

Site Characterisation Methodologies for DNAPLs in Fractured South African Aquifers

By

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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, Institute for
Groundwater Studies, University of the Free State, Bloemfontein, South Africa.**

May 2007

Promoter: Dr. B.H. Usher

Acknowledgement

I must begin by expressing my heartfelt appreciation to my promoter and mentor Dr. Brent Usher for his endless support and continuous guidance throughout the research period. Without his efforts, I would never have achieved this goal.

I would like to acknowledge to Prof. Gerrit van Tonder and Dr. Allen Shapiro for their assistance and encouragement in various parts of the research.

My special thanks go to Jennifer Pretorius and Sechaba Elmon Lenong for their extensive and useful assistance during most of my fieldworks and in the shaping of my thesis.

I wish to express my sincere thanks to Mehari T. Menghistu, Dr. Danie Vermeulen, Eelco Lucas, Dr. Ingrid Denis, Professor Frank Hodgson, Elna De Necker, Lore-Mari Cruywagen, Jane van den Heever and everybody in IGS for their hospitality, encouragement and contribution in many forms of the thesis.

Thanks to Catherine Bitzer for proof-reading while she was in predicament of maternity.

A special thanks to WRC, especially Dr. Kevin Pietersen, for the funding of the research that ran for three years.

Finally, I would like to have a special word of thank to my parents for their uninterrupted moral support.

TABLE OF CONTENTS

1	INTRODUCTION.....	1
1.1	INTRODUCTION TO DNAPLS	1
1.2	HISTORICAL ISSUES.....	3
1.2.1	<i>Groundwater Contamination by DNAPLS</i>	5
1.2.2	<i>Scope of the Problem in South Africa</i>	5
1.3	DNAPL CHARACTERISATION CHALLENGE IN FRACTURED AQUIFERS.....	6
1.4	CHARACTERISATION APPROACH	8
1.5	AIM OF THESIS	8
1.5.1	<i>Thesis Structure</i>	9
2	DNAPL PROPERTIES	10
2.1	PHYSICAL PROPERTIES.....	10
2.1.1	<i>Interfacial Tension</i>	10
2.1.2	<i>Wettability and Contact Angle</i>	11
2.1.3	<i>Density</i>	13
2.1.4	<i>Solubility</i>	14
2.1.5	<i>Viscosity</i>	15
2.1.6	<i>Capillary Pressure</i>	15
2.1.7	<i>Bulk Retention Capacity</i>	17
2.1.8	<i>Relative Permeability</i>	18
2.1.9	<i>Vapourisation</i>	20
2.1.10	<i>Volatilisation</i>	21
2.1.11	<i>Sorption and Partitioning Coefficient</i>	21
2.1.12	<i>Saturation</i>	23
2.1.12.1	<i>Residual Saturation</i>	23
2.1.12.2	<i>Pooled DNAPL</i>	25
2.2	BIOTRANSFORMATION OF DNAPLS	26
2.3	USE OF DNAPLS.....	27
2.3.1	<i>Chlorinated solvents</i>	27
2.3.2	<i>Polychlorinated biphenyls (PCBs)</i>	30
2.3.3	<i>Creosote</i>	30
2.3.4	<i>Coal tar</i>	30
2.4	PHYSIOCHEMICAL PROPERTIES OF THE COMMON DNAPLS	31
2.4.1	<i>Chlorinated Solvents</i>	31
2.4.2	<i>Polychlorinated biphenyls (PCBs)</i>	34
2.4.3	<i>Creosote and Coal Tar</i>	35
2.4.4	<i>Miscellaneous DNAPLS</i>	36
2.4.5	<i>Potential DNAPL Sources in South Africa</i>	40
2.4.5.1	<i>Industrial and Mining Activities</i>	40
2.4.5.2	<i>Agricultural Activities</i>	48
2.4.5.3	<i>Municipal/Domestic Activities</i>	50
3	MIGRATION OF DNAPLS IN FRACTURED AQUIFERS	51
3.1	OVERVIEW OF DNAPLS IN THE VADOSE ZONE	51
3.2	OVERVIEW OF DNAPLS IN THE SATURATED POROUS MEDIA	53
3.3	DNAPL MIGRATION IN FRACTURED NON-POROUS MEDIA.....	55
3.3.1	<i>DNAPL Entry into Fractures</i>	56
3.3.2	<i>DNAPL Flow Rates in Vertical Fractures</i>	60
3.3.3	<i>DNAPL Mobilisation due to Pumping</i>	61
3.3.4	<i>Influence of Interfacial Tension in the Fracture Network</i>	62
3.3.5	<i>Influence of Fracture Orientation</i>	63
3.3.6	<i>DNAPL Elevation in a Borehole in a Fractured Network</i>	64
3.4	DNAPL MIGRATION IN DUAL-POROSITY MEDIA.....	65
3.4.1	<i>DNAPL Diffusion in Dual-Porosity Aquifer</i>	66
3.4.1.1	<i>Dissolved-phase Transport in Dual-Porosity Media</i>	68
4	SIGNIFICANCE OF FRACTURED SOUTH AFRICAN AQUIFERS TO DNAPL CONTAMINATION.....	70

4.1	SOUTH AFRICAN AQUIFERS AND DNAPLS	70
4.1.1	Primary Porosity Aquifers	72
4.1.2	Fractured Non-porous Aquifers	73
4.1.2.1	DNAPLS and Dykes	75
4.1.2.2	DNAPLS and Sills	75
4.1.3	Karst	76
4.1.4	Dual-porosity Aquifers	78
5	DNAPL SITE CHARACTERISATION STRATEGIES WITH FOCUS ON FRACTURED AQUIFERS.....	82
5.1	DIFFERENCE OF DNAPLS FROM OTHER CONTAMINANTS	82
5.2	TOOLBOX APPROACH FOR DNAPL CHARACTERISATION	84
5.2.1	Establishing Goals and Objectives	85
5.2.2	Planning and Conducting Site Investigations	86
5.2.3	Site Conceptual Model Development	88
5.2.3.1	Source and Release Characterisation	89
5.2.3.2	Geochemistry Impacting Natural Biodegradation	91
5.2.3.3	Free-Phase DNAPL	91
5.2.3.4	Contaminant Dissolution, Transport and Fate	95
5.2.3.5	Nature and Extent of Contamination	97
5.2.3.6	Fracture and Hydrogeologic Characterisation	98
5.2.3.7	Duration of Site Characterisation	100
5.2.3.8	Evaluation of Contamination Potential	101
6	FINDINGS OF SITE CHARACTERISATION IN FRACTURED SOUTH AFRICAN AQUIFERS.....	102
6.1	INTRODUCTION TO TEST SITE 1	102
6.1.1	Site Description	102
6.1.2	Geology and Hydrogeology	104
6.1.2.1	Regional Geology	104
6.1.2.2	Regional Hydrogeology	107
6.1.2.3	Local Geology	108
6.1.2.4	Local Hydrogeology	108
6.1.3	Topography	108
6.1.4	Climatic Conditions	109
6.2	INTRODUCTION TO CAMPUS TEST SITE	111
6.2.1	Site Description	111
6.2.2	Geology and Hydrogeology	112
6.2.2.1	Regional Geology and Hydrogeology	112
6.2.2.2	Local Geology	112
6.2.2.3	Local Hydrogeology	113
6.2.3	Climatic Conditions	114
6.3	NON-INVASIVE TECHNOLOGIES	114
6.3.1	General Assessment of Test Site 1	115
6.3.1.1	Gasworks Plant	115
6.3.1.2	The Electroplating Workshop	117
6.3.1.3	Types of Chemicals	118
6.3.1.4	Assessment of Site Operations	119
6.3.2	Hydrocensus	120
6.3.2.1	Hydrogeological Findings	121
6.3.2.2	Inorganic Results	121
6.3.2.3	Organic Results	122
6.3.3	Direct Observations	123
6.3.3.1	UV Analysis	124
6.3.3.2	Sudan IV Dye Shake Test	124
6.3.3.3	Findings from Direct Observation	125
6.3.4	Soil Gas Surveys	125
6.3.4.1	Results of Soil Gas Survey	126
6.3.5	Surface and Airborne Geophysics	130
6.3.5.1	Airborne Geophysics	130
6.3.5.2	Surface Geophysics	130
6.4	INVASIVE TECHNIQUES	131
6.4.1	Test Pits	131

6.4.1.1	Geological Findings	132
6.4.1.2	Chemical Results.....	133
6.4.2	<i>Drilling</i>	137
6.4.2.1	Percussion Drilling.....	137
6.4.2.2	Auger Drilling	138
6.4.2.3	Core Drilling	139
6.4.2.4	Borehole and Piezometer Construction	140
6.4.2.5	Precautions during Drilling	142
6.4.3	<i>Soil Sampling</i>	143
6.4.3.1	Mineralogy	143
6.4.3.2	Organic Chemical Results.....	143
6.4.3.3	Visual and Enhanced Visual Observations.....	145
6.4.3.4	Vapour Analyses	145
6.4.4	<i>Water sampling</i>	146
6.4.4.1	Inorganic Parameters.....	147
6.4.4.2	Organic Parameters	150
6.4.5	<i>Geochemical Borehole Logging</i>	151
6.4.5.1	EC – Logging	151
6.4.5.2	Interface Probe	152
6.4.5.3	Multi-parameter Probe	153
6.4.6	<i>Borehole Geophysics</i>	153
6.4.6.1	One-arm Caliper.....	154
6.4.6.2	Natural Gamma	155
6.4.6.3	Spontaneous Potential (SP).....	155
6.4.6.4	Resistivity Probe	156
6.4.6.5	Full Wave Sonic (FWS).....	157
6.4.6.6	Neutron-neutron Probe.....	158
6.4.7	<i>Aquifer Tests</i>	159
6.4.7.1	Slug Test.....	159
6.4.7.2	Pumping Tests	160
6.4.7.3	Diagnostic plots.....	161
6.4.8	<i>Tracer Tests</i>	163
6.5	EFFECTIVE MATRIX DIFFUSION COEFFICIENT ESTIMATION.....	163
6.5.1	<i>Introduction</i>	163
6.5.2	<i>Assumptions and Methodology</i>	165
6.5.3	<i>Data Analysis</i>	169
6.5.4	<i>Formation Factor</i>	172
6.5.5	<i>Mass Flux</i>	174
6.6	EFFECTIVE POROSITY ESTIMATION	175
6.6.1	<i>Introduction</i>	175
6.6.2	<i>Objective</i>	175
6.6.3	<i>Assumptions</i>	176
6.6.4	<i>Methodology</i>	176
6.6.5	<i>Data Analysis</i>	180
6.6.6	<i>Limitation</i>	180
6.7	PARTITIONING INTERWELL TRACER TEST (PITT)	182
6.7.1	<i>Introduction</i>	182
6.7.2	<i>Objective</i>	183
6.7.3	<i>Methodology</i>	183
6.7.3.1	Evaluation of the Natural Organic Carbon of the Sand.....	184
6.7.3.2	Controlled Release of TCE	186
6.7.4	<i>PITT Analysis</i>	188
6.7.4.1	Conclusion.....	189
6.8	CONCEPTUAL MODEL OF TEST SITE 1	190
6.8.1	<i>Site Geology</i>	190
6.8.1.1	Unconsolidated Lithology	191
6.8.1.2	Bedrock Geology	194
6.8.2	<i>Fracture Networks</i>	195
6.8.2.1	Fractures due to Weathering	195
6.8.2.2	Fractures of Stress or Tectonic Origin	197
6.8.2.3	Calcite Enclaves	198
6.8.2.4	Calcite Veins	199
6.8.2.5	Slickensides.....	200
6.8.3	<i>Summary of the Fracture Network</i>	201

6.8.4	<i>Hydrogeology</i>	202
6.8.4.1	Water Level	202
6.8.4.2	Hydrogeological Conceptual Model	205
6.8.5	<i>Conceptual Model of DNAPL Phase Migration</i>	205
6.8.6	<i>Conceptual Model of the Dissolved Plume</i>	206
6.9	FRACTURE CHARACTERISATION IN THE CAMPUS TEST SITE	207
6.9.1	<i>Hydraulic and Transport Parameters of the Fracture</i>	207
6.9.1.1	Hydraulic parameters	208
6.9.1.2	Transport Parameters	211
6.9.2	<i>Fracture Connectivity</i>	211
6.9.2.1	Borehole Spacing and Connectivity	213
6.9.2.2	Borehole Depth and Connectivity	213
6.9.2.3	Estimated Fracture Connectivity	214
6.9.3	<i>Apparent Fracture Aperture</i>	218
6.9.3.1	Borehole-video Cameras	218
6.9.3.2	Apparent Aperture	220
6.9.4	<i>Fracture Orientation (Dip, Strike and Depth)</i>	221
6.9.4.1	Depth of the fracture	221
6.9.4.2	Dip and Strike of the Fracture	223
7	PROPOSED METHODOLOGY FOR SOUTH AFRICAN CONDITIONS	226
7.1	NON-INVASIVE CHARACTERISATION METHODOLOGIES	226
7.1.1	<i>General Site Assessment</i>	227
7.1.1.1	Types of Chemicals	227
7.1.1.2	Site Operations	227
7.1.1.3	Assessment of Potential DNAPL Migration	228
7.1.2	<i>Arial Photo and Map Interpretations</i>	229
7.1.3	<i>Surface and Airborne Geophysics</i>	229
7.1.4	<i>Initial Site Conceptual Model</i>	230
7.2	INVASIVE METHODS	231
7.2.1	<i>Visual and Visual-Enhanced Examination of Soil/Rock Samples</i>	232
7.2.2	<i>Test Pits</i>	233
7.2.3	<i>Drilling</i>	235
7.2.3.1	Drilling Techniques	236
7.2.3.2	Core Drilling	238
7.2.3.3	Borehole Construction	239
7.2.3.4	Compatibility of Construction Materials	240
7.2.4	<i>Soil Gas Surveys</i>	241
7.2.4.1	Vapour analyses of soil samples	242
7.2.5	<i>Soil samples</i>	243
7.2.5.1	Sample collection	243
7.2.6	<i>Borehole logging</i>	244
7.2.6.1	Geophysical Borehole Logging	244
7.2.6.2	Flow logging	247
7.2.6.3	Video logging	248
7.2.6.4	Geochemical logging	248
7.2.6.5	Interface meter	249
7.2.7	<i>Pumping Tests</i>	250
7.2.8	<i>Tracer Tests</i>	250
7.2.9	<i>Partitioning Interwell Tracer Tests (PITTs)</i>	251
7.3	SITE CONCEPTUAL MODEL	252
7.3.1	<i>Geology and Hydrogeology</i>	252
7.3.2	<i>Characterisation of DNAPL Source Zone and Dissolved Plume</i>	253
7.3.3	<i>Flowchart for DNAPL Site Characterisation</i>	253
8	CONCLUSIONS AND RECOMMENDATIONS	256
8.1	CONCLUSIONS	256
8.2	RECOMMENDATIONS	263
	REFERENCES	265
	ABSTRACT	279
	OPSOMMING	281

TABLE OF FIGURES

Figure 2-1: Obtuse contact angle when DNAPL is the non-wetting fluid.....	12
Figure 2-2: Acute contact angle when DNAPL is the wetting fluid.	12
Figure 2-3: Neutrally wetting fluids forming a contact angle of 90^0	13
Figure 2-4: Pore-scale interfaces between DNAPL and water in a porous medium (modified from Pankow and Cherry, 1996).	16
Figure 2-5: Capillary pressure-saturation relationship for two-fluid system (Cohen and Mercer, 1993).....	17
Figure 2-6: (a) water-NAPL relative permeability; (b) ternary diagram showing the relative permeability of NAPL as a function of phase saturation (Cohen and Mercer, 1993).....	19
Figure 2-7: Residual DNAPL in (a) unsaturated and (b) saturated porous media (Kueper <i>et al.</i> , 2003).	24
Figure 2-8: Typical maximum pool heights for the common DNAPLs, DNAPL perched above a variety of capillary barriers (Kueper <i>et al.</i> , 2003).....	26
Figure 2-9: Biotransformation of PCE and TCE (Weidermeier, 1998)	27
Figure 2-10: Structural formula of (a) TCE, (b) 1,1,1-TCA, and (c) PCE.....	34
Figure 2-11: Chemical structure of PCBs.....	34
Figure 2-12: Specific gravity versus absolute viscosity of some DNAPLs. DNAPL mobility increases with an increasing density:viscosity ratio (Cohen and Mercer, 1993).....	40
Figure 2-13: Annual production of organic compounds in South Africa (Hohne, 2004).	42
Figure 2-14: Distributions of various industrial and mining activities that potentially produce DNAPLs (after Hohne, 2004).	43
Figure 3-1: Conceptual model of a simplified vadose zone contaminated with DNAPL. (a) No vapour plume (wet and cold environment or low vapour pressure); (b) vapour plume with the effects of sorption (to aquifer material) and diffusion of the gaseous phase to the matrix porosity. (modified from Cohen and Mercer, 1993).....	52
Figure 3-2: DNAPL migration pathways in unsaturated sands. DNAPL presence shows red due to SUDAN IV dye. Bedding dips 30° below horizontal (Poulsen and Kueper, 1992).	53
Figure 3-3: Conceptual model of a simplified saturated porous media contaminated with DNAPL (after Cohen and Mercer, 1993).	54
Figure 3-4: DNAPL movement in the saturated zone following the slope of the geology, opposite to the groundwater flow (adopted from Shapiro (2006)).	55
Figure 3-5: Fractured migration in fractured aquifer (Mackay and Cherry, 1989)	56
Figure 3-6: Forces acting on a DNAPL/water interface.	56
Figure 3-7: Pool height vs. fracture aperture invaded provided in Table 3-1.....	59
Figure 3-8: Pool of TCE in bedrock depression. TCE can enter progressively smaller aperture fractures with depth as a result of an increase in capillary pressure brought about by vertical accumulations (Pankow and Cherry, 1996).	60
Figure 3-9: Time taken for a first arrival of DNAPL to move 5 m versus fracture aperture (Pankow and Cherry, 1996).....	61

Figure 3-10: Mobilisation of DNAPL pool due to pumping (Pankow and Cherry, 1996).	62
Figure 3-11: a) DNAPL migration pathways for a low interfacial tension system; b) DNAPL migration pathways for a light interfacial tension system (Pankow and Cherry, 1996).	63
Figure 3-12: DNAPLs migrate preferentially through big aperture fractures and continue to enter small fractures only when their capillary pressure exceeds the entry pressure.	64
Figure 3-13: Elevation of DNAPL in boreholes located in a fracture network (after Pankow and Cherry, 1996).	65
Figure 3-14: A hypothetical conceptual model of DNAPL migration in an aquifer system composed of different layers of different matrix and fracture porosities (www.dnapl.group.shef.ac.uk).	66
Figure 3-15: Conceptual model for a DNAPL in a fracture disappearing into the matrix porosity due to diffusion (after Pankow and Cherry, 1996).	67
Figure 3-16: Dissolved mass transport in fractured clay (Harrison <i>et al.</i> , 1992).	69
Figure 4-1: Simplified geology of the Karoo Supergroup.	71
Figure 4-2: A granite sample with fracture but no significant void porosity. Flow is entirely controlled by the fracture orientation and properties of the DNAPL.	74
Figure 4-3: A dolerite dyke from the Karoo Supergroup with noticeable weathering along the contact zone with the host rock.	75
Figure 4-4: A dolerite sill from the Karoo Supergroup with horizontal and vertical fractures making it an unreliable barrier to DNAPL migration, both horizontally and vertically.	76
Figure 4-5: Conceptual model of DNAPL migrating through dolerite sill.	76
Figure 4-6: A hypothetical model of DNAPL migration in a karst aquifer.	78
Figure 4-7: Fractured-porous rocks, with fractures of varying orientations typical in the Karoo aquifer.	79
Figure 4-8: Geohydrological conceptual model of the various rocks and structural features in a dyke/sill intersection zone, Queenstown (after Vandoolaeghe, 1980).	80
Figure 4-9: A conceptual model of DNAPL transport process in the dyke/sill intersection zone, Queenstown.	81
Figure 5-1: Components of site conceptual model (after EPA, 1993; AFCEE, 2000)	90
Figure 5-2: Borehole GB3, showing that the depth of interest for characterisation could always be greater than believed.	100
Figure 6-1: Aerial photo of Test Site 1 (coordinates are not provided to keep the confidentiality of site location).	104
Figure 6-2: The Karoo Supergroup (after Tankard <i>et al.</i> , 1982).	105
Figure 6-3: Schematic distribution of major Late Tertiary - Early Quaternary fluvial terrace and pedocrete (excluding gypcrete) deposits of the Main Karoo Basin (From Woodford <i>et al.</i> , 2002).	106
Figure 6-4: Average climatic parameters of Bloemfontein (from http://www.weathersa.co.za).	109

Figure 6-5: Annual rainfall records for Bloemfontein Weather Station (1910 - 2003)	110
Figure 6-6: Borehole distribution at the Campus Test Site (coordinate in Transverse Mercator with central meridian of Lo27, measured in metres)	111
Figure 6-7: Geological profiles of 24 percussion boreholes drilled on the Campus Test Site (from Botha <i>et al.</i> , 1998)	112
Figure 6-8: Geological profiles of the two inclined core holes drilled on the Campus Test Site (from Botha <i>et al.</i> , 1998)	113
Figure 6-9: Schematic diagram of the lithology and aquifers present at the CTS (modified from Botha <i>et al.</i> , 1998)	114
Figure 6-10: Aerial photo of target areas at Test Site 1	116
Figure 6-11: On-going spillage from tar loading	116
Figure 6-12: Lime treating and wastewater holding facility	117
Figure 6-13: Topographical map of Test Site 1 (in pink) and the hydrocensus boreholes	120
Figure 6-14: STIFF diagram of the hydrocensus boreholes	122
Figure 6-15: UV fluorescence of three samples with values of 0, 1 and 2 respectively	124
Figure 6-16: Detection of LNAPL droplet using the water-soil shake test with Sudan IV dye	125
Figure 6-17: Drill holes where PID measurements were taken	126
Figure 6-18: VOC distribution measured by the PID	127
Figure 6-19: TPH distribution measured by the PID	128
Figure 6-20: Methane distribution measured by the PID	128
Figure 6-21: O ₂ distribution measured by the PID	129
Figure 6-22: CO ₂ distribution measured by the PID	129
Figure 6-23: A test pit 20 m south of the gasworks	131
Figure 6-24: The distribution of test pits on the site	132
Figure 6-25: (A) Soil profile, and (B) visual observation of dark coloured NAPL on clay fracture plane from a test pit	133
Figure 6-26: Intensity of UV fluorescence in the gasworks area	134
Figure 6-27: Position of boreholes (circles), piezometers and core holes (squares) on the site (due to crowding, only few boreholes are labelled)	137
Figure 6-28: Auger drilling: (A) Hollow-stems stuck in the clay layer during auger drilling, (B) <i>In-situ</i> soil samples from direct push drilling	138
Figure 6-29: Solid-stem auger drilling on the site	139
Figure 6-30: Drilling of Core hole GC1	140
Figure 6-31: Summarised geologic profile of Core Holes EC1 and GC1	140
Figure 6-32: Construction of the shallow boreholes	141
Figure 6-33: Construction of the deep boreholes	141
Figure 6-34: Piezometer drilled by solid-stem auger	142

Figure 6-35: Hand-held PID reading VOCs of soil gas from a plastic container.....	146
Figure 6-36: Durov diagram of the test site boreholes	147
Figure 6-37: STIFF diagrams of the test site boreholes.	148
Figure 6-38: EC profile for Borehole EB1.....	148
Figure 6-39: A comparison of water quality in EB1 in the unconsolidated section (EB1-s) and bedrock (EB1-d).....	149
Figure 6-40: EC (mS/m) distribution of boreholes (circles) and piezometers (squares) on test site.....	149
Figure 6-41: Piper diagram of the hydrocensus samples as compared to the Test Site 1.	150
Figure 6-42: Geochemical logging of Borehole FB1.	153
Figure 6-43: Comparison between drilling borehole log and caliper log in Borehole GB9.....	155
Figure 6-44: Gamma, SP and resistivity logs in Borehole EB1.	156
Figure 6-45: Full wave sonic profile of Borehole EB1.	158
Figure 6-46: Neutron-neutron log of Borehole FB1 showing an anomaly at the water level.	159
Figure 6-47: Log-log plot of tests conducted in GB4, showing a slope of 0.5.	162
Figure 6-48: Linear drawdown versus square root of time plot, proving the early linear flow.	162
Figure 6-49: EC versus depth in Borehole UO5 at the start of the <i>in-situ</i> matrix diffusion experiment on 7 February 2005.....	166
Figure 6-50: EC measurements in Borehole UO5 at depths of 27 and 36 m following the purging.	168
Figure 6-51: Comparison of EC at depths of 27 and 26 m and model results.....	169
Figure 6-52: Model results of EC versus time for different values of the matrix porosity, keeping the effective diffusion coefficient constant.	171
Figure 6-53: Estimates of the effective matrix diffusion coefficient for the matrix porosity of 0.03.	171
Figure 6-54: Estimates of the effective matrix diffusion coefficient for the matrix porosity of 0.05.	172
Figure 6-55: Point dilution test set-up.	177
Figure 6-56: EC vs. time in Borehole GB5 at depths of 16 and 17 m.....	179
Figure 6-57: Comparison of EC curves at early and late times.	181
Figure 6-58: Widening of curves in position of high flow anomaly at late stage in Borehole GB2.	181
Figure 6-59: Simulated concentration curves using MT3DMS showing concentration curves at different time stages.	182
Figure 6-60: Column used for PITT experiment.....	184
Figure 6-61: Normalised EC and benzene concentration curves before the sand was heated (lagging of benzene).	185
Figure 6-62: Normalised EC and benzene concentration curves after the sand was heated (no lagging of benzene).	186

Figure 6-63: Tracer concentration curves from the first experiment.....	189
Figure 6-64: Tracer concentration curves from the second experiment.....	189
Figure 6-65: Expected arrival times of 2E1H and 2-octanol.....	190
Figure 6-66: Geologic logs of Boreholes GB7 and GB8.....	191
Figure 6-67: NAPL nodules in the clay layer of Borehole GB2.....	192
Figure 6-68: Calcrete at a depth of 10 m in Borehole GB2.	193
Figure 6-69: A representative geologic profile of all the deep boreholes.	194
Figure 6-70: Highly weathered shale below the unconsolidated section in EC1.....	195
Figure 6-71: A closer look of the weathered shale in EC1.	196
Figure 6-72: Small-aperture horizontal fractures with weathered zone indicative of flow paths.....	197
Figure 6-73: Big-aperture vertical and horizontal fractures at various locations.	198
Figure 6-74: Enclaves within the mudstone layer providing preferential flow paths through their boundaries.	199
Figure 6-75: Calcite vein filling fractures to different degrees.	200
Figure 6-76: Slickensides showing shiny and grooved surface.....	201
Figure 6-77: Contour map of groundwater elevation.....	203
Figure 6-78: Ground surface versus water-level elevation.....	204
Figure 6-79: Time series of water level in the different boreholes.....	204
Figure 6-80: Conceptual model of Test Site 1.....	205
Figure 6-81: DNAPL phase movement in the developed conceptual model.....	206
Figure 6-82: Conceptual model of vapour, dissolved and free DNAPL phases in Test Site 1.....	207
Figure 6-83: Distribution of the DNAPL boreholes (circles) and core holes (squares) in the Campus Test Site.....	208
Figure 6-84: Estimation of fracture transmissivity using Cooper-Jacob 2 method from drawdown data after 5 minutes (UP16 was abstracted, while D4, D2 and D3 were used for monitoring).	209
Figure 6-85: Estimation of fracture transmissivity using Cooper-Jacob 2 method from drawdown data after 2 minutes (UP16 was abstracted, while UO29, UO30 and D1 were used for monitoring).....	210
Figure 6-86: Estimation of fracture transmissivity using Cooper-Jacob 2 method from drawdown data after 2 minutes (UO23 was abstracted, while D3, D2 and D4 were used for monitoring).	211
Figure 6-87: Water elevation versus time when UP16 was pumped.....	212
Figure 6-88: Drawdown versus distance of the boreholes from UP16 after 6 hours of pumping.	213
Figure 6-89: Drawdown versus depth of the boreholes after 6 hours of pumping UP16.....	214
Figure 6-90: A reasonable estimate of the fracture (shaded) connectivity.	217
Figure 6-91: A conservative estimate of the fracture (shaded) connectivity.....	217
Figure 6-92: An exaggerated estimation of the fracture (shaded) connectivity.	218

Figure 6-93: Video camera used to log the Campus Test Site boreholes. A compass was attached to the base of the televiewer to position the direction of the fracture apertures.....	219
Figure 6-94: Video camera of Borehole D3 with accurate depth measurement and aperture of the fracture.	219
Figure 6-95: Apparent fracture aperture in Borehole UO23.	220
Figure 6-96: Apparent fracture aperture in Borehole D2.	220
Figure 6-97: Apparent fracture aperture in Borehole D3.	221
Figure 6-98: Caliper, FWS and NN logs of Borehole UO23.	222
Figure 6-99: Geologic log and EC profile of Borehole UO23.	222
Figure 6-100: Drawdown versus time graph of UO23.	223
Figure 6-101: Relationship between true dip and apparent dip.....	224
Figure 6-102: A simplified conceptual model of the fracture in the Campus Test Site.	225
Figure 7-1: Example of excavated container with organic contaminants in a test pit at Test Site 1.....	234
Figure 7-2: Caking of sand and clay slurry during auger drilling.	238
Figure 7-3: Geophysical logging of boreholes at research site - Test Site 1.	245
Figure 7-4: Flowchart for DNAPL site characterisation.	255

LIST OF TABLES

Table 1-1: List of activities that could be sources for DNAPL release to the groundwater.....	5
Table 2-1: Results of contact angle experiments using DNAPLs (from Cohen and Mercer, 1993).....	13
Table 2-2: 1986 U.S. production of chlorinated organic solvents (after Pankow and Cherry, 1996).....	29
Table 2-3: Common DNAPL usage (from Cohen and Mecer, 1993; Pankow and Cherry, 1996).....	30
Table 2-4: Organic compounds that are DNAPLs.....	31
Table 2-5: Chemical and Physical Properties of Chlorinated Hydrocarbons.....	33
Table 2-6: Composition (percent) and selected properties of various Aroclors excluding carrier fluids (adapted from Cohen and Mercer, 1993).....	35
Table 2-7: Composition of creosote and coal tar, solubility of pure coal tar compounds, proposed RCRA groundwater action levels, and prevalence in groundwater at wood-treating sites (Cohen and Mercer, 1993).....	37
Table 2-8: Case studies of mainly organic groundwater contamination related to organic compounds (and DNAPL) in South Africa (modified from Usher <i>et al.</i> , 2004).....	46
Table 2-9: Case studies of agricultural contamination (modified from Usher <i>et al.</i> , 2004).....	49
Table 2-10: Contaminants associated with organic pollution sources from urban-based agriculture (Usher <i>et al.</i> , 2004).....	50
Table 3-1: Minimum pool height required for DNAPLs to enter a fracture (Kueper <i>et al.</i> , 2003).....	58
Table 4-1: Simplified flow mechanisms in South African aquifers (modified from Pretorius, 2007; Pietersen, 2004).....	72
Table 5-1: Single-component concentrations potentially indicative of NAPL (CLU-IN, 2000).....	96
Table 5-2: Dissolved concentration typically observed in multi-component DNAPL zones (CLU-IN, 2000).....	97
Table 5-3: Bedrock properties to determine during site investigations (Kueper <i>et al.</i> , 2003).....	99
Table 6-1: Climate data of Bloemfontein based on monthly averages of 30 years (1961 - 1990) (from Weather SA).....	110
Table 6-2: Preliminary list of potential contaminants, depending on the activities at Test Site 1.....	118
Table 6-3: List of chemicals used in the electroplating workshop.....	119
Table 6-4: Organic chemical results of the hydrocensus boreholes.....	123
Table 6-5: Comparison between laboratory and UV analysis.....	134
Table 6-6: Organic contaminants composition of the test pit soil, coal tar and sludge samples (mg/Kg).....	136

Table 6-7: Organic contaminant composition of the soil samples from boreholes and piezometers (ppm).	144
Table 6-8: Laboratory determined f_{oc} for selected soil samples.	145
Table 6-9: UV-value of soil samples from Boreholes GB1 and GB2.	145
Table 6-10: Average VOC values in auger-drilled holes.	146
Table 6-11: Boreholes that tested positive for chlorinated solvents.	151
Table 6-12: Slug test results.	160
Table 6-13: EC measurements in Borehole UO5 following the purging.	167
Table 6-14: Parameters assigned for model results.	170
Table 6-15: Estimates of the formation factor for the estimated effective diffusion coefficients at 27 m for various values of the matrix porosity.	173
Table 6-16: Estimates of the formation factor for estimated effective diffusion coefficients at 36 m for various values of the matrix porosity.	174
Table 6-17: Parameter-values used to estimate the effective porosity in Borehole GB5.	180
Table 6-18: Estimated effective porosity in Borehole GB5.	180
Table 6-19: Partitioning coefficient of the alcohols with respect to TCE and water.	186
Table 6-20: Parameters of the first PITT experiment.	187
Table 6-21: Parameters of the second PITT experiment.	188
Table 6-22: Depth and elevation of the contact zone (main water strike) between the sandy gravel and shale.	196
Table 6-23: Water strikes, anomalies and their elevations.	202
Table 6-24: Summary of transport parameters estimated from the tracer tests.	211
Table 6-25: List of boreholes that intersect and do not intersect the fracture.	216
Table 6-26: Borehole coordinates and fracture depth (from the collar height) and elevation (from mean annual sea level) at the Campus Test Site.	223
Table 6-27: Dip and dip direction of the fracture in the DNAPL Boreholes.	225
Table 7-1: Factors facilitating or inhibiting DNAPL penetration (adapted from Pankow and Cherry, 1996).	228
Table 7-2: Contaminant characteristics to establish during site investigations (Kueper <i>et. al.</i> , 2003).	231
Table 7-3: Well (borehole) construction design and the effect it has on DNAPL thickness in borehole (adapted from Cohen and Mercer, 1993).	241
Table 7-4: Geophysical borehole logging tools and their fields of application (adapted from Woodford and Chevalier, 2000).	247
Table 8-1: Applicability of the various characterisation techniques for different sites.	262

1 Introduction

Groundwater is an important drinking water supply source to many communities in South Africa. It contributes about 14% to the total water use in South Africa (Pietersen, 2005), which is only 16% of the total harvest potential for the country, estimated to be at $19 \times 10^9 \text{ m}^3$ a year. It is likely that groundwater use will increase for domestic, industrial or irrigational purposes. For those who rely on it, it is critical that their groundwater be unpolluted and relatively free of undesirable contaminants.

Unfortunately, not all types of groundwater are fit for use. Due to the belief that the soil and sediment layers above an aquifer acted as a barrier to pollutants, a significant amount of contamination has been released into the soil and groundwater. One such type of pollutants are DNAPLs which are discussed in the next section.

No previous research on DNAPLs has been done in South Africa, and this thesis aims to address this issue in the context of South African aquifers, regulatory conditions, budgetary constraints and available technologies. The thesis is based on three-years of research on DNAPLs in South African aquifers to address these issues.

1.1 Introduction to DNAPLs

Groundwater contaminants could be of natural or unnatural origin and include microbial, radioactive, inorganic and organic compounds. A very problematic class of contaminants is known as DNAPLs (dense non-aqueous-phase liquids), which comprise a group of organic contaminants with similar physical properties. DNAPLs are single or multi-component liquid compounds that are denser than water and relatively insoluble in water. Unlike DNAPLs, LNAPLs (light non-aqueous-phase liquids), such as gasoline and heating oil, are less dense than water and float on top when they contaminate groundwater. Both DNAPLs and LNAPLs are grouped under NAPLs (non-aqueous-phase liquids) that are immiscible with water and have very low solubility. For an organic contaminant (or mixture of contaminants) to be considered as a DNAPL, it must have a fluid density greater than 1.01 g/cm^3 , a solubility in water of less than 2% (or 20000 mg/l) and a vapour pressure of less than 300 torr (40 kPa) (Pankow and Cherry, 1996). However, in addition to the physical properties, toxicity of the chemical to the environment should also be considered in classifying DNAPL contaminants.

Many of the DNAPLs could be assigned to one of four groups, largely based on their manufacturing origins or end use:

- Chlorinated solvents,
 - trichloroethene – TCE,

- tetrachloroethene – PCE and
- trichloroethane – TCA).
- Creosote and coal tars,
- Polychlorinated biphenyls (PCBs), and
- Miscellaneous or mixed DNAPLs

It is also common to find metals (such as mercury), certain types of crude oil, and hexavalent chromium (ITRC, 2003) as DNAPL components dissolved in the chlorinated solvents. The physical properties of a single DNAPL are different from when combined with other DNAPL compounds. Compounds typically found as DNAPLs can also be found in LNAPLs if these miscible fluids have been co-mingled in the subsurface.

DNAPLs are toxic to various life forms. They can pose serious health risks by contaminating drinking water and impacting on indoor air quality in areas of high water table fluctuations. Exposure from these chemicals can occur through direct ingestion of contaminated groundwater, and/or inhalation of toxic vapours (Cheremisinoff, 1990), as contaminated groundwater permeates into the basements of buildings. DNAPL vapour intrusion is a new but rapidly developing field of science, in which the EPA is actively searching policing options and cultivating an understanding of the complex exposure pathways. Cohen and Mercer (1993) state that the potential for seriously harmful long-term contamination of groundwater by DNAPL chemicals is exacerbated due to their limited solubility (but much higher than drinking water limits), and their significant migration potential in soil gas, groundwater, and/or as a separate phase. Further complicating matters are organisms present in soil and groundwater that biodegrade these chemicals, changing the properties for remediation of impacted soil and groundwater.

Due to their low solubility, DNAPLs in the subsurface may become a source of dissolved phase groundwater contamination for many years. Their immiscibility allows them to preferentially remain in a separate non-aqueous phase, dissolving slowly over time. the transport of dissolved DNAPLs is influenced by groundwater advection, including the effects of mechanical dispersion, molecular diffusion, chemical partitioning between groundwater and porous media, and other chemical reactions (e.g., degradation). However, for the DNAPL free-phase (undissolved immiscible phase), since the specific gravity is greater than one, they tend to migrate downward in groundwater under the influence of gravity, capillary effects and stratigraphy, and to a lesser extent by groundwater flow. Groundwater flow direction may play some role, especially for DNAPLs with a specific gravity close to 1. Therefore it is common for DNAPLs to be located in locations other than those expected by determining advective transport, making them difficult to characterise.

As is common in some South African aquifers, the thickness and type of unconsolidated materials may prevent DNAPL releases from reaching bedrock. However, once the DNAPL phase reaches the bedrock, any fracture or solution channel may become a pathway for DNAPL migration, while uncontaminated fractures or solution channels can be found in very close proximity to the contaminated pathway, if not interconnected or with small aperture for DNAPLs to enter. Once in a fracture or solution channel, the DNAPL can migrate significantly longer distances than in porous media, as the open spaces are usually larger and more continuous than those found in the matrix. This makes them less likely to be trapped as residual in small ganglia. However, residue can be formed in irregularly shaped or dead-end fractures.

1.2 Historical Issues

Particularly since 1940, DNAPLs have been used in a wide range of manufacturing industries. As a result of widespread production, transportation, use, and unchecked disposal, there are numerous DNAPL contamination sites across the world. The severity and scale of groundwater contamination by these compounds went largely unrecognised until the late 1970s (Schwille, 1988).

Until relatively recently, the significance of the presence of DNAPL in groundwater was not well understood, or was ignored at most sites. This was particularly true for fractured sites (Divine, 2003), where detection and accurate characterisation of the source and geology of an area is substantially more difficult than for inorganic and LNAPL-contaminated sites. The recent development of several promising characterisation and remediation technologies has increased the interest in DNAPL removal. The increase in DNAPL research in recent years is exemplified by the fact that searching for “DNAPL” in Google.com in July 2004 would generate only 4000 matches, while this increased to 185,000 by May 2007.

DNAPLs are characterised by their lack of noticeable taste, odour and higher density relative to water, making them extremely difficult to detect and monitor. In contrast, petroleum spills float on top of the water table and are usually volatile, with a distinctive taste and odour. Although appropriate analytical methods actively existed since the mid 1950s, there was no drive to investigate groundwater for the presence of DNAPLs. Scientists concentrated their efforts on alkyl benzene sulphonate (ABS) detergents and organic pesticides such as DDT and aldrin (Rivett *et al.*, 1990). The surreptitious nature of DNAPLs caused them to be disregarded as groundwater contaminants until much later.

The first significant recognition in the research community of the potential DNAPL character of chlorinated solvents in groundwater is attributable to Schwille. As a result of two case studies in West Germany during the late 1960s and early 1970s

involving chlorinated solvents, he developed conceptual models and conducted physical model studies on the behaviours of these compounds. Schwillie studied chlorinated solvent movements into unsaturated and saturated sand and fractured media. The detailed evolution of knowledge regarding the threat posed by DNAPLs to groundwater is given in provided by Pankow and Cherry (1996) and can be summarised as follows:

- **Prior to mid-1960s:** It was generally assumed that groundwater quality was largely unaffected by man. The subsurface was believed to be particularly capable of absorbing organic contaminants. In one of the earliest textbooks on groundwater, Thomas (1951) stated that “*organic wastes are the easiest to eliminate (through the) natural processes of separation, filtration, dilution, oxidation, and chemical reaction*”, and that if “*powerful influences of protection or purification were not at work in nature, it would be almost impossible to find unpolluted groundwater anywhere.*” Thus, in the nascent field of contaminant hydrogeology, organic contaminants were receiving very little attention. The contaminant that received the most attention in the early decades of the field was salt, mostly from seawater intrusion.
- **Mid-1960s to 1972:** toxic organic compounds are detected in some drinking water supplies.
- **1972 to 1975:** first chlorinated VOCs found in drinking water; trihalomethanes.
- **1976 to 1979:** widespread testing for THMs in drinking water reveals the presence of other VOCs, coming to the conclusion that many important aquifers are contaminated with chlorinated solvents.
- **1980 to 1981:** The evidence that chlorinated solvents are widespread groundwater contaminants becomes overwhelming.
- **1982 to late 1980s:** The issue of DNAPLs in groundwater had evolved from the stage wherein the problem was being discovered and understood, to a stage wherein the goal was to have contamination contained, remediated, and prevented. However, the world was entirely unaware of two facts: 1) that DNAPL-phase solvent could be present in large amounts in the subsurface at sites contaminated with chlorinated solvents; and 2) that such a presence posed many difficult problems in remediating such sites.
- **Late 1980s to the present:** Efforts to characterise DNAPLs especially in fractured aquifers and remediation efforts with proper conceptual model development approach. This is where this thesis aims to play a role by putting this into context of South African fractured rock aquifers.

1.2.1 Groundwater Contamination by DNAPLs

The late 1980s marked a huge influx of groundwater contamination reports (Rivett *et al.*, 1990). The main reason for the high incidence rate and sheer magnitude of groundwater contamination by DNAPLs such as chlorinated solvents was the way in which the chemicals were handled and disposed of. The standard disposal method involved the tipping of solvent onto dry ground or ash; justification of this method was derived from the assumption that the high volatility of the various solvents caused them to completely volatilise to the atmosphere, when in actual fact gaseous diffusion and infiltration caused the DNAPLs to migrate into the subsurface.

It is clear that, if more had been known of the behaviour of DNAPLs in the subsurface and their potential to contaminate groundwater, it is very likely that much of the contamination of groundwater would have been averted. Several factors contributed to this knowledge deficit. For example, the lack of relevant environmental studies into the behaviour of DNAPLs in the ground delayed the implementation of better practices for solvent disposal. Table 1-1 lists the major activities that could be sources of DNAPL releases to the groundwater.

Table 1-1: List of activities that could be sources for DNAPL release to the groundwater.

DNAPL release	Mechanism of groundwater contamination
Storage	Leakage of solvent from cracks in tanks may easily go unnoticed. Poor facilities for the storage of corroding equipment may liberate solvents.
Disposal	The belief that DNAPLs' high volatility would result in their dispersal to the atmosphere resulted in the common disposal practice of simply pouring the waste solvents onto waste ground.
Transit	Spillage during highway accidents and derailments. Malfunctioning of transporting equipments. Leaking, buried chemical distribution pipelines.
Handling	The misguided practice of washing down large machines and oily floors would lead to penetration of the subsurface through cracks in the walls and floor.

1.2.2 Scope of the Problem in South Africa

South Africa has laws that protect groundwater resources, but the public awareness of the laws and health effects of toxic pollutants is not widespread. At the same time, due to areas of prospective population growth, it is likely that groundwater demand will increase. The limited published data on DNAPL contamination from solvent mixtures, available in South Africa, indicate:

- Usher *et al.* (2004): In the major urban areas of South Africa, 36 out of a possible 50 sources are DNAPL contamination.

- Usher *et al.* (2004): In major urban areas, 64 out of 110 contaminants listed in the national prioritization list could be considered as DNAPL contaminants.
- Morris *et al.* (2000): Solvent contamination from a metal plating facility in Cape Town, with measured levels of TCE ranging between 6 µg/l to 4 089 µg/l.
- Palmer & Cameron-Clarke (2000): Total chlorinated hydrocarbon concentrations of 100 000 ppb at a depth of 30 metres below surface was measured at an industrial hazardous waste site in Durban.

Although these reports indicate that some sites may be potentially contaminated and some highly contaminated, the incidents could be non-representative of the actual contamination from the huge number of organic chemicals used for various industrial purposes. In addition, 90% of South African aquifers are fractured, making DNAPL characterisation an extremely important part of evaluating the quality of the water and assessing remedial issues.

The challenge therefore lies in developing appropriate site characterisation methods for South Africa, bearing in mind the limited research done locally on the topic, the types of aquifers encountered, the budgetary and regulatory constraints and the availability of the technology in this country.

1.3 DNAPL Characterisation Challenge in Fractured Aquifers

The objective of a DNAPL site characterisation in an aquifer is to collect data sufficient to define the nature and extent of DNAPLs, in order to assess risk and select appropriate remedial measures. There are numerous consequences of a poorly investigated or inadequately characterised DNAPL site. Improperly conducted environmental site investigations at DNAPL sites can result in an inaccurate assessment of risk; and an inadequate remedial design basis can cause cross-contamination of aquifers, and expand the contaminated area. Moreover, inadequate characterisation of a DNAPL source zone can lead to the implementation of costly remedies in an ineffective manner (e.g., treating a much larger volume than needed with an expensive technology). Poor DNAPL site characterisation also dramatically increases the risk of ineffective remedial performance as a portion of the source may be left out and not be treated or controlled.

However, due to the physical properties of DNAPLs, it is difficult to adequately characterise the volume and extent of DNAPL releases to the soil and groundwater, and particularly finding and delineating multiple DNAPL source zones in fractured media. As stated these are the types of aquifers most likely to be encountered in South Africa, thus this characterisation merits further investigation. It may be fairly easy to characterise dissolved-phase contaminant plumes using conventional tools such as

monitoring wells. Free-phase DNAPLs follow fractures where their density, aperture and connectivity are some of the most difficult part of hydrogeology to characterise. DNAPLs have been shown to sink into fractures to depths of greater than 60 m (ITRC, 2003) and migrate great distances horizontally. Once in the fracture, they can diffuse into the primary porosity and effectively disappear, in part or entirely (Parker *et al.*, 1994; Shapiro, 2001).

Usually DNAPL sites are composed of various components which have a different physical property than the individual components. The physical properties and their nature of following fractures make DNAPL characterisation exceptionally challenging. The application of conventional tools and investigative strategies that is productive to characterise relatively homogeneous distribution of contaminants is not effective to detect the relatively unpredictable behaviour and heterogeneous distribution of the DNAPLs. Moreover, DNAPLs are commonly present in sufficient amounts to cause significant dissolved-phase contamination in the subsurface, but not enough to be readily mapped using standard subsurface investigation methods.

It is common for DNAPLs to exist as small ganglia that are disconnected from each other. These ganglia and small isolated lenses of DNAPLs are very difficult to discover using standard investigation techniques such as soil borings and monitoring wells because of their small size and distribution. It is easy to miss a discrete ganglia or a lense of DNAPL existing between boreholes spaced less than even a metre apart.

While they can be released as a chemical product (as manufactured and sold), DNAPLs are often discharged as spent solvents or wastes that contain appreciable fractions of other organic chemicals. These co-contaminants may represent a wide range of organic (halogenated and non-halogenated volatiles, and semi-volatile compounds such as waste grease and various oils, as well a stabilisers and rust inhibitors) and inorganic chemicals that are miscible with the DNAPL, and therefore migrate along with it in the subsurface. The other components can significantly influence the overall chemical and physical properties of the DNAPL and can both aid detection and complicate remediation (Dwarakanath *et al.*, 2002). These compounds can be found above and below the water table at sites where DNAPLs releases occur.

In summary, locating DNAPLs in fractured bedrock is complicated by a highly variable spatial distribution of the fractures and by the lack of resolution typical of most characterisation technologies. The more complex the fractures, the more difficult it is to characterise a DNAPL release. A site with a complicated fracture network will generally have a greater number of preferential pathways of varying size, as well as more confining layers to trap large and small amounts of DNAPLs. Characterising a DNAPL release can also be difficult even in formations that appear to be homogeneous. Column tests by Schwille (1988) and field tests by Poulsen and Kueper (1992) demonstrated the control on DNAPL migration by preferential flow pathways

in what appeared to be homogeneous materials. This is exacerbated in heavily heterogeneous fractured aquifers, making it even more difficult to determine the location of residual and potentially mobile DNAPLs.

1.4 Characterisation Approach

DNAPL site characterisation, especially in fractured aquifers, is an emerging science not only in South Africa but also in the developed world. Recognising the significance of DNAPL contamination has grown only in the past two decades (Schwille, 1988). Traditional site investigation techniques may be sufficient to delineate dissolved plume, but not to characterise free-phase DNAPLs. This is because complex fracture patterns can make it very difficult to delineate the subsurface DNAPLs that follow them. A standardised tool box cannot be descriptive of all DNAPL-contaminated sites, which is highly dependent on the geological set-up and site-specific DNAPL composition.

Knowledge of previous operations and waste disposal practices at a facility will provide insight and information about whether DNAPL may have been released, and whether it has become a source of groundwater contamination. Investigation of both the site geology, and the properties and distribution of the DNAPL is extremely important for successful fractured site characterisation (Pope and Wade, 1995). The DNAPL investigation should be based on a strong conceptual model and utilise a combination of investigation techniques that are best fitted to the site and chemicals of concern. They should be characterised using a flexible and iterative refinement of the conceptual model.

The characterisation toolbox may need to include strategies to either better locate the fractures based on a knowledge of DNAPL-specific fate and transport characteristics, or must include assumptions regarding the subsurface fracture distribution. An extensive fracture tracing will likely be expensive and probably not find all of the fractures at a site; therefore, DNAPL presence and distribution may need to be inferred. A fracture hunt in the Campus Test Site, a typical Karoo aquifer, showed that the connectivity and hydraulic property of a fracture network may change on a metre scale, and is extremely difficult to delineate.

1.5 Aim of Thesis

This research is sponsored by the Water Research Commission (WRC) of South Africa for the study of DNAPLs in South Africa. As discussed in subsequent sections, fractures are often the most important factors in the transport of DNAPLs in the subsurface, and therefore much of this thesis is focussed on characterising fractures properly in South African aquifers. There is no recipe for DNAPL site characterisation because each site presents variations of contaminant transport

conditions and issues, especially in South Africa where 95% of the aquifers are fractured and heterogonous. The purpose of this thesis is:

- To provide a detailed overview of the most important physio-chemical properties of different DNAPLs, the influence this has on transport of these contaminants and the interactions of these contaminants in different types of aquifers
- To combine the lessons learned from three years of DNAPL characterisation experience, with an emphasis on fractured aquifers.
- To produce a document with a more realistic approach to DNAPL characterisation at contaminated sites, with a proper site conceptual model development in fractured rock aquifers.
- To discuss efficient and cost-effective scientific approaches and strategies used for DNAPL characterisation in fractured South African aquifers that are known or suspected to be contaminated. This includes the development of new methods of testing and integration of data to understand fractures and their impact on DNAPL transport.
- To provide site investigators, site owners, environmental managers, governmental regulators and the public sector with guidance in conducting site investigations in assessing DNAPL impacts.

1.5.1 Thesis Structure

The first two chapters will discuss the theoretical aspects of DNAPLs. In Chapter 2, the physical, chemical and biochemical properties of common DNAPLs are explained. Chapter 3 contains the behaviour of DNAPLs as they migrate in fractured aquifers of various orientations.

South African aquifers are mainly fractured; therefore Chapter 4 discusses the South African aquifer systems and the implications for DNAPL contamination in detail. Chapter 5 addresses DNAPL site characterisation strategies in fractured media. Steps to follow before and during the characterisation will be discussed as part of a toolbox approach to site characterisation. This approach was then applied to two case studies to characterise fractures for DNAPL sites; this is discussed in Chapter 6. The investigation protocol and results obtained are integrated in these sections.

Based on the findings and understanding obtained, site-specific methodologies for South African aquifers will be proposed in Chapter 7. Conclusions and recommendations, with the focus of the fractured aquifers of the country, are provided in Chapter 8.

2 DNAPL Properties

In this section various potential of DNAPL sources in South Africa are discussed first. Then the physical, chemical properties of fluid and media associated with DNAPL flow are described. It builds a foundation of fundamental concepts and definitions that are helpful in fully understanding the geological settings and types of DNAPLs to which proper site characterisation can be applied. The influence of these properties on DNAPL transport at contaminated fractured aquifers is examined further in Chapter 3. It should be recognised that the success or failure of remedial activity at a particular DNAPL site will be determined largely by the degree to which the geology (particularly fractures) and contaminant distribution are characterised. If the geology and contaminant distribution are not adequately understood, decisions regarding the applicability of remedial activities should not be made. Although various literature sources were referred as indicated in the respective sections, the main source of information on the physio-chemical properties of DNAPLs discussed in this chapter is adapted from EPA's Hazardous Waste Clean-Up Information (CLU-IN) web site (<http://clu.in.org/>).

2.1 Physical Properties

There are several physical properties that make DNAPLs problematic with regard to groundwater contamination.

2.1.1 Interfacial Tension

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, known as interfacial tension. It is a representation of the co-existence of liquids at different pressures, causing the interface to contract into as small an area as possible. This force imbalance in the curved interface demonstrates that the pressures in each fluid are different.

This force arises due to mutual attraction between similar molecules in the vicinity of the interface, and a mutual dislike for molecules on the opposite side of the interface. Interfacial tension results in the interface between immiscible liquids taking the shape of the minimum area. If there were no interfacial tension between water and the liquids of concern, they would be termed aqueous phase liquids rather than non-aqueous phase liquids. In other words, they would be fully miscible with water. Therefore, interfacial tension is one of the most important physicochemical properties controlling multi-phase fluid (DNAPL) migration in the subsurface. The importance

of interfacial tension in multiphase flow is reflected in the fact that the migration equations (Equation 3-4) are more sensitive to interfacial tension relative to other physicochemical properties such as contact angle, viscosity, etc.

For many laboratory-grade organic compounds such as chlorinated solvents, the interfacial tension with water is on the order of 0.040 to 0.050 N/m (note that 1 N/m=1000 dynes/cm). As comparison, the interfacial tension between pure water and air (often referred to as surface tension) is approximately 0.072 N/m. At industrial waste sites, the interfacial tension between DNAPL and water is typically between 0.005 and 0.035 N/m, depending on the specific components that comprise both the NAPL and the water. If some of the components act as surface active agents (surfactants), the interfacial tension will tend to be toward the lower end of this range, and possibly even less. Examples of such surfactants include additives in various fuels and cleaners. Interfacial tension is therefore a site-specific parameter that must be measured for an actual sample of DNAPL obtained from the subsurface. It is important to note that the application of a surfactant or cosolvent flood will usually result in lowering the DNAPL-water interfacial tension (Fountain *et al.*, 1991).

2.1.2 Wettability and Contact Angle

When two fluids are in contact with solid, one usually has a greater affinity for the solid than the other. Wettability is a measure of a liquid's relative affinity for a solid. The wetting fluid will preferentially spread over the solid surface at the expense of the non-wetting fluid. Figure 2-1, Figure 2-2 and Figure 2-3 illustrate a drop of DNAPL resting on a solid surface in the presence of water. As shown, the liquid-liquid interface meets the solid surface at a specific angle, referred to as a contact angle. The fluid, through which this angle is measured as less than 90 degrees, is referred to as the wetting phase. The other fluid, through which the angle is measured as greater than 90 degrees, is referred to as the non-wetting phase. In the event that one phase spontaneously spreads to coat the entire solid surface, the contact angle is zero, and that phase is referred to as being perfectly wetting. In such cases, the non-wetting phase does not physically touch the solid surface, but is separated from the solid surface by a thin layer of the wetting phase.

For most contaminated sites, NAPL can be assumed to be non-wetting with respect to water, provided that the aquifer solids contain little organic matter (Pankow and Cherry, 1996). When DNAPL is non-wetting, it means that water occupies the smaller pore spaces and preferentially spreads across solid surfaces, while the DNAPLs are restricted to the larger openings. Above the water table, it is usually appropriate to assume that water is wetting with respect to DNAPL, and that DNAPL is wetting with respect to air. Extra care should be taken, however, when dealing with coal tar or creosote sites. These DNAPLs are typically complex mixtures that may contain a

significant portion of highly insoluble (and possibly polymerised) pitch. This pitch may be reactive and has the potential to significantly alter the wettability of aquifer solids (CLU-IN, 2000). For coal tar and creosote sites, wettability should be measured and not assumed.

Wettability between a DNAPL and water in a given geologic setting depends not only on the individual components that comprise the DNAPL and the water, but also on the surface chemistry of the solid in question. Wettability is therefore site-specific and may even vary within a particular site, in which case the site is said to exhibit mixed wettability. A reliable method of establishing whether a NAPL is wetting or non-wetting at a site is to measure a capillary pressure-saturation curve using the DNAPL, porous medium, and other fluid in question.

Figure 2-1 shows a common case where 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). The DNAPL produces an obtuse contact angle (between 90° and 180°).

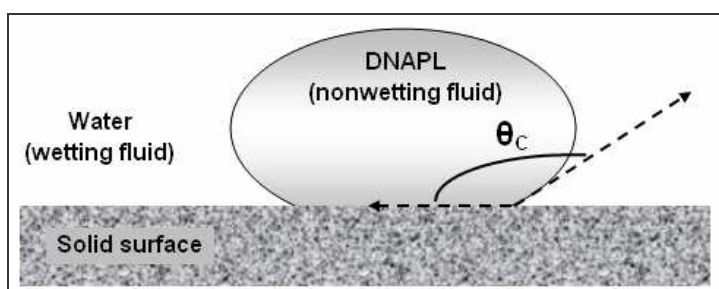


Figure 2-1: Obtuse contact angle when DNAPL is the non-wetting fluid.

Figure 2-2 shows a rare case where a DNAPL has a greater affinity for a solid (wetting) than water (non-wetting). The DNAPL produces an acute contact angle (between 0° and 90°).

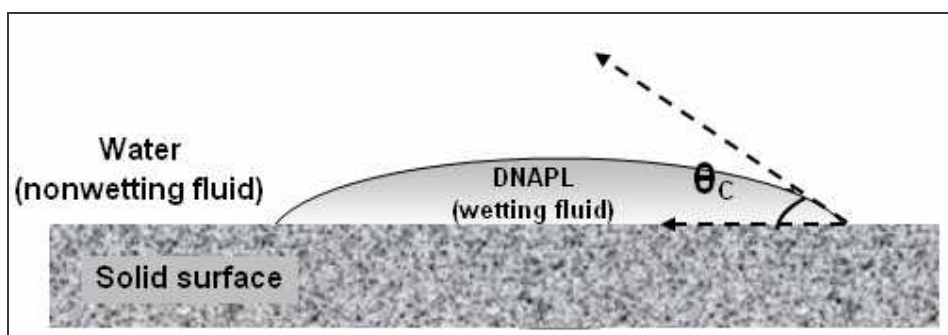


Figure 2-2: Acute contact angle when DNAPL is the wetting fluid.

From the above cases, it follows that it is theoretically possible to attain a contact angle of 90° (Figure 2-3). This neutral condition is approached by mixtures such as

crude oil-water, and coal tar-water, in which the NAPL can be referred to as neutrally wetting. In fact, phases with contact angles ranging between 75° and 105° are considered neutrally wetting (Kueper *et al.*, 2003).

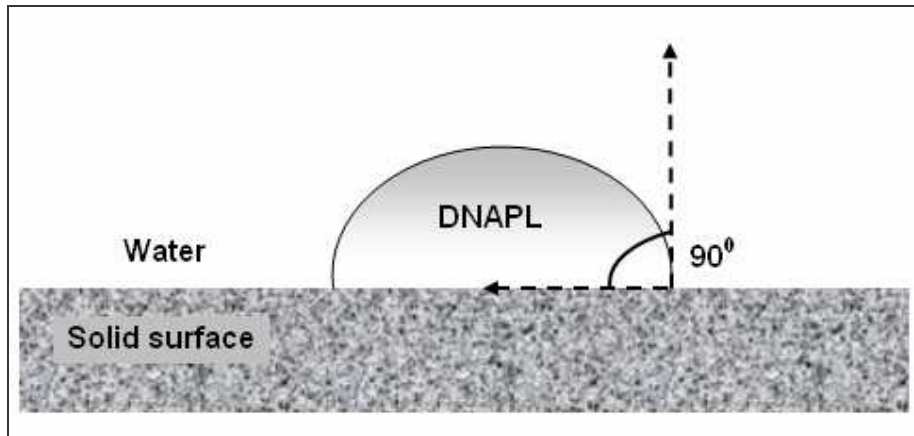


Figure 2-3: Neutrally wetting fluids forming a contact angle of 90°.

Results of contact angle experiments using several DNAPLs and various substrates are provided in Table 2-1.

Table 2-1: Results of contact angle experiments using DNAPLs (from Cohen and Mercer, 1993).

DNAPL	substrate	Medium	Contact Angle (°)
Tetrachloroethene	clay	APL*	23-48
Tetrachloroethene	clay	air	153-148
1,2,4-Trichlorobenzene	clay	APL	28-38
1,2,4-Trichlorobenzene	clay	air	153
Hexachlorobutadiene	clay	water	32-48
Hexachlorocyclopentadiene	clay	water	32-41
2,3-Dichlorotoluene	clay	water	30-38
4-Chlorobenzotrifluoride	clay	water	30-52
Carbon Tetrachloride	clay	water	27-31
Chlorobenzene	clay	water	27-34
Chloroform	clay	water	29-31

*APL refers to aqueous phase liquids (water containing dissolved chemicals).

2.1.3 Density

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. Cohen and Mercer (1993) states that density differences of ~ 1% influence fluid movement in the subsurface, in many situations NAPL densities differ from that of water by 10-50%. The relatively high

density of DNAPLs means that they may penetrate the water table and flow downward, directed by paths of least capillary resistance (possibly against the direction of groundwater flow).

If the DNAPL of concern is a single component, then its density can be estimated using a textbook value. However, the density of a multi-component DNAPL is unlikely to be listed in a handbook and will need to be measured using a sample of recovered liquid. Density is a weak function of temperature for the range of temperatures usually encountered in the subsurface. Most DNAPLs exhibit a slight increase in density with a decrease in temperature.

DNAPLs may contain a small amount of contaminants, which in their pure form are LNAPLs. DNAPLs may also contain some components that are solids in their pure form. Since the majority of components are liquids that are denser than water, however, a DNAPL phase exists. The implication is that it is possible to detect lighter-than-water components such as toluene far below the water table without the presence of an actual LNAPL source in the subsurface. It is also clear that the density of DNAPLs will be site-specific because these properties depend upon component composition.

2.1.4 Solubility

The solubility of DNAPL components in groundwater is important because it influences the level of contamination. It is reported (e.g., Mackay *et al.*, 1985) that organic compounds are commonly found in groundwater at concentrations less than ten percent of NAPL solubility limits, even where NAPL is known or suspected to be present. The discrepancy between field and laboratory measurements is probably caused by heterogeneous field conditions, such as non-uniform groundwater flow, complex NAPL distribution, and mixing of stratified groundwater in a borehole, and to a lesser extent, NAPL-water mass transfer limitations (Feenstra and Cherry, 1988; Mackay *et al.*, 1985; Powers *et al.*, 1991).

DNAPLs vary widely in their aqueous solubility. Factors affecting solubility include temperature, cosolvents, salinity, and dissolved organic matter. Although the aqueous solubility of most organic chemicals rises with temperature, the direction and magnitude of this relationship is variable (Lyman *et al.*, 1982). Similarly, the effect of cosolvents (multiple organic compounds) on chemical solubility depends on the specific mix of compounds and concentrations.

Subsurface NAPL trapped as ganglia at residual saturation and contained in pools, such as DNAPL trapped in depressions along the top of a capillary barrier, are long-term sources of groundwater contamination. Factors influencing NAPL dissolution and eventual depletion include the effective aqueous solubility of NAPL components, groundwater velocity, NAPL-water contact area, and the molecular diffusivity of the

NAPL chemicals in water (Feenstra and Cherry, 1988; Anderson, 1988; Hunt *et al.*, 1988a; Schwillie, 1988; Anderson *et al.*, 1992a, b; Pfannkuch, 1984; Miller *et al.*, 1990; Mackay *et al.*, 1991).

2.1.5 Viscosity

Viscosity is a measure of a liquid's resistance to flow derived from the internal friction from molecular cohesion. Lower DNAPL viscosity results in the deeper penetration of an aquifer in a given time. Certain DNAPLs, such as some chlorinated solvents, are characterised by viscosities less than that of water, implying that they are highly mobile in the subsurface. Other DNAPLs, such as coal tar, are significantly more viscous than water. Viscosity is very dependent on temperature and should always be evaluated at the temperature of interest. As with density, the viscosity of a single-component DNAPL can be obtained from a handbook (e.g., Verschueren, 1983). The viscosity of a multi-component DNAPL, however, will be site-specific and should be measured from a recovered sample.

2.1.6 Capillary Pressure

Capillary pressure refers to the pressure imbalance that exists across a curved interface separating two immiscible fluids. This pressure difference exists because of the interfacial tension in the fluid-fluid interface separating the two fluids. The fluid on the concave side of the interface is at a higher pressure.

The concept of contact angle permits one to relate the pressure difference across an interface, as discussed in detail in Section 56. It is worth to note that higher capillary pressures are required for the non-wetting phase to enter finer-grained materials. As a result, DNAPL migration below the water table is typically confined to the relatively coarser-grained lenses and laminations. This is illustrated clearly in the work of Kueper *et al.* (1989).

In a two-phase system, such as DNAPL and water below the water table, the non-wetting phase will always be present on the concave side of the interface separating the liquids in question. The wetting phase will be present on the convex side of the interface and will preferentially reside in the smaller pores and pore-throats. This small-scale distribution of fluids is illustrated schematically in Figure 2-4. It is assumed, in this figure, that DNAPL is the non-wetting phase, and that water is perfectly wetting on the grain surfaces. Note that DNAPL does not occupy all the pores in the figure and that water can therefore flow past the DNAPL-water interfaces, thereby allowing contact with injected agents such as surfactants and cosolvents.

