

**DNAPLS IN SOUTH AFRICAN FRACTURED AQUIFERS:
OCCURRENCE, FATE AND MANAGEMENT**

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**Submitted in fulfillment of the requirements for the degree of Doctor of
Philosophy in the Faculty of Natural Sciences and Agriculture, Department of
Geohydrology, University of the Free State, Bloemfontein, South Africa.**

May 2007

Acknowledgements

The research in this report emanated from a project funded by the Water Research Commission entitled: **“Field investigations to study the fate and transport of dense non-aqueous phase liquids (DNAPLs) in groundwater”**

The financing of the project by the WRC and contributions by members of the Reference Group, especially Kevin Pietersen (Chairman), are gratefully acknowledged.

I hereby wish to express my sincere thanks to a large number of people who have helped me to complete this thesis:

- To Brent Usher my supervisor, thank you for all your advise, support, patience, personal input, and friendship with both the research project and my thesis.
- To Robel Gebrekristos my research partner on the project, thank you for all your hard work in the field, personal input and friendship.
- From the Institute for Groundwater Studies the following personnel and students need to be thanked for their contributions: Ingrid Dennis, Gerrit van Tonder, Sechaba Lenong, Michelle Pienaar, Adrie van Wyk, Mehari Mengistu, and Sakhile Mndaweni, Eelco Lucas, and Jane van den Heever.
- International experts Allen Shapiro from the USGS and Dave Kreamer from the University of Nevada, are thanked for their review of documentation and results of the WRC project, and insights from their wealth of international experience on NAPL site characterisation and data interpretation.
- Employees from Test Site 1 for access to the site and data, and for funding and assisting in drilling. In this regard, Jaap Vermeulen, Johan Mans and Hottie Harris are thanked.
- For making the down-hole geophysical equipment from DWAF, available for use at the research sites, Eddie van Wyk is thanked. Barry Venter, Nico de Meillion, and Lukas Smith were responsible for applying and interpretation of techniques.
- Pieter and Andre Groenenstein from Prestige Besproeiing, are thanked for design and construction of laboratory and field equipment for use during experiments.
- My parents, Attie and Bettie Cowley, for your support and prayers throughout my studies.
- And last but not least, to my family Jan, Elizabeth and Willem: Thank you for your support throughout the past four years, enduring many hours of my absence, late hours, and moods. Without you this thesis would not have been possible, I love you very much!

Key Words

Dense Non-Aqueous Phase Liquids (DNAPLs)

Occurrence

Fate and Transport

Natural Attenuation

Fracture characterisation

Critical factors

Fracture flow

Aquifers

South Africa

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List of Abbreviations

| ABBREVIATIONS | DEFINITION |
|----------------------|---|
| CF | CHLOROFORM |
| CHC | CHLORINATED HYDROCARBONS |
| DCA | DICHLOROETHANE |
| DCE | DICHLOROETHENE |
| DNAPL | DENSE NON-AQUEOUS PHASE LIQUID |
| DO | DISSOLVED OXYGEN |
| EC | ELECTRICAL CONDUCTIVITY |
| FOC | FRACTION OF ORGANIC CARBON IN SOLID MATERIAL |
| LNAPL | LIGHT NON-AQUEOUS PHASE LIQUID |
| MBGL | METERS BELOW GROUND SURFACE |
| NAPL | NON-AQUEOUS PHASE LIQUID |
| ORP | OXIDATION/REDUCTION POTENTIAL |
| PAH | POLYAROMATIC HYDROCARBONS |
| PCE | PERCHLOROETHENE/PERCHLOROETHYLENE/TETRACHLOROETHENE |
| PCR | POLYMERASE CHAIN REACTION |
| PID | PHOTOIONISATION DETECTOR |
| PVC | POLYVINYLCHLORIDE |
| TCE | TRICHLOROETHENE/TRICHLOROETHYLENE |
| TPH | TOTAL PETROLEUM HYDROCARBONS |
| VC | VINYL CHLORIDE |
| VOC | VOLATILE ORGANIC COMPOUNDS |

1 Introduction

Dense Non-Aqueous Phase Liquids (DNAPLs) are water-immiscible organic liquids with a density greater than that of water. The most prevalent types of DNAPLs are the halogenated organic solvents (including trichloroethene, “TCE”, and tetrachloroethene, “PCE”), but many sites are contaminated with other types of DNAPLs including coal tar and creosotes (complex hydrocarbon mixtures consisting of polycyclic aromatic hydrocarbons and other aromatic hydrocarbons), polychlorinated biphenyl (PCBs), and certain pesticides (Cohen and Mercer, 1993).

Numerous references provide detailed information on the physical and chemical properties of DNAPLs (e.g., Mercer and Cohen, 1990; Cohen and Mercer, 1993; Pankow and Cherry, 1996; USEPA, 1991, and Kueper *et al.*, 2003). Although there was broad recognition of groundwater contamination from chlorinated solvents in the 1970s and early 1980s, the crucial role of DNAPLs as the primary source of this contamination was overlooked until the mid-1980s. Schwille (1988) is credited for the pioneering work on the fate of DNAPLs in the subsurface leading to a greater understanding of the role of DNAPLs in groundwater contamination.

Pankow and Cherry (1996) provide a comprehensive history of the growth of knowledge regarding the role of DNAPLs in groundwater contamination. Since the early 1990s, however, the significance of the longterm the presence of DNAPL in groundwater has been fully recognized.

The physical, chemical, and biotic degradation properties of DNAPLs determine the threats that these organic chemicals pose to the environment (Pankow and Cherry, 1996). Rates of migration are dependent on the properties of the DNAPLs (viscosity, density, interfacial tension), and the geologic characteristics of the subsurface. DNAPLs can migrate relatively easily in the saturated zone under gravity forces, penetrate deeply into aquifers, and in some cases, travel substantial horizontal distances away from the original source area. DNAPLs exhibit relatively low aqueous solubility (typically in the milligrams per liter range or parts per million (ppm)), but the solubility levels generally exceed drinking water standards (typically in the microgram per liter range or parts per billion, ppb) by several orders of magnitude. Some DNAPL compounds, such as chlorinated solvents, are relatively volatile in pure phase, and can thus partition into soil gas, causing further migration of those DNAPL constituents in

the vadose zone.

Efforts to identify potential contaminants in groundwater resources of South Africa, have shown that a diversity of dissolved organic contaminants and NAPLs are likely to be found in urbanised areas (Pretorius *et al.*, 2003; Usher *et al.*, 2004). The research to date has highlighted the paucity of data, targeted monitoring or regulations related to these contaminants.

The true extent of the problem, the critical factors governing the flow and migration of DNAPLs in South African aquifers and means of managing these problems has not previously been addressed and filling these data gaps forms the focus of the research contained in this thesis.

The research in this thesis has illustrated the technical challenges of properly characterising fractured rock aquifers where this type of contamination has occurred, the potential depths of investigation required and the difficulties of understanding these problems with limited resources and technical capacity locally. Out of this, recommendations regarding regulation of DNAPL contaminants and monitored natural attenuation (MNA) in South Africa have arisen from this research and a way forward to promote awareness, standardisation of guidelines and increased capacity amongst decision makers is proposed. The structure of the thesis is provided later in this chapter.

1.1 Background to the research

This thesis is a culmination of several research projects undertaken from 2003, in which the author was involved. These projects include the following:

1. Research for the establishment of regulatory processes for dealing with leaking underground storage tanks in South Africa, (Pretorius, *et al.*, 2003).
2. Research for identification and prioritisation of groundwater contaminants in South Africa's urban catchments, (Usher *et al.*, 2004).
3. Research for field investigations to study the fate and transport of dense non-aqueous phase liquids (DNAPLs) in groundwater. (Usher, *et al.*, 2007).

Specific topics from these projects that are included in this thesis and were researched by the author are:

- Literature review regarding all aspects of NAPL contamination.
- Regulatory requirements for dealing with NAPL contamination in South Africa, including several environmental acts, DWAF and DEAT regulations, and international environmental legislation.
- Occurrence, fate and transport of NAPLs in South African Aquifers. This included:
 - The inventory of activities in urban environments, associated with these contaminants,
 - The inventory of chemicals associated with the above activities, and their properties,
 - Definition of what “typical” South African aquifer systems are, and
 - Factors and properties influencing the migration, transport, and fate of these contaminants in typical South African aquifers.
- Field and laboratory testing of critical factors that influence transport in the subsurface of these contaminants.

Much of the fieldwork and interpretation of the results from Test Site 1 was done as part of the DNAPL WRC project. Gebrekristos completed a PhD thesis “*Site characterization Methodologies for DNAPLs in Fractured South African Aquifers*”, for the same project (Gebrekristos, 2007). The necessary reference is made where work from Gebrekristos’ thesis, or interpretation of results was used. Pienaar completed the microbial study for the Monitored Natural Attenuation (MNA) investigation of the project (Usher, *et al.*, 2007). These results and interpretation is included in the discussion and referenced.

1.2 Aims

The aim of this thesis is to provide an understanding of the extent of the DNAPL problem, the critical factors which control the fate and transport of DNAPL in South African aquifer systems, and provide recommendations for management and regulation of the DNAPL problem in South Africa.

The aims will be achieved through the following:

- Extensive literature review of local and international publications, journal articles, legislation and regulatory guidelines, and chemical and groundwater databases.
- Applying applicable research and site assessment methodologies at two research field sites.
 - Test Site 1, is a large industrial site where it was suspected that large quantities of DNAPL type chemicals were stored, used and disposed of.
 - The Campus Test site is a research site where extensive research has contributed to the understanding of fracture flow in aquifer systems.
- Testing and evaluating fracture characterisation methods at both sites.
- Flow characterization in the laboratory through controlled fracture apertures in typical sedimentary rocks.
- Characterising DNAPL fracture flow by injecting a surrogate DNAPL in a fracture system at the Campus site.
- Determination of retardation and attenuation processes of different DNAPLs at Test Site 1.
- Determination of DNAPL properties
- Testing of suitable borehole construction material
- Using Multi-phase Flow Numerical Modeling to simulate DNAPL transport in fracture systems.

1.3 Structure of the Thesis

The thesis is structured that Chapter 2 describes the extent of the DNAPL problem, types of DNAPLs and the existing regulation governing (ground)water contamination in South Africa.

Chapter 3 is a description of the how contaminant and aquifer properties influence the transport and fate of DNAPLs in South African aquifer systems. Transport mechanisms for both the free phase and dissolved phases of DNAPLs are discussed. Attenuation and degradation mechanisms are also discussed. As a summary of the chapter, generalised conceptual models of major South African aquifer systems and how DNAPLs could

affect these systems are given.

Chapter 4 gives the most important issues highlighted from the research with regard to site assessment and prediction techniques, including a case study of the multi-phase modelling.

In Chapter 5 the critical factors which influence DNAPL flow in aquifers are discussed within context of the two research sites where techniques were tested and evaluated. An overview of the research field sites used during the duration of the research period is given with the results of the field and laboratory tests and experiments.

Chapter 6 discusses the management a regulatory framework recommended for DNAPL contaminated sites in South Africa. Focus areas that are highlighted include: Water Quality Standards; trigger values for clean-up; Risk Based Approaches; and MNA implementation in South Africa.

Chapter 7 gives the major conclusions from the research.

2 Extent of Problem

2.1 Inventory and prioritisation of potential of DNAPL contaminants and sources in major urban areas of South Africa

As part of the research for this thesis, investigation into groundwater contaminants in urban catchments of South Africa (Usher, *et al.*, 2004) a contaminant inventory and priority list of potential groundwater contaminants in these environments was compiled for urban related activities. All possible sources (activities) were identified within the urban environment and expected contaminants assigned to each source. These were prioritized according to set criteria.

The contaminant source inventory is one of the most important elements in water resource assessment. It identifies potential sources of contamination associated with specific activities, industries, and land uses located within an area. The contaminant inventory should serve three important functions:

- Assess past and present activities that may pose a threat to the water supply based on their contamination potential. Activities covered include transporting, storing, manufacturing, producing, using, or disposing of potential contaminants;

- Identify the locations of activities and operations that pose the greatest risks to the water supply; and
- Educate managers and the public about the potential threats to the water supply posed by various activities.

A typical approach to a contaminant inventory will be iterative, starting simple and moving to more complex methods as experience and resources grow. The first step will be to identify the most significant or serious sources of contamination. Activities and land uses that manufacture, produce, store, use, dispose or transport these regulated contaminants within the area will be identified.

There are many potential sources of contaminants that can seep into the ground and move through the soil to the water table. Potential contamination sources include everything from septic tanks, dry cleaners and underground storage tanks to landfills, urban runoff and pesticides applied on farm fields. A typical contaminant inventory list will include the most common sources of groundwater contamination but is by no means a complete listing of all potential sources, since virtually anything spilled or placed on the ground has the potential to leach to groundwater.

The approach taken to compile a groundwater contaminant inventory for South Africa's urban areas was similar to that described in several US regulatory publications. The first step was to identify potential sources and activities which can pose a threat to groundwater resources in South Africa. From this expected/ potential contaminants (chemicals) were identified that could emanate from these sources. The result was a generic contaminant inventory (or baseline) from which the individual urban centers' inventories were compiled.

The applicable information that was taken from the generic table was verified by means of real data or case studies. A column was added in the tables for specific reference sources. The data used to verify the contaminants were typical from literature searches, which was followed by contacts of individuals at various organizations, such as Department of Water Affairs and Forestry (DWAF), municipalities, water boards and private consulting companies. Contamination incident reports, databases, DWAF publications, consultant reports, internet searches and other relevant publications are examples of data used to verify the information.

In Table 2-1, an adapted version of the contaminant inventory (Usher *et al.*, 2004) is given. Only organic contaminants are included in the list. It must be noted that some contaminants listed (e.g. petroleum hydrocarbons), can rather be classified as LNAPLs, therefore implying a density or specific gravity less than that of water. The reason for inclusion can be attributed to the complex behaviour of NAPLs and the changes that take place when contaminant mixtures are considered, as opposed to single component contaminants. These mixtures would more often than not, rather behave as a DNAPL than as a LNAPL. (This behaviour will be discussed in detail in Section 2.5.)

After the contaminant inventory was completed the contaminants were then prioritized according to set criteria. The groundwater contaminants were first grouped according to the criteria below and then rated within each group:

4. Fate in the environment
5. Human health impacts:
 - 5.1. Non-harmful substances, which have no observed effects on human health
 - 5.2. Toxic substances, which cause various effects on the body from short-term exposure or long term accumulation, ranging in severity depending on the dose e.g. nausea, rashes, kidney failure or neurotoxic effects.
 - 5.3. Carcinogenic substances, which are known to cause cancer.

Weights were assigned to each contaminant according to health effects associated with that contaminant. The highest ranking (priority) contaminant was the one, which is often persistent in the environment, frequently encountered and harmful to human health and the environment.

Out of the 50 possible sources, 36 are sources of DNAPL contamination (see Table 2-2). Out of the top ten ranked sources only on-site sanitation, cemeteries and feedlot/poultry farms are excluded from this list. From this prioritization, a picture of the widespread occurrence and extent of the DNAPL problem in South Africa is emerging. **Error! Reference source not found.** This is also adapted from Usher *et al.* (2004), only the NAPL type contaminants with their ranking are included. Out of the 119 contaminants listed in the national prioritization list, 62 can be considered to be

DNAPL contaminants. However, not all the contaminants listed have the physical properties of a DNAPL. Many of the contaminants listed are often either used as intermediates to synthesize compounds with DNAPL properties, or are found at sites often associated with the better known and more common DNAPL contaminants (e.g. solvent use). The properties of the contaminant mixture found in the aquifer, will determine the behaviour of the NAPL source.

From this prioritisation, it can be seen that the extent of the DNAPL problem in South Africa's urban areas is potentially much greater than expected. The problem is not confined to large urban centers, but many of the potential sources (e.g. auto workshops, dry-cleaners) are found in all types of settlements across the country. The development of groundwater resources for supply, in urbanized areas, is thus very likely to be affected by potential contamination from DNAPLs.

Table 2-1: Contaminant Prioritisation – NAPL contaminants with ranking (Adapted from Usher, *et al.*, 2004).

| Contaminant prioritisation (from highest to lowest risk) * | | | |
|--|----------------------------|-----|----------------------|
| 1 | Chlordane | 46 | Ethylene oxide |
| 2 | HCH | 47 | Ethylene Dibromide |
| 3 | Lindane | 48 | Dioxane 1,4 |
| 4 | DDD | 49 | Chlorine Dioxide |
| 5 | Butadiene | 50 | Carbon Tetrachloride |
| 6 | Trichloroethylene | 52 | Benzidine |
| 8 | Dichloromethane | 53 | Trichlorobenzene |
| 9 | Tetrachloromethane | 54 | Toluene |
| 10 | Phenol | 56 | Dichloroethylene |
| 11 | Atrazine | 57 | DDE |
| 12 | TCA | 59 | Chloroform |
| 13 | Formaldehyde | 61 | Diuron |
| 14 | Creosote | 62 | Heptane |
| 15 | Dichlorobenzene | 63 | Chlorobenzene |
| 16 | MEK | 66 | Tetrachlorobenzene |
| 19 | Acrylonitrile | 72 | Ethylbenzene |
| 20 | Vinyl Chloride | 73 | Ethyl Alcohol |
| 22 | Trichlorophenol 2,4 | 74 | Ethyl Acetate |
| 23 | Dichloropropane 1,2 | 79 | Tri-n-Nutyltin Oxide |
| 24 | Dichlorophenol 2,4 | 81 | Styrene |
| 28 | Benzene | 89 | PCE |
| 29 | Arsenic | 91 | Naphthalene |
| 30 | Methylene Chloride | 94 | Glycol |
| 31 | Tebuthiuron | 95 | Fluorocarbon 113 |
| 33 | Monosodium-Methyl Arsenate | 96 | Fluorobenzene |
| 34 | Isopropanol | 97 | Chloropyrifos |
| 35 | Acetone | 98 | Chlorofluoroethane |
| 41 | Aldicarb | 101 | Butane |
| 42 | Xylenes | 103 | Acetylene |
| 43 | Trichloroethane 1,1,1,- | 104 | Phthalates |
| 44 | Pentachlorophenol | | |

* PCB's were not included in the list, as this is a descriptive name of a group of contaminants. The Individual contaminants must be entered into the URA software with their properties to obtain a ranking. However, due to the known toxic and carcinogenic properties of the PCB group, these contaminants are likely to be in the top ten ranking.

Table 2-2: Prioritisation list of sources of possible DNAPL groundwater contamination in urban environments (Adapted from Usher, *et al.*, 2004).

| Ranking | Type of source |
|---------|--|
| 2 | Production of agricultural chemicals (fertilizers, herbicides, pesticides) |
| 4 | Metallurgical |
| 5 | Metal (predominately gold) and coal mining |
| 6 | Transport |
| 7 | Petrol Service Stations (Underground Storage Tanks) |
| 8 | Wood processing and preserving |
| 10 | Manufacturing - Chemicals |
| 11 | Workshops (Mechanical and electrical) |
| 12 | Stormwater/ sewer systems |
| 13 | Automotive manufacturing |
| 13 | Automotive refinishing and repair |
| 14 | Other metal product manufacturing |
| 15 | Railroad yards |
| 18 | Agriculture (General and crop cultivation) |
| 19 | Paper/ pulp industry |
| 20 | Research and educational institutions |
| 24 | Munitions manufacturing |
| 25 | Hazardous waste sites |
| 26 | Marine maintenance industry |
| 27 | Dry cleaning activities |
| 28 | General/ Domestic waste sites |
| 29 | Wastewater treatment |
| 30 | Textile manufacture |
| 31 | Rubber and plastics |
| 33 | Leather manufacturing |
| 35 | Printing industry |
| 38 | Auto Salvage/Metal Recyclers |
| 39 | Electrical and electrical products manufacturing |
| 40 | Electricity generation |
| 41 | Photographic manufacturing and uses |
| 42 | Paint/ink manufacturing and coatings |
| 43 | Pharmaceuticals and cosmetics manufacturing |
| 44 | Adhesives and sealants |
| 48 | Hospitals / Health Care |
| 49 | Glass manufacturing |
| 50 | Incinerators |

2.2 Types of DNAPL contaminants

The first step in the assessment of a potential DNAPL site is the consideration of the potential chemicals that might be present at the site. A wide variety of chemical products and wastes may comprise a DNAPL. In general, a DNAPL is defined as a heavier-than-water organic liquid that is only slightly soluble in water. All DNAPLs can be characterised by their physical properties such as: density, viscosity, and interfacial tension with water, component composition, and solubility in water, vapour pressure and wettability. For a chemical (or chemical mixture) to be considered as a DNAPL, it must have a fluid density greater than 1.01g/cm^3 , a solubility in water of less than 2%

(or 20000 mg/l) and a vapour pressure of less than 300 torr (Pankow and Cherry, 1996).

The major DNAPL types include: halogenated hydrocarbons, especially *solvents, coal tar and creosote, Polychlorinated Biphenyls (PCBs), some pesticides, and miscellaneous or mixed DNAPLs*. Of these types, the most extensive subsurface contamination is associated with halogenated (primarily chlorinated) solvents, either alone or within mixed DNAPL sites, due to their widespread use and properties (high density, low viscosity, significant solubility, and high toxicity) (Pankow and Cherry, 1996). The most prevalent DNAPL types are outlined in Appendix A1, with summary information on DNAPL density and viscosity, appearance, and usage.

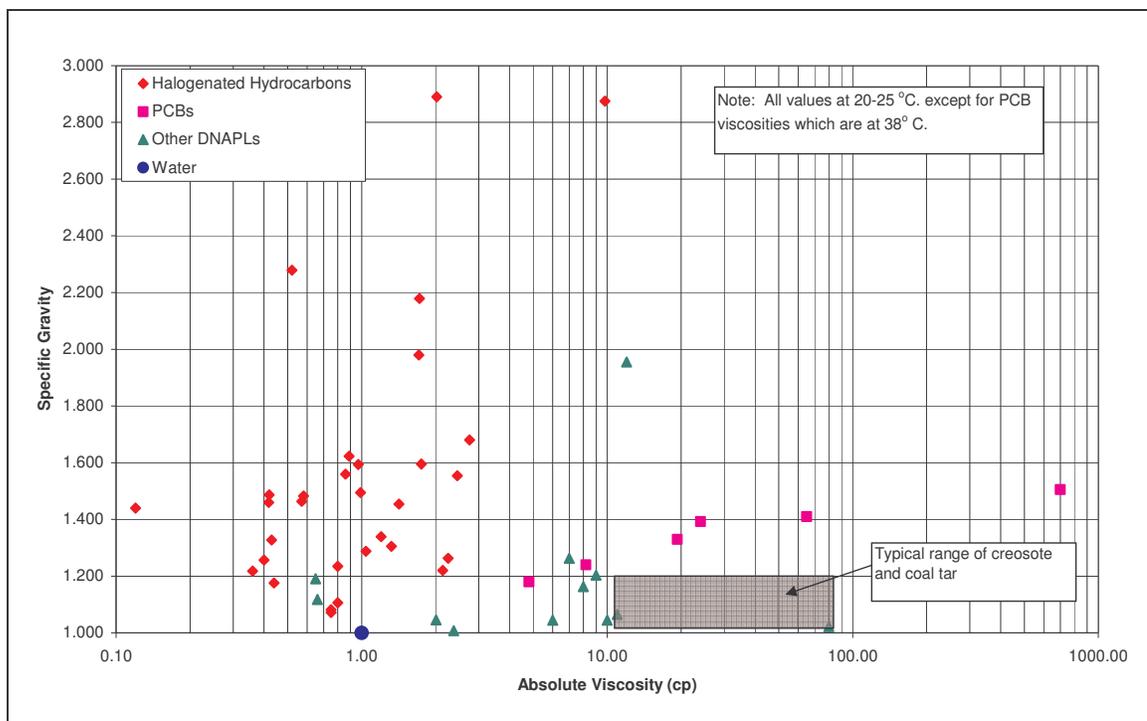


Figure 2-1 shows that, due to their relatively high density:viscosity ratios (Figure 2-2), pure chlorinated solvents (red) are generally far more mobile than creosote/coal tar, PCB oil mixtures and other DNAPLs.

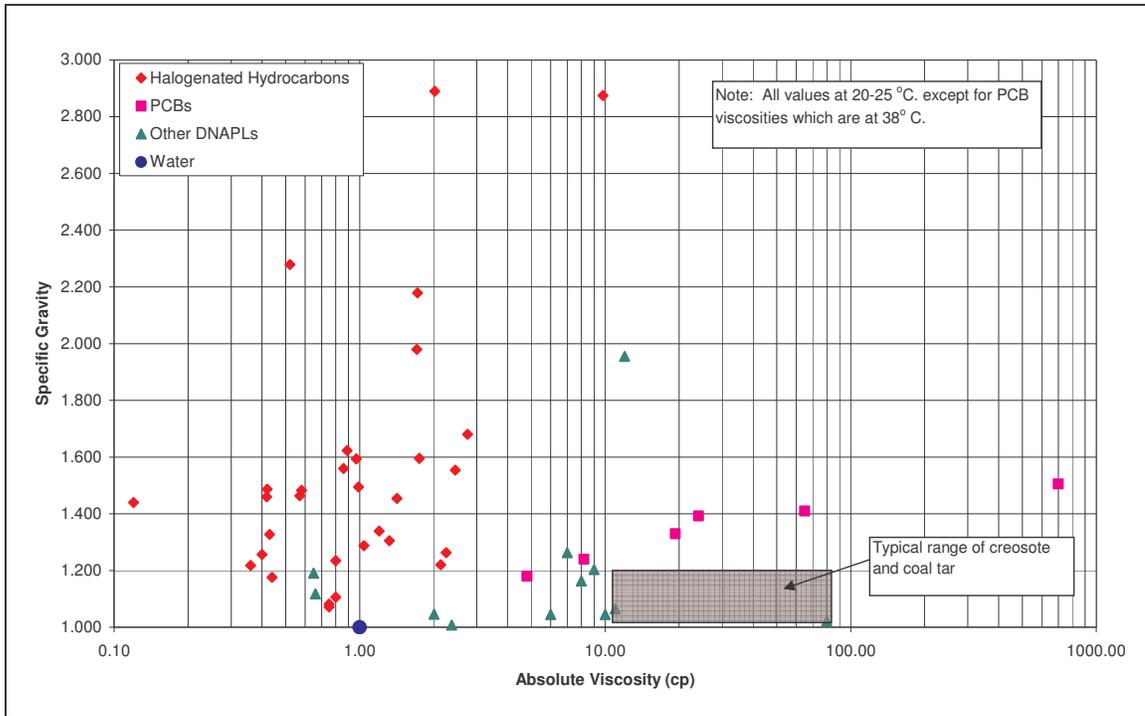


Figure 2-1: Density versus absolute viscosity for some DNAPLs. (Adapted from Cohen and Mercer, 1993)

An increase in Density: Viscosity ratio relates to increased mobility of a DNAPL (Figure 2-2) (Discussed in more detail in Appendix A).

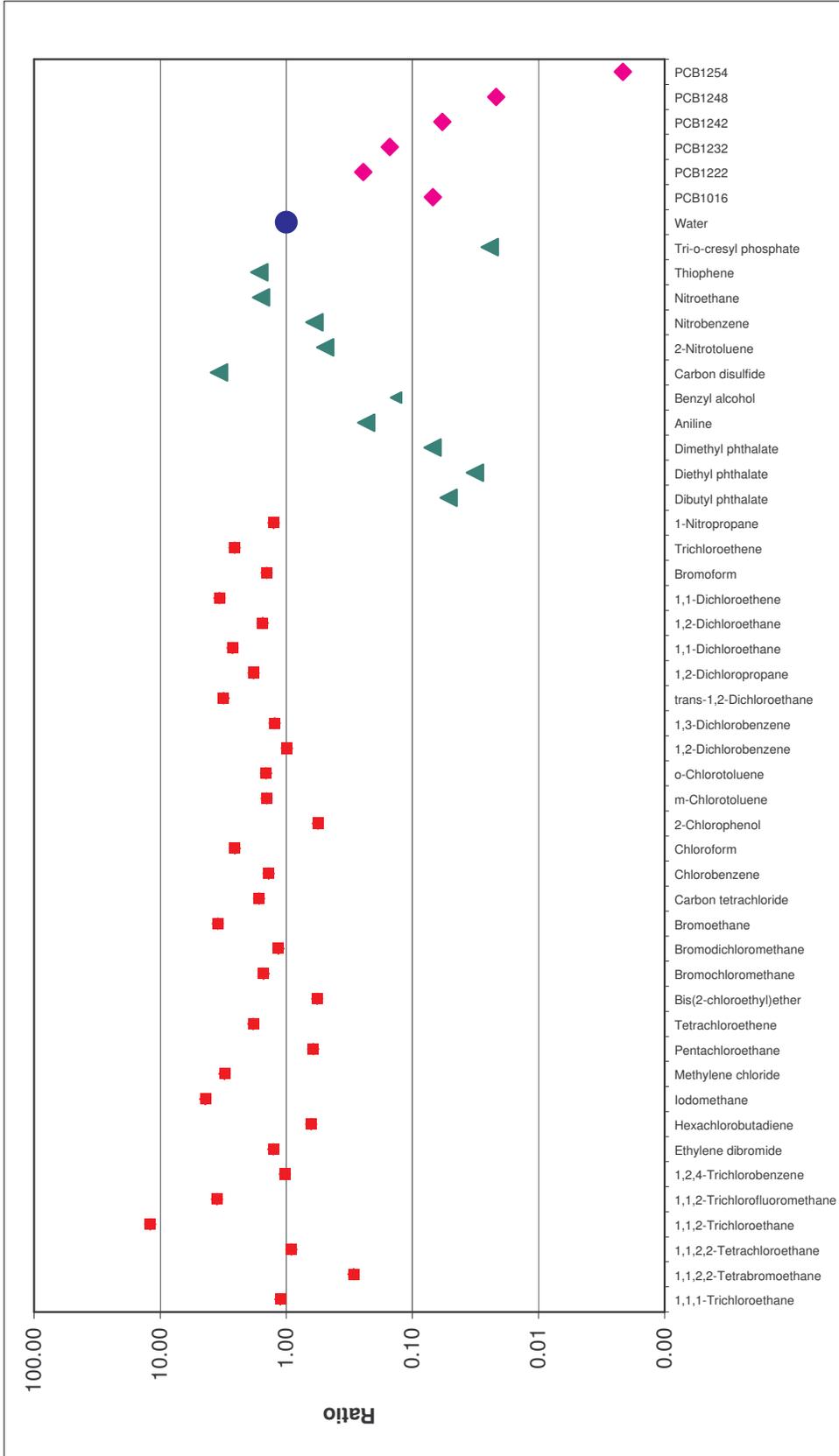


Figure 2-2: Density:Viscosity ratios for selected DNAPL contaminants, mobility increases with increased ratio.)

2.2.1 Halogenated Solvents

Halogenated solvents, particularly chlorinated hydrocarbons, and brominated and fluorinated hydrocarbons to a much lesser extent, are DNAPL chemicals encountered at contamination sites. These halocarbons are produced by replacing one or more hydrogen atoms with chlorine (or another halogen) in petrochemical precursors such as methane, ethane, ethene, propane, and benzene. Many bromocarbons and fluorocarbons are manufactured by reacting chlorinate hydrocarbon intermediates (such as chloroform or carbon tetrachloride) with bromine and fluorine compounds, respectively (Cohen and Mercer, 1993).

Although most chlorinated solvents were first synthesized during the 1800s, large-scale production generally began around the middle of the 1900s. Typical uses of these chemicals include dry cleaning, metal degreasing, pharmaceutical production, pesticide formulation and chemical intermediates. Chlorinated solvents typically enter the subsurface as a result of past disposal directly onto land, storage and disposal into unlined evaporation ponds and lagoons, leaking storage tanks and vapour degreasers, leaking piping and accidental spills during handling and transportation. Chlorinated solvents can be encountered as single component DNAPLs or as part of a multi-component DNAPL containing other organic compounds such as PCB oils, mineral oils and fuels. The four principal chlorinated solvents are: perchloroethylene (PCE), trichloroethylene (TCE) 1,1,1-trichloroethane (1,1,-TCA) and dichloromethane (DCM). Fluorocarbons were discovered in the search for improved refrigerants in 1930. Fluorocarbon is used as refrigerants, foam blowing agents, solvents, fluoropolymers (such as teflon), and as aerosol propellants. Prior to 1974, when concerns arose regarding atmospheric ozone depletion, aerosol propellants were the main end use of fluorocarbons (Cohen and Mercer, 1993). Most of domestic bromine output is used to manufacture ethylene dibromide (EDB) for use in engine fuel antiknock fluids to prevent lead oxide deposition. Use of EDB for this purpose, will diminish with the phase out of leaded petrol internationally (Moldan, Pers. Comm, 2003). Brominated hydrocarbon DNAPLs are also used as fire retardants and fire extinguishing agents, and in a variety of other products (www.epa.gov/safewater/contaminants/).

The halogenated solvents present an extremely high contamination potential due to their extensive production and use, relatively high mobility as a separate phase (high density:viscosity ratio), significant solubility and high toxicity (Cohen and Mercer, 1993). Most of the chlorinated solvents have densities that range from 1.1 g/cm³ to 1.63 g/cm³. Viscosities are less than or similar to water. The solubilities are as much as a hundred thousand times higher than the respective drinking water standards (USEPA, 1991).

Industries and industrial processes potentially associated with halogenated solvents in South Africa would include:

- Electronics manufacturing (metal cleaning);
- Solvent production (metal machining);
- Pesticide/herbicide manufacturing (tool and die operations);
- Dry cleaning (vapour and liquid degreasers);
- Instrument manufacturing (paint stripping);
- Solvent recycling (storage and transfer of solvents);
- Engine manufacturing;
- Steel product manufacturing;
- Chemical production;
- Rocket engine/ fuel manufacturing;
- Aircraft cleaning/ engine degreasing; and
- Rail and road transport.

Limited published data is available in South Africa on DNAPL contamination from solvent mixtures. Morris *et al.*, (2000) measured levels of TCE ranging between 6 µg/l to 4 089 µg/l. A pump and treat system was used as containment and rehabilitation method. Total chlorinated hydrocarbon concentrations of 100 000 ppb at a depth of 30 meters below surface was measured at an industrial hazardous waste site in Durban (Palmer and Cameron-Clarke, 2000).

In a high profile court case (www.legal-aid.co.za/publications/case_studies/cs),

subsistence farmers alleged that a steel works has poisoned their water, harming their health and that of their livestock by pumping harmful industrial effluent into the environment. The farmers' lawyers argued that the primary cause of the pollution lies in the plant's vast "evaporation" and furnace sludge dams that cover an area of about 140 ha. The dam closest to the applicants' properties received dangerous contaminants including benzene, toluene and xylene. The borehole water has at times given off a strong smell of naphthalene, which is toxic and can cause cancer, respiratory depression and lung tumours (DEAT, 2003).

2.3 Coal tar and Creosote

Coal tar and creosote are complex chemical mixture DNAPLs derived from the destructive distillation of coal in coke ovens and retorts. These oily DNAPLs are generally translucent brown to black, and are characterized by specific gravities that range between 1 and 1.20, viscosities much higher than water (typically 10 to 70 centi-Poise (cP)), and the distinctive odour of naphthalene (moth balls) (Cohen and Mercer, 1993).

Coal tar was historically produced as a by-product of manufactured gas operations up until approximately 1950, and is currently still produced as a by-product of blast furnace coke production. The tars are made up of 500 to 3000 different compounds, typically toxic to humans, mammals, and plant life. Tar is not to be considered equivalent to asphalt, which is a residual of natural petroleum deposits and of oil refineries. Also associated with gas manufacturing were captured impurities such as ammonia, cyanide, sulphur and heavy metals, particularly arsenic. Coal tar contains hundreds of hydrocarbons, including light oil fractions, middle oil fractions, heavy oil fractions, anthracene oil and pitch. The density of coal tar typically ranges from 1,010 to 1,100 kg/m³ and the viscosity from 20 to 100 cP. The relatively low density and high viscosity of coal tar implies that it may still be migrating as a DNAPL at sites where it was introduced to the subsurface many years earlier. With respect to the impact on groundwater, most investigators typically select a subset of compounds to assess the impact on water quality. These may include the suite of BTEX compounds (benzene, toluene, ethylbenzene and xylenes), as well as poly-aromatic hydrocarbons (PAHs) including benzo[a]pyrene, naphthalene and phenanthrene (Kueper *et al.*, 2003).

Creosote is composed of various coal tar distillates and was commonly used to treat

wood products such as railway sleepers and telegraph poles. It is still used today in certain timber-treating operations and as a component of roofing and road tars. Creosote contains many hydrocarbons, primarily, polycyclic aromatic hydrocarbons (PAHs) and phenolic compounds. Creosote may be blended, however, with up to 50% of a carrier fluid such as diesel fuel prior to use. The density of creosote typically ranges between 1,010 and 1,130 kg/m³, depending on the amount and type of any carrier fluid. Creosote is therefore one of the least dense DNAPLs of environmental interest. It often takes a long time for movement to cease following initial release into the subsurface because creosote is only slightly denser than water and has a relatively slow downward (gravity-driven) migration. The relatively high viscosity of creosote, which typically ranges between 20 and 50 cp, also facilitates the long migration timescale (Kueper *et al.*, 2003).

Creosote and coal tar contamination of the subsurface is associated with wood-treating plants, former manufactured gas plants, coal tar distillation plants, and steel industry coking plants. No published data with exception of the court case referred to previously was found related to coal tar and creosote contamination of South African aquifers. This does, however, not imply that the potential for this type of contamination is unlikely in South Africa.

It is known that several coal gasification works were constructed at large industrial sites, as an additional power/fuel supply during the oil embargo of the early 1980's in South Africa. Perhaps the most famous and largest of these plants is from Sasol, a world-leader in the commercial production of liquid fuels and chemicals from coal and crude oil, the Sasol I plant in Sasolburg. Following the success of Sasol I, Sasol II and III, located in Secunda, came on line in 1980 and 1982, respectively. The Moss gas plant which converts natural gas to products using a high temperature process and an iron catalyst started up in 1992.

2.4 Polychlorinated biphenyls (PCBs)

PCBs are extremely stable, nonflammable, dense, and viscous liquids that are formed by substituting chlorine atoms for hydrogen atoms on a biphenyl (double benzene ring) molecule. PCBs were sold between 1929 and 1977 under the Aroclor trademark for use primarily as dielectric fluids in electrical transformers and capacitors. PCBs were also sold for use in oil-filled switches, electromagnets, voltage regulators, heat transfer

media, fire retardants, hydraulic fluids, lubricants, plasticizers, carbonless copy paper, dedusting agents, etc.

Commercial PCBs are a series of technical mixtures, consisting of many isomers and compounds. A four-digit number e.g. 1254 identifies each Aroclor. The first two digits, “12”, indicate the number of carbons in the biphenyl double ring. The last two digits indicate the weight percent chlorine in the PCB mixture, such as 54% chlorine in Aroclor 1254. Aroclor 1016, which contains approximately 41% chlorine, however, was not named using this convention. Aroclors become more dense and viscous and less soluble with increasing chlorine content. The lower chlorinated formulations (Aroclors 1016 to 1248) are colorless mobile oils. Aroclor 1254 is a viscous yellow liquid, and Aroclor 1260 is a black sticky resin (Cohen and Mercer, 1993).

PCBs were frequently mixed with carrier fluids prior to use. For example, PCBs were typically diluted with up to 70% carrier fluid, usually chlorobenzenes or mineral oil, in askarel (Askarel is a generic name for fire-resistant dielectric fluids). The mix of Aroclor and carrier fluid type and content, therefore, determines the physical properties of the PCB fluid, including its density, viscosity, solubility and volatility. Depending on the particular combination of congeners present and the type of carrier fluid, the density of most PCB oils encountered in practice ranges from approximately 1,100 to 1,500 kg/m³, while the viscosity ranges from approximately 10 to 50 cP (Kueper *et al.*, 2003). The relatively high density of PCB oils indicates that the timescale of migration may be relatively short, but their relatively high viscosity results in an intermediate range of timescales of migration.

With respect to impact on groundwater, most congeners are extremely hydrophobic and therefore sorb strongly onto soils and rock. Consequently, if PCBs are detected in groundwater samples, the DNAPL source is typically immediately up gradient of the monitoring location. Exceptions are sites where colloid-facilitated transport is occurring or where the PCBs are dissolved in other organic contaminants such as oils (Kueper *et al.*, 2003). Carrier organic liquids may be LNAPLs as well as DNAPLs. PCB DNAPLs are often encountered at former solvent and waste oil recycling facilities where they have been co-disposed with a variety of other organic liquids such as chlorinated solvents and aromatic compounds.

Worldwide production of PCBs has now ceased, mainly in response to recognition of their toxicity and their tendency to bioaccumulate in animal tissues. However, they remain in limited use and may be present as impurities in locations where they were used previously.

In South Africa PCBs have been used in the past as electrical insulating liquid for transformers and capacitors. Problems are often caused when there is a fire in the establishment, or the electrical device leaks. Eskom (the country's electricity service provider) has used PCBs in the past but is in a process of phasing these out. Eskom has about 150,000 L of oil containing PCBs, which it plans to eliminate before 2025. Industry, railways, mines, and municipalities also have equipment that may contain PCBs. Eskom is providing training and education about the dangers and methods of phasing out PCBs, but there is still much ignorance in dealing with the substance. Eskom has persuaded the oil companies that process the electrical oils to reject any oil with a PCB concentration > 20 ppm. This is having a positive impact by pressuring current PCB users to phase the use of PCBs out, but progress is slow. South African law does not control PCBs other than the occupational exposure limits laid out in the Occupational Health and Safety Act (DEAT, 2003).

2.5 Miscellaneous and Mixed DNAPLs

Miscellaneous DNAPLs refer to dense, immiscible fluids that are not categorized as halogenated solvents, coal tar, creosote, or PCBs. These include some herbicides and pesticides, phthalate plasticizers, and various exotic compounds (Cohen and Mercer, 1993). Mixed DNAPL sites refer to landfills, lagoons, chemical waste handling or reprocessing sites, and other facilities where various organic chemicals were released to the environment and DNAPL mixtures are present. Typically, these mixed DNAPL sites include a significant component of chlorinated solvents.

At these mixed DNAPL sites the DNAPL that is composed of two or more chemical compounds can be referred to as a multi-component DNAPL. Creosote and coal tar are examples of multi-component DNAPLs. At a typical industrial waste disposal site, a combination of chlorinated solvents, PCBs and a variety of aromatic compounds, can be found. This implies that each component is available to dissolve from the DNAPL into groundwater. Some of the components can be less dense than water, but it is the combined density that gives the mixture its DNAPL character.

The physical/chemical properties of the DNAPL may vary spatially at a site. The degree of spatial variability that may exist at a site with respect to the physicochemical properties of the DNAPL, will depend among others, on the site's use and history. Regardless of site history, however, DNAPLs encountered in the subsurface may have different physical and chemical properties from reagent grade non-aqueous phase liquids (NAPLs). This may be the result of industrial processes in which they were used prior to disposal or as a result of contact with naturally occurring substances present in the soil zone (Kueper, *et al.*, 2003).

Many of the DNAPL contaminated sites in South Africa contain complex mixtures of DNAPLs. Most commonly, these mixtures are found at regulated waste sites, industrial waste sites, and industrial complexes where a variety of interdependent industrial activities take place.

2.6 Regulatory Framework (with reference to DNAPLs)

The South African mission for groundwater quality (DWAF, 2000) is “To manage groundwater quality in an integrated and sustainable manner within the context of the National Water Resources Strategy and thereby to provide an adequate level of protection to groundwater resources and secure the supply of water of acceptable quality.” Policy goals have been identified and will be implemented through the following strategies:

1. Establish an understanding of the vulnerability to pollution of the country's groundwater resources
2. Establish an understanding of the relationship between polluting activities (sources) and changes in the quality of groundwater
3. Regulate and prohibit land-based activities which may affect the quantity and quality of water.
4. Control practices and use measures to lessen the polluting effects of activities which threaten groundwater quality, and
5. Control the aggregate impact of certain prescribed activities.

Several acts exist in South Africa pertaining to waste management, actions to be taken against potential polluters, as well as remedial action. The National Water Act, Act 36

of 1998 (NWA), requires site remediation, but very little regulatory guidelines exist on how this is to be attained. Little guidance exists on the processes that must be followed to get from the stage where the problem is identified up to the point of remediation. The task is made more difficult by the fact that all the laws of the different departments must be harmonized in such a way that all the legal implications of a decision are considered so as to prevent illegal processes from occurring. Regulations should drive cleanups and hence site characterization at polluted sites and hazardous waste sites and it is thus imperative that South Africa develops guidelines for site characterization for different types of pollution.

The environmental law and proceedings and remedies as practiced in South Africa, are set out in Figure 2-3 (DWAF, 2001).

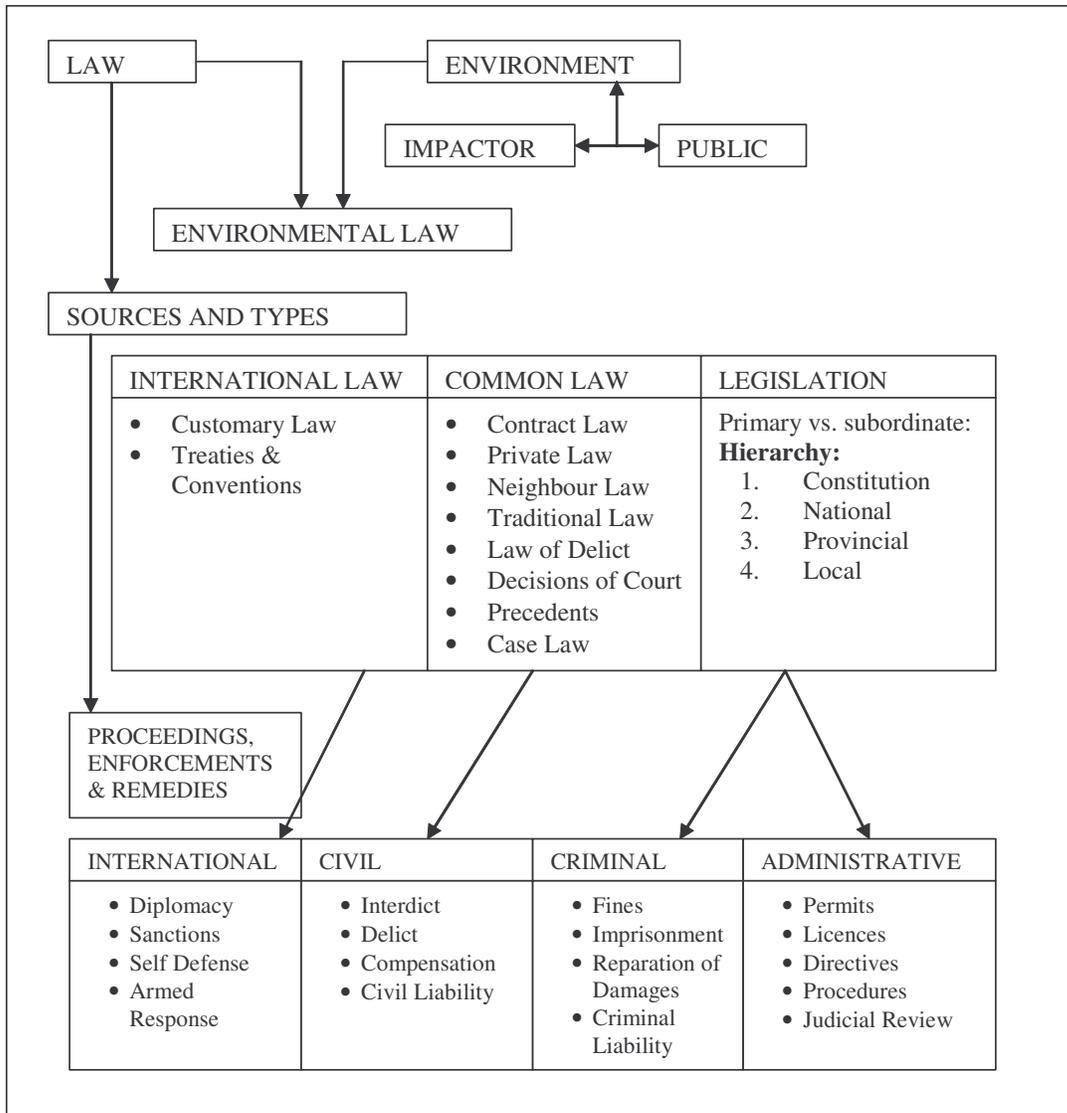


Figure 2-3: The environmental law and proceedings and remedies as practiced in South Africa (DWAF, 2001)

When applying legislation, it must be determined which legislation has the authority to overrule the other. A distinction must be made between original (primary) legislation and subordinate legislation. Original (primary) legislation pertains to Acts of Parliament, as well as laws made by any of the nine Provinces (DWAF, 2001). Subordinate legislation derives its authority from primary legislation. This includes regulations, ordinances, proclamations and authorizations such as licenses, general authorizations, permits and even policy (DWAF, 2001).

A listing of the legislation in South Africa in their relative statutory importance is given as follows:

- Constitution
- Parliamentary or National Legislation (Acts of parliament) – (National Environmental Management Act - NEMA, National Water Act - NWA, Water Services Act - WSA)
- Provincial Legislation
- Laws from 1994
- Proclamations between 1986-1994
- Ordinances before 1986
- Local authority bylaws

This implies that the Constitution is the only legislation that has the authority over the NEMA and NWA, and these acts have authority over provincial laws. The following sections highlight the applicable sections of the various acts and the possible importance to groundwater contamination and remediation.

2.6.1 National Water Act of 1998 (Act 36 of 1998)

The Department of Water Affairs empowered, through the National Water Act (NWA) of 1998 (Act 36 of 1998) to fulfill obligations set out in the Act relating to the use, allocation and protection of, and access to, water resources. The National Water Act thus provides the framework within which the Department can manage the protection, use, development, conservation and control of South Africa's water resources.

There are eleven uses of water in accordance with the National Water Act. The eleven uses are *not rights* and may generally take place only in terms of an authorisation or license.

National government is empowered through the Act to establish suitable institutions and to ensure that they have appropriate community, racial and gender representation. The Act will thus enable the Department to effectively implement its new policies (or regulations) regarding groundwater quality management. The following will be important with regard to groundwater quality management (DWAF, 2000):

1. Groundwater no longer enjoys the status of private water and is now subject to the same control measures as surface water;
2. Powers to monitor, assess, plan and audit performance of all water users have been provided for in the Act;
3. The Department can within its available resources provide extension and support services and play a role in building capacity at community level; and
4. The Department will be able to influence land-use-planning decisions, to regulate or prohibit land-based activities, to develop and implement Best Practice standards and to implement source controls where necessary. Implementation of Best Practice standards as conditions of authorisation managed by other organs of state will be particularly important.

With regard to water pollution the Act allows Government to prosecute any person who “*unlawfully and intentionally or negligently commit any act or omission which pollutes or is likely to pollute a water resource*”. Sections (19) and (151) deals with these offences. The Act requires that the responsible person that caused water pollution, will also be responsible for the remediation of such a site. This is commonly known as “the polluter pays” principal.

The Minister of Water Affairs is further allowed, under the Act, to make any regulations related to the Act (section (69)). An example of such regulations are the “Water Quality Management Series” Documents No. M.1.0 to M.5.0, which are guidelines on management of mining related activities, which may have an impact on water resources.

2.6.2 Environment Conservation Act of 1989 (Act 73 of 1989)

The Department of Environmental Affairs and Tourism is responsible for issuing waste disposal site permits under the Environment Conservation Act of 1989 (Act 73 of 1989). The Department, together with other government departments, has set a waste regulatory system in place (DWAF, 1998).

In terms of Section 20 of the Environment Conservation Act (ECA), 1989 (Act 73 of 1989), waste can only be disposed of at a waste disposal facility that has a permit issued by the Minister of Environmental Affairs and Tourism. Such a facility must be sited, designed, operated and monitored strictly in accordance with the permit conditions.

These conditions will include the requirements, standards and procedures set out in the Department of Water Affairs' Waste Management Series, "Minimum Requirements" documents (1998). To date, three documents were published in 1998; and a third edition was published in 2005.

These are:

- Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste
- Minimum Requirements for Waste Disposal by Landfill, and
- Minimum Requirements for Water Quality Monitoring at Waste Disposal Facilities.

The documents are intended to enforce the permit system and the environmentally acceptable disposal of waste. They also are intended to raise waste management standards in South Africa and to facilitate conformance with the international standards. The approach adopted is the Integrated Waste Management Approach. The aim is to curtail the risks associated with handling and disposal of waste to the point where they are acceptable to man and the environment. Waste management must therefore be carefully planned in advance and take place in the following order (DWAf 1998):

Waste prevention: the prevention and avoidance of the production of a waste, perhaps by regulation.

Waste minimisation: the reduction of the volume of waste during production by means of different processes or clean technology.

Resource recovery: recycling of waste or the recovery of energy through incineration and biodegradation.

Treatment: the treatment of waste to reduce volume or hazardousness

Disposal: the safe disposal of waste so that it will not pollute the environment or cause health hazards.

The Department strongly recommends that waste be managed in accordance with the above principles. Waste prevention, minimisation and resource recovery are the best

options for the management of waste. Further, waste is classified as either general waste or hazardous waste, depending on the risk that the waste poses to the environment.

2.6.3 DNAPLs within the Regulatory Framework

From the above discussion it can be seen that the legal tools do exist by which pollution of water resources from contaminants, including DNAPLs, can be regulated. However, due to the complex transport mechanisms of DNAPLs in the subsurface, specific guidance should be provided by Regulatory bodies regarding the following aspects:

- Site characterisation methods
- Monitoring and sampling guidelines
- Remediation Techniques – especially with reference to Monitored Natural Attenuation (MNA).

The “Minimum Requirements for Water Quality Monitoring at Waste Disposal Facilities” (DWAF, 1998) provides clear guidance on the type of monitoring, frequency of monitoring, number of monitoring boreholes and construction of the boreholes. However, these requirements only take into account inorganic contaminants and do not take into account the unique behaviour of NAPLs in the subsurface which results in complex NAPL distributions. Planning of a site assessment of a DNAPL contaminated site as well as the design of a monitoring network will have to take this behaviour of the contaminants into account. Currently no regulations are available in South Africa to help guide site owners, site assessors and authorities in this regard.

3 Transport and Fate of DNAPLs in the Subsurface

3.1 Introduction

Dense Non-Aqueous Phase Liquids (DNAPLs) behave differently from other contaminants in the subsurface. DNAPLs can occur either as pure compounds, a mixture of compounds, or dissolved in water. The unique behaviour results in the complex DNAPL distributions, which are strongly influenced by geologic heterogeneities and the physical properties of the compounds. DNAPL behaviour differs not only in different aquifer material but also from the vadose to the saturated groundwater zone.

The physiochemical and aquifer properties that control the behaviour of DNAPLs are discussed in Appendix A.

When spilled, DNAPLs will move downward through the unsaturated zone, trapping some (residual) DNAPL in the pore space. If a large volume of DNAPL is spilled and permeability exists in the subsurface, the DNAPL will penetrate past the water table and continue moving downward through the saturated zone due to gravity. The subsequent subsurface migration of DNAPLs is not solely a function of conventional groundwater transport mechanisms (i.e. advection, dispersion and diffusion), but rather a function of geological structures (i.e. fissures, bedding planes, etc.) and gravity (including the bedrock topography). However, soluble constituents of DNAPLs will dissolve into groundwater and their distribution is a function of the hydraulic gradient, resulting in a groundwater plume down gradient from the contaminant source. The potential depth of DNAPL penetration through the vadose zone and into the groundwater will depend on the properties of the DNAPL, the nature of the DNAPL release, and the properties and geological structure within the vadose and groundwater zones.

Up to now the discussion has mostly taken into account the movement of the DNAPL phase. However, DNAPLs tend to partition among different phases (free, aqueous and gaseous) in the subsurface and the *four partitioning processes* which play a role in the fate and transport of DNAPLs are:

- Dissolution into water phase
- Volatilisation of dissolved chemicals from water phase to air phase
- Vapourisation of DNAPL into air phase, and
- Sorption of dissolved chemicals from water to solids.

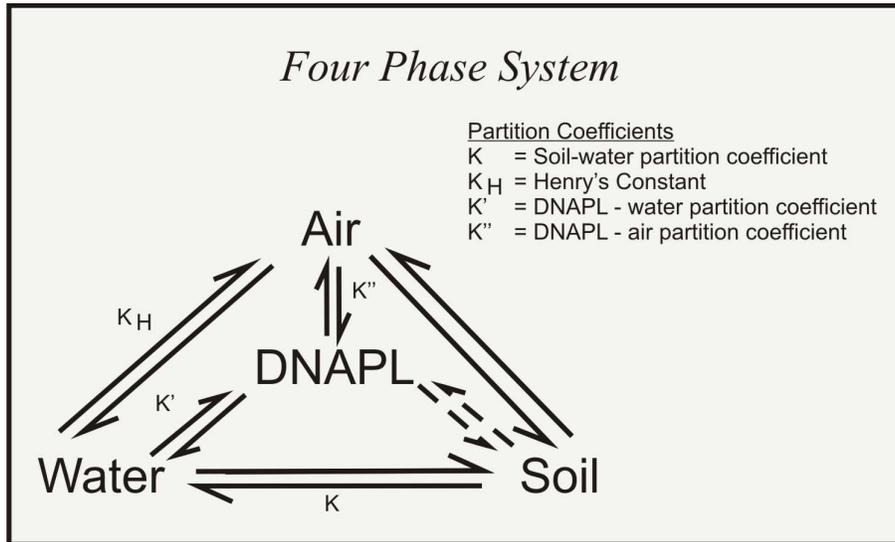


Figure 3-1: Distribution of DNAPL between the four phases found in the vadose zone (From Huling and Weaver, 1991).

The concept of phase distribution is critical in all decision making. Understanding the phase distribution of a DNAPL introduced into the subsurface provides significant insight in determining which tools are viable options with respect to site characterization and remediation. DNAPL represented by residual saturation in the four-phase diagram (Figure 3-1) is largely immobile under the usual subsurface pressure conditions and can migrate further only: (1) In water according to its solubility; or (2) In the gas phase of the unsaturated zone.

DNAPL components adsorbed onto the soil are also considered immobile. The mobile phases are, therefore, the soluble and volatile components of the DNAPL in the water and air, respectively (Huling and Weaver, 1991).

3.2 DNAPLs in the Vadose Zone

Studies at most industrial sites show that DNAPLs will tend to penetrate through the vadose zone into the groundwater zone where most of the DNAPL mass will accumulate and then cause persistent contamination (Pankow and Cherry, 1996). It is

however possible where the water table is exceptionally deep or where the volume is small that the entire mass of DNAPL may reside within the vadose zone.

Residual DNAPL, in the form of disconnected blobs and ganglia of organic fluid, is formed at the trailing end of a migrating DNAPL body. The individual blobs and ganglia of organic liquid comprising residual DNAPL are typically between 1 and 10 grain diameters in length (Kueper *et al.*, 2003). Residual DNAPL is held in place by capillary forces that arise because the interface between the DNAPL and water, and the interface between DNAPL and air, is in a state of tension.

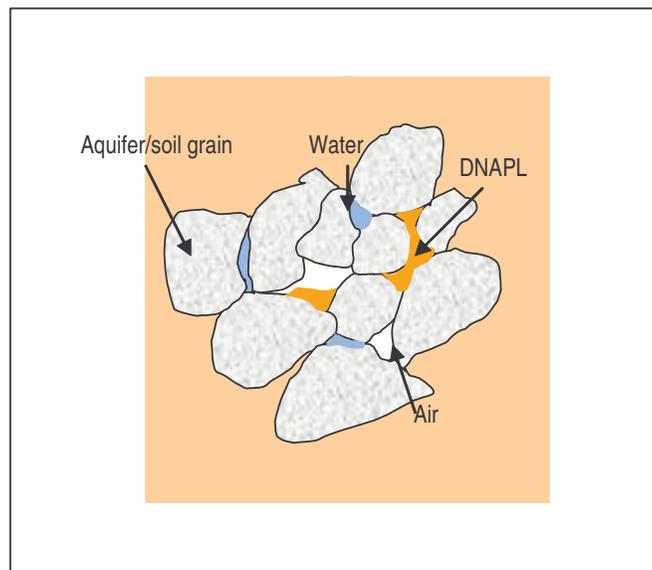


Figure 3-2: Residual DNAPL in the unsaturated or vadose zone (From Kueper *et al.*, 2003)

The residual DNAPL is exposed to both air and water. This allows for both vapourisation into the air phase across DNAPL-air interfaces and dissolution into infiltrating water across DNAPL-water interfaces. Once present in soil moisture, dissolved contaminants will be available for partitioning across air-water interfaces (volatilisation).

Because the vapour pressure of many DNAPL compounds is relatively high, the lifespan of residual DNAPL in the unsaturated zone can be much less than the lifespan of residual DNAPL below the water table. This will not eliminate the presence of vapour phase, absorbed phase and aqueous phase contamination in the unsaturated zone, but it can lead to an absence of the DNAPL phase. The vapourisation process can deplete residual chlorinated solvent DNAPLs such as TCE and PCE within 5-10 years

in relatively warm and dry climates (Kueper *et al.*, 2003).

This vapourisation process causes a vapour plume to develop in the surrounding air in the soil. The vapour plumes can contribute to the dissolved mass in the groundwater in several ways:

1. When infiltrating water comes into contact with this vapour plume a groundwater plume can develop
2. In the case of DNAPLs with greater vapour densities, density driven advection in high permeability media, can enhance downward movement of vapour to the water table
3. A fluctuating water table can also trap vapour in the water table zone
4. Diffusion of DNAPL vapour across the capillary fringe can also contribute to the dissolved mass in the groundwater zone

Thus, the absence of a DNAPL in the unsaturated zone at a site should not, in general, be used as a basis for concluding that past releases of DNAPL did not occur at that site or that past releases of DNAPL failed to reach the water table.

3.3 DNAPLs in the Groundwater (Saturated) Zone

If the release of NAPL is large enough, and the density is higher than that of water, the DNAPL will move through the vadose zone and penetrate to below the water table into the saturated zone. The distribution of DNAPL and other phases will therefore be a function of the NAPL properties and the aquifer media.

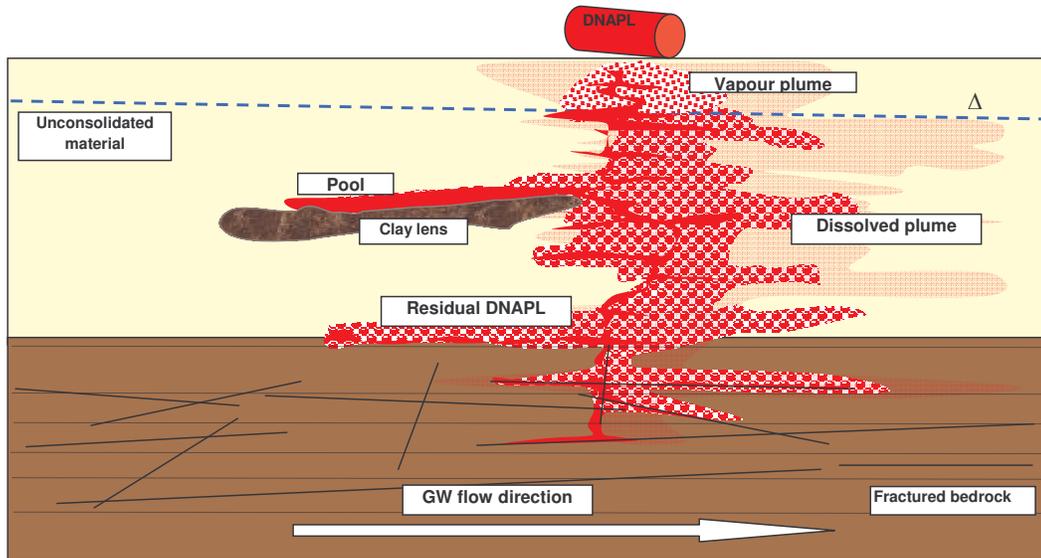


Figure 3-3: DNAPL distributions in unconsolidated deposits and fractured bedrock

Due to the lack of air (or gaseous phase), the saturated zone containing DNAPL is considered a three-phase system consisting of the solid (soil), water, and immiscible fluid (DNAPL).

Figure 3-4 indicates the three phases and the transfer of the mass of contaminant between the phases. There are therefore only three pathways of phase distribution in the saturated zone, except at the water table.

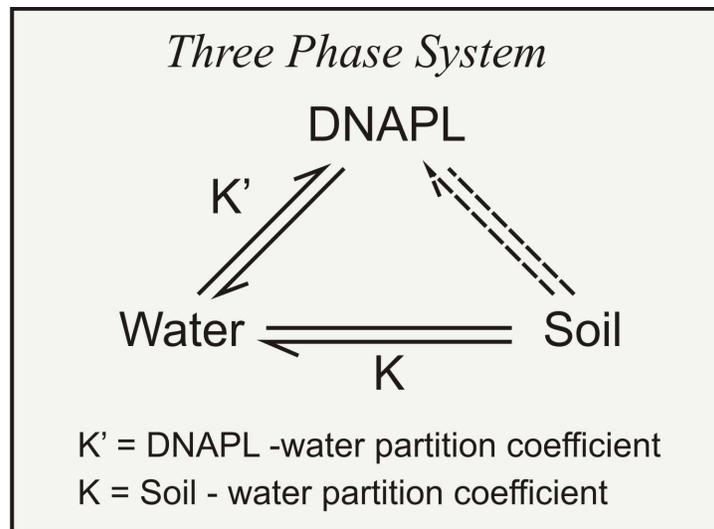


Figure 3-4: Distribution of DNAPL between the three phases found in the saturated zone (From Huling and Weaver, 1991).

3.3.1 Porous Media

The bulk of literature on DNAPL fate and transport is focused on porous or intergranular flow aquifer systems. The reason being that many of North America and Europe's water supply comes from these types of aquifers. The transport and fate in these systems have thus been well researched and documented (Pankow and Cherry, 1996).

The DNAPL phase will be distributed in porous media depending on the layering or bedding planes. As the DNAPL moves downwards, some residual DNAPL will be entrapped on the pathway downwards. Any contrast in grain size distribution (permeability) will cause a change in entry pressure (Pankow and Cherry, 1996). A higher entry pressure will be encountered at any change to a smaller grain size and, this will cause lateral spreading of the DNAPL phase. The DNAPL will accumulate (pool) on the finer grained layer and continue to spread laterally until the height of the layer (pool) exceeds the entry pressure for the layer (Figure 3-5).

Residual and pooled DNAPL collectively form what is referred to as the DNAPL source zone. It is within the DNAPL source zone that dissolution into groundwater occurs and aqueous phase plumes originate. The DNAPL migration along these multiple pathways, in a very tortuous manner; is sometimes referred to as dendritic form (Figure 3-5) due to its resemblance to the branches of a tree (Schwille, 1988). The specific migration pathways will be governed by the variations in permeability and capillary characteristics, and the ultimate depth of migration is a function of the source release strength and the porous media structure (Kueper, *et al.*, 1993). Migration will also occur along pathways such as bedding plane structures on the scale of millimetres to metres. In horizontally bedded media, significant amounts of lateral spreading can be expected, including in directions not coincident with the direction of groundwater flow.

Predicting the exact pathway of the DNAPL source zone is therefore very difficult and requires detailed and complex determination.



Figure 3-5: Example of a two-layer bead medium, initially saturated with water. Entry of smaller pore space by DNAPL only after sufficient pressure as result from pool height (From Schwille, 1988).

The height of DNAPL that can accumulate above a capillary barrier below the water table can be estimated using Equation 19 (Kueper *et al.*, 1993):

$$H = (P_c'' - P_c') / (P_D - P_w)g \quad \text{Equation 1}$$

Where:

H is the height of pooled DNAPL; P_c'' is the capillary pressure at the base of the pool; P_c' is the capillary pressure at the top of the pool; P_D is the DNAPL density; P_w is the groundwater density; g is the acceleration due to gravity.

Larger pool heights can form for higher DNAPL-water interfacial tension, lower DNAPL density and lower capillary barrier permeability. For chlorinated solvents and PCB DNAPLs, pool heights typically range from a few centimetres to several tens of centimetres. For creosote and coal tar, DNAPL pool heights are generally larger than those associated with PCB and chlorinated solvent DNAPLs because of the lower density of these compounds. This had led to a useful rule of thumb that in horizontally bedded media, 'DNAPL must migrate sideways in order to migrate down' (Kueper *et al.*, 2003).

The goal of a site characterization should be to define the lateral extent of the DNAPL source zone, without specific delineation of residual DNAPL and DNAPL pools within the overall source zone. Given the complex nature of DNAPL migration, it follows that the majority of porous media within a DNAPL source zone will contain neither residual nor pooled DNAPL. The probability of directly encountering residual or pooled DNAPL with conventional site investigation methods (including drilling) is therefore relatively small. It is now commonly accepted that direct visual observation of DNAPL does not occur at most DNAPL sites.

The overall bulk retention capacity of porous media within a DNAPL source zone is generally thought to range from approximately 0.5 to 3 %. This retention capacity is defined as the volume of DNAPL (as both residual DNAPL and pools) divided by the overall bulk volume of the source zone. These values are lower than local-scale residual saturations (5 - 20 % of the pore space) because they are expressed in relation to the bulk volume impacted and because not all lenses and laminations within the impacted zone will have been invaded by the DNAPL. Exceptions will occur at some sites, with some source zones containing bedding structures and capillary properties capable of retaining higher amounts (Kueper *et al.*, 2003).

3.3.2 Fractured Non-Porous Media

The pattern of DNAPL migration in a fractured media will be controlled by the orientation and interconnection of the fractures. DNAPL will move laterally along horizontal fractures and downward along vertical fractures.

DNAPL will enter fractures in bedrock both above and below the water table. Analogous to unconsolidated deposits, both residual DNAPL and pools will form in rock fractures, with a higher likelihood of pool formation in horizontal to sub-horizontal features. Fracture entry pressures are directly proportional to interfacial tension and inversely proportional to fracture aperture. This results in preferential DNAPL migration through the larger aperture fractures of a fracture network. Once DNAPL enters a fracture network, it is likely that downward and lateral migration will occur until the DNAPL source is exhausted.

The scenario that DNAPL will pool on top of a fractured formation is unlikely and it would rather continue the downward migration through the fracture system (Figure 3-3).

The reason being, that capillary pressure increases linearly with depth in a hydrostatic system, which implies that a fracture aperture would need to be extremely small to support the overlying distribution of DNAPL. The fracture aperture required to stop migration denotes the largest aperture that can exist at a corresponding depth such that DNAPL migration is arrested. It should however be considered that all fractures are rough walled and exhibit a range of apertures within a fracture plane. This is analogous to the concept of pore throat in a porous medium, and the DNAPL will enter only the fracture aperture (or pore throat) large enough to support the required entry pressure.

For chlorinated solvents such as TCE, fracture apertures need to decrease quickly with depth in order to prevent further downward migration. Experience has shown that fractures can remain open to depths of many hundreds of metres in many rock types, with measured apertures in the order of hundreds of micrometers at many sites (Kueper, *et al.* 2003).

It is calculated for less dense DNAPLs such as creosote and coal tar that a less drastic reduction in fracture aperture with depth is required to arrest downward migration, but that significant reductions are still required to support an accumulation of DNAPL. It is therefore very likely that by the time a site investigation has started that a more dense and less viscous DNAPL (e.g. solvents) would have stopped downward migration, as opposed to a less dense, more viscous DNAPL (creosote or coal tar). This behaviour was observed at Test Site 1 (Section 5.3.4.2).

The overall ability of fractured bedrock to retain residual and pooled DNAPL is relatively small given the low fracture porosity of most rock types. A typical fractured rock, for example, may exhibit fracture porosities in the range of 0.001 to 0.01. Assuming that DNAPL will occupy on average 20 percent of the fracture pore space, this range of fracture porosities corresponds to bulk retention capacities ranging from 0.0002 m³ DNAPL per m³ of bedrock to 0.002 m³/m³ (that is, between 200 ml and 2 litres of DNAPL per m³ of rock). This implies, for example, that one drum of DNAPL containing 205 litres (0.205 m³) of product will occupy a bulk bedrock volume of 103 - 1025 m³. From this it is clear that relatively small volumes of DNAPL have the potential to impact relatively large volumes of bedrock. This conclusion holds for many of the hard rock aquifer types in South Africa.

The maximum depth to which a DNAPL will penetrate in a fracture network therefore depends on fracture aperture, number and type of fracture connections, the physical properties of the DNAPL and the height of the column of continuous DNAPL above the fractures at the front of the DNAPL zone. At some sites it is known that DNAPLs have penetrated to depths of several hundreds meters below surface (Pankow and Cherry, 1996).

From the above it is evident that geologic structure and the in situ stress fields control the occurrence of fractures, which are the predominant mechanism for NAPL movement. No formation is uniformly fractured, and thus the assumptions of formation homogeneity and even anisotropy that are commonly applied in porous media are not appropriate for the description of NAPL movement in fractured rocks. Any site characterisation in fractured rock should focus on the spatial distribution of the hydraulic properties such as conductive fractures or other geologic features (Shapiro, 2003).

3.3.3 Fractured Porous Media

The discussion above has focused on the migration of DNAPL through hard rock fractures, and assuming very little or no matrix porosity. In cases where the rock matrix is relatively porous, some entry of DNAPL into the rock matrix may also occur. This is generally not a concern in crystalline rocks, but is a concern in the formations such as sandstones, fractured clay and porous dolomites. In South Africa most of the aquifer types utilized on large scale, fall within this category. These include the Karoo aquifers, Table Mountain sandstone aquifers and dolomitic aquifers.

In fractured porous media the relative large volume of pore space or voids in the matrix will influence the migration of the dissolved plume, the persistence of the DNAPL phase and the design of the monitoring and remediation efforts (Pankow and Cherry, 1996). As in fractured media the DNAPL phase in the fractures will gradually dissolve. However, in fractured porous media the dissolved phase can enter the water in the matrix and sorb to the matrix solids through matrix diffusion. Matrix diffusion refers to the process whereby solutes dissolved in groundwater diffuse into and out of the rock matrix due to concentration difference. This process therefore causes a change in physical state of the DNAPL mass, to dissolved and sorbed phases.

Matrix diffusion will occur in all rock types exhibiting a finite matrix porosity. If concentrations are higher in the open fracture, the diffusion process will result in dissolved contaminants moving into the matrix (forward diffusion). If concentrations are higher in the matrix, dissolved contaminants will move out of the matrix and into water in the open fractures (back diffusion). This process of forward and backward diffusion can lead to persistence of contaminants in an aquifer long after the DNAPL source has disappeared.

Parker (2003) reported that from analysing thousands of core samples of shales, limestones, and dolomites, at chlorinated solvent contaminated sites, that matrix diffusion caused complete dissolution of the contaminants from the fractures over several decades. The measurements showed that matrix diffusion halos along fractures are large and measurable and that nearly all the contaminant mass resides within the rock matrix rather than in the fracture system.

The matrix diffusion process causes solute plumes in fractured porous media, to migrate slower than the rate of groundwater flow. The rate of plume advance, can therefore be significantly attenuated relative to the rate of groundwater migration, with attenuation rates as high as 100 or more (Kueper, *et al.*, 2003). The attenuation is greater for smaller aperture fractures, higher matrix porosity and slower moving groundwater. This explains why solute plumes in fractured porous media are often smaller in spatial extent than predicted by groundwater velocity calculations alone.

The timescale of remediation in fractured rocks is often controlled by the back diffusion process and not by the presence of DNAPL in fractures. The concentration gradient driving back-diffusion is typically less than the initial concentration gradient driving forward-diffusion into the matrix while residual DNAPL is present in the fracture. In fractured environments exhibiting matrix diffusion, conventional technologies such as pump-and-treat should be viewed as either a source zone containment technology, or a plume interception technology, not as a technology capable of restoring groundwater to near-pristine quality within short periods. The effectiveness of many remedial techniques is diffusion limited and this process needs to be considered during development of a remedial strategy, and selection of a remedial technique.

In fractured porous media the volume of pore space available for contaminant mass is

measured as, the total fracture porosity, plus the matrix porosity. In situations where DNAPL in the fracture network continues (e.g. continues source), the maximum storage capacity is attained when all the pore water in the matrix is at solubility limit (Pankow and Cherry, 1996).

Apart from matrix diffusion, the process whereby a change in the wetting phase occurs, displacement of the DNAPL into the matrix can also occur. E.g. the DNAPL is wetting or becomes wetting, with respect to water, then spontaneous imbibition (displacement) of the DNAPL into the matrix can occur (Kueper, *et al.*, 2003). This is not a common phenomenon with DNAPLs but is sometimes observed in case of coal tars.

3.4 Plumes from DNAPLs

Both the residual and pooled DNAPL (source zone) will give rise to an aqueous (water) phase plume. From the above discussion, it is evident that the nature and extent of the aqueous phase plumes will be determined by the spatial distribution of the DNAPL source, and the aquifer media and lithology. These plumes could thus achieve great spatial variability within the aquifer. Measuring concentrations through sampling of observation boreholes can thus be misleading and several factors have to be considered.

The influence from dispersion on aqueous plumes of DNAPLs is similar to that on inorganic plumes. The plume would be long and narrow for weak dispersion, and wide and fan-shaped for strong dispersion (Pankow and Cherry, 1996). Dispersion always occurs in the subsurface and results in a lowering of concentrations along the centreline of a plume in the downstream direction. This is because contaminant concentrations decrease in the transverse direction (both horizontally and vertically) away from the plume centre line.

The maximum concentrations can thus only be observed immediately adjacent to the DNAPL source zone, and this maximum will not be observed anywhere down-gradient of the source zone.

In-borehole dilution can lead to the measuring of lower concentrations than actual concentrations in the aquifer. This refers to the fact that the monitoring borehole draws in both the local contaminant plume as well as surrounding uncontaminated water. The result is a mixing of clean and contaminated water in the monitoring well, and a

resulting lowering of concentrations in the obtained sample relative to what may be present in the aquifer immediately adjacent to the borehole. In addition to mixing during purging, this in-borehole dilution effect can occur naturally if vertical flow gradients exist within the borehole (Kueper *et al.*, 2003). Biotic and abiotic degradation can also result in the lowering of concentrations in the down-gradient direction within a contaminant plume.

Therefore, the net effect of hydrodynamic dispersion, in-borehole dilution, monitoring borehole placement and potential degradation processes is that contaminant concentrations in a sample obtained from a monitoring borehole downstream of a DNAPL source zone may be significantly less than the aqueous solubility of the DNAPL of interest.

Experience has shown that a DNAPL source may be present upstream of a monitoring borehole, if the water sample concentrations exceed 1 per cent of the effective solubility of the component of interest (USEPA, 1993). The 1 per cent 'rule of thumb' has been criticised because it does not provide guidance on how far upstream the DNAPL source zone is located. It is clear that a variety of site-specific factors influence the magnitude of sampled contaminant concentrations and that some of these factors cannot be determined. The 1 per cent 'rule of thumb' should be used as a means of establishing that DNAPL may be present upstream of the monitoring point in question, and therefore as a means of justifying the use of additional site investigation techniques to confirm or refute the presence of DNAPL (Kueper *et al.*, 2003).

Once DNAPL is present in a fractured aquifer, it will also slowly dissolve into groundwater flowing through open fractures, giving rise to aqueous phase plumes. The plumes will generally migrate in the hydraulically down-gradient direction subject to advection, dispersion, sorption to fracture walls, possible biodegradation and matrix diffusion. As with plume migration in unconsolidated deposits, the chemical composition of the plume will be a function of the chemical composition of the DNAPL.

If the DNAPL of interest is composed of a mixture of components, these components will not dissolve into groundwater at their single component, textbook solubility values. Rather, the dissolution of a multi-component NAPL will be according to Raoult's law.

The dissolution of a multi-component DNAPL into groundwater will be characterised by the preferential depletion of the higher effective solubility components at an early time. The lower effective solubility components will display slower rates of concentration decrease with time; with some components displaying moderate increases in concentration with time. The total concentration of all components will decrease with time.

3.5 Attenuation and Degradation Processes affecting DNAPLs

Natural attenuation (NA) processes include a variety of physical, chemical or biological processes that, under favourable conditions, act ‘without human intervention’ to reduce the mass, toxicity, mobility, volume or concentration of contaminants in soil or groundwater. Biological degradation of DNAPL in source zones is based on the ability of micro-organisms to transform chemical constituents within close proximity to the DNAPL surfaces (the order of 100 μm), thereby resulting in enhanced rate of dissolution of the DNAPL constituents (Carey, 2000).

The processes that affect solute contaminant transport may be divided into three groups:

1. Physical (dispersion, diffusion, dilution and volatisation),
2. Geochemical (sorption and chemical or abiotic reactions), and
3. Biochemical (biodegradation) processes.

Some of these processes result in a loss in contaminant mass (destructive, such as degradation); some transfer contaminant from the mobile phase to an immobile phase (retardation) and some may simply redistribute contaminant within the mobile phase (dispersion).

It should be noted that in the NAPL form, rather than dissolved in water or sorbed on soil particles, organic contaminants are not readily degraded biotically or abiotically. Additionally, dispersion, dilution and sorption of the NAPL are slow. Therefore, it is important to determine where this NAPL may be at a polluted site, in order to remove or contain as much of this source, as possible, because the processes of natural attenuation would not effectively remediate most of this material in a reasonable time (USEPA, 1998).

Table 3-4 gives the dominant attenuation mechanisms for principal groundwater

contaminant groups. (Contaminant types include more than DNAPL contaminants; other contaminants listed are often associated with DNAPL contaminated sites.)

Table 3-1: Dominant attenuation mechanisms for principal contaminant groups (Modified from Carey *et al.*, 2000)

| Contaminant type | Examples | Non-degradative attenuation mechanisms | | | | | | Degradative attenuation mechanisms | | | | | |
|---|--|--|---------------------------------|----------------------|------------|-----------|----------------|---|--|---|--------------|---------------|---------------------|
| | | Methylation | Precipitation & cation exchange | Sorption and binding | Dispersion | Diffusion | Volatilisation | Aerobic degradation (contaminant as electron donor) | Anaerobic degradation (contaminant as electron acceptor) | Reductive dehalogenation (contaminant as electron acceptor) | Fermentation | Co-metabolism | Oxidation/reduction |
| Chlorinated Solvents* ≥ 3 chlorine atoms ≤ 3 chlorine atoms | PCE, TCE, TCA, TCM DCM, VC, DCE | | | x | | | x | x? | x | xx | | x | x |
| | | | | x | x | x | x | xx | x | | x | x | |
| Petroleum hydrocarbons | BTEX, middle distillates | | | x | x | x | x | xx | x | | x | x | |
| Oxygenates | MBTE, EBTE, | | | | x | x | x | xx | | | | x | |
| PAHs* | Naphthalene | | | xx | x | x | | x | x | | | x? | |
| Creosote* | Phenols and phenolics | | | | x | x | x | xx | xx | | x | x | |
| Pesticides* | Chlorinated; organophosphate; pyrethroid; triazine; phenyl urea; phenoxyacid; cationic | | | x | x | x | | x | x | x? | | x? | |

xx = primary importance; x = secondary importance; x? = some doubt exists over the process

* Contaminant groups are classified mainly as DNAPL contaminants

Certain contaminant characteristics can favour NA processes. These are typically:

1. Low toxicity (or low solubility relative to toxicity-based environmental standard) – this minimises the risk of exceeding an environmental quality standard;
2. Moderate solubility – this reduces the risk of a high contaminant loading developing which, depending upon the groundwater velocity and dispersion, may present a risk to receptors and inhibit degradation;
3. Non-reversible (destructive) mechanisms are preferred to (non-destructive) reversible processes; and
4. Rapid degradation (for example, low half-life) relative to groundwater velocity to reduce the risk that the contaminant may “break through” at a receptor;

The physical properties of an aquifer that have the greatest impact on the application of NA are the flow rate and flow mechanism present and the hydraulic conductivity. Preferential groundwater pathways, including fractures, joints and solution channels result in higher contaminant velocities, which in turn, may lead to rapidly expanding contaminant plumes where attenuation is limited. Groundwater flow under these conditions is highly unpredictable, making plume characterisation difficult. Intergranular flow is more predictable and the travel rates are lower, providing greater time for degradation to occur and longer exposure of contaminants to active biodegradative/ mineral sites (Keuper, *et al.* 2003).

The hydraulic conductivity of an aquifer depends upon a number of physical factors including porosity and particle size distribution. The favoured aquifer characteristics for the assessment of NA are isotropic, intergranular flow mechanisms, as these provide the opportunity to predict groundwater flow patterns and attenuation processes with the greatest confidence. By contrast, characterisation of the hydraulic regime in fractured aquifers is complicated by the highly heterogeneous nature of the system. Long-term predictions in the performance of NA are, therefore, likely to be inherently uncertain.

3.5.1 Non-degradative attenuation mechanisms

The non-degradative mechanisms discussed in this section may reduce the concentration of a contaminant, but do not necessarily affect its mass, toxicity or mobility.

Table 3-2: Non-degradative mechanisms that may reduce the concentration of a contaminant in the system (Adapted from Carey, 2000).

| Mechanism | Result | When is it important? |
|--|---|---|
| Dilution: mixing of contaminated water by unpolluted groundwater | <ul style="list-style-type: none"> • Reduce groundwater concentrations • Infiltration may be important in introducing electron acceptors where contaminants are being microbiologically degraded. | <ul style="list-style-type: none"> • Small quantities of contaminant • Recharge from uncontaminated infiltration of precipitation away from the source area • Contaminated groundwater discharging to a clean surface water resource or mixing with clean water before an abstraction point. |
| Dispersion: value of dispersion will directly reflect the heterogeneity of the system | <ul style="list-style-type: none"> • Reduce concentrations by spreading the contaminant | <ul style="list-style-type: none"> • Heterogeneous systems • When scale of the plume or system increases, dispersion also increase • May facilitate biodegradation by reducing contaminant concentrations below toxic thresholds and spreading the plume into areas with electron acceptors. |
| Diffusion: slow in comparison to mechanical dispersion | <ul style="list-style-type: none"> • Movement of contaminants from regions of higher concentration to lower concentration | <ul style="list-style-type: none"> • Only significant in no-flow or very low-flow systems or over very long time-scales. • For dual-porosity systems, e.g. Karoo aquifers, diffusion of contaminants from the mobile 'fracture' water to the less mobile 'pore' water may be an important mechanism in retarding contaminant movement. Reverse diffusion from the pore water may act as a persistent secondary source of contamination. |
| Solution/precipitation: | <ul style="list-style-type: none"> • E.g. precipitation as insoluble sulphides and carbonates • But may be dissolved back into solution • | <ul style="list-style-type: none"> • When physiochemical conditions change, e.g. pH, redox changes result in changes to solubility and influence dissolved concentrations. |

| Mechanism | Result | When is it important? |
|---|---|---|
| <p>Sorption: interaction of a contaminant between water and soil/rock matrix</p> <ul style="list-style-type: none"> • adsorption, the attachment of a solute to a solid surface; • absorption, the movement of a solute (diffusion) into the structure of a porous particle where it sorbs onto an internal surface • ion exchange, the replacement of a sorbed ion by the contaminant | <ul style="list-style-type: none"> • Reduce contaminant concentrations by their removal from solution • Retard the rate at which contaminants move through the system | <ul style="list-style-type: none"> • Desorption is generally slower than sorption therefore sorbed contaminant may represent a longer-lasting source • Extent of contaminant sorption may influence the efficiency of other attenuating mechanisms, such as biodegradation • Sorption is a function of: <ul style="list-style-type: none"> ○ Nature of the contaminant (conservative or non-conservative) ○ Contaminant concentration in solution ○ Nature and concentration of other contaminants (competition with other contaminants may reduce the number of sites for sorption or some organic contaminants may provide additional sites for further sorption) ○ Nature of the soil/rock matrix, including available surface area ○ the presence of clay, organics and oxyhydroxides which may provide ideal sites for sorption ○ pH and redox potential of the system may influence sorption ○ Flow rate may influence the time available for sorption. • For non-polar organic and inorganic contaminants, sorption occurs preferentially to soil organic matter or to clay minerals. In most aquifers, sorption to organic matter is the dominant process, except where the organic content is low and then sorption to mineral surfaces (i.e. iron oxides) is the main process (Karirickhoff, Brown, and Scott, 1979). |
| <p>Volatilisation</p> | <p>Removal of contaminant mass, but is not destructive.</p> | <ul style="list-style-type: none"> • Physicochemical characteristics of the contaminant • Site-specific conditions incl. temperature, depth to water and porosity. • Primarily in the unsaturated zone |

3.5.2 Degradative attenuation mechanisms

Not all the mechanisms actually remove mass from the plume. It is often difficult or impossible to determine in the field the exact mechanisms functioning to transform the contaminants. However, an understanding of the geochemical environment and the patterns of contaminant degradation are essential to discerning the likely degradative processes at a site. Knowledge of the degradative mechanisms will help the investigator determine the effectiveness of a natural attenuation remedy, the need for supplemental remediation and to design a long-term monitoring programme.

Unlike metals which cannot readily be destroyed, the mass of organic and inorganic compounds (such as ammonia) may be reduced by (bio)chemical reactions comprising hydrolysis (reaction with water, acids and bases), photolysis (reaction with sunlight or with reactive radicals produced by light energy), biodegradation (reaction with enzymes or other biogenic compounds), oxidation, and reduction/elimination reactions (Carey, *et al.* 2000).

3.5.2.1 Abiotic reactions

Abiotic reactions include the chemical transformation of contaminants. The transformation products may be in a less mobile, less reactive or less toxic form. Examples of abiotic reactions are *hydrolysis*, (reaction with either water or a hydroxide ion to produce an alcohol), *substitution* (reaction with another anion as the nucleophilic agent), *elimination* (two adjacent groups within the molecule are lost, resulting in the formation of a double bond) and *oxidation/reduction* (transfer of electrons from one compound to another). Rates of abiotic degradation may vary from days to hundreds of years, but this process is generally slower than biodegradation.

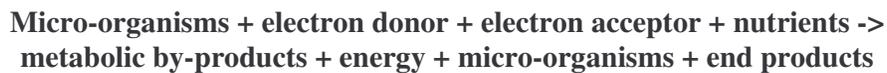
The most common abiotic reactions are hydrolysis (the halogen is replaced with a hydroxyl (OH-) group) and dehydrohalogenation (an elimination reaction that removes a halogen and a hydrogen from adjacent carbon atoms in an alkane and produces an alkene). Substitution and abiotic oxidation reactions also occur for NAPLs. Abiotic degradation primarily affects chlorinated and brominated methanes and ethanes. The kinetics of abiotic reactions varies greatly with each contaminant, such that intermediates tend to accumulate. Often, biotic processes (which change pH and redox

potential) are necessary to stimulate abiotic reactions (Wiedemeier *et al.*, 1998).

The most well-documented abiotic degradation reactions involve carbon tetrachloride, chloroform, chloromethane, trichloroethane (TCA) and chloroethane.

3.5.2.2 Biotic reactions

Biotic (biological) degradation is the dominant process controlling the fate and transport of many organic contaminants. Organic compounds are biodegraded via biological oxidation when electron donors, electron acceptors and nutrients are combined by micro-organisms to produce metabolic by-products and energy for microbial growth. Depending on groundwater geochemistry, microbial population and contaminant properties, biodegradation may occur under aerobic and/or anaerobic conditions. Dissolved contaminants such as trichloromethane are transformed into innocuous by-products such as carbon dioxide, chloride, methane and water. However, intermediates may be generated which are more toxic and mobile than the original compounds. This may be represented by the following generalised equation:



All degradative mechanisms involve the transfer of electrons to or from the contaminant molecule. Micro-organisms almost always mediate this transfer of electrons. The oxidative state of the environment as well as the contaminant determines the direction of the electron transfer and whether a particular transfer is likely to occur. Biodegradation of chlorinated compounds in groundwater occurs via three basic mechanisms (Carey, *et al.*, 2000):

1. As a primary growth substrate (i.e., micro-organisms use the contaminant as food for energy and growth)
2. As an electron acceptor (i.e., micro-organism 'breathes' the contaminant)
3. Through co-metabolism (i.e., the contaminant is fortuitously degraded without producing energy for the micro-organism)

Microbial degradation requirements include: electron donors (availability of a carbon source), electron acceptors (e.g., oxygen, nitrate, iron (III), manganese (IV), sulphate, and carbon dioxide in this energy sequence), essential nutrients and proper

environmental conditions (proper range of pH, temperature, salinity, redox potential).

With regard to this discussion, enzymes are responsible for the degradation of organic carbon, which is used by the bacterial cell to produce both the building blocks of life and energy. The degradation of any organic molecule, including contaminants, requires the production and efficient utilisation of enzymes. In most instances, degradation is merely a complex oxidation/reduction reaction. The electrons or reducing equivalents (hydrogen or electron-transferring molecules) produced must be transferred to a terminal electron acceptor (TEA). During the transfer process, energy is produced which is utilised by the cell. With regard to TEAs, bacteria are generally grouped into three categories:

1. Aerobic bacteria — bacteria which can only utilise molecular oxygen as a TEA. Without molecular oxygen, these bacteria are not capable of degradation.
2. Facultative aerobes/anaerobes — bacteria, which can utilise molecular oxygen or when oxygen concentrations are low or non-existent, may switch to nitrate, manganese oxides or iron oxides as electron acceptors.
3. Anaerobes — bacteria which cannot utilise oxygen as an electron acceptor and for which oxygen is toxic. Though reactions may utilise nitrate or other electron acceptors, it may be said that they generally utilise sulphate or carbon dioxide as electron acceptors.

In general, all ‘types’ of bacteria (e.g., aerobic, anaerobic) are present at all sites. However, all bacteria involved in all of the potential biodegradation pathways for chlorinated solvents are not necessarily present at every site. For example, it is believed that all of the bacteria needed for the reductive dechlorination of PCE or TCE to DCE are present at approximately 90% of all sites and all of the bacteria needed for the reductive dechlorination of PCE or TCE to ethene are present at approximately 75% of all sites (Weidemeier, *et al.*,1999).

McCarty (1997) provides a general review of the redox-dependent biodegradability of chlorinated ethenes. In summary, the complete transformation from PCE and TCE to ethene will occur only under methanogenic conditions. Under less reducing conditions, PCE and TCE may be transformed to DCE, but will not be transformed further to vinyl chloride or ethene. Reductive dechlorination of these chlorinated ethenes will not occur

in the nitrate reducing zone.

Table 3-3: Common degradation processes for different chlorinated hydrocarbons

| Degradation Process | | PCE | TCE | DCE | VC | TCA | CT | CF | DCM |
|-----------------------------------|---------------------------|-----|-----|-----|----|-----|----|----|-----|
| Aerobic Biodegradation | Primary Substrate | N | N | Y | N | N | N | N | Y |
| | <i>Methane/Alkanes</i> | N | Y | Y | Y | Y | N | Y | Y |
| | <i>Aromatics</i> | N | Y | Y | Y | N | N | N | N |
| | <i>Ammonia</i> | N | Y | Y | Y | Y | N | Y | Y |
| <i>Cometabolism supported by:</i> | | | | | | | | | |
| Anaerobic Biodegradation | Primary Substrate | N | N | N | Y | N | N | N | Y |
| | <i>Denitrification</i> | Y | Y | Y | Y | N | Y | Y | Y |
| | <i>Iron Reduction</i> | Y | Y | Y | Y | Y | Y | Y | Y |
| | <i>Sulphate reduction</i> | Y | Y | Y | Y | Y | Y | Y | Y |
| | <i>Methanogenesis</i> | Y | Y | Y | Y | Y | Y | Y | Y |
| Chemical Degradation | | N | N | N | N | Y | Y | N | N |

The parameters to measure for biotic degradation of chlorinated solvents may include:

- Temperature
- Redox potential
- Dissolved Oxygen
- Sulphide
- Iron (II)
- Methane, ethane/ethene
- Alkalinity
- pH
- Sulphate
- Nitrate
- Chloride
- Dissolved Organic Carbon (DOC)
- Hydrogen

Aerobic degradation is a transformation and/or elimination of an organic compound by micro-organisms in the presence of oxygen. This is often the most thermodynamically favoured reaction, providing the greatest energy to the micro-organism.

The three modes of contaminant degradation have already been referred to. The aerobic case occurs when the contaminants, for example, petroleum hydrocarbons, are utilised by bacteria as a sole source of carbon. Petroleum hydrocarbons are degraded through a series of enzymatic reactions to produce needed cellular constituents. While this may seem incidental to DNAPL Monitored Natural Attenuation (MNA) processes, many of

the sites are not 'pure DNAPL' sites and as part of the cocktail of contaminants that may occur, petroleum hydrocarbons and diesel may occur in many cases. Electrons or reducing equivalents must be regenerated. If a contaminant serves as a sole source of carbon and energy, conditions must be within acceptable pH, Eh and temperature limits and the appropriate TEA must be present. In this case, the rate of degradation will be determined by the rate of dissolution of toxic end products away from the microbial population and the rate at which the TEA is replenished. Some of the lesser chlorinated solvents, such as dichloroethene (DCE), may also serve as sole sources of carbon; however, tetrachloroethene (PCE) and trichloroethene (TCE) are not thought to serve as sole sources of carbon.

In the case of TCE (and lesser chlorinated solvents), degradation may occur through co-metabolic processes. Under aerobic conditions, the enzymes necessary for the degradation, however, must be induced. Inducible enzymes are those that are not produced unless an inducer compound is present within the bacterial cell. Pertinent to this discussion are the inducers for methane mono-oxygenase and various mono- and dioxygenase enzymes produced by aromatic degrading bacteria.

In the presence of oxygen and methane, methanotrophic bacteria are known to produce the enzyme methane mono-oxygenase (Hanson and Hanson, 1996; Patel *et al.*, 1982). The substrate for this enzyme is methane, but it has been shown to have a broad substrate specificity including chlorinated solvents (Mayer *et al.*, 1988). Methanotrophs downgradient from a chlorinated solvent event may feed on methane produced within the anaerobic portion of the plume and co-metabolically degrade some chlorinated solvents. Oxygenase enzymes produced by bacteria capable of degrading aromatic hydrocarbons are capable of degrading chlorinated solvents. Aromatic compounds, such as toluene and phenol, have been shown to induce the responsible enzymes. In contaminated aquifers which contain both aromatic hydrocarbons and chlorinated solvents, degradation of both may occur.

Of the chlorinated ethenes, vinyl chloride is the most susceptible to aerobic oxidation under natural groundwater conditions. While laboratory studies have shown TCE may degrade oxidatively, there is no field evidence to support this. Cis-1,2-dichloroethene (cis-DCE), and 1,2-dichloroethane (1,2-DCA) may be subject to aerobic biodegradation. Chloroethane tends to hydrolyse (an abiotic reaction) preferentially over aerobic or

anaerobic biodegradation. VC rapidly degrades aerobically, particularly in comparison to reductive dechlorination. Chloromethane (CM) and dichloromethane (DCM) are degraded aerobically (Leisinger, *et al.*, 1994). Chlorobenzene and polychlorinated benzene (up to tetrachlorobenzene) are degraded aerobically, similar to benzene (Wiedemeier *et al.*, 1998). Co-metabolism of chlorinated ethenes is generally of little significance, unless a suitable electron donor (e.g. methane, ammonia, or phenol) is present (McCarty, 1997).

Anaerobic degradation is a transformation and/or elimination of an organic compound by micro-organisms in the absence of oxygen. Compounds other than oxygen act as electron acceptors. The processes include, denitrification, Fe(III) reduction, sulphate reduction, methanogenesis i.e. NO_3^- , Fe, SO_4^{2-} and CO_2 (in that order), plus chlorinated solvents acting as electron acceptors. VC and DCM are the only known examples of chlorinated solvents that undergo anaerobic degradation as electron donors. Highly chlorinated solvents do not degrade aerobically. Decreases in the concentration of electron acceptors and the corresponding increase in the concentration of metabolic by-products provide indirect evidence for degradation.

The degradation process may also vary in different parts of the plume, e.g. anaerobic degradation may occur at the centre of the plume and aerobic degradation at the margin of the plume.

The transformation of chlorinated ethenes requires consortia of many micro-organisms which then ferment these products to alcohols and fatty acids for energy. Secondly, other microbes oxidise the alcohols and organic acids, producing acetate and molecular hydrogen (H_2). Thirdly, another set of microbes oxidises the acetate and hydrogen as electron donors, using either the contaminant or naturally available chemicals. *Dehalococcoides ethenogenes* is the only anaerobic micro-organism that is known to completely dechlorinate chlorinated ethenes in the laboratory. Other species of *Dehalococcoides* working together with a group of micro-organisms called a 'consortium' may also dechlorinate chlorinated ethenes. Hendrickson *et al.*, 2002, have shown that *Dehalococcoides* species were found in 21 of 24 soil and groundwater samples contaminated with chlorinated ethenes collected in North America and Europe. At the sites where *Dehalococcoides* was not found, chlorinated degradation proceeded only to 1,2-DCE which then accumulated in the groundwater.

PCE and TCE are readily reduced as a result of their oxidative states; the more reduced daughter products (DCE and VC) are less prone to reductive processes. These intermediates tend to accumulate in anaerobic aquifers where contaminants are allowed to naturally attenuate (Lesage *et al.*, 1990). This may also be a function of the concentration of degradable organic matter within the contaminated system. Co-metabolism of TCE by autotrophic bacterial populations, obtained from soil and groundwater, has been demonstrated; this route of removal is limited only to low concentrations of TCE. The co-metabolism of TCE proceeds in the presence of methane, ammonia or toluene as co-substrate. Due to the inherent toxicity of TCE to micro-organisms responsible for degradative process and because of the competitive inhibition between a co-substrate and the secondary substrate for oxygenase enzymes, special attention to concentrations of TCE and its co-substrate is warranted (McCarty, 1997).

The process can be summarised by the figure below. Different types of microbes are involved at each stage. The bottom step shows that PCE must compete for electrons with sulphate, iron and carbon dioxide, meaning that a large amount of organic electron donors may be needed to supply enough electrons.

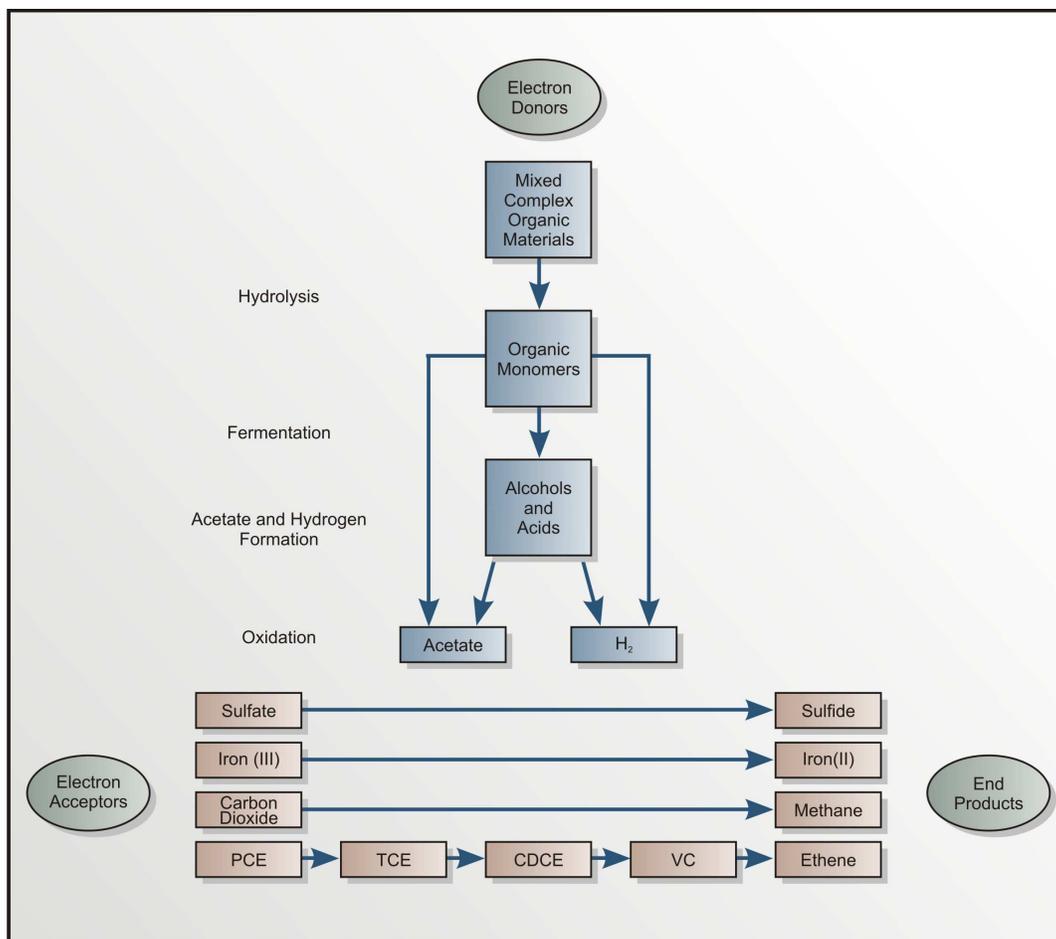


Figure 3-6: Steps in the process of biodegradation of PCE by reductive dechlorination. As shown, biodegradable organic matter is required as an electron donor to initiate the process. (After McCarty, 1997.)

PAHs biodegrade very slowly, and the fate of PAHs in subsurface systems is governed largely by their hydrophobic nature (the reason for their low solubility and tendency to attach to surfaces). PAH molecules held within NAPLs or adsorbed to surfaces cannot be biodegraded. Consequently, understanding dissolution (Ghoshal *et al.*, 1996) and the sorption processes (Luthy *et al.*, 1994) for PAHs is often the key to understanding biodegradation and natural attenuation potential.

3.6 Review Major Aquifer Systems in South Africa

3.6.1 Introduction

An understanding of the nature and occurrence of groundwater in South Africa aquifer systems is a prerequisite for assessment, monitoring and management of DNAPL contaminated sites. “An aquifer is an underground formation, capable of yielding sustainable amounts of water for the potential user(s) thereof” (DWAf, 2000). In the

wider definition, an aquifer only becomes a groundwater resource once it is utilised as a source of water. Although the focus of this thesis is on (intergranular) fractured aquifers, the following discussion will include other major aquifer types recognized in South Africa, i.e. intergranular flow aquifers, and dolomitic (karst) aquifers. The field testing was done in intergranular fractured aquifer systems (Campus Test Site and Test Site 1).

The physical properties of an aquifer that have the greatest impact on the fate and transport of DNAPL contaminants, are the flow rate and flow mechanism present, and the hydraulic conductivity. Therefore the major South African aquifer systems are classified and discussed in relation to the dominant flow mechanisms and flow characteristics.

Preferential groundwater pathways, including fractures, joints and solution channels result in higher contaminant velocities, which in turn can lead to rapidly expanding contaminant plumes where attenuation is limited. Groundwater flow under these conditions is highly unpredictable, making plume characterisation difficult. Intergranular (porous) flow is more predictable and the travel rates are generally lower, providing greater time for degradation to occur, and longer exposure of contaminants to active biodegradative/mineral sites.

The hydraulic conductivity of an aquifer depends upon a number of physical factors including porosity and particle size distribution. The favoured aquifer characteristics for transport characterization are isotropic, intergranular flow mechanisms, as these provide the opportunity to predict groundwater flow patterns and attenuation processes with the greatest confidence. By contrast, characterisation of the hydraulic regime in fractured/fissured aquifers is complicated by the highly heterogeneous nature of the system.

Most South African aquifers occur in fractured rock ranging in age from earliest Pre-Cambrian to Jurassic. Aquifers consisting of recent to Tertiary formations are restricted to coastal dune belts and unconsolidated deposits associated with rivers and aeolian sands. Characterisation of these fractured rock resources has been limited. The dominant occurrence of groundwater in fractured rocks implies that these aquifer systems are more difficult to manage and to protect (Pietersen, 2004).

Most of the research on groundwater in South Africa, has been focused on the main Karoo Basin. This is to a large degree understandable because of the Karoo Basin being the largest aquifer system in areal extent in South Africa. The aquifers support the domestic and agricultural needs of a number of small towns and rural communities. The dolomite and Table Mountain Group (TMG) aquifers have also been studied in some detail. The key challenge for the dolomite aquifer system relates to the management of the resource which is threatened by various land use impacts and the protection of aquifer integrity. This will require an integrated aquifer management arrangement. The rest of the hydrogeological domains have been investigated in lesser detail (Pietersen, 2004).

For this discussion the South African aquifers have been broadly divided into four groups according to the dominant flow mechanism. Table 3-4 gives a summary of these systems.

Table 3-4: Flow mechanisms of main aquifer systems in South Africa.

| Dominant flow mechanism | Porosity type | Hydrogeological domains | Examples | Rock type |
|--------------------------------|----------------------|---|--------------------------------------|------------------------------|
| Intergranular | Primary | Quaternary and Tertiary deposits | Alluvium, Cape Flats, Kalahari Sands | Unconsolidated sands |
| Intergranular and fractured | Dual | Sedimentary rock and composite rock regions | Table Mountain Group, Karoo Group | Sandstones, shales, arenites |
| Fracture flow | Fracture | Crystalline metamorphic and igneous regions, Intrusive and extrusive rock regions | West Rand Group, Basement | Granites |
| Karst | Karstic | Sedimentary rock regions and composite rock regions | Karst Belt, Ghaap plateau | Dolomite |

The properties of selected South African aquifers are shown in the following section, related to the dominant flow mechanisms and flow characteristics.

3.6.2 Intergranular flow systems

Intergranular flow occurs through the pore spaces between individual grains. Intergranular permeability can also be referred to as primary permeability. Most examples of material in which intergranular flow is the dominant flow mechanism are unconsolidated deposits such as sands and gravels. These aquifers usually have a low rate of flow and a high storage content due to the volume of pore spaces- however, flow

rates may be higher depending upon the permeability and topography, for example in coarser grained gravels.

The aquifer systems that represent this flow mechanism, include the major aquifers of the Cape flats in the Western Cape and the Kalahari Sands of the Northern Cape. Also included in this group are alluvial deposits across the country.

The Cape Flats Aquifer is a sand unit from the Sandveld Group, of Cenozoic age, that was deposited on top of the impervious Malmesbury shales and Cape granites. The bedrock comprises the Cape Granite Suite and the metasediments of the Malmesbury Group overlain by Late Tertiary to Recent sediments, up to 50 m thick. The bedrock topography shows that there is a Palaeo-valley reaching more than 40 m below mean sea level towards the north-eastern portion of the area. The sand body is generally stratified horizontally and several lithostratigraphic units can be recognized. The aquifer sands are well sorted and rounded resulting in hydraulic conductivities of 30-40 m/d in the central area and 15-50 m/d in the eastern portion. The groundwater recharge varies between 15% and 37% of the annual precipitation (Adelana and Xu, 2006).