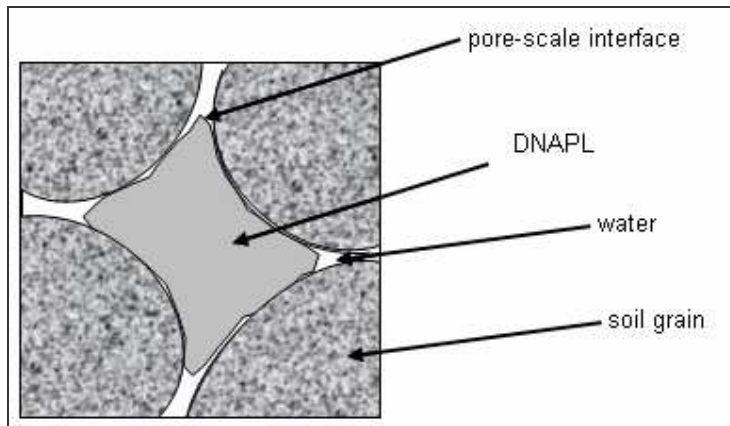
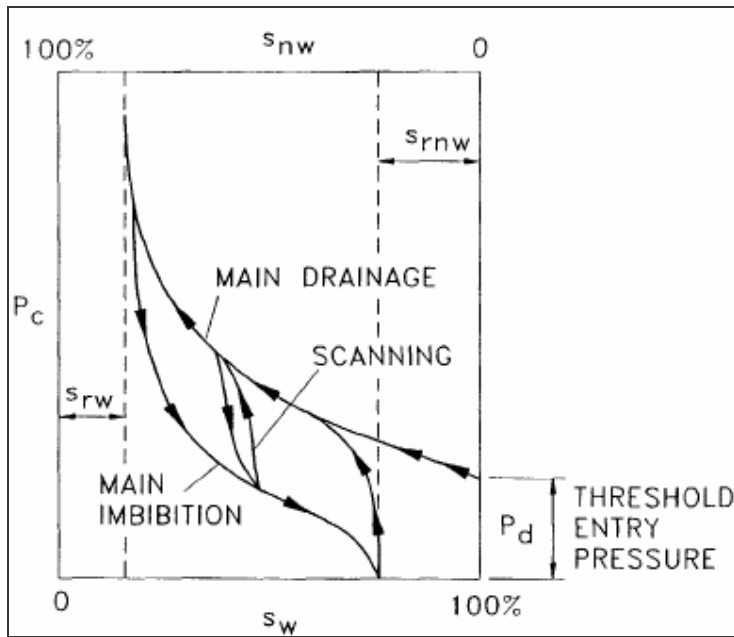


Figure 2-4: Pore-scale interfaces between DNAPL and water in a porous medium (modified from Pankow and Cherry, 1996).

In the majority of cases, it is not possible to define the pore-scale geometry of a geological material such that the positions of individual fluid interfaces can be calculated. If this were possible, however, the relationship between capillary pressure and the relative amounts of DNAPL and water in a porous/fractured medium (fluid saturation) could be established. As an alternative, it is customary to represent the relationship between capillary pressure and fluid saturation by means of a capillary pressure-saturation curve (or capillary pressure curve) measured at the macroscopic scale. The macroscopic scale represents an average over many pores and pore throats.

Figure 2-5 presents a typical capillary pressure-saturation curve for a two-phase system in porous media. A similar curve would apply to a two-phase system in a rough-walled fracture (Reitsma and Kueper, 1994). The wetting and non-wetting phase saturations are expressed as an average percentage of pore space. It is important to note that the capillary pressure-saturation relationship is hysteric; that is, the curve is at least double legged, with one leg valid during the drying cycle (drainage) and the one during the wetting cycle (wetting). Moreover, since the subsurface of the earth could intermittently be subjected to both drying and wetting cycles, the curve can change abruptly from the wetting (imbibition) to the drainage leg, and conversely. As can be seen in Figure 2-5, a higher degree of non-wetting saturation can only be attained with higher capillary pressures. This corresponds to the fact that progressively smaller pores and pore throats will be invaded at higher capillary pressures. The threshold capillary pressure required to invade an initially wetting-phase saturated porous medium is referred to as the entry pressure.



S_w = wetting phase saturation, S_{nw} = non-wetting phase saturation, S_{rw} = residual wetting phase, S_{rnw} = residual non-wetting phase, main imbibition = main wetting

Figure 2-5: Capillary pressure-saturation relationship for two-fluid system (Cohen and Mercer, 1993).

The shape of the capillary pressure-saturation curve depends on many factors, including grain sorting, contact angle, interfacial tension, and hydraulic conductivity. Of greatest practical interest at a site is the variation of the capillary pressure-saturation relationship with hydraulic conductivity. In general, a lower hydraulic conductivity material or a smaller aperture fracture will exhibit a higher entry pressure. A suite of capillary pressure curves for an aquifer containing a wider range of materials (e.g., silt through gravel) would exhibit a wider range of entry pressures.

2.1.7 Bulk Retention Capacity

The bulk retention capacity of a porous or fractured medium is defined as the volume of DNAPL divided by the overall volume of medium within which the DNAPL migration pathways occurred. This overall volume includes the total volume of soil, gas, and liquid through which the DNAPL migrates. In other words, the overall volume of medium includes both the lenses and laminations in which residual and pooled DNAPL is present and the adjacent lenses and laminations void of DNAPL. 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 DNAPL.

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 field deposits

will generally 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% and 3% by bulk volume (CLU-IN, 2000), with the lower values applicable to more heterogeneous deposits without 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).

2.1.8 Relative Permeability

The conductance of fluid flow that a porous or fractured medium exhibits is referred to as its permeability. Finer-grained materials exhibit a lower permeability, while coarser-grained materials generally exhibit a higher permeability. Permeability is a function of the medium only, not of the fluids present in the medium. For a medium saturated with water, it is customary to define the term hydraulic conductivity. Unlike permeability, hydraulic conductivity takes into account the particular fluid that is present in the medium. In an isotropic medium, hydraulic conductivity is defined as:

$$K = \frac{k\rho g}{\mu}$$

Equation 2-1

where

- K = hydraulic conductivity,
- k = permeability,
- ρ = fluid density,
- g = acceleration due to gravity, and
- μ = fluid viscosity.

It is clear from Equation 2-1 that K incorporates both medium (k) and fluid (ρ, μ) properties.

When the pore space of a porous or fractured medium is occupied by two or more fluids, the permeability of the medium to any one of the fluids is reduced. The presence of a second or third fluid reduces the number of pores and pore throats available for flow and increases the tortuosity of available flow paths. To account for the reduction in permeability due to the presence of additional fluids, a relative permeability can be defined as follows:

$$k_r = \frac{k_{eff}}{k}$$

Equation 2-2

where

k_r = relative permeability of the fluid of interest and

k_{eff} = effective permeability of the fluid of interest.

If only one fluid occupies the medium of interest, the effective permeability would equal the permeability and relative permeability to the one fluid, which would be 1. As increasing amounts of a second or third fluid occupy the medium, the relative permeability to the first fluid would decrease. Numerous studies have demonstrated that relative permeability is a function of fluid saturation (Bear, 1972; Corey, 1986). Figure 2-6 (a) and (b) present the typical relationship between relative permeability and fluid saturation in a multi-phase system. It is clear that, as the relative permeability to one phase increases, the relative permeability to the other phase decreases. Although relative permeability curves for a two-phase system generally follow the trends exhibited in Figure 2-6(a), the specific shapes of the curves are a function of many factors, including interfacial tension and medium structure.

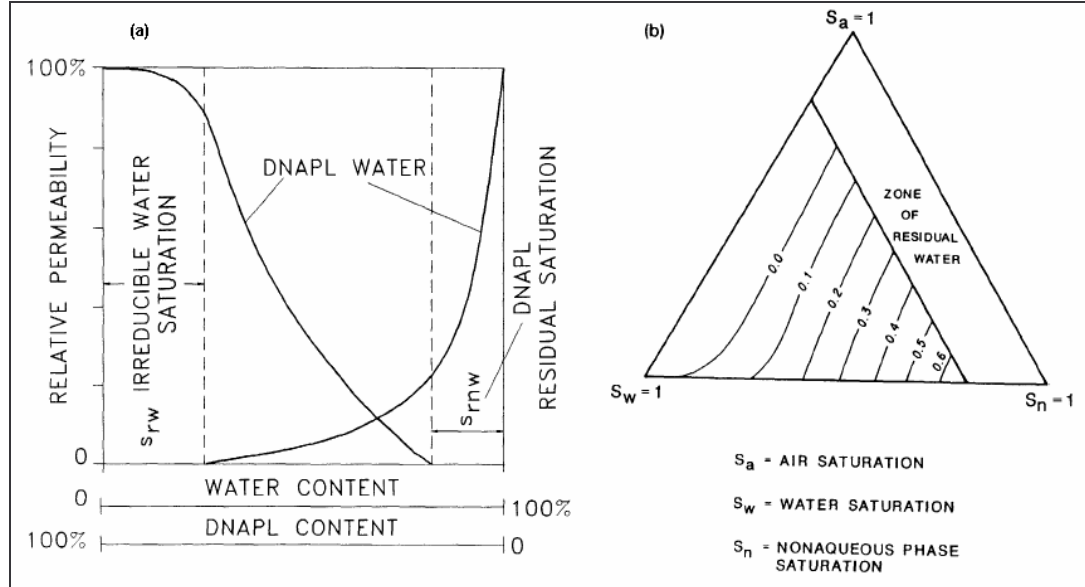


Figure 2-6: (a) water-NAPL relative permeability; (b) ternary diagram showing the relative permeability of NAPL as a function of phase saturation (Cohen and Mercer, 1993).

Relative permeability curves are required to calculate the fluid flux for a multi-phase system. For a single-phase system, Darcy's Law can be used to calculate the fluid flux as follows (after Pankow and Cherry, 1996):

$$q_w = -\frac{k_{ij}k_{rw}}{\mu_w} \left(\frac{\partial P_w}{\partial x_j} - \rho_w g_j \right)$$

Equation 2-3

$$q_{nwi} = -\frac{k_{ij}k_{rnw}}{\mu_w} \left(\frac{\partial P_{nw}}{\partial x_j} - \rho_{nw} g_j \right)$$

Equation 2-4

where

i and j = indices that extend over the three Cartesian coordinates.

In Equation 2-3 and Equation 2-4, q is the volume flux, k is the permeability, k_r is the relative permeability, P is the pressure, ρ is the density, μ is the dynamic viscosity, and the subscripts w and nw denote the wetting fluid (water) and non-wetting fluid (DNAPL), respectively. By convention, the repeated index, j, implies a summation of j = 1, 2, and 3.

At first glance, Equation 2-3 and Equation 2-4 appear to be uncoupled. This is not the case, however, because the relative permeability k_{rw} and k_{rnw} are strong functions of the saturation. It was previously pointed out that fluid saturation is a function of capillary pressure. Therefore, the relative permeabilities are functions of $P_c = P_{nw} - P_w$, and Equation 2-3 and Equation 2-4 are strongly coupled.

It should be noted that Darcy's Law is valid for steady-state, laminar fluid flow. At a site where fluid flow is transient, the partial differential equation describing fluid flow must be solved. Transient flow will occur in response to events such as groundwater pumping and infiltration of rainwater or snow melt. There are several commercially available groundwater flow models suitable for simulating transient, single-phase flow in a wide range of geological environments. Simulating the flow of multiple fluids, such as LNAPL or DNAPL migration in groundwater, requires the use of a multiphase flow model. A multi-phase flow model, however, is considerably more challenging to use than a groundwater flow model. Some of the difficulties associated with parameter estimation and output uncertainty in multi-phase flow modelling are discussed by Kueper and Frind (1996).

2.1.9 Vapourisation

The transfer of components from the DNAPL phase directly to the air phase is referred to as vapourisation (CLU-IN, 2000). Vapourisation will lead to the formation of contaminant vapours in unsaturated media. These vapours can advect and disperse through the continuous air pathways present in unsaturated media, thereby spreading contamination beyond the immediate area of the DNAPL. The rate of vapourisation and magnitude of air-phase concentrations is proportional to a compound's vapour

pressure (the pressure exerted in the air phase above the pure compound in a closed container), which is a strong function of temperature. Vapour pressure typically increases with higher temperatures.

Certain DNAPLs, such as trichloroethylene (TCE), have a significant vapour pressure and can therefore give rise to large vapour plumes. Vapourised contaminants may diffuse into soil moisture, up through the ground surface, down to the water table, and into infiltrating water. The vapour pressure and resulting maximum air phase concentrations for typical NAPLs can be found in handbooks such as Verschueren (1983) and Mackay *et al.* (1993). For a multi-component DNAPL, a compound's effective vapour pressure should be calculated. For structurally similar compounds, the use of Raoult's Law, which stipulates that the effective vapour pressure of the component in question will equal the product of its single-component vapour pressure and its mole fraction in the NAPL phase, has been found to be appropriate for calculating vapour pressures in a multi-component system. The behaviour of contaminant vapour in unsaturated media is further discussed by Mendoza *et al.* (1996).

2.1.10 Volatilisation

The partitioning of components from the dissolved DNAPL phase to the air phase is referred to as volatilisation. The magnitude of concentrations arising from volatilisation is described by Henry's Constant, which is defined as the equilibrium concentration in the air phase divided by the equilibrium concentration in water. A high Henry's Constant indicates a high affinity for the air phase. Care should be taken when using a Henry's Constant in calculations, because various units can be used to define this parameter in handbooks. It should also be noted that if groundwater contains dissolved compounds at their aqueous solubility, the same air phase concentration will arise from the volatilisation process and from the vapourisation process. The Henry's Constant for typical organic contaminants encountered at hazardous waste sites can be found in handbooks such as Verschueren (1983).

2.1.11 Sorption and Partitioning Coefficient

The partitioning of components from the water phase to solid matter such as sand grains 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 both the type of organic compound and the degree of organic carbon on solid surfaces.

At sites where sorption is occurring, the leading edge of 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 characterised by the retardation factor:

$$R = 1 + \frac{\rho_b}{\phi} K_d = \frac{\bar{v}}{v_c}$$

Equation 2-5

where

- R = retardation factor,
- ρ_b = dry bulk density of the medium,
- ϕ = medium porosity,
- K_d = distribution coefficient,
- $\bar{v}$ = average linear groundwater velocity, and
- v_c = contaminant velocity.

Equation 2-5 assumes an equilibrium sorption process. Modifications need to be made in cases where the sorption process is rate limited. Fetter (2005) presents an introductory discussion of non-equilibrium sorption.

The distribution coefficient, K_d , is often approximated as:

$$K_d = K_{oc} f_{oc}$$

Equation 2-6

where

- K_{oc} = organic carbon partition coefficient and
- f_{oc} = 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, 2005). 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.

It is clear that the degree of retardation experienced by a particular contaminant 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 presence of cosolvents such as alcohols in groundwater will also influence the sorption process.

2.1.12 Saturation

The saturation of a fluid is the volume fraction of the total void volume occupied by that fluid. Saturations range from zero to one and the saturations of all fluids sum to one. Saturation is important, because it is used to define the volumetric distribution of DNAPL, and because other properties, such as relative permeability and capillary pressure, are functions of saturation.

Photographs showing variable DNAPL distribution and saturation states observed during laboratory experiments are presented by Schwille (1988) and Wilson *et al.* (1990).

In the saturated zone, non-wetting DNAPL flows selectively through the big aperture fracture or coarse grains, more permeable portions of heterogeneous media, averting the finer-grained zones that provide greater capillary resistance to entry. As a result, mobile DNAPL is present as blobs connected along fractures, macropores, and the larger pore openings. Water occupies the smaller pores and tends to be retained as a film between the non-wetting DNAPL globules and media solids. The fluid distribution is more complex in the vadose zone, where DNAPL migration occurs by displacing soil gas and sometimes water from pore throats and bodies (Figure 2-7(a)). Residual saturation and pooled DNAPL are varieties of the saturation states to be discussed in the following sections. Figure 2-7 (b) shows a saturated porous medium where the pores are filled with water and DNAPL.

Measuring saturation presents a costly sampling and analysis problem. Numerous samples will generally be needed to assess the distribution of subsurface DNAPL; and sampling, sample preservation, and analytical methods must be carefully selected and implemented to produce reliable results. Cary *et al.* (1991) demonstrated a procedure to extract NAPL from soil by shaking a soil-water suspension with a strip of hydrophobic, porous polyethylene in a glass jar for several hours. Estimates of NAPL content were determined by weighing the strips before and after the extraction procedure. Saturation can also be estimated gravimetrically in conjunction with various organic solvent extraction techniques and specialised distillations (Cary *et al.*, 1989a, b). Chemical analyses can be made to estimate total contaminant concentration and NAPL saturation. Finally, drilling and sampling, pumping tests, and geophysical borehole logging can be used to facilitate field estimates of saturation. These estimates are qualitative, subject to considerable error and uncertainty, and the methods used are largely undocumented (Cohen and Mercer, 1993).

2.1.12.1 Residual Saturation

Residual DNAPL refers to the presence of small, disconnected blobs and ganglia of organic liquid that are trapped in the pore spaces of porous media or fractures by capillary forces. Residual DNAPL is formed at the trailing end of a migrating DNAPL

body by snap-off and by-passing mechanisms. In porous media, blobs of residual DNAPL are typically between 1 and 10 pore throats in length (CLU-IN, 2000). It is currently understood that DNAPL migration cannot take place through the subsurface without the formation of residual DNAPL (CLU-IN, 2000).

In the unsaturated zone, components will partition from residual DNAPL to the air phase, giving rise to vapour plumes, and from residual DNAPL to soil moisture and infiltrating water, giving rise to aqueous phase contamination. Below the water table, residual DNAPL will dissolve into flowing groundwater, resulting in dissolved contaminant plumes. The degree of residual DNAPL formed in a particular medium is a function of many factors, including DNAPL density, DNAPL viscosity, interfacial tension, medium permeability, and the maximum capillary pressure attained during the original migration process. In general, residual NAPL saturations will vary from between 2% and 30% of pore space (approximately 1 to 10% of bulk volume), and will be spatially variable at a site (CLU-IN, 2000). It must be noted, however, that this saturation refers to the amount of DNAPL actually present in the lenses, laminations, or fractures invaded by the migrating DNAPL. As will be discussed further, the concept of bulk retention capacity is more useful for estimating the volume of NAPL retained in the subsurface at real sites. Figure 2-7(a) and shows residual DNAPL in an unconsolidated lithology where the pores are filled with air, water and DNAPL. Figure 2-7(b) shows residual DNAPL in a consolidated lithology where the pores are filled with water and DNAPL.

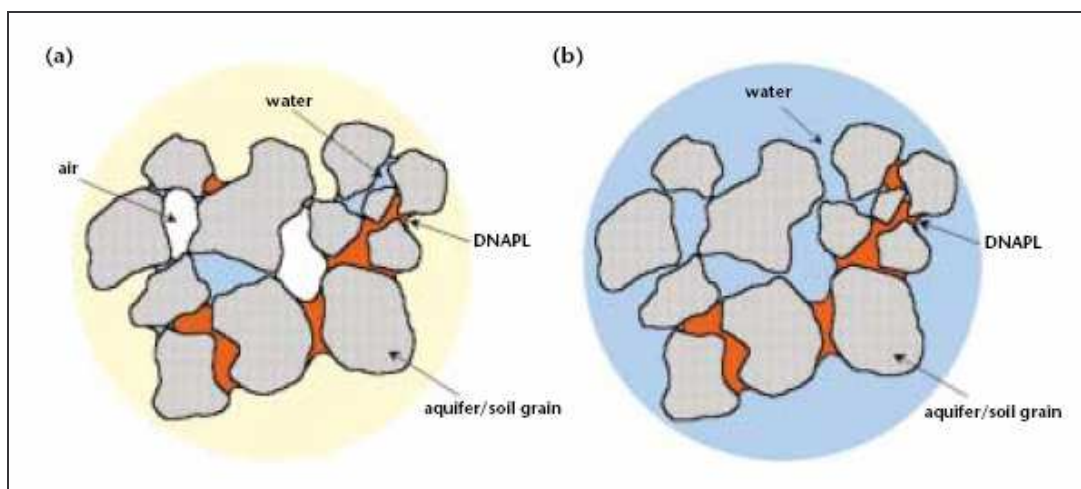


Figure 2-7: Residual DNAPL in (a) unsaturated and (b) saturated porous media (Kueper *et al.*, 2003).

2.1.12.2 Pooled DNAPL

Pooled DNAPL refers to the presence of DNAPL at saturations higher than the residual DNAPL. Pooled DNAPL is distinctly different from residual DNAPL in that pooled DNAPL represents a continuous fluid distribution, and is potentially mobile in the subsurface. While the relative permeability assigned to residual DNAPL is zero, pooled DNAPL has a finite relative permeability determined by the degree of saturation. In general, pools contain DNAPL saturations of between 30% and 80% of pore space (CLU-IN, 2000).

DNAPL pools tend to form above capillary barriers. Below the water table, with DNAPL being non-wetting with respect to water, DNAPL would pool on fine-grained lenses. LNAPL would tend to pool on high-water content layers in the unsaturated zone. Significant pooling of LNAPL may also occur in the vicinity of the water table. Due to the heterogeneous nature of subsurface deposits, DNAPL pools can form at all elevations and not necessarily just on lower permeability units such as clay aquitards and bedrock surfaces.

The presence of pooled DNAPL can be problematic at sites because drilling through DNAPL pools can lead to vertical short-circuiting. DNAPL pools can also be mobilised in response to groundwater pumping, which can be an advantage if extraction wells are properly placed, but a disadvantage if mobilization occurs into previously uncontaminated regions of the subsurface. DNAPL pools also can be mobilized if injected agents such as surfactants and cosolvents lower the DNAPL-water interfacial tension. For the case of DNAPL below the water table, the height of pooled DNAPL can be calculated by considering a force balance in a one-dimensional, hydrostatic system (Kueper *et al.*, 1993) and the mathematical equations are given in Section 56. Figure 2-8 shows a typical maximum pool heights for the common DNAPLs, with the DNAPL perched above a variety of capillary barriers

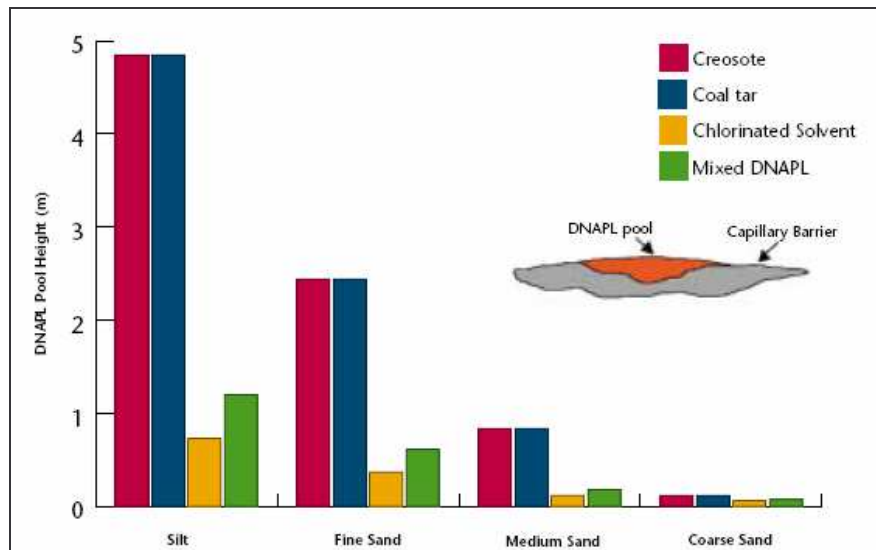


Figure 2-8: Typical maximum pool heights for the common DNAPLs, DNAPL perched above a variety of capillary barriers (Kueper *et al.*, 2003).

2.2 Biotransformation of DNAPLs

A further complication is the bio-transformations of the DNAPLs in soil and groundwater. In the early 1980s, chloroethene, *cis*- and *trans*-1,2-dichloroethene were detected in groundwater beneath industrial sites that traditionally only used TCE and PCE as degreasers or solvents. Since micro-organisms in the recharge sources were found to be active in the decomposition of organic matter, researchers speculated that the organisms could also act on the hydrocarbons, resulting in exotic organic byproducts that are themselves poisonous (Chrinemnoff, 1990). Parsons (1984) concluded that some organisms can promote successive transformation of PCE to TCE, and of PCE and TCE to other compounds. Some of the chemical transformations are illustrated in Figure 2-9. As a result, bio-transformations complicate characterisation in the identification of the source of contamination and mobility of DNAPLs.

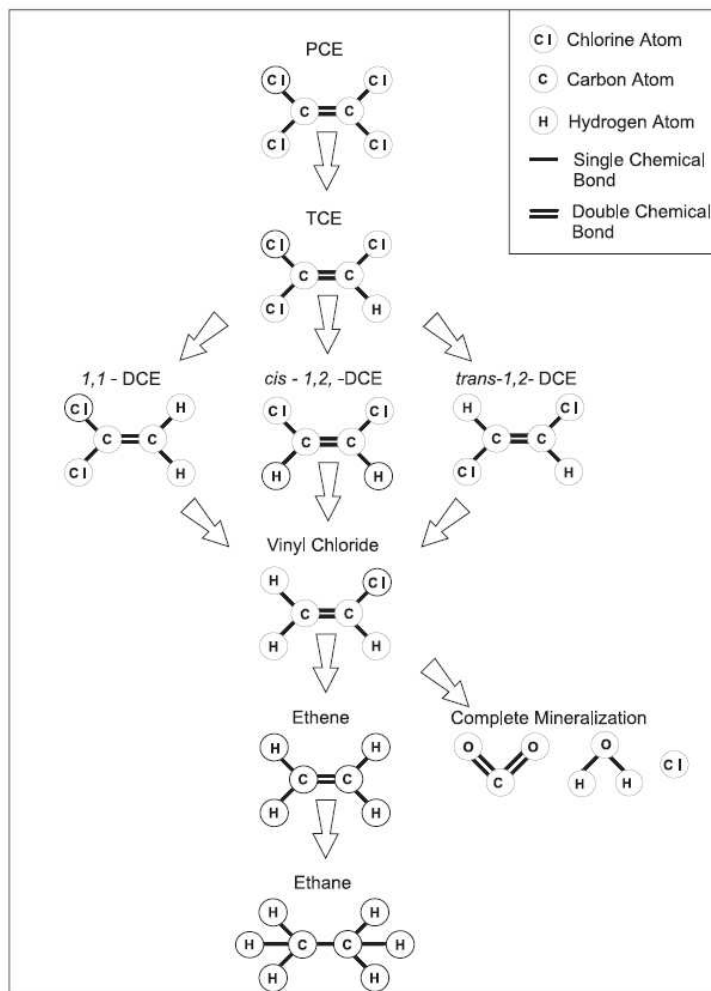


Figure 2-9: Biotransformation of PCE and TCE (Weidermeier, 1998)

2.3 Use of DNAPLs

As discussed in Section 1.1, the major DNAPL types include chlorinated solvents, coal tar and creosote, PCB oils, and miscellaneous or mixed DNAPLs. Of these types, the most extensive subsurface contamination is associated primarily with chlorinated solvents, either alone or within mixed DNAPL sites. This is due to their widespread use and properties (they possess a combination of physical and chemical properties that impart a high propensity for widespread groundwater contamination). For example, some other DNAPL chemicals are much less soluble than the chlorinated solvents, and so they are much less mobile because they partition strongly to soil materials. As another example, important soluble components of creosote and coal tar are more degradable in the groundwater zone than are most chlorinated solvents. Table 2-2 lists the common chlorinated solvent production in mass and volume in 1986 in the United States, while Table 2-3 summarises the uses of the common DNAPL contaminants.

2.3.1 Chlorinated solvents

Chlorinated solvents have been produced in large quantities throughout the world since the middle of the 20th century. Typical uses of these chemicals include dry cleaning, metal degreasing, pharmaceutical production, pesticide formulation and chemical intermediates (Cohen and Mercer, 1993). 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 (for example, at a former solvent or waste oil recycling facility). The following section discusses the chlorinated solvents highly encountered in DNAPL contaminated aquifers as summarised from Cohen and Mercer (1993); Kueper *et al.*, (2003); and Leonard, (2003).

- **1,2-Dichloroethane (EDC):** is a raw material for polychlorinated vinyl (PVC) and is therefore manufactured in large quantities. EDC is also used as a degreaser and a component in cleaning agents, pesticides, adhesives, paints, and varnishes. It is made by the chlorination of boiling ethylene in the presence of metal complex catalysts. EDC has a high chlorine content, which makes it expensive to incinerate. EDC is listed in the EPA's Toxic Release Inventory and is considered a mutagen and a possible carcinogen.
- **1,1,1-Trichloroethane (1,1,1-TCA):** is found in building materials, cleaning products, paints, and metal degreasing agents and is similar to trichloroethylene. Exposure to 1,1,1-TCA usually occurs by breathing

contaminated air. Inhaling high levels of 1,1,1-trichloroethane can cause dizziness and lightheadedness. Exposure to much higher levels can cause unconsciousness and other effects.

- **1,1,2-Trichloroethane (1,1,2-TCA):** is used as a feedstock for making 1,1-dichloroethene and as a solvent and is not commonly found in drinking water. It has been detected in some boreholes at fairly small concentrations (31 ppb) (ATSDR, 1989). It is more commonly found in air and industrial wastewater. There is little information about the effects of exposure to 1,1,2-TCA for humans. Animals exposed to high doses suffer liver cancer, and die at very high exposures.
- **Trichloroethylene (TCE):** is used as a degreasing solvent. TCE is also an ingredient in typewriter correction fluids, paint removers/strippers, adhesives, spot removers, and rug-cleaning fluids. Before it was banned for health reasons, TCE was used in foods, beverages (decaffeination of coffee), pet foods, pharmaceuticals, and cosmetics. TCE is produced from either acetylene or ethylene. Beginning with acetylene, the acetylene is chlorinated to tetrachloroethylene and pyrolysis produces TCE. TCE is considered as a possible human carcinogen. Its effects on reproductive/developmental functions are not conclusive.
- **Tetrachloroethylene or perchloroethylene (PCE):** is used mainly in dry cleaning and textile processing. It is also an important chemical intermediate, especially for aerosols and refrigerants, and an industrial metal degreaser (Chenier, 1992). It is a significant groundwater contaminant with a low water standard of 5 µg/L, like TCE. Disposal practices in the past, such as using unlined trenches or ponds, have resulted in substantial contamination of soils and aquifers.
- **1,1-Dichloroethylene:** is often the number one derived organic chemical manufactured annually and is made in excess of 4.5 billion kg/yr (Chenier, 1992). Dichloroethylene is used to produce vinyl chloride, PCE, methyl chloroform and other industrial chemicals.
- **Cis-1,2-Dichloroethylene:** is used in the manufacturing of solvents and often occurs in mixtures with its isomer, trans-1,2-dichloroethylene. The EPA has found that cis-1,2-DCE is not classifiable as a human carcinogen. However, exposure to cis-1,2-DCE has been shown to cause decreased numbers of red blood cells in animals and affect the liver.
- **Trans-1,2-Dichloroethylene:** animals exposed to trans-1,2-DCE have suffered damage to their lungs and liver. At very high levels, the animals had

damage to their hearts. No EPA classification exists for the carcinogenicity of trans-1,2-DCE.

- **Vinyl chloride:** is used in the manufacture of polyvinyl chloride (PVC), which is used to make a variety of plastic products such as pipe, coatings for wire and cable, and upholstery. Vinyl chloride is also a product of the degradation of many of the other chlorinated hydrocarbons. The Department of Human Health and Services (USA) has classified vinyl chloride as a human carcinogen.

Table 2-2: 1986 U.S. production of chlorinated organic solvents (after Pankow and Cherry, 1996).

Compound	Abbreviation	Mass (10 ⁶ kg)	Volume (200 L)
1,2-Dichloroethane	1,2-DCA	5,871	22,900,000
1,1,1-Trichloroethane	1,1,1-TCA	294	1,100,000
Carbon tetrachloride	CTET	284	890,000
Methylene chloride	DCM	255	960,000
Chloroform	TCM	191	640,000
Tetrachloroethylene	PCE	184	560,000
Trichloroethylene	TCE	75	260,000

Table 2-3: Common DNAPL usage (from Cohen and Mecer, 1993; Pankow and Cherry, 1996)

Chlorinated Solvents	PCBs	Creosote and coal tar
Electronics manufacturing	Capacitors	Wood treating
Solvent production	Transformers	Coal tar distillation
Pesticide/herbicide manufacturing	Printing inks	Steel coking operations
Dry cleaning	paints	Coal gasification
Instrument manufacturing	Pesticides	Roofing tars
Solvent recycling	Adhesives	Road tars
Engine manufacturing	Gas-transmission turbines	
Steel product manufacturing	Hydraulic fluids	
Chemical production	Plasticizer in rubbers	
Rocket engine/fuel manufacturing	Heat transfer medium	
Aircraft cleaning/engine degreasing	Wax extender	
Adhesives	Vacuum pumps	
Chemical intermediate	Carbonless reproducing paper	
Pain removal/stripping	Dedusting agent	

2.3.2 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a class of over 200 chemical compounds referred to as congeners, in which between one and ten chlorine atoms are attached to a biphenyl molecule (Kueper *et al.*, 2003). The synthesis of PCBs was first reported in 1881, with full recognition of their industrial uses developing in the 1930s. The majority of PCBs were manufactured for use in capacitors, transformers, printing inks, paints, pesticides and other applications. PCBs were marketed under the trade name Aroclor, distributing a variety of formulations differing from each other with respect to the amount and particular types of congeners present.

Worldwide production of PCBs has now ceased, mainly in response to recognition of their toxicity and their tendency to bio-accumulate in animal tissues. However, they remain in limited use, and groundwater contamination is dominantly in locations where they were used and discarded previously.

2.3.3 Creosote

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.

2.3.4 Coal tar

As creosote, coal tar is a complex mixture of hydrocarbons produced through the gasification of coal. Coal tar was historically produced as a byproduct of

manufactured gas operations up until approximately 1950, and is currently still produced as a by-product of blast furnace coke production.

2.4 Physiochemical Properties of the Common DNAPLs

Because of their physical properties and environmental toxicity, organic compounds that fall in the DNAPL category are listed in Table 2-4.

Table 2-4: Organic compounds that are DNAPLs.

Compound class	Compounds
Chlorinated solvents	Tetrachloroethylene, Trichloroethylene, 1,1,1-Trichloroethane, Dichloromethane, Chloroform, Carbon tetrachloride, 1,2-Dichloroethane, Chlorobenzene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,1,2-Trichloroethane, 1,2,4-Trichlorobenzene,
Other halogenated organics	Benzyle chloride, Bromobenzene, Bromochloromethane, Bromodichloromethane, Bromoform, 4-Bromophenyl phenyl ether, bis(2-Chloroethyl)ether, 2-Chloroethyl vinyl ether, bis(2-Chloroisopropyl)ether, 1-Chloro-1-nitropropane, 4-Chloropropyl phenyl ether, Dibromochloromethane, 1,1-Dichloroethane, 1,2-Difluorotetrachloroethane, 1-Iodopropane, Hexachlorobutadiene, Pentachloroethane, 1,1,2,2-Tetrabromoethane, 1,1,2,2-Tetrachloroethane, 1,2,3-Trichloropropane, 1,1,2-Trichloro-1,2,2-Trifluoroethane
Substituted aromatics, phthalates, and miscellaneous organics	Chloroanilines, Chlorotoluenes, Nitrotoluenes, Benzyl butyl phthalate, Di-n-butyl phthalate, Diethyl phthalate, o-Anisidine, Phenyl ether, Tri-o-cresol phosphate
PCB mixtures	Aroclor 1221, Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254
Pesticides	Chlorodane, Chloropicrin, 1,2-Dibromo-3-chloropropane, 1,2-Dichloropropane, 1,2-Dichloropropylene, Dichlorvos, Disulfoton, Ethion, Ethylene dibromide, Malthion, Parathion

2.4.1 Chlorinated Solvents

In addition to the facts that large quantities of DNAPL solvents have been produced and used and these solvents have been able to enter the subsurface environment due to a variety of different source types, it is important to recognise that the physical, chemical and biological properties of the chlorinated solvents have made these chemicals particularly likely causes of groundwater contamination. The chemical and physical properties of chlorinated solvents are provided in Table 2-5. Pankow and Cherry (1996) summarise these properties and their implications as follows:

- The high vapour pressure of the chlorinated solvents led to a false sense of security regarding how these chemicals must be handled. Historically, it was believed that chlorinated solvent released to the unsaturated zone would easily vapourise to the atmosphere. Thus, when poured on dry ground, although a chlorinated solvent may appear to be entirely lost to the atmosphere, some will be transported into the subsurface by gaseous diffusion, by infiltration of contaminated water, and as a moving DNAPL phase. Once contamination reaches the saturated zone (including direct releases to the saturation zone), high volatility is of little assistance in removing the solvents: transport across the capillary fringe can be exceedingly slow (McCarthy and Johnson, 1992).
- The high densities of the chlorinated solvents (1.2 to 1.7 g/cm^3) relative to that of water (1 g/cm^3) mean that if a sufficient volume of a typical chlorinated solvent is spilled, then liquid solvent may be able to penetrate the water table. In the saturated zone, the unstable nature of the solvent flow causes the solvent to form thin “finger” that can lead to the collection of large amounts of solvent in one or more pools on the top of less permeable layers. Since a pool presents a very low cross-section to on-coming groundwater flow, absolute removal rates of dissolved solvent from the pool will usually be very low (Johnson and Pankow, 1992).
- The relatively low viscosities of the chlorinated solvents allow a relatively rapid downward movement in the subsurface. The chlorinated solvent mobility in the subsurface increases with increasing density/viscosity ratios (Cohen and Mercer, 1993).
- The low interfacial tension between a liquid chlorinated solvent phase and water allows a liquid chlorinated solvent to easily enter into small fractures and pore spaces, facilitating deep penetration into the subsurface. Low interfacial tension also contributes to the low retention capacities of soils for chlorinated solvents.
- The low absolute solubilities of the chlorinated solvents (typically on the order of hundreds of $\mu\text{g/L}$) mean that when a significant quantity of such a compound is spilled on the ground surface, liquid solvent will be able to migrate as a DNAPL phase in the subsurface, potentially accumulating as one or more pools on the tops of low permeability layers. The low solubility will then permit such pools to persist for decades to centuries (Johnson and Pankow, 1992).
- The high relative solubilities of the chlorinated solvents mean that a solvent spill can cause groundwater contamination at levels that are high relative to the concentrations that appear harmful to human health.

- The low partitioning to soil materials exhibited by the chlorinated solvents means that soil and rock materials will bind these compounds only weakly. This applies to both the unsaturated and saturated zones. Thus, sorption to soils will not significantly retard the movement of a chlorinated solvent, and zones of contamination can essentially grow as quickly as the groundwater can move.
- The low degradabilities of the chlorinated solvent compounds, either by biological means, or by the abiotic-chemical reactions, mean that the subsurface lifetimes of these chemicals can be very long.

Table 2-5: Chemical and Physical Properties of Chlorinated Hydrocarbons.

Chemical	Molecular Weight	Density (g/mL)	Solubility (mol/L)	Vapour Pressure (atm)	Henry's Law Constant (L atm/mol)	Octanol-Water Partition Coefficient
Vinyl chloride	62.5	0.9106a	4.47E-02 ^b	2.57E-01 ^b	22.3872 ^b	3.9811 ^b
Trans-1,2-Dichloroethylene	96.9	1.2565a	6.50E-02 ^c	4.29E-01 ^c	9.3758 ^e	114.815 ^d
Cis-1,2-Dichloroethylene	96.9	1.2837a	3.61E-02 ^d	2.63E-01 ^d	4.046 ^e	72.444 ^d
1,1-Dichloroethylene	96.9	1.218a	4.13E-03 ^c	6.50E-01 ^c	26.104 ^f	30.200 ^f
1,1-Dichloroethane	99	1.1757a	5.01E-02 ^b	3.02E-01 ^b	6.0256 ^b	61.6595 ^b
1,2-Dichloroethane	99	1.2351a	8.51E-02 ^b	9.12E-02 ^b	1.072 ^b	29.5121 ^b
Trichloroethylene	131.4	1.4642a	9.12E-03 ^b	9.77E-02 ^b	10.715 ^b	263.027 ^b
1,1,2-Trichloroethane	133.4	1.4397a	3.31E-02 ^c	3.99E-02 ^c	9.10E-01 ^f	239.8833 ^f
1,1,1-Trichloroethane	133.4	1.339a	8.51E-03 ^b	1.66E-01 ^b	19.498 ^b	301.995 ^b
Tetrachloroethylene	165.8	1.6227a	9.12E-04 ^b	2.51E-02 ^b	27.542 ^b	758.578 ^b

a=CRC (1983); b=Schwarzenbach *et al.* (1993); c=Mackay & Shiu (1981); d=Howard (1990); e=Gossett (1987);

f=Mackay & Shiu (1990)

The structural formula of TCE, 1,1,1-TCA and PCE are shown in Figure 2-10.

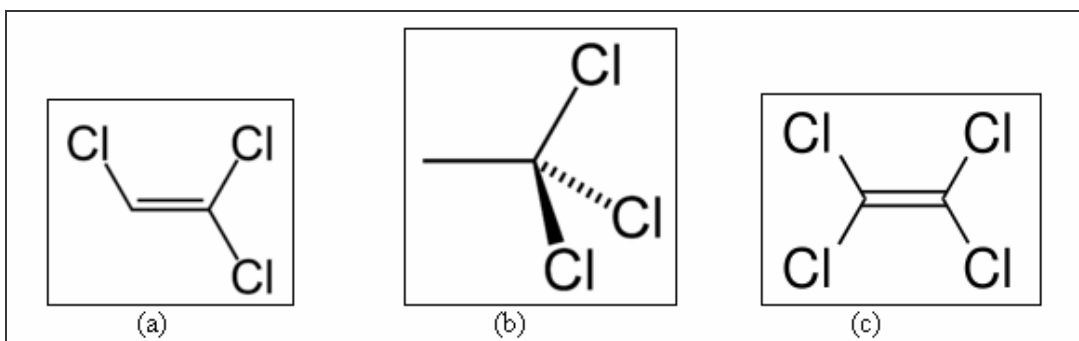


Figure 2-10: Structural formula of (a) TCE, (b) 1,1,1-TCA, and (c) PCE.

The high mobility of pure chlorinated solvents as compared to creosote/coal tar and PCB oil mixtures due to their relatively high density:viscosity ratios, is shown in Figure 2-12.

2.4.2 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. In the U. S., the only large producer of PCBs was Monsanto Chemical Co., which sold them between 1929 and 1977 under the Aroclor trademark for use primarily as dielectric fluids in electrical transformers and capacitors.

They were distributed in a variety of formulations differing from each other with respect to the amount and particular types of congeners. PCBs are formed when one to ten chlorine atoms are attached to a biphenyl molecule (Figure 2-11). Each Aroclor can be identified by a four-digit code. In most formulations, the first two digits in the code designate the number of carbon atoms in the biphenyl ring, while the last two digits designate the weight percent of chlorine. Aroclor 1254, for example, contains 12 carbon atoms in each biphenyl ring and 54% chlorine by weight. The composition and selected properties of various Aroclors are provided in Table 2-9.

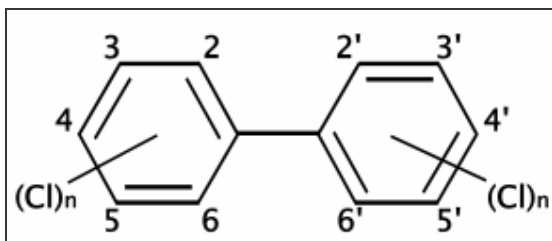


Figure 2-11: Chemical structure of PCBs.

2.4.3 Creosote and Coal Tar

Coal tar and creosote are oily DNAPLs that are generally translucent brown to black, are characterised by specific gravities that range between 1.01 and 1.20. Their viscosities are much higher than water (typically 10 to 70 cp), and have a distinctive odour of naphthalene (moth balls).

Creosote and coal tar are complex mixtures containing more than 250 individual compounds. Creosote is estimated to contain 85% polycyclic aromatic hydrocarbons (PAHs), 10% phenolic compounds, and 5% N-, S-, and O- heterocyclic compounds. The composition of creosote and coal tar are quite similar, although coal tar generally includes a light oil component (<5% of the total), consisting of monocyclic aromatic compounds such as benzene, toluene, ethylbenzene, and xylene (BTEX). Chemical composition data for coal tar and creosote are given in Table 2-7.

Table 2-6: Composition (percent) and selected properties of various Aroclors excluding carrier fluids (adapted from Cohen and Mercer, 1993).

Composition	AROCLOR						
	1221	1232	1016	1242	1248	1254	1260
Biphenyl	11.0	6.0	trace	-	-	-	-
Monochlorobiphenyl	51.0	26.0	1.0	1.0	-	-	-
Dichlorobiphenyl	32.0	29.0	20.0	17.0	1.0	-	-
Trichlorobiphenyl	4.0	24.0	57.0	40.0	23.0	-	-
Tetrachlorobiphenyl	2.0	15.0	21.0	32.0	50.0	16.0	-
Pentachlorobiphenyl	0.5	0.5	1.0	10.0	20.0	60.0	12.0
Hexachlorobiphenyl	-	-	trace	0.5	1.0	23.0	46.0
Heptachlorobiphenyl	-	-	-	-	-	1.0	36.0
Octachlorobiphenyl	-	-	-	-	-	-	6.0
Specific Gravity (at 25 – 15 °C)	1.2	1.3	1.4	1.4	1.4	1.5	1.6
Absolute Viscosity (cp at 38 °C)	5.0	8.0	20.0	24.0	70.0	700.0	resin
Solubility (µg/L at 25 °C)	200.0	-	240.0	240.0	54.0	12.0	2.7
Vapour Pressure (mm at 25 °C)	0.0067	0.0046	0.0004	0.0004	0.0004	0.00008	0.00004
Log K _{ow}	2.8	3.2	4.4	4.1	6.1	6.5	6.9

2.4.4 Miscellaneous DNAPLs

Miscellaneous DNAPLs refer to dense, immiscible fluids that are not categorized as chlorinated 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.

Table 2-7: Composition of creosote and coal tar, solubility of pure coal tar compounds, proposed RCRA groundwater action levels, and prevalence in groundwater at wood-treating sites (Cohen and Mercer, 1993).

CREOSOTE/COAL TAR FRACTION and compounds	1=Commercial creosote (USEPA, 1990d) 2=U.S. creosote (USDA, 1980) 3=German creosote (USDA, 1980) 4=Creosote (Mueller <i>et al.</i> , 1989) (Note: Relative weight percents of dominant compounds in each fraction given for creosote no. 4.)				1=Coal tar (GRL, 1987) 6=British coal tar (USDA, 1980) 7=U.S. coal tar (USDA, 1980)			Aqueous Solubility of Pure Compound (mg/L) (Montgomery and Welkom, 1990; and Mueller <i>et al.</i> , 1989)	Groundwater Action Levels Proposed 7/5/91 (mg/L)	GW Samples from 5 wood- treating Sites (Rosenfeld and Plumb, 1991)	Concentration in Groundwater Samples at 5 Wood- treating Sites (mg/L) Rosenfeld and Plumb, 1991)
	1	2	3	4	5	6	7				
VOLATILE AROMATICS					5%						
Benzene					0.10%	0.25%	0.12%	1780	0.005	22%	0.033
Ethylbenzene						0.02%	0.02%	152	0.7	19%	0.039
Toluene					0.20%	0.22%	0.25%	515	2	20%	0.048
Xylene					1%	0.19%	0.14%	200	10	18%	0.094
Styrene						0.04%	0.02%	300	0.005		
ACID EXTRACTABLES				10%	5%	-					

Phenol				20	0.70%	0.57%	0.61%	82000	20	12%	1.537
Cresols				30	1.10%	0.10%	0.97%	24000	2		
Pentachlorophenol				10				20	0.2		
Xylenols				35	0.20%	0.48%	0.36%	5000			
2,4-Dimethylphenol									0.02	13%	1.219
2,3,5-Trimethylphenol				5							
BASE/NEUTRALS				85%	28%						
Naphthalene	17.0%	3.0%	7.3%	13	10.9%	8.9%	8.8%	32	0.1	35.0%	3.312
Methylnaphthalenes	10.0%	2.1%	4.2%	21	2.4%	2.0%	1.9%	25		27.0%	0.563
Dimethylnaphthalenes				8	3.3			2			
Biphenyl	1.9%	80.0%		8				7			
Acenaphthene	7.8%	9.0%	4.1%	4	1.3%	0.96%	1.06%	3	2	38.0%	0.805
Fluorene	6.0%	10.0%	9.6%	8	1.6%	0.88%	0.84%	2	0.002	34.0%	0.661
Phenanthrene	19.4%	21.0%	12.6%	13	4.0%	6.30%	2.66%	1	0.002	29.0%	1.825
Anthracene	2.5%	2.0%		13	1.1%	1.00%	0.75%	0.07		21.0%	1.825
Fluoranthene	11.8%	10.0%	6.8%	4				0.3	1	22.0%	0.425
Pyrene	8.4%	8.5%	5.0%	2				0.1	1	22.0%	1.025
Chrysene	4.2%	3.0%	2.8%	2				0.002	0.0002	22.0%	0.666
Anthraquinone				1						13.0%	0.249

2,3-Benzo[b]fluorene				1				0.002	0.00005		
Methylantracene		4.0%		1				0.04			
Benzo[a]pyrene				1				0.003	0.0002		
Diphenyldmethylnaphth.			3.2%							8%	0.057
Diphenyloxide			3.4%			1.50%					
N,S,O- HETROCYCLICS				5.0%							
Quinoline				10				6700			
Isoquinoline				10				4500			
Caronzole	5.1%	2.0%		10	1.1%	1.3%	0.6%	1			
2,4-Dimethylpyridine				10							
Benzo[b]thiophene				10				130			
Dibenzothiophene				10				2			
Dibenzofuran				10				10		28%	0.332
PITCH					62.0%	59.8%	63.5%				
TOTAL	94.1%	75.40%	59.3%		91.0%	84.5%	82.6%				

RCRA = Resource Conservation and Recovery Act.

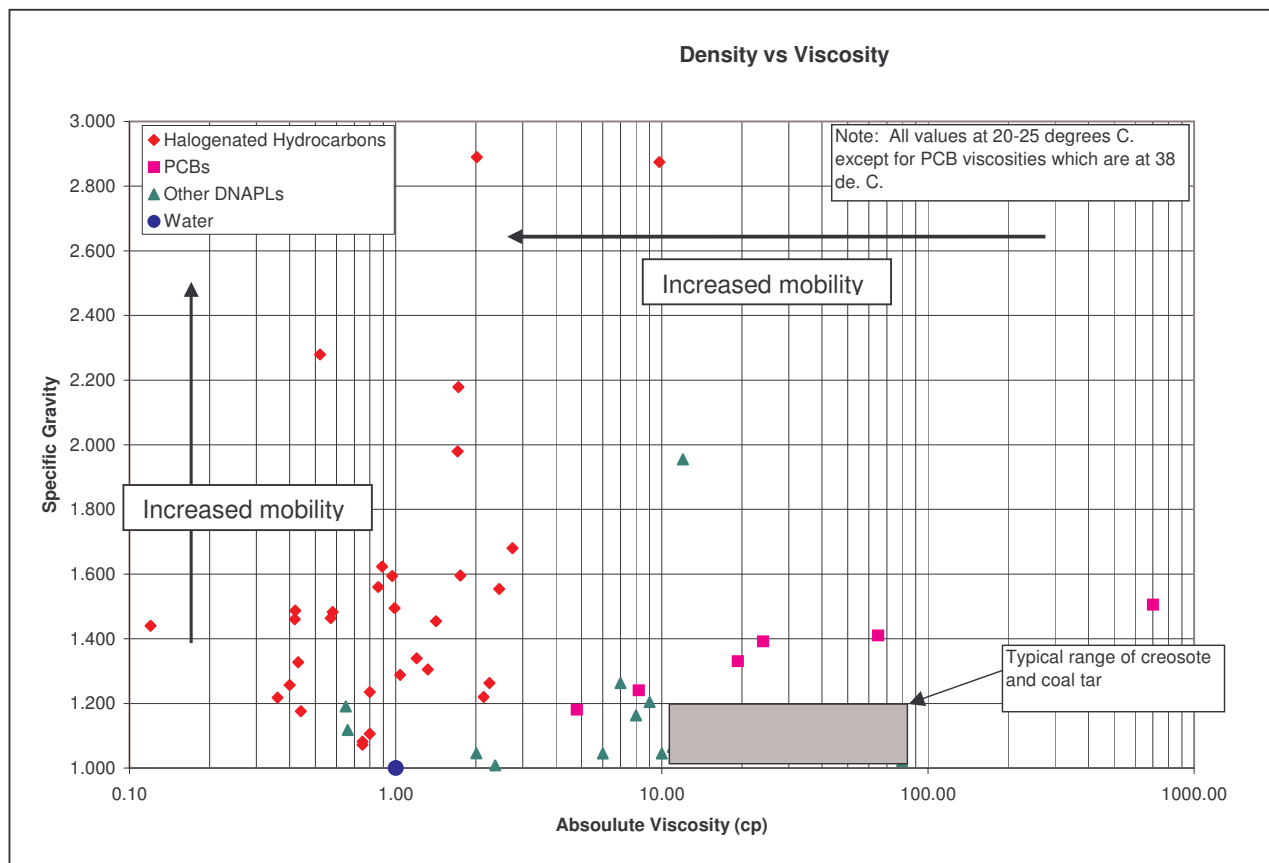


Figure 2-12: Specific gravity versus absolute viscosity of some DNAPLs. DNAPL mobility increases with an increasing density:viscosity ratio (Cohen and Mercer, 1993).

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 of the components is available to dissolve from the DNAPL into groundwater. Some of the components can even be less dense than water, but it is the combined density that gives the mixture its DNAPL character.

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.

2.4.5 Potential DNAPL Sources in South Africa

2.4.5.1 Industrial and Mining Activities

In South Africa, industrialisation dates back to the early discovery of minerals in the 1880s. Ever since, industrial activities have increased and spread all over the country. These include mining, agricultural and other domestic firms providing the growing

demands of civilization. Especially after World War II, there was a sharp increase in metal productions; particularly in iron, steel and other engineering products (Lumby, 1995).

Chemical industries arose in the nineteenth century as a result of the demand for explosives and chemicals to support the mining industry (Mbendi, 2003; Hohne, 2004).

Sasol and Secunda are large synthetic oil-from-coal plants established in the early 1980s for the purpose of strategic self-sufficiency fuel production. They are the major sources of chemical feedstocks and intermediates in South Africa (Mbendi, 2003). A plant for polyvinyl chloride (PVC) was established in 1955, and plants for polyethylene in 1966, polystyrene in 1964, synthetic rubbers in 1964 and latex in 1968 (Hohne, 2004).

South Africa's chemical industry is of substantial economic significance to the country; for example, the petrochemical industry is widely dispersed across various sectors of the economy. In general, organic chemical products from the petrochemical activity can be summarised as follows (after Hohne, 2004):

- Organic chemicals produced from the petrochemical industry, including ethylene, propylene, butadiene, benzene, toluene, xylenes, and methanol. Although as pure compounds, most of these are LNAPLs, when mixed with DNAPLs, the overall mixture density could be higher than water and behave like DNAPLs.
- Sasol produces about two million tonnes of a range of various olefins for the petrochemical industry per annum. About 0.6 million tonnes of olefins are used by the chemical industry, and the remaining 1.4 million tonnes are used in fuels.
- The Engen Refinery in Durban produces some benzene and other aromatics. Modest amounts of propylene are produced at the Sapref refinery in Durban. The Mosref plant generates mixed alcohol and ketone streams.
- Many byproducts such as solvents, phenols, tars, plastics, and rubbers are produced as intermediate chemicals from Sasol. While the major organic products are polyethylene, polypropylene, polyvinyl chloride, as well as nylon, polyester and acrylic fibers.
- Some of the main end products include: plastics, paints, explosives, and fertilisers. Chemicals like pharmaceuticals, agro-chemicals, bio-chemicals, food, fuel and plastics additives fall into this category, and are also produced as special end products.

The figure below (Figure 2-13) shows organic chemically based products manufactured annually in the country. Petroleum products are by far the highest production; however, potential DNAPL containing compounds could also be produced in large quantities, for example, in the industrial organic chemicals and fertilisers.

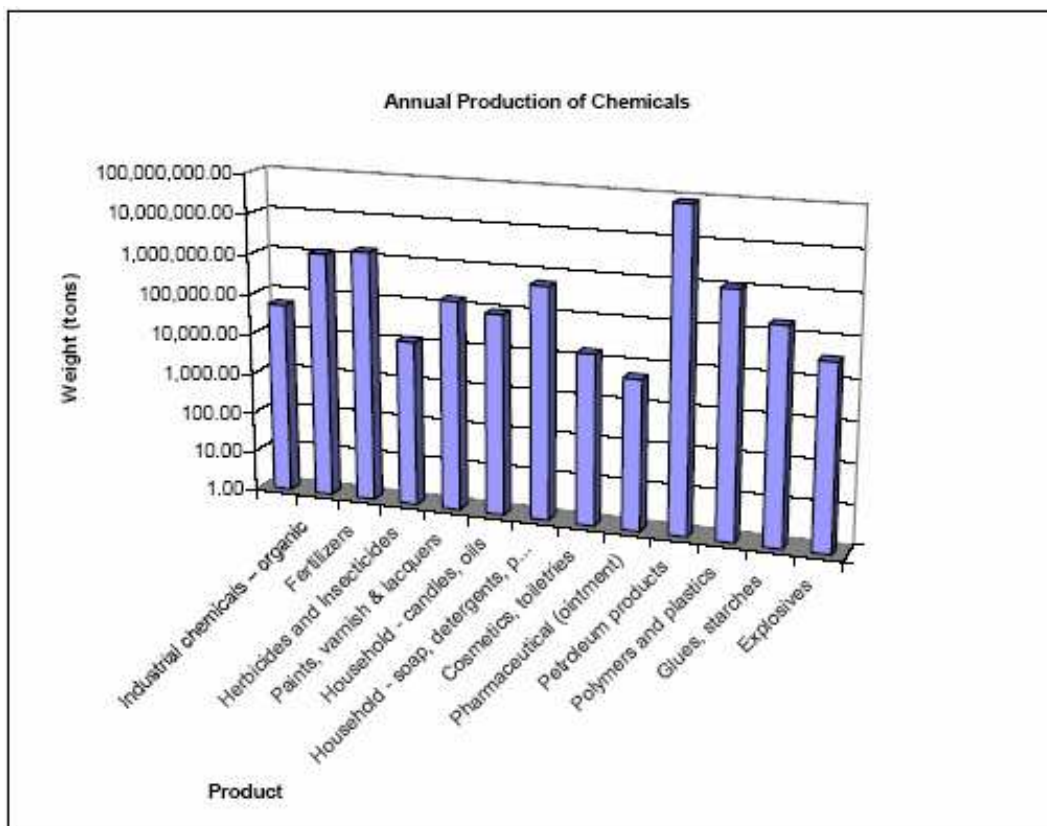


Figure 2-13: Annual production of organic compounds in South Africa (Hohne, 2004).

Distributions of various industrial and mining activities that potentially produce DNAPLs are plotted in Figure 2-14. In a text box below each industrial/mining map, the organic variables and DNAPLs most likely to be found as contaminants are listed. These do not represent all the contaminants that can be found in association with the specific industry.

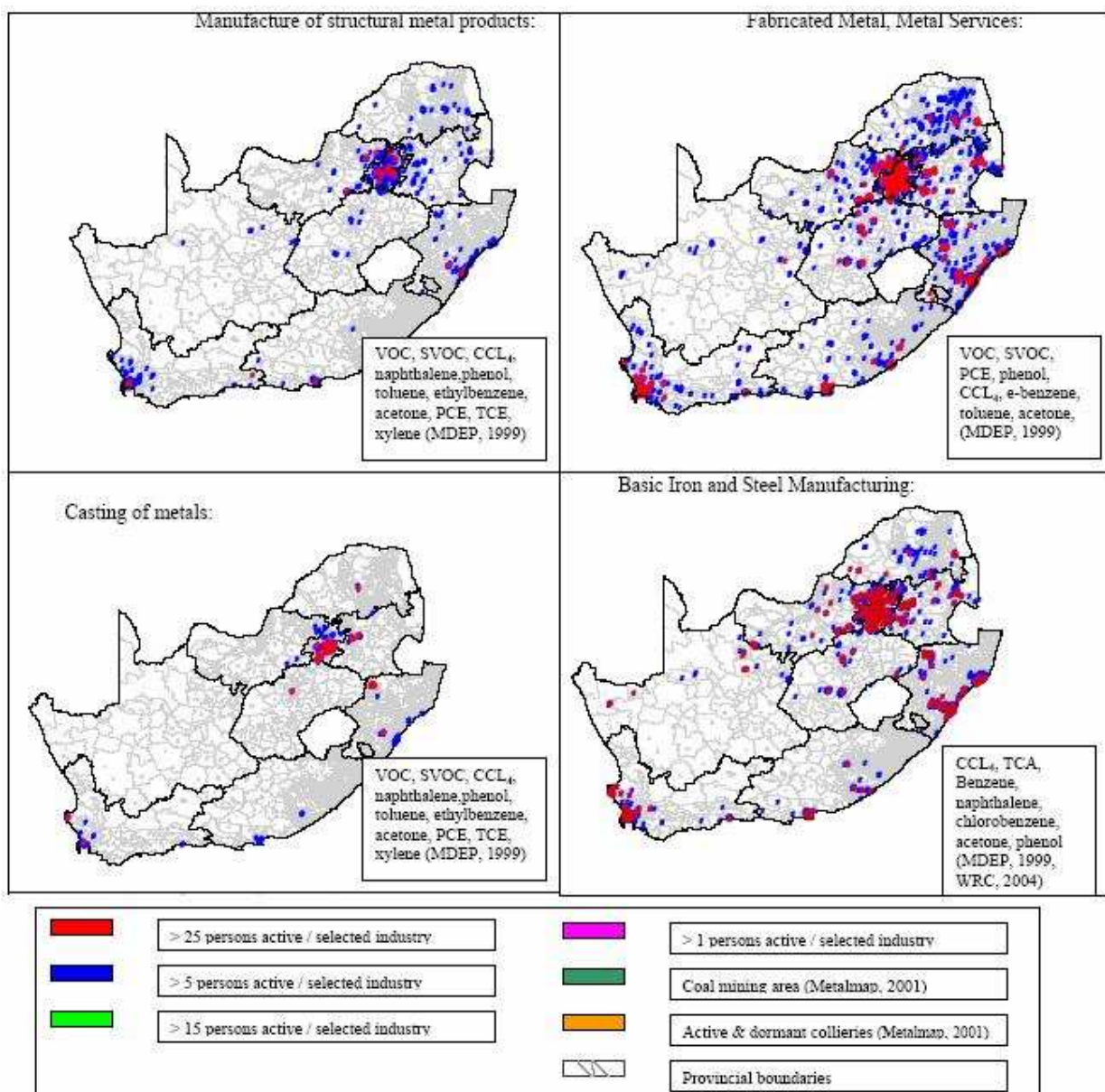


Figure 2-14: Distributions of various industrial and mining activities that potentially produce DNAPLs (after Hohne, 2004).

Due to a large number of chemical industries producing organic compounds, DNAPL contamination to the groundwater is highly probable. However, due to few studies and/or unreported incidents, cases of known DNAPL contamination are limited. A study was done by Usher *et al.*, (2004) on the identification and prioritisation of groundwater contaminants and sources in South Africa's urban catchments. The objectives of the investigations were to:

- identify and prioritise the type of contaminants and their associated sources that present a threat to groundwater, the environment and health in South Africa's urban catchments;

- Formulate strategies to better understand the impacts of polluting activities on groundwater resources in urban catchments;
- Establish a data information system on South Africa's contaminants.

From this study, a national South African priority list of contaminants and contaminant sources in urban areas has been established. This prioritization used the commonly cited example of a method for assessing groundwater pollution risk developed by Foster and Foster and Hirata (1988), as an initial step. Classification and prioritisation of groundwater contaminants is the first step in the method, to obtain "subsurface contaminant load" (SCL). Hirata & Johansson (2002) also refer to this step as establishing the "contaminant potential" in their later modification of the method. Foster and Hirata's (1998) procedures for the assessment of groundwater pollution risk were developed in the Latin American-Caribbean region and should be applicable for the type of urbanization that characterizes developing countries such as South Africa. The approach followed was also to consider contaminant class, intensity of contamination, mode of contaminant disposition and duration of contaminant load. For the research by Usher *et al.*, 2004, the potential toxicity and persistence was added to this approach, with persistence and transport also qualitatively considered, using a fuzzy logic framework to assist with ranking. In a similar way therefore to Johansson and Hirata (2002) a prioritisation of various generalised sources of groundwater contamination was done with activities classified into industrial, urban settlement, mining and waste disposal categories in the South African groundwater contaminant inventory.

Shockingly, the priority lists have shown that several high priority contaminants have not yet received adequate attention in terms of water management. A list of possible sources of organic contamination in South African groundwater is provided by Usher *et al.* (2004). The sources amount to 50 in number, 36 of which are NAPL contamination sources. Of the top ten ranked sources only on-site sanitation, cemeteries and feedlot/poultry farms are excluded from the list, indicating the possibility of DNAPL contamination.

As shown in the contaminant prioritisation list of Usher *et al.* (2004), 110 contaminants were listed as national prioritisation, out of which, 64 can be considered NAPL contaminants. For this prioritisation, it is possible to estimate the extent and seriousness of the NAPL problem in South Africa, as discussed by Pretorius (2007).

Table 2-8 lists examples of reported organic groundwater contamination in South Africa's urban catchments, originating from industrial activities. Although few in number, they provide some insight of the seriousness of NAPL contamination in groundwater. It is worth highlighting some of the serious pollution incidents listed in the table:

- A TCE contamination of up to 6 mg/L originated from a metal plating industry in Cape Town (Morris *et al.*, 2000).
- Chlorinated hydrocarbons of 100 mg/L originated from Umbogentweni Industrial Complex, in Durban (Palmer *et al.*, 2000).

Table 2-8: Case studies of mainly organic groundwater contamination related to organic compounds (and DNAPL) in South Africa (modified from Usher *et al.*, 2004).

Title	Urban area	Source	Major contaminants	Aquifer type	General findings	Lessons learnt	Reference
Metal plating industry	Cape Town	Leaks and spills in storage and production areas, improper treatment and disposal of wastes.	Cyanide (15-210 mg/kg in soils), and trichloroethene (TCE, 6-4089µg/l). Chromium, nickel, cadmium and zinc are also potential contaminants.	Unconfined primary sand aquifer.	Removal of contaminated soil and pump-and-treat programme (to control the contamination plume) were successful in decreasing TCE concentrations.	Potentially toxic metal ions react with ligands and alter their behaviour in the subsurface.	Morris <i>et al.</i> (2000)
Umbogentweni Industrial Complex	Durban	Seepage from unlined slimes dams, mercury ponds and buried drums (containing tar and chlorinated hydrocarbons).	Chlorinated hydrocarbons (100 mg/l), including 1,2-dichloroethane, tetrachloroethene, trichloroethene, cis-1,2-dichloroethene & vinyl chloride.	Shallow primary and deeper weathered secondary aquifers.	Both inorganic and organic contamination occur.	Hydraulic containment had to be implemented to avoid plume from reaching an informal settlement close by.	Palmer <i>et al.</i> (2000)
Shell Sapref Refinery	Durban	Underground pipelines that deliver the refinery's finished products to nearby industrial complex.	Alkanes and BTEX	Shallow primary and deeper weathered secondary aquifers.	Noted as the largest petrol spill in the history of South Africa more than 1 million litres of petrol has been recovered from remediation site up to date (ongoing to 2004). Five residences had to be evacuated due to fumes from contaminated soil.	Sound inspections and maintenance techniques are a necessity with regard to underground pipelines	Verweij (2003)

Title	Urban area	Source	Major contaminants	Aquifer type	General findings	Lessons learnt	Reference
Dow Sentrachem	Chloorkop industrial suburb of Ekurhuleni Metro	Seepage from wastewaters discharged to a channel from the production facility to the nearby evaporation ponds	Chloroform, tetrachloromethane, di-, tri- and tetra-chlorinated benzenes and chlorinated alkanes, hexachlorocyclohexane (HCH), DDT and degradation products , 2,4-dichlorophenol, etc.	Shallow primary and deeper weathered secondary aquifers.	Surface and groundwater, as well as soil and sediment, have been contaminated with the contaminants emanating from the discharge channel.	Organophosphates and their degradation products can be very persistent in soil and groundwater even years after the original source was removed.	Santillo, <i>et al.</i> (2002)
Hydrogeology of the Main Karoo Basin	Free State Towns	Leakage from petrol stations and fuel depots	Benzene, Toluene, Ethylbenzene-Xylenes.	Weathered fractured rock aquifers.	Concentrations several orders above suggested limits. Dissolved phase contamination severe even where no free phase was detected	Low permeability rocks can still cause widespread contaminant plumes. Absence of free phase does not indicate there is no pollution. Even in small towns NAPL pollution can be very problematic.	Woodford and Chevalier (eds). (2002)

2.4.5.2 Agricultural Activities

Agricultural activities began with the early civilisations in the country and have been recognised as a source of potential groundwater contamination in South Africa (Conrad *et al.*, 1999). This is mainly due to the intensive use of increased quantities of fertilisers (including sewage sludge and treated wastewater available from urban wastewater treatment plants) and pesticides/herbicides.

Agricultural activities that may cause DNAPL contamination in groundwater include (Conrad *et al.*, 1999; Usher *et al.*, 2004):

- Application of sewage sludge as a soil amendment
- Irrigation with wastewater
- Application of pesticides and herbicides
- Disposal of wastewater from abattoirs
- Accidental spills of agrichemicals
- Sludge application
- Pesticides
- Irrigation

The inappropriate use of pesticides in vineyards and orchards in Cape Town's urban areas poses a threat to groundwater (Usher *et al.*, 2004). Although most of their research was conducted on surface waters, there are a number of reports on detected pesticides in groundwater (Dalvie *et al.*, 2003; Solomons *et al.*, 2003; London *et al.*, 2000). An indication of possible threats of specific pesticides to groundwater can also be obtained from their sales and usage figures (Jovanovic and Maharaj, 2004). The causes of pollution can be attributed to normal usage via direct applications to agricultural land, as well as incorrect usage, handling, storage and disposal of current and obsolete pesticides. Obsolete chemicals include those that are banned, discarded and expired such as DDT and dieldrin, among others (Naidoo and Buckley, 2003).

Table 2-9 lists examples of reported organic groundwater contamination in South Africa's urban catchments, originating from agricultural activities. Although few, they provide insight of the seriousness of NAPL contamination in groundwater.

Table 2-9: Case studies of agricultural contamination (modified from Usher *et al.*, 2004)

Title	Urban area	Source	Major contaminants	Aquifers	General findings	Reference
The quality of surface and groundwater in the rural Western Cape with regard to pesticides	Hex River Valley, Piketberg, Grabow, outside major metro areas	Agriculture (predominantly vineyards and orchards)	Azinphos-methyl, chlorpyrifos, deltamethrin, endosulfan, iprodione, penconazole, prothiofos, simazine, vanmidothion	Table Mountain Group	Several pesticide species were detected in both surface and groundwaters in the peri-urban agricultural areas around Cape Town metro.	London <i>et al.</i> (2000), Dalvie <i>et al.</i> (2003), Solomons <i>et al.</i> (2003)
A preliminary survey of pesticide levels in groundwater from a selected area of intensive agriculture in the Western Cape	Hex River Valley, Western Cape, outside major metro areas	Agriculture (predominantly vineyards and orchards)	Aldicarb, bromopropylate, chlorpyrifos, copper oxychloride, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, dichlorovos, dimethoate, dinocap, diquat, endosulfan, fenamiphos, fenthion, fenvalerate, folpet, glyphosate, hexaconazole, iprodione, mancozeb, etc.	Table Mountain Group	The preliminary survey did not indicate groundwater contamination, despite high usage of pesticides.	Weaver (1993)
Intensive animal husbandry	Cape Town	Agricultural: vineyards, wheat farming, 1200 cows.	Pesticides, fertilisers, nitrate, ammonia, potassium, microbial	Shallow, unconfined, weathered zone of the Cape granite	Waste management is not practised efficiently at this site.	Conrad et al. (1999)

The potential organic contaminants associated with agricultural activities are predominantly synthetic organic pesticides. For the urban-agricultures, they are summarised as shown in Table 2-10.

Table 2-10: Contaminants associated with organic pollution sources from urban-based agriculture (Usher *et al.*, 2004).

Source	Synthetic organics
Sewage sludge	traces of industrial chemicals e.g. PAH
Wastewater irrigation	traces of industrial chemicals
Pesticide & herbicide application	carbarnates, chlorinated insecticides, chlorophenols, naphthalene, organo-phosphates, phenols, phthalates
Animal wastes	Hormones and steroids
Abattoirs	Pesticides, biogenic amines

2.4.5.3 Municipal/Domestic Activities

Although sources of DNAPL contamination from municipal activities is not fully studied yet, potential sources of groundwater contamination from waste disposal associated with municipal or domestic activities include (Usher *et al.*, 2004):

- Leakage of leachate from formal landfill sites
- Infiltration of leachate from informal solid waste dumps
- Infiltration of liquid wastes from industrial effluent lagoons
- Effluent irrigation on land
- Effluent discharge to rivers

Groundwater monitoring data from formal waste disposal sites suggest that, where sites are unlined or liners have failed, leachate from the waste site causes groundwater contamination. Accidents and polluting incidents primarily occur where waste disposal sites are poorly managed and/or not properly lined.

Liquid effluents may leach through the vadose zone into the aquifer undetected and contaminate the groundwater if the site is unlined, and plume migration is not controlled or effectively monitored. Early warning systems as well as controls should be in place to minimise the impacts of pollution and allow the timely control of contamination incidents.

3 Migration of DNAPLs in Fractured Aquifers

Understanding the physical behaviour of DNAPLs in the subsurface guides site investigation strategies and defines their migration pathways. DNAPLs can enter the subsurface as a separate non-aqueous phase liquid (NAPL), an aqueous phase (i.e., dissolved in water), and/or as a vapour phase. The different phases are the result of the geologic media, properties of the chemicals, and nature of DNAPL release to the subsurface (e.g. ongoing, episodic, or a one-time event release).

The movement, occurrence and ultimate distribution of DNAPLs after their release to the ground surface may be in one or more of the four aquifer types:

- Unsaturated zone
- Saturated porous aquifer
- Fractured non-porous aquifer
- Fractured porous (dual-porosity) aquifer

This chapter describes conceptual models for the behaviour of DNAPLs in ideal hydrogeologic settings. A brief overview and conceptual models on the migration of DNAPLs in unsaturated and saturated porous media is given in Section 3.1 and Section 3.2, respectively. A detailed explanation on DNAPL migration in fractured non-porous and fractured porous media is given in Section 3.3 and Section 3.4, respectively. The conceptual models are based on laboratory studies, field experiments, mathematical model results, as well as observations from many chemical spill and waste disposal sites in South Africa, and across the world.

3.1 Overview of DNAPLs in the Vadose Zone

When released to the subsurface, gravity causes DNAPL to migrate downward through the unsaturated zone to a capillary barrier. Due to capillary forces and heterogeneous grain sizes, lateral spreading may also occur. In this zone, DNAPLs migrate as a free-phase or volatiles in the soil gas. As the DNAPL migrates downward through the unsaturated zone, a significant portion is trapped at residual saturation by dead-end pores and interfacial tension with the individual grains.

In cases where the released volume is small and/or the thickness of the unsaturated zone great, the DNAPL may be immobilised above the water table. Figure 3-1 shows a conceptual model of a simplified vadose zone contaminated with DNAPL. DNAPLs are typically wetting with respect to air, thus they imbibe into dry, finer-grained layers. DNAPL in the unsaturated zone will therefore typically exist at negative pressure and will not flow into an open borehole or excavation (CLU-IN, 2000).

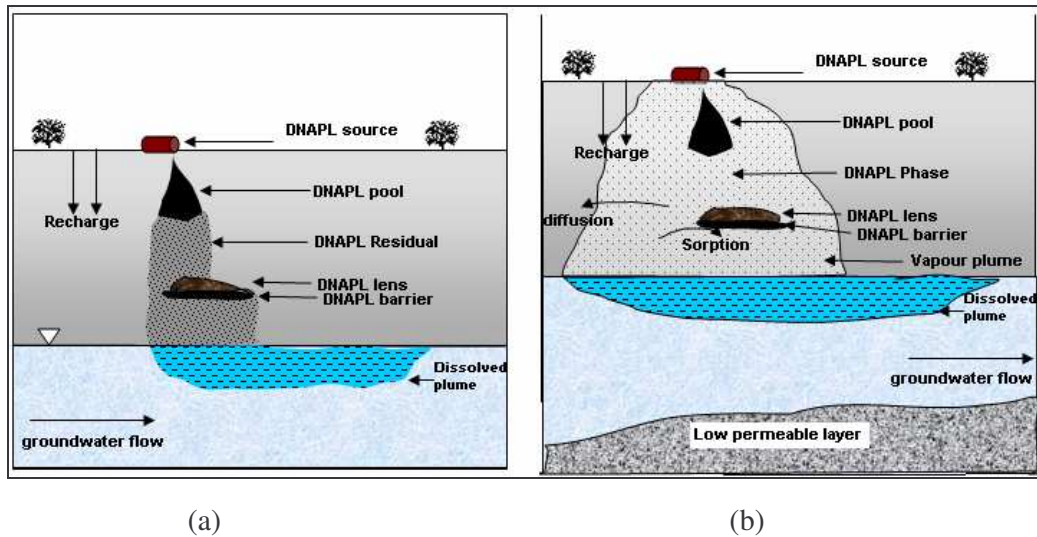


Figure 3-1 Conceptual model of a simplified vadose zone contaminated with DNAPL. (a) No vapour plume (wet and cold environment or low vapour pressure); (b) vapour plume with the effects of sorption (to aquifer material) and diffusion of the gaseous phase to the matrix porosity. (modified from Cohen and Mercer, 1993)

DNAPL migration through unsaturated porous media is extremely sensitive to bedding structure as a result of capillary forces. Figure 3-2 shows an experiment carried out by Poulsen and Kueper (1992) illustrating the migration pathways of DNAPL (PCE) in the unsaturated zone of a sandy aquifer. In this case, DNAPL was found to migrate distinctly through certain lenses and laminations and not through others. DNAPL migration was governed by gravity and geologic structures, with migration pathways always following the strike and dip of individual lenses and laminations. At times, the lenses and laminations through which DNAPL migration occurred were no more than a few millimetres in thickness. This subtle variation in hydraulic conductivity at the millimetre to centimetre scale, although sufficient to govern DNAPL migration, would be almost impossible to characterize at contaminated sites.



Figure 3-2: DNAPL migration pathways in unsaturated sands. DNAPL presence shows red due to SUDAN IV dye. Bedding dips 30° below horizontal (Poulsen and Kueper, 1992).

Once present in unsaturated media, residual and pooled DNAPL may vapourise, giving rise to vapour plumes. In dry and warm environments, vapourisation may deplete all residual and pooled DNAPLs in as little as a few years, depending on the vapour pressure of the particular DNAPL. However, if the subsurface temperature is low, the vapour phase, aqueous phase, and sorbed phase contamination may persist for several decades or longer.

3.2 Overview of DNAPLs in the Saturated Porous Media

With sufficient volume, DNAPL will migrate downward to the capillary fringe and saturated zone (provided enough is present after the residual is trapped left behind in the vadose zone). In porous media, the water and contaminant movement can occur in the connected pore spaces between the solid grains or particles. Below the water table, DNAPLs are found in an immiscible mobile phase, residual within the pores, or dissolved in water and forming plumes of contamination that travel in the direction of the groundwater flow. Due to their higher density, DNAPL may displace water and continue to migrate downwards, or laterally if high capillary layers are encountered. Figure 3-3 presents a general scenario illustrating the distribution of DNAPL in the saturated porous media.

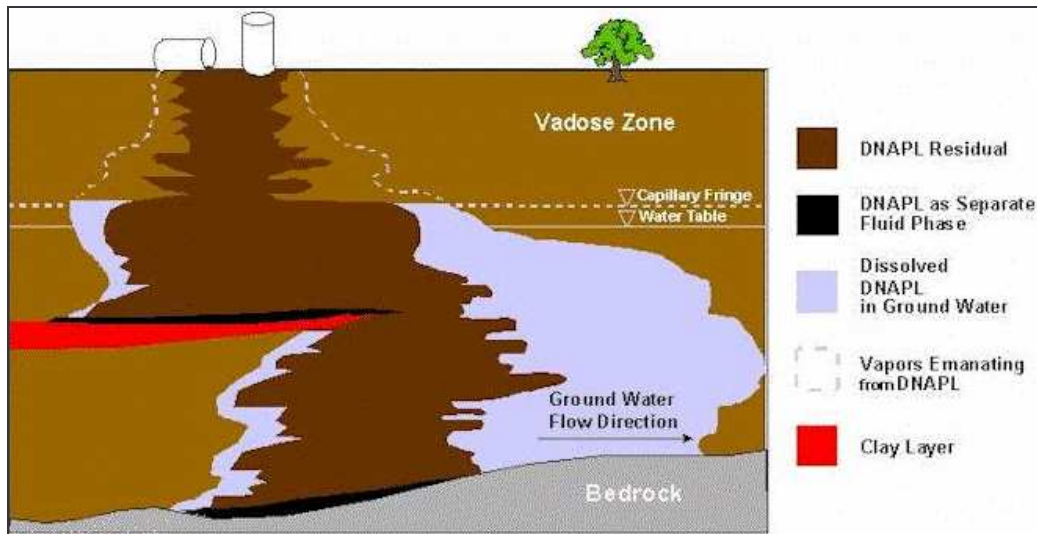


Figure 3-3: Conceptual model of a simplified saturated porous media contaminated with DNAPL (after Cohen and Mercer, 1993).

DNAPL is typically non-wetting with respect to water, and migration will tend to take place in coarser-grained materials. DNAPLs migrating below the water table will ultimately come to rest as both residual and pools when they reach the capillary barrier. DNAPL pools are most likely to form wherever a variation in permeability exists. DNAPL pooled below the water table exists at positive pressure and will therefore freely enter a borehole or excavation.

At a contaminated site, the spatial distribution of DNAPL migration pathways below the water table will be governed by geological structure, with migration not necessarily coincident with the direction of groundwater flow. During migration, DNAPL has the potential to pool and flow laterally whenever the capillary pressure at the leading edge of the migrating DNAPL body can no longer overcome the displacement pressure of an encountered lens or lamination (as shown in Figure 3-3). Since entry pressures are, in general, correlated with hydraulic conductivity, there is the potential for lateral or vertical DNAPL flow change wherever a variation in hydraulic conductivity exists.

As in the unsaturated zone, the field experiments conducted by Kueper *et al.* (1993) demonstrated that small-scale variations in hydraulic conductivity can govern the locations of residual and pooled DNAPL in the saturated zone. In general, the migration pathways of DNAPL in the porous media will be very tortuous and sparsely distributed making it extremely difficult to locate all individual DNAPL pools and residual zones. Mobile and immobile DNAPLs in the saturated zone will dissolve into the flowing groundwater, and thereby act as a source of long-term groundwater contamination.

Just as in the unsaturated zone, DNAPL transport upon a low permeability layer will be governed in large part by the layer's slope. If the layer slopes in a direction opposite to that of the groundwater flow direction, DNAPL may migrate in a direction opposite to the flow following the slope (Figure 3-4).

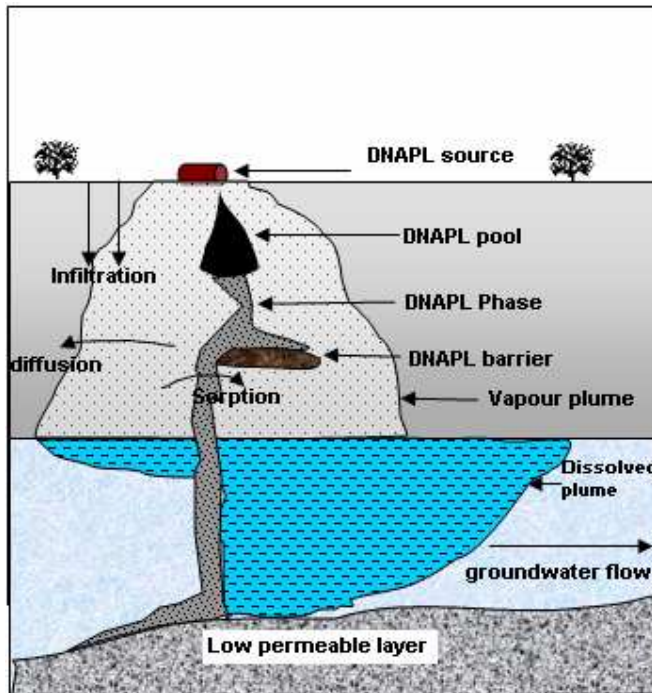


Figure 3-4: DNAPL movement in the saturated zone following the slope of the geology, opposite to the groundwater flow (adopted from Shapiro (2006)).

3.3 DNAPL Migration in Fractured Non-Porous Media

In some South African aquifers it was observed that the thickness and type of unconsolidated materials may prevent DNAPL releases from reaching bedrock. The amount of DNAPL retained in the sediments depends on the physical and chemical properties of the unconsolidated sediments as well as the DNAPL. However, the bulk retention capacity of most types of porous media to chlorinated solvents is low and even small volumes will in general have the potential to migrate down to the base of these overburden deposits. The DNAPL forms pools on the surface of the bedrock and if the capillary pressure at the bottom of the pool exceeds the entry pressure of the fracture, will proceed to enter the fracture as shown in Figure 3-5.

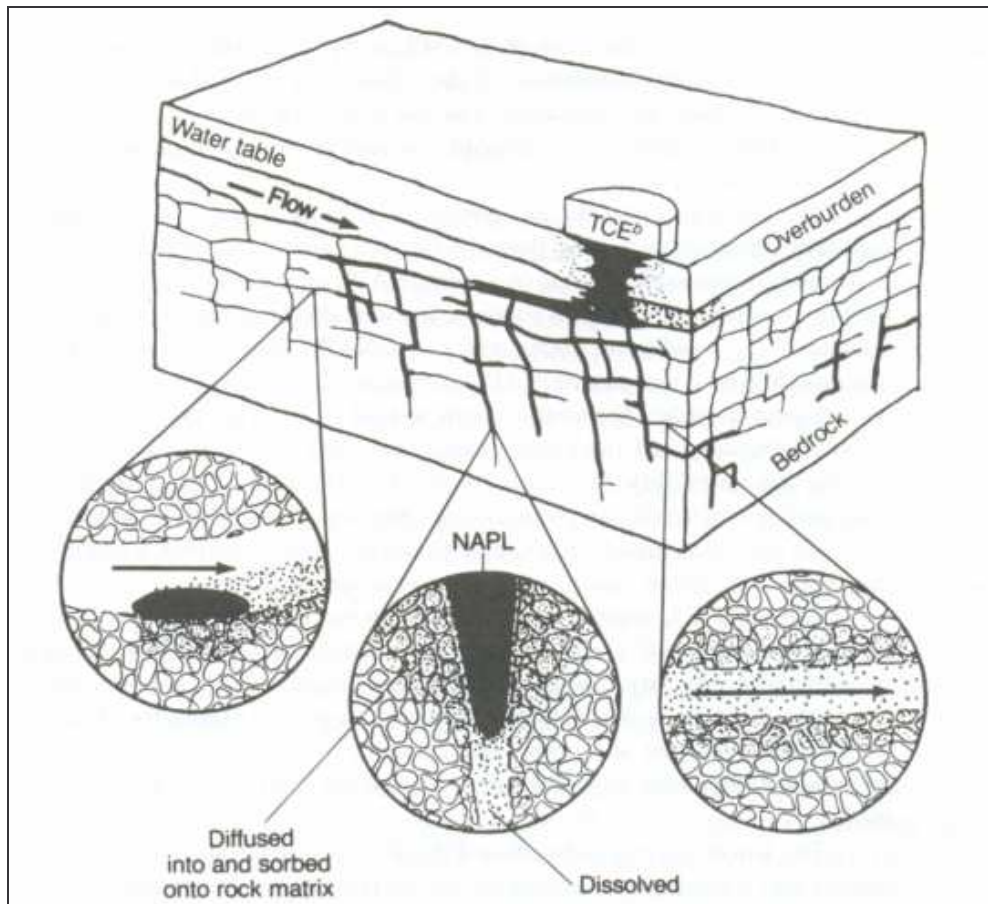


Figure 3-5: Fractured migration in fractured aquifer (Mackay and Cherry, 1989)

3.3.1 DNAPL Entry into Fractures

If the capillary pressure at the base of a pool is greater than the entry pressure of the fracture, the DNAPL enters the fracture underlying the pool. Schematically, this relationship is shown in Figure 3-6. The fluid on the concave side of the interface is at a higher pressure.

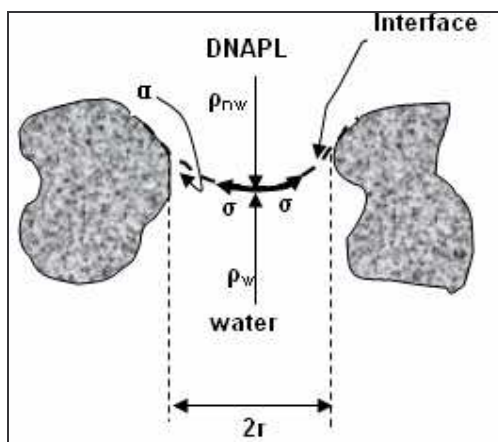


Figure 3-6: Forces acting on a DNAPL/water interface.

Since the DNAPL is usually non-wetting with respect to water, assuming a hydrostatic equilibrium in the system, the capillary pressure at the base of the pool is given by the difference in absolute pressures of the non-wetting (P_{nw}) and wetting (P_w) phases.

$$P_c = P_{nw} - P_w$$

Equation 3-1

Which may also be expressed as:

$$P_c = (\rho_{nw} - \rho_w)gh$$

Equation 3-2

where

P_c = capillary pressure (Pascal, Pa)

ρ_{nw} = density of the non-wetting phase, DNAPL (kg/m^3)

ρ_w = density of wetting phase, water

g = gravitational constant (m/s^2)

h = height of the pool (m).

Equation 3-2 assumes that the top of the pool exists at a capillary pressure of zero. According to Keuper and McWhorter (1991), the entry pressure of a rough-walled fracture is:

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

Equation 3-3

where

P_e = entry pressure of the fracture (Pa)

σ = interfacial tension between DNAPL and water (N/m)

θ = contact angle on the fracture walls (degrees)

e = fracture aperture (m)

By combining Equation 3-1 and Equation 3-2, one can derive an equation for the minimum pool height required for a DNAPL to enter a fracture:

$$H = \frac{2\sigma \cos \theta}{(\rho_{mw} - \rho_w)ge}$$

Equation 3-4

where

H = minimum pool height required to enter a fracture (m)

From Equation 3-4, it is clear that much greater pool heights are required for a low density DNAPL to start to enter fractures for a given interfacial tension. The minimum pool height required for entry into a fracture is directly proportional to the DNAPL-water interfacial tension, and inversely proportional to the difference in fluid densities and the fracture aperture. It is also important to note that the minimum pool height indicated by Equation 3-4 is independent of depth below the water table. This is consistent with the fact that capillary pressures dictate the behaviour of the two-phase systems, with absolute pressure having very little influence in near-surface environments (Pankow and Cherry, 1996).

Table 3-1 lists the vertical accumulation of various DNAPLs in a fracture network. The fracture aperture (in μm) required to support the accumulation of DNAPLs is given by assuming water density to be equal to 1000 kg/m^3 and gravitational acceleration as 9.806 m/s^2 . These data are produced by using Equation 3-4 above.

Table 3-1: Minimum pool height required for DNAPLs to enter a fracture (Kueper *et al.*, 2003).

Height of accumulation (m)	Mixed composition DNAPL (μm)	Coal tar/creosote (μm)	TCE (μm)
0.1	407.9	815.8	88.7
0.2	203.9	407.9	44.3
0.5	81.6	163.2	17.7
1.0	40.8	81.6	8.9
2.0	20.4	40.8	4.4
3.0	13.6	27.2	2.9
4.0	10.2	20.4	2.2

All three DNAPLs are assigned interfacial tension of 0.020 N/m . DNAPL densities are: $1,100 \text{ kg/m}^3$ (mixed composition); $1,050 \text{ kg/m}^3$ (coal tar/creosote) and $1,460 \text{ kg/m}^3$ (TCE).

Figure 3-7 illustrates the data in Table 3-1. For chlorinated solvents such as TCE, fracture apertures need to decrease quickly with depth in order to prevent further downward migration. Even a 1 m accumulation of TCE in fractured rock would require apertures to be no larger than $9 \mu\text{m}$ at the base of the accumulation in order to prevent further downward migration (Kueper *et al.*, 2003). (By way of comparison, a

human hair is approximately 50 μm thick). Kueper *et al.* (2003) explain that fractures remain open to depths of many hundreds of metres in many rock types, with measured apertures in the order of hundreds of micrometres at many sites.

Figure 3-7 assumes that water is wetting with respect to the DNAPL of interest. Less dense DNAPLs such as creosote and coal tar do not require such drastic reduction in fracture aperture with depth to block downward migration, but significant reductions are still required to support an accumulation of DNAPLs. A head of creosote or coal tar of 2 m, for example, would require all fracture apertures below the DNAPL to be less than 41 μm to prevent downward migration. All fractures are rough-walled and therefore exhibit a range of apertures within the fracture plane. In the above example, the largest aperture within the fracture plane needs to be restricted to 41 μm or less in order to arrest downward DNAPL migration.

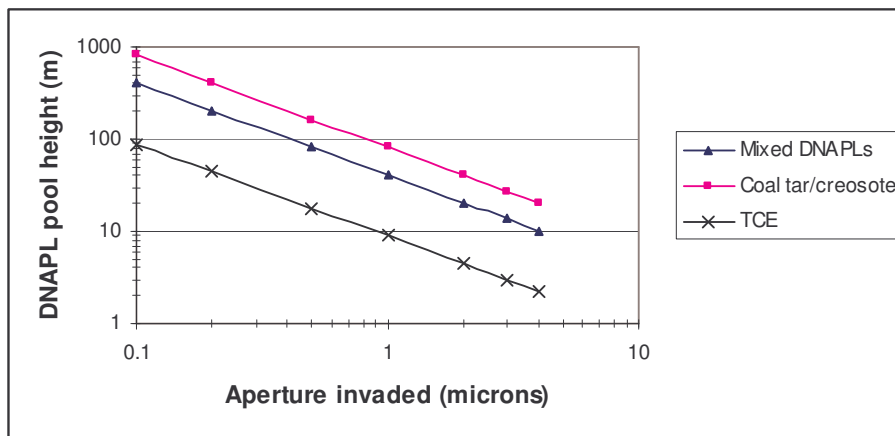


Figure 3-7: Pool height vs. fracture aperture invaded provided in Table 3-1.

Once a DNAPL enters a fracture or fracture network, if the DNAPL is allowed to extend itself vertically while remaining a continuous phase, progressively smaller aperture fractures will be invaded. This means, the capillary pressure at the base of the DNAPL accumulation is a function of not only the pool height in the overburden overlying fractures in question, but also the height of DNAPL accumulated in fractures beneath this pool (Pankow and Cherry (1996). This can be explained by the scenario discussed by Pankow and Cherry (1996): Figure 3-8 shows a 0.25 m high accumulation of TCE in a local bedrock depression. The TCE-water interfacial tension is assumed to be 0.04 N/m. The capillary pressure at point A is 1,127.7 Pa, implying that fractures as small as 70 μm will be invaded (Equation 3-4 for vertical flow). In Figure 3-8, the aperture at point A is greater than this and DNAPL enters the fracture network. If the DNAPL were to stop moving and reach a static distribution as shown, the capillary pressure at points B and C would be 5,638.5 Pa and 10,149.2 Pa, respectively. This would require that the fracture apertures at points B and C be no larger than 14.2 μm and 7.9 μm , respectively. Since such a rapid reduction in fracture

aperture with depth is not likely in a rock environment, it is probable that the pool will not come to rest as shown, but will rather continue to drain into the fracture network until it is completely depleted.

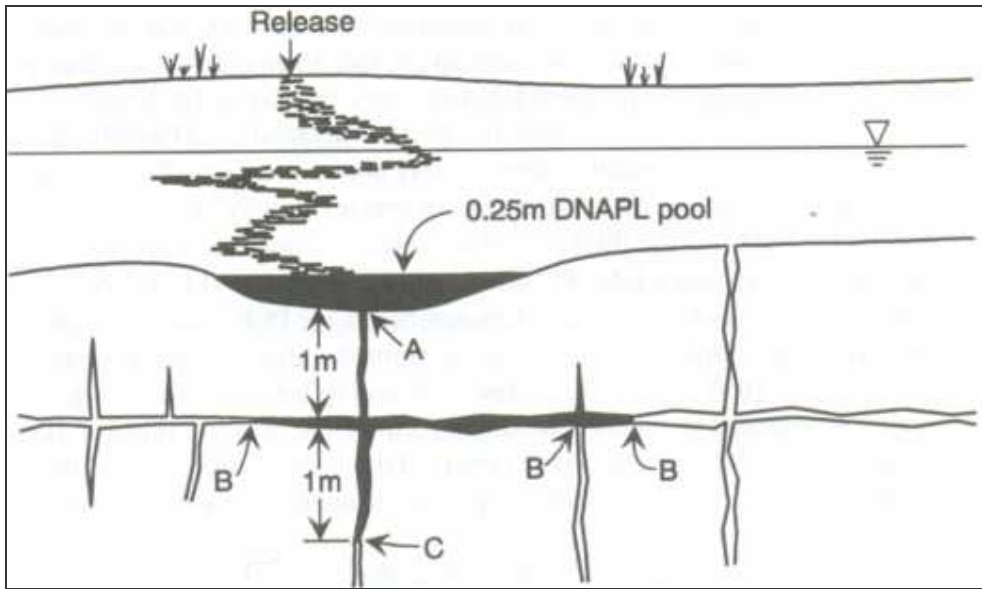


Figure 3-8: Pool of TCE in bedrock depression. TCE can enter progressively smaller aperture fractures with depth as a result of an increase in capillary pressure brought about by vertical accumulations (Pankow and Cherry, 1996).

3.3.2 DNAPL Flow Rates in Vertical Fractures

As demonstrated in Equation 3-4, larger fracture apertures provide the least entry pressure and DNAPLs flow through them preferentially. DNAPLs will continue to invade smaller fractures, depending on their capillary pressures, and will move vertically or laterally, as dictated by the orientation of the fractures. To investigate the rates at which DNAPLs can traverse a fractured aquifer, numerical simulations were carried out by Pankow and Cherry (1996) using the DNAPL fracture migration model developed by Kueper and McWhorter (1991).

A DNAPL pool height of 5 m was assumed to rest on top of bedrock with vertical fracture. Then the invasion rate of the DNAPL was evaluated at various fracture apertures. Figure 3-9 presents a plot of the time taken for DNAPL to first reach the lower aquifer as a function of fracture aperture. Two cases are shown, one for the DNAPL density of 1200 kg/m^3 and one for a density of 1460 kg/m^3 . It is clear that the first arrival times are very sensitive to fracture aperture, which is consistent with the fact that fracture transmissivity is proportional to the cube of the aperture (De Marsily, 1986). For the higher density case, very short first arrival times are exhibited for fracture apertures larger than $50 \text{ }\mu\text{m}$. The lower curve approaches an asymptote at an aperture of $39.9 \text{ }\mu\text{m}$, which is the smallest aperture that can be invaded by the 5 m high pool. For the lower density case, the first arrival times are longer and the

asymptotic aperture is higher since the 5 m pool height generates a smaller capillary pressure, and since the gravity driving force is reduced. It follows that larger pool heights and lower viscosities will generally bring about quicker first arrival times.

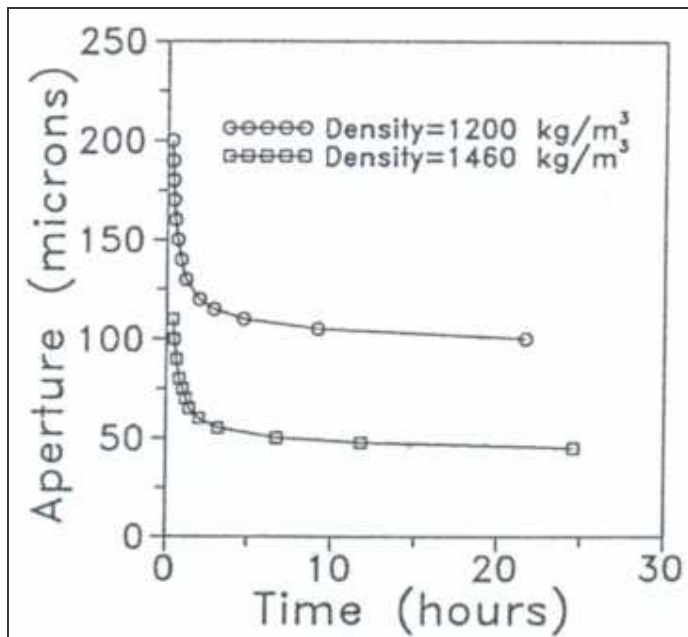


Figure 3-9: Time taken for a first arrival of DNAPL to move 5 m versus fracture aperture (Pankow and Cherry, 1996).

3.3.3 DNAPL Mobilisation due to Pumping

DNAPL pools can be mobilised by pumping because of the increase in capillary pressure created during head decrease. Assume a DNAPL pool is formed above a fractured aquifer as shown in Figure 3-10, such that the capillary pressure at the base of the DNAPL pool is insufficient to bring about entry into fractures. Water pressure in the aquitard will be lowered from below if pumping at high rate is done in a borehole situated beneath the fractured aquitard. This will result in an increase in capillary pressure at the base of the DNAPL pool, promoting the entry of DNAPL into fractures, and the extent of contamination will be worsened. If the height of the DNAPL pool above the fracture is very close to the minimum height required for fracture entry, even pumping at a lower rate that creates small decrease in pressure from below is potential for DNAPL migration to previously not invaded fractures.

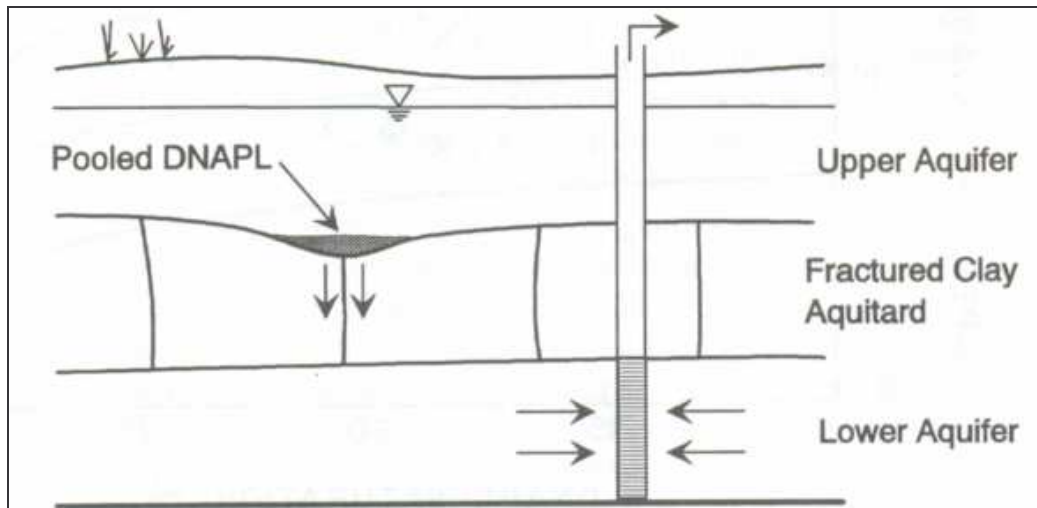


Figure 3-10: Mobilisation of DNAPL pool due to pumping (Pankow and Cherry, 1996).

3.3.4 Influence of Interfacial Tension in the Fracture Network

As discussed previously, once the initial entry into a fracture network takes place, a DNAPL will preferentially migrate through larger aperture fractures, entering intersecting fractures only if the local capillary pressure exceeds the entry pressure of the newly encountered fractures. One fluid parameter that has a dramatic influence on the overall migration pathways of DNAPL is interfacial tension (see Equation 3-3).

Figure 3-11 shows a fracture network with intersecting horizontal and vertical fractures of different permeabilities and a source of DNAPL release on the top of the network. The upper section of the fracture network has higher permeability (bigger apertures) than the lower part of the network. Figure 3-11 (a) shows the conceptualised DNAPL migration pathways when the DNAPL has a lower interfacial tension. As can be seen, a larger number of individual fractures are invaded because the fracture entry pressures are low. This results in little lateral spreading through the fracture system and larger ultimate depths of migration.

Figure 3-11 (b) illustrates the movement pathways due to a DNAPL with higher interfacial tension with water. In this case, not as many individual fractures are invaded because fracture entry pressures are higher. The pool height in the lagoon and the density driving force can only generate capillary pressures that are sufficient to enter the largest aperture fractures. In addition, substantial lateral flow takes place above the less permeable rock unit since high capillary pressures are required for invasion. Even if the lower permeability rock unit becomes invaded, lateral flow will continue above it since the relative permeability to DNAPL will be higher in the overlying, more fractured unit. As shown in the figure, large amounts of lateral spreading can occur through major bedding partings. Since the DNAPL-water interfacial tension largely dictates what the ultimate lateral and vertical extent of

DNAPL migration will be in a fracture network, care should be taken to have this value measured whenever a sample of the DNAPL of interest can be obtained.

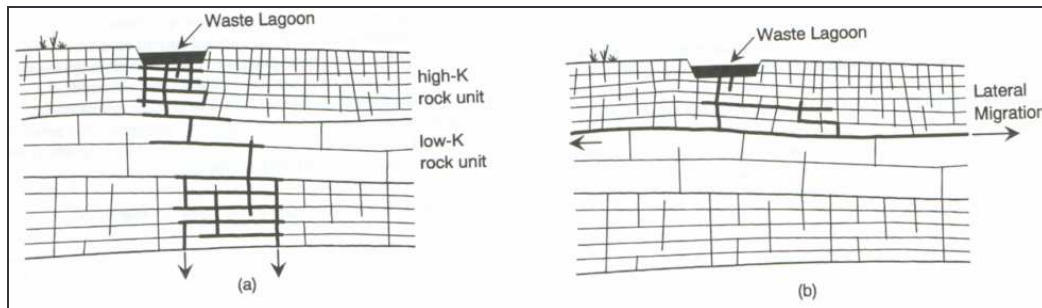


Figure 3-11: a) DNAPL migration pathways for a low interfacial tension system; b) DNAPL migration pathways for a light interfacial tension system (Pankow and Cherry, 1996).

3.3.5 Influence of Fracture Orientation

DNAPL movement in fracture networks is not only determined by the physiochemical properties of the DNAPLs, but also by the fracture density, orientation and connectivity, as shown in Figure 3-12. As in the porous media, DNAPL movement is largely controlled by geologic structures. DNAPL will migrate through those pathways that offer the least capillary resistance. These pathways will not necessarily be the same as those involved in the flow of the groundwater. Moreover, since hydraulic gradients in most natural groundwater systems are typically very low, they will have little influence on the direction of DNAPL migration through the fractures. A comprehensive monitoring program in fractured media should therefore focus on having boreholes placed according to geologic structure, and not necessarily according to the direction of groundwater flow. Although the fractures comprise a complex system, their presence or position follow some tectonic rules that should be observed to help in a mapping.

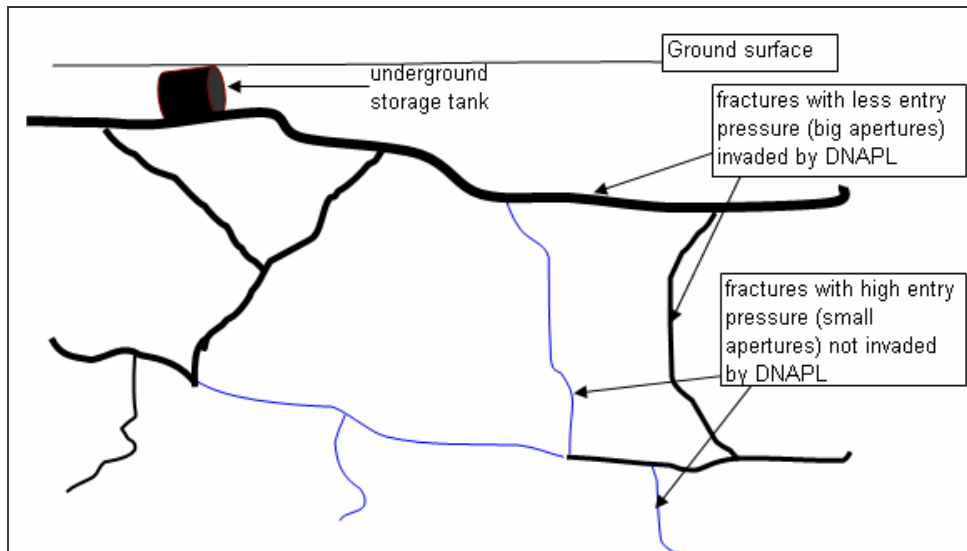


Figure 3-12: DNAPLs migrate preferentially through big aperture fractures and continue to enter small fractures only when their capillary pressure exceeds the entry pressure.

3.3.6 DNAPL Elevation in a Borehole in a Fractured Network

DNAPL elevation and thickness measurements are made in boreholes to assist the determination of fluid potentials, flow directions, and immiscible fluid distributions. With knowledge of DNAPL entry areas, the surface slope of capillary barriers, hydraulic data, and other observations of DNAPL presence, borehole data can be evaluated to infer the directions of DNAPL migration. The interpretation of data from boreholes containing DNAPL may be complicated by several factors related to the measurement method, fluid properties, borehole design, or borehole location. DNAPLs in boreholes should therefore be evaluated in conjunction with evidence from geologic conditions and DNAPL presence obtained during drilling.

Figure 3-13 presents a series of figures where boreholes have intersected a DNAPL pool in fractured media. In Case A, the presence of DNAPL in the borehole corresponds to the presence of DNAPL in the formation at the same general elevation. If the top of the pool in the formation exists at a capillary pressure of zero, the elevation of the water-DNAPL interface in the borehole will equal the elevation of the top of the pool in the formation. What is not known, however, is the distance to which the pool extends below the borehole.

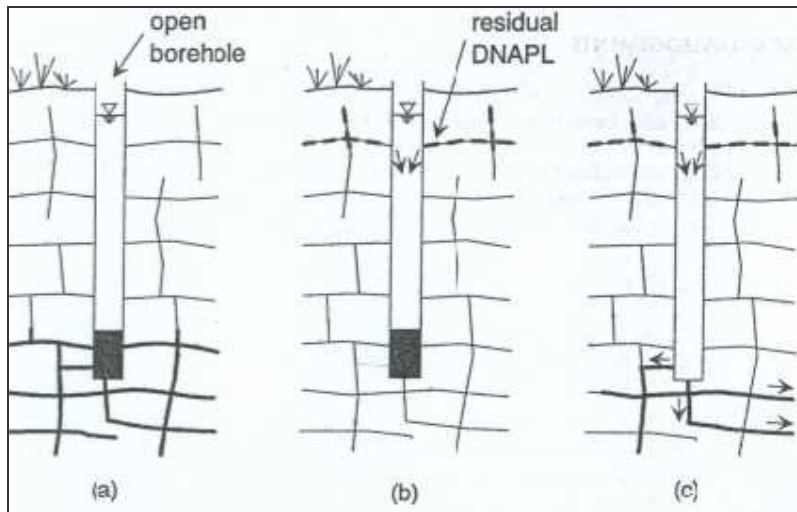


Figure 3-13: Elevation of DNAPL in boreholes located in a fracture network (after Pankow and Cherry, 1996).

In Case B, the identical height of DNAPL exists in the borehole as in Case A, but no DNAPL is present in the formation at this elevation. In this case, DNAPL has entered from an upper elevation and accumulated at the base of the borehole. The DNAPL does not exit the borehole because the height of accumulation is insufficient to generate the capillary pressure in excess of the entry pressure of the local fractures. Case C illustrates a case of borehole short-circuiting where the capillary pressure has exceeded the fracture entry pressures, resulting in penetration of fracture at a lower elevation.

3.4 DNAPL Migration in Dual-porosity Media

For certain field situations, the fractured medium has an insufficient matrix porosity to allow significant contaminant mass, either as the DNAPL phase itself, or dissolved in groundwater, to enter the matrix. For others, however, the porosity of the matrix material can have important effects on the fate and behavior of DNAPLs in fracture networks. Fractured geologic media, in which the matrix porosity is most likely to have a significant influence on DNAPL behaviour, include sedimentary rocks in which matrix porosity is appreciable; for example, shales, siltstones, sandstones, limestones and dolomites. Most rocks in the TMG and Karoo Supergroups in South Africa are typically dual-porosity aquifers. Crystalline rocks such as granites and marble generally have insignificant matrix porosity. Figure 3-14 illustrates a hypothetical conceptual model of DNAPL migration in an aquifer system composed of layers of different matrix and fracture porosities.

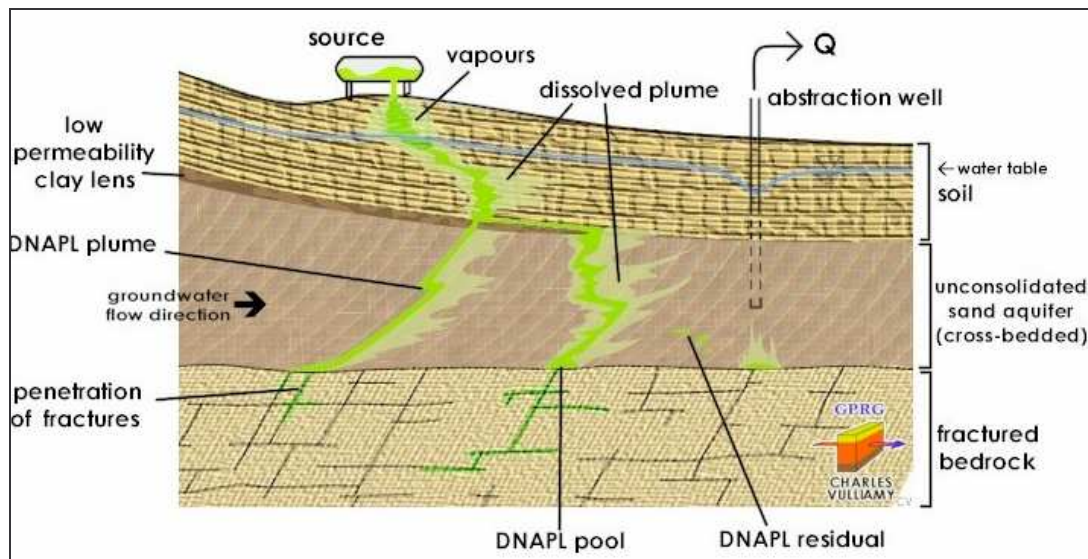


Figure 3-14: A hypothetical conceptual model of DNAPL migration in an aquifer system composed of different layers of different matrix and fracture porosities (www.dnapl.group.shef.ac.uk).

3.4.1 DNAPL Diffusion in Dual-Porosity Aquifer

Once DNAPL is present in fractured porous rock in the form of residual and pools, dissolution into flowing groundwater will occur, giving rise to aqueous-phase plumes. Dissolution will also occur in the matrix as a result of molecular diffusion, resulting in contaminants being stored in the aqueous phase and sorbed to solid particles. The rate of DNAPL diffusion into the matrix of fractured rock is dependent upon a variety of factors; primarily the aqueous solubility of the DNAPL (concentration) and the porosity of the matrix. For a highly soluble DNAPL and/or a moderate to high matrix porosity, the dissolution rate can be high (Parker *et al.*, 1994).

If the matrix has the capacity to store more contaminant mass than is present in the fractures in the form of residual and pooled DNAPL, the DNAPL will eventually completely deplete itself as a result of molecular diffusion as illustrated in Figure 3-15. At early times, Figure 3-15 (a), immobile DNAPL and water co-exist in the fractures; the DNAPL is the non-wetting fluid and is present in the largest aperture regions in the fractures, in accordance with capillary pressure considerations. In Figure 3-15 (b), a significant amount of the DNAPL has dissolved, thereby causing the remaining DNAPL to disconnect and redistribute within the larger fracture aperture regions so as to achieve minimal interfacial energy between the two fluids. Eventually (Figure 3-15 (c)), the DNAPL dissolves completely, resulting in its disappearance as a separate phase. The chemical mass then exists as diffusion haloes around the fractures that once contained DNAPL. The time periods required for complete DNAPL phase disappearance are specific to the chemical and porous medium conditions. Subsequent flushing of the fractures with uncontaminated

groundwater will cause diffusion out of the matrix and into the moving groundwater as the concentration gradient is reversed.

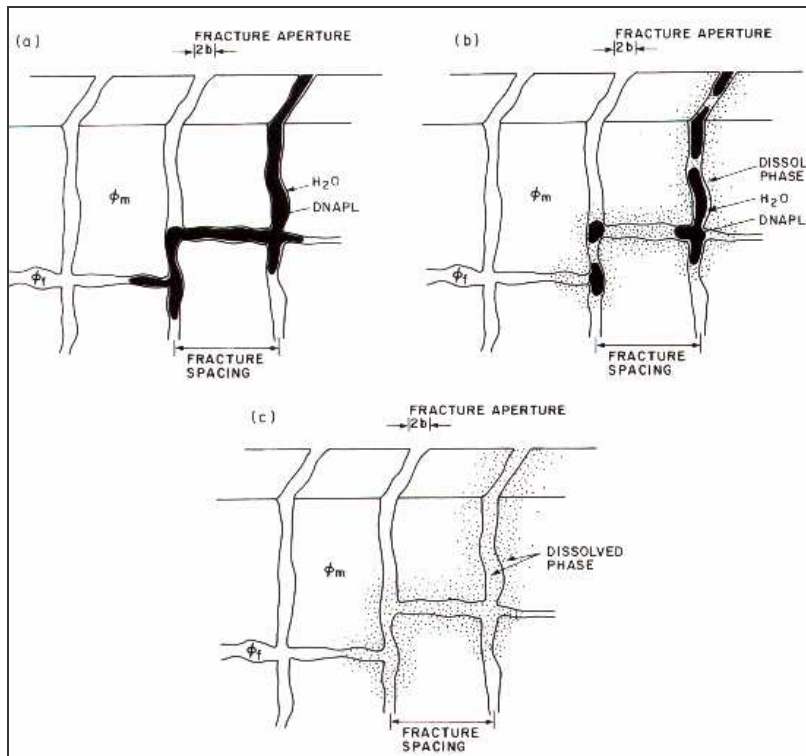


Figure 3-15: Conceptual model for a DNAPL in a fracture disappearing into the matrix porosity due to diffusion (after Pankow and Cherry, 1996).

The advantage of this situation is that it may be possible to drill through fractured rock without risking vertical DNAPL mobilization, because the contaminant is no longer present as an immiscible phase. The disadvantage is that an extremely long time period will be required to remediate the fractured rock environment because of reverse diffusion of contaminants from the matrix back to the open fractures. The matrix can store mass both in the aqueous form and sorbed to solid particles. Higher matrix porosity will allow larger amounts of aqueous phase storage, while higher organic carbon content will result in larger amounts of sorbed storage. Parker *et al.* (1994), and Pankow and Cherry (1996) present mathematical solutions to estimate the lifespan of DNAPL in fractured porous media for a variety of source configurations.

With respect to DNAPL dissolution into flowing groundwater in fractured rock, the same general principles apply as for porous media. One additional important consideration with respect to the evaluation of the dissolved plume, however, is the influence of matrix diffusion. Dissolved DNAPL contaminants in groundwater flowing through the fracture network will diffuse into a porous matrix. The effect of matrix diffusion is to slow the rate of solute migration relative to that of groundwater. In other words, matrix diffusion acts as a retardation mechanism in fractured rock. The advantage of this is that contaminants will not be migrating as quickly through

fractured rock as may be thought by considering groundwater velocity alone. The disadvantage is that pump-and-treat methods designed to remove aqueous plumes from fractured rock will need to operate for extremely long periods of time, because the mass removal process will be limited by the rate of contaminant diffusion from the matrix back into the open fractures where groundwater is flowing.

3.4.1.1 Dissolved-phase Transport in Dual-Porosity Media

Like the other contaminants, dissolved DNAPLs transport is influenced by groundwater advection, including the effects of mechanical dispersion, molecular diffusion, chemical partitioning between groundwater and porous media, and other chemical reactions (e.g., degradation). As with the flow of DNAPLs in fractures, groundwater flow in fractured porous media occurs predominantly in the fractures. If the fracture apertures are large, then the groundwater velocity and down-gradient transport of contaminants can be rapid. Dissolved contaminants are subject to diffusion into the out of the matrix.

Plumes of dissolved contaminants can result from groundwater infiltrating through zones of dissolved or DNAPL-phase contamination above the water table, from the dissolution of DNAPLs in the source zone below the water table, or from dissolved chemical mass residing in the matrix blocks between the fractures. As with the dissolution and diffusion of DNAPL material in the fractures, the influence of matrix dissolution in the overall solute transport in fractures depends upon the combined chemical and geologic characteristics of the system of interest.

Harrison *et al.* (1992) developed a numerical model to assess the importance of vertical planar fractures on solute transport downward through a 15 m thick aquitard overlying a sand aquifer. Figure 3-16 shows the conceptual setting adopted by Harrison *et al.* (1992), and Table A 1 in the Appendix provides the hydraulic conditions and porous media properties used as input parameters. The fractured clayey aquitard with a shallow water table overlies a sand aquifer where flow is horizontal. Flow is downward through the aquitard. Contaminants emanate from a near-surface waste zone in the aquitard. The waste zone is generic in the sense that it could represent any type of source. The simulation of the contaminant migration through the aquitard into the underlying aquifer provides insight into how a small number of narrow vertical fractures in an aquitard can allow significant leakage of dissolved contaminants through the aquitard.

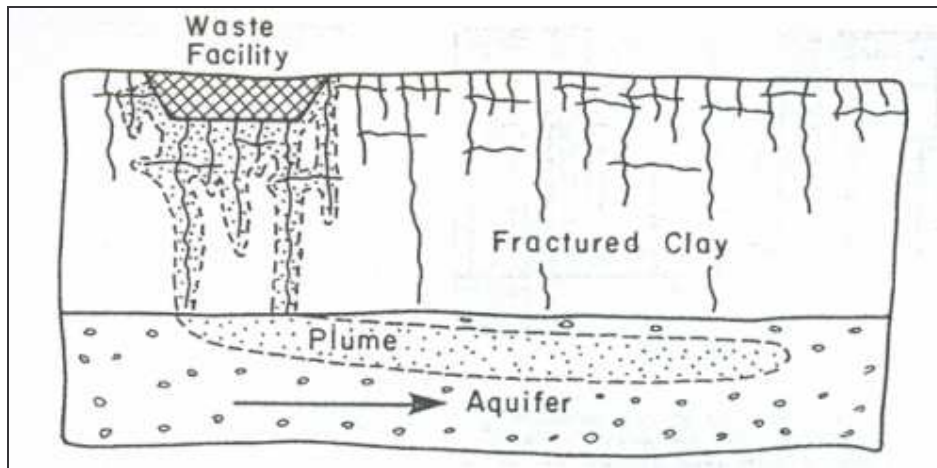


Figure 3-16: Dissolved mass transport in fractured clay (Harrison *et al.*, 1992)

4 Significance of Fractured South African Aquifers to DNAPL Contamination

This chapter addresses the main geological compositions and structural features of South African aquifers. Two case study sites were investigated during this research. Being a subset of South African aquifers, their local geology and structural features will be briefly summarised. The implication to South African aquifers of various settings to the potential DNAPL contamination will then be explained.

4.1 South African Aquifers and DNAPLs

The age of South African rocks range from Precambrian to Jurassic. Aquifers younger than the Tertiary period are usually restricted to the coastal zones and are generally consolidated. The unconsolidated aquifers are the youngest and are composed of fluvial and aeolian deposits. Clay units within the unconsolidated aquifers are often fractured during the dry seasons, which could be good pathways for DNAPL chemicals. Although some local data are available, the study in the patterns of the fracture networks of basement rocks is limited. This could be due to fracture heterogeneity and complexity.

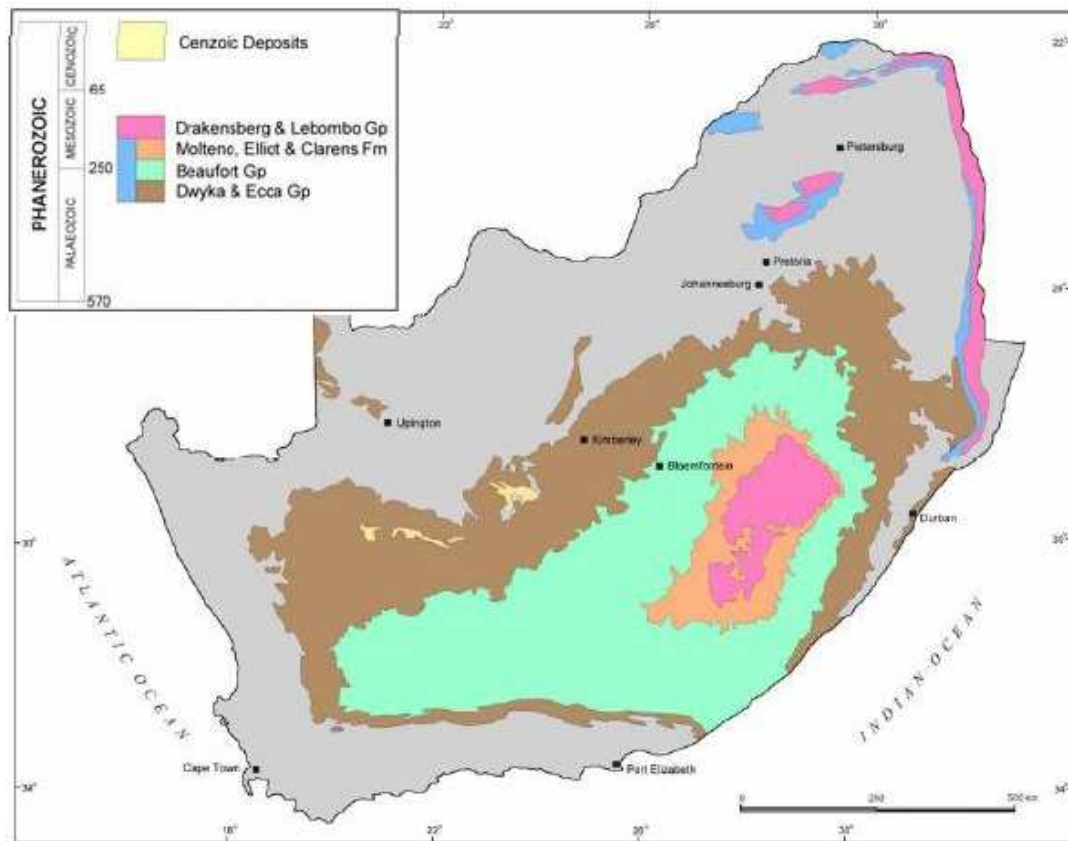


Figure 4-1: Simplified geology of the Karoo Supergroup.

The Karoo Basin (hence aquifers in the Basin are referred to Karoo Aquifers) covers about 50% of the country (Figure 4-1). Many rural communities and small towns rely on these aquifers as their main source of water for domestic, agricultural and/or small-scale firms. This is mainly because of the absence of significant surface waters. The second largest aquifer system is the Table Mountain Group (TMG) aquifers and dolomites with significantly high storage capacity of solution cavities. The rest of the geological formations cover smaller areas and have been investigated in less detail (Pietersen, 2004), therefore, their significance to the contribution of the South African groundwater is not fully evaluated.

Generally, the rock units and aquifer systems could be classified into three groups: porous, fractured, fractured-porous aquifers, and the solution caverns of carbonations rocks. These groups are listed in Table 4-1, with their geological composition and dominant locations in South Africa.

Table 4-1: Simplified flow mechanisms in South African aquifers (modified from Pretorius, 2007; Pietersen, 2004).

Aquifer porosity	Hydrogeological domains	Examples	Rock type
Matrix/primary porosity	Tertiary and later deposits	Alluvium, Cape Flats, Kalahari Sands	Unconsolidated sands
Fracture non-porous	Crystalline metamorphic and igneous regions, Intrusive and extrusive rock regions	West Rand Group, Basement	Granites
Dual porosity	Fractured rock containing significant matrix porosity (e.g. fractured sandstone)	Table Mountain Group, Karoo Group	Fractured sandstones, shales, and mudstones
Karst	Sedimentary rock regions and composite rock regions	Karst Belt, Ghaap plateau	Dolomite

4.1.1 Primary Porosity Aquifers

As observed in some South African aquifers, the thickness and type of unconsolidated materials may prevent DNAPL releases from reaching the bedrock. The amount of DNAPLs retained depends on the physical and chemical properties of the unconsolidated sediments, as well as the DNAPLs.

Just like the groundwater, DNAPL flows entirely through the interconnected voids in porous aquifers. However, since DNAPLs are the non-wetting fluid with respect to water, they flow through wider voids and small pores only if their capillary pressure is higher than the entry pressure of the voids. Therefore, DNAPL residual and pools are expected and lateral migration of the contaminant is possible because of the heterogeneity of permeabilities.

Many local or large scale unconsolidated (or partially consolidated) sediments form from erosion, weathering and other forces that shape the South African topography. The eroded material is largely transported away by rivers and wind, while colluvial soils have developed on the hill slopes and terrace surfaces. Localised alluvial, aeolian, colluvial and calcrete deposits occur in the major rivers, basins and valleys, and are common all over the country. Botha *et al.* (1998) state that sources of groundwater in the area covered by the Karoo aquifers do not only originate from the Karoo formation, but more recent sedimentary deposits also form extensive aquifers. For example, the town of Ficksburg in the Eastern Free State obtains approximately

50% of its water from alluvial beds in the Caledon River (Botha *et al.*, (1998). Porous aquifers are common in the Cape Flats of the Western Cape and the Kalahari Sands of the Northern Cape.

The Cape Flats Aquifer is a sand unit from the Sandveld Group, of Cenozoic age 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 horizontally stratified, and several lithostratigraphic units can be recognised. 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 northwest of the Northern Cape, undifferentiated inland deposits of unconsolidated to semi-consolidated sediments, including sands, calcrete, aeolianite, gravel, clay and calcrete of Tertiary-Quaternary age make up the Kalahari Group (Pretorius and Dennis, 2004).

4.1.2 Fractured Non-porous Aquifers

Crystalline rocks of metamorphic and igneous origin in South Africa are found mainly in the Northern provinces. They have limited water storage capacities but may also have with very high transmissivity, depending on the fracture apertures and connectivities. The crystalline rocks that lack void porosity include: the Makoppa Dome, Limpopo Granulite Gneiss Belt, Pietersberg Plateau, Lowveld, Bushmanland, and Namaqualand.

In the Karoo Aquifers, the deposition of the sediments ended with the outpouring and covering of basaltic lava, known as the Drakensberg Formation (Marsh *et al.*, 1997; Botha *et al.*, 1998; Woodford and Chevallier, 2002). Basalt has been extruded flow upon flow to a thickness of at least 1450 m. The huge aerial extent of individual flows (Figure 4-1) shows that the flood basalts were highly mobile.

Figure 4-2 shows granite that has fractures porosity but lacks void porosity. The DNAPL flow in such aquifers is almost entirely controlled by the orientation and aperture of the fractures and physiochemical properties of the DNAPL, with a very limited diffusion to the rock matrix.



Figure 4-2: A granite sample with fracture but no significant void porosity. Flow is entirely controlled by the fracture orientation and properties of the DNAPL.

Pietersen (2004) states that the average yield from such aquifers is less than 1 L/s. However, high yields are associated with weathered zones and fractures. For example, the groundwater resources of the Namaqualand region are located in the crystalline metamorphic and igneous basement aquifers, upon which rural communities largely depend. A summary of these crystalline aquifer systems can be derived from Lloyd (1999). They are generally poor aquifer materials and their yield occurs almost entirely from secondary features; their primary structures and lithological composition (weather igneous or metamorphic) have little to do with their hydraulic property. The rock materials are such hard that weathering does not contribute to the hydraulic properties and the fracture network is inconsistent with unpredictable spatial distribution. If contaminated with DNAPLs, the free phase and dissolved phase are likely to travel through the fractures with negligible matrix diffusion.

When the DNAPL is introduced to the fractured rock, it follows a complex pathway based on the distribution of fractures in the original matrix. The number, density, size and direction of the fractures often cannot be determined due to the heterogeneity of the fractured system. Relatively small volumes of DNAPL can penetrate deeply into fractured systems, due to the low retention capacity of the fractures and the ability of some DNAPLs to migrate through small fractures.

The fractured-rock aquifers could be exposed at or near land surface and could be highly susceptible to DNAPL contamination. Contaminant transport and fate is fundamentally different from those for the porous/unconsolidated media discussed above, for example the unconsolidated fluvial deposits. Significantly more uncertainty

exists regarding the direction and rate of contaminant migration, as well as the processes and factors that control chemical and microbial transformations.