In the north-west of the Northern Cape, undifferentiated inland deposits of unconsolidated to semi-consolidated sediments including sands, calcrete, aeolianite, gravel, clay and silcrete of Tertiary-Quaternary age, make up the Kalahari Group. The Kalahari group primary (sand/gravel) aquifers and clay formations' quality is often naturally poor with TDS values ranging from 1500 mg/l and higher. Some groundwater utilisation for small rural settlements, takes place from primary or porous aquifers from the Kalahari group, but the quality and yields are often variable and not good (Pretorius & Dennis, 2004).

Little is known regarding true riverbed sand aquifers in South Africa. General characteristics of riverbed aquifers can be summarized as (Pretorius & Dennis, 2004):

- Coarse gravels and sands are more typical of alluvial deposits. However, flood plains consist mainly of fine silt. Towards the end of a river's course, the river slows down dumping some of the heavier materials on these flood plains.
- Alluvial deposits grain size varies considerably; fine and coarse materials are intermixed. The hydraulic conductivities vary between 10-3 to 103 m/d and

their porosities vary between 25 – 70%. However, flood plain porosities usually range 35 – 50% and the hydraulic conductivities vary between 10⁻⁸ – 10⁻¹ m/d.

- In general riverbed aquifers are high recharge areas and often recharge deeper underlying aquifers and are unconfined in nature.

3.6.3 Intergranular and fractured

The two most studied and utilized intergranular and fractured (or dual porosity) aquifer systems in South Africa are the Karoo and Table Mountain Group (TMG) aquifers.

The main Karoo Basin encompasses an area of approximately 630 000 km². A major characteristic of the Karoo Supergroup, which consists mainly of sandstone, mudstone, shale and siltstone, is the low permeability. The Dwyka diamictite and shale have very low hydraulic conductivities, and virtually no primary voids. Water is confined to within narrow discontinuities like jointing and fracturing. The Dwyka Group is not considered an ideal unit for large-scale development of groundwater. The Ecca Group consists mainly of shales, with thicknesses varying from 1 500 m in the south to 600 m in the north. Significant tracts of land are irrigated from groundwater found in the Ecca shales. This is surprising because this formation is considered dense. Aquifers in the Beaufort Group are multi-layered and multi-porous with variable thickness. The characteristics and depositional history of the Molteno Formation would indicate better groundwater potential. The sediment bodies are more persistent than those of the Beaufort Group. The Elliot Formation consists mostly of red mudstone. This Formation thus presents more of an aquitard than an aquifer. The Clarens Formation consists almost entirely of well-sorted, medium- fine-grained sandstones, deposited as thick consistent layers. Although the Formation has a relatively high and uniform porosity (average 8.5%), it is poorly fractured and has a very low permeability. The formation may therefore be able to store large volumes of water, but is unable to release it quickly (Woodford and Chevallier, 2002).

Dolerite intrusives are prevalent throughout the Karoo Basin. The country rock is often fractured during and after dyke emplacement. These discontinuities represent zones of relatively higher permeability which act as conduits for groundwater flow within the aquifer. Most successful boreholes show some relationship with the dolerite intrusives. (Woodford and Chevallier, 2002).The aperture and areal extent of water-yielding

fractures in Karoo Formations are limited, and therefore unable to store large quantities of water (Botha *et al.*, 1998). The rock matrix is considered as the main storage units for water in Karoo aquifers. Major flow in Karoo aquifers occurs from the rock matrix to the fracture, which supplies the borehole with water (Woodford and Chevallier, 2002).

The dominantly arenitic Table Mountain Group (TMG) is well exposed within the Cape Fold Belt, which straddles the west and south coasts of South Africa (De Beer, 2002). The TMG formations have been exposed through two major tectonic events, the Cape Orogeny and the fragmentation of southwestern Gondwana during the Mesozoic (De Beer, 2002). Due a combination of favourable factors, such as structure and climate, the TMG forms one of the major fractured rock aquifers in South Africa. From a hydrogeological point of view, the TMG rocks represent a multi-porous medium that essentially consists of two major components, namely (Woodford, 2002):

- (a) Fractures and
- (b) Inter-fracture blocks or rock matrix.

TMG rocks are generally considered to form dual-porosity, fractured rock aquifer systems, where it is difficult to simultaneously quantify the groundwater flow within fractures and the rock matrix (Woodford, 2002). The main groundwater intersections in the TMG aquifer are commonly at depths of > 100m below ground surface and geothermal evidence from hot springs indicates groundwater circulation to depths of up to 2000 m (Rosewarne, 2002).

3.6.4 Fractured Flow

In sub-Saharan Africa, crystalline metamorphic and igneous rocks occupy 40% of the land area and 220 million people live in rural areas underlain by such rocks (MacDonald *et al.* 2002). Crystalline metamorphic and igneous aquifers have limited storage capacity and groundwater is generally rapidly depleted. Economic quantities of groundwater are associated with the weathered overburden. The most productive zone for groundwater is considered to be the lowest zone of the weathered profile and the top of the fractured bedrock. Viable yields are found where the weathering profile extends below the piezometric surface. The average yields are generally considered to be less than 1 L/s (Pietersen, 2004).

Crystalline metamorphic and igneous terrains are found extensively in the northern provinces of South Africa. In South Africa, the following groundwater regions are characterised by crystalline igneous and metamorphic basement rocks: Makoppa dome, Limpopo granulite gneiss belt, Pietersberg Plateau, Lowveld, Bushmanland, and Namaqualand. The availability of significant groundwater resources is therefore crucial for sustainable rural livelihoods. Groundwater is, more often than not, the only viable water supply to local communities. The groundwater resources of the Namaqualand region are a prime example of resources derived from crystalline metamorphic and igneous basement aquifers, upon which rural communities are heavily dependent (Pietersen, 2004).

The occurrence of groundwater depends on the existence in the rock formation of a thick weathered zone (the uppermost 10 – 30 m) or the occurrence of deeper fracture zones (MacDonald *et al.* 2002). Lloyd (1999) concludes the following about igneous and metamorphic basement rocks:

- (a) They are poor aquifer materials,
- (b) Their primary aquifer characteristics are negligible,
- (c) Lithology is not notably significant in influencing aquifer characteristics,
- (d) Fracturing is the most important aspect of aquifer potential but is inconsistent both spatially, and in depth
- (e) Weathering does not appear to generally enhance fractured hard rock aquifer potential

3.6.5 Karst Flow

In South Africa, the regions that are mostly dominated by dolomite formations are regions characterised by Vaalian Strata: Western Bankeveld and Marico Bushveld, Soutpansberg Hinterland, Karst Belt, Eastern Bankeveld, and Ghaap Plateau.

The dolomite aquifers cover an area of about 5000 km², with storage estimated at 5000 million m³ (Bredenkamp, 2002). It is estimated that available groundwater resources are 300 million m³.

Since these aquifers are in part overlain by areas of intensive land use and urbanisation, they are potentially susceptible to water quality deterioration. However, groundwater contamination by substances such as oil, fertilizer nitrate and other sources of pollution does not seem to be serious in the dolomite areas. The groundwater quality of dolomite aquifers in the Northwest Province seems to be generally good (Bredenkamp, 2002). The Gauteng Dolomite Aquifer covers a large area in the highest populated province in South Africa (Van Wyk, 2002). The aquifer consists of a CaMgHCO_3 rich limestone overlying older sedimentary successions of which one of them is gold bearing Witwatersrand Super Group. The total thickness of the dolomite is of the order of 250 to 1000m. The system is highly compartmentalised due to presence of near-vertical intrusive dyke rock, which plays a major role in the groundwater flow regime, causing several large springs, which drain the dolomite compartments (Van Wyk, 2002).

3.7 Conceptual Models for DNAPL Transport in South African fractured aquifers

In Sections 3.2 to 3.4 a generalised description of DNAPL fate and transport and in aquifer systems is given. The following section discusses issues and implications with regard to DNAPLs in specific South African aquifers (as discussed in Section 3.6). Each aquifer system is graphically conceptualised with an illustration.

3.7.1 Intergranular flow systems

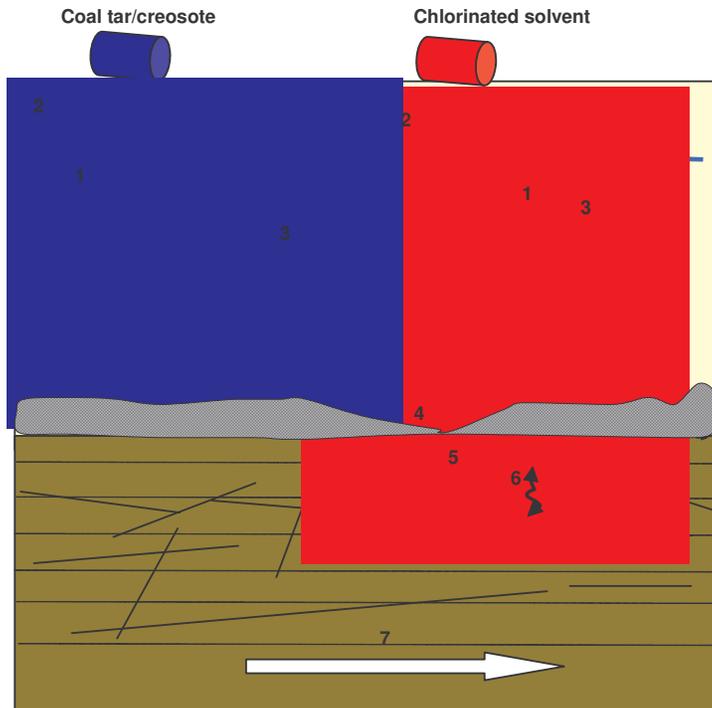
The issues and implications with regard to DNAPL fate and transport are as listed below, and illustrated in the conceptualisation in Figure 3-7.

1. **Primary aquifer systems are often “thin” aquifers with shallow water tables**
- This implies that the aquifer is highly susceptible to contamination. However, due to this characteristic, site characterization and remediation techniques are translated most easily from US and other international experiences. A wide range of well established techniques are available to the site assessor.
2. **Thin unsaturated zone** allows for easy access to contaminated zone and less chances for vapour plume development and transport.
3. **High permeability** – implies higher groundwater velocities
4. **High porosity** causes larger dissolved plumes.

5. **High organic and clay content** of these systems allows for higher attenuation, nutrient availability, and thus degradation rates when considering monitored natural attenuation (MNA) as a remedy.
6. **Variable lithology and permeability** –heterogeneity of the system will cause a tortuous and varied pathway for the vertical and sub-vertical flow of the DNAPL phase.

In Figure 3-7 the difference between a coal tar/creosote vs. chlorinated solvent contaminated system is shown. From this it can be seen due to the difference in physical properties (density and viscosity) of the contaminant, the transport processes will differ. The free phase of solvents, are more likely to migrate deeper but less horizontal in the source zone, than the coal tar/creosote mix. The source zone area containing residual and pooled DNAPL at the coal tar/creosote spill tend to be more spread out horizontally.

Primary porosity, intergranular flow systems, e.g. Quaternary and Tertiary deposits, Cape Flats, Kalahari Sands, Alluvium (Unconsolidated sands, gravel and clay)



Unconsolidated sand
 Clay
 Shale

Features

- 1 Residual and pooled DNAPL in unconsolidated sand
- 2 Vapour plume
- 3 Aqueous phase plume migration
- 4 Lateral discontinuity in fractured clay layer
- 5 DNAPL entry into fractured rock
- 6 Matrix diffusion from aqueous phase and DNAPL
- 7 Groundwater flowdirection

Issues and implications

- Thin aquifer systems
- Shallow water table - thin unsaturated zone
- High porosity - larger plumes
- High organic and clay content assist in attenuation processes
- Nutrient availability for biological degradation
- Variable lithology and permeability
- Site characterisation methods well established for these systems

Figure 3-7: Conceptualisation of DNAPL fate and transport in intergranular flow systems.

3.7.2 Intergranular and fractured

The issues and implications with regard to DNAPL fate and transport in dual porosity systems are as listed below, and illustrated in the conceptualisation in Figure 3-8.

1. **Generally “deep” aquifer systems with thick unsaturated zone** – This makes translating of US and other international experiences with regard to site assessment and characterization difficult. Many of these methodologies cannot be applied in hard rock and/or at great depths. Also high cost of investigation in thick aquifers/ deep unsaturated zones.
2. **High fracture permeability, low matrix permeability** – Slow groundwater velocities in matrix but localized high flow in preferred pathways (fractures). This gives rise to smaller dissolved plumes than in porous media, but migration could be further.
3. **Multi-layered aquifer due to presence of hydraulic variance in horizons** – The resulting contaminated zones will be strongly influenced by the hydraulic variance leading to irregular distribution of NAPL and dissolved plumes. This is important for the construction of boreholes and interpretation of sampling results. Layering may also limit vertical dispersion
4. **Fracture aperture, strike, and dip.** Fracture entry pressures are directly proportional to interfacial tension and inversely proportional to fracture aperture. This results in preferential DNAPL migration through the larger aperture fractures of a fracture network. The strike and dip of the more permeable fractures will therefore control the primary directions of DNAPL migration in a fracture network.
5. **Horizontal and vertical flow** must be considered, but density driven flow through vertical fractures will result in deep penetration of DNAPL.
6. **Matrix diffusion** - Matrix diffusion refers to the process whereby solutes dissolved in groundwater diffuse into and out of the rock matrix. If concentrations are higher in the open fracture, the diffusion process will result in dissolved contaminants moving into the rock matrix (forward diffusion). If concentrations are higher in the rock matrix, dissolved contaminants will move

out of the rock matrix and into water in the open fractures (back diffusion). Matrix diffusion will occur in all rock types exhibiting a finite matrix porosity. This process causes the contamination to be persistent over time and makes remediation techniques such as “pump-and-treat” not feasible in the long-term in dual porosity systems.

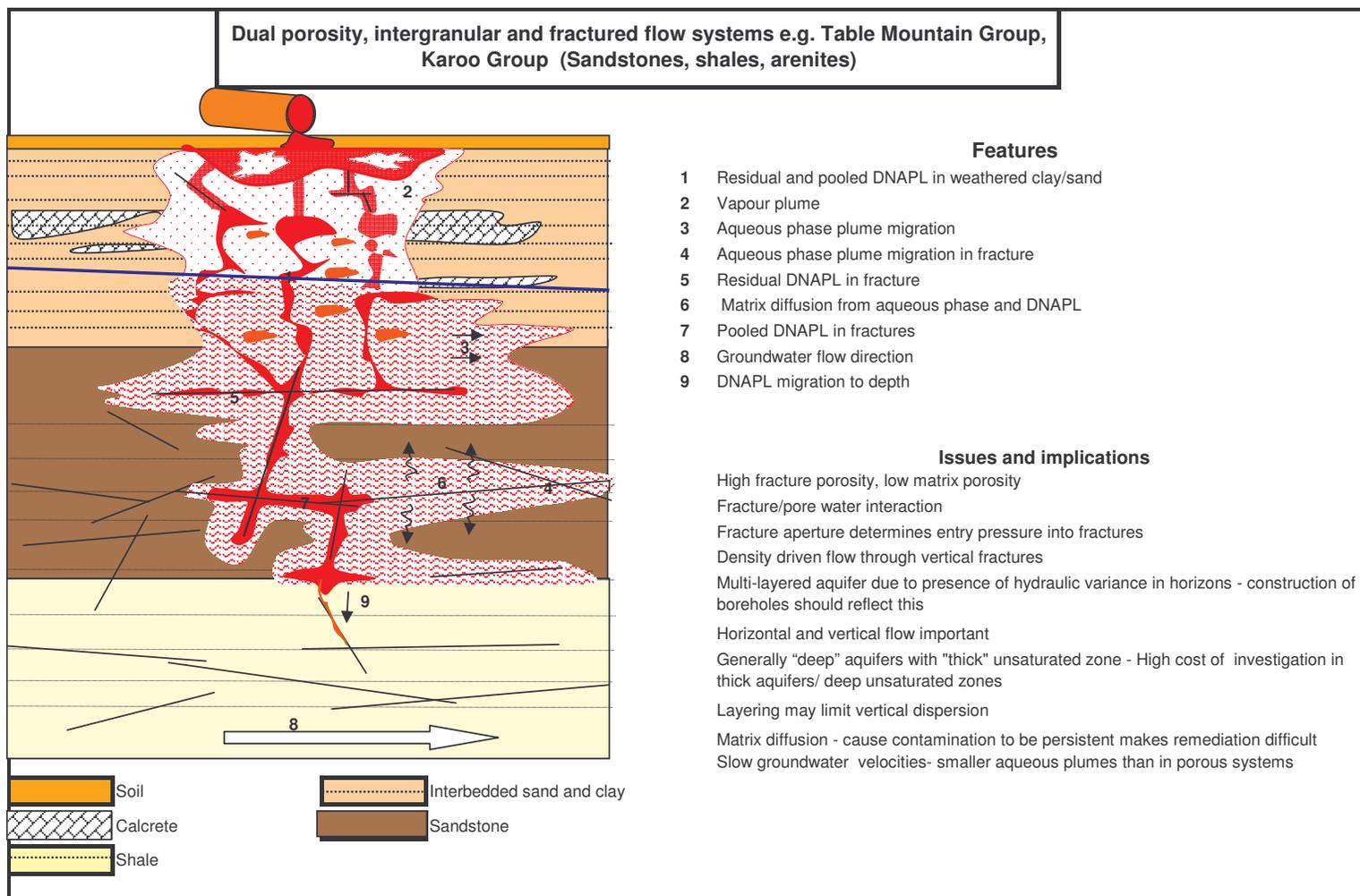


Figure 3-8: Conceptualisation of DNAPL fate and transport in intergranular and fractured (dual porosity) flow systems.

3.7.3 Fractured Flow

The issues and implications with regard to DNAPL fate and transport in fractured systems are as listed below, and illustrated in the conceptualisation in Figure 3-9.

1. **Fracture flow** is the dominant flow mechanism. Micro-fissures store most of the water, which gets transmitted by the large fractures. This also results in rapid flow rates which imply that contaminants can be rapidly transported along interconnected fractures both horizontally and vertically.
2. **Preferential pathways** – Results in significant variation in vertical and horizontal permeability. Siting of observation and monitoring boreholes are important in relation to preferential pathways. It is difficult to be confident about representative nature of monitoring results and delineation of dissolved phase plumes.
3. **Low matrix porosity** – Thus negligible matrix diffusion, dissolved plume is confined to fractures and "matrix" around fractures

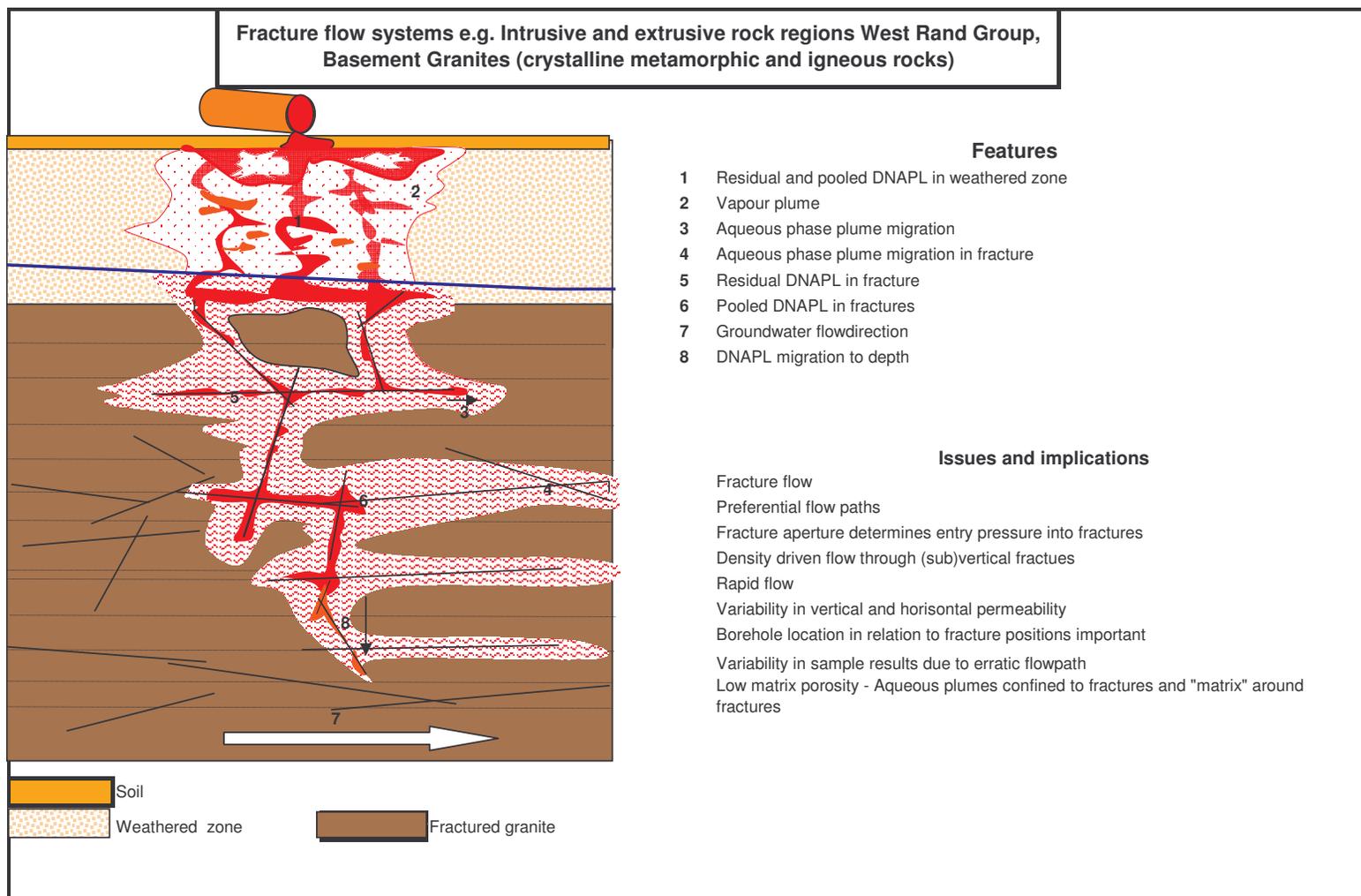


Figure 3-9: Conceptualisation of DNAPL fate and transport in fractured flow systems.

3.7.4 Karst Flow

The issues and implications with regard to DNAPL fate and transport in fractured systems are as listed below, and illustrated in the conceptualisation in Figure 3-9.

1. **Karst and fracture flow** is the dominant flow mechanism. Micro-fissures store most of the water, which gets transmitted by the connected solution features and larger fractures. This also results in rapid flow rates, which implies that contaminants can be rapidly transported along interconnected features both horizontally and vertically.
2. Although rapid flow rates are possible in interconnected features, **variable travel times** need to be considered in assessing viability of attenuation processes, siting of monitoring boreholes and frequency of monitoring. If boreholes are drilled into discontinuous cavities and fractures, high residence times can result in higher measured concentrations, than in the surrounding aquifer.
3. **Preferential pathways** – Results in significant variation in vertical and horizontal permeability. Siting of observation and monitoring boreholes are important in relation to preferential pathways. Difficult to be confident about representative nature of monitoring results and delineation of dissolved phase plumes.
4. **Regional variations in behaviour of the aquifer** e.g. solution features and compartmentalizing (i.e. through dykes and sills)
5. **Low matrix porosity** – Thus negligible matrix diffusion, dissolved plume is confined to solution cavities and fractures and "matrix" around fractures. This will be dependant on the karstification of the system.
6. Karst aquifers are often associated with **large seasonal water table variations**. This can result in short-circuiting of normal flow during high water tables.
7. **Thick aquifers and deep unsaturated zones** -This makes translating of US and other international experiences with regard to site assessment and characterization difficult. Many of these methodologies cannot be applied in hard rock and/or at great depths. Also high cost of investigation in thick aquifers/ deep unsaturated zones.

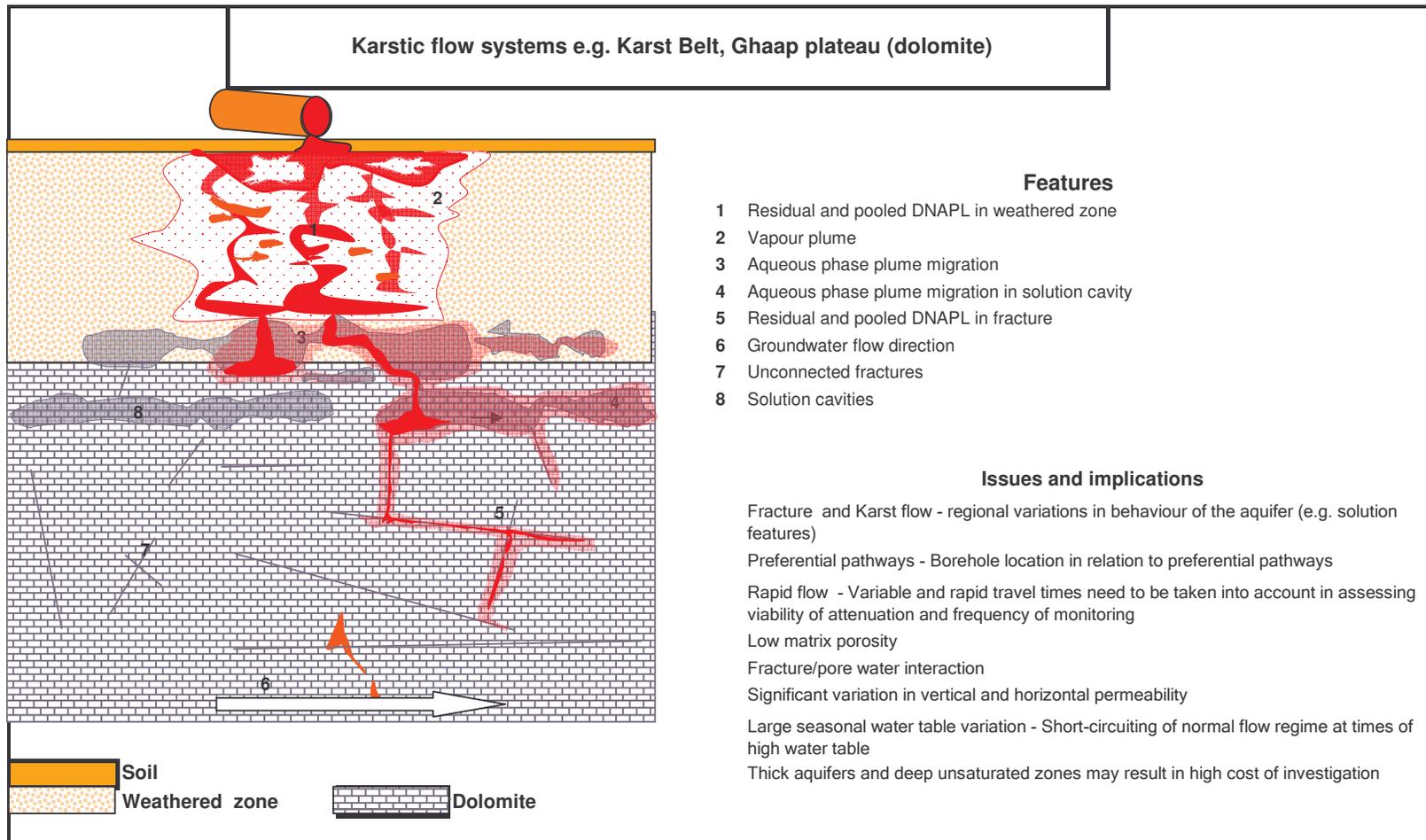


Figure 3-10: Conceptualisation of DNAPL fate and transport in karst flow systems.

4 DNAPL Site Assessment and Transport Prediction

4.1 Introduction

In natural subsurface systems dominated by heterogeneity, the delineation and even the detection of sparingly soluble, dense contaminants can be extremely difficult. Several techniques can be applied for the characterization of a site contaminated with DNAPLs. Therefore, this section highlights the importance of a site-specific characterisation methodology and applicability of techniques when investigating DNAPL contaminants in South Africa. Transport prediction techniques are discussed and a simple case study presented. For more detail on site assessment techniques refer to Gebrekristos (2007) thesis'.

DNAPL contaminated sites tend to be more complex than light non aqueous phase liquid (LNAPL) or aqueous contaminated sites because the physical and chemical characteristics of dense, sparingly soluble contaminants add additional complexity to heterogeneous geology and hydrogeology at most sites. While LNAPL contamination is usually constrained to the top of the water table and above, and aqueous phase contamination follows the hydrology of the site, DNAPL movement is controlled by gravity and capillary pressure of sediments, and can move against the hydraulic gradient.

A *general assessment* of an industrial or waste disposal site can be made to determine the potential presence of DNAPL in the groundwater zone. This general assessment is usually made early in a site investigation program using existing information about the site. The site assessor must consider if the chemicals found at the site, or expected at the site, could comprise DNAPLs, and if the activities at the site could have resulted in the release of significant quantities of DNAPL into the subsurface.

Given the selective and tortuous nature of DNAPL migration, it follows that the majority of porous media within a DNAPL source zone will contain neither residual nor pooled DNAPL (Kueper, et al, 2003). The probability of directly encountering residual or pooled DNAPL with a conventional drilling programme is therefore relatively small. Instead, the presence of DNAPL is inferred using alternative lines of evidence.

Many site assessment techniques have been developed during the past few decades. However, it is not possible to apply all of the methods at the same time because of practical reasons. Cost, availability, and the nature of the site and DNAPL are some of the factors that determine which technique to be used.

At sites contaminated by DNAPL, detailed characterisation of the presence and transport potential must be done because:

- The behaviour of subsurface DNAPL cannot be adequately defined by *investigating miscible contaminant transport* due to differences in properties and principles that govern DNAPL and solute transport,
- DNAPL can *persist for decades or centuries as a significant source* of groundwater and soil vapour contamination; and
- Without adequate precautions or understanding of DNAPL presence and behaviour, *site characterization activities may result in expansion of the DNAPL contamination* and increased remedial costs.

4.2 “Toolbox” Approach

The specific objectives of DNAPL site evaluation will differ from a solute contaminated site to include the following:

- Estimation of the quantities and types of DNAPLs released and present in the subsurface,
- Delineation of DNAPL release source areas;
- Determination of the subsurface DNAPL zone;
- Determination of site stratigraphy (especially fracture locations, and dips of strata and fracture);
- Determination of immiscible fluid properties;
- Determination of fluid-media properties; and
- Determination of the nature, extent, migration rate, and fate of contaminants in all the phases.

The overall objectives of DNAPL site evaluation are to facilitate adequate

assessments of site risks and remedies, and to minimize the potential for inducing unwanted DNAPL migration during remedial activities. Delineation of subsurface geologic conditions is critical to site evaluation because DNAPL movement can be largely controlled by the capillary properties of subsurface media. It is particularly important to determine, if practicable, the spatial distribution of fine-grained capillary barriers and preferential DNAPL pathways (e.g., fractures and coarse-grained strata).

Site characterization should be a continuous, iterative process, whereby each phase of investigation and remediation is used to refine the conceptual model of the site. During the initial phase, a conceptual model of chemical presence, transport, and fate is formulated based on available site information and an understanding of the processes that control chemical distribution. The potential presence of DNAPL at a site should be considered in the initial phase of site characterization planning. Determining DNAPL presence should be a high priority at the onset of site investigation to guide the selection of site characterization methods. Knowledge or suspicion of DNAPL presence requires that special precautions be taken during field work to minimize the potential for inducing unwanted DNAPL migration.

Below is a framework with the required steps to complete a DNAPL site assessment. Note that the construction and update of the site conceptual model is an integral part of the process and updated throughout the investigation.

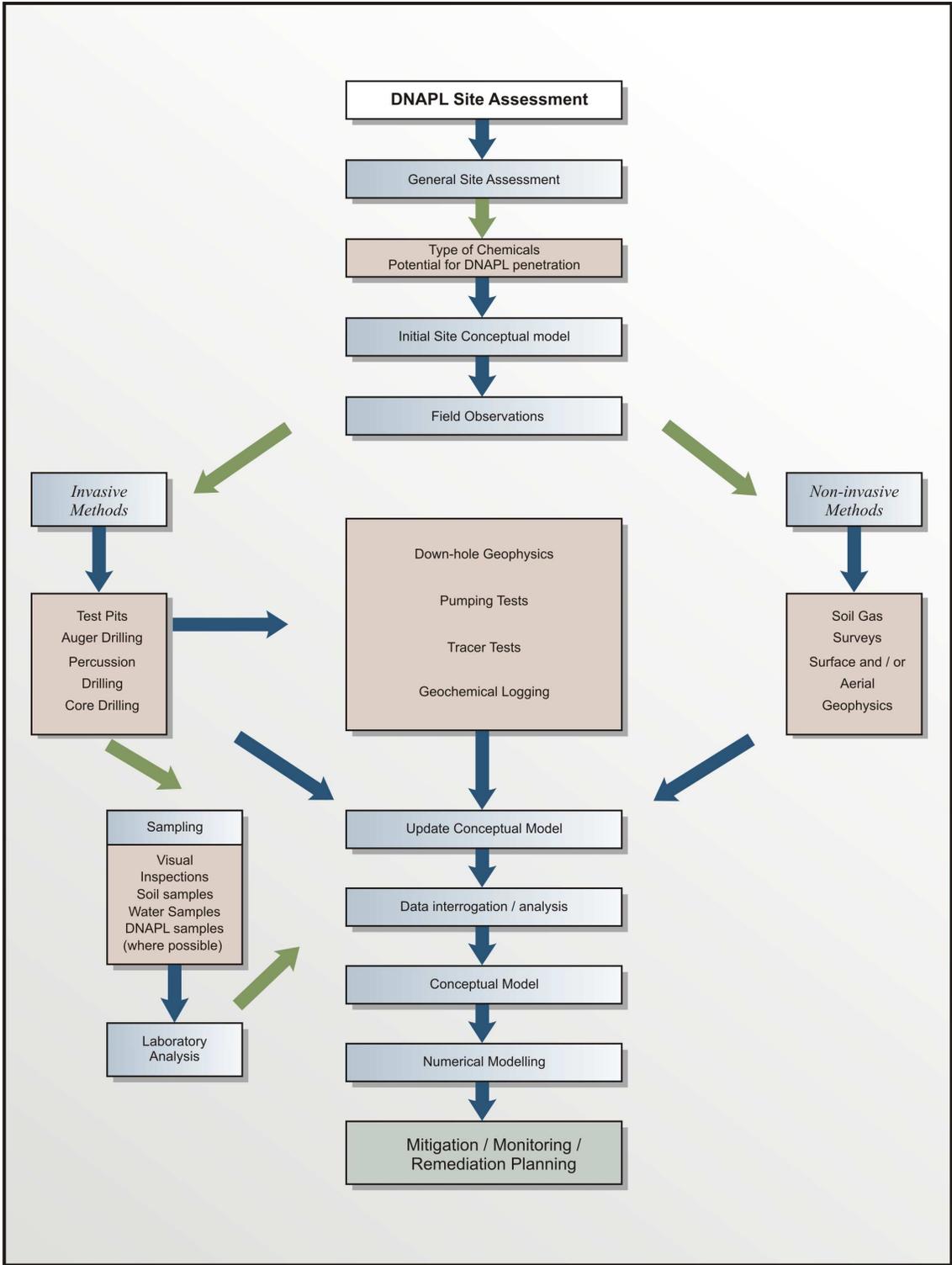


Figure 4-1: Framework for DNAPL site assessment.

Following development of the initial site conceptual model based on available information collected during the general site assessment, a combination of non-invasive and invasive field methods/techniques will generally be required to advance site characterization and enable the investigator to conduct risk and remedy assessments.

Several technologies for the characterization of sites contaminated with DNAPLs have recently been developed. These include geophysical techniques, tracer tests, and direct sampling or sensing methods. The innovative methods provide some significant advances over conventional sampling-based approaches but the real value of these methods is in their addition to a “toolbox” approach to DNAPL characterization (Rossabi, *et al.*, 2000).

The toolbox approach recognizes that all characterization methods contribute to the conceptual model of the site. The strategic selection of technology and results from each application must contribute to the evolution of this conceptual model. The ultimate goal is the absolute knowledge of the contamination at the site. This, of course, can never be reached but using the right suite of tools and comprehensive integration of the data, the most accurate understanding is obtained.

Non-invasive methods can often be used during the early phases of field work to optimize the cost-effectiveness of a DNAPL site characterization program. Specifically, surface geophysical surveys, soil gas analysis, and photo interpretation can facilitate characterization of contaminant source areas, geologic controls on contaminant movement, and the extent of subsurface contamination. Conceptual model refinements derived using these methods reduce the risk of spreading contaminants during subsequent invasive fieldwork.

Various means of subsurface exploration are utilized to directly observe and measure subsurface materials and conditions. Generally, the invasive activities include: drilling and test pit excavation; and monitoring borehole installation. Monitoring boreholes are used to sample the groundwater, conduct water level surveys, hydraulic testing (pump testing and tracer testing), and borehole geophysical surveys.

More than 90% of South African aquifers are fractured, and research for this thesis has shown that very detailed fracture characterization is required at DNAPL contaminated sites to conceptualise the potential DNAPL contaminated zones and plume distribution. Techniques that were found to be specifically focussed on fracture characterisation of a site include the following:

- Comparing samples and cores from different drilling techniques
- Pump tests to determine hydraulic connectivity between boreholes
- Down-hole geophysical and geochemical logging to determine more conductive zones in boreholes
- Video or acoustic video logging for fracture positions, relative fracture apertures, and possible fracture orientations
- Tracer tests to determine preferred pathways for solute transport

Specific fracture characterisation methods tested during this research are discussed in Section 5.2.5.

Figure 4-2; provide a brief summary of the parameters that should be measured, and the general techniques to be applied as part of the “toolbox” approach at a DNAPL contaminated site during field investigations.

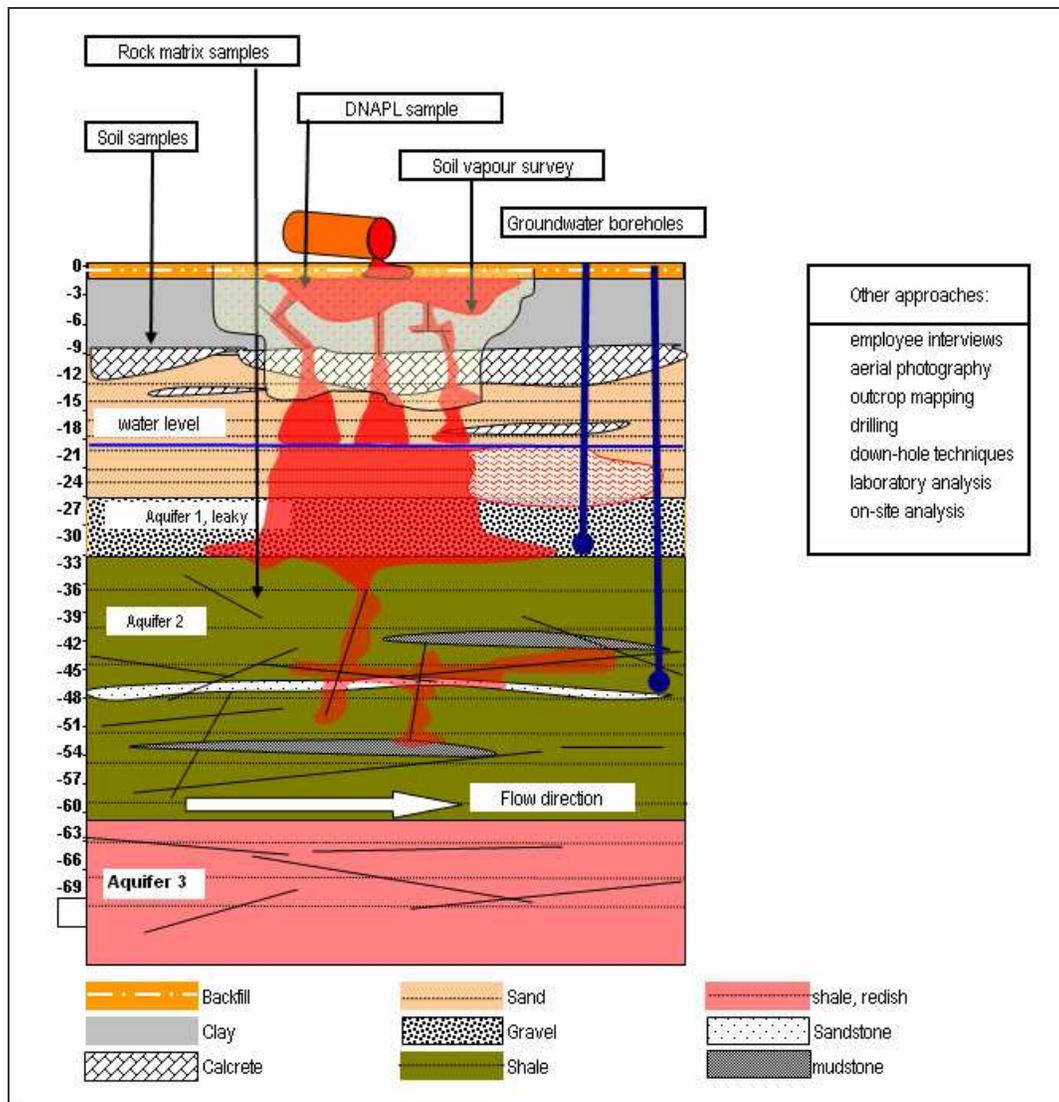


Figure 4-2: Site assessment techniques (Adapted from, Kueper, *et al.*, 2003 and Gebrekristos, 2007))

4.3 Prediction Techniques

4.3.1 Background

Following the release of DNAPLs at surface, DNAPLs migrate in intricate patterns through the subsurface as a separate fluid, creating a complex source zone composed of vertical trails of immobile residual blobs and horizontal accumulations of non-aqueous phase pools. Dissolution of both DNAPL residual and pools results in the development of dissolved-phase contaminant plumes. The toxic, dissolved-phase constituents transported to environmentally sensitive receptors are the primary hazard associated with DNAPL contaminated sites

Numerical modelling is an effective tool for designing laboratory and field-scale

experiments and can be used to perform sensitivity and uncertainty analysis in the study of DNAPL migration and remediation. Numerous multiphase flow models have been developed for use in a contaminant hydrogeology. Most such models account for the migration but not the dissolution of the non-aqueous phase. (Grant and Gerhard, 2004).

A groundwater model is a (computer-based) representation of a natural geohydrological system that uses the laws of science and mathematics. The basic steps involved in modelling can be summarised as:

1. Collecting and interpreting field data
2. Conceptualising the natural system
3. Deciding on a model
4. Calibration and sensitivity analysis
5. Validation
6. Modelling scenarios
7. Presenting results

The most important component of a groundwater model is the *conceptual model*. The conceptual model is representation of the investigator's geohydrological understanding of the essential flow processes of the system. The development of *conceptual models* though detailed site characterization is key to successful management of DNAPL sites. The integration of results from the different techniques is needed to develop a conceptual model for different aspects of a DNAPL site. The most important aspects would include determination of preferred DNAPL pathways and the size, orientation and density of the fracture network.

The mathematical model is a set of equations, which, subject to certain assumptions, quantifies the physical processes active in the aquifer system being modelled. While the model itself obviously lacks the detailed reality of the groundwater system, the behaviour of a valid model approximates that of the aquifer. If the model represents the groundwater system to an adequate level of detail it will provide a predictive tool to quantify the effects on the system of specified hydrological conditions.

The numerical model solves both complex and simple problems. Transport of aqueous-phase contaminants dissolved in groundwater is described by the Advection-Dispersion equation. Numerous transport models solving the Advection-Dispersion equation have been developed, including MT3D (Zheng, 2004). However, the majority of these models do not incorporate the effects of immobile DNAPL presence or transient DNAPL flow. Some numerical models are capable of simulating multi-phase flow, dissolution and contaminant transport (i.e. UTCHEM). These models have extremely large data requirements and are therefore of limited use for simulating field-scale scenarios. To simulate DNAPL dissolution, numerical models rely on mathematical representations of the complex physio-chemical phenomena involved (Grant and Gerhard, 2004).

Once the numerical model is completed, various scenarios can be simulated.

4.3.2 Multiphase Modelling

Multi-phase modelling is a very important consideration in DNAPL assessment. Due to the complexity of these multi-phase interactions, the models which deal with these problems in a quantitative manner are, of necessity, therefore also generally very complex. For these models to have relevance, the data requirements of such models are also extensive.

Models have several limitations, of which users must be aware when embarking on these modelling exercises, and of which regulators, site owners and other decision-makers should consider when taking action based on numerical or analytical models. Lichtner (1996) puts it as follows:

“Computer models can provide, if not a direct quantitative description, at least a far better qualitative understanding of the geochemical and physical processes than might otherwise be possible.”

It is important to note that the uncertainties related to multiphase models are not unique in the groundwater environment. Any model is a simplified version of reality, based on various assumptions. Apart from the assumptions made to construct the conceptual model, there is major uncertainty with several input parameters and the results should always be interpreted with these considerations.

4.3.2.1 Data requirements

The data requirements for such models are intensive and would include the following parameters (UT, 2000 and Reynolds and Kueper, 2004):

- Dimensions
- Mesh size
- Pore volume
- Boundary conditions
- Initial pressure
- Initial DNAPL saturation
- Aquifer pore volume
- Total aquifer DNAPL volume
- List of Reactive Species
- Capillary pressure endpoint
- Concentration: Water, DNAPLs
- Density of fluids
- Diffusion coefficient (m^2/d)
- Dispersivity (m)
- Soil/Aquifer/Bulk density (g/cc)
- Interfacial tension (dyne/cm)
- Permeability (m/d)
- Aquifer dip angles
- Saturation fraction
- Temperature ($^{\circ}\text{C}$)
- Viscosity of wetting and non-wetting phases
- Phase Behaviour
- Phase Saturations
- Capillary Pressure
- Relative Permeability Curves

Additional input parameters may be required, depending on the model code used. For these the user needs to refer to the specific model's user manual.

4.3.2.2 Outline of methodology for NAPL modelling

Modelling multiphase flow and transport requires a similar rationale to groundwater

reactive mass transport modelling. As such, the guidance provided for codes such as MT3D and MT3D-MS (Zheng, 2004), is an applicable approach to follow. As highlighted in many documents providing guidance on modelling, the proper conceptualisation of the problem, as achieved with a detailed conceptual model of the aquifer, the source of DNAPLs, their properties and the likely interactions expected, will hold the key to the successful modelling of a multiphase transport model of DNAPL.

In every model study the natural system is represented by a conceptual model. A conceptual model includes designing and constructing equivalent but simplified conditions for the real-world problem that is acceptable in view of the objectives of the modelling and the associated management problems. Converting the real-world situation into an equivalent model system, which may then be solved using existing programme codes, is a crucial step in groundwater and multiphase flow and transport modelling in aquifers.

A critical and cost-effective use of modelling lies in understanding and evaluating the analysis of proposed or alternative future conditions i.e., the model is used as a management or decision-making tool to help answer “what if” questions (Donagian and Rao, 1986). Models also may be used to approximate and estimate the rates and extent of migration that may be expected at the field-scale under varying conditions. Attempting to answer such questions through data collection programmes would be expensive and very difficult in many situations. For example, information can be generated to evaluate the effects of differing hydraulic, NAPL or microbial activity properties for the site.

Therefore, modelling may be used to assist in the design of the field characterisation, ensuring that the most important factors are included and evaluated adequately and therefore, to assist in focusing available resources (time and money).

A suggested flow path for such modelling has been suggested by Carey *et al.*, 1995.

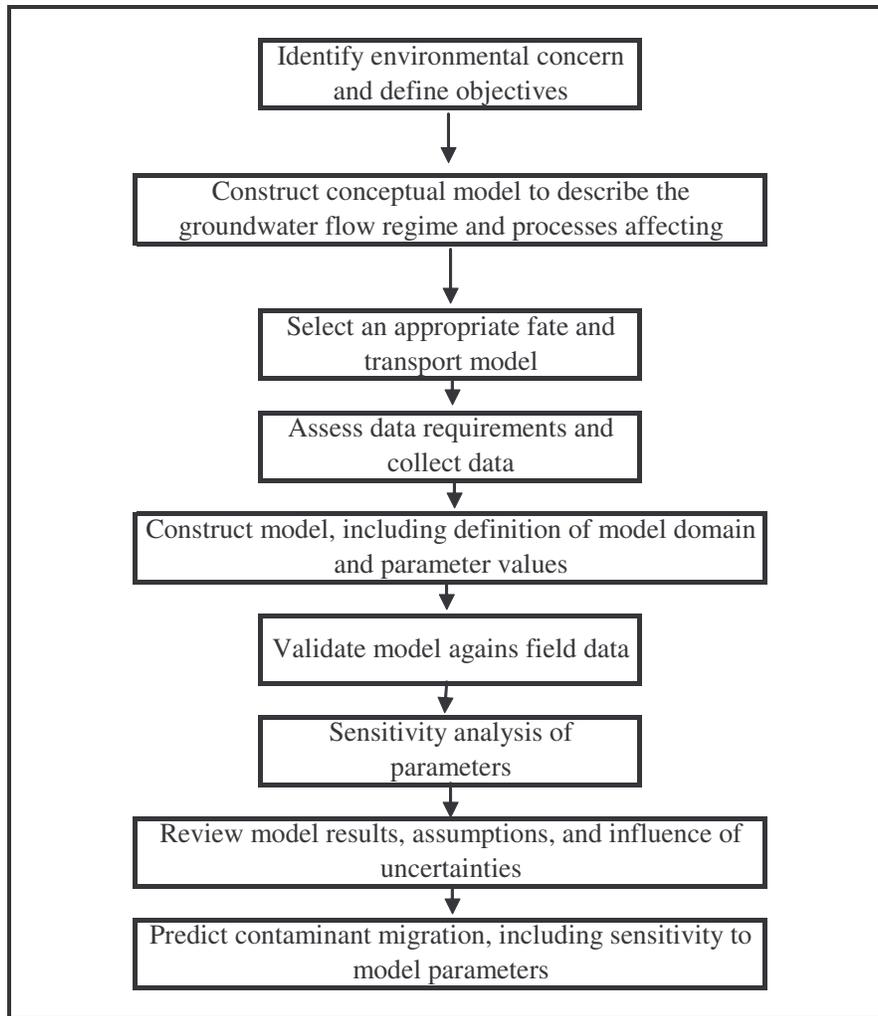


Figure 4-3: Suggested outline of approach (adapted from Carey *et al.*, 1995)

Anderson *et al.*, 1992 suggests that concentration distributions in the groundwater zone may be highly spatially variable. In addition to dispersion, vertically-averaged sampling from conventional monitoring wells may lead to observed concentrations which are substantially below the maximum values present in the aquifer. Unless caution is observed when those averaged results are being interpreted, incorrect conclusions about the distribution of organic contaminants in the subsurface may be drawn.

4.3.2.3 UTCHEM

Pioneering research was conducted at The University of Texas at Austin to provide a scientific and engineering basis for modeling the enhanced recovery of oil and the enhanced remediation of aquifers through the development and application of compositional simulators. This research has resulted in the development and

application of UTCHEM, a 3-D, multi-component, multiphase, compositional model of chemical flooding processes which accounts for complex phase behavior, chemical and physical transformations and heterogeneous porous media properties, and uses advanced concepts in high-order numerical accuracy and dispersion control and vector and parallel processing (UT, 2000). The simulator was originally developed by Pope and Nelson in 1978 to simulate the enhanced recovery of oil using surfactant and polymer processes. Generalizations by Bhuyan *et al.* in 1990 have extended the model to include other chemical processes and a variety of geochemical reactions between the aqueous and solid phases. In this simulator, the flow and mass-transport equations are solved for any number of user-specified chemical components (water, organic contaminants, surfactant, alcohols, polymer, chloride, calcium, other electrolytes, microbiological species, electron acceptors, etc.). These components can form up to four fluid phases (air, water, oil, and micro-emulsion) and any number of solid minerals depending on the overall composition.

In 2002 Delshad *et al.*, further developed UTCHEM to include a multi-component dual porosity model, in order to evaluate the potential of current characterization and remediation technologies of non-aqueous phase liquids (NAPLs) in fractured porous media. The dual porosity formulation allows flow in both the matrix and the fracture. Mass transfer between the fracture and matrix rock includes diffusion, convection, imbibition, and gravity drainage.

All of these features taken together, but especially the transport and flow of multiple phases with multiple species and multiple chemical and biological reactions make UTCHEM unique. UTCHEM groundwater applications:

- NAPL spill and migration in both saturated and unsaturated zones
- Partitioning interwell test in both saturated and unsaturated zones of aquifers
- Remediation using surfactant/cosolvent/polymer
- Remediation using surfactant/foam
- Remediation using cosolvents
- Bioremediation
- Geochemical reactions (e.g., heavy metals and radionuclides)

There are other multi-phase codes, but this is the most widely code for NAPL transport in groundwater, probably due the fact that it is available in the public domain.

4.3.3 Dissolved phase and degradation modelling

It is again emphasised that the dissolved phases can only be accurately modelled if the NAPL transport is considered. Therefore, dissolved phase degradation numerical models can be used if the NAPL source zones and flow pathways have been accurately determined in the aquifer.

The question is often posed: “Which is the best modelling tool/package for prediction?” The answer to this is none; each modelling code or method has particular advantages and disadvantages as far as availability, cost, ease of use and inherent assumptions and weaknesses. The only answer is that the appropriate code or method must be used based on the type of answer required.

Carey *et al.*, 1995 gives an overview of some available codes. This has been used with additional codes and comments added in Appendix B. The usefulness of these models and their basic data requirements, along with the uncertainties involved in reactive transport or multiphase flow models, the user/researcher are listed.

4.4 Uncertainty and limitations in multiphase or reactive transport modelling.

As analogues to the real-life situation, multiphase models are due to their inherent nature very limited in what may be achieved. There is a wide range of complexity from simple approaches which make several simplifying assumptions or corrections (and are consequently easier to populate, construct and simulate), to detailed models which attempt to be more comprehensive (requiring far more data, expertise, computing power and time for simulation). While the simpler models are attractive for the ease of use and simplicity, unfortunately, it appears that they can be very misleading.

Gerhard and Kueper, (2003) developed a comprehensive multiphase model and compared these results to simpler methods. Some of their findings include:

1. None of the simpler or more conventional constitutive models employed was able to reproduce, within $\pm 10\%$, the spatial and temporal migration of the non-wetting fluid body at late time predicted by the base case.
2. Not accounting for hysteresis functions in the constitutive model demonstrated a relatively small effect on the spatial distribution of non-wetting fluid, but significantly influenced imbibition rates and total growth cessation times.
3. Not accounting for non-wetting phase trapping, even when the maximum non-wetting phase residual value is less than 10%, is found to increase the mobility of the non-wetting fluid profoundly, resulting in a wider and deeper extent of DNAPL predicted to occur over a time-frame order of magnitude greater than when trapping is incorporated.
4. The non-wetting fluid distribution is tortuous and highly sensitive to the order of the encounter of permeability and capillary properties, with this sensitivity increasing upon termination of the source.
5. Not accounting for the abrupt extinction of imbibition, caused the time predicted for the cessation of non-wetting fluid migration to approximately double.
6. Typical hysteretic constitutive models based on the van Genuchten function appear to be unsuitable for simulating DNAPL migration in heterogeneous media below the water-table.

The conclusion from the research on multiphase flow modelling by Gerhard and Kueper is very sobering to all practitioners in this field. This conclusion reads as follows:

“The practical implication of this study is that in addition to fluid and porous media properties, source characteristics, and the specific distribution of permeability beneath a release location, all of the examined constitutive model hysteresis and trapping phenomena may need to be incorporated, and appropriate values for the corresponding function parameters may need to be known, in order to accurately simulate the redistribution and immobilisation of a non-wetting fluid release below the water table in both space and time.”

Grant and Gerhard (2004) also described two practical implications of multiphase

flow modelling after studying the sensitivity of DNAPL migration, dissolution and transport simulations in homogeneous and heterogeneous porous media to the choice of mass transfer expression using six published, experimentally derived correlation models:

1. Predicted dissolved phase concentrations down-gradient of a realistic DNAPL release are quite sensitive to the chosen mass transfer expression, and
2. A more robust and comprehensive correlation model is likely necessary for accurate simulations.

This study suggested that attempting to infer DNAPL source configuration from down gradient concentrations or to predict site remediation times remains uncertain until such time as a comprehensive mass-transfer expression is derived and validated.

The above discussions highlight the difficulties and uncertainties of multi-phase modelling in porous media. In fractured media all of the above difficulties similarly apply, but the fractures add an order of the magnitude of complexity and uncertainty in the simulations. Groundwater flow modelling in fractured media is in its infancy and whereas for many applications on a larger scale, the effects of individual fractures may be averaged out in the equivalent porous media. However, the scale effect is not applicable to DNAPL migration. The consequence of this is that the models must explicitly accommodate fractures and the current conundrum is that the select few models that can accommodate fractured flow; do not coincide with the few codes that properly consider multiphase flow. The modelling attempts must therefore be done on only very well characterised sites or considered as alternative scenarios used to highlight critical factors that must be quantified.

The amount of detailed information required on a heterogeneous site to describe the system accurately would be impossible to gather and thus attempts to quantify these flows accurately are fraught with uncertainty. Thompson and Jackson (1996) put it as strongly as this: *“From the perspective of contaminant hydrology, the impact of geologic heterogeneity is difficult to consider in practice,”* and *“(Therefore) oversimplified conceptualisations of system behaviour are used.”* Thus, through no

fault of modellers or modelling codes, which would need to be too complex to be practical if such heterogeneities were incorporated, oversimplifications usually occur.

The problem with codes that can accommodate these features is that they cannot be verified. It is somewhat paradoxical that as more and more sophisticated representations of heterogeneous porous media are developed, it becomes increasingly difficult to compare the resulting calculations with experimental or field observations to validate model predictions. This is because of the greater burden placed on the detail of observation required to compare with the model calculations (Lichtner, 1996).

Where several interactions are considered and the sequential differentiation of the plume or NAPL occurs along the flow path, the uncertainties are likely to increase. Research on geochemical kinetics has revealed a wealth of possible mechanisms and rates by which minerals, organisms and aqueous species may interact (Steeffel and MacQuarrie, 1996). Thus, in the best-case situation, even by adopting the best-constrained independent input parameters, one must accept at least one order of magnitude uncertainties in each parameter. It follows *that the results of reactive transport calculations performed using independently constrained parameters, will also most likely have uncertainties of several orders of magnitude, at best* (Oelkers, 1996).

Despite all of this, models may still be regarded as useful tools, provided the results are presented and evaluated with these limiting factors clearly reported and understood.

4.5 Case Study

Results from numerical modelling from the capability of the numerical model to represent geological reality and the ability to measure fractures and fracture networks at the scale of interest are subject to potential biases. During the course of this research, two numerical models have been identified as suitable for the simulation of DNAPL movement within the fractured South African aquifers. MODFLOW is the ideal tool to assist in the conceptual modelling and dissolved phase transport, while UTCHEM is the more complex tool which can be used in detailed simulations taking into account phase differences.

This case study was mainly done to compare results for the two model codes, for the simulation of the movement of DNAPL phase in a typical horizontal fracture system. The conceptual model used, was based on the bedding plane fracture (mode 1 fracture) in the sandstone layer of the Campus Test Site (Section 5.2).

4.5.1.1 Model Setup

The following model domain dimensions and parameters were used:

The **network** constructed for the main sandstone aquifer consists of 56 x 40 cells in the x and y directions respectively. Figure 4-4 is a schematic representation of the network. The cell size varied from 13 m at the edge of the modelling area to 1.6 m in the vicinity of the DNAPL boreholes. The modelled area is 131 m in the x direction and 169 m in the y direction, the total area covered being 22139 m². The network is rotated by -25o to ensure it is parallel with the flow direction, thereby minimizing numerical errors. The model network extends over a larger area than the area under investigation to ensure that the model boundaries will not affect simulated results. The same network was used for both the MODFLOW and UTCHEM simulations.

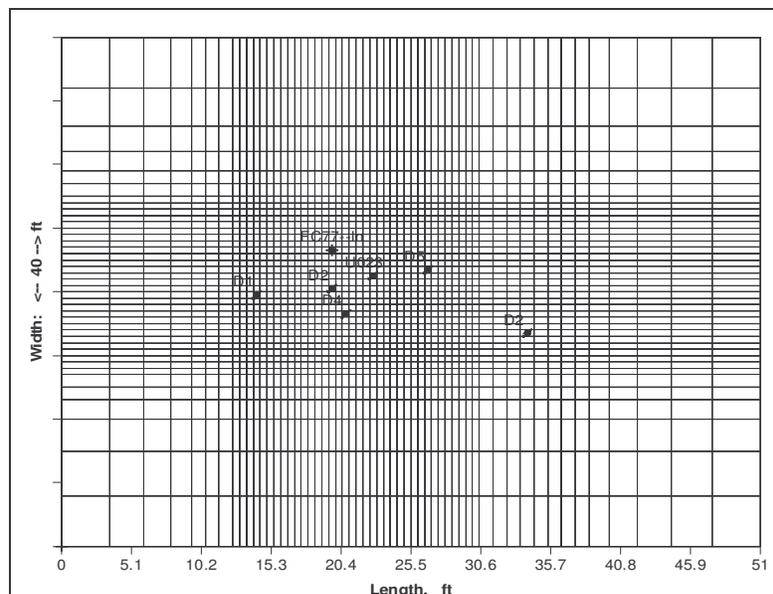


Figure 4-4: Model Network

Boreholes together with their positions are listed below.

Table 4-1: Boreholes included in the models

| Borehole name | Cell in x direction | Cell in y direction |
|----------------------|----------------------------|----------------------------|
| D1 | 11 | 22 |
| D2 | 22 | 21 |
| D3 | 22 | 15 |
| D4 | 24 | 25 |
| D5 | 36 | 18 |
| UO23 | 28 | 19 |
| UO30 | 47 | 28 |

The models are 3-dimensional. It is assumed that the sandstone aquifer is 10 m thick, therefore the **layers** were chosen as:

- Layer 1: 16 – 18 mbgl
- Layer 2: 18 – 20 mbgl
- Layer 3: 20 – 20.5 mbgl
- Layer 4: 20.5 – 21 mbgl
- Layer 5: 21 – 21.4 mbgl
- Layer 6: 21.4 – 21.6 mbgl (fracture zone)
- Layer 7: 21.6 – 22 mbgl
- Layer 8: 22 – 22.5 mbgl
- Layer 9: 22.5 – 23 mbgl
- Layer 10: 23 – 24 mbgl
- Layer 11: 24 – 26 mbgl

It is assumed that the **fracture zone has a thickness** of 20 cm. The network is refined in the vicinity of the fracture to ensure numerical stability.

The **total number of cells** in the model is 24640.

The left and right hand **boundaries** were as Dirichlet boundaries. This is to ensure that the water levels throughout the modelling exercise remain constant and that the groundwater flux is constant throughout the simulations.

Initial conditions were specified as follows: Groundwater within the model is flowing from left to right, with a head of difference of 0.1 m. The initial DNAPL concentration for the study area is set to 0.

Sources and sinks can be defined as recharge and abstraction sources in the aquifer. These can be either water or contaminant sources and sinks. In this model the only

source assigned was to borehole D3 which is injecting 6.9618 l/d of DNAPL into the aquifer. The concentration of the DNAPL (FC77) was set to 1.

A **hydraulic conductivity** of 1 m/d was assigned to all the layers except the fracture, for which a hydraulic conductivity of 250 m/d was assigned. The vertical hydraulic conductivity was set to a factor 10 smaller.

A value of 6% was assigned for **kinematic porosity** to the modelled area, except in the fracture where a value of 25% was used.

A **longitudinal dispersivity** value of 0.007 m was selected for the simulations. Bear and Verruijt (1992) estimated the average transversal dispersivity to be 10 to 20 times smaller than the longitudinal dispersivity. An average value of 0.0007 m was selected for this parameter during the simulations.

4.5.1.2 Numerical model: MODFLOW and MT3D

A numerical flow and mass transport model was set up in MODFLOW and MT3D as discussed in the previous section. The model was then run for a period of 2 days. The NAPL phase was treated as if it was a conservative solute that was injected into the model domain. The numerical model was setup with the fracture dipping be approximately 2 degrees between the injection borehole D3 and borehole D2. The results of the model after 2 days are shown in Figure 4-5.

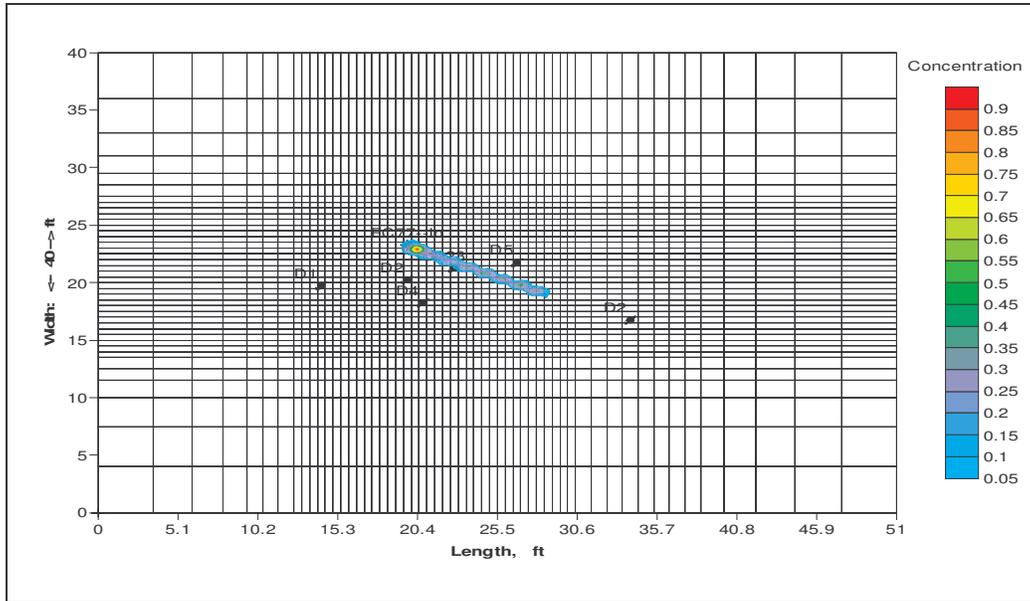


Figure 4-5: Results of the simulation after 2 days (in fracture)

4.5.1.3 Numerical model: UTCHEM

The same model as the PMWIN model was set up in UTCHEM. Additional parameters entered in the model for which MODFLOW and MT3D do not account for are listed in Table 4-2.

Table 4-2: Additional parameters entered in UTCHEM

| Parameter | Value |
|-----------------------------|------------------------|
| Interfacial tension | 1.65 mN/m |
| Solubility of FC77 in water | 0.00015 |
| Viscosity of FC77 | 0.89 |
| Density of FC77 | 1.78 g/cm ³ |

It should be noted that the results are given in the figures are for the fracture layer (layer 6) only, and for the DNAPL (oil) phase only.

The results of the simulation after 1 & 2 days are shown in Figure 4-6 and Figure 4-7.

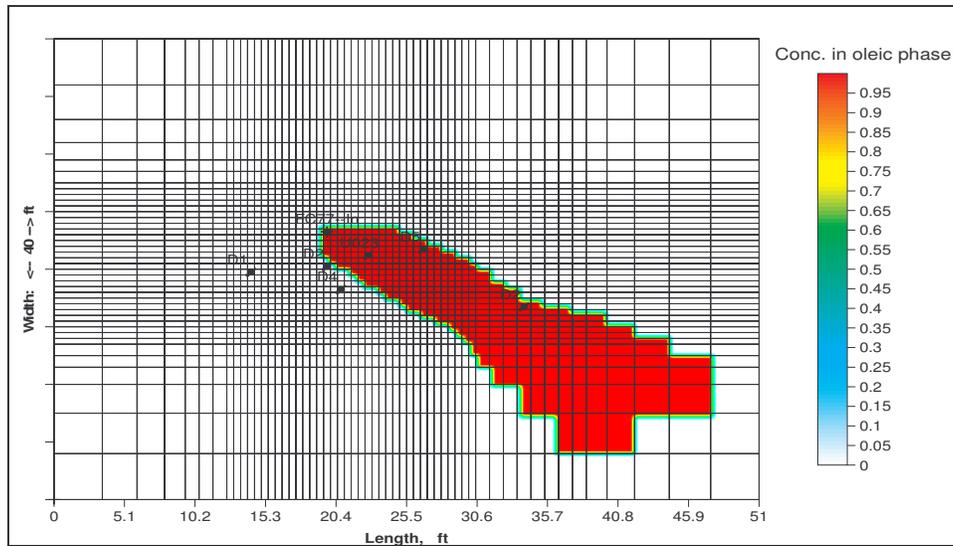


Figure 4-6: Simulation of FC77 after 1 day (in fracture)

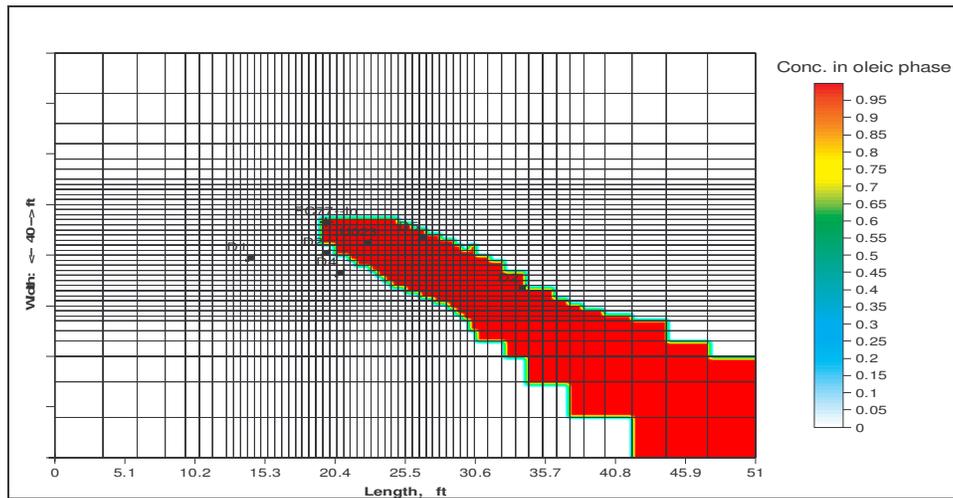


Figure 4-7: Simulation of FC77 after 2 days (in fracture)

The results from the UTCHEM model differs dramatically from those obtained from the MODFLOW/MT3 model (Figure 4-5). One of the main reasons for this is that MODFLOW does not take into account the dip of the fracture. The flow in MODFLOW is dependant on the change in piezometric heads and the groundwater and associated (dissolved) contamination will flow from a higher pressure to a lower piezometric head. In this case the change in piezometric head over the study area is small and therefore there is very little movement of the contaminant over a period of 2 days.

4.5.1.4 Sensitivity Analysis

The purpose of sensitivity analyses is to demonstrate the model responses to variations in uncertain input parameters. The results of a sensitivity analysis can be used to identify sensitive input parameters for the purpose of guiding additional field data collection and, perhaps, focusing calibration efforts.

In this section a sensitivity analysis is performed on the UTCHEM campus model. Various input parameters are adjusted and the results observed. A potential key parameter in real life simulations would be the fracture aperture, but since in this scenario the DNAPL is injected into the system on the fracture layer, this aperture does not play a significant role in determining the expected flow.

4.5.1.4.1 Dip of the fracture

The dip of the fracture in Figure 4-6 and Figure 4-7 is 2° . In this scenario the dip doubled, halved, halved again, totally removed and changed to the opposite direction of water flow. The results of the models after 1 & 2 days are shown in Figure 4-9 to Figure 4-15.

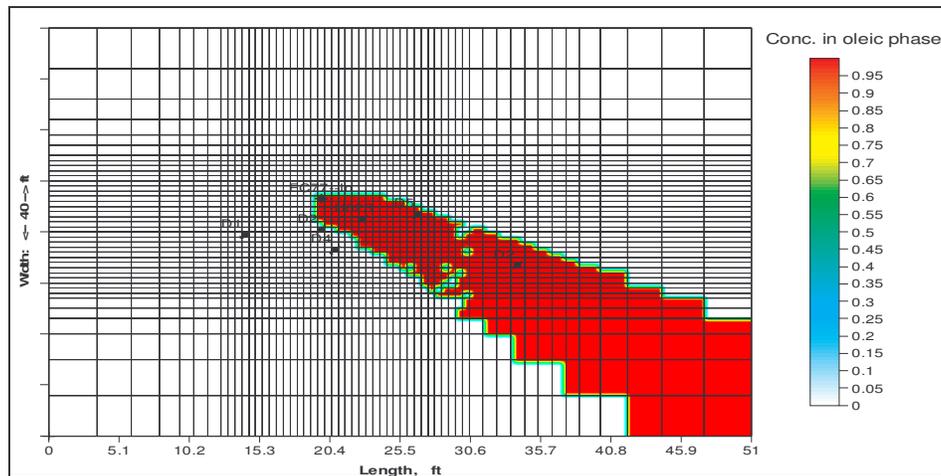


Figure 4-8: Simulation of FC77 after 1 day where the dip is doubled to 4° (in fracture)

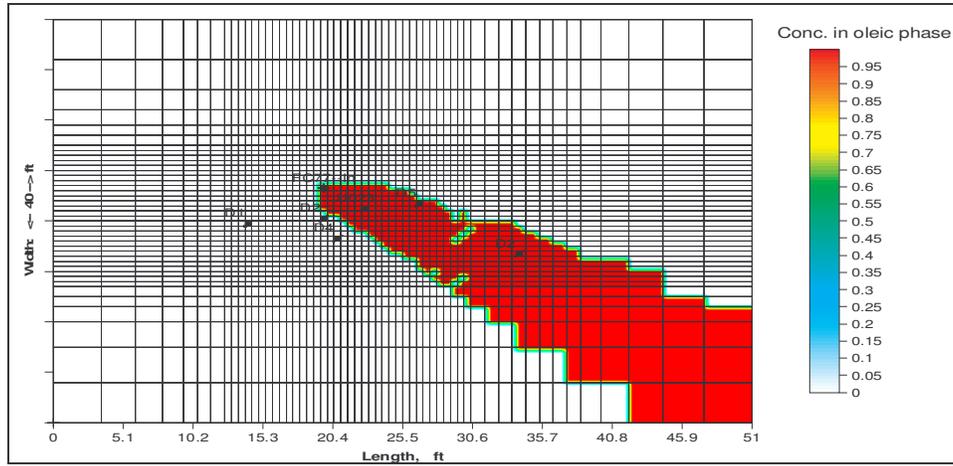


Figure 4-9: Simulation of FC77 after 2 days where the dip is doubled to 4° (in fracture)

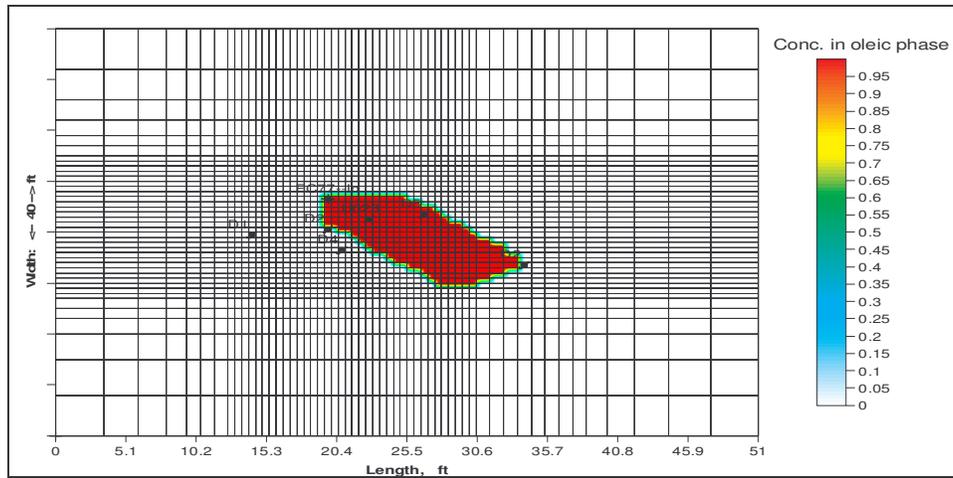


Figure 4-10: Simulation of FC77 after 1 day where the dip is halved to 1° (in fracture)

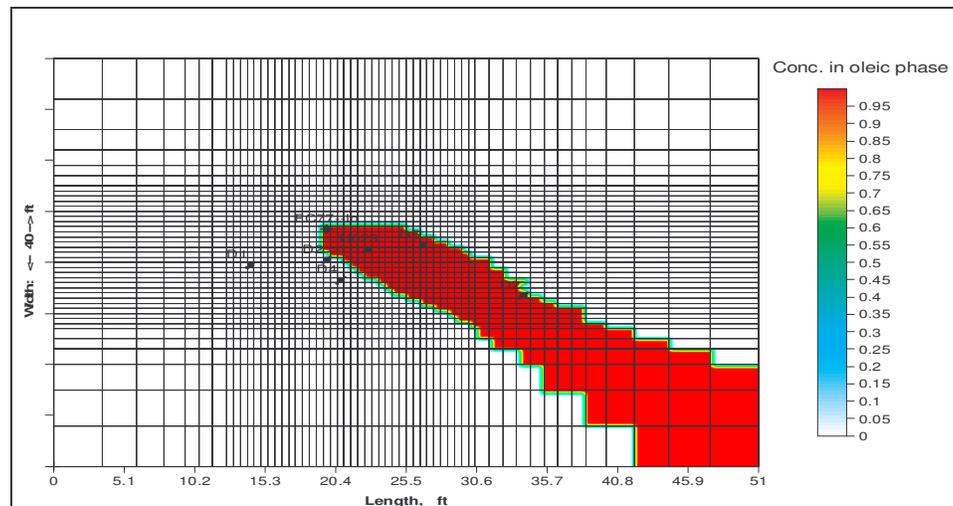


Figure 4-11: Simulation of FC77 after 2 days where the dip is halved to 1° (in fracture)

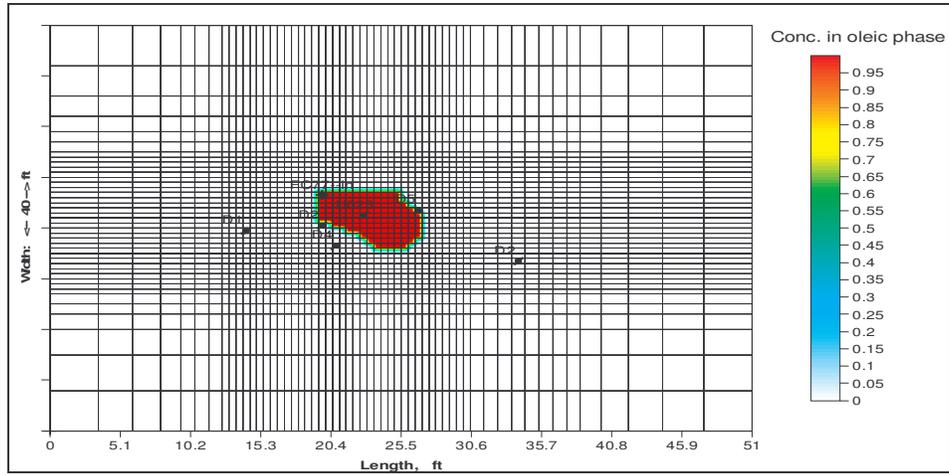


Figure 4-12: Simulation of FC77 after 1 day where the dip is reduced to 0.5° (in fracture)

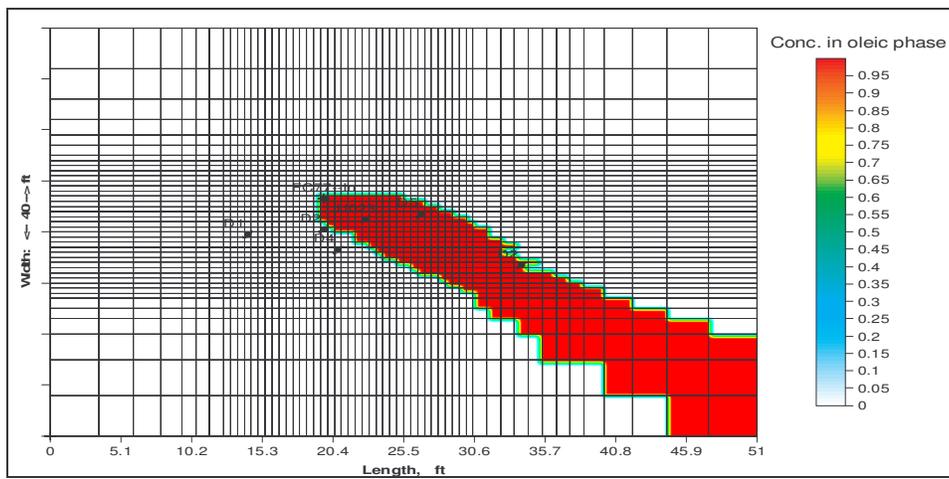


Figure 4-13: Simulation of FC77 after 2 days where the dip is reduced to 0.5° (in fracture)

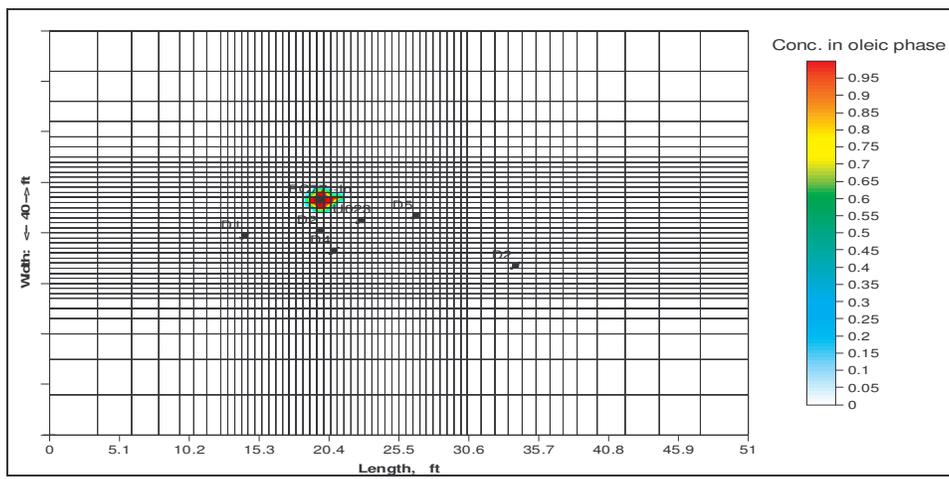


Figure 4-14: Simulation of FC77 after 1 day where there is no dip (in fracture)

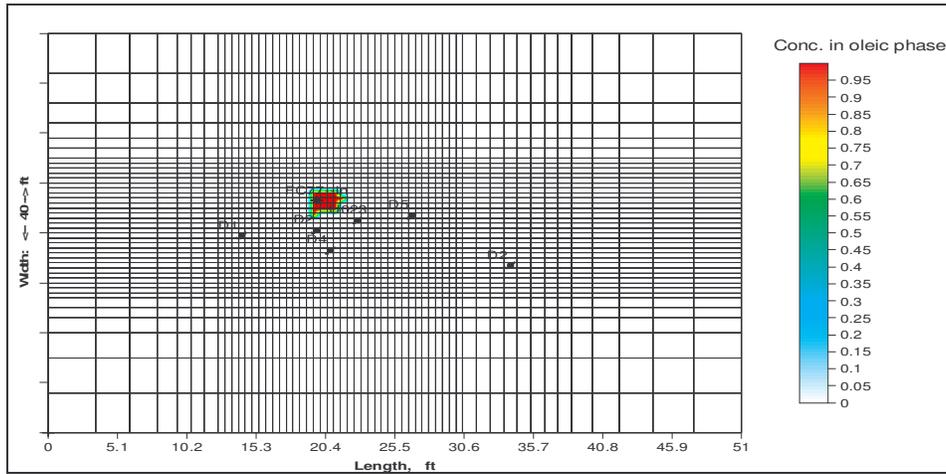


Figure 4-15: Simulation of FC77 after 2 days where there is no dip (in fracture)

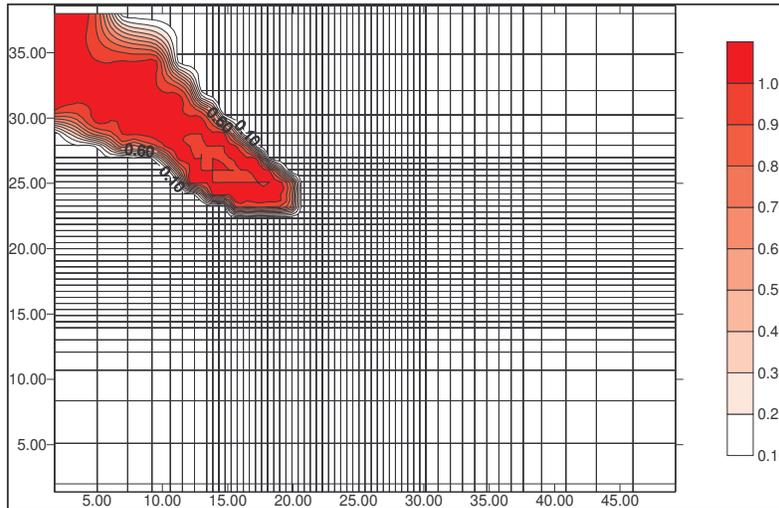


Figure 4-16: Simulation of FC77 after 1 day where the dip is at 2° opposite direction to water flow (in fracture) (Refer to figure 4-4 for positions of boreholes).

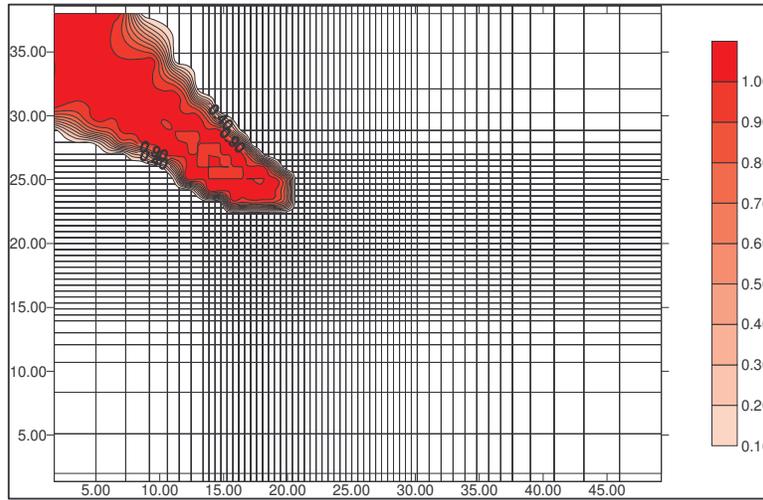


Figure 4-17: Simulation of FC77 after 2 days where the dip is at 2° opposite direction to water flow (in fracture) (Refer to figure 4-4 for positions of boreholes).

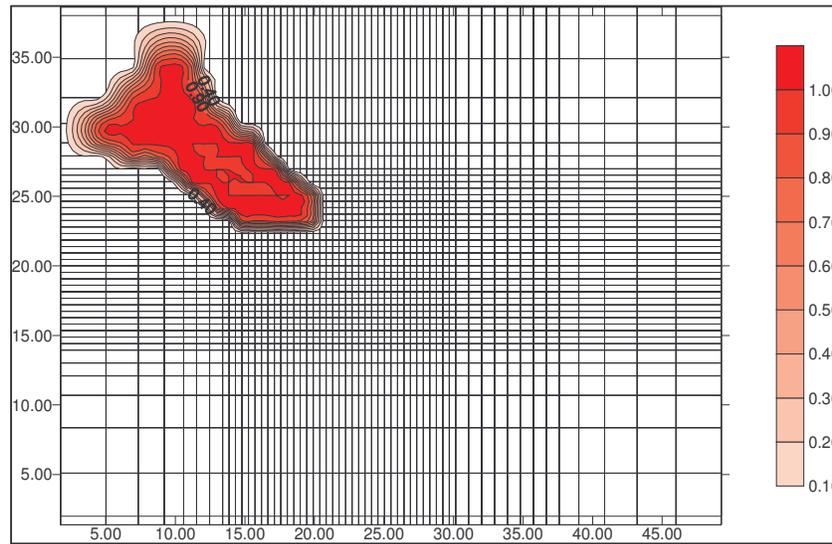


Figure 4-18: Simulation of FC77 after 1 day where the dip is at 1° opposite direction to water flow (in fracture) (Refer to figure 4-4 for positions of boreholes).

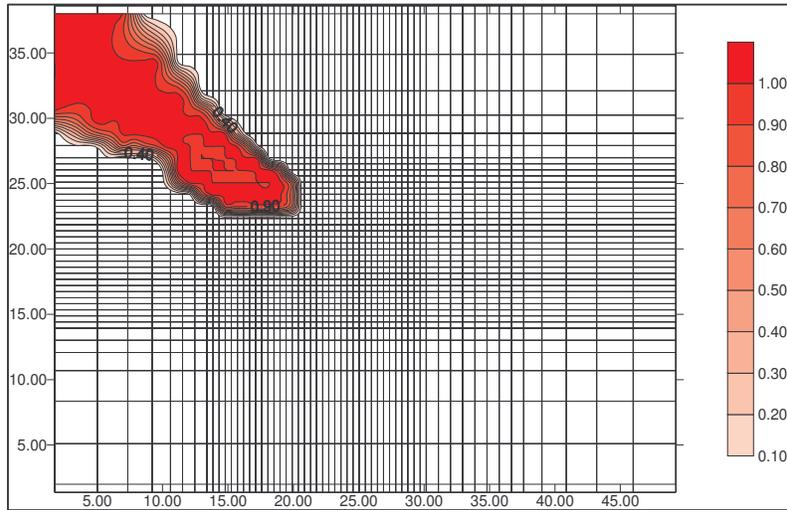


Figure 4-19: Simulation of FC77 after 2 days where the dip is at 1° opposite direction to water flow (in fracture) (Refer to figure 4-4 for positions of boreholes).

From the modeling results it is clear that the model is very sensitive to the dip of the fracture and it is therefore important to quantify this correctly. The no dip simulation correlates very well to the MT3D simulation given in Figure 4-5. The apparent lower concentrations in the direction of flow are as a result of preferred pathways that form. As the layer becomes oil wet, the relative oleic permeability increases, facilitating DNAPL flow and leading to an increase in tortuosity in the direction of flow.

4.5.1.4.2 Hydraulic conductivity of the fracture

In this scenario the dip of the fracture is 1°. The hydraulic conductivity of the fracture was increased by a factor 10, then decreased by a factor 10 and factor 100. The model would not run when the hydraulic conductivity was set to 2500 m/d. The results are shown in Figure 4-20 to Figure 4-23.

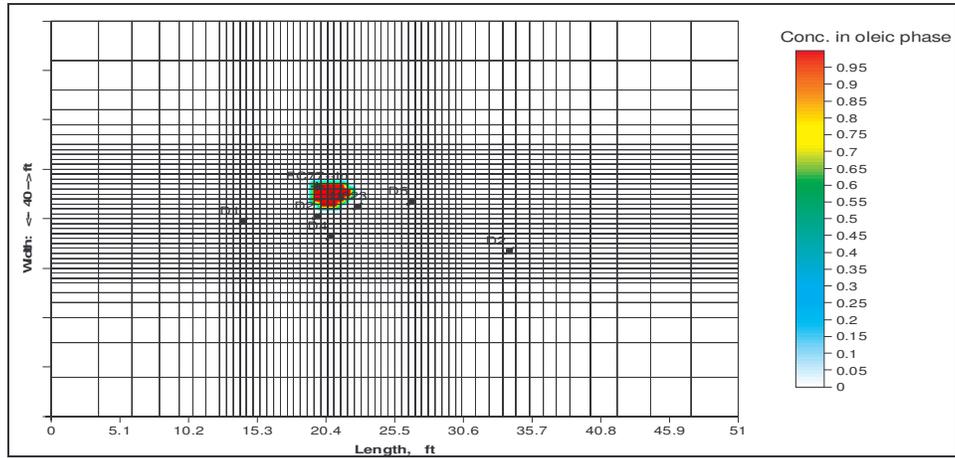


Figure 4-20: Simulation of FC77 after 1 day with the fracture hydraulic conductivity set as 25 m/d

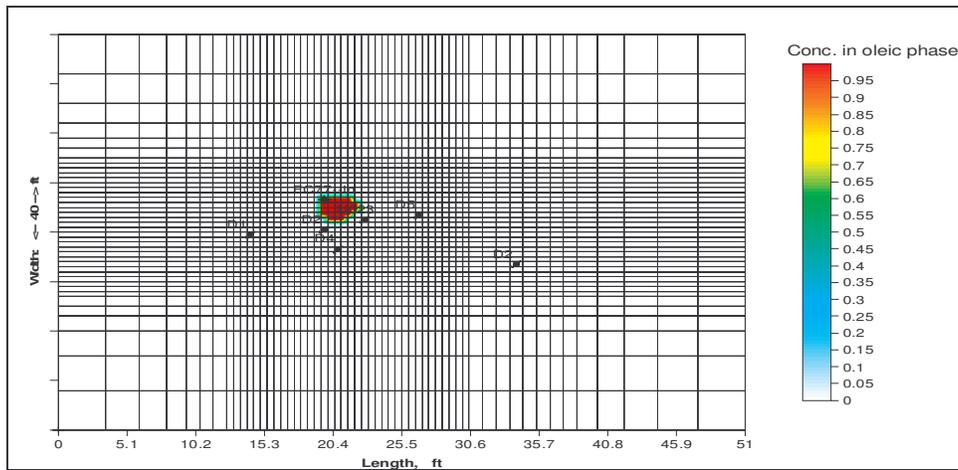


Figure 4-21: Simulation of FC77 after 2 days with the fracture hydraulic conductivity set as 25 m/d

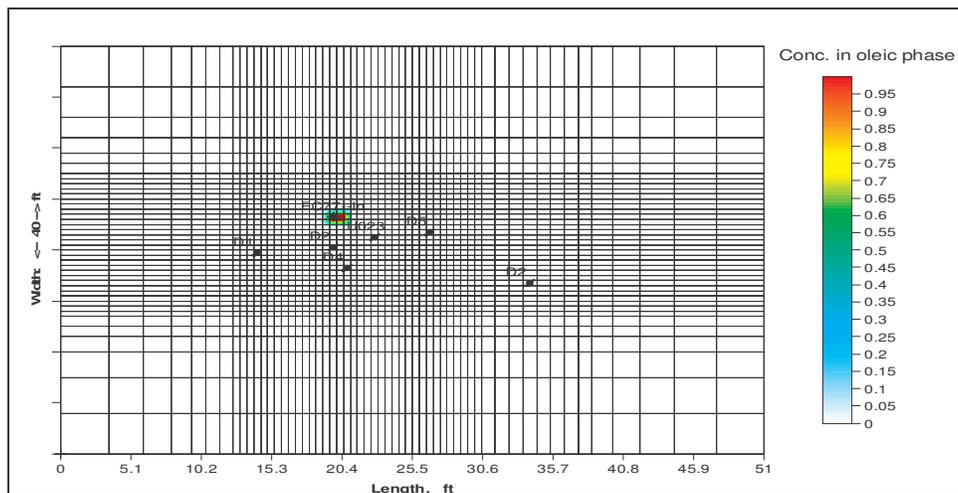


Figure 4-22: Simulation of FC77 after 1 day with the fracture hydraulic conductivity set as 2.5 m/d

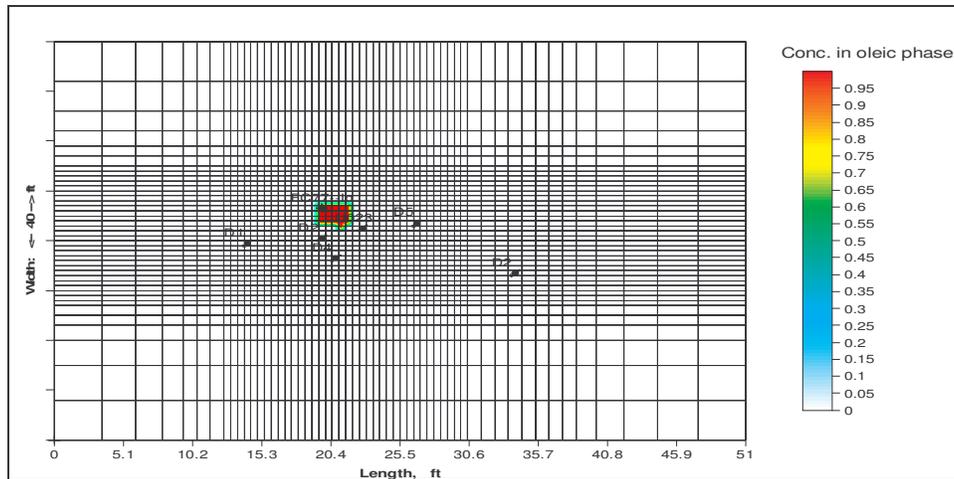


Figure 4-23: Simulation of FC77 after 2 days with the fracture hydraulic conductivity set as 2.5 m/d

The results can be compared to Figure 4-10 and Figure 4-11, where the model was run under the same conditions except the hydraulic conductivity in the fracture is 250 m/d. Because of the dramatic influence of hydraulic conductivity on the movement of the DNAPL an additional scenario was run where the 250 m/d was halved to 125 m/d. The results are shown in Figure 4-24 and Figure 4-25.

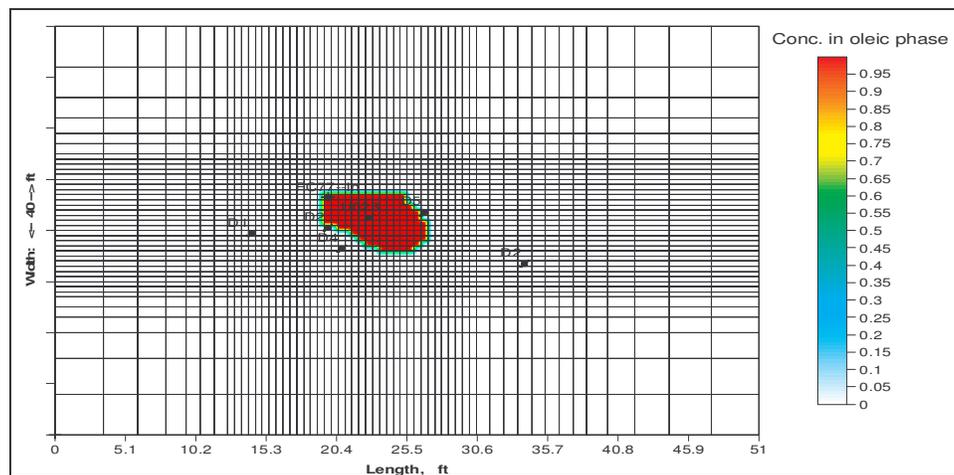


Figure 4-24: Simulation of FC77 after 1 day with the fracture hydraulic conductivity set as 125 m/d

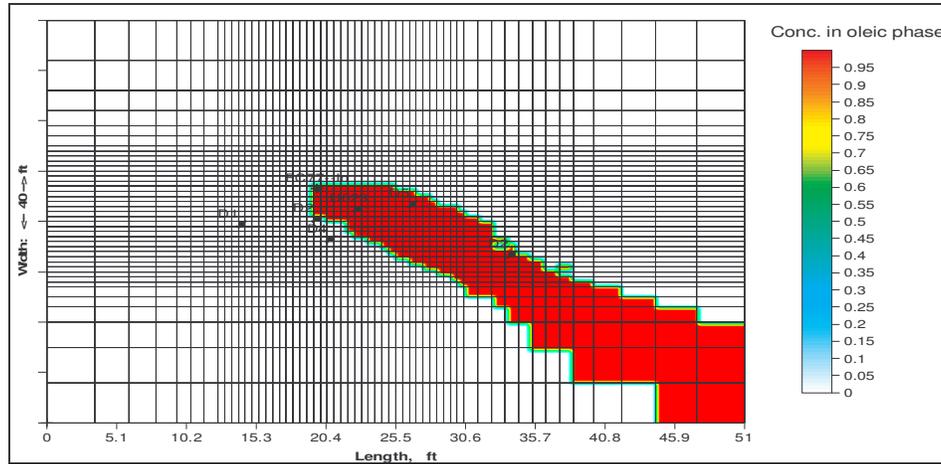


Figure 4-25: Simulation of FC77 after 2 days with the fracture hydraulic conductivity set as 125 m/d

The model is sensitive to changes in hydraulic conductivity in the fracture and therefore this parameter must be known to ensure the simulations are correct.

The results can be compared to Figure 4-10 and Figure 4-11, where the model was run under the same conditions except the interfacial tension parameter is set to 1.65 mN/m. There is no difference in the plumes when changing this interfacial tension parameter. The reason for this being that in the model formulation this factor only plays a role when mobilization with, for example cosolvents, are simulated.

However, interfacial tension will play a role is in the selection of the input parameters of the Van Genuchten relationship with capillary pressure. The selection of the curve which is dependant on the water saturation and capillary pressure (thus interfacial tension) relationship, and the calculated parameters will play a role in the transport mechanism and migration pathway.

4.5.1.4.3 Comparison between FC77 and Trichloethylene (TCE)

The same model as shown in Figure 4-10 and Figure 4-11 was run for TCE. The parameters associated with TCE are listed in Table 4-3.

Table 4-3: Parameters associated with TCE

| Parameter | Value |
|------------------|------------------------|
| Solubility | 1100 mg/l |
| Viscosity | 0.39 |
| Density | 1.46 g/cm ³ |

The results are shown in Figure 4-26 and Figure 4-27.

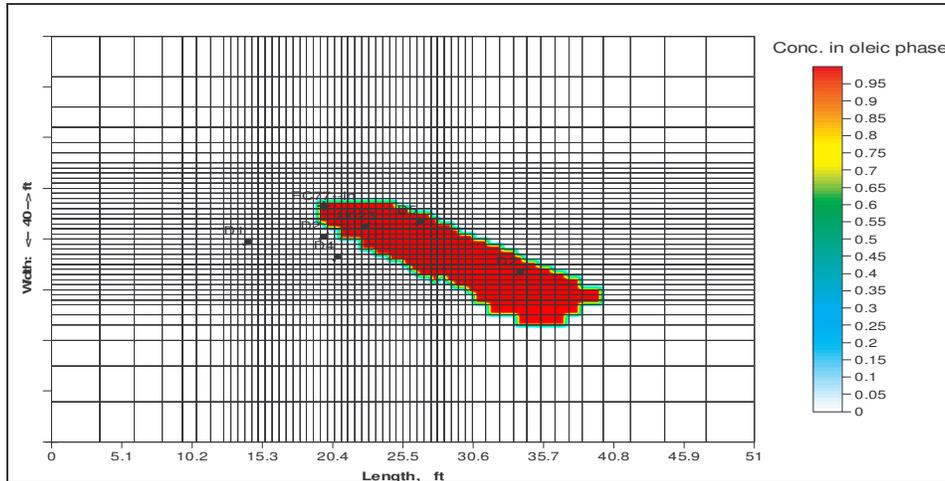


Figure 4-26: The movement of TCE in fracture after 1 day

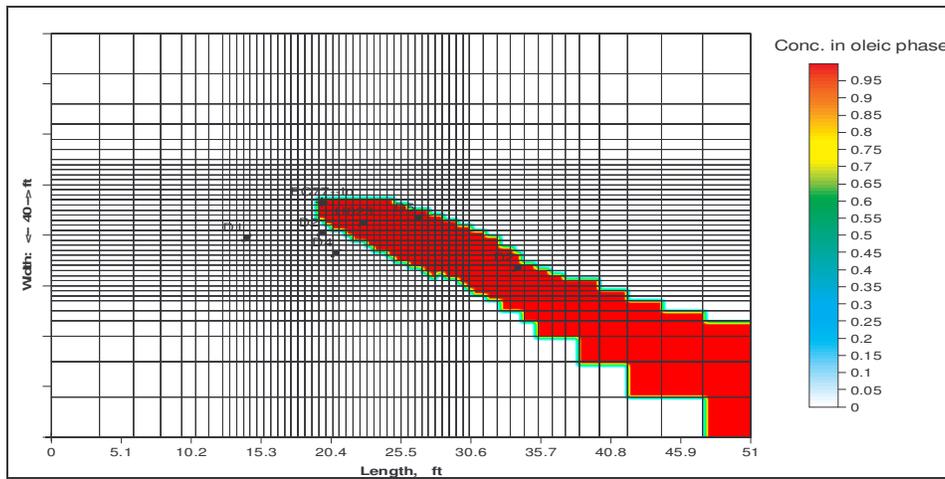


Figure 4-27: The movement of TCE in fracture after 2 days

Modelled results are similar to that of the FC77 simulations. This is a result of similar input parameters for the two substances. The dissolved phase simulation should however, differ significantly due to difference in solubility.

4.6 Discussion

From the results of the modelling the following conclusions can be drawn:

1. A “traditional” numerical model such as MODFLOW does not take into account the properties of the DNAPL fluid and can therefore not simulate the fluid movement within a fractured aquifer system.
2. A numerical model such as MODFLOW will be useful to simulate dissolved transport at a DNAPL contaminated only after site and the fracture

characterization was performed to determine the potential extent of the NAPL source zone.

3. The sensitivity analysis showed that the UTCHEM model is very sensitive to the fracture parameters, especially the hydraulic conductivity and fracture dip.
4. Results from proper fracture characterization, needs to be incorporated into the conceptual model, because even small scale heterogeneities in the fracture network can influence the flow paths of the NAPL fluid.

5 Determination of critical factors for transport of DNAPLs in fractured and fractured porous systems

5.1 Introduction

Field and laboratory studies were undertaken to determine critical factors for the fate and transport of DNAPL contaminants in (porous) fractured aquifer systems in South Africa. Two research field sites were used to test field methodologies, evaluate field measurements/results, and conduct field scale experiments on. The Campus Test Site is uncontaminated by DNAPLs, and was used to serve as an experimental site. Test Site 1, was used to test site assessment techniques on, and evaluate results from a DNAPL contaminated site. This chapter will discuss these techniques, experiments, and results completed for this research on the field sites. Also included in the chapter are, results from laboratory experiments.

5.2 Experiments at the Campus Test Site

5.2.1 Background

The Campus Test Site is located at the University of the Free State, Bloemfontein. The site has been studied with various hydrogeological and geophysical experiments by postgraduate students and researchers since 1991. The aquifer system is composed of porous and fractured porous sedimentary layers. Due to the extensive work which has been done on the site, the hydrogeological properties and geological features have been characterized in great detail over a period of almost twenty years. There are thirty-five percussion and seven core-boreholes in the site and covers an area of 180 x 190 m.

The site is uncontaminated by DNAPLs, and was used to serve as an experimental site for understanding critical factors for DNAPL flow and for the field injection of a DNAPL-surrogate. The campus test site provides the opportunity to investigate different site characterization methods and results obtained over the various research projects, and from this compare site characterization techniques and understand DNAPL flow in a real field situation, but without the obvious complications of a contaminated industrial site.

Previously 30 percussion boreholes were drilled, and for this research, an additional 6 percussion boreholes and two core boreholes were drilled. The distribution of boreholes is provided in Figure 5-1.

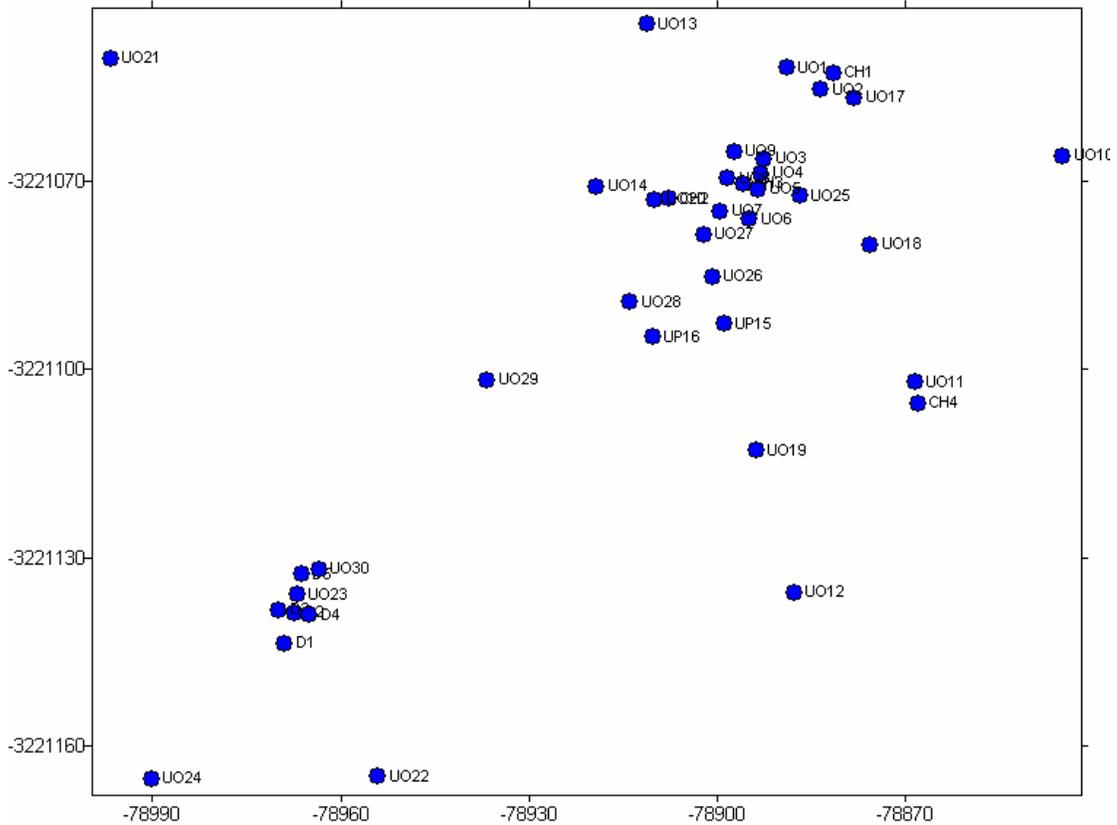


Figure 5-1: Location of boreholes in the Campus Site.

The conceptual model of the site was discussed in depth by Botha *et al.* (1998). The site is composed of three aquifers as shown in Figure 5-2. The first aquifer is a phreatic aquifer that occurs in a laminated alternation of mudstones and siltstones (6-9 m thick) and a fine grained rhythmite sequence (1-6 m thick). A black carbonaceous shale layer (0.5 - 4 m thick) separates the first aquifer from the second and main aquifer. This aquifer occurs in the 8-11 m thick sandstone layer, and is confined. The third aquifer, also a confined aquifer, occurs in a succession of interbedded mudstone, siltstone and fine-grained sandstone. Aquifer 2 has high yield because of a horizontal fracture with aperture of 1 mm.

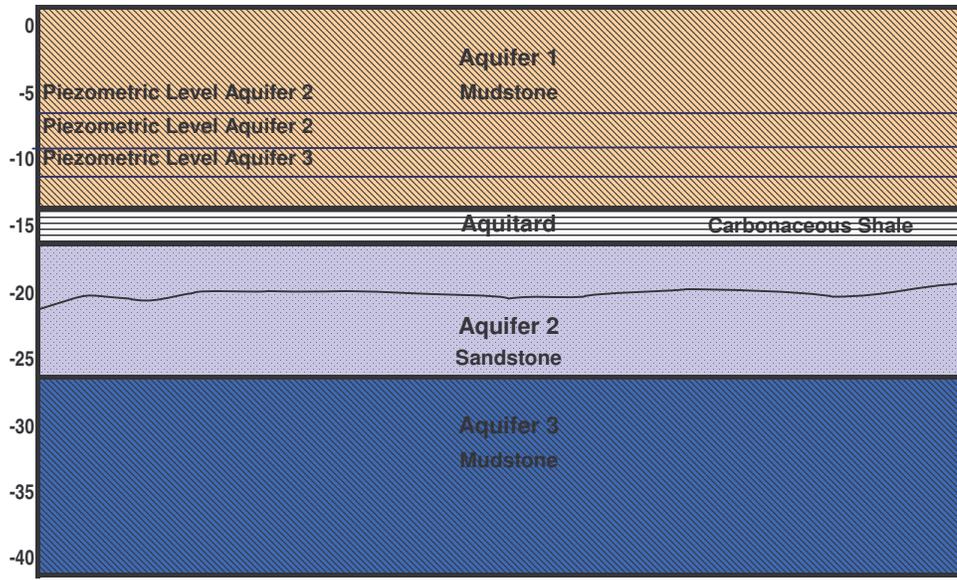


Figure 5-2: Conceptual model of Campus Test Site (after Botha *et al.*, 1998).

5.2.2 Geology

The Campus Test Site is underlain by a series of mudstones and sandstones from the Adelaide Supergroup of the Beaufort Group of formations in the Karoo Sequence (Botha *et al.* 1998). Mapping of geological outcrops around the Campus Site reveals the existence of extensional fractures (mode 1) and shearing fractures (mode 2). The dominant type of fractures recognised in the sediments includes sub-horizontal bedding-parallel fractures and orthogonal and diagonal fractures with dominant north-west, north-east and east-west trends.

The mode 1 fracture is the most significant fracture on the Campus Site and all boreholes with high yields (11 have yields in excess of 3 l/s) intersected this bedding-plane fracture. The yields of the other 19 percussion boreholes are less than 0.6 l/s because the mode 1 fracture was not intersected during drilling. It is clear from both the borehole geophysical logs and video cameras that the mode 1 fracture is located about 21 m below the surface. It consists of fracture zone with a thickness that varies between 100-200 mm (i.e. the fracture zone has developed as consequence of the weathering of the rock between two bedding-plane fractures that were close together (Riemann *et al.* 2002), and it is sub-horizontal.

For the purpose of DNAPL experiments, six new air percussion boreholes were

drilled, located in the south-east section of Figure 5-1. They were labelled from D1 to D6, shown in close-up in Figure 5-3.

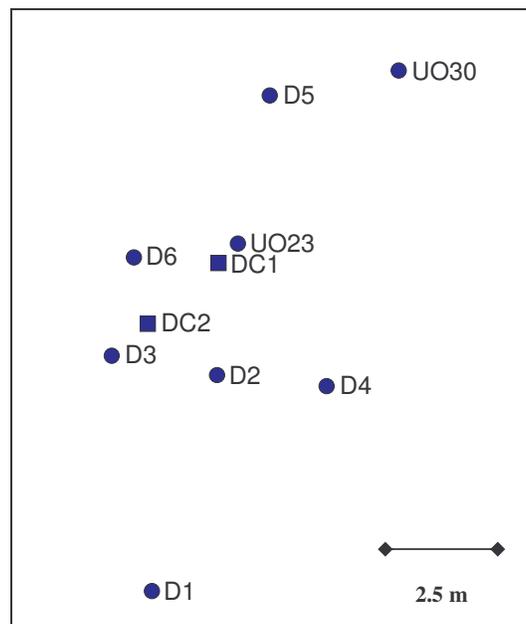


Figure 5-3: Distribution of the DNAPL boreholes.

Three of the boreholes, namely D2, D3 and D4, had blow yields of greater than 3 L/s, which indicates that they intersect the mode I fracture network. The intersection of the fracture by the boreholes was confirmed through slug tests, pump tests, video camera logging, and borehole geophysics. The remaining boreholes, D1, D5, and D6, have blow yields of less than 0.6 L/s and do not intersect the fracture.

The geological profile of the DNAPL boreholes is very similar to that of the pre-existing boreholes. The geological log of borehole D3 is given in Figure 5-4 as an example. The figure also shows EC log of the borehole showing an anomaly at the position of the mode 1 fracture. The geologic profile in the rest of DNAPL profile can be represented by that of D3. Selected boreholes' (D1, D2, D4, D5, and D30) geological profiles are provided in Appendix D1.

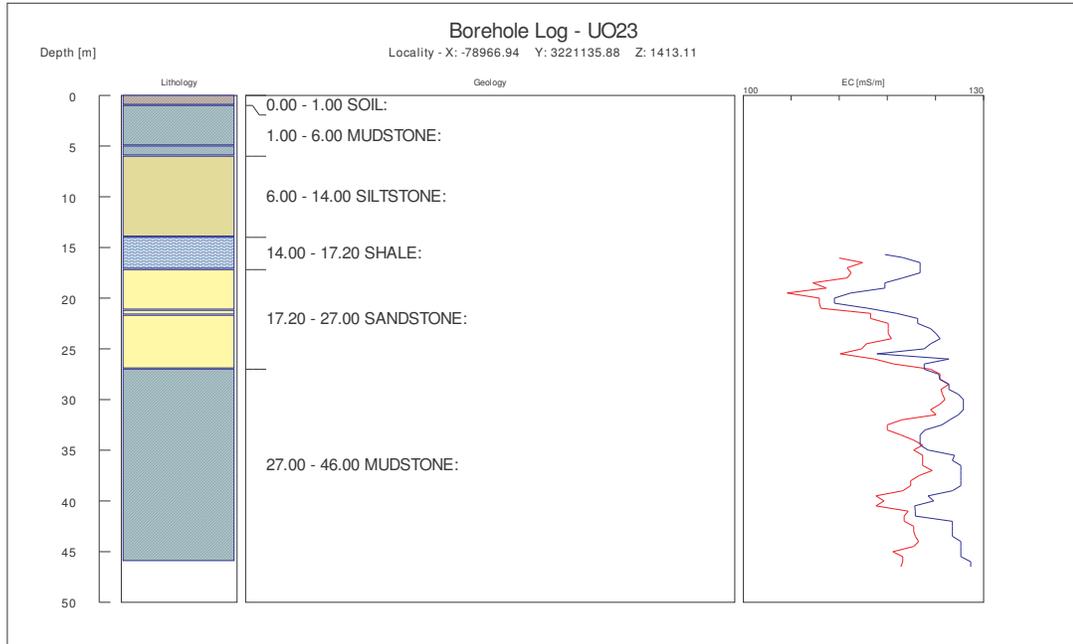


Figure 5-4: Geologic and EC profile of borehole UO23.

The mode 1 fracture (referred to from hereon as “the fracture”) is the most significant feature that determines the yield of the boreholes on the site. From drilling, aquifer testing, video camera logging, and down-hole geophysics the position of the fracture is around 20 – 22m below the ground surface and it is roughly parallel to the geological layers with an almost horizontal dip.

Fracture mapping has also been done on available outcrops near the site, and this has not shown good correlation with detailed hydraulic and down-the-hole fracture characterization methods. The orientation of the fracture plane was investigated; however, the exact dip and strike of the fracture plane results showed large variation for different borehole pairs. Table 5-5 lists the calculated dip and strike values from different borehole combinations. Generally for the site, the fracture orientation is in a north easterly direction. The variability in strike and direction of dip is expected in heterogenous fractured media.

5.2.3 Additional Field Investigations

As previously stated the Campus Test Site has been used in past research projects and extensive site characterisation and hydraulic testing have previously been done at the site. However, for the purpose of this research 8 new boreholes were drilled to the south-west of the site. The purpose of these boreholes was to study fracture

characterisation methods, and investigate subsurface DNAPL flow within a fracture system, of a surrogate DNAPL.

Table 5-1 gives a summary of the field investigations completed at the site for the purpose of this research. Various borehole geophysical techniques were applied to locate the fracture (Section 5.2.5.1.2). The resolution of the techniques was sometimes insufficient to locate fractures to within a few centimetres. In order to obtain the best result from a borehole log, as much information as possible was compiled and compared, using the multiple toolbox approach. Sometimes the fracture did not give a unique response to a single technique, but by comparing the response to other techniques, a better interpretation was reached. The aquifer testing (pump tests and tracer tests) was repeated several times using the same or different sets of borehole combinations (See Section 5.2.5.5).

Table 5-1: Summary of field investigations at the Campus Test Site

| Site Assessment Method | Location | Results/Application |
|--|-------------------------------------|---|
| Drilled air percussion boreholes | D1, D2, D3, D4 ,D5, and D6 | Access to subsurface Geology of the site Lithologic profile Identification of fracture positions D2, D3, D4 and D6 intersect fracture D1 slightly intersect fracture D5 does not intersect fracture Conceptual model development |
| Diamond core drilling | DC1 and DC2 | Fracture and fracture zone positions Lithologic profile Conceptual model development Injection for FC-77. |
| Slug tests | D1, D2, D3, D4 ,D5, and D6 | D2, D3, D4, UO23 higher yielding boreholes D1, D5 lower yielding boreholes |
| Water level measurements | D1, D2, D3, D4 ,D5, D6, DC1 and DC2 | Water level values: D2, D3, D4, UO23 and UO30 \pm 15 m D1 \pm 12 m D5 \pm 7 m. Two aquifer systems identified Time series, seasonal fluctuations |
| Pump test | UO30,D3, UO23, UP16, DC2, and D2 | T of D3 about 17 m ² /day T of UO23 about 17 m ² /day T of D2 about 18 m ² /day UO30 Dewatered in 20 minutes DC2 is connected to other boreholes Fracture connectivity |
| Multi-parameter profiling of DNAPL boreholes | D1, D2, D3, D4 ,D5, D6, DC1 and DC2 | Anomalies associated with fracturing and flow paths |

| | | |
|---|----------------------------|---|
| Point dilution tests | UO23, D3 | Estimation of Darcy and seepage velocity Comparison of results of different tests |
| Radial convergent tests | UO23, D3 | Estimation of : Darcy and seepage velocity Fracture position Fracture thickness Dispersivity Fracture velocity Conceptual model development Preferential flow paths for DNAPLs Comparison of results of different tests |
| Video logging | D1, D2, D3, D4 ,D5, and D6 | Measuring tape for depth measurement Compass for fracture direction Apparent Aperture of fracture Conceptual model development Preferential flow paths |
| Down-hole Geophysics (One-arm Caliper Natural Gamma; Spontaneous Potential; Resistivity, Full Wave Sonic, and Neutron-neutron) | D1, D2, D3, D4 ,and D5 | Used in fracture characterization and confirmation of preferential flow paths |
| Brine experiment | Injected into DC2 | Supersaturated NaCl solution to simulated density driven flow Flow was towards D3 Preparation for FC-77 experiment |
| FC-77 experiment | Injected into DC2 | Injected surrogate DNAPL to observe NAPL flow in fracture system in aquifer Video logged procedure in D3 Flow was towards D3 |

5.2.4 Conceptual site model

The site is characterised by the presence of different fracture sets at different orientations. For example, a borehole video camera of D3 shows that two fractures zones, each with a thickness of about 15 cm, are found at depths of ~20.3 m and ~20.5 m. The fracture at 20 m was detected in D2, which is 2.4m away from D3, but the fracture at 20.3 m was not found. On the other hand, the fracture at 20.3 m was located in borehole UO23, which is 3.6 m away from D3, but the fracture at 20 m was not found. This shows that the orientation and density of the fractures vary within few meters. Figure 5-5 shows a preliminary conceptual model of the site.

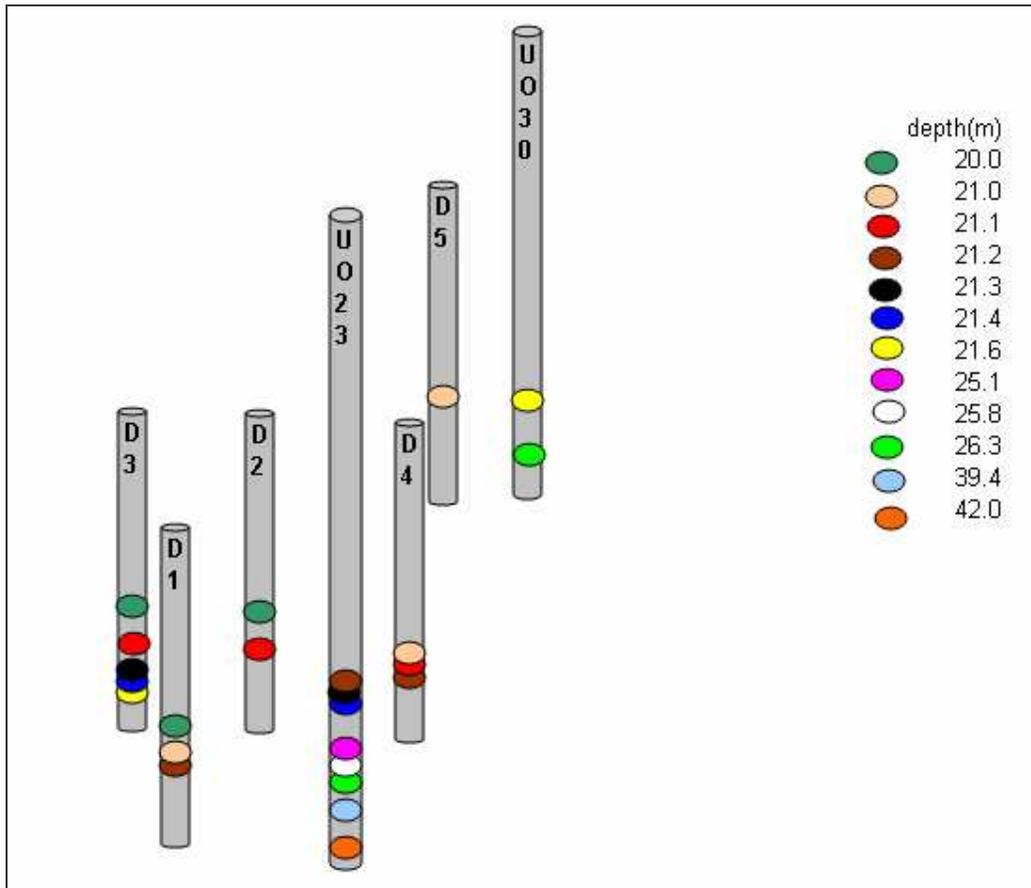


Figure 5-5: Fractures and anomalies detected in the DNAPL boreholes.

While the above figure provides a good indication of the fractures and other features on site, for the purposes of understanding the degree of connectivity between the boreholes, an integrated geological model (Figure 5-6 and Figure 5-7) of these

boreholes was constructed using the information. Since these boreholes have been targeted for the DNAPL surrogate field experiment, a detailed understanding of these features was required to design the experiment correctly and also do construct feasible conceptual models for numerical modelling. The data were consolidated and the Rockworks package again used to portray this visually.

The results are shown below, and indicate the zones of high connectivity in the different boreholes at a depth of around 21m below surface. In the deeper boreholes there is another feature which may be important if the surrogate DNAPL penetrates vertically.

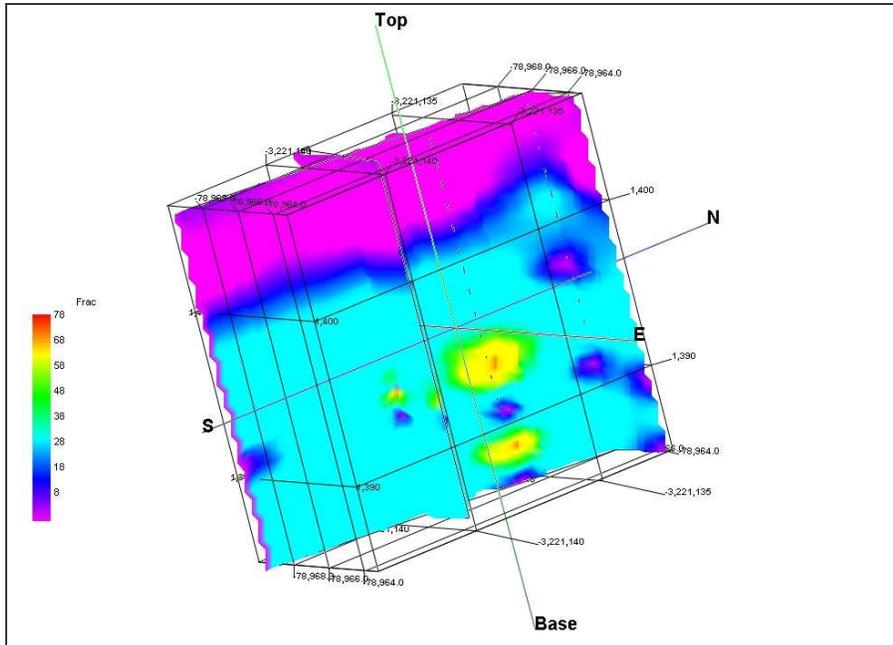


Figure 5-6: Fractures and anomalies integrated into a conceptual geological model of the DNAPL boreholes.

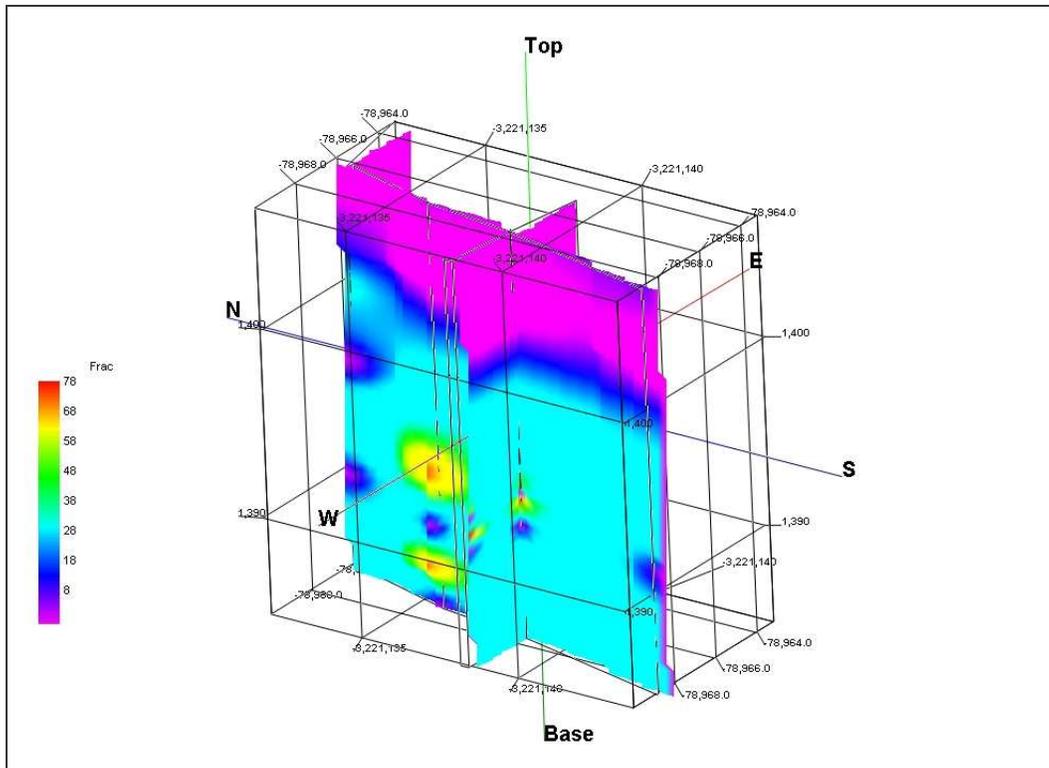


Figure 5-7: Fractures and anomalies integrated into a conceptual geological model of the DNAPL boreholes (yellow to red higher density of anomalies related to fracture zone).

The site is characterised by a bedding parallel fracture that water and contaminant transport due to the transmissivity of the fracture. There were some reports (such as Botha et al, 1998 and Riemann, 2002) stating the depth of the fracture in certain

boreholes, but they were with uncertainty of 10 - 20 cm. Estimating the fracture depth with such uncertainty may result in experimental errors, because the fracture size varies on a millimetre scale in some locations.

Table 5-2 lists the average elevation of the mode 1 fracture in the DNAPL boreholes.

Table 5-2: Campus Test Site average mode 1 fracture elevation.

| Borehole | fracture elevation (m) |
|----------|------------------------|
| D3 | 1391.91 |
| D2 | 1391.82 |
| D4 | 1391.99 |
| UO23 | 1391.76 |
| DC1 | 1391.82 |
| DC2 | 1392.05 |
| UO5 | 1388.08 |
| UO7 | 1388.47 |
| UO26 | 1387.74 |
| UO20 | 1389.44 |
| UO14 | 1388.72 |

The mode 1 fracture is not continuous; instead it is irregular and disconnects at short intervals, making it difficult to estimate its areal extent. As an example, Borehole D5 and UO23 are only 3.5 m apart; however, D5 does not intersect the fracture, while UO23 does. Evaluation of drilling and pump tests shows that most of the boreholes intersect the fracture to some extent. A list of boreholes that intersect and do not intersect the fracture is given in Table 5-3.

Table 5-3: List of boreholes that intersect and do not intersect the fracture (Gebrekristos, 2007).

| Intersecting Bhs | | Non-intersecting Bhs |
|------------------|------|----------------------|
| UO6 | UO23 | D1 |
| CH1 | UO25 | D5 |
| CH3 | UO26 | UO13 |
| D2 | UO27 | UO2 |
| D3 | UO28 | UO24 |
| D4 | UO29 | UO3 |
| DC1 | UO30 | UO10 |
| DC2 | UO4 | UO11 |
| UO1 | UO5 | UO12 |
| UO14 | UO7 | UO21 |
| UO18 | UP15 | UO22 |
| UO19 | UP16 | UO17 |
| UO20 | UO8 | |
| UO9 | | |

The following Section shows, how the during this research the connectivity and therefore the potential fluid (or NAPL) active features of the mode 1 fracture on the Campus Site in the vicinity of the DNAPL boreholes was characterised.

5.2.5 Fracture Characterisation for DNAPL flow

In Section 5.2.4, the hydrogeological conceptual model of the Campus Test Site was discussed. From this it is clear that the bedding plane fracture or mode 1 fracture at approximately 21 meter below surface is the controlling hydraulic feature at the site. All the boreholes that intersect this fracture have borehole yields in excess of 3 l/s.

Characterising DNAPL source zones requires reliable estimates of the mass distribution of the DNAPL in the subsurface, based on the nature of release, the geological structure, and the physiochemical properties of the DNAPL (Lerner, *et al.*, 2002). The depth of penetration is controlled by the connectivity of the fracture network and fracture apertures. Description of connectivity in the literature is generally limited to the physical fracture network, defined as network connectivity. A more useful approach would be to define a connectivity expression based on the fluid active fractures, which form a sub-set of the entire fracture network (Lerner, *et al.*, 2002).

Statistical approaches as described by Wealthall, *et al.*, (2001) can lead to potential bias for principal fracture network parameters. These are summarised below:

Table 5-4: Sources of potential bias for fracture network parameters (Adapted from Wealthall *et al.*, 2001).

| Parameter | Derived fracture network property | Potential bias |
|------------------|--|---|
| Orientation | Inclination, strike and fracture set | Outcrops are subject to weathering and stress relief and give inaccurate measurements. |
| Trace length | Apparent size | Due to the scale of observation (outcrop and borehole) it is difficult to determine true fracture size. |
| Termination mode | Connectivity | Fracture map generation is based on 2D tracemaps and to not represent 3D connectivity. |
| Aperture | Apparent aperture | Hydraulic apertures underestimate aperture, mass balance apertures (from tracer test) may be more representative of fracture porosity. Calculating hydraulic aperture by assigning equal transmissivity to each of the fractures are an unlikely hydrogeological model. |
| Infill | Percentage open for fluid flow | Infill of fractures cannot be incorporated in transport models. |

The aim of this section is to highlight some of the techniques used during this research to characterise fluid active features of the mode 1 fracture on the Campus Site in the vicinity of the DNAPL boreholes.

The approach followed for the fracture characterisation is based on the “toolbox approach” where it is recognized that all characterization methods contribute to the conceptual model, or in this case to the fracture characterisation of the site. A suite of tools are used together with comprehensive integration of the data, until the most accurate understanding is obtained.

The suite of tools used for the fracture characterisation includes the following:

1. Down-hole techniques
2. Geochemical profiling
3. Borehole geophysics
4. Video logging
5. Core drilling
6. Aquifer Testing
7. Pump tests
8. Tracer tests

5.2.5.1 Down-hole techniques

5.2.5.1.1 *Geochemical profiling*

The electrical conductivity (EC) profiles and other geochemical profiles were found to be effective and inexpensive in locating the fractures and other hydraulic features at the site. The ease and cost effectiveness of especially EC profiling, make it an effective part of the fracture characterization toolbox.

In-situ determination of the water quality with a down-the-hole multi-parameter probe is a particularly useful tool to assist in understanding an aquifer system interactions and controls on the water quality. The parameters measured generally included pH, EC, temperature, dissolved oxygen and redox potential. Using all the parameters the hydrochemical description of the system can be improved and correlation with geological and hydrogeological features can be evaluated. The dissolved oxygen, redox and temperature values can also provide useful information regarding the reactions occurring in the immediate environment of the profile, such as inflow of water from recharge areas.

An example of a multi-parameter log of borehole UO23 is given in Figure 5-8. EC (and temperature) profiling was repeated at different times, shown in the figure. The logs show the same trend and show anomalies at depths of 20.5, 25.1, 33 and 40 m. The anomaly at 20.5 m is likely to be the fracture position while the others could either be fractures or geologic boundaries between different rock layers. These values were compared to other results from other down-hole techniques.

Geochemical profiles for the other DNAPLs are shown in Appendix D2. The fracture position was confirmed for most of the boreholes through this method.

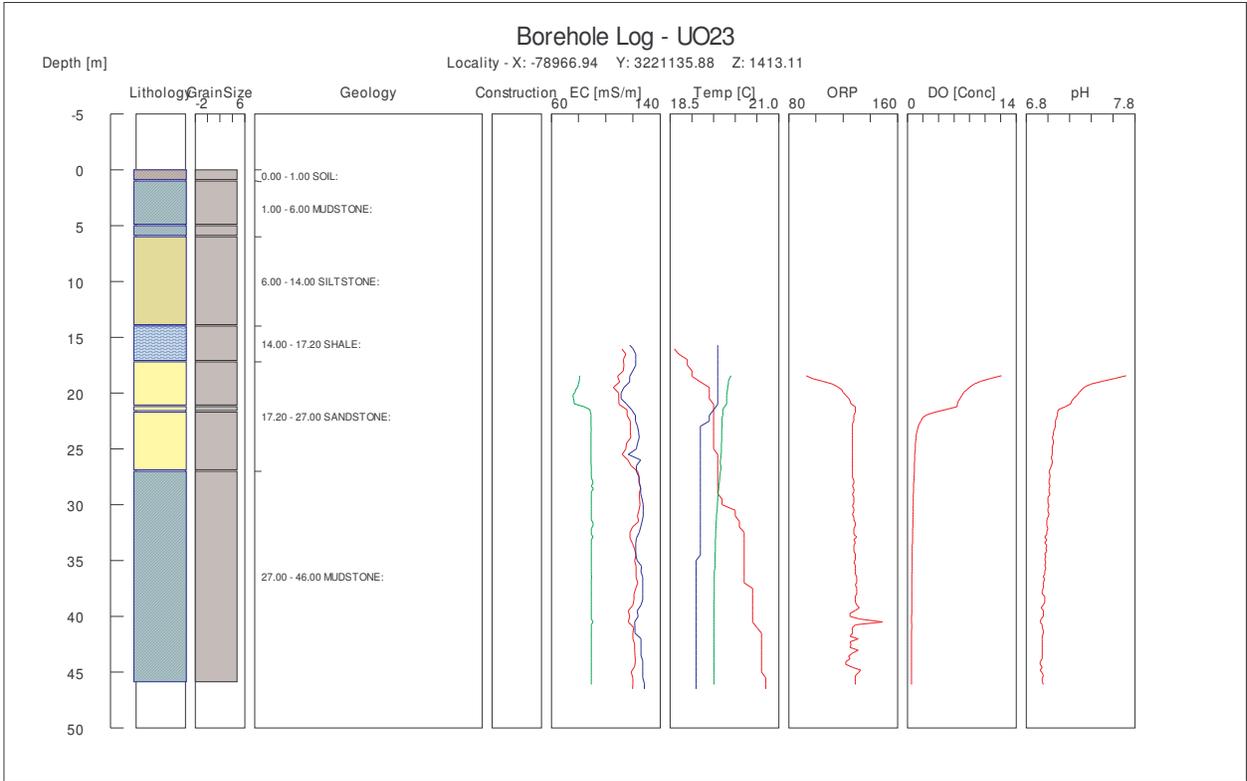


Figure 5-8: Multiparameter geochemical profile of borehole UO23.

5.2.5.1.2 Borehole geophysics

A number of borehole geophysical methods were applied at the Campus Test Site. In the following sections selected profiles are discussed. Full results of the geophysical survey of the DNAPL boreholes are given in AppendixD1.

5.2.5.1.2.1 One-arm Caliper

The one-arm caliper is used to measure the maximum diameter of a borehole. This caliper had only one arm and therefore measured in one dimension. Figure 5-9 shows a calliper profile of borehole UO23. The calliper log showed anomalies at depths of 21.2, 26.2, and 42 m.

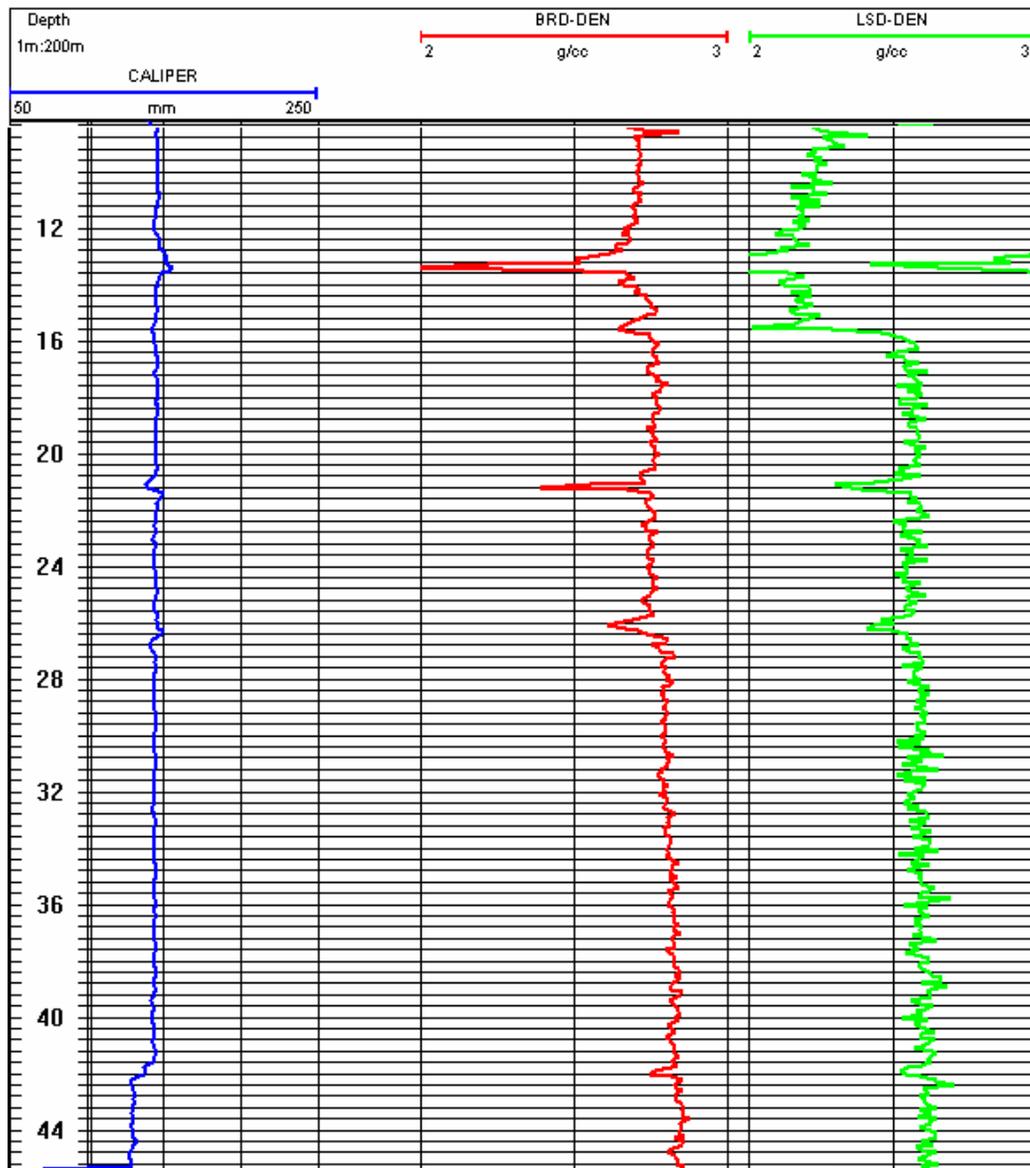


Figure 5-9: Caliper profile of borehole UO23.

5.2.5.1.2.2 Natural Gamma

Natural radioactive isotopes are used to characterise the stratigraphy of boreholes. This technique measures the amount of naturally emitted gamma rays across the borehole profile and anomalies in radioactive isotopes were used to delineate the different geologic units.

Figure 5-10 show natural gamma profile of borehole UO23. This technique does not seem to show anomalies associated with fracturing as some of the other techniques, and location of the fracture could not be identified from this profile. The sharp anomaly above the water level is caused by the borehole's steel casing.

The anomaly at 26 meters is associated with the change in lithology from sandstone to mudstone.

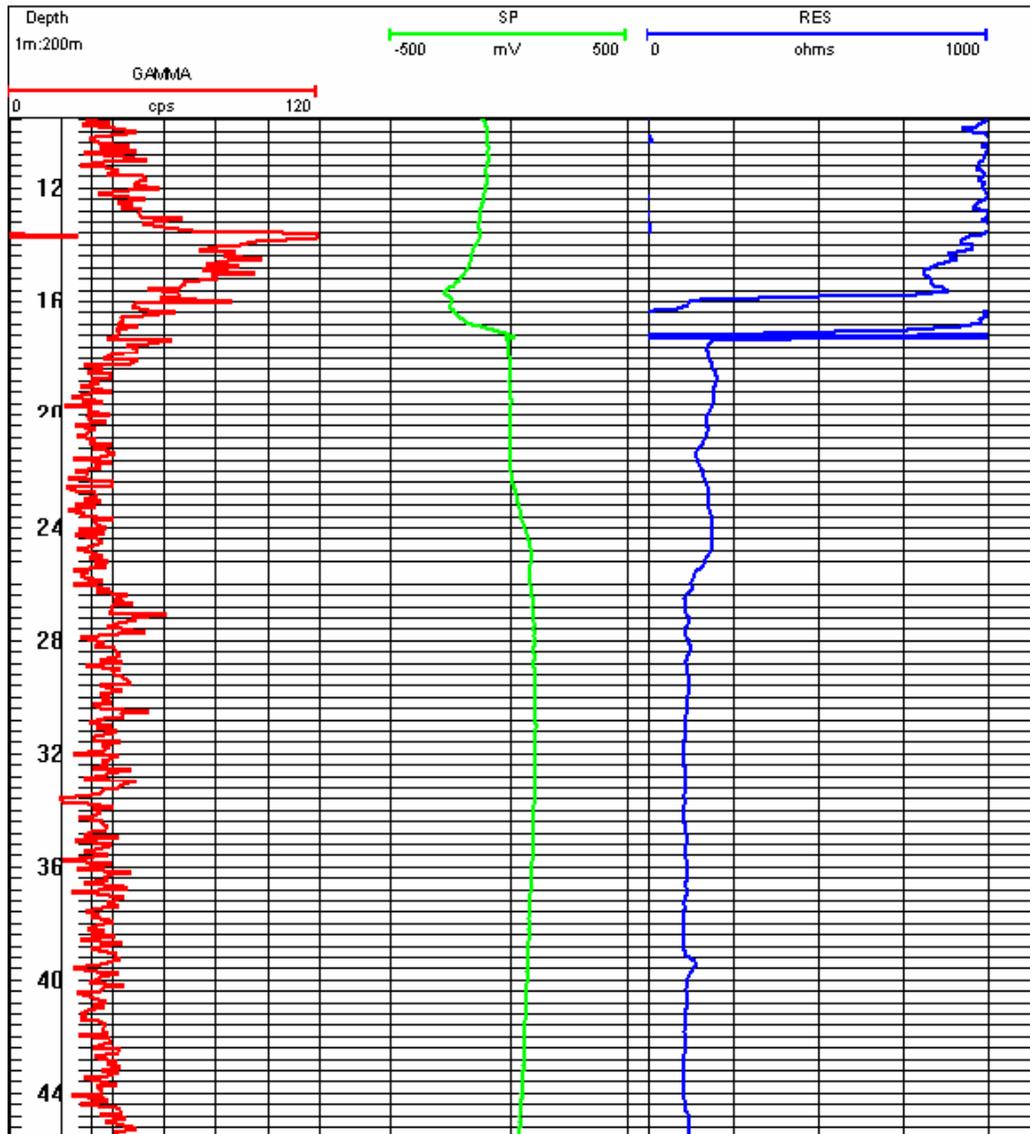


Figure 5-10: Gamma, SP and resistivity log of borehole UO23.

5.2.5.1.2.3 Spontaneous Potential

The spontaneous potential (SP) probe measures change in voltage between the stratigraphies inside a borehole. The spontaneous potential of borehole UO23 is given in Figure 5-10. Similar to the gamma profile, there is no anomaly associated with fractures or the different geologic units. However, the position of the water level is marked by sudden increase in the potential difference at a depth of 16.2 m.

5.2.5.1.2.4 Resistivity

This method measures the electrical resistance of geologic units across the borehole profile, to identify different layers from the resistivity contrast. An example of resistivity profile of borehole UO23 is given in Figure 5-10. The first anomaly at a depth of 16.2 m is the water level; this position was also detected by the gamma and SP methods. Other anomalies are detected at depth of 26 and 39.3 m which could be indicative of changes in lithological units.

5.2.5.1.2.5 Full Wave Sonic (FWS)

Sonic waves travel with different velocities in different lithologic units and can be used to identify these layers. Full wave sonic (FWS) is used to measure formation strength and difference in FWS is indicative of formation difference.

An example of FWS is given in Figure 5-11 which shows the profile of borehole UO23. Anomalies can be seen at depths of 21, 26.5, 39.5, and 45 m. The anomaly at a depth of 21 m is likely associated with the mode 1 fracture. The second anomaly at a depth of 26.5 m is likely due to the boundary between the sandstone and mudstone layers (Figure 5-2). The anomaly at a depth of 39.5 m can be correlated with the anomalies detected by the geochemical profiling and resistivity profiles (Figure 5-10), and are likely a fracture in the mudstone layer.

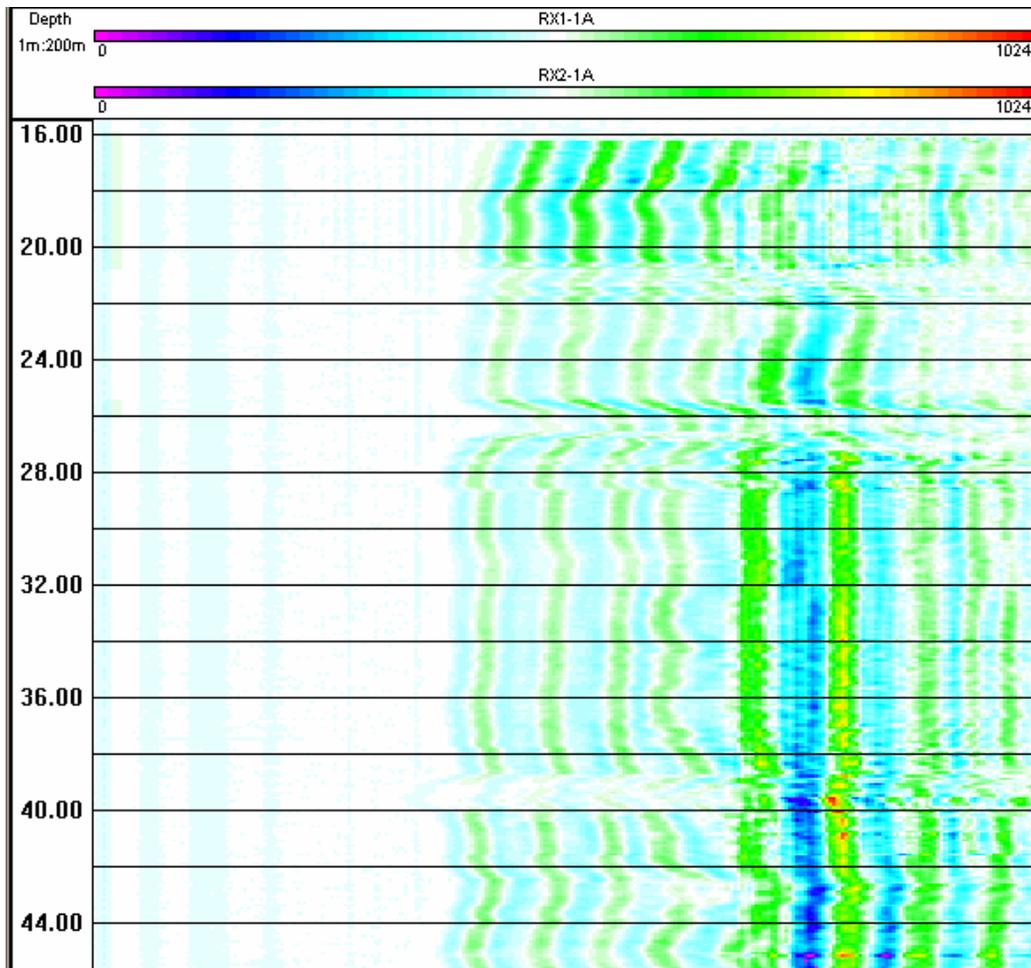


Figure 5-11: FWS log of borehole UO23.

5.2.5.1.2.6 Neutron-Neutron

The neutron-neutron probe measures the rate at which an artificial source of emitted neutrons loses energy by collisions with hydrogen atoms. Most naturally occurring hydrogen in the earth's crust is associated with water, the results are related to the amount of water in the formation.

An example of neutron profile of borehole UO23 is given in Figure 5-12. Three anomalies can be identified, at depths of 15.8, 21.1, and 26.2 m. The first anomaly is associated with the water level. The anomaly at 21.1 m is likely due to the mode 1 fracture and can be correlated with the geochemical, Caliper and FWS profiles. The anomaly at a depth 26.6 m is most likely by the boundary between the sandstone and mudstone layers.

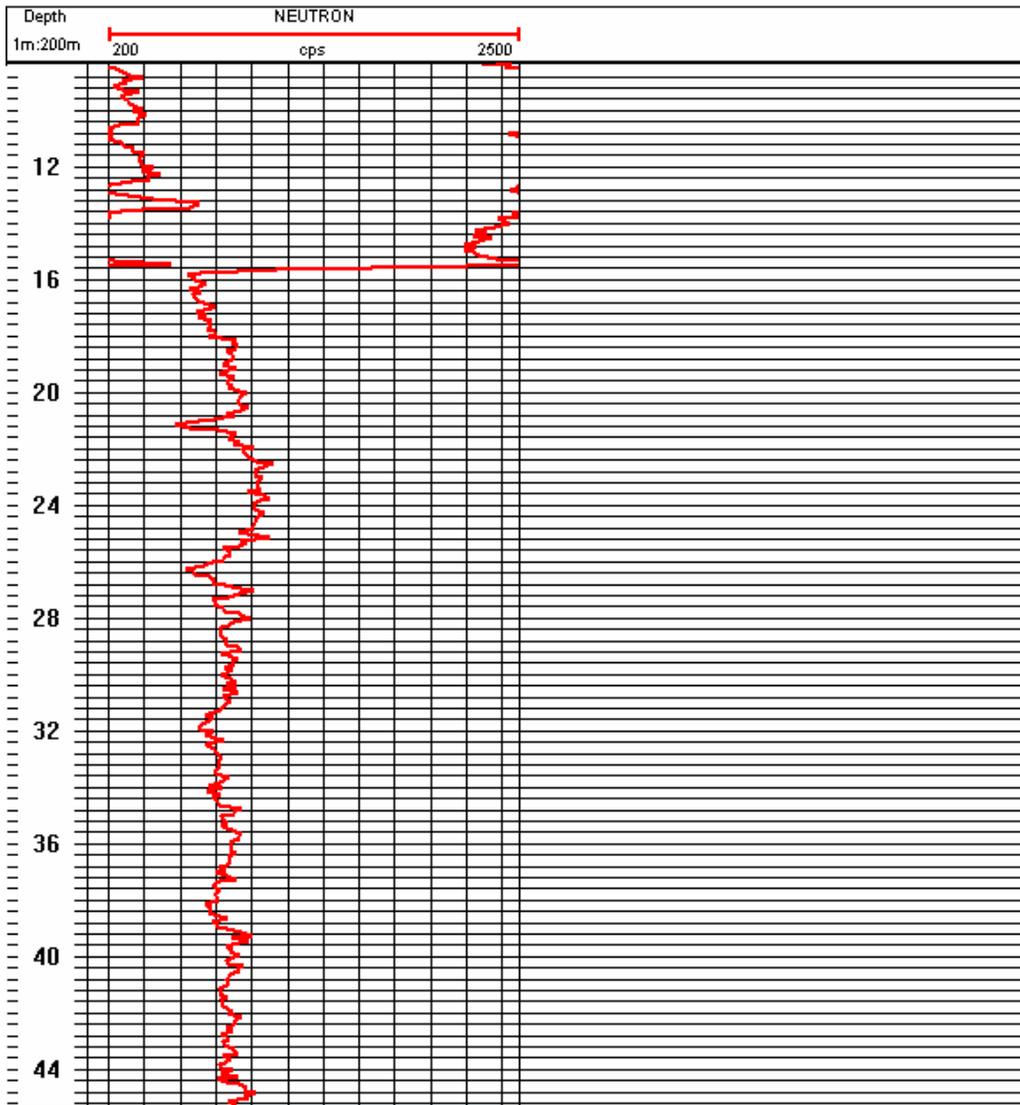


Figure 5-12: Neutron profile of borehole UO23.

5.2.5.2 Video logging

Video logging involves the lowering of the borehole camera down the borehole, similar to the other geophysical probes described above. The advantages of the method include:

- Determination or confirmation of borehole construction (depth, casing type, etc)
- Inspection of casing attributes (e.g. damage, clogging)
- Determination of fracture positions and orientation
- Geological profiling

At the Campus Site orientation of fracture openings were determined by the use of a

compass attached to the camera. Borehole videos are useful to confirm the presence of vertical fractures in boreholes, which can not be detected by use of other geophysical methods (except with optic televiewer). Detection of vertical fractures at a site is very important as these fractures may greatly influence the depth of DNAPL penetration and can explain dissolved concentration found at great depth in the aquifer system.



Figure 5-13: Video camera image of Borehole D3 with accurate depth measurement of the fracture.

All of the percussion drilled boreholes at the mini test site were video logged and orientation of the visible open fractures was determined with use of an attached compass to the camera. Table 5-5 lists the calculated dip and strike values from different borehole combinations.

Table 5-5: Summary of dip and strike of the fracture plane from different combination of boreholes (From Gebrekristos, 2007).

| Borehole Combination | θ (fracture dip and strike) |
|----------------------|------------------------------------|
| UO14, UO7, UO23 | 2.24, N20 ⁰ E |
| UO23, D4, D3 | 1.02, N64 ⁰ W |
| UO14, UO7, D3 | 2.2, N20 ⁰ E |
| UO23, D4, D2 | 0.91, N82 ⁰ W |
| UO23, D2, D3 | 0.46, N80 ⁰ W |
| UO20, UO7, D3 | 44.62, N35 ⁰ W |
| UO14, UO20, D3 | 15.65, N120 ⁰ |

Visual confirmation of fractures that could not be detected through other methods was done in some of the boreholes, etc. D3 at 21.29 and 21.54 m. This was also confirmed through the tracer testing.

5.2.5.3 Summary

The location of anomalies identified by the down-hole techniques did not coincide as expected. For example the position of the fracture in D3 was located at 21.3 m by the resistivity method, 21.4 using the 1-caliper and 21.6 using the EC method. This discrepancy could be result of different elevations used as of point of reference. For some of the measurements the collar height was taken as zero-reference and in other measurements the ground surface was taken as a zero-reference. Summary of the anomalies of geologic features are given in Table 5-6.

Table 5-6: Summary of anomalies detected from borehole geophysics (Gebrekristos, 2007).

| Depth m | D1 | D2 | D3 | D4 | D5 | UO7 | UO14 | UO20 | UO23 | UO30 |
|---------|---------|------------------------|----------|---------|---------|------------|------------------|---------|---------------|---------|
| 12.8 | | | | | V | | | | | |
| 13.3 | | | | | C,B,L,F | | | | | |
| 17.8 | | | | | | | C, B, L | | | |
| 20.0 | V | V | V | | | | | | | |
| 21.0 | B, L, F | | | B, L, G | F | | | | | |
| 21.1 | | G, R, F, N, E, D | F | F | | | | | | |
| 21.2 | E, O | | | F | | | | | C, B, L, N | |
| 21.3 | | | R, N,V | | | | | | F,V | |
| 21.4 | | | C, B, L | | | | | | E, O, D, pH | |
| 21.6 | | | E, D, pH | | | B, L | C, B, L | | | E, D |
| 22.2 | | | | | | F | | F | | |
| 22.6 | | | | | | C, B, L, N | | | | |
| 24.8 | | | | | | | | C, B, L | | |
| 25.1 | | | | | | | | | V | |
| 25.3 | | | | | | | | | V | |
| 25.8 | | | | | | | | F, N | E, | |
| 26.3 | | | | | | | | | C, B, L, F, N | C, B, L |
| 28.2 | | | | | | | C, B, L, F, N | | | |
| 28.8 | | | | | | | F, N | | | |
| 29.2 | | | | | | | | C, B, L | | |
| 39.4 | | | | | | | | | F | |
| 42.0 | | | | | | | | | C, B, L | |
| 45.2 | | | | | | | C, B, L | | | |
| 46.8 | | | | | | | F, N | | | |
| 54.6 | | | | | | | G, S, R, F | | | |
| 55.8 | | | | | | | B, L, F | | | |

- C = calliper
- B = BRD
- L = LSD
- N = Neutron
- F = FWS
- G = gamma
- S = SP
- R = Resistivity
- E = EC
- O = ORP (redox potential)
- D = DO (dissolved oxygen)
- V = borehole video camera

5.2.5.4 Core Drilling

Two core boreholes were drilled at the Campus Test Site with the purpose of obtaining detail on geologic features such as fracture depths and lithology boundaries.

The degree of weathering, fracture orientations and preferential flow paths were studied. The following figures are the geological logs for the two core holes.

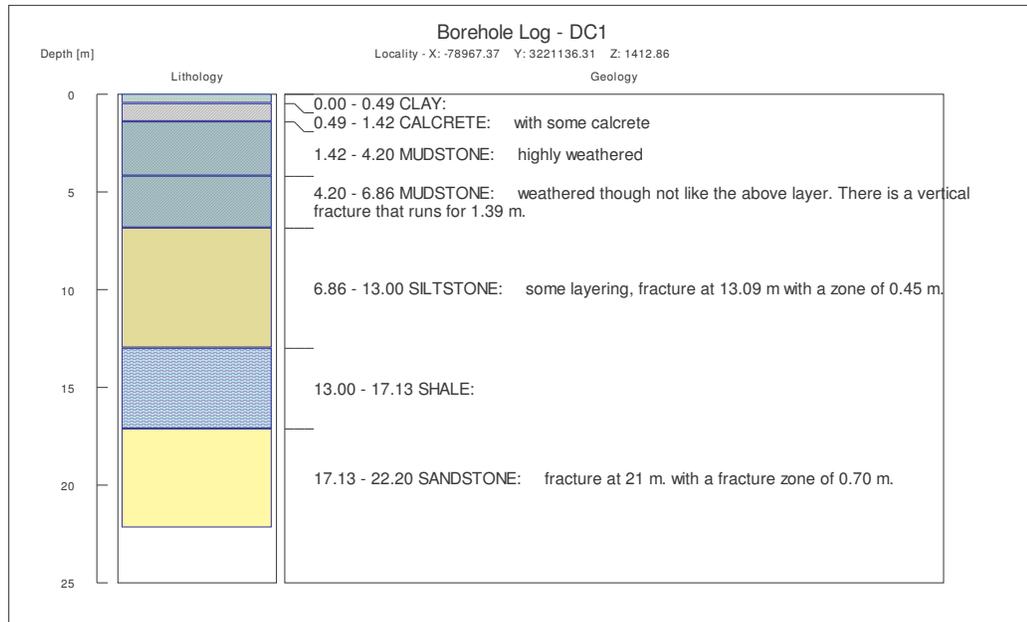


Figure 5-14: Borehole log for Core hole DC1.

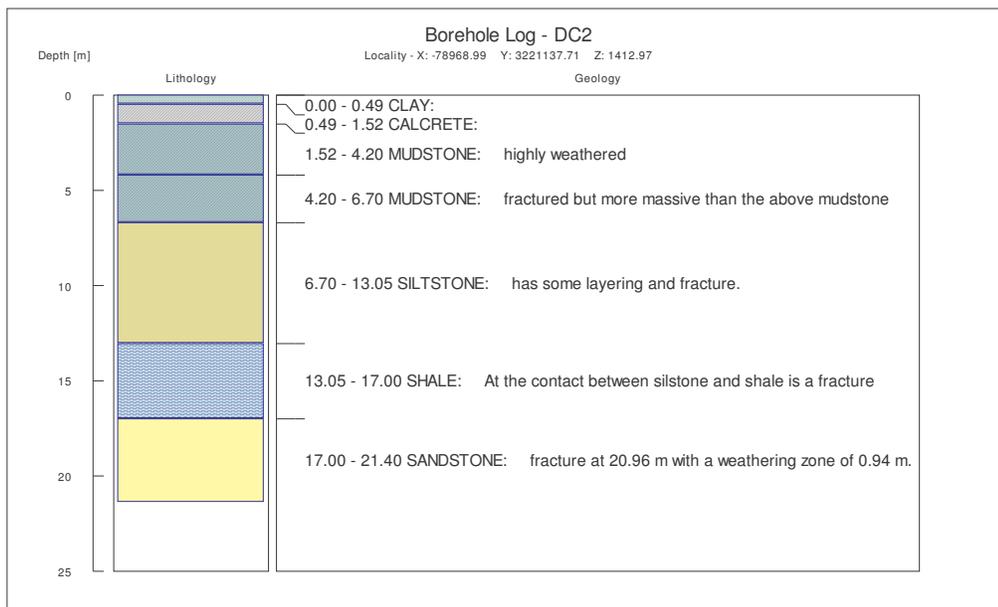


Figure 5-15: Borehole log for Core hole DC2.

The holes were drilled to about 0.3 meters below the mode 1 fracture at ~21 meters. Several vertical and horizontal fracture zones were identified. It could be seen from

the discolouration of the cores, that weathering of the sandstone took place in a 0.6 m zone adjacent to the mode 1 fracture (Figure 5-16).



Figure 5-16: Vertical fracture in DC1 at ~5 m (top) and mode 1 fracture at 21 m (bottom) in DC1.



Figure 5-17: Mode 1 fracture in DC2 at 20.96 m.

The core drilling added valuable data to the fracture characterization of the site. However, care had to be taken when measuring the core lengths to account for potential core loss due to highly weathered zones. This could result in inaccuracy when determining the depth of the fracture. Core drilling is especially important for vertical fractures and identification of potential preferential flow zones. It allows the accurate delineation of different magnitudes of fracture and this information will lead to improved conceptual models for DNAPL sites.

5.2.5.5 Aquifer Testing

5.2.5.5.1 Slug Tests

Slug tests are used during site assessment to determine first estimates for aquifer parameters such as transmissivity and borehole yield. These first estimates are often used as guidance to select optimal pump rates for pump tests. In the case of the Campus Site the slug tests provided information regarding the intersection of the DNAPL boreholes to the mode 1 fracture.

Recovery time and estimated borehole yields from the slug test are provided in Table 5-7. Boreholes that do not intersect the fracture have yields of less than 0.6 L/s. From the slug tests, it is evident that boreholes D1, D5 and UO30 do not intersect the fracture while the rest of the boreholes do. This was later confirmed other methods.

Table 5-7: Slug test results on boreholes that do not intersect fracture.

| Borehole | Time (sec) | Yield (L/s) |
|----------|------------|-------------|
| D2 | 5 | >3 |
| D3 | 2 | >3 |
| D4 | 16 | >3 |
| UO23 | 7 | >3 |
| D1 | >600 | <0.2 |
| D5 | >600 | <0.2 |
| UO30 | >600 | <0.2 |

5.2.5.5.2 Pump Tests

The principle of a pump test is that if water is pumped from a borehole and the discharge and the drawdown of the borehole is measured in the borehole and in observation boreholes at known distances from the borehole, the measurements may be substituted into an appropriate well-flow equation. These may used to calculate the hydraulic characteristics of the aquifer (Kruseman and De Ridder, 1994).

The interpretation of pump test data is based on mathematical models that relate drawdown response to discharge in the abstraction and/or monitoring borehole. In fractured-rock aquifers, the geometry and permeability of the system have a large influence on the drawdown. The scale of heterogeneity in a fractured-rock system may be large in relation to the scale of the test. Therefore, conventional models developed for homogeneous porous aquifers might not be viable in fractured-rock systems. Specific methods and software developed to analyse pump tests conducted in fractured-rock systems should be used when considering the estimation of hydraulic parameters in these fractured systems.

Estimation of the correct aquifer parameters is used for the construction of the correct conceptual model in combination with the geological set-up. In cases of contaminated groundwater, the aquifer parameters are important for planning and management during risk assessments and/or groundwater remediation. Depending on the objectives, several observation boreholes and piezometers at different depths may be used for measurements.

From the points above, it is clear that the principles for conducting and analysing pump tests depend on the objectives of the investigation. During DNAPL investigations, pump tests are used to estimate the hydraulic parameters and for finding principal hydraulic features of the system. Pump tests are rarely used in isolation for aquifer parameter estimation and the use of a suite of aquifer testing methods, such as slug testing, pump tests, flow logging, and tracer testing is preferred by site investigators (Cohen and Mercer, 1993; Pankow and Cherry, 1996; Sara, 2003).

At the Campus Site many pump tests were done to determine the aquifer parameters. For the purpose of this research, a series of pump tests were done to determine the aquifer parameters and the connectivity of the mode 1 fracture between boreholes and the subsequent response of the fracture system during pumping (Results are given Appendix D3).

The following section is a discussion of hydraulic parameters calculated from aquifer testing at the Campus Test Site, and then two pump tests (UP16 and DC2) are discussed in more detail with regard to the connectivity of the fracture system.

5.2.5.5.2.1 Hydraulic Parameters

Riemann *et al.* (2002) estimate that the horizontal K-value of the fracture as 3600 m/day, if multiplied with the thickness of the fracture zone of about 0.2 m, a T-value of 750 m²/day is obtained. T-value of the formation (both fracture and matrix) was estimated as 19 m²/day. A summary of hydraulic parameters for the aquifer on the Campus Test Site as estimated with a three-dimensional numerical model is given in Table 5-8.

Table 5-8: Summary of hydraulic parameters of the Campus Test Site (after Riemann *et al.*, 2002).

| Parameter | Estimated values |
|------------------|-----------------------|
| K_{hm} (m/day) | 0.158 |
| K_{vm} (m/day) | 5.82×10^{-3} |
| S_{sm} (m-1) | 5.65×10^{-5} |
| K_{hf} (m/day) | 3.6×10^3 |

K_{hm} = horizontal matrix
 K_{vm} = vertical matrix,
 S_{sm} = matrix specific storage,
 K_{hf} = fracture.

Pump test results obtained in this research estimate similar parameter values as listed in Table 5-9. The T-value of the fracture was estimated using the Barker method while that of the formation was estimated using Cooper-Jacob method. Estimated T-value of the fracture was less than that estimated in previous studies (Table 5-8). This could be either due to the difference in analytical and numerical methods used for estimation or that the transmissivity is smaller at the DNAPL mini test caused by spatial variability across this site.

Table 5-9: Pump test results in the Campus Site.

| Pumped Borehole | Tf (m ² /d) | Tfm (m ² /d) |
|-----------------|------------------------|-------------------------|
| UO23 | 149 | 17 |
| UO23 | 150 | 15 |
| D3 | 83 | 16 |
| D3 | 178 | 17 |
| D2 | 149 | 16 |

Tf = fracture,
Tfm = formation

A pump test was done in July 2005 in borehole UO23 with abstraction rate of 3.5 L/s. The drawdown increased suddenly after about two hours at a depth of 21.74 m (shown in Figure 5-18). This occurred due to of the dewatering of the fracture zone.

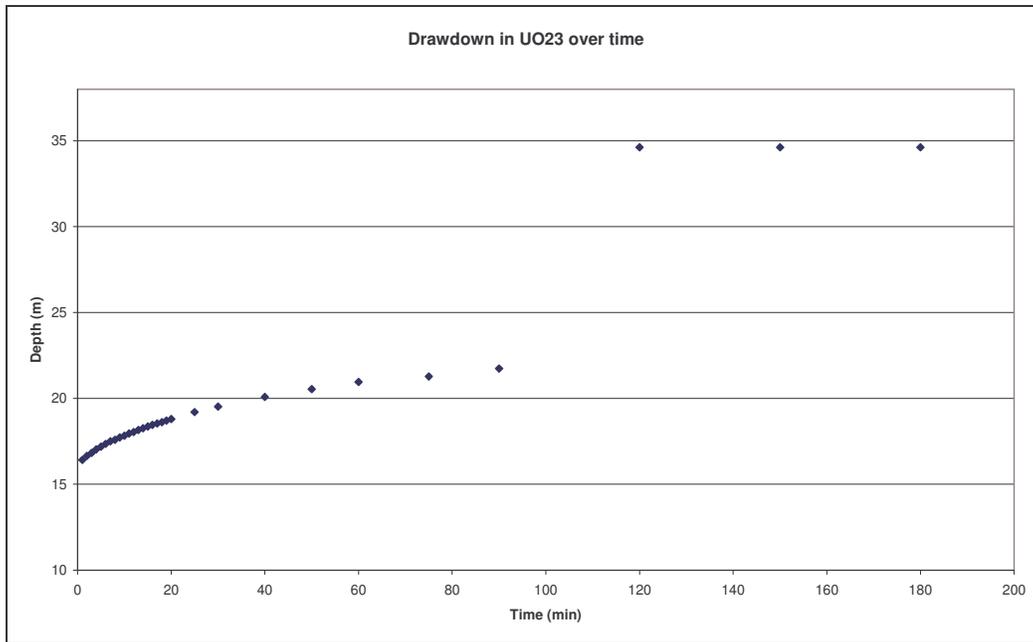


Figure 5-18: Drawdown graph of UO23.

Riemann (2002) explained that early time drawdown data could be used to estimate the T-value of the fracture zone using Cooper-Jacob 2 (CJ2) method. However, in this experiment the estimated T-values using CJ2 are misleading. If boreholes UO29, UO30 and D1 are used the calculated T-value is 52.93 m²/day and if D4, D2 and D3 are used the T-value was 26.73 m²/day. However, UO30 and D1 are weak boreholes that do not intersect the fracture and theoretically they should have very low T-values and D4, D2, D3 all intersect the fracture and theoretically should result in higher T-values. The reason for this therefore lies in applying the wrong conceptual model to the interpretation and analysis of results.

It was expected that all the observation boreholes UO29, UO30, D1, D4, D2 and D3 would respond similarly, as discussed by Riemann (2002) but this did not happen. Another example of this occurred when UO23 was pumped and D2, D3, and D4 were used as observation boreholes. All the boreholes intersect the fracture and were expected to give high T-value of the fracture. However, the data were scattered widely and it was not possible to fit a single line. Different sets of observation boreholes resulted in different values of transmissivity, illustrating the anisotropy of the fracture network.

5.2.5.5.3 UP16 Pump Test

A constant rate test was with UP16 as abstraction borehole. Groundwater was abstracted for seven hours at a rate of 2 L/s and the water level was measured in all the boreholes of the Campus Site. The groundwater elevation versus time curve of the test is given in Figure 5-19. UP16 is one of the boreholes that intersect the fracture and all the boreholes that intersect the fracture showed similar drawdown curves. The boreholes can be categorized into three groups. One group showed no drawdown at all, the second group showed intermediate drawdown, the third group had significant drawdown.

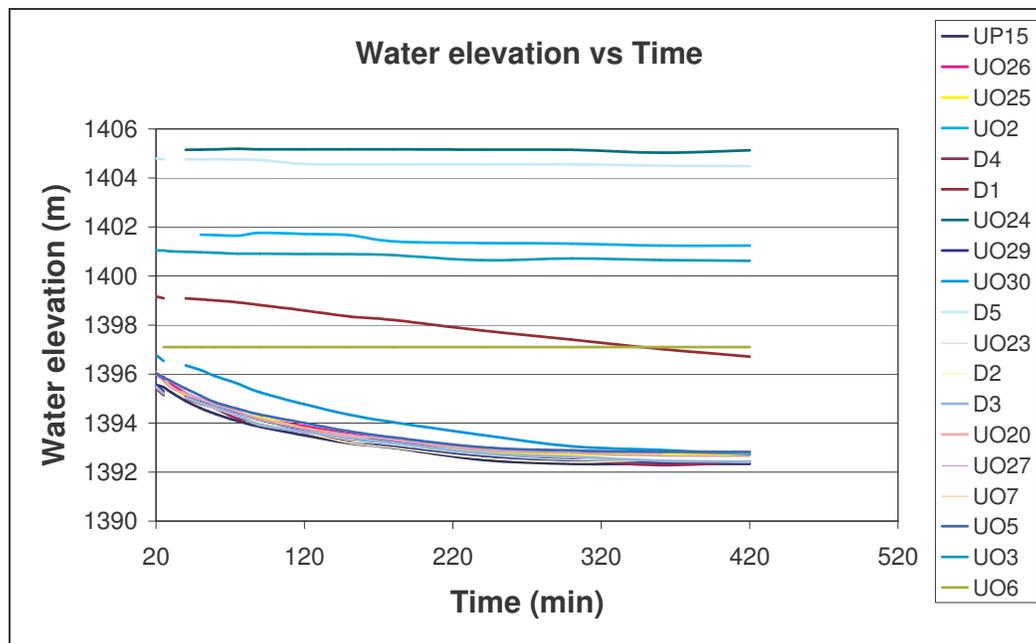


Figure 5-19: Pump test when UP16 was abstracted.

The effect of the distance of the boreholes from the abstraction borehole (UP16) was almost insignificant to the drawdown observed. The drawdown, after 6 hours of pumping, versus the distance of the boreholes from UP16 is given in Figure 5-20. For example, UO6 was only 23.8 m away from UP16; however, there was no drawdown at all. Furthermore, D3 was 74 m away from UP16 but the drawdown was 5 m.

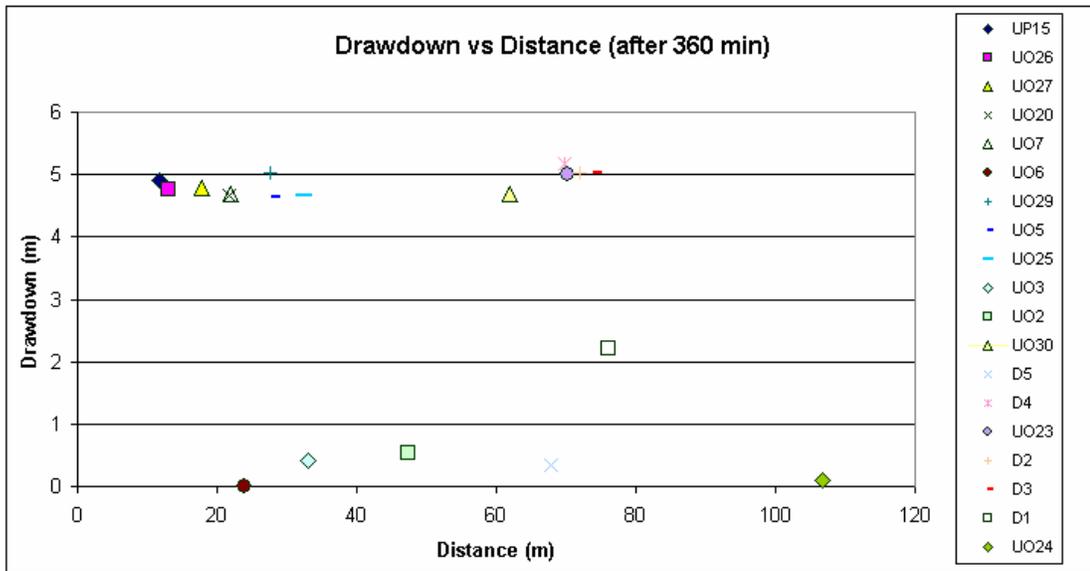


Figure 5-20: Drawdown vs. distance of the boreholes from UP16 after 6 hours of pumping.

The depth of the boreholes was also insignificant in affecting the drawdown. UP16 was 41m deep and the pump was below the fracture zone. The drawdown of the boreholes, after 6 hours of pumpUP16, versus the depth of the boreholes is given on Figure 5-21. For example, UO6 was 41 m and UO24 was 30m deep, respectively, and no drawdown was observed in both of them. At the same time, boreholes D3, UO23 and D2 were 23, 46 and 23 m deep, respectively, and had drawdown of 5 m (Figure 5-20).

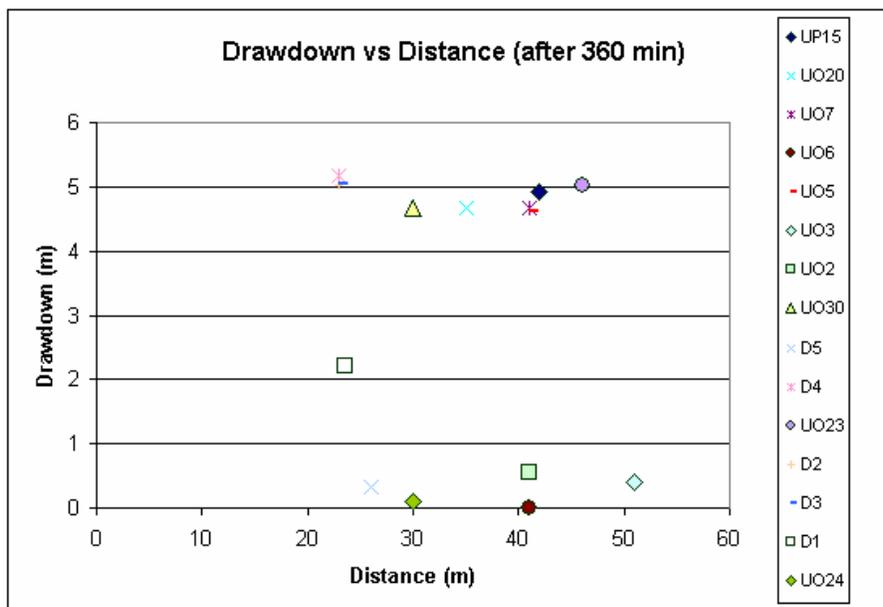


Figure 5-21: Drawdown vs. depth of the boreholes after 6 hours pump of UP16.

It can be concluded that the drawdown in the observation boreholes was mainly due to the fracture connectivity, hydraulic conductivity of the connection and the fracture density. The conceptual model developed by Botha *et al.* (1998), given in Figure 5-2, is a simplified form of the site and cannot explain this behaviour.

As a further example, Borehole D1 did not intersect the fracture from evidence provided by video cameras, water level measurements and slug tests. However, as pumping of UP16 progressed, drawdown in D1 increased (Figure 5-19). This could show that D1 was linked with UP16 with low transmissive fracture.

Another example is UO30 which had static water level equal to those that intersect the fracture. Upon pumping of UP16, it showed almost the same hydraulic head response to those of the strong boreholes that intersect mode 1 fracture (Figure 5-19). According to the conceptual model of Botha *et al.* (1998), the borehole was located in sandstone aquifer and intersected the fracture zone. However, UO30 did not intersect the fracture as obtained from borehole video camera, pump test and slug test. When UO30 was pumped at a rate of 0.86 L/s, it was dewatered within 7 minutes and the recovery analysis showed that it had a T-value of 1.2 m²/day, indicating that the fracture has a much lower transmissivity than the mode 1 fracture. However, the static water level of UO30 is similar to the other boreholes that intersect the mode 1 fracture and UO30 reacted similar to these boreholes during the pump test of UP16. From this it can be concluded that the transmissivity of the fracture will be dependent on the aperture and the degree of connectivity, or the “fluid active” features of the fracture.

5.2.5.5.4 DC2 Pump Test

From previous tests and interpretation of the tests, the conceptualisation of the fracture connectivity has been established. In order to ensure that the core holes (DC1 and DC2) also intersected the fracture zone a 2 hour constant rate (0.1 l/s) pump test was done on 26 January 2007, in DC2 and the pressure response from the DNAPL boreholes recorded with Solonist pressure transducers.

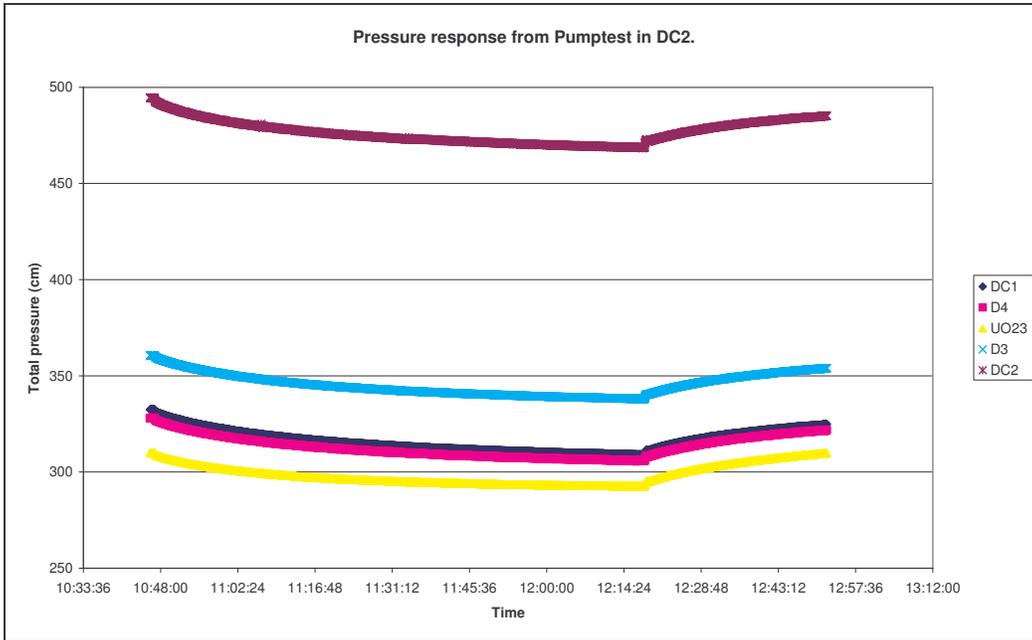


Figure 5-22: Total pressure response from pump test in DC2.

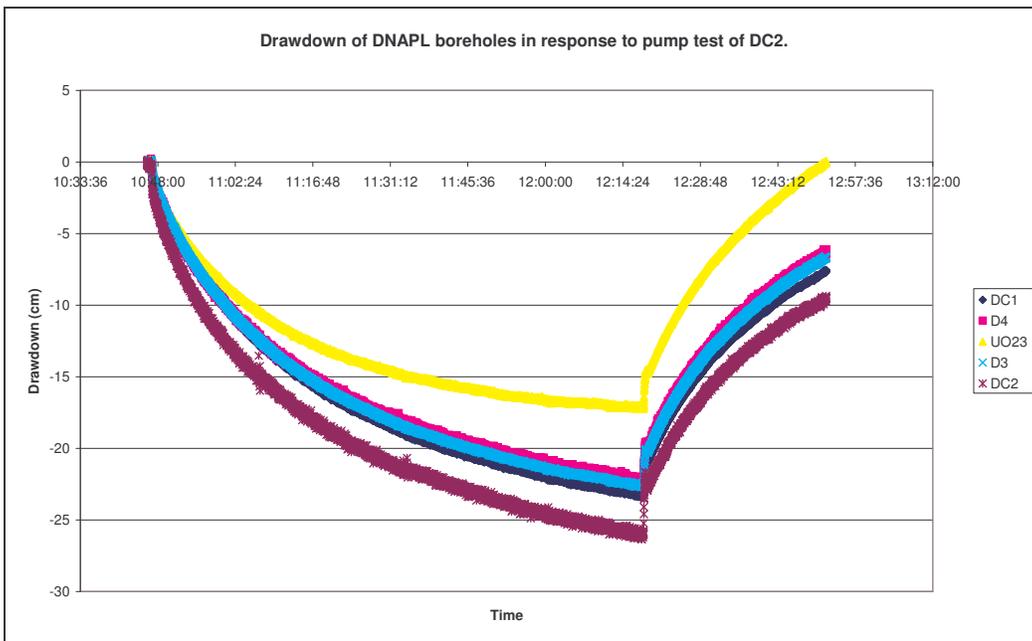


Figure 5-23: Drawdown in boreholes during pump test of DC2.

The pressure response was converted to drawdown and the following table gives the maximum drawdown response and the distance from DC2, of the boreholes after two hours of pumping.

Table 5-10: Maximum drawdown measured during DC2 pump test.

| Borehole ID | DC1 | D4 | UO23 | D3 | DC2 |
|-----------------------|---------|---------|--------|---------|---------|
| Drawdown (cm) | -23.178 | -22.218 | -17.13 | -22.538 | -26.169 |
| Distance from DC2 (m) | 2.2 | 4.27 | 2.8 | 1 | 0 |

These results correspond to the results from the UP16 pump test although the testing was done at a much smaller scale. The effect of the distance of the boreholes from the abstraction borehole (DC2) was almost irrelevant to the drawdown observed. D3, D4, and DC1 are connected to the same system but UO23 is more weakly connected. The results thus show there is some degree of connectivity to the mode 1 fracture in all the observation boreholes but the “fluid active” features are not all the same. The transmissivity of the fracture connections can therefore vary, even over a distance of a few meters.

5.2.5.6 Tracer Tests

5.2.5.6.1 Introduction

Understanding the processes controlling subsurface transport is a key element in site characterisation and for the design and implementation of effective contaminant remediation. Subsurface transport is complex, controlled by the transport parameters such as groundwater velocity, kinematic porosity and dispersion. According to Riemann (2002), these parameters normally have to be analysed from field-scale tracer tests. Conventional field methods such as pump tests are adequate for most water supply investigations, but do not yield sufficient information for understanding aqueous mass transport.

During a tracer test an identifiable substance (the tracer) is injected under controlled conditions and is then used to infer the general behaviour of a flow in the transport medium. The selection of the tracer to be used will depend on the nature of the investigation. For instance, if the advective properties of a medium are investigated, care should be taken that the tracer is physically compatible with the fluid, while a study of the diffusive flow through a porous medium will require attention to the diffusion constants and the molecular size of the tracer.

Tracer tests aim to relate the concentration of chemical, biological or solid substances measured in observation boreholes to the flow velocity. A variety of single-well and

multiple-well tracer tests with their analysing methods, are available for use at NAPL contaminated sites. A single-well tracer test is conducted in one borehole only, meaning that injection of the tracer and measurement of the concentration take place in the same borehole. Multiple-well tracer tests under natural gradient are usually conducted with one injection borehole and one or more observation boreholes.

The transport and spread of the tracer plume is controlled by advection (i.e. flow velocity) and longitudinal and transversal dispersion, while the concentration at time t and position (x,y) is also a function of matrix diffusion, retardation due to non-ideal tracing behaviour and decay (Fetter, 1999).

The disadvantages of these tests are the time necessary to carry out the test and the difficulties in measuring the tracer concentration in the observation boreholes. The measurement tool should not disturb the natural flow field. On the other hand, the real concentration in the flow path (i.e. the fracture zone) is required, which cannot be realised properly in open boreholes. Another practical problem related to this test is the position of the boreholes, which are often not located exactly in the flow direction. Moreover, the flow direction is often not known exactly or may change along the flow path. Some of these difficulties were overcome during the research project by the determination of fracture orientations (and therefore flow paths) using data from other fracture characterisation methods.

As discussed above, the aim of a tracer test is to estimate transport parameters of the aquifer for the dissolved phase. Although the movement of DNAPL through a geologic medium depends on the density and viscosity of the DNAPL, the transport parameters also play a vital role in the extent of DNAPLs in the subsurface and their study is important in the site characterisation and fate of the DNAPLs.

5.2.5.6.2 Point Dilution Test: Natural Gradient - Single-well tests D3

From the fracture characterisation of the DNAPL boreholes on the Campus Test Site, it was determined that D3 has two fracture zones located at 21.29 and 21.54 meters below surface (Figure 5-24). Natural gradient point dilution tracer tests were conducted at these two fractures to determine the properties of these two fractures. It was already evident from in situ measurement of EC during the radial convergent tracer tests, that the lower fracture was the preferred pathway for solute transport.

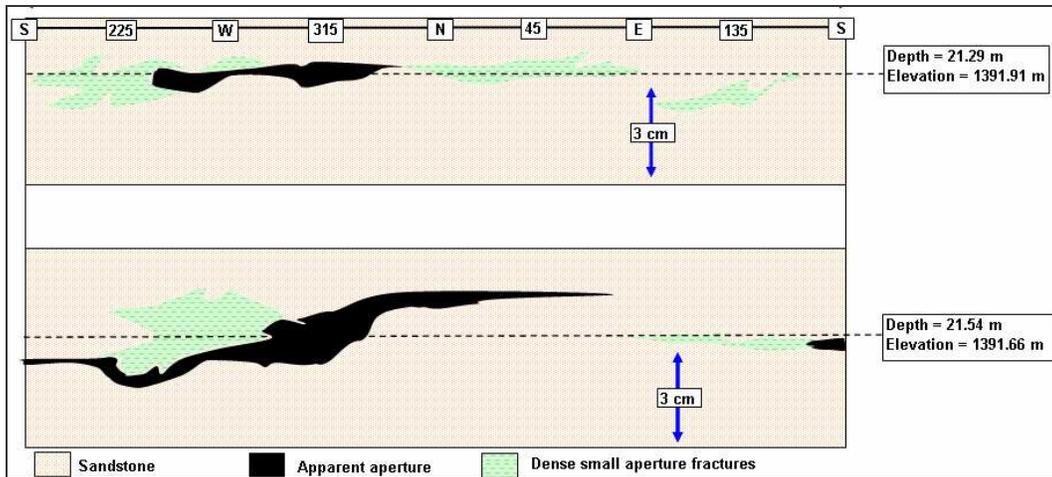


Figure 5-24: Apparent fracture aperture and fracture positions in Borehole D3 (From Gebrekristos, 2007).

The point dilution tests were conducted over a 0.15 m interval across the two fractures. A mass of 100g of NaCl was injected during the tests.

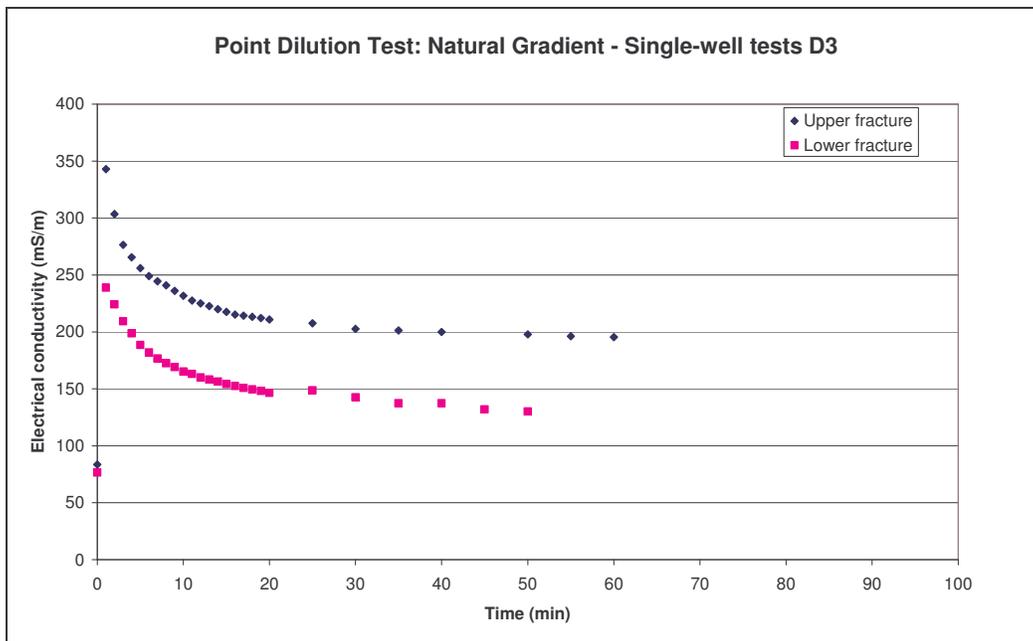


Figure 5-25: Results for Point Dilution Test: Natural Gradient - Single-well tests D3

The TRACER program was used to analyse the data of all three tracers. See Figure 5-26 and Figure 5-27 for graphs. From these, the Darcy velocities for the upper and lower fracture of 2.01 m/d and 3.05 m/d, respectively, were calculated.

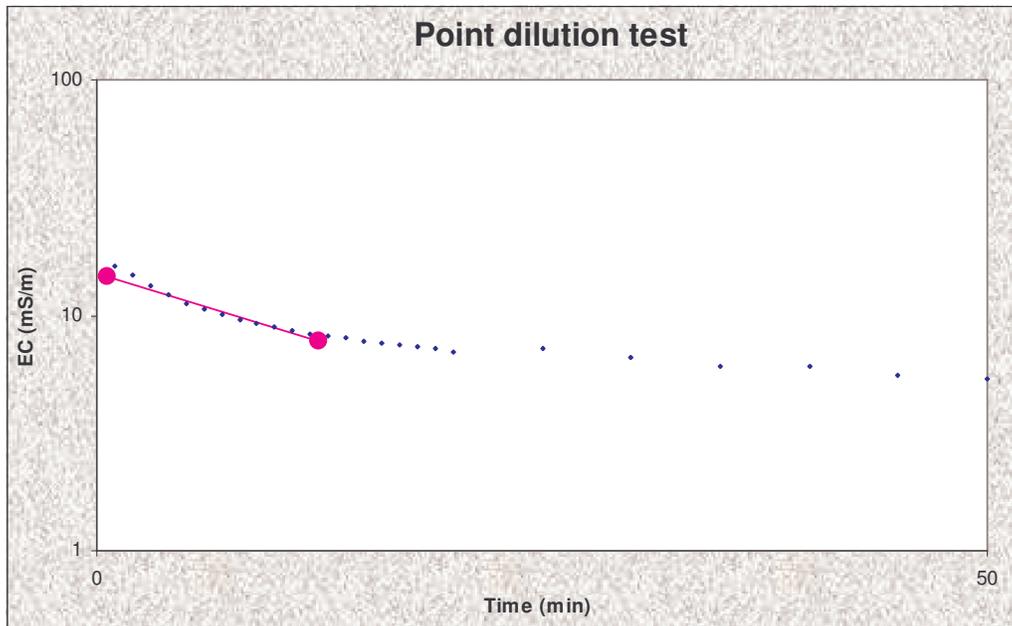


Figure 5-26: TRACER fits of point dilution test for lower fracture in D3.

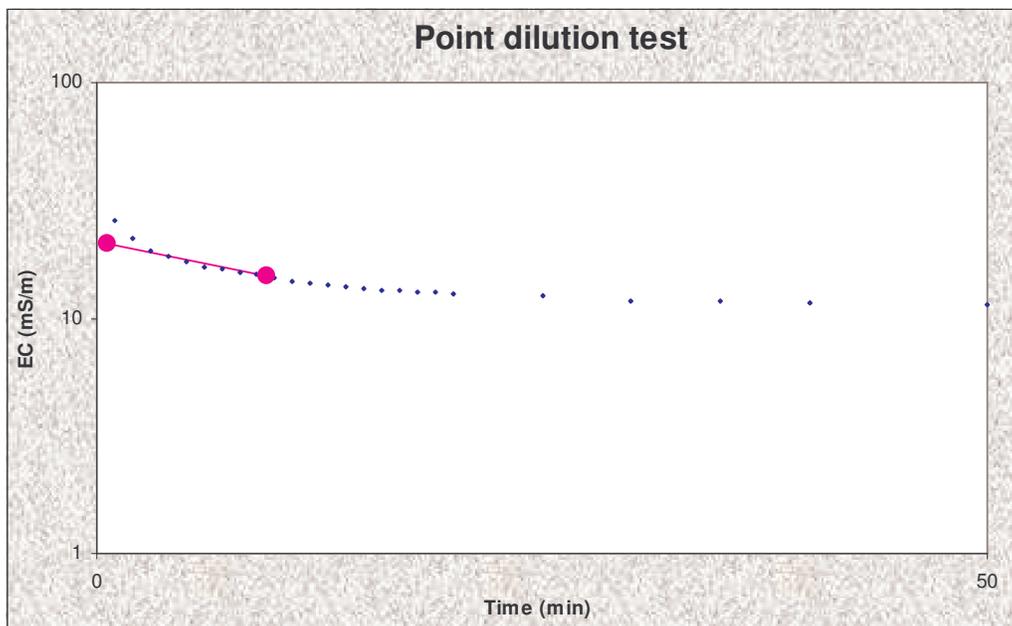


Figure 5-27: TRACER fits of point dilution test for upper fracture in D3.

Since the seepage velocity can be defined as:

$$v = Ki/n_e \quad \text{Equation 2}$$

Where, v is the seepage velocity, K is the hydraulic conductivity, i is the hydraulic gradient, and n_e is the effective porosity.

If it is assumed that the effective porosity of the fracture is similar for both fractures, and the hydraulic gradient is equal, the seepage velocity for the lower fracture also be higher than for the upper fracture. This result thus confirms the assumption made through other test results that the preferred pathway for dissolved transport should be through the lower fracture.

5.2.5.6.3 Point Dilution Test: Natural Gradient - Single-well tests UO23

A similar point dilution test as in D3 was conducted over the fracture zone at 21.35 meters in UO23. The test was repeated and similar results were obtained. The average calculated Darcy velocity (m/d) for the fracture zone was 1.25.

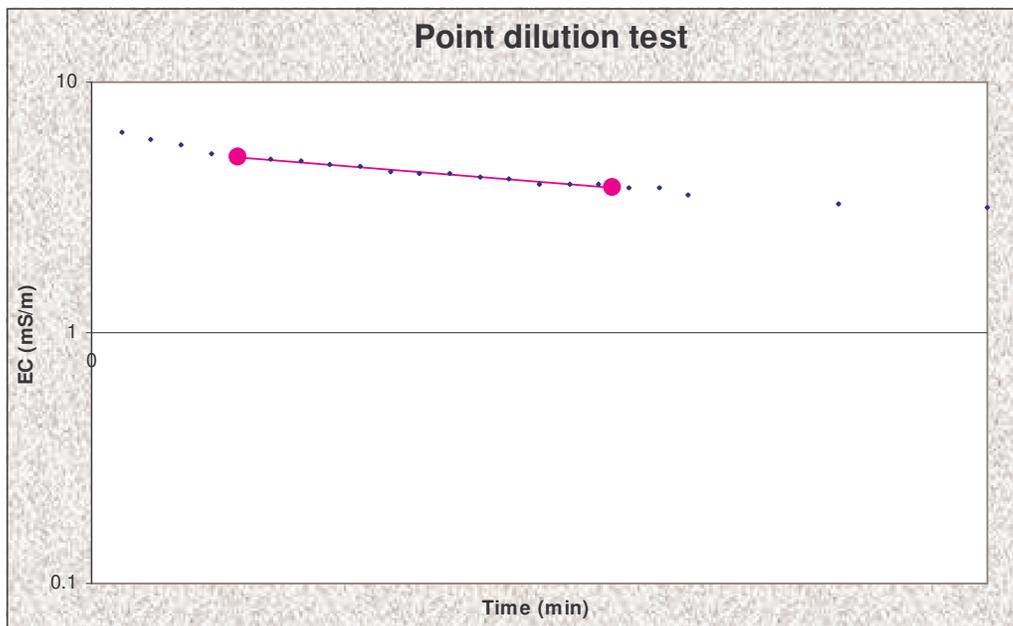


Figure 5-28: Results of point dilution test for fracture zone in UO23 (14/11/2006).

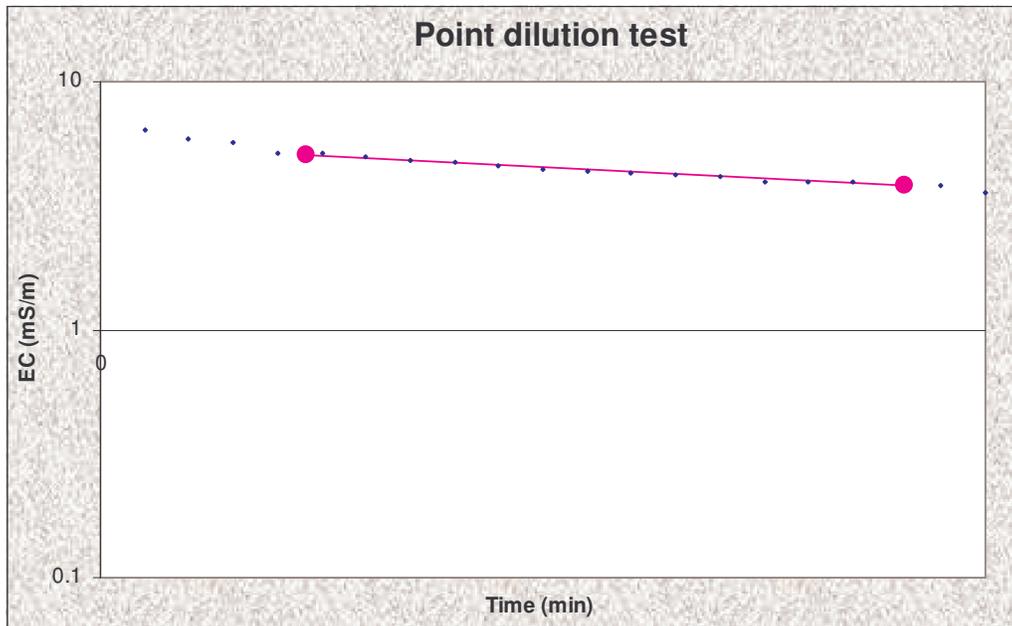


Figure 5-29: Results of point dilution test for fracture zone in UO23 (15/11/2006).

If the same assumptions are made for the fracture porosity and hydraulic gradient as in D3, the Darcy velocity can be used to compare seepage velocity for the fracture in UO23. Therefore, if comparing the relative seepage velocities, it confirms the results of the faster breakthrough of tracer mass towards D3, during the radial convergent tests between D3 and UO23.

5.2.5.7 Conclusion

Through using multiple techniques from the fracture characteristics of the model fracture at the DNAPL “mini” test site, have been done. This research proved that multiple techniques are required for fracture characterisation and that each technique has advantages and limitations. The geophysical down-hole techniques were effective in locating geological features, geochemical logging provided information of flow zones and with video logging orientations of fractures could be determined. The hydraulic testing provided information on the hydraulic connectivity and mass transport within the fracture network.

Based on the results above it can be seen that the fracture characteristics are highly heterogenous at the scale of a few meters. In terms of implications for DNAPL flow, any uncertainty in representing the fracture network can lead to a wide range of calculated values for bulk retention capacity and DNAPL penetration depth, particularly at low capillary pressures (See Appendix A).

5.2.6 Flow characterization through controlled fracture apertures in typical sedimentary rocks

5.2.6.1 Introduction

For DNAPL migration, aspects such as the fracture aperture, fracture orientation, fracture roughness and matrix diffusion are very important considerations. The aim of this set of experiments was to gauge the importance of each of these aspects by controlling these aspects in bench-scale experiments. This laboratory testing was especially important to design and compare to the field application of a surrogate DNAPL as described in Section 5.2.7.

Hydraulic and tracer tests through rock fractures and artificial fractures have been performed by many researchers in both laboratory experiments (Cliffe *et al.*, 1993; Dronfield and Silliman, 1993; Grisak and Pickens, 1981; Moreno *et al.*, 1985; Sonnenborg *et al.*, 1999) and field experiments (Becker and Shapiro, 2000; McKay *et al.*, 1993; Novakowski and Lapcevic, 1994). Modeling flow and transport through fractures can be challenging because of the heterogeneous nature of variable aperture fractures. A simplified concept of modeling a fracture as two parallel plates (Snow, 1969) has often been used in analyzing data from hydraulic and tracer tests (Cliffe *et al.*, 1993; Novakowski and Lapcevic, 1994; Sonnenborg *et al.*, 1999). These aspects were incorporated in the interpretation of results.

The concept of the sandstone parallel plate fracture experiment was inspired by the research done by Hill and Sleep (2001). Laboratory-scale experiments were performed by Hill and Sleep (2001) to assess the effects of biofilm growth on flow and transport through a sandblasted glass parallel plate fracture. In the experiment of Hill and Sleep (2001), the fracture for the experiment was constructed from two sandblasted glass plates, 6 mm thick, 21 cm wide and 28 cm long. The aperture of the fracture was 560 μ m (0.56 mm).

5.2.6.2 Laboratory fracture experiment

Hydraulic and tracer tests were performed prior to NAPL injection to establish baseline conditions. A hydraulic conductivity of approximately 6000 m/d was calculated for the fracture with the cubic law by Van Wyk, (2006). Laboratory experiments were performed to assess the transport through a controlled sandstone fracture. This apparatus was built to represent the Mode 1 fracture at the campus test

site.

5.2.6.2.1 Materials and set-up of experiment

Van Wyk, 2006 undertook several tests using this apparatus. The apparatus was made of glass. The dimensions for the apparatus were as follows: 0.5 m high, 1 m long, and 0.4 m in width. See Figure 5-30 for set-up of the apparatus. The apparatus was divided into three sections (see Figure 5-31):

The upper section was constructed above the sandstone fracture. This area was sealed from the other sections and filled with water to represent a saturated aquifer above the fracture.

The centre section (fracture section) consisted of two sandstone plates (0.8 m long, 0.4 m in diameter and 0.02 m thick). The aperture between the two sandstone plates was 0.0013 m (1.3 mm). The plates were separated using 12 plastic shims (0.02m long, 0.01 m in diameter and 0.013 m thick). The fracture section is connected to the in- and outlet areas. These are both 0.5 m high, 0.4 m in diameter and 0.1 m in length. The in- and outlet areas represent the injection and abstraction boreholes of the field experiment. Although the shims represent some deviation from a perfect parallel plate, their presence makes the experiment more representative of the field conditions.

The bottom section is located below the sandstone plates. This area was also filled with water to represent saturated conditions. Water level controllers were installed at the inlet side of the fracture. The purpose of the water level controllers was to regulate the gradient at the injection side.

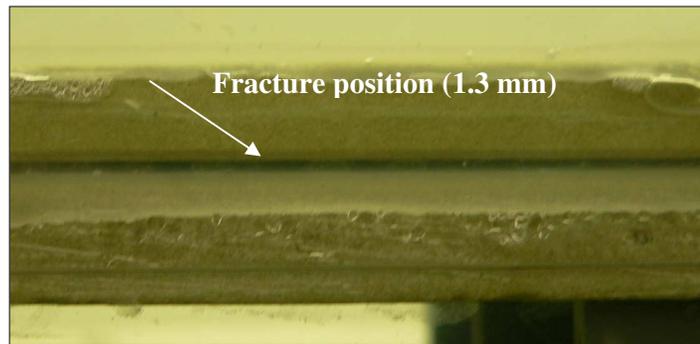
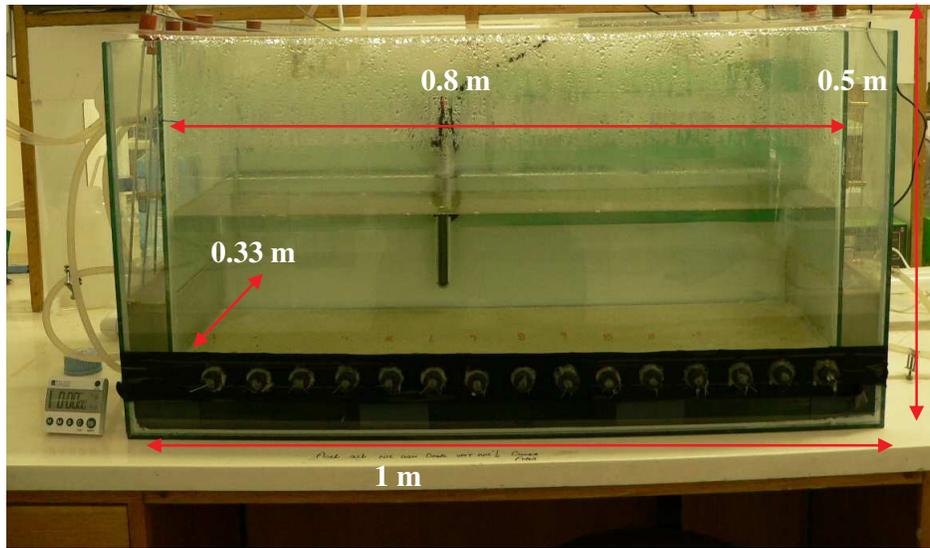


Figure 5-30: Set-up of the sandstone parallel plate experiment apparatus.

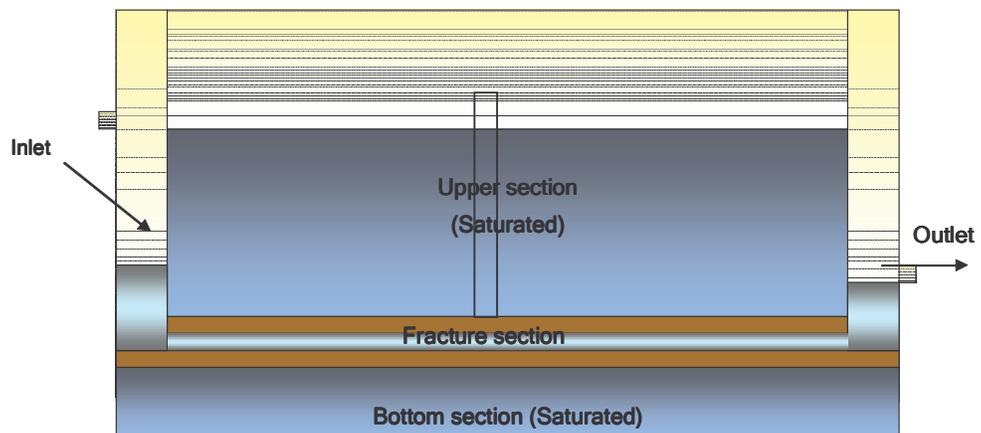


Figure 5-31: Horizontal parallel plate fracture apparatus showing the three sections and the "borehole" in the middle).

5.2.6.2.2 Conservative transport tests

Hydraulic and tracer tests were performed by Van Wyk (2006) before the NAPL injection to establish baseline conditions for the experimental setup. Researchers in the field of fracture flow used to consider a rock fracture as a pair of parallel plates separated by a constant distance, b , which represented the aperture of the fracture. Since fractures consist of rough walls, channelling and closings, they cannot be represented correctly by a unique fracture aperture.

Therefore the term “equivalent aperture” was introduced to describe the effective aperture contributing to flow or transport in the fractured rock. There are three common definitions and estimations of the “equivalent aperture” with respect to different measurements. According to Tsang (1992), they are called mass balance aperture, frictional loss aperture and cubic law aperture (Riemann, 2002). The hydraulic conductivity of the fracture was calculated using the parallel plate theory. A hydraulic conductivity of approximately 17000 m/d was calculated for the fracture with an aperture of 1.3 mm.

NaCl and NaBr tracers were used to determine the conservative migration through the created fracture (van Wyk, 2006). A tracer velocity of 147 m/d was calculated for the conservative tracer in a fracture with an aperture of 1.3 mm, and a dispersivity of 0.06 m and a tracer velocity of 151 m/d were calculated for the conservative tracer transport through the fracture aperture of 0.8 mm, showing that advection dominates.

5.2.6.3 Comparison of hydraulic response of NAPL and brine

The hydraulic response of FC-77 injection into a controlled aperture fracture was undertaken. FC-77 is one of the fluorinert-type chemicals, which have similar physical properties to expected DNAPLs such as PCE (Table 5-11).

Fluorinert liquids are a family of clear, colourless, odourless, inert per-fluorinated fluids having a viscosity similar to water but approximately 75% greater density. Fluorinert liquids are thermally and chemically stable, compatible with sensitive materials, including metals, plastics and elastomers, and are practically non-toxic. Fluorinert liquids are completely fluorinated, containing no chlorine or hydrogen atoms. The strength of the carbon-fluorine bond contributes to their extreme stability and inertness. This chemical structure also results in very low intermolecular forces,

low surface tension and essentially no solvent action on non-fluorinated compounds.

Flourinert's chemical and physical properties can be summarised as follows:

- Completely fluorinated organic liquid
- Stable
- Inert
- No solvent action on non-fluorinated compounds
- Non-toxic

Table 5-11: Physical similarity of FC-77 and DNAPLs.

| Fluorinert Liquid | FC-77 | PCE | TCE |
|-------------------------------|--------------|------------|------------|
| Average molecular weight | 415 | 165.5 | 131.4 |
| Boiling point, °C | 97 | 121 | 87 |
| Pour point, °C | -95 | | |
| Density, g/cm ³ | 1.78 | 1.6 | 1.45 |
| Viscosity, cs | 0.8 | 0.84 | 0.54 |
| Vapour pressure, torr | 42 | 18.2 | 69 |
| Surface Tension, dynes/cm | 15 | 73 | 34 |
| Solubility of Water, ppm(wt.) | 13 | 200 | 1100 |

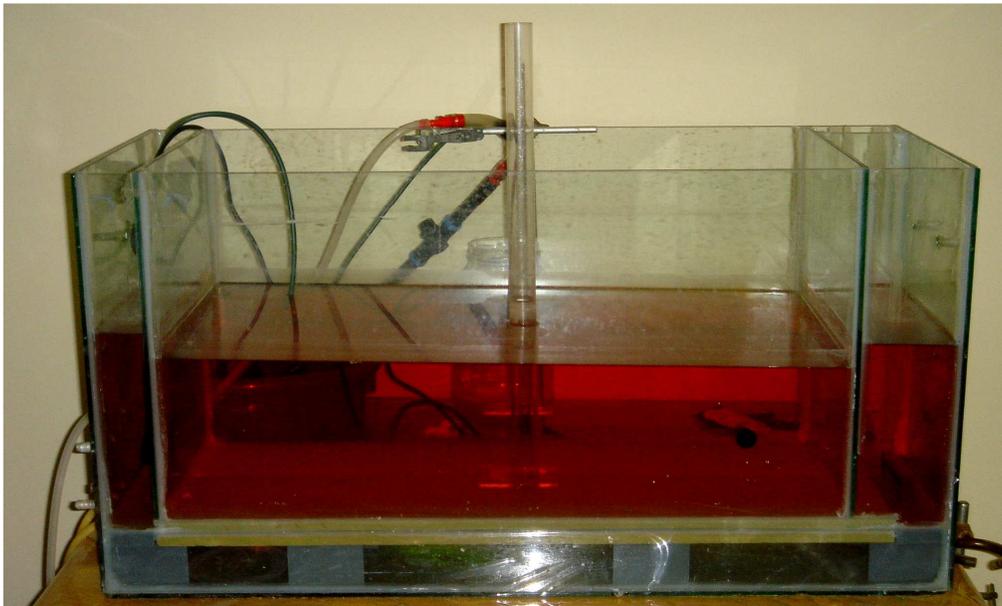


Figure 5-32: Modified experimental set up

The response of NAPL injection was contrasted with the injection of a high density NaCl brine. This was prepared by preparing a supersaturated NaCl solution and using the supernatant as a density-driven aqueous liquid.

5.2.6.3.1 Hydraulic response of brine and FC-77 injection

The hydraulic response of the brine and NAPL was determined by construction of a “borehole” into the parallel sandstone plates (Figure 5-32 and Figure 5-30). Three Solinst Diver pressure transducers were used to measure the pressure response, respectively, in the injection tube and in areas up and down gradient of the injection. The apparatus was inclined to the right by ~1 degree. Measurements were taken at half-second intervals, and barometric pressure compensation was done using a Solinst Barologger to measure barometric pressure over the duration of the experiment.