4.1.2.1 DNAPLs and Dykes

Dykes of various thicknesses, orientations and origins are common in South Africa. For example the dolerite dykes in the Karoo Aquifer are believed to be feeders of the basalt flows of Drakensberg Formation. The numerous dykes crisscross the Karoo Basin, cut through the sedimentary rocks and die out at various levels within the basalt flows (Botha *et al.*, 1998). The dykes are formed subsequent to the deposition of the sedimentary rocks and contemporaneous with the outpouring of lavas. They were injected with feeder channels of lava that have solidified into dolerite plugs, dykes, sills and inclined bodies of various sizes and shapes.

The dolerites are generally fine or medium grained, dense, hard rock of great durability and may generally be considered as DNAPL barriers. However, they occasionally coincide with faults and the host rock is sheared with slickensides. Weathering is usually noticeable along contacts (Figure 4-3) and where it penetrates deeper into the basalts. This zone could be a promising location to drill a strong borehole, but **makes the dykes unreliable as DNAPL barriers.**

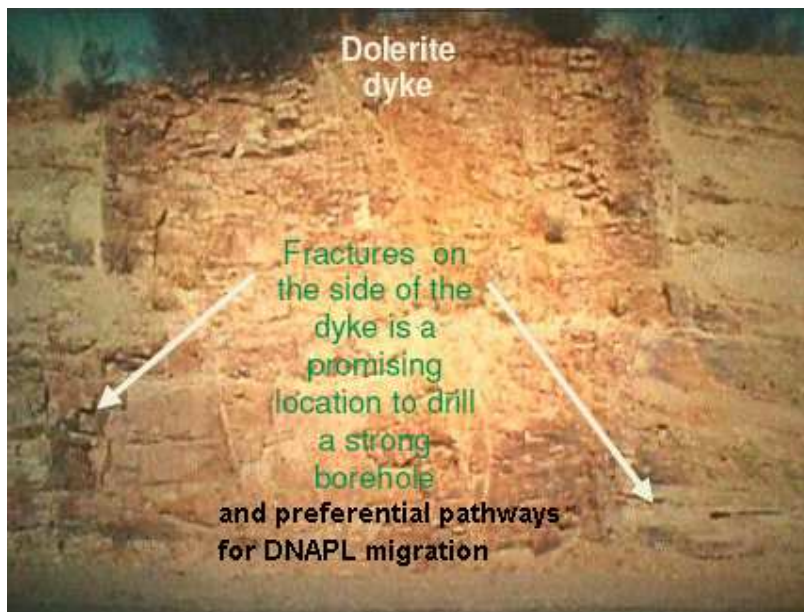


Figure 4-3: A dolerite dyke from the Karoo Supergroup with noticeable weathering along the contact zone with the host rock.

4.1.2.2 DNAPLs and Sills

Just like the dykes, sills are also common in South Africa. For example, the sills in the Karoo formations are part of the Drakensberg dolerite intrusions that tend to follow the bedding planes of the formations concordantly (Woodford and Chevallier, 2002).

The dolerite sills may generally be considered DNAPL barriers from vertical migration due to the property of the dolerite. However, they could be fractured horizontally and vertically, which provide a pathway for DNAPL invasion (Figure 4-4). Weathering is common on the contact of the sills and the host rock. Therefore, **the sills are also not reliable barriers for DNAPL migration.**



Figure 4-4: A dolerite sill from the Karoo Supergroup with horizontal and vertical fractures making it an unreliable barrier to DNAPL migration, both horizontally and vertically.

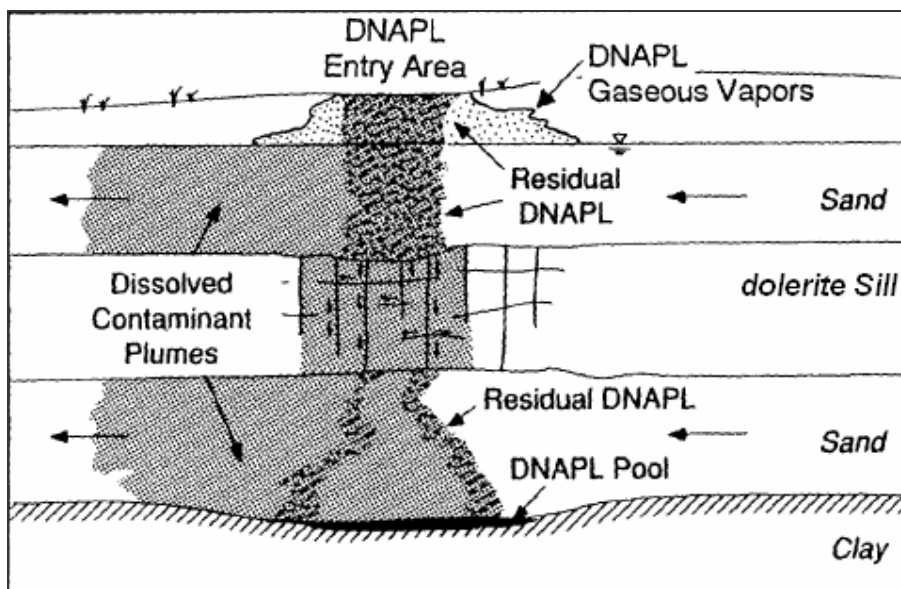


Figure 4-5: Conceptual model of DNAPL migrating through dolerite sill.

4.1.3 Karst

Dolomite formations are common in regions located in the Vaalian Strata, such as Western Bankeveld and Marico Bushveld, Soutpansberg Hinterland, Karst Belt, Eastern Bankeveld, and Ghaap Plateau. Dolomite aquifers are estimated to cover an

area of about 5000 km², with storage estimated at 5000 million m³ (Bredenkamp, 2002) and an estimated available groundwater resource of 300 million m³.

Usually the dolomite aquifers are overlain by areas of intensive land use and urbanisation, and are therefore potentially susceptible to water quality deterioration. The total thickness of the dolomite is of the order of 250 to 1000m. The system is highly compartmentalised due to the presence of a near-vertical intrusive dyke rock, which plays a major role in the groundwater flow regime, causing several large springs draining the dolomite compartments (Van Wyk, 2002). Solution cavities in dolomite or carbonation rocks could be large and groundwater flow could be simulated by high turbidity rivers (Figure 4-6). The implications of a karst aquifer to DNAPLs are:

- Due to high groundwater velocity, even the denser DNAPLs may be forced to follow the groundwater flow. The dissolved phase has the potential to migrate faster and contaminate larger areas in shorter periods of time.
- Solution caverns could sometimes be disconnected and serve as a dead-end storage for DNAPLs. Samples collected from such karsts could be unrepresentative of the overall contamination concentration.
- Mass loss due to diffusion is relatively negligible, because of the large storage capacity of the solution caverns.

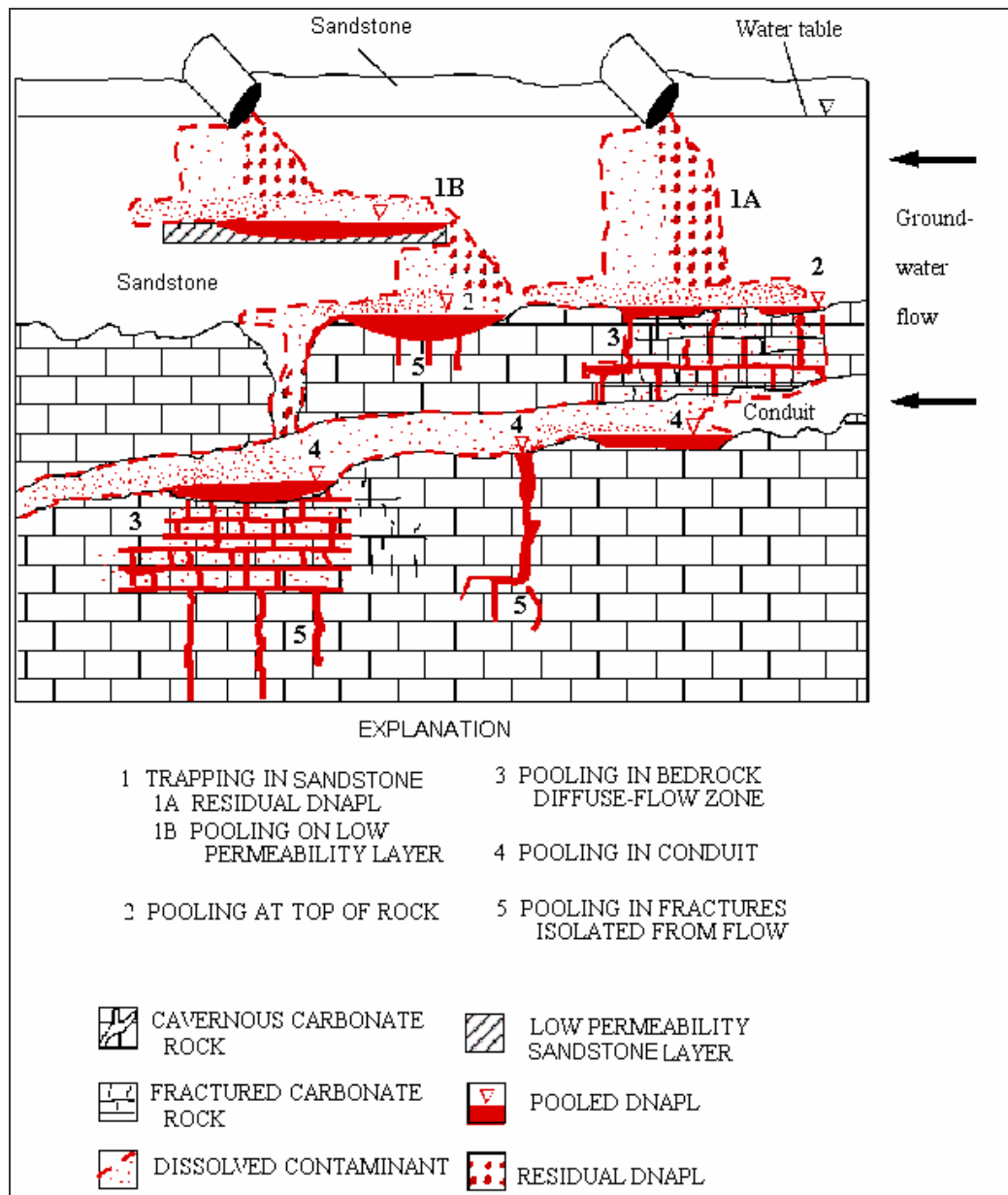


Figure 4-6: A hypothetical model of DNAPL migration in a karst aquifer.

4.1.4 Dual-porosity Aquifers

The Karoo Supergroup and TMG are the most studied and main groundwater resources with fractured-porous aquifers. An example of dual-porosity rocks from the Karoo aquifers is shown in Figure 4-7. The fracture networks are complicated with variable fracture apertures, orientations and depths.

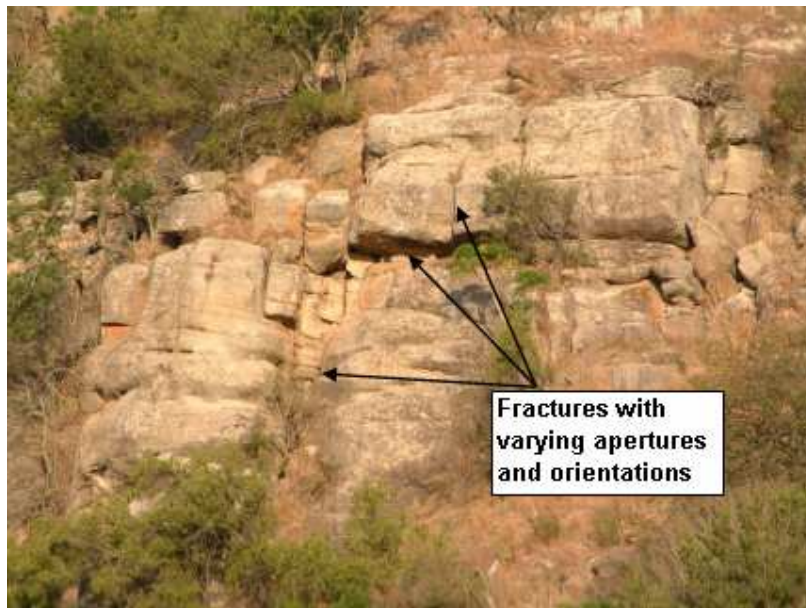


Figure 4-7: Fractured-porous rocks, with fractures of varying orientations typical in the Karoo aquifer.

At some locations, the heterogeneity of the fracture-porous aquifers is complicated by the intrusion of intersecting dykes and sills with the weathering of the rocks to various degrees. Large volumes of groundwater are often intercepted in these locations in open fractures or fissures that transgress the dyke, and extend some distance into the country rock. For example, the geological conceptual model shown in Figure 4-8 reflects the complexity of the structural features near Queenstown. The fractures are commonly sub-horizontal ($< 50^\circ$) in attitude (Woodford and Chevallier, 2002). Vandoolaeghe (1980) concluded that horizontal and oblique fractures within the dolerite and adjacent sediments are the dominant water-bearing features in the Queenstown area.

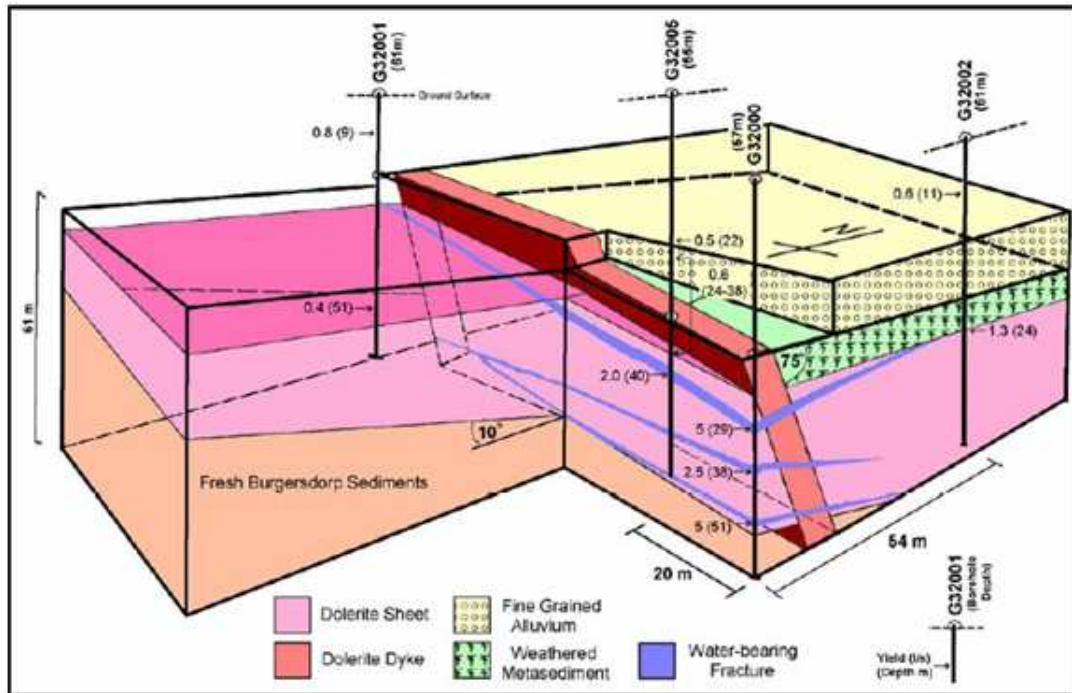


Figure 4-8: Geohydrological conceptual model of the various rocks and structural features in a dyke/sill intersection zone, Queenstown (after Vandoolaeghe, 1980).

The fractures occasionally extend several tens of metres away from the dyke into the country rock. At some locations, young fractures cut the intrusive rocks and extend about 100 m (Woodford and Chevallier, 2002) to the host sedimentary rocks.

When DNAPL contamination implications are considered in such aquifers, they tend to be more complicated than any other aquifer systems. This could be partly due to the matrix diffusion that can potentially disappear DNAPLs from the fracture networks. Therefore, DNAPLs contamination to fractured-porous aquifers can pose a serious threat to the Nation's groundwater resources. Figure 4-9 shows a conceptual model of the DNAPL transport process in a conceptual model of the Queenstown geology.

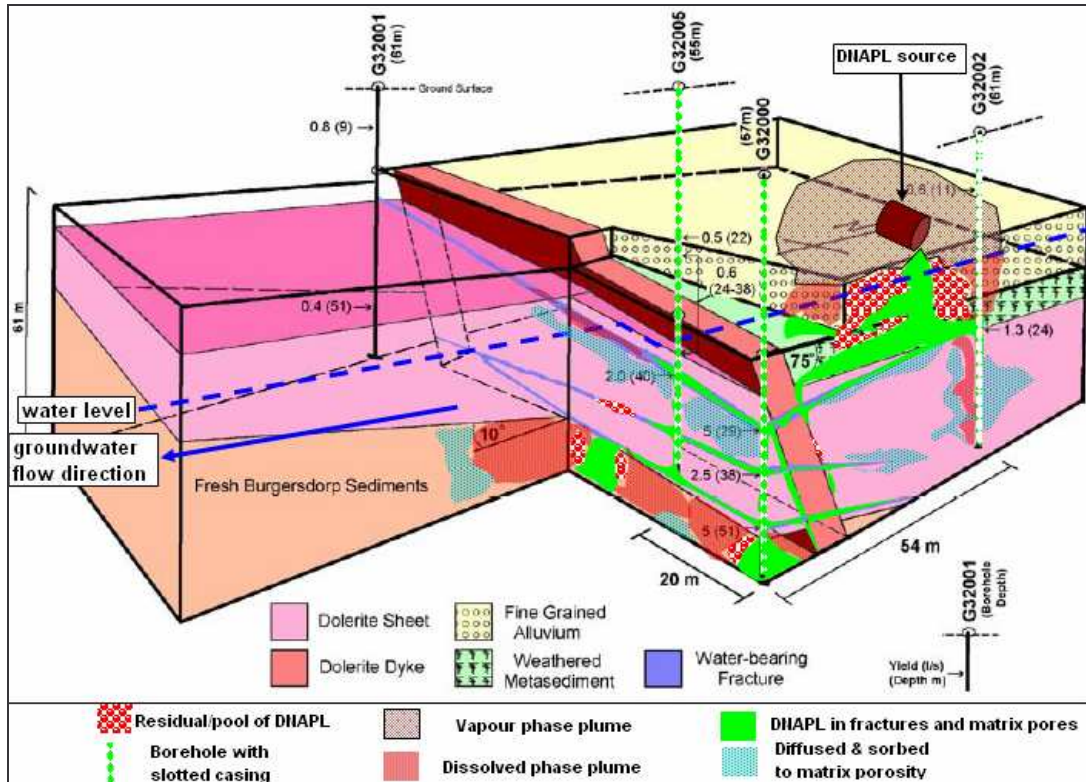


Figure 4-9: A conceptual model of DNAPL transport process in the dyke/sill intersection zone, Queenstown.

Because of the huge areal extent of the Karoo and TMG, many industrial centres in South Africa are located in the piedmont physiographic region, where fractured porous aquifers are common. Improper disposal methods, leaking tanks and pipes, and chemical spills could potentially contaminate aquifers in and around many industrial centres. The complexity of the fracture network (and matrix porosity) worsened by the physical, chemical and microbial processes of DNAPLs, may make restoration and protection of groundwater quality in these aquifers extremely difficult.

5 DNAPL Site Characterisation Strategies with Focus on Fractured Aquifers

Since the ultimate objective of characterising a contaminated site is to be able to assess risk and select appropriate remedial measures, site characterisation is an essential process that must be planned scientifically and in phases. During the initial phase, a hypothesis or 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 as part of this early hypothesis (Cohen and Mercer, 1993), and the conceptual model should be developed from existing data that will be improved iteratively as more information is gathered. A variety of conceptual models for general hydrogeological settings and South African cases are described in Chapter 3 and 4, respectively.

Based on the initial hypothesis, a data collection program is designed in the second phase to test and improve the site conceptual model. As such, site characterisation efforts should focus on obtaining fracture data and their implication for DNAPLs. After analysing the newly acquired data within the context of the initial conceptual model, an iterative step of refining the hypothesis is performed using the results of the analysis, and additional data may be collected. As knowledge of the site increases and becomes more complex, the working hypothesis may take the form of either a numerical or analytical model. Data collection must continue until the hypothesis is proven sufficiently. This chapter discusses the specific objectives, strategies, and challenges related to DNAPL site investigation in fractured aquifers.

5.1 *Difference of DNAPLs from Other Contaminants*

Due to the unique migration patterns of DNAPLs in the subsurface, conventional site characterisation techniques involve the risk of enlarging the zone of DNAPL contamination. In particular, drilling, borehole installation and pumping activities are major causes of spreading the contamination. The difficulty in characterisation DNAPLs is compounded by the following factors (USEPA, 1992; Cohen and Mercer, 1993; Pankow and Cherry, 1996).

- The relative importance of the forces that control the rate, flow direction, and ultimate fate of DNAPL is different from the relative importance of those that control the distribution of dissolved phase plumes. DNAPL behaviour is only loosely coupled with that of groundwater. DNAPL movement is remarkably sensitive to the capillary properties of the fractures, and the distribution of those fractures controls the distribution of the DNAPL. Thus, knowledge of

geologic conditions is relatively more important than knowledge of hydrologic conditions for the adequate characterisation of DNAPL sites.

- DNAPL in fractured media poses exceptionally difficult problems for site investigation because fracture networks are complex, DNAPL retention capacity (mass of DNAPL per volume of rock) is generally small, and the depth to which DNAPL may penetrate can be very large.
- Obtaining a detailed delineation of subsurface DNAPL distribution is difficult and may be impractical when using conventional site characterisation techniques. DNAPL migrates preferentially through relatively permeable soil and rock fractures and is influenced by small-scale heterogeneities (such as bedding dip and slight textural changes, as discussed in Chapter 3) due to density, capillary forces, and viscous forces. As a result, the movement and distribution of DNAPL is difficult to determine even at sites with relatively homogeneous soil and a known, uniform DNAPL source. This difficulty is compounded by fractured bedrock, heterogeneous strata, complex DNAPL mixtures, etc.
- The failure to directly observe DNAPLs in fractures does not mean that it does not exist. Often, only very low aqueous concentrations of DNAPL constituents are detected in monitoring boreholes at known DNAPL sites. These concentrations, however, may greatly exceed drinking water standards.
- DNAPLs can be broadly classified on the basis of physical properties such as density, viscosity, and solubility. Of the various types of DNAPLs found in the subsurface, chlorinated solvents and creosote/coal tar are apparently the most common. These two types of DNAPLs, however, present huge characterisation problems of a very different nature, due to the differences in their physical properties. Some of the conclusions applicable to the one are not generally applicable to the other. Physical characteristics can guide the choice of characterisation.
- The risk of causing DNAPL remobilisation must be assessed during site investigation. Conventional drilling technologies have a high potential for promoting vertical DNAPL movement. The appropriate investigation strategy is dependent on site-specific conditions, including the geology and the type of DNAPL.
- Non-intrusive, low-risk investigation methods such as surface geophysical techniques and reviews of site history and existing data should first be used to develop and improve the conceptual model of DNAPL presence and diminish the risks associated with subsequent drilling. Currently, surface geophysical methods are incapable of delineating DNAPLs. However, even routine, non-

invasive geophysical techniques can be used to evaluate fractures, which have a great influence on DNAPL migration.

- Site characterisation should be a continuous, iterative process, whereby each phase of investigation and remediation is used to refine the conceptual model of the site. The time required to define site characteristics cannot easily be reduced because of the heterogeneous, site-specific nature of subsurface environments and the investigatory process required.
- The complexity of the DNAPL problem requires a sophisticated knowledge of DNAPL contaminant hydrology. Most decisions regarding site investigations depend on site-specific conditions.
- Data collecting for DNAPL site characterisation is expensive.

The need to characterise the complexities associated with DNAPL presence at contamination sites derives from the following (USEPA, 1992; Cohen and Mercer, 1993; Pankow and Cherry, 1996).

1. The behaviour of subsurface DNAPL, especially in fractures, cannot be adequately defined by investigating miscible contaminant transport due to differences in properties (fluid and media) and principles that govern DNAPL and solute transport.
2. DNAPL can persist for decades or centuries as a significant source of groundwater and soil vapour contamination.
3. Without adequate precautions or understanding of DNAPL presence and behaviour, site characterisation activities such as drilling and aquifer testing may result in the expansion of the DNAPL contamination zone, and increased remedial costs.

Thus, DNAPL presence characterisation, transport, and fate are required to perform an adequate assessment of site risks and remedies, and to minimise the potential for inducing unwanted DNAPL migration during remedial activities.

5.2 Toolbox Approach for DNAPL Characterisation

In natural subsurface systems dominated by heterogeneity, the delineation and even the detection of slightly soluble, dense contaminants can be extremely difficult. The performance assessment of clean-up at these sites is therefore more complex. Several technologies for the characterisation 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 resides in their addition to a toolbox approach to DNAPL characterisation.

The toolbox approach recognises that all characterisation methods contribute to the conceptual model of the site (Rossabi *et al.*, 2000). The strategic selection of technology and the results from each application must contribute to the evolution of the conceptual model. The ultimate goal is the absolute knowledge of 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.

The evolving conceptual model and toolbox approach are simply a framework for the ideal understanding of a site. Generally, characterisation methods should progress from less invasive to more invasive, and from less expensive to more expensive. Simple, long-term observations should also not be overlooked (e.g. water-level fluctuations in existing boreholes) and can often provide inexpensive and important keys to understanding a site. Of course, these are general guidelines and should not prevent the use of a very expensive but very useful method at the beginning of an investigation if justified for a particular site.

DNAPL-contaminated sites tend to be more complex than 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.

The conceptual model is the realisation of the site at a particular time (Rossabi *et al.*, 2000). It is optimally constructed through historical process information, the complete set of physical, chemical, geologic, and hydrogeologic data and understanding of the dynamic processes, experiential knowledge of similar sites, the risk scenarios related to the site and its contaminants, and the type and scope of remediation envisioned. The model is updated and refined by subsequent data and information, and the process is iterative.

5.2.1 Establishing Goals and Objectives

Although difficult, it is generally possible to characterise a DNAPL site sufficiently to reduce the level of uncertainty regarding the nature and extent of contamination. Before scoping the investigation and developing a work plan, it is necessary to establish reasonable goals and objectives. The following is a list of some of the more important goals and objectives for a typical DNAPL investigation in a fractured site:

- Determine if the contamination poses a threat to human health and the environment.
- Make decisions regarding present and future risks caused by DNAPLs.

- Assess the feasibility and potential benefits of the DNAPL characterisation as compared with the expense of collecting data.
- To minimise time and budget, the characterisation should focus on the usefulness of the data in lowering uncertainty rather than turning the assessment into a research effort that eliminates all uncertainty.

5.2.2 Planning and Conducting Site Investigations

Some issues to consider and address when planning a DNAPL site investigation include (The Interstate Technology & Regulatory Council (ITRC), 2003; Cohen and Mercer, 1993), but are not limited to:

- **If a DNAPL was used or stored at a site, there is a high potential that DNAPL release occurred.** Knowledge of previous operations and waste disposal practices at a facility will provide insight and information about whether DNAPLs have been released, and whether this has become a source of groundwater contamination.
- **Standard site investigation techniques do not work well in characterising DNAPLs.** Complex and discrete DNAPL migration patterns can make it very difficult to delineate subsurface DNAPL using standard investigation techniques. DNAPL-specific site investigation techniques are required. The investigator may need to develop strategies to either better locate the DNAPL based on a knowledge of DNAPL-specific fate and transport characteristics, or make assumptions regarding the subsurface DNAPL distribution. An extensive DNAPL hunt will likely be expensive and will probably not find all of the DNAPL at a site; therefore, DNAPL presence and distribution may need to be inferred.
- **DNAPL tends to migrate via discrete preferential pathways; mainly fractures.** Since DNAPL follows the path of least resistance, it can migrate in unexpected directions whenever fractures are encountered. Being able to predict the DNAPL transport pathways is important since these migration pathways may be put to use as pathways for enhanced DNAPL extraction. As such, the investigation needs to focus on discovering transport pathways to successfully characterise.
- **Effect of DNAPL distribution on groundwater samples.** A long borehole screen intersecting DNAPL ganglia or a thin DNAPL lense may allow groundwater sample dilution and indicate contamination that does not indicate that the borehole intersected a DNAPL zone. In addition, monitoring boreholes can easily miss discrete DNAPL zones and, depending on site-

specific conditions, boreholes drilled very close to subsurface DNAPL may fail to provide a clear indication of the nearby DNAPL mass.

- **The effect of DNAPL distribution on fractures.** DNAPL confined to small fractures can easily be missed by core holes. If a small amount of DNAPL is collected in a core, it can easily be missed when collecting a rock sample from the core or even diluted by in the sample container depending upon the sample collection technique. It can escape easily if it is volatile. Crushing the rock and field extraction with methanol may be applied. Hydrophobic dyes and other visual sample examination techniques may fail to indicate the presence of DNAPL if the ratio of the non-DNAPL rock/soil sample to DNAPL is too high for easy detection.
- **DNAPL that flows counter to the groundwater flow direction can confound the delineation of the source and dissolved contamination zones.** DNAPL moving counter to groundwater flow may extend the contamination source areas and thereby create additional plumes of dissolved phase contamination in unexpected areas. This results in increased uncertainty regarding the spatial distribution of the source zone. Thus, when monitoring for dissolved contaminants at assumed downgradient locations to delineate the up-gradient presence of source (DNAPL) zones and/or the extent of dissolved contamination, an increased degree of monitoring is appropriate. This should include additional samples in assumed up-gradient directions to ensure the detection of wandering source zones and associated dissolved contamination plumes.
- **Reasonable precautions should be taken when planning and implementing the DNAPL site investigation.** Reasonable measures should be taken to control the risks of expanding the zone of chemical contamination or developing misleading chemical concentration data by the use of invasive site characterisation methods (e.g., dragging down of residual DNAPL during drilling).
- **The DNAPL at a site may not have the same composition as the original chemical purchased from a chemical supply company.** As DNAPLs are used, they become contaminated with impurities and may not have the same physical and chemical characteristics as the original pure chemical. These need to be taken into account and samples of the DNAPL should be collected, if possible, and analysed for parameters that could affect the subsurface behaviour. These parameters are discussed in Section 2.1, and include such as viscosity and density.

- **The age of the release and when the chemicals were purchased may be a factor in determining DNAPL composition.** It is important to know the approximate age or time frame of the release and/or chemical purchase, since this may provide clues regarding the chemical composition of the DNAPL. Manufacturing processes change over time. Knowledge of the exact chemical composition manufactured during a certain period may help the investigator explain the presence or absence of daughter products in the dissolved phase plume. The date of release can also help the investigator in determining fate and transport-related issues including but not limited to source area delineation (release points), liability, discrete/mixed plumes, natural attenuation, etc.
- **It must be recognised that, for almost all fractured rock sites, the governing flow features are discrete fractures.** Characterisation should focus on those fractures and whether or not they can be lumped together to assign an effective parameter. At some sites, there may only be a few interconnecting fractures, which are the primary players in contaminant transport. The location of these fractures and their hydraulic properties must be identified and defined. At a more densely fractured-porous site, the characterisation should include major processes like diffusion.

Investigations at DNAPL and potential DNAPL sites should be designed to collect and manage large amounts of data in order to specifically address the above issues. The data collection techniques should be designed to collect data that indicate where the DNAPL may be present in the subsurface, and how it contributes to the aqueous groundwater contamination and unsaturated zone soil gas plumes.

5.2.3 Site Conceptual Model Development

An accurate site conceptual model is critical for evaluating the true risk of DNAPL contamination, as well as the possibilities and limitations of site remediation. In order to characterise a DNAPL site, the investigation strategy must be designed to incorporate DNAPL physics, flow dynamics, and fate. Central to this strategy is the development of an initial site conceptual model that addresses the potential presence of DNAPL and will guide the site investigation. As discussed earlier, site conceptual model is dynamic and has to be improved as the study of the site is intensified. A complete conceptual model should include a visual representation of contaminant source and release information, site geology and hydrology, contaminant distribution, fate and transport parameters, and risk assessment features such as current and future land use and potential exposure pathways and receptors.

Figure 5-1 provides an example of a conceptual model for a chlorinated solvent spill. It is extremely important to include a source area conceptual model within the overall site conceptual model. This will detail the properties of the DNAPL and the fracture

system in which it is located. The source area conceptual model is a tool that will help the investigator organise the available data and understand the characteristics of the source.

5.2.3.1 Source and Release Characterisation

The site conceptual model should include a description of the source of contamination and what is known about the timing and quantity of the release. Most site characterisations begin by locating areas where DNAPLs were originally released to the subsurface. In many cases, the distinct source of contamination is known to be a former underground storage tank, disposal pit, gasworks, area, etc. However, many industrial source areas are dispersed and difficult to find.

At old sites, it is often impossible to pinpoint the exact source of contamination. Soil gas surveys can be used to locate these areas at sandy, permeable sites. However, at sites with low permeability soils, locating dispersed sources will often require excavation and removal of contaminated soils along underground utilities. This level of intrusive characterisation may not be possible along active utility corridors or base rocks. The timing and amount of DNAPLs released may equally be difficult to estimate in old sites (AFCEE, 2000). Historical records on DNAPLs use are usually difficult to obtain.

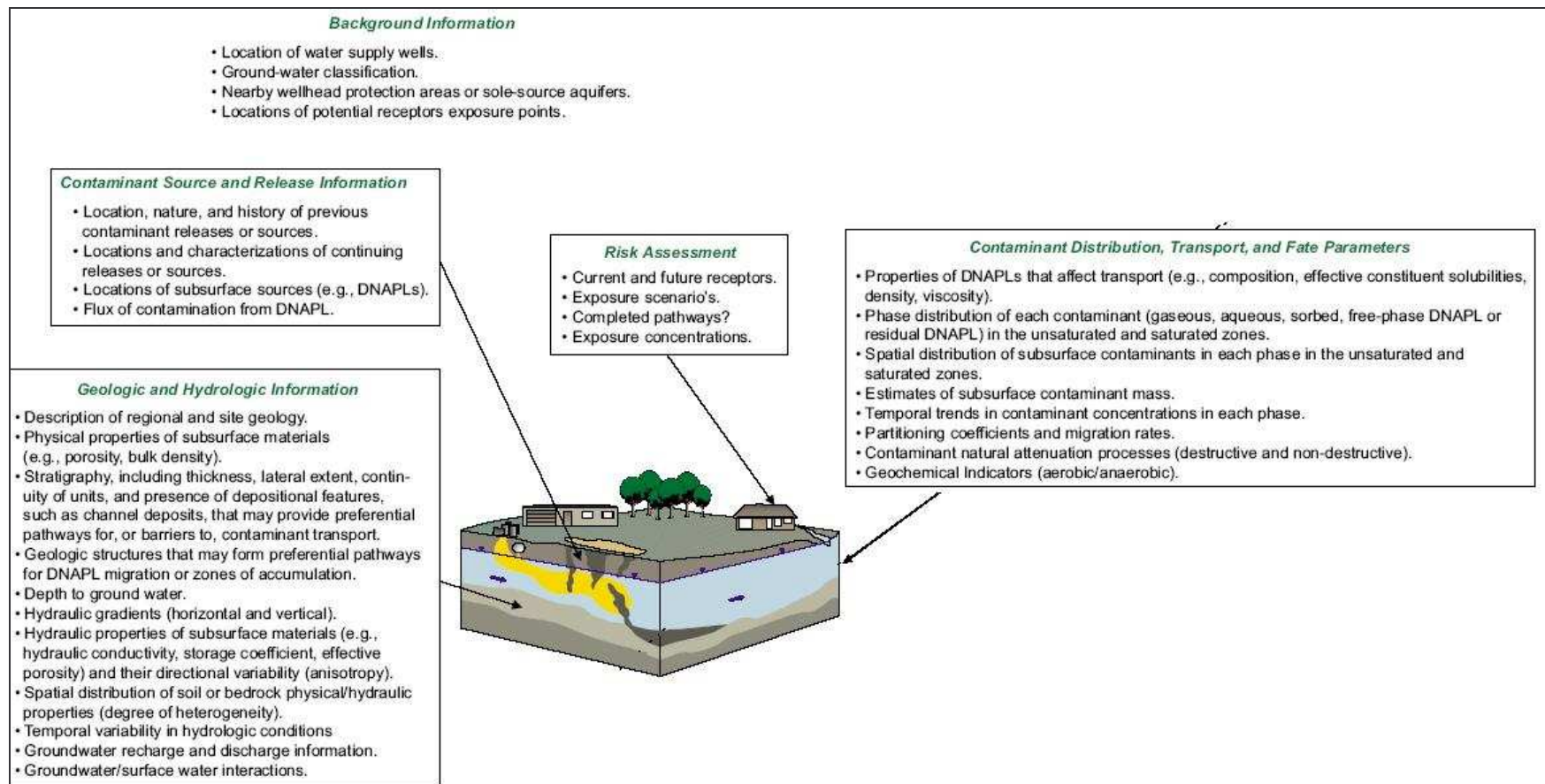


Figure 5-1: Components of site conceptual model (after EPA, 1993; AFCEE, 2000)

In unconsolidated soils, the amount of DNAPLs remaining in the subsurface can be roughly estimated based on a comprehensive soil gas survey in a known source area. Average soil gas concentrations of DNAPLs can be equated to soil concentrations in order to estimate the mass of solvents in an impacted volume of soil. Likewise, average groundwater concentrations can be used as a coarse estimate of the amount of DNAPLs dissolved in a volume of impacted aquifer. However, these methods are generally ineffective estimators of contaminant mass in fractures. Due to the unique challenges posed by fractures, soil and groundwater DNAPL contamination should be a rough guide for the potential of fractures to be contaminated by DNAPLs.

The main limitation of the soil sampling method is that only a very small portion of the subsurface, the recovered volume of the core barrel is sampled. A further complication is that conventional soil sampling is rarely designed to increase the likelihood of finding DNAPLs. Conventional soil sampling methods generally specify that samples be taken at predetermined intervals (e.g., 5 or 10 m) often with little regard for subsurface material. Generally, only the sediment very near the predetermined interval is recovered, so selection of a sampling interval is limited although occasionally a screening instrument (e.g., Photo Ionization Detector (PID)) is used to guide the sample location. Given the conceptual model for DNAPL, it is probable that DNAPL will be missed when using this strategy.

Surface geophysical methods, including ground penetrating radar, complex resistivity, and electromagnetic induction methods have successfully detected aqueous and non-aqueous phase organic contaminants at a very limited number of sites (Cohen and Mercer, 1993).

5.2.3.2 Geochemistry Impacting Natural Biodegradation

At many sites, geochemical conditions may support the natural biodegradation of DNAPLs. The biodegradation can influence the DNAPL contamination potential at a site. Geochemical indicators such as dissolved oxygen, nitrate, iron, manganese, sulfate, methane, and hydrogen ion concentrations should be reported in the site conceptual model. The relative distribution of primary solvents such as PCE and TCE, and daughter products such as DCE and vinyl chloride should be discussed in relation with the geochemical profile (AFCEE, 2000).

5.2.3.3 Free-Phase DNAPL

Special precautions are required to avoid the inadvertent creation or enhancement of DNAPL migration pathways during the course of hydrogeologic investigations. Given the ability of DNAPL materials to move downward through very small fractures (e.g. 20 microns) within the soil mass, conventional grouting procedures may not prove effective for soil borings or boreholes drilled directly through a DNAPL perching

stratum and into an underlying, clean unit. In developing a DNAPL detection/delineation work plan, the following concepts should be applied (Newell and Connor, 1992):

- **"Outside-In" Approach:** Prior to penetrating a suspected DNAPL zone, critical stratigraphic features should first be identified by investigations conducted outside of the area concerned. These preliminary data should be analysed to identify potential perching strata or capillary barriers beneath the DNAPL zone. All drilling subsequently conducted within the area must be terminated at the depth of the uppermost, continuous capillary barriers safety net" stratum. In thick, fractured rock settings, such perching strata may not be present, and the risks associated with drilling inside the DNAPL zone must be carefully weighed against the need for vertical delineation data.
- **Soil Borings and Boreholes:** To avoid inadvertent penetration of perching layers within DNAPL zones, soil borings should be sampled continuously with depth and terminated at or near the surface of such confining strata. For the detection of free-phase DNAPL, observation boreholes must be screened across the upper surface of a perching layer. However, under no conditions should the borehole boring penetrate the full thickness of the base stratum. Boreholes should be constructed with short screen sections and double-cased through the depth of any overlying DNAPL-contaminated sections.
- **Non-Invasive Site Investigation Techniques:** Where applicable, non-invasive techniques should be employed to indicate DNAPL presence or characterise site stratigraphy. Geophysical methods can be applied to define the presence and topography of perching strata. In addition, shallow soil gas sampling above the DNAPL zone has proven to be a useful indicator of DNAPL presence in some cases.

Overall, the DNAPL detection/delineation program is conducted in three steps (from Newell and Connor, 1992):

Step 1: Detailed Characterisation of Stratigraphic Profile

- Prior to drilling through known or suspected DNAPL zones, a sufficient number of soil borings should be drilled and continuously sampled outside the area concerned to provide a detailed characterisation of both principal and micro-stratigraphic features. In unconsolidated sediments, cone penetrometers can provide a cost-effective alternative to conventional drilling techniques, providing a continuous detailed record of minor sand, silt, and clay strata. Geologic data should be analysed to identify the uppermost stratum serving as a capillary barriers for prevention of downward DNAPL migration (e.g., a laterally continuous clay stratum). Subsequent investigations conducted in the

zone of DNAPL occurrence must be designed to prevent artificial penetration of this base confining layer.

Step 2: DNAPL Detection Sampling

- To detect or confirm the presence of residual or free-phase DNAPL within the suspected zone, a series of soil borings and observation boreholes should be created over the depth interval determined in Step 1. Soil borings should be drilled and continuously sampled to the depth of the base perching layer, with caution to minimise breaching any overlying perching strata. If DNAPL is encountered within the soil column, observation boreholes should be screened across the surface of the base perching stratum to detect pool accumulation. Sampling and testing procedures should include the following:
 - Visual Inspection of Soil Samples: In the field, soil samples must be inspected for visual evidence of DNAPL presence. Particular emphasis is placed on inspecting secondary porosity features; in some cases DNAPL will weep out fractures while the sample is inspected. Although the presence of DNAPL is obvious in some samples, small amounts of residual DNAPL are often difficult to see. To increase the likelihood of observing small amounts of DNAPL, the soil material may be mixed with water in a sample jar, and the water inspected for an immiscible liquid film or droplets. Alternatively, a soil/water mixture may be run through a paint filter, and inspected for the presence of a free-phase liquid or film.
 - Organic Vapour Analyses: The concentration of organic vapours on the soil sample should be measured in the field with a portable vapour monitoring instrument, using sample jar or headspace techniques. High organic vapour concentrations can be indicative of volatile DNAPL in the soil matrix.
 - Laboratory Analyses: Selected soil samples, particularly samples with organic vapour concentrations, are analysed for gross indicators of contamination, such as Total Petroleum Hydrocarbons, as well as specific organic constituents. Soil samples containing more than 10,000 mg/kg of hydrocarbon contamination (1% of soil mass) commonly contain DNAPL (Feenstra *et al.*, 1991). However, it is important to note that gross indicator analyses may not provide adequate sensitivity to detect residual DNAPL concentrations on the soil mass. For this purpose, compound specific analyses for major components of the DNAPL source material should be conducted using

ppb-level analytical methods and the results evaluated in accordance with the partitioning procedure discussed below.

- Partitioning Calculation: On the basis of laboratory data, a partitioning calculation, evaluating the potential for dissolved-phase versus separate phase organic constituent occurrence, can be used to evaluate the presence/absence of residual mass. By using the concentration of organics on the soil and the partitioning calculation, a theoretical porewater concentration of organics in groundwater is determined. If the theoretical porewater concentration is greater than the estimated solubility of the organic constituent of interest, then DNAPL may be present at the site.
- Installation of Observation Boreholes: The final element of the DNAPL detection program is the installation of observation boreholes on top of the bottom perching layer. These boreholes are constructed to 1) minimise the volume of gravel pack and unscreened borehole section below the screens, and 2) have the bottom of the screened section set as close as possible to top of the perching layer. This borehole construction methodology will help ensure that at least some of the DNAPL accumulates in the borehole rather than in the borehole/gravel pack.

Step 3: DNAPL Zone Delineation

- Once DNAPL is detected at a site, the DNAPL zone is delineated to the best degree possible with the following procedure.
 - Free-phase DNAPL Zone: The topography of the base perching layer should be further defined with additional drilling or, where applicable, with other techniques. Based on this surface definition, additional borings or observation boreholes should be completed in the topographic lows of the principal perching layer(s) to detect and delineate DNAPL pools. The apparent depth of DNAPL accumulation on the base perching layer may be estimated using an interface probe, a double check-valve bailer, or a weighted cotton string. Although this information provides a qualitative estimate of the volume of DNAPL in the subsurface, accurate quantification is frustrated by uncertainties regarding where the DNAPL is coming from, where the borehole is screened in relation to the DNAPL pool, and other unknowns (Waterloo Centre for Groundwater Research, 1991).
 - Residual DNAPL Zone: To define the lateral extent of the residual DNAPL zone, a series of step-out drillings are made from the source

area. Samples are collected and observed visually, analysed for organic vapours, as well as chemical constituents and gross contaminant indicators in the laboratory. Additional step-out borings are made in an iterative fashion until an apparent clean zone (i.e. no DNAPL) is identified and confirmed with laboratory samples. To define the vertical extent of the residual DNAPL zone, each boring is sampled continuously until either a) no further DNAPL is visually observed or detected from vapour monitoring data, or b) the bottom perching stratum is reached.

5.2.3.4 Contaminant Dissolution, Transport and Fate

In addition to describing the source of contamination, the site conceptual model should include a summary of the chemical, physical, and biodegradation properties of key contaminants of concern and describe their distribution, movement, and fate in the subsurface environment. DNAPL dissolution may continue for decades or centuries due to the undiluted nature of the DNAPL and limits on solubility and groundwater flow rates. DNAPL migration can greatly expand the vertical and horizontal extent of subsurface contamination. This is because gravity may force DNAPL to sink to depths and in directions that are not hydraulically down-gradient from the DNAPL entry location (the initial source area). Therefore, a primary focus of many DNAPL site characterisation studies will be to delineate the presence of mobile DNAPL to facilitate the assessment of containment and recovery options. At a minimum, the site conceptual model for a DNAPL site should include:

- Chemical and physical properties of DNAPL compounds that impact subsurface transport (e.g., partitioning coefficients, solubility, vapour pressure, Henry's Constant, density, viscosity)
- An estimate of the phase distribution of each contaminant (free-phase DNAPL, sorbed, in soil vapour, or dissolved) in the saturated and unsaturated zone.
- Temporal trends in contaminant concentrations in each phase.
- Geochemical evidence of contaminant natural attenuation processes.

Often, DNAPLs at a site are not observed directly for a number of reasons: DNAPL distribution may be sparse, some DNAPLs are colourless, and residual DNAPL will not flow to a borehole. Under these conditions, a rough estimate of DNAPL extent can be drawn from water quality data. As a rule of thumb, if dissolved concentrations are at or above 1% of effective solubility, it is likely that the borehole is completed in the vicinity of a DNAPL zone (EPA, 2000). This effective solubility relationship for dissolved constituents in DNAPL zones reflects the slow rates of mass transfer from

DNAPL bodies to the aqueous phase, hydrodynamic dispersion, and borehole dilution. Using the 1% rule of thumb, concentrations that indicate the likely presence of some common single-component NAPLs are presented in Table 5-1.

Table 5-1: Single-component concentrations potentially indicative of NAPL (CLU-IN, 2000).

Compound	1% of Single Compound solubility (µg/L)
Carbon Tetrachloride (CTET)	7.6
1,2-Dicloroethane (DCA)	85
1,2-Dichloroethene(cis) (DCE)	35
Methylene Chloride	200
Tetrachloroethene (PERC)	1.5
Trichloroethane (TCA)	15
Trichloroethene (TCE)	11
Benzene	18
Toluene	5.4

If the DNAPL is a mixture of compounds, such as petroleum fuels, creosote-based wood-treating oils, coal oil, or mixed solvents, the effective solubility of individual compounds is a function of the compound's mole fraction in the DNAPL and its pure-phase solubility. This relationship is described through Raoult's Law as:

$$C_i = X_i S_i$$

Equation 5-1

where

C_i = effective solubility of component i ,

X_i = mole fraction of component i in the DNAPL phase, and

S_i = single-component or "textbook" aqueous solubility of component i .

Use the above relationship requires knowledge of the primary DNAPL components. This can be obtained by collecting and analysing a representative set of DNAPL samples for the individual compounds. A second method is to use the dissolved phase concentrations in groundwater and apportion the mole fractions in the same ratio. The second approach may show a bias if any of the primary compounds are naturally attenuated through either biological or physical processes. Application of Raoult's Law is described in detail in Feenstra (1990), and Pankow and Cherry (1996).

Table 5-2 provides a summary of dissolved concentrations detected in boreholes completed through actual, multi-component DNAPL zones at various types of industrial sites. Site-specific concentrations that indicate the presence of DNAPL can be verified by measuring dissolved concentrations in boreholes completed in known DNAPL zones (e.g., where DNAPL was directly observed) and using those concentrations as a threshold for other areas with similar soils and borehole completions.

Table 5-2: Dissolved concentration typically observed in multi-component DNAPL zones (CLU-IN, 2000)

Type of Site	NAPL	Parameter	Typical Dissolved Concentration Range (mg/L)
Wood-Treating	Creosote Based Wood-Treating Oils (DNAPL)	Total Polycyclic Aromatics Hydrocarbons	1-10
Manufactured Gas	Coal Tar (DNAPL)	Total Polycyclic Aromatics Hydrocarbons	1-10
Fuel Production/Storage	Gasoline (LNAPL)	BTEX	1-10
	Diesel (LNAPL)	BTEX	
	Jet Fuel (LNAPL)	BTEX	1-10
	Natural Gas Condensate (LNAPL)	BTEX	1-10
Chlorinated Solvent Storage/Disposal	Chlorinated Solvents (DNAPL)	Total Volatile Organic Compounds	1-10

5.2.3.5 Nature and Extent of Contamination

DNAPL chemicals may contaminate soil, bedrock, groundwater, surface water, surface water sediments, and air. Focusing on groundwater, this assessment includes an analysis of groundwater flow and chemical transport. Emphasis is often placed on the latter component through intensive groundwater quality monitoring. This information is used to help:

- Identify contaminants,
- Determine the distribution and concentration of contaminants,
- Determine contaminant sources, and
- Determine the contaminant phase - dissolved, sorbed or non-aqueous.

In determining the nature and extent of groundwater contamination, it is important to estimate the hydrogeologic characteristics that influence the contaminant distribution. These characteristics include:

- Stratigraphy,
- Hydraulic properties of aquifers and confining beds,
- Hydraulic gradients,
- Recharge/discharge rates, and
- Sorption potential.

If fractures are present, an evaluation should be made of their orientation, spacing, and vertical and lateral extent. The spatial distribution of hydraulic properties, gradients, and contaminants can be very complex, requiring vertical as well as horizontal assessment. Groundwater contamination is often conceptualised as forming plumes. At some sites, however, heterogeneities in hydraulic properties (especially in fractured media) and a complex distribution of contaminant sources may result in very erratic contaminant distributions.

5.2.3.6 Fracture and Hydrogeologic Characterisation

Table 5-3 lists a variety of parameters that can be determined as part of fractured porous aquifer site investigations. The matrix porosity, matrix dry bulk density and matrix fraction organic carbon need to be measured for samples from a core. Each major rock type should be sampled as these parameters exhibit spatial variability.

The orientation of major fracture sets is typically determined through outcrop mapping and down-the-hole geophysical surveys. The fracture spacing is typically determined by the results of down-the-hole hydraulic testing in conjunction with core logs and an optical televiewer. It should be noted that the core may contain mechanical breaks that can be difficult to distinguish from natural fractures.

The fracture porosity is usually determined from estimates of fracture spacing and aperture, determined from hydraulic testing. The bulk hydraulic conductivity is generally determined through pumping and slug tests. The bulk retention capacity of the rock mass for DNAPL is typically estimated from fracture porosity.

Table 5-3: Bedrock properties to determine during site investigations (Kueper *et al.*, 2003).

Parameter	Example use of information
Matrix porosity	Diffusion calculations
Matrix dry bulk density	Estimate of remediation timeframe
Matrix fraction organic carbon	Estimate of (retarded) plume velocity
Orientation of major fracture sets	Determine direction of plume migration Directions of DNAPL migration
Fracture spacing	Diffusion calculations
Fracture porosity and connectivity	Plume velocity calculation
Bulk rock hydraulic conductivity	Plume velocity calculation Design of extraction wells
Hydraulic head distribution	Directions of groundwater flow and velocity of groundwater
Bulk retention capacity	DNAPL mass estimate
Contact angle	DNAPL-rock-water wetting relationship
Spatial extent of DNAPL source zone	Guide remedy selection
Spatial extent of plume	Guide remedy selection; risk analysis

In summary, since fractures control the DNAPL fluid movement and chemical migration, the following aspects should be the focus of studying fractures.

- Rock type and fracturing
- Regional geologic structures
 - Regional geologic mapping (may not be sufficient for detailed site characterisation)
 - Lithologies (may vary locally with differing groundwater yields.)
- Fracture evolution/chronology
- Fracture properties
 - Fracture location and orientation
 - Fracture connectivity
 - Fracture trace length
 - Fracture density
 - Fracture aperture

- Fracture roughness
- Mineralisation and alteration
- Primary/Intrinsic porosity

5.2.3.7 Duration of Site Characterisation

In order to fully characterise a DNAPL site, large amounts of data are usually needed. Even when using field analytical methods and scientific work plans, large amounts of money can be spent on a DNAPL site investigation, without determining the precise location of all of the DNAPL mass and fractures. Without a clear set of objectives, there can seem to be an almost endless need for collecting data and spending large amounts of money. There is always the issue of not being able to quantitatively demonstrate the bounds of uncertainty in fractured rock and, hence, make the argument that characterisation is complete. At some sites, it may never be possible to completely characterise the site with the current technologies, and what has been characterised has to be good enough. For example, at Test Site 1, the upper part of the aquifer was “well-characterised” and showed no major contaminant carrying pathways. To determine the geologic profile, a deeper borehole (GB3) was drilled (Figure 5-2). A large fracture that provided pathways for contaminant migration was identified at a depth of 53 m. This fracture would not have been found without drilling a deeper borehole. Therefore, a complete characterisation may not be possible, but it is important to decide when to stop the work.

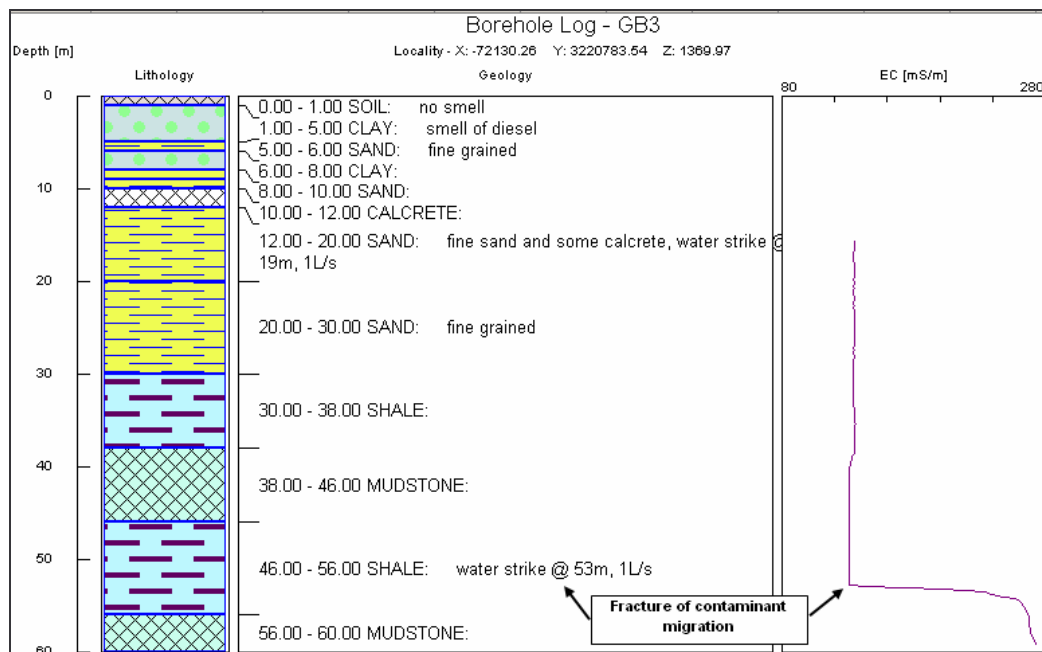


Figure 5-2: Borehole GB3, showing that the depth of interest for characterisation could always be greater than believed.

5.2.3.8 Evaluation of Contamination Potential

Although the complexity of risk assessment will vary from one site to another and one regulatory environment to another, there are several common elements that should be included in every site conceptual model:

- An analysis of potential receptors (current and future) which could be impacted by contamination.
- An analysis of potential exposure pathways that could allow DNAPL compounds to impact receptors.
- A determination of what level of contaminant exposure will not present an unacceptable risk to impacted receptors (risk-based cleanup goals).
- Measurement of contaminant concentrations at potential exposure points or estimation of exposure point concentrations using fate and transport models. These exposure concentrations are then compared to risk-based cleanup goals.

Most site investigators evaluate the concentration of dissolved phase based upon the assumption that the risk is primarily located in drinking water. However, high risk exists through inhaling VOC escaping from the vapour zone, or even from the shallow water level in dry environment.

Potential receptors include utility and construction workers and non-intrusive office workers. Potential exposure pathways include soil gas inhalation, direct soil contact, direct groundwater contact and inhalation of groundwater volatiles. The reduction or removal of risk can be accomplished by limiting contaminant migration pathways or restricting receptors to prevent unacceptable exposure concentrations.

6 Findings of Site Characterisation in Fractured South African Aquifers

DNAPL site characterisation studies on contaminated aquifers are internationally done on a number of sites, using different techniques and approaches. Results from such research may not be valid in Southern Africa, as the soil, aquifer types, and climatic conditions are very different from those overseas. However, international experience does represent an important knowledge base, and this understanding is utilised, according to its suitability.

Site characterisation investigations were carried out on two sites (Test Site 1 and Campus Test Site) in South Africa to evaluate characterisation technologies for fractured aquifers. First an introduction of the sites and reasons for their selection are discussed. After elaborating the objective of the chapter, a detailed discussion will be given on the site characterisation techniques, methodologies applied, and the results obtained.

The site characterisation procedure is phased. It started with the non-invasive techniques that provide rapid and cost-effective ways for screening. After developing the initial conceptual model from the non-invasive techniques, the investigation proceeds to invasive techniques that provide more information on DNAPLs and fractures on a local scale. These techniques and results are addressed after the non-invasive methods.

6.1 *Introduction to Test Site 1*

6.1.1 Site Description

Test Site 1 is an industrial site with potential DNAPL contamination located in the Free State, South Africa. According to an agreement with the site owners, the exact location and name of the site remains confidential, but an aerial photo is provided in Figure 6-1. Test Site 1 was selected as a main research site for relevant field characterisation methodologies for the following reasons:

- **Site activities.** Several industrial activities take place at Test Site 1, which entail known potential NAPL contamination sources. DNAPL releases to the subsurface are suspected at multiple sources within the site. These include electric and mechanical workshops, above and underground storage tank facilities, spray painting and electroplating workshops, metal foundry, and coal gasification plant. Due to the usage of various chemicals, the site is expected to be a mixed DANPL contamination source.

- **Accessibility of the site.** The site is located close to the University of the Free State, which makes it preferable for time-intensive research activities without the restraint of added cost and time.
- **Geological composition.** Although no previous geological studies were available, the site is located on the Karoo Supergroup. The assessment of DNAPLs at the site could be inferred for an understanding and evaluation of DNAPL behaviours in the Karoo aquifers. As discussed in Section 1.5, the objective of this research is to characterise DNAPLs in fractured aquifers, and since Karoo aquifers are predominantly fractured and contain most elements of typical South African aquifer conditions, the site was considered appropriate to address the objective. It is suitable for the application of a number of rapid and detailed site characterisation methods and an understanding of the behaviour of various DNAPL phases in the Karoo Aquifer. By characterising of Test Site 1, the following knowledge is expected to be gained:
 - The nature of residual and gaseous DNAPL phase in the unsaturated zone,
 - Vapour, dissolved, diffused and free-phase DNAPLs in the matrix porosity of the unconsolidated sediments of the saturated zone, and
 - Preferential migration of dissolved and free-phase DNAPLs in the fractured porous media and natural degradation in the complex aquifer system can be assessed.
- **Site Hydrogeology.** No previous hydrogeological investigations were conducted on the site. This implies that no previous disturbances of the groundwater regime have taken place to date, and the migration of the DNAPL source zones can be investigated without changes. This also allows for the design of the field observation and monitoring boreholes to be sited based on the objectives of this research.

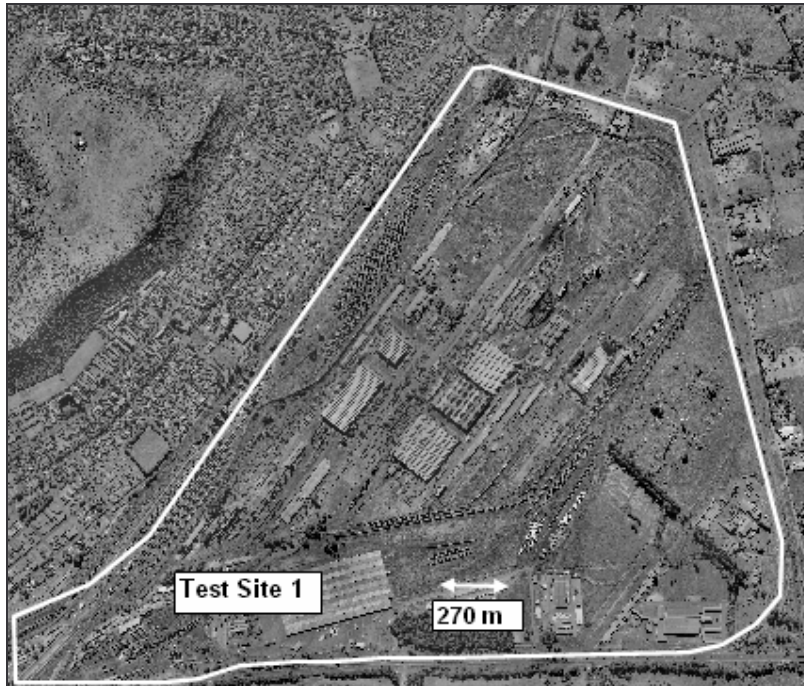


Figure 6-1: Aerial photo of Test Site 1 (coordinates are not provided to keep the confidentiality of site location).

6.1.2 Geology and Hydrogeology

6.1.2.1 Regional Geology

A regional study of the site may not be important for the detailed characterisation of DNAPLs in fracture networks. However, an initial conceptual model can be developed by integrating regional geological data with the available site information. Test Site 1 is located within the Karoo Supergroup, and the regional geology is focused on a summary of the Karoo aquifers.

The geological succession of the Karoo Supergroup (shown in Figure 6-2) is composed of the Dwyka, Ecca, Beaufort and Stormburg Groups, from older to younger respectively. Following the sedimentary Groups is the Drakensberg lavas, which define the uppermost Karoo Aquifer.

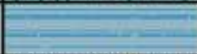
Drakensberg Volcanics			Basalt	Jurassic
Stormberg Group	Clarens		Cross-bedded sandstone	Triassic
	Elliott		Red mudstone and sandstone	
	Molteno		Sandstone, conglomerate and mudstone	
Beaufort Group	Tarkastad Subgroup		Burgersdorp Formation	Permian
			Katberg Sandstone	
	Adelaide Subgroup		Green, grey and purple mudstones	
			Sandstone	
Ecca Group			Shale and sandstone	
Dwyka Group			Tillite and diamictite	Carboniferous

Figure 6-2: The Karoo Supergroup (after Tankard *et al.*, 1982).

These formations are not the only sources of groundwater in areas underlain by the Karoo Supergroup. More recent unconsolidated formations; mainly alluvium, colluvium and calcrete, often form extensive aquifers. These unconsolidated sediments form a thick layer on Test Site 1, estimated to be more than 20 m. They lie on the upper beds of the Adelaide Subgroup of the Beaufort Group (Botha *et al.*, 1998), while beds of the Tarkastad Subgroup crop out 30-40 km south and east of the site. The regional geology of the Adelaide Subgroup and Quaternary sediments can be summarised as follows:

- **Adelaide Subgroup:** The late Permian-aged Adelaide Subgroup comprises of sedimentary rocks such as fine-grained sandstone, siltstone, blue-grey massive mudstone and occasional clay-pellet conglomerate.
 - It attains a maximum thickness of about 5000 m in the southeast, which decreases rapidly to about 800 m in the centre of the Karoo Basin and thereafter more gradually to around 100 – 200 m in the extreme north.
 - In the southern and central parts of the Karoo Basin, the Adelaide Subgroup consists of alternating bluish-grey, greenish-grey or greyish-red mudrock and grey, very fine to medium-grained, lithofeldspathic sandstone. Sandstone generally constitutes 20 – 30% of the total thickness, but in certain areas may be as little as 10%, while some sandstone-rich intervals may in places contain up to 60% sandstone. Individual sandstone units are thickest in the south (averaging 6 m; maximum 60 m) and generally become thinner northwards and extend laterally for a few hundreds metres to a few kilometres, but many are

markedly lenticular. Calcareous concretions 20-100 cm in diameter are present in some sandstone layers (Woodford *et. al.*, 2002).

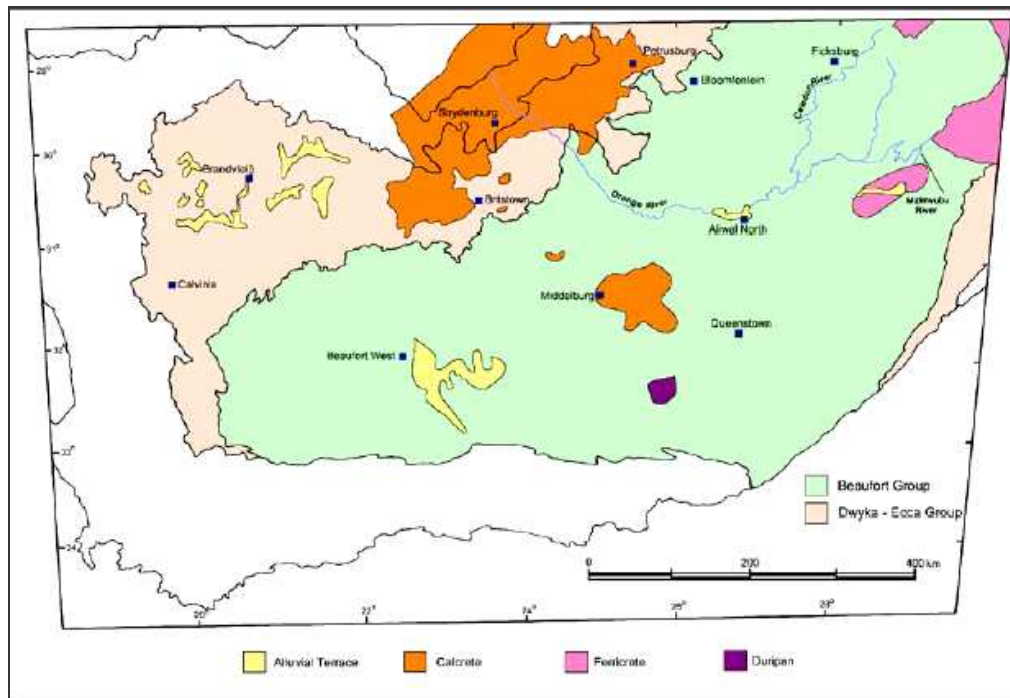


Figure 6-3: Schematic distribution of major Late Tertiary - Early Quaternary fluvial terrace and pedocrete (excluding gypcrete) deposits of the Main Karoo Basin (From Woodford *et. al.*, 2002).