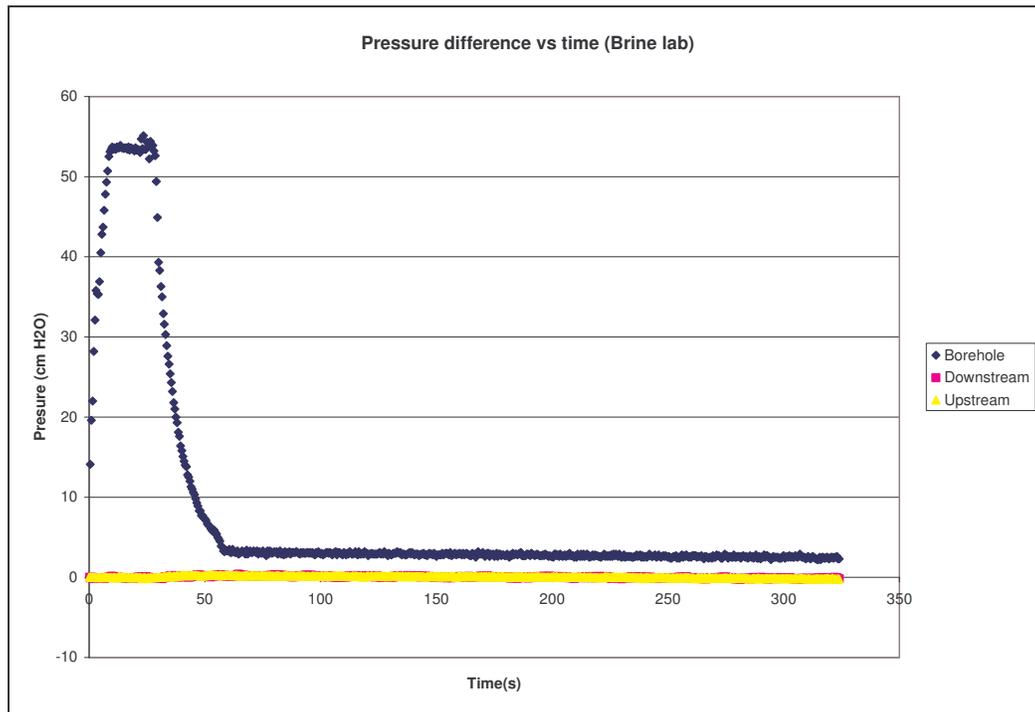


Figure 5-33: Pressure response over time in injection tube for the brine injection (See Figure 3.54 for detail of observation points).

The pressure response shows the pressure increasing in the tube as the brine is added (Figure 5-33). This is followed by an instantaneous release of the brine into the fracture at time of 31.5 seconds (earlier data has been removed for clarity and the brine addition only commenced once the system had stabilized). It is interesting that the up gradient and down gradient transducers show an instantaneous response to the release and that this occurs at the same time up- and down-gradient (Figure 5-34).

Since the injection occurred equidistantly from each position and the fracture is the only flow path, this is expected.

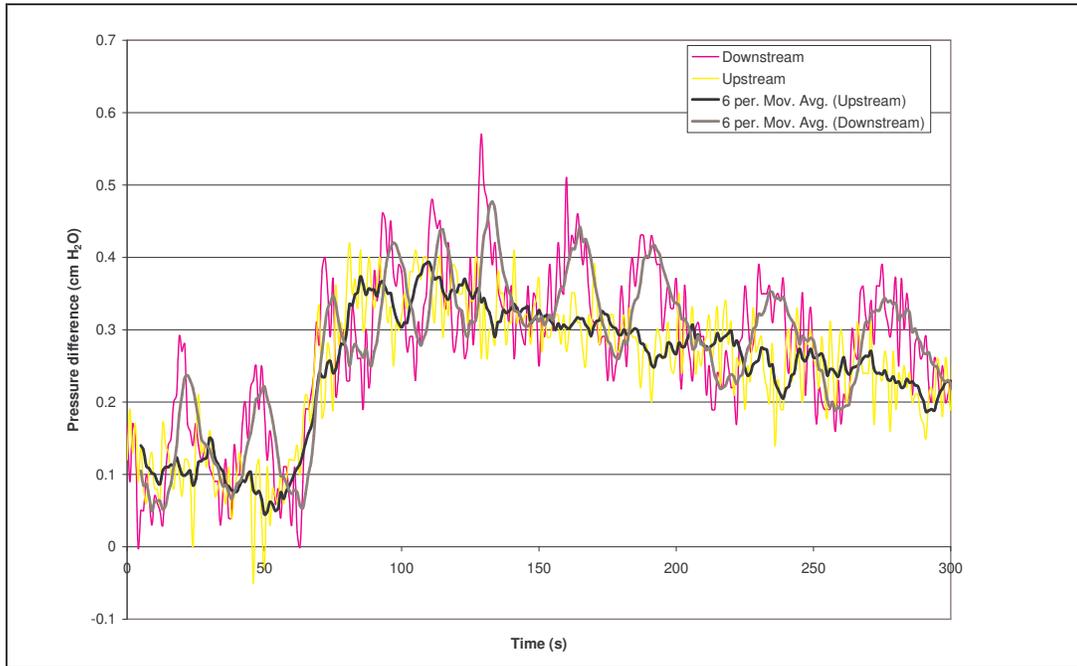


Figure 5-34: Pressure response to brine injection at up and down-gradient positions

For the FC-77 injection the same methodology was used, and the pressure response noted.

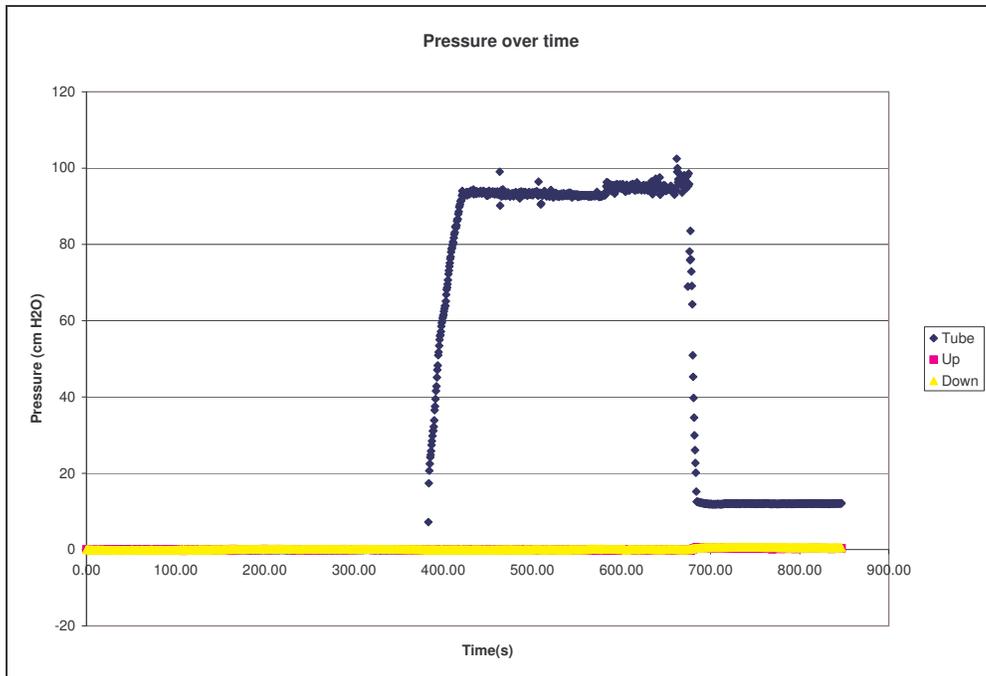


Figure 5-35: Pressure response over time in injection tube for the FC-77 injection (See Figure 5.36 for detail of observation points).

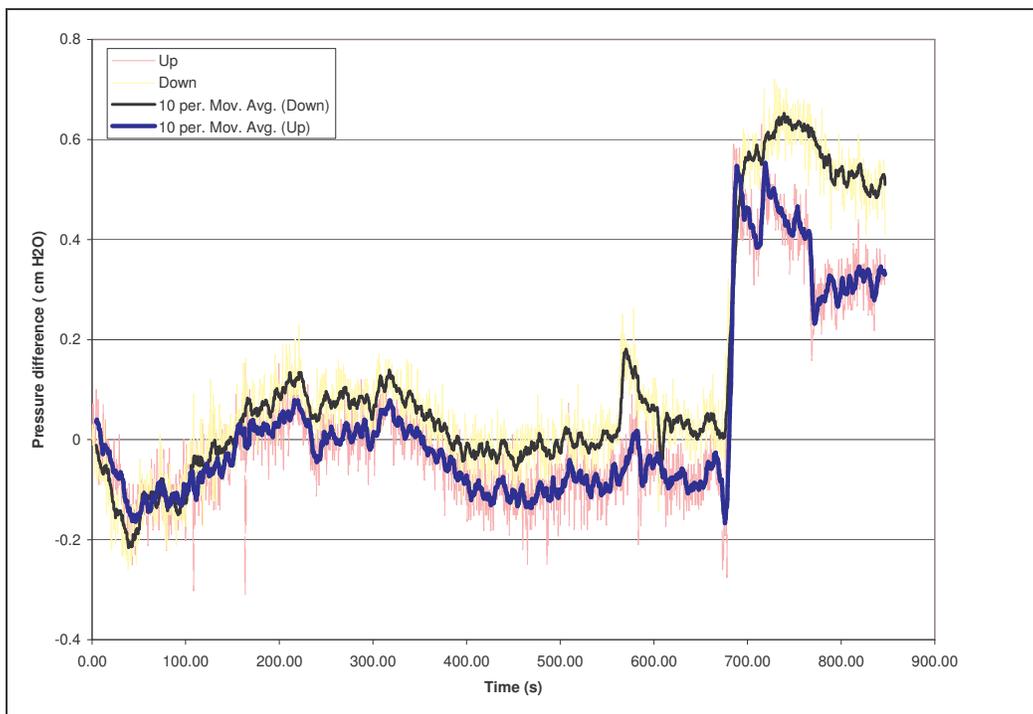


Figure 5-36: Pressure response to FC-77 injection at up and down-gradient positions

Using the Bouwer-Rice mode within the Flow Characteristics application of van Tonder *et al.*, (2002), the pressure response was used to determine the equivalent

hydraulic conductivity. Based on these responses, the K-value determined by the two injections is 60 m/s and 42 m/s respectively.

If,

$$K = k\rho g/\mu \quad \text{Equation 3}$$

And, k is the intrinsic permeability of the fracture which is constant for the experiment, the density difference is taken into account by using the total pressure response. Therefore, the difference between the two calculated K-values (0.7) is attributed to the viscosity (μ) difference of the two fluids. FC-77's viscosity is 0.8 cs, therefore, the theoretical and measured values are fairly well aligned.

5.2.7 Characterising DNAPL fracture flow in the field using surrogate DNAPL

A unique field technique was applied to determine the nature of the DNAPL phase flow in South African aquifers using a surrogate DNAPL. FC-77 is one of the fluorinert-type chemicals, which have similar physical properties to expected DNAPLs such as PCE.

DNAPLs are non-wetting on geologic solids with regard to water. Therefore, they will always preferentially enter and flow in the largest available space. In strata having significant dual permeability such as fractured sandstones, migration will preferentially be in fractures, as fractures apertures are typically greater than the largest pore throats. Once in a fracture network, DNAPL migration can be rapid, and will be governed by geological structure. DNAPL will preferentially migrate through the larger aperture pathways of a fracture plane since these provide the least capillary resistance to movement. The complex geometry and connections of fracture networks prevent complete characterization by conventional investigation techniques.

Fractures usually have rough walls and variable apertures, and consequently the internal properties of individual fractures that control DNAPL migration are poorly known. DNAPL migration through fractured media is relatively new area of interest. There is a scarcity of information available in the literature on in situ fracture apertures because of the inherent difficulties in obtaining data. Measurement of fractured apertures is however extremely important in solving contaminant transport and DNAPL penetration depth problems for the fractured domain

Numerical simulation of NAPL migration in fracture systems is complex and constrained by the lack of data. Whilst fracture orientations, intensities and lengths are relatively easily recorded in the field by detailed measurement, the apertures of these fractures, which control migration, are very difficult to measure due to their small size and high variability. The modelling studies during this research (Section 4.5) have shown that the spreading of DNAPLs within fracture networks may be affected by characteristics of the fracture network such as spatial variations in fracture apertures and zones of closure. It has also been shown that aperture variability may control the distribution of DNAPL and water within the fracture plane, and hence the ability of the fracture to transmit these fluids.

The results from the laboratory experiments on the flow of FC-77 under controlled conditions was used to design the experiment

5.2.7.1 Experimental set up

5.2.7.1.1 Borehole selection

The DNAPL test site at the Campus Test Site, referred to previously was used for this experiment. Six percussion boreholes, number D1 to D6 were drilled in close proximity of the previous boreholes UO23 and UO30. In addition, two core boreholes were drilled in the interval between boreholes D3 and UO23, for the purposes of detailed fracture characterization, and specifically for the injection of the surrogate DNAPL. As such, the core boreholes were drilled until the mode 1 fracture was intersected and drilling was then stopped, leaving only a short interval below the fracture. The position between D3 and UO23 was chosen due to the well-developed hydraulic properties of the fracture in these two boreholes and the fact that the interval between them was relatively short (Figure 5-37). Furthermore, the generalised dip of the mode 1 fracture is roughly in the same direction and the strike of the line between UO23 and D3.

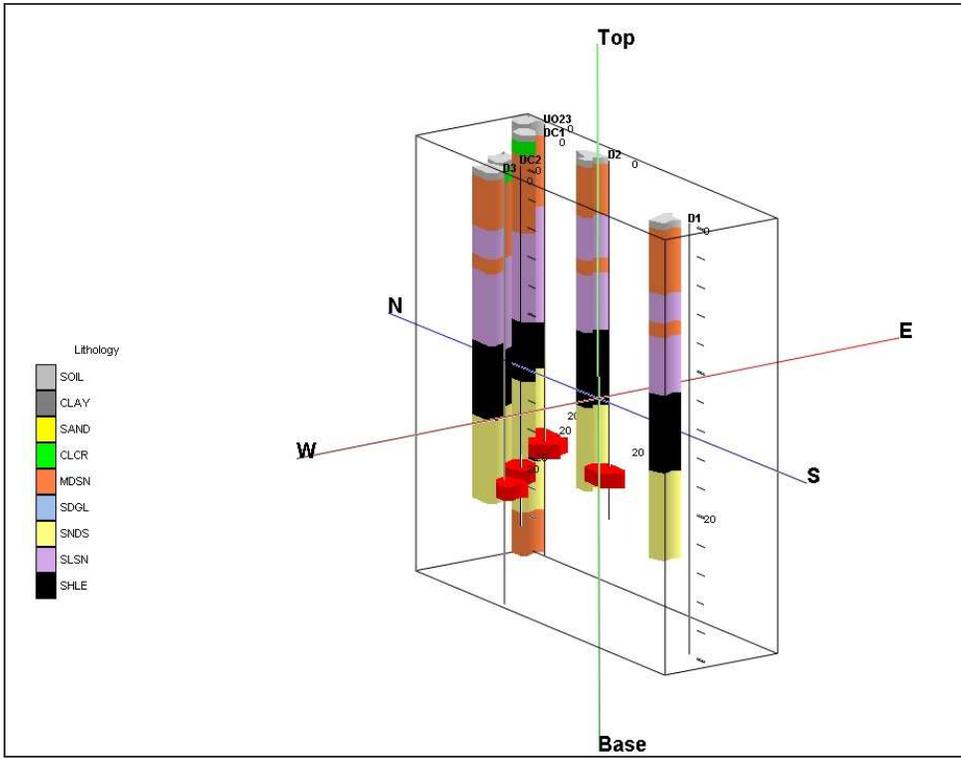


Figure 5-37: Position of fractures in DNAPL test site on Campus

5.2.7.1.2 *Experimental approach*

The position of the fractures in each borehole was identified, and characterised by a variety of methods. Point dilution and injection withdrawal tracer tests were done to assess the mass transport properties of the mode 1 fracture in this part of the test site. This allowed accurate determination of fracture depths and properties. From this determination, core borehole DC2 was selected for the injection due to its better interception of the fracture and the slightly higher elevation of the fracture in this borehole. The injection was done just above the fracture position that had been determined. The bottom of the DC2 and all of the other observation boreholes, were plugged with bentonite to prevent the FC-77 from migrating downwards.

To execute the DNAPL injection experiment more accurately, a series of water and later brine injection was done prior to the FC-77 injection. The aims of the brine injection were to optimise the experimental procedure, equipment and observations for DNAPL injection.

A supersaturated NaCl solution was prepared by mixing ~7 kg of NaCl with 10 L of water, with an estimated specific gravity of ~ 1.1.

Since FC-77 is denser than the water and the brine, its capillary pressure (P_c) is also higher. Therefore, the applied pressure is expected to be less than that required for the brine to infiltrate the fracture.

$$P_c = (\rho_{nw} - \rho_w)gh \quad \text{Equation 4}$$

Where,

ρ_{nw} = non-wetting phase density

ρ_w = wetting phase density

g = gravitational acceleration constant

h = height of the pool of DNAPL

Therefore, as compared to brine, a lesser amount of FC-77 can exceed the threshold entry pressure (P_c):

$$P_e = \frac{2\sigma \cos \theta}{e} \text{ Equation (23)}$$

Where,

σ = interfacial tension between the fluid and water.

θ = contact angle on the fracture walls

e = fracture aperture

The threshold entry pressure (P_e) can be calculated as follows:

- The fracture (zone) aperture is estimated at 0.2 m.
- The interfacial tension of FC-77 is 15 dynes/cm

The capillary pressure that is needed to allow the FC-77 to infiltrate the fracture can be calculated with the following:

- Density of the FC-77 is 1.78 g/cm³
- Density of water is 1 g/cm³

The required entry pressure to enter a fracture will therefore be dependant on the density and interfacial tension of NAPL fluid. According to this approach, the required head in mm of FC-77 to enter a fracture of 1 mm will only be 3.17 mm of fluid (Figure 5-38). The capillary pressure depends on the height, but not on the volume of the tube. In the injection borehole, therefore a narrow but long tube was used, to ensure the injection pressure (applied capillary pressure) would be far greater than the threshold entry pressure.

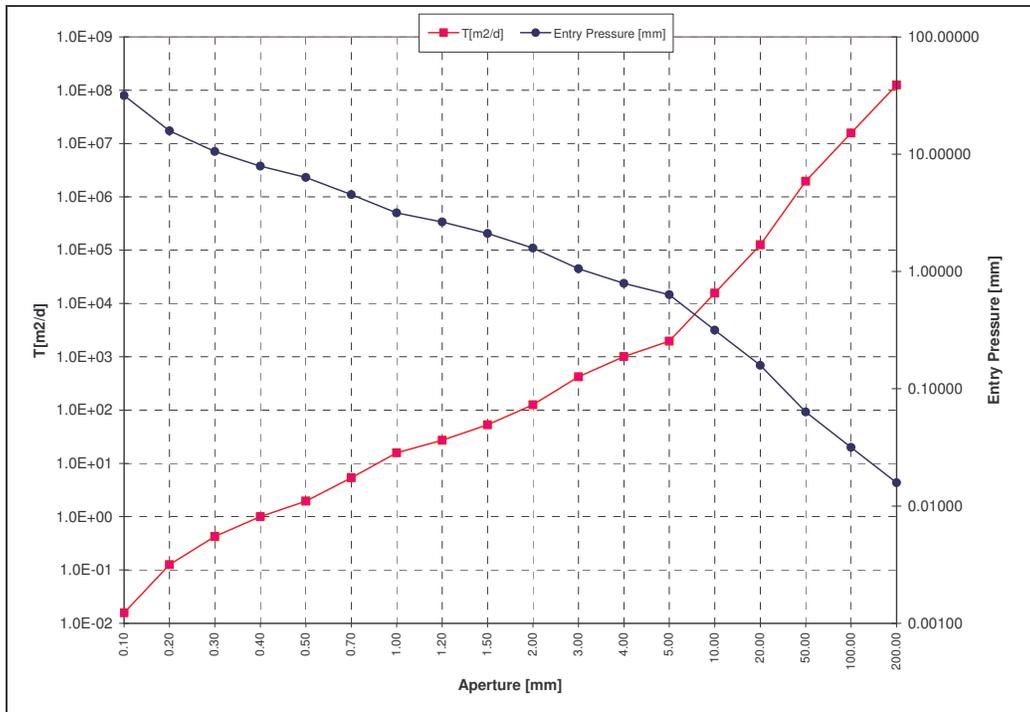


Figure 5-38: Required entry pressure (expressed as mm pool height) vs. fracture aperture and calculated transmissivities for FC-77 fluid.

If the calculated transmissivity values of $\sim 150 \text{ m}^2/\text{day}$ (Table 5-9) from the pump tests are compared with this graph, an aperture of approximately 2.2 mm can be expected which implies that 1.44 mm of FC-77 will be required to overcome the required entry pressure. The implication of this is that an accumulation of DNAPL less than fracture aperture is required to penetrate the fracture. At apertures greater than a certain threshold for different DNAPLs, the required capillary pressure becomes of no practical significance.

In the injection borehole, the following was done:

- The small diameter core borehole was selected (internal diameter 76 mm)
- A smaller diameter internal tube was used for injection (internal diameter = 22 mm)
- The pressure differential was measured over time with Solinst pressure transducers in the injection and observation boreholes

5.2.7.1.3 Apparatus

Apparatus was custom-designed and constructed for these experiments. The challenge

was to use inert materials in a small diameter borehole, in which the rate of pressure change had to be measured. The equipment also had to allow instantaneous release of fluid and be robust enough for repeated usage.

The equipment used consisted of a series of PVC pipes which could provide enough head (as the driving force for the injection) with a release mechanism on the lower end. This release valve was optimized through experimentation, until a metallic mechanical release valve was selected as providing the best response in terms of controlled release. The pressure differentials were measured using Solinst Divers in the injection apparatus and in the observation boreholes.

A photograph of the apparatus is shown below:



Figure 5-39: Apparatus used for the injection

An important aspect of the apparatus was the inclusion of rubber skirts or flanges above the release mechanism. These were included to prevent upward flow of the injected fluid, so that a true measure of the pressure response into the fracture could be obtained, rather than the decrease in pressure as fluid pushed up the borehole. Measurements of EC in the brine test showed that these skirts were effective in preventing upward flow of high-density fluids in the injection borehole.

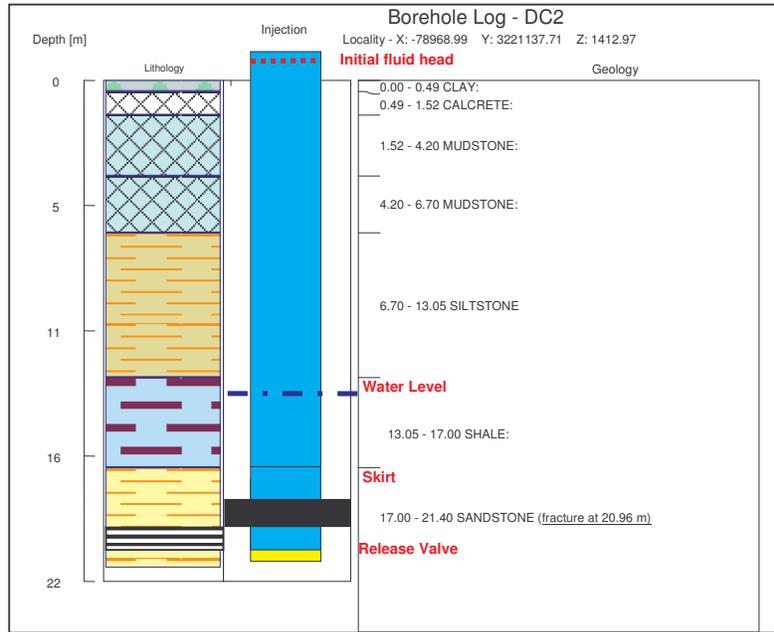


Figure 5-40: Schematic representation of experimental apparatus

5.2.7.2 Results

5.2.7.2.1 Brine injection

The brine injection achieved two objectives apart from optimizing the experimental procedure, namely establishing a baseline hydraulic response to injection of high-density fluid and the identification of boreholes where the surrogate DNAPL was most likely to be located after injection.

In Figure 5-41 the pressure response of two closely timed brine injections of approximately 2L of brine solutions are shown.

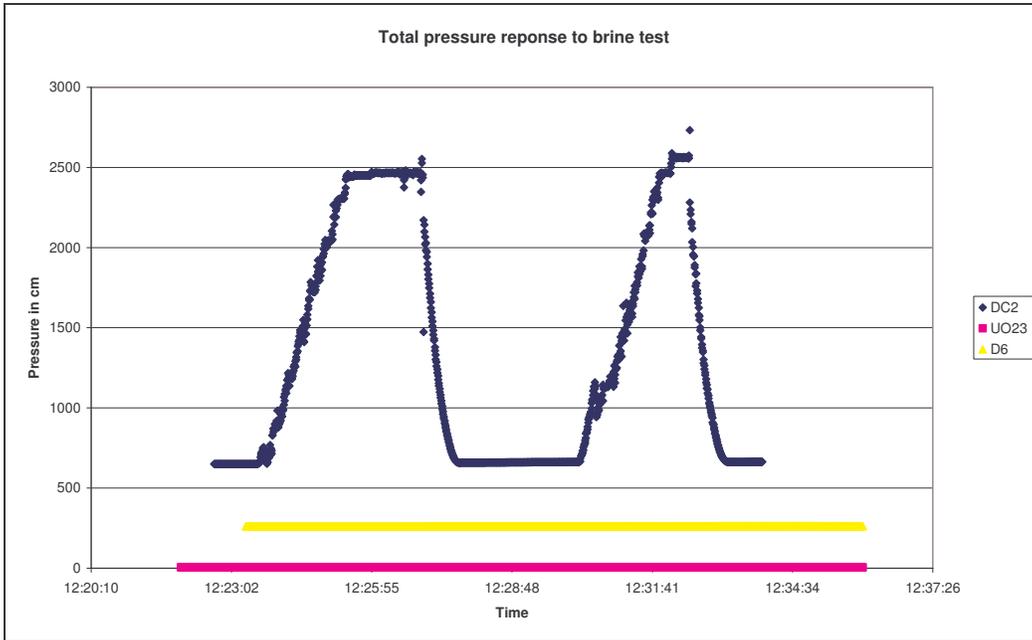


Figure 5-41: Brine injection pressure response in injection and observation boreholes. See Figure 5-42 for detail of observation boreholes).

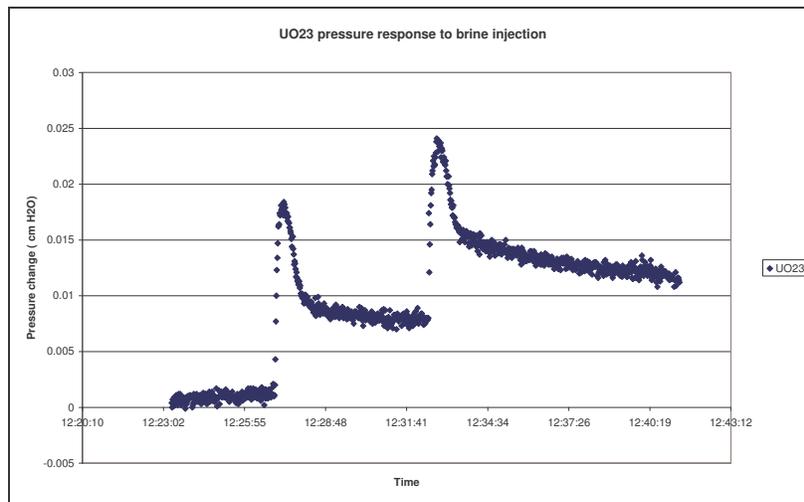


Figure 5-42: Brine injection pressure response in UO23

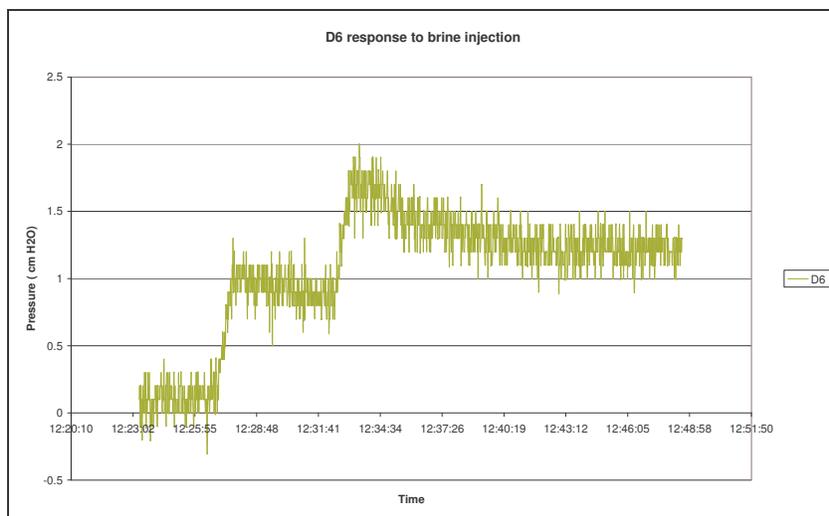


Figure 5-43: Brine injection pressure response in D6.

The pressure responses of the different boreholes show the degree of connectivity and, as will be shown in the Flourinert injection, the differential response in different boreholes and the time lag indicates the degree to which the fractures in each of the reacting boreholes is interconnected. Distance from the injection does play a role but the response is not radial and is more strongly influenced by the degree of fracture interconnectivity.

After the completion of each test, Borehole D3 was pumped for 6 - 8 hours until the measured EC returned to background values in all of the boreholes.

The brine injection was repeated several days after the initial test. During this injection the EC variation in different boreholes was assessed to determine where the brine had migrated to and therefore where Flourinert may flow towards (Figure 5-44). Of significance out of this determination was the fact that in borehole D3 adjacent to the injection, the brine showed a stronger response in the lower of the two closely spaced fractures (See Section 5.2.5.6.2).

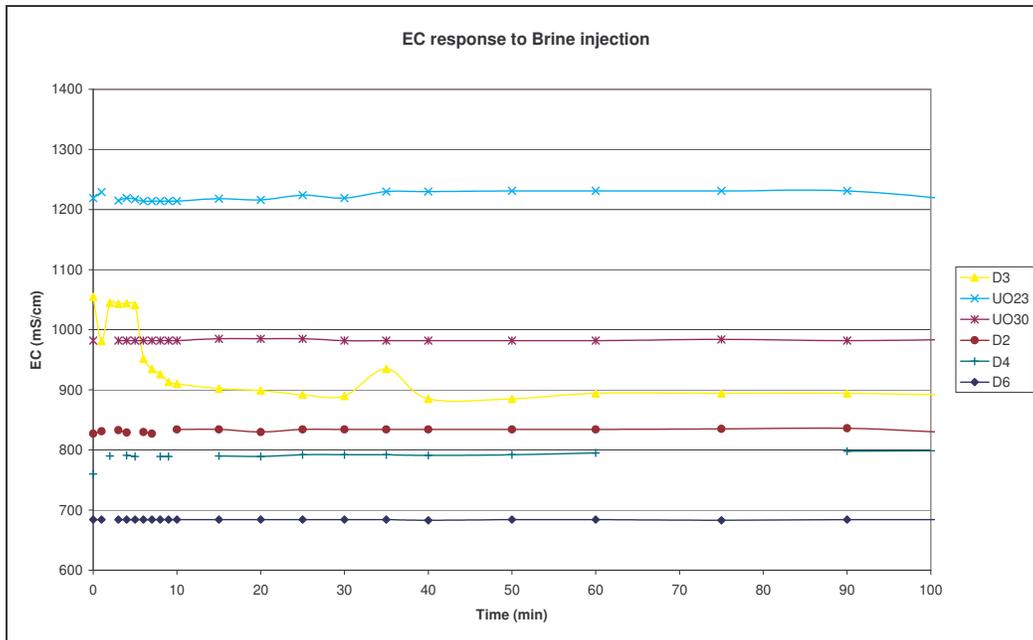


Figure 5-44: EC response after brine injection

The pattern of EC detection in the surrounding boreholes shows an interesting trend. It is clear from Figure 5-45 that D3 which is adjacent to DC2 shows a strong response, with lesser detection in UO23 and very small increases in EC in DC1, D2 and D6.

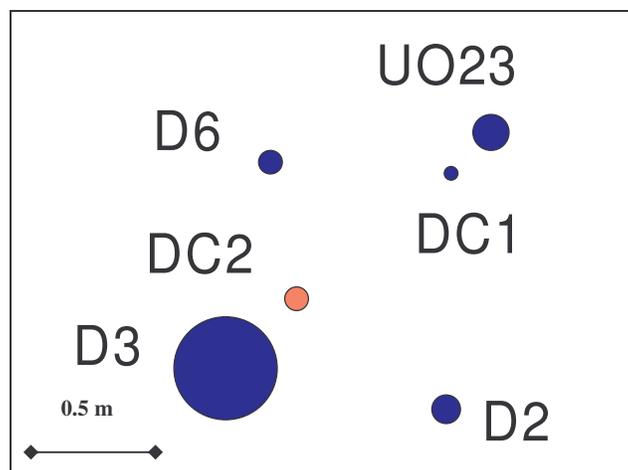


Figure 5-45: Proportional EC response to brine injection

The difference in the NAPL injection will lie in the fact that there is no dissolved phase migration down gradient according to the head distribution in the aquifer.

5.2.7.2.2 Injection of FC-77

The injection of the FC-77 was done in a similar manner to the brine injection described in the preceding section.



Figure 5-46: Field set up of the FC injection

In addition to the pressure transducers installed in the injection and observation boreholes, Solinst interface meters were used to detect the presence of the FC-77 in the observation boreholes and above the rubber skirts to assess pooling of NAPL in the injection borehole. It was also decided to install a borehole video camera in observation borehole D3. Since the FC-77 is colourless, sodium fluorescein dye was inserted in the borehole, in order to be able to observe a colour contrast. The depth of installation of the camera was determined by the brine injection, which indicated that the lower fracture within the fracture zone was most likely to facilitate density-driven flow.

The pressure response in the injection borehole and the observation boreholes are provided for discussion. It can be seen that the injection apparatus was effective in terms of allowing the FC-77 to build up a head of in excess of 30 m, with the stepwise increase in pressure indicative of the addition of each litre of the surrogate DNAPL. In total 7L of fluid was injected. The graph also indicates an instant release of the pressure, from which the relative hydraulic conductivity can be obtained (Figure 5-47).

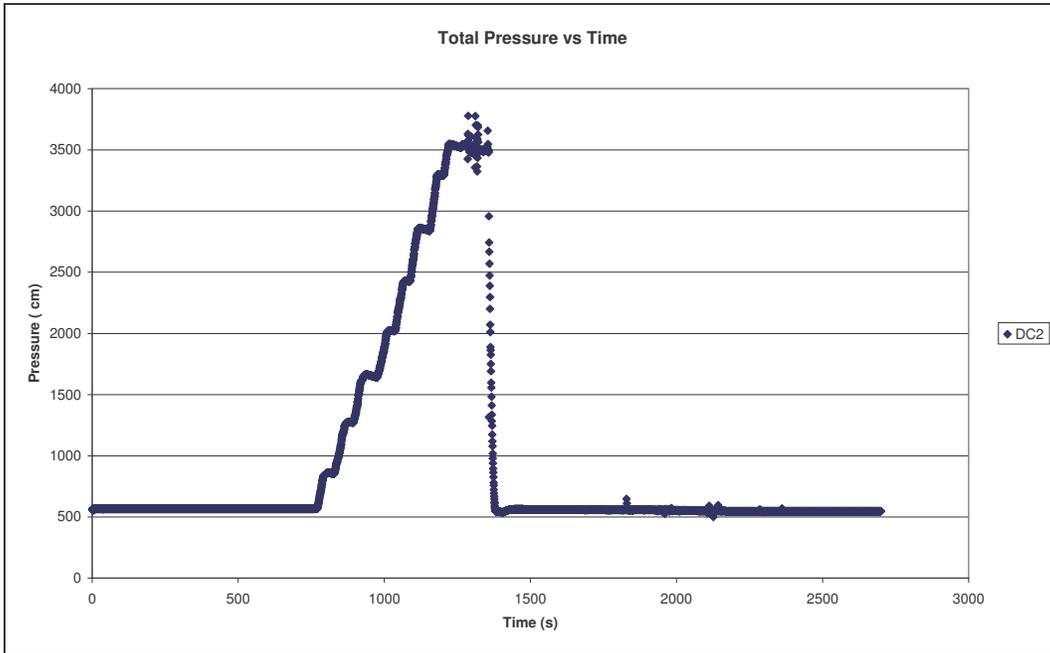


Figure 5-47: Pressure increase and recession in the injection borehole

The response in the observation boreholes shows the very rapid response in each of the observation boreholes (Figure 5-48). This is a very similar response to that observed for the brine injection (Figure 5-42 and Figure 5-43), with the magnitude of the response proportional to the distance from the injection and the connectivity to the fracture.

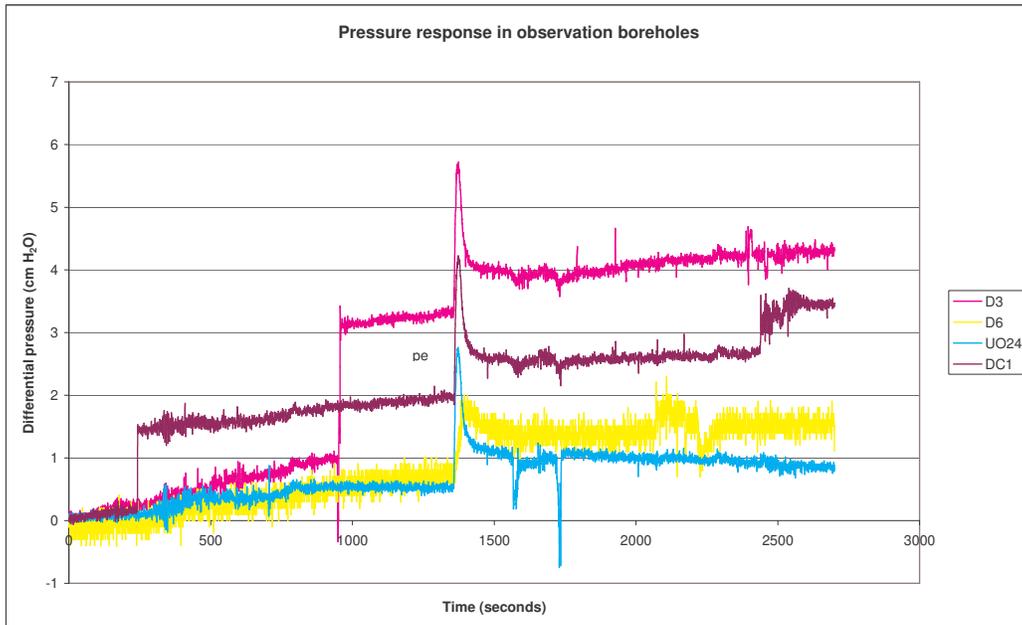


Figure 5-48: Observation boreholes' hydraulic response

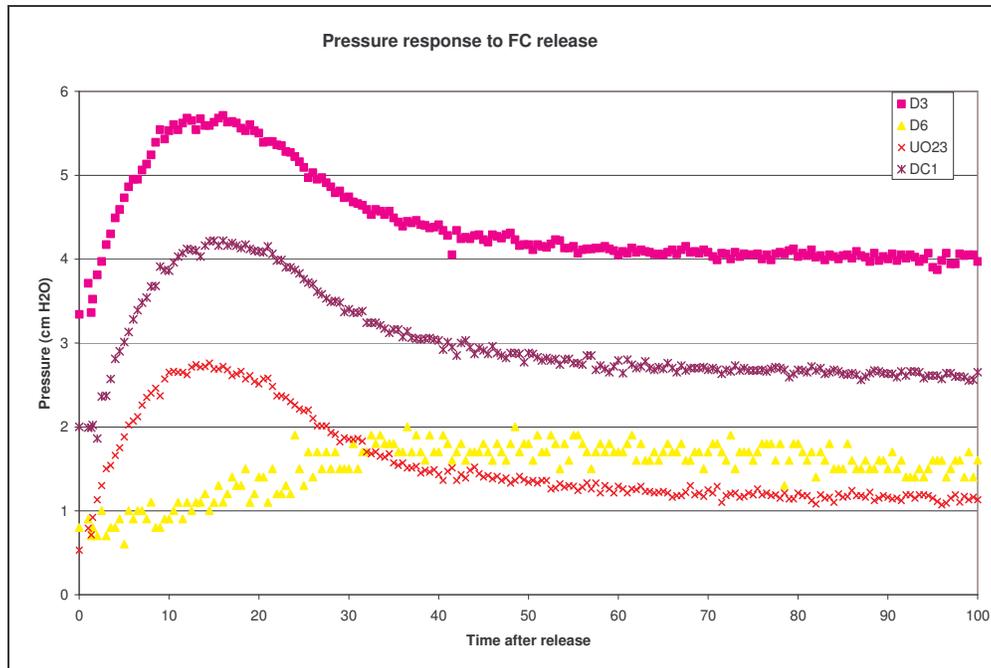


Figure 5-49: Detail of response in observation boreholes (Time=0 reflects the injection of FC-77 time= 1350 s on Figure 5-47)

The magnitude of the response appears to be roughly distance related (Figure 5-49), whereas the timing of the response is related to the degree of hydraulic connectivity or the hydraulic conductivity of the pathway, rather than the proximity to the injection. As such, D3 begins to peak after approximately 9 seconds, UO23 with 10 seconds, DC1 in approximately 12 seconds after injection and D6 again give a very turbulent response that starts to peak at approximately 25 seconds after injection. The gradient of the responses are also slightly steeper in the more rapid reacting boreholes. This would confirm the other hydraulic observations that UO23 and D3 are generally high yielding with high transmissivities, and strongly connected.

The decrease in pressure in the injection borehole gives an indication of the apparent NAPL hydraulic conductivity. Plotting this response against the log of the time suggests a slight change in conditions after approximately 8 to 9 seconds. If this pressure recession is more rapid after 10 seconds it would suggest that this is the DNAPL filling the available space between the bottom of the injection apparatus and the bottom of the borehole. Whereas, if this was less steep it would suggest some resistance to flow as the NAPL had to overcome some of the capillary pressures due to its non-wetting nature.

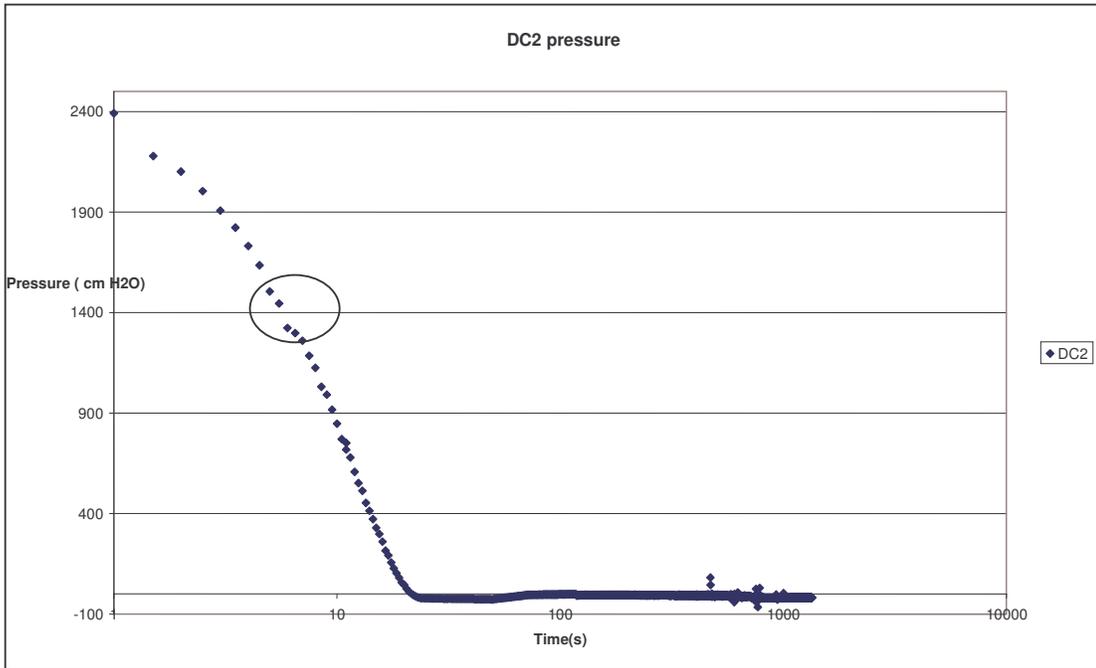


Figure 5-50: Detail of the pressure recession in the DNAPL injection borehole (change in gradient at 8 seconds evident)

The hydraulic responses of the brine and NAPL injections have been analysed using the Bouwer and Rice analysis method.

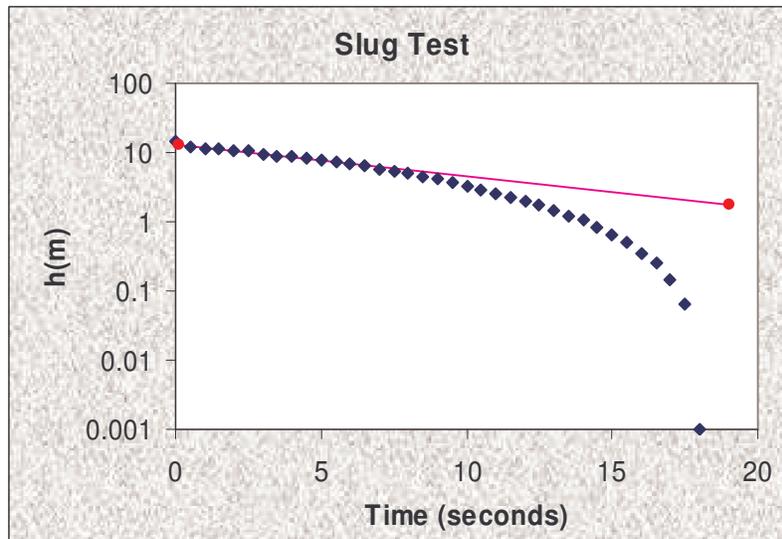


Figure 5-51: Brine injection (K-value of 134 m/d)

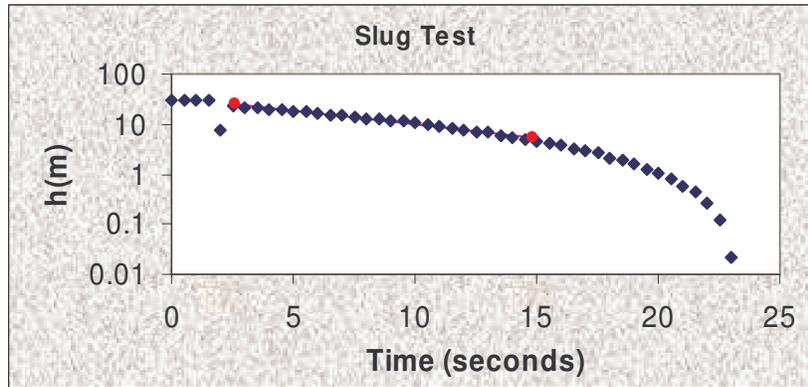


Figure 5-52: DNAPL injection (K-value 140 m/d) for later time

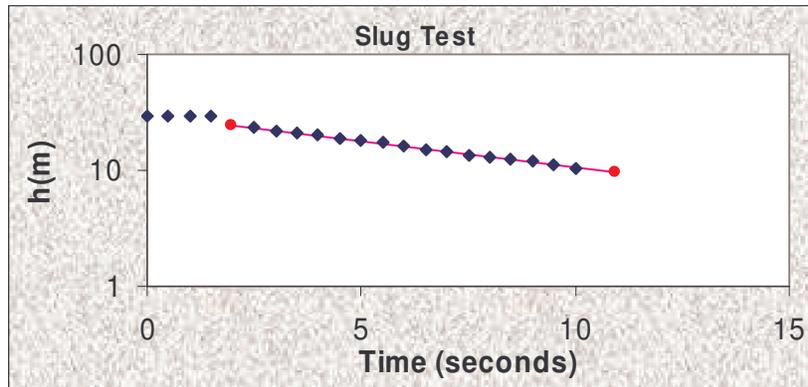


Figure 5-53: DNAPL injection at early time (K-value 120 m/d)

This indicates that the apparent hydraulic conductivity increases in later time, which suggests that initially the NAPL has to overcome some wetting/non-wetting resistance but that as soon as the fracture becomes NAPL wet the K-value of the NAPL exceeds that of the brine injection, probably due to the reduced viscosity of the DNAPL.

These factors would suggest that DNAPL migration would have occurred easily and widespread from the injection borehole. Apart from the pressure response measured in the boreholes, an interface meter was used to measure the free phase in the boreholes. The only borehole in which any free phase NAPL was measured was D3, the first indication of NAPL occurred approximately two minutes after the injection. The maximum amount of DNAPL measured was approximately 4 cm of DNAPL or roughly 80 to 100 ml of FC-77 in the borehole, 10 minutes after injection of and this remained constant throughout the observation period.

24 Hours after the experiment the interface meter was used again and no NAPL could be detected in any of the boreholes. From this observation it can be assumed that the FC-77 has migrated downwards and/or laterally and that the fluid exists as residual

close to the injection borehole.

The success of the accurate fracture determination was verified by the visual observations recorded in borehole D3. The precise position where the borehole video camera was installed, yielded the first recorded field observation of DNAPL emanating from fractures in the subsurface. While the DNAPL observations are not that clear in still shots (Figure 5-54), the series below indicates the DNAPL flowing from the fracture, with shots of the initial period and after the DNAPL flow had ceased. (See attached CD for video clip.)

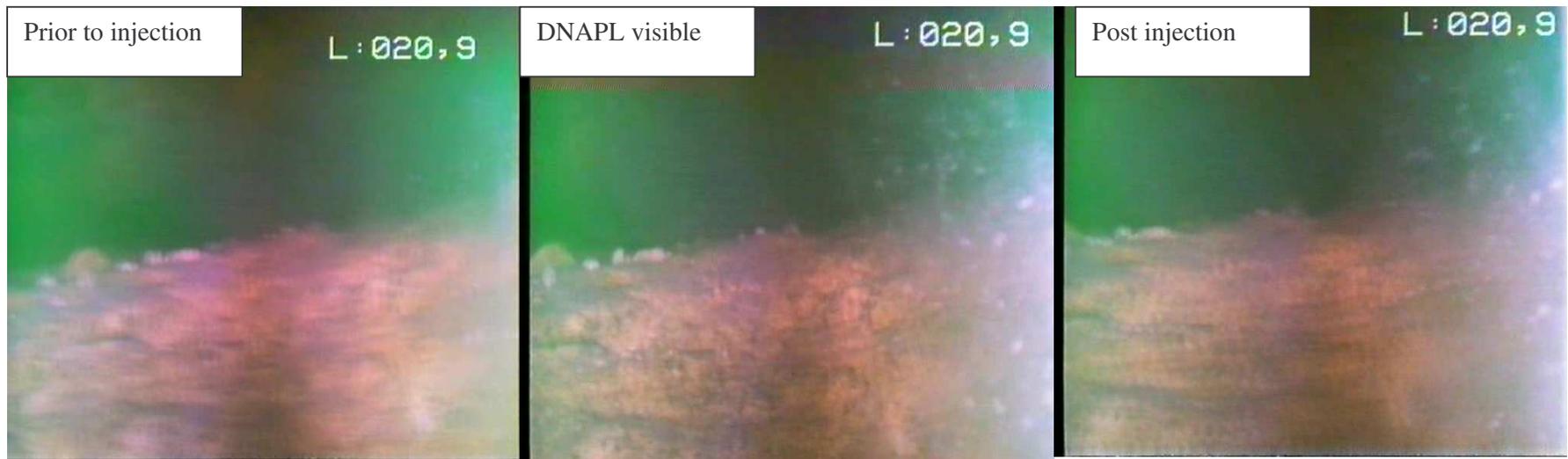


Figure 5-54: Clips of borehole video of FC-77 flow out of fracture Borehole D3.

5.2.7.3 Discussion

Laboratory testing of water, brine and FC-77, into a fixed aperture sandstone fracture constructed as a parallel plate provided confirmation of the established critical factors for fracture mass transport of dissolved, density driven and DNAPL flow. These results were used to precisely define the field injection of the surrogate DNAPL. The detailed field characteristic of this site and the results of the injection of brine and a surrogate DNAPL have provided some important findings. The most pertinent of these are as follows:

1. DNAPL injection into fractured rock elicits a different response to a high density aqueous liquid (brine), emphasizing the importance of NAPL flow, as opposed to aqueous density driven flow.
2. At field scale, DNAPLs have the ability of migrating in the direction opposite to groundwater flow.
3. Local variations in fracture strike and dip play a far more important role in DNAPL flow than the regional fracture dip or groundwater flow directions.
4. The pressure response of boreholes surrounding the injection is not radial in fractured rock, and is a function of the hydraulic conductivity and the distance from the injection point.

Even under very controlled injection of DNAPL, the location of DNAPL mass distribution at field scale is very difficult, and large amounts of the DNAPL reside in local depressions within the fracture network as residual, which cannot be easily recovered. This supports the observations from field scale DNAPL remediation (Kueper *et al.*, 2003, Fetter, 1999 and Pankow and Cherry, 1996), where the solubility and volatility of the DNAPL are key factors to recovery, rather than mobilization and recovery of free phase DNAPL.

Accurate fracture identification and characterization are the most important considerations in understanding DNAPL flow in the majority of South African aquifers.

5.3 Determination of fate and transport of DNAPLs at an industrial site

5.3.1 Background

Test Site 1 was selected as a potential DNAPL research site because of the diversity of activities and chemicals used at the site. It is a large industrial complex where several activities related to the transport industry take place and of which some date back to as early as 1919.

There were no existing monitoring or abstraction boreholes on site, therefore the presence and extent of pollutants were unknown. After the initial site investigation, the researchers compiled a list of the activities and potential groundwater contaminants. Three target sites within the property were then selected for intensive site characterisation, namely the gasworks, foundry and electroplating workshop areas. Figure 5-55: shows the distribution of these target areas on the site.

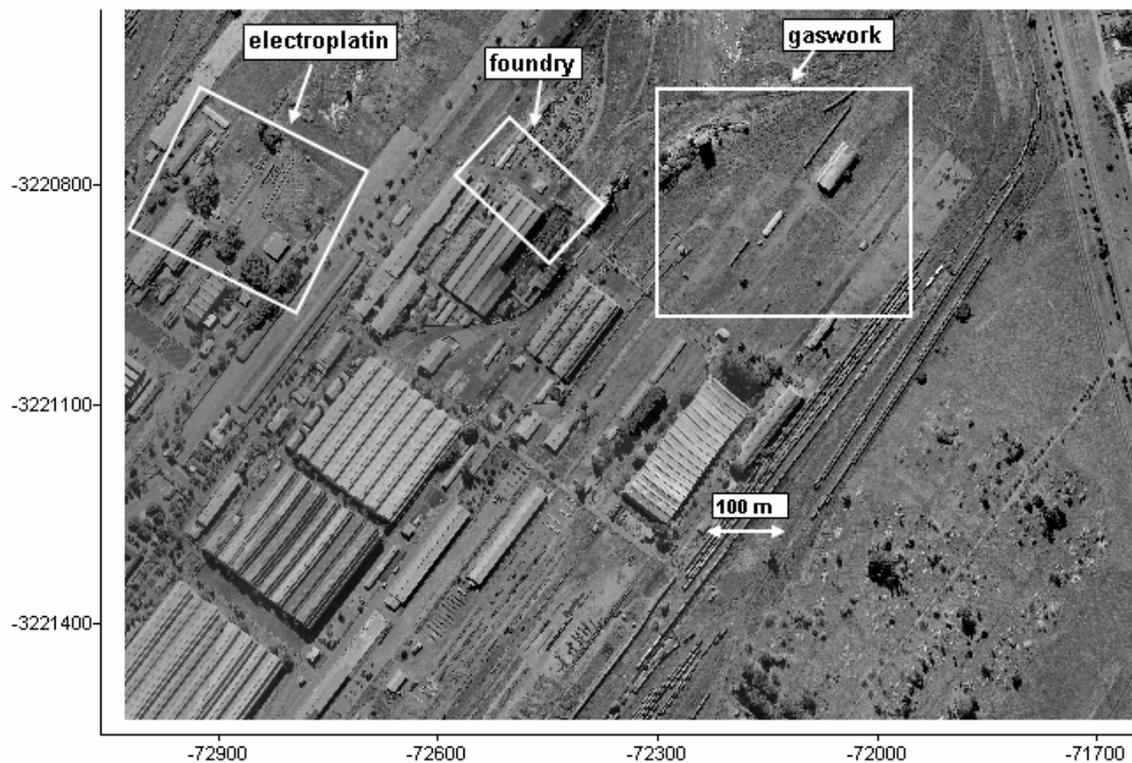


Figure 5-55: Aerial photo of Test Site 1 and target areas.

5.3.1.1 General Site Assessment

Several technologies for the characterization of sites contaminated with DNAPLs are available. These include geophysical techniques, tracer tests, and direct sampling or sensing methods. The innovative methods provide some significant advances over conventional sampling-based approaches but the real value of these methods is in their addition to a “toolbox” approach to DNAPL characterization (Rossabi, *et. al.*, 2000).

A general assessment of a contaminated site was made to determine the potential presence of a DNAPL in the groundwater zone at the site. This general assessment is usually made early on in the investigation and use is made of existing information about the site. The site investigator must consider whether the chemicals found at a site or expected at a site, could comprise DNAPLs and if the activities at the site could have resulted in the release of significant quantities of the DNAPL to the surface.

5.3.1.1.1 Types of chemicals

A large variety of chemicals was stored, used, produced as by-products of processes, and disposed of at Test Site 1. Many of these chemicals have properties of NAPL contaminants.

The site comprises an area of 1.01 Km² of diverse workshops, above and underground storage tank facilities, rail lines, a metal foundry and coal gasification plant. The types, quantities, use, storage, and disposal of chemicals used, were identified by referring to documents, chemical inventories, aerial photos, interviews with current and former employees, old engineering construction plans and site inspection.

There were no existing monitoring or abstraction boreholes in the area, and the presence and extent of pollutants were unknown. The areas identified where DNAPL contamination was suspected, are the foundry, old redundant gasworks, and the electroplating workshop (Figure 5-56 and Figure 5-57).



Figure 5-56: View of the decommissioned gasworks, with spillage from tar loading tanks, still visible.



Figure 5-57: Electroplating workshop, from the outside

Table 5-12 lists a preliminary list of potential contaminants depending on the activities at the site.

Table 5-12: List of activities and potential contaminants at Test Site 1.

| Area | Possible contaminants | Comment |
|-------------------------|--|--|
| Tank/truck washing bay | Bitumen (brand name – “autocoat”), oil/diesel, inorganics, coal residue | Previous sandblasting of trucks/tankers to clean Only cement and coal trucks No chemical tankers Wash water is allowed to run on soil (or in storm water drain) Dumping of coal/bitumen residue from trucks |
| Electroplating workshop | CN, chrome and other heavy metals, chlorinated solvents (PCE and TCE), acids, inorganics, paint components | Electroplating activities ceased 2003 The risk office provided a chemical inventory Pump station/ sump still filled with waste water/chemicals Spills from the pump house in the past Field in the back most likely used as a dumping site in earlier years Now used as a small component painting shop Storeroom with acid, paint, solvents Workshops all have cement floors |
| Redundant gasworks | Coal tar, inorganics, coal residue, asbestos, unknown contaminants dumped in field | Built in late seventies Only used for a few years Coal tar loading bay Spillages along rail line from load bay In field several old “pond” dump sites Asbestos dumped illegally |
| Foundry | Heavy metals, solvents, oils/greases, cutting oils (including PCBs) | Smelting, casting of metal components Boilers Slag and coal discard dumped |
| Other | Inorganics, diesel/oil/petrol/paraffin, heavy metals | Soda Ash storage tank USTs for diesel, petrol, paraffin Channels, storm water and sewage pipes/lines/sewers |

5.3.1.1.2 Assessment of site operations

It was suspected that, during the operation of the gasworks, large volumes of coal tar, phenols and oils were spilled on the site. Little information was found on the history of storage, spillage or disposal of the wastes. It was however evident from the site inspection that the tar loading bay was subjected to numerous spillages through the years of operation. More than 21 years after decommissioning of the plant, there is still tar residue within the storage tanks that leak onto the soil. An old sump near the loading bay is also filled with coal tar and wastewater.

Interviews with employees yielded significant information regarding the operation, management and waste disposal at the electroplating. Electroplating of mechanical and other parts took place in the closed-off workshop area. Any wastewater generated was pumped to a lime treatment facility just outside the workshop. For many years of operation, the “treated” water was disposed of either in the storm water system or in the open veld. Subsequently a holding facility was built, where the sludge was settled and excess water disposed of via the sewer system. Sludge has been removed and disposed at a regulated waste facility in the recent past, but in earlier years the sludge was disposed of on site.

In an area east of the sludge treatment facility, the land was used as an informal dumping ground for a variety of wastes, including building rubble, sludge, empty solvent containers and oil drums. It is suspected that possible groundwater contamination from the operations would include inorganic wastes, such as heavy metals, and typical chlorinated solvents. The site owner has provided a list of chemicals used during the last two years of operations in the electroplating, as shown in Table 5-13.

Table 5-13: List of chemicals used in the electroplating workshop.

| Chemicals Used | |
|------------------------------------|---|
| Solvents and degreasers including: | <i>TetraSolve, RanSolve, Methoklone and Oxyprep</i> (The solvent ingredients consist mostly of Tetrachloroethene (PCE), Dichloromethane (DCM), ethylene glycol monobutylether or a mix of chlorinated hydrocarbons.) |
| Number of acids including: | Sulphuric-, hydrochloric-, nitric-, chromic-, ortho phosphoric-and , boric acid |
| Other: | Nickel Chloride; Nickel Sulphate; Sodium Cyanide; Calcium Hypo-chloride; Zinc Oxide; Copper Cyanide; Copper Sulphate; Sodium Carbonate; Caustic Soda |

From interviews with employees, indications are that diesel, used motor oil and greases were also spilled in the area. The potential NAPL contaminants are more than just the dense chlorinated hydrocarbons, and this site is thus representative of a mixed DNAPL site.

5.3.1.1.3 Assessment of potential DNAPL migration

There was limited hydrogeological information available before the field investigations were initiated. Old engineering construction diagrams showed that the subsurface is composed of thick (more than 20 m) unconsolidated sediments and the vadose zone depth was estimated at least 10 m to 13 m thick. The site is located on typical Beaufort sediments from the Karoo Group. It could therefore be assumed that DNAPL transport would be influenced by fracture flow, matrix diffusion and bedding plane features in the bedrock.

Considering the age of the industry, DNAPL contaminants were expected to migrate down to the saturated zone. Since some of the disposal sites were used for many years, it is suspected that natural attenuation could also have taken place. Therefore, daughter products, could also be found in the vadose and saturated zones. The possibility of vapour plumes in the vadose zone is also expected as there were multiple sources of contamination many of which potentially housed volatile organic chemicals.

5.3.1.2 Climate

The study area has a fairly arid climate with very hot summers and cool to cold winters, and a predominantly summer rainfall. Figure 5-58 below gives the average monthly climatic parameters for the Bloemfontein weather station.

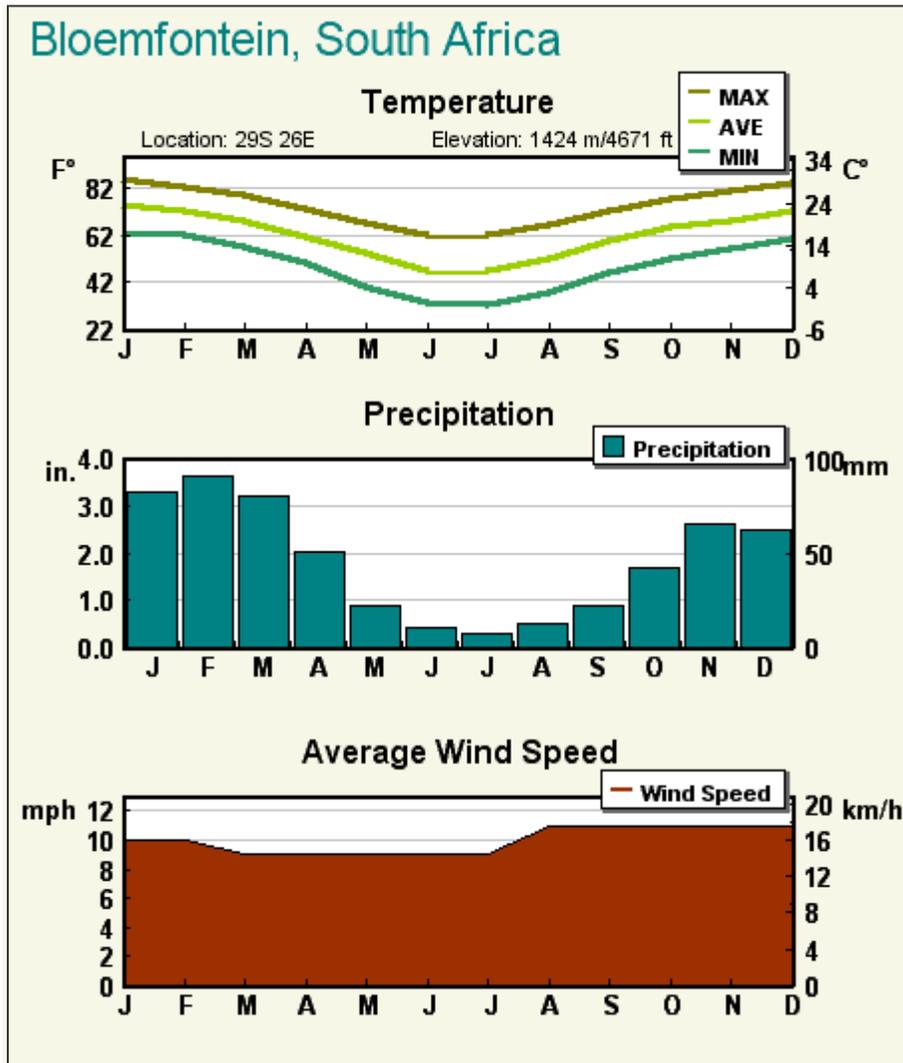


Figure 5-58: Average climatic parameters for the Bloemfontein (From <http://www.weathersa.co.za>)

5.3.1.3 Hydrocensus

Since no hydrogeological information was available it was decided to do hydrocensus of the surrounding properties to Test Site 1. Information that was collected included water use, water level, pump rates and water quality. The hydrocensus was done mainly in the groundwater flow direction. The distribution of the hydrocensus boreholes in relation to the test site is shown in Figure 5-59.

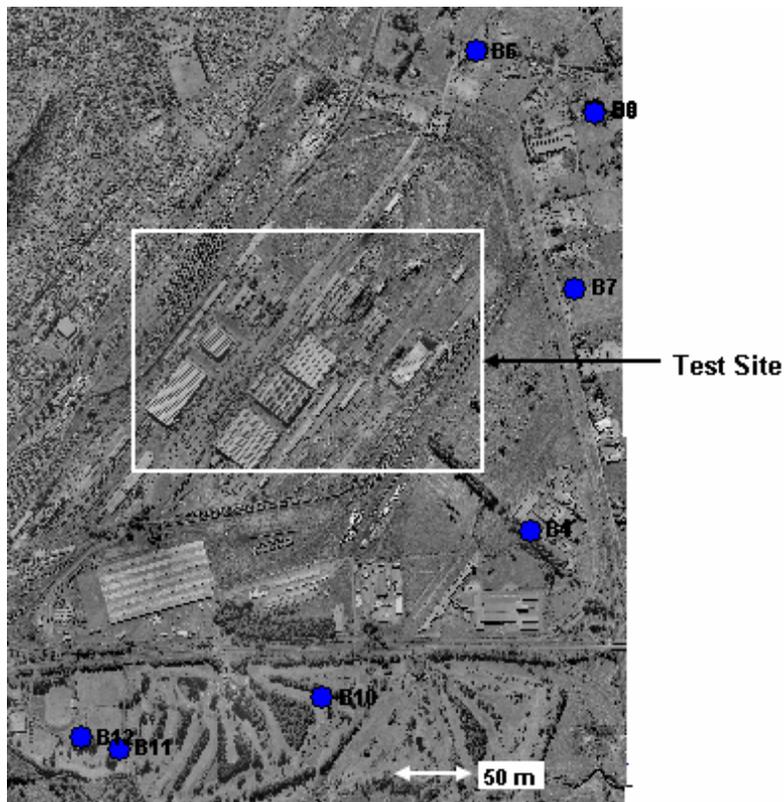


Figure 5-59: Location of the hydrocensus boreholes.

The hydrocensus boreholes were used for various applications, including domestic, light industrial and/or agricultural purposes. Some boreholes were constructed in such a way that neither water levels nor samples could be taken. There was good cooperation from property owners and a total of ten boreholes were evaluated, namely B1, B4, B5, B6, B7, B8, B9, B10, B11 and B12. Where there was access to open boreholes, samples were collected using a specific depth sampler, and where boreholes were equipped, pumped samples were taken on surface at the outlets. Evaluation of water quality and possible sources of contaminants, found in the samples, were compounded by the diverse land use of the area. The area is zoned as light industrial but include a number of residential plots, a fresh produce market, feedlot, abattoir, transport companies, brickworks, automotive workshops and plant nurseries.

5.3.1.4 Field Investigation

After the initial target areas were identified at Test Site 1, the field investigations were initiated. The field investigation was done with a phased approach and took

approximately three years to complete. Several non-invasive and invasive methodologies were applied at the site. A number of samples (soil and water) were taken, and water level data was collected which provided the researchers with time series data.

The following table is a short summary of the site assessment methodologies applied at Test Site 1. A brief description of the results is also given.

Table 5-14: Summary of site assessment methodologies applied at Test Site 1.

| Site Assessment Method | Location | Results/Application |
|--|--|--|
| Non-invasive: | | |
| Hydrocensus | Surrounding properties | Ten boreholes tested. Various contaminants incl. BTEX and chlorinated solvents where found. |
| Soil gas survey | Electroplating and Gasworks areas | Distribution of VOC, TPH, Methane, CO ₂ and O ₂ . Correlation with rail lines |
| Geophysics: | | |
| Airborne Geophysics (Magnetic and radiometric) | Complete site | Regional structures i.e. dykes were located |
| Surface Geophysics (ESS, Magnetic, EM) | Gasworks | Confirmation of dyke |
| Invasive: | | |
| Test Pits | 25 test pits were dug at Electroplating and Gasworks areas | Provided access to shallow soil profile, identified areas where shallow contamination of PAHs occur. |
| Drilling | | |
| Air Percussion | Outside-in approach was applied, 13 boreholes drilled across site, up and downstream. | Provided access to subsurface and groundwater for hydraulic testing, sampling, etc. Borehole nests of different depths gave information regarding different aquifer systems. . |
| Auger | 7 Auger holes were drilled using Hollow-stem, Direct push, and Solid-core methods. Electroplating and Gasworks areas | Four piezometers installed. Soil profile documented down to 18 meters, soil samples taken and VOC measurements taken at regular intervals. Contaminants in soil profile differ from contaminants in groundwater. |
| Diamond core | Two core holes drilled using split core method drilled down to 60 meters at | Cores provided detailed geological information and fracture types and |

| | | |
|------------------------|---|---|
| | Electroplating and Gasworks areas | positions. |
| Sampling: | | |
| Soil | Soil samples taken from surface, test pits, auger, percussion and core boreholes | Analysed samples for organic contaminant content. Contaminants in soil and unconsolidated portions of the aquifer differ from that in groundwater, mostly PAHs and concentrations higher than that were found in groundwater. Evidence of strong retardation in clay layers. |
| Water | Water taken from all boreholes and piezometers where groundwater was intersected. | Groundwater analysed for inorganic and organic contamination. Contaminants found in groundwater differ between shallower unconsolidated part of the aquifer system to that of the deeper bedrock system. Concentrations of VOCs lower than expected and evidence of degradation (micro-organisms and daughter products of Chloroform, PCE and TCE). Toxicity testing with battery of test, to determine health risks. Results were inconclusive with regard to organics, due to presence of inorganic contaminants. |
| Geochemical profiling: | | |
| Multi-parameter probe | All boreholes and piezometers where groundwater was intersected | Down-hole profiles of DO, Redox potential, EC, pH, and Temp. Used in fracture characterization and confirmation of preferential flow paths. Also determined redox conditions which are favourable for degradation of contaminants. |
| Conductivity probe | All boreholes and piezometers where | Down-hole profiles EC and Temp. Used |

| | | |
|--|---|--|
| | groundwater was intersected | in fracture characterization and confirmation of preferential flow paths. |
| Interface meter | All boreholes and piezometers where groundwater was intersected | Used to identify boreholes or piezometers with free phase NAPL. No free phase was detected in any of the boreholes. |
| Other down-hole techniques: | | |
| Down-hole Geophysics (One-arm Caliper Natural Gamma; Spontaneous Potential; Resistivity, Full Wave Sonic, and Neutron-neutron) | Boreholes at Electroplating and Gasworks areas | Used in fracture characterization and confirmation of preferential flow paths |
| Video logging | Boreholes at Electroplating and Gasworks areas | Identified vertical and sub-vertical fracture zones in bedrock |
| Aquifer Testing: | | |
| Slug tests | All percussion boreholes | First estimate of hydraulic conductivity for further testing |
| Pump tests | All percussion boreholes short duration tests (6 hours), GB9 a 6 and 26 hour test | Determined variation of transmissivity: (Higher T obtained during shorter tests (T of fracture) and lower T at longer test (T of formation)) |
| Tracer tests | Point dilution tracer test GB2, EB3, EB1, GB4, GB5, GB3, and FB1 | Obtained Darcy velocity, Seepage velocity and location of fracture zones |

5.3.2 Determination of Composition of DNAPL at Test Site 1

The physical properties of the organic compounds affect their behaviour in the subsurface (Appendix A). Some of these physical properties are, for example, interfacial tension and wettability, density, viscosity, solubility, Henry's law constants, capillary pressure, and relative permeability. From the previous discussions it can be seen that determination of these properties are critical in the understanding of the behaviour of the NAPL phase in the subsurface. Many of these properties can be obtained from literature for pure phase organic fluids. However, many DNAPL wastes that are produced in manufacturing and industrial operations are complex mixtures of organic compounds. The behavior of such chemically complex mixtures of organic compounds can vary significantly from the single component DNAPLs and, consequently, should be considered when assessing or remediating sites with complex, multi-component DNAPLs. It is therefore important that, if possible, during a site assessment that a sample of the NAPL should be taken and the components and properties be analysed for.

5.3.2.1 NAPL samples from Test Site 1

At Test Site 1, no free phase NAPL was encountered during invasive investigations. However, at the electroplating a sludge dam from the electroplating and paint works shops contained left over sludge. At the gasworks a sump filled with coal tar from the gasification process was discovered (Figure 5-60).



Figure 5-60: Sump at gasworks (left) and sludge pond at electroplating (right)

Since it was assumed that most of the contamination will be related to these two types of wastes samples from these sources were taken for organic analysis.

5.3.2.1.1 Organic Analyses results

The samples were analysed for VOCs, SVOCs and PAHs. As was expected the sample contained mostly PAH and SVOC components (Figure 5-61 and Table 5-15)

However, the laboratory could only account for ~ 9% of the composition and classified the remainder of the sample as coal tar pitch. Of this 9 %, naphthalene (5%), Fluorene (2%) and Phenanthrene (1%) accounted for the majority of the PAHs in the sample. Although this analysis was unlikely to reflect the composition of the NAPL in the subsurface, it did provide some guidance towards the focus of analyses of soil and water samples.

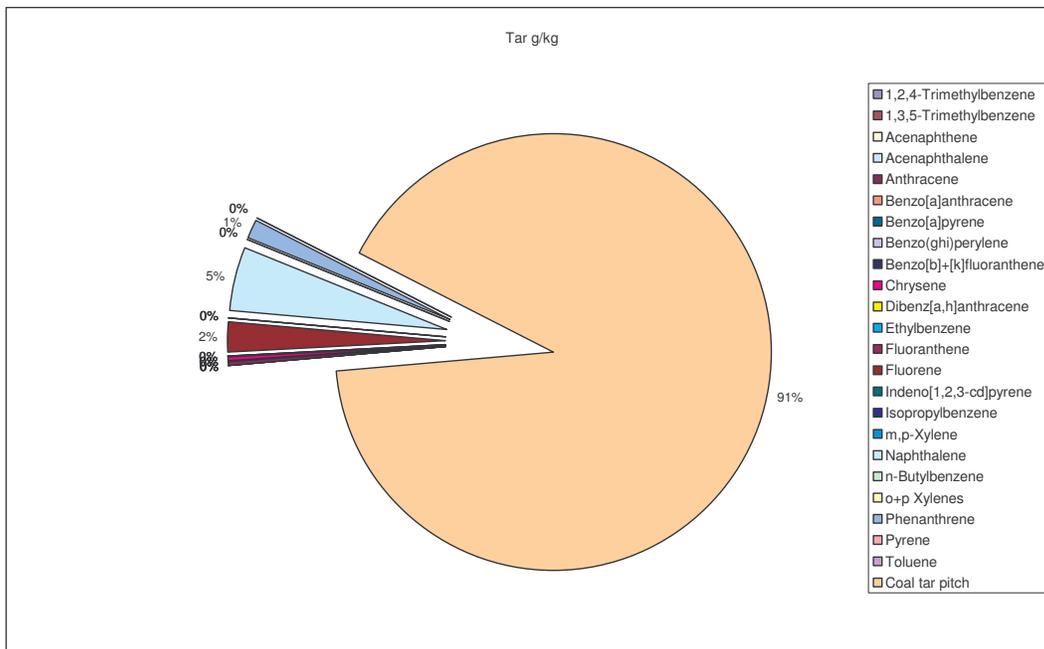


Figure 5-61: Composition of the coal tar sample

Table 5-15: Analysis of coal tar sample in g/kg.

| | Tar g/kg |
|--------------------------|----------|
| 1,2,4-Trimethylbenzene | 0.174 |
| 1,3,5-Trimethylbenzene | 0.067 |
| Acenaphthene | 0.087 |
| Acenaphthalene | 0.84 |
| Anthracene | 0.766 |
| Benzo[a]anthracene | 0.143 |
| Benzo[a]pyrene | 0.107 |
| Benzo(ghi)perylene | 0.02 |
| Benzo[b]+[k]fluoranthene | 0.234 |
| Chrysene | 2.399 |
| Dibenz[a,h]anthracene | 0.01 |
| Ethylbenzene | 0.019 |
| Fluoranthene | 0.262 |
| Fluorene | 22.874 |
| Indeno[1,2,3-cd]pyrene | 0.068 |
| Isopropylbenzene | 0.002 |
| m,p-Xylene | 0.048 |
| Naphthalene | 47.269 |
| n-Butylbenzene | 0.066 |
| o+p Xylenes | 0.061 |
| Phenanthrene | 12.29 |
| Pyrene | 0.324 |
| Toluene | 0.045 |

The sludge sample was also submitted for organic analysis. These results accounted for less than 1% of the contents and included the VOCs TCE, PCE and toluene (Table 5-16 and Figure 5-62). The sample did confirm the potential presence of PCE and TCE as contaminants in the subsurface.

Table 5-16: Analysis of sludge sample in g/kg.

| | Sludge (g/kg) |
|-------------------------|---------------|
| Tetrachloroethene (PCE) | 1.705 |
| Toluene | 0.044 |
| Trichloroethene (TCE) | 0.435 |

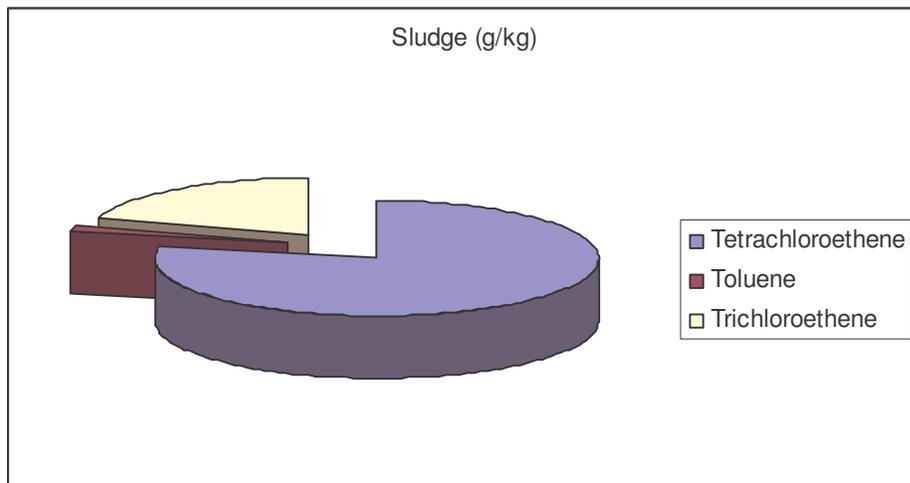


Figure 5-62: Organic components of sludge sample.

Whenever a sample of the suspected DNAPL is obtained during a site investigation it is important to use the sample to determine the physiochemical properties of the fluid. This allows the site investigator to make more accurate predictions on the potential migration rates of the DNAPL in the subsurface. However, due to the amount of time that these samples were exposed to the elements on surface, it was assumed that the physical properties were not representative of the DNAPL contaminants in the subsurface, and could thus not be used to determine the properties of the suspected DNAPL. Although the sludge sample contained solvents, the properties of the sludge were not representative of the solvents, which have entered into the subsurface. The samples were thus only used to guide field investigations and analyses of soil and water samples (also see Section 5.3.3.3).

5.3.3 Conceptual site model

All the information collected during the site investigation was used to construct a conceptual site model for Test Site 1. This includes the geological, hydrogeological, and contaminant transport and fate information.

5.3.3.1 Geology

During the drilling of boreholes and piezometers a large quantity of geological information was collected.

The area is underlain by the Adelaide Subgroup of the Beaufort Group of the Karoo Supergroup (Botha *et al.*, 1998). Quaternary deposits of alluvium, colluvium and calcrete are found throughout the formation.

The lithology of the site can be divided into the upper unconsolidated and lower bedrock units. The unconsolidated part is generally composed of clay, calcrete, sand, and gravel, with a thickness of about 30m. The first water strike is approximately at 15 m, and the main water strike is at the contact between the unconsolidated and the bedrock formation (± 30 m). The consolidated rock is composed of shale with interbedded mudstone and sandstone layers. Additional water strikes are encountered in boreholes where fractures are intersected. The geologic logs of all the boreholes and piezometers are provided in Appendix D1.

The site is underlain by a 30 meter layer of unconsolidated sediments. From top to bottom, it is composed of backfill, soil, clay, calcrete, sand and sandy gravel. However, the interbedding of layers is common. Thin layers of sand are commonly found interbedded between clay and calcrete. The thickness and extent of each unit is highly variable. For example, boreholes GB7 and GB8 (Figure 5-63) are only 10 m apart, but still their geological logs show considerable variation.

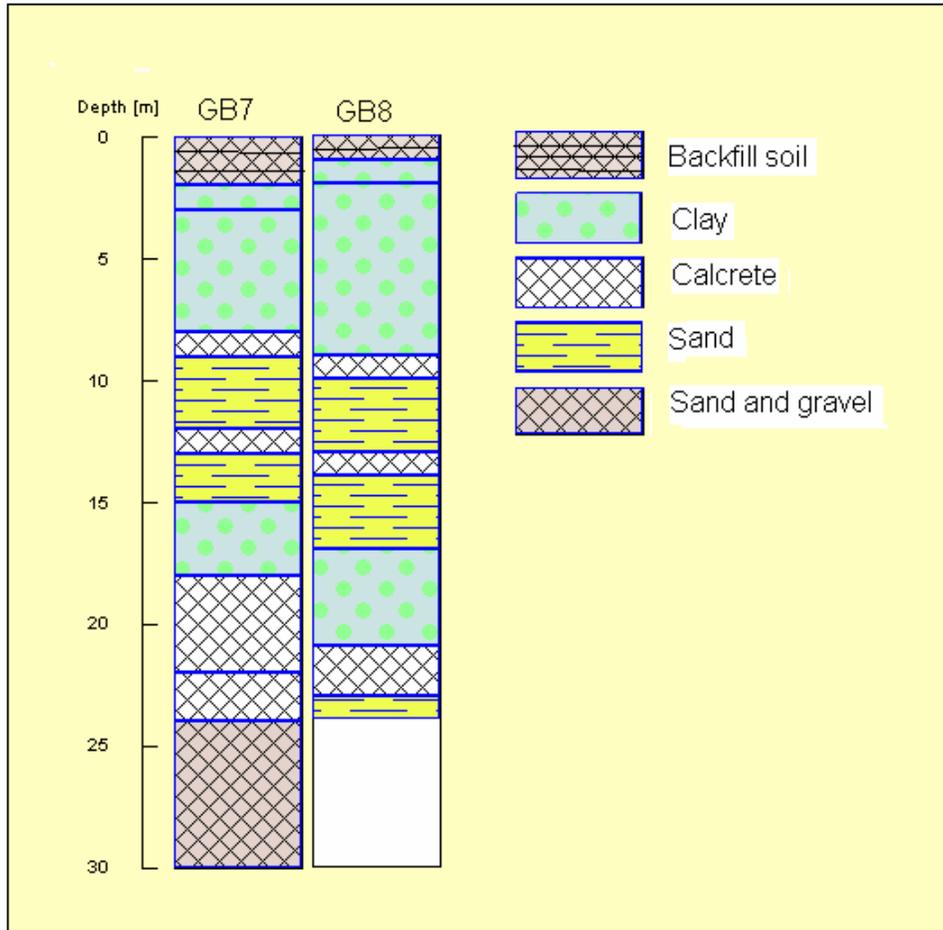


Figure 5-63: Geologic logs of Boreholes GB7 and GB8.

Most of the site is covered with backfilled material consisting of coal ash, building rubble, and gravel. At some locations it appears as if asphalt and possibly coal tar have been used as part of the backfill. Below the backfill, a layer, approximately 10 meters thick, of black or dark red clay is found. With depth, the clay becomes silt enriched. The clay exhibits an expanding nature, which is exacerbated when it is exposed to moisture. Following the clay a variable calcrete layer is found. At some sections it is as thick as 4 m. The grain size is variable, with calcrete gravels and fine grained calcrete commonly found together. This layer is not composed of pure calcrete, but is mixed with the other layers at varying ratios.

Below this a fine-grained sand is intersected. The water strike in the unconsolidated aquifer is associated with this layer. The sand generally is graded and becomes coarser towards the bedrock, where an unsorted gravel layer is found at the interface.

The bedrock formation consists of shale with some interbedded siltstone, sandstone and mudstone units. The shale, siltstone, and mudstone exhibit a very low primary porosity. The sandstone is fine grained. From the down-hole geophysics, video logging and core samples it was evident that the orientation and intensity of the fractures vary within the formations. Some bedding plane fracturing was visible as well as vertical, and subvertical fracturing.

The fracturing in the shale is dense and with random orientation, as shown in Figure 5-64. The shale was likely exposed to the atmospheric environment for a long time before the deposition of the unconsolidated sediments that resulted in its weathering.

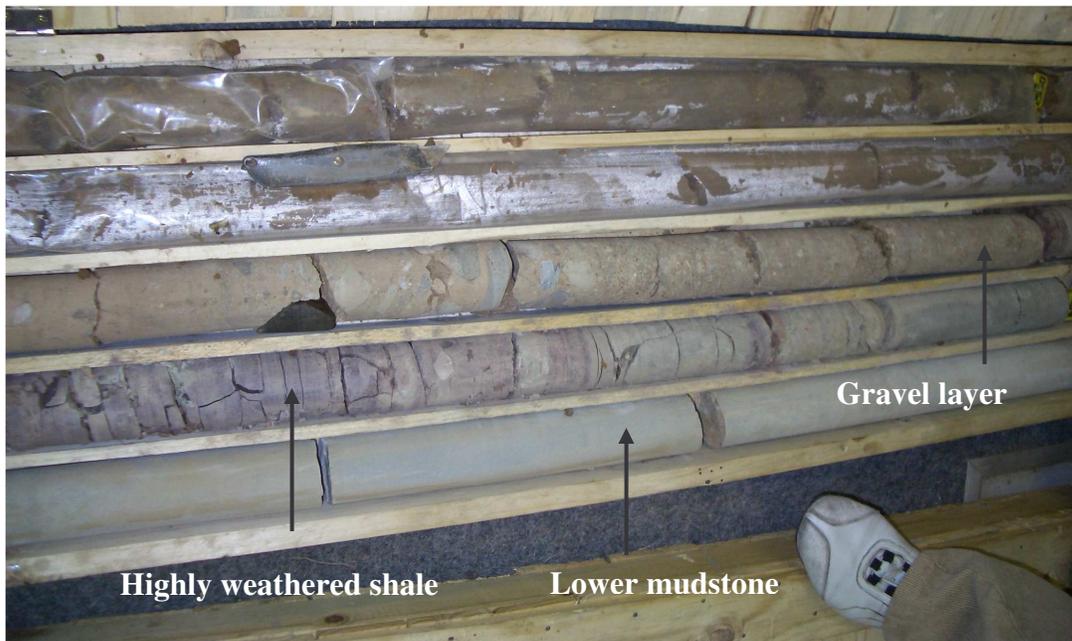


Figure 5-64: Highly weathered shale below the unconsolidated section in EC1.

The presence of this dense and highly connected fracture network will act as preferential pathways for DNAPLs and the associated dissolved plumes. Since the orientation and intensity of the fractures is highly variable, it was difficult to characterise the precise pathway of any DNAPL. The weathered shale is followed by interbedded mudstone, shale, sandstone and siltstone. Although the layers are of varying thicknesses at different locations, the primary porosity is relatively low in all of the layers. Secondary porosity (fractures) will be important for contaminant migration. Examples of the variation in the

size, orientation and intensity of fractures were evident from the core samples, Figure 5-65).



(A) Vertical fracture around 36 m in EC1

(B) Horizontal fracture around 51 m in EC1



(C) Fracture zone around 41 m in GC1

Figure 5-65: Vertical and horizontal fractures in the core samples from Test Site 1.

Some of the fractures displayed infilling with calcite. This decreases the transmissivity of the fracture and could limit DNAPL migration within these fractures. Often the calcite vein is more competent than the fracture zone, which is usually weathered through oxidation. Slickensides were observed in the shale in GC2 at a depth of about 53 m. Although there are indicators of fracturing (filled with calcite) followed by the displacement of the rocks relative to each other, the compactness of the rocks on both sides of the slickensides was so high that that is unlikely that these features will act as

conduits for DNAPL of water flow.

The major fracture zones were observed at 30 - 38, 42, 48 – 52 meters below surface. Most of the more conductive fractures or features were confirmed through additional site assessment methods.

5.3.3.2 Hydrogeology

In the test site, the elevation of the groundwater was found to follow the topography. It decreases with distance away from the koppie adjacent to the site, towards the east. The water level is approximately 15 m below the ground surface. Ground surface versus water level elevations were plotted to obtain a mathematical relationship between the two. There is a linear relationship with an R^2 value of 0.9, as shown in the following figure.

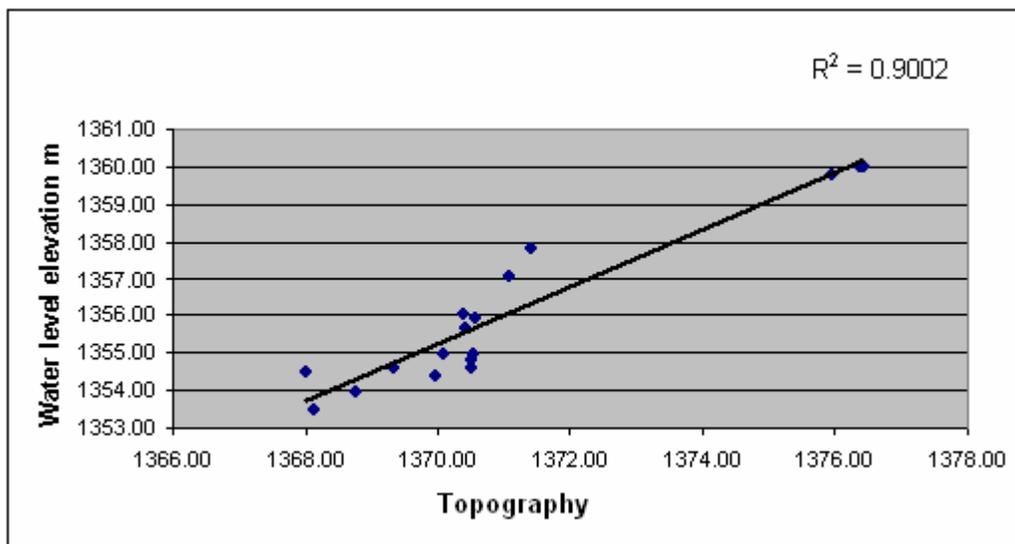


Figure 5-66: Topography vs. water level elevation (Gebrekristos, 2007).

Figure 5-68 shows the contour lines of the groundwater elevation. The figure is plotted by compensating the collar height from the respective boreholes. From this figure it can be seen that there is high hydraulic head around Borehole FB1, which does not follow the topography. FB1 is the deepest borehole on the site, with a depth of 61 m. All of the other boreholes are shallower and have lower hydraulic heads. It is therefore possible that FB1 is drilled into a fracture system with a relatively higher T-value. A time series of water level elevation for all the boreholes and piezometers on the site is given in the following

figure. The measurement was taken for two years and shows that the water level was stable with little seasonal variation. There are no production boreholes on the site.

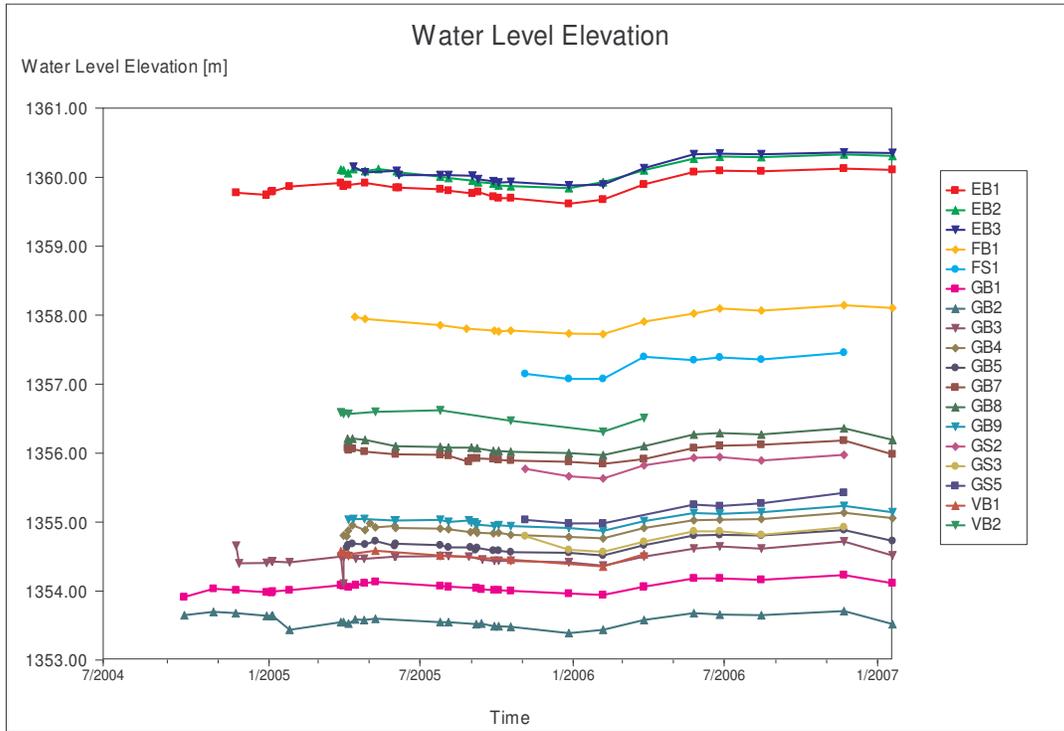


Figure 5-67: Time series of water level in the different boreholes (Gebrekristos, 2007).

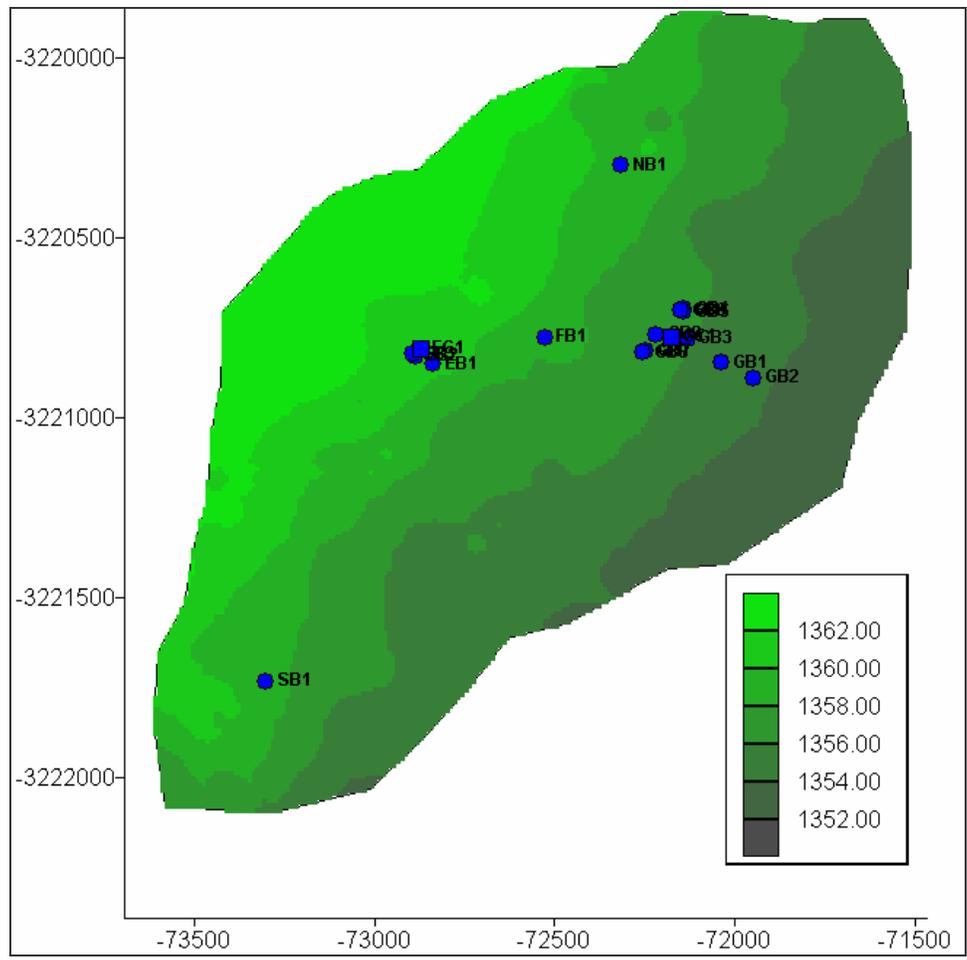


Figure 5-68: Contour map of groundwater elevation (Usher *et al.*, 2007).

Prior to the pump test, slug tests were performed to estimate the hydraulic conductivity and yield of the boreholes. The analysis was done using the Bouwer-Rice method. An average estimated yield of 4.4 L/s was calculated for the boreholes on site (Gebrekristos, 2007).

The results of the pump tests on Test Site 1 show that the aquifer systems generally have high T-values. The aquifer system is divided into two systems, depending on the estimated transmissivity values. These are the unconsolidated aquifer, and the bedrock aquifer. This division was supported by the water level measurements. Pump tests were done on both aquifer systems, and the T-value of the unconsolidated aquifer is found to be significantly lower than that of the bedrock aquifer. Table 5-17 shows a summary of the results. Both the drawdown and recovery data were considered in estimating the T-value and analysed using the Cooper-Jacob method. The T-value of the upper aquifer

ranges from 61 m²/day in GB1 and EB3 to 98 m²/day in GB5. The variation in transmissivity could be due to local differences in geologic formations and/or borehole construction. The bedrock or lower aquifer has a relatively higher T-value, ranging from 216 m²/day in GB7 to 797 m²/day in GB9. A large range in transmissivity was found. This could be caused by the duration and pump rate during the testing. Local variance in geologic formations and/or borehole construction could also contribute to these variations (Gebrekristos, 2007).

Table 5-17: Summary of T-value (m²/day) of the Test Site 1 boreholes (Gebrekristos, 2007).

| Borehole | Average T (m ² /day) |
|----------|---------------------------------|
| EB1 | 408 |
| EB2 | 285 |
| EB3 | 61 |
| GB1 | 61 |
| GB2 | 92 |
| GB3 | 571 |
| GB4 | 449 |
| GB5 | 98 |
| GB7 | 216 |
| GB8 | 308 |
| GB9 | 797 |
| FB1 | 306 |

The calculated hydraulic parameters, confirmed the conceptualisation of a two aquifer system. The hydraulic head difference between the aquifers is very small. It is therefore likely that a leaky boundary separates the systems. A third aquifer system, linked to deeper fracturing within the shale, was evident in the deeper boreholes (FB1, EC1, and GC1). A hydraulic head difference was measured in these boreholes. However, there was little evidence that this deeper aquifer system played a major role in the contaminant transport at the site.

In summary:

- The upper unconsolidated aquifer is about 30 m thick and is composed of primary porosity. It has lower transmissivity as compared to the lower bedrock aquifer with an average value of 120 m²/day.

- The bedrock aquifer consisting of interbedded sedimentary rock layers of dual porosity. The fracture network is composed of variable density and size of fractures resulting in variable transmissivity. The formation T-value of this system was averaged to be 450 m²/day.
- The aquifer system is described as a leaky because no aquitard was found from geologic data that separates the two aquifers. This is further confirmed by the presence of an almost equal hydraulic head in both aquifers and that the water levels follow the topography.

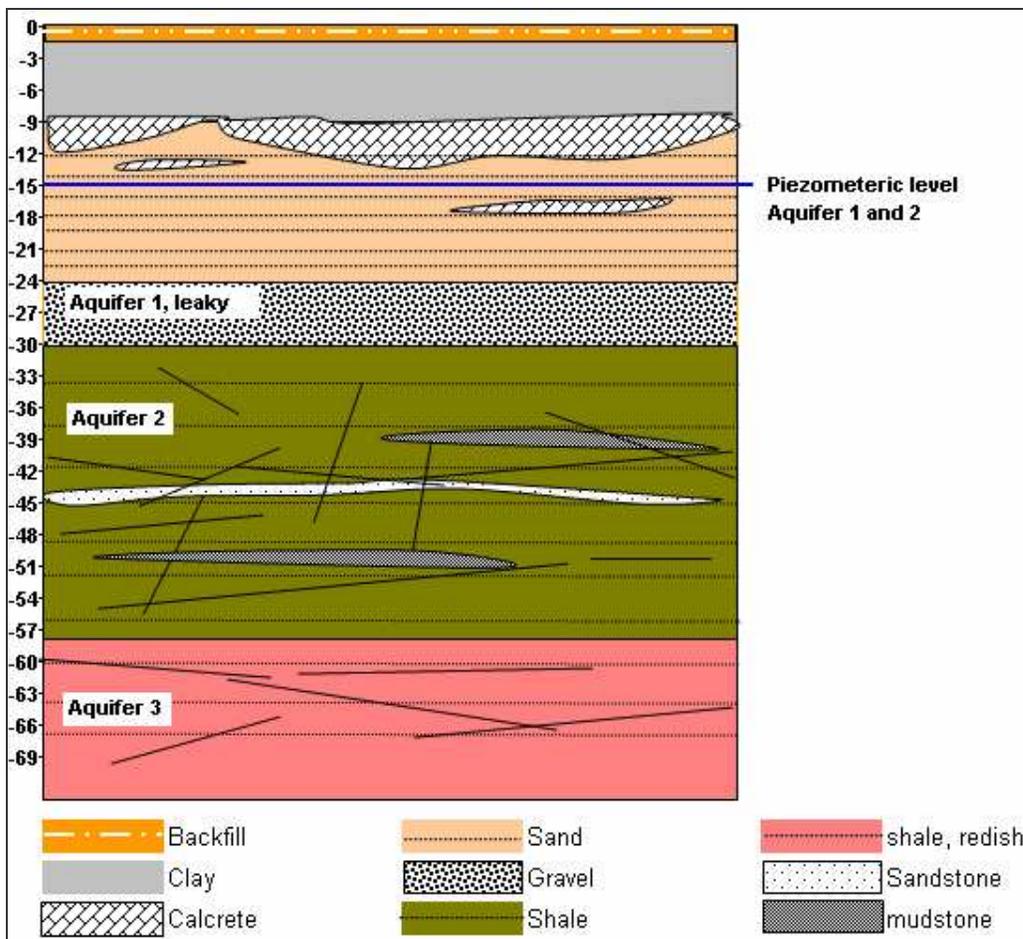


Figure 5-69: Geological Conceptual model of Test Site 1 (Usher, *et al.*, 2007; Gebrekristos, 2007)

5.3.3.3 Contaminant Fate and Transport

5.3.3.3.1 Sample Collection

Soil and water samples were collected at various stages of the field investigation using different methods.

The first soil samples were collected during the reconnaissance survey of the site, by hand auger. The aim was to roughly locate possible DNAPL source zones in the upper portion of the soil profile. Following this, deeper ($\pm 2 - 3.5$ meters below surface) test pits were dug with a back-actor, at the electroplating and gasworks areas. During percussion, auger, and core drilling, soil and rock samples were collected at various depths (up to 60 meters below surface) and geologic units.

The water samples were taken over a three year period at varying depths from observation boreholes and piezometers. Sampling was aimed at detecting the concentration of possible dissolved DNAPL contaminants and delineating the resulting plume.

Samples were collected in suitable glass vials and the containers (provided by the laboratories) and filled completely, with no headspace. During many of the sample runs, three sets of water samples were collected: one for organic analyses, the second for inorganic analysis, and the third for microbial and/or toxicity testing.

Samples were taken several days/weeks after drilling from purged boreholes with depth specific bailers. Results from various sample techniques, were compared. The analysis results did not conclusively prove that concentrations varied between samples taken, before, during and after purging. This could be as a result of the low concentrations of the contaminants, or borehole effect, e.g. volatilisation.

Generally, samples were taken from both the unconsolidated and consolidated portions of the aquifer system. Boreholes and piezometers were constructed to separate the two systems. Sampling depths were selected depending on the water strikes, anomalous EC-values, geochemical and geophysical borehole profiles.

5.3.3.3.2 Sample analysis results

Evidence of the presence and distribution of DNAPLs can be obtained by careful observation and field testing during drilling or collection of soil and rock samples.

DNAPL presence can be determined directly by visual or olfactory examination of soil and groundwater samples rather than indirectly by more costly chemical analyses. In certain circumstances, DNAPL in soil or rock is obvious. Abundant dark-coloured DNAPL at high residual saturation or in layers and pools is usually readily visible in soil cores (Pankow and Cherry, 1996). This is often true for coal tar or creosote when released in large quantities. It is less common to visually identify DNAPLs such as chlorinated solvents, because of the nature of the liquid and the variability in source zones. The integrity of the sample, (e.g. core samples from hollow stem technique) will also influence visual identification of possible DNAPL presence. Visual identification of DNAPLs can be enhanced by using methods such as ultraviolet (UV) fluorescence and soil-water shake tests (with or without hydrophobic dye such as Sudan IV. Many of the aromatic and polycyclic aromatic hydrocarbons (PAHs), and unsaturated aliphatic hydrocarbons (e.g. TCE and PCE) fluoresce (Pankow and Cherry, 1996).

Organic chemical analyses of samples were done using USEPA protocols, and employing gas chromatography-mass spectrometry methods.

For the reconnaissance survey, the analysis was aimed at obtaining quick and qualitative results, so that potential source DNAPL areas would be identified for further study. The samples were collected from the top soil, and considerable amounts of VOCs were expected to volatilise naturally. However, 19 of the 25 soil samples, fluoresced. Although this was not a quantitative measure of DNAPL concentration, the exercise suggested that organic contaminants were present in the subsurface, and possibly deeper in the groundwater.

Based on the screening of soil samples with UV fluorescence, selected samples were sent for laboratory analysis. The chemical analysis results obtained from the laboratory is provided in Appendix C2. (Tar pitch, an integral part of the tar sample, is not considered in this analysis.)

From these results, it can be concluded that most of the contaminants found in the shallow soil zone are from a coal tar or creosote origin. This is confirmed by the historical land use and activities at Test Site 1. The informal waste site at the

electroplating was used to dispose of empty drums and containers of used oils, solvents and creosote. At the gasworks, coal tar (produced as a waste product from coal gasification) was spilled adjacent to the plant and south-east of the gas plant, the area was used for treatment of wood railway sleepers with creosote. The contaminants found in the soil samples are similar to the components found in the coal tar sample from the gas plant sump.

During the drilling of the observation boreholes and piezometers, several soil samples were collected for UV testing and chemical analysis. The results of the samples that tested positive for the contaminants analysed, are presented in Appendix D2. The samples analysed from the deeper portions of the aquifer below the water table (20 m or more below surface), tested below detection limits for the contaminants analysed. It was also noted that the contaminants found in the shallow subsurface (from the test pits) were different from the contaminants in the deeper subsurface, and in much lower concentrations. No chlorinated solvents were detected. This suggests that most of the contamination from the coal tar and creosote sources is attenuated strongly by the thick clay layer above the water table. Some of the more mobile contaminants, e.g. toluene did however migrate to deeper layers.

The chemical analyses results from the hydrocensus water samples were used to classify the regional or background hydrochemical environment. There are two patterns of chloride concentration. Most of the boreholes have concentration values of between 90 – 163 mg/L, while others range from 22 - 25 mg/L. These variations are probably due to a difference in recharge sources, which may imply two different aquifer systems. Boreholes B1 and B4 have lower Cl^- and NO_3^- values compared to the others. As a result, they fall slightly distant from the other boreholes in the Piper diagram (Figure 5-70).

Table 5-18: Inorganic water quality of the hydrocensus boreholes.

| SiteName | B1 | B4 | B5 | B6 | B8 | B9 | B10 | B11 | B12 |
|----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| pH | 7.70 | 7.87 | 7.68 | 7.43 | 7.78 | 7.80 | 7.23 | 7.24 | 7.77 |
| EC mS/m | 50.30 | 37.40 | 114.00 | 134.00 | 113.00 | 125.00 | 152.00 | 137.00 | 136.00 |
| Ca mg/l | 38.58 | 25.18 | 100.18 | 113.14 | 101.09 | 117.38 | 149.67 | 135.59 | 131.73 |
| Mg mg/l | 21.09 | 14.18 | 70.08 | 77.19 | 69.69 | 74.77 | 68.98 | 68.33 | 64.00 |
| Na mg/l | 38.13 | 32.42 | 36.29 | 60.16 | 31.31 | 32.99 | 92.48 | 65.73 | 70.38 |
| K mg/l | 1.78 | 5.26 | 0.65 | 1.44 | 4.37 | 0.95 | 1.81 | 1.46 | 0.87 |
| MALK mg/l | 209.00 | 140.00 | 395.00 | 379.00 | 370.00 | 304.00 | 366.00 | 326.00 | 325.00 |
| Cl mg/l | 22.00 | 25.00 | 110.00 | 163.00 | 124.00 | 140.00 | 150.00 | 102.00 | 90.00 |
| SO4 mg/l | 18.10 | 15.15 | 45.90 | 116.00 | 79.00 | 150.00 | 260.00 | 265.00 | 295.00 |
| N NO3mg/l | 0.09 | 0.41 | 11.12 | 10.14 | 0.02 | 12.46 | 15.84 | 22.10 | 17.70 |
| F mg/l | 0.50 | 0.03 | 0.27 | 0.08 | 0.11 | 0.06 | 0.36 | 0.22 | 0.24 |
| Br mg/l | | | 0.28 | 0.52 | 0.37 | 0.67 | 0.68 | 0.45 | 0.44 |
| N Ammonia mg/l | 0.14 | 0.15 | 0.14 | 0.15 | 2.20 | 0.28 | 0.66 | 0.20 | 0.30 |

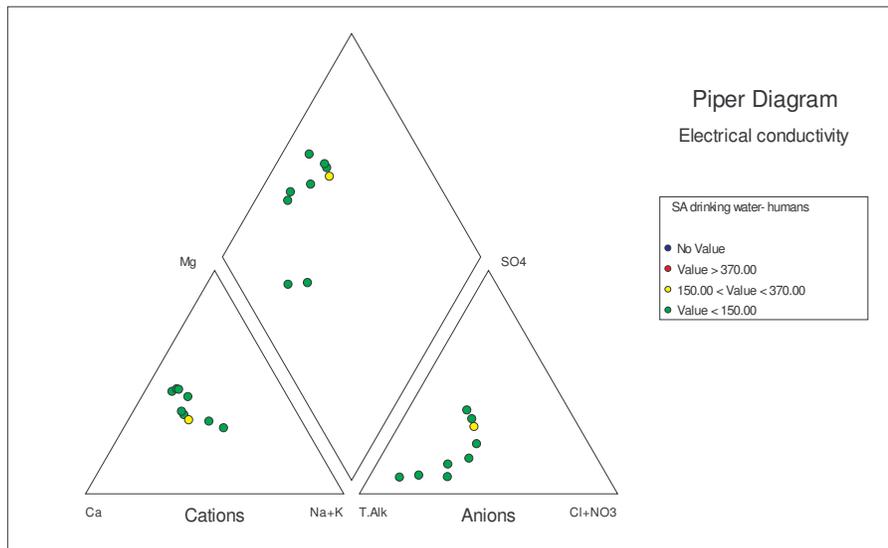


Figure 5-70: Piper diagram of hydrocensus water samples.

If the results are compared to that of the water samples at the Test site, it can be seen that with the exception of B1 and B4 the hydrocensus boreholes are of similar hydrochemical signature than most of the boreholes on the test site, and can be classified into one of the three groupings identified, namely from the shallow, deep or mixed aquifer systems.

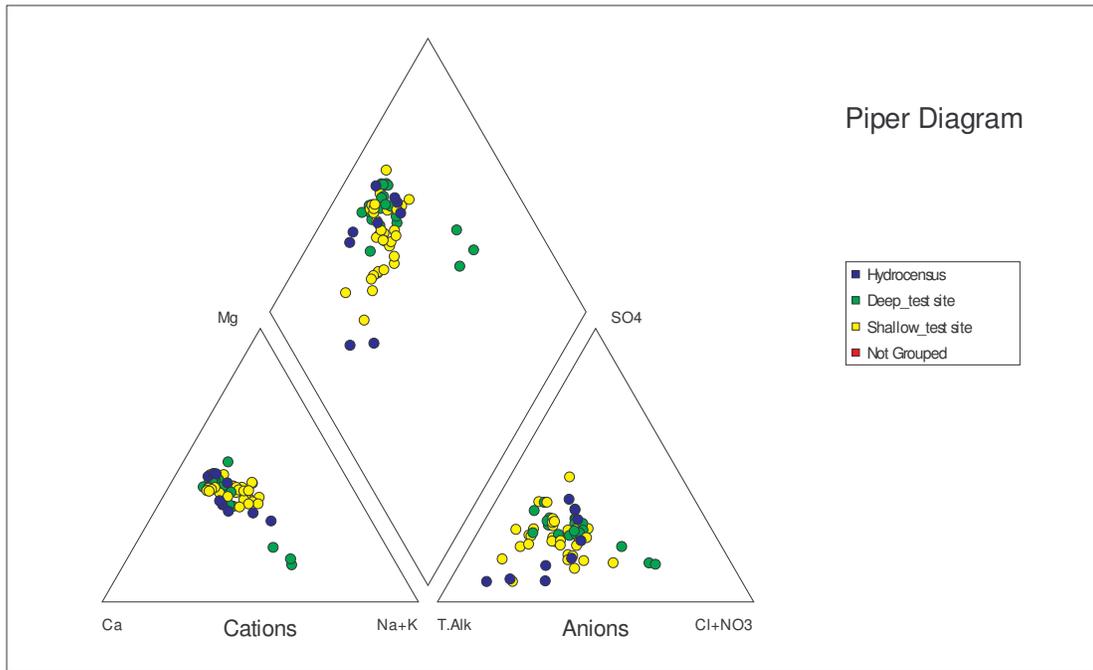


Figure 5-71: Piper diagram of hydrocensus water samples compared to the test site water samples. The inorganic content of the site boreholes is provided in Appendix C3. A Durov diagram of the table is also given in Figure 5-72. They all have similar hydrochemical compositions. The groundwater can generally be classified as a Ca-bicarbonate type. From Durov and Stiff diagrams it can be seen that there is an enrichment of Mg towards the east of the site, in the vicinity of the gasworks (GB boreholes). The relatively high alkalinity is likely due to the calcrete soil in the unconsolidated aquifer and the calcite cementation in the pores and in certain infilled fractures. The relative low chloride content could be attributed to the recent age of the water and may indicate that it was recently recharged. The groundwater is also relatively depleted in Na^+ and K^+ and enriched in Mg^{2+} content.

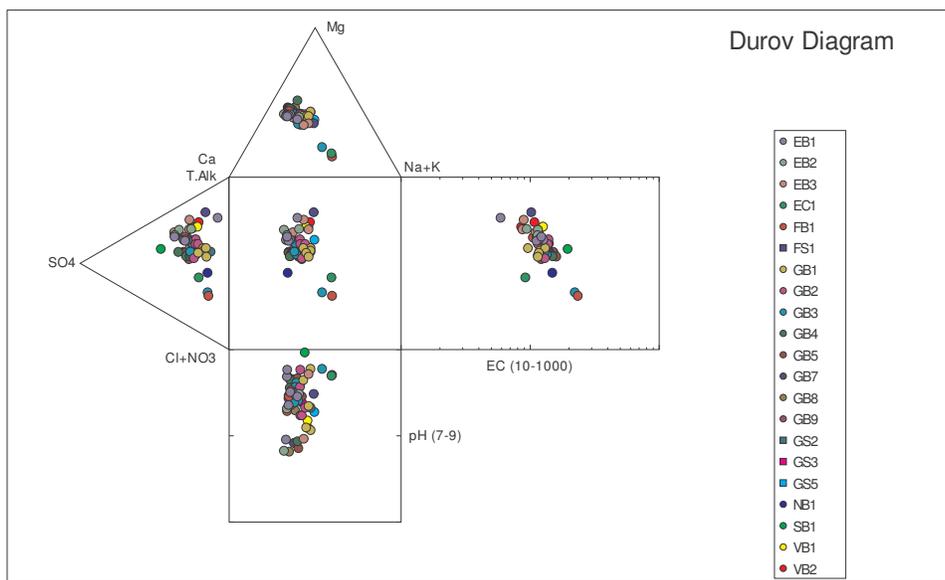


Figure 5-72: Durov diagram of the Test site boreholes

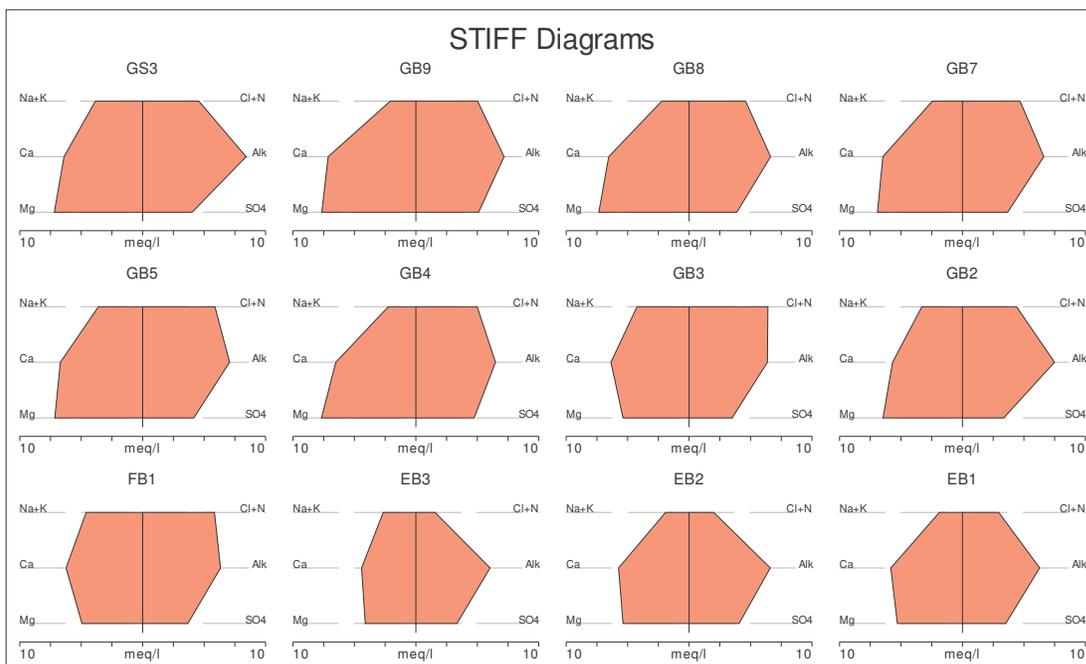


Figure 5-73: Stiff diagrams of the Test site boreholes.

There is some differentiation between water type of the boreholes drilled in only the shallower unconsolidated aquifer system (GS5, GS2, FS1, & GB1), and that of the deeper

fractured rock system. In borehole EB1 which is constructed to intercept both aquifer systems, the water quality varies at different depths (Figure 5-74 and Figure 5-75). The EC value at shallow depths (EB1-s) is for example lower than at deeper depths (EB1-d). The water quality changes significantly below the fracture, indicating that water of poorer quality flows through the fracture. However, there is only slight differences to the water type of the deeper boreholes, which supports the assumption of a “leaky aquifer” system with no aquitard dividing the two systems.

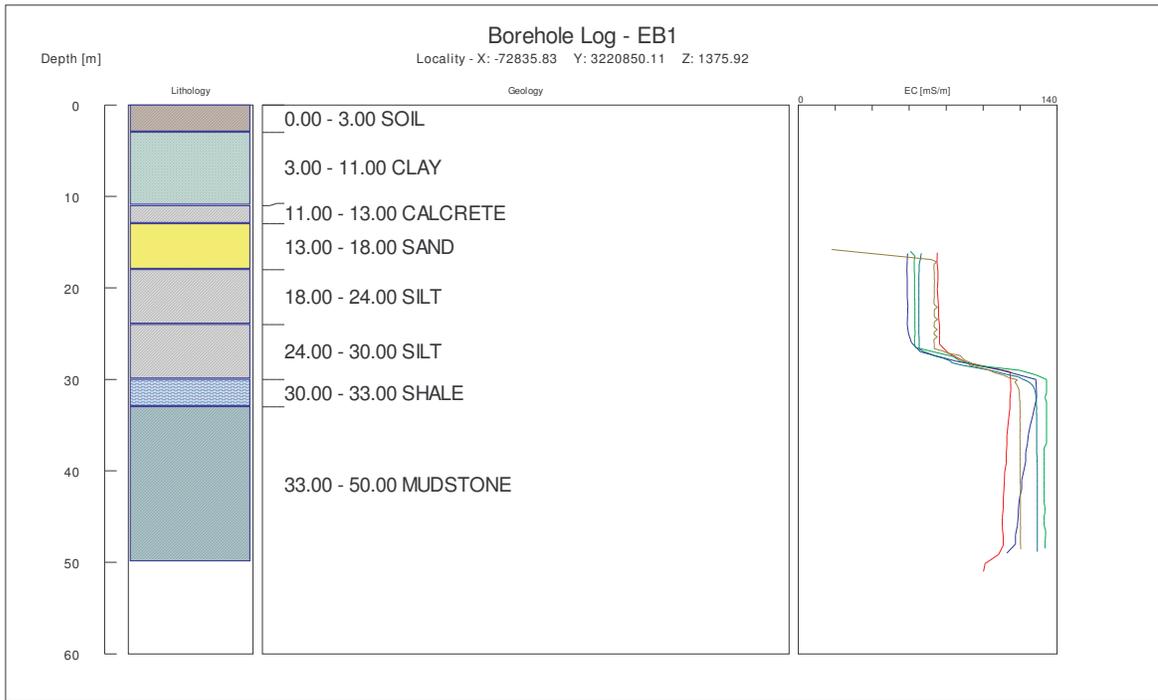


Figure 5-74: EC profile for Borehole EB1.

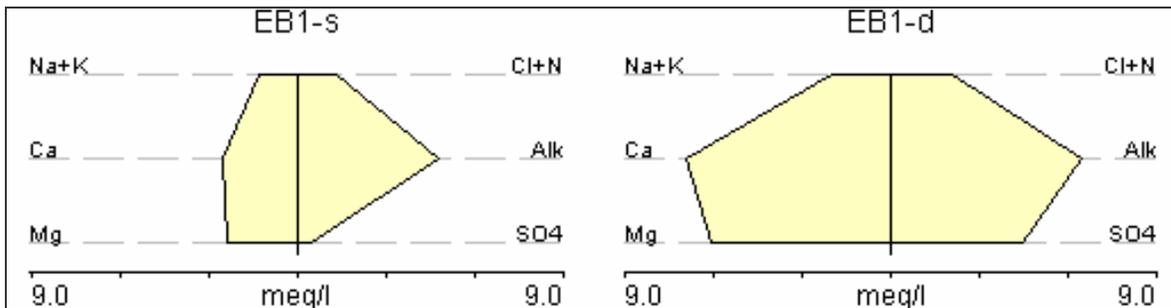


Figure 5-75: Stiff diagram comparison of EB1 at shallow and deep water sample depths.

Boreholes SB1, NB1 and EC1, do not show the similar classification as the rest of the boreholes. These boreholes are likely connected to different recharge areas or aquifer systems.

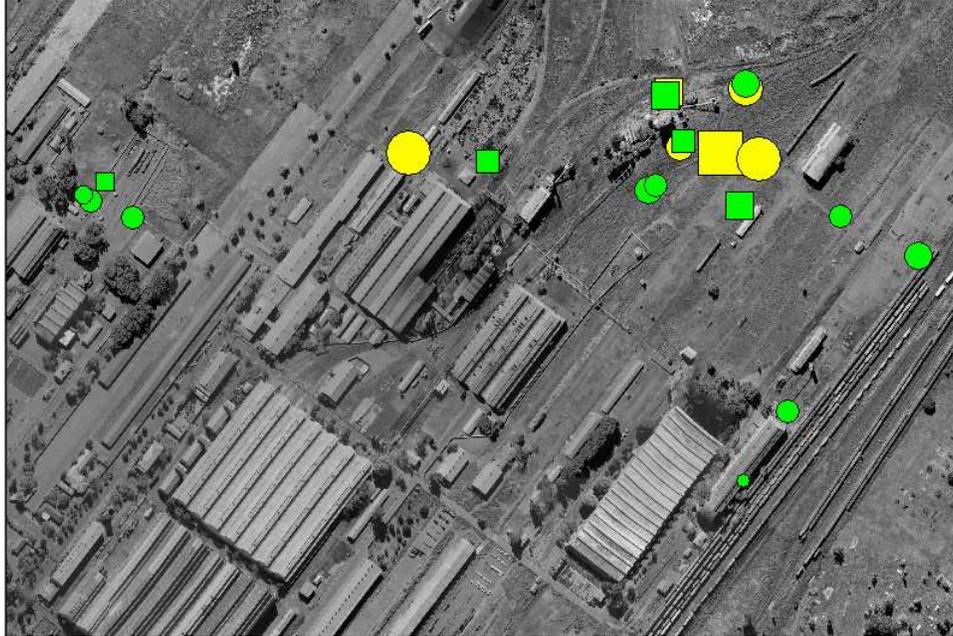


Figure 5-76: Relative EC (mS/m) distribution of boreholes on Test site.

The boreholes the gasworks, have higher EC values than the electroplating boreholes. Generally the EC increases towards the east (Figure 5-76) and with depth (Figure 5-74). However, they are no health threats from the inorganic quality as most of the boreholes, EC values are below the maximum recommended drinking water standards (150 mSm). Other inorganic parameters which were evaluated to investigate lines of evidence for natural attenuation and degradation processes are: Nitrate, sulphate, and selected metals. This will be discussed in more detail in Section 5.3.4.

From the organic chemistry results of the hydrocensus borehole data, the contaminants found consisted mostly of the BTEX group of components. These contaminants are associated with petroleum product spillage such as petrol. The source of these contaminants can be explained due to a number of petrol stations, automotive workshops, and transport companies in the area.

Concentration of 13 $\mu\text{g/L}$ trichloroethene was measured in borehole B5. Trichloroethene

is a DNAPL and has a maximum permissible concentration limit of 5 µg/L in the US (Pankow and Cherry 1996). The source of the contaminant is potentially from an automotive workshop located close by and unlikely from the Test site. Table 5-19 lists the concentration of dissolved phase of NAPL contaminants that was above detection limits, attained from the lab analysis for the hydrocensus boreholes.

Table 5-19: Dissolved phase of NAPL contaminants in the hydrocensus boreholes (µg/L)

| Site Name | B1 | B10 | B11 | B12 | B4 | B5 | B6 | B8 | B9 |
|------------------------|----|-----|-----|-----|----|-----|-----|-----|----|
| 1,2,4 Trimethylbenzene | | | | | | 0.3 | 0.3 | 0.3 | |
| 1,3,5 Trimethylbenzene | | | | | | | | 0.1 | |
| Bromoform | | | | | 12 | | | | |
| Ethylbenzene | | | | | | 0.4 | | | |
| m-Xylene | | | | | | 0.5 | | | |
| o+p Xylenes | | | | | | 0.6 | | | |
| Tert Butylbenzene | | | | | | 0.3 | | | |
| Toluene | | | | | | 1.3 | | | |
| Trichloroethene | | | | | | 13 | | | |

Appendix D4 lists the organic contaminants detected in the groundwater at Test site 1. A variety of organic contaminants was detected in the groundwater at the site. The concentrations of most of the contaminants were very low, and seldom exceeded values of 5 µg/l. Cognizance should however be taken of the fact that available water quality standard limits (e.g. USEPA and Dutch Standards) are often very low and in ranges of 1 to 5 µg/l, and the water quality should be evaluated in terms of health and environmental risk to users and receptors.

The type of organic contaminants present in the groundwater system at the site consists of a number of PAHs associated with the coal tar and creosote contaminants, and halogenated hydrocarbons associated with solvent use. Three types of commonly used pesticides were detected, i.e. Atrazine, Simazine, and Terbutylazine. A number of miscellaneous organic components were also found, which included: Biphenyl, TPHs, 4-chloro-3-methylphenol, 3/3,5-Dimethylphenol, 4-thylphen, and Pentachlorophenol.

The contaminants of particular interest for this thesis are the ones associated with DNAPL contamination i.e. the PAHs and chlorinated solvents.

The concentrations of PAHs detected in the groundwater were confined to the shallow auger drilled piezometers (FS1, GS1, GS2, GS3 and GS5). These concentrations (Figure 5-77) are at least an order or two lower than the ones measured in the soil samples including the clay and sand layers. This confirms the conceptualization of the coal tar and creosote contaminants being attenuated in the upper unconsolidated layers and only small amounts leaching to the shallow groundwater system.

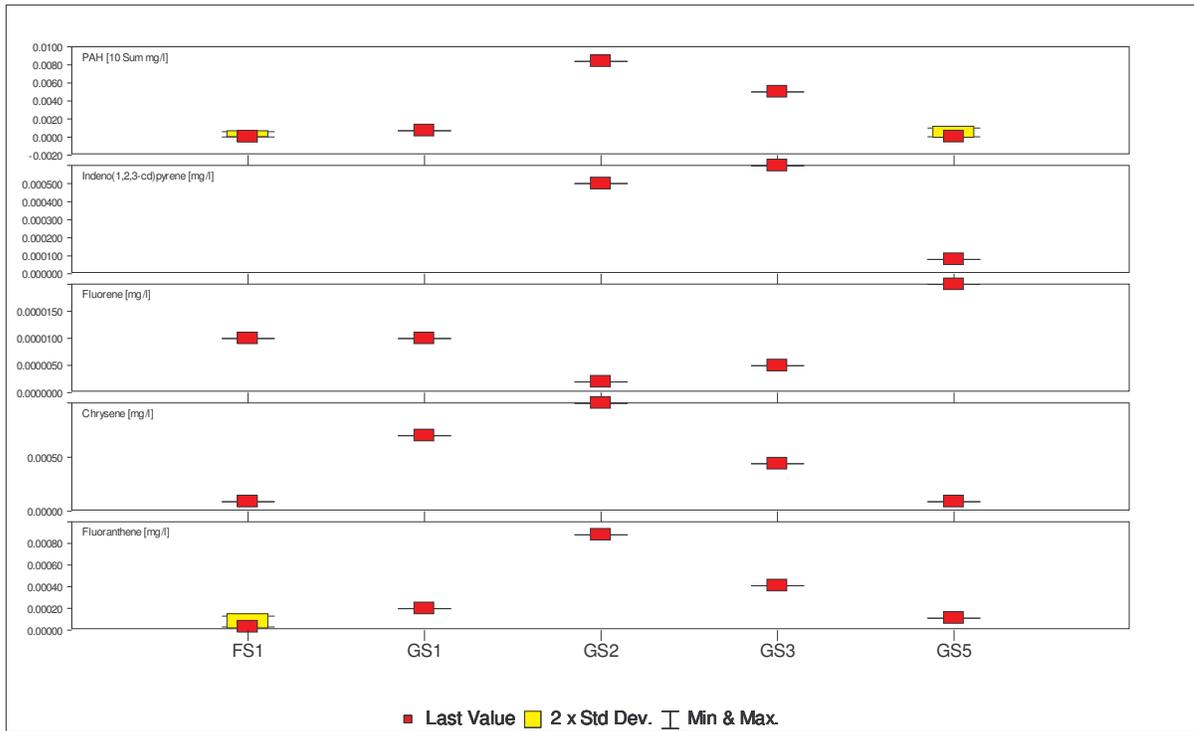


Figure 5-77: Selected PAHs components and PAH total concentrations measured in the piezometers FS1, GS1, GS2, GS3 and GS5.

The solvents found at the site consist mostly of trichloroethene (TCE), chloroform (CF) and to smaller extent tetrachloroethene (PCE). As previously discussed, the concentration of chlorinated hydrocarbons detected in the groundwater is very low. From data collected on volume and type of solvent use, storage and disposal at the site; much higher concentrations were expected. This can be the result of one or more of the following scenarios:

1. Biotic and abiotic degradation can result in the lowering of concentrations in the down-gradient direction within a contaminant plume (Kueper, *et al.*, 2003).

Evidence of degradation was found at the site (e.g. daughter products and microbial populations).

2. In very hot, dry climates, coupled with a deep unsaturated zone, it is possible that a large portion of the contaminants can be volatilized before the contaminants reach the groundwater zone (Pankow and Cherry, 1996, and Fetter, 1999).
3. Matrix diffusion could have caused all NAPL fluid to dissolve out of the fractures into the formation matrix (Parker, 2003). Thus the bulk of the contaminant mass is likely to reside within the matrix and will slowly back-diffuse into the fracture system.
4. Various factors influence the magnitude of contaminant concentrations obtained from observation boreholes samples relative to the actual concentrations in the aquifer (Kueper, *et al.*, 2003). These include placement of boreholes relative to plume centre line, construction of boreholes, and heterogeneity of the aquifer system. If the borehole (and/or screened intervals) were placed offset from the plume centre line, sampled concentrations would be lower than in the aquifer. This is because contaminant concentrations decrease in the transverse direction (both horizontally and vertically) away from the plume centre line.
5. DNAPL source zone characterization in fractured rock aquifer systems is notoriously complicated (Mercer and Cohen, 1993, and Pankow and Cherry, 1996). It is possible due to the size and activities at Test site 1, coupled with limited funding and available technology that the site assessments methods applied were inadequate to characterize the DNAPL source zones.

Table 5-20: Boreholes that tested positive for chlorinated solvents.

| TCE | CF | PCE |
|-------------------|-----------------|------------|
| EB2,3 | EB1,2,3 | EB2 |
| EC1 | FB1 | EC1 |
| FB1 | FS1 | NB1 |
| FS1 | GB1,3,4,5,7,8,9 | |
| GB1,2,3,4,5,7,8,9 | GS2,3,5 | |
| GC1 | NB1 | |
| GS2,3,5 | SB1 | |
| NB1 | | |
| SB1 | | |

The maximum concentration limit (MCL) for chloroform is 0.08 mg/L and for TCE 0.005 mg/L (www.epa.gov), and none of the detected concentrations exceeds the MCL. Even though both chloroform and TCE are below the MCL, it is worth observing their concentrations in the various boreholes, as shown in Figure 5-78 and Figure 5-79. Concentrations are slightly higher towards the gasworks area.

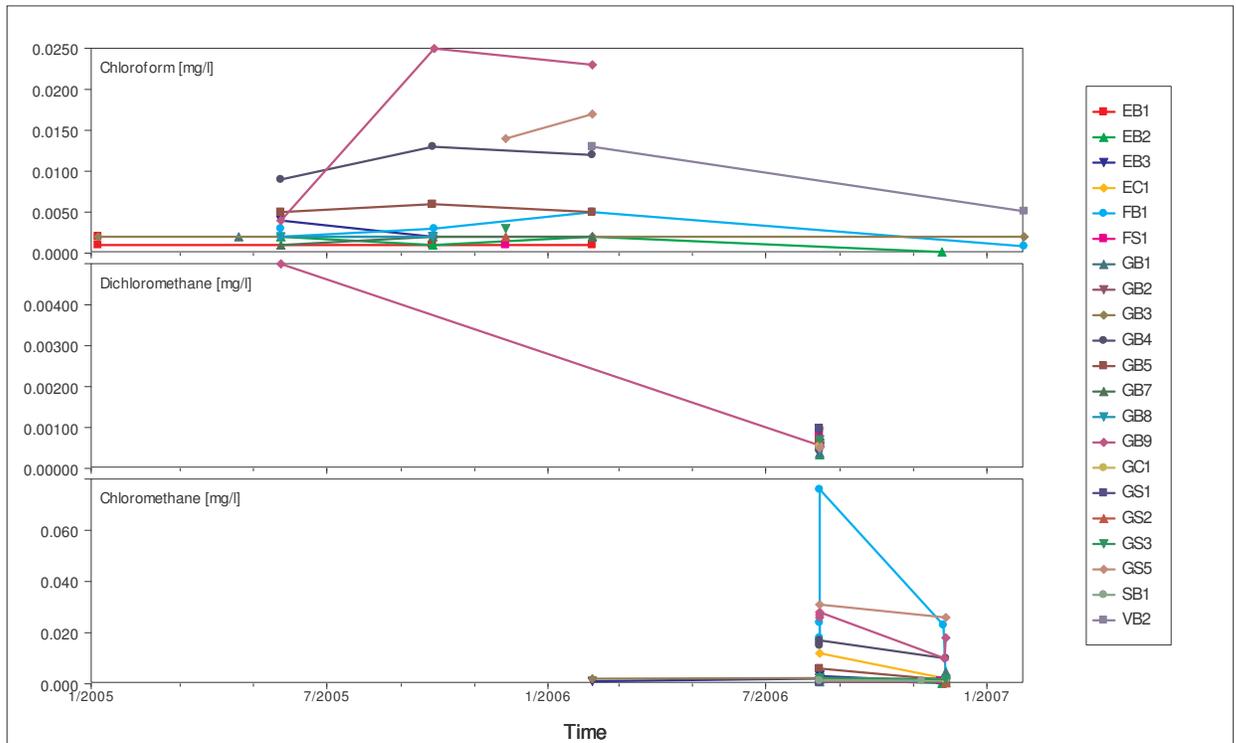


Figure 5-78: Concentrations of Chloroform and degradation products.

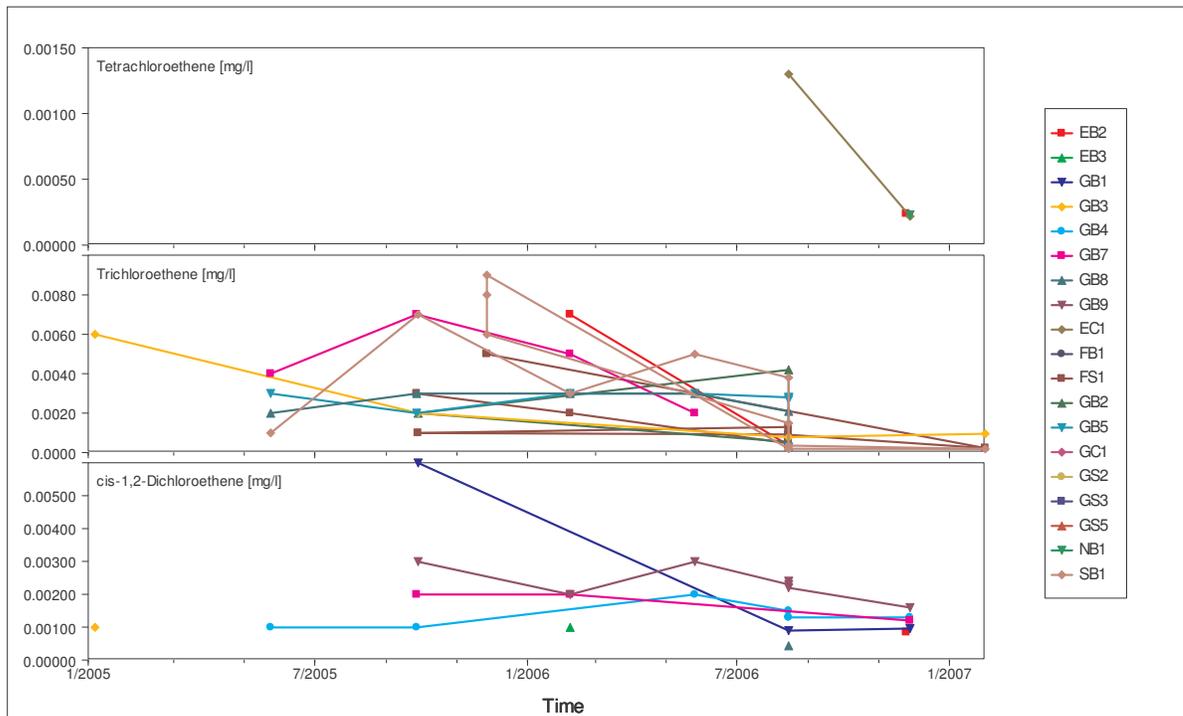


Figure 5-79: Concentrations of PCE, TCE and cis-DCE.

Even though the concentrations of the contaminants are very low, evidence of degradation pathways and associated daughter products can be seen from the above figures. The daughter products; cis-1,2-dichloroethene, chloromethane, and dichloromethane were all detected in boreholes with TCE, PCE and chloroform. Samples were taken and analysed for methane, ethene and ethane, however only in EB2 some low concentrations of methane were detected. (Also see Section 5.3.4).

5.3.3.3 Contaminant conceptualisation

As discussed in the previous section, dark coloured NAPL were visible in the unconsolidated part of the aquifer. This is an indication that the NAPL phase had migrated through the layers, but that the contamination source is either depleted or removed so that the NAPL phase does not have enough capillary pressure to form NAPL free phase.

Free NAPL phase was not encountered on any of the drilled boreholes. The migration of NAPL phase in the conceptual model is provided in Figure 5-80. It is believed that the

DNAPL movement through the clay layer is mainly via fractures, as the clay was found to be almost impermeable unless fractured. Mineralogy analysis of the solid samples confirmed the presence the expanding clay mineral montmorillonite, and other associated clay minerals (illite and koalinite) in the upper unconsolidated lithologies.

However, if there is any thick deposit of DNAPLs in such a way that the capillary pressure is greater than the entry pressure of the clay, DNAPLs can move downward through the clay matrix. Calcrete, sand and gravel are porous where DNAPLs can move downward easily. Due to their higher density, the DNAPLs are expected to move further down until the impermeable layer is encountered. Once they reach the fracture zone, this will determine the flow rate and direction.

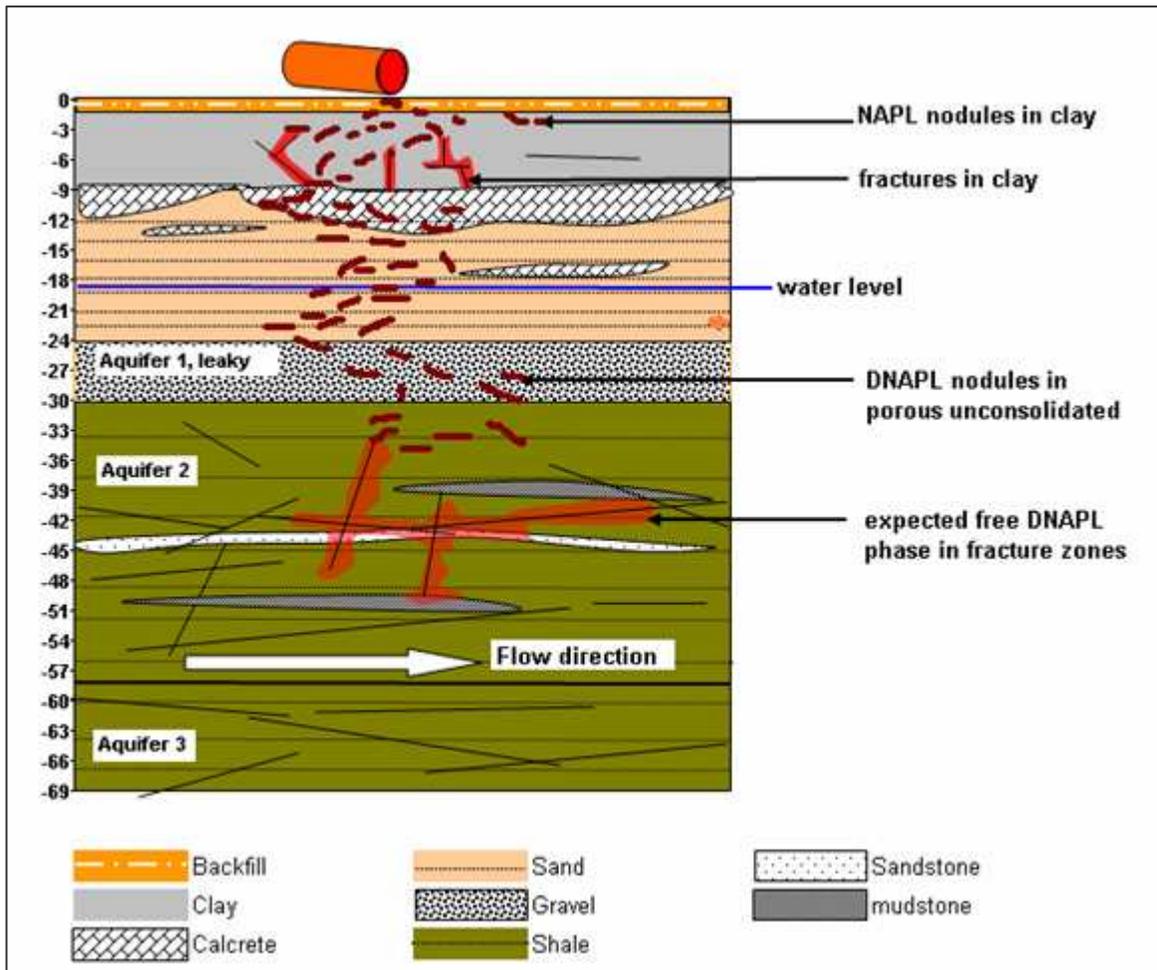


Figure 5-80: NAPL phase movement in the developed conceptual model. (Usher, *et al.*, 2007; Gebrekristos, 2007)

Chemical analysis of water samples indicates that the dissolved plume of NAPLs is present at various concentrations and locations. However, the concentrations are very low. The presence of the vapour plume in the vadose zone was also confirmed by soil samples and soil surveys.

By drawing various cross sections of different parameters across the site, an understanding of the dissolved phase interactions can be obtained. The TCE profiles show an increase from west to east across the site. This is corroborated by the TOX (total halogen components) increase across the site. It is interesting to note that the EC variation provides a very similar pattern.

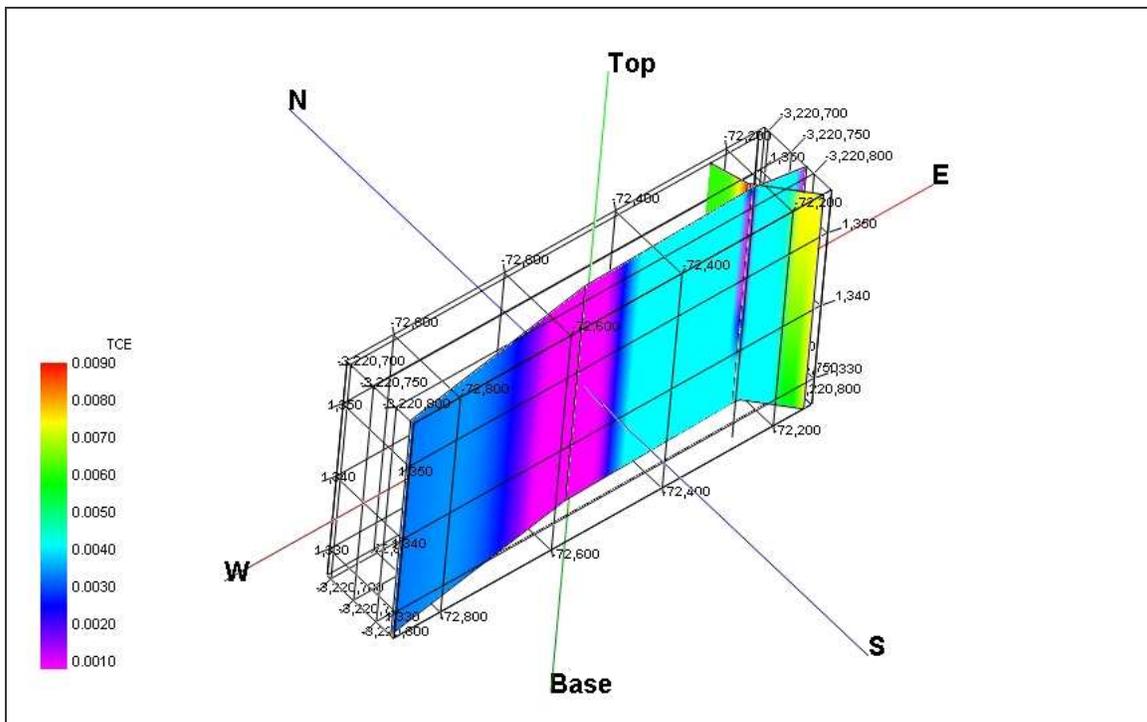


Figure 5-81:TCE distribution across Test Site 1

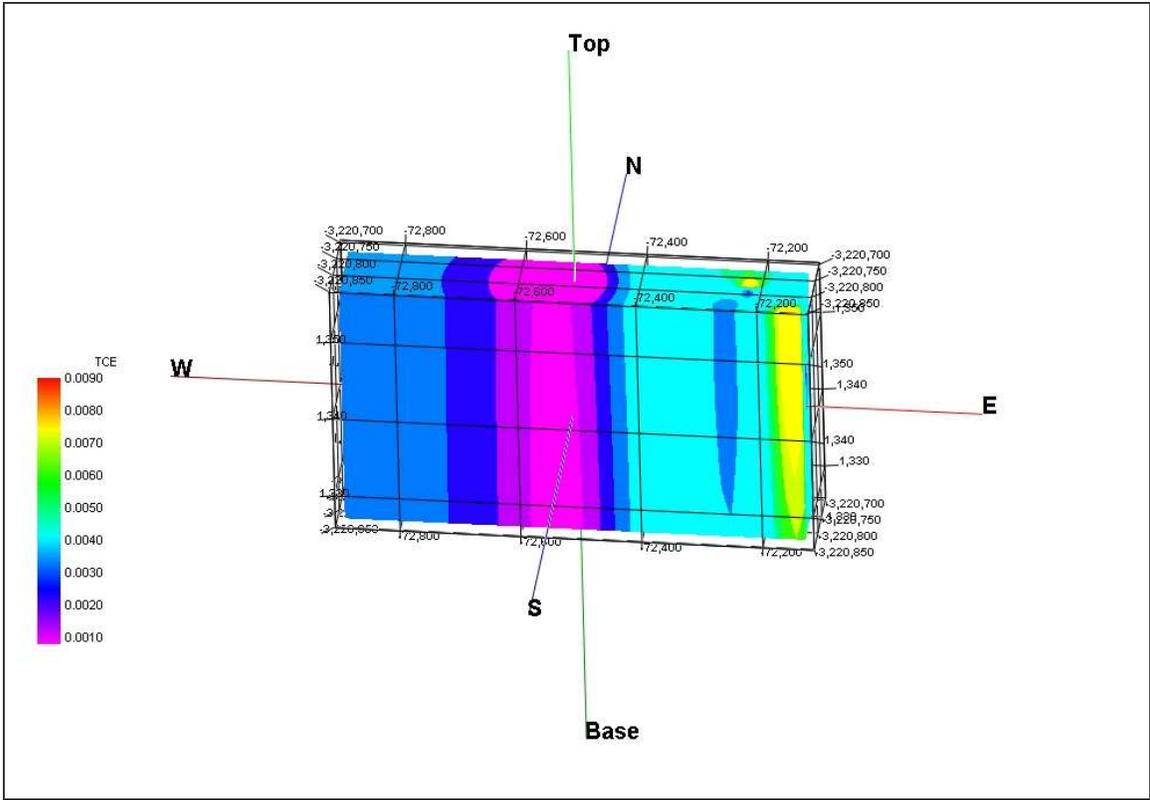


Figure 5-82: TCE distribution across Test Site 1

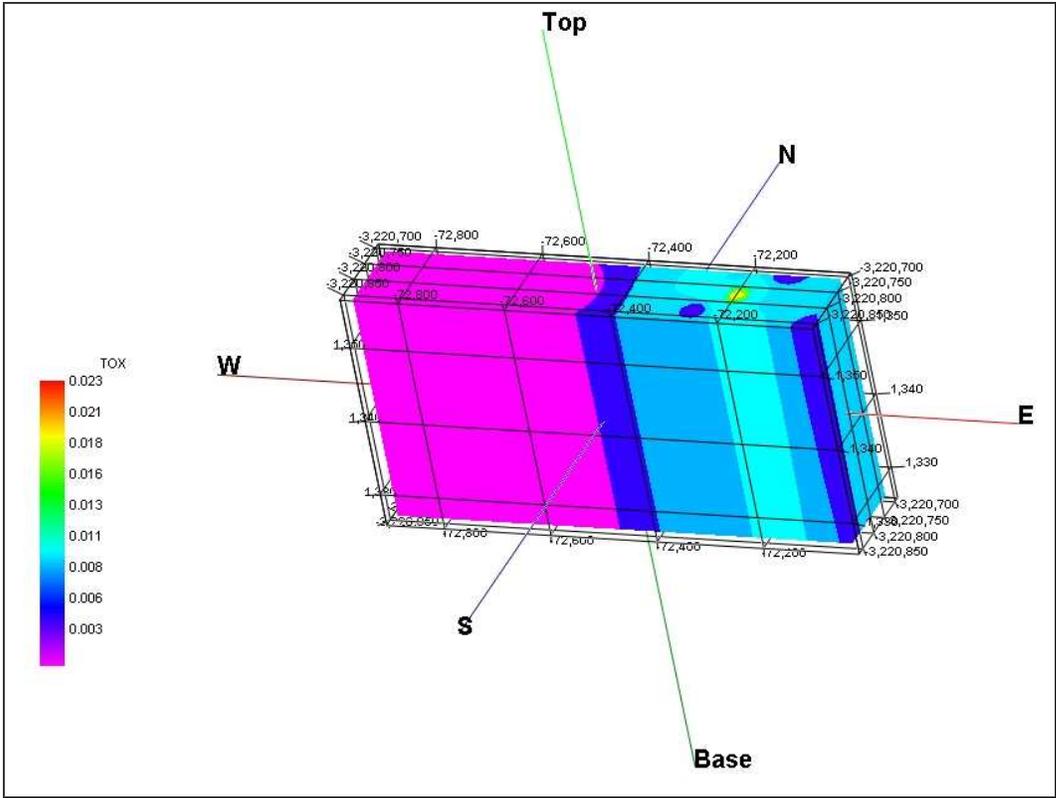


Figure 5-83: TOX (total halogen components) distribution across Test Site 1

A hypothetical DNAPL plume migration in the vadose zone and saturated zone is given in Figure 5-84.

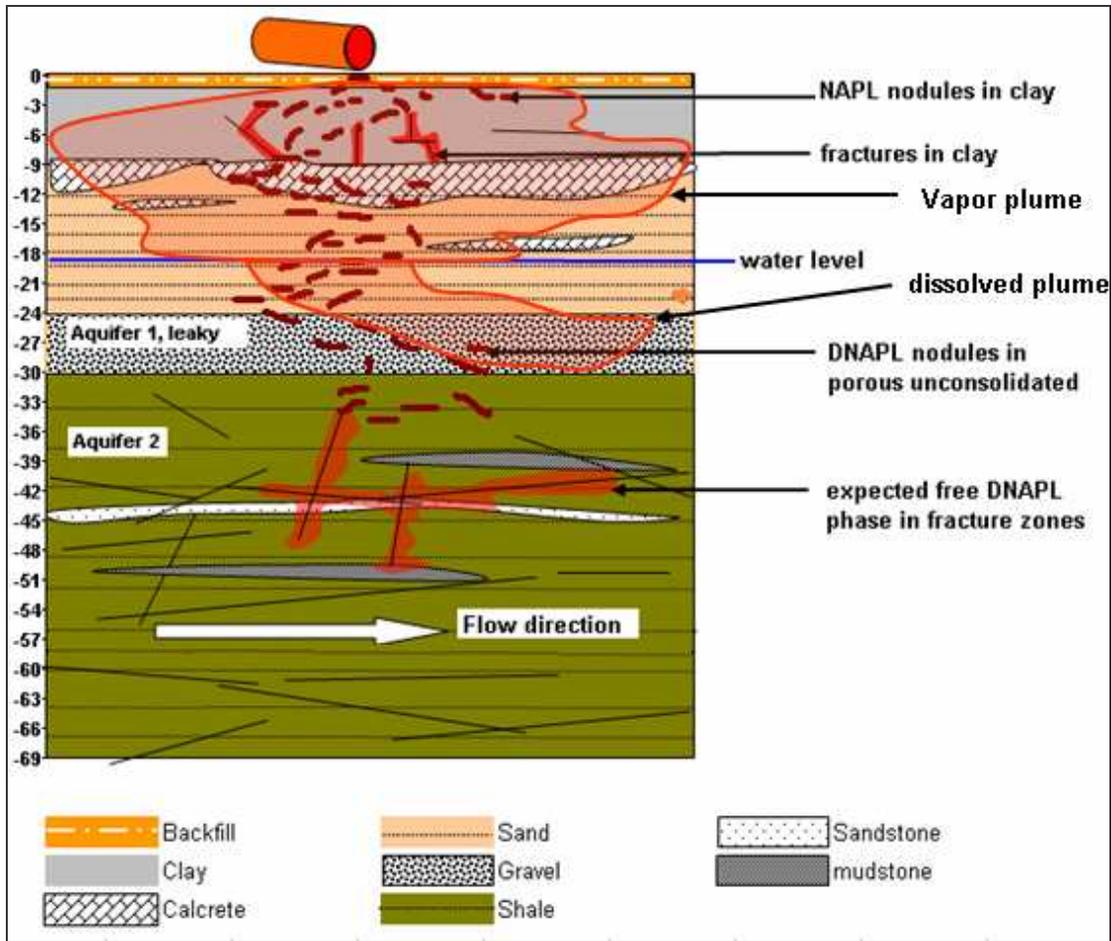


Figure 5-84: Hypothetical vapour and dissolved DNAPL plumes. (Usher, *et al.*, 2007; Gebrekristos, 2007)

Although evidence of “pooled” DNAPL phase was not found at the site, residual DNAPL, dissolved phase, sorbed phase and vapour phase contamination were identified. It is also likely that the bulk of the contaminant mass resides in the porous matrix of the bedrock formations.

The lithology is heterogeneous, composed of thick unconsolidated sediments, and underlain by a porous fractured aquifer system. The complexity of the site geology associated with the various components of DNAPL sources and compositions makes it challenging for any remedial approach.

The removal of all NAPL sources and DNAPL components in the subsurface so that the site would restore to its initial uncontaminated state is impractical. The other alternative

is the removal of sufficient DNAPL mass from the source zones to subject the length of the resulting aqueous phase plume downstream of the source zone to effective natural attenuation processes that stabilise and subsequently reduce the plume.

However, it is not easy to estimate the amount of DNAPL source mass to be removed for a specific reduction in dissolved DNAPL in the groundwater. No information was available to estimate the total mass of contaminants in the subsurface. It has been established that there is no a linear relationship between mass removal and end-point groundwater concentrations (Kueper *et al.*, 2003).

The partial removal of DNAPL sources may not bring about a significant short-term reduction in groundwater contaminant concentrations, but it is likely to reduce the duration over which the plume persists. If the removal of DNAPL source zones is not possible, source zone containment is an achievable remediation goal. With this technique, source zones should be separated properly from the aquifer system by physical barriers, and groundwater can be maintained by the pump-and-treat technique.

The contaminants of concern at the site are found at such low concentrations, that monitored natural attenuation (MNA) is the recommended remedial procedure for the site. Strong evidence exist (Sections 5.3.4) that NA is already occurring and reducing contaminant concentrations on site. By monitoring and relying on the naturally occurring processes to degrade and retard contaminants, plumes may shrink. However, an appropriate monitoring well network and several years of groundwater quality data to establish trends in the concentration time will be needed (See section 6.4).

5.3.4 Determination of retardation and attenuation processes

In Appendix A a summary of the retardation and attenuation processes affecting contaminant transport was given. Determination of these processes is also what is described as “lines of evidence” when monitored natural attenuation (MNA) is considered as a remedy at a site. At Test Site 1 these retardation and attenuation processes or “lines of evidence” were investigated and documented to determine whether MNA will be a viable option at the site as recommended remedy.

The USEPA (1999) prescribe a three-tiered approach to collecting evidence, where successively more detailed information is collected as necessary, to provide a specified level of confidence on the estimates of attenuation rates and remediation timeframe. In South Africa no such guidelines exists, so these were used to assess the processes at Test Site 1.

1. ***Historical groundwater and/or soil chemistry data*** that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. In the case of a groundwater plume, the decreasing concentrations should not be solely the result of plume migration.
2. ***Hydrogeological and geochemical data*** that may be used to demonstrate indirectly the *types of NA processes* active at the site and the rate at which such processes will reduce contaminant concentrations to required levels. For example, characterisation data may be used to quantify the rates of contaminant sorption, dilution or volatilisation or to demonstrate and quantify the rates of biological degradation processes occurring at the site.
3. ***Data from field or microbial studies*** (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of a particular NA process at the site and its ability to degrade the contaminants of concern.

The first line of evidence alone does not prove that contaminants are being degraded. Reduction in contaminant concentration could be the result of non-degradative mechanisms. In order to evaluate remediation by natural attenuation at most sites, the investigator will have to determine whether contaminant mass is being *destroyed*. This is done using either or both, of the second or third lines of evidence. The second line of evidence relies on chemical and physical data to show that contaminant mass is being destroyed and not just being diluted or sorbed to the aquifer matrix. Microcosm studies (third line of evidence) may be necessary to demonstrate physically that natural attenuation is occurring. Microcosm studies may also be used to show that indigenous biota are capable of degrading site contaminants at a particular rate. Although numerical modelling is not considered a line of evidence, it is useful for examining the relative importance of the processes influencing the transport of organic compounds.

Evidence for natural attenuation is often circumstantial, so it is always necessary to seek multiple lines of evidence, particularly where the level of uncertainty is high and the sensitivity of the site is significant.

5.3.4.1 Data collected at Test Site 1

In Section 5.3.3.3 the water quality of Test Site 1 is discussed. The following sections highlight the lines of evidence found on which the recommendation is based to recommend MNA at Test Site 1 as a potential remedy.

5.3.4.2 Evidence of potential PAH retardation and degradation.

In Section 5.3.3.3 it is shown that the contaminants associated with the coal tar and creosote contamination is only found in the upper unconsolidated part of the aquifer system in the soil samples and the shallow piezometers.

Evidence that support the retardation properties and degradation potential of this zone, especially in the clay layer, includes the following:

A few selected soil samples at various depths have been selected to determine the f_{oc} values, in order to calculate the potential of retardation of the clay layer. It is assumed that the clay layer is consistent over the site and located at between 2 to 10 meters below surface. An average value for the organic carbon content (f_{oc}) of 0.17 is calculated for the clay layer. This implies that the retardation of organic contaminants to the clay layer would be high.

Table 5-21: Laboratory determined f_{oc} for selected soil samples.

| SiteName | Depth | F _{OC} |
|----------|-------|-----------------|
| ES1 | 14 | 0.17 |
| FS1 | 2 | 0.26 |
| GS4 | 3.4 | 0.08 |
| GS5 | 18 | 0.09 |

Mineralogy results of selected soil samples showed that the upper clay rich layers were rich in montmorillonite and illite minerals. Both these minerals are known to have high absorption properties.

Table 5-22: Mineralogy results for selected soil samples

| Borehole no. & depth | Quartz | Montm | Illite | Calcite | Albite | Orthoclase | Kaolinite |
|----------------------|--------|--------|--------|---------|--------|------------|-----------|
| GS1-2m | >40% | 2-10% | | | | 2-10% | |
| GB3-4m | >40% | >40% | | | | 2-10% | |
| GS5-6m | >40% | >40% | 2-10% | 2-10% | | 1-2% | |
| GS5-8m | >40% | 10-40% | | 1-2% | | 1-2% | |
| FS1-8m | >40% | 10-40% | 2-10% | | | 2-10% | |
| ES1-9m | >40% | 2-10% | | 10-40% | 2-10% | 2-10% | |
| GB2-10m | >40% | 10-40% | 2-10% | >40% | 1-2% | | |
| ES1-11m | >40% | 10-40% | 2-10% | 10-40% | | 1-2% | |
| GS1-12m | >40% | 2-10% | | 10-40% | | 1-2% | |
| GS5-12m | >40% | 2-10% | | 1-2% | | 2-10% | |
| ES1-13m | >40% | 10-40% | | 10-40% | | 2-10% | |
| EB1-14m | >40% | 10-40% | | | | 2-10% | |
| GS5-15m | >40% | 10-40% | | 2-10% | | 2-10% | |
| EB1-20m | >40% | 10-40% | | | | 2-10% | |
| GB9-25m | >40% | >40% | | | 10-40% | | 1-2% |
| GB7-33m | >40% | 10-40% | 2-10% | | | 2-10% | 10-40% |
| GB7-37m | >40% | 2-10% | 2-10% | | 10-40% | | 2-10% |
| GB9-37m | >40% | 10-40% | 2-10% | | | 2-10% | 10-40% |
| GB3-57m | >40% | 2-10% | 10-40% | 2-10% | | 10-40% | 2-10% |

Dark coloured NAPL was visible on calcrete and clay nodules during excavation of shallow test pits. Enhanced visual techniques such as fluorescence with UV light also confirmed the presence of aromatic hydrocarbons in the oil samples. PAH results from soil analyses were at least an order higher (>0.01 ppm) than that of the water samples (<0.001 ppm). Only shallow boreholes tested positive for PAH contaminants and no PAHs were found in the water or soil of the deeper boreholes.

Unfortunately there was no time series of data for soil samples, and therefore no comparisons could be made whether concentrations were decreasing in the soil. Long-term monitoring of the shallow boreholes should provide this information.

Microbial studies (Usher *et al.*, 2007) on water samples from the site, gave the following results: The clones sequenced A and C gave accurate (99%) BLAST results with particular species. **Clone A** aligned well with a known sequence of *Oxalobacteraceae bacterium*. Species from this genus has been documented to be involved with bioremediation of Polychlorinated biphenyls PCB's. The mature biofilm was found to degrade pentachlorinated PCB congeners, which may be then reductively dechlorinated to trichlorobiphenyls and eventually aerobically metabolized (Macedo *et al.*, 2005).

Clone C gave 99% alignment with the DNA of *Pseudomonas saccharophila*, these bacteria are also known as a possible bioremediation agents and is known to degrade PAH including Pyrene by co-metabolising with various other organism in consortia (Kazunga and Aitken, 2000).

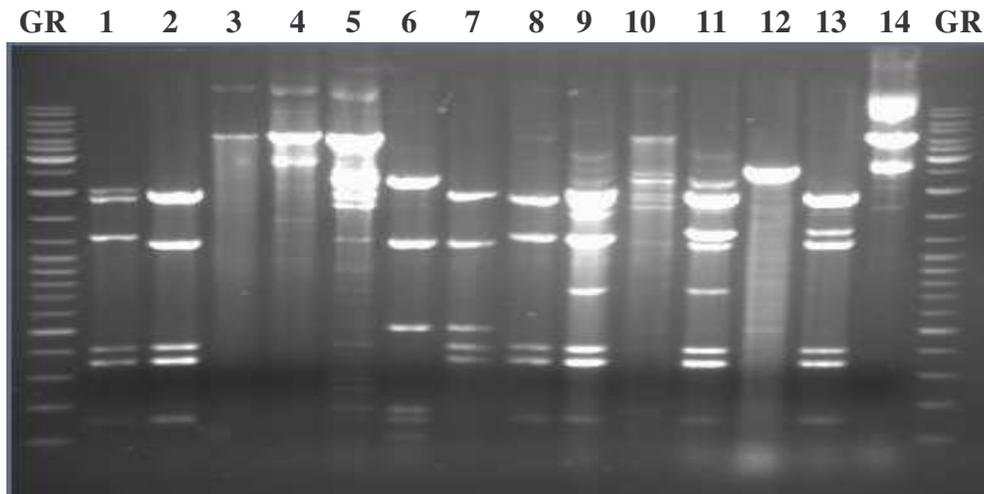


Figure 5-85: Representation of the restriction digestion of the 14 clones with the four base pair cutter *Rsa*

5.3.4.2.1 Evidence for Reductive Dechlorination

Reductive dechlorination is the common biological process for degradation of chlorinated hydrocarbons. The oxidation-reduction (redox) state of an aquifer is critical in determining the degradation reaction that contaminants are likely to undergo. The degradation of chlorinated compounds with 3 or 4 chlorine atoms are subject primarily to reductive dechlorination. The chlorinated compound serves as an electron acceptor and a chlorine atom is removed sequentially from the core carbon molecule (e.g., ethene, ethane or methane).

Reductive dechlorination occurs under *strongly reducing conditions* ($ORP < -100mV$) and requires carbon as a food source for the microbes. Less chlorinated compounds (those with 1 or 2 chlorine atoms) are also subject to reductive dechlorination but the degradation rates are usually slower than for the more highly chlorinated compounds. Complete reductive dechlorination produces ethene, ethane, or methane and CO_2 . Although the optimal range for $ORP < -100mV$ during reductive dechlorination, reaction

can still take place in the range up to <50 mV, if other factors are also optimal.

Even though the concentrations of the chlorinated solvents at Test Site 1 were very low, evidence of degradation pathways and associated daughter products can be seen Figure 5-78 and Figure 5-79. The daughter products; cis-1,2-dichloroethene, chloromethane, and dichloromethane were all detected in boreholes with TCE, PCE and chloroform (Figure 5-86). Samples were taken and analysed for methane, ethane and ethane, however only in EB2 some low concentrations of methane was detected.

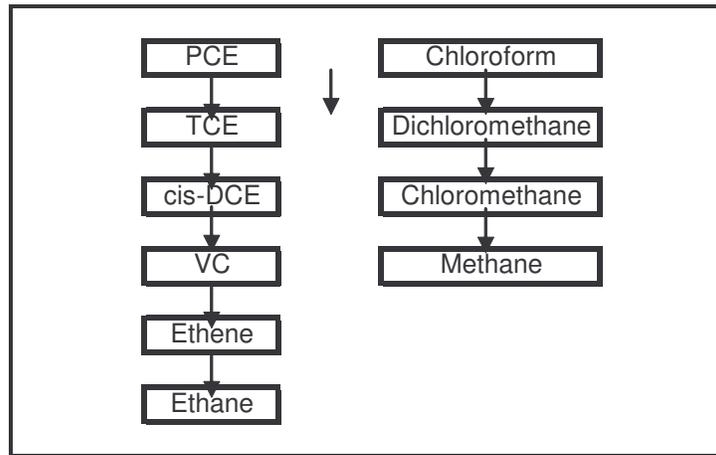


Figure 5-86: (Simplified) Degradation pathways for reductive dechlorination of PCE, TCE, and Chloroform (Adapted from Pankow and Cherry, 1996).

The following figures show the dissolved oxygen (DO) and ORP logs for the boreholes where other evidence of reductive dechlorination was found. Contaminants that are degraded by anaerobic bacteria require *the absence of dissolved oxygen*. In some cases, contaminants can act as electron acceptors and therefore can be degraded only after dissolved oxygen has been depleted. It must be noted that redox conditions were never such that methanogenic conditions were reached, and therefore degradation to vinyl chloride is not expected to occur.

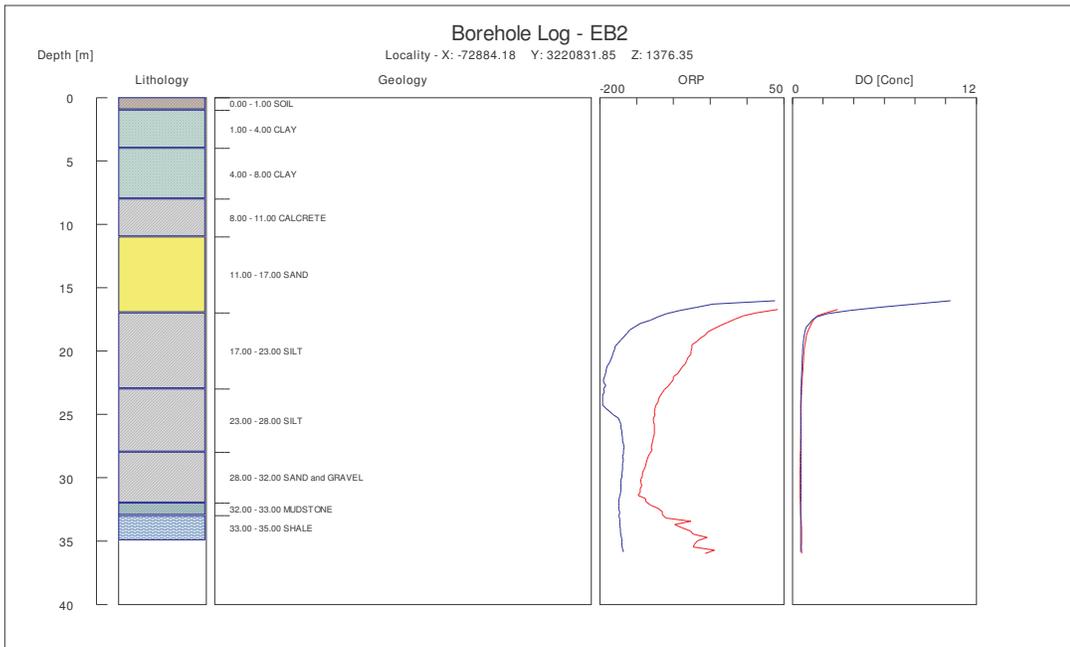


Figure 5-87: DO and ORP logs for Borehole EB2.

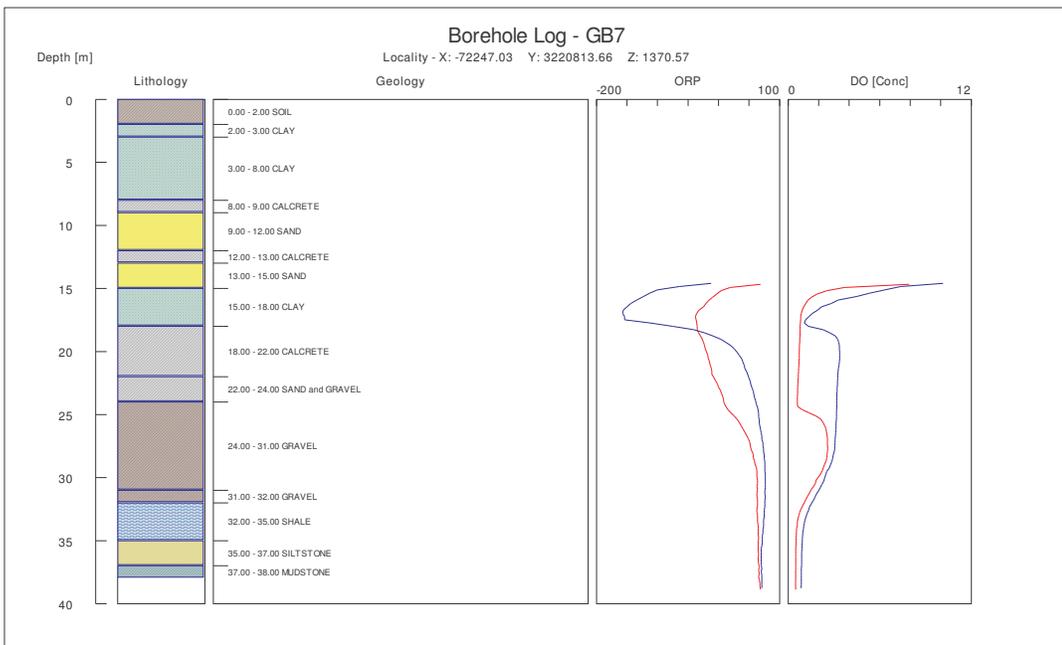


Figure 5-88: DO and ORP logs for Borehole GB7

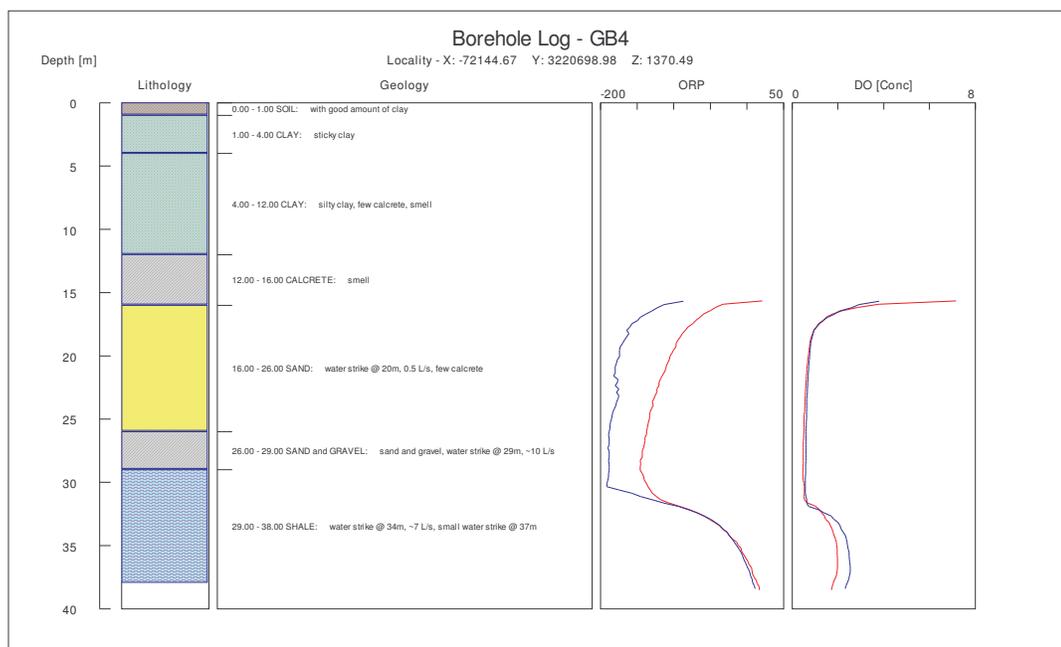


Figure 5-89: DO and ORP logs for Borehole GB4.

From the above logs it can be seen that optimal DO (low) and ORP conditions for degradation is found in the shallower unconsolidated part of the aquifer system.

Chloride concentrations, in boreholes where evidence of reductive dechlorination was found, were compared to solvent concentrations (Figure 5-90). Chloride would move much more rapidly than DNAPLs, thus there may be a disconnect between the chloride concentration increase and the solvent concentration decrease. The comparisons, show promise but due to the low solvent concentrations were not conclusive.

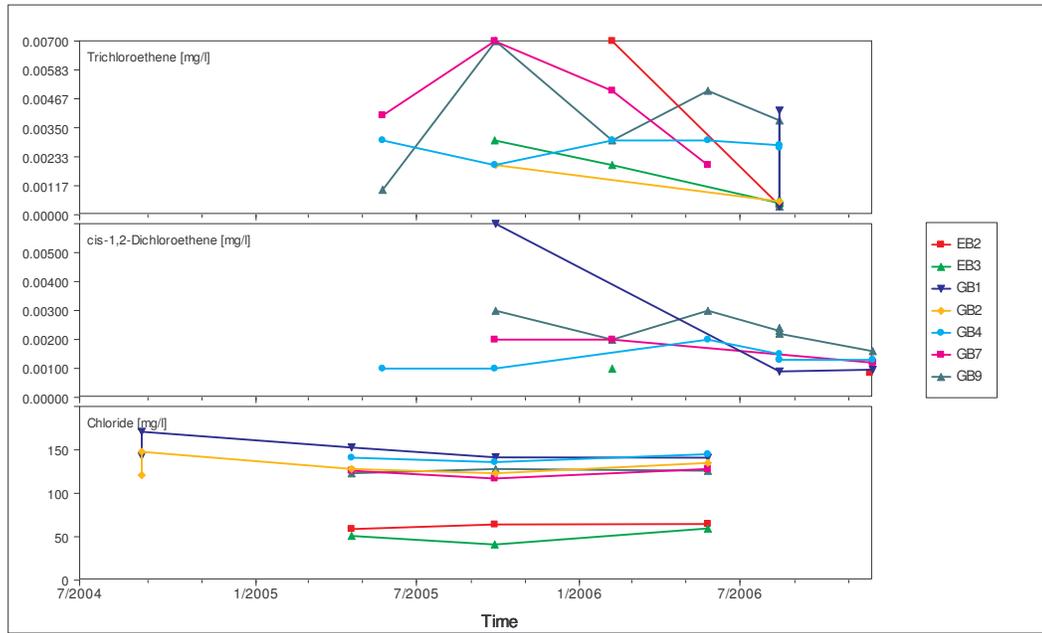


Figure 5-90: Comparison of chloride concentrations with TCE and cis-TCE concentrations. Other inorganic parameters which were evaluated to investigate lines of evidence for natural attenuation and degradation processes are: Nitrate, sulphate, and selected metals.

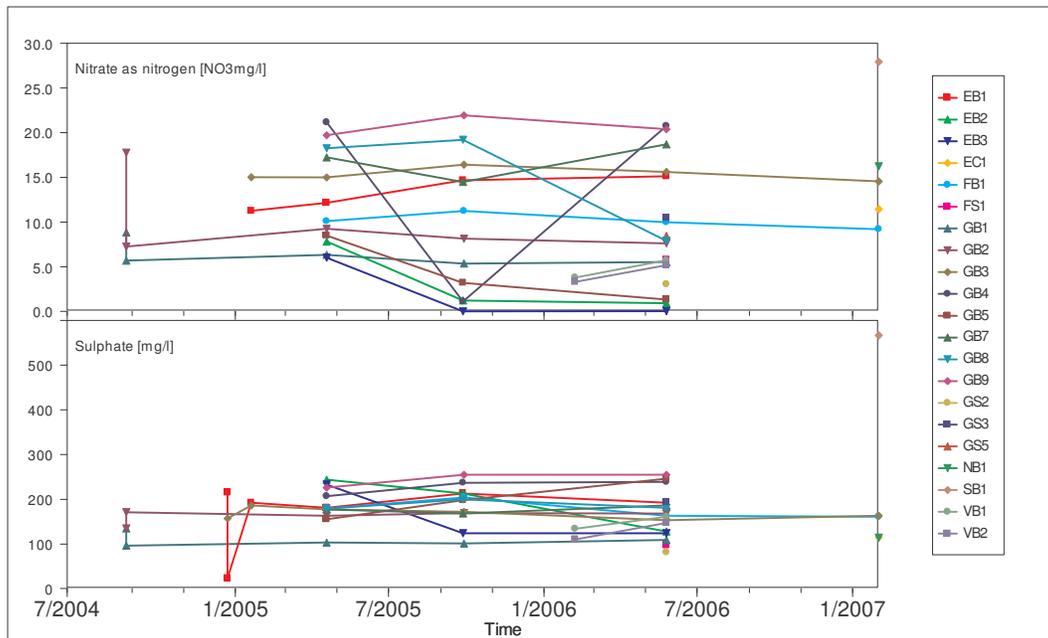


Figure 5-91: Nitrate and Sulphate values measured in boreholes at Test site.

Slight decreases to nitrate and sulphate values can be observed in boreholes where other lines of evidence for reductive dechlorination are present. i.e. EB2, EB3 and GB2. In boreholes with elevated nitrate values, reductive dechlorination is not expected.

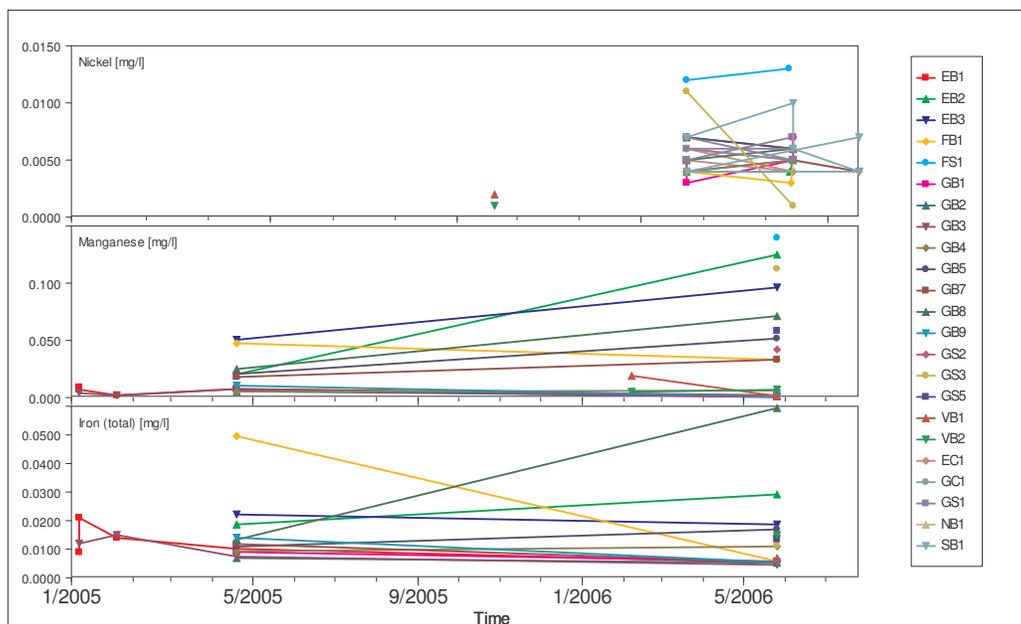


Figure 5-92: Ni, Mn, and Fe values measured in boreholes at Test site.

The data from the metal concentrations were inconclusive due to the lack of differentiation between metal species. Only total metal concentrations were determined.

The following was concluded from the microbial analysis with regard to species capable of chlorinated hydrocarbon degradation:

The dechlorinating bacteria *Dehalococcoides*, may be present but this could not be conclusively determined. Other studies on the genetic diversity at chlorinated-organics contaminated sites have found that the species of this genus may be present but only in limited numbers, and thus difficult to detect using clone library screening (Macbeth *et al.*, 2004). The sequence results however did give some promising results as most of the clone were associated with a variety of organic pollution degradation. The species found included *Oxalobacteraceae bacterium*; *Ralstonia sp*; *Pseudomonas saccharophila*. Most of these bacteria work in consortia to clean up a variety of toxic pollutants and in some instances are associated with consortia able to degrade chlorinated hydrocarbons.

5.3.4.3 Discussion

The BIOCHLOR Natural Attenuation screening protocol software was used to estimate the likelihood of anaerobic biodegradation of chlorinated organics at Test Site 1 (Available at: <http://www.epa.gov/ada/csmos/models/biochlor.html>). The BIOCHLOR Natural Attenuation software is based on a sequential, first order, coupled reactive transport model. Figure 5-93 shows by using the input parameters from the site an overall score of 22 was calculated. This falls into the range where there is “*strong evidence for anaerobic biodegradation of chlorinated organics*” at the site.

Although from the above results strong evidence exists with regard to degradation of contaminants at Test Site 1 it is recommended that the following steps be completed before MNA can be applied as a remedy at the site:

1. Similar data need to be collected for other sources of contamination. During this research only three relative small areas were investigated of the total site consisting of 111 ha.
2. Several more monitoring boreholes need to be drilled and constructed according to acceptable MNA practices.
3. Several more years of water analysis data will need to be collected to make conclusions on long-term trends.
4. A comprehensive risk assessment needs to be conducted for all potential receptors from the site.

| Natural Attenuation Screening Protocol <small>The following is taken from the USEPA protocol (USEPA, 1998). The results of this scoring process have no regulatory significance.</small> | | Interpretation | | Score | Score: 22 <i>Scroll to End of Table</i> |
|--|------------------------------------|--|----------------------------------|----------------------------------|---|
| | | Inadequate evidence for anaerobic biodegradation* of chlorinated organics | | 0 to 5 | |
| | | Limited evidence for anaerobic biodegradation* of chlorinated organics | | 6 to 14 | |
| | | Adequate evidence for anaerobic biodegradation* of chlorinated organics | | 15 to 20 | |
| | | Strong evidence for anaerobic biodegradation* of chlorinated organics | | >20 | |
| Analysis | Concentration in Most Contam. Zone | Interpretation | Yes | No | Points Awarded |
| Oxygen* | <0.5 mg/L | Tolerated, suppresses the reductive pathway at higher concentrations | <input checked="" type="radio"/> | <input type="radio"/> | 3 |
| | > 5mg/L | Not tolerated; however, VC may be oxidized aerobically | <input type="radio"/> | <input checked="" type="radio"/> | 0 |
| Nitrate* | <1 mg/L | At higher concentrations may compete with reductive pathway | <input type="radio"/> | <input checked="" type="radio"/> | 0 |
| Iron II* | >1 mg/L | Reductive pathway possible; VC may be oxidized under Fe(III)-reducing conditions | <input type="radio"/> | <input checked="" type="radio"/> | 0 |
| Sulfate* | <20 mg/L | At higher concentrations may compete with reductive pathway | <input type="radio"/> | <input checked="" type="radio"/> | 0 |
| Sulfide* | >1 mg/L | Reductive pathway possible | <input type="radio"/> | <input type="radio"/> | |
| Methane* | >0.5 mg/L | Ultimate reductive daughter product, VC Accumulates | <input checked="" type="radio"/> | <input type="radio"/> | 3 |
| Oxidation Reduction Potential* (ORP) | <50 millivolts (mV) | Reductive pathway possible | <input checked="" type="radio"/> | <input type="radio"/> | 1 |
| | <-100mV | Reductive pathway likely | <input checked="" type="radio"/> | <input type="radio"/> | 2 |
| pH* | 5 < pH < 9 | Optimal range for reductive pathway | <input checked="" type="radio"/> | <input type="radio"/> | 0 |
| TOC | >20 mg/L | Carbon and energy source; drives dechlorination; can be natural or anthropogenic | <input checked="" type="radio"/> | <input type="radio"/> | 2 |
| Temperature* | >20°C | At T >20°C biochemical process is accelerated | <input checked="" type="radio"/> | <input type="radio"/> | 1 |
| Carbon Dioxide | >2x background | Ultimate oxidative daughter product | <input type="radio"/> | <input type="radio"/> | |
| Alkalinity | >2x background | Results from interaction of carbon dioxide with aquifer minerals | <input type="radio"/> | <input checked="" type="radio"/> | 0 |
| Chloride* | >2x background | Daughter product of organic chlorine | <input type="radio"/> | <input checked="" type="radio"/> | 0 |
| Hydrogen | >1 nM | Reductive pathway possible, VC may accumulate | <input type="radio"/> | <input type="radio"/> | |
| Volatile Fatty Acids | >0.1 mg/L | Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source | <input type="radio"/> | <input type="radio"/> | |
| BTEX* | >0.1 mg/L | Carbon and energy source; drives dechlorination | <input type="radio"/> | <input checked="" type="radio"/> | 0 |
| PCE* | | Material released | <input checked="" type="radio"/> | <input type="radio"/> | 0 |
| TCE* | | Daughter product of PCE ^{a/} | <input checked="" type="radio"/> | <input type="radio"/> | 2 |
| DCE* | | Daughter product of TCE. If cis is greater than 80% of total DCE it is likely a daughter product of TCE ^{a/} ; 1,1-DCE can be a chem. reaction product of TCA | <input checked="" type="radio"/> | <input type="radio"/> | 2 |
| VC* | | Daughter product of DCE ^{a/} | <input type="radio"/> | <input checked="" type="radio"/> | 0 |
| 1,1,1-Trichloroethane* | | Material released | <input type="radio"/> | <input type="radio"/> | |
| DCA | | Daughter product of TCA under reducing conditions | <input type="radio"/> | <input type="radio"/> | |
| Carbon Tetrachloride | | Material released | <input checked="" type="radio"/> | <input type="radio"/> | 0 |
| Chloroethane* | | Daughter product of DCA or VC under reducing conditions | <input checked="" type="radio"/> | <input type="radio"/> | 2 |
| Ethene/Ethane | >0.01 mg/L | Daughter product of VC/ethene | <input type="radio"/> | <input type="radio"/> | |
| | >0.1 mg/L | Daughter product of VC/ethene | <input type="radio"/> | <input type="radio"/> | |
| Chloroform | | Daughter product of Carbon Tetrachloride | <input checked="" type="radio"/> | <input type="radio"/> | 2 |
| Dichloromethane | | Daughter product of Chloroform | <input checked="" type="radio"/> | <input type="radio"/> | 2 |

* required analysis.
a/ Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

End of Form

Figure 5-93: BIOCHLOR Natural Attenuation Decision Support System: Natural Attenuation Screening Protocol applied for Test Site 1.

5.4 Borehole construction material experiments

5.4.1 Introduction

The compatibility of borehole construction materials with NAPLs and highly contaminated groundwater should be an important consideration during borehole design. Borehole construction materials (e.g. screens, casings, sealants) are subject to degradation or corrosion in the natural environment. Materials exposed to NAPLs may also be degraded or corroded, which may lead to structural failure. This vulnerability applies to materials exposed to these chemicals in both the subsurface and above ground. The EPA, (1995) recommends that at sites where the presence of NAPLs is suspected, a materials' compatibility review should be conducted. Since the time requirements for either monitoring (or subsurface remediation systems) at contaminated sites are usually long-term, it is economically and technically important that these systems be constructed of materials with known chemical resistance qualities to provide reliable service over many years.

There are two types of effects that NAPLs have on materials used in borehole construction (sampling and remediation): firstly, the structural integrity of a material may be compromised by corrosion or solvation. Secondly, dissolved groundwater contaminants from NAPLs can sorb to or leach from monitoring materials, which affect groundwater quality measurements. Another way of viewing these two effects is from a concentration perspective. Sorption to monitoring surfaces may have the greatest effect on water quality measurements when contaminants are present at low dissolved concentrations. Conversely, sorption of contaminants present as NAPLs or in high dissolved concentrations, may have a minimal effect on water quality measurements, while the effects on the structural integrity of the materials may be at a maximum.

McCaulou, *et al.* (1995) published a "Chemical Compatibility Table". The compatibility in this paper is defined as "a material's ability to withstand corrosion or degradation under specific experimental conditions". This refers to the effects that NAPLs and high concentrations of dissolved organic compounds have on the structural integrity of materials.

For this research, commonly used (in South Africa), borehole construction materials were tested. Results of these experiments are given in the following sections.

5.4.2 Experiments

Borehole construction material was tested with various TCE concentrations for a period of 18 months. Samples of PVC, Steel and HDPE were submersed in solutions of TCE with water and the effects observed after 18 months. The materials were taken out from the solution and visually inspected for any changes. To assist in the visual observations hydrophobic dyes and UV light was used.

Table 5-23: Summary of experiments with casing material

| | Concentrations of TCE |
|-----------------|-------------------------------------|
| PVC | ~ 3 g/l water |
| PVC | ~1.4 g/l water (dyed with Sudan IV) |
| PVC | ~ 7 g/l water |
| | |
| Steel | ~ 3 g/l water |
| Steel | ~1.4 g/l water (dyed with Sudan IV) |
| Steel | ~ 7 g/l water |
| | |
| HDPE | ~1.4 g/l water (dyed with Sudan IV) |
| Steel (control) | Water |
| | |

The samples of PVC in solutions with free phase TCE both showed signs of solvation and sorption. The following photograph shows how the TCE (dyed red with Sudan IV) has sorbed to the PVC and after 18 months, the PVC has become completely plasticised (Figure 5-94).



Figure 5-94: Sample of PVC after 18 months in solution with ~ 1.4 g/l TCE.

TCE concentrations also increased the corrosion of the steel casing material (Figure 5-95 top left) and where NAPL was present, it sorbed to the steel casing material to some extent (Figure 5-96); however, not as strongly as to the PVC, and once the sample was removed from the solution it was no longer visible.



Figure 5-95: Effect of TCE (dyed red) on casing material after 18 months of exposure.



Figure 5-96: Sorption of TCE on Steel sample.

HDPE, (which was inspected by means of UV fluorescence in order to determine the extent of sorption and/or corrosion) showed no signs of sorption or corrosion (Figure 5-95 top right and Figure 5-97). Therefore, from the results of these simple experiments it is evident that care should be taken to select the correct construction material to ensure long-term stability and to prevent water quality errors during sampling.

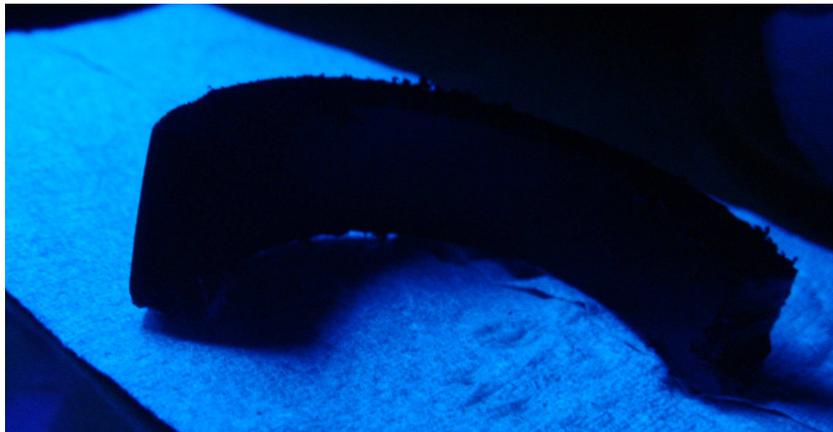


Figure 5-97: HDPE sample inspected under UV after exposure to TCE in solution.

It is recommended that the selection of construction materials be done on a site-specific basis. Once the contaminants of concern are known, the Chemical Compatibility Table of McCaulou, *et al.* (1995) may be used to select suitable materials.

Bentonite was tested as a sealant of a borehole bottom. It was found that under the correct application (the bentonite must remain submersed in water); the integrity of the bentonite is not affected by a NAPL such as TCE. However, if the bentonite is not correctly applied, cracks may develop which cause preferential pathways for the NAPL to migrate downwards.

6 Management and Regulation of DNAPLs in South Africa

6.1 General

The need for South African-specific guidelines for dealing with DNAPLs should be a high priority. Currently, for organic groundwater contaminants, consultants and researchers use a multitude of different quality guidelines and standards. Guideline concentrations and maximum contaminant levels from several other countries are often referred to, which has led to an *ad hoc* approach to appropriate trigger concentrations for actions.

There is an urgent need for a consistent approach to allow the groundwater community, the regulators and the site owners to apply the same rationale consistently and be subjected to the same expectations for acceptable concentrations.

In view of this, it is recommended that a common framework with a systematic methodology be applied. In a country such as South Africa, such a framework must be flexible, pragmatic, consistent and cost-effective. It is therefore considered appropriate that a risk-based approach be followed, with a set of screening trigger values for different common groundwater contaminants. This approach is consistent with the methodologies recommended by the USEPA, the UK Environmental Agency, Australian regulations and the trend in much of the rest of the world.

6.2 Risk-Based Approaches

A risk assessment is an analysis that uses information about toxic substances at a site to estimate a theoretical level of risk for people/receiving environments potentially exposed to these substances. The information comes from scientific studies and environmental data from a site. A risk assessment provides a comprehensive scientific estimate of risk to persons who could be exposed to these hazardous materials (ATSDR, 2004).

The UK approach is outlined in the following steps:

- Prioritisation of sites and contaminants on site with screening methods
- Quantification of potential risk, using simple analytical methods, advanced analytical equations and detailed numerical modelling

- Identification and implementation of appropriate actions

Such an approach is in line with the widely used Risk-Based Correction Action used widely internationally. Regulators have indicated the increasing acceptability of risk-based approaches, provided that they are supported by a high quality scientific and consistent methodology. The common approach in all these methods is the ‘Source-Pathway-Receptor’ philosophy. Such an approach will allow each aquifer to receive the appropriate protection and result in the site investigation, mitigation and remediation being funded, requisite with the risks posed to the receiving environment (users and water resources) and the importance of the resource as a supply or as a strategic reserve.

A typical framework for the implementation of such a methodology is provided by below:

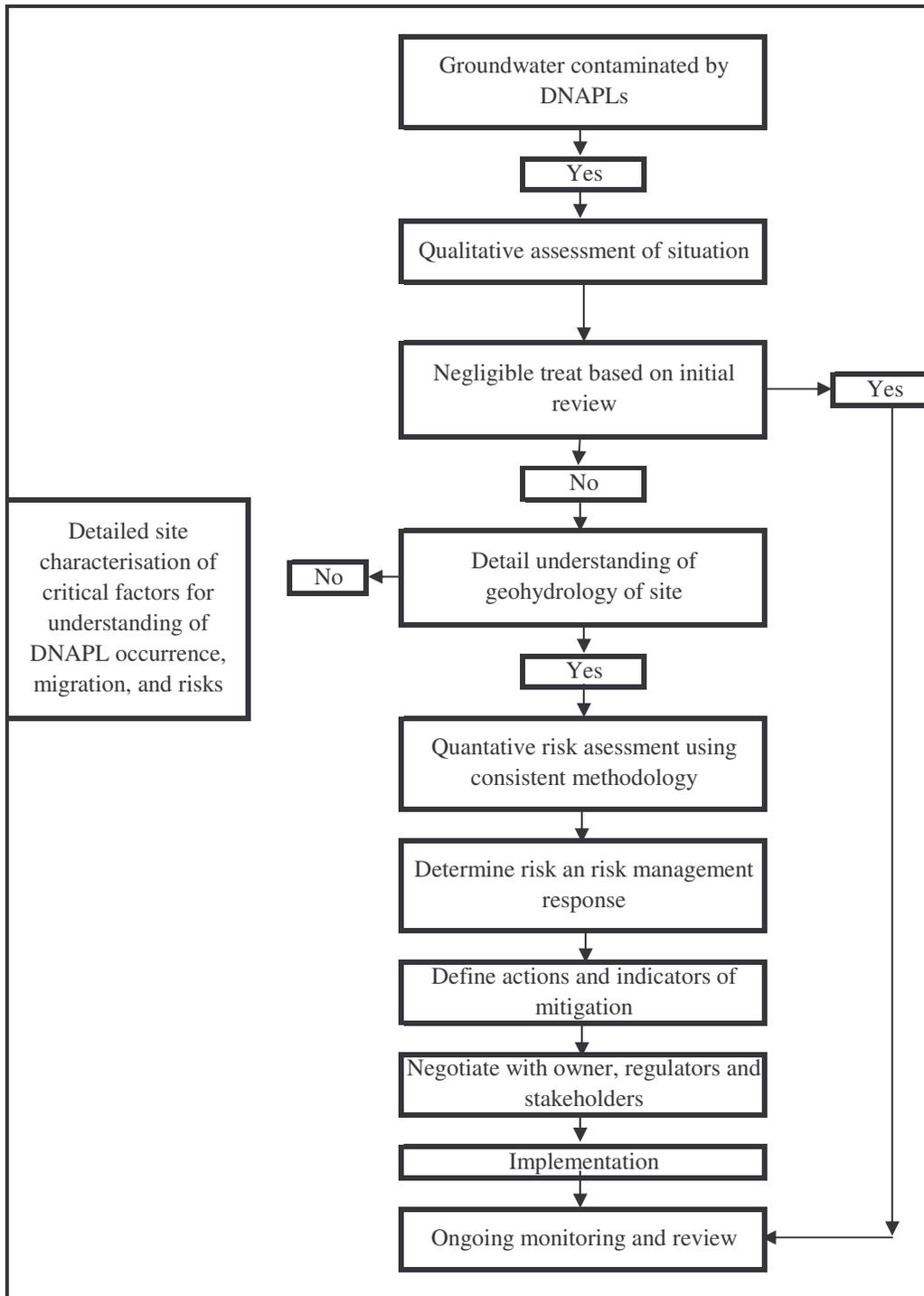


Figure 6-1: Proposed methodology for setting and implementing standard approaches for organic contaminants in South Africa (from Carey *et al.*, 1995)

It is critical to have conservative safety margins as an integral component of the accepted risk assessment analysis to ensure adequate protection of the receptors. Each risk assessment prepared in support of decision-making should include a risk characterisation

that follows the principles and reflects the values outlined in South African policy.

A risk characterisation should be prepared in a manner that is clear, transparent, reasonable and consistent with the relevant regulations available to the regulator for enforcement and environmental, water resource or public health protection. Furthermore, discussion of risk in all reports, presentations, decision packages and other documents should be substantively consistent with the risk characterisation. The nature of the risk characterisation will depend upon the information available, the regulatory application of the risk information and the resources (including time) available. In all cases, however, the assessment should identify and discuss all the major issues associated with determining the nature and extent of the risk and provide commentary on any constraints limiting fuller exposition (USEPA, Science Policy Council, 1995).

In all cases, the process should include risk assessment and risk management, discussion of uncertainties/confidence level of the risk determination, a full conceptual model of the site with available information, full disclosure of results and risk perspectives. As part of this Hazard Identification, Dose Response Assessment and Exposure Assessment must be provided in the context of the ‘Source-Pathway-Receptor’ paradigm.

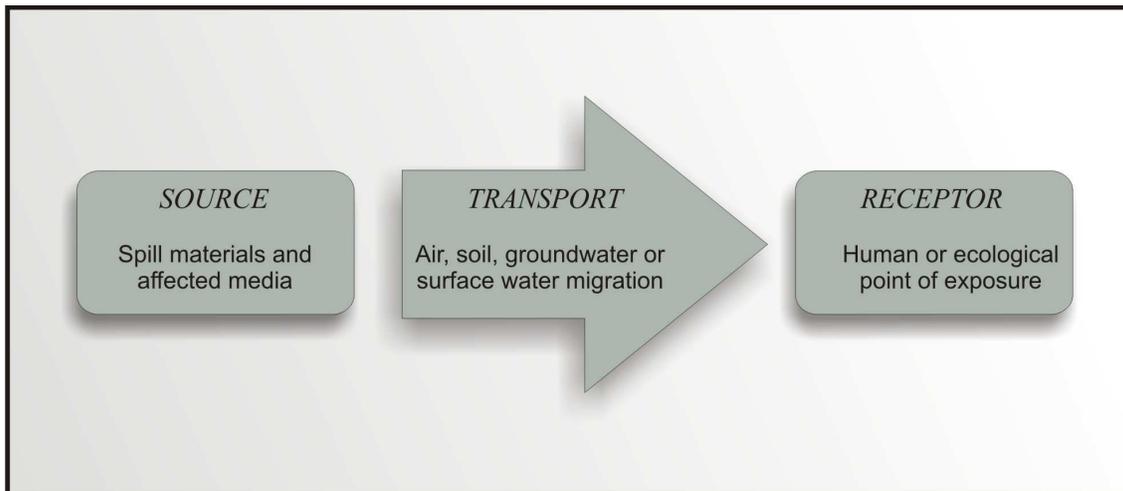


Figure 6-2: Risk Assessment Overview

While the general approach and procedures should be similar to the well established methodologies such as those described in the ASTM Risk-Based Corrective Action procedure, it is important that the method is focused on the protection of water resources

and specifically recognises the statutory responsibilities of DWAF and other agencies as a function of South African legislation.

6.3 Trigger values for action

A difficulty for regulators and site owners is the initial decision of whether action should be taken. It is suggested that an initial screening methodology be established. Such a methodology could follow several approaches. The simplest, but not necessarily the most effective, would be to follow an ultraconservative approach. Such an approach would include listing tables of common organic contaminants and the associated guideline values from different countries. The difficulty here lies in selecting the most appropriate value for each parameter. This is not as easily achieved as might be expected, as indicated by the comparison between different guideline concentrations (Appendix F) from the Dutch and EPA groundwater guidelines (two of the most common references used in South Africa available at: <http://www.cleanuplevels.com> and <http://www.sanaterre.com>).

In the table, the big differences between two equally well respected and widely used guidelines may be seen for various parameters. This understandably leads to inconsistent application. It is suggested that the Intervention Value of the Dutch guidelines be used where available, due to the more extensive nature of the available list and that as a precaution, a trigger value of 0.01% of maximum solubility of any contaminant not found on the list, be used. Solubility data for a vast range of organics are available in the public domain, including in the URA software developed for the WRC as part of the Identification and Prioritisation of Groundwater Contaminants in South African urban environments (Usher et al., 2004). This trigger value could be used as a first level of action, but risk-based decisions are more appropriate and therefore recommended.

6.4 Monitored Natural Attenuation

Natural attenuation makes use of natural processes to contain the spread of contamination from chemical spills and reduce the concentration and amount of pollutants at contaminated sites. Natural attenuation means that environmental contaminants remain in place while natural attenuation works on them. Natural attenuation is often used as one part of a site clean-up that also includes the control or

removal of the contamination source.

Where conditions are favourable, natural attenuation processes may reduce contaminant mass or concentration at sufficiently rapid rates and therefore achieve remediation objectives at some sites without the aid of other (active) remedial measures.

When monitoring of groundwater confirms that natural attenuation processes are acting at a sufficient rate to ensure that the wider environment is unaffected and that remedial objectives will be achieved within a reasonable timescale and are fast enough to limit risks to potential receptors, the process is referred to as *Monitored Natural Attenuation* (MNA). MNA is an excepted mitigation strategy of organic contaminated sites in the US and Europe, is sufficient proof is provided that the processes are occurring at a site.

Natural attenuation occurs to some degree at every site; however, depending on site conditions, there may be definite limits to its effectiveness as an interim or long-term solution, because natural attenuation does not necessarily imply that contaminants are removed. Furthermore, the site-specific conditions that often limit the effectiveness of natural attenuation as a contaminant removal/destruction process are rarely properly evaluated.

It is very important to note that MNA is not a “do nothing” approach. The evidence required to select it as a mitigation strategy and to prove that it occurs to the required degree, shifts the onus squarely onto the site owner to show that the risks associated with allowing natural attenuation are acceptable. It follows that detailed monitoring is an integral part of successfully applying MNA at a site.

It is recommended that the approach for assessing and implementing MNA in South Africa be a *risk-based* management strategy. The methodology should be based on a multi-stage process, involving structured decision-making and iterative data collection and analysis. The key steps are summarised in the flow chart below.

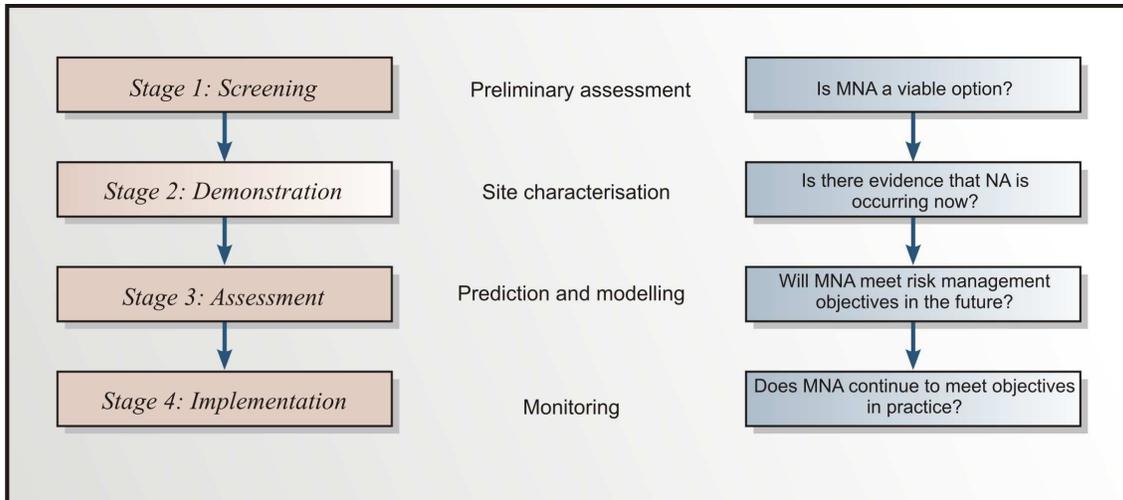


Figure 6-3: Overall procedure for the assessment of natural attenuation

The initial stage will be to determine whether natural attenuation is likely to occur at sufficient rates on the site under investigation. After reviewing screening factors to determine the viability of MNA, a detailed site characterisation should be performed as part of the next stage.

The purpose of the *demonstration stage* is to show quantitatively that natural attenuation is occurring at a rate that will achieve the objectives in a reasonable time frame. Demonstrating effectiveness involves obtaining data to test and calibrate the conceptual model. The process is iterative, in which data are used to refine the model that in turn guides any necessary additional site characterisation.

The key to MNA demonstration in South Africa is a '*lines of evidence*' approach.

1. Primary lines of evidence involve the use of historical monitoring data to demonstrate a trend of reduced pollutant concentrations down-gradient of the source, along the groundwater flow path.
2. Secondary lines of evidence involve measuring changes in chemical and geochemical analytical data to prove a loss of contaminant mass.
3. Tertiary lines of evidence use data from laboratory microbiological testing to show that on-site bacteria are capable of degrading site contaminants.

Evidence for natural attenuation is often circumstantial, so it is often necessary to seek

multiple lines of evidence, particularly where the level of uncertainty is high and the sensitivity of the site is significant. However, where the weight of evidence from a primary line of evidence is overwhelming, then it may be judged unnecessary to collect secondary and tertiary data.

The objectives of the site characterisation are twofold: to provide data to demonstrate and quantify NA along the lines of evidence approach and to provide sufficient site-specific input data to forecast the future behaviour of contamination using solute fate and transport models.

Table 6-1 presents a description of physical, chemical, biological and geochemical parameters and their use in demonstrating natural attenuating mechanisms. The process of selecting appropriate determinants from this list will depend upon the nature of contamination, the biogeochemical environment at a site and the dominant attenuation processes under consideration.

Table 6-1: Data Collection required for Evaluation and Implementation of Natural Attenuation (Adapted from Sara, 2003)

| Parameter | Data Type | Ideal Use, Value, Status and Comments | Method |
|------------------------|--|--|--|
| Geological | | | |
| Area geology | Topography/soil type/surface water/climate | Provides information of groundwater flow systems, recharge/discharge areas, infiltration rates, evaluation of geological deposits with regard to aquifer/aquitard properties | Geological/soil/topographic maps, aerial photographs and field geological mapping. |
| Hydrogeological | | | |
| Subsurface geology | Lithology/stratigraphy/structure | Identify water-bearing units, thickness, confined/unconfined aquifers, effect on groundwater flow and direction (anisotropy) | Hydrogeologic surveys/maps |
| | | | Review soil boring and borehole logs |
| | | | Surface and subsurface geophysics |
| Velocity | Hydraulic conductivity/permeability | Saturated hydraulic conductivity of geological matrix. Calculate specific discharge and if site is complex vertical and horizontal conductivity | Estimate range base on geology |
| | | | Pump or slug tests |
| | | | Grain size analyses |
| | | | Permeability testing |
| | | | Downhole flowmeter |
| | | | Tracer and dilution tests |
| | Gradient | Measure potential of fluid to move (hydraulic gradient) | Water table and piezometric surface measurements |
| | Porosity | Measures the soil/matrix pore space. Specific discharge divided by porosity gives average groundwater velocity | Estimate range base on geology Measure bulk and particle mass density |

| Parameter | Data Type | Ideal Use, Value, Status and Comments | Method |
|--------------------------|--|---|--|
| Direction | Flow field | Estimate direction of groundwater flow | Water and piezometric contour maps Downhole flowmeter |
| Dispersion/sorption | f_{oc} | Fraction of organic carbon is used to estimate the retardation of chemical migration relative to the average groundwater velocity | Measure from soil/rock samples, estimate from published values or use reactive and non-reactive tracers in groundwater |
| | Dispersion | Longitudinal and horizontal dispersion spreads out the chemical(s) along the flow path | Estimate based on the distribution of chemicals or use tracer testing |
| Chemistry | | | |
| Organic chemistry | VOCs | Identify parent chemicals and degradation products, and assess distribution. Certain isomers/degradation products provide direct evidence of biodegradation while others are formed due to abiotic degradation. Some aromatic hydrocarbons and ketones can support biodegradation of VOCs | Purge and trap GC-MS analyses (Based on USEPA method 8260) |
| | Semi-VOCs | Selected SVOCs can support biodegradation of VOCs | GC-MS analyses (Based on USEPA method 8270) |
| | Volatile Fatty Acids | Some organic chemicals (e.g. acetic acid) can provide insight into microbial activity | Standard analytical methods, published modified methods using ion chromatography |
| | Methane, ethane, ethene, propane and propene | Provides evidence of dechlorination of chlorinated methanes, ethenes and ethanes. Methane also indicates activity of methanogenic bacteria. Isotope analysis of methane can be used to determine its origin. | Modified analytical methods, GC-FID |
| | TOC/BOD/COD/TPH | Potential availability of general growth substrates. | Analytical method depended on parameter and laboratory |

| Parameter | Data Type | Ideal Use, Value, Status and Comments | Method |
|----------------------------|------------------|---|--|
| Inorganic Chemistry | Alkalinity | Increased levels is indicative of carbon dioxide production | Analytical method depended on parameter and laboratory |
| | Chloride | Provides evidence of dechlorination. Possible use in mass balancing and as conservative tracer. Care should be taken when interpreting chloride data. | Analytical method depended on parameter and laboratory |
| | Conductivity | Assess overall water quality of water samples and indicate possible flow patterns across the well depth. | Field electrode measurement and downhole probe measurement. |
| | Dissolved Oxygen | Indicator of aerobic environments, electron acceptor. | Preferable to take field measurement/ downhole probe or through flow cell. |
| | Iron | Nutrient, ferrous indicates activity of iron reducing bacteria. Ferric is used as electron acceptor. | Analytical method depended on parameter and laboratory |
| | Manganese | Nutrient, indicator of iron and manganese reducing conditions. | Analytical method depended on parameter and laboratory |
| | Nitrate | Used as electron acceptor by denitrifying bacteria, or is converted to ammonia for assimilation. | Analytical method depended on parameter and laboratory |
| | Nitrite | Produced from nitrate under anaerobic conditions. | Analytical method depended on parameter and laboratory |
| | Phosphorous | Limiting nutrient | Analytical method depended on parameter and laboratory |
| | Sulphate | Used as electron acceptor. Changes in its concentration may provide evidence of activities of sulphate reducing bacteria. | Analytical method depended on parameter and laboratory |
| | Sulphide | May provide evidence of sulphate reduction. May not be detected because it may react with various oxygenated chemical species and metals. | Analytical method depended on parameter and laboratory |
| | Toxic metals | Presence of these metals may reduce microbial activity. | Analytical method depended on parameter and laboratory |

| Parameter | Data Type | Ideal Use, Value, Status and Comments | Method |
|--------------------------------|--|---|--|
| Physical/ inorganic | pH | Measurement of suitability of environment to support range of microbial species. Activity tends to be reduced in pH range outside of 5 – 9. Anaerobic organisms more sensitive to pH extremes. | pH can change rapidly and measurements are best taken on site with pH probe immediately after sample is taken or through a flow cell. |
| | Redox Potential | Measure of oxidation-reduction potential of the environment. Site and species specific and gives indication of aerobic or anaerobic conditions. | Field measurements with redox electrode. Flowcell or downhole measurements. |
| | Temperature | Help to correct temperature sensitive parameters and measuring devices. | |
| Microbiology | | | |
| Biomass | Micro-organisms Per Unit Soil or Groundwater | Microbial population density between impacted and non-impacted/treated areas can be compared to assess whether microbial populations are responsible for observed degradation. The value of biomass measurements is still being explored for VOC biodegradation. | There are three general techniques available: culturing (plate counts, BioLog, MPN enumerations); direct counts (microscopy); and indirect measurement of cellular components (ATP, phospholipid fatty acids). |
| | Biodegradation Rate and Extent | Demonstrate the indigenous micro-organisms are capable of performing the predicted transformations. Determine nutrient requirements and limitations. Measure degradation rates and extent. | Varied. Shake flasks, batch, column, bioreactors designs. |
| | Species/Genera/ Functional Group | The presence of certain microbial species of functional groups (e.g., methanogenic bacteria) that have been correlated with VOC biodegradation may be assessed. Research is being conducted to identify patterns of microbial composition that are predictive of successful VOC biodegradation. | There are three general techniques available: culturing and direct counts; indirect measurement of cellular components; and molecular techniques (16s RNA, DNA probes, RFLP). |

When the *assessment stage* of the investigation is reached, it is assumed that adequate information has been obtained to define the site and to demonstrate that natural attenuation is occurring and by what processes. Acceptance of MNA as a remedial option should be dependent on demonstrating that:

1. Natural attenuation processes are protecting receptors and will continue to do so;
2. Any further migration of the contaminant plume will not result in significant additional pollution of groundwater; and
3. The period over which contaminant concentrations are reduced by natural attenuation is reasonable.