- **Quaternary Deposits:** River terraces are present along most of the major rivers in the Karoo Basin. The main fluvial deposits are shown on Figure 6-3. They are Miocene or Plio-Pleistocene in age (late Tertiary - early Quaternary) and occur up to 60 m above the elevation of the present river channel. They mainly consist of gravels, comprising well-rounded cobbles and boulders, sometimes cemented by calcrete (Woodford *et. al.*, 2002).
 - **Calcrete** deposits of unknown thickness occur widely distributed in the study area on the Tierberg shales (De Kock, 2001). Calcrete deposits may attain a thickness in excess of 30 m, but are rarely homogeneous over depths exceeding 1 to 5 m. They are thought to be of two basic origins: (1) groundwater and (2) pedogenic.
 - In the groundwater type, carbonate is precipitated above a fluctuating, shallow water table or by lateral seepage of groundwater. In the pedogenic type the carbonate is transported downwards through the soil by infiltrating rainwater.
 - The carbonate may originate from the soil, may be transported on dust particles, or within the rainwater itself. Calcrete is usually formed in

arid and semi-arid areas, or as a weathering product of dolerite (Woodford *et. al.*, 2002).

6.1.2.2 Regional Hydrogeology

Since Test Site 1 is composed of the quaternary deposits overlying the Adelaide subgroup, this section is focused on the most important hydrogeologic characteristics of this part of the Karoo Aquifers.

- **Adelaide Subgroup:** The main sediment source area for the Beaufort rocks (and hence Adelaide Subgroup) occurs along the high-lying, southern margin of the Karoo Basin. The coarser-grained rocks are, therefore, found near the Cape Fold Belt (alluvial fan and braided stream environments), while mudstone, shale and fine-grained sandstones dominate the more distant central and northern portion (meandering river and floodplain environment) of the Basin. The sedimentary units in the Group therefore usually have very low primary permeability.
 - The geometry of these aquifers is complicated by the lateral migration of meandering streams over a floodplain. The aquifers in the Beaufort Group will thus not only be multi-layered, but also multi-porous with variable thickness. The contact plane between two different sedimentary layers will cause a discontinuity in the hydraulic properties of the composite aquifer. The pumping of a multi-layered aquifer will thus cause the piezometric pressure in the more permeable layers to drop faster than in the less permeable layers.
 - It is therefore possible to completely extract the more permeable layers of the multi-layered Beaufort aquifers, without materially affecting the piezometric pressure in the less permeable layers. This complex behaviour of aquifers in the Beaufort Group is further complicated by the fact that many of the coarser, and thus more permeable, sedimentary bodies are lens shaped. The life span of a high-yielding borehole in the Beaufort Group may therefore be limited, if the aquifer is not recharged frequently (Woodford *et. al.*, 2002).
- **Quaternary Deposits:** Calcrete deposits often form excellent, albeit localised, sources of groundwater due to a higher rate of recharge from rainfall than the average of 2 – 5% for Karoo aquifers (Kirchner *et al.*, 1991), and dissolution of the calcrete.
 - Due to the relatively higher recharge rate of the calcrete, some of the best Karoo aquifers are situated in calcrete deposits. Farmers in the central Free State district of Petrusburg, for example, often tap calcrete

aquifers up to 30 m thick for irrigational purposes. Weaver *et al.* (1993) also target valley calcrete with good results after boreholes sites along dolerite dykes failed to yield enough water for the town of Strydenburg in the Northern Cape Province.

6.1.2.3 Local Geology

Although no previous studies on the local geology are available, Test Site 1 is located within the Karoo Supergroup. From initial field visits and regional geology, the sediments are composed of clay, calcrete, sand and gravel units, with thicknesses varying locally. The sediments appear to be alluvial deposits from paleo-rivers flowing in the basin. However, the sediments could also be colluvial soils. As explained by Botha *et al.* (1998), calcrete is usually formed in arid and semi-arid areas and from the weathering of dolerites that are rich in calcium.

The detailed geological composition of the site is discussed in Section 6.8.1 as more information was obtained from the drilling process, test pits and other geological observations. By integrating and correlating this information, a conceptual model of the site is provided in Section 6.8.4.2.

6.1.2.4 Local Hydrogeology

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 to 13 m thick. Depending on regional geology, the bedrock is expected to be composed of shale, mudstone, siltstone and sandstone aquifers characterised by dual porosity. As is common in the Karoo aquifers, the fracture network is expected to vary in orientation and depth, which could result in complicated DNAPL migration pathways. Considering the age of the industry and amount of chemicals used, DNAPL contaminants were expected to migrate through the unconsolidated sediments to the fractured rocks.

The detailed hydrogeologic composition of the site is discussed in subsequent chapters as more information was obtained from drilling processes, pump tests, tracer tests, borehole geophysical loggings and other hydrogeological observations. By integrating and correlating this information, a hydrogeological conceptual model of the site is provided in Section 6.8.4.2.

6.1.3 Topography

The site is situated on a relatively flat terrain on unconsolidated sediments with an elevation of 1384 m on the northwest part and gradually decreasing to 1368 m on the southeast. A small hill is located about 1 km northeast of the site with an elevation of

approximately 1480 m. The topographical map of the site is provided in Figure 6-13, where Test Site 1 is marked in pink.

6.1.4 Climatic Conditions

Test Site 1 has a fairly arid climate, with very hot summers, a cool to cold winters, and a predominantly summer rainfall. Figure 6-4 gives the average monthly climatic parameters from the Bloemfontein weather station.

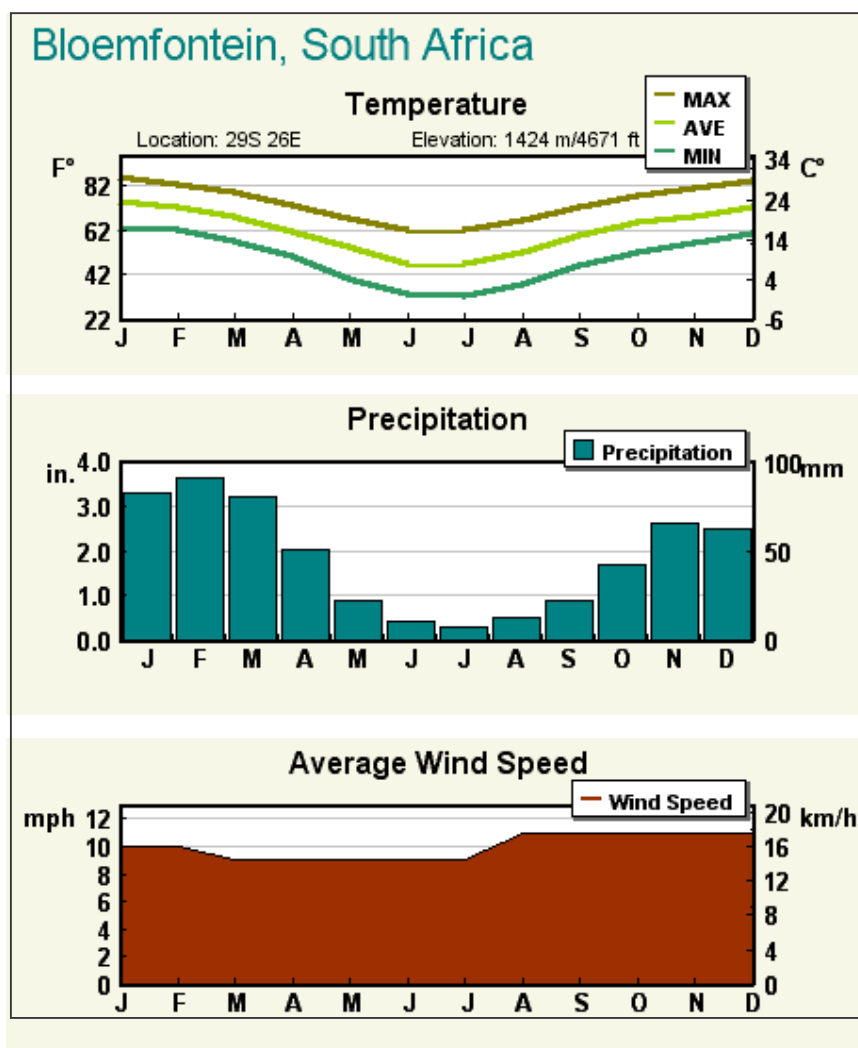


Figure 6-4: Average climatic parameters of Bloemfontein (from <http://www.weathersa.co.za>).

Table 6-1 shows climate information according to the World Meteorological Organization (WMO) prescriptions, based on monthly averages for the 30-year period between 1961 - 1990. The average daily maximum and minimum temperatures range from 24 to 8 °C, respectively. While the recorded maximum and minimum temperatures were 39 and -10 °C, respectively.

A more detailed record of the rainfall is provided by the annual rainfall over time for Bloemfontein in Figure 6-5.

**Table 6-1: Climate data of Bloemfontein based on monthly averages of 30 years (1961 – 1990)
(from Weather SA).**

Month	Temperature (° C)				Precipitation		
	Highest Recorded	Average Daily Maximum	Average Daily Minimum	Lowest Recorded	Average Monthly (mm)	Average Number of days with >= 1mm	Highest 24 Hour Rainfall (mm)
January	39	31	15	6	83	11	62
February	39	29	15	4	111	11	142
March	35	27	12	1	72	11	56
April	33	23	8	-3	56	9	45
May	30	20	3	-9	17	4	32
June	25	17	-2	-9	12	3	26
July	24	17	-2	-10	8	2	37
August	29	20	1	-10	15	3	54
September	34	24	5	-7	24	4	46
October	35	26	9	-3	43	7	48
November	37	28	12	0	58	9	46
December	38	30	14	3	60	10	48
Year	39	24	8	-10	559	84	142

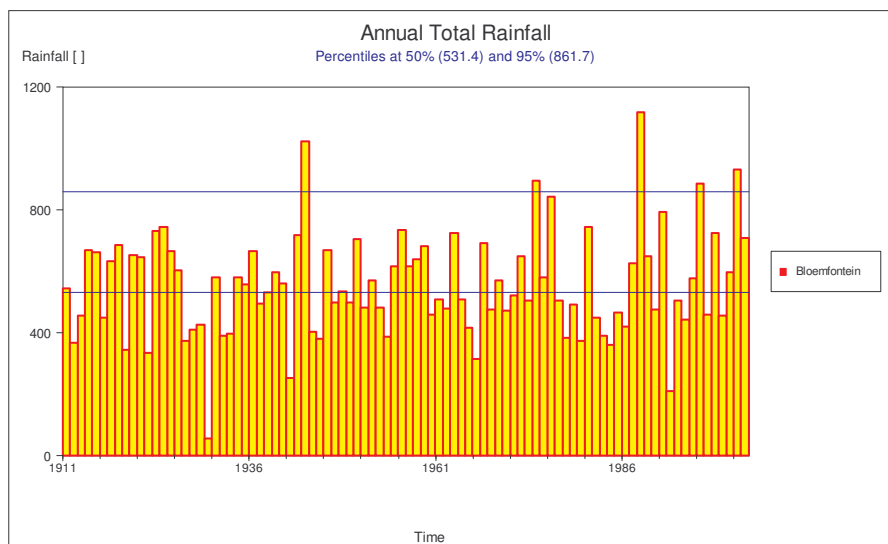


Figure 6-5: Annual rainfall records for Bloemfontein Weather Station (1910 – 2003)

6.2 Introduction to Campus Test Site

6.2.1 Site Description

The Campus Test Site is an uncontaminated aquifer used as an additional site for the study of the behaviour of fractures and means of characterising them. It is located on the grounds of the University of the Free State in Bloemfontein, South Africa. It covers an area of approximately 35 000 m², and has been used as a facility to conduct various geophysical, hydraulic, and chemical transport investigations in fractured sedimentary rocks (Botha *et al.*, 1998; Riemann, 2002). Before the start of this research, there were 30 percussion boreholes and seven core holes drilled by previous investigators.

The Campus Test Site is a DNAPL-free area and was selected for the characterisation of fractures, particularly for the accurate investigation of the bedding-parallel fracture already identified by previous researchers. Additionally, six percussion boreholes and two core holes were drilled for a further geological and hydrogeological investigation of the site, and are labelled as DNAPL boreholes in Figure 6-6.

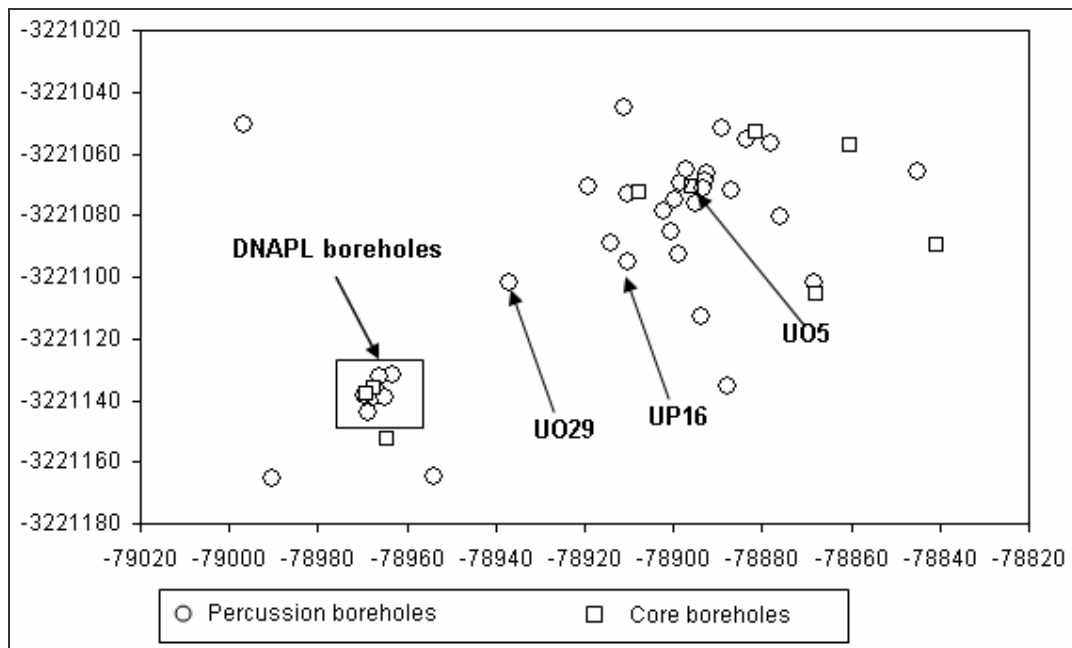


Figure 6-6: Borehole distribution at the Campus Test Site (coordinate in Transverse Mercator with central meridian of Lo27, measured in metres).

6.2.2 Geology and Hydrogeology

6.2.2.1 Regional Geology and Hydrogeology

As in the case of Test Site 1, the Campus Test Site is underlain by a series of mudstones and sandstones from the Adelaide Subgroup of the Beaufort Group of the Karoo Supergroup. The regional geology and hydrogeology discussed in Sections 6.1.2.1 and 6.1.2.2, respectively, are also applicable to the Campus Test Site.

6.2.2.2 Local Geology

All holes in the Campus Site were vertically oriented, with the exception of two core holes that were at an inclination of 45^0 , to identify subvertical fractures. The geological profiles of the percussion and two inclined core holes (CH5 and CH6) are shown in Figure 6-7 and Figure 6-8, respectively.

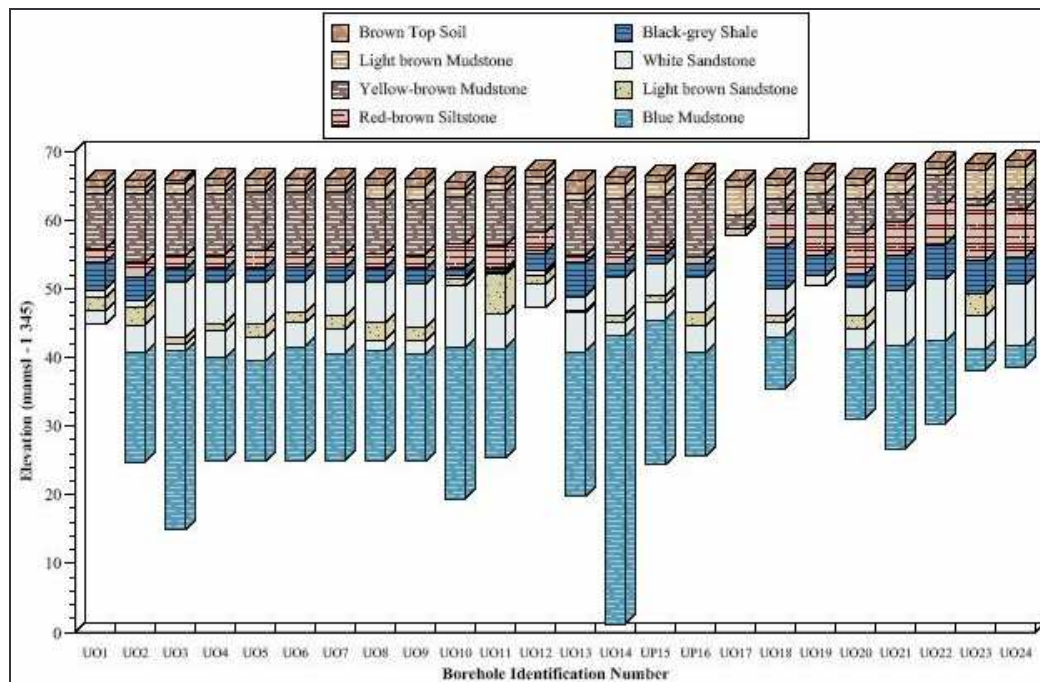


Figure 6-7: Geological profiles of 24 percussion boreholes drilled on the Campus Test Site (from Botha *et al.*, 1998).

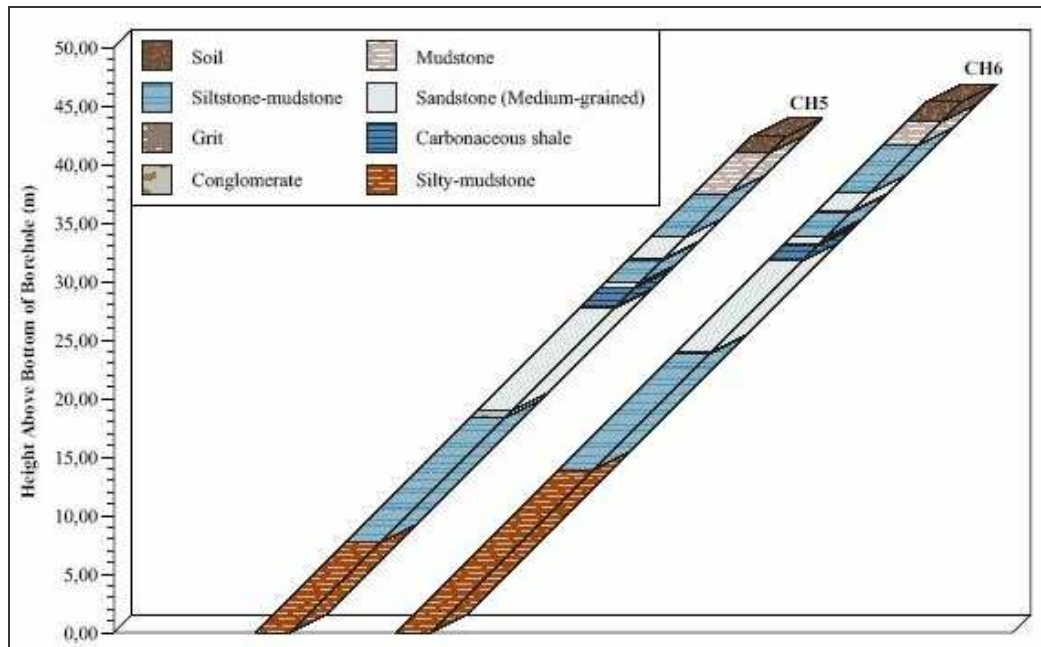


Figure 6-8: Geological profiles of the two inclined core holes drilled on the Campus Test Site (from Botha *et al.*, 1998).

6.2.2.3 Local Hydrogeology

For the purpose of this research, the Campus Test Site can generally be described as a site composed of subhorizontal, sedimentary units. From the land surface downward, these units are mudstone, carbonaceous shale, sandstone, and a second mudstone unit. The thickness of each unit varies slightly in the boreholes at the site. Figure 6-9 shows a conceptual model of the vertical distribution of the sedimentary units at the site.

The top mudstone is unconfined and extends roughly to a depth of 14 meters (m) below land surface, and is characterised by a very low yield. The carbonaceous shale acts as an aquitard, separating the upper unconfined aquifer from the transmissive sandstone aquifer. The high transmissivity in this unit is attributed to the horizontal fracture that is characteristic of this layer. The mudstone unit at the bottom of the sequence also has a low yield similar to the unconfined aquifer. The water levels associated with the aquifer units are schematically shown in Figure 6-9. In general, the hydraulic heads in the upper and lower mudstone units are higher than the hydraulic head in the sandstone.

At the Campus Test Site, the transmissivity of the sandstone aquifer is dominated by a single, areally extensive subhorizontal bedding-plane fracture that intersects boreholes at approximately 20.0 to 23.0 m below land surface (Figure 6-9). Van Tonder and Vermeulen (2005) estimated the transmissivity of the fracture to be about $580 \text{ m}^2/\text{d}$, whereas the transmissivity of the sandstone matrix was approximately $3 \text{ m}^2/\text{d}$. Subvertical fractures have also been detected in the sandstone, but they are regarded as being hydraulically insignificant because of their low transmissivity. All the

boreholes intersected with the fracture have significant yields, and all the remaining boreholes have insignificant yields. The fracture itself has an aperture of approximately 10 mm, but the adjacent 200 mm of the sandstone is also highly permeable, and therefore the aperture is considered to be 200 mm. This is a typical Karoo aquifer, where horizontal fractures serve as the conduits of water towards boreholes in the aquifers, but the water is stored in the Karoo formations themselves (Botha *et al.*, 1998).

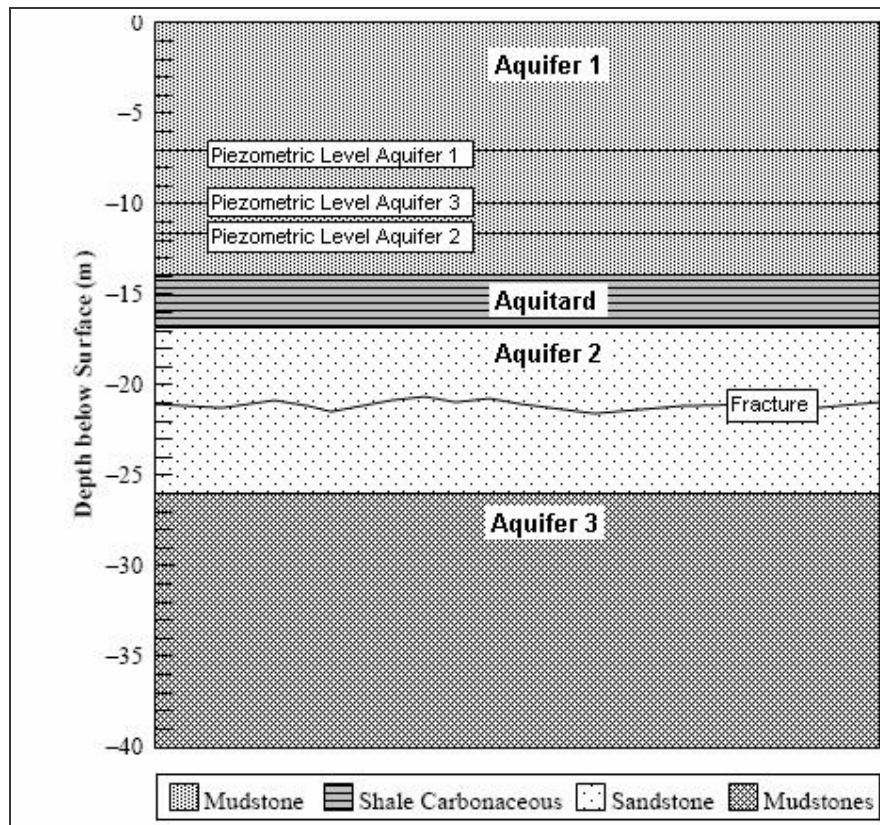


Figure 6-9: Schematic diagram of the lithology and aquifers present at the CTS (modified from Botha *et al.*, 1998).

6.2.3 Climatic Conditions

The Campus Test Site is located in the Free State and has similar climatic conditions to Test Site 1. Therefore, the discussion of Section 6.1.4 also applies to the Campus Test Site.

6.3 Non-Invasive Technologies

As discussed above, Test Site 1 was a potential DNAPL contamination source. Therefore, DNAPL characterisation technologies were applied to in this site, but not the Campus Test Site. To minimise the risk of DNAPL migration due to site

characterisation techniques and develop a conceptual model in a cost-and time-effective manner, non-invasive techniques were applied first.

Although they are not applicable for direct DNAPL characterisation in fractured aquifers, understanding DNAPL in the shallow unconsolidated aquifers is essential in evaluating the DNAPL-release zones. The applied non-invasive techniques include:

- General assessment of Test Site 1 by site visiting, interviewing employees, documentation studies and aerial photo analysis.
- Hydrocensus of boreholes located in the surrounding areas.
- A reconnaissance survey on the site and direct observing for DNAPL contamination with the aid of UV light and Sudan IV shake tests.
- Soil gas surveys by using various models of PIDs to delineate the organic vapour plume.
- Surface geophysics for outlining of major structures and geologic features that may play an important role for DNAPL migration pathways.

The detailed procedures followed during the non-invasive assessment and results obtained are discussed in the following sections.

6.3.1 General Assessment of Test Site 1

Test Site 1 is an industrial site with diverse activities related to the manufacture and maintenance of transport-related products. Various chemicals have been used for different purposes since its establishment in 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, a list of activities that may result in the release of DNAPLs and potential groundwater contaminants were collected. Then three target areas within the property were identified as potential DNAPL sources and selected for intensive site characterisation. These areas are the electroplating workshop, gasworks and foundry, as shown in Figure 6-10.

6.3.1.1 Gasworks Plant

The gasworks plant was erected for the purpose of on-site gas supply. It started to operate in 1980 and decommissioned three years later. Since then, no rehabilitation of the site has taken place. It is suspected that, during 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. At present, there is still tar residue within the storage tanks of the plant, which is leaking onto the soil, shown in Figure 6-11. An old

sump near the loading bay is also filled with coal tar and wastewater, suspected to be a potential release of DNAPLs to the subsurface.

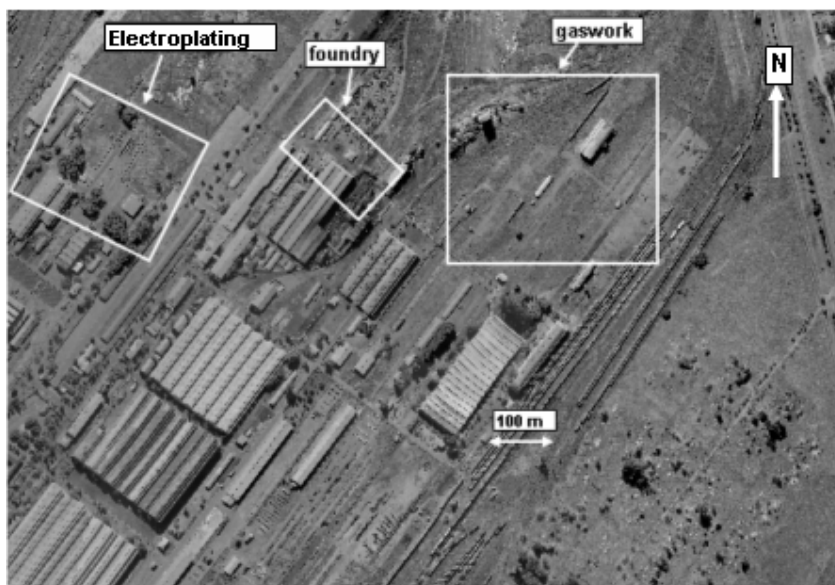


Figure 6-10: Aerial photo of target areas at Test Site 1.



Figure 6-11: On-going spillage from tar loading.

Gas plants are known to produce a variety of organics characterised by the variable densities of dominant liquid wastes. Among these are aromatic hydrocarbons, including the tar-acid phenols and cresols; the mono-cyclical aromatic hydrocarbons (MAHs) more commonly known as the BTEX series (benzene, toluene, ethylbenzene and xylene); the duocyclical aromatic hydrocarbons (DAHs) mainly represented by

the base-neutral naphthalene; the polycyclical aromatic hydrocarbons (PAHs) represented by the medium and heavy oils (the "tars"), as well as various forms of cyanogens, sulfur, and some heavy metals concentrated from the trace metals of the coal and some of the enrichment oils (www.hatheway.net). The coal tar "mix" or waste will commonly have the properties of a DNAPL, with a combined density greater than that of water.

6.3.1.2 The Electroplating Workshop

The electroplating workshop operated for 30 years until it was decommissioned in August 2003. Interviews with employees yielded some significant information regarding the operation, management and waste disposal at the site. Electroplating of mechanical and other parts took place in the closed-off workshop area. Wastewater was pumped to a lime treatment facility just outside of the workshop. In previous years, the "treated" water was either disposed of in the stormwater system or in the open field. Later a holding facility was built, where sludge was allowed to settle and the excess water disposed of via the sewer system (Figure 6-12). In the past few years, the sludge was removed and disposed of at a regulated waste facility, but in earlier years the sludge was disposed of on site. In the area opposite the lime treating and holding facility an open field was used as a dumping ground for a variety of wastes, including building rubble, sludge, empty solvent containers and oil drums.



Figure 6-12: Lime treating and wastewater holding facility.

It is suspected that possible groundwater contamination as a result of the operation would include inorganic and organic wastes, such as heavy metals, and typical chlorinated solvents. The site owner provided a list of chemicals used during the last two years of operation.

The ingredients of the solvents consist mostly of PCE (Tetrachloroethene), Dichloromethane, ethylene glycol monobutylether or a mix of chlorinated hydrocarbons. All of these chemicals are known DNAPL contaminants. From interviews with employees, it is also evident that used motor oil and greases were spilled in the area. The potential NAPL contaminants can thus possibly be more than just the dense chlorinated hydrocarbons, and this site is thus representative of a mixed DNAPL site. According to the US EPA, sludge from electroplating works is classified as hazardous and should be disposed of at a registered waste facility. A number of Superfund sites indicate former electroplating activities that resulted in typical groundwater contaminants such as trichloroethene (TCE), vinyl chloride, chromium, copper, and zinc (www.epa.gov).

6.3.1.3 Types of Chemicals

Different types of chemicals were used on this site, making the site a potential DNAPL-contaminated site. 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, aerial photos, interviewing employees, old engineering construction plans, and site investigations. Table 6-2 provides a preliminary list of suspected contaminants, depending on the activities at the site.

Table 6-2: Preliminary list of potential contaminants, depending on the activities at Test Site 1.

Area	Comments	Possible contaminants
Tank/truck washing bay	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 stormwater drain) Dumping of coal/bitumen residue from trucks	Bitumen (brand name – “autocoat”), oil/diesel, inorganics, coal residue
Electroplating workshop	Electroplating activities ceased 2003 The risk office has a complete list of chemicals used in processes 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	CN, chrome, solvents, acids, inorganics

Area	Comments	Possible contaminants
	Storeroom with acid, paint, solvents, Workshops all cement floors	
Redundant gasworks	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	Coal tar, inorganics, coal residue, unknown contaminants dumped in field
Foundry	Smelting, casting of metal components Boilers Slag and coal discard dumped	Heavy metals, solvents, oils/greases, cutting oils (including PCBs)
Other	Soda Ash storage tank USTs for diesel and petrol Channels, stormwater and sewage pipes/lines/sewers	Inorganics, diesel/oil/petrol, heavy metals

6.3.1.4 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.

East from the sludge treatment facility of the electroplating area, the land was used as an informal dumping ground for a variety of wastes, including building rubble, sludge, empty solvent containers and oil drums. From interviews with the employees, a list of chemicals used in the electroplating workshop is given in Table 6-3.

Table 6-3: List of chemicals used in the electroplating workshop.

Chemicals Used	
Solvents and degreasers including:	TetraSolve, RanSolve, Methoklone and Oxyprep
Number of acids including:	sulphuric-, hydrochloric-, nitric-, chromic-, ortho phosphoric-and , boric acid
Caustic Soda	Nickel Chloride
Nickel Sulphate	Copper Cyanide

Sodium Cyanide	Copper Sulphate
Calcium Hypo-chloride	Sodium Carbonate

6.3.2 Hydrocensus

As part of the data collection phase, a hydrocensus of the surrounding properties were completed. The purpose was to obtain an idea of the extent of the groundwater use and quality in the area. It was attempted to obtain a representative data set of different water users in the vicinity. Land and water use ranged from light industrial (e.g. auto workshops), food produce, agriculture and household use. The distribution of the hydrocensus boreholes in relation to the test site is shown in Figure 6-13 and general information of the boreholes is provided in Table A2 of the Appnedix. The hydrocensus was also aimed at understanding the water level and conceptualise the general flow direction.

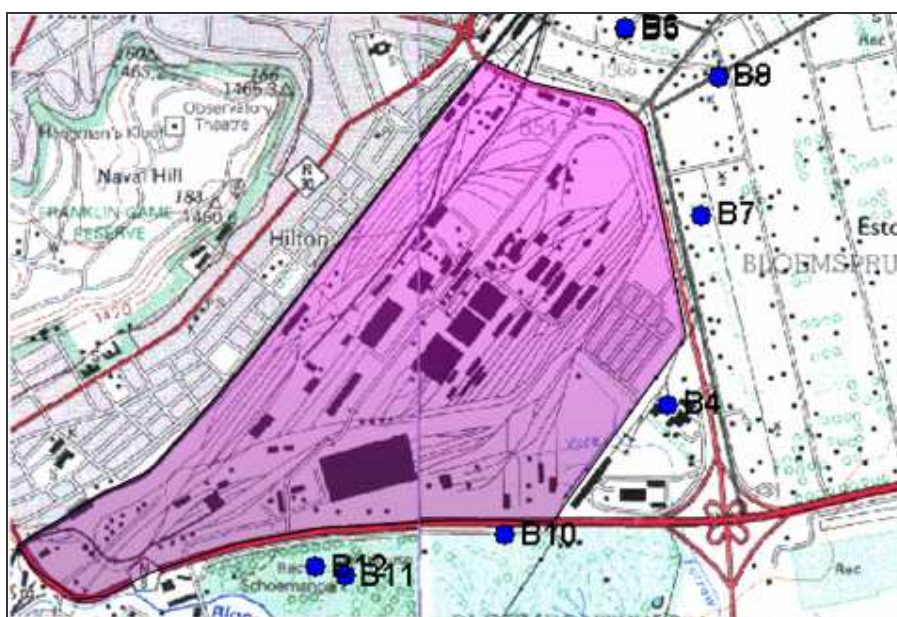


Figure 6-13: Topographical map of Test Site 1 (in pink) and the hydrocensus boreholes.

The boreholes were used for various applications, including domestic, industrial and/or agricultural purposes. Some boreholes were capped 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. Borehole pairs B5 and B6, B8 and B9, B1 and B4 are so closely spaced that they overlap on the map scale and are difficult to see in Figure 6-13.

6.3.2.1 Hydrogeological Findings

Water levels were found to be greatly variable across the area and ranged from approximately 6 m below the collar height to deeper than 50 m. Boreholes B8 and B9 are only 4 m apart but their water levels are 17.5 m and more than 50 m respectively. This indicates that the boreholes are most likely located in different aquifers.

6.3.2.2 Inorganic Results

The water sampling, storage and transportation procedures during the hydrocensus are the same as the procedures for water sampling of the boreholes drilled in Test Site 1. These procedures are discussed in Section 6.4.4.

Inorganic analysis was performed at the laboratory of the Institute for Groundwater Studies (IGS), University of the Free State. The chemical results are illustrated with STIFF diagram in Figure 6-14, and the data is provided in Table A 3 of the Appendix. Although the pH was generally neutral in all the boreholes, the water quality was found to be greatly variable. For example, the electrical conductivity (EC) ranges from 50.3 to 136 mS/m, while the potassium concentration ranged from 0.65 to 5.26 mg/L. However, all the samples are within acceptable drinking water standards, depending on the electrical conductivity values. From the preliminary interpretation of the results, it can be concluded that there is no conclusive evidence that there was off-site migration of the suspected contaminants from Test Site 1 to the surrounding groundwater users.

The water quality of Borehole B9 shows that more Ca^{+2} and NO_3^- than is present in Borehole B8. The difference in chemistry coincides with the difference in water level discussed in Section 6.3.2.1, which further indicates different aquifer systems or alternative hydrochemical sources.

Further investigation reveals that there are two patterns of chloride concentrations. Most 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. It is important to note that the chloride concentrations of Boreholes B8 and B9 are similar, 124 and 140 mg/L, respectively.

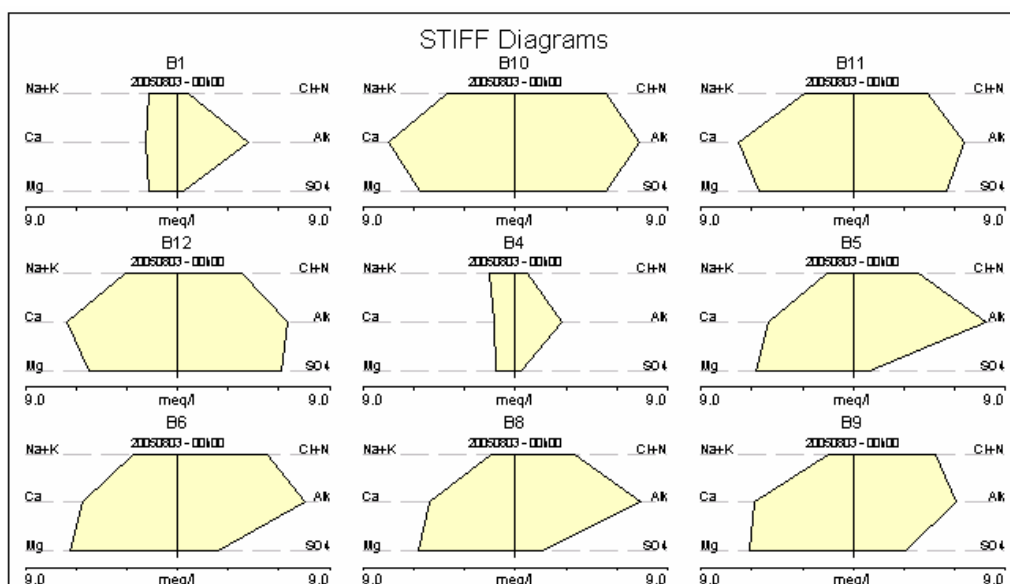


Figure 6-14: STIFF diagram of the hydrocensus boreholes.

All the boreholes, except B1 and B4, have similar chemistry. B1 and B4 are located close together and coincide on the map (Figure 6-13). They are found inside an abattoir region. As can be seen on the STIFF diagrams in Figure 6-14, they have a lower salinity than the rest of the boreholes, with lower calcium content.

6.3.2.3 Organic Results

The water quality was analysed for volatile organic compounds (VOCs) by UIS Analytical Services (Pty) Ltd. The laboratory is a private independent chemistry company with a wide range of analytical methods and consulting services located in Pretoria, South Africa.

The results are given in Table 6-4, and it can be seen that some of the VOCs showed elevated levels. These can most likely be attributed to on-site activities such as automotive workshops and transport-related industries. An important discovery is the existence of trichloroethene (TCE) in Borehole B5, with a concentration value of 13 µg/L. As discussed in Section 2.3.1, TCE is a common DNAPL and has a maximum permissible concentration level of 5 µg/L. However, it was not easy to unequivocally pinpoint the source of the contaminant, as there is a small industry that manufactures bricks in the borehole area, as well as several smaller-scale workshops where solvents may be used.

No polycyclic aromatic hydrocarbons (PAHs) were found in any of the samples analysed. Relatively higher concentrations of VOCs were detected in Borehole B5, located in a golf course, but this can most likely be attributed to a petrol spill from a nearby underground storage tank at a service station. Organic analysis shows the

contamination of Borehole B4 with bromoform. However, the concentration was only 12 µg/L, which was below the maximum concentration limit set at 20 µg/L.

Table 6-4: Organic chemical results of the hydrocensus boreholes.

Volatile Organic Compounds	B4 µg/L	B5 µg/L	B6 µg/L	B8 µg/L	B12 µg/L
Trichloroethene	<1	13.0	<1	<1	<1
Toluene	<1	1.3	<1	<1	<1
Ethylbenzene	<1	0.4	<1	<1	<1
o+p Xylenes	<1	0.6	<1	<1	<1
m-Xylene	<1	0.5	<1	<1	<1
Bromoform	12.0	<1	<1	<1	<1
1,3,5 Trimethylbenzene	<1	<1	<1	0.1	<1
Tert Butylbenzene	<1	0.3	<1	<1	<1
1,2,4 Trimethylbenzene	<1	0.3	0.3	0.3	<1
Dichlorobenzene	<1	<1	<1	<1	<1
Total	12.0	16.4	0.3	0.4	0.0

6.3.3 Direct Observations

A reconnaissance survey was done for a preliminary assessment and shallow soil samples were taken for organic contaminant analysis. Scoops, shovels and hand-augers were used for sampling. Due to the hardness of the unconsolidated sediments and the limited nature of manual work, 30 cm was the maximum depth sampled.

Duplicate samples were collected in amber glass bottles and transparent plastic bottles. To avoid cross contamination during sampling, the equipment was cleaned after every sampling. Since the loss of volatiles is a critical factor related to the chemical analysis of soil samples, care was taken in sample collection, storage and transportation.

Samples were taken from seven sites around the gasworks and from six sites at the electroplating area. Two or three samples were taken from each site at about 10 cm intervals. Samples were also taken from the tar pooled in an old sump at the gasworks. Additional sludge samples were taken from the old waste disposal pond in the electroplating area. In total, 25 soil samples and three possible source material samples were collected.

6.3.3.1 UV Analysis

The visual identification of DNAPLs can be enhanced by using methods such as ultraviolet (UV) fluorescence and soil-water shake tests (with or without dye), as discussed in Section 7.2.1. The plastic bottles used were transparent and it was not difficult to observe even small-scale fluorescence. If the sample did not fluoresce at all, its value was labeled “0”. If the intensity of the fluorescence was high, then it was labeled “2”, and intensities between “0” and “2” were labeled “1”. Figure 6-15 shows the fluorescence of three soil samples with values of 0, 1, and 2 respectively.

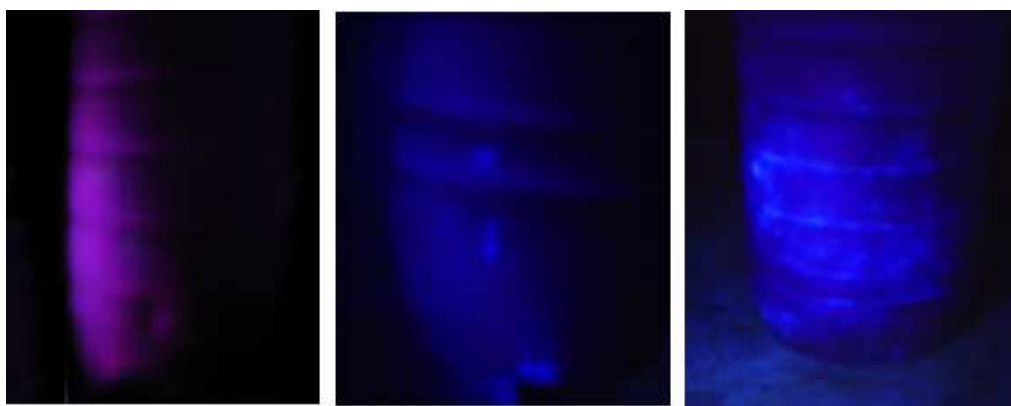


Figure 6-15: UV fluorescence of three samples with values of 0, 1 and 2 respectively.

6.3.3.2 Sudan IV Dye Shake Test

Soil-water shake tests involve the transfer of a soil sample to a clear, sealed container (tube) with an equal volume of water. The container is shaken by hand and/or centrifuged and then inspected for DNAPL at the bottom of the container. The test can be enhanced by the addition of a hydrophobic dye such as Sudan IV. Sudan IV is a relatively inexpensive reddish-brown powder that dyes organic fluids red upon contact, but is practically insoluble in water at ambient temperatures. This method can be used on site during drilling and sampling exercises. Figure 6-16 shows an example of LNAPL droplet detected using Sudan IV dye (the droplet turns red when the dye is mixed with water).



Figure 6-16: Detection of LNAPL droplet using the water-soil shake test with Sudan IV dye.

6.3.3.3 Findings from Direct Observation

The analysis of soil samples using UV and Sudan IV from the reconnaissance survey was aimed at obtaining quick and qualitative results, so that potential source DNAPL areas would be identified for further study. Since the samples were stored in transparent plastic bottles, small amount of fluorescence could be detected.

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.

The soil-water shake tests were found to be ineffective. Only two of the 17 samples showed visible NAPL droplets with the Sudan IV. The failure of the experiment could be attributed to the low concentrations of residual NAPL, and the poor colour contrast between the soil and the indicator. Soil suspensions were dark to reddish brow.

It can be concluded that visual and enhanced visual identification (especially UV fluorescence) can be recommended as first-order screening methods, but consideration has to given to the limitations of the soil-water shake tests.

6.3.4 Soil Gas Surveys

DNAPLs generally enter subsurface environments through unsaturated soil. Therefore, a soil and soil gas analysis may reveal rapid and indirect information about the quality of the groundwater. In principle, if a soil gas survey is conducted properly, the vapor plume in the unsaturated zone can be delineated (Pankow and Cherry, 1996). Although the factors that control the movement and distribution of the DNAPLs in the unsaturated zone are different from those in the saturated zone, the

idea of detection of a groundwater plume by vapour sampling in the unsaturated zone helps in characterising DNAPLs in the saturated zone.

A soil gas survey was done using a multi-parameter photo-ionisation detector (PID) known as the Ecolab PID®. Using this instrument, VOC, methane, total petroleum hydrocarbons (TPH), carbon dioxide and the oxygen content of the top 40 cm soil were measured. At each point selected for measurement, a hole was drilled to a depth of 40 cm. Immediately after drilling, the PID inlet is inserted into the hole, with the mouth of the hole sealed to prevent gas losses. Soil gas concentrations were then measured by the PID to obtain the levels of different components in the soil gas.

A total of 71 readings were taken, six in the electroplating area and 65 in the gasworks. The distribution of the drill holes where readings were taken is given in Figure 6-17. The VOC, TPH, Methane, O₂ and CO₂ values obtained are plotted in contour maps and provided in the following section.

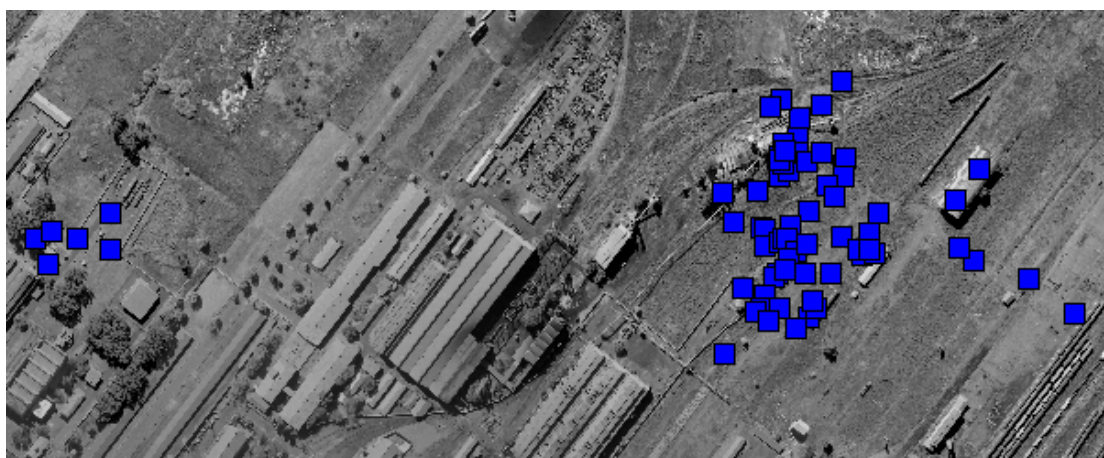


Figure 6-17: Drill holes where PID measurements were taken.

6.3.4.1 Results of Soil Gas Survey

A contour map plotted from the VOC values in the gasworks is shown in Figure 6-18. It seems that the distribution of the anomalies coincides with railway lines. They have a similar orientation to the UV fluorescence values obtained from the test pits (Figure 6-26). This provides further information that the VOCs are related to transportation and are most likely the result of spills during chemicals transport.

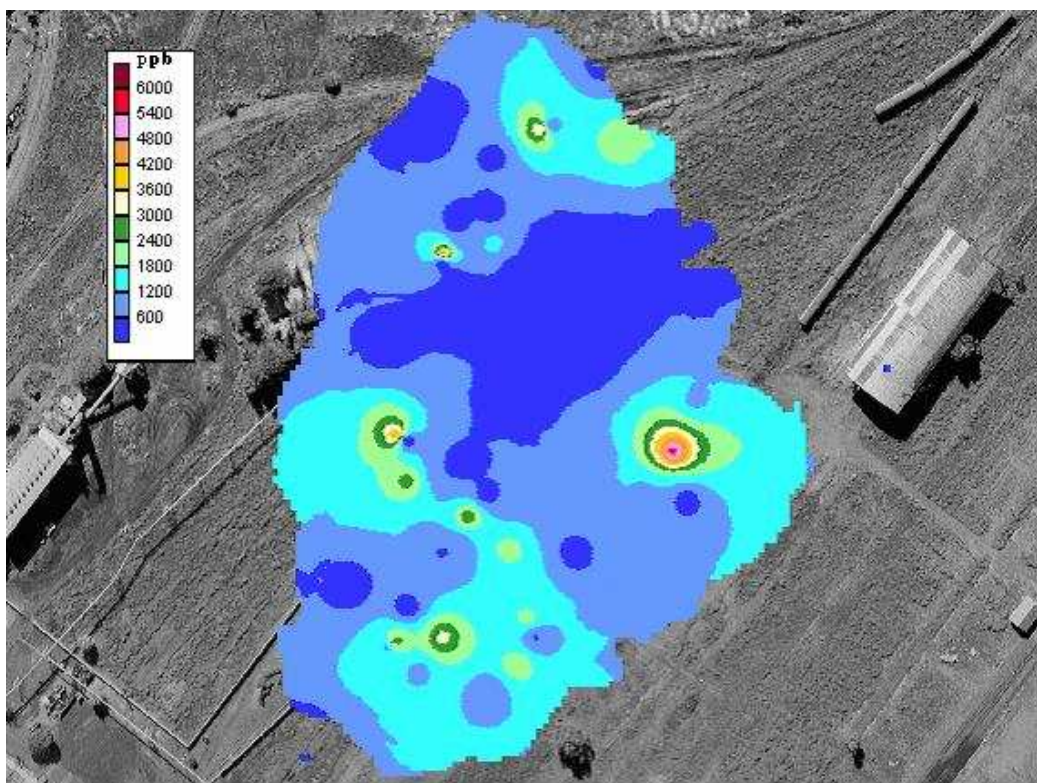


Figure 6-18: VOC distribution measured by the PID.

Figure 6-19 illustrates a contour map of TPH distributions. The high values around the middle of the map agree with the high VOC of Figure 6-18. These values are along railway lines; however, this does not mean that all railway lines are characterised by such high TPHs or VOCs. As shown on the figures, some sections of the railways have low distributions, which may indicate that there was no spillage along them. It is interesting to note in Figure 6-19, that soil vapour in the gasworks has low relative TPH values. The TPH content of the soil also coincides with that of methane.

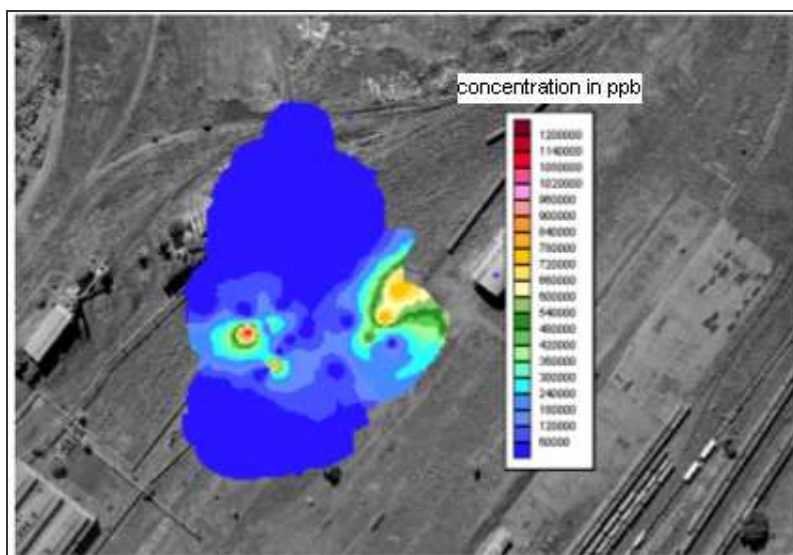


Figure 6-19: TPH distribution measured by the PID.

Methane is common in a reducing (non-oxidising) environment. A comparison of Figure 6-20 and Figure 6-21 shows that areas rich in O_2 (oxidising environment) has low methane (reducing environment). These distributions also indirectly provide information on the types of microbes that can be expected on different parts of the site. For example, we would expect aerobic bacteria to dominate in areas where O_2 is high. However, plants and bushes may also deplete the oxygen content of the soil.

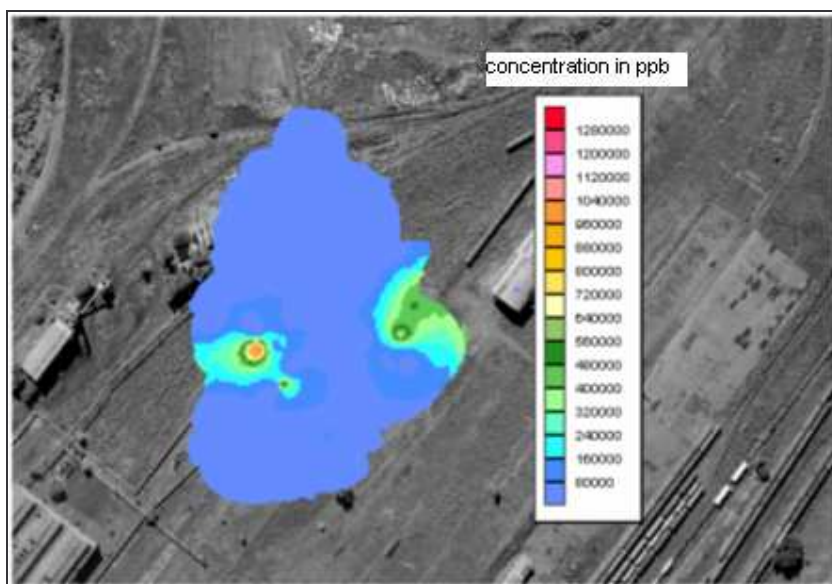


Figure 6-20: Methane distribution measured by the PID.

Unlike the other parameters, the O_2 content is low along the railway lines. This is possibly related to the degradation of organic compounds by microbes that consume oxygen as a preferred electron acceptor. The micro-organisms or plants use organic

compounds as a source of energy, and consume O_2 in the process. This explains why the O_2 is lower in areas where TPHs and VOCs are high.

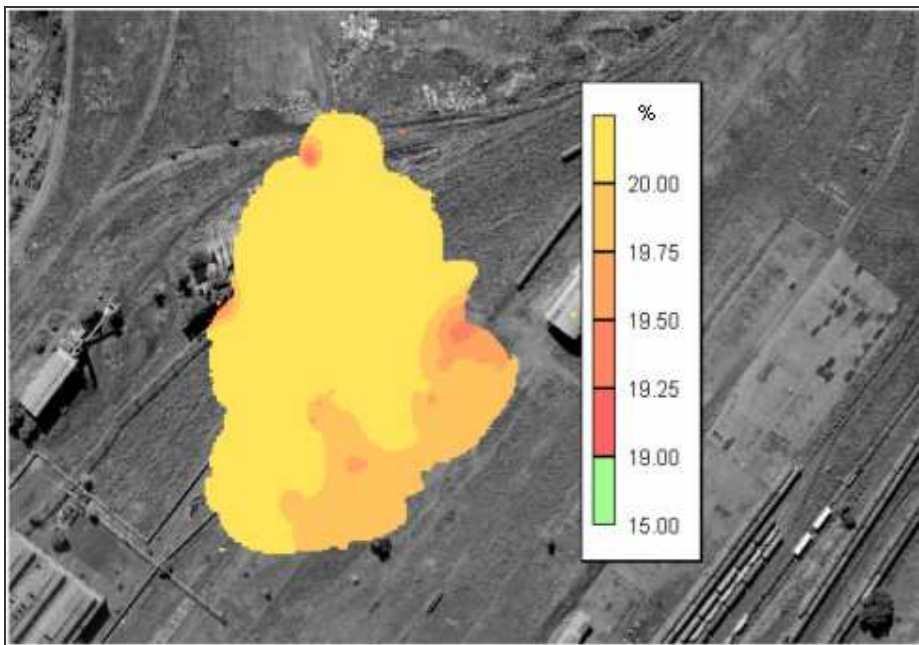


Figure 6-21: O_2 distribution measured by the PID.

Most microbes use organic compounds and O_2 , and release CO_2 as a product. Therefore, it is expected the distribution of CO_2 should follow the same spatial extent as the degradation distribution of TPHs and/or VOCs.

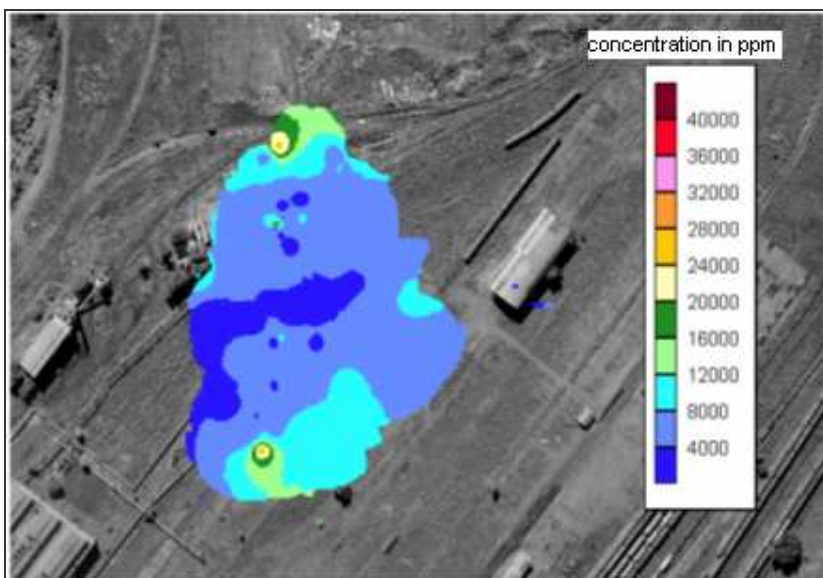


Figure 6-22: CO_2 distribution measured by the PID.

6.3.5 Surface and Airborne Geophysics

Non-invasive methods such as geophysical surveys can be useful to define subsurface geologic or contaminant conditions at contaminant sites by avoiding the mobilisation of DNAPLs during drilling and other invasive techniques. The most obvious choice for non-invasive methods, beyond evaluating historical records and using existing infrastructure, is geophysical techniques.

6.3.5.1 Airborne Geophysics

The airborne geophysical survey was performed under the supervision of the South African Council of Geosciences. The survey was high resolution and was aimed at detecting linear features that may influence the movement of groundwater in the area, which can act as pathways for the migration of DNAPL pollutants. During the survey magnetic and radiometric data were collected, as shown in Figure A 1 and Figure A 2, respectively, in the Appendix. A side product of the survey is a digital terrain model (Figure A 3) of the area, which is a higher resolution dataset than the normal topographical contour data and could assist in interpreting the flow directions of groundwater in the area. During the survey, low-flying birds caused a loss of 10% of the data; however, the most important parts were recovered.

As can be seen on the airborne survey figures, no geologic feature could be delineated with specific lineation or orientation. This is either due to the geologic composition of the site, or the immense population with cultural noise originating from power lines, railway lines, metal structures and waste dumps. However, the airborne geophysics conducted indicates trace of lineaments in the surroundings of Test Site 1.

6.3.5.2 Surface Geophysics

Various surface geophysical surveys were also conducted under the supervision of the South African Council of Geosciences. These include magnetic, frequency-domain electromagnetic, time-domain electromagnetic and resistivity surveys. As with the airborne geophysical results, no geophysical anomaly was detected that may provide preferential pathways to DNAPLs. This could either be due to the geological composition of the site or noise interference generated from industrial activities.

An electro-seismic survey (ESS) was conducted by Du Preez (2005) on the test site to delineate high permeability zones around the gasworks area. The lines were perpendicular to the assumed groundwater flow direction, so that possible fractured zones and subsurface structures could be identified. However, like the other geophysical surveys, there were no structural lineaments identified, either because of cultural interference or the nature of the subsurface geology.

6.4 Invasive Techniques

Invasive methods were used in a phased manner to test and advance the site conceptual model. The purpose of the invasive techniques were to define the stratigraphic, lithologic, structural, and/or hydraulic controls on the movement and distribution of the contamination (in all phases); characterise the fluid and fluid-media properties that affect DNAPL migration; estimate or determine the nature and extent of contamination, and the rates and directions of contaminant transport; evaluate exposure pathways; and design monitoring and remedial systems. The detailed procedures followed during the invasive assessment and results obtained are discussed in the following sections.

6.4.1 Test Pits

Test pits can provide more information regarding the shallow portions of the subsurface than borehole drilling. Test pits allow for a detailed visual examination of geologic structures and the lithologic composition of the shallow subsurface. At Test Site 1, the top layer is mainly composed of clay, and preferential vertical pathways could be investigated in the pits. Such features are difficult to identify in boreholes. An example of a test pit from the site is depicted in Figure 6-23.

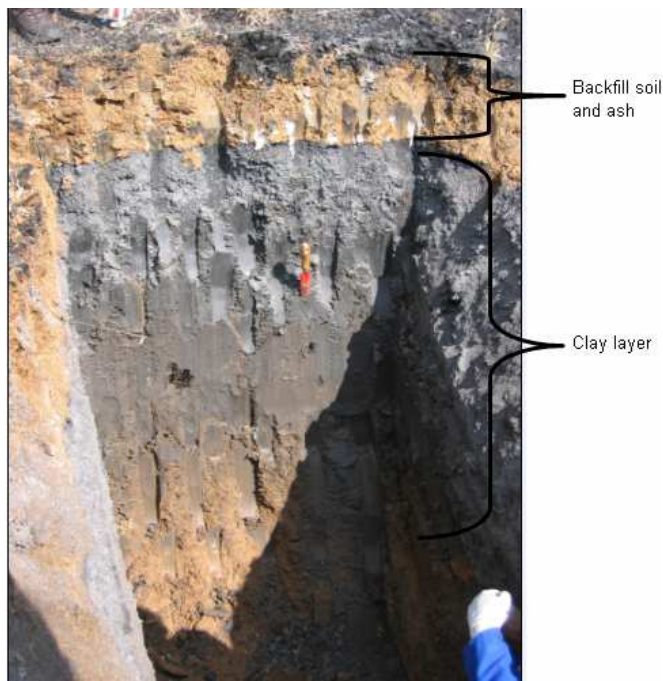


Figure 6-23: A test pit 20 m south of the gasworks.

Test pits also facilitate the visual examination of potential DNAPL distribution and their relationship with the geological features. Since DNAPL distribution and geological structures may be visible in the test pits in at least two dimensions, soil samples selected for chemical analysis have the potential to be more representative

than those collected from boreholes. However, the test pits are shallow, and investigations of depths greater than 3 m are not easy. At sites with limited unconsolidated material, test pits may not be as practical as borehole drilling.

Test pits can be excavated using a backhoe (back-actor) or power shovel to a depth of up to 8 m. The depth and size of the test pits are determined by the purpose of the investigation, strength of the excavator, sidewall stability, and worker safety regulations (Pankow and Cherry, 1996). A back-actor was used to unearth the pits on the site, with depths ranging from 1.5 to 3 m. Test pits were located in vicinity of suspected DNAPL source areas. A total of 25 test pits were dug (Figure 6-24); six in the electroplating and 19 in the gasworks area. After lithologic investigation and sample collection, the test pits were buried to avoid any short-circuiting of DNAPLs through the pits.

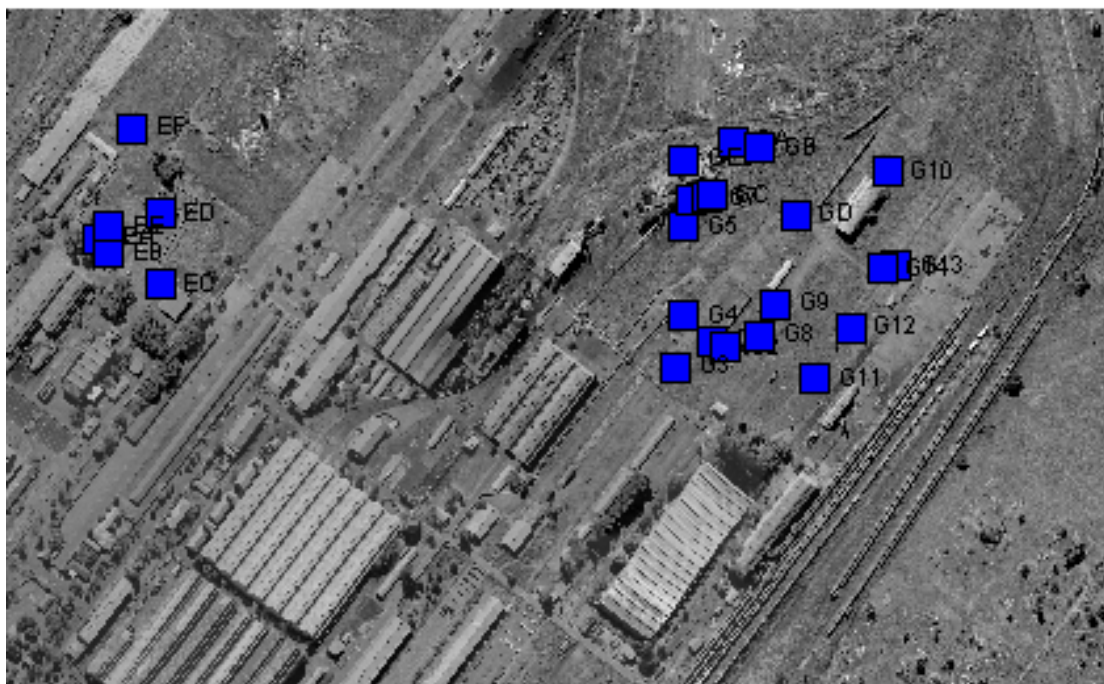


Figure 6-24: The distribution of test pits on the site.