A decision to *implement an MNA* monitoring programme should now be made in consultation with the Regulatory agency. The monitoring programme will need to be designed on a site-specific basis and should consider:

1. The number of monitoring boreholes required, their location and construction details;
2. The sampling methodology;
3. The sampling frequency and duration of monitoring;
4. Quality assurance (QA) procedures for sampling;
5. Methods of chemical analysis;
6. Reporting requirements to the Regulator; and
7. The basis for ceasing monitoring or to trigger the implementation of contingency measures.

It is important that the criteria for ceasing monitoring should be defined as part of the monitoring plan. Typically, monitoring will continue until: contaminant concentrations in the plume have reached background levels; remedial objectives accepted by the Regulator have been met and natural attenuation can be relied on to further reduce contaminant levels; or remedial objectives have been substantially met and declines in contaminant concentrations have been defined to the extent that there is a high degree of confidence that the remedial objectives will be achieved within a time-frame acceptable to the Regulator or that the *proven* risks are acceptable.

The monitoring plan should include a *contingency plan*, in case natural attenuation proves to be ineffective or insufficient on its own as a remedial technique. This plan should include:

- the basis for implementing the contingency plan;
- the measures that will be implemented and the time-scale during which these measures will be implemented.

Criteria for implementing the contingency plan or for reviewing the MNA conceptual model may include the following:

- contaminant concentrations in monitoring boreholes exceed remedial targets;
- contaminant concentrations do not decrease at a sufficient rate to meet remedial objectives;
- changes in groundwater or land use adversely influencing the effectiveness of NA;
- increases in contaminant concentrations that indicate continued release of contaminants to groundwater.

Thus, for MNA to be considered, a detailed study of the contaminated site is required. Natural attenuation is not an appropriate option at all sites. The rates of the attenuation processes may be too slow to meet the objectives, and in certain cases, the incomplete degrading of pollutants may increase potential risks. It is also important to note that, in more complex environments such as the aquifer conditions common in much of South Africa, where geological formations such as fractured rock aquifers or dolomite occur, these areas will be less likely candidates for natural attenuation. This is because groundwater conditions often have great subsurface variability that makes the prediction of groundwater flow and the associated migration of contamination difficult.

6.4.1 Practical implementation in a South African Context

The section above provides a clear overview of the approaches that need to be followed for MNA to be successfully applied to South African sites that have been impacted on by DNAPLs. Implicit in these methodologies are the four basic steps outlined in Figure 6-3 of screening for suitability, detailed site characterisation of the impacted site, assessment of natural attenuation processes and then monitoring to ensure that these processes will continue to meet the set criteria.

The suggested approach in a South African context is summarised by the figure below:

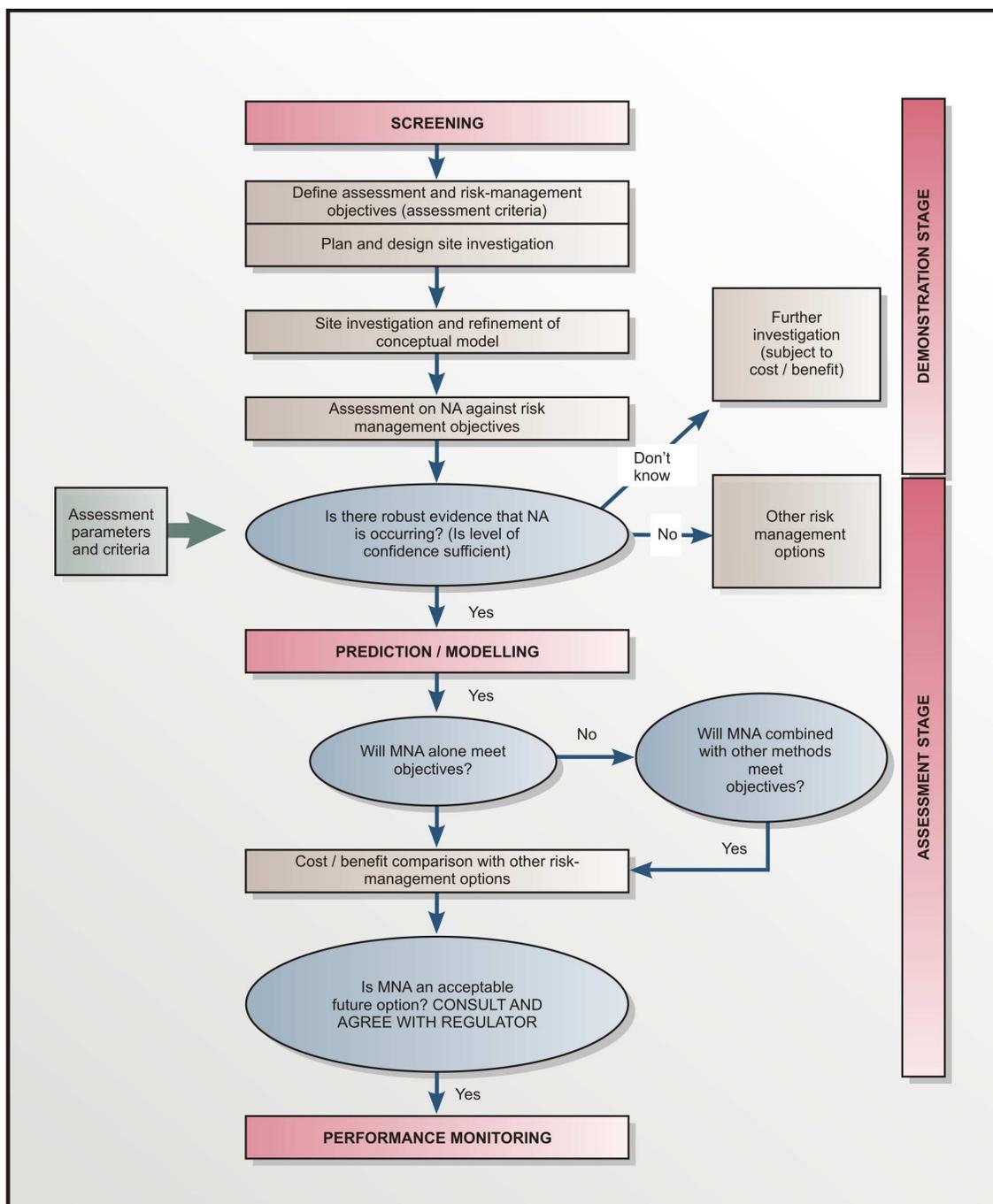


Figure 6-4: Suggested approach for MNA in a South African context.

The application of MNA in this country will not succeed without the acceptance of risk-based approaches and the standardisation of the requirements for site assessment, monitoring and remediation. Under the correct conditions, MNA along with source remediation, long-term monitoring and conservative risk determination might be more

appropriate than other conventional technologies, provided there is clear understanding that it is not a 'do nothing' alternative. There will be sites where monitored attenuation will not be acceptable due to the conditions on site or the receptors affected.

There are some key areas that need to be addressed for MNA to be implemented successfully:

- There is a lack of specific regulations addressing aspects such as site characterisation and monitoring and remediation policies to deal with dissolved organic contaminants and NAPLs in groundwater in this country.
- There is a very urgent need to establish South African water quality guidelines/standards for these types of contaminants. Several international guidelines exist but standardisation in South Africa for consistent decision-making and management is needed.
- The South African regulatory framework allows for risk-based decision-making to be applied in the management of groundwater contamination. Consensus on the acceptance of this approach and the application thereof is required, as is guidance for regulators, site owners and environmental specialists to apply this consistently in South Africa.
- There is very little specific guidance and policy on the remediation of these contaminants in groundwater in South Africa. Aspects such as site clean-up levels, monitored natural attenuation and Best Practice for these technologies should receive attention.

7 Conclusions

7.1 Occurrence of DNAPLS in South Africa

For a chemical (or chemical mixture) to be considered as a DNAPL, it must have a fluid density greater than 1.01g/cm^3 , a solubility in water of less than 2% (or 20000 mg/l) and a vapour pressure of less than 300 torr (Pankow and Cherry, 1996). The major DNAPL types include: halogenated hydrocarbons, especially *solvents, coal tar and creosote, Polychlorinated Biphenyls (PCBs), some pesticides, and miscellaneous or mixed DNAPLS.*

From the contaminant inventory and prioritization done as part of this research (Usher *et al.*, 2004) a picture of the widespread occurrence and extent of the DNAPL problem in South Africa emerged. Out of the 50 possible sources, 36 are sources of DNAPL contamination (see Table 2-2). Out of the top ten ranked sources only on-site sanitation, cemeteries and feedlot/poultry farms are excluded from this list. Out of the 119 contaminants listed in the national prioritization list, 62 can be considered to be NAPL contaminants.

The extent of the DNAPL problem in South Africa's urban areas is potentially much greater than expected. The problem is not confined to large urban centers, but many of the potential sources (e.g. auto workshops, dry-cleaners) are found in all types of settlements across the country. The development of groundwater resources for supply, in urbanized areas, is thus very likely to be affected by potential contamination from DNAPLS.

7.2 Critical factors for transport of DNAPLS in fractured and intergranular (porous) fractured aquifer systems in South Africa

A basic understanding of the nature and occurrence of groundwater in South Africa aquifer systems is a prerequisite for assessment, monitoring and management of DNAPL contaminated sites.

When spilled, DNAPLS will move downward through the unsaturated zone, trapping some (residual) DNAPL in the pore space. If a large volume of DNAPL is spilled and

permeability exists in the subsurface, the DNAPL will penetrate past the water table and continue moving downward through the saturated zone due to gravity. The subsequent subsurface migration of DNAPLs is not a function of conventional groundwater transport mechanisms (i.e. advection, dispersion and diffusion), but rather a function of geological structures (i.e. fissures, bedding planes, etc.) and gravity (including the bedrock topography). However, soluble constituents of DNAPLs will dissolve into groundwater and their distribution is a function of the hydraulic gradient, resulting in a groundwater plume down gradient from the contaminant source. The potential depth of DNAPL penetration through the vadose zone and into the groundwater will depend on the properties of the DNAPL, the nature of the DNAPL release, and the properties and geological structure within the vadose and groundwater zones.

The physical properties of an aquifer that have the greatest impact on the fate and transport of DNAPL contaminants, are the flow rate and flow mechanism present, and the hydraulic conductivity. Therefore the major South African aquifer systems are classified in relation to the dominant flow mechanisms and flow characteristics, namely:

- Intergranular flow systems
- Intergranular and fractured flow systems
- Fractured flow systems
- Karst flow

The DNAPL and dissolved phase migration will be influenced by the geologic and hydraulic features of each flow system. Since dissolved compounds in groundwater are carried mainly by advective transport, any aqueous phase contaminant (the dissolved phase of the DNAPL) is likely travel in the direction of groundwater flow. However, from the results of the study it has become clear that preferential pathways in fractured rock will determine the flow path of any DNAPL phase contamination. Aqueous plumes of DNAPL contaminants will therefore be influenced by these pathways (dissolving and or diffusing from the NAPL into the water in fractures and matrix) which can result in spatially variable aqueous plumes in these aquifer systems.

Features which will influence the migration pathways and extent of DNAPL penetration are:

1. **The depth to water table and thickness of the unsaturated zone** – In fractured rock aquifers in semi-arid regions this is often greater than in porous media which makes translating of US and other international experiences with regard to site assessment and characterization difficult. Many of these methodologies cannot be applied in hard rock and/or at great depths. Also this implies high cost of investigation in thick aquifers/ deep unsaturated zones.
2. **High fracture permeability, low matrix permeability** – This will cause slow groundwater velocities in matrix of fractured aquifers, but localized high flow in preferred pathways (fractures). This gives rise to smaller dissolved plumes than in porous media, but potential migration could be further.
3. **Multi-layered aquifer due to presence of hydraulic variance in horizons** – The resulting contaminated zones will be strongly influenced by the hydraulic variance leading to irregular distribution of NAPL and dissolved plumes. This is important for the construction of boreholes and interpretation of sampling results. Layering may also limit vertical dispersion.
4. **Fracture aperture, connectivity, strike, and dip** - Fracture entry pressures are directly proportional to interfacial tension and inversely proportional to fracture aperture. This results in preferential DNAPL migration through the larger aperture fractures of a fracture network. The strike and dip of the more permeable fractures will therefore control the primary directions of DNAPL migration in a fracture network. The fractures also need to be connected to facilitate continued migration in a preferential direction.
5. **Horizontal and vertical flow** must be considered in fractured rock. Density driven flow through vertical fractures will result in deep penetration of DNAPL.
6. **Matrix diffusion** - Matrix diffusion refers to the process whereby solutes dissolved in groundwater diffuse into and out of the rock matrix. If concentrations are higher in the open fracture, the diffusion process will result in dissolved

contaminants moving into the rock matrix (forward diffusion). If concentrations are higher in the rock matrix, dissolved contaminants will move out of the rock matrix and into water in the open fractures (back diffusion). Matrix diffusion will occur in all rock types exhibiting a finite matrix porosity. This process causes the contamination to be persistent over time and makes remediation techniques such as “pump-and-treat” not feasible in the long-term in dual porosity systems.

Laboratory testing of water, brine and FC-77, into a fixed aperture sandstone fracture constructed as a parallel plate provided confirmation of the established critical factors for fracture mass transport of dissolved, density driven and DNAPL flow. These results were used to precisely define the field injection of the surrogate DNAPL. The field test showed DNAPL injection into fractured rock elicits a different response to injection of high density aqueous liquid (brine), emphasizing the importance of NAPL flow, as opposed to aqueous density driven flow. At field scale, the injection showed that DNAPLs have the ability of migrating in the direction opposite to groundwater flow. The local variations in fracture strike and dip play a far more important role in DNAPL flow than the regional fracture dip or groundwater flow directions. The importance of scale issues was thus highlighted, and the results suggest that local scale fracture orientation and inclination play a far more important role in the migration of the DNAPL phase than previously indicated.

The pressure response of boreholes surrounding the injection is not radial in fractured rock, and is a function of the hydraulic conductivity and the distance from the injection point. This also showed that even under very controlled injection of DNAPL, the location of DNAPL mass distribution at field scale is very difficult, and large amounts of the DNAPL reside in local depressions within the fracture network as residual, which cannot be easily recovered. This supports the observations from field scale DNAPL remediation, where the solubility and volatility of the DNAPL are key factors to recovery, rather than mobilization and recovery of free phase DNAPL. This experiment confirmed that accurate fracture identification and characterization are the most important considerations in understanding DNAPL flow in the majority of South African aquifers.

Biotic and abiotic degradation can result in the lowering of concentrations in the down-

gradient direction within a contaminant plume (Kueper, *et al.*, 2003). Evidence of degradation was found at Test Site 1 (e.g. daughter products and microbial populations). In very hot, dry climates, coupled with a deep unsaturated zone, it is possible that a large portion of the contaminants can be volatilized before the contaminants reach the groundwater zone (Pankow and Cherry, 1996, and Fetter, 1999), which can result in low aqueous organic concentrations in the saturated zone.

The natural attenuation assessment on Test Site 1 indicated that natural attenuation processes are important consideration under South African conditions. Relatively high organic carbon in the shallow zones assists in retardation of the organic contaminants, while the large unsaturated zone, arid climate and high temperatures leads to significant loss of contaminant mass through volatilization. All three of the standard “lines of evidence” were found on this site. This information can be used to quantify the risks of the onsite activities. The assessment also showed that a significant body of evidence over a period of time would be required to prove that natural attenuation is occurring on a site. The use of molecular microbiology to determine microbial diversity and populations supported the other lines of evidence for MNA, and provided useful insights into the occurrence or absence of specific daughter products from degradation.

7.3 Site Assessments at DNAPL sites

The standard approaches to site assessment undertaken at most contaminated sites, will not yield the required results in the case of a DNAPL contaminated site. The field investigations for this research have showed that a markedly different approach is needed, and that detailed and accurate understanding of the fractures and their influence on the flow and transport of DNAPLs and their dissolved constituents is required. This can be achieved by using a toolbox of diverse techniques to obtain the required information.

The laboratory measurements, field experiments and multiphase modelling indicated the importance of fractures in controlling DNAPL fate and transport. In the majority of South African aquifers, identification and detailed understanding of the fracture systems is vital. This research indicated that *multiple techniques* must be used to *characterize fractures* and multi-criteria decision-making techniques are required at such sites. At the campus test site, very little correlation was found between outcrop mapping of fractures and the

precise dip and orientation of the controlling fractures.

General site assessments focusing on onsite activities can yield a wealth of valuable information regarding potential pollutants, especially on older industrial sites. In many cases, product sheets and interviews give excellent results in terms of identifying potential groundwater contaminants. This step is vital in successfully targeting the priority contaminants areas and identifying most likely groundwater contaminants, and forming the initial site conceptual model. From this, the decision can be made if the site is a potential DNAPL site and the results can be used to guide the early stages of site assessment.

It is very important to approach drilling at a DNAPL site as an iterative process. This allows improvements to be made in borehole design, materials used, and locations and depths of boreholes and results are obtained, as was done in this project. A once-off drilling program is unlikely to succeed at most DNAPL contaminated sites. An outside-in approach is vital at DNAPL sites, and the most appropriate approach for each site must be followed. Percussion drilling was found to be cost effective and rapid and is appropriate for drilling outside the DNAPL source zone. This type of drilling limits the amount of information on smaller fractures, vertical features and accurate geological description that can be obtained during the invasive phase of an investigation. The method may lead to volatilization of VOCs. Although core drilling is a more expensive technique, the results obtained under controlled and industrial site conditions show that it gives vital information for detailed fracture characterization. Core drilling is especially important for vertical fractures and identification of potential preferential flow zones. It allows the accurate delineation of different magnitudes of fracture and this information will lead to improved conceptual models for DNAPL sites in this country. It is strongly recommended that where fractures play an important role in the transport of DNAPLs, the drilling of at least one or two core boreholes be part of the site characterization since the benefits should greatly exceed the increased costs.

Laboratory and field observations showed that the material for casing used is very important and consideration must be given to inertness in terms of NAPLs. The position

of casings and screens is very important; otherwise, the measurements do not reflect the true concentrations within a plume. The field experiment using a surrogate DNAPL indicated the importance of installation of sumps and plugs for DNAPL contaminated sites.

The research also showed that the considerations for *design and borehole siting* for the initial drilling, the detailed site characterisation and for MNA and other remediation are very different, and the objectives of each borehole need to be clearly defined prior to commencement of each drilling program.

The hydraulic observations are often more valuable than other measurements in determining preferential flow. At both test sites, it was shown that multiple boreholes are required to correlate fracture positions and determine regional and local dip of fracture. The results on both test sites have shown slug tests to provide a good first order indication of the hydraulic properties of importance in mass transport. Comparison of results from differing durations of pumping indicates that longer duration tests provide better information on the fracture connectivity across the study area.

Point dilution tracer tests are cost effective and fairly rapid methods of determining major flow zones in aquifer. The experiment evaluates the Darcy and seepage velocity of fractures or sections of an aquifer that are important in estimating the migration rate of dissolved DNAPL phases. The estimated velocities and fracture positions must be correlated with the pumping test for a better conceptual model development. Tracer testing using *radial convergent* forced gradient tests showed that in fractured rock, anisotropic mass transport occurs. This has very important implications for remediation of DNAPLs and the success of remediation in South Africa.

Soil quality results are very important for the mass balance and to determine the distribution of contaminants between different portions of the subsurface. Test Site 1 indicated the importance of determining f_{oc} in soils so that retardation can be estimated. It was also evident that the less mobile phases such as PAHs are more likely to be found in the soils, implying that the relative concentration of organic contaminants determined in the soils will not be indicative of the expected distribution within fractured rock aquifers.

Inorganic water quality must not be overlooked in characterization of DNAPL sites. It was found that these values provide useful information on different sources/aquifers and changes in conditions. This information was also vital information for MNA assessment and must be included in the assessment of DNAPL sites. Furthermore it was seen that the distribution of different inorganic parameters yields important information of the flow paths, which could be very useful for the delineation of aqueous phase plumes from DNAPL sites.

Organic concentrations measured in observation boreholes can often be lower than the true concentration existing in the adjacent aquifer matrix. This can be the result of incorrect placement and/or construction of the borehole relative to a plume centre line and inherent heterogeneity of the aquifer system. The correct sampling position within the borehole must be selected based on the intersection of preferential flow paths. If the borehole (and/or screened intervals) were placed offset from the plume centre line, sampled concentrations would be lower than in the aquifer. This is because contaminant concentrations decrease in the transverse direction (both horizontally and vertically) away from the plume centre line.

The development of conceptual models through detailed site characterization is key to successful management of DNAPL sites. The field investigations showed the integration of results from the different techniques is needed to develop conceptual model for different aspects of DNAPL site investigation. The most important aspects would include determination of preferred DNAPL pathways and the size, orientation and density of the fracture network. The work done on both field sites showed that this is a continuous process of improvement in understanding. The available information is utilized in different ways for optimization of sampling, monitoring design, modelling and consideration of natural attenuation and/or remediation.

Numerical modelling is an effective tool for designing laboratory and field-scale experiments and can be used to perform sensitivity and uncertainty analysis in the study of DNAPL migration and remediation (Grant and Gerhard, 2004).

A “traditional” numerical model such as MODFLOW does not take into account the

properties of the DNAPL fluid and can therefore not simulate the fluid movement within a fractured aquifer system. A numerical model such as MODFLOW will be useful to simulate dissolved transport at a DNAPL contaminated only after site and the fracture characterization was performed to determine the potential extent of the NAPL source zone. UTCHEM is a 3-D, multi-component, multiphase, compositional model of chemical flooding processes which can account for complex phase behaviour, chemical and physical transformations and heterogeneous media properties, can be used for multi-phase modeling. The sensitivity analysis showed that the UTCHEM model is very sensitive to the fracture parameters, especially the hydraulic conductivity and fracture dip, and therefore the results from proper fracture characterization, needs to be incorporated into the conceptual model.

Research was undertaken by Grant and Gerhard (2004), comparing six published multi-phase flow models. They concluded that attempting to infer DNAPL source configuration from down gradient concentrations or to predict site remediation times remains uncertain until such time as a comprehensive mass-transfer expression is derived and validated.

7.4 Management and Regulation of DNAPLs in South Africa

The need for South African-specific guidelines for dealing with DNAPLs was identified as a high priority. It was recommended that a *common framework with a systematic methodology be applied*. In a country such as South Africa, such a framework must be flexible, pragmatic, consistent and cost-effective. It is therefore considered appropriate that a risk-based approach be followed, with a set of screening trigger values for different common groundwater contaminants. Such a *risk based approach* should include risk assessment and risk management, discussion of uncertainties/confidence level of the risk determination, a full conceptual model of the site with available information, full disclosure of results and risk perspectives. As part of this Hazard Identification, Dose Response Assessment and Exposure Assessment must be provided in the context of the ‘Source-Pathway-Receptor’ paradigm. The method chosen must be focused on the protection of water resources and specifically recognises the statutory responsibilities of

DWAF and other agencies as a function of South African legislation.

As a first step for regulators to take appropriate action at a DNAPL contaminated site, *trigger values* that could be used as a first level of action is recommended. It is suggested that the Intervention Value of the Dutch guidelines be used where available, due to the more extensive nature of the available list and that as a precaution, a trigger value of 0.01% of maximum solubility of any contaminant not found on the list, be used.

Natural attenuation makes use of natural processes to contain the spread of contamination from chemical spills and reduce the concentration and amount of pollutants at contaminated sites. When monitoring of groundwater confirms that natural attenuation processes are acting at a sufficient rate to ensure that the wider environment is unaffected and that remedial objectives will be achieved within a reasonable timescale and are fast enough to limit risks to potential receptors, the process is referred to as *Monitored Natural Attenuation* (MNA). MNA should not be seen as a “do nothing” approach. The evidence required to select it as a mitigation strategy and to prove that it occurs to the required degree, shifts the onus squarely onto the site owner to show that the risks associated with allowing natural attenuation are acceptable. It is recommended that the approach for assessing and implementing MNA in South Africa be a *risk-based* management strategy. The methodology should be based on a multi-stage process, involving structured decision-making and iterative data collection and analysis.

Thus, for MNA to be considered, a detailed study of the contaminated site is required. Natural attenuation is not an appropriate option at all sites. It should be noted that, in more complex environments such as the aquifer conditions common in much of South Africa, where geological formations such as fractured rock aquifers or dolomite occur, these areas will be less likely candidates for natural attenuation. This is because groundwater conditions often have great subsurface variability that makes the prediction of groundwater flow and the associated migration of contamination difficult.

The application of MNA in this country will therefore not succeed without the acceptance of risk-based approaches and the standardisation of the requirements for site assessment, monitoring and remediation.

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ABSTRACT

The potential for the widespread contamination of groundwater by Dense Non-aqueous Liquids (DNAPLs) in South Africa is substantial, because of the extensive production, transport, utilisation, and disposal of large volumes of DNAPL chemicals. There are a great number of potential sites where DNAPLs may have been released to the subsurface in varying quantities. A basic understanding of the nature and occurrence of groundwater in South Africa aquifer systems is a prerequisite for assessment, monitoring and management of DNAPL contaminated sites.

The physical properties of an aquifer that have the greatest impact on the fate and transport of DNAPL contaminants, are the flow rate and flow mechanism present, and the hydraulic conductivity. The major South African aquifer systems have been classified in relation to the dominant flow mechanisms and flow characteristics. The majority of the utilised South African aquifers can be classified as intergranular fractured aquifers. From the results of this study, which included laboratory experiments and the controlled injection of a surrogate DNAPL in the field, it is clear that preferential pathways in fractured rock will determine the flow path of any DNAPL phase contamination. Aqueous plumes of DNAPL contaminants will also be influenced by these pathways (dissolving and or diffusing from the NAPL into the water in fractures and matrix) which can result in spatially variable aqueous plumes in these aquifer systems. The local variations in fracture strike and dip play a far more important role in DNAPL flow than the regional fracture dip or groundwater flow directions.

Natural attenuation processes are important consideration under South African conditions. Relatively high organic carbon in the shallow zones assists in retardation of the organic contaminants, while the large unsaturated zone, arid climate and high temperatures leads to significant loss of contaminant mass through volatilization.

Although the National Water and Environmental Acts of South Africa are very clear on prevention of pollution to, and management of water resources, no guidelines exist on how to deal with DNAPL contaminated sites. Recommendations have been made relating to the regulations that are required for:

- Site assessment
- Sampling and monitoring
- Implementation of monitored natural attenuation

OPSOMMING

Die potensiaal vir wydverspreide besoedeling vanaf “Dense Non-aqueous Liquids” (DNAPLs) in Suid Afrika is substansieel, as gevolg van die omvangryke produksie, vervoer, gebruik en wegmaking van groot volumes DNAPL chemikalië. Daar is ‘n groot aantal potensiële terreine waar DNAPLs in wisselende hoeveelhede vrygelaat is ondergronds. ‘n Basiese insig oor die tipe en voorkoms van grondwater en akwifere stelsels in Suid Afrika, is ‘n voorvereiste vir die ondersoek, monitering en bestuur van DNAPL besoedelde terreine.

Die fisiese eienskappe van ‘n akwifer wat die grootste impak op die beweging en uiteinde van DNAPL kontaminante het, is die vloeï spoed, vloeï meganisme en hidroliese konduktiwiteit. Die meerderheid Suid Afrikaanse akwifere kan as intergranulêre gefrakteerd geklassifiseer word. Die resultate van die navorsing, wat laboratorium toetse en ‘n gekontroleerde vrylating in die veld van ‘n surrogaat DNAPL ingesluit het, het bewys dat die voorkeur vloeipaaie, die vloeipad van die DNAPL fase sal bepaal. Opgeloste pluime van DNAPL kontaminante sal dus ook langs hierdie vloeipaaie beweeg (of deur oplossing en/of deur diffusie na die water in die frakture en matriks) wat kan lei tot ruimtelike variëring van opgeloste pluime in die akwifer. Die lokale variasies in die fraktuur helling en strekking speel ‘n belangriker rol as regionale fraktuur helling of grondwater vloei rigtings.

Onder Suid Afrikaanse kondisies is natuurlike attenuasie prosesse belangrik om te konsidereer. Relatiewe hoë organiese koolstof in die vlak sones sal retardasie van organiese kontaminante aanhelp, terwyl die groot onversadigde zone, droë klimaat en hoë temperature volatilisasie aanhelp.

Alhoewel die Nasionale Water en Omgewings wetgewing baie duidelik is oor voorkoming en bestuur van besoedeling van waterbronne, is daar geen riglyne oor wat by DNAPL gekontaminateerde terreine te doen nie. Aanbevelings is gemaak in verband met regulasies wat benodig word vir:

- Terrein ondersoek
- Monsterneming en Monitering
- Implimentering van gemoniteerde natuurlike attenuasie.

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Appendix A

PHYSIOCHEMICAL PROPERTIES OF DNAPLS, AQUIFER MEDIA, AND ASSOCIATED IMPLICATIONS FOR FATE AND TRANSPORT OF DNAPL

Introduction

Dense Non-Aqueous Phase Liquids (DNAPLs) behave differently from other contaminants in the subsurface. DNAPLs can occur either as pure compounds, a mixture of compounds, or dissolved in water. The unique behaviour results in the complex DNAPL distributions, which are strongly influenced by geologic heterogeneities and the physical properties of the compounds. DNAPL behaviour differs not only in different aquifer material but also from the vadose to the saturated groundwater zone. In this section the factors controlling the behaviour of DNAPLs will be discussed, as well as the distinctive behaviour in different aquifer types, namely porous media, fractured media and porous fractured media. It is especially the latter two types of aquifer media, which are applicable to South African conditions.

Physiochemical properties of DNAPLs

The physical properties of the organic compounds affect their behaviour in the subsurface (Fetter, 1999). Some of these physical properties are, for example, interfacial tension and wettability, density, viscosity, solubility, Henry's law constants, capillary pressure, and relative permeability. Table 1 summarises some of the important physical properties of DNAPL compounds and how these affect their behaviour as groundwater contaminants.

The following sections give a brief overview of some of the properties listed in the table below, and how it relates to the physical concepts of DNAPL migration.

Table 1: Physical properties of DNAPLs which affect their behaviour (Adapted from Fetter, 1999).

| Parameter [and Units] | Derivation | Behaviour |
|--|--|--|
| Melting Point [°C] or Boiling Point [°C] at 1 atm. | Specific phase dependant on temperature | Compound will be present as gas, liquid or vapour as a function of temperature |
| Specific Gravity | Ratio of weight of a given volume of a substance (at 20°C) to weight of same volume of water (at 4 °C) | Substance will float on water if specific gravity of pure substance < 1. Substance will sink in water if specific gravity of pure substance > 1 |
| Water Solubility [ppm or ppb] | A measure of how readily a substance will dissolve in water. Liquids: solubility is a function of the temperature of the water and the nature of the substance. Gases: water solubility must be measured at a given vapor pressure. | More soluble substances have a greater potential mobility. The solubility of organic compounds can range from being completely miscible with water to being totally immiscible (insoluble) with water. |
| Octanol-Water Partition Coefficient (K_{ow}) | A measure of the degree to which an organic substance will preferentially dissolve in water or an organic solvent. The coefficient is the ratio of the equilibrium concentrations of the substance in two immiscible fluids, water and octanol. | The greater the coefficient, the greater the tendency for the substance to dissolve in an organic liquid/solvent and the less mobile the substance will be in the aqueous environment. |
| Distribution Coefficient (K_d) | A measures of how strongly a substance adheres to soil as opposed to remaining dissolved in water or the ratio of the mass of a substance adsorbed per unit mass of soil to the mass of the substance remaining in solution at equilibrium. | Substances with high K_d values are not very water soluble and will preferentially adhere to soils. Such substances are unlikely to be transported as dissolved constituents but rather transported adhered to sediment particles. |
| Vapour Pressure [Pa or mm Hg or psi or atm] | The pressure of the gas in equilibrium with the liquid or solid at a given temperature. A measure of the tendency of a substance to pass from solid or liquid states to a vapour state (i.e. a measure of how readily a substance will evaporate). | The greater the vapor pressure, the more volatile the substance. |
| Vapour Density (of a gas) | The vapour density is related to the equilibrium vapour pressure, the gram molecular weight of the gas and the temperature. | Indicates whether a gas will rise (i.e. gas lighter than air) or sink (i.e. gas denser than air) in the atmosphere. |

| Parameter [and Units] | Derivation | Behaviour |
|-----------------------|--|--|
| Henry's Law Constant | Relates to a linear relation between the partial pressure of a gas above a liquid and the mole fraction of the gas dissolved in the liquid. Can also be applied to organic compounds that are volatile liquids when dissolved in water | The greater the Henry's Law constant, the greater the rate of volatilization from soil or water. |

Density and Viscosity

Density, defined as mass per unit volume, is closely related to specific gravity, which is the ratio of a substance's density to that of water. Mercer and Cohen (1990) states that density differences of ~ 1%, can influence fluid movement in the subsurface, in many situations NAPL densities differ from that of water by 10-50%. The relatively high density of chlorinated solvents means that they may penetrate the water table and flow downward, directed by paths of least capillary resistance, even possibly against the direction of groundwater flow.

Viscosity is a measure of a liquid's internal resistance to flow. Lower DNAPL viscosity results in deeper penetration of an aquifer in a given time. Coal tars and creosote are examples of DNAPLs with high viscosities and thus lower mobility rates as opposed to the halogenated solvents (with low viscosities).

Solubility

When organic chemicals are released into the environment from a mixture like a petroleum hydrocarbon fuel, the water solubilities of the chemicals are typically far lower than their published solubilities. For example, the solubility of benzene is around 1750 mg/l, but typical maximum benzene concentrations resulting from equilibrium between petrol and water are only 20 to 40 mg/l (US EPA, 2001). This occurs because the concentration (or effective solubility) depends on the relative abundance of the chemical in the fuel. This behaviour is based on an extension of Raoult's Law and is related to the relative mole fraction of the contaminant within the total spill or release of organics (Schwarzenbach *et al.*, 1993). This can be calculated as:

$$C_w = x_o S \quad \text{Equation 1}$$

where C_w is the effective solubility, x_o is the mole fraction (of the organic compound in the mixture) and S is its solubility. The mole fraction is calculated from:

$$x_o = MF_x MW_o / MW_x \quad \text{Equation 2}$$

where MF_x is the mass fraction of the selected organic compound in the mixture, MW_o is the average molecular weight of the mixture and MW_x is the molecular weight of the selected compound.

In many studies, the octanol-water partition coefficient, K_{ow} , is used to describe the degree to which an organic substance will preferentially dissolve in water or an organic solvent. The substance is mixed with equal amounts of two immiscible fluids, water and octanol. The coefficient is given by the ratio:

$$K_{ow} = C_{octanol} / C_{water} \quad \text{Equation 3}$$

where $C_{octanol}$ is a measure of the equilibrium concentration of the substance in octanol and C_{water} the equilibrium concentration in water. K_{ow} is usually reported as a logarithm. The greater the value of $\log K_{ow}$, the greater the tendency of the organic substance to dissolve in the organic liquid, rather than in the water. Thus, the larger the octanol-water partition coefficient, the less mobile the compound is in the environment (Fetter, 1999).

Volatility

The pure phase of each contaminant will have its own specific capacity to mobilise from the liquid to gaseous phase. The Henry's Law constant of a compound defines the partitioning of that compound between the air and water phases:

$$K_h = C_a / C_w \quad \text{Equation 4}$$

where K_h is the dimensionless Henry's constant, C_w and C_a are the concentration in mass per volume units in water and air, respectively. This law can be applied to organic compounds that are volatile liquids when they are dissolved in water. The greater the Henry's law constant, the greater the rate of volatilisation from soil to air (Fetter, 1999).

Interfacial Tension

Interfacial tension is a representation of the co-existence of liquids at different pressures, is the most important physicochemical property controlling multiphase fluid migration in the subsurface (Kueper *et al.*, 2003).

At the interface between two liquid phases, the cohesive forces acting on the molecules in either phase are unbalanced: this exerts tension on the interface - similar to that on a stretched membrane - causing the interface to contract to as small an area as possible. A force balanced on a curved interface between two fluids leads to the conclusions that the pressure in the fluids on either side of the interface is not equal, the difference being given by equation:

$$\Delta P = 2\sigma/r \quad \text{Equation 5}$$

Where ΔP is the pressure difference across the interface, σ is the interfacial tension, and r is the radius of curvature of the interface (Pankow and Cherry, 1996).

Interfacial tension is the property that permits two fluids to exist in contact at different pressures. Values of interfacial tension range from about 20 to 50 dynes/cm for most water-DNAPL pairs (Mercer and Cohen, 1990).

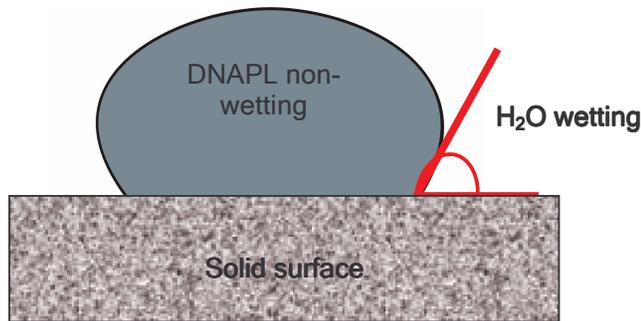
It is important to remember that DNAPLs at field sites have often undergone changes due to weathering or mixing with other compounds, therefore where possible, the interfacial tension of the DNAPL found at the site should be measured.

Wettability

Wettability is a measure of a liquid's relative affinity for a solid. Where two liquid phases are present, the 'wetting' fluid will preferentially spread over the solid surface at the expense of the 'non-wetting' fluid. Wettability is depicted by the concept of a contact angle, the angle subtended by the liquid-liquid interface and the solid surface.

Since wettability conventionally refer to the non-aqueous phase, the angle is measured through the aqueous phase as seen below:

It is commonly the case that DNAPLs are non-wetting relative to water; this relationship is illustrated by the fact that although both fluids are in contact with the solid, the water has a greater affinity for the surface (wetting), which produces a contact angle of less than 90° . This implies that, the majority of DNAPL contaminants will rather be restricted to the larger openings, while water occupies the smaller pore spaces and preferentially



spreads across solid surfaces.

Figure 1: Wettability: Contact angle $< 90^\circ$ then DNAPL equals non-wetting fluid, water equals wetting fluid.

In the rarer case of a DNAPL having greater affinity for a solid (wetting) than water (non-wetting), the contact angle is will be greater than 90° . This is often referred to as an oil-wet surface.

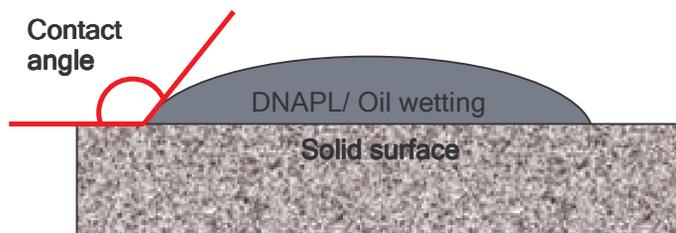


Figure 2: Wettability: Contact angle $> 90^\circ$, DNAPL equals the wetting phase.

From the above cases, it follows that it should be theoretically possible to attain a contact angle of 90° . This neutral condition is approached by mixtures such as crude oil and water and coal-tar and water in which the NAPL can be termed 'neutrally wetting'. In actual fact, phases with contact angles ranging between 75° and 105° are considered neutrally wetting.

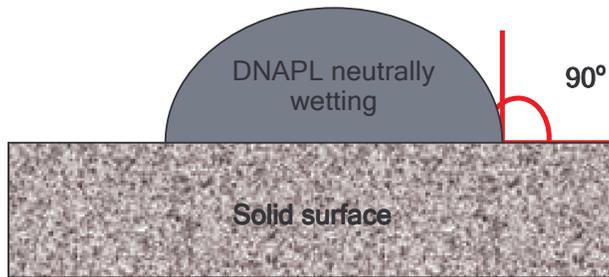


Figure 3: Wettability: Contact angle = 90°, DNAPL is considered neutrally wetting

Although most problematic DNAPLs are non-wetting, taking into account the variation of groundwater composition, DNAPL composition and the characteristics of the solid surfaces, the possibility of complex wettability relationships must be considered at actual field sites.

Capillary Pressure

As explained above, DNAPLs tend to be the non-wetting fluid in aquifers. The curved interface between two fluid phases, DNAPL and water, is determined by the difference in fluid pressure between the wetting and non-wetting phase, and this difference in pressure is termed the capillary pressure (P_c):

$$P_c = \Delta P = P_{nw} - P_w \quad \text{Equation 6}$$

where P_{nw} is the pressure of the non-wetting fluid (DNAPL) and P_w is the pressure of the wetting fluid (water) (Pankow and Cherry, 1996).

Capillary pressure is related to interfacial tension, pore size and contact angle by the following equation:

$$(P_c) = (2 \sigma \cos \theta)/r \quad \text{Equation 7}$$

where σ is the interfacial tension, r is the radius water-filled pore and θ is the contact angle (Mercer and Cohen, 1990).

The geometry of the interstitial pore space is highly complex. If the network of interstitial spaces is seen to be connected by pore throats of smaller dimension, equation (7) would predict the threshold value of the capillary pressure that must be exceeded for DNAPL to pass through a pore throat of radius. There will be no DNAPL access to an interstitial pore until the capillary pressure exceeds the threshold value associated with the largest throat already in contact with the DNAPL. The water-DNAPL interface will then migrate across regions of pore space that support radii of curvature consistent with the prevailing capillary pressure. If the capillary pressure is increased, successively smaller pore throats will be invaded by DNAPL (Pankow and Cherry, 1996).

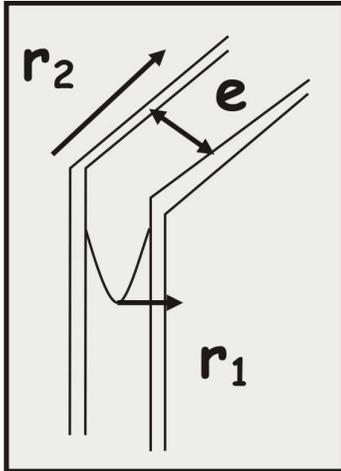


Figure 4: Explanation of capillary pressure between parallel plates/ fracture plane

Equation (7) can be adapted for parallel flat plates (or a fracture plane) to the following:

$$P_c = \sigma (1/r_1 + 1/r_2) \quad \text{Equation 8}$$

If it assumed that the length of the fracture $r_2 = \infty$ then:

$$r_1 = e/2 \quad \text{Equation 9}$$

Where e is the fracture aperture and then:

$$P_c = (2\sigma \cos \theta)/e \quad \text{Equation 10}$$

(Thomson, 2004).

The following figure shows the relationship between fracture aperture, transmissivity and the required entry pressure (in mm head), that needs to be overcome, to enter the fracture for TCE. The graph below shows this relationship.

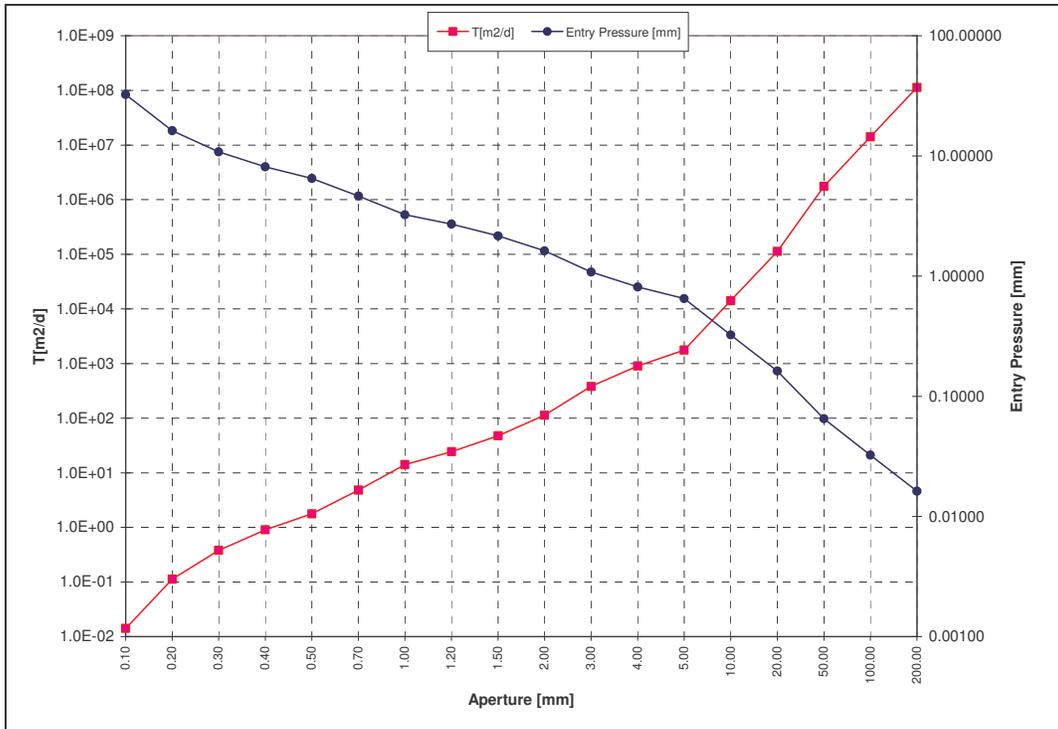


Figure 5: Entry pressure and transmissivity vs. Fracture aperture

From this graph it can be seen that the relationship of transmissivity to fracture aperture is non-linear and almost logarithmic. As a consequence the required entry pressure decreases non-linearly for larger fracture apertures. For example a fracture aperture of 0.2 mm will require ± 16.24 mm of “pooled” TCE to enter into the fracture. A fracture aperture of 2 mm will require only 1.62 mm of “pooled” TCE to enter into the fracture.

Capillary pressure, Saturation and Hysteresis

The above equations describe capillary pressure for ideal homogeneous porous media or flat parallel plates. Geologic media however is made up of various interface geometrics and radii of curvature at each pore or pore throat. The macroscopic average capillary pressure is needed to describe the relationship between DNAPL invasion and the water saturation in the media. This relationship is known as the capillary pressure-saturation function or sometimes as the capillary pressure curve (Pankow and Cherry, 1996).

The fluid contents are expressed in terms of the fraction of the total interstitial void volume occupied by each fluid. If V_v is the void volume in a representative element of bulk porous medium, then:

$$S_w = V_w/V_v \quad \text{Equation 11}$$

$$S_{nw} = V_{nw}/V_v \quad \text{Equation 12}$$

$$S_w + S_{nw} = 1 \quad \text{Equation 13}$$

Where V_w and V_{nw} are the volumes of wetting and non-wetting fluids, respectively, and S_w and S_{nw} are the relative volumes of wetting and non-wetting fluids expressed as a fraction of the pore volume. These relative volumes are referred to as saturations (Pankow and Cherry, 1996).

The capillary pressure saturation function $P_c(S_w)$ is measured in experimental cells, where a NAPL source is allowed to invade a saturated porous medium (at incremental increased NAPL pressures) and the subsequent volume of displaced water is measured at these pressure intervals. Capillary pressure-saturation curves can then be derived for different media and DNAPL components. Figure 6 is an example of such a curve.

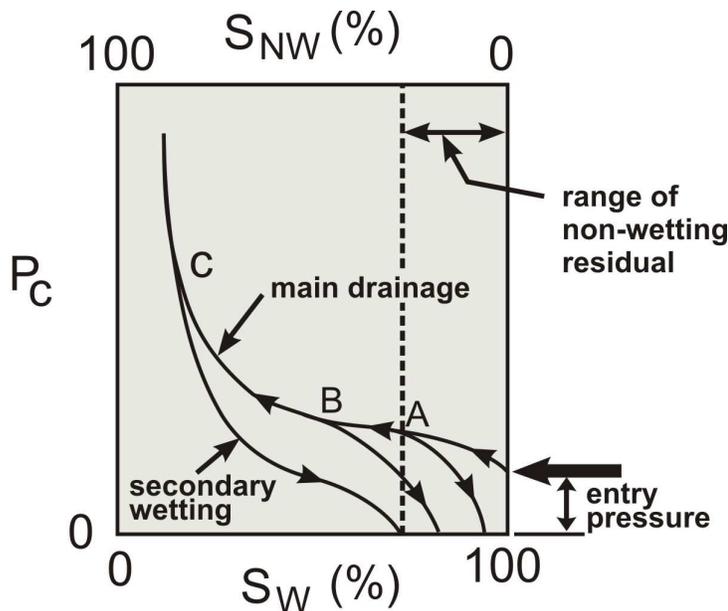


Figure 6: Capillary pressure-saturation curve (From Thomson, 2004).

From the derived curves, it was found that as was previously stated by equation (7), the DNAPL would only start to invade the media continuously once the threshold value has been reached. This capillary pressure is known as the *entry pressure* (also see Figure 5 and Figure 6). For most materials entry pressure corresponds to a water saturation in the range 0.8 to 0.95 (Pankow and Cherry, 1996).

These curves have been derived under conditions where the water saturation first has decreased and the capillary pressure increased as a result of the DNAPL invasion, this process is known as drainage. Once the source of DNAPL is exhausted, the DNAPL will continue to migrate away from the source and will be replaced by water in that zone. The situation has now changed from one of increasing water saturation to decreasing capillary pressure, known as wetting. The capillary pressure is less during the wetting process than during the drainage. The relationship between drainage and wetting is however not equal, which leads to a type of hysteresis.

This results in what is known as residual DNAPL saturation ($1-S_m$) where S_m is the maximum water saturation achievable during the wetting process. What is known as residual DNAPL, is typical blobs and fingers of DNAPL which have been cut off and disconnected from the continuous DNAPL body by invading water.

Based on the understanding of these pore level processes, estimations of hydrostatic conditions in actual field investigations can be made. Such invasion relationships will typically be DNAPL pool heights required for invasion across a capillary barrier, or fracture aperture required to stop downward migration. These relationships will be discussed in more detail in the following sections.

Aquifer Media parameters

Relative Permeability

Permeability or hydraulic conductivity (K) is the single-phase fluid conductivity of a porous material, and defined in terms of measurable quantities by Darcy's law equation:

$$K = q\mu L / A\Delta P \quad \text{Equation 14}$$

Where μ is the viscosity of a compressible fluid, which is forced to flow at a flow rate q , through a porous medium of length L , and with a cross section A , such that the pressure difference across the length of the porous medium is ΔP . The value of this permeability is determined by the structure of the rock. In a fractured rock, the permeability will depend on the density and the width of the apertures.

In the case where two or more fluids are flowing simultaneously through a porous medium, a *relative permeability* for each of the fluids can be defined. This describes the extent to which one fluid is hindered by the other. The relative permeability is defined by setting the Darcy equation individually for each phase (i) that flow in the pore space:

$$q_i = (Kk_{ri}/\mu_i)A \Delta p_i / \Delta x \quad \text{Equation 15}$$

Where, k_{ri} is the relative permeability for phase i . The usual assumption is that k_{ri} is a function of the saturation of the phase i , and constitutes a rock property.

Bulk retention capacity

The bulk retention capacity of a porous or fractured medium is defined as the volume of NAPL divided by the overall volume of medium within which the NAPL migration pathways occurred. This overall volume includes the total volume of soil, gas, and liquid through which the NAPL has migrated. In other words, this overall volume of medium includes both those lenses and laminations in which residual and pooled NAPL is present and the adjacent lenses and laminations void of NAPL. The concept of bulk retention capacity is particularly useful at real sites where it is virtually impossible to detect each individual lens and lamination containing residual and pooled NAPL.

The bulk retention capacity is dependent upon several factors, including the nature of the release (e.g., slow dripping versus catastrophic spill), interfacial tension, and the bedding structure of the medium. The bulk retention capacity of natural deposits generally will be much less than laboratory-derived values because of the heterogeneous nature of field deposits. For typical silt, sand, and gravel deposits exhibiting structure, DNAPL bulk retention capacities are expected to range between 0.25 percent and 3 percent by bulk volume, with the lower values in this range applicable to more heterogeneous deposits not having laterally extensive capillary barriers. This range of bulk retention capacities is based on a variety of field experiments involving the release of DNAPL into a natural sand aquifer (Kueper, *et al.*, 1993; Poulsen and Kueper, 1992; Brewster, *et al.*, 1995).

Retardation factors

The partitioning of components from the water phase to solid matter such as on soil particles and fracture walls is referred to as sorption. Sorption can be classified as *adsorption*, which refers to the partitioning of components to the actual surface of solid matter, and *absorption*, which refers to the diffusion of components into the pore space within soil grains. Having diffused into a grain or other solid particle, components may also adsorb to the interior surfaces of these particles. For typical organic contaminants, the degree of adsorption is a function of the type of organic compound, the degree of organic carbon present on the solid surfaces, and the mineral type.

At sites where sorption is occurring, the contaminant plume will migrate at a slower rate than the groundwater. This process is commonly referred to as retardation. The ratio of groundwater velocity to contaminant velocity can be characterized by the retardation factor:

$$R = 1 + \frac{B_d}{\theta} K_d \quad \text{Equation 16}$$

and

$$v_c = v_x/R \quad \text{Equation 17}$$

Where R is the retardation factor, B_d is the dry bulk density of the medium, θ is the medium porosity, K_d is the distribution coefficient. u_c is the average linear groundwater velocity, and u_x is the velocity of the contaminant front. Equation (16) assumes an equilibrium sorption process. Modifications need to be made in cases where the sorption process is rate limited (Fetter, 1999).

The distribution coefficient, K_d , is often approximated as:

$$K_d = K_{oc} f_{oc} \quad \text{Equation 18}$$

Where K_{oc} is the organic carbon partition coefficient and f_{oc} is the fraction organic carbon present on the solid matter. K_{oc} can be estimated using empirical relationships that are a function of either K_{ow} , the octanol-water partition coefficient, or the aqueous solubility of the compound of interest (Fetter, 1999). These estimation methods are subject to a certain degree of uncertainty. If accurate definitions of K_d or R are required, laboratory batch tests, column tests, and pilot field tests should be considered.

Rivett and Allen-King (2003) performed controlled field experiments with multi-component DNAPLs, to investigate the effect on the dissolved plume retardation. The results showed that when plumes contain mixed solutes sorption will be nonlinear. It is clear that the degree of retardation experienced by a particular contaminant (or contaminant mixture) is a function of both the medium through which solute transport is occurring and the nature of the particular contaminant. Retardation factors will therefore be site-specific.

The following sections are a summary of the main processes affecting contaminant transport and therefore, cause natural attenuation. Emphasis is placed on the degradation pathways of chlorinated hydrocarbons (CHCs), as examples of common DNAPLs.

Influence of Chemical complexity on DNAPL behaviour

The discussion above has focused on the behavior of pure phase organic fluids. However, many DNAPL wastes that are produced in manufacturing and industrial operations are complex mixtures of organic compounds. The behavior of such chemically complex mixtures of organic compounds can vary significantly from the single component DNAPLs and, consequently, should be considered when assessing or remediating sites with complex, multi-component DNAPLs. The following sections describe some of the impacts of complex chemical composition on DNAPL transport and distribution in the subsurface.

Effect of Polar or Ionizable Constituents on Capillary Phenomena

The presence of polar or ionizable compounds in DNAPLs can significantly affect NAPL-water interfacial tension and the wetting character of the DNAPL (Dawson and Illangasekare, 1999). As shown before, these parameters are integral to the definition of capillary pressure. Lower DNAPL-water interfacial tension will lead to a greater degree of miscibility between the fluids and therefore a greater potential for DNAPL to enter into smaller pore spaces.

Single component, non-polar organic liquids, such as the aliphatic and aromatic hydrocarbons, have interfacial tensions ranging from 20 to 50 dynes/cm. The same is true of multi-component or mixed DNAPLs composed only of non-polar organic compounds (Mercer and Cohen, 1990). Dawson and Illangasekare (1999), observed lower interfacial tensions for DNAPLs that contain some fraction of polar or ionizable organic components, particularly amphiphilic compounds such as surfactants that have an affinity for both the aqueous and organic liquid phases. Similar reductions in interfacial tension have been observed with the introduction of organic acids into water-NAPL systems. DNAPLs, such as coal tar, containing ionizable organic components have also been shown to be pH-dependent (Dawson and Illangasekare, 1999). Figure 7 shows dramatic decreases in NAPL-water interfacial tension were observed when ionizable organic constituents were present in anionic (high aqueous pH), neutral form (low aqueous pH). In contrast, the interfacial tension of non-polar compounds such as trichloroethylene does not vary with pH (Barranco *et al.*, 1997).



Figure 7: Photomicrographs of a coal tar-water system and aqueous pH 7 and pH 12. (Needle size for scale: o.d. = 0.52 mm). (Barranco and Dawson, 1998)

Significant reduction in interfacial tension occurs as a function of increasing ionic strength. This phenomenon presumably occurs because an increase in the concentration of aqueous ions promotes stronger interactions with the functional groups of polar constituents in the NAPL phase (Dawson and Illangasekare, 1999).

Wettability

As described earlier, contact angles less than 90° generally indicate that water is the wetting phase relative to the DNAPL, whereas contact angles greater than 90° indicate the DNAPL is the wetting phase relative to water. In general, the wetting fluid will tend to coat mineral surfaces and occupy the smaller pore openings in porous media. Many factors influence the wettability of a system, including DNAPL and aqueous-phase composition, presence of organic matter, mineralogy, and saturation history (Dawson and Illangasekare, 1999). Changes in wettability, will affect a number of properties that influence multiphase flow, including capillary pressure, relative permeability, and residual saturation.

Strong water wetting conditions exist for most aquifers containing DNAPLs composed of non-polar (e.g., saturated hydrocarbons) or relatively non-polar constituents (e.g., chlorinated organic hydrocarbons) (Barranco et al, 1997). This condition exists because interaction between non-polar, hydrophobic DNAPL constituents and hydrophilic minerals (e.g., quartz) is energetically unfavorable. However, wetting behavior that deviates from that observed for non-polar DNAPLs has been observed for systems containing polar or ionizable organic compounds. These include typically high-molecular-weight compounds found in mixtures with coal tar, creosote, and some fuel oils (Barranco and Dawson, 1998).

The wettability of systems containing water and NAPLs with ionizable organic constituents is dependent upon the type and concentration of the ionizable constituents as well as the aqueous chemistry. If the sign of the mineral surface charge is opposite to that of an ionized organic constituent, then electrostatic attraction between the organic molecule and the surface will occur at the mineral surface or in the thin film of surrounding water. Conversely, ionizable organic constituents with the same sign charge as the surface will be repulsed from the near-surface water (Dawson and Illangasekare, 1999).

Wettability is also dependent on aqueous pH, since pH influences the speciation of ionizable organic constituents as well as the charge of the mineral surfaces present. Figure 9 shows that quartz wettability changes from coal tar-wet to water wet as pH is varied from 7 to 12 (Barranco and Dawson, 1998).

Changes in NAPL Character over Time or Space

DNAPL wastes may exhibit a range of properties, depending on the mix of constituents that comprise the DNAPL. The composition can vary due to the altering of pure chemical substances by industrial processes, prior to disposal. Degradation and transport processes will also cause changes to the chemical structure and character of the DNAPL over time and space in the subsurface.

The combination of higher molecular weight constituents, with lower molecular weight components can cause an increase in the bulk density of a DNAPL. Coal tar, an example of a multi-component DNAPL, generally has a density slightly greater than 1 gm/cm^3 as a result of a number of high-molecular weight, asphaltenic constituents, even though most coal tars are composed predominantly of low density mono-aromatic hydrocarbons (EPRI, 1993).

Viscosity can also varies considerably among constituents of DNAPLs. As with density, the viscosity of multi-component DNAPLs increases with increasing content of higher molecular-weight constituents in the mixture. For example, coal tar has a

significantly higher viscosity (approximately 20 cP;) than its mono-aromatic hydrocarbon constituents (e.g., benzene: 0.65 cP) (EPRI 1993).

Mixing of such NAPLs in the subsurface, due to repeated spills of different NAPLs or both LNAPLs and DNAPLs, can significantly alter the character of the NAPL over time and space. The multi-component nature of complex NAPL wastes may result in changes in their properties over time or as the NAPL migrates due to differential volatilization, dissolution, sorption and degradation of constituents (Cohen and Mercer, 1993). For example, lighter, more volatile components of fuels may volatilize over time, leaving a heavier, less volatile NAPL in the subsurface. This process is typically referred to as weathering (or degradation). The weathered product may have transport characteristics that are considerably different than the original product. Awareness of the possible changes to the character and migration properties of a DNAPL is very important when decisions regarding site characterization or remediation options are made.

Appendix B1

Selected DNAPLs with Viscosity (cp) and Specific Gravity Appearance/occurrence and uses. (Sources: Cohen & Mercer, 1993, www.epa.gov/safewater/contaminants/; www.epa.gov/iris/; www.chemicaland21.com/; www.eco-usa.net/toxics/; www.atsdr.cdc.gov/ and www.speclab.com/)

| DNAPL | Acronym | Absolute viscosity | Specific Gravity | Appearance and Use |
|------------------------------|------------------------------|--------------------|------------------|---|
| Halogenated Hydrocarbons | | | | |
| 1,1,1-Trichloroethane | 1,1,1-TCA, Methyl chloroform | 1.20 | 1.339 | It is a colorless liquid with a sharp, sweet odor and does not occur naturally in the environment. It is found in many common products such as glue, paint, industrial degreasers, and aerosol sprays. |
| 1,1,2,2-Tetrabromoethane | Acetylene tetrachloride | 9.79 | 2.875 | Clear to pale yellow liquid with pungent odour. It is used as a flame retardant/fire extinguishing ingredient, solvent for fats, oils, greases, and a chemical intermediate. It is also used in separating minerals. |
| 1,1,2,2-Tetrachloroethane | Acetylene tetrabromide | 1.75 | 1.595 | It is a manufactured, colorless chemical and has a sweet odor. It does not burn easily but is volatile. In the past, it was used in large amounts to produce other chemicals and as a solvent, to clean and degrease metals, and in paints and pesticides. It presently is used only as a chemical intermediate in the production of other chemicals. |
| 1,1,2-Trichloroethane | 1,1,2-TCA | 0.12 | 1.440 | It is an organic liquid with a chloroform-like odor. It does not burn easily, can be dissolved in water, and evaporates easily. It is used as a solvent and as an intermediate in the production of the chemical, 1,1-dichloroethane. Major Industries where it can be found: Alkalies, chlorine, photograph equipment, meat packing plants, petroleum refining, blast furnaces, and steelworks. |
| 1,1,2-Trichlorofluoromethane | Freon 11 | 0.42 | 1.487 | It is used as a solvent, chemical intermediate, blowing agent for polyurethane foams and polymeric foams, dry cleaning agent, aerosol propellant and in fire extinguishers. It is also used in the manufacturing of aerosol sprays, commercial refrigeration equipment, as an "inert" ingredient in pesticides and cleaning compounds. Very resistant to chemical and biological degradation and likely to be a persistent contaminant if it reaches groundwater. |

| DNAPL | Acronym | Absolute viscosity | Specific Gravity | Appearance and Use |
|------------------------|----------------------|--------------------|------------------|---|
| 1,2,4-Trichlorobenzene | 1,2,4-TCB | 1.42 | 1.454 | It is an aromatic, colorless organic liquid. The greatest use of 1,2,4-trichlorobenzene is primarily as a dye carrier. It is also used to make herbicides and other organic chemicals; as a solvent; in wood preservatives; and in abrasives. It was once used as a soil treatment for termite control. Major environmental releases of 1,2,4-trichlorobenzene are due to its manufacture and use as a dye carrier from textile finishing industries. |
| Ethylene dibromide | EDB | 1.72 | 2.179 | EDB is a colorless liquid with a mild sweet odor, like chloroform. It is used as an additive to leaded petrol; as a fumigant to protect against insects and pests in a number of crops and on turf; spot treatment of milling machinery; and is also used as an intermediate for dyes, resins, waxes, and gums. |
| Hexachlorobutadiene | HCBD | 2.45 | 1.554 | Hexachlorobutadiene is a colorless liquid with a turpentine-like odor. It is mainly used to make rubber compounds. It is also used as a solvent, and to make lubricants, in gyroscopes, as a heat transfer liquid, and as a hydraulic fluid. |
| Iodomethane | Methyl iodide | 0.52 | 2.279 | It is a colourless liquid with a sweet, pungent odour. The primary use is as a chemical intermediate in the manufacture of certain pharmaceuticals and pesticides. It is also used in methylation processes and in the field of microscopy. To a lesser extent, it has been used in fire extinguishers and as an insect fumigant. |
| Methylene chloride | Dichloromethane | 0.43 | 1.327 | Methylene chloride is a colorless liquid with a mild, sweet odor. It is used as an industrial solvent and as a paint stripper. It may also be found in some aerosol and pesticide products and is used in the manufacture of photographic film. |
| Pentachloroethane | Ethane pentachloride | 2.75 | 1.680 | Colourless liquid with chloroform smell. Used as solvent for oil and grease in metal cleaning; separation of coal from impurities, dry cleaning; in soil sterilisation; in organic synthesis as a drying agent for timber immersed in it at temperatures greater than 100 deg C. Also is used as a solvent for cellulose acetate, certain cellulose ethers, resins and gums. |

| DNAPL | Acronym | Absolute viscosity | Specific Gravity | Appearance and Use |
|-------------------------|------------------------|--------------------|------------------|---|
| Tetrachloroethene | Perchloroethylene, PCE | 0.89 | 1.623 | It is a nonflammable, colorless liquid at room temperature which readily evaporates into air and has an ether-like odor. It is a manufactured chemical that is widely used in the dry-cleaning of fabrics. It is also used for degreasing metal parts and in manufacturing other chemicals. It is found in consumer products, including some paint and spot removers, water repellents, brake and wood cleaners, glues, and suede protectors. |
| Bromochloromethane | Chlorobromoethane | 0.99 | 1.495 | Clear colourless to pale yellow liquid, with sweet chloroform like odour. As a chemical intermediate and limited use as fire extinguishing agent. |
| Bis(2-chloroethyl)ether | | 2.14 | 1.220 | It is a colorless, nonflammable liquid with a strong unpleasant odor. It dissolves easily in water, and some of it will slowly evaporate to the air and does not occur naturally. Most of it is used to make pesticides. Some of it is used as a solvent, cleaner, component of paint and varnish, rust inhibitor, or as a chemical intermediate to make other chemicals. |
| Bromodichloromethane | Dichlorobromomethane | 1.71 | 1.980 | It is a colorless, nonflammable liquid. Algae in the oceans form small amounts naturally. The small quantities that are produced are used in laboratories or to make other chemicals. However, most bromodichloromethane is formed as a by-product when chlorine is added to drinking water to kill bacteria. |
| Bromoethane | Ethyl bromide | 0.42 | 1.460 | Colorless to yellow liquid with ether like odor. Ethyl bromide is used as a solvent, as an anesthetic in medicine, as a refrigerant, as a fumigant. It is an ethylating agent in organic synthesis and is used in petrol. |
| Carbon tetrachloride | Tetrachloromethane | 0.97 | 1.594 | It does not occur naturally. It is a clear liquid with a sweet smell that can be detected at low levels. It is most often found as a colorless gas. It is not flammable and does not dissolve in water easily. It was used, but are now banned, in the production of refrigeration fluid, propellants for aerosol cans, as a pesticide, as a cleaning fluid and degreasing agent, in fire extinguishers, and in spot removers. |

| DNAPL | Acronym | Absolute viscosity | Specific Gravity | Appearance and Use |
|---------------------|--------------------------|--------------------|------------------|---|
| Chlorobenzene | Benzene chloride | 0.80 | 1.106 | It is a colorless, flammable liquid with an aromatic, almond-like odor. Some of it will dissolve in water, but it readily evaporates into air. It does not occur naturally in the environment. It was used in the past to make other chemicals, such as phenol and DDT. The greatest use of chlorobenzene is in the manufacture of other organic chemicals, dyestuffs, and insecticides. It is also a solvent for adhesives, drugs, rubber, paints and dry-cleaning, and as a fiber-swelling agent in textile processing. |
| Chloroform | Trichloromethane | 0.58 | 1.483 | Chloroform is a colorless liquid with a pleasant, nonirritating odor and a slightly sweet taste. It was used in the past as an inhaled anesthetic during surgery. Today, chloroform is used to make other chemicals and can be formed in small amounts when chlorine is added to water. |
| m-Chlorotoluene | | 0.75 | 1.072 | Clear liquid slightly soluble. It is used as a solvent and as an intermediate for organic synthesis especially for dyes. |
| o-Chlorotoluene | 2-Chloro-1-methylbenzene | 0.75 | 1.082 | Clear liquid slightly soluble. It is used as a solvent and as an intermediate for organic synthesis especially for dyes. |
| 1,2-Dichlorobenzene | o-Dichlorobenzene | 1.32 | 1.305 | It is a colorless to pale yellow liquid with a pleasant odor. Dichlorobenzenes belong to the group of organic halogen compounds replacing two hydrogen atoms in benzene by chlorine atoms. There are three isomers. It is used as a solvent, a chemical intermediate to manufacture dyes, agrochemicals, pharmaceuticals, and other organic synthesis. It is an insecticide and a fumigant. The effluents from industrial and sewage treatment plants; pulp and paper mill effluents; effluents from iron and steel manufacturing, and petroleum refinery effluents have been identified a sources to the environment of this chemical. |
| 1,3-Dichlorobenzene | m-Dichlorobenzene | 1.04 | 1.288 | |

| DNAPL | Acronym | Absolute viscosity | Specific Gravity | Appearance and Use |
|--------------------------|---------------------------------|--------------------|------------------|--|
| trans-1,2-Dichloroethane | trans-1,2-DCE | 0.40 | 1.257 | It is a colorless liquid with a sharp, harsh odor. It is used to produce solvents and in chemical mixtures. Also solvent; degreasing agent; paint remover ingredient; aerosol products ingredient; blowing agent in foams; refrigerant. |
| 1,2-Dichloropropane | Propylene dichloride | 0.86 | 1.560 | It is a colorless, flammable liquid with a chloroform-like odor. It was used in the past as a soil fumigant, chemical intermediate, and industrial solvent and was found in paint strippers, varnishes, and furniture finish removers. Most of these uses were discontinued. Today, almost all of the 1,2-dichloropropane is used as a chemical intermediate to make perchloroethylene and several other chlorinated chemicals. |
| 1,1-Dichloroethane | 1,1-DCA | 0.44 | 1.176 | Industrial chemical that is not found naturally in the environment. It is a colorless liquid with a mild, sweet smell. It is used to make certain plastics, such as flexible films like food wrap, and in packaging materials. It is also used to make flame retardant coatings for fiber and carpet backings, and in piping, coating for steel pipes, and in adhesive applications. |
| 1,2-Dichloroethane | Ethylene dichloride; 1,2-DCA | 0.80 | 1.235 | It is a clear liquid and has a pleasant smell and sweet taste. The most common use is in the production of vinyl chloride which is used to make a variety of plastic and vinyl products including polyvinyl chloride (PVC) pipes, furniture and automobile upholstery, wall coverings, housewares, and automobile parts. It is also used to as a solvent and is added to leaded petrol to remove lead. |
| 1,1-Dichloroethene | Vinylidene chloride; 1,1-DCE | 0.36 | 1.218 | Colourless liquid, with chloroform like smell. (spacing required) Virtually all it produced is used in the production of copolymers with vinyl chloride or acrylonitrile. A small percentage (4%) is used as chemical intermediates. It is used to make certain plastics, such as flexible films like food wrap, and in packaging materials. It is also used to make flame retardant coatings for fiber and carpet backings, and in piping, coating for steel pipes, and in adhesive applications. |

| DNAPL | Acronym | Absolute viscosity | Specific Gravity | Appearance and Use |
|---|-----------------------------|--------------------|------------------|--|
| Bromoform | Tribromomethane | 2.02 | 2.890 | It is colorless to yellow, heavy, nonflammable, liquid with a sweet odor. Plants in the ocean form small amounts naturally. They are somewhat soluble in water and readily evaporate into the air. Most of it that enters the environment is formed as byproducts when chlorine is added to drinking water to kill bacteria. Only small quantities are produced, it was used in the past as solvents and flame retardants, or to make other chemicals, but now it is used mainly as laboratory reagents. Also used in synthesis of sedative, antitussive and antiseptic medication; as a heavy liquid floatation agent in mineral separation, sedimentary petrographical surveys, and purification of materials such as quartz; as an industrial solvent in liquid-solvent extractions, in nuclear magnetic resonance studies; as a catalyst, initiator, or sensitizer in polymer reactions, and in vulcanization of rubber. |
| Trichloroethene | TCE | 0.57 | 1.464 | Trichloroethylene is a heavy, stable, toxic, nonflammable liquid with a chloroform aroma. Because of concerns about its toxicity, the use is declining. It is prohibited to use in food, drugs and cosmetics. It is now mainly used in vapor degreasing of fabricated or assembling metal parts. It is also used as an industrial solvent in extraction processes, as a diluent in paints and adhesives, in textile processing, and other ways. It is used as a chain terminator for PVC production. It is also used as a refrigerant, as a heat exchange liquid, as a chemical intermediate or raw material in the production of chloroacetic acid, pesticides, gums, resins, tars, paints and varnishes. It is used in dry cleaning operations. |
| Other (incl. components of coal tar and creosote) | | | | |
| Dibutyl phthalate | Dibutyl-n-phthalate; DBP | 20.30 | 1.046 | Clear liquid, slight odor, slightly soluble. DBP, a member of the phthalic acid ester plasticizer, imparts flexibility and impacts strength of plastics. It is used as an ingredient of insect repellent, a solvent in lacquer and perfume fixative, a dye carrier, and as a textile lubricating agent and solid rocket propellant. |

| DNAPL | Acronym | Absolute viscosity | Specific Gravity | Appearance and Use |
|--------------------|-------------|--------------------|------------------|--|
| 1-Nitropropane | UN 2608 | 0.80 | 1.008 | Almost colorless liquid with a mild, fruity odor. Solvent for cellulose acetate, vinyl resins, lacquers, synthetic rubbers, fats, oils, dyes and protective coatings; rocket propellant; organic intermediate for agrochemicals and pharmaceuticals; solvent-extraction processes; and fuel additive. |
| Diethyl phthalate | DEP | 35.00 | 1.118 | It is a colorless liquid that has a bitter, disagreeable taste. This synthetic substance is commonly used to make plastics more flexible. Products in which it is found include toothbrushes, automobile parts, tools, toys, and food packaging. It can be released fairly easily from these products, as it is not part of the chain of chemicals (polymers) that makes up the plastic. It is also used in cosmetics, insecticides, and aspirin. |
| Dimethyl phthalate | DMP | 17.20 | 1.191 | It is clear oily liquid, slightly soluble. It is used as an ingredient of insect repellent. It is used as a solvent in lacquer and paint and as a dye carrier. It is used as a textile lubricating agent and solid rocket propellant. Also cosmetic ingredient, fluidized bed coating in manufacture of poly(vinylidene fluoride); plasticizer in cellulose acetate and nitrocellulose and plastics, resins, rubber; constituent of rubber. |
| Aniline | Benzenamine | 4.40 | 1.022 | It is a pale brown liquid with a characteristic odor, is slightly soluble in water, and mixes readily with most organic solvents. It is obtained commercially from chlorobenzene by heating with ammonia in the presence of copper catalyst or from a product of coal tar (nitrobenzene) through the reduction reaction. It is the starting material in the dye manufacturing industry and as in the manufacture of others. Aniline is converted into sulfanilic acid which is the parent compound of the sulfa drugs. It is also important in the manufacture of rubber-processing chemicals, antioxidants and varnishes. Amines take part in many kinds of chemical reactions and offer many applications include in agrochemicals, dyestuffs (the best known being aniline), pharmaceuticals, and corrosion inhibitors. |

| DNAPL | Acronym | Absolute viscosity | Specific Gravity | Appearance and Use |
|------------------|-------------------------|--------------------|------------------|---|
| Benzyl alcohol | Benzenemethanol | 7.76 | 1.045 | It is a clear, colorless liquid with a mild pleasant aromatic odor. Benzyl alcohol, featuring good solvency, low toxicity, and low vapor pressure, is used as a general solvent for inks, paints, lacquers, and epoxy resin coatings. It is also used as a raw material of various esters, used in the soap, perfume, and flavor industries. It is also used as a photographic developer and in perfumes, flavor industries, pharmaceuticals as a bacteriostatic. |
| Carbon disulfide | Carbon disulfide | 0.37 | 1.263 | Pure carbon disulfide is a colorless liquid with a pleasant odor that is like the smell of chloroform. The impure carbon disulfide that is usually used in most industrial processes is a yellowish liquid with an unpleasant odor, like that of rotting radishes. It is prepared from preheated hydrocarbons (natural gas) with vaporized sulfur in the presence of a catalyst. One of the most important uses is in the production of viscose rayon fibers, which are used to produce rayon filament yarn, rayon tire yarn, rayon stable fibre and Cellophane film. It is widely used as a solvent in the industrial fields of refining rubber. |
| 2-Nitrotoluene | 1-Methyl-3-nitrobenzene | 2.37 | 1.163 | Yellowish liquid at ordinary temp, weak aromatic odor. Production of toluidine, tolidine, fuchsine and various dyes. |
| Nitroethane | UN2842 | 0.66 | 1.045 | Clear liquid with a mild fruity odor. It is a suitable solvent in coatings and inks. It is used as an extraction solvent of rosin and some inorganic materials such aluminum chloride used as a Friedel-Crafts reaction catalyst. |
| Nitrobenzene | Nitrobenzol | 2.01 | 1.204 | Nitrobenzene is an industrial chemical. It is an oily yellow liquid with an almond-like odor. It is produced in large quantities for use in industry. Most of the nitrobenzene is used to manufacture a chemical called aniline. Nitrobenzene is also used to produce lubricating oils such as those used in motors and machinery. A small amount of nitrobenzene is used in the manufacture of dyes, drugs, pesticides, and synthetic rubber. |

| DNAPL | Acronym | Absolute viscosity | Specific Gravity | Appearance and Use |
|---------------------------|---------------------|--------------------|------------------|--|
| Thiophene | Thiacyclopentadiene | 0.65 | 1.065 | Clear to yellow liquid, slightly soluble. It is used as a solvent and chemical intermediate. Its derivatives are widely used in manufacturing dyes, aroma compounds and pharmaceuticals. They are used as monomers to make condensation copolymers. 2-Thiophene Ethanol is used as an intermediate of such as antiplatelet drugs (Clopidogrel, Ticlopidine) used to lessen the chance of heart attack or stroke. |
| Tri-o-cresyl phosphate | o-Creasil phosphate | 80.00 | 1.955 | Clear liquid, slightly soluble. Tricresyl Phosphate is used as a plasticizer for PVC, rubber and plastics. It is used as an ingredient for flame-retardant in plastics, rubbers and in hydraulic systems. It is used as a heat exchange medium. It is used a solvent and thinner for nitrocellulose, paints and varnishes. It is also used as an additive in high-pressure cooling lubricants and a lead scavenger in petrol. |
| Polychlorinated Biphenyls | | | | |
| PCB1016 | Aroclor 1016 | 19.30 | 1.330 | Polychlorinated biphenyls are mixtures of up to 209 individual chlorinated compounds (known as congeners). There are no known natural sources of PCBs. PCBs are either oily liquids or solids that are colorless to light yellow. PCBs are mixtures of synthetic organic chemicals with the same basic chemical structure and similar physical properties ranging from oily liquids to waxy solids. Due to their non-flammability, chemical stability, high boiling point and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics and rubber products; in pigments, dyes and carbonless copy paper and many other applications. |
| PCB1222 | Aroclor 1222 | 4.80 | 1.180 | |
| PCB1232 | Aroclor 1232 | 8.20 | 1.240 | |
| PCB1242 | Aroclor 1242 | 24.00 | 1.392 | |
| PCB1248 | Aroclor 1248 | 65.00 | 1.410 | |
| PCB1254 | Aroclor 1254 | 700.00 | 1.505 | |

Appendix B2

List of sources of possible DNAPL groundwater contamination in urban environments (Adapted from Usher, et. al., 2004).

| Ranking | Type of source | Expected contaminants | Comment |
|---------|--|---|---|
| 2 | Production of agricultural chemicals (fertilizers, herbicides, pesticides) | Chlorinated insecticides, ethylbenzene, naphthalene, organophosphates, phenols, phthalates, toluene, xylene, other herbicides | Not a common industry, limited to large industrial premises, but mobility and type of contaminants pose a great contaminant risk to groundwater. |
| 4 | Metallurgical | Mineral oils, organic solvents; chlorobenzenes; PCBs, coal tars | Usually large industrial premises, variety chemicals used, often have own waste disposal areas/ ponds which pose great contaminant risk to groundwater. |
| 5 | Metal (predominately gold) and coal mining | Petroleum hydrocarbons, chemicals/ reagents used in benefiacion processes, PCBs, PAHs | Potential for groundwater contamination high but not often found within urban area (except Gauteng) |
| 6 | Transport | Benzene, toluene, xylenes (BTEX), alkanes, TPH, PAH, any other chemicals transported resulting from accidents or spills | Accidents and spills in urban area often cleaned up quickly after reporting. Wide variety of chemicals |
| 7 | Petrol Service Stations (Underground Storage Tanks)* | Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), alkanes, TPH, PAH any other chemicals stored in USTs | Leakage from UST common due to corrosion of systems |
| 8 | Wood processing and preserving | Creosote, PAHs, pentachlorophenol, phenol, PCB | Spills and accidents more likely the greater the operation. |

| Ranking | Type of source | Expected contaminants | Comment |
|---------|--|--|---|
| 10 | Manufacturing - Chemicals | VOCs (Acetylene, Benzene, Butane, Chloroform, Ethyl Alcohol, and Methane), PAHs, chloroform, tetrachloromethane, di-, tri- and tetra-chlorinated benzenes, chlorinated alkanes, hexachlorocyclohexane (HCH), DDT (DDD and DDE), 2,4-dichlorophenol, HCH, ketones, toluene, xylene; carbon tetrachloride, chlorofluoroethanes, dichloroethylene, methylene chloride, PCE, TCE, vinyl chloride, 1,1,1-trichloroethane, PCBs, PAHs, coal tars | Usually large industrial premises, variety of base and more complex chemicals (used and produced), often have own waste disposal areas/ponds, which pose great contaminant risk to groundwater. |
| 11 | Workshops (Mechanical and electrical) | PAHs, diesel, benzene, alkanes, chlorinated solvents | Spills and wash water directed to sewers or stormwater drains |
| 12 | Stormwater/ sewer systems | Hydrocarbons, diverse industrial chemicals | Likelihood of groundwater contamination dependant on the type and integrity of the network |
| 13 | Automotive manufacturing | Hydrocarbons, solvents, paints | Little waste generation of groundwater importance; spillage, accidents, illegal disposal |
| 13 | Automotive refinishing and repair | Paint; waste oils; toluene, acetone, perchloroethylene, xylene, gasoline and diesel fuel, carbon tetrachloride | Spills and wash water directed to sewers or stormwater drains |
| 14 | Other metal product manufacturing | Benzene, trichloroethane and trichloroethylene, other VOCs; degreasing agents; waste oils | Diverse |
| 15 | Railroad yards | Petroleum hydrocarbons; VOCs; BTEX; solvents; fuels; oil and grease; lead; PCBs | Widespread, with long histories |
| 18 | Agriculture (General and crop cultivation) | Volatile organic compounds (VOC); carbon tetrachloride, ethylene dibromide, and methylene chloride; pesticides; insecticides; herbicides; grain fumigants | Activities mostly irrigation crop cultivation, some vineyards (Cape Town) but not common within urban boundaries |

| Ranking | Type of source | Expected contaminants | Comment |
|---------|---------------------------------------|--|--|
| 19 | Paper/ pulp industry | Acrylates, chlorinated solvents, mercury, phenols, styrene, chloroform | Industries vary between small-scale to very large scale. Paper mills pose greater threat to groundwater but often located on outskirts of urban area due to aesthetic reasons. |
| 20 | Research and educational institutions | Organic solvents; photographic waste; waste oil; paint, pesticides | Chemicals flushed to sewer network |
| 24 | Munitions manufacturing | Solvents | Not a common industry, limited to large industrial premises, but mobility and type of contaminants pose a great contaminant risk to groundwater. |
| 25 | Hazardous waste sites | Various chemical mixtures | Only 6 H:H sites in SA, all permitted. There are however many private H:H sites. |
| 26 | Marine maintenance industry | Solvents; paints; VOC emissions; heavy metal sludge; degreasers | Only relevant to coastal urban centers with large port facilities |
| 27 | Dry cleaning activities | VOCs such as chloroform and tetrachloroethane; various solvents; spot removers; fluorocarbon 113 | Spills often occur at chemical storage area and below machinery. |
| 28 | General/ Domestic waste sites | Various chemicals | Most legal domestic waste sites are located on outskirts of urban area due to aesthetic reasons, groundwater contamination will vary with size, type and management of each site |
| 29 | Wastewater treatment | Diverse industrial chemicals | Depending on the type of water treatment process and management of the system, the likelihood of groundwater contamination may increase. |

| Ranking | Type of source | Expected contaminants | Comment |
|---------|--|--|---|
| 30 | Textile manufacture | Ammonium, arsenic, cadmium, chromium, ethyl acetate, nickel, hexane, oxalic acid, phenols, phthalates, toluene, lead | Common industry varying in type and size. Some more likely to cause groundwater contamination (e.g. wool washing) |
| 31 | Rubber and plastics | Acrylonitrile, antimony, benzene, butadiene, cadmium, chloroform, chromium, dichloroethylenes, lead, phenols, phthalates, styrene, sulphur, vinyl chloride, toluene, heptane, formaldehyde | Industries vary between small-scale to very large scale. Rubber conversion industry pose greater threat than plastic conversion. |
| 33 | Leather manufacturing | Toluene; benzene; solvents | Very few large tanneries in SA, number of small-scale operations, but due to nature of chemicals used the risk for groundwater contamination is great. |
| 35 | Printing industry | Waste oils; toluene; MEK; xylene, TCE | Very common industry widely distributed throughout urban area but often chemicals are flushed to sewer network |
| 38 | Auto Salvage/Metal Recyclers | CBs, hydraulic fluids and lubricating oils, fuels, and solvents | Most of these types of industries are relative small. |
| 39 | Electrical and electrical products manufacturing | Petroleum hydrocarbons, isopropanol, methanol, salinity, trichloroethylene, arsenic, silane, metals | Most of these types of industries are relative small. |
| 40 | Electricity generation | PCBs, PAHs | Widespread, with long histories |
| 41 | Photographic manufacturing and uses | Solvents; photographic products | Chemicals flushed to sewer network |
| 42 | Paint/ink manufacturing and coatings | Chlorinated solvents, glycol ethers, ketones, methylene chloride, mineral spirits, phthalates, styrene, terpenes, toluene, anthraquinones, benzidine, ethyl acetate, hexane, oxalic acid, phenol | Industries vary between small-scale to very large scale. Larger manufacturing (opposed to "mixing") industries will pose greater threat to groundwater. |

| Ranking | Type of source | Expected contaminants | Comment |
|---------|---|--|--|
| 43 | Pharmaceuticals and cosmetics manufacturing | Dyes, glycols, mineral spirits, dichlorobenzene, methylene chloride | Most of this type of industries are relative small and does not manufacture own base chemicals. |
| 44 | Adhesives and sealants | Benzene, toluene, methyl-ethyl ketone (MEK) | Most of these types of industries are relative small. |
| 48 | Hospitals / Health Care | Formaldehyde;photographic chemicals; solvents; mercury; chemotherapy chemicals | Waste often not disposed of or incinerated on site |
| 49 | Glass manufacturing | Arsenic; lead | Not a common industry, with limited contaminant risk to groundwater. |
| 50 | Incinerators | Dioxin; various municipal and industrial waste | Most incinerators are permitted and strict compliance to storage of waste and ash must be followed |

Appendix C

Applicable Dissolved transport Codes:

1. AT123D

AT123D is based on an analytical solution for transient one-, two- or three-dimensional transport in a homogeneous isotropic aquifer with uniform regional flow. AT123D computes the spatial-temporal concentration distribution of wastes in the aquifer system and predicts the transient spread of a contaminant plume through a groundwater aquifer. The fate and transport processes accounted for in AT123D are advection, dispersion, adsorption and biological decay. AT123D estimates all the above components on a monthly basis for up to 99 years of simulation time.

2. BIOSCREEN

Based on the Domenico analytical solute transport model, BIOSCREEN is a screening model which simulates remediation through natural attenuation of dissolved hydrocarbons at petroleum fuel release sites. (Available at <http://www.epa.gov/ada/csmos/models/bioscrn.html>) The software, programmed in the Microsoft Excel spreadsheet, has the ability to simulate advection, dispersion, adsorption and aerobic decay, as well as anaerobic reactions that have been shown to be the dominant biodegradation process at many petroleum release sites. It includes three different model types: (1) solute transport without decay, (2) solute transport with biodegradation modelled as a first-order decay process (simple, lumped-parameter approach) and (3) solute transport with biodegradation modelled as an instantaneous biodegradation reaction with multiple soluble electron acceptors, including dissolved oxygen, nitrate and sulphate. The model is designed to simulate biodegradation by both aerobic and anaerobic reactions.

3. BIOPLUME II & III

BIOPLUME II is a two-dimensional, finite difference, two-dimensional model for simulating transport of a single dissolved hydrocarbon species under the influence of oxygen-limited biodegradation, first order decay, linear sorption, advection and dispersion. The aquifer may be heterogeneous and anisotropic.

The BIOPLUME III model simulates both aerobic and anaerobic biodegradation processes in addition to advection, dispersion, sorption and ion exchange. BIOPLUME III simulates the biodegradation of organic contaminants using a number of aerobic and anaerobic electron acceptors: oxygen, nitrate, iron (III), sulphate, and carbon dioxide. BIOPLUME III is based on the U.S. Geologic Survey (USGS) Method of Characteristics Model (MOC) dated July 1989 (Konikow and Bredehoeft).

4. FATE 5

A new groundwater attenuation modeling tool (FATE 5) has been developed to assist users with determining site-specific natural attenuation rates for organic constituents dissolved in groundwater. FATE 5 is based on and represents an enhancement to the Domenico analytical groundwater transport model (Domenico, 1987). These enhancements include use of an optimization routine to match results from the Domenico model to actual measured site concentrations, an extensive database of chemical property data, and calculation of an estimate of the length of time needed for

a plume to reach steady state conditions. FATE 5 was developed in Microsoft ® Excel and is controlled by means of a simple, user-friendly graphical interface

5. MODFLOW: MT3D/ MT3DMS

MT3D is a transport model that is used in conjunction with any block-centred finite difference flow model, such as MODFLOW. MT3D is a three-dimensional transport model for simulation of advection, dispersion and chemical reactions of dissolved constituents in groundwater systems. It includes linear or non-linear sorption and first-order irreversible decay or biodegradation.

A later version of MT3D, MT3DMS (where MT3D stands for the Modular 3-Dimensional Transport model, while MS denotes the Multi-Species structure), is also now available. MT3DMS has a comprehensive set of options and capabilities for simulating advection, dispersion/diffusion and chemical reactions of contaminants in groundwater flow systems under general hydrogeologic conditions. MT3DMS is unique in that it includes three major classes of transport solution techniques in a single code, i.e.:

The standard finite difference method;

The particle-tracking-based Eulerian-Lagrangian methods; and

The higher-order finite-volume TVD method.

Since no single numerical technique has been shown to be effective for all transport conditions, the combination of these solution techniques, each having its own strengths and limitations, is believed to offer the best approach for solving the most wide-ranging transport problems with the desired efficiency and accuracy.

6. RT3D

RT3D is based on MT3D and is used for simulating three-dimensional, multi-species, reactive transport in groundwater. RT3D can accommodate multiple sorbed and aqueous phase species with user-defined reaction frameworks. It allows instantaneous biodegradation, kinetically limited reaction, non-equilibrium sorption/desorption, NAPL dissolution, dual porosity, anaerobic and aerobic biodegradation.

As part of a natural attenuation evaluation, RT3D may be used to predict the fate and transport of groundwater plumes. A sensitivity analysis may be performed to evaluate the range of potential outcomes. Such predictions may be used to define a long-term monitoring programme that will feed back into future reactive transport simulations and model refinement.

Active remediation may also be simulated, whether it be air sparging, chemical oxidation or accelerated bioremediation. The key is understanding the reaction kinetics of the remediation process and applying that knowledge in a user-defined reaction module. Reactive transport simulations could potentially be applied to scenarios involving contaminants such as heavy metals, explosives, petroleum hydrocarbons, and/or chlorinated solvents.

7. PHT3D

PHT3D is a multi-component transport model for three-dimensional reactive transport in saturated porous media. The model incorporates the codes MT3DMS for the simulation of three-dimensional advective-dispersive, multi-species transport and the

geochemical model PHREEQC-2 for the quantification of reactive processes. PHT3D uses PHREEQC-2 database files to define equilibrium and kinetic (e.g., biodegradation) reactions.

PHT3D has been applied to a number of (bio)geochemical transport modelling studies:

- Natural attenuation of hydrocarbons
- *In situ* remediation of metal-contaminated groundwater
- Artificial recharge and aquifer storage and recovery
- Transport of chlorinated solvents in a permeable Fe(0)-filled reactive barrier
- Natural attenuation of landfill leachates
- Transport and attenuation of ammonium-contaminated groundwater

8. SUTRA

SUTRA simulates fluid movement and transport of either energy or dissolved substances in a variably saturated system environment. Solute transport is restricted to a single reacting species and accounts for solute sorption (linear, Freundlich or Langmuir equilibrium isotherm), zero and first-order decay and zero-order production, hydrodynamic dispersion (including corrections for anisotropy) and molecular diffusion.

SUTRA employs a two-dimensional hybrid finite-element and an integrated finite-difference method to approximate the governing equations that describe the two interdependent processes that are simulated: (1) fluid density-dependent saturated or unsaturated ground water flow and either (2a) transport of a solute in the groundwater, in which the solute may be subject to equilibrium adsorption on the porous matrix and both first-order and zero-order production or decay; or (2b) transport of thermal energy in the ground water and solid matrix of the aquifer.

9. BIOCHLOR

BIOCHLOR is a screening model that simulates remediation by natural attenuation of dissolved solvents at chlorinated solvent release sites. BIOCHLOR may be used to simulate solute transport without decay and solute transport with biodegradation modelled as a sequential first-order process within one or two different reaction zones.

BIOCHLOR simulates remediation by natural attenuation (RNA) of dissolved solvents at chlorinated solvent release sites. The software, programmed in the Microsoft Excel spreadsheet environment and based on the Domenico analytical solute transport model, has the ability to simulate 1-D advection, 3-D dispersion, linear adsorption and biotransformation via reductive dechlorination (the dominant biotransformation process at most chlorinated solvent sites). Reductive dechlorination is assumed to occur under anaerobic conditions and dissolved solvent degradation is assumed to follow a sequential first-order decay process (Available at: <http://www.epa.gov/ada/csmos/models/biochlor.html>). BIOCHLOR includes three different model types:

- Solute transport without decay
- Solute transport with biotransformation modelled as a sequential first-order decay process
- Solute transport with biotransformation modelled as a sequential first-order decay process with two different reaction zones (i.e., each zone has a different set of rate coefficient values).

Appendix D1

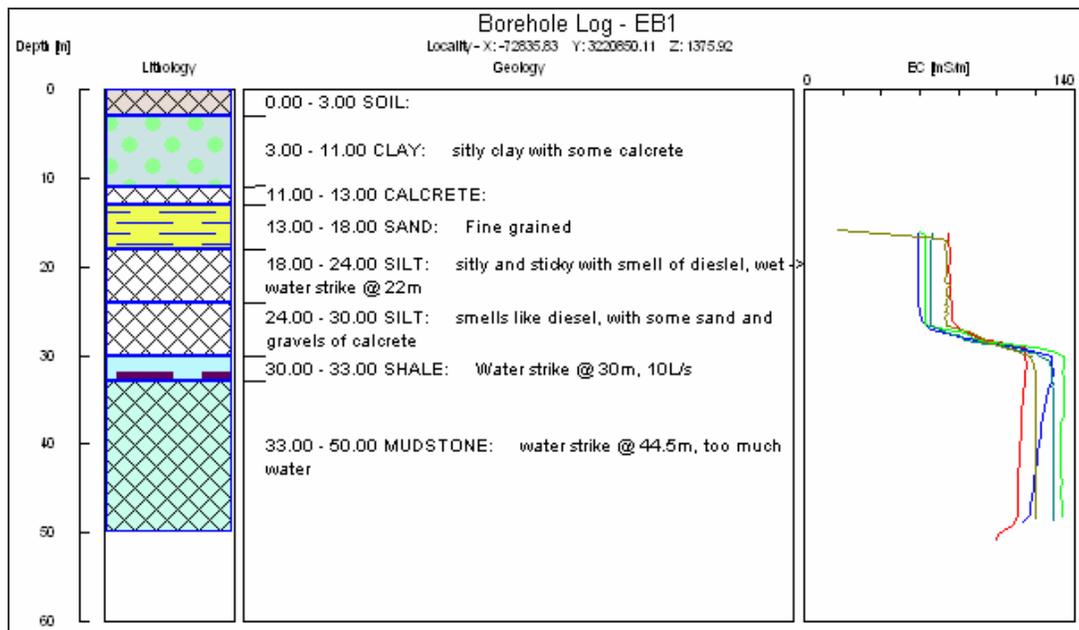


Figure 8: Geologic and EC log of Borehole EB1.

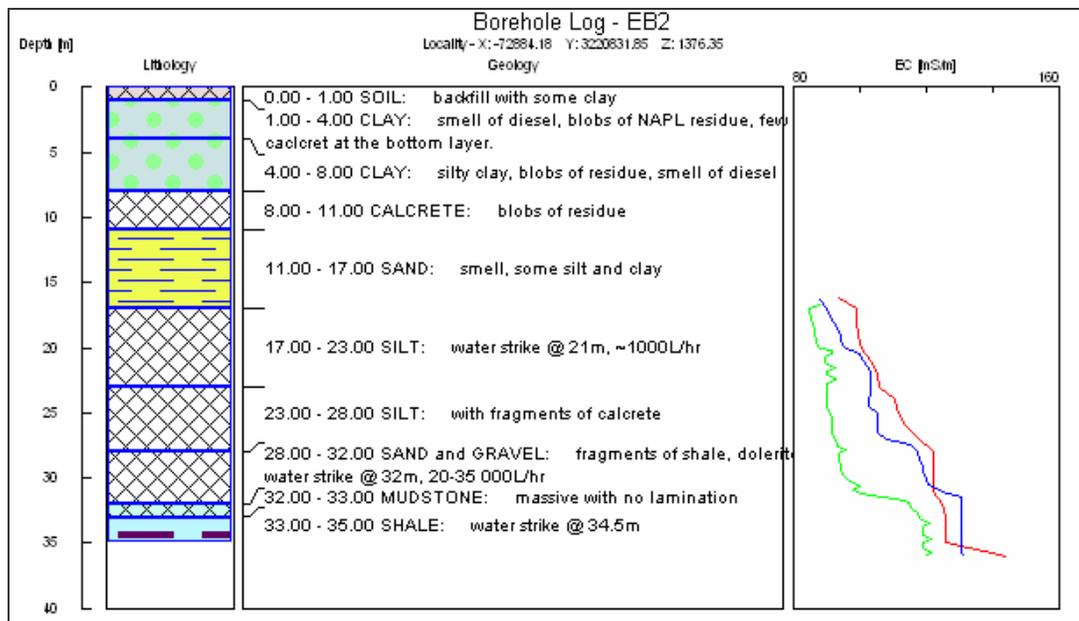


Figure 9: Geologic and EC log of Borehole EB2.

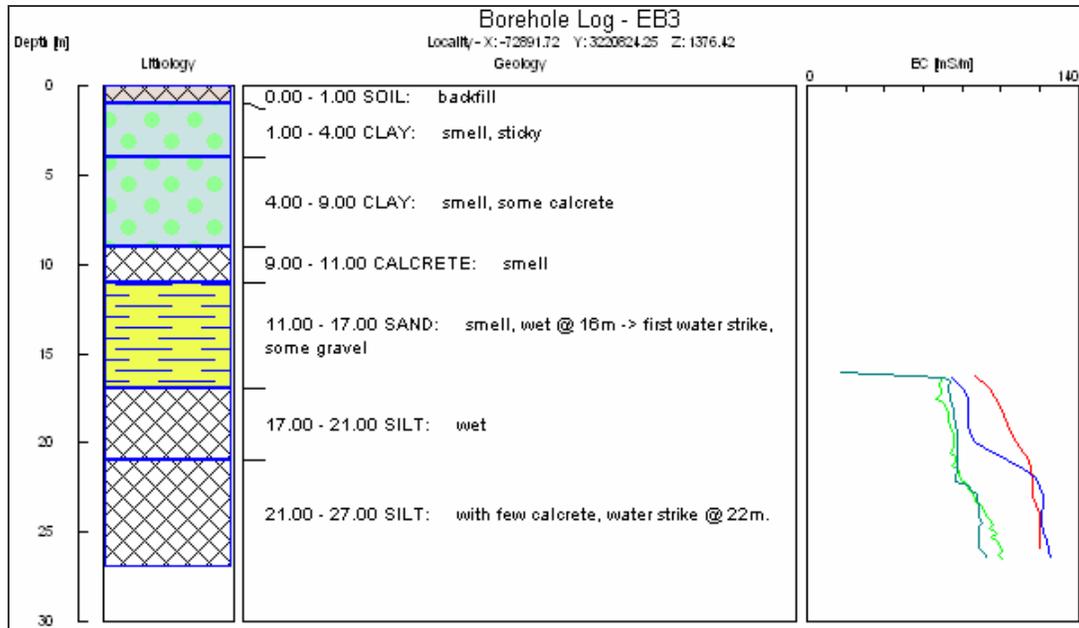


Figure 10: Geologic and EC log of Borehole EB3.

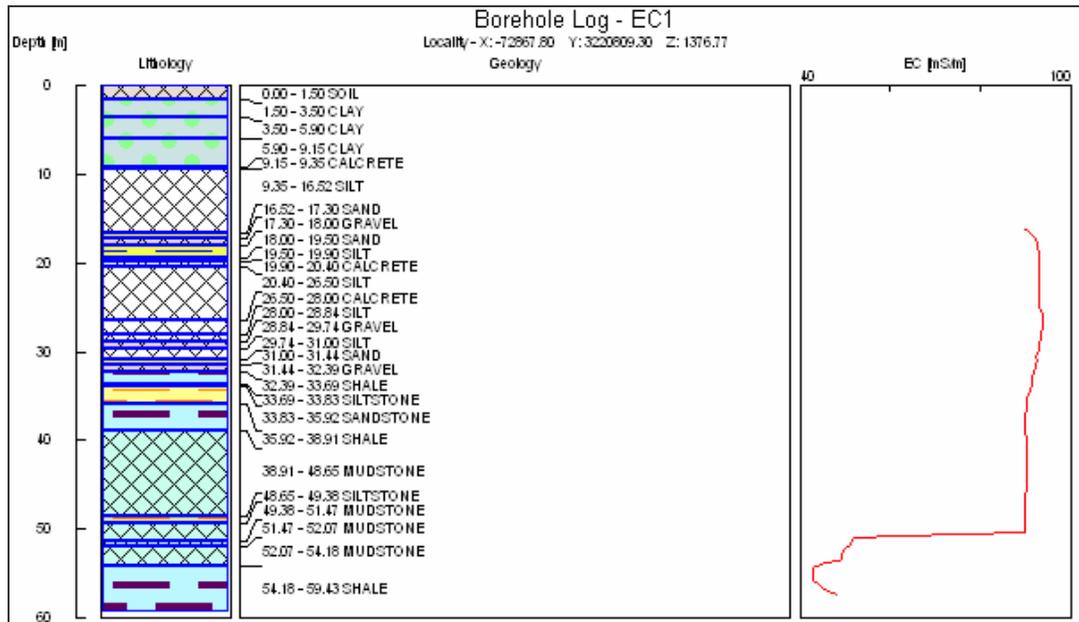


Figure 11: Geologic and EC log of Borehole EC1.

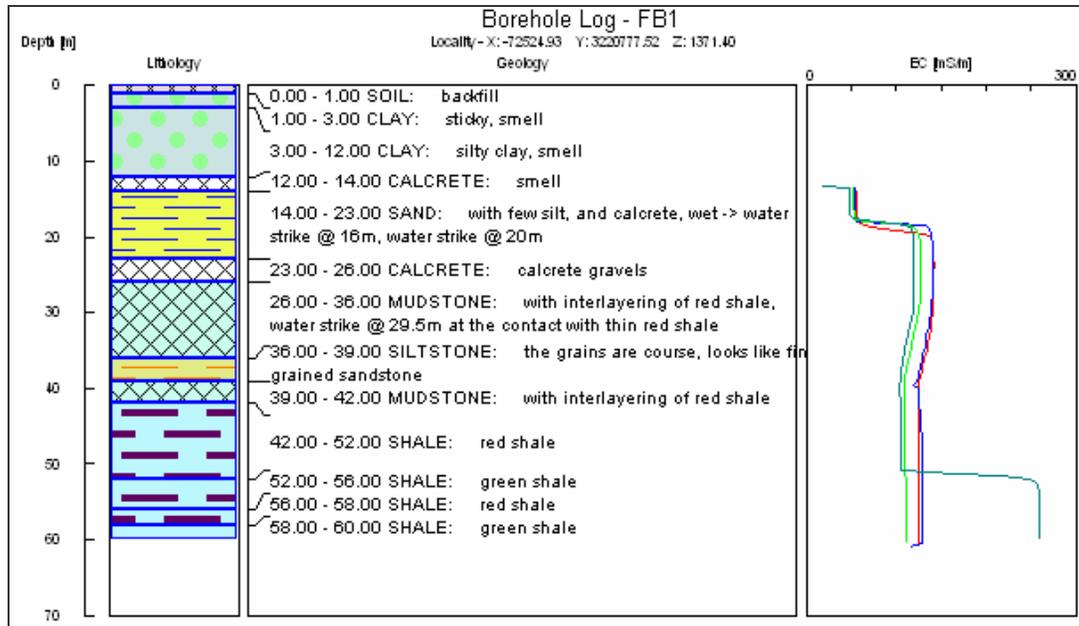


Figure 12: Geologic and EC log of Borehole FB1.

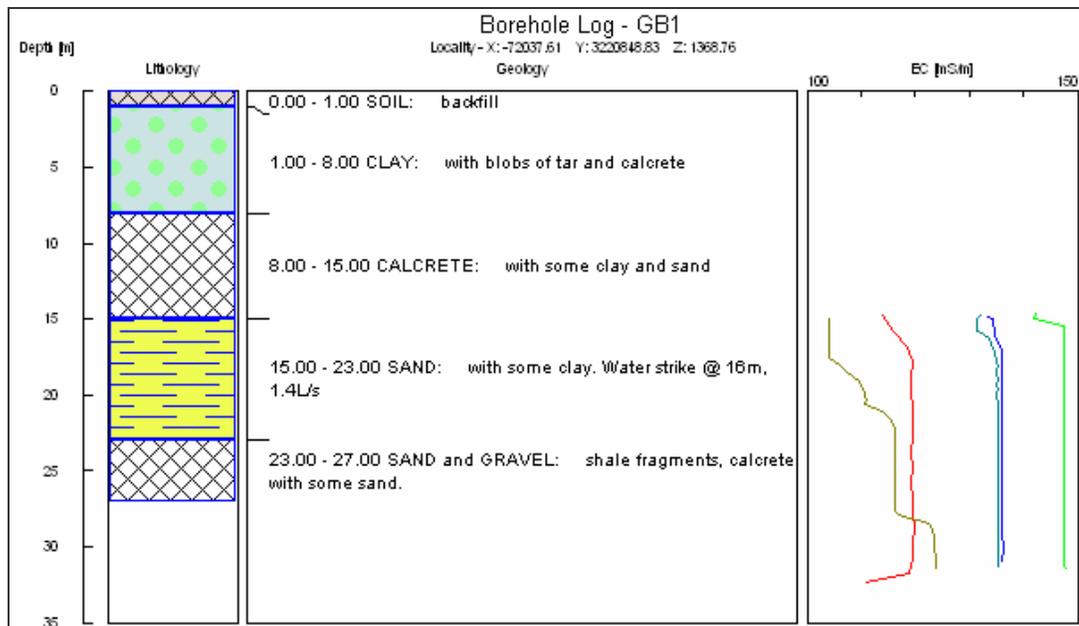


Figure 13: Geologic and EC log of Borehole GB1.

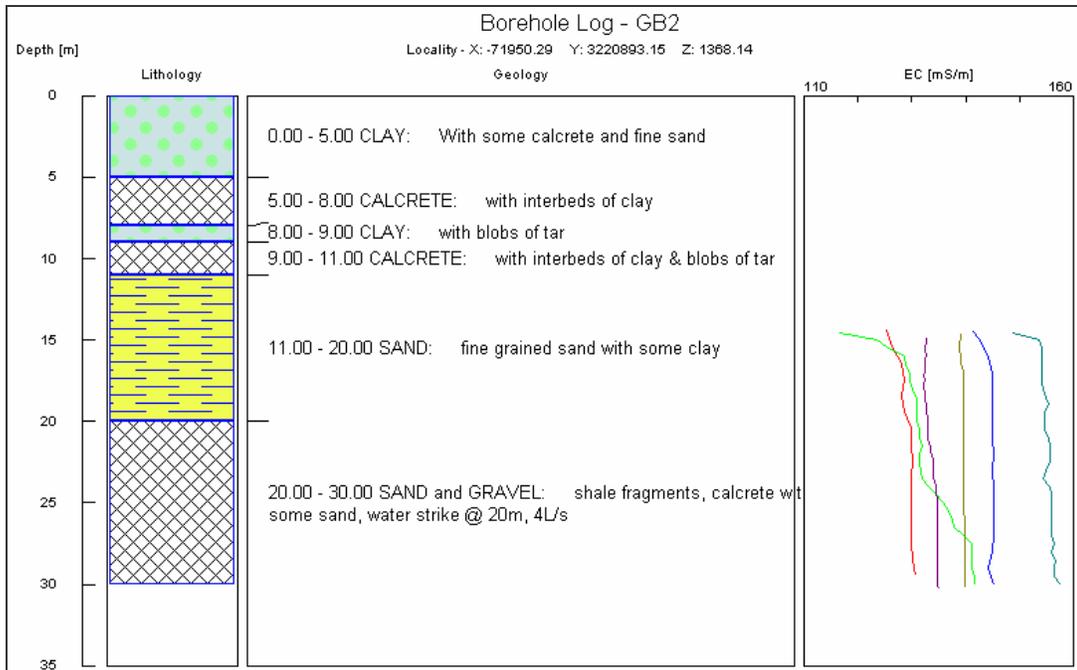


Figure 14: Geologic and EC log of Borehole GB2.

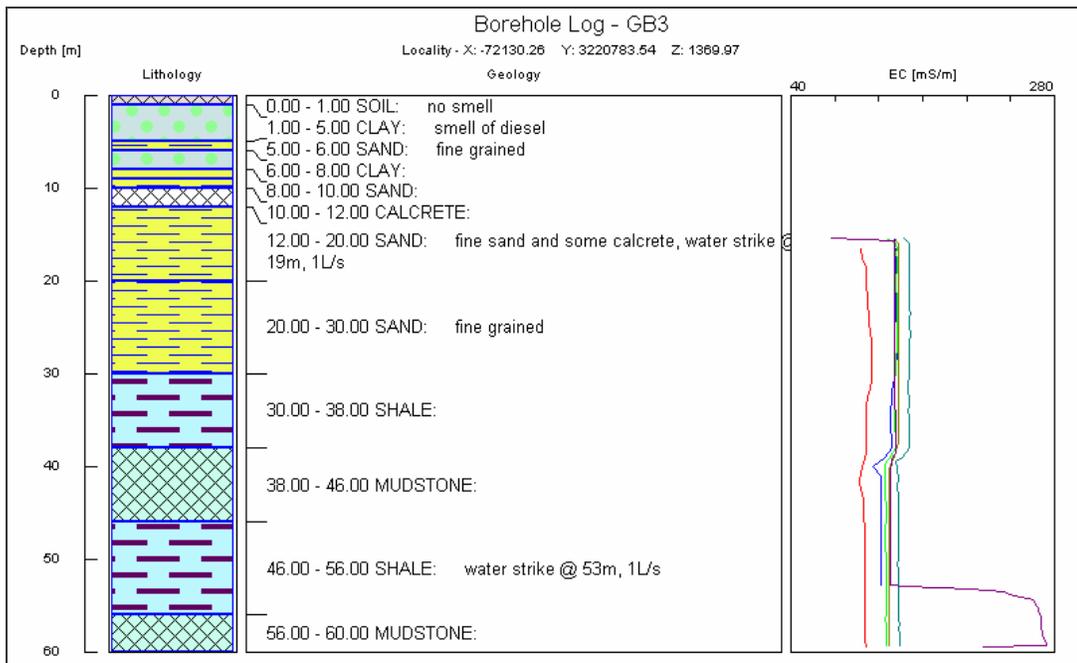


Figure 15: Geologic and EC log of Borehole GB3.

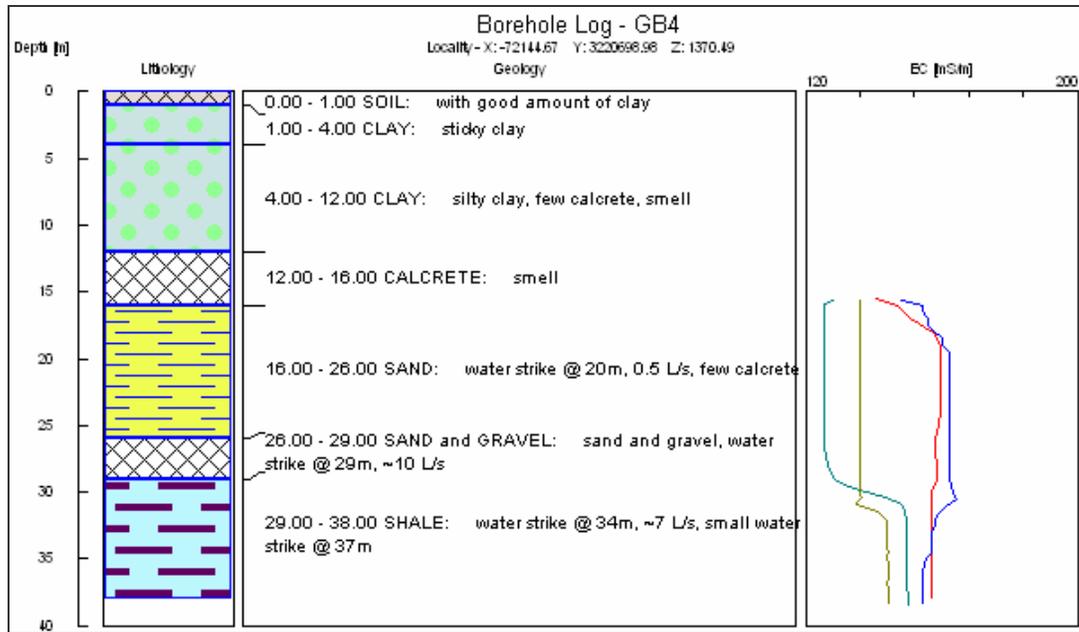


Figure 16: Geologic and EC log of Borehole GB4.

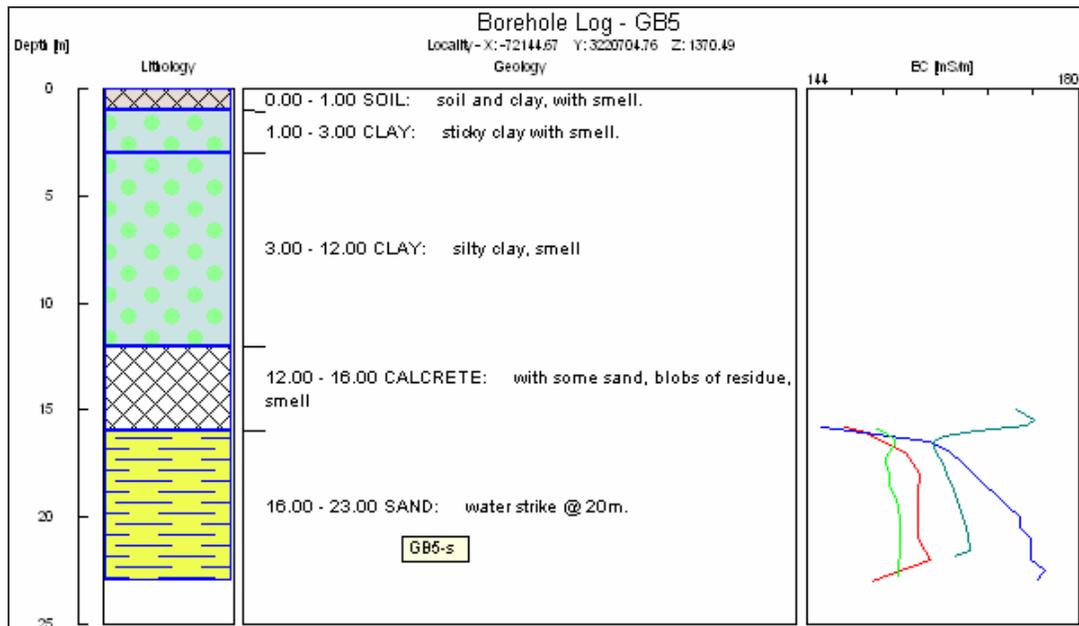


Figure 17: Geologic and EC log of Borehole GB5.

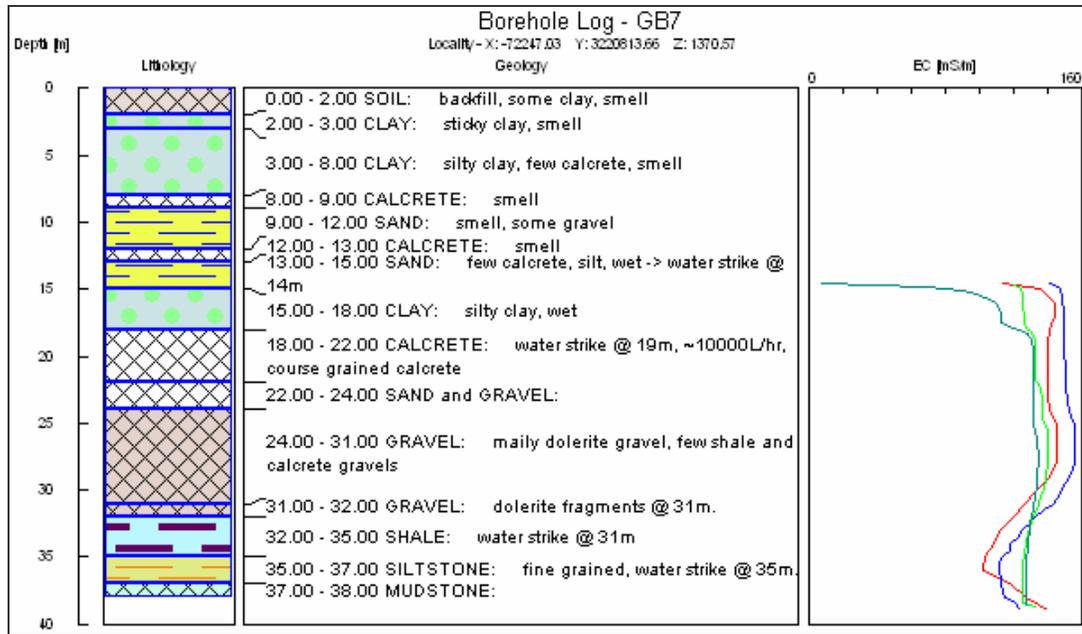


Figure 18: Geologic and EC log of Borehole GB7.

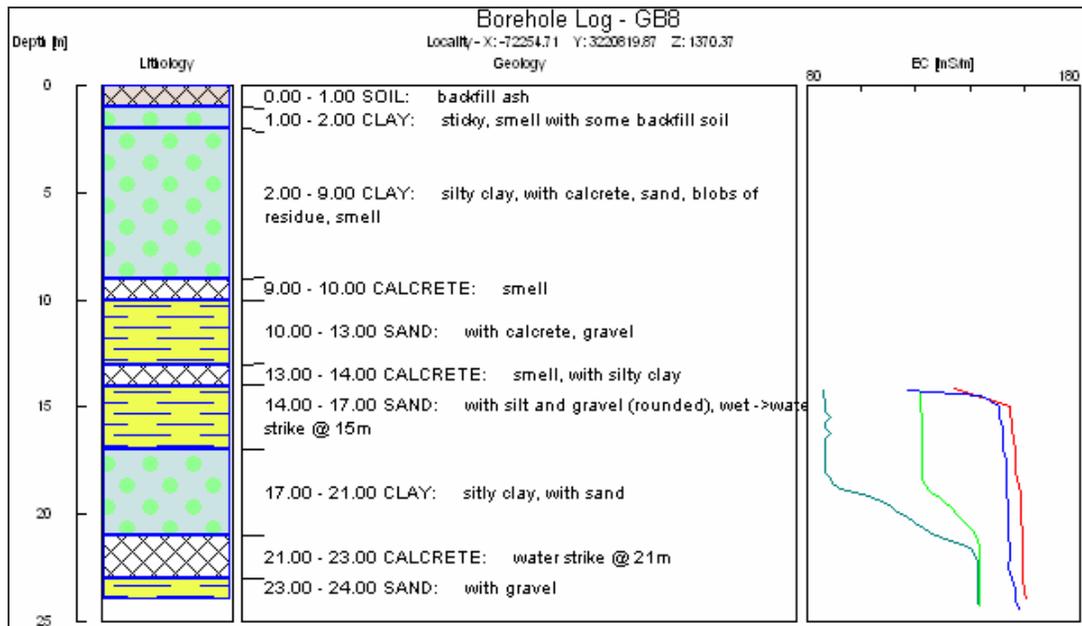


Figure 19: Geologic and EC log of Borehole GB8.

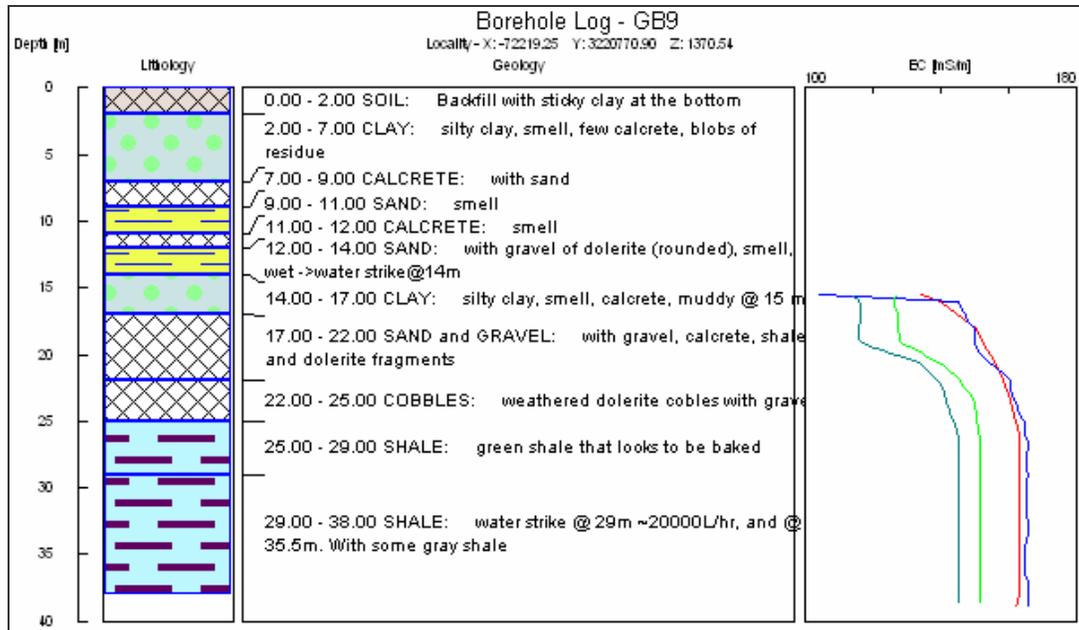


Figure 20: Geologic and EC log of Borehole GB9.

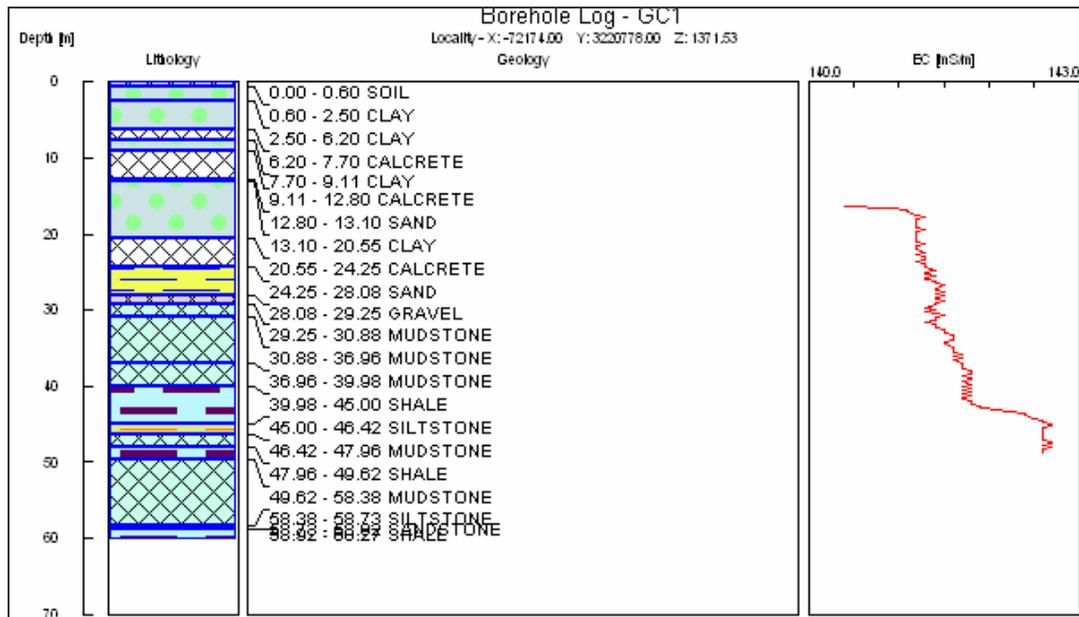


Figure 21: Geologic and EC log of Borehole GC1.

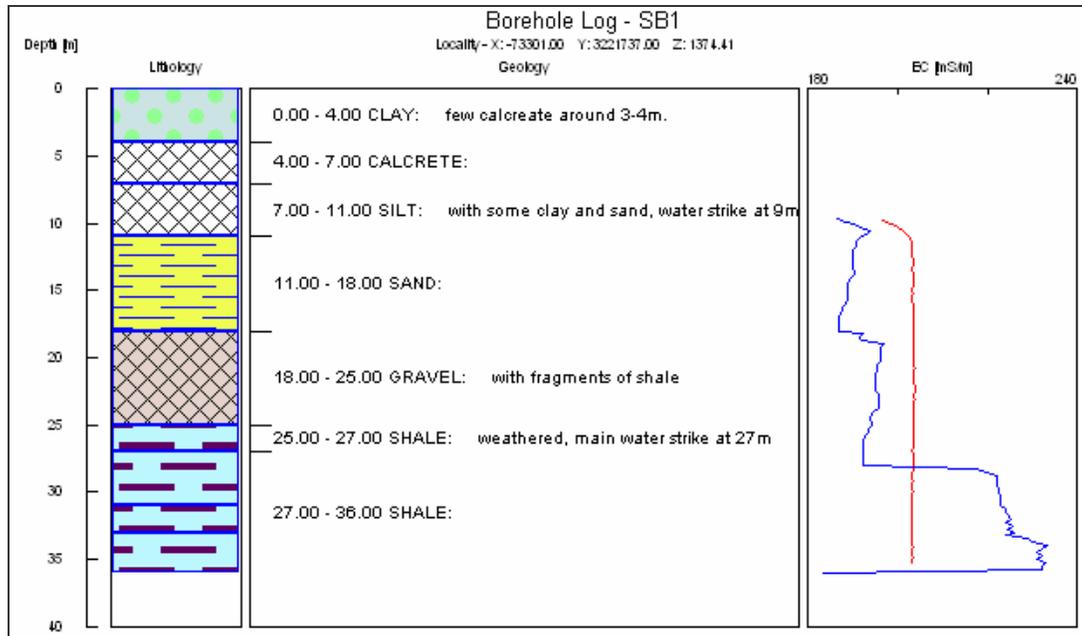


Figure 22: Geologic and EC log of Borehole SB1.

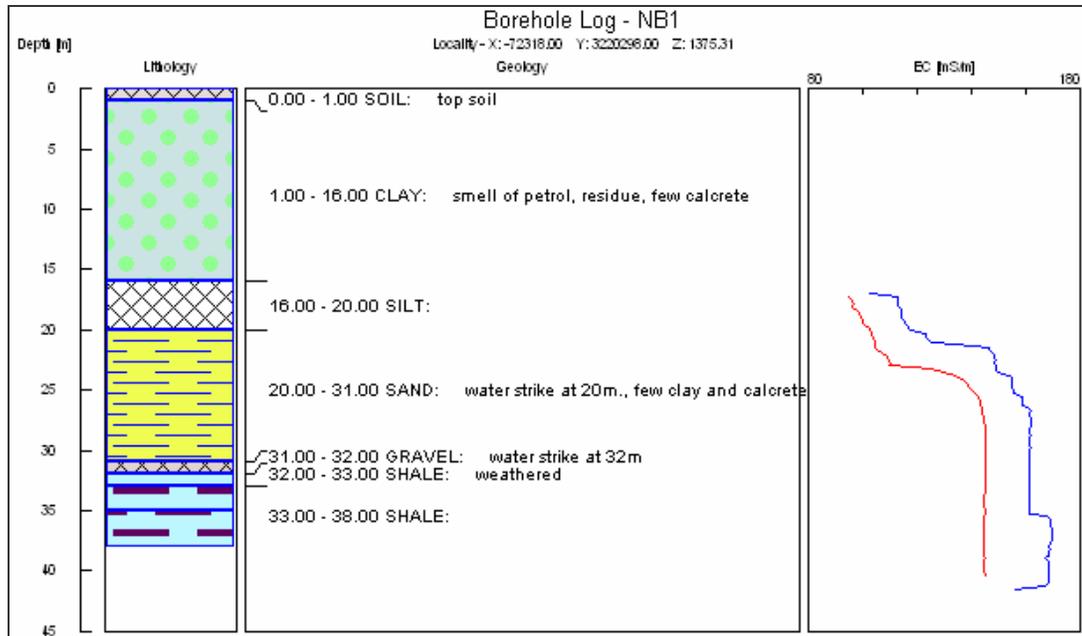


Figure 23: Geologic and EC log of Borehole NB1.

Appendix D2

Organic contaminants composition of the test pit soil, coal tar and sludge samples (ppm).

| Organic contaminant | TAR | Sludge | GE2 | GD1 | GC4 | GC3 | GC1 | GB2 | GB3 | GB1 | GA1 | EF2 | EE1 | ED2 | ED1 | EB3 | EC2 | EB2 | B-G7B | H-G13 | L-G9B | M-G7B | N-G2C | O-G12 |
|-----------------------------|---------|--------|------|-------|--------|------|------|------|------|-------|-------|-------|-------|------|------|------|------|------|-------|-------|-------|-------|-------|-------|
| 1,2,4 Trimethylbenzene | 173.523 | | | | | | | | | 0.023 | 0.035 | | | | | | | | | | 0.002 | | | |
| 1,3,5 Trimethylbenzene | 66.5 | | | | | | | | | | | | | | | | | | | | | | | |
| 1,4-Dichlorobenzene | | | | | | | | | | | | | | | | | | | | | | | | |
| Acenaphthalene | 840 | | | | | | | | | | | | | | | 0.03 | | | | | | | | |
| Acenaphthene | 87 | | | | | | | | | | | | | | | 1.03 | | | | | | | | |
| Anthracene | 766 | | 0.06 | | 0.31 | | | | | 0.06 | | | | | | 0.86 | | 0.03 | | | | | | |
| Benzo(a)anthracene | 143 | | | 0.07 | | | | | | 0.04 | 0.18 | | | | | 0.47 | | 0.18 | | | | | | |
| Benzo(a)pyrene | 107 | | | | | | 0.41 | | | 0.04 | 0.08 | | | | | 0.76 | | 0.23 | | | | | | |
| Benzo(ghi)perylene | 20 | | | | | | | | | | | | | | | | | | | | | | | |
| Benzo(k+b)fluoranthene | 234 | | | 0.06 | | | 0.44 | | | 0.1 | 0.15 | | | | | 0.77 | | 0.49 | | | | | | |
| Bis (2-Ethylhexyl)phthalate | | | | | | | | | | | | 2.27 | | 1.46 | | | 0.12 | | | | | | | |
| Bromodichloromethane | | | | 0.425 | | | | | | 1.86 | 3.462 | | | | | | | | | | | | | |
| Bromoform | | | | | | | | | | | | | | | | | | | | | | | | |
| Chrysene | 2256 | | | 0.09 | 0.01 | | | | | 0.31 | 0.21 | | | | | 0.11 | | 0.12 | | | | | | |
| Dibenzo(a,h)anthracene | 9.7 | | | | | | | | | | | | | | | | | | | | | | | |
| Diethyl phtalate | | | | | | | | | | 0.05 | | | | | | | | | | | | | | |
| Di-n-butylphthalate | | | | | | | | | | | | 29.6 | 25.83 | | | | | | | | | | | |
| Ethylbenzene | 18.835 | | | | | | | | | 0.011 | | | | | | | | | 0.001 | 0.001 | 0.003 | 0.004 | 0.003 | 0.002 |
| Fluoranthene | 262 | | 0.06 | 0.1 | 0.05 | 0.03 | | | 0.03 | 0.14 | 0.18 | | 0.02 | 0.1 | 0.08 | 2.83 | | 0.51 | | | | | | |
| Fluorene | 22874 | | | | 66.83 | | | | | 30.79 | 1.12 | | | | | 0.34 | | | | | | | | |
| Indeno(1,2,3-cd)pyrene | 67.9 | | | | | | | | | | | | | | | | | | | | | | | |
| Isopropylbenzene | 2.341 | | | | | | | | | | | | | | | | | | | | | | | |
| m-Xylene | 48.469 | | | 0.018 | | | | | | 0.042 | 0.053 | | | | | | | | 0.002 | 0.002 | 0.004 | 0.006 | 0.003 | 0.002 |
| Naphthalene | 73615 | | 3.27 | | 107.59 | | | | | 19.2 | 2.52 | | | 4.94 | 1.05 | 2.96 | | 6.96 | | | | | | |
| n-Butylbenzene | 66.365 | | | | | | | | | | | | | | | | | | | | | | | |
| o+p Xylenes | 61.079 | | | 0.012 | | | | | | 0.021 | 0.028 | | | | | | | | 0.002 | 0.002 | 0.004 | 0.006 | 0.004 | 0.002 |
| Phenanthrene | 12290 | | | | 3.85 | | 0.32 | 0.02 | | 2.98 | 5.3 | 29.64 | 25.83 | 0.16 | 0.06 | 5.39 | | 0.85 | | | | | | |
| Pyrene | 324 | | 0.05 | 0.12 | 0.03 | 0.03 | 0.14 | | 0.02 | 0.09 | 0.17 | | 0.02 | 0.07 | 0.13 | 2.84 | | 0.57 | | | | | | |
| Sec-Butylbenzene | | | | | | | | | | 0.005 | | | | | | | | | | | | | | |
| Tert-Butylbenzene | | | | | | | | | | | | | | | | | | | | | | | | |
| Tetrachloroethene | | 1.705 | | | | | | | | | | | | | | | | | | | | | | |
| Toluene | 45.302 | 0.044 | | 0.243 | | | | | | 0.076 | 0.061 | | | | | | | | | | | 0.008 | | |
| Trichloroethene | | 0.435 | | | | | | | | | | | | | | | | | | | | | | |

*The samples highlighted in blue, contains compounds also found in the coal tar sample from the site.

Organic contaminants composition of the soil samples from boreholes and piezometers (ppm).

| SiteName | ES1-14 | FS1-2 | GB1-(10+11) | GB1-16 | GB1-5 | GB2 | GB2-(5+6) | GB2-10 | GS4-3.4 | GS5-18 | Sludge | Tar |
|----------------------------|--------|-------|-------------|--------|-------|------|-----------|--------|---------|--------|--------|----------|
| 1,2,4 Trimethylbenzene ppm | | | | | | | | | | | | 173.52 |
| 1,3,5 Trimethylbenzene ppm | | | | | | | | | | | | 66.50 |
| 1,4-Dichlorobenzene ppm | | | | | | | | | | | | |
| Acenaphthalene ppm | | | | | | | | | | | | 840.00 |
| Acenaphthene ppm | | | | | | | | | | | | 87.00 |
| Anthracene ppm | | | | | | | | | | | | 766.00 |
| Benzo(a)anthracene ppm | | | | | | | | | | | | 143.00 |
| Benzo(a)pyrene ppm | | | | | | | | | | | | 107.00 |
| Benzo(ghi)perylene ppm | | | | | | | | | | | | 20.00 |
| Benzo(k+b)fluoranthene ppm | | | | | | | | | | | | 234.00 |
| Chrysene ppm | | | | | | | | | | | | 2256.00 |
| Dibenzo(a,h)anthracene ppm | | | | | | | | | | | | 9.70 |
| Di-n-octylphthalate ppm | | | | | | | | | | | | |
| Ethylbenzene ppm | | | | | | | | | | | | 18.84 |
| Fluoranthene ppm | | | | | | | | | | | | 262.00 |
| Fluorene ppm | | | | | | | | | | | | 22874.00 |
| Indeno(1,2,3-cd)pyrene ppm | | | | | | | | | | | | 67.90 |
| Isopropylbenzene ppm | | | | | | | | | | | | 2.34 |
| m-Xylene ppm | | | | | | | | | | | | 48.47 |
| Naphthalene ppm | | | | | | | | | | | | 73615.00 |
| n-Butylbenzene ppm | | | | | | | | | | | | 66.37 |
| o+p Xylenes ppm | | | | | | | | | | | | 61.08 |
| Phenanthrene ppm | | | | | | 0.02 | | | | | | 12290.00 |
| Toluene ppm | | | 0.09 | 0.02 | 0.12 | | 0.38 | 0.03 | | | 0.04 | 45.30 |
| Diethyl phtalate ppm | | | | | | | | | | | | |
| Di-n-butylphthalate ppm | | | | 8.17 | | | | | | | | |
| PAH mg/L | 14 | 14 | | | | | | | 14 | 15 | | |
| Bromodichloromethane ppm | | | | | | | | | | | | |
| Bromoform ppm | | | | | | | | | | | | |
| Sec-Butylbenzene ppm | | | | | | | | | | | | |
| Tert-Butylbenzene ppm | | | | | | | | | | | | |
| Tetrachloroethene ppm | | | | | | | | | | | 1.71 | |
| Trichloroethene ppm | | | | | | | | | | | 0.44 | |
| FOC % | 0.17 | 0.26 | | | | | | | 0.08 | 0.09 | | |

*The samples highlighted in blue, contains compounds also found in the coal tar sample from the site.

Appendix D3

| SiteName | DateTimeMeas | pH | EC mS/m | TDS mg/l | Ca mg/l | Mg mg/l | Na mg/l | K mg/l | MALK mg/l | Cl mg/l | SO4 mg/l | N NO3mg/l | F mg/l |
|----------|------------------|-------|---------|----------|---------|---------|---------|--------|-----------|---------|----------|-----------|--------|
| B1 | 2004/08/03 00:00 | 7.70 | 50.30 | -1.00 | 38.58 | 21.09 | 38.13 | 1.78 | 209.00 | 22.00 | 18.10 | 0.09 | 0.50 |
| B10 | 2004/08/03 00:00 | 7.23 | 152.00 | -1.00 | 149.67 | 68.98 | 92.48 | 1.81 | 366.00 | 150.00 | 260.00 | 15.84 | 0.36 |
| B11 | 2004/08/03 00:00 | 7.24 | 137.00 | -1.00 | 135.59 | 68.33 | 65.73 | 1.46 | 326.00 | 102.00 | 265.00 | 22.10 | 0.22 |
| B12 | 2004/08/03 00:00 | 7.77 | 136.00 | -1.00 | 131.73 | 64.00 | 70.38 | 0.87 | 325.00 | 90.00 | 295.00 | 17.70 | 0.24 |
| B4 | 2004/08/03 00:00 | 7.87 | 37.40 | -1.00 | 25.18 | 14.18 | 32.42 | 5.26 | 140.00 | 25.00 | 15.15 | 0.41 | 0.03 |
| B5 | 2004/08/03 00:00 | 7.68 | 114.00 | -1.00 | 100.18 | 70.08 | 36.29 | 0.65 | 395.00 | 110.00 | 45.90 | 11.12 | 0.27 |
| B6 | 2004/08/03 00:00 | 7.43 | 134.00 | -1.00 | 113.14 | 77.19 | 60.16 | 1.44 | 379.00 | 163.00 | 116.00 | 10.14 | 0.08 |
| B8 | 2004/08/03 00:00 | 7.78 | 113.00 | -1.00 | 101.09 | 69.69 | 31.31 | 4.37 | 370.00 | 124.00 | 79.00 | 0.02 | 0.11 |
| B9 | 2004/08/03 00:00 | 7.80 | 125.00 | -1.00 | 117.38 | 74.77 | 32.99 | 0.95 | 304.00 | 140.00 | 150.00 | 12.46 | 0.06 |
| EB1 | 2005/05/03 00:00 | 7.50 | 118.00 | -1.00 | 119.16 | 69.46 | 46.94 | 0.74 | 320.00 | 72.00 | 181.00 | 12.16 | 0.07 |
| EB1 | 2005/02/03 00:00 | 7.65 | 113.00 | -1.00 | 117.00 | 65.00 | 42.00 | 1.76 | 329.00 | 81.00 | 192.00 | 11.25 | 0.11 |
| EB1 | 2005/01/06 00:00 | 7.24 | 123.10 | -1.00 | 131.00 | 70.00 | 45.00 | 1.03 | 290.00 | 73.00 | 215.00 | -1.00 | 0.16 |
| EB1 | 2005/10/11 10:00 | 8.05 | 128.00 | -1.00 | 146.35 | 77.48 | 46.52 | 1.17 | 353.00 | 75.00 | 213.00 | 14.67 | 0.09 |
| EB1 | 2005/01/06 00:00 | 7.55 | 59.50 | -1.00 | 51.00 | 29.00 | 29.00 | 1.22 | 237.00 | 47.00 | 23.00 | -1.00 | 0.07 |
| EB1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB1 | 2006/06/09 00:00 | 7.32 | 124.00 | -1.00 | 135.29 | 74.93 | 44.78 | 0.73 | 357.00 | 79.00 | 192.00 | 15.13 | 0.08 |
| EB1 | 2006/12/12 00:00 | 7.40 | 130.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB2 | 2005/05/03 00:00 | 7.69 | 115.00 | -1.00 | 128.44 | 71.67 | 41.97 | 0.71 | 336.00 | 59.00 | 244.00 | 7.82 | 0.05 |
| EB2 | 2005/10/11 10:00 | 8.18 | 116.00 | -1.00 | 127.95 | 69.24 | 34.50 | 1.20 | 351.00 | 64.00 | 213.00 | 1.23 | 0.15 |
| EB2 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB2 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB2 | 2006/06/09 00:00 | 7.52 | 95.00 | -1.00 | 88.99 | 55.20 | 54.39 | 0.71 | 303.00 | 64.80 | 128.00 | 0.92 | 0.16 |
| EB2 | 2006/08/29 00:00 | 7.60 | 110.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB2 | 2006/12/09 00:00 | 7.90 | 80.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB2 | 2006/12/12 00:00 | 7.60 | 120.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB3 | 2005/05/03 00:00 | 7.51 | 111.00 | -1.00 | 109.31 | 61.40 | 50.56 | 1.36 | 329.00 | 51.00 | 233.00 | 6.01 | 0.08 |
| EB3 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB3 | 2005/10/11 10:00 | 8.04 | 90.00 | -1.00 | 82.74 | 44.36 | 62.89 | 2.10 | 303.00 | 41.10 | 124.00 | 0.01 | 0.03 |
| EB3 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB3 | 2006/06/09 00:00 | 7.29 | 88.00 | -1.00 | 73.77 | 44.68 | 67.32 | 1.12 | 273.00 | 59.60 | 124.00 | 0.04 | 0.05 |
| EB3 | 2006/08/29 00:00 | 7.20 | 100.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB3 | 2006/08/29 00:00 | 7.40 | 110.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB3 | 2006/08/29 00:00 | 7.40 | 110.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EB3 | 2006/12/12 00:00 | 7.30 | 90.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EC1 | 2006/08/29 00:00 | 7.60 | 95.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| EC1 | 2006/12/12 00:00 | 7.50 | 100.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FB1 | 2005/05/03 00:00 | 7.55 | 114.00 | -1.00 | 114.21 | 70.78 | 39.53 | 0.78 | 319.00 | 65.00 | 179.00 | 10.09 | 0.08 |
| FB1 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FB1 | 2005/10/12 10:00 | 7.72 | 119.00 | -1.00 | 112.59 | 66.63 | 35.28 | 0.93 | 341.00 | 72.00 | 204.00 | 11.23 | 0.62 |
| FB1 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FB1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FB1 | 2006/06/09 00:00 | 7.48 | 106.00 | -1.00 | 108.59 | 62.58 | 44.79 | 0.65 | 309.00 | 67.00 | 163.00 | 9.97 | 1.05 |
| FB1 | 2006/08/29 00:00 | 7.60 | 110.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FB1 | 2006/08/29 00:00 | 7.40 | 120.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FB1 | 2006/08/29 00:00 | 7.50 | 110.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FB1 | 2006/12/10 00:00 | 7.60 | 56.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FB1 | 2006/12/12 00:00 | 7.60 | 110.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FS1 | 2005/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FS1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FS1 | 2006/06/09 00:00 | 7.52 | 103.00 | -1.00 | 92.17 | 61.04 | 101.38 | 1.92 | 466.00 | 45.00 | 97.00 | 5.78 | 0.14 |
| FS1 | 2006/08/29 00:00 | 7.40 | 120.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| FS1 | 2006/12/08 00:00 | 7.30 | 120.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB1 | 2005/05/03 00:00 | 7.36 | 132.00 | -1.00 | 105.92 | 72.38 | 76.70 | 1.18 | 359.00 | 153.00 | 103.00 | 6.33 | 0.10 |
| GB1 | 2004/09/08 00:00 | 7.91 | 118.00 | -1.00 | 90.40 | 63.70 | 72.60 | 2.50 | 313.00 | 143.00 | 135.00 | 8.85 | 0.26 |
| GB1 | 2004/09/08 00:00 | 7.66 | 116.00 | -1.00 | 85.00 | 62.80 | 75.70 | 2.32 | 309.00 | 171.00 | 96.00 | 5.69 | 0.16 |
| GB1 | 2005/10/12 10:00 | 7.23 | 120.00 | -1.00 | 71.35 | 61.34 | 68.19 | 1.22 | 308.00 | 141.60 | 101.00 | 5.35 | 0.08 |
| GB1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB1 | 2006/06/09 00:00 | 7.94 | 97.00 | -1.00 | 85.33 | 72.88 | 82.69 | 1.20 | 332.00 | 141.00 | 109.00 | 5.52 | 0.13 |
| GB1 | 2006/08/29 00:00 | 7.30 | 130.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB1 | 2006/08/29 00:00 | 7.50 | 96.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB1 | 2006/12/12 00:00 | 7.40 | 130.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB1 | 2006/12/12 00:00 | 7.30 | 210.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB2 | 2005/05/03 00:00 | 7.24 | 139.00 | -1.00 | 122.42 | 83.86 | 76.81 | 1.33 | 380.00 | 128.00 | 163.00 | 9.24 | 0.10 |
| GB2 | 2004/09/08 00:00 | 7.68 | 116.00 | -1.00 | 89.40 | 65.10 | 68.00 | 2.71 | 346.00 | 121.00 | 135.00 | 7.26 | 0.14 |
| GB2 | 2004/09/08 00:00 | 7.77 | 131.00 | -1.00 | 117.00 | 81.20 | 78.30 | 2.88 | 313.00 | 148.00 | 171.00 | 17.76 | 0.17 |
| GB2 | 2005/10/12 10:00 | 7.44 | 140.00 | -1.00 | 111.03 | 75.84 | 68.58 | 1.58 | 420.00 | 123.00 | 169.00 | 8.14 | 0.10 |
| GB2 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB2 | 2006/06/09 00:00 | 7.77 | 116.00 | -1.00 | 128.77 | 86.87 | 81.36 | 1.28 | 413.00 | 135.00 | 168.00 | 7.62 | 0.06 |
| GB2 | 2006/08/29 00:00 | 7.40 | 150.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB2 | 2006/12/12 00:00 | 7.30 | 140.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB3 | 2005/05/03 00:00 | 7.39 | 136.00 | -1.00 | 121.02 | 73.17 | 65.50 | 1.12 | 311.00 | 132.00 | 177.00 | 14.99 | 0.12 |
| GB3 | 2005/02/03 00:00 | 7.62 | 131.00 | -1.00 | 119.00 | 74.00 | 57.00 | 1.22 | 328.00 | 125.00 | 186.00 | 15.03 | 0.12 |
| GB3 | 2005/10/12 10:00 | 7.60 | 135.00 | -1.00 | 115.60 | 59.09 | 71.19 | 1.66 | 318.00 | 137.00 | 172.00 | 16.42 | 0.16 |
| GB3 | 2005/01/06 00:00 | 7.44 | 129.60 | -1.00 | 124.00 | 70.00 | 65.00 | 1.59 | 329.00 | 124.00 | 157.00 | -1.00 | 0.11 |

| SiteName | DateTimeMeas | Al mg/l | Fe mg/l | Mn mg/l | N_Amonia | N NO2mg/l | Br mg/l | PO4 mg/l | As mg/l | Ba mg/l | Cd mg/l | Cu mg/l | Ni mg/l |
|----------|------------------|---------|---------|---------|----------|-----------|---------|----------|---------|---------|---------|---------|---------|
| B1 | 2004/08/03 00:00 | -1.00 | -1.00 | -1.00 | 0.14 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| B10 | 2004/08/03 00:00 | -1.00 | -1.00 | -1.00 | 0.66 | -1.00 | 0.68 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| B11 | 2004/08/03 00:00 | -1.00 | -1.00 | -1.00 | 0.20 | -1.00 | 0.45 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| B12 | 2004/08/03 00:00 | -1.00 | -1.00 | -1.00 | 0.30 | -1.00 | 0.44 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| B4 | 2004/08/03 00:00 | -1.00 | -1.00 | -1.00 | 0.15 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| B5 | 2004/08/03 00:00 | -1.00 | -1.00 | -1.00 | 0.14 | -1.00 | 0.28 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| B6 | 2004/08/03 00:00 | -1.00 | -1.00 | -1.00 | 0.15 | -1.00 | 0.52 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| B8 | 2004/08/03 00:00 | -1.00 | -1.00 | -1.00 | 2.20 | -1.00 | 0.37 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| B9 | 2004/08/03 00:00 | -1.00 | -1.00 | -1.00 | 0.28 | -1.00 | 0.67 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| EB1 | 2005/05/03 00:00 | -1.00 | 0.01 | 0.01 | -1.00 | -1.00 | 0.49 | -1.00 | 0.0064 | 0.0720 | -1.0000 | 0.0186 | -1.0000 |
| EB1 | 2005/02/03 00:00 | 0.01 | 0.01 | 0.00 | -1.00 | -1.00 | 0.50 | -1.00 | -1.0000 | -1.0000 | -1.0000 | 0.0070 | -1.0000 |
| EB1 | 2005/01/06 00:00 | 0.01 | 0.01 | 0.01 | -1.00 | -1.00 | 0.35 | -1.00 | -1.0000 | 0.0950 | -1.0000 | 0.0240 | -1.0000 |
| EB1 | 2005/10/11 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.49 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| EB1 | 2005/01/06 00:00 | 0.02 | 0.02 | 0.01 | -1.00 | -1.00 | 0.17 | -1.00 | -1.0000 | 0.0500 | -1.0000 | 0.0320 | -1.0000 |
| EB1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| EB1 | 2006/06/09 00:00 | 0.00 | 0.01 | 0.00 | 0.06 | 0.07 | 0.43 | -1.00 | -1.0000 | 0.0917 | -1.0000 | -1.0000 | -1.0000 |
| EB1 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1400 | -1.0000 | -1.0000 | 0.0050 |
| EB2 | 2005/05/03 00:00 | -1.00 | 0.02 | 0.02 | -1.00 | -1.00 | 0.22 | -1.00 | -1.0000 | 0.0784 | -1.0000 | 0.0180 | -1.0000 |
| EB2 | 2005/10/11 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.43 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| EB2 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| EB2 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| EB2 | 2006/06/09 00:00 | 0.00 | 0.03 | 0.13 | 0.20 | -1.00 | 0.35 | -1.00 | -1.0000 | 0.0469 | -1.0000 | -1.0000 | -1.0000 |
| EB2 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0640 | -1.0000 | -1.0000 | 0.0040 |
| EB2 | 2006/12/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0260 | -1.0000 | -1.0000 | 0.0040 |
| EB2 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0660 | -1.0000 | -1.0000 | 0.0050 |
| EB3 | 2005/05/03 00:00 | 0.01 | 0.02 | 0.05 | -1.00 | -1.00 | 0.19 | -1.00 | -1.0000 | 0.0721 | -1.0000 | 0.0192 | -1.0000 |
| EB3 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| EB3 | 2005/10/11 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.13 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| EB3 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| EB3 | 2006/06/09 00:00 | 0.00 | 0.02 | 0.10 | 0.10 | -1.00 | 0.35 | -1.00 | -1.0000 | 0.0167 | -1.0000 | -1.0000 | -1.0000 |
| EB3 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0490 | -1.0000 | -1.0000 | 0.0040 |
| EB3 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.7800 | -1.0000 | -1.0000 | 0.0040 |
| EB3 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.7800 | -1.0000 | -1.0000 | 0.0050 |
| EB3 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0400 | -1.0000 | -1.0000 | 0.0040 |
| EC1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1100 | -1.0000 | -1.0000 | 0.0060 |
| EC1 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1000 | -1.0000 | -1.0000 | 0.0050 |
| FB1 | 2005/05/03 00:00 | -1.00 | 0.05 | 0.05 | -1.00 | -1.00 | 0.43 | -1.00 | -1.0000 | 0.0852 | -1.0000 | 0.0159 | -1.0000 |
| FB1 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| FB1 | 2005/10/12 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.45 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| FB1 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| FB1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| FB1 | 2006/06/09 00:00 | 0.00 | 0.01 | 0.03 | 0.06 | 0.02 | 0.41 | -1.00 | -1.0000 | 0.0873 | -1.0000 | -1.0000 | -1.0000 |
| FB1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1800 | -1.0000 | -1.0000 | 0.0040 |
| FB1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0860 | -1.0000 | -1.0000 | 0.0040 |
| FB1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1200 | -1.0000 | -1.0000 | 0.0050 |
| FB1 | 2006/12/10 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0360 | -1.0000 | -1.0000 | 0.0030 |
| FB1 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0840 | -1.0000 | -1.0000 | 0.0050 |
| FS1 | 2005/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| FS1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| FS1 | 2006/06/09 00:00 | 0.01 | 0.01 | 0.14 | 0.09 | -1.00 | 0.22 | -1.00 | -1.0000 | 0.0918 | -1.0000 | -1.0000 | -1.0000 |
| FS1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1200 | -1.0000 | -1.0000 | 0.0120 |
| FS1 | 2006/12/08 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1200 | -1.0000 | -1.0000 | 0.0130 |
| GB1 | 2005/05/03 00:00 | 0.01 | 0.01 | 0.01 | -1.00 | -1.00 | 0.73 | -1.00 | -1.0000 | 0.0984 | -1.0000 | 0.0160 | -1.0000 |
| GB1 | 2004/09/08 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.49 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| GB1 | 2004/09/08 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.45 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| GB1 | 2005/10/12 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.64 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| GB1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| GB1 | 2006/06/09 00:00 | 0.00 | 0.01 | 0.00 | 0.04 | -1.00 | 0.64 | -1.00 | -1.0000 | 0.0802 | -1.0000 | -1.0000 | -1.0000 |
| GB1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1000 | -1.0000 | -1.0000 | 0.0050 |
| GB1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0040 | -1.0000 | -1.0000 | 0.0030 |
| GB1 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.0980 | -1.0000 | -1.0000 | 0.0050 |
| GB1 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1600 | -1.0000 | -1.0000 | 0.0070 |
| GB2 | 2005/05/03 00:00 | -1.00 | 0.01 | 0.01 | -1.00 | -1.00 | 0.84 | -1.00 | -1.0000 | 0.1173 | -1.0000 | 0.0167 | -1.0000 |
| GB2 | 2004/09/08 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.52 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| GB2 | 2004/09/08 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.57 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| GB2 | 2005/10/12 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.77 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| GB2 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| GB2 | 2006/06/09 00:00 | 0.00 | 0.01 | 0.00 | 0.03 | -1.00 | 0.82 | -1.00 | -1.0000 | 0.0962 | -1.0000 | -1.0000 | -1.0000 |
| GB2 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1300 | -1.0000 | -1.0000 | 0.0070 |
| GB2 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.0000 | 0.1200 | -1.0000 | -1.0000 | 0.0060 |
| GB3 | 2005/05/03 00:00 | -1.00 | 0.01 | 0.01 | -1.00 | -1.00 | 0.83 | -1.00 | -1.0000 | 0.1437 | -1.0000 | 0.0193 | -1.0000 |
| GB3 | 2005/02/03 00:00 | 0.01 | 0.02 | 0.00 | -1.00 | -1.00 | 0.88 | -1.00 | -1.0000 | -1.0000 | -1.0000 | 0.0070 | -1.0000 |
| GB3 | 2005/10/12 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.78 | -1.00 | -1.0000 | -1.0000 | -1.0000 | -1.0000 | -1.0000 |
| GB3 | 2005/01/06 00:00 | 0.01 | 0.01 | 0.00 | -1.00 | -1.00 | 0.81 | -1.00 | -1.0000 | 0.1510 | -1.0000 | 0.0260 | -1.0000 |

Appendix D4

| SiteName | DateTimeMeas | Biphenyl mg/l | TPH C22- C30 mg/l | TPH C30 - C40 mg/l | Bromodichlorometh ane mg/l | Atrazine mg/l | Simazine mg/l | Terbuthyla zine mg/l | 4chloro3m ethylphen ol mg/l | Trichlorofl uorometha ne mg/l | 2,3/3,5- Dimethylp henol + 4- Ethylphen mg/l | Dibenzo(a h)anthrac ene | Pentachlor ophenol mg/l |
|----------|------------------|------------------|----------------------|-----------------------|-------------------------------|------------------|------------------|-------------------------|-----------------------------------|-------------------------------------|--|-------------------------------|-------------------------------|
| GB5 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB5 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB7 | 2005/05/03 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB7 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB7 | 2005/10/11 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB7 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB7 | 2006/06/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB7 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 |
| GB8 | 2005/05/03 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB8 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB8 | 2005/10/11 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB8 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB8 | 2006/06/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB8 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB8 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2005/05/03 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2005/10/12 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2006/06/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2006/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 |
| GB9 | 2006/12/12 00:00 | 0.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GC1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GC1 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS1 | 2006/08/29 00:00 | -1.00 | 0.03 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS2 | 2005/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS2 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS2 | 2006/06/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS2 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | 0.00 | -1.00 |
| GS3 | 2005/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS3 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS3 | 2006/06/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS3 | 2006/08/29 00:00 | -1.00 | 0.11 | -1.00 | 0.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS3 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 |
| GS5 | 2005/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS5 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS5 | 2006/06/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS5 | 2006/08/29 00:00 | 0.00 | 0.16 | -1.00 | 0.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS5 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| NB1 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| NB1 | 2006/11/22 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| NB1 | 2007/02/15 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| NB1 | 2007/02/15 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| SB1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| SB1 | 2006/11/22 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| SB1 | 2007/02/15 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| SB1 | 2007/02/15 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| VB1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| VB1 | 2006/06/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| VB2 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| VB2 | 2006/06/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |

| SiteName | DateTimeMeas | 1,2,4 Trimethylbenzene mg/l | 1,3,5 Trimethylbenzene mg/l | Benzene mg/l | Bromform mg/l | cis-1,2-Dichloroethene mg/l | Chloroform mg/l | Chloromethane mg/l | Dichloromethane mg/l | Trichloroethene mg/l | Tetrachloroethene mg/l |
|----------|------------------|-----------------------------|-----------------------------|--------------|---------------|-----------------------------|-----------------|--------------------|----------------------|----------------------|------------------------|
| GB5 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.01 | 0.00 | 0.00 | -1.00 |
| GB5 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 |
| GB7 | 2005/05/03 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB7 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | 0.00 | -1.00 |
| GB7 | 2005/10/11 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | 0.00 | -1.00 | -1.00 | 0.01 | -1.00 |
| GB7 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | 0.00 | -1.00 | -1.00 | 0.01 | -1.00 |
| GB7 | 2006/06/09 00:00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 |
| GB7 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 |
| GB8 | 2005/05/03 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB8 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | 0.00 | -1.00 |
| GB8 | 2005/10/11 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | 0.00 | -1.00 |
| GB8 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 |
| GB8 | 2006/06/09 00:00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 |
| GB8 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | 0.00 | 0.00 | -1.00 |
| GB8 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2005/05/03 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GB9 | 2005/10/12 10:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | 0.03 | -1.00 | -1.00 | 0.01 | -1.00 |
| GB9 | 2005/06/07 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | 0.01 | 0.00 | -1.00 |
| GB9 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | 0.02 | -1.00 | -1.00 | 0.00 | -1.00 |
| GB9 | 2006/06/09 00:00 | 0.03 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 | 0.01 | -1.00 |
| GB9 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | 0.03 | 0.00 | -1.00 | -1.00 |
| GB9 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | 0.03 | 0.00 | 0.00 | -1.00 |
| GB9 | 2006/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.01 | -1.00 | -1.00 | -1.00 |
| GB9 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | 0.02 | -1.00 | -1.00 | -1.00 |
| GC1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | 0.00 | 0.00 | -1.00 |
| GC1 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 |
| GS1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | 0.00 | -1.00 | -1.00 |
| GS2 | 2005/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | 0.01 | -1.00 |
| GS2 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS2 | 2006/06/09 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS2 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 |
| GS3 | 2005/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.01 | -1.00 |
| GS3 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS3 | 2006/06/09 00:00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS3 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | 0.00 | -1.00 | -1.00 |
| GS3 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS5 | 2005/12/11 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.01 | -1.00 | -1.00 | 0.01 |
| GS5 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.02 | -1.00 | -1.00 | -1.00 |
| GS5 | 2006/06/09 00:00 | 0.03 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| GS5 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.03 | 0.00 | 0.00 | -1.00 |
| GS5 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.03 | -1.00 | -1.00 | -1.00 |
| NB1 | 2006/12/12 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | 0.00 |
| NB1 | 2006/11/22 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.03 | -1.00 | -1.00 |
| NB1 | 2007/02/15 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.0015 | -1.00 | -1.00 | 0.0002 | -1.00 |
| NB1 | 2007/02/15 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| SB1 | 2006/08/29 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | 0.00 | -1.00 |
| SB1 | 2006/11/22 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.00 | -1.00 | -1.00 | -1.00 |
| SB1 | 2007/02/15 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.0051 | -1.00 | -1.00 | -1.00 | -1.00 |
| SB1 | 2007/02/15 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| VB1 | 2006/02/21 00:00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| VB1 | 2006/06/09 00:00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |
| VB2 | 2006/02/21 00:00 | 0.00 | -1.00 | -1.00 | -1.00 | -1.00 | 0.01 | -1.00 | -1.00 | -1.00 | -1.00 |
| VB2 | 2006/06/09 00:00 | 0.02 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 | -1.00 |

Appendix E1

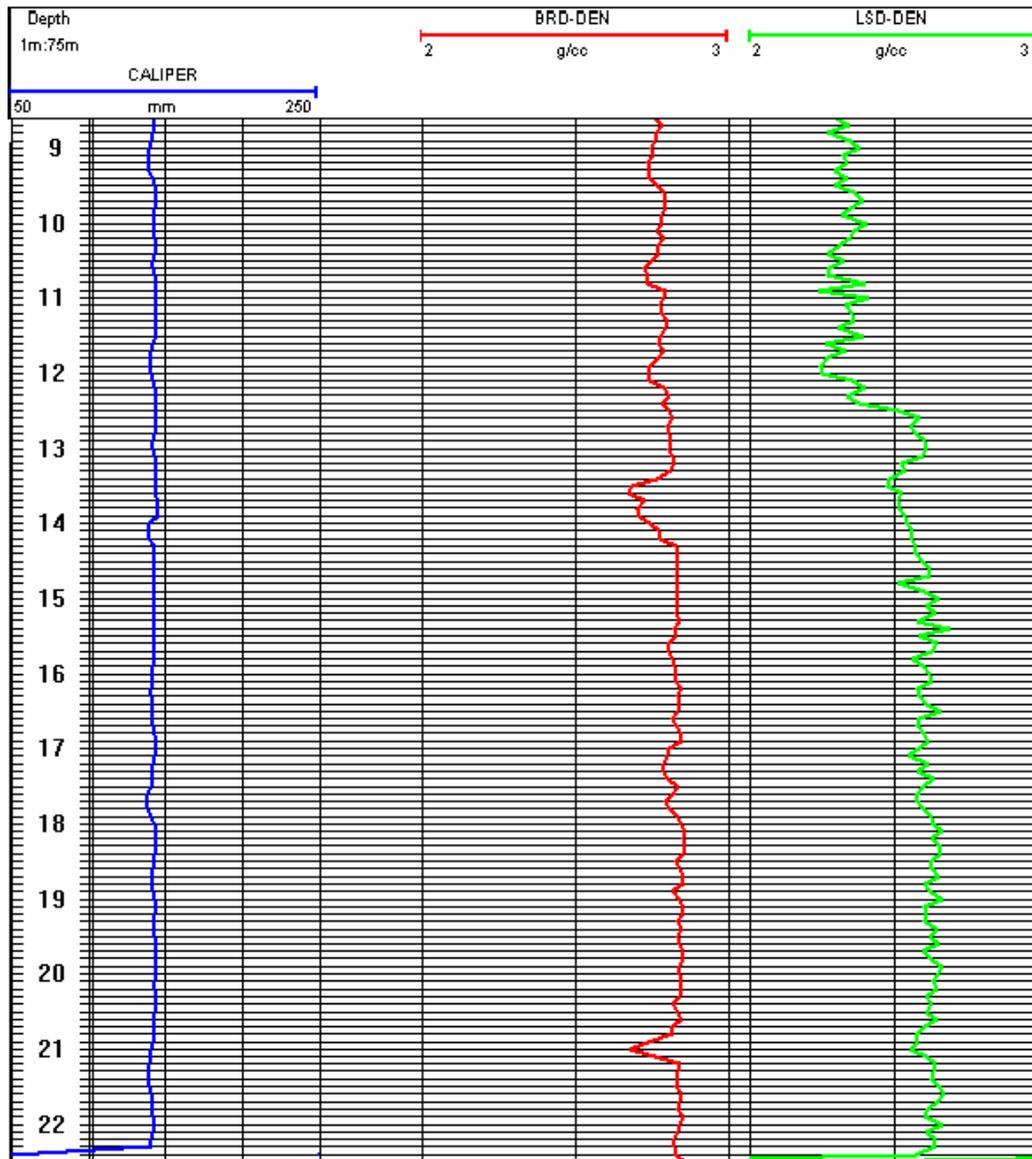


Figure 24: Caliper profile of borehole D1.

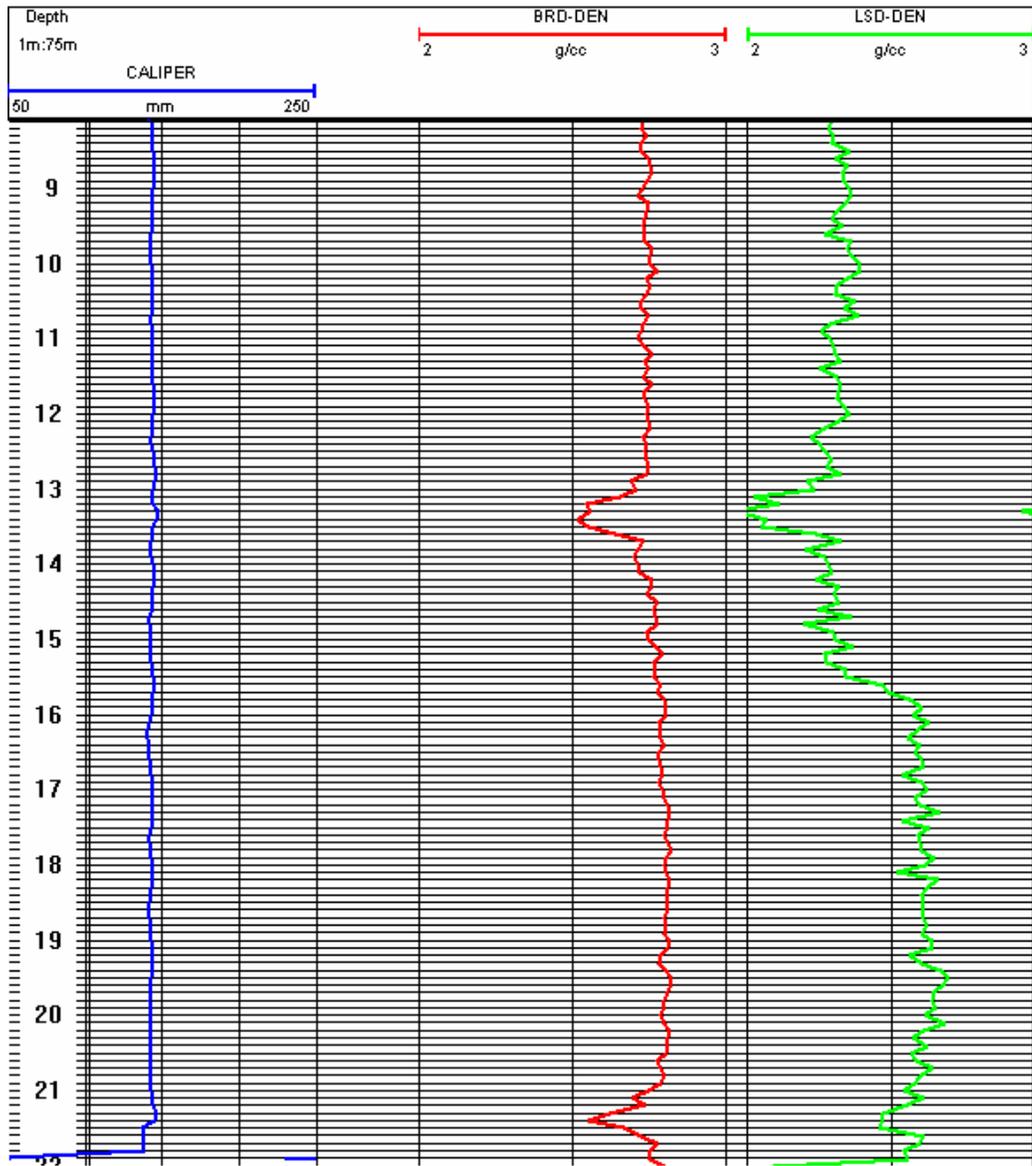


Figure 25: Caliper log of borehole D3.

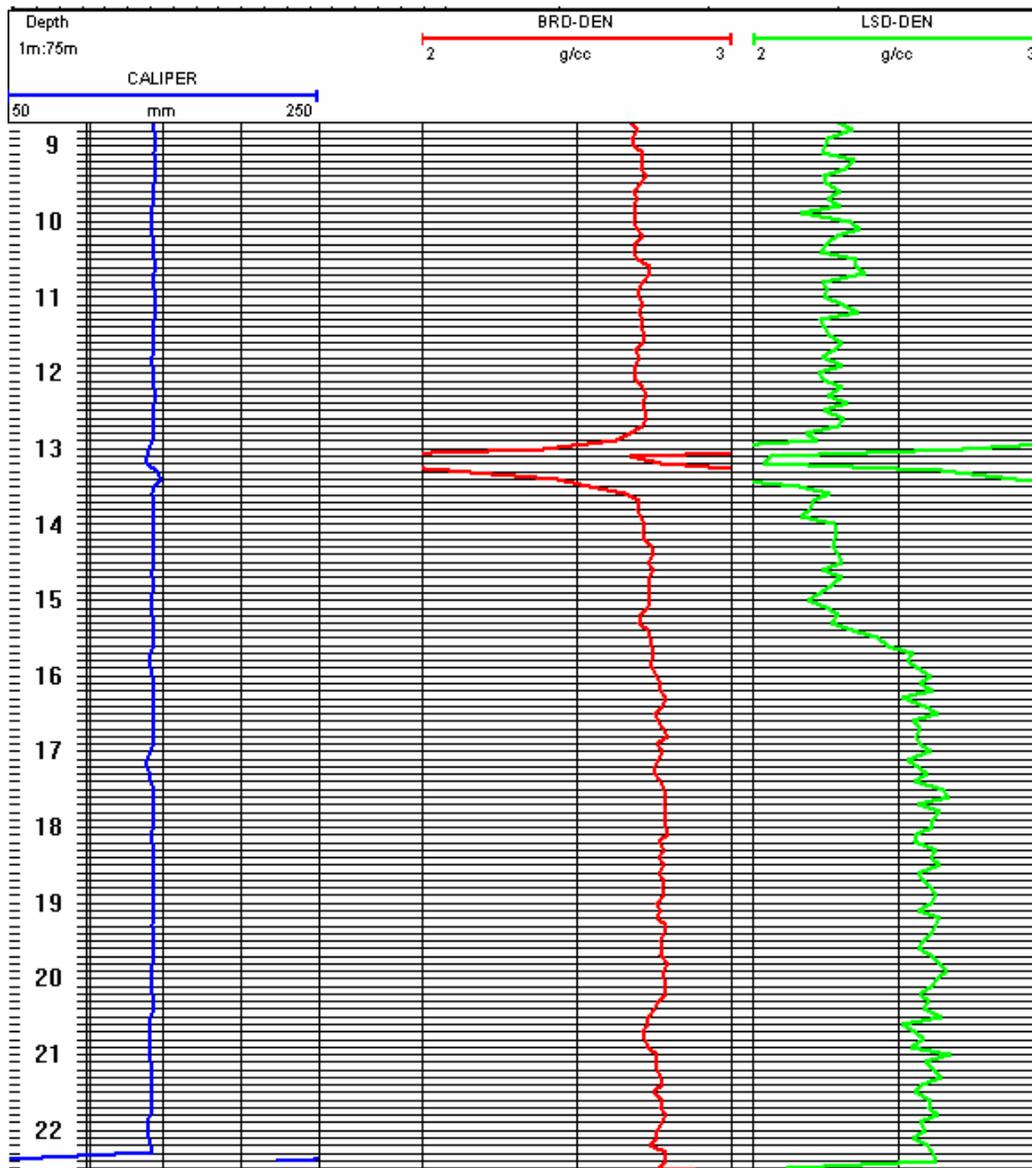


Figure 26: Caliper profile of borehole D4.

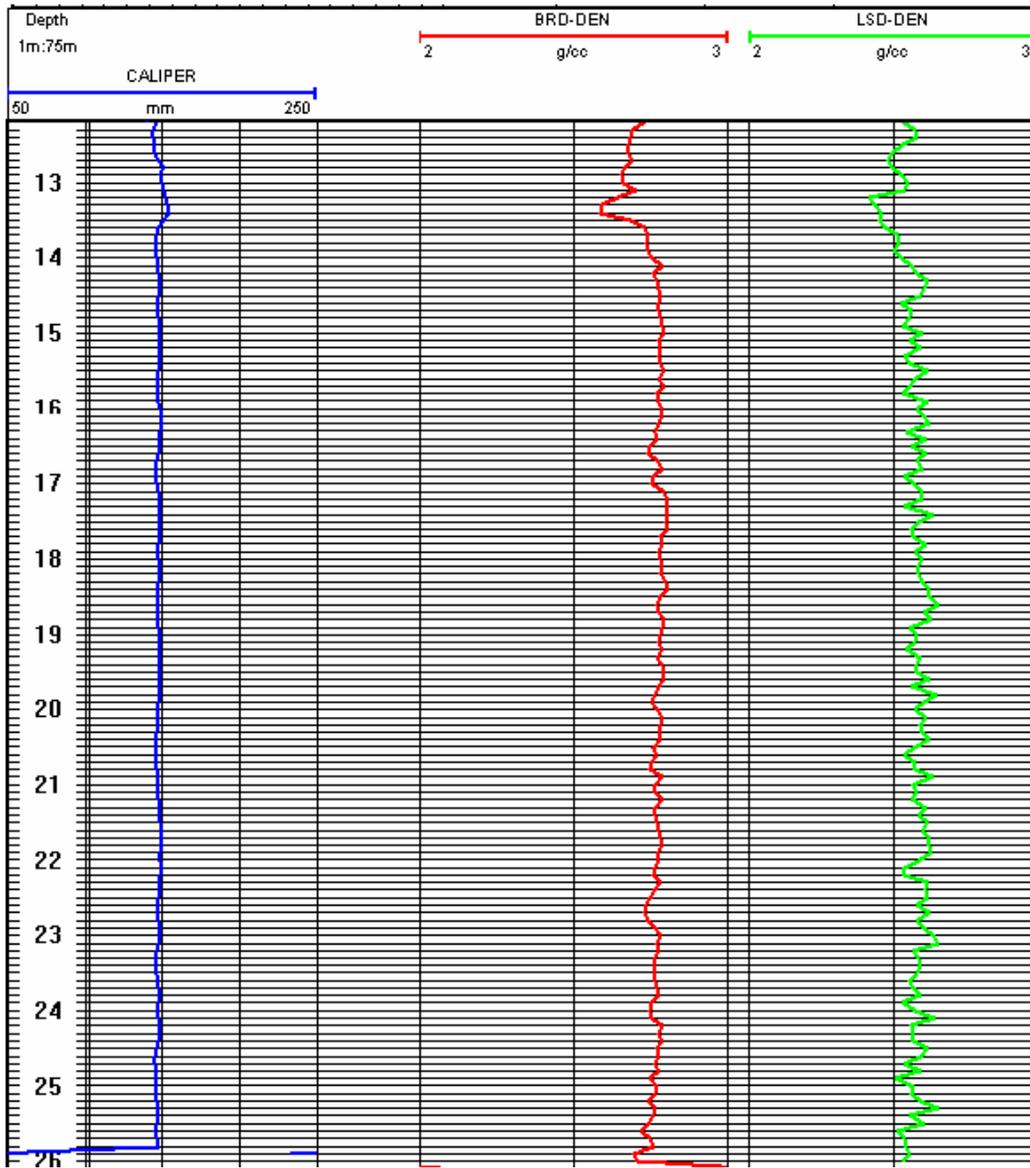


Figure 27: Caliper profile of borehole D5.

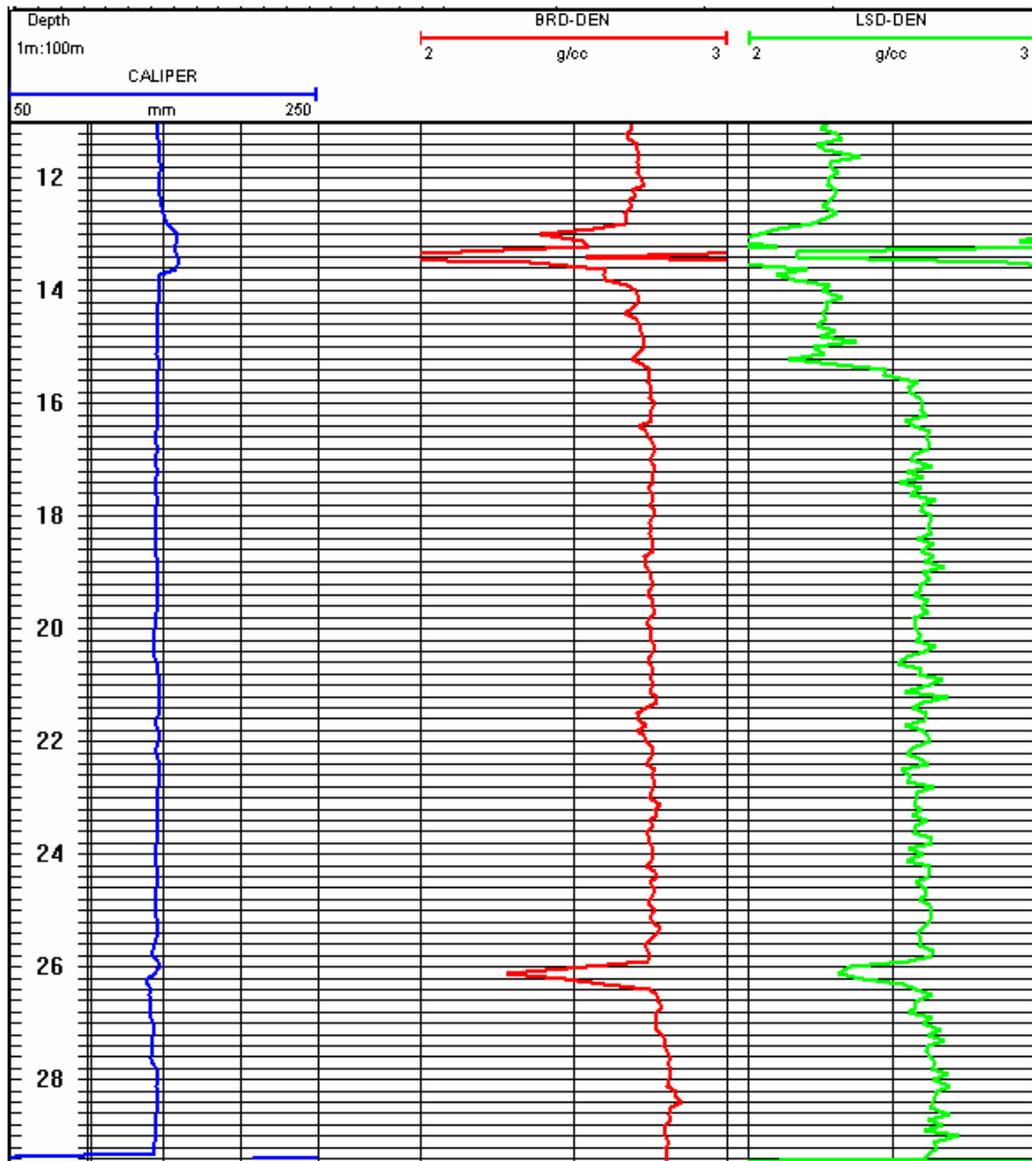


Figure 28: Caliper profile of borehole UO30.

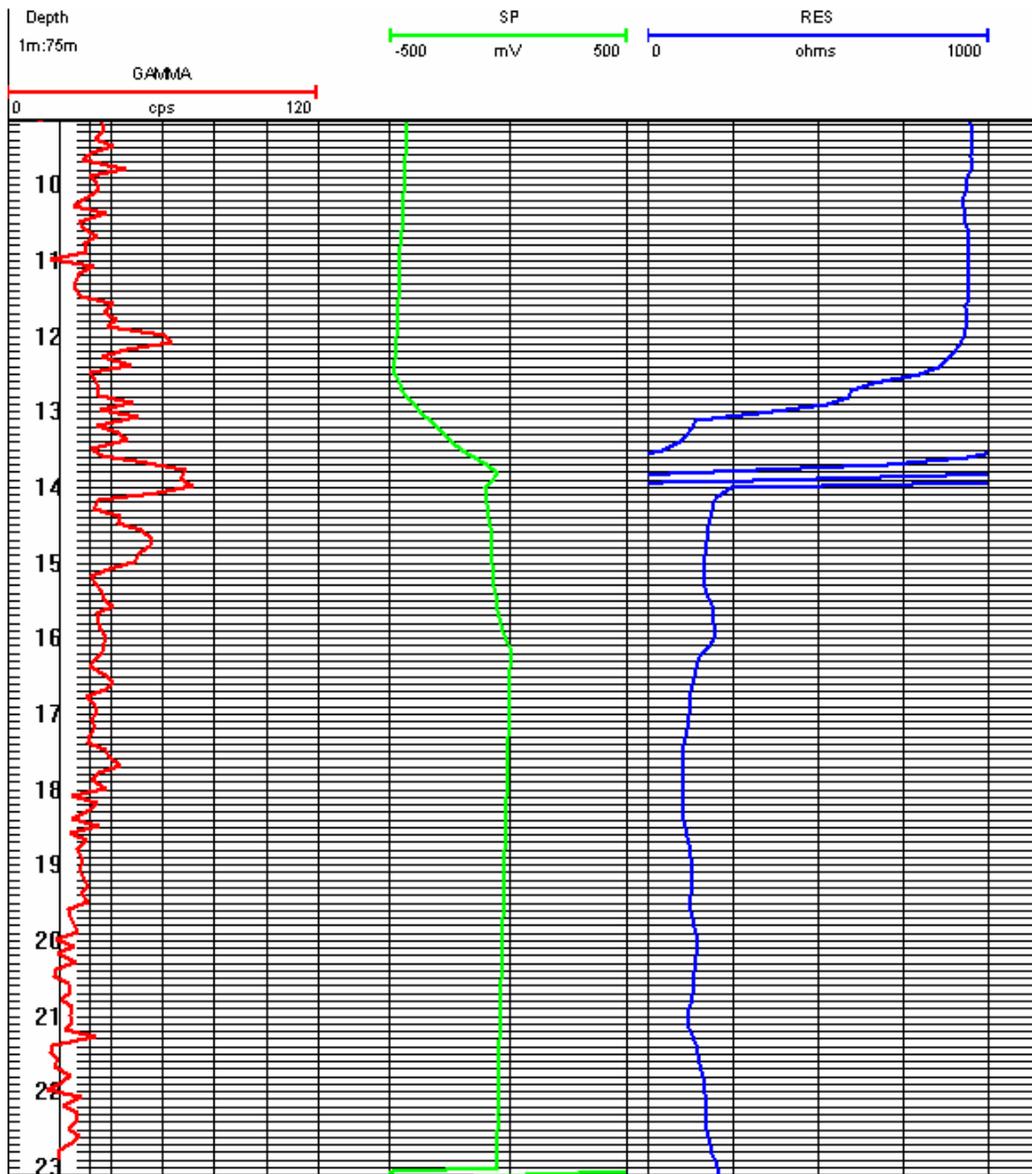


Figure 29: Gamma, SP and Resistivity logs of borehole D1.

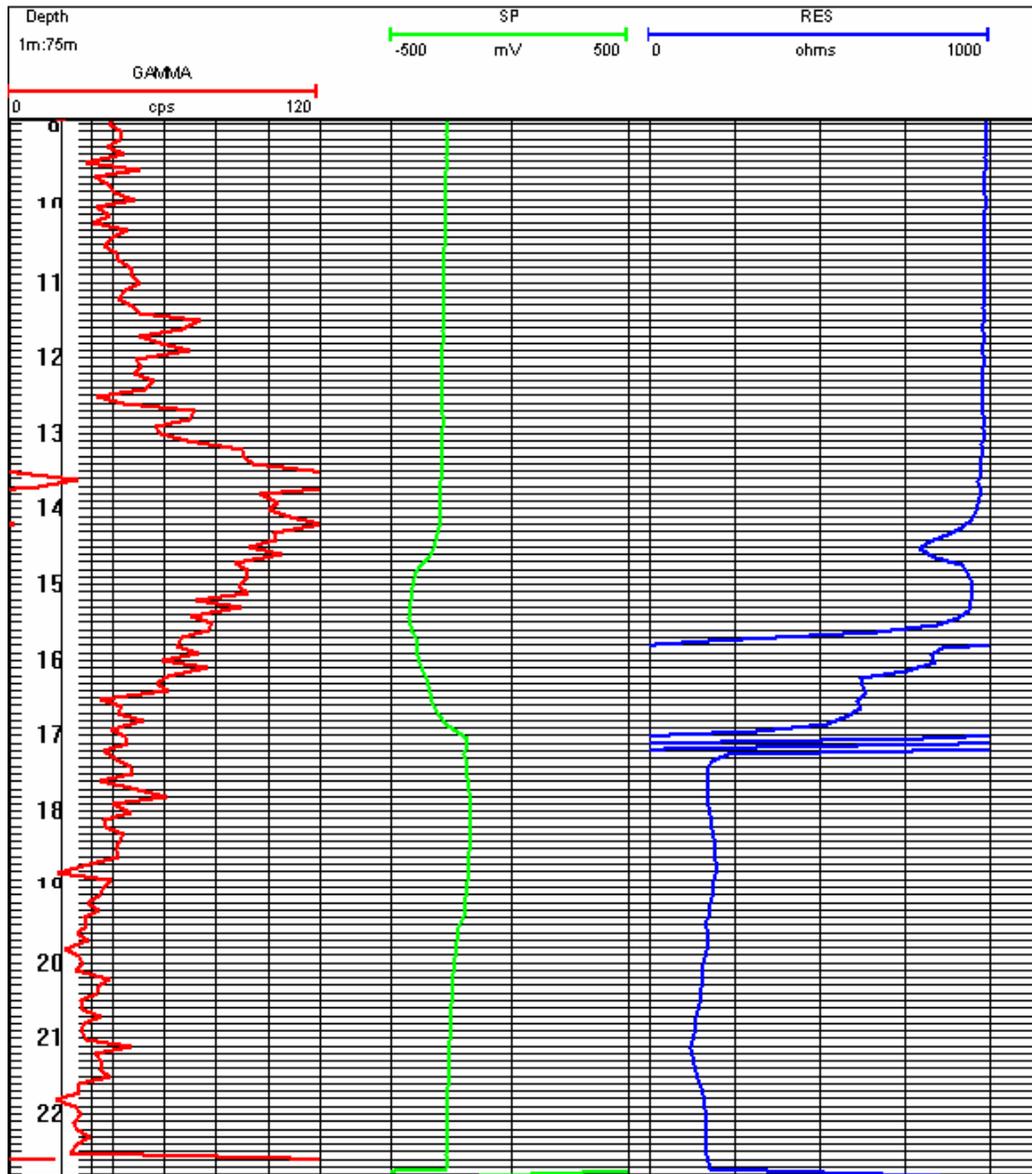


Figure 30: Gamma, SP and resistivity logs of borehole D2.

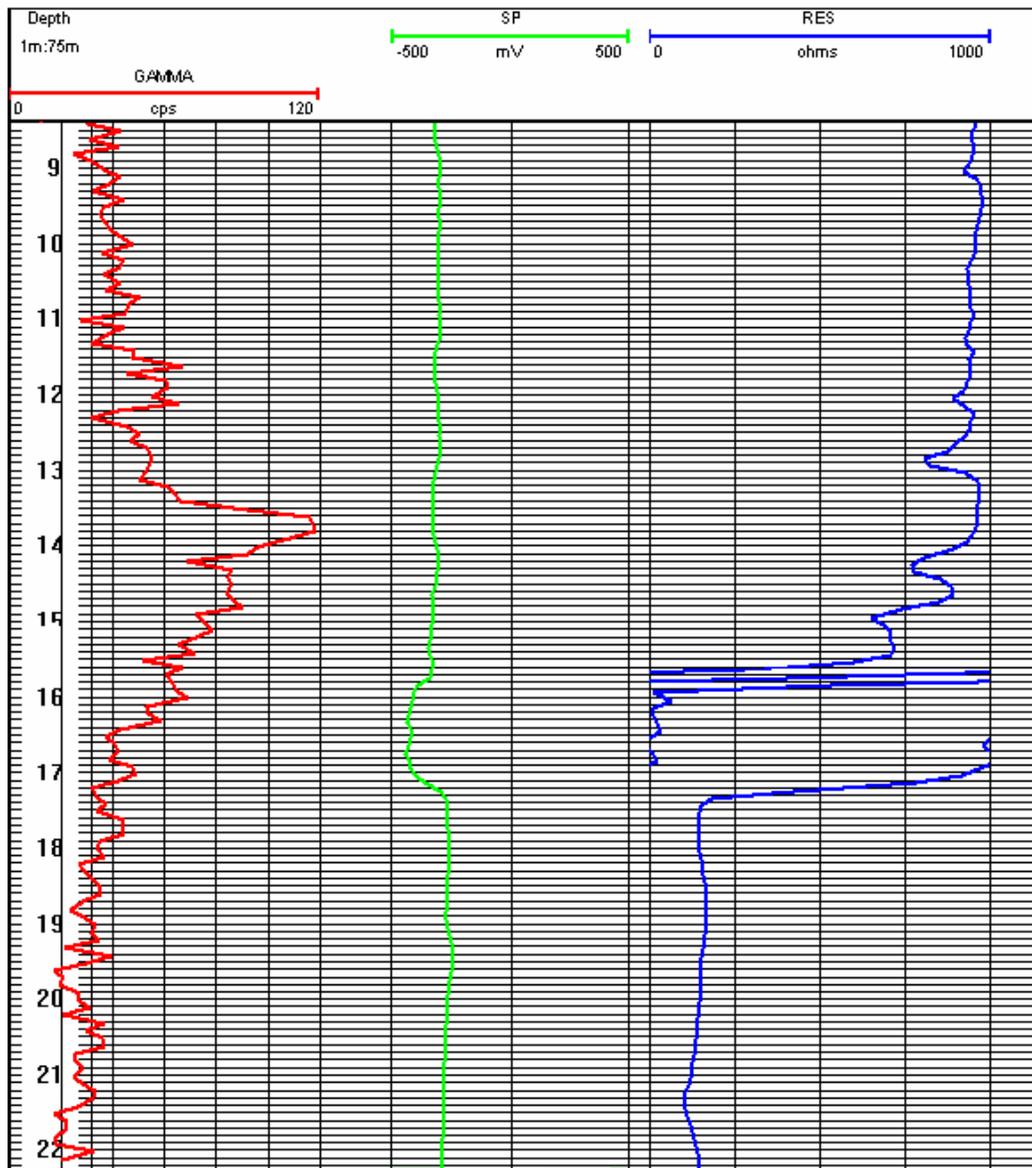


Figure 31: Gamma profile of borehole D3.

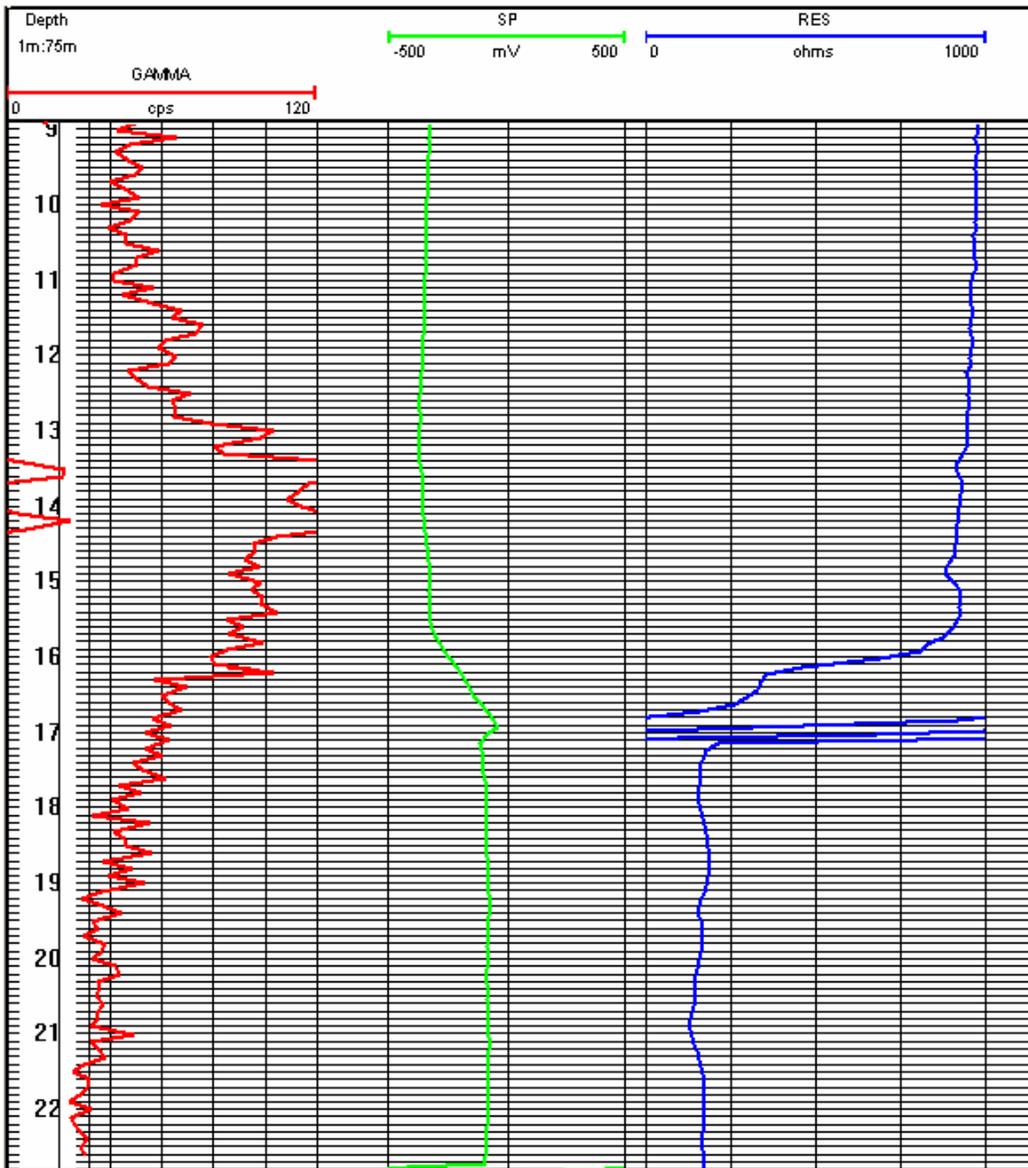


Figure 32: Gamma, SP and resistivity profile of borehole D4.

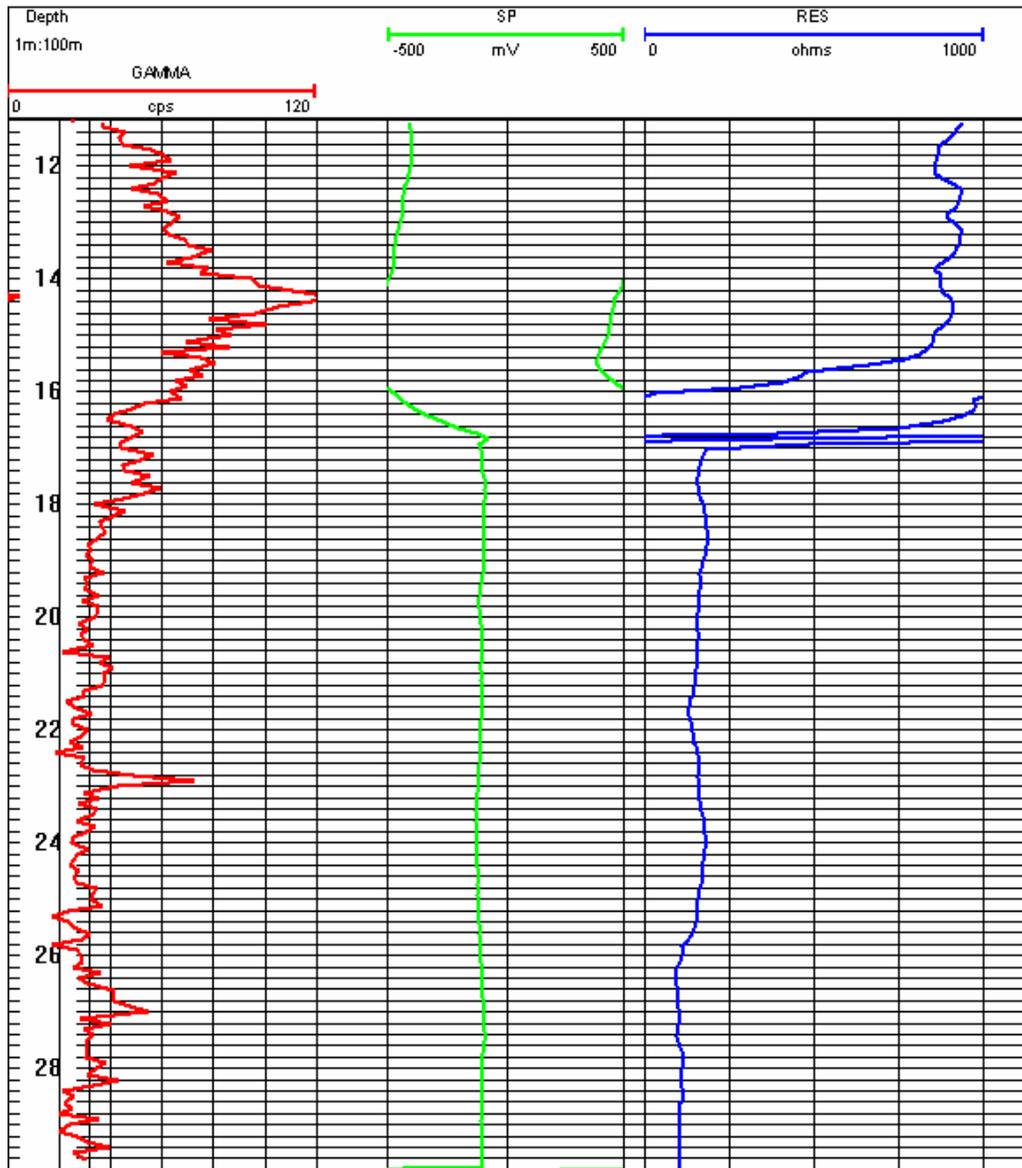


Figure 33: Gamma, SP and resistivity logs of borehole UO30.

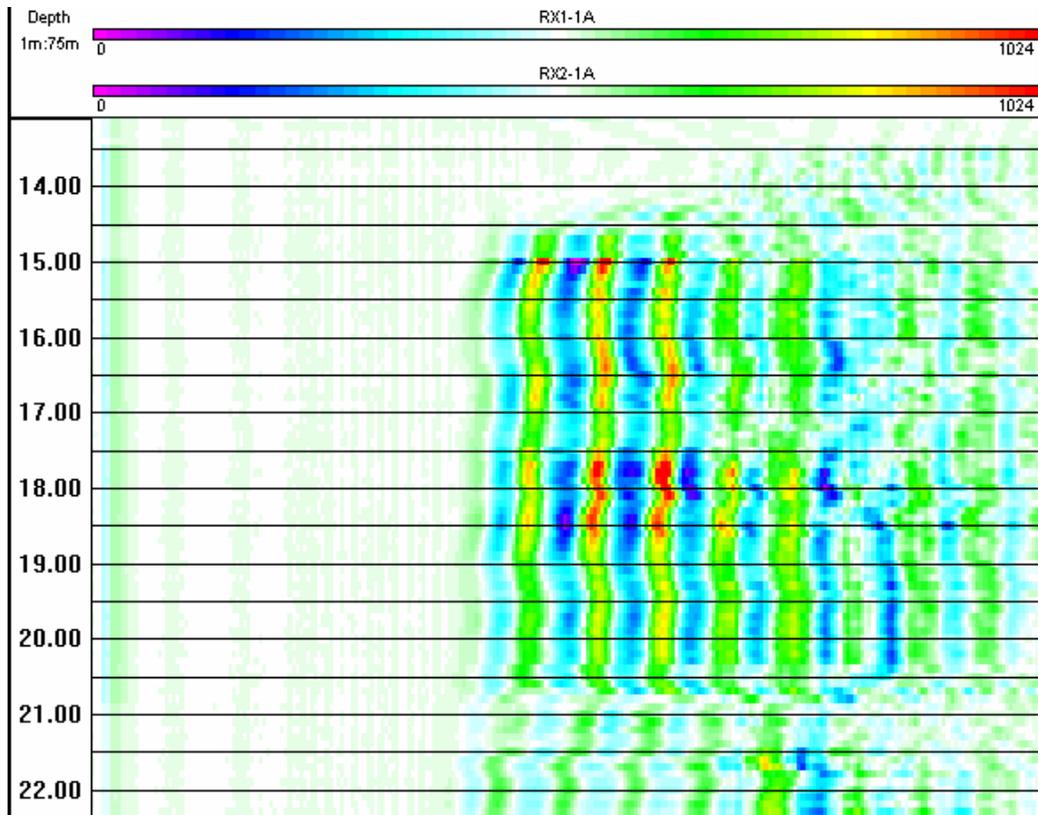


Figure 34: FWS log of borehole D1.

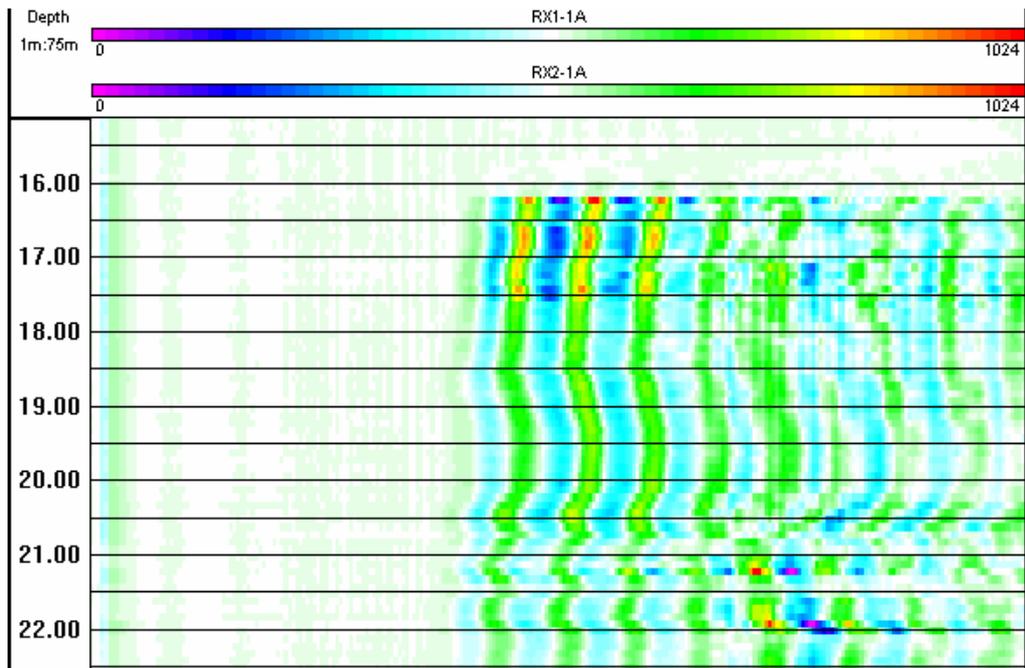


Figure 35: FWS logs of borehole D2.

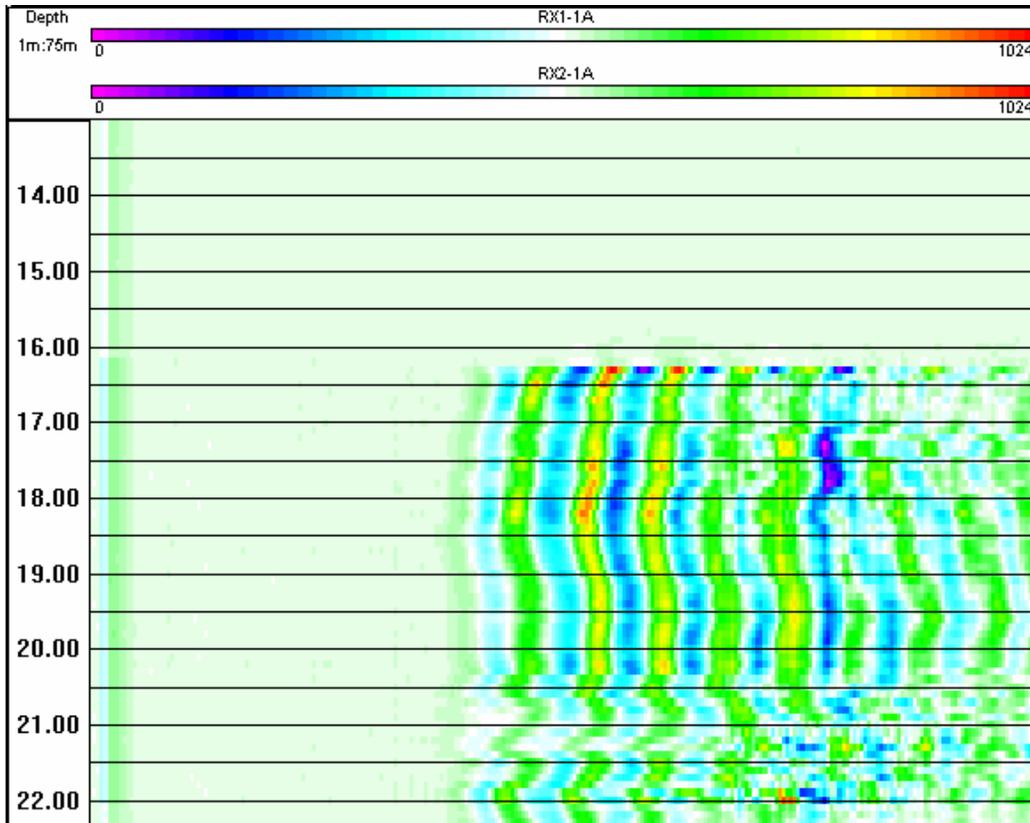


Figure 36: FWS log of borehole D3.

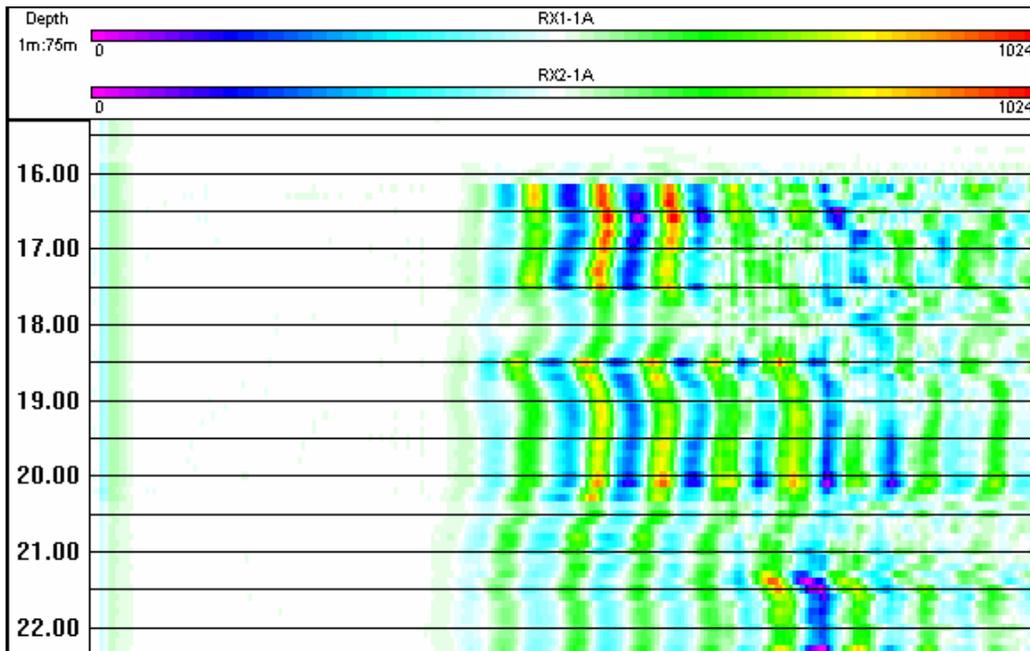


Figure 37: FWS log of borehole D4.

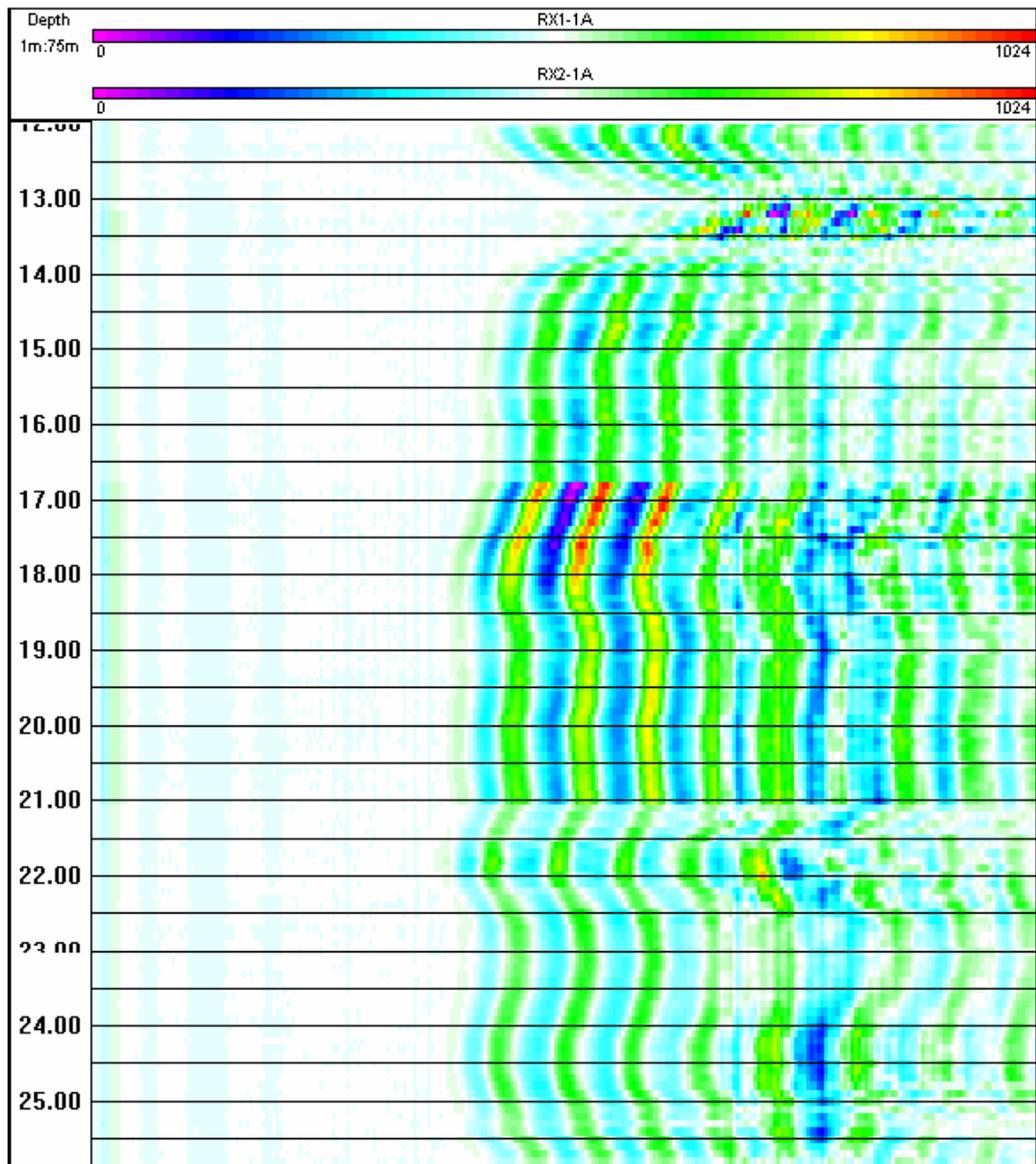


Figure 38: FWS log of borehole D5.

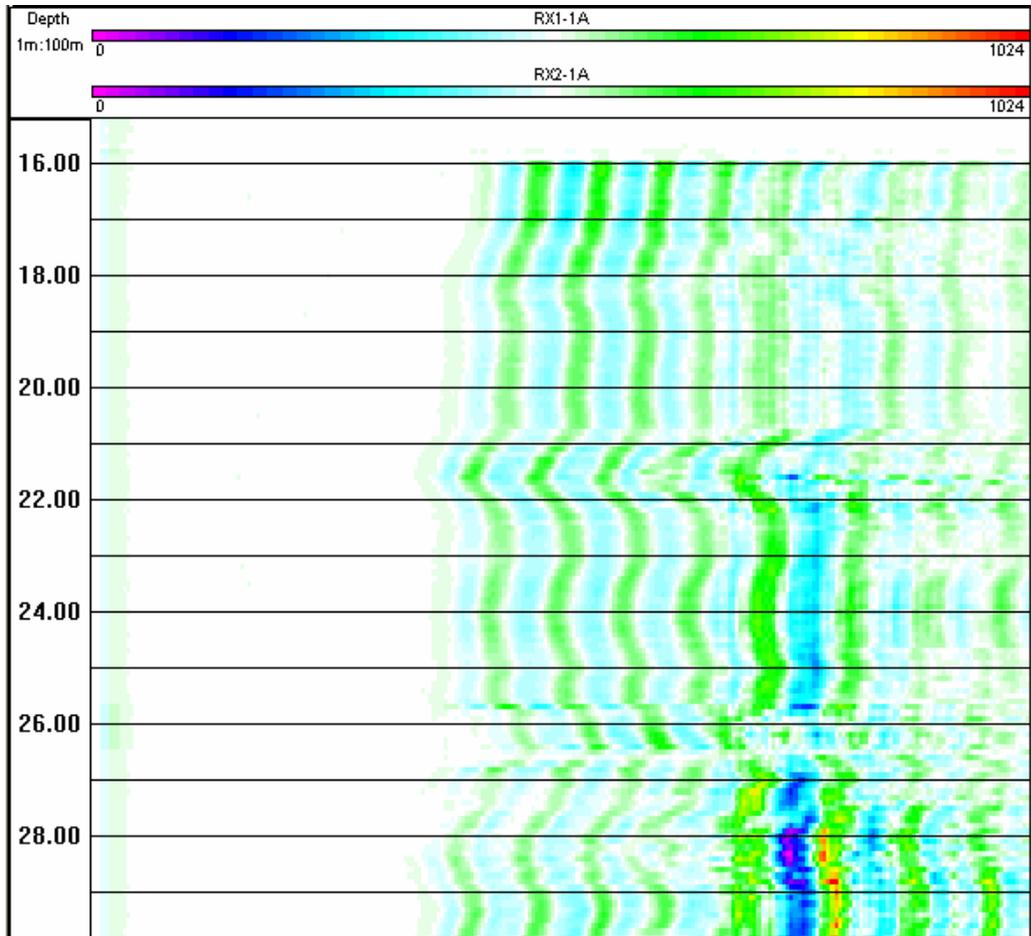


Figure 39: FWS profile of borehole UO30.