6.4.1.1 Geological Findings

Soil sampling procedures from the test pits are similar to those used for boreholes and piezometers and are discussed in Section 6.4.3. As can be seen in Figure 6-25(A), the top soil is composed of backfill soil, followed by clay of varying thicknesses and colours. The clay layer appears to be very competent when moist. This implies that NAPLs will have few preferential pathways to migrate to lower layers and will be strongly attenuated by this layer. However, during dry conditions, the clay can form small fractures. Figure 6-25(B) shows a small-scale fracture plane within the clay, where dark-coloured NAPLs are visible.

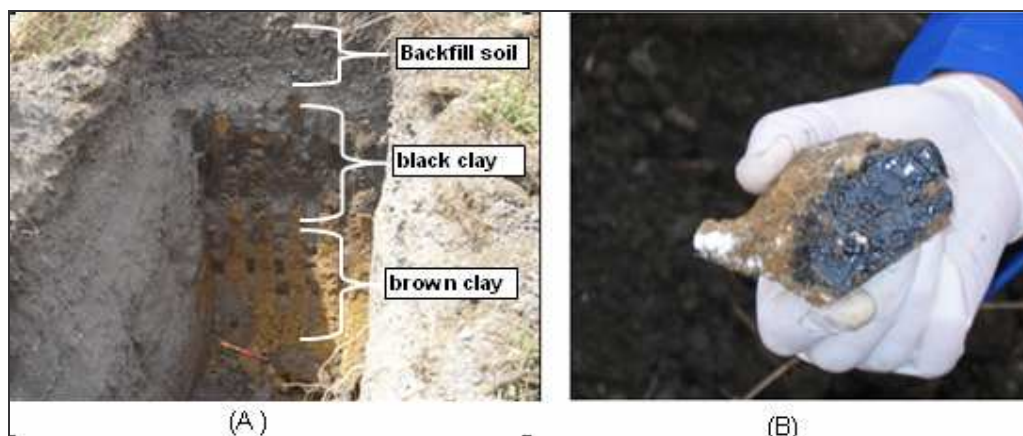


Figure 6-25: (A) Soil profile, and (B) visual observation of dark coloured NAPL on clay fracture plane from a test pit.

6.4.1.2 Chemical Results

During the excavation of the test pits, on average three samples were taken per test pit. Since the spatial distribution of DNAPLs can vary on a centimetre scale, they were collected so that they would be representative, both horizontally and vertically in a specific. Samples were collected *in-situ*, using hand-held scoops. After every sampling, the scoop was cleaned to avoid cross-contamination. From each sample, sub-sample portions were taken, one set being stored in plastic bottles and another in amber glass bottles. The samples in the plastic bottles were analysed using the UV light, while the glass bottles were sent to the laboratory for chemical analysis.

An important discovery that has to be emphasised is that soil samples from almost all the test pits had an odour of organic compounds. During the excavation at an area close to the electroplating workshop, an old plastic can containing used solvent was unearthed. This area was used as a waste disposal area and could potentially be a source of DNAPL pollution. A strong organic chemical smell was detected during excavations at the gasworks, which strongly suggests that the clay layer attenuated many of the contaminants spilled there.

UV fluorescence results from the reconnaissance survey and test pits were plotted to obtain a possible distribution of organic contaminants of the shallow subsurface, and is given as a contour map Figure 6-26. The UV intensity distribution seems to coincide with the railway lines. The likely cause of this is chemical spills during transportation. This distribution also shows a good correlation with the soil-vapour survey results (See Section 6.3.4).

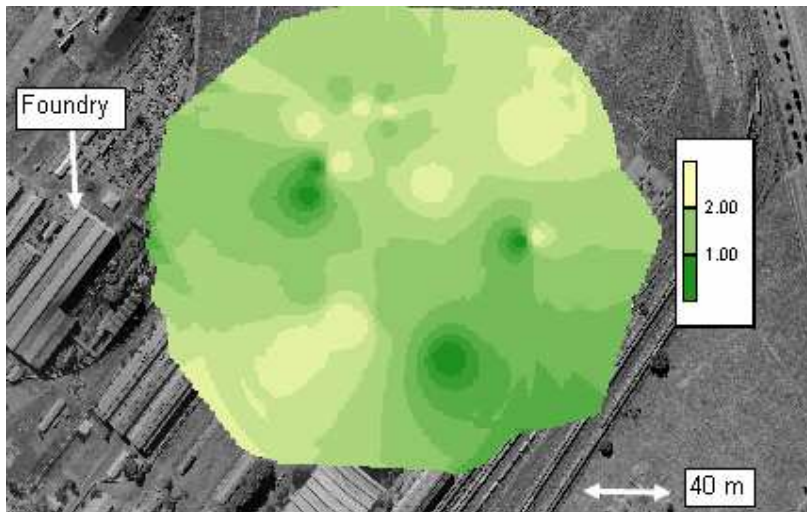


Figure 6-26: Intensity of UV fluorescence in the gasworks area.

Based on the screening of soil samples with UV fluorescence, selected samples were sent for laboratory analysis. A comparison between UV fluorescence and laboratory results is shown in Table 6-5. The column “Organic Compounds” indicates whether any VOCs, SVOCs or PAHs were detected in the sample. It was noted that some samples that fluoresced under the UV light did not contain any organic contaminants. Samples EA2, EC1, GC2, and GC5 fluoresced under the UV light, but did not contain any detectable organic compounds when analysed. This could be caused by volatilisation during storage, transportation, or handling in the laboratory before and/or during analysis.

Table 6-5: Comparison between laboratory and UV analysis.

Sample Code	UV	Organic Compound	Sample Code	UV	Organic Compound
EA2	1	Not detected	GA1	2	Detected
EB2	1	Detected	GB1	2	Detected
EB3	2	Detected	GB2	1	Detected
EC1	1	Not detected	GB3	2	Detected
EC2	2	Detected	GC1	2	Detected
ED1	2	Detected	GC2	2	Not detected
ED2	2	Detected	GC3	1	Detected
EE1	2	Detected	GC4	2	Detected
EE2	2	Detected	GC5	1	Not detected
EF2	1	Detected	GD1	2	Detected
GE2	2	Detected	GD3	0	Not detected

During a follow-up test pit excavation and sample run, soil samples were preserved with methanol. Efficient extraction of VOCs from the matrix materials can be achieved with methanol due to its strong affinity for these compounds and favourable wetting properties (ASTM D 4547, 1998). However, this technique did not result in the detection of additional VOC contaminants or higher levels of VOCs already detected.

The chemical results obtained from the laboratory are provided in Table 6-6 (tar pitch, an integral part of the tar sample, is not considered in this analysis). From this, it can be concluded that most of the contaminants found in the shallow soil zone are of a coal tar or creosote origin. No chlorinated solvents were detected in any of the samples. Coal tar and creosote are complex chemical mixture DNAPLs derived from the destructive distillation of coal in coke ovens and retorts. Coal tar contains hundreds of hydrocarbons, including light oil fractions, middle oil fractions, heavy oil fractions, anthracene and coal tar pitch. 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 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.

This is confirmed by 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 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.

Table 6-6: Organic contaminants composition of the test pit soil, coal tar and sludge samples (mg/Kg).

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 phthalate										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 contain compounds also found in the coal tar sample from the site.

6.4.2 Drilling

Test pits are restricted to the top part of an unconsolidated lithology. Soil and water sample analysis from boreholes and core holes can be useful in the investigation of free and dissolved DNAPL phases deep in the aquifer.

Boreholes were installed to evaluate subsurface stratigraphic, hydrogeologic, and contaminant conditions. Selection of borehole sites, depths, and methods was based on available information regarding site conditions. 17 percussion drilled borehole, seven auger drilled piezometers, and two diamond core holes were drilled in the course of the investigation.

6.4.2.1 Percussion Drilling

The purpose of the drilling was to investigate the distribution and amount of DNAPLs in the groundwater and soil profiles. An outside-in approach was applied, i.e. boreholes were first drilled further from the suspected sources, moving progressively closer. The distribution of the boreholes drilled by the percussion, auger and core drilling methods on the test site is shown in Figure 6-27. This technique was cheaper, but because of the extensive air applied during drilling, VOC could easily escape before sample storage. Boreholes SB1 and NB1 were drilled in the southwestern and northeastern part of the site for a better understanding of the flow direction in the latter part of the research to allow for better hydraulic understanding and for hydrogeologic, plume and geochemical delineation. The list of boreholes, their drilling dates and depths is provided in Table A 4, in the Appendix.

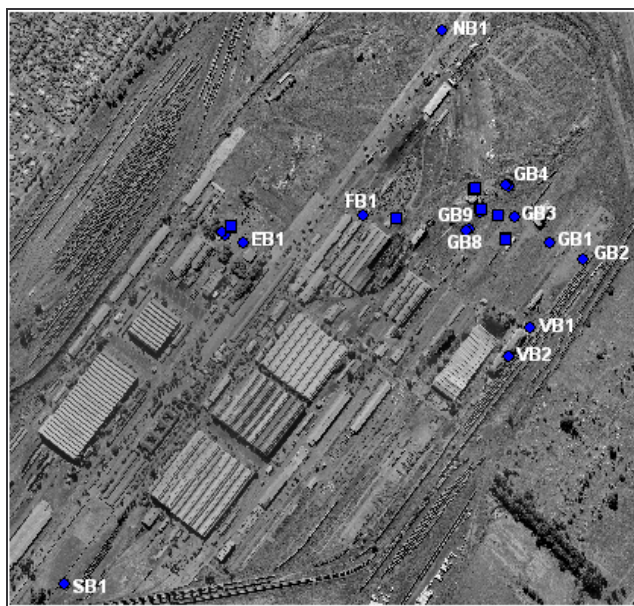


Figure 6-27: Position of boreholes (circles), piezometers and core holes (squares) on the site (due to crowding, only few boreholes are labelled).

6.4.2.2 Auger Drilling

Hollow-stem, direct-push and solid-stem drilling technologies were applied on the site. Auger drilling poses a smaller risk of mobilising DNAPLs than percussion drilling (USEPA, 1991), because there is less vibration during drilling and usually the borehole diameter is smaller. The purpose of this drilling was to investigate the unconsolidated section in relation to its DNAPL. This technique could have an advantage over percussion drilling, because intact samples can be obtained with hollow stem drilling or direct push techniques and the risks of volatilising VOCs is reduced when compared to air-percussion drilling that requires pressured air to remove the drill cuttings. Lithologic profiles could also be constructed more precisely, because there is no mixing of soils from different layers. The auger holes were developed to piezometers, and their distribution is shown in Figure 6-27. Limitations include that this drilling techniques has a limited penetration of more competent or consolidated rock

6.4.2.2.1 Hollow-stem Drilling

The hollow stem was aimed at obtaining undisturbed *in-situ* samples of the vadose zone soils. However, the technique was ineffective, as it was difficult to penetrate the clay layer. The moist clay had become impenetrable and was difficult to drill through. As a result, the stem was stuck in the clay, as shown in Figure 6-28 (A).



Figure 6-28: Auger drilling: (A) Hollow-stems stuck in the clay layer during auger drilling, (B) *In-situ* soil samples from direct push drilling.

6.4.2.2.2 Direct- Push Drilling

Direct-push drilling was attempted in the gasworks area. It was a good technique to obtain *in-situ* soil samples (Figure 6-28(B)). However, the unconsolidated layer, especially the calcrete, was so hard that only a few metres could be drilled, and the method was abandoned.

6.4.2.2.3 Solid-stem Drilling

Solid- or core-stem drilling was effective compared to the other two auger drilling techniques. The technique does not allow exact *in-situ* sampling like the hollow-stem and direct push methods; however, with solid-stem augering it was possible to drill through the clay and calcrete layers. All the piezometers developed were drilled by solid-stem auger. Figure 6-29 illustrates solid-stem drilling in the electroplating area.



Figure 6-29: Solid-stem auger drilling on the site.

6.4.2.3 Core Drilling

The core drilling was important in studying the geological composition and NAPL residue distribution by providing intact samples that were not possible with percussion or auger drilling. Although the drilling rate was slow (as slow as 3 m per day in hard rocks), detailed information on DNAPLs and geologic features was obtained. Boundaries between geologic layers were clearly identified. The degree of weathering, fracture orientations and preferential flow paths were thoroughly studied.

The first core hole (EC1) was drilled in the electroplating area to a depth of 59.43 m, while the second (GC1) was drilled in the gasworks area to a depth of 60.27 m. The location of the core holes is shown in Figure 6-27. The diameter of each core hole was

6 cm and slotted PVC casing was inserted to the unconsolidated part of the aquifer. A core hole drilling in GC1 is shown in Figure 6-30.



Figure 6-30: Drilling of Core hole GC1.

Core drilling was useful in defining the boundaries between the different geologic units more accurately than the percussion drilling. As revealed from the core drilling, the site is composed of unconsolidated sedimentary successions, followed by sedimentary rocks of shale and mudstone layers. The simplified lithologic profile of Core Holes EC1 and GC1 is shown in Figure 6-31.

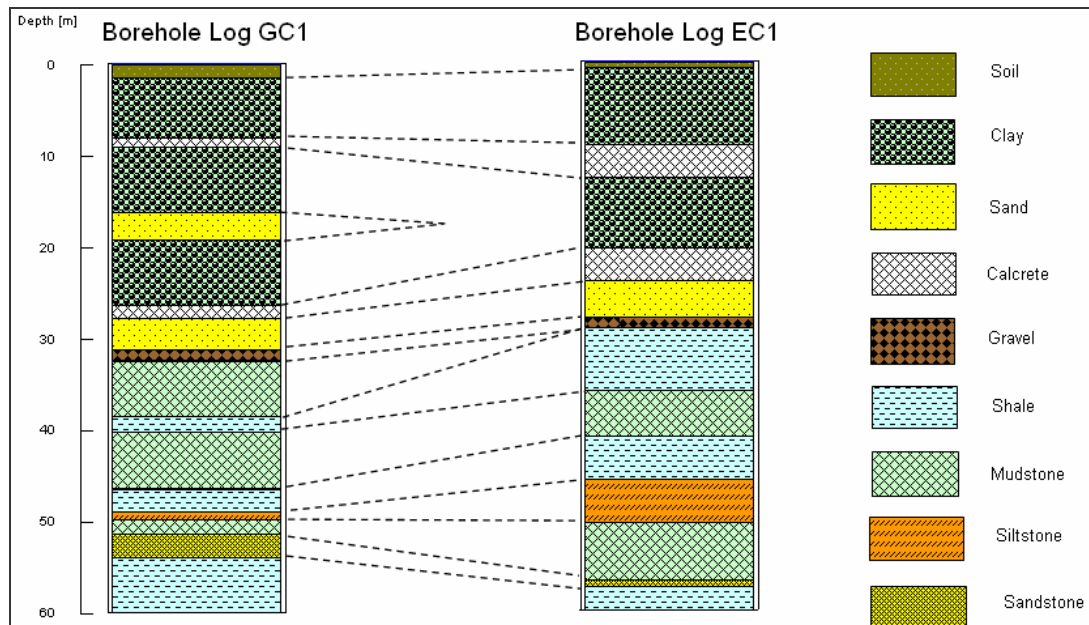


Figure 6-31: Summarised geologic profile of Core Holes EC1 and GC1.

6.4.2.4 Borehole and Piezometer Construction

6.4.2.4.1 Borehole Construction

The first four boreholes (GB1, GB2, GB3 and EB1) that were drilled have a similar construction. They have PVC casing with an internal diameter of 14 cm. The

unconsolidated part has interchanging PVCs, where one is cased and the next screened. Those that penetrate to the hard rock, GB3 and EB1, are left without casing. The bottom part of the boreholes is lined by bentonite to avoid vertical contamination. Figure 6-32 (A) shows the borehole construction of this group.

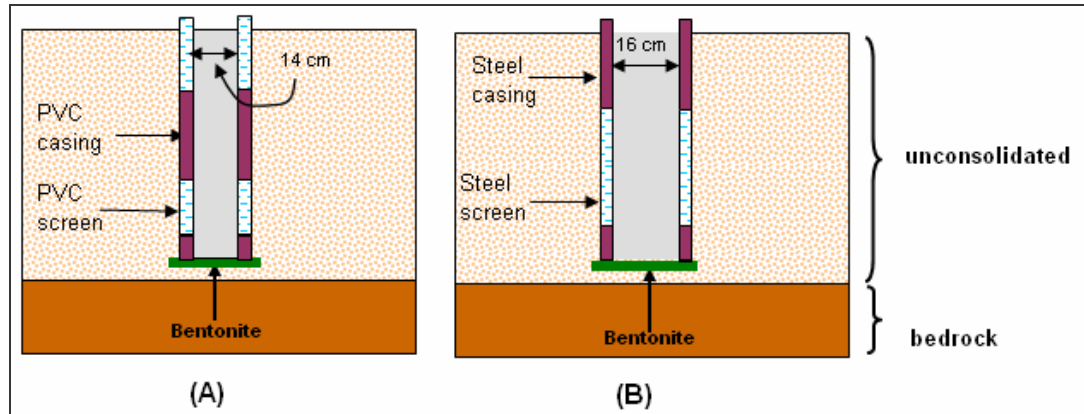


Figure 6-32: Construction of the shallow boreholes.

Boreholes GB5, GB6, GB8 and EB3 have a similar construction in that they are all in the unconsolidated aquifer. They are 16 cm in diameter, have a solid steel casing of about 5 m and the rest of the borehole section is slotted steel-screen. Figure 6-32(B) shows an illustration of this group of boreholes.

Boreholes GB4, GB7 and EB2 have a similar construction. They all penetrate to the hard rock and have an internal diameter of 16 cm. The unconsolidated part is steel cased, while the consolidated part is left open. The outer part of the boreholes is filled by bentonite at the contact between the unconsolidated and hard rock. This was done to avoid cross-contamination of DNAPLs from the two aquifer systems. Finally, the bottom part of the boreholes was lined by bentonite. This group of boreholes is depicted in Figure 6-33(A).

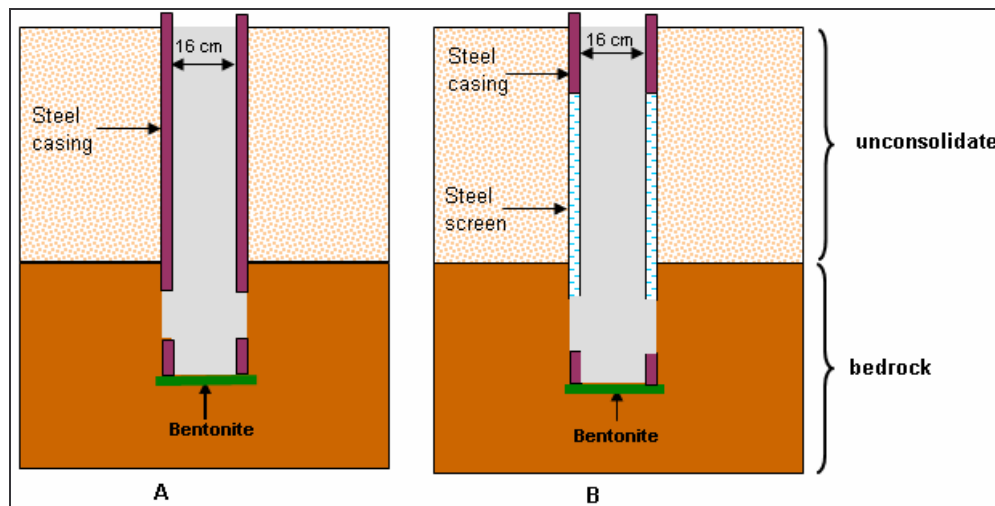


Figure 6-33: Construction of the deep boreholes.

Boreholes GB9 and FB1 have a similar construction. Both are drilled to the hard rock, but they are different from the other groups in that the entire section of the borehole is screened. Therefore, mixed water is supplied from the unconsolidated and hard rock aquifers. Figure 6-33(B) shows a sketch of this group of boreholes.

6.4.2.4.2 Piezometer Construction

As stated above, all the piezometers were drilled by the solid-stem auger technique. Three holes were drilled in the gasworks area and developed to piezometers. One piezometer was constructed in the foundry vicinity. A hole drilled in the electroplating was not developed to a piezometer. The internal diameter of the piezometers is 4.5 cm. Figure 6-34 shows a piezometer (GS3) in the gasworks area.



Figure 6-34: Piezometer drilled by solid-stem auger.

Table A 5 in the Appendix summarises the construction information of the piezometers. Both the solid and screened sections are made up of HDPE. The slotted section contains 84 slots within a 20 cm length. Each slot is 4 cm long and 2 mm wide. The depth column in Table A 5 shows the maximum depth reached during drilling; however, some of the piezometers collapsed later and are shallower.

6.4.2.5 Precautions during Drilling

Caution was exercised to prevent the further migration of contaminants via boreholes, especially in the form of dense DNAPL migration. The recommended strategy of drilling near the expected DNAPL zones only after subsurface conditions have been characterised by drilling in surrounding areas (the **outside-in** strategy) was followed on Test Site 1. The gasworks plant is the expected source of DNAPLs; therefore the first borehole, GB1, was drilled in the far southeast, the next (GB3) closer and the following (GB9) even closer to the source area (Figure 6-27).

Because DNAPLs are denser than water, invasive site characterisation procedures may inadvertently spread the contamination zone. For example, conventional drilling and well installation methods often create vertical pathways for DNAPL movement. The bottom of all the boreholes and piezometers on the site were lined with bentonite

to avoid such vertical movement. Unnecessary drilling within the suspected DNAPL source zone was also avoided to minimise the risk of contaminant spreading.

6.4.3 Soil Sampling

Soil samples were also taken whenever test pits, boreholes and piezometers were drilled from various layers. The time interval between digging, sampling and storing was as quick as possible to minimise loss of VOCs due to volatilisation. Soil samples were kept in a cooler box until they are analysed.

The drilling provided soil and rock samples from deeper sections of the subsurface than the test pits. As it was in the test pits, samples were taken in plastic bottles for UV analysis, and another in amber glass containers for organic analysis. Samples were also collected for mineralogical analysis and determination of the fraction of organic carbon (f_{oc}).

6.4.3.1 Mineralogy

Soil samples and rock chips were collected during the percussion and auger drilling for the analysis of mineralogy. The mineralogical analysis was done at the Geology Department at the University of the Free State, and the results are provided in Table A 6 in the Appendix. Quartz is the dominant mineral, probably because of its resistance to weathering. The relatively high content of calcite is mainly due to the calcrete layer common on the site. The presence of montmorillonite, illite and kaolinite in higher proportion are indicative that the site is rich in clay minerals.

6.4.3.2 Organic Chemical Results

The results of the samples that tested positive for the organic contaminants are presented in Table 6-7. The samples from the deeper portions of the aquifer (20 m or more below surface) tested below detection limits for the contaminants analysed. As compared to the test pits, it was noted that the organic contaminants found at greater depths were different, and in much lower concentrations. No chlorinated solvents were detected.

Table 6-7: Organic contaminant 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.

A few selected samples at various depths were selected to determine the fraction of organic carbon (f_{oc}) in order to calculate the potential of retardation in the clay layer. The analysis is done at Brethby, UK and the result is given in Table 6-8.

Table 6-8: Laboratory determined f_{oc} for selected soil samples.

Site Name	Depth	F_{OC}
ES1	14	0.17
FS1	2	0.26
GS4	3.4	0.08
GS5	18	0.09

6.4.3.3 Visual and Enhanced Visual Observations

During the drilling of the first boreholes, namely GB1 and GB2, soil samples were taken for UV analysis. Table 6-9 shows the results of this analysis. A considerable number of the samples fluoresced under the UV light. Samples from GB1 and GB2 fluoresced at depths of 15 and 16 m, respectively, which indicates the minimum depth of contamination. The values of the UV indicated by 0, 1 or 2 are discussed in Section 6.3.3.1.

Table 6-9: UV-value of soil samples from Boreholes GB1 and GB2.

Borehole name	Depth (m)	UV		Borehole Name	Depth (m)	UV		Borehole Name	Depth (m)	UV
GB1	2	1		GB1	13	2		GB2	6	2
GB1	3	1		GB1	14	2		GB2	7	2
GB1	4	2		GB1	15	2		GB2	8	0
GB1	5	2		GB1	16	0		GB2	9	2
GB1	6	2		GB1	19	0		GB2	10	1
GB1	7	1		GB2	1	2		GB2	12	1
GB1	9	1		GB2	2	0		GB2	14	2
GB1	11	2		GB2	3	1		GB2	16	1
GB1	12	0		GB2	4	0		GB2	18	0

6.4.3.4 Vapour Analyses

During auger drilling, vapour “head space” tests were performed on soil samples as they were collected during the process to measure the VOCs using a hand-held PID, shown in Figure 6-35.



Figure 6-35: Hand-held PID reading VOCs of soil gas from a plastic container.

Readings of VOCs using the PID was done in every 1 m depth of during the auger drilling. The maximum VOC reading scale of the instrument was 10000 ppm. Several of the samples recorded values of the maximum scale, which may indicate that their concentrations are actually above 10000 ppm. However, readings in some of the samples were very low. The values at every interval within a borehole are averaged and provided in Table 6-10.

The significantly low value in GS4 could be associated with the drilling, as it was the only borehole drilled using the direct-push. Of great interest is the fact that very few of the values recorded by the PID were confirmed by laboratory analyses.

Table 6-10: Average VOC values in auger-drilled holes.

Borehole Name	VOC ppm
ES1	2115.79
FS1	3351.41
GS1	5263.83
GS2	3506.89
GS3	1771.13
GS4	39.16
GS5	1344.83

6.4.4 Water sampling

Water samples in Test Site 1 were collected with the same procedure to that of the hydrocensus. A Solinst® depth-specific sampler was used to obtain the water samples. In Test Site 1, water samples were taken over a three year period at varying depths selected depending on the water strikes, anomalous EC-values, geochemical and geophysical borehole profiles. Before each sampling, the bailer was washed with

The objective of the water sampling was to detect the concentration of dissolved DNAPL contaminants and delineate the plume. Samples were collected in suitable glass vials provided by the laboratories and were completely filled, with no headspace. During many of the sample runs, two sets of water samples were collected, for inorganic analyses and organic analysis.

The inorganic content of the site boreholes is illustrated with a Durov and STIFF diagrams as shown in Figure 6-36 and Figure 6-37, respectively. All the boreholes have similar hydrochemical compositions. The groundwater can generally be classified as a Ca-bicarbonate type. From the 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 fractures. The 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^+ as compared to the Mg^{2+} content.



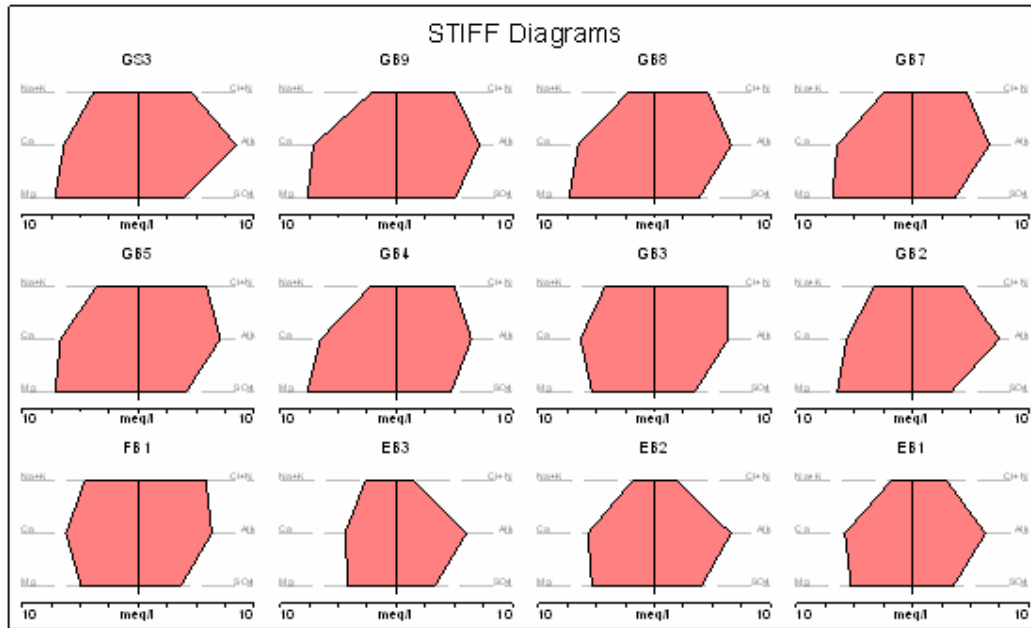


Figure 6-37: STIFF diagrams of the test site boreholes.

There is some difference in water quality between the boreholes in the unconsolidated section and those in the bedrock. In Borehole EB1, which is constructed to intercept both aquifer systems, the water quality varies at different depths (Figure 6-38 and Figure 6-39). 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 poor quality seeps through the fracture. However, there is only slight differences in the water type of the deeper boreholes, which supports the assumption of a “leaky aquifer” system with no aquitard dividing the two systems.

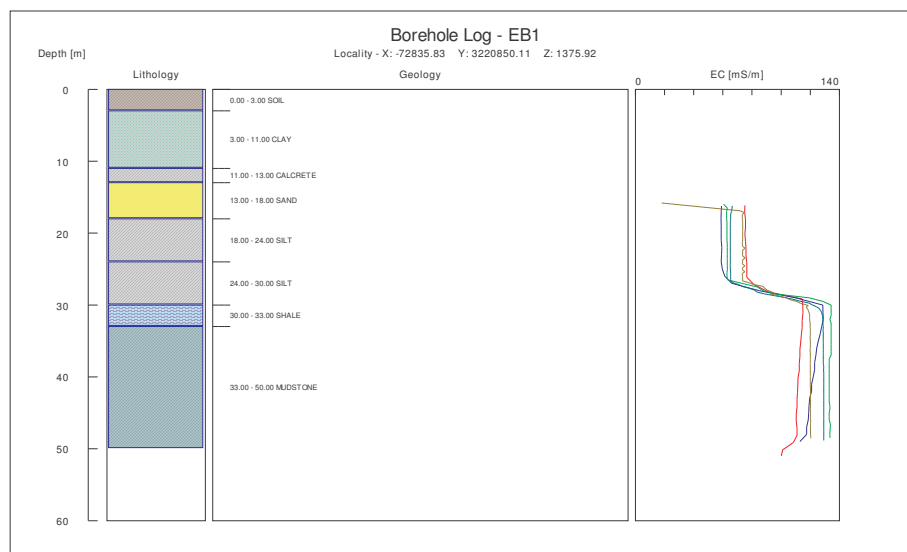


Figure 6-38: EC profile for Borehole EB1.

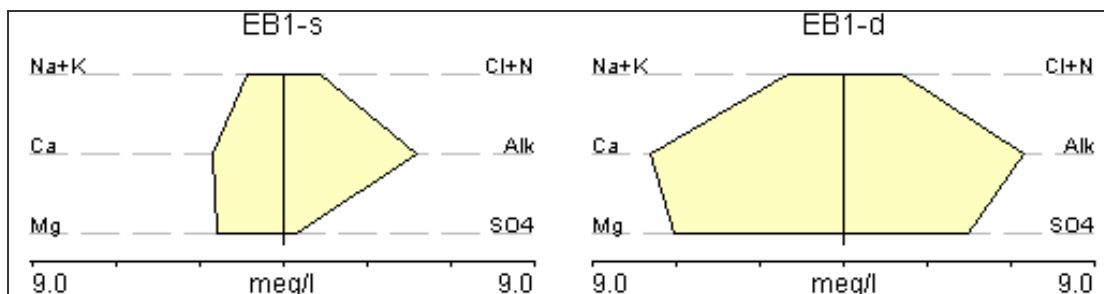


Figure 6-39: A comparison of water quality in EB1 in the unconsolidated section (EB1-s) and bedrock (EB1-d).

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



Figure 6-40: EC (mS/m) distribution of boreholes (circles) and piezometers (squares) on test site.

The boreholes at the gasworks have higher EC values than the electroplating boreholes. Generally the EC increases towards the east (Figure 6-40) and with depth (Figure 6-38). However, there are no health threats from inorganic substances, as most of the boreholes comprise EC values below the maximum recommended drinking water standards.

Other inorganic parameters that were evaluated to investigate lines of evidence for natural attenuation and degradation processes are nitrate, sulphate, and selected metals. A slight increases to nitrate and sulphate values are observed in boreholes where other lines of evidence for reductive dechlorination are present. i.e. EB2, EB3 and GB2. The data from the metal concentrations were inconclusive due to a lack of

differentiation between metal species. Only total metal concentrations were determined.

If the inorganic results of the hydrocensus is 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 more 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. The comparison of the hydrocensus and Test Site 1 inorganic chemical results can be done in Figure 6-41.

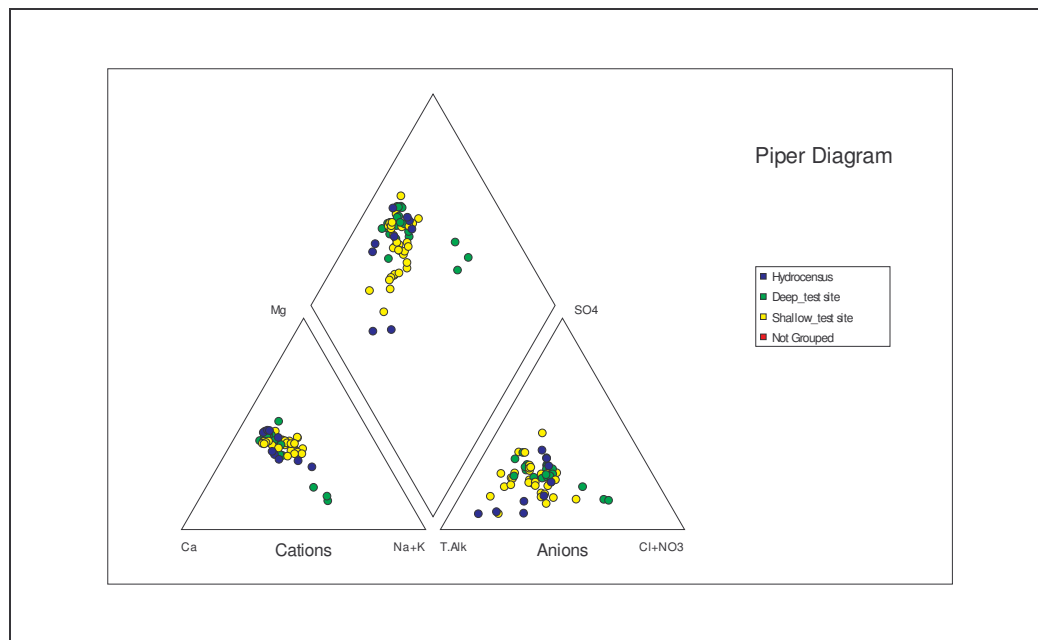


Figure 6-41: Piper diagram of the hydrocensus samples as compared to the Test Site 1.

6.4.4.2 Organic Parameters

A variety of organic contaminants were detected where most of the concentrations were low, seldom exceeding 5 µg/L. Cognisance should however be taken of the fact that available water quality standard limits (e.g. US EPA and Dutch Standards) are often very low 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 in the groundwater of the site consists 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, Atrazine, Simazine, and Terbutylazine. A number of miscellaneous organic components were also found, which include: Biphenyl, TPHs, 4-chloro-3-methylphenol, 3,3,5-Dimethylphenol, 4-thylphen, and Pentachlorophenol.

The contaminants of particular interest for this research 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 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 conceptualisation of the coal tar and creosote contaminants being attenuated in the upper unconsolidated layers, and only small amounts leaching to the shallow groundwater system.

Table 6-11 lists the boreholes tested positive for chlorinated solvents, where the major constituents are trichloroethene (TCE), chloroform (CF) and, to a smaller extent, tetrachloroethene (PCE).

Table 6-11: 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 and PCE 0.005 mg/L (www.epa.gov), and none of the detected concentrations exceeds the MCL.

6.4.5 Geochemical Borehole Logging

6.4.5.1 EC – Logging

EC profiling is an inexpensive yet effective method in locating fracture zones and other physical features that control water quality. Due to its ease of use and cost-effectiveness, it was applied to all the boreholes.

The advantages of this type of profiling include the determination of hydraulic variation within the vertical profile of the subsurface and identification of important features in the system. Using this, features such as fractures or layers that transport different salinity groundwater can be identified. As stand-alone measurements, these observations have a limited value; however, when viewed in conjunction with the geological logs or other down-the-hole measurements, a far more detailed conceptual

understanding of the most important geohydrological features can be obtained. These features are important for the dissolved phase plumes from NAPLs, and also for the NAPL transport itself, since they identify the stratigraphic horizons along which these are most likely to be transported.

On the test site, the Solinst TLC® was used for down-the-hole EC and temperature profiling. The Solinst TLC meter displays accurate measurements of conductivity and temperature on an LCD display. Water-level and probe depth measurements are read from the accurate flat-tape, marked in millimetres. The tape is housed on a standard reel. These features make the TLC meter ideal for profiling conductivity and temperature in wells and open water.

The results of the profiling are incorporated with the multi-parameter results discussed section 6.4.5.3. An example is given in Figure 6-38, which shows the geologic and EC profiling of Borehole EB1. A water strike fracture was detected during drilling at a depth of 30 m, and again by EC logging. The EC value of Borehole EB1 increases below the fracture, which may indicate that contaminated water is flowing through the fracture.

These are hydraulic conductive layers, along which more contaminated groundwater, and therefore most likely any solute plumes from DNAPL sources, may be transported. It should be noted that the transport of the dissolved phase of a DNAPL is not density driven, but governed by the same mechanisms as all other dissolved contaminants in groundwater. This was confirmed by the inorganic and organic chemical analytical results of the boreholes. Both organic and inorganic contaminant concentrations were found to be much higher in this highly transmissive zone than at other parts of the aquifer.

The TLC profiler was thus very effective in indicating specific hydraulic features in the aquifer system, and guided the research to target specific depths for sampling dissolved phase contaminants.

6.4.5.2 Interface Probe

The accumulation of DNAPL in the bottom of a monitoring well can be determined effectively by the use of interface probes, or by sampling at the bottom of the well. Interface probes are down-the-hole sensors on a graduated cable or tape. They commonly use an optical sensor for detecting the air/water interface, and a conductivity sensor for detecting the water/DNAPL interface.

The Solinst Interface Meter® is an instrument that works on the principle stated above, and was applied to the site boreholes. Under ideal conditions, a DNAPL and/or LNAPL thickness of about 2 mm or greater can be detected. However, a DNAPL is difficult to detect by these means when mixed with fine sediment at the bottom of the well when it is conductive, or when it preferentially wets the probe materials.

Benzene and TCE were used as testing fluids for LNAPLs and DNAPLs, respectively. The limitation of the interface probe is that it cannot detect NAPLs if their thickness is less than 2 mm. No free DNAPL phase was detected in any of the boreholes or piezometers.

6.4.5.3 Multi-parameter Probe

A multi-parameter probe YSI 600 XLM® was used to log all the boreholes through time. These parameters include electrical conductivity (EC), temperature, oxidation reduction potential (ORP), dissolved oxygen (DO) and pH values. In addition to locating fractures and geological anomalies, these parameters are useful in analysing microbial activities that could biodegrade DNAPLs. As an example, a geochemical logging of Borehole FB1 is given in Figure 6-42. The loggings were done in different dates and are indicated by different colours. Except for the temperature, the parameters were good in identifying fracture positions and anomalies coincided with drilling information. Since the water table is more exposed to the atmosphere than the lower section of the aquifer water, it is no surprise to observe higher dissolved oxygen in the water table area in all the boreholes.

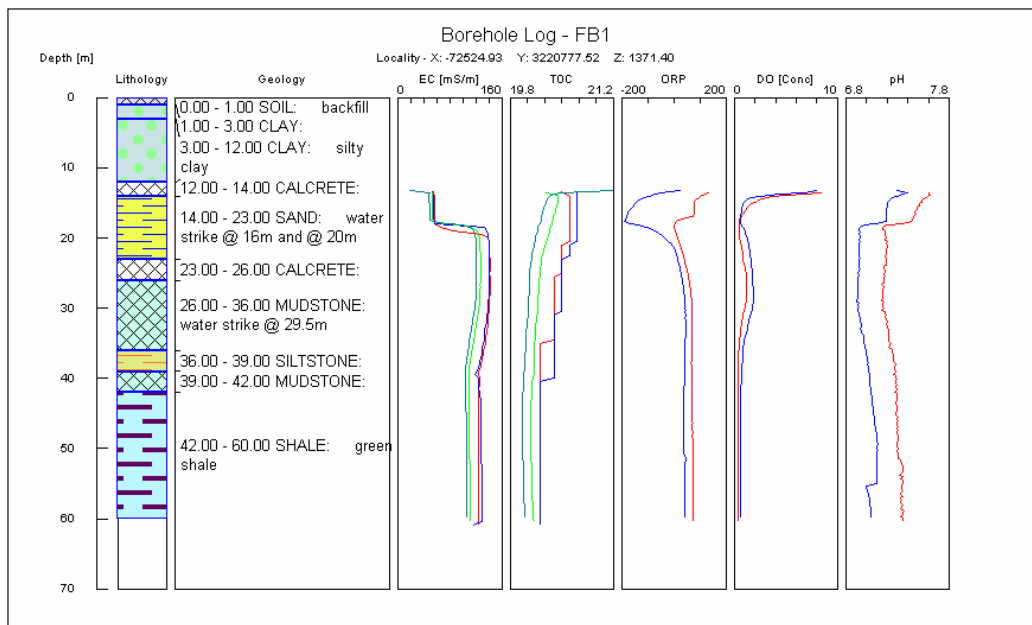


Figure 6-42: Geochemical logging of Borehole FB1.

6.4.6 Borehole Geophysics

The borehole geophysical loggings were conducted under the supervision of the Department of Water Affairs and Forestry (DWAF). Geophysical methods provide qualitative and quantitative information on subsurface conditions. They can be deployed in a number of ways: purely surface survey, surface to borehole, borehole to

borehole, and single borehole. Single borehole geophysics was applied to the test site and the techniques with their results are discussed in this section.

The geophysical methods do not measure the extent and distribution of NAPLs. They are used to measure the physical properties of subsurface materials. Changes in these properties are used to interpret changes in the materials that are important in developing the conceptual model (ITRC, 2004). For example, examining fracture size and orientation in bedrock provides information on potential preferential flow paths of DNAPLs.

Sometimes, the resolution of the techniques could be insufficient to locate thin preferential pathways for small pockets of NAPLs. In order to obtain the best result from a borehole log, as much information as possible must be compiled and compared. Usually formations do not give a unique response to a single function, but by comparing the response to other functions, a better interpretation can be obtained.

6.4.6.1 One-arm Caliper

The caliper is used to measure the maximum diameter of a borehole. It is helpful in logging caving sections, eroded intervals, fractures, changes in drilling diameter, casing sizes and the position of screens. The caliper has one arm and measured in only one dimension. The continuation of the anomaly in the other dimensions must be confirmed by correlating other geophysical techniques.

On the left-hand side of Figure 6-43, the borehole geologic log of GB9 can be seen, and on the right is the borehole's caliper log. The drilling information indicates that there are few water strikes, of which one is at approximately 35.5 m. The caliper log shows an anomaly at a depth of 36 m, which may be the fracture zone that was detected during drilling. The above water strikes could not be detected by the caliper, as the borehole is cased to a depth of 31 m.

The caliper is used primarily to verify fracture positions that could possibly be preferential pathways to DNAPLs.

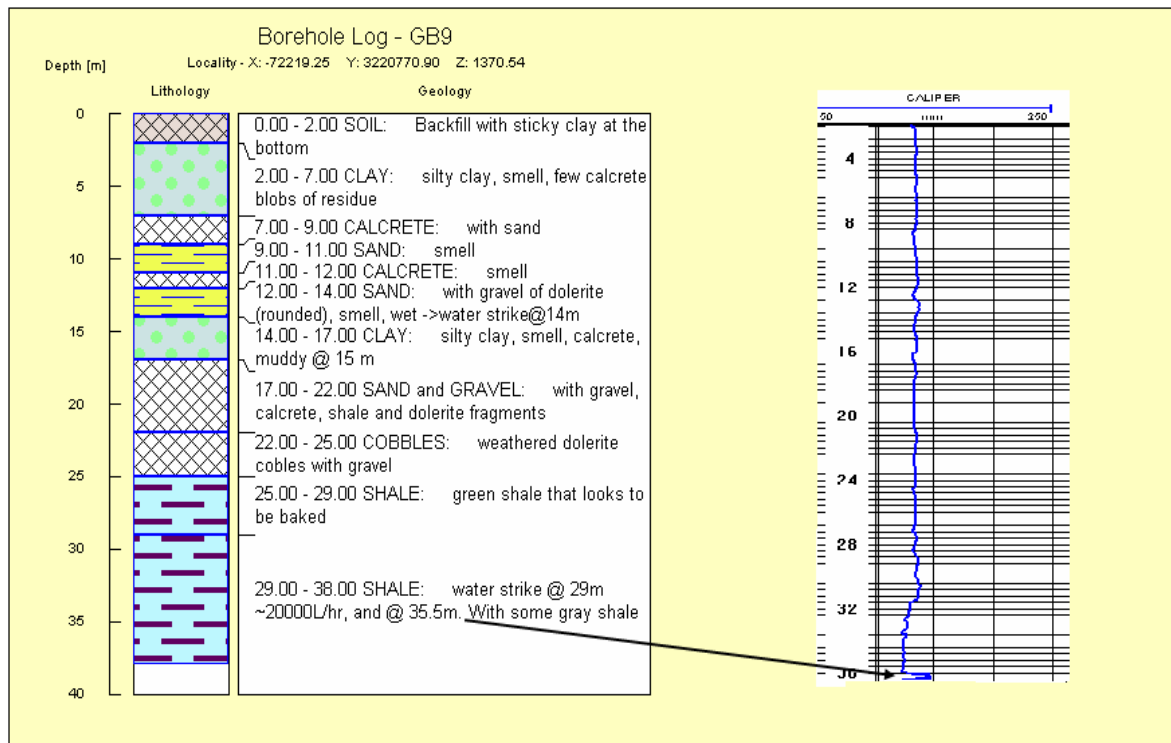


Figure 6-43: Comparison between drilling borehole log and caliper log in Borehole GB9.

6.4.6.2 Natural Gamma

Natural radioactive isotopes, mainly potassium, uranium and thorium, emit gamma rays detected by the sensors in the probe. While no soil or rock material has a characteristic level of natural radiation, the different matrices within a borehole can be differentiated by relative activities. For example, clays and shales contain potassium-rich minerals like mica and clay minerals; they are more radioactive than sand and dolomite.

Natural gamma is primarily used to verify the stratigraphy on the site conceptual model. A log of natural gamma in Borehole EB1 is given on Figure 6-44, in comparison with spontaneous potential and resistivity. The anomaly at a depth of 31.3 m is not detected by the gamma method, illustrating that geophysical results should be correlated for a better interpretation. The small anomaly at a depth of 44.5 m, however, could be correlated with the spontaneous potential and resistivity logs and is a fracture. The fracture was also identified during drilling, as shown in the borehole log.

6.4.6.3 Spontaneous Potential (SP)

The spontaneous potential probe measures the voltage change in millivolts between an electrode located on the probe and one at the surface. The potential between these electrodes is measured as the electrode travels through the conductive fluid in the borehole. The spontaneous potential method is used to measure bed thicknesses, and

can be used to measure water quality. It is also helpful in indicating corrosion severity in a steel casing.

It is not known whether this has any potential for locating anomalies due to DNAPL. A spontaneous potential log of Borehole EB1 is shown on Figure 6-44. An anomaly is shown at a depth of 31.3 m, which is probably the end of the casing. A little anomaly at the depth of 44.5 m is suspected to be a fracture. The fracture was also identified during drilling, as shown in Figure 6-44.

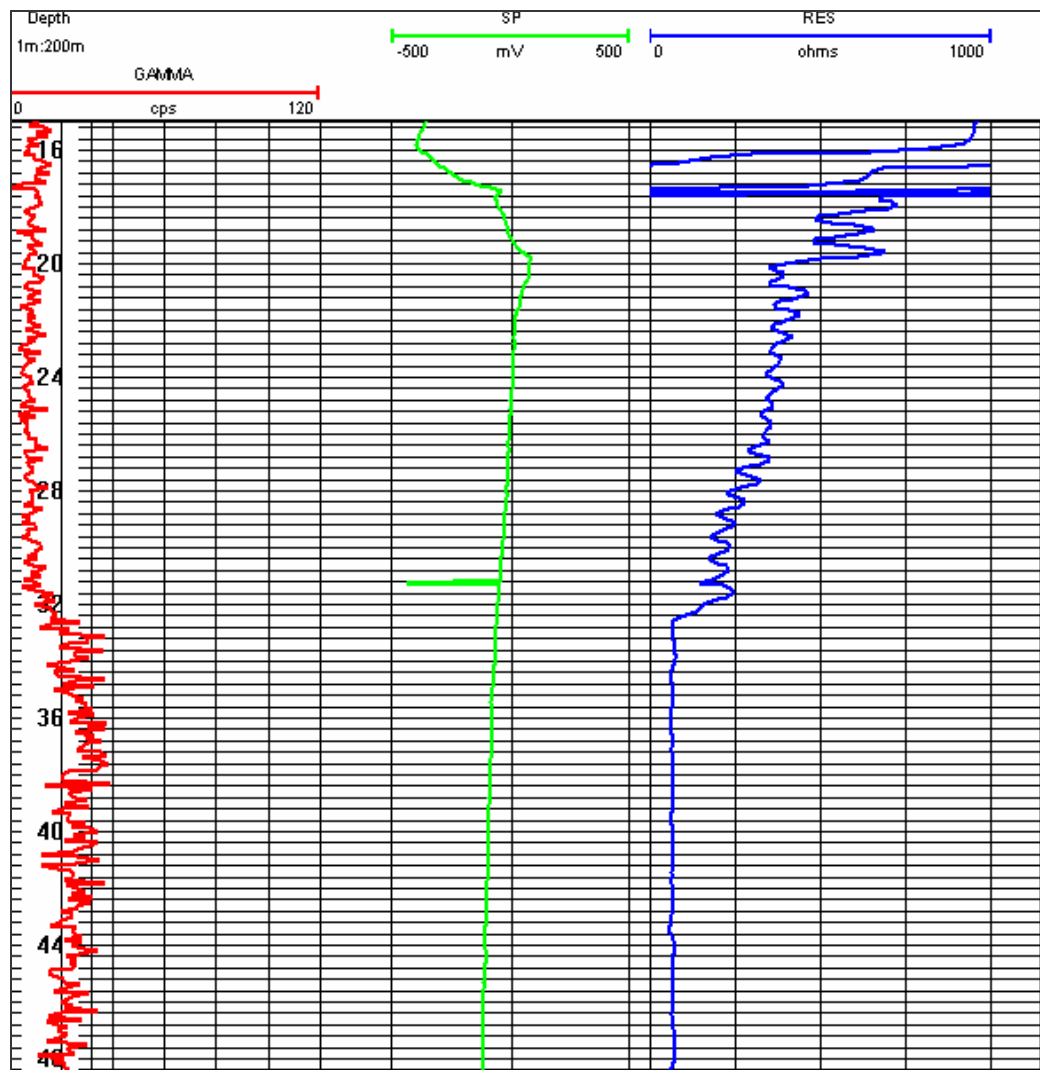


Figure 6-44: Gamma, SP and resistivity logs in Borehole EB1.

6.4.6.4 Resistivity Probe

This method measures the electrical resistance between an electrode on the probe and one at the surface. The resistivity method is mostly used to define formation boundaries, joints and fractures, the water level, the end of casing and the location of screens. Resistivity is the inverse of conductivity; therefore, water of high resistivity means low in conductivity and vice versa.

Borehole resistivity is useful in developing a conceptual model of bedrock stratigraphy and the potential preferential pathways of DNAPLs. In Figure 6-44, a resistivity anomaly is noted at the depth of 31.3 m, which is also detected by the spontaneous potential and is likely due to the casing end. A little anomaly at the depth of 44.5 m is suspected to be a fracture, which is also detected by the gamma and SP techniques. The fracture was also identified during drilling. The profiles given in Figure 6-38 and Figure 6-44 were done in Borehole EB1, and it can be clearly seen the conductivity is the inverse of resistivity.

6.4.6.5 Full Wave Sonic (FWS)

The full wave sonic is used to measure formation strength. The wave travels at different velocities in different lithologic units and is useful in demarcating the boundaries. Figure 6-45 shows the FWS profile in Borehole EB1. A clear anomaly could be identified at a depth of 33.5 m. Closer inspection also reveals small anomalies at the depths of 20.3, 26.3, 31, 33, 36 and 44 m. The 33.5 and 44 m depth anomalies agree with those discussed in Sections 6.4.6.2, 6.4.6.3 and 6.4.6.4. The anomaly is the casing end, and the second is a fracture, which can be correlated with Figure 6-44.

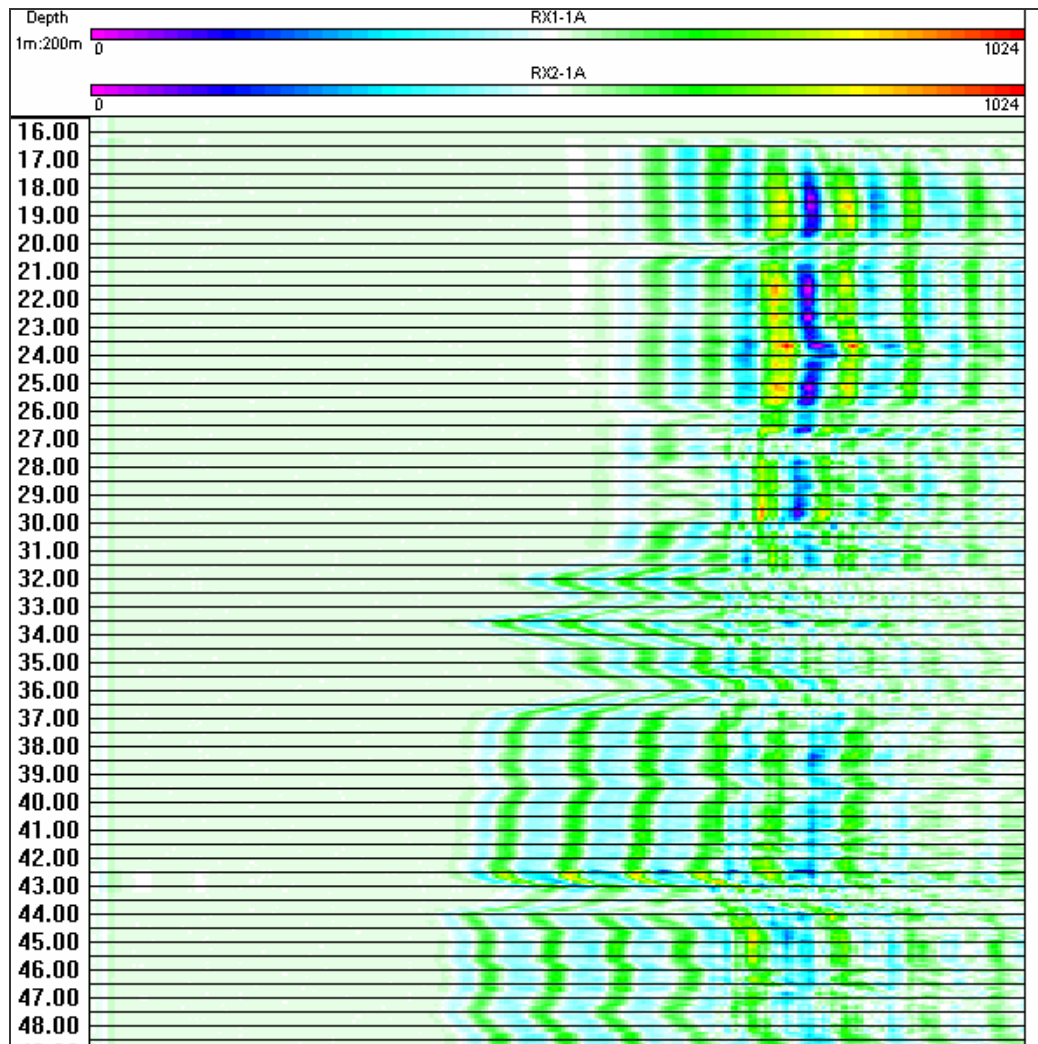


Figure 6-45: Full wave sonic profile of Borehole EB1.

6.4.6.6 Neutron-neutron Probe

Figure 6-46 shows the neutron-neutron profile of Borehole FB1. The anomaly at a depth of 13.3 m is due to the water level.

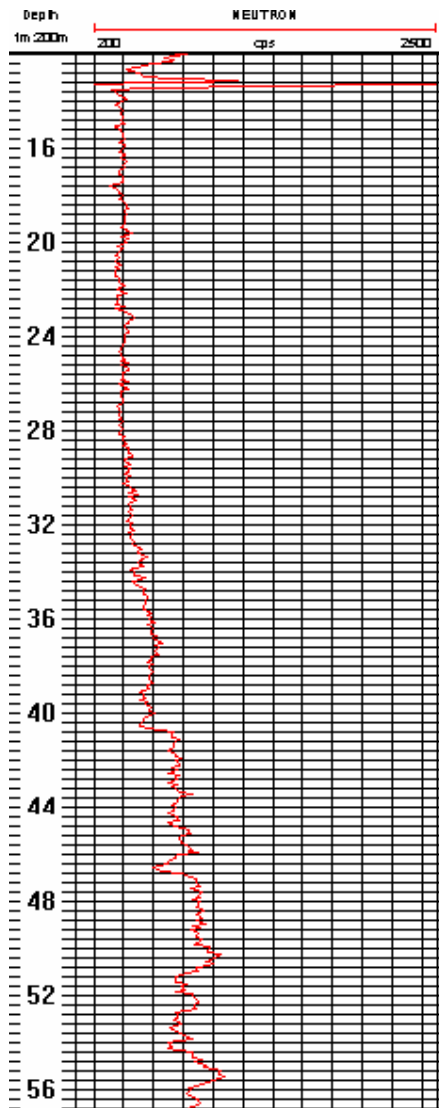


Figure 6-46: Neutron-neutron log of Borehole FB1 showing an anomaly at the water level.

6.4.7 Aquifer Tests

6.4.7.1 Slug Test

Prior to the pump test, slug tests were performed to estimate the hydraulic conductivities and yields of the boreholes. The analysis was performed using the Bouwer-Rice method. A summary of the results is shown in Table 6-12. The column K_{fm} is the estimated hydraulic conductivity of the formation. The term “formation” in this context means an average hydraulic conductivity of the porous matrix and fracture zone. K_f is the estimated hydraulic conductivity of the fracture zone only. The thickness of the fracture aperture in the boreholes is not precisely known. Therefore, in all the boreholes the fracture zones are assumed to have a thickness of 0.2 m to calculate the K_f . Generally speaking, K_f and estimated yields are proportional with an R^2 -value of 0.81.

Table 6-12: Slug test results.

Borehole	K_{fm} (m/d)	K_r (m/d)	Estimated Yield (L/s)
EB2	16.75	90.05	3.17
EB3	2.07	18.37	2.65
GB4	4.98	78.32	4.99
GB5	1.10	31.25	2.65
GB7	6.32	71.14	4.80
GB8	5.10	85.50	3.03
GB9	11.18	409.55	8.80
GB1		120.40	3.40
GB2		76.86	3.71
GB3		181.77	6.29
EB1		131.76	5.32

Van Tonder *et al.* (2005) state that the estimated K-value (and thus KD-value) determined by the total thickness of the formation in a slug-test analysis, does not represent the T-value of the formation. Therefore, the estimated K_{fm} in Table 6-12 is just an approximate value because of its dependency on the flow thickness (thickness of the part of the aquifer in which flow occurs due to the slug input).

6.4.7.2 Pumping Tests

The results of the pump tests on Test Site 1 show that the aquifer systems generally have high T-values. Broadly speaking, the system can be divided into two aquifers, depending on the estimated transmissivity values and the geology. These are the unconsolidated aquifer (which will be noted as Aquifer 1), and the consolidated aquifer (which will be noted as Aquifer 2). This division was also supported by the water level measurements discussed in Section 6.8.4.1.

Pumping tests were done on both aquifer systems, and the T-value of Aquifer 1 is found to be significantly lower than that of Aquifer 2. The T-value of Aquifer 1 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. As observed in three boreholes (namely GB1, GB5 and EB3), Aquifer 1 will be dewatered within 15 minutes if pumped at a rate of greater than or equal to 3 L/s.

Aquifer 2 has a relatively higher T-value, ranging from 216 m²/day in GB7 to 797 m²/day in GB9. There could be many causes for the large range in transmissivity. Two main factors include the abstraction rate during the test and the duration of the test. For example, if we consider GB9, the rest water level was at 15.55 m and the main water strike at 29 m. Although the test was performed for five hours, the abstraction rate was very low (2.9 L/s) and the total drawdown was only 0.63 m. Therefore, the T-value that could be estimated is mainly the response of the fracture. It can be concluded that the 797 m²/day is the T-value of the fracture, while the 216 m²/day is the value of the formation (matrix and fracture). Another possibility for the variation of T-values is local differences in geologic formations and/or borehole construction.

Aquifer 2 has a relatively higher T-value, ranging from 216 m²/day in GB7 to 797 m²/day in GB9. Since this is a fractured aquifer, there could be many causes for the large range in transmissivity, such as fracture aperture, connectivity and density, heterogeneity of the porous matrix, abstraction rate and the duration of the test.

For example, in GB9 the rest water level was at 15.55 m and the main water strike at 29 m. Initially the pump test was performed for 5 hours at a pumping rate of 2.9 L/s. As a result of the low pumping rate, the drawdown was only 0.63 m and the estimated T-value was 797 m²/d. However, when the borehole was pumped at rate of 4 L/s for 26 hours, the drawdown was 1.09 m and the estimated T-value was 216 m²/day. The high T-value estimated during the lower pumping rate is probably due to the fracture reaction. However, when the borehole was stressed for a longer period and at a higher pumping rate, the response was from the fracture and the matrix and the estimated T-value of formation (matrix and fracture).

6.4.7.3 Diagnostic plots

Three pumping tests in GB4 were sequentially performed with abstraction rates of 7, 6.5 and 2.6 L/s, respectively. In the first two tests, the results were similar and a drawdown of 12.50 m was obtained in the first minute. At first, it was thought that the rapid drawdown was due to well bore storage, but log-log diagnostic plots show that the early time curve had a slope of 0.5 (Figure 6-47). This indicates a linear flow (mainly from the fracture) with no or minor well bore storage effect. As time increases, the flow dimension increases, indicating that Aquifer 2 has a dual porosity.

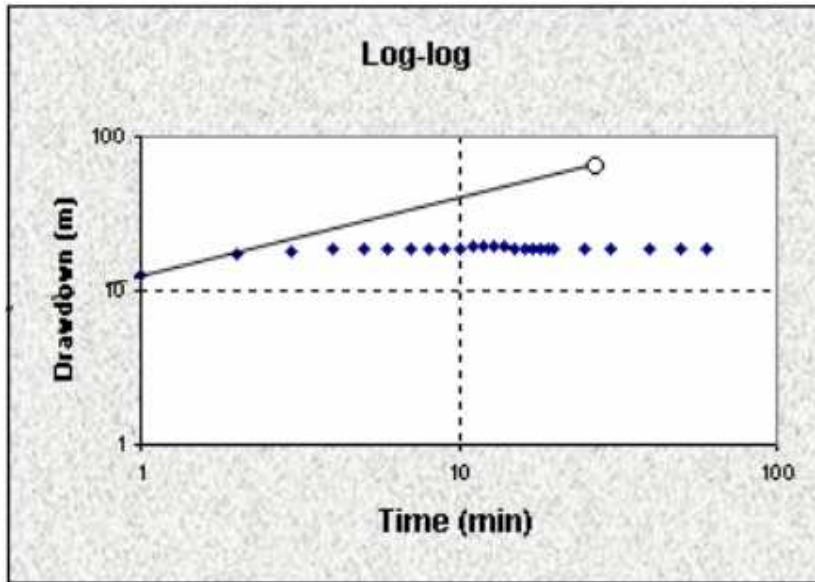


Figure 6-47: Log-log plot of tests conducted in GB4, showing a slope of 0.5.

The linear-flow nature of the aquifer system at an early stage can also further be seen by the square root of time curves, as shown in Figure 6-48.

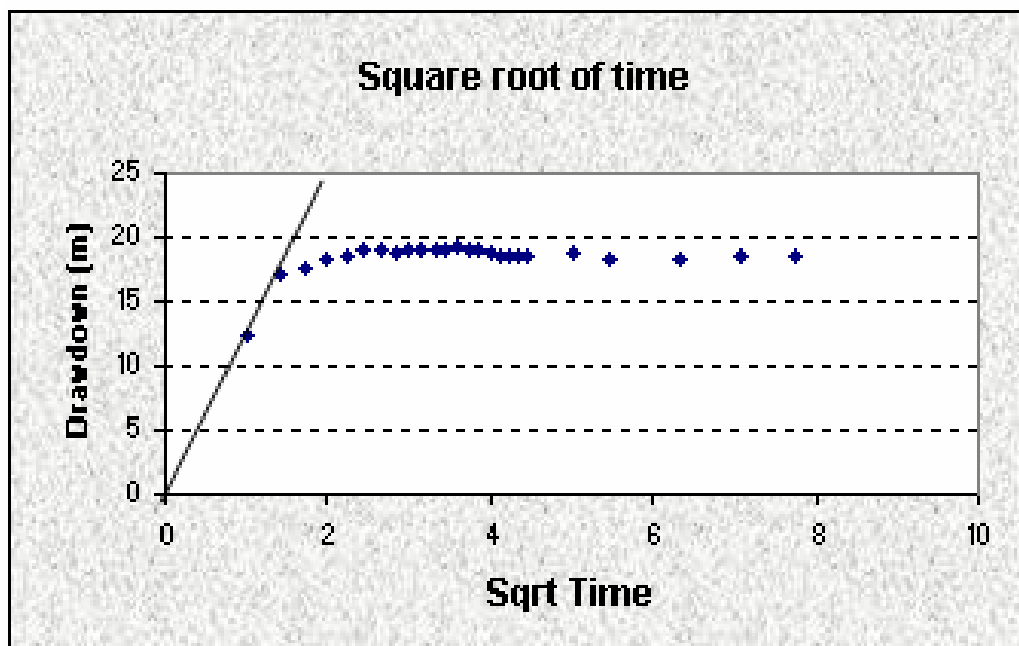


Figure 6-48: Linear drawdown versus square root of time plot, proving the early linear flow.

The presence of early linear flow indicates the presence of a fracture zone where the aquifer response occurs at an early stage. This fracture zone could be a preferential pathway for DNAPLs.

Depending on the pump test results and hydraulic parameters, two aquifers are identified, denoted as Aquifer 1 and Aquifer 2, respectively. Apparently, there is no

significant head difference between Aquifer 1 and 2, although their hydraulic parameters are different. This scenario is possible if there is a leaky boundary that separates Aquifer 1 from Aquifer 2. However, the higher head in GB9 than in GB8 and GB7 is in disagreement with the conceptual model of the aquifer system, and is probably caused by improper borehole construction. The schematic representation of the conceptual model is given in Figure 6-80.

6.4.8 Tracer Tests

Point dilution tracer experiments were performed to evaluate the flow velocity through the lithologies or fractures on Test Site 1. The tracer tests were conducted in six boreholes, namely, GB2, GB3, GB4, GB5, EB3 and FB1. The tests were done in section intervals that ranged from the water level (about 15 m) to a depth of 55 m from the ground surface. Experiments in the unconsolidated section were done in Boreholes GB2, GB5 and EB3; the experiment in the contact zone between the unconsolidated and consolidated was done in Borehole GB4; while the studies in the consolidated aquifer were done in Boreholes GB3 and FB1.

NaCl was used as a tracer. Changes in concentration were measured in terms of electrical conductivity (EC). From experimental results, the concentration of NaCl, in mg/L, was found to be four times the EC (mS/m) value.

The Darcy and Seepage velocities in the unconsolidated section were estimated to be approximately 0.5 and 1 m/d, respectively. However, the velocities in the bedrock were variable depending on the strength of the fractures. The Darcy and Seepage velocities ranged from 1 to 10 m/d.

6.5 Effective Matrix Diffusion Coefficient Estimation

6.5.1 Introduction

As discussed in the previous sections, fractures are the principal pathways through which most groundwater moves, and thus, fractures are responsible for the fluid advection and mechanical dispersion of dissolved constituents. In some crystalline rocks, the matrix porosity may range from less than 1 to greater than 3 percent (%) (Wood *et al.*, 1996); the matrix porosity of sedimentary rocks may be much higher (Finley and Tyler, 1986; Mace and Hvorka, 2000). In many instances, the permeability of the matrix porosity is not capable of transmitting significant quantities of fluid. The matrix porosity, however, can act as a fluid-filled reservoir in contact with the fluid in the fractures. Dissolved constituents may diffuse from fractures into the rock matrix or vice versa, depending on the direction of the concentration gradients.

In situations where contaminants have been introduced into the groundwater of fractured-rock aquifers, the diffusion and retention of chemical constituents in the rock matrix is a significant problem in the design and implementation of groundwater remediation strategies (Parker *et al.*, 1994). Pumping may readily remove the contaminated groundwater from fractures, but the migration of the contaminants from the rock matrix to the fractures will be limited by chemical diffusion. In instances where contaminated groundwater in fractures has been in contact with the rock matrix for months, years, or decades, the time frame for the diffusion of contaminants out of the rock matrix may extend to hundreds of years. Quantifying the magnitude of the chemical diffusion into or out of the rock matrix in different types of fractured-rock aquifers is extremely important in managing water resources and designing groundwater remediation strategies.

The diffusion of a constituent dissolved in the groundwater of a rock matrix is governed by the following differential equation

$$\frac{\partial C}{\partial t} - D\nabla^2 C = 0$$

Equation 6-1

where

C = concentration of the dissolved constituent per volume of water,

t = time,

D = effective diffusion coefficient of the dissolved constituent in the fluid of the rock matrix, and

∇^2 = Laplacian operator, which will take different forms depending on the coordinate system associated with the diffusion process.

In Equation 6-3 it is assumed that the chemical constituent under consideration is nonreactive with fracture surfaces and the rock matrix, and there is no fluid advection in the rock matrix.

Ohlsson and Neretnieks (1995) summarised the results of numerous laboratory-scale diffusion experiments conducted in crystalline rocks and identified a range of formation factors and the effective diffusion coefficients for various chemical constituents. Van der Voort (2001) conducted laboratory-scale diffusion experiments in samples of sandstone, shale, and quartzite using NaCl and sodium sulfate (Na_2SO_4) as the tracing solutions. In addition, van der Kamp *et al.* (1996) and Novakowski and van der Kamp (1996) describe an experimental procedure and method of interpreting laboratory-scale radial diffusion experiments conducted on core samples.

Controlled *in-situ* experiments conducted by injecting tracer solutions into fractures under forced hydraulic gradient conditions have also been conducted to estimate the magnitude of the effective diffusion coefficients (Garnier *et al.*, 1985; Becker and Shapiro, 2000). Such tests are usually conducted over distances of metres to tens of metres in the formation, and the tracer breakthrough curves are examined to estimate the effective diffusion coefficient and the formation factor.

In addition, concentrations of environmental tracers (for example, tritium and chlorofluorocarbons) have been used to estimate the effective diffusion coefficient under *in situ* conditions. Environmental tracers are chemical constituents or dissolved gases that are entrained in precipitation and eventually recharge the groundwater (Maloszewski and Zuber, 1991; Shapiro 2001). The application of environmental tracers, however, is used to infer the magnitude of the matrix diffusion over regional flow regimes that may extend over hundreds of metres to kilometres.

Methods of estimating the effective diffusion coefficient under laboratory conditions require a significant investment in precision equipment. Estimating the effective diffusion coefficient into or out of a rock matrix under *in-situ* conditions (e.g., under forced hydraulic gradients, or from the interpretation of environmental tracers) can be greatly affected by the groundwater flow regime (Becker and Shapiro, 2003; Shapiro, 2001). In some instances, an effective matrix-diffusion coefficient that is greater than the free-water diffusion coefficient can arise as an artifact of the fluid velocity (Shapiro, 2001).

6.5.2 Assumptions and Methodology

The objective of this section is to describe an *in-situ* tracer experiment conducted in a borehole in contact with the rock matrix to estimate the magnitude of the effective diffusion coefficient on the Campus Test Site. The experiment considers the diffusion of a tracer into or out of the rock matrix along a section of a borehole that is in contact with intact unfractured rock. It is also assumed that there is no ambient borehole flow to disturb the distribution of the dissolved constituent in the borehole.

Over the past decade, many tracer tests were conducted at the Campus Test Site (Van Wyk, 1998; Riemann, 2002), which involved numerous injections of tracers, in particular, NaCl. Although most of the tracer tests involved procedures to recover the injected tracer mass, a considerable amount of the residual tracer solution has remained in the aquifer and diffused into the rock matrix over time. Electrical conductivity (EC) surveys of boreholes at the Campus Test Site show elevated levels of dissolved constituents in the borehole below the dominant permeable subhorizontal, bedding-plane fracture. EC measurements as high as 2,900 micro-Siemens per metre (mS/m) have been recorded in the stagnant water of boreholes

below the bedding-plane fracture. In contrast, the EC of water in the bedding-plane fractures is approximately 90 mS/m. The lower EC in the bedding-plane fracture is indicative of fresh water recharging the aquifer and migrating in the most permeable feature of the formation.

Since water with high EC has been resident in the lower part of the borehole in contact with the rock matrix of the mudstone for an extended period, it is hypothesised that the concentration of the water in the rock matrix of the mudstone is equivalent to the concentration of the water in the borehole. The tracer test to estimate the effective diffusion coefficient of the mudstone matrix is conducted by introducing water into the lower part of the borehole that has low EC, and then monitoring the time-varying change in EC in the lower part of the borehole as a function of time. Alternatively, a test could be conducted by introducing a tracer solution into the borehole and monitoring its time-varying concentration as it diffuses into the rock matrix. In the subsequent discussion, EC is used as a surrogate for concentration.

Borehole UO5 (Figure 6-6), which intersects the bedding-plane fracture at a depth of 23.0 m, was selected for the matrix diffusion study. A Solinst TLC meter was used for *in situ* measurements of EC with depth in the borehole. Measurements were conducted by moving the probe up and down the borehole, while monitoring the depth of the probe with a tape accurate to one millimetre. Before the start of the test, EC measurements as a function of depth in the borehole were taken on 07 February 2005 and plotted in Figure 6-49. The EC increases abruptly below the position of the fracture, indicating the section of the borehole with stagnant water. Estimates of the effective diffusion coefficient of the mudstone will be made at depths of 27 and 36 m; the pre-test EC values at these depths were 2540 and 2910 mS/m, respectively.

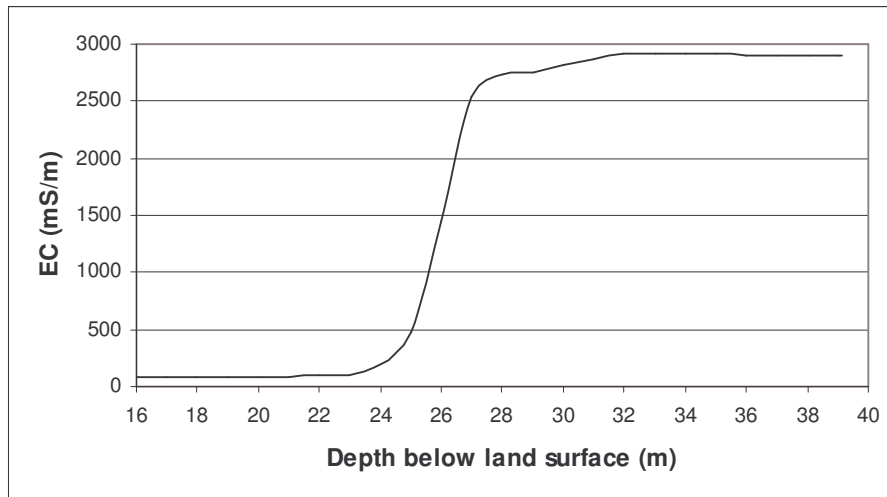


Figure 6-49: EC versus depth in Borehole UO5 at the start of the *in-situ* matrix diffusion experiment on 7 February 2005.

On 02 April 2005, the borehole was purged for 40 minutes, after which the EC as a function of depth in the borehole was measured. As the borehole was purged, low salinity groundwater entered the borehole from the bedding-plane fracture at 23 m below land surface. Following the purging, the EC was measured nine times during the subsequent 34 days; measurements were stopped on 06 May 2005.

After purging the borehole, the concentration gradient is reversed with water having low EC residing in the borehole, whereas water in the adjacent rock matrix has higher EC. Consequently, solute in the fluid of the rock matrix starts to diffuse into the borehole in response to the concentration gradient. Table 6-13 lists the EC measured with time at depths of 27 and 36m below land surface in Borehole U05; this information is also shown graphically in Figure 6-50. The first measurement was taken immediately after purging.

Table 6-13: EC measurements in Borehole U05 following the purging.

Date and Time	Elapsed time after purging, in days	EC, in mS/m, at 27 m below land surface	EC, in mS/m, at 36 m below land surface
2005/04/02 16:00	0	90.9	92.2
2005/04/03 10:30	0.8	97.1	100.1
2005/04/04 17:15	2.1	101.1	105.4
2005/04/05 15:16	3.0	102.1	108.4
2005/04/06 15:24	4.0	103.8	110.5
2005/04/08 14:05	5.9	105.4	113.6
2005/04/13 14:22	10.9	109.0	120.9
2005/04/22 08:47	19.7	112.9	130.5
2005/05/06 14:30	33.9	122.7	147.2

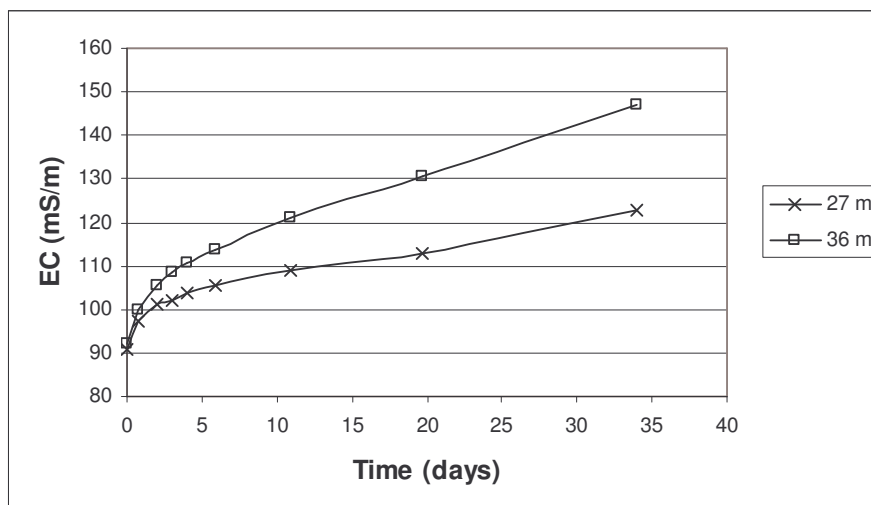


Figure 6-50: EC measurements in Borehole UO5 at depths of 27 and 36 m following the purging.

The increase in EC over time in Borehole UO5, shown in Figure 6-50 is hypothesised to be the result of diffusion from the rock matrix into the borehole. The concentration with depth in the borehole prior to the start of the test is hypothesised to be the spatially varying concentration in the rock matrix with depth along the length of the borehole. EC values near the bedding-plane fracture at 23 m below land surface are not considered in the estimation of the matrix diffusion, because groundwater advection through the fracture may influence the EC in the borehole immediately adjacent to the fracture. After 34 days, the EC in the borehole at 27 m below land surface recovered from 90.90 to 122.70 mS/m, whereas at 36 m below land surface the EC rose from 92.20 to 147.20 mS/m.

Because the EC measurements show variability with depth in the borehole, vertical concentration gradients in the fluid column of the borehole are also likely to affect the time-varying EC measurements in the borehole. It is anticipated that this phenomena will have the greatest effect immediately after the purging of the borehole, and the effect should diminish over the duration of the monitoring. Disturbances in the distribution of EC with depth in the borehole could also arise from lowering and raising the EC probe in the fluid column. This, however, is assumed to have a nominal effect on the EC distribution in the borehole, because the cross-sectional area of the probe is small relative to the diameter of the borehole. Thus, a minimal volume of fluid is displaced as the probe is moved in the borehole. Furthermore, EC measurements were taken infrequently over the duration of the test to avoid continuously disturbing the fluid column in the borehole. The potential effect of these disturbances on the estimates of the effective diffusion coefficient will be evaluated by estimating the effective diffusion coefficient at both 27 and 36 m below land surface and comparing the results.

6.5.3 Data Analysis

The effective diffusion coefficient of the mudstone is estimated by interpreting the time-varying EC measurements at depths of 27 and 36 metres in the Borehole UO5. To interpret the data shown in Figure 6-50, the equations governing the radial diffusion from the rock matrix to the borehole are solved. The equations governing the radial diffusion of a chemical constituent are given by Novakowski and van der Kamp (1996). Following the approach of Novakowski and van der Kamp (1996), the governing equations and the Laplace transform solution are given in Appendix B. From these equations, curves of EC versus time are generated, and the effective diffusion coefficient is varied so that model results best reproduce the measured time-varying EC values.

Typical solutions for EC in the borehole for different values of the effective matrix diffusion coefficient are shown in Figure 6-51. The physical parameters describing the borehole and the mudstone that were used to generate the curves in are listed in Table 6-14. In the curves of concentration versus time shown in Figure 6-51, a 1-metre long section of the borehole is assumed to represent the fluid volume in the borehole in contact with the rock matrix. Thus, the concentration in the rock matrix at a given elevation is assumed to be constant over a 1 m section of the rock matrix. The results in Figure 6-51 show that larger effective diffusion coefficients result in a more rapid increase in the EC following the purging.

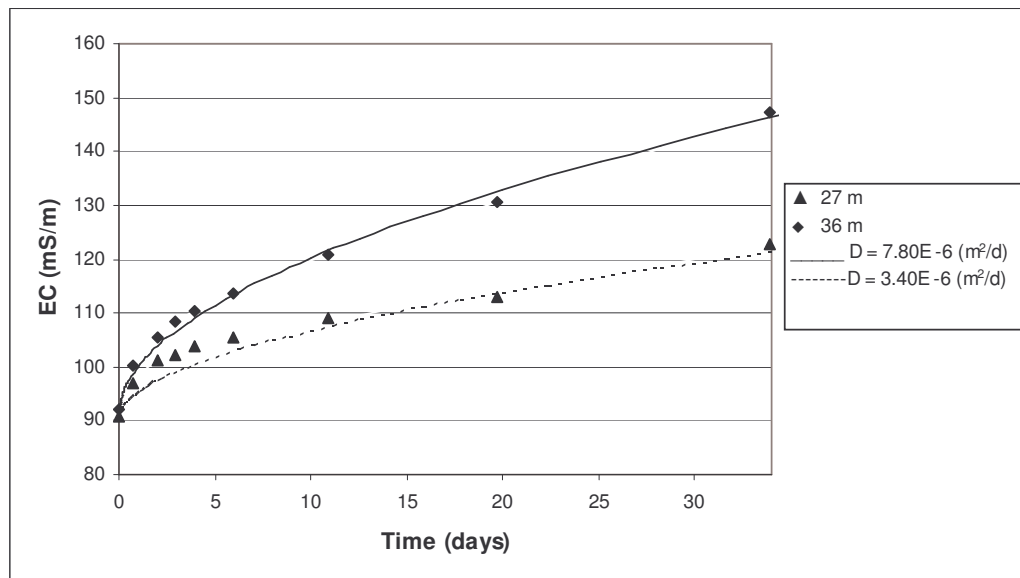


Figure 6-51: Comparison of EC at depths of 27 and 26 m and model results.

Also shown in Figure 6-51, the measured values of EC as a function of time at 27 and 36 m below land surface in Borehole UO5 are plotted with the model curves. These data are compared to the modelled time-varying EC from the solution to radial diffusion into the borehole from the rock matrix to estimate the values of the effective

diffusion coefficients that best reproduce this data. The best fit for the EC data measured at 27 and 36 m below land surface are 3.4×10^{-6} and 7.8×10^{-6} m²/day, respectively. The estimated effective diffusion coefficient at 27 m below land surface is approximately half the estimated effective diffusion coefficient estimated from the EC data at 36 m below land surface.

Table 6-14: Parameters assigned for model results.

Depth	27 m	36 m
Average porosity of matrix	0.04	0.04
Initial EC (after purging)	91 mS/m	91 mS/m
EC in the matrix	2540 mS/m	2910 mS/m
Borehole radius	0.08 m	0.08m
Length of borehole section	1 m	1 m
Borehole surface area	0.5 m ²	0.5 m ²
Borehole volume	0.02 m ³	0.02 m ³

This difference between the estimated effective diffusion coefficients at 27 and 36 m below land surface in borehole U05 could be the result of the vertical diffusion of chemical constituents in the borehole at the start of the test after purging the borehole or the result of minor variability in formation properties. In the model calculations shown in Figure 6-51, the porosity of the mudstone was assumed to be 0.04; however, the actual porosity may vary between 0.03 and 0.05 (Riemann, 2002; Van der Voort, 2001). Figure 6-52 shows the effect of varying the porosity of the mudstone from 0.03 to 0.05, while maintaining the effective diffusion coefficient estimated from the EC data at 36 m below land surface in Borehole U05. Larger values of the matrix porosity result in more mass diffusion into the borehole and larger solute concentrations in comparison to model results using smaller values of the matrix porosity.

Consequently, to reproduce the measured time-varying EC values assuming a smaller value of the matrix porosity requires a larger value of the effective matrix diffusion. Conversely, a larger value of the matrix porosity would require a smaller value of the effective diffusion coefficient to reproduce the measured time-varying EC values.

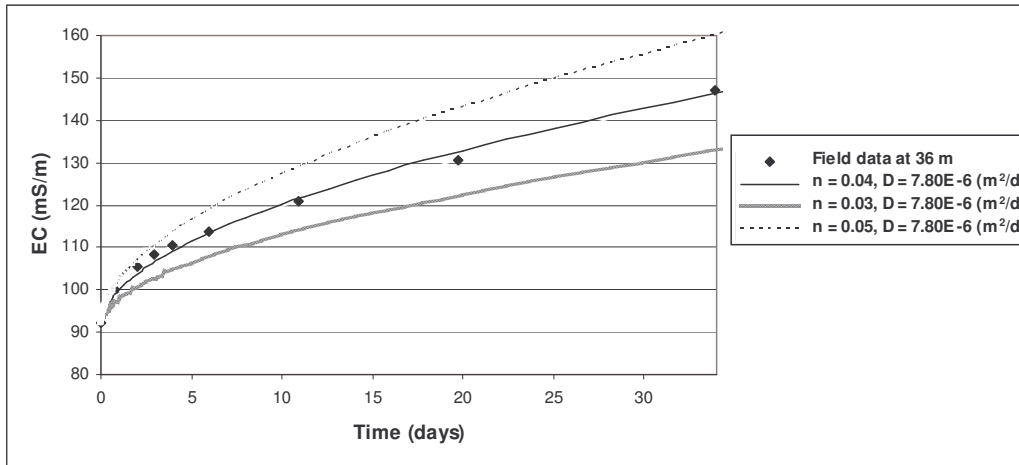


Figure 6-52: Model results of EC versus time for different values of the matrix porosity, keeping the effective diffusion coefficient constant.

For the measured time-varying EC values in Borehole U05 at 36 m below land surface, and an assumed mudstone matrix porosity of 0.03, the effective matrix diffusion coefficient that best reproduces the data is $1.27 \times 10^{-5} \text{ m}^2/\text{day}$ (Figure 6-53). Also, for an assumed mudstone matrix porosity of 0.05, the effective diffusion coefficient that best reproduces the measured EC data at 36 m below land surface is $5.00 \times 10^{-6} \text{ m}^2/\text{day}$ (Figure 6-54). If the variability in the matrix porosity is also considered in the evaluation of the time-varying EC data at 27 m below land surface in Borehole U05, the estimates of the effective diffusion coefficient from the two elevations in the borehole overlap within the range of the sensitivity of the estimated values.

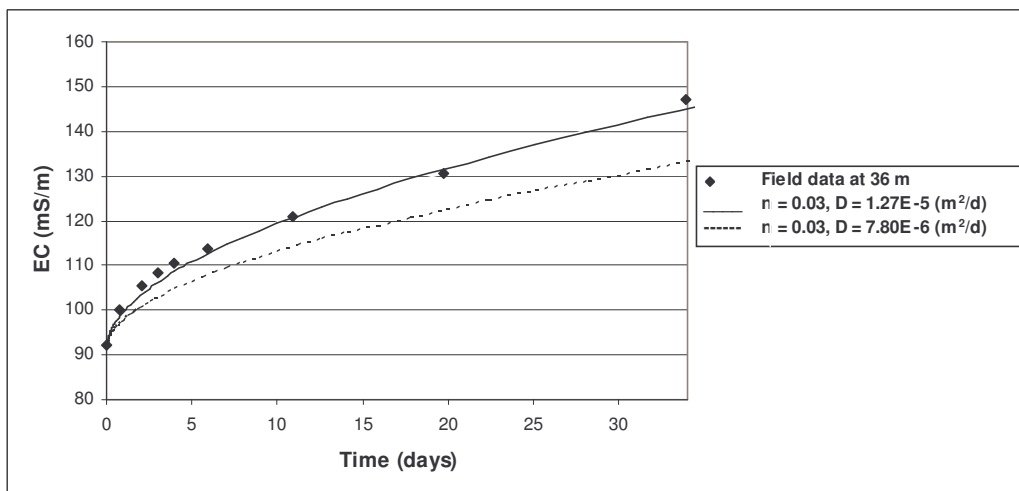


Figure 6-53: Estimates of the effective matrix diffusion coefficient for the matrix porosity of 0.03.

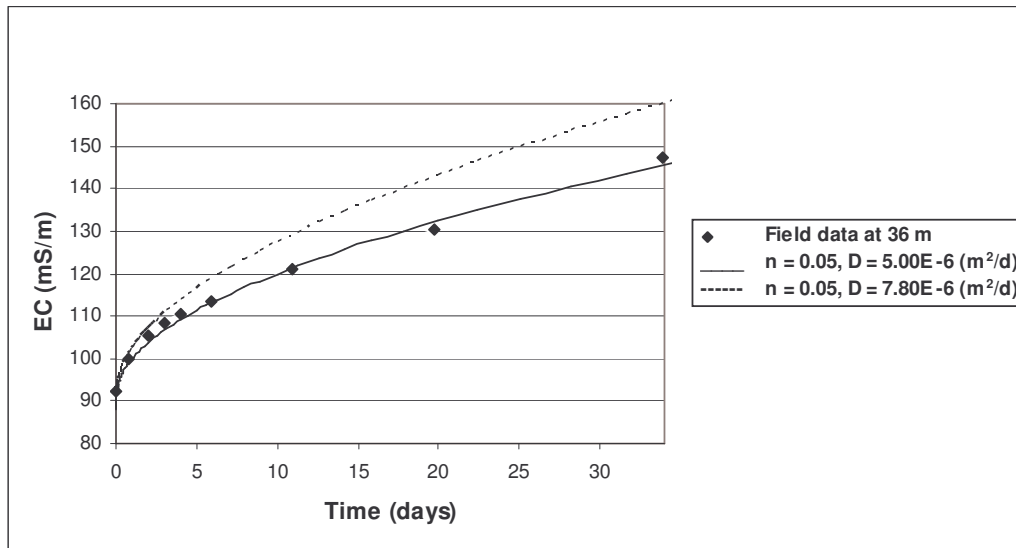


Figure 6-54: Estimates of the effective matrix diffusion coefficient for the matrix porosity of 0.05.

6.5.4 Formation Factor

The effective diffusion coefficient, D , is dependent on the diffusion coefficient of the dissolved constituent in water and the pore structure of the rock matrix,

$$D = \phi D_d$$

Equation 6-2

where

D_d = the free-water diffusion coefficient of the dissolved constituent, and

ϕ = the formation factor that scales the free-water diffusion coefficient to account for diffusion in the tortuous pore structure of the rock matrix.

The formation factor is a dimensionless term that is less than 1 and can range over several orders of magnitude, depending on the type of rock under consideration (Novakowski and Van der Kamp, 1996).

The effective diffusion coefficient is a combination of the free-water diffusion coefficient, D_d , for the dissolved constituent under consideration and a formation factor, ϕ , that scales D_d (Equation 6-2). If D_d is known, estimates of the formation factor, ϕ , can be obtained from estimates of the effective diffusion coefficient. Knowledge of the formation factor is important for extending the results of this investigation to other dissolved constituents in the groundwater.

In this investigation, it is assumed that chloride is the principal component of the dissolved species in the groundwater causing the elevated values of EC. From

experimental results it was found that the concentration of chloride (in mg/l) in the groundwater was equal to four times the EC (in mS/m). Values of EC in the borehole prior to the test at 27 and 36 m below land surface were 2540 and 2910 mS/m, respectively. These correspond to chloride concentrations of 10160 and 11640 mg/L chloride, respectively. The free-water diffusion coefficient for these concentrations of chloride in solution can be interpolated from the results given in Robinson and Stokes (1965). Robinson and Stokes (1965) give values of the free-water diffusion coefficient for sodium chloride solutions of various concentrations at 25 degrees Celsius ($^{\circ}\text{C}$). Correcting for the water temperature in the borehole, which was 18.9°C , the free-water diffusion coefficient for the sodium-chloride solution is estimated to be $1.25 \times 10^{-4} \text{ m}^2/\text{d}$ at both 27 and 36 m below land surface in Borehole U05.

Using the estimated free-water diffusion coefficient for the tracer solution, estimates of the formation factor from the time-varying EC measurements at 27 m below land surface range from 0.053 to 0.018, with an average value of 0.027, depending on the porosity (Table 6-15). In contrast, the estimates of the formation factor from the time-varying EC measurements at 36 m below land surface range from 0.102 to 0.040 with an average value of 0.062 (Table 6-16). The estimates of ϕ at these elevations in the borehole overlap and could be an artifact of the variability in the matrix porosity. Other authors have reported similar values for the formation factor from laboratory experiments conducted on other types of sedimentary rocks (see, e.g., Novakowski *et al.*, 1999), and a similar range in the formation factor is also found in laboratory experiments conducted on crystalline rocks (Ohlsson and Neretnieks, 1995; 1997).

Table 6-15: Estimates of the formation factor for the estimated effective diffusion coefficients at 27 m for various values of the matrix porosity.

Matrix Porosity	Effective Diffusion Coefficient, m^2/d	Formation Factor
0.03	6.6×10^{-6}	0.053
0.04	3.4×10^{-6}	0.027
0.05	2.2×10^{-6}	0.018

Table 6-16: Estimates of the formation factor for estimated effective diffusion coefficients at 36 m for various values of the matrix porosity.

Matrix Porosity	Effective Diffusion Coefficient, m²/d	Formation Factor
0.03	1.27×10^{-5}	0.102
0.04	7.8×10^{-6}	0.062
0.05	5.0×10^{-6}	0.040

6.5.5 Mass Flux

The Laplace transformation solution for the mass entering the borehole during the *in-situ* test is given in Equation (A.26) of Appendix B. An inversion algorithm is used to estimate the chloride mass that enters the borehole from the rock matrix of the mudstone as a function of time. For the effective diffusion coefficient estimated from the EC data at 36 m below land surface in Borehole U05, and an assumed matrix porosity of 0.04, approximately 4.4 milligrams (mg) of chloride enter the borehole over the 34 days of the test. These calculations are based on a conversion between EC and the chloride concentration note previously. This calculation only considers a 1-m long section of the borehole. The total chloride mass that enters the borehole can be estimated by multiplying this result by the length of the borehole being considered in the experiment. If the length of the borehole associated with the experiment is assumed to be the distance from the bedding-plane fracture to the bottom of Borehole U05, the total mass entering the borehole during the experiment is 70.4 mg. In reality, the mass entering the borehole is a function of depth in the borehole, because of vertical concentration gradients. Thus, this estimate of total chloride mass entering over the entire length of the borehole should be regarded as an upper limit.

For comparison, the total mass in a volume of the rock matrix surrounding the borehole can also be calculated. If the initial chloride concentration measured in borehole U05 at 36 m below land surface is assumed to represent the chloride concentration in the rock matrix of the mudstone at the start of the test, a cubic metre (m³) of the mudstone around the borehole contains approximately 4.7×10^5 mg chloride. In comparison, only 4.4 mg of chloride enter a 1-m section of the borehole. Thus over the time frame of the test, the diffusion of chloride into the borehole constitutes a minuscule mass of the chloride that is resident in the rock matrix adjacent to the borehole. One can use the solution for the mass entering the borehole given in Appendix B to extrapolate to later times. For example, after 100 days, 9 mg of chloride would enter the borehole, after 1,000 days, 29 mg of chloride would enter

the borehole; and after 10,000 days, 103 mg of chloride would enter the borehole. Again, these calculations are for a 1-m section of the borehole.

These results illustrate the slow rate of diffusion into the borehole and the minimal amount of mass that will diffuse out of the rock matrix in response to perturbations in the concentration imposed in the borehole. At sites where there has been groundwater contamination and contaminants have diffused into the rock matrix, diffusion will be a limiting factor in remediating the groundwater. Estimates of mass removal from the rock matrix to fractures can be made once the effective diffusion coefficient has been estimated.

6.6 Effective Porosity Estimation

6.6.1 Introduction

Although aquifers are normally heterogeneous, the average value of aquifer parameters can usually be measured without difficulty. For example, the hydraulic conductivity and storativity can be estimated from pumping tests. The effective porosity is, however, traditionally measured on rock/soil samples from the aquifer. The sampling process could, however, result in the alteration of the inherent porosity of the aquifer. At greater depths, sediments are compacted and the porosity is smaller than in a laboratory tested sample.

An easy and inexpensive alternative for measuring effective porosity is the use of the point dilution test. The theory behind point dilution dates back a couple of decades (Drost *et al.*, 1968; Halevy *et al.*, 1967). Based on these theories, recent experiments were also done by Riemann (2002) to estimate the groundwater flow velocity in a fracture. The single-well point dilution test aims to relate the observed rate of tracer dilution in a borehole or a segment isolated in a borehole to the groundwater velocity. Since groundwater velocity is a function of the effective porosity, the effective porosity can be evaluated as shown in this experiment.

6.6.2 Objective

As it will be discussed in section 6.5, the disappearance of dissolved contaminants due to diffusion from fractures to the matrix porosity is very sensitive to the porosity of the matrix. For example, in the Campus Test Site mudstone at a depth of 36 m, a change of matrix porosity from 0.04 to 0.03 resulted in a change of the effective diffusion coefficient of the matrix by 94%, (i.e., from 3.4×10^{-6} to 6.6×10^{-6} m²/d). Therefore, for accurate assessment of dissolved DNAPL disappearance from the fracture, the porosity of the aquifer must be measured as accurately as possible. Porosity measurements on soil samples will usually not reflect the *in-situ* value; the

objective of this experiment is to estimate the effective porosity of the matrix *in-situ* from a point dilution tracer test.

6.6.3 Assumptions

In theory, if groundwater-flow is the only factor controlling the tracer movement, more dilution is expected at sections where the flow is higher. Experimental results have shown that Darcy velocity can be evaluated from such dilution rates (Freeze and Cherry, 1979). However, before the equation for the estimation of Darcy velocity is developed, the following assumptions are made (from Halevy *et al.*, 1967; Drost *et al.*, 1968; Lamontagne *et al.*, 2002):

- The tracer is mixed completely within the borehole.
- Steady state flow exists.
- The distribution of the tracer across the section is homogenous with no density gradient due to tracer concentration.
- No forced groundwater flow exists in the vicinity of the well (i.e. no pumping or injection).
- Tracer does not move by diffusion or dispersion but advection.
- No displacement of tracers due to improper release exists.

6.6.4 Methodology

The experimental set-up was as shown in Figure 6-55. The pump inlet was positioned at the bottom of the tested section, while the injection pipe outlet was at the top of the section. The abstraction and injection pipes were connected by a flow cell on the surface. The flow cell also had a hole through which the tracer was injected and the electrical conductivity (EC) probe could be inserted for EC measurements inside the flow cell. Water was abstracted and flowed through the flow cell and injection pipe back to the upper section of the tested section.

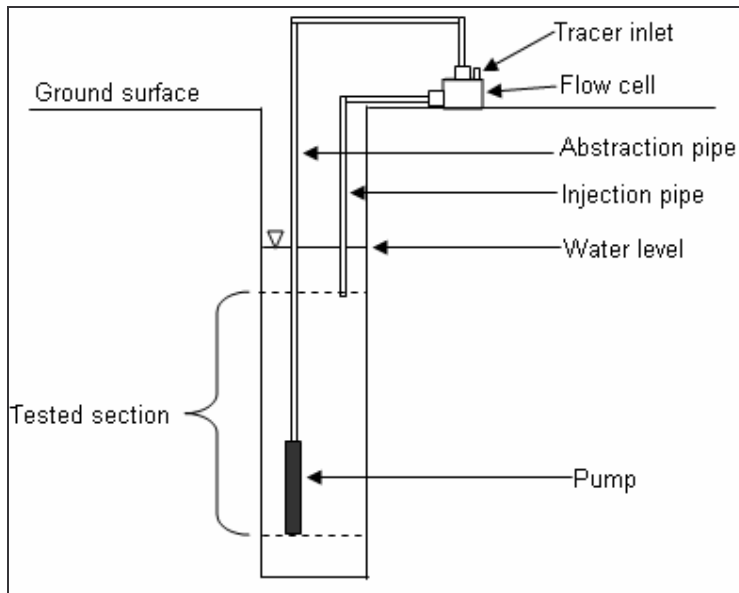


Figure 6-55: Point dilution test set-up.

A flow cell was found to be more effective in circulating the water than an open container, as suggested by Ellington (2003). If an open container is used, the injection and pumping rates have to be equal, and this adjustment may take some time, during which water may overflow from the open container.

Once the set-up of the equipment was completed, water circulated from the pump and through the flow cell back to the injection pipe. Depending on the pumping rate and volume of section, all the tracer solution was inserted uniformly in a single well-volume. The insertion of the tracer is very important. Improper insertion could result in an error regarding borehole profile and estimated effective porosity.

The time required for a single-well volume to circulate is discussed by Riemann (2002). The amount of tracer solution introduced should be high enough to be distinguished from the background EC of the borehole. If the concentration is too high, however, it may create a density gradient and vertical movement of the solution may occur. If the velocity is expected to be high, the influence of solution movement by density gradient would be insignificant, and a higher concentration of tracer could be applied. From the experimental observations, a tracer amount that increases the background concentration by 50 to 300% was sufficient.

In the case of borehole profiling, the tracer was circulated for at least one well volume following its release, so that the solution would mix completely. Pumping was stopped and EC measurements taken. The measurement position was selected from the background EC profile and geologic data (if available). A Solinst TLC® meter was used for *in-situ* measurements of EC with depth in the borehole. Measurements were conducted by shifting the probe up and down the borehole, while monitoring the depth of the probe with a tape accurate to one millimetre.

During the borehole-mixing process, activities that may result in the increase of the rate at which tracer moves out of the well, termed dispersion by Lamontagne *et al.* (2002), should be avoided. Tracer dispersion results in the dilution of the tracer at higher rates at an early stage. The reason for this is that some of the tracer that is initially displaced upstream by dispersion will later re-enter the well by advection.

The vibration of the pump, accidental compression of the pipes and removing the pump before the test is completed, are some of the factors that may result in dispersion. Turbulent flow due to a high pumping rate could also result in dispersion; therefore, the optimal circulation velocity may be a compromise between greater mixing and less dispersion. Measuring continued until the solution in the borehole was sufficiently dilute. If an average effective porosity of a tested section is needed, the test should proceed as suggested by Riemann (2002), where the reading is taken at one fixed position and the circulation must continue until the solution is diluted to approach the background value.

Prior to the data analysis, it is recommended that the measured concentration be normalised so that the background concentration is subtracted. The data were normalised as follows:

$$C_o = C_i - C_b$$

$$C(t) = C - C_b$$

Equation 6-3

$$C_N = \frac{C(t)}{C_o}$$

Equation 6-4

where:

C_b = background concentration

C_i = initial concentration inserted at time $t = 0$.

C = concentration at time t .

C_N = normalised concentration

When there is a complete mixing of the inflow water and tracer before the solution leaves the open well, the concentration of the tracer will gradually decrease exponentially. This is demonstrated in Figure 6-56, where the depletion of the tracer was measured in Borehole GB5 at depths of 16 and 17 m over a period of 5 hours.

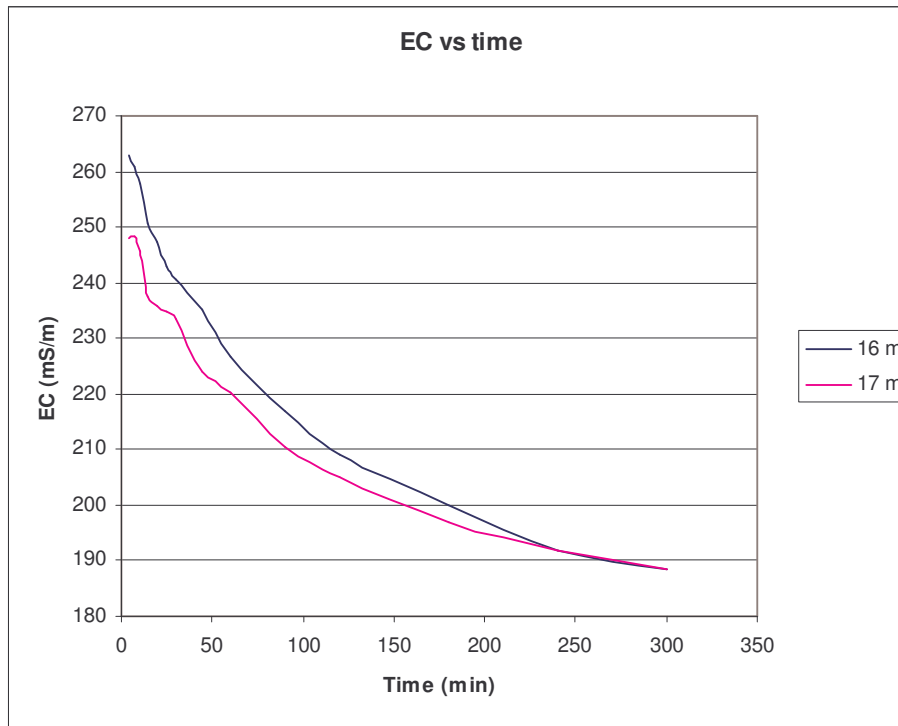


Figure 6-56: EC vs. time in Borehole GB5 at depths of 16 and 17 m.

As shown in Figure 6-56, the rate of tracer dilution at any point of time is directly proportional to the current concentration, i.e. the higher the concentration of a tracer in the well water, the higher the concentration in the out flowing water. This can be expressed mathematically (Freeze and Cherry, 1979) by:

$$n = \frac{V}{(K \cdot i) \alpha A \cdot t} \ln \left(\frac{C_o}{C(t)} \right)$$

Equation 6-5

where

V = volume of borehole segment used for the tracer test

A = vertical cross-sectional area through the center of the borehole segment.

α = borehole distortion factor, which can be approximated to 2.

n = effective porosity

K = hydraulic conductivity (m/s)

i = hydraulic gradient

By analysing the data with Equation 6-5, the effective porosity of some boreholes were estimated, as an example the effective porosity estimated in Borehole GB5 will be provided here. However, before discussing the estimated porosity, the parameters needed in the equation are explained.

6.6.5 Data Analysis

The average hydraulic gradient around Borehole GB5 was first evaluated from the combination of static water elevations of the surrounding boreholes and was found to be 0.02. From a pump test the transmissivity of GB5 was estimated to be 120 m²/d (Section 6.4.7.2). As shown in Borehole GB5 was conducted in 6 m interval; therefore, the hydraulic conductivity was taken as 18.33 m/d. The list of the parameters of Borehole GB5 used in the estimation of effective porosity is given in Table 6-17.

Table 6-17: Parameter-values used to estimate the effective porosity in Borehole GB5.

Hydraulic conductivity (m/d)	Hydraulic gradient	Borehole radius (m)	Flow volume to area ratio	Borehole distortion factor	Tested Section (m)
18.33	0.02	0.07	0.13	2	1

After the insertion of the parameter values in Equation 6-5, the effective porosity of GB5 was estimated at specific depths, as given in Table 6-18. The main water strike from drilling was around 20 m. This position coincides with this result, where the highest effective porosity was estimated around 19 m.

It should be noted that since the hydraulic conductivity and gradient are average values of the entire 6 m section, the estimated effective porosity at the specific section can be considered as a first-hand estimate. If the hydraulic conductivity and gradient were evaluated using packer at every metre within the 6 m interval, the estimated effective porosity would have been accurate.

Table 6-18: Estimated effective porosity in Borehole GB5.

Depth (m)	Effective porosity
16	0.17
17	0.25
18	0.27
19	0.30
20	0.27
21	0.13

6.6.6 Limitation

One of the assumptions for the data interpretation was that no density gradient of tracer concentration exists. However, it was found that the vertical movement of

tracers due to density or concentration gradients influences the experiment, especially if the hydraulic conductivity within the borehole profile changes significantly due to fracture and matrix contrast. This scenario can be better explained by taking two points, A and B, as shown in Figure 6-57, where point A is located at the fracture and B at the matrix. EC values at early time are less affected by the concentration gradient, and the positions of the fractures were detected more accurately. However, at a late stage, the dilution spread will be wider, making it difficult to locate fractures precisely. Moreover, the velocity at point A will be underestimated, and overestimated at point B. This scenario was proven using MODFLOW and MT3DMS modeling of PMWIN as shown in Figure 6-59. Figure 6-58 shows a similar result point dilution in Borehole GB2.

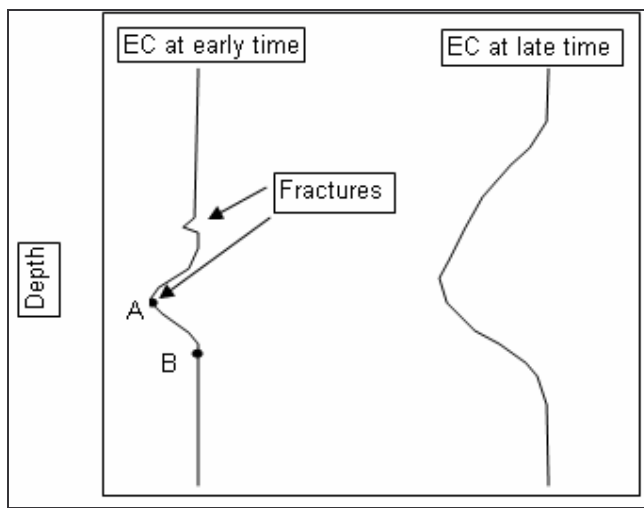


Figure 6-57: Comparison of EC curves at early and late times.

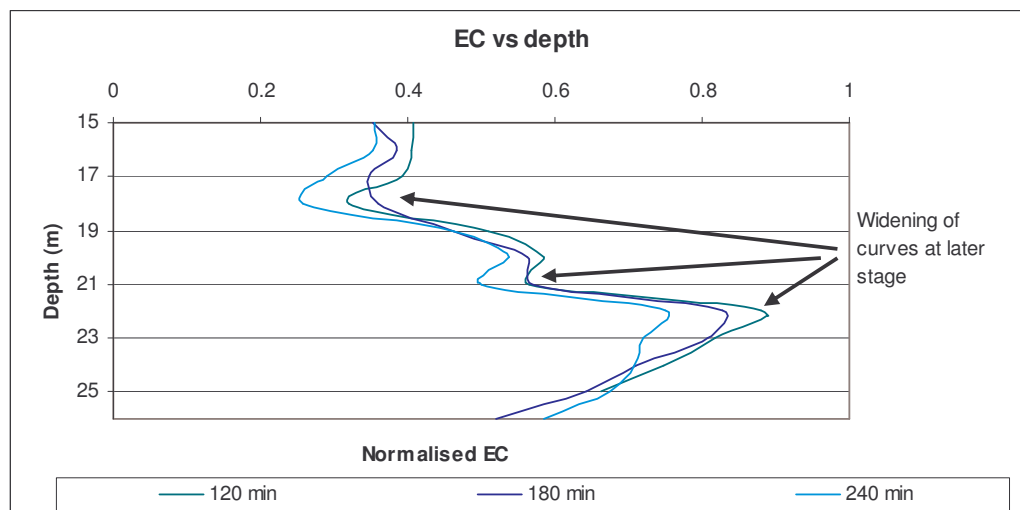


Figure 6-58: Widening of curves in position of high flow anomaly at late stage in Borehole GB2.

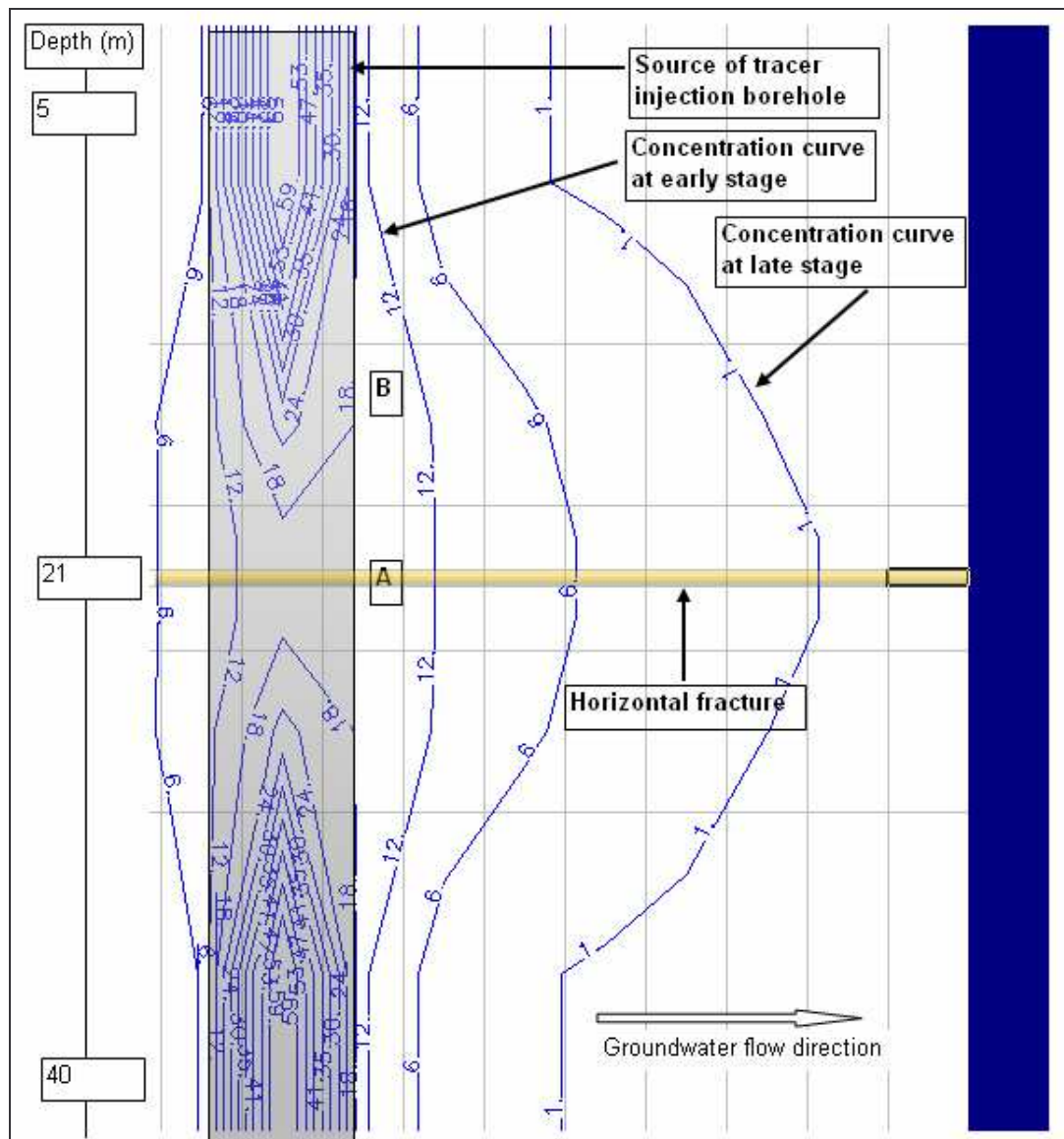


Figure 6-59: Simulated concentration curves using MT3DMS showing concentration curves at different time stages.

6.7 Partitioning Interwell Tracer Test (PITT)

6.7.1 Introduction

Traditional soil and water sampling methods provide information at only discrete points. Due to financial constraints and other practical reasons, it is not possible to sample every point in a contaminated area, especially if the contamination is extensive. This increases the likelihood of undetected localised DNAPL residuals and pools.

This difficulty created an interest in the use of Partitioning Interwell Tracer Tests (PITT) for characterising the occurrence, quantity, and distribution of NAPL

saturation in subsurface systems. The use of partitioning tracer tests to measure immiscible organic-liquid saturation in the subsurface was developed by the petroleum industry in the 1970s as a means to determine residual oil saturation in oil fields. Since then, numerous partitioning tracer tests have been conducted to characterise NAPL residue in an aquifer (Pope *et al.*, 1994; Jin *et al.*, 1995).

The principle behind a PITT test is, when tracers with different partitioning coefficients are injected into the aquifer, the non-partitioning tracers stay in the water phase while the molecules of the partitioning tracers move back and forth between the water and NAPL phases. When the tracer molecules are in the water phase, they move with the velocity of the water and when they are in the NAPL phase, they move with the velocity of the NAPL. If the NAPL phase is a residual saturation, the tracer molecules move only in the water phase.

The net result is that the partitioning tracer pulse lags behind the non-partitioning tracers. The extent of the separation of the tracer pulses depend on the fraction time of the tracer spends in the NAPL phase compared to that in the water, which is a function of NAPL saturation and the partitioning coefficient. The greater the observed chromatographic separation of the tracers, the greater the NAPL saturation in the soil.

By analysing the abstraction borehole tracer response, the amount of residual NAPL in the subsurface environment can be determined. PITT tests sample a much larger volume of the porous medium than do core samples or geophysical logs; consequently, the NAPL saturation estimated from tracer data represents an average over a larger volume.

However, due to the high cost of design and implementation of PITT on the field scale tends to limit the deployment of this technology. The experiments are applicable to the unconsolidated section only and reliability decreases as the heterogeneity increases.

6.7.2 Objective

PITT has never been applied in South Africa. The aim of this test was to evaluate how accurately the saturation of a DNAPL can be estimated from a PITT test. The experiment was conducted in a sand-column with a known saturation of TCE (a common DNAPL), so that the estimated saturation from the PITT test can be compared. During PITT experiments, it is assumed that the conservative and partitioning tracers are influenced by advective transport and partitioning only. Other parameters such as sorption to the soil matrix are assumed to be insignificant.

6.7.3 Methodology

The PITT experiment was conducted in a column with a height of 50 cm and internal diameter of 4.5 cm, as shown in Figure 6-60. In order to avoid TCE and tracer

sorption the experiment materials, the column was made of HDPE pipe and the outlet pipe of copper. Galvanised rings were inserted in the column to force water flow through the centre by avoiding preferential pathways along the column wall. To control the residence time of the tracer and ensure complete saturation, water was pumped from below and the samples collected from the top outlet. This ensures that the column is fully saturated, and can represent the saturated portion of the subsurface. Quartz sand was used for the experiment, with an effective porosity of 0.38 and a hydraulic conductivity of 30 m/d. Therefore, considering the dimension of the column, the volume of void was 302 ml and later verified in the laboratory.



Figure 6-60: Column used for PITT experiment.

6.7.3.1 Evaluation of the Natural Organic Carbon of the Sand

The partitioning tracers could partition to the natural organic content of the soil, especially if NAPL saturation is low, and considerations must be taken to compensate this effect. Before the experiment was conducted in this research, the natural organic carbon of the sand was evaluated. Benzene is not a good tracer for PITT experiment mainly because of its toxicity. However, the experiment was done in a controlled environment and due to the availability of the chemical and cost effective concentration measuring instrument, the SiteLab®; benzene was used for the

evaluation of the natural organic carbon of the sand as a partitioning tracer, while chloride was used as a conservative tracer.

A slug of 10 ml containing NaCl and benzene at concentrations of 2.5 g/L and 250 mg/L was injected into the column. The water flow through the column was at a rate of 20 ml/min and samples were collected every one minute. The concentration of chloride was measured in terms of the EC (relationship between EC and chloride concentration is discussed in Section 6.5). The plot of normalised concentration versus cumulative produced volume is provided in Figure 6-61. The normalised concentration is calculated by dividing the concentration of the sample by the maximum concentration measured during the experiment. This normalization is not essential for the interpretation. However, since the concentration of chloride is very high compared to that of benzene, normalisation assists in the identification.

The figure clearly shows that the benzene is lagging behind the conservative chloride. This indicates that the sand has some natural organic carbon that partitions the benzene. Then the sand was heated for 30 hours at a temperature of 150 °C to destroy any natural organic compound in the sand. Then the experiment was repeated and the result obtained is plotted in Figure 6-62. The arrival of the peak of benzene and chloride at the same time is an indication of absence of natural organic carbons.

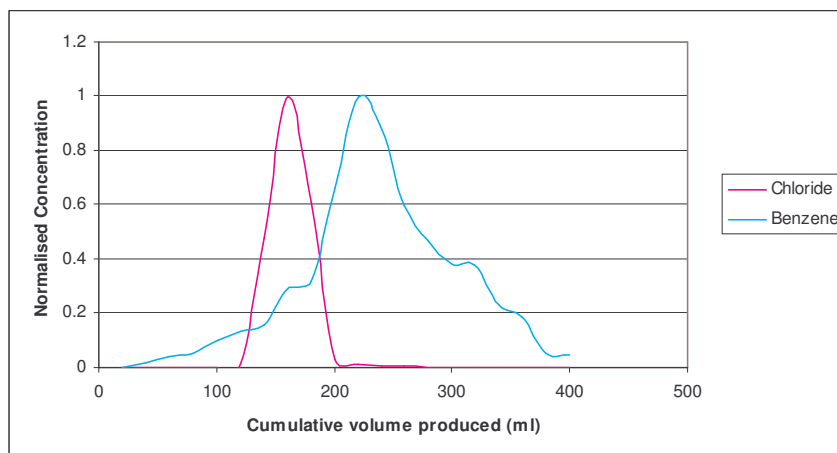


Figure 6-61: Normalised EC and benzene concentration curves before the sand was heated (lagging of benzene).

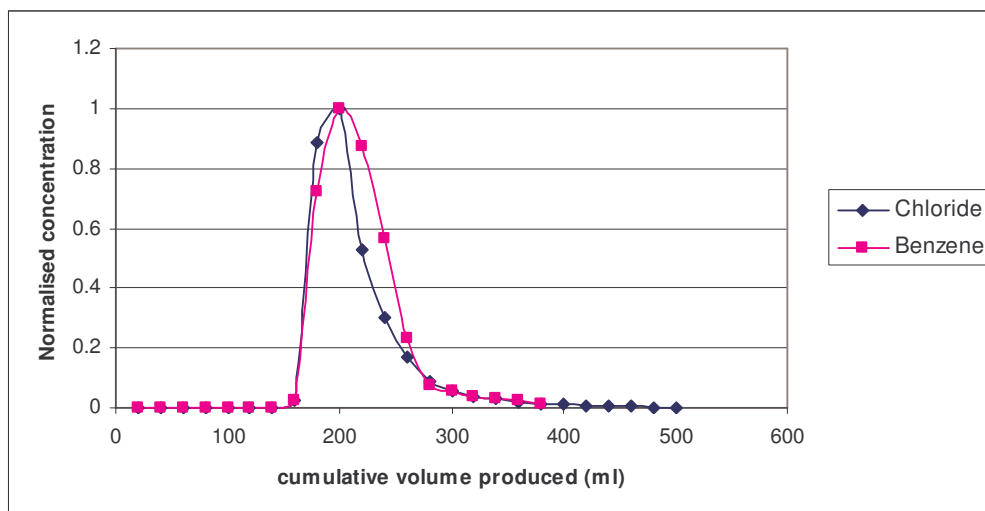


Figure 6-62: Normalised EC and benzene concentration curves after the sand was heated (no lagging of benzene).

6.7.3.2 Controlled Release of TCE

The PITT experiment was conducted twice by changing the concentration of tracers and TCE residual in the column. In the first experiment, a slug of 30 ml of trichloroethylene (TCE) was injected into the column from the top. To remove any free phase TCE, the column was flushed with water by five times its pore volume and 1.5 ml of TCE was flushed out. Therefore, since the volume of void of the sand column was 302 ml, the saturation of TCE is 0.094. In the second experiment, a slug of 15 ml of TCE was injected. To remove any free phase TCE, the column was flushed with water by five times its pore volume but no TCE was flushed out; therefore, the saturation of the TCE is 0.05.

In both experiments, chloride was used as a conservative tracer while alcohols, namely 1-pentanol, 1-hexanol, 2-octanol and 2-ethyl-1-hexanol (2E1H), were used as partitioning tracers. The partitioning coefficients of the tracers between TCE and water were evaluated before the beginning of the experiment by the CSIR laboratory as listed in Table 6-19.

Table 6-19: Partitioning coefficient of the alcohols with respect to TCE and water.

Tracer	K_p
1-pentanol	4.2
1-hexanol	18.4
2-ethyl-1-hexanol	107.5
2-octanol	302

A list of the parameters used for the first and second experiments are given in Table 6-20 and Table 6-21, respectively.

Table 6-20: Parameters of the first PITT experiment.

Parameter	Value
Volume of TCE injected (ml)	30
Volume of flushing water volume (ml)	1500
TCE flushed out (ml)	1.5
volume of tracer slug injected (ml)	15
Conc. of 1-pentanol (g/L) in the slug	10
Conc. of 1-hexanol (g/L) in the slug	5
Conc. of 2-octanol (g/L) in the slug	0.7
Conc. of 2-ethyl-1-hexanol (g/L) in the slug	0.7
Conc. of NaCl (g/L) in the slug	20
Average pumping rate (ml/min)	1.4
Test length of the experiment (min)	2380

Table 6-21: Parameters of the second PITT experiment.

Parameter	Value
Volume of TCE injected (ml)	15
Volume of flushing water volume (ml)	1500
TCE flushed out (ml)	0
volume of tracer slug injected (ml)	15
Conc. of 1-pentanol (g/L) in the slug	5
Conc. of 1-hexanol (g/L) in the slug	2.5
Conc. of 2-octanol (g/L) in the slug	0.7
Conc. of 2-ethyl-1-hexanol (g/L) in the slug	0.7
Conc. of NaCl (g/L) in the slug	10
Average pumping rate (ml/min)	1.4
Test length (min)	3510

6.7.4 PITT Analysis

After plotting the concentration or normalised concentration versus the cumulative volume produced, the saturation can be estimated using the equation:

$$S_N = \frac{V_p - V_n}{(K_p - 1)V_n + V_p}$$

Equation 6-6

where

S_N = saturation of the DNAPL

V_p = volume at which the center of mass of the partitioning flows out

V_n = volume at which the center of mass of the non-partitioning flows out

K_p = partitioning coefficient of the non-partitioning tracer

The concentration of the alcohol tracers in the out flowing water was also analysed in the CSIR laboratory. Tracer concentration curves from the first experiment are shown in Figure 6-63. By applying Equation 6-6, the saturation of TCE was estimated to be 0.088 by 1-pentanol and 0.098 by 1-hexanol. This range shows that saturation is estimated with 95% accuracy. Tracers 2-octanol and 2E1H were too partitioning to arrive in the first 1680 ml cumulative volume of water produced.

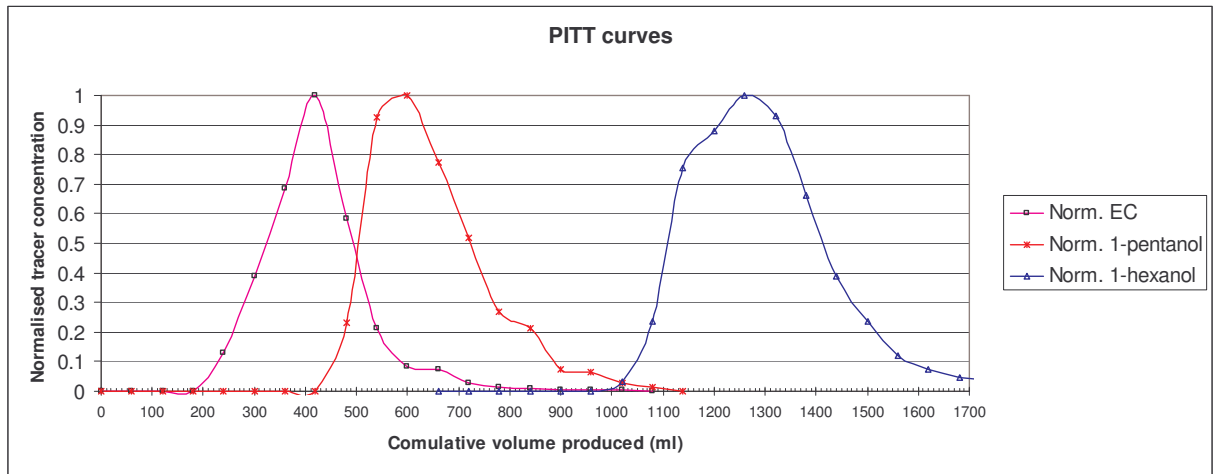


Figure 6-63: Tracer concentration curves from the first experiment.

Tracer concentration curves from the second experiment are shown in Figure 6-64. By applying Equation 6-6, the saturation of TCE was estimated to be 0.052 by 1-pentanol and 0.0512 by 1-hexanol. This range shows that the saturation is estimated with 96.9% accuracy. Although the saturation of TCE was less as compared to the previous experiment, 2-octanol was still too partitioning to arrive in the first 2300 ml cumulative volume of water produced. However, 2E1H started to arrive after 1800 ml but it was also too partitioning for the center of mass concentration to arrive in 2340 ml cumulative volume.

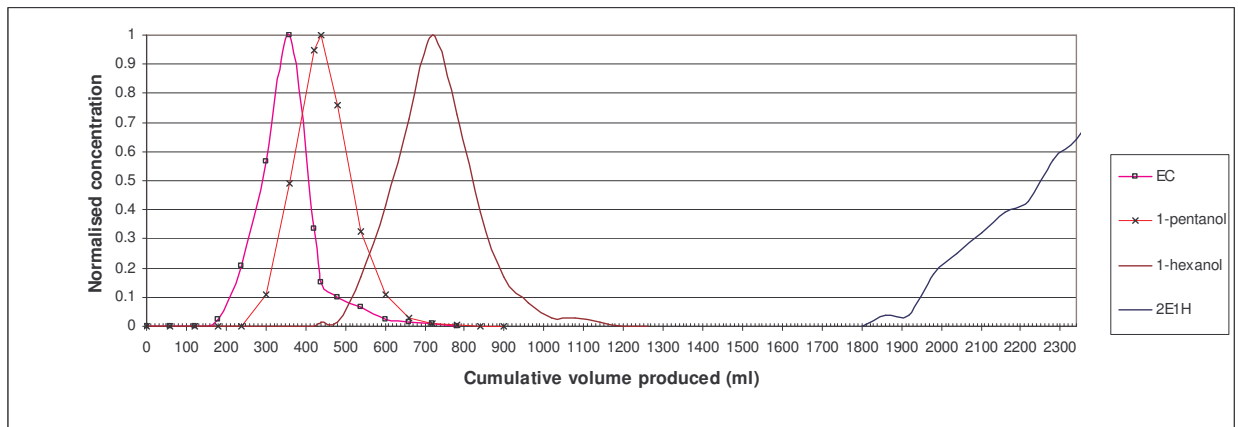


Figure 6-64: Tracer concentration curves from the second experiment.

6.7.4.1 Conclusion

From the results, it can be concluded that it was possible to estimate the saturation with an accuracy of 95%. However, the sand used was homogenous and the environment was controlled. Therefore, it does not mean that PITT can be applied with similar accuracy in the heterogeneous unconsolidated aquifers usually encountered in South Africa.

From the experiment, it can be deduced that if the residual saturation is expected to be high, a partitioning tracer with lower partitioning coefficient must be used, otherwise the time of experiment will be extended unnecessarily until the highly partitioning tracer arrives at the abstraction boreholes. Likewise, if the saturation is expected to be low, a partitioning tracer with lower partitioning coefficient will act like a non-partitioning tracer and a tracer with high partitioning coefficient is recommended for the experiment.