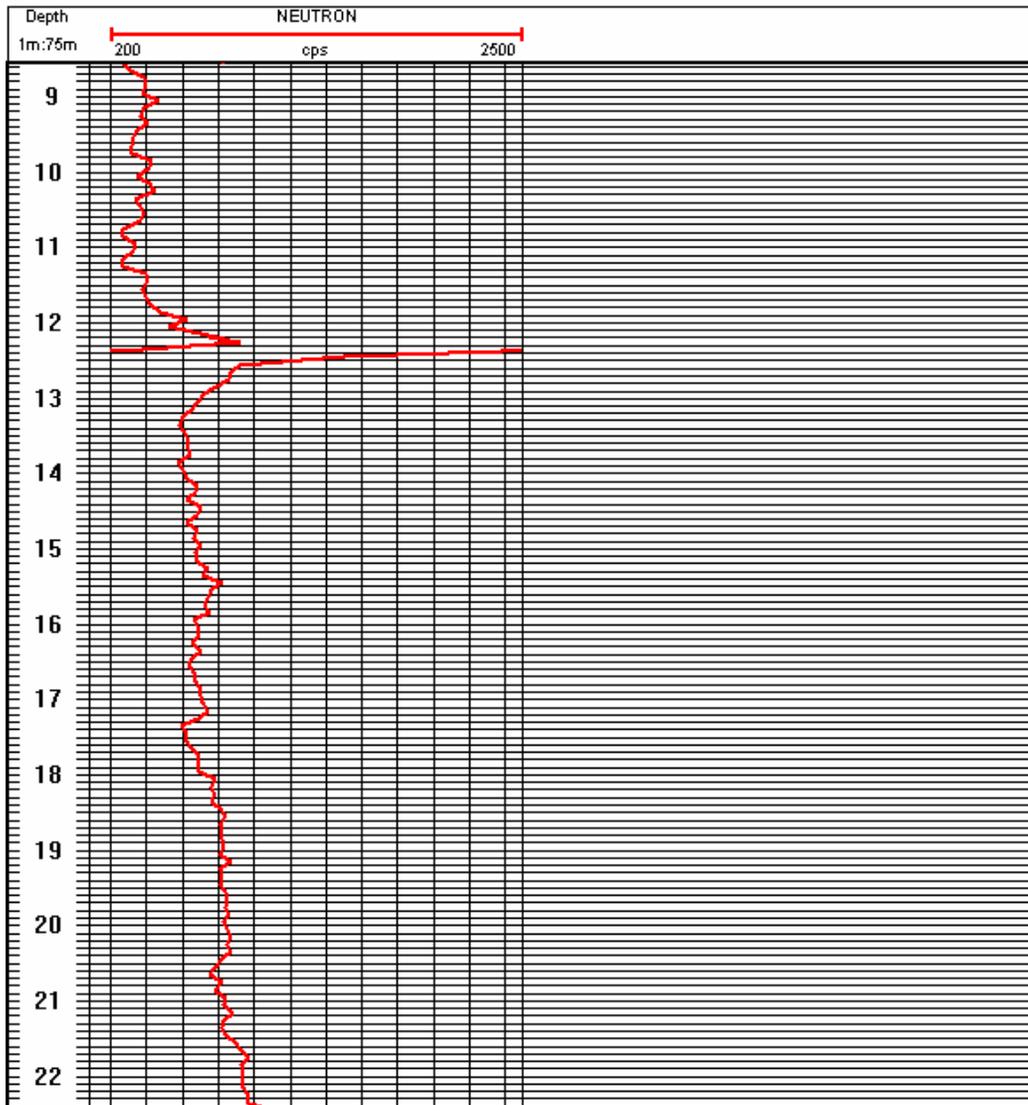


Figure 40: Neutron log of borehole D1.

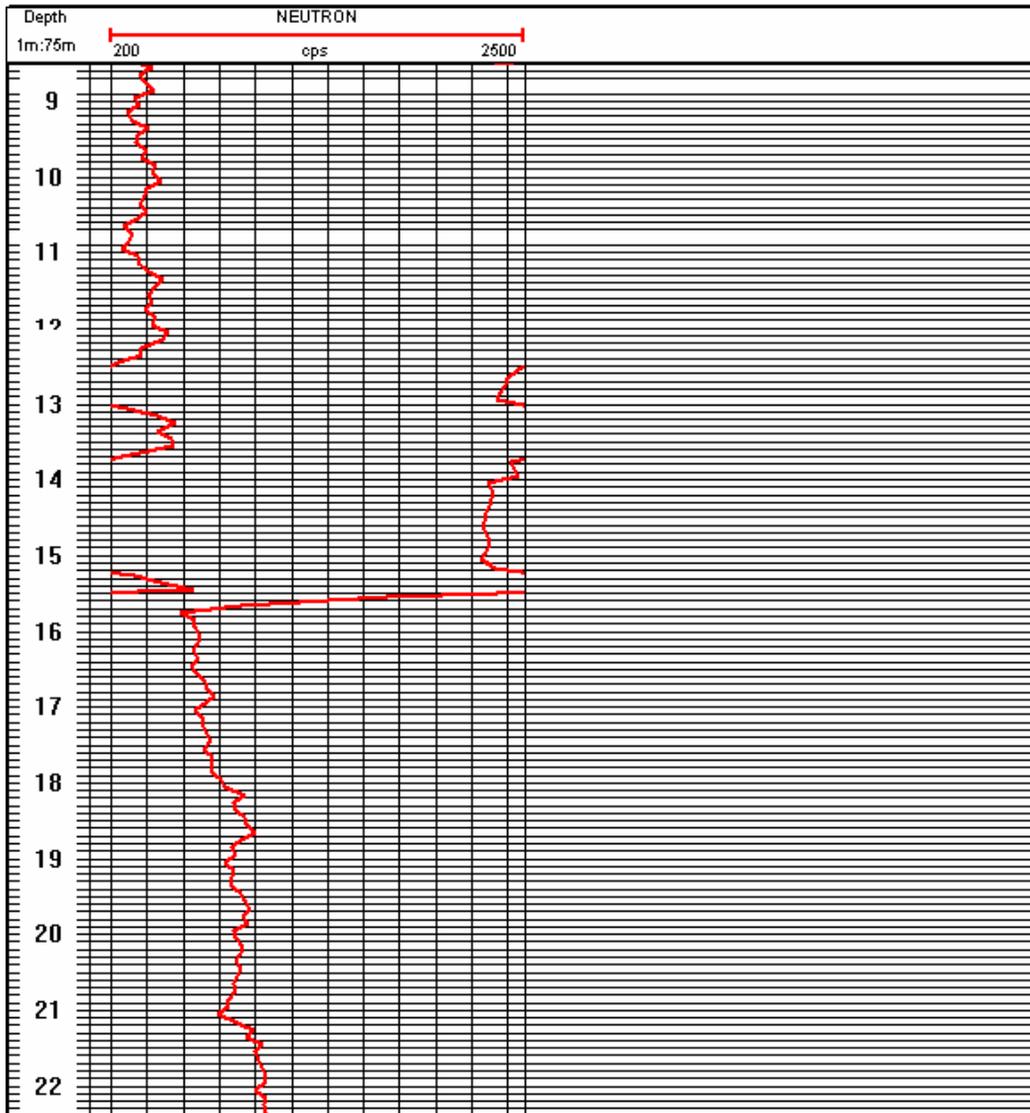


Figure 41: Neutron profile of borehole D2.

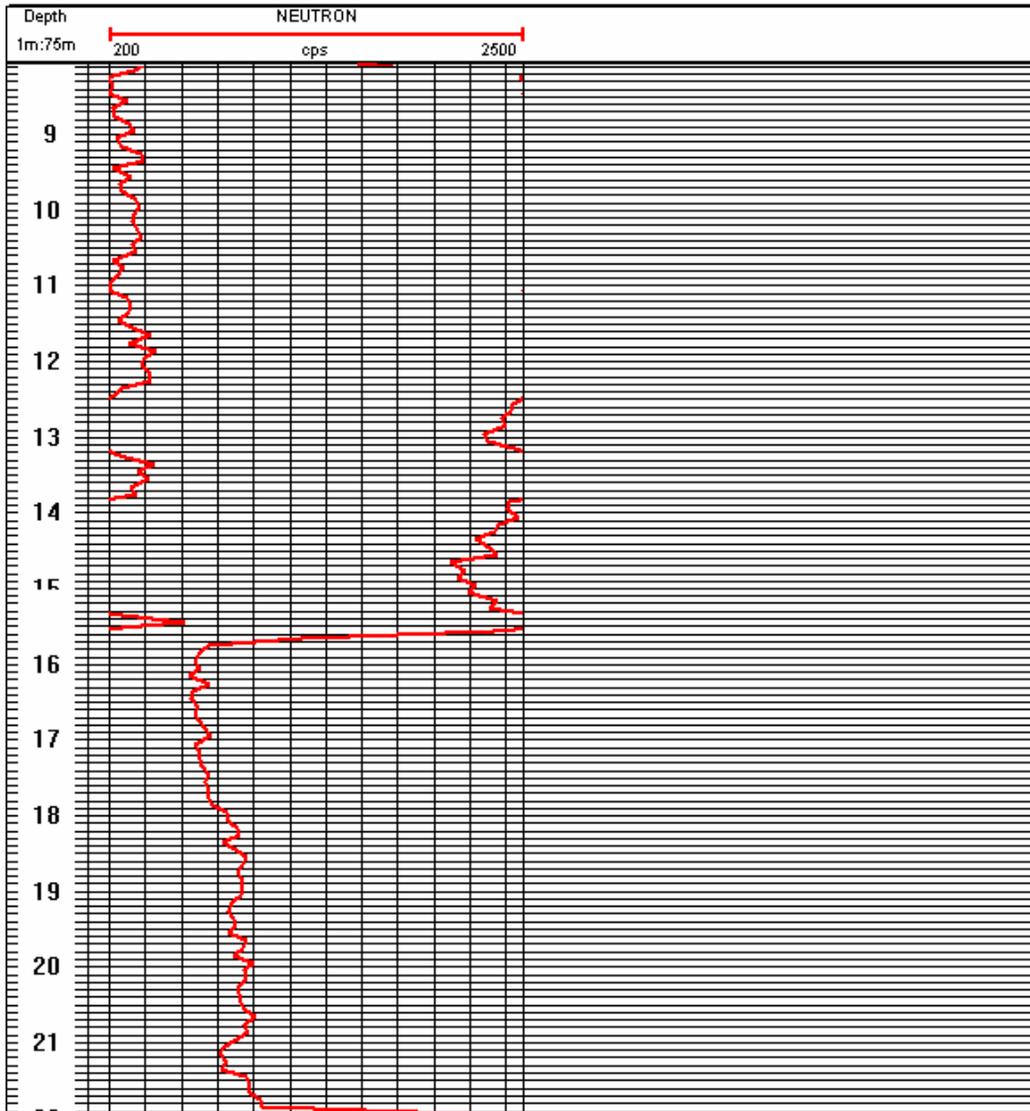


Figure 42: Neutron profile of borehole D3.

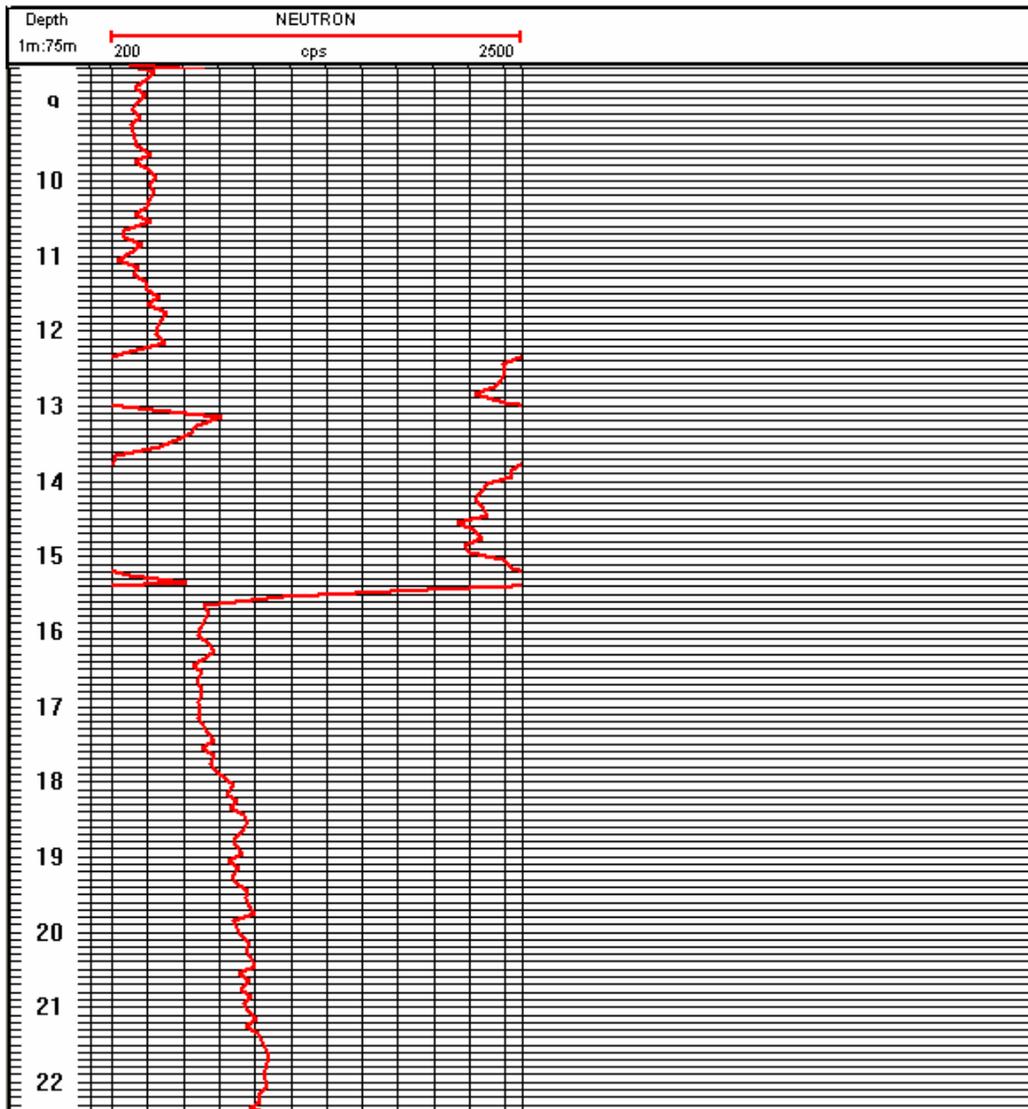


Figure 43: Neutron profile of borehole D4.

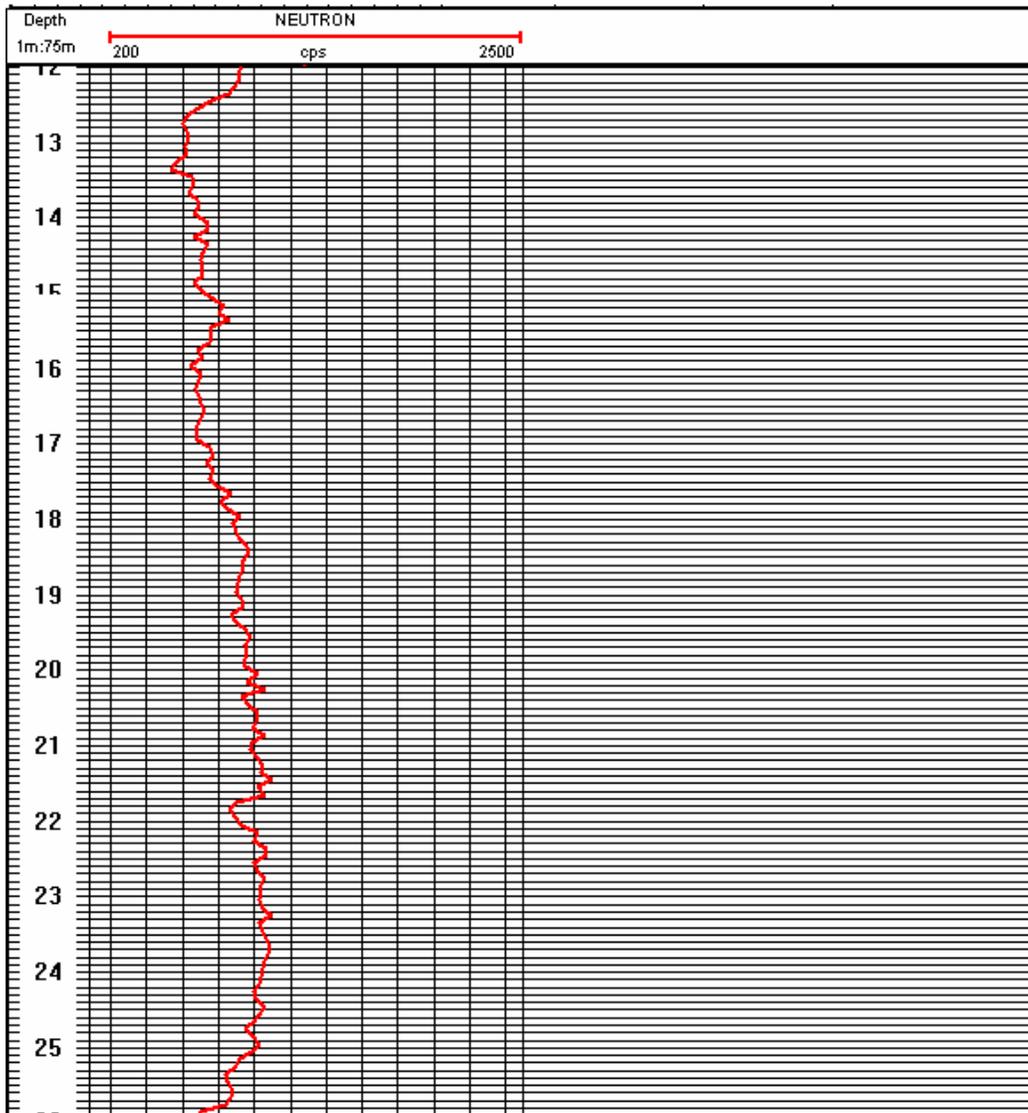


Figure 44: Neutron profile of borehole D5.

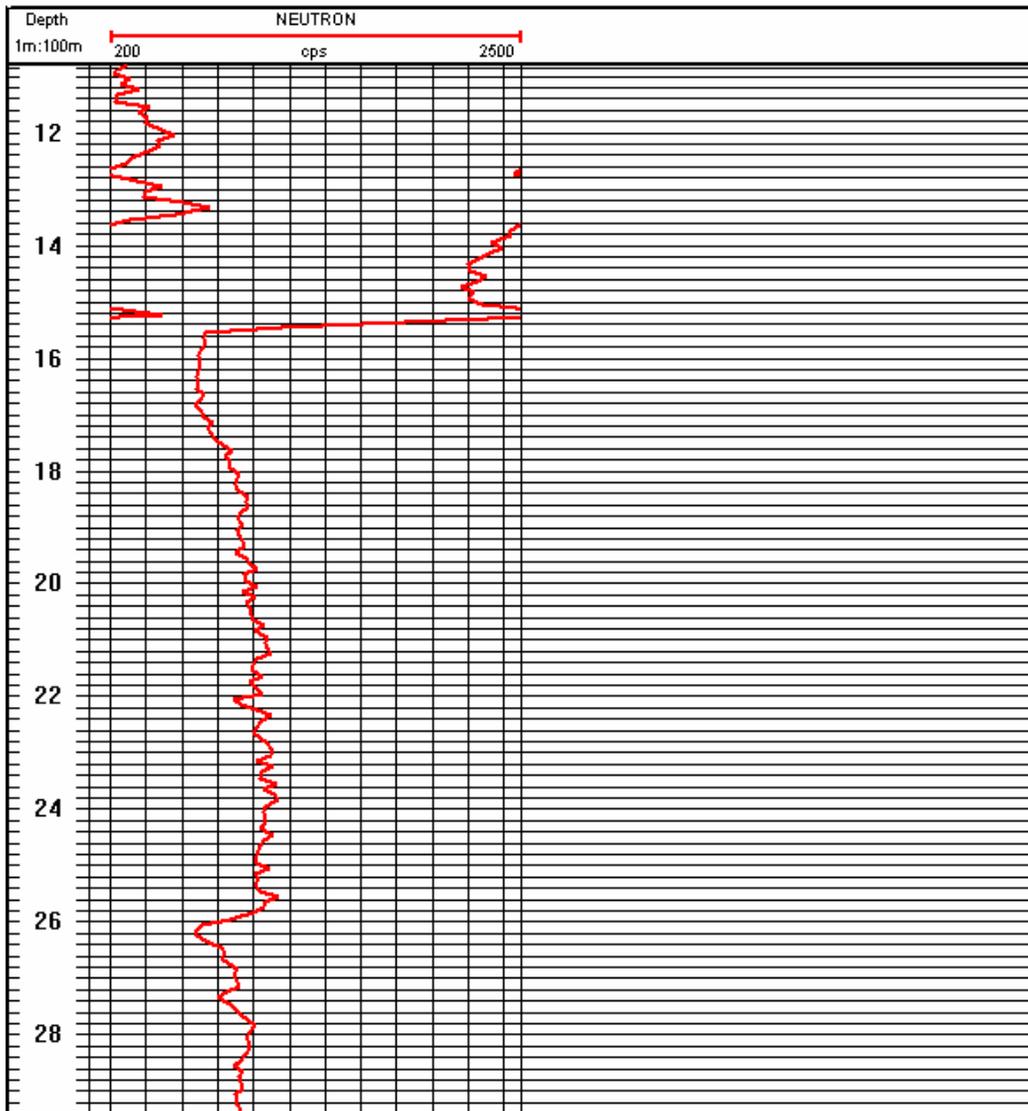
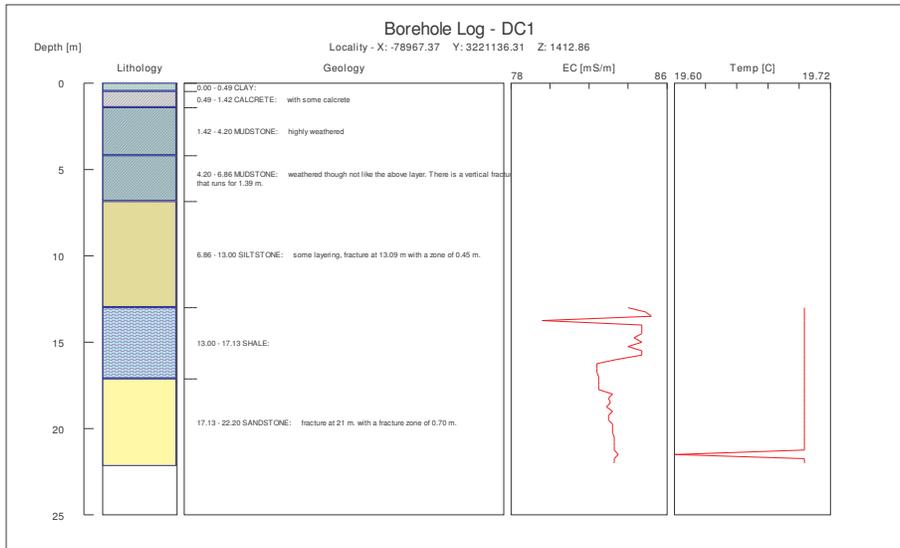
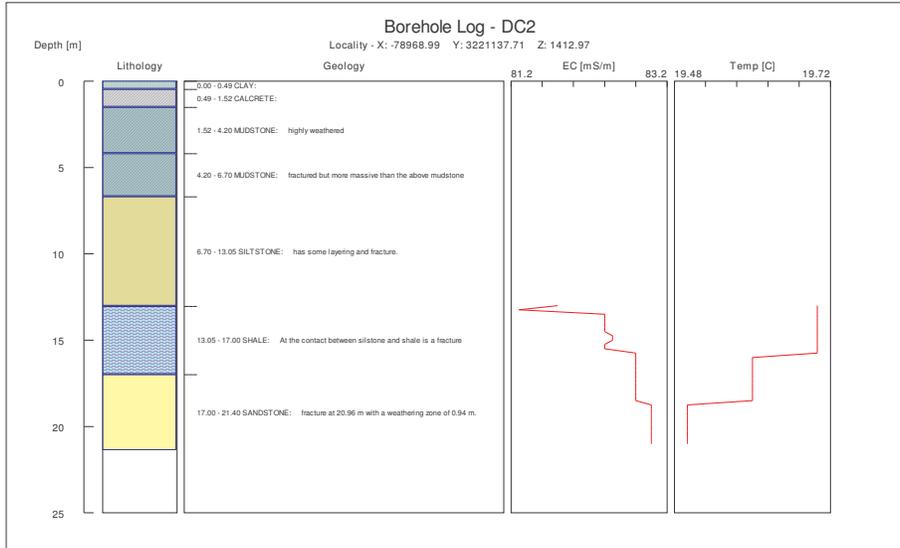
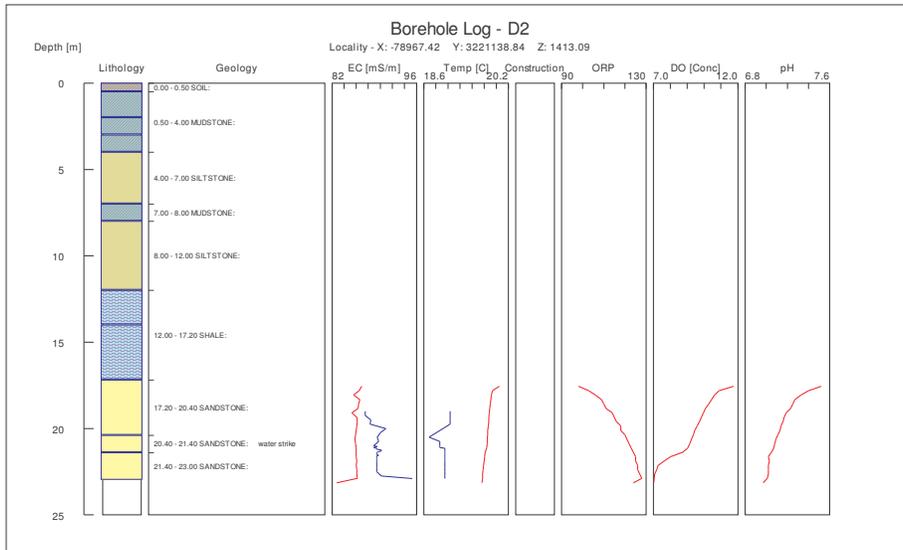
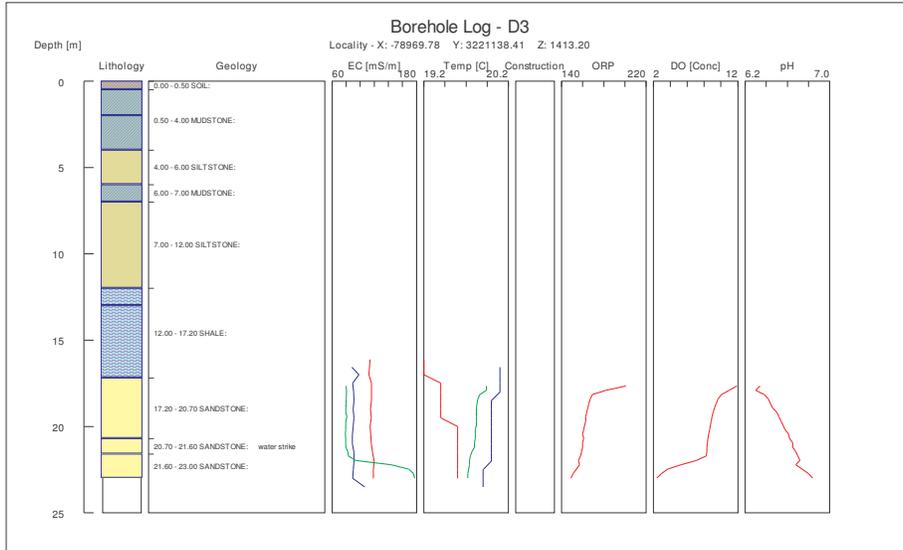
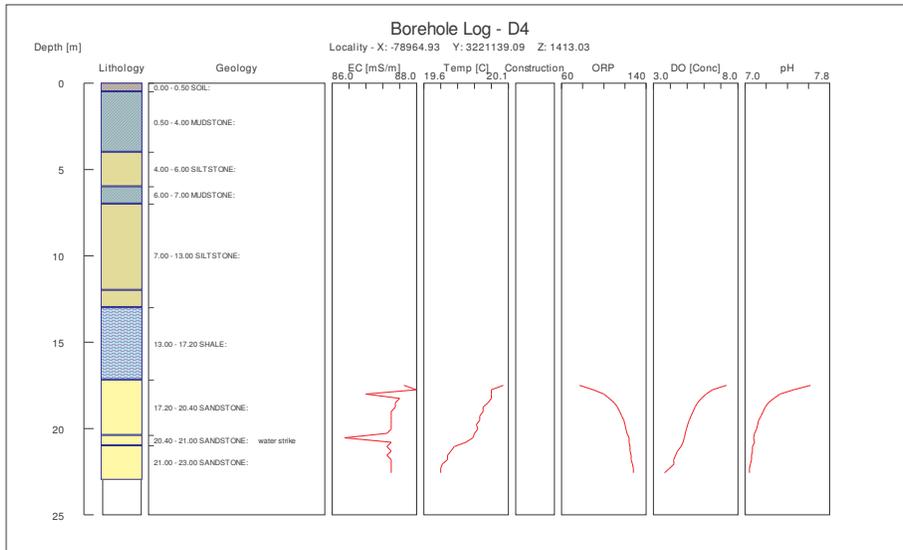
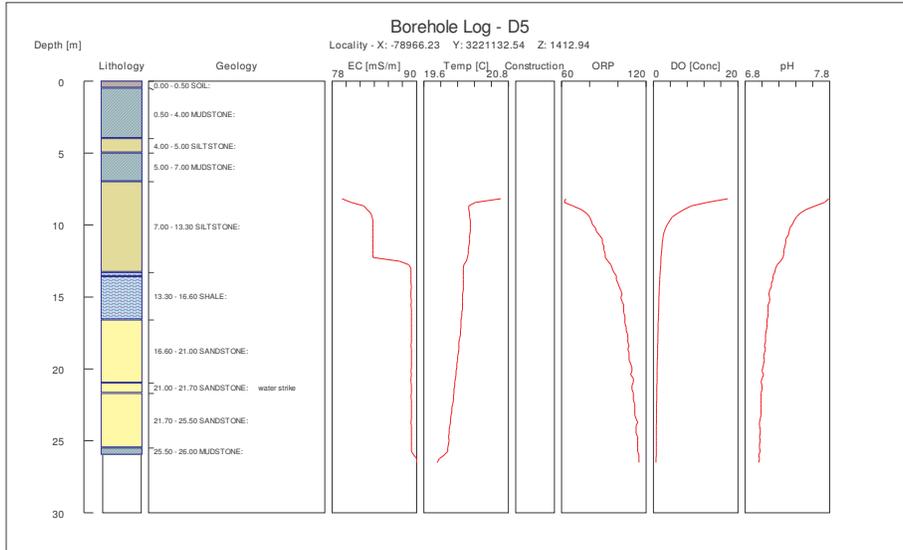


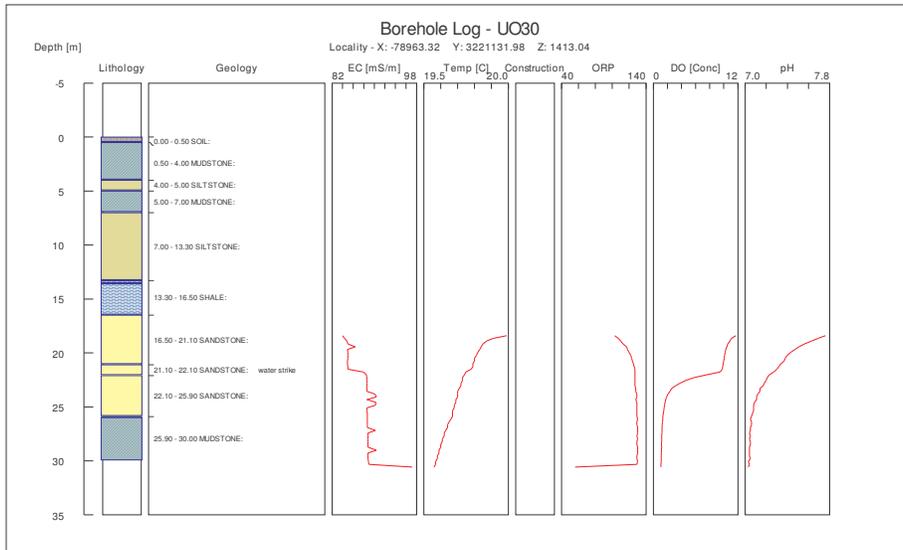
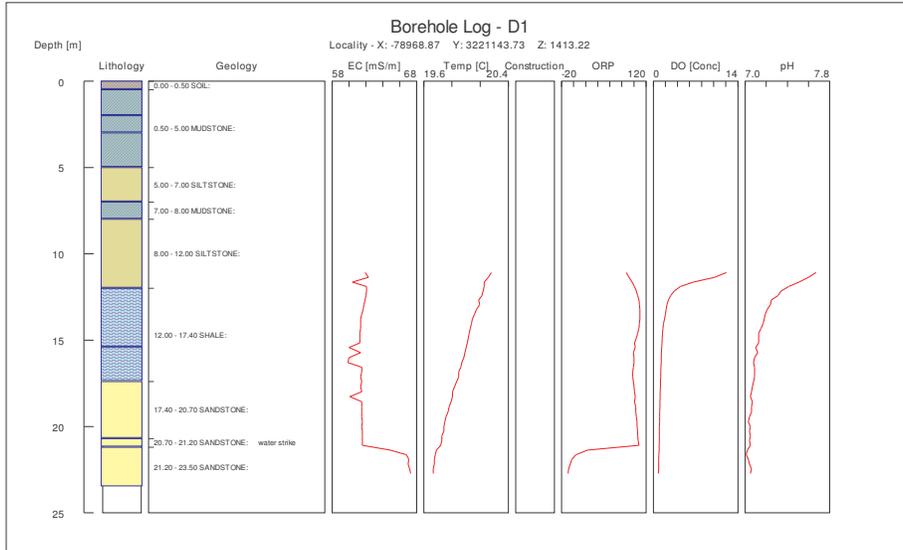
Figure 45: Neutron profile of borehole UO30.

Appendix E2









Appendix E3

Table 2: Pumping test data of Borehole D3

| | |
|--------------|------------|
| Date Started | 2005/07/04 |
| Time Started | 08:15 |

| Pumping Borehole Information | | | | |
|------------------------------|--------------|-------------|------------|--------------|
| Borehole Name | | D3 | | |
| Depth of Pump (m) | | 22.5 | | |
| Static WL (m) | | 15.62 | | |
| Time (min) | Drawdown (m) | Yield (L/s) | Time (min) | Recovery (m) |
| 1 | 16.52 | 3.25 | 1 | 21.35 |
| 2 | 16.69 | 3.25 | 2 | 21.25 |
| 3 | 16.92 | 3.25 | 3 | 21.2 |
| 4 | 17.07 | 3.25 | 4 | 21.1 |
| 5 | 17.23 | 3.25 | 5 | 20.94 |
| 6 | 17.38 | 3.25 | 6 | 20.8 |
| 7 | 17.51 | 3.25 | 7 | 20.72 |
| 8 | 17.66 | 3.25 | 8 | 20.62 |
| 9 | 17.79 | 3.25 | 9 | 20.56 |
| 10 | 17.91 | 3.25 | 10 | 20.49 |
| 11 | 18 | 3.25 | 11 | 20.43 |
| 12 | 18.09 | 3.25 | 12 | 20.37 |
| 13 | 18.17 | 3.25 | 13 | 20.32 |
| 14 | 18.26 | 3.25 | 14 | 20.26 |
| 15 | 18.36 | 3.25 | 15 | 20.21 |
| 16 | 18.47 | 3.25 | 16 | 20.16 |
| 17 | 18.53 | 3.25 | 17 | 20.1 |
| 18 | 18.64 | 3.25 | 18 | 20.05 |
| 19 | 18.72 | 3.25 | 19 | 20 |
| 20 | 18.8 | 3.25 | 20 | 19.96 |
| 25 | 19.23 | 3.25 | 25 | 19.76 |
| 30 | 19.53 | 3.25 | 30 | 19.55 |
| 40 | 20.08 | 3.25 | 40 | 19.18 |
| 50 | 20.56 | 3.25 | 50 | 18.86 |
| 60 | 20.99 | 3 | 60 | 18.57 |
| 75 | 21.44 | 2.03 | 75 | 18.2 |
| 90 | 22.53 | 2.03 | 90 | 17.9 |
| 120 | 22.78 | 2.3 | 120 | 17.4 |
| 150 | | | 150 | 17.08 |
| 180 | | | 180 | 16.81 |
| 240 | | | 240 | 16.54 |
| 300 | | | 300 | 16.31 |

| Observation Borehole Information | | | | | | |
|----------------------------------|--------|--------|--------|--------|--------|--------|
| Borehole Name | D5 | UO23 | UO30 | D4 | D1 | D2 |
| Distance (m) | 8.8 | 4.3 | 9.9 | 5 | 5.5 | 2.6 |
| Static WL (m) | 7.92 | 15.43 | 15.36 | 15.37 | 12.72 | 15.45 |
| Time (min) | wl (m) |
| 1 | | | | | | 16.25 |
| 2 | | | | | | 16.43 |
| 3 | | 16.6 | | | | 16.6 |
| 4 | | | | 15.75 | | |
| 5 | 7.95 | | 15.5 | | 12.9 | |
| 6 | | | | | | 17.3 |
| 7 | | 17.32 | | | | 17.38 |
| 8 | | 17.4 | 15.75 | | | |
| 9 | 8 | | | | | |
| 10 | | | | 17.3 | | |
| 11 | | 17.85 | | 17.4 | | |
| 12 | | | | | 12.8 | |
| 13 | | 17.88 | | | | |
| 14 | 8.17 | | 16.03 | | | 18.1 |
| 15 | | | | | | 18.15 |
| 16 | | | | | | |
| 17 | | | | 17.54 | | |
| 18 | | 18.5 | | | 12.81 | |
| 19 | | | | | | 18.58 |
| 20 | 8.2 | 18.67 | 16.26 | | | |
| 25 | 9.2 | 18.89 | 16.4 | 18.66 | 12.96 | 19.02 |
| 30 | 9.73 | 19.48 | 17.09 | 19.64 | 13.02 | 19.58 |
| 40 | 10 | 19.94 | 17.22 | 20.2 | 13.14 | 19.8 |
| 50 | 10.28 | 20.41 | 18.01 | 20.3 | 13.28 | 20.32 |
| 60 | 10.24 | 20.87 | 18.2 | 20.75 | 13.45 | 20.74 |
| 75 | 9.57 | 21.19 | 19.1 | 21.1 | 13.88 | 21.18 |
| 90 | 9.4 | 21.36 | 19.64 | 21.14 | 14.12 | 21.34 |
| 120 | 9.5 | 21.25 | 19.5 | 21.19 | 14.5 | 21.39 |
| 150 | | | | | | |
| 180 | | | | | | |
| 240 | | | | | | |
| 300 | | | | | | |

Table 3: Pumping test data of Borehole UO23

| | |
|--------------|------------|
| Date Started | 2005/07/05 |
| Time Started | 08:35 |

| Pumping Borehole Information | | | | |
|------------------------------|--------------|-------------|------------|--------------|
| Borehole Name | | UO23 | | |
| Depth of Pump (m) | | 35 | | |
| Static WL (m) | | 15.68 | | |
| Time (min) | Drawdown (m) | Yield (L/s) | Time (min) | Recovery (m) |
| 1 | 16.42 | 3.25 | 1 | 25.89 |
| 2 | 16.65 | 3.25 | 2 | 21.4 |
| 3 | 16.83 | 3.25 | 3 | 21.33 |
| 4 | 17.03 | 3.25 | 4 | 21.24 |
| 5 | 17.19 | 3.25 | 5 | 21.19 |
| 6 | 17.35 | 3.25 | 6 | 21.16 |
| 7 | 17.5 | 3.25 | 7 | 21.1 |
| 8 | 17.59 | 3.25 | 8 | 21 |
| 9 | 17.73 | 3.25 | 9 | 20.9 |
| 10 | 17.83 | 3.25 | 10 | 20.82 |
| 11 | 17.96 | 3.25 | 11 | 20.75 |
| 12 | 18.05 | 3.25 | 12 | 20.69 |
| 13 | 18.16 | 3.25 | 13 | 20.64 |
| 14 | 18.26 | 3.25 | 14 | 20.61 |

| Observation Borehole Information | | | | | | | | | |
|----------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Borehole Name | UO5 | D2 | D3 | UO24 | D4 | UO30 | UO29 | D5 | D1 |
| Distance (m) | 98 | 3.2 | 4.3 | 36.2 | 3.7 | 5.6 | 45.9 | 5.7 | 8.6 |
| Static WL (m) | 13.63 | 15.65 | 15.74 | 8.7 | 15.58 | 15.58 | 15.4 | 8.94 | 14.52 |
| Time (min) | wl (m) |
| 1 | | | 16.45 | | 16.25 | | | | |
| 2 | | | | | | | | | |
| 3 | | 16.7 | | | | 15.4 | | | |
| 4 | | | 17.1 | | | 15.7 | | | |
| 5 | | 17.2 | | | 17 | | | | |
| 6 | | | | | | | 16.73 | | |
| 7 | | | | 8.69 | | | 16.83 | | |
| 8 | | | 17.63 | | | 15.87 | | | |
| 9 | | 17.61 | | | | 15.93 | | | |
| 10 | | 17.79 | 17.86 | | 17.7 | | | | |
| 11 | | 17.92 | 18.02 | | 17.8 | | | | |
| 12 | | | | | | | 17.46 | | |
| 13 | | 18 | | | | | 17.56 | | |
| 14 | | | 18.24 | | | 16.18 | | | |

| | | | | |
|-----|-------|------|-----|-------|
| 15 | 18.36 | 3.25 | 15 | 20.55 |
| 16 | 18.46 | 3.25 | 16 | 20.5 |
| 17 | 18.54 | 3.25 | 17 | 20.44 |
| 18 | 18.62 | 3.25 | 18 | 20.41 |
| 19 | 18.71 | 3.25 | 19 | 20.36 |
| 20 | 18.8 | 3.25 | 20 | 20.32 |
| 25 | 19.2 | 3.25 | 25 | 20.16 |
| 30 | 19.52 | 3.25 | 30 | 20.02 |
| 40 | 20.09 | 3.25 | 40 | 19.75 |
| 50 | 20.54 | 3.25 | 50 | 19.51 |
| 60 | 20.96 | 3.09 | 60 | 19.27 |
| 75 | 21.28 | 3.09 | 75 | 18.92 |
| 90 | 21.74 | 3.09 | 90 | 18.6 |
| 120 | 34.62 | 2.41 | 120 | 18.1 |
| 150 | 34.62 | 2.41 | 150 | 17.67 |
| 180 | 34.62 | 2.32 | 180 | 17.37 |
| 240 | | | 240 | |
| 300 | | | 300 | |

| | | | | | | | | | |
|-----|-------|-------|-------|------|-------|-------|-------|------|-------|
| 15 | | | | 8.7 | | 16.2 | | | |
| 16 | | | | | 18.28 | | | | |
| 17 | | | 18.54 | | 18.31 | | | | |
| 18 | | 18.5 | | | | | 17.97 | | |
| 19 | | | 18.75 | | | | 18.06 | | |
| 20 | | 18.7 | 18.87 | | 18.7 | 16.53 | 18.12 | 9.04 | |
| 25 | 16.77 | 19.08 | 19.27 | | | 16.4 | 18.48 | 9.05 | 14.73 |
| 30 | | 19.52 | 19.54 | 8.7 | 19.63 | 17.1 | 18.95 | 8.96 | 14.71 |
| 40 | | 20.06 | 20.23 | 8.68 | 19.9 | 17.38 | 19.33 | 8.78 | 14.92 |
| 50 | | 20.44 | 20.67 | 8.69 | 20.58 | 17.85 | 20 | 8.72 | 15 |
| 60 | 17.5 | 20.94 | 21 | 8.69 | 20.97 | 18 | 20.25 | 8.6 | 15.1 |
| 75 | 18.16 | 21.21 | 21.34 | 8.7 | 21.1 | 18.66 | 20.56 | 8.5 | 15.34 |
| 90 | 18.2 | 21.3 | 21.44 | 8.7 | 21.09 | 19.14 | 20.74 | 8.45 | 15.53 |
| 120 | 18.29 | 21.34 | 21.46 | 8.7 | 21.09 | 19.74 | 20.74 | 8.53 | 15.87 |
| 150 | | 21.34 | 21.47 | 8.7 | 21.1 | 20.26 | 20.74 | 8.59 | 16.16 |
| 180 | 18.17 | 21.3 | 21.43 | 8.7 | 21.08 | 21.01 | 20.76 | 8.68 | 16.41 |
| 240 | | | | | | | | | |
| 300 | | | | | | | | | |

Table 4: Pumping test data of Borehole UP16

| | |
|--------------|------------|
| Date Started | 2005/07/11 |
| Time Started | 09:30 |
| | |

| Pumping Borehole Information | | |
|------------------------------|--------------|-------------|
| Borehole Name | | UP16 |
| Depth of Pump (m) | | 33 |
| Static WL (m) | | |
| Time (min) | Drawdown (m) | Yield (L/s) |
| 1 | | 2 |
| 2 | | 2 |
| 3 | | 2 |
| 4 | | 2 |
| 5 | | 2 |
| 6 | | 2 |
| 7 | | 2 |
| 8 | | 2 |
| 9 | | 2 |
| 10 | | 2 |
| 11 | | 2 |
| 12 | | 2 |
| 13 | | 2 |
| 14 | | 2 |
| 15 | | 2 |
| 16 | | 2 |
| 17 | | 2 |
| 18 | | 2 |
| 19 | | 2 |
| 20 | | 2 |

| Observation Borehole Information | | | | | | | | | | | | | | |
|----------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| BH | UP15 | UO26 | UO25 | UO18 | D4 | UO29 | UO23 | D2 | D3 | UO14 | UO20 | UO27 | UO7 | UO5 |
| Distance (m) | | | | | | | | | | | | | | |
| Static WL (m) | 14.16 | 14.19 | 13.74 | 11.52 | 15.56 | 15.35 | 15.61 | 15.59 | 15.7 | 13.91 | 13.87 | 14.02 | 13.77 | 13.65 |
| Time (min) | wl (m) |
| 1 | 14.38 | | | 13.96 | | | | | | | | | 14 | |
| 2 | | | | | | | | | | | | | | 13.9 |
| 3 | | 14.38 | | | | | | | | 14.44 | 13.7 | | | |
| 4 | 14.72 | | | | | | | | | | | | | |
| 5 | | 14.77 | | 14.7 | 16.57 | 15.93 | 16.44 | 16.57 | 16.62 | | | 14.45 | | |
| 6 | | | 14.04 | | | | | | | | | | 14.41 | |
| 7 | 15 | | | | | | | | | | | | | 14.3 |
| 8 | | | | | | | | | | | | | 14.53 | |
| 9 | | 15.05 | | | | | | | | | | | | |
| 10 | | | 14.32 | | 17.01 | 16.6 | 16.96 | 17.04 | 17.1 | 14.88 | | | 14.7 | |
| 11 | | | | | | | | | | | 14.87 | | | 14.6 |
| 12 | 15.33 | | | | | | | | | | | | | |
| 13 | | | | | | | | | | | | | | |
| 14 | | | 14.35 | | | | | | | | | 15.15 | 14.77 | |
| 15 | | | | | 17.33 | 16.95 | 17.32 | 17.38 | 17.45 | 15.2 | | | | 14.78 |
| 16 | | 15.23 | | | | | | | | | | | 14.97 | |
| 17 | | | | | | | | | | | | | | 14.9 |
| 18 | | | 15.14 | | | | | | | | 15.16 | | | |
| 19 | | | | | | | | | | | | | | |
| 20 | 15.85 | 15.68 | | | 17.61 | 17.28 | 17.6 | 17.63 | 17.73 | | | 15.49 | 15.17 | 15.08 |

| | | |
|-----|--|------|
| 25 | | 2 |
| 30 | | 2 |
| 40 | | 2 |
| 50 | | 1.91 |
| 60 | | 1.91 |
| 75 | | 1.91 |
| 90 | | 1.91 |
| 120 | | 1.91 |
| 150 | | 1.91 |
| 180 | | 1.71 |
| 240 | | 2.16 |
| 300 | | 2.24 |
| 360 | | 2 |
| 420 | | 2 |

| | | | | | | | | | | | | | | |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 25 | 15.95 | 15.89 | 15.44 | | 17.88 | 17.54 | 17.89 | 17.91 | 18 | 15.35 | 15.37 | 15.74 | 15.35 | 15.25 |
| 30 | 16.15 | 16.08 | 15.64 | | | | | | | 15.85 | 15.8 | 16.04 | 15.6 | 15.4 |
| 40 | 16.51 | 16.44 | 16 | 12.42 | 18.03 | 17.74 | 18.05 | 18.08 | 18.16 | 16.1 | 16.11 | 16.21 | 15.9 | 15.71 |
| 50 | 16.8 | 16.71 | 16.23 | 14 | 18.24 | 17.98 | 18.27 | 18.3 | 18.38 | 16.43 | 16.31 | 16.5 | 16.14 | 16 |
| 60 | 17.04 | 16.96 | 16.47 | 14.1 | 18.43 | 18.16 | 18.48 | 18.51 | 18.57 | 16.53 | 16.5 | 16.74 | 16.42 | 16.27 |
| 75 | 17.33 | 17.25 | 16.75 | 14.15 | 18.85 | 18.47 | 18.76 | 18.81 | 18.89 | 17 | 16.82 | 17 | 16.68 | 16.53 |
| 90 | 17.56 | 17.47 | 16.9 | 14.16 | 19 | 18.77 | 19.05 | 19.08 | 19.28 | 17.28 | 17.12 | 17.3 | 16.93 | 16.77 |
| 120 | 17.91 | 17.79 | 17.32 | 12.55 | 18.4 | 19.15 | 19.46 | 19.47 | 19.55 | 17.36 | 17.51 | 17.7 | 17.27 | 17.11 |
| 150 | 18.23 | 18.1 | 17.61 | 14.98 | 19.71 | 19.47 | 19.79 | 19.9 | 19.8 | 17.98 | 17.8 | 17.92 | 17.61 | 17.45 |
| 180 | 18.42 | 18.36 | 17.88 | 15.1 | 19.75 | 19.75 | 20 | 20.1 | 20.01 | 18.08 | 17.94 | 18.17 | 17.86 | 17.7 |
| 240 | 18.91 | 18.76 | 18.25 | 15.5 | 20.35 | 20.16 | 20.4 | 20.52 | 20.43 | 18.42 | 18.38 | 18.58 | 18.26 | 18.1 |
| 300 | 19.07 | 18.91 | 18.38 | 16.15 | 20.52 | 20.35 | 20.61 | 20.68 | 20.58 | 18.6 | 18.4 | 18.68 | 18.41 | 18.23 |
| 360 | 19.07 | 18.94 | 18.4 | 16.64 | 20.74 | 20.39 | 20.62 | 20.61 | 20.74 | 18.63 | 18.53 | 18.8 | 18.45 | 18.28 |
| 420 | 19.07 | 18.96 | 18.44 | 17 | 20.6 | 20.44 | 20.7 | 20.69 | 20.78 | 18.67 | | 18.81 | 18.5 | 18.29 |

Table 5: Pumping test data of Borehole UO14

| | | | | |
|-------------------------------------|---------------------|--------------------|-------------------|---------------------|
| Date Started | 2005/08/03 | | | |
| Time Started | 08:15 | | | |
| Pumping Borehole Information | | | | |
| Borehole Name | UO14 | | | |
| Depth of Pump (m) | 34 | | | |
| Static WL (m) | 14.77 | | | |
| Time (min) | Drawdown (m) | Yield (L/s) | Time (min) | Recovery (m) |
| 1 | 18.6 | 3.25 | 1 | 20.69 |
| 2 | 19.2 | 3.25 | 2 | 19.22 |
| 3 | 19.46 | 3.25 | 3 | 19.09 |
| 4 | 19.66 | 3.25 | 4 | 19.02 |
| 5 | 19.79 | 3.25 | 5 | 18.99 |
| 6 | 19.87 | 3.25 | 6 | 18.94 |
| 7 | 19.97 | 3.25 | 7 | 18.93 |
| 8 | 20.09 | 3.25 | 8 | 18.92 |
| 9 | 20.09 | 3.25 | 9 | 18.91 |
| 10 | 20.19 | 3.25 | 10 | 18.89 |
| 11 | 20.26 | 3.25 | 11 | 18.89 |
| 12 | 20.33 | 3.25 | 12 | 18.88 |
| 13 | 20.43 | 3.25 | 13 | 18.88 |
| 14 | 20.49 | 3.25 | 14 | 18.87 |
| 15 | 20.66 | 3.25 | 15 | 18.865 |
| 16 | 20.73 | 3.25 | 16 | 18.86 |
| 17 | 20.78 | 3.25 | 17 | 18.86 |
| 18 | 20.85 | 3.25 | 18 | 18.85 |
| 19 | 20.92 | 3.25 | 19 | 18.84 |
| 20 | 20.99 | 3.25 | 20 | 18.83 |
| 25 | 21.25 | 3.25 | 25 | 18.81 |
| 30 | 21.5 | 3.25 | 30 | 18.79 |
| 40 | 21.95 | 3.25 | 40 | 18.74 |
| 50 | 22.31 | 3.25 | 50 | 18.54 |
| 60 | 24.66 | 3 | 60 | 18.38 |
| 75 | 24.8 | 2.03 | 75 | 18.14 |
| 90 | 27.59 | 2.03 | 90 | 17.93 |
| 120 | 29.06 | 2.3 | 120 | 17.6 |
| 150 | 29.64 | | 150 | 17.31 |
| 180 | 29.645 | | 180 | 17.04 |
| 240 | 29.65 | | 210 | 16.76 |
| 300 | 29.78 | | 225 | 16.6 |

Table 6: Pumping test data of Borehole UO23

| | | | | | | | | | | | | | | | | | | | | | |
|-------------------------------------|------------|---------------------|---|--------------------|------|-------------------|--|----------------------|-----|-------|------|-------|-------|-------|-------|--|--|--|--|--|--|
| Date Started | 2005/08/15 | | | | | | | | | | | | | | | | | | | | |
| Time Started | 08:13 | | | | | | | | | | | | | | | | | | | | |
| Pumping Borehole Information | | | Observation Borehole Information | | | | | | | | | | | | | | | | | | |
| Borehole Name | | | | | UO23 | | | | | | | | | | | | | | | | |
| Depth of Pump (m) | | 38 | | | | | | Distance (m) | | | | | | | | | | | | | |
| Static WL (m) | | 18.3 | | 2 | | | | Static WL (m) | | 18.28 | 8.31 | 18.32 | 18.06 | 18.3 | 18.3 | | | | | | |
| Time (min) | | Drawdown (m) | | Yield (L/s) | | Time (min) | | Recovery (m) | | | | | | | | | | | | | |
| 1 | 18.38 | 0.72 | 1 | 19.02 | | | | | 1 | | | | 18.17 | | 18.4 | | | | | | |
| 2 | | 0.72 | 2 | 19 | | | | | 2 | 18.34 | | | 18.15 | 18.38 | 18.42 | | | | | | |
| 3 | 18.46 | 0.72 | 3 | 18.97 | | | | | 3 | | | | | 18.4 | | | | | | | |
| 4 | 18.46 | 0.72 | 4 | 18.94 | | | | | 4 | | | 18.39 | | | | | | | | | |
| 5 | 18.47 | 0.72 | 5 | 18.91 | | | | | 5 | 18.31 | | | | | 18.46 | | | | | | |
| 6 | 18.47 | 0.72 | 6 | 18.9 | | | | | 6 | | | | 18.16 | 18.42 | | | | | | | |
| 7 | 18.51 | 0.72 | 7 | 18.88 | | | | | 7 | | | | 18.17 | | 18.5 | | | | | | |
| 8 | 18.54 | 0.72 | 8 | 18.87 | | | | | 8 | | | 18.47 | | 18.45 | | | | | | | |
| 9 | 18.55 | 0.72 | 9 | 18.85 | | | | | 9 | | | | 18.16 | | 18.6 | | | | | | |
| 10 | 18.56 | 0.72 | 10 | 18.84 | | | | | 10 | | | | | | | | | | | | |
| 11 | 18.57 | 0.72 | 11 | 18.82 | | | | | 11 | 18.41 | | 18.52 | | 18.5 | | | | | | | |
| 12 | | 0.72 | 12 | 18.81 | | | | | 12 | 18.43 | | | | | 18.62 | | | | | | |
| 13 | 18.58 | 0.72 | 13 | 18.8 | | | | | 13 | | | | 18.18 | 18.55 | | | | | | | |
| 14 | 18.59 | 0.72 | 14 | 18.78 | | | | | 14 | | | | 18.18 | | 18.65 | | | | | | |
| 15 | 18.6 | 0.72 | 15 | 18.77 | | | | | 15 | 18.45 | | | | | | | | | | | |
| 16 | | 0.72 | 16 | 18.76 | | | | | 16 | | | | | 18.59 | | | | | | | |
| 17 | 18.63 | 0.72 | 17 | 18.75 | | | | | 17 | | | 18.59 | | | 18.69 | | | | | | |
| 18 | 18.64 | 0.72 | 18 | 18.73 | | | | | 18 | | | 18.6 | | 18.62 | | | | | | | |
| 19 | 18.65 | 0.72 | 19 | 18.72 | | | | | 19 | | | 18.62 | | | | | | | | | |
| 20 | 18.66 | 0.72 | 20 | 18.71 | | | | | 20 | | | 18.64 | | | 18.73 | | | | | | |
| 25 | 18.69 | 0.72 | 25 | 18.67 | | | | | 25 | 18.58 | 8.31 | 18.66 | 18.26 | 18.66 | 18.71 | | | | | | |
| 30 | 18.72 | 0.72 | 30 | 18.62 | | | | | 30 | 18.63 | 8.31 | 18.71 | 18.27 | 18.72 | | | | | | | |
| 40 | 18.77 | 0.72 | 40 | 18.55 | | | | | 40 | 18.67 | 8.31 | 18.77 | 18.36 | 18.73 | 18.78 | | | | | | |
| 50 | 18.82 | 0.72 | 50 | 18.42 | | | | | 50 | 18.74 | 8.31 | 18.8 | 18.4 | 18.8 | 18.85 | | | | | | |
| 60 | 18.84 | 0.72 | 60 | 18.36 | | | | | 60 | 18.74 | | 18.85 | 18.46 | 18.85 | 18.89 | | | | | | |
| 75 | 18.9 | 0.72 | 75 | 18.3 | | | | | 75 | 18.8 | 8.31 | 18.88 | 18.54 | 18.88 | 18.94 | | | | | | |
| 90 | 18.94 | 0.72 | 90 | | | | | | 90 | 18.85 | 8.31 | 18.93 | 18.61 | 18.93 | 19 | | | | | | |
| 120 | 18.96 | 0.72 | 120 | | | | | | 120 | 18.89 | | 19 | 18.69 | 18.98 | 19.02 | | | | | | |
| 150 | 19 | 0.72 | 150 | | | | | | 150 | 18.94 | | 19.07 | 18.73 | 19.01 | 19.07 | | | | | | |
| 180 | 19.05 | 0.72 | 180 | | | | | | 180 | 18.96 | | 19.09 | 18.79 | 19.06 | 19.1 | | | | | | |
| 240 | 19.1 | 0.72 | 240 | | | | | | 240 | 19.03 | 8.31 | 19.14 | 18.84 | 19.1 | 19.16 | | | | | | |
| 300 | 19.1 | 0.67 | | | | | | | 300 | 19.07 | 8.29 | 19.14 | 18.84 | 19.12 | 19.2 | | | | | | |
| 360 | 19.1 | 0.67 | | | | | | | 360 | 19.08 | 8.28 | 19.17 | 18.82 | 19.17 | 19.24 | | | | | | |

| | | | | | | | | | | |
|-----|-------|------|--|-----|-------|------|-------|-------|-------|-------|
| 420 | 19.11 | 0.67 | | 420 | 19.08 | 8.26 | 19.18 | 18.89 | 19.18 | 19.25 |
| 480 | 19.11 | 0.67 | | 480 | 19.1 | 8.26 | 19.2 | 18.9 | 19.18 | 19.27 |
| 570 | 19.16 | 0.67 | | 570 | 19.15 | 8.26 | 19.25 | 18.95 | 19.2 | 19.28 |
| | | | | | | | | | | |

Table 7: Pumping test data of Borehole D3

| | |
|--------------|------------|
| Date Started | 2005/08/16 |
| Time Started | 07:00 |

| Pumping Borehole Information | | | | |
|------------------------------|--------------|-------------|------------|--------------|
| Borehole Name | | D3 | | |
| Depth of Pump (m) | | 23.1 | | |
| Static WL (m) | | 17.4 | | |
| Time (min) | Drawdown (m) | Yield (L/s) | Time (min) | Recovery (m) |
| 1 | 17.66 | 0.72 | 1 | 19.01 |
| 2 | 17.68 | 0.72 | 2 | 18.93 |
| 3 | 17.69 | 0.72 | 3 | 18.9 |
| 4 | 17.71 | 0.72 | 4 | 18.87 |
| 5 | 17.71 | 0.72 | 5 | 18.86 |
| 6 | 17.76 | 0.72 | 6 | 18.83 |
| 7 | 17.79 | 0.72 | 7 | 18.8 |
| 8 | 17.82 | 0.72 | 8 | 18.79 |
| 9 | 17.85 | 0.72 | 9 | 18.77 |
| 10 | 17.87 | 0.72 | 10 | 18.76 |
| 11 | 17.89 | 0.72 | 11 | 18.74 |
| 12 | 17.91 | 0.72 | 12 | 18.72 |
| 13 | 17.92 | 0.72 | 13 | 18.7 |
| 14 | 17.94 | 0.72 | 14 | 18.7 |
| 15 | 17.96 | 0.72 | 15 | 18.68 |
| 16 | 17.97 | 0.72 | 16 | 18.67 |
| 17 | 17.99 | 0.72 | 17 | 18.65 |
| 18 | 18 | 0.72 | 18 | 18.64 |
| 19 | 18.03 | 0.72 | 19 | 18.63 |
| 20 | 18.04 | 0.72 | 20 | 18.61 |
| 25 | 18.11 | 0.72 | 25 | 18.56 |
| 30 | 18.17 | 0.72 | 30 | 18.51 |
| 40 | 18.26 | 0.72 | 40 | 18.43 |
| 50 | 18.32 | 0.72 | 50 | 18.38 |
| 60 | 18.39 | 0.72 | 60 | 18.3 |
| 75 | 18.48 | 0.72 | 75 | 18.24 |
| 90 | 18.52 | 0.72 | 90 | 18.15 |
| 120 | 18.61 | 0.72 | 120 | 18.08 |
| 150 | 18.7 | 0.72 | 150 | 18 |
| 180 | 18.75 | 0.72 | 180 | 17.95 |
| 240 | 18.81 | 0.72 | 240 | 17.88 |
| 300 | 18.85 | 0.7 | | |
| 360 | 18.91 | 0.7 | | |

| Observation Borehole Information | | | | | | |
|----------------------------------|--------|--------|--------|--------|--------|--------|
| Borehole Name | D2 | UO23 | D4 | D5 | UO30 | UO29 |
| Distance (m) | | | | | | |
| Static WL (m) | 17.52 | 17.38 | 17.39 | 8.23 | 17.25 | 17.16 |
| Time (min) | wl (m) |
| 1 | | 17.5 | 17.43 | 8.23 | 17.28 | 17.16 |
| 2 | | | | | 17.29 | |
| 3 | 17.59 | | 17.43 | | 17.24 | |
| 4 | 17.69 | 17.67 | | | | |
| 5 | 17.69 | | 17.59 | | 17.28 | |
| 6 | | 17.72 | | | 17.28 | |
| 7 | 17.73 | 17.75 | | | | |
| 8 | 17.76 | | | | | 17.43 |
| 9 | 17.77 | 17.82 | | | | 17.45 |
| 10 | | | | | | 17.46 |
| 11 | 17.8 | | 17.73 | | | |
| 12 | 17.81 | 17.82 | | | | 17.5 |
| 13 | | | | | | 17.51 |
| 14 | | | 17.77 | | | 17.54 |
| 15 | 17.85 | 17.88 | | | | 17.56 |
| 16 | 17.9 | | 17.8 | | | |
| 17 | 17.92 | 17.91 | | | | 17.59 |
| 18 | 17.92 | 18.5 | 17.84 | | | |
| 19 | | | | | 17.32 | |
| 20 | 17.96 | 17.96 | 17.87 | | 17.32 | |
| 25 | 18.03 | 18.03 | 17.95 | | 17.41 | 17.74 |
| 30 | 18.09 | 18.08 | 17.97 | | 17.52 | 17.77 |
| 40 | 18.17 | 18.16 | 18.05 | | 17.62 | 17.88 |
| 50 | 18.24 | 18.24 | 18.2 | 8.23 | 17.71 | 17.93 |
| 60 | 18.32 | 18.35 | 18.25 | | 17.81 | 18.02 |
| 75 | 18.38 | 18.41 | 18.31 | | 17.95 | 18.08 |
| 90 | 18.43 | 18.47 | 18.37 | | 18.01 | 18.14 |
| 120 | 18.55 | 18.55 | 18.46 | 8.23 | 18.18 | 18.24 |
| 150 | 18.6 | 18.62 | 18.53 | | 18.29 | 18.31 |
| 180 | 18.68 | 18.68 | 18.57 | | 18.35 | 18.38 |
| 240 | 18.73 | 18.75 | 18.66 | | 18.48 | 18.43 |
| 300 | 18.78 | 18.81 | 18.72 | | 18.53 | 18.47 |
| 360 | 18.83 | 18.84 | 18.75 | | 18.55 | 18.51 |

| | | | | | | | | | | |
|-----|-------|------|--|-----|-------|-------|-------|--|-------|-------|
| 420 | 18.95 | 0.7 | | 420 | 18.87 | 18.88 | 18.78 | | 18.61 | 18.55 |
| 480 | 18.99 | 0.69 | | 600 | 18.98 | 18.91 | 18.83 | | 18.65 | 18.61 |
| 600 | 19.09 | 0.69 | | | | 19 | 18.92 | | 18.74 | 18.68 |

Table 8: Pumping test data of Borehole D2

| Pumping Borehole Information | | | | |
|------------------------------|--------------|-------------|------------|--------------|
| Borehole Name | | D2 | | |
| Depth of Pump (m) | | 23 | | |
| Static WL (m) | | 16.51 | | |
| Time (min) | Drawdown (m) | Yield (L/s) | Time (min) | Recovery (m) |
| 1 | 16.67 | 0.86 | 1 | 18.28 |
| 2 | 16.72 | 0.86 | 2 | 18.23 |
| 3 | 16.78 | 0.86 | 3 | 18.2 |
| 4 | 16.84 | 0.86 | 4 | 18.17 |
| 5 | 16.84 | 0.86 | 5 | 18.15 |
| 6 | | 0.86 | 6 | 18.13 |
| 7 | 16.89 | 0.86 | 7 | 18.1 |
| 8 | 16.91 | 0.86 | 8 | 18.08 |
| 9 | 16.94 | 0.86 | 9 | 18.06 |
| 10 | 16.96 | 0.86 | 10 | 18.04 |
| 11 | 16.99 | 0.86 | 11 | 18.03 |
| 12 | | 0.86 | 12 | 18.01 |
| 13 | 17.04 | 0.86 | 13 | 17.99 |
| 14 | 17.06 | 0.86 | 14 | 17.96 |
| 15 | 17.08 | 0.86 | 15 | 17.94 |
| 16 | 17.11 | 0.86 | 16 | 17.93 |
| 17 | | 0.86 | 17 | 17.91 |
| 18 | 17.14 | 0.86 | 18 | 17.9 |
| 19 | 17.16 | 0.86 | 19 | 17.88 |
| 20 | 17.18 | 0.86 | 20 | 17.87 |
| 25 | 17.31 | 0.86 | 25 | 17.81 |
| 30 | 17.32 | 0.86 | 30 | 17.73 |
| 40 | 17.47 | 0.86 | 40 | 17.65 |
| 50 | 17.54 | 0.86 | 50 | 17.57 |
| 60 | 17.63 | 0.86 | 60 | 17.51 |
| 75 | 17.72 | 0.86 | 75 | 17.43 |
| 90 | 17.79 | 0.86 | 90 | 17.38 |
| 120 | 17.86 | 0.86 | 120 | 17.27 |
| 150 | 17.97 | 0.86 | 150 | 17.17 |
| 180 | 18.01 | 0.86 | 180 | 17.1 |
| 240 | 18.14 | 0.86 | 240 | 17 |
| 300 | 18.24 | 0.86 | 300 | 16.94 |
| 360 | 18.24 | 0.86 | | |
| 420 | 18.32 | 0.86 | | |
| 480 | 18.39 | 0.86 | | |
| 600 | 18.46 | 0.86 | | |

| Observation Borehole Information | | | | | | |
|----------------------------------|--------|--------|--------|--------|--------|--------|
| Borehole Name | D3 | D1 | D4 | UO23 | UO29 | UO30 |
| Distance (m) | | | | | | |
| Static WL (m) | 16.58 | 12.05 | 16.4 | 16.49 | 16.27 | 16.4 |
| Time (min) | wl (m) |
| 1 | | | | 16.61 | 16.46 | |
| 2 | 16.6 | | 16.56 | | | 16.18 |
| 3 | | | | 16.7 | 16.52 | |
| 4 | 16.82 | | 16.65 | | | 16.45 |
| 5 | | | | 16.78 | 16.57 | |
| 6 | 16.88 | | | 16.8 | | 16.42 |
| 7 | | | | | 16.64 | |
| 8 | | | 16.75 | | | 16.48 |
| 9 | | | 16.78 | | 16.7 | |
| 10 | | | | 16.92 | | 16.48 |
| 11 | 16.83 | | | 16.94 | 16.77 | |
| 12 | 17.05 | | 16.87 | | | 16.43 |
| 13 | | | | | 16.8 | |
| 14 | 17.06 | | | | | 16.53 |
| 15 | | | | 17 | 16.9 | |
| 16 | | | 16.94 | | | 16.6 |
| 17 | 17.15 | | 16.97 | | 16.9 | |
| 18 | | | | 17.07 | | 16.63 |
| 19 | | | 17 | | 16.94 | |
| 20 | 17.21 | | 17.04 | 17.12 | | 16.56 |
| 25 | 17.32 | | 17.11 | 17.21 | 17 | 16.56 |
| 30 | 17.35 | | 17.16 | 17.27 | 17.04 | 16.67 |
| 40 | 17.49 | | 17.28 | 17.35 | 17.1 | 16.74 |
| 50 | 17.55 | | 17.37 | 17.45 | 17.2 | 16.85 |
| 60 | 17.62 | | 17.45 | 17.53 | 17.28 | 17 |
| 75 | 17.74 | | 17.53 | 17.65 | 17.4 | 17.14 |
| 90 | 17.8 | | 17.58 | 17.67 | 17.44 | 17.23 |
| 120 | 17.81 | 12.1 | 17.67 | 17.76 | 17.52 | 17.5 |
| 150 | 17.93 | 12.12 | 17.74 | 17.86 | 17.65 | 17.54 |
| 180 | 18.04 | 12.14 | 17.83 | 17.93 | 17.7 | 17.75 |
| 240 | 18.15 | 12.17 | 17.98 | 18.07 | 17.75 | 18 |
| 300 | 18.22 | | 18.04 | 18.1 | 17.82 | 17.82 |
| 360 | 18.26 | | 18.12 | 18.22 | 17.87 | 17.95 |
| 420 | 18.32 | | 18.13 | 18.23 | 17.97 | 18.6 |
| 480 | 18.37 | | 18.21 | 18.27 | 18 | 18.02 |
| 600 | 18.45 | 12.37 | 18.3 | 18.36 | | |

Table 9: Pumping test data of Borehole UO30

| | | | | |
|-------------------------------------|---------------------|--------------------|-------------------|---------------------|
| Date Started | 2005/08/27 | | | |
| Time Started | 05:40 | | | |
| Pumping Borehole Information | | | | |
| Borehole Name | | UO30 | | |
| Depth of Pump (m) | | 30.3 | | |
| Static WL (m) | | 16.2 | | |
| Time (min) | Drawdown (m) | Yield (L/s) | Time (min) | Recovery (m) |
| 1 | 18.83 | 0.86 | 1 | 30.11 |
| 2 | 20.9 | 0.86 | 2 | 30.09 |
| 3 | 23.3 | 0.86 | 3 | 30.07 |
| 4 | 25.43 | 0.86 | 4 | 30.06 |
| 5 | 26.91 | 0.86 | 5 | 30.06 |
| 6 | 28.75 | 0.86 | 6 | 30.06 |
| 7 | 30.12 | 0.86 | 7 | 30.06 |
| 8 | | | 8 | 29.94 |
| 9 | | | 9 | 29.72 |
| 10 | | | 10 | 29.6 |
| 11 | | | 11 | 29.51 |
| 12 | | | 12 | 29.38 |
| 13 | | | 13 | 29.3 |
| 14 | | | 14 | 29.19 |
| 15 | | | 15 | 29.08 |
| 16 | | | 16 | 28.98 |
| 17 | | | 17 | 28.85 |
| 18 | | | 18 | 28.72 |
| 19 | | | 19 | 28.66 |
| 20 | | | 20 | 28.56 |
| 25 | | | 25 | 27.95 |
| 30 | | | 30 | 27.48 |
| 40 | | | 40 | 26.92 |
| 50 | | | 50 | 26 |
| 60 | | | 60 | 24.48 |
| 75 | | | 75 | 23.38 |
| 90 | | | 90 | 22.15 |

Table 10: Pumping test data of Borehole UP16

| | |
|--------------|------------|
| Date Started | 2006/07/04 |
| Time Started | 10:15 |

| Pumping Borehole Information | | | | |
|------------------------------|--------------|-------------|------------|--------------|
| Borehole Name | | UP16 | | |
| Depth of Pump (m) | | 40 | | |
| Static WL (m) | | 11.36 | | |
| Time (min) | Drawdown (m) | Yield (L/s) | Time (min) | Recovery (m) |
| 1 | 11.38 | 1.9 | 1 | 16.6 |
| 2 | 11.93 | 1.9 | 2 | 16.01 |
| 3 | 12 | 1.9 | 3 | 15.94 |
| 4 | 12.1 | 1.9 | 4 | 15.87 |
| 5 | 12.18 | 1.9 | 5 | 15.79 |
| 6 | 12.27 | 1.9 | 6 | 15.7 |
| 7 | 12.34 | 1.9 | 7 | 15.64 |
| 8 | 12.4 | 1.9 | 8 | 15.57 |
| 9 | 12.48 | 1.9 | 9 | 15.51 |
| 10 | 12.54 | 1.9 | 10 | 15.42 |
| 11 | 12.61 | 1.9 | 11 | 15.36 |
| 12 | 12.66 | 1.9 | 12 | 15.29 |
| 13 | 12.72 | 1.9 | 13 | 15.29 |
| 14 | 12.76 | 1.9 | 14 | 15.23 |
| 15 | 12.82 | 1.9 | 15 | 15.18 |
| 16 | 12.89 | 1.9 | 16 | 15.13 |
| 17 | 12.92 | 1.9 | 17 | 15.06 |
| 18 | 13.04 | 1.9 | 18 | 15.01 |
| 19 | 13.1 | 1.9 | 19 | 14.97 |
| 20 | 13.16 | 1.9 | 20 | 14.91 |
| 25 | 13.43 | 1.9 | 25 | 14.86 |
| 30 | 13.67 | 1.9 | 30 | 14.66 |
| 40 | 14.04 | 1.9 | 40 | 14.41 |
| 50 | 14.37 | 1.9 | 50 | 14.09 |
| 60 | 14.58 | 1.9 | 60 | 13.83 |
| 75 | 14.89 | 1.9 | 75 | 13.58 |
| 90 | 15.11 | 1.9 | 90 | |
| 120 | 15.52 | 1.9 | 120 | |
| 150 | 15.81 | 1.9 | 150 | |
| 180 | 16.05 | 1.9 | 180 | |
| 240 | 16.4 | 1.9 | 240 | |
| 300 | 16.71 | 1.9 | 300 | 12.32 |

| Observation Borehole Information | | |
|----------------------------------|--------------|--------------|
| Borehole Name | UO5 | UO3 |
| Distance (m) | 28.92 | 33.62 |
| Static WL (m) | 10.61 | 8.24 |
| Time (min) | Drawdown (m) | Drawdown (m) |
| 1 | 10.84 | |
| 2 | 10.9 | |
| 3 | | |
| 4 | 11.06 | 8.24 |
| 5 | | |
| 6 | | |
| 7 | | |
| 8 | | |
| 9 | | |
| 10 | | 8.24 |
| 11 | | |
| 12 | 11.52 | |
| 13 | 11.69 | |
| 14 | 11.74 | |
| 15 | 11.77 | |
| 16 | 11.81 | |
| 17 | | |
| 18 | | |
| 19 | | |
| 20 | 12.07 | 8.25 |
| 25 | 12.37 | 8.28 |
| 30 | 12.48 | 8.3 |
| 40 | 12.89 | 8.32 |
| 50 | 13.14 | 8.32 |
| 60 | 13.43 | 8.36 |
| 75 | 13.68 | 8.39 |
| 90 | 13.96 | 8.42 |
| 120 | 14.31 | 8.44 |
| 150 | 14.59 | 8.45 |
| 180 | 14.79 | 8.47 |
| 240 | 15.1 | 8.51 |
| 300 | 15.46 | 8.56 |

Table 11: Pumping test data of Borehole D3

| | |
|--------------|------------|
| Date Started | 2006/11/15 |
| Time Started | 10:00 |

| Pumping Borehole Information | | | | |
|------------------------------|--------------|-------------|------------|--------------|
| Borehole Name | | D3 | | |
| Depth of Pump (m) | | 22.5 | | |
| Static WL (m) | | 13.71 | | |
| Time (min) | Drawdown (m) | Yield (L/s) | Time (min) | Recovery (m) |
| 1 | 14.51 | 2.3 | 1 | 17.86 |
| 2 | | 2.3 | 2 | 17.7 |
| 3 | | 2.3 | 3 | 17.53 |
| 4 | | 2.3 | 4 | 17.41 |
| 5 | 15.27 | 2.3 | 5 | 17.26 |
| 6 | 15.44 | 2.3 | 6 | 17.14 |
| 7 | 15.54 | 2.3 | 7 | |
| 8 | 15.66 | 2.3 | 8 | 17.05 |
| 9 | 15.76 | 2.3 | 9 | 16.91 |
| 10 | 15.89 | 2.3 | 10 | 16.84 |
| 11 | 15.96 | 2.3 | 11 | 16.71 |
| 12 | 16.11 | 2.3 | 12 | 16.64 |
| 13 | 16.17 | 2.3 | 13 | |
| 14 | 16.29 | 2.3 | 14 | 16.52 |
| 15 | 16.35 | 2.3 | 15 | 16.44 |
| 16 | 16.44 | 2.3 | 16 | 16.35 |
| 17 | 16.5 | 2.3 | 17 | 16.3 |
| 18 | 16.59 | 2.3 | 18 | 16.24 |
| 19 | 16.66 | 2.3 | 19 | 16.18 |
| 20 | 16.74 | 2.3 | 20 | 16.11 |
| 25 | 17.04 | 2.3 | 25 | 15.86 |
| 30 | 17.33 | 2.3 | 30 | 15.54 |
| 40 | 17.77 | 2.3 | 40 | |
| 50 | 18.11 | 2.3 | 50 | |
| 60 | 18.42 | 2.3 | 60 | |

| Observation Borehole Information | | | | | | | |
|----------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Borehole Name | D2 | DC2 | D1 | DC1 | UO23 | UO30 | D4 |
| Distance (m) | | | | | | | |
| Static WL (m) | 13.63 | 13.46 | 13.72 | 13.42 | 13.63 | 13.66 | 13.54 |
| Time (min) | wl (m) |
| 1 | | | | | 14.45 | | |
| 2 | 14.49 | 14.49 | | 13.42 | | | |
| 3 | | | 14.74 | | | 13.67 | |
| 4 | | | | | 14.91 | 13.63 | |
| 5 | | | | | | | 14.98 |
| 6 | | | | | 15.19 | | |
| 7 | | | | | | 13.65 | 16.13 |
| 8 | | | | 15.24 | 15.5 | | 15.5 |
| 9 | | | | | | 13.67 | |
| 10 | | | | 15.51 | 15.72 | | 15.68 |
| 11 | | | | | | | 15.68 |
| 12 | | | | | 15.88 | | 15.9 |
| 13 | | | | | 16.05 | | |
| 14 | | | | 15.91 | | | |
| 15 | | | | | 16.13 | | |
| 16 | | | | 15.99 | 16.23 | | 16.1 |
| 17 | | | | 16.47 | | 13.77 | |
| 18 | | | | 16.2 | 16.37 | | |
| 19 | | | | 16.27 | 16.46 | 13.8 | |
| 21 | 16.61 | 16.61 | | 16.4 | 16.6 | | 16.47 |
| 25 | 16.92 | 16.92 | 16.87 | 16.6 | 16.8 | 13.91 | 16.7 |
| 32 | 17.24 | 17.24 | 17 | 16.97 | 17.13 | 14 | 17.05 |
| 40 | 17.63 | 17.63 | 17.33 | 17.4 | 17.58 | 14.18 | 17.54 |
| 53 | 18.03 | 18.03 | 17.76 | 17.73 | 17.94 | 14.46 | 17.81 |
| 62 | 18.28 | 18.28 | 18.05 | 18.24 | 18.28 | 14.67 | 18.12 |

Appendix E4

| | | | | | |
|---|------------|-----------------|-------------------------------------|------------|-----------------|
| Date and Time 05/12/2006 00:00 | | | | | |
| Tracer Type Radial convergent | | | | | |
| Injection Borehole D3 | | | Monitoring Borehole DC2 | | |
| Injection Pipe Depth 20.3 | | | Monitoring Pipe Depth 20.92 | | |
| Solute Mass (Kg) 0.4 NaCl /0.02 NaBr | | | Distance from Injection BH | | |
| | | | Distance from Abstraction BH | | |
| Point dilution data | | | Monitoring BH Data | | |
| Time (min) | Conc. (mS) | Water Level (m) | Time (min) | Conc. (mS) | Water Level (m) |
| 0 | 77.4 | | 0 | 83.1 | |
| 0.5 | 1000 | | 0.5 | 76.9 | |
| 1 | 884.3 | | 1 | 76.2 | |
| 1.5 | 794.9 | | 1.5 | 76.5 | |
| 2 | 716.4 | | 2 | 76.9 | |
| 2.5 | 674.1 | | 2.5 | | |
| 3 | 728.4 | | 3 | | |
| 3.5 | 652.1 | | 3.5 | 77.7 | |
| 4 | 595.9 | | 4 | | |
| 4.5 | 619.5 | | 4.5 | | |
| 5 | 577 | | 5 | 70 | |
| 5.5 | 578.7 | | 5.5 | | |
| 6 | 584.6 | | 6 | 76.6 | |
| 6.5 | 551.7 | | 6.5 | 77 | |
| 7 | 522.8 | | 7 | 77.6 | |
| 7.5 | 514.9 | | 7.5 | 70 | |
| 8 | 496 | | 8 | 77.7 | |
| 8.5 | 504.4 | | 8.5 | 77.3 | |
| 9 | 496 | | 9 | 76.9 | |
| 9.5 | 474 | | 9.5 | 70 | |
| 10 | 468.1 | | 10 | | |
| 11 | 458.3 | | 11 | 77 | |
| 12 | 436.1 | | 12 | 77.1 | |
| 13 | 418.2 | | 13 | 77.4 | |
| 14 | 408.9 | | 14 | 77.7 | |
| 15 | 412.2 | | 15 | 70.3 | |
| 16 | 405.8 | | 16 | 77.7 | |
| 17 | 400.8 | | 17 | 76.7 | |
| 18 | 384.3 | | 18 | 75.9 | |
| 19 | 384.2 | | 19 | 76 | |
| 20 | 365.6 | | 20 | 76.4 | |
| 25 | 363.5 | | 25 | 77.7 | |
| 30 | 340 | | 30 | 74.1 | |
| 40 | 301.6 | | 40 | 76.6 | |
| 50 | 274.2 | | 50 | 75.7 | |
| 65 | 235.5 | | 65 | 74 | |
| 75 | 214.5 | | 75 | 72.8 | |
| 90 | 185.2 | | 90 | 74.3 | |
| 120 | 141.3 | | 120 | 72.8 | |
| Abstraction Borehole UO23 | | | Monitoring Borehole DC1 | | |
| Abstraction Pipe Depth 23.3 | | | Monitoring Pipe Depth (m) | | |
| Abstraction Rate (l/s) 2 | | | Distance from Injection BH | | |
| | | | Distance from Abstraction BH | | |
| Abstraction Borehole Data | | | Monitoring BH Data | | |
| Time (min) | Conc. (mS) | Water Level (m) | Time (min) | Conc. (mS) | Water Level (m) |
| 0 | 89.3 | | 0 | 109.3 | |
| 0.5 | 80.7 | | 1 | 108.8 | |
| 1 | 82.1 | | 2 | 108.8 | |
| 1.5 | 82.1 | | 3 | 109.1 | |
| 2 | 83.6 | | 4 | 109.4 | |
| 2.5 | 85.4 | | 5 | 109.4 | |
| 3 | 86.3 | | 6 | 109.4 | |
| 3.5 | 92 | | 7 | 109.4 | |
| 4 | 94.5 | | 8 | 109.4 | |
| 4.5 | 95.6 | | 9 | 109.4 | |
| 5 | 96 | | 10 | 109.4 | |
| 5.5 | 99 | | 11 | 109.4 | |
| 6 | 97 | | 12 | 109.4 | |
| 6.5 | 98.6 | | 13 | 109.4 | |
| 7 | 100.1 | | 14 | 109.4 | |
| 7.5 | 100 | | 15 | 109.4 | |
| 8 | 99 | | 16 | 109.4 | |
| 8.5 | 102 | | 17 | 109.4 | |
| 9 | 106.8 | | 18 | 109.4 | |
| 9.5 | 97 | | 19 | 109.4 | |
| 10 | 93.9 | | 20 | 109.4 | |
| 11 | 89.7 | | 25 | 109.4 | |
| 12 | 87.7 | | 30 | 109.4 | |
| 13 | 87 | | 35 | 109.4 | |
| 14 | 86 | | 40 | 109.4 | |
| 15 | 83 | | 45 | 109.4 | |
| 16 | 86.8 | | 50 | 109.4 | |
| 17 | 88 | | 55 | 109.4 | |
| 18 | 89.5 | | 60 | 109.4 | |
| 19 | 91.1 | | 70 | | |
| 20 | 90.4 | | 80 | | |
| 25 | 88.5 | | 90 | | |
| 30 | 87.2 | | 105 | | |
| 40 | 86.2 | | 120 | | |
| 50 | 88.3 | | 135 | | |
| 65 | 91.4 | | 150 | | |
| 75 | 86.3 | | 180 | | |
| 90 | 87.7 | | 210 | | |
| 120 | 87.9 | | 240 | | |
| 270 | | | 270 | | |
| 300 | | | 300 | | |
| 330 | | | 330 | | |
| 360 | | | 360 | | |

| | |
|-----------------------------|----------------------|
| Date and Time | 17/11/2006 08:00 |
| Tracer Type | Radial convergent |
| Injection Borehole | UO23 |
| Injection Pipe Depth | 20.3 |
| Solute Mass (Kg) | 0.4 NaCl + 0.02 NaBr |

Injection Borehole Data

| Time (min) | Conc. (mS) | Water Level (m) |
|------------|------------|-----------------|
| 0 | 85.6 | 13.46 |
| 0.5 | 316 | |
| 1 | 417 | |
| 1.5 | 523.7 | |
| 2 | 326 | |
| 2.5 | 300 | |
| 3 | 303.7 | |
| 3.5 | 267 | |
| 4 | 248 | |
| 4.5 | 218.9 | |
| 5 | 215 | |
| 5.5 | 238 | |
| 6 | 213.9 | |
| 6.5 | 209.8 | |
| 7 | 210.2 | |
| 7.5 | 179.3 | |
| 8 | 201.6 | |
| 8.5 | 167 | |
| 9 | 183 | |
| 9.5 | 147 | |
| 10 | 189.6 | |
| 11 | 174.4 | |
| 12 | 164.9 | |
| 13 | 153.9 | |
| 14 | 137.8 | |
| 15 | 144.3 | |
| 16 | 135.9 | |
| 17 | 130.6 | |
| 18 | 107.5 | |
| 19 | 127.1 | |
| 20 | 107.4 | |
| 25 | 104.7 | |
| 30 | 89.6 | |
| 40 | 85.9 | |
| 150 | | |
| 180 | | |

| | |
|-------------------------------|-------|
| Abstraction Borehole | D3 |
| Abstraction Pipe Depth | 22.35 |
| Abstraction Rate (l/s) | 1.15 |

Abstraction Borehole Data

| Time (min) | Conc. (mS) | Water Level (m) |
|------------|------------|-----------------|
| 0 | 97.7 | |
| 0.5 | 97.6 | |
| 1 | 112.58 | |
| 1.5 | 156.5 | |
| 2 | 186.9 | |
| 2.5 | 201.2 | |
| 3 | 203.9 | |
| 3.25 | 206.3 | |
| 3.5 | 202 | |
| 4 | 196.7 | |
| 4.5 | 188.2 | |
| 5 | 183.5 | |
| 5.5 | 178.3 | |
| 6 | 166.8 | |
| 6.5 | 164.1 | |
| 7 | 159.6 | |
| 7.5 | 154.6 | |
| 8 | 150 | |
| 8.5 | 145.1 | |
| 9 | 143.2 | |
| 9.5 | 137.2 | |
| 10 | 136.4 | |
| 11 | 131.6 | |
| 12 | 127.1 | |
| 13 | 121.9 | |
| 14 | 118.7 | |
| 15 | 118.4 | |
| 16 | 117.8 | |
| 17 | 117.2 | |
| 18 | 114.5 | |
| 19 | 114.3 | |
| 20 | 114.9 | |
| 25 | 108.3 | |
| 30 | 105.6 | |
| 40 | 101.2 | |
| 50 | 98.2 | |
| 150 | | |

| | | | | | |
|---------------------------------------|------------|-------------------------------------|-------------------------------------|------------|-----------------|
| Date and Time 16/11/2006 08:00 | | | | | |
| Tracer Type Radial convergent | | | | | |
| Injection Borehole UO23 | | Monitoring Borehole DC2 | | | |
| Injection Pipe Depth 20.35 | | Monitoring Pipe Depth (m) | | | |
| Solute Mass (Kg) 0.4 | | Distance from Injection BH | | | |
| | | Distance from Abstraction BH | | | |
| Point dilution data | | | Monitoring BH Data | | |
| Time (min) | Conc. (mS) | Water Level (m) | Time (min) | Conc. (mS) | Water Level (m) |
| 0 | 87.5 | | 0 | 88.6 | |
| 1 | 542 | | 1 | 87.1 | |
| 2 | 470.5 | | 2 | 88.5 | |
| 3 | 436.7 | | 3 | 87.1 | |
| 4 | 405.9 | | 4 | 86.2 | |
| 5 | 341.6 | | 5 | 87.1 | |
| 6 | 305.5 | | 6 | 87.5 | |
| 7 | 270.7 | | 7 | 87.1 | |
| 9 | 266.4 | | 8 | 86.2 | |
| 10 | 258.3 | | 9 | 86.2 | |
| 11 | 223.3 | | 10 | 84.7 | |
| 12 | 220.5 | | 11 | 84.7 | |
| 13 | 213.5 | | 12 | 85.5 | |
| 14 | 199.6 | | 13 | 85.2 | |
| 15 | 192.1 | | 14 | 85.5 | |
| 16 | 173.2 | | 15 | 85.2 | |
| 17 | 174 | | 16 | 84.3 | |
| 18 | 171.9 | | 17 | 84.7 | |
| 19 | 161.5 | | 18 | 85.1 | |
| 20 | 150.7 | | 19 | 84.3 | |
| 25 | 134.2 | | 20 | 84.3 | |
| 26 | 132.6 | | 25 | 84.7 | |
| 27 | 126.7 | | 30 | 84.3 | |
| 28 | 123.4 | | 35 | 84.7 | |
| 29 | 122.5 | | 40 | 84.9 | |
| 30 | 119 | | 50 | 85 | |
| 35 | 106.2 | | 55 | | |
| 40 | 102.3 | | 60 | | |
| 50 | 99.2 | | 70 | | |
| 60 | 95.6 | | 80 | | |
| 80 | | | 90 | | |
| 90 | | | 105 | | |
| 105 | | | 120 | | |
| 120 | | | 135 | | |
| 135 | | | 150 | | |
| 150 | | | 180 | | |
| 180 | | | 180 | | |
| 210 | | | 210 | | |
| 240 | | | 240 | | |
| 270 | | | 270 | | |
| 300 | | | 300 | | |
| 330 | | | 330 | | |
| 360 | | | 360 | | |
| Abstraction Borehole D3 | | | Monitoring Borehole DC1 | | |
| Abstraction Pipe Depth 23.3 | | | Monitoring Pipe Depth (m) | | |
| Abstraction Rate (l/s) 1.2 | | | Distance from Injection BH | | |
| | | | Distance from Abstraction BH | | |
| Abstraction Borehole Data | | | Monitoring BH Data | | |
| Time (min) | Conc. (mS) | Water Level (m) | Time (min) | Conc. (mS) | Water Level (m) |
| 0 | 112.4 | | 0 | 109.3 | |
| 1 | 179 | | 1 | 108.8 | |
| 2 | 220.3 | | 2 | 108.8 | |
| 3 | 201.8 | | 3 | 109.1 | |
| 4 | 186.4 | | 4 | 109.4 | |
| 5 | 179.3 | | 5 | 109.4 | |
| 6 | 174.3 | | 6 | 109.4 | |
| 7 | 167.1 | | 7 | 109.4 | |
| 8 | 159.6 | | 8 | 109.4 | |
| 9 | 157.5 | | 9 | 109.4 | |
| 10 | 154.7 | | 10 | 109.4 | |
| 11 | 152.4 | | 11 | 109.4 | |
| 12 | 149.5 | | 12 | 109.4 | |
| 13 | 144.3 | | 13 | 109.4 | |
| 14 | 141.7 | | 14 | 109.4 | |
| 15 | 140.4 | | 15 | 109.4 | |
| 16 | 137.2 | | 16 | 109.4 | |
| 17 | 135.7 | | 17 | 109.4 | |
| 18 | 132.9 | | 18 | 109.4 | |
| 19 | 130.7 | | 19 | 109.4 | |
| 20 | 129.7 | | 20 | 109.4 | |
| 25 | 124.7 | | 25 | 109.4 | |
| 30 | 119.9 | | 30 | 109.4 | |
| 35 | 116.4 | | 35 | 109.4 | |
| 40 | 113.6 | | 40 | 109.4 | |
| 50 | 113.9 | | 45 | 109.4 | |
| 60 | 112.6 | | 50 | 109.4 | |
| 55 | | | 55 | 109.4 | |
| 60 | | | 60 | 109.4 | |

| | | | |
|---------------------------------------|------------------------|-------------------------------------|--------------------|
| Date and Time 15/11/2006 08:00 | | | |
| Tracer Type Radial convergent | | | |
| | | | |
| Injection Borehole | D3 | Monitoring Borehole | DC2 |
| Injection Pipe Depth | 20.3 | Monitoring Pipe Depth (m) | |
| Solute Mass (Kg) | 0.4 | Distance from Injection BH | |
| rest water level 14.18 | | Distance from Abstraction BH | |
| | | | |
| Point dilution data | | Monitoring BH Data | |
| Time (min) | Conc. (mS) | Time (min) | Conc. (mS) |
| | Water Level (m) | | Water Level |
| 0 | 102.7 | 0 | 84.5 |
| 1 | 491.8 | 1 | 86.6 |
| 2 | 537 | 2 | 87.1 |
| 3 | 505.9 | 3 | 84.9 |
| 4 | 463.1 | 4 | 84.3 |
| 5 | 483.4 | 5 | 83.6 |
| 6 | 446.1 | 6 | 83.5 |
| 7 | 422 | 7 | 84.7 |
| 8 | 422.5 | 8 | 86.2 |
| 9 | 390.4 | 9 | 83.5 |
| 10 | 393.1 | 10 | 84.3 |
| 11 | 380.4 | 11 | 83.6 |
| 12 | 367.5 | 12 | 83.2 |
| 13 | 342.7 | 13 | 84.7 |
| 14 | 346.2 | 14 | 85.2 |
| 15 | 331.1 | 15 | 84.9 |
| 16 | 323.2 | 16 | 83.6 |
| 17 | 318.4 | 17 | 84.4 |
| 18 | 309.9 | 18 | 85.5 |
| 19 | 301.1 | 19 | 83.5 |
| 20 | 298.7 | 20 | 80.6 |
| 25 | 291.2 | 30 | 87.2 |
| 30 | 288.5 | 35 | 82.8 |
| 35 | 280.9 | 40 | 84.7 |
| 40 | 290.1 | 45 | 82.5 |
| 45 | 271.7 | 50 | 82.6 |
| 50 | 262.1 | 55 | 82.7 |
| 55 | 280.4 | 60 | 79.3 |
| 60 | 233 | 70 | 79.5 |
| 70 | 214 | 80 | 80 |
| 80 | 229.4 | 90 | 79.8 |
| 90 | 231.4 | 105 | 78.8 |
| 105 | 206.9 | 120 | 78.7 |
| 120 | 196.8 | 135 | 79 |
| 135 | 204.7 | 150 | 79.3 |
| 150 | 183 | 180 | 80.5 |
| 180 | 161 | 180 | 80.5 |
| 210 | | 210 | |
| 240 | | 240 | |
| 270 | | 270 | |
| 300 | | 300 | |
| 330 | | 330 | |
| 360 | | 360 | |
| | | | |
| Abstraction Borehole UO23 | | Monitoring Borehole DC1 | |
| Abstraction Pipe Depth 23.42 | | Monitoring Pipe Depth (m) | |
| Abstraction Rate (l/s) 1 | | Distance from Injection BH | |
| | | Distance from Abstraction BH | |
| | | | |
| Abstraction Borehole Data | | Monitoring BH Data | |
| Time (min) | Conc. (mS) | Time (min) | Conc. (mS) |
| | Water Level (m) | | Water Level |
| 0 | 81.9 | 0 | 108.5 |
| 1 | 81.9 | 1 | 106.3 |
| 2 | 81.6 | 2 | 101.2 |
| 3 | 79.9 | 3 | 99.7 |
| 4 | 78.7 | 4 | 97.4 |
| 5 | 79.5 | 5 | 98.6 |
| 6 | 80.1 | 6 | 97.8 |
| 7 | 77.4 | 7 | 96.8 |
| 8 | 78.1 | 8 | 96.2 |
| 9 | 79.3 | 9 | 95.1 |
| 10 | 79.7 | 10 | 96 |
| 11 | 80.1 | 11 | 95.1 |
| 12 | 79.3 | 12 | 95.1 |
| 13 | 79.6 | 13 | 95.1 |
| 14 | 77.7 | 14 | 94.7 |
| 15 | 80.2 | 15 | 95.1 |
| 16 | 78.3 | 16 | 92.7 |
| 17 | 78.7 | 17 | 92.9 |
| 18 | 79.3 | 18 | 93.6 |
| 19 | 78.8 | 19 | 92.6 |
| 20 | 80.4 | 20 | 93.3 |
| 25 | 84 | 25 | 103.8 |
| 30 | 70.2 | 30 | 91.1 |
| 35 | 88.5 | 35 | 94.2 |
| 40 | 91.1 | 40 | 98.6 |
| 45 | 88.5 | 45 | 98.7 |
| 50 | 95.4 | 50 | 102.6 |
| 55 | 86.1 | 55 | 100 |
| 60 | 86.1 | 60 | 99.1 |
| 70 | 86.1 | 70 | 98.4 |
| 80 | 88.4 | 80 | 100.9 |
| 90 | 83.8 | 90 | 97.8 |
| 105 | 84.7 | 105 | 95.7 |
| 120 | 83.9 | 120 | 95.1 |
| 135 | 86.3 | 135 | 90.2 |
| 150 | 84.1 | 150 | 102.7 |
| 180 | 84.4 | 180 | 87 |

| | |
|----------------------|-------------------|
| Date and Time | 14/11/2006 11:30 |
| Tracer Type | Radial convergent |

| | |
|-----------------------------|------|
| Injection Borehole | D3 |
| Injection Pipe Depth | 20.3 |
| Solute Mass (Kg) | 0.2 |

Point dilution data

| Time (min) | Conc. (mS) | Water Level (m) |
|------------|------------|-----------------|
| 0 | 80.8 | |
| 1 | 248 | |
| 2 | 282.5 | |
| 3 | 304.2 | |
| 4 | 274.4 | |
| 5 | 270 | |
| 6 | 265 | |
| 7 | 258 | |
| 8 | 255 | |
| 9 | 249.4 | |
| 10 | 256.7 | |
| 11 | 252.9 | |
| 12 | 251.2 | |
| 13 | 246.5 | |
| 14 | 241.5 | |
| 15 | 235 | |
| 16 | 238.3 | |
| 17 | 231.7 | |
| 18 | 235.2 | |
| 19 | 233.2 | |
| 20 | 233 | |
| 25 | 225.1 | |
| 30 | 222 | |
| 35 | 220.3 | |
| 40 | 220.2 | |
| 45 | 217 | |
| 50 | 213.1 | |
| 55 | 209.5 | |
| 60 | 205.7 | |
| 70 | 202.1 | |
| 80 | 194.4 | |
| 90 | 187.6 | |
| 110 | 183.5 | |
| 120 | 174.8 | |
| 150 | 164.5 | |
| 150 | | |
| 180 | | |
| 210 | | |
| 240 | | |
| 270 | | |
| 300 | | |
| 330 | | |
| 360 | | |

| | |
|-------------------------------|-------|
| Abstraction Borehole | UO23 |
| Abstraction Pipe Depth | 22.42 |
| Abstraction Rate (l/s) | 0.65 |

Abstraction Borehole Data

| Time (min) | Conc. (mS) | Water Level (m) |
|------------|------------|-----------------|
| 0 | 87.5 | |
| 1 | 80.5 | |
| 2 | 79.5 | |
| 3 | 79.1 | |
| 4 | 78 | |
| 5 | 78 | |
| 6 | 78 | |
| 7 | 78 | |
| 8 | 77.8 | |
| 9 | 76.7 | |
| 10 | 76.8 | |
| 11 | 74.6 | |
| 12 | 77 | |
| 13 | 75.3 | |
| 14 | 78 | |
| 15 | 76 | |
| 16 | 74.6 | |
| 17 | 73.3 | |
| 18 | 76.7 | |
| 19 | 76.7 | |
| 20 | 75.9 | |
| 25 | 78 | |
| 30 | 78 | |
| 35 | 78.8 | |
| 40 | 78.6 | |
| 45 | 78.8 | |
| 50 | 79.9 | |
| 55 | 78.3 | |
| 60 | 79.5 | |
| 70 | 73.7 | |
| 80 | 79.6 | |
| 90 | 79.6 | |
| 110 | 77.7 | |
| 120 | 80.7 | |
| 150 | 82.3 | |

| | |
|-------------------------------------|-----|
| Monitoring Borehole | DC2 |
| Monitoring Pipe Depth (m) | |
| Distance from Injection BH | |
| Distance from Abstraction BH | |

Monitoring BH Data

| Time (min) | Conc. (mS) | Water Level (m) |
|------------|------------|-----------------|
| 0 | 87.8 | |
| 1 | 88.1 | |
| 2 | 85 | |
| 3 | 82.4 | |
| 4 | 82.8 | |
| 5 | 81.2 | |
| 6 | 82.1 | |
| 7 | 82.3 | |
| 8 | 82.8 | |
| 9 | 81.7 | |
| 10 | 81.2 | |
| 11 | 81.7 | |
| 12 | 81.2 | |
| 13 | 80.5 | |
| 14 | 82 | |
| 15 | 80.5 | |
| 16 | 79.8 | |
| 17 | 79.3 | |
| 18 | 79 | |
| 19 | 79.8 | |
| 20 | 79.8 | |
| 25 | 80.7 | |
| 30 | 79 | |
| 35 | 78.8 | |
| 40 | 78.8 | |
| 45 | 77.8 | |
| 50 | 79 | |
| 55 | 77.7 | |
| 60 | 76.5 | |
| 70 | 77.3 | |
| 80 | 76.9 | |
| 90 | 77.2 | |
| 110 | 75.7 | |
| 120 | 77.9 | |
| 150 | 75.9 | |
| 150 | | |
| 180 | | |
| 210 | | |
| 240 | | |
| 270 | | |
| 300 | | |
| 330 | | |
| 360 | | |

| | |
|-------------------------------------|-----|
| Monitoring Borehole | DC1 |
| Monitoring Pipe Depth (m) | |
| Distance from Injection BH | |
| Distance from Abstraction BH | |

Monitoring BH Data

| Time (min) | Conc. (mS) | Water Level (m) |
|------------|------------|-----------------|
| 0 | 108.1 | |
| 1 | 106.7 | |
| 2 | 106.7 | |
| 3 | 102.5 | |
| 4 | 98.6 | |
| 5 | 98.5 | |
| 6 | 98.6 | |
| 7 | 97.3 | |
| 8 | 93.4 | |
| 9 | 91.7 | |
| 10 | 94.3 | |
| 11 | 94.7 | |
| 12 | 92.4 | |
| 13 | 91.7 | |
| 14 | 89.4 | |
| 15 | 88.5 | |
| 16 | 89.4 | |
| 17 | 90.2 | |
| 18 | 90.2 | |
| 19 | 90.2 | |
| 20 | 90.2 | |
| 25 | 91.7 | |
| 30 | 91.6 | |
| 35 | 89.2 | |
| 40 | 88.1 | |
| 45 | 90.5 | |
| 50 | 91 | |
| 55 | 88.5 | |
| 60 | 90.6 | |
| 70 | 88.8 | |
| 80 | 89 | |
| 90 | 89.5 | |
| 110 | 87.8 | |
| 120 | 87 | |
| 150 | 86.9 | |

| | |
|----------------------|---------------------|
| Date and Time | 04/11/2006 08:40 |
| Tracer Type | Point-dilution Test |

| | |
|-----------------------------|-------|
| Injection Borehole | D3 |
| Injection Pipe Depth | 20.42 |
| Solute Mass (Kg) | 0.3 |

Point-dilution data

| Time (min) | Conc. (mS/m) |
|------------|--------------|
| 0 | 64.5 |
| 1 | 385.2 |
| 2 | 356.6 |
| 3 | 302.1 |
| 4 | 286.5 |
| 5 | 302.6 |
| 6 | 298.7 |
| 7 | 285 |
| 8 | 285 |
| 9 | 265 |
| 10 | 268 |
| 11 | 263 |
| 12 | 275 |
| 13 | 250.2 |
| 14 | 282 |
| 15 | 273.2 |
| 16 | 251.5 |
| 17 | 277.9 |
| 18 | 282.5 |
| 19 | 283.2 |
| 20 | 272.9 |
| 25 | 251.1 |
| 30 | 233.9 |
| 40 | 241.2 |
| 50 | 202.3 |
| 60 | 220 |
| 75 | 229.8 |
| 90 | 227.4 |
| 120 | 220.6 |
| 160 | 215.3 |

| | |
|-------------------------------|-------|
| Abstraction Borehole | D3 |
| Abstraction Pipe Depth | 22.42 |
| Abstraction Rate (l/s) | 0.78 |

Injection-Withdrawal data

| Time (min) | Conc. (mS/m) |
|------------|--------------|
| 0 | 182 |
| 1 | 194.2 |
| 2 | 194.1 |
| 3 | 194 |
| 4 | 193.9 |
| 5 | 193.6 |
| 6 | 194.1 |
| 7 | 193.9 |
| 8 | 194.2 |
| 9 | 194.8 |
| 10 | 194.2 |
| 11 | 194.3 |
| 12 | 194.4 |
| 13 | 193.9 |
| 14 | 194 |
| 15 | 194.4 |
| 16 | 194.2 |
| 17 | 195 |
| 18 | 195 |
| 19 | 195 |
| 20 | 195 |
| 25 | 195.5 |
| 30 | 195.6 |
| 35 | 194.9 |
| 40 | 194.2 |
| 45 | 195 |
| 50 | 193.8 |
| 55 | 193.2 |
| 60 | 190.5 |
| 70 | 189.6 |

Appendix F

Table Comparison of Dutch and EPA concentration limits for selected organics

| Parameter | DUTCH | | US EPA | |
|--|----------------------|-------------------------|-----------|-----------------|
| | reference value mg/l | Intervention value mg/l | MCLG mg/l | MCL or TTI mg/l |
| benzo(a)pyrene | 0.0000005 | 0.00005 | zero | 0.0002 |
| 1,1,1-trichloroethane | 0.00001 | 0.3 | 0.2 | 0.2 |
| 1,1,2-trichloroethane | 0.00001 | 0.13 | 0.003 | 0.005 |
| 1,1-dichloroethane | 0.007 | 0.9 | zero | 0.005 |
| 1,1-dichloroethene | 0.00001 | 0.01 | 0.007 | 0.007 |
| 1,2 butylacetate | - | 6.3 | | |
| 1,2-dichloroethane | 0.007 | 0.4 | 0.07 | 0.07 |
| 1,2-dichloroethene (cis. trans) * | 0.00001 | 0.02 | 0.1 | 0.1 |
| 4-chloromethylphenols | - | 0.35 | | |
| aldrin | 0.00000009 | - | zero | 0.002 |
| atrazine | 0.000029 | 0.15 | 0.003 | 0.003 |
| benzene | 0.0002 | 0.03 | zero | 0.005 |
| carbofuran | 0.000009 | 0.1 | 0.04 | 0.04 |
| carbon tetrachloride | 0.00001 | 0.01 | zero | 0.005 |
| chlordane | 0.00000002 | 0.0002 | zero | 0.002 |
| chlorobenzene (sum) | - | - | 0.1 | 0.1 |
| <i>EPA distinguishes between cis and trans</i> | 0 | 0 | 0.6 | 0.6 |
| dichlorobenzenes (sum) | 0.003 | 0.05 | 0.075 | 0.075 |
| dichloromethane | 0.00001 | 1 | zero | 0.005 |
| dichlorophenols (sum) | 0.0002 | 0.03 | | |
| dichloropropanes | 0.0008 | 0.08 | zero | 0.005 |
| dioxin | - | - | zero | 0.00000003 |
| endrin | - | - | 0.002 | 0.002 |
| ethyl benzene | 0.004 | 0.15 | 0.7 | 0.7 |
| heptachlor | 0.000000005 | 0.0003 | zero | 0.0004 |
| heptachlor-epoxide | 0.000000005 | 0.003 | zero | 0.0002 |
| hexachlorobenzene | 0.00000009 | 0.0005 | zero | 0.001 |
| pentachlorophenol | 0.00004 | 0.003 | zero | 0.001 |
| styrene (vinylbenzene) | 0.006 | 0.3 | 0.1 | 0.1 |
| tetrachloroethene | 0.00001 | 0.04 | zero | 0.005 |
| toluene | 0.007 | 1 | 1 | 1 |
| trichloroaniline | - | 0.01 | 0.07 | 0.07 |
| trichloroethylene | 0.024 | 0.5 | zero | 0.005 |
| vinyl chloride | 0.00001 | 0.005 | zero | 0.002 |
| xylene | 0.0002 | 0.07 | 10 | 10 |