In the experiments conducted, if the time had been extended for a longer period, the more partitioning tracers, 2E1H and 2-octanol, would have arrived. The hypothetical arrival of the peak concentration in terms of the cumulative volume of solution produced was calculated with Equation 6-6. By assuming the parameter values used in the second experiment (Table 6-21), the curves produces by extending the experimental time, are shown in Figure 6-65.

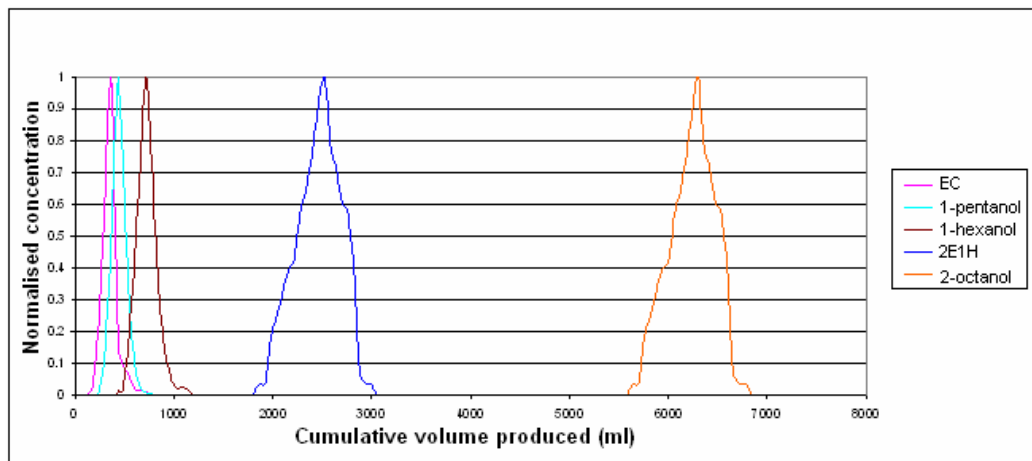


Figure 6-65: Expected arrival times of 2E1H and 2-octanol.

6.8 Conceptual Model of Test Site 1

6.8.1 Site Geology

This section addresses the geological formations as interpreted from drilling and improves the geological conceptual model discussed in section 6.1.2.3. The lithology of the site can be divided into the upper unconsolidated and lower consolidated units. The unconsolidated part is generally composed of clay, calcrete, sand, and gravel, with a thickness of about 30m. The first water strike is at about 15 m, and the main water strike is at the contact between the unconsolidated and consolidated sections (30 m). The consolidated rock is composed of fractured shale with some mudstone and sandstone layers. In most boreholes, the main water strike is around 30-35 m, although there are deeper and stronger water strikes in some boreholes.

6.8.1.1 Unconsolidated Lithology

The site is underlain by thick unconsolidated sediments, roughly 30 m thick. They play a significant role in the groundwater and contaminant distribution of the area. From top to bottom, it is composed of backfill soil, clay, calcrete, sand and sandy gravel. However, the intercalation (interbedding) of layers is common. For example, a thin layer of sand may be encountered between clay and calcrete at some localities. The thickness and extent of each unit is highly variable. As an example of this variability, Boreholes GB7 and GB8 in Figure 6-66 are only 10 m apart, but their geological logs still show considerable variation.

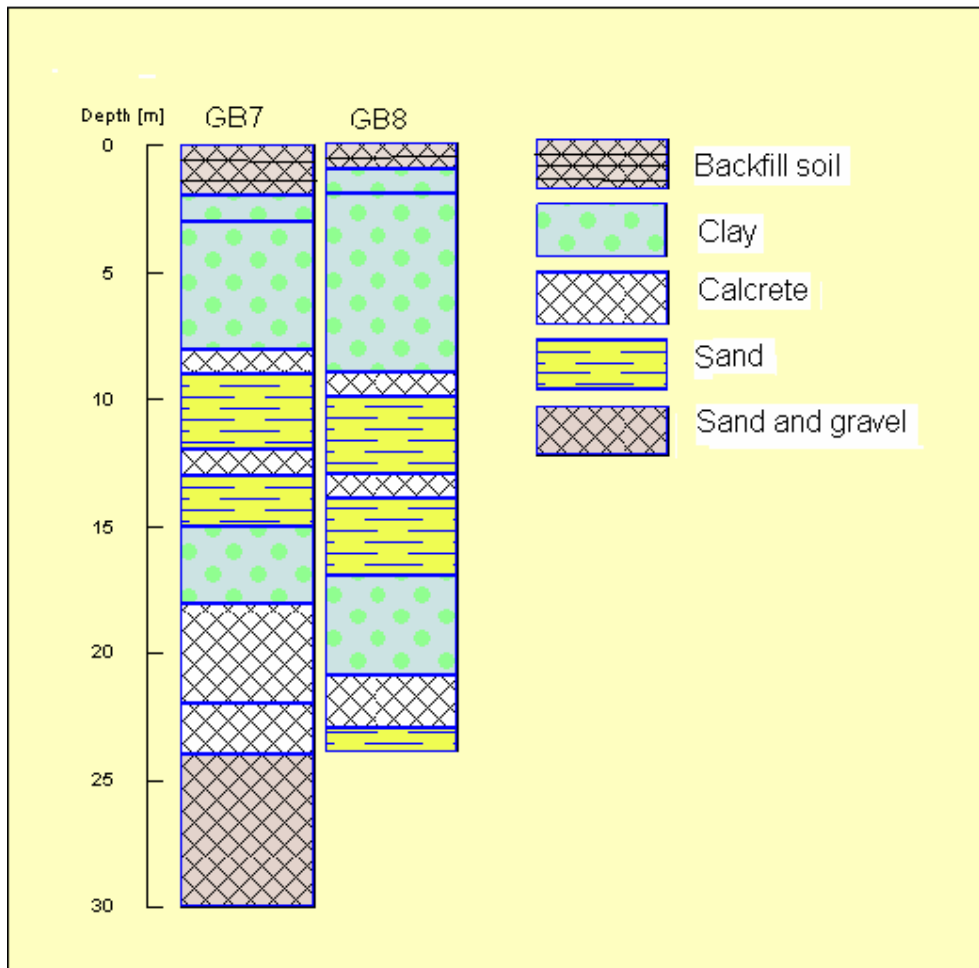


Figure 6-66: Geologic logs of Boreholes GB7 and GB8.

6.8.1.1.1 Backfill Soil

The top section of much of the site is covered by backfilled ash, soil and rock fragments, probably for infrastructural purposes. This backfill covers almost the entire test site, but with differing thicknesses.

The variation in grain size and poor sorting of the backfill could create preferential vertical and lateral pathways for DNAPL migration. In certain instances, it appears as if asphalt and possibly coal tar were used as part of the backfill. This could lead to a false impression of the VOC distribution on the site.

6.8.1.1.2 Clay

Below the backfill, a layer of black or dark red clay is common. With depth, the clay becomes silt-enriched. This section of the lithology is characterised by the **smell of organic compounds**. Soil samples collected from the excavated test pits and percussion drilling had this smell, although the intensity varied.

The expanding nature of the clay is exacerbated when it is exposed to moisture. The clay minerals expand and become impermeable. This helps to prevent the further downward movement of contaminants including DNAPLs. The thickness of the clay layer could be up to 10 m, so it is possible that a considerable amount of DNAPL can accumulate on or within this layer. The low capillary pressure prevents downward migration. When the layer is completely dry, however, it is possible that fractures can form. These fractures could be favorable pathways for DNAPLs. In Borehole GB2, some nodules of dark NAPLs within silty clay were also observed (Figure 6-67).

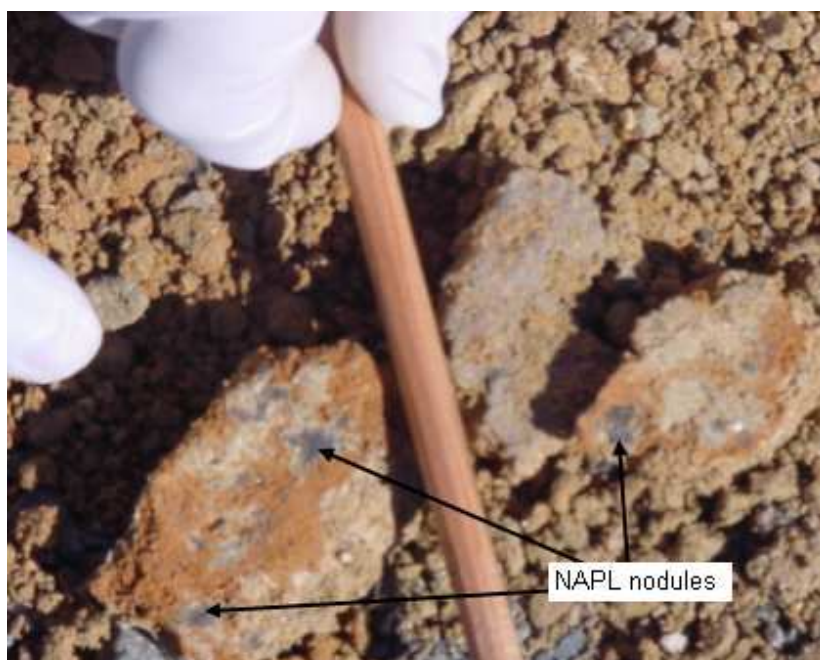


Figure 6-67: NAPL nodules in the clay layer of Borehole GB2.

6.8.1.1.3 Calcrete

The calcrete layer is ubiquitous and also displays a disparity in thickness and depth. 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. An example of calcrete collected from Borehole GB2 at a depth of 10 m is shown in Figure 6-68 .



Figure 6-68: Calcrete at a depth of 10 m in Borehole GB2.

Due to the light colour of the calcrete, NAPL nodules are clearly visible in this layer. The unit is also characterised by a strong odour of organic chemicals, possibly due to its larger grain size compared to the layers above and below the calcrete. This unit does not expand with moisture and the coarser nature of the layer could create a pathway for DNAPL movement.

6.8.1.1.4 Sand

This layer is composed of fine-grained sand. The water strike in the unconsolidated aquifer is located within this layer. Although the sand is fine grained, it is coarse enough for a preferential DNAPL pathway and the elevated transmissivity of this layer could facilitate aqueous contaminant transport.

6.8.1.1.5 Sandy Gravel

On contact with the bedrock, the grain size increases and gravel starts to dominate. Sometimes the grains are as large as pebbles or even cobbles. Because of its grain size, this layer provides a preferential pathway for DNAPLs. Below this sandy gravel unit is consolidated shale with lower effective porosity, and it is expected that once the DNAPL reaches, this layer it will find it easier to move laterally along the dip of

this contact rather than vertically into the consolidated rock. However, the vertical fractures within the shale, confirmed by the core drilling, will allow the DNAPL to penetrate the shale until an impermeable section is encountered.

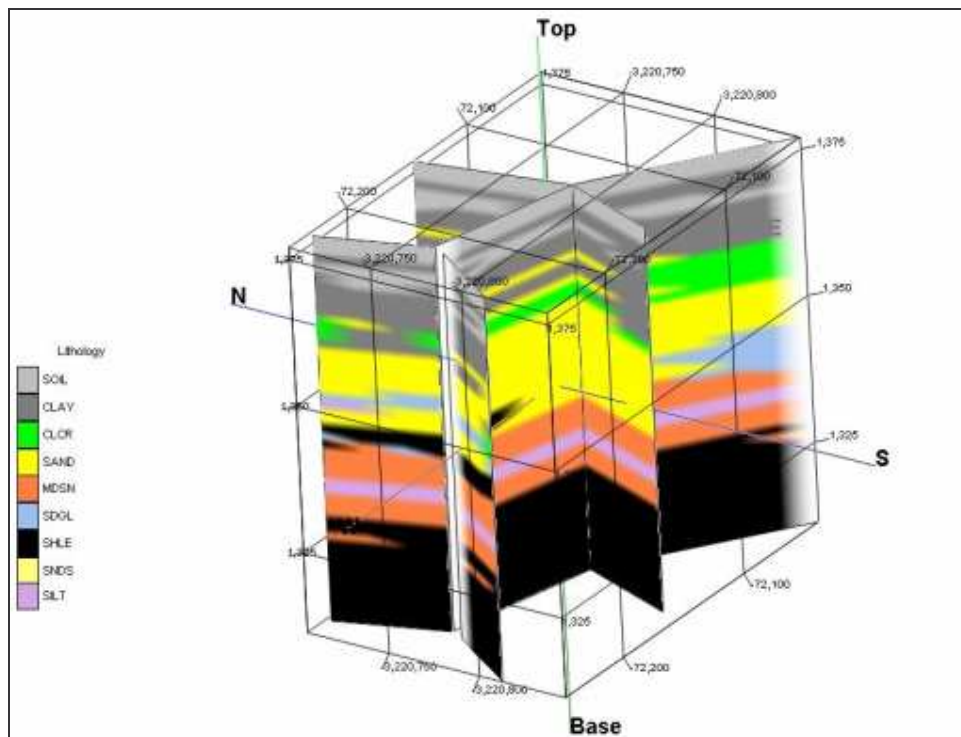
6.8.1.2 Bedrock Geology

6.8.1.2.1 Shale

Below the unconsolidated lithology is shale with some intercalations of sandstone and mudstone units. The major water strike in the base rock is intersected at a depth of around 30 m. Other minor water strikes were also encountered in the boreholes whenever a small fracture is penetrated.

The shale and mudstone have a very low primary porosity, which is not favourable for DNAPL movement. The sandstone is also fine grained, which results in high capillary pressure. However, the presence of fractures in the rocks creates preferential pathways for DNAPL and dissolved species. Since the orientation and intensity of the fractures vary, DNAPL entering the system could be very difficult to predict, locate and remediate.

A three-dimensional geologic profile mapped from the boreholes in the gasworks area is provided in Figure 6-69. It shows a section through the unconsolidated and consolidated geology.



6.8.1.2.2 Sandstone, Mudstone and Siltstone

Layers of sandstone, mudstone and siltstone are interbedded within the shale layer. Their thickness may vary from 10 m (Borehole FB1) to 0 m (Borehole GB9). Some fractures were also found in these rock units, but their depth and orientation were random.

All the layers are fine grained and are expected to prevent the downward migration of DNAPL, except where vertical and horizontal fractures with large enough apertures that minimizes the required capillary pressure.

6.8.2 Fracture Networks

6.8.2.1 Fractures due to Weathering

The shale below the unconsolidated lithology is highly weathered as observed in all the boreholes and core holes. The fractures are randomly oriented and dense, as shown in

Figure 6-70 and Figure 6-71. The shale was probably exposed to the atmospheric environment for a long time before the deposition of the unconsolidated sediments that resulted in its weathering.



Figure 6-70: Highly weathered shale below the unconsolidated section in EC1.



Figure 6-71: A closer look of the weathered shale in EC1.

The position of the contact between the unconsolidated and consolidated units in the boreholes is listed in Table 6-22. This zone is characterised by a high yield, which is the main water strike in the aquifer system.

Table 6-22: Depth and elevation of the contact zone (main water strike) between the sandy gravel and shale.

Borehole	Main water strike (m)	Elevation of main water strike (m)
EB1	30	1345.92
EB2	32	1344.35
EC1	32	1343.96
FB1	39	1332.40
GB1	27	1341.76
GB2	30	1338.14
GB3	30	1339.97
GB4	29	1341.49
GB7	32	1338.57
GB9	25	1345.54
GC1	46	1323.05
SB1	25	1348.20

Borehole	Main water strike (m)	Elevation of main water strike (m)
NB1	32	1341.80
VB1	28	1340.02
VB2	27	1342.42

The shale has very low primary porosity, which is not favourable for DNAPL movement. Movement of DNAPLs or even groundwater flow would have been almost impossible. However, the presence of a dense and highly connected fracture network will definitely create preferential pathways for DNAPLs. Because of the big aperture of the fractures, a small amount of DNAPL head is needed to migrate both laterally and vertically. Since the orientation and intensity of the fractures vary, it is difficult to characterise the free DNAPL phase.

6.8.2.2 Fractures of Stress or Tectonic Origin

6.8.2.2.1 Small-aperture Fractures

The weathered shale is followed by interlayers of mudstone, shale, sandstone and siltstone. While they have different thicknesses and depths at different locations, they have one thing in common; their primary porosity is very low. Although the sandstone is relatively coarse grained with higher effective porosity, high capillary pressure is needed for DNAPLs to migrate through.

However, the presence of secondary fractures makes the rocks important for DNAPL movement. Figure 6-72 (a) and (b) show a fracture with an aperture of less than 1 mm, but about a 1 cm zone of weathering.



(A) Siltstone at 49 m in GC1



(B) Mudstone at 37 m in GC1

Figure 6-72: Small-aperture horizontal fractures with weathered zone indicative of flow paths.

6.8.2.2.2 *Big-aperture Fractures*

Big-aperture fractures were found frequently and at various orientations. For example, in EC 1, a fracture was located at a depth of 36 m within the massive shale that has a weathering zone of 1.14 m (Figure 6-73 (A)). Another fracture in Borehole EC1 was encountered at 51 m that appears to be horizontally dipping, as shown in Figure 6-73 (B). A fracture zone of 1 m is also found in GC1 at a depth of about 41 m with big fractures, as shown in Figure 6-73 (C).



(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 6-73: Big-aperture vertical and horizontal fractures at various locations.

6.8.2.3 **Calcite Enclaves**

Enclaves of calcite nodules or small rock fragments were found within the mudstone layer, as shown in Figure 6-74. The enclaves are loosely attached to the matrix of the mudstone and a preferential flow path is created around them. This flow path could

easily be identified by the weathered zone formed around them. Without the core samples, these features, being small in scale, could hardly be detected by geophysical techniques or available down-the-hole investigations.



Figure 6-74: Enclaves within the mudstone layer providing preferential flow paths through their boundaries.

6.8.2.4 Calcite Veins

Another important feature is calcite vein that fill some of the fractures. The calcite veins are believed to be solution precipitates formed from the groundwater that moved through the fractures. Some of the veins are fully grown and completely fill the fracture aperture. The veins decrease the transmissivity of the fracture, but also block DNAPL movement. Usually the calcite vein is stronger than the fractured zone, which is usually weathered due to oxidation, as water flows through. Examples of the veins filling horizontal and vertical fractures and/or big fracture zones are shown in Figure 6-75 (A) to (G).



(A) Fracture partially filled with calcite vein

(B) Laminae of intact calcite vein completely filling the fracture



(c) Plan view of a fracture filled with calcite vein (vein broken during drilling)



(d) Calcite vein filling a vertical fracture



(e) Partially filled vertical fracture



(f) Partially filled horizontal fracture



(g) Fracture zone filled with calcite veins

Figure 6-75: Calcite vein filling fractures to different degrees.

6.8.2.5 Slickensides

Slickensides were observed in the shale in GC2 at a depth of about 53 m. The slides are characterised by shiny and grooved surfaces, as shown in Figure 6-76. Although

they were indicators of fracturing 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 no water could flow through the fracture. The fresh surface with no weathering due to oxidation or deposition of calcite veins is an indication of the impermeability of the fracture; therefore, they are insignificant in the hydrogeology of the system and DNAPL migration.



Figure 6-76: Slickensides showing shiny and grooved surface.

6.8.3 Summary of the Fracture Network

As discussed above, the core holes revealed the existence of different types of pathways that are potential for DNAPL migration. The position of water strikes, fractures and anomalies in the Test Site 1 boreholes is provided in Table 6-23. A summary of the position and nature of fracturing in both core holes is given in Table A 7, in Appendix A.

Table 6-23: Water strikes, anomalies and their elevations.

Bh*	Water Strikes and anomalies	Elevation (m)	Bh	Water Strikes and anomalies	Elevation (m)	Bh	Water Strikes and anomalies	Elevation
SB1	11	1363.41	EB1	26.7	1349.22	EB2	34.5	1341.85
GB1	19	1352.76	SB1	27	1347.41	EC1	34.94	1341.83
GB3	19	1350.97	GB4	29	1341.49	GB7	35	1335.57
GB7	19	1351.57	GB9	29	1341.54	GB9	35.5	1335.04
GB9	19	1351.54	GC1	29.25	1342.28	EC1	36.11	1340.66
GB2	20	1348.14	FB1	29.5	1341.90	FB1	37.5	1333.90
GB4	20	1350.49	GB3	30	1339.97	EC1	38.17	1338.60
GB5	20	1350.49	EB1	30	1345.92	EC1	38.91	1337.86
FB1	20	1351.40	GC1	30.88	1340.65	GB3	39	1330.97
NB1	20	1355.31	GB7	31	1339.57	EB1	44.5	1331.42
GB8	21	1349.37	EB2	32	1344.35	GC1	48.37	1323.16
EB2	21	1355.35	NB1	32	1343.31	FB1	51	1320.40
EB1	22	1353.92	EC1	32.39	1344.38	EC1	51.95	1324.82
EB3	22	1354.42	EC1	33.69	1343.08	GB3	53	1316.97
EB2	24	1352.35	GB4	34	1336.49	EC1	53.77	1323.00

*Bh = Borehole

6.8.4 Hydrogeology

6.8.4.1 Water Level

At the test site, the elevation of the groundwater was found to follow the topography and decreases with distance from the koppie adjacent to the site towards the southeast. The water level is approximately 13 to 15 m below the collar heights of the boreholes. A contoured view of the groundwater elevation generated using Bayesian Interpolation is given in Figure 6-77. The groundwater elevation follows the topography and flows from the northwest to the southeast.

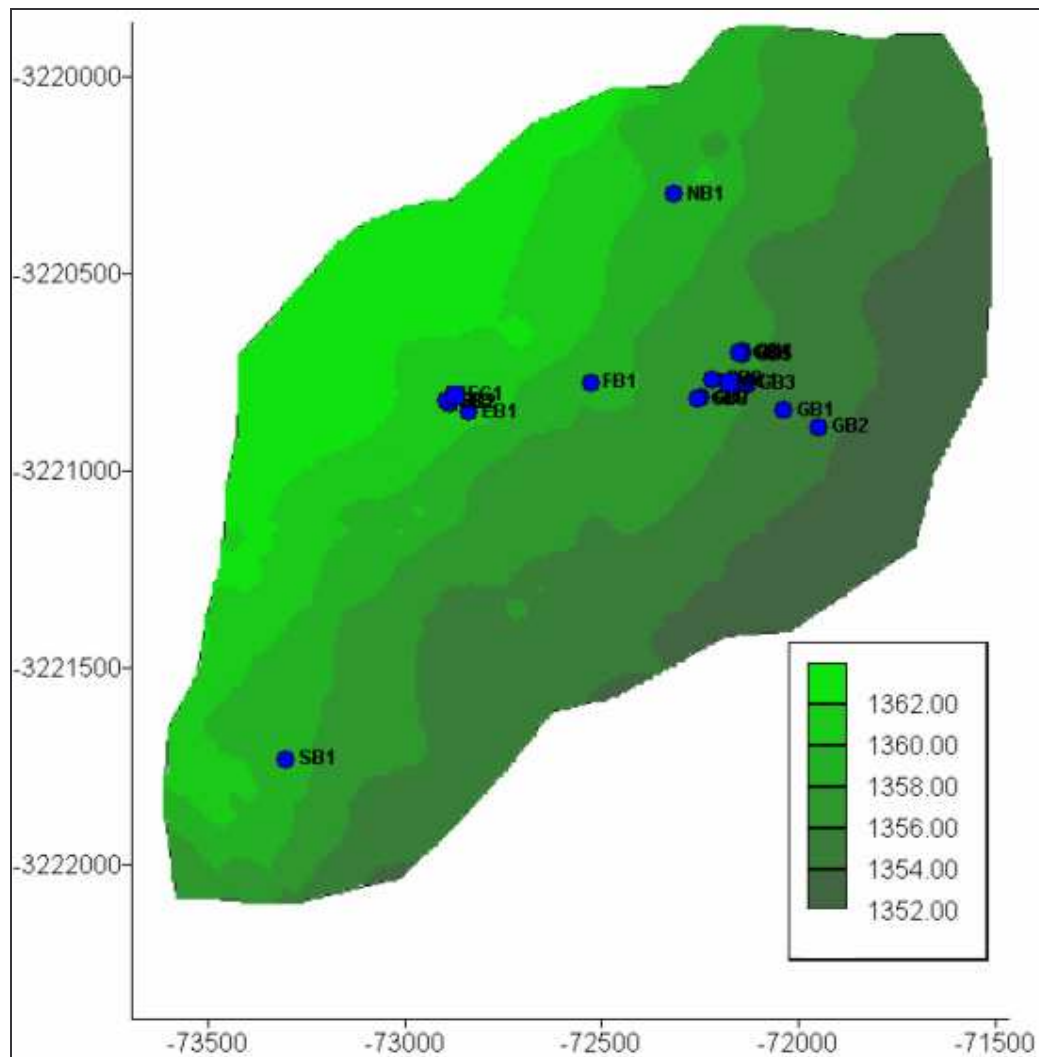


Figure 6-77: Contour map of groundwater elevation.

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 Figure 6-78.

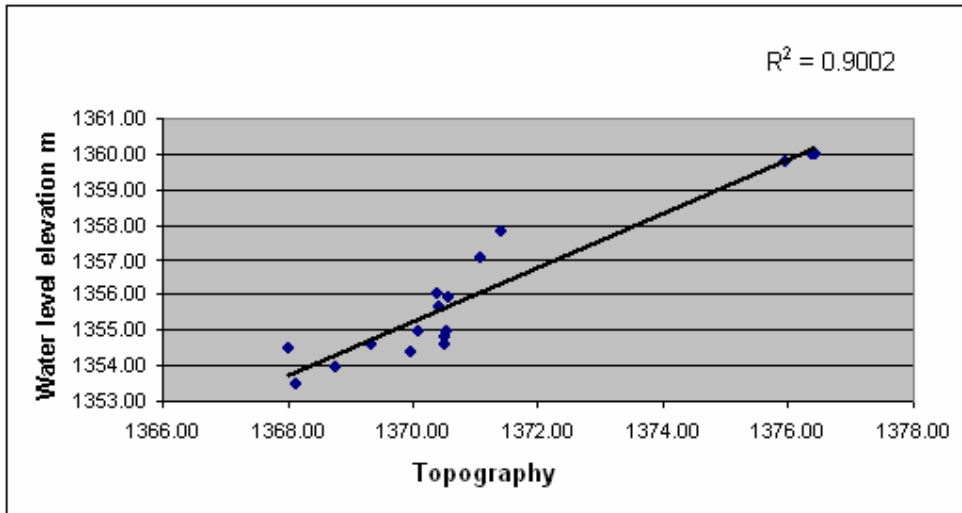


Figure 6-78: Ground surface versus water-level elevation.

A time series of water level elevation for all the boreholes and piezometers on the site is given in Figure 6-79. The measurement was taken for the past two and half years and shows that the water level was more or less in the same position. There are no abstraction boreholes on the site, the minor fluctuation is due to recharge from rainfall.

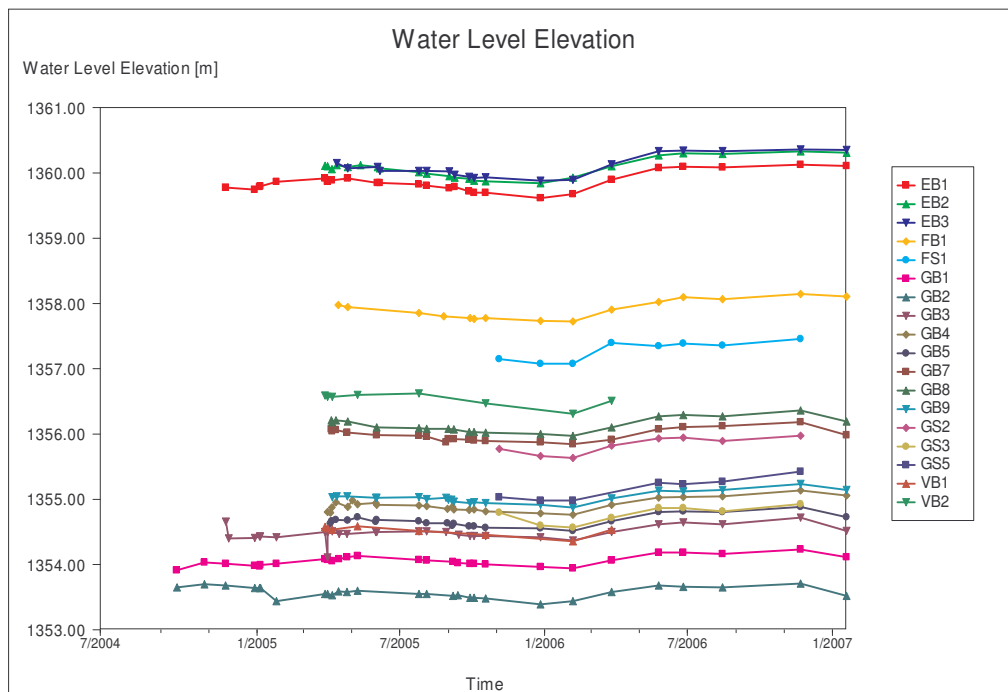


Figure 6-79: Time series of water level in the different boreholes.

6.8.4.2 Hydrogeological Conceptual Model

After integrating the information obtained from pumping test, drilling and other techniques; a hydrogeological conceptual model of the site is developed (Figure 6-80). The system is composed of two aquifers, Aquifer 1 and Aquifer 2 as discussed in section 6.4.7.2. Since there is no aquitard (from drilling information) that separates the two aquifers, they are characterised by a leaky contact. This is further confirmed by the presence of equal static hydraulic head in both aquifers

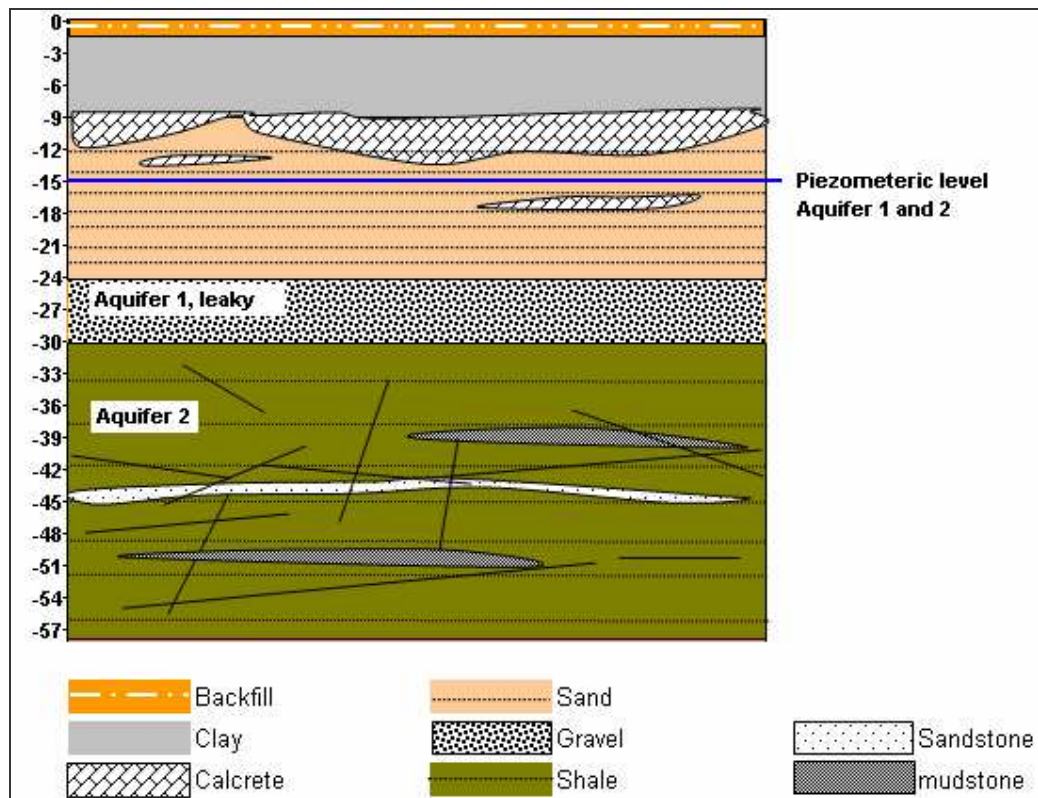


Figure 6-80: Conceptual model of Test Site 1.

6.8.5 Conceptual Model of DNAPL Phase Migration

As discussed in section 6.8.1.1, NAPL nodules were encountered 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. Although nodules were common in the clay and calcrete layers, free-phase NAPL was not encountered in any of the drilled boreholes.

The migration of NAPL phase in the conceptual model is provided in Figure 6-81. It is believed that the DNAPL movement through the clay layer is mainly through

fractures, as the clay was found to be almost impermeable. However, if there is any thick deposit of DNAPLs in such a way that the capillary pressure is greater than the porosity entry pressure of the clay, DNAPLs can move downward through the clay matrix. Calcrete, sand and gravel are porous, where DNAPLs can easily move downward, especially if the DNAPL pool is high. 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, fractures determine the flow rate and direction.

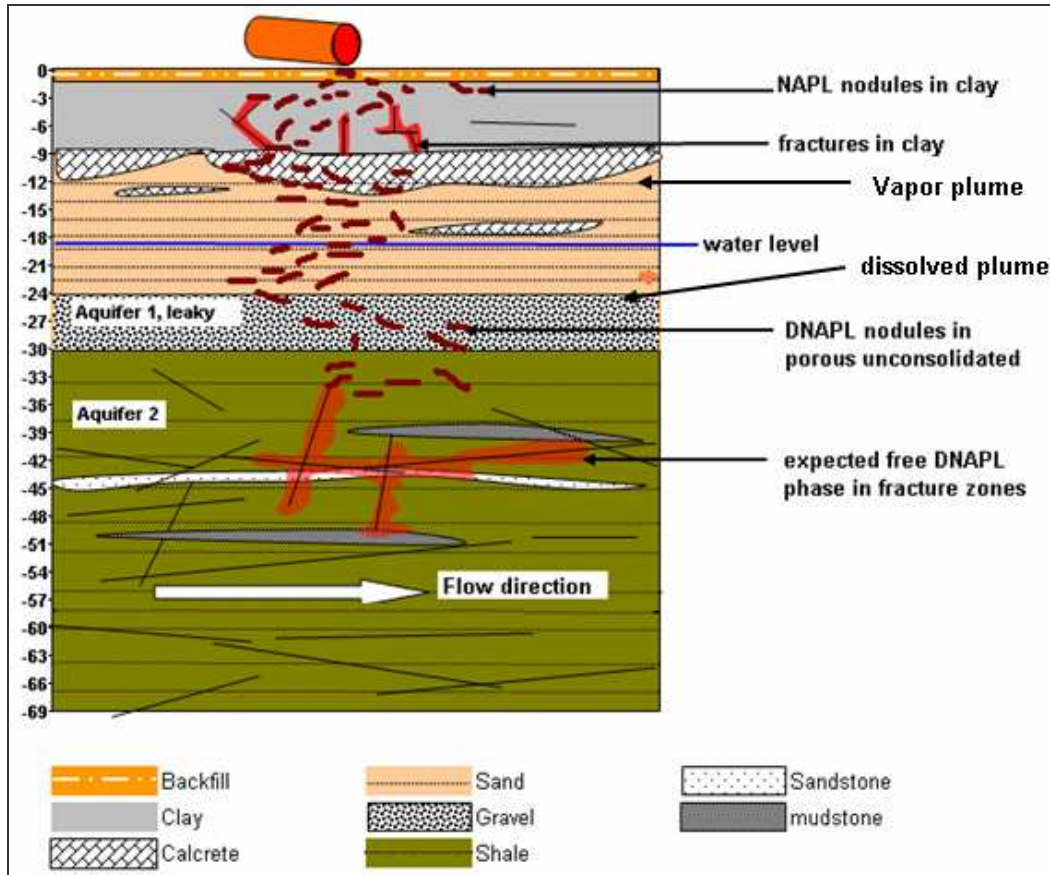


Figure 6-81: DNAPL phase movement in the developed conceptual model.

6.8.6 Conceptual Model of the Dissolved Plume

Chemical analysis of water samples indicates that the dissolved plume of NAPLs is present at various concentrations and locations. 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, a detailed understanding of the dissolved-phase interactions can be obtained. These profiles are provided in Appendix A, from Figure A 4 to Figure A 9. The TCE profiles show an increase from west to east across the site. This is corroborated by the TOX increase across the site and also the chloroform distribution. It is interesting to note that the EC variation

provides a very similar pattern. By integrating this information, a hypothetical DNAPL plume migration in the vadose zone and saturated zone is given in Figure 6-82.

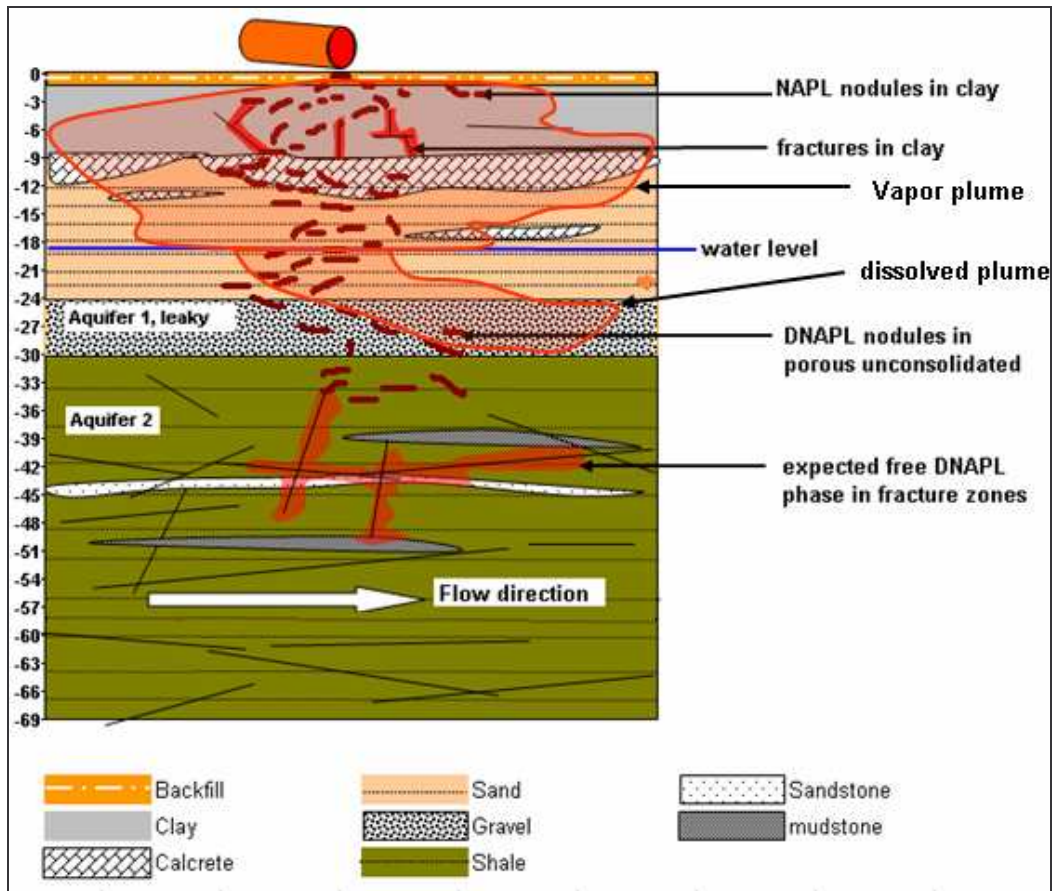


Figure 6-82: Conceptual model of vapour, dissolved and free DNAPL phases in Test Site 1.

6.9 Fracture Characterisation in the Campus Test Site

As discussed in section 6.2.2.3, the hydrogeological conceptual model of the Campus Test Site was fairly understood from previous studies. However, accurate position, dip and strike, aperture and connectivity of the bedding parallel fracture were not studied. Various techniques were applied to “hunt” the fracture so that its orientation would be evaluated in detail. In this section, the new findings of the fracture properties will be discussed.

6.9.1 Hydraulic and Transport Parameters of the Fracture

Six boreholes and two core holes were drilled at the Campus Test Site during this research. The distribution of the boreholes relative to the previously drilled boreholes is shown in Figure 6-6, marked with “DNAPL boreholes”. A close look of the

DNAPL boreholes is given in Figure 6-83. Boreholes UO23 and UO30 are some of the old boreholes but due to their location, were used in this research for the fracture characterisation; therefore, they will be included with the DNAPL boreholes in this discussion.

The hydraulic and transport parameters of the bedding-parallel fracture in the site are discussed by Riemann (2002), Van Wyk (1998), and Botha *et al.*, (1998). Although the parameters of the fracture in the DNAPL boreholes are not expected to be very different, this study was done to evaluate if the parameters differ locally due to the fracture heterogeneity.

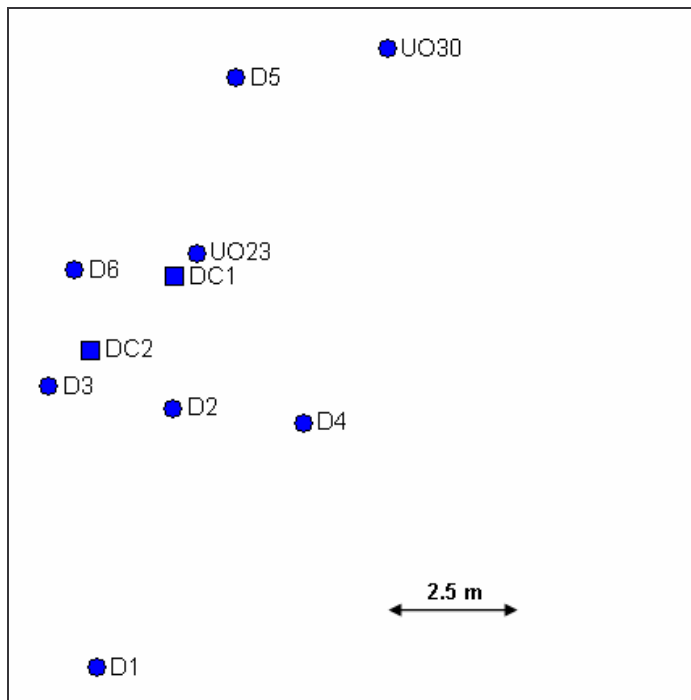


Figure 6-83: Distribution of the DNAPL boreholes (circles) and core holes (squares) in the Campus Test Site.

6.9.1.1 Hydraulic parameters

From drilling, it was identified that D2, D3, D4, D6, UO23, DC1 and DC2 intersect the fracture, while D1, D5 and UO30 do not. From previous investigations (Riemann, 2002), it was found that the boreholes that intersect the fracture have a yield of about 6 L/s while boreholes that don't intersect the fracture have a yield of less than 0.2 L/s. A slug test was done in the DNAPL boreholes to further confirm the strength of the boreholes and intersection to the fracture. The result obtained from the slug test coincided with the information obtained from drilling.

As discussed in section 6.2.2.3, Van Tonder and Vermeulen (2005) estimated the transmissivity of the fracture as 580 m²/day and that of the matrix to be 3 m²/d.

Riemann (2002) estimated the transmissivity of formation (an average of the fracture and matrix combined) as $19 \text{ m}^2/\text{d}$. Similar values were obtained when the DNAPL boreholes were pump tested during this research.

Riemann (2002) explained that early time drawdown data could be used to estimate the transmissivity of the fracture zone using Cooper-Jacob 2 (CJ2) method. However, in this experiment estimated transmissivity using CJ2 did not give any physical meaning. For example, UP16 was pumped and the DNAPL boreholes and UO29 were used as monitoring boreholes (see Figure 6-6 for the positions of UP16 and UO29). The Microsoft Excel based software, **FC_excel**, developed by IGS to characterise fracture hydraulic parameters was used for the interpretation. Boreholes D4, D2 and D3 intersect the fracture, therefore, the transmissivity is expected to be around $750 \text{ m}^2/\text{d}$. However, as it can be seen in Figure 6-84, the estimated fracture transmissivity was only $21.99 \text{ m}^2/\text{d}$. Boreholes UO30 and D1 do not intersect the fracture, and the transmissivity is expected to be around $3 \text{ m}^2/\text{d}$. However, as it can be seen in Figure 6-85, the estimated transmissivity was $52.09 \text{ m}^2/\text{d}$, which is higher than that estimated by the boreholes intersecting the fracture.

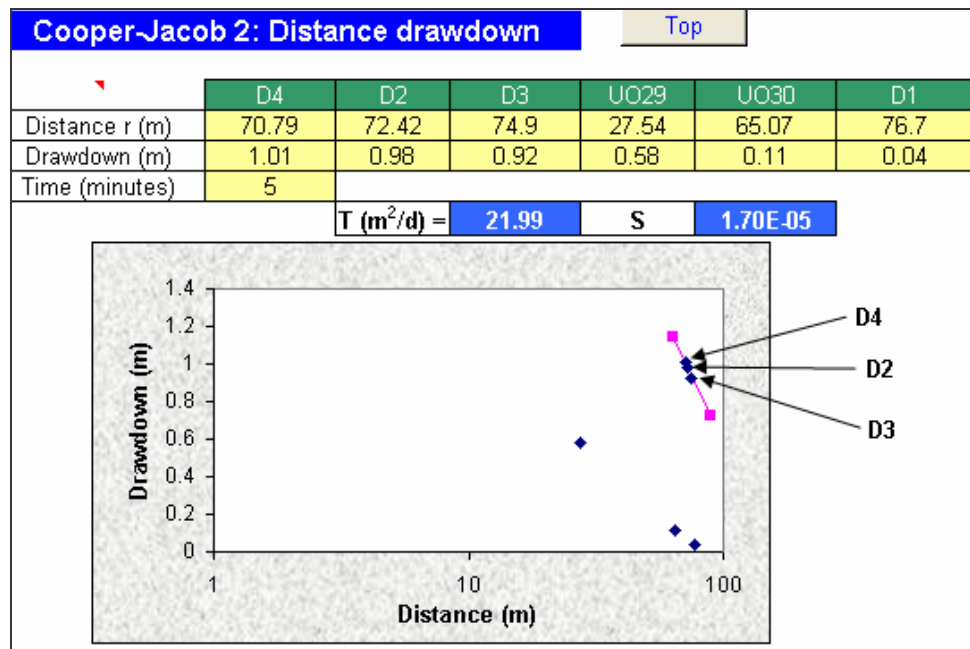


Figure 6-84: Estimation of fracture transmissivity using Cooper-Jacob 2 method from drawdown data after 5 minutes (UP16 was abstracted, while D4, D2 and D3 were used for monitoring).

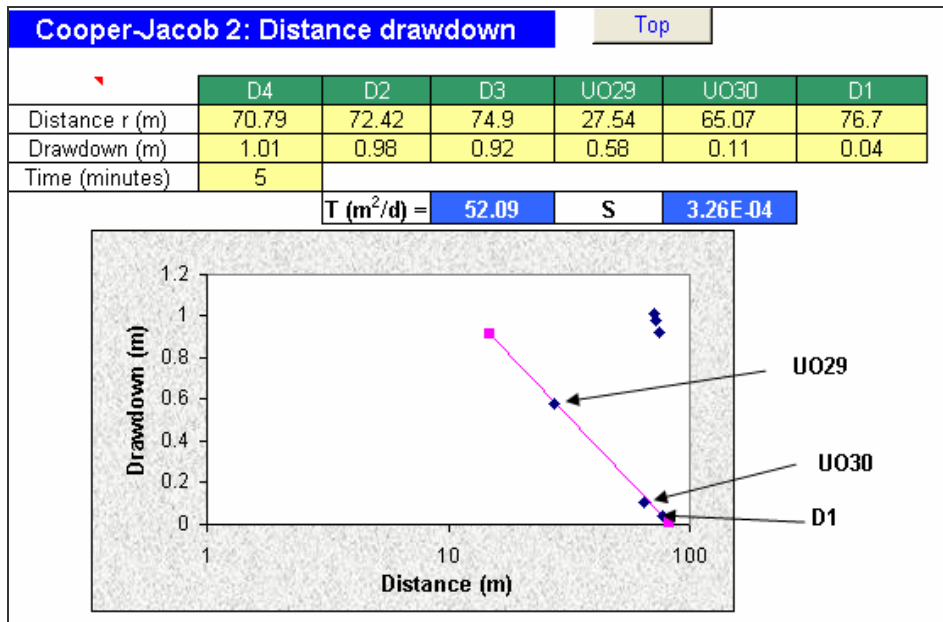


Figure 6-85: Estimation of fracture transmissivity using Cooper-Jacob 2 method from drawdown data after 2 minutes (UP16 was abstracted, while UO29, UO30 and D1 were used for monitoring).

Another example is given in Figure 6-86 where UO23 was pumped and D2, D3, and D4 were used for monitoring. All the boreholes intersect the fracture and were expected to give high transmissivity estimate. However, the boreholes were scattered widely and it was not possible to fit a single line on them. Different sets of monitoring boreholes result in different values of transmissivity.

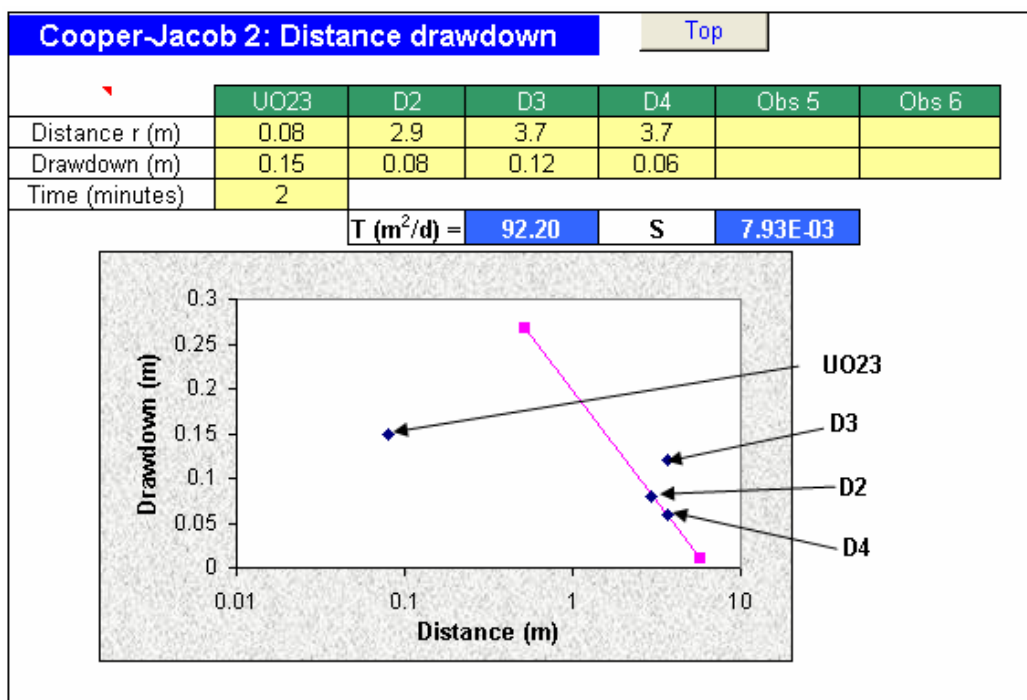


Figure 6-86: Estimation of fracture transmissivity using Cooper-Jacob 2 method from drawdown data after 2 minutes (UO23 was abstracted, while D3, D2 and D4 were used for monitoring).

6.9.1.2 Transport Parameters

Riemann (2002) conducted point dilution and radial convergent tracer tests and estimated various transport parameters of the fracture in the site. The parameters estimated in the DNAPL boreholes were very similar to those of Riemann (2002) and are summarised in Table 6-24.

Table 6-24: Summary of transport parameters estimated from the tracer tests.

	UO23	UO23	UO23	D3	D3	D3
Method	Point Dilution	Injection-withdrawal	Radial-convergent	Point Dilution	Injection-withdrawal	Radial-convergent
Darcy Velocity (m/d)	4.71		6.02	5.27		10.82
Seepage velocity (m/d)	10.47	17.36		11.72	11.65	
Forced Flow velocity (m/d)			24.09			24.04
Dispersivity (m)			1.8			1.9
Effective Porosity			0.114			0.67
Abstraction BH			D3			UO23

6.9.2 Fracture Connectivity

To evaluate the connectivity of the boreholes by the fracture, a constant rate pumping test was conducted in UP16 and the rest of the boreholes in the Campus Site were used to observe the drawdown. It was known from previous studies (Riemann, 2002)

that UP16 is one of the boreholes that intersect the fracture. The test was conducted for seven hours at a rate of 2 L/s and the water level was measured in all the other boreholes continuously during the test. The groundwater elevation versus time curves of the observation boreholes are given in Figure 6-87.

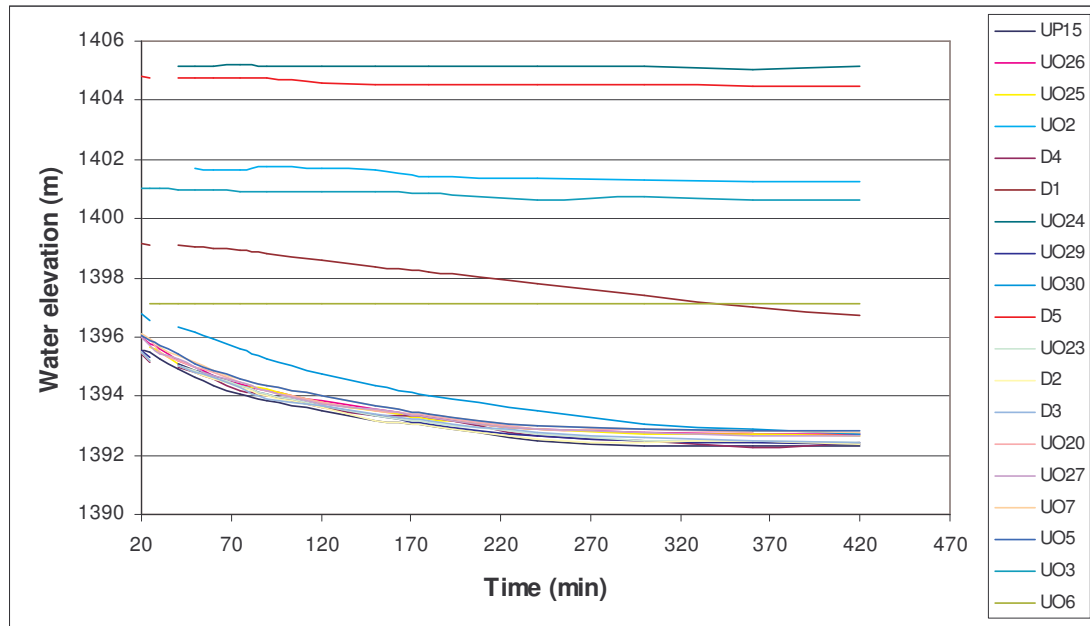


Figure 6-87: Water elevation versus time when UP16 was pumped.

Depending on the drawdown curves, the boreholes can be categorised into three groups. One group showed no drawdown at all times during the test, indicating that they don't intersect the fracture. The second group showed a slight drawdown, indicating that they are connected to UP16 by a low transmissivity fracture. The third group had significant drawdown, indicating that they are well connected with UP16 by the fracture.

It can be concluded that the drawdown in the observation boreholes was mainly due to the fracture connectivity and transmissivity. The conceptual model developed by Botha *et al.* (1998), given in Figure 6-9 is a simplified form of the site and cannot explain the behaviour of the boreholes satisfactorily. For example, Borehole D1 did not intersect the fracture as observed by borehole video cameras and slug test done in the borehole. However, as pumping of UP16 progressed, drawdown in D1 increased (Figure 6-87). This shows that the fracture that connects D1 with UP16 has low transmissivity.

Another example is UO30, which had a static water level equal to those that intersect the fracture (Figure 6-87). Even when UP16 was pumped, it showed almost the same hydraulic head response to those that intersect the fracture. According to the conceptual model of Botha *et al.* (1998), the borehole is located in Aquifer 2 (Section 6.2.2.3) and intersects the fracture zone. However, UO30 does not intersect the

fracture, as shown from video camera, slug test and pumping test conducted in the borehole. 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 has a transmissivity of $1.2 \text{ m}^2/\text{d}$, indicating that it does not intersect the fracture. Therefore, UO30 is slightly connected by the fracture; as a result the static water level of the borehole is the same as those that intersect the fracture. However, the transmissivity of the fracture is very low, to the extent that when UO30 was pumped, there was no enough inflow into the borehole through the fracture and was dewatered within 7 minutes.

6.9.2.1 Borehole Spacing and Connectivity

The effect of the distance between the monitoring boreholes and the abstraction borehole (UP16) was almost insignificant, as shown in Figure 6-88. The figure shows the drawdown observed after 6 hours of pumping verses the distance of the observation boreholes from UP16. For example, UO6 and D3 are 23.8 and 74 m way from UP16, respectively; however, there was no drawdown in UO6 but 5 m drawdown was observed in D3. This shows that the main factor that controls the drawdown in the observation boreholes is the connectivity with the abstraction borehole but not their distance.

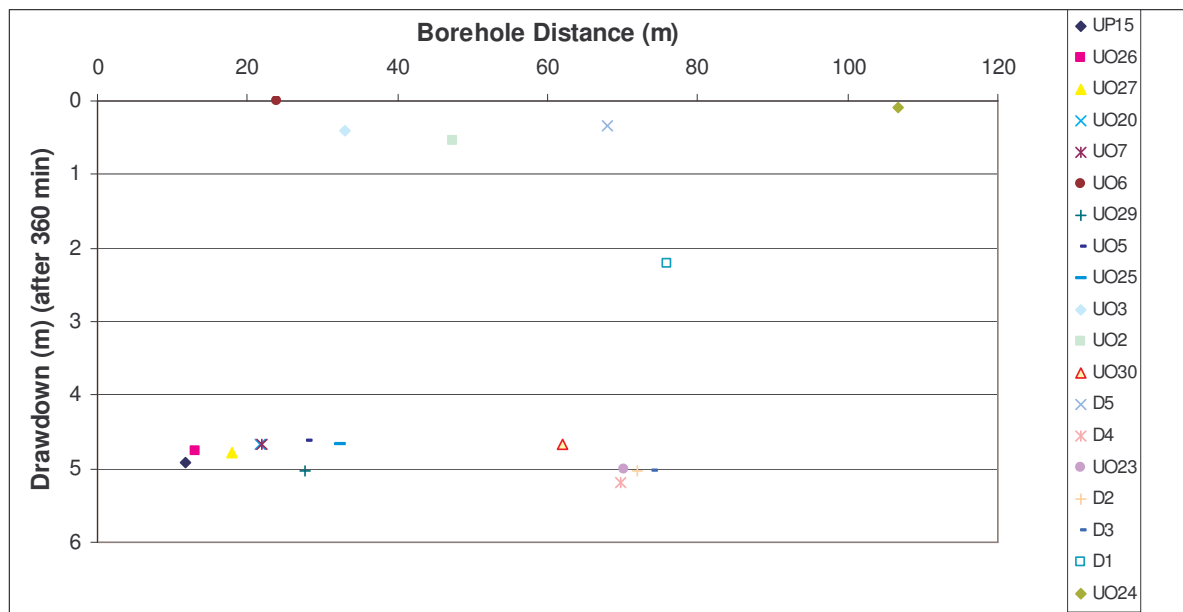


Figure 6-88: Drawdown versus distance of the boreholes from UP16 after 6 hours of pumping.

6.9.2.2 Borehole Depth and Connectivity

The depth of the observation boreholes was also studied if it contributes to the amount of drawdown. From previous studies (Riemann, 2002) and pumping test conducted during this research, UP16 intersects the fracture at about 23 m from the ground surface. UP16 is 41 m deep and the pump was installed close to the bottom of the

borehole. The drawdown of the boreholes after 6 hours of pumping versus the depth of the boreholes is given in Figure 6-89. For example, UO6 and UO24 are 41 and 30 m deep, respectively; and no drawdown was observed in both boreholes.

Boreholes D2, D3 and UO23 are 23, 23 and 46 m deep, respectively; however, a drawdown of 5 m was observed in all of them (Figure 6-88). This further proves that the main factor that controls the drawdown in the observation boreholes is the fracture connectivity of the monitoring boreholes with the abstraction borehole.

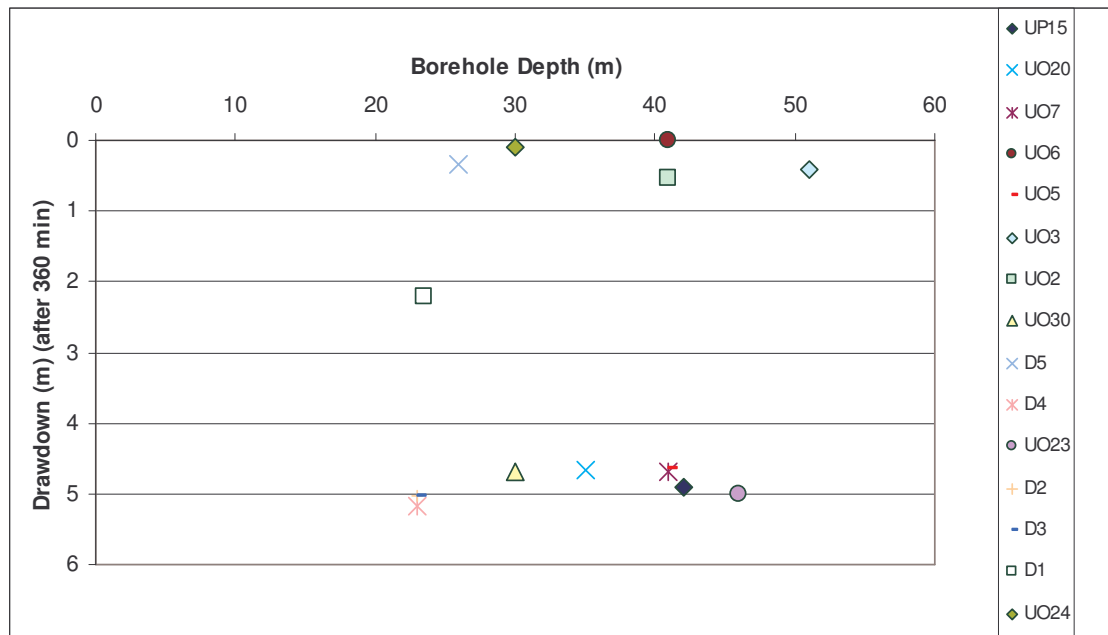


Figure 6-89: Drawdown versus depth of the boreholes after 6 hours of pumping UP16.

6.9.2.3 Estimated Fracture Connectivity

The fracture on the CTS is not continuous; instead it is irregular and disconnects at short intervals, making it difficult to estimate its connectivity. As an example, Borehole D5 and UO23 are only 3.5 m apart; however, D5 does not intersect the fracture, while UO23 does. It was practically impossible to track the fracture from drilling.

As observed during this research, because of the complex and difficult to predict nature of fracture systems, estimation of the spatial distribution of fractures using the non-invasive and invasive techniques is extremely difficult. Various techniques were applied to characterise the connectivity of the fracture in the Campus Test Site. These techniques include:

- Drilling
 - Percussion drilling
 - Core drilling

- Borehole geophysical logging
 - One-arm Caliper
 - Natural Gamma
 - Spontaneous Potential
 - Resistivity Probe
 - Full Wave Sonic (FWS)
 - Neutron-neutron Probe
- Borehole Geochemical logging
 - Electrical conductivity (EC)
 - pH
 - Dissolved oxygen
 - Redox potential and
 - Temperature
- Aquifer test
 - Slug test
 - Pumping test
 - Tracer Test
 - Point dilution tests
 - Radial-convergent tests
- Borehole video camera
- Surface geophysical survey
 - Electromagnetic seismic survey (ESS).

Although the pumping test provided most of the information needed for the evaluation of the fracture connectivity, the final connectivity understanding is developed by integrating the various techniques. After identifying the borehole that intersects the fracture, a conceptual model of the fracture connectivity was developed. The developed conceptual model shows that there are **infinite possibilities** of fracture connectivity.

A list of boreholes that intersect and do not intersect the fracture is given in Table 6-25. Due to accessibility problem, the fracture status in some boreholes and core holes was not evaluated; therefore, these boreholes are not listed in the table.

Table 6-25: List of boreholes that intersect and do not intersect the fracture.

Boreholes intersecting the fracture			Borehole that do not intersect the fracture.
CH1	UO25		D5
CH3	UO26		UO10
D1	UO27		UO11
D2	UO28		UO12
D3	UO29		UO13
D4	UO30		UO17
D6	UO4		UO2
DC1	UO5		UO21
DC2	UO6		UO22
UO1	UO7		UO24
UO14	UO8		UO3
UO18	UO9		
UO19	UP15		
UO20	UP16		
UO23			

Figure 6-90 shows a reasonable connectivity of the fracture, however, the actual connectivity could be much smaller than that with a conservative estimate shown in Figure 6-91. The connectivity could also be much larger than the reasonable estimate where most of the site being covered by the fracture as shown in Figure 6-92.

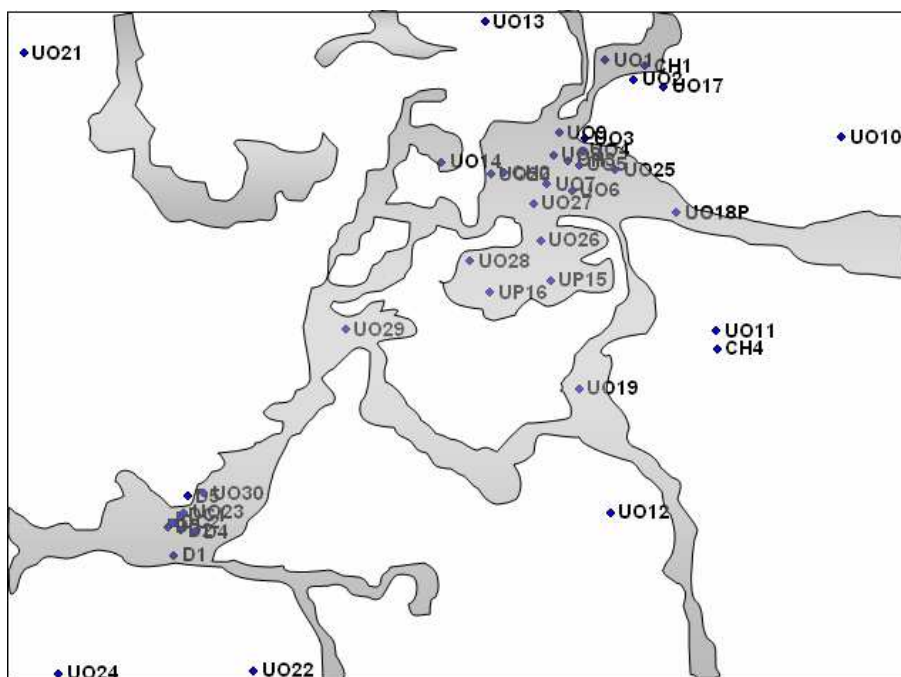


Figure 6-90: A reasonable estimate of the fracture (shaded) connectivity.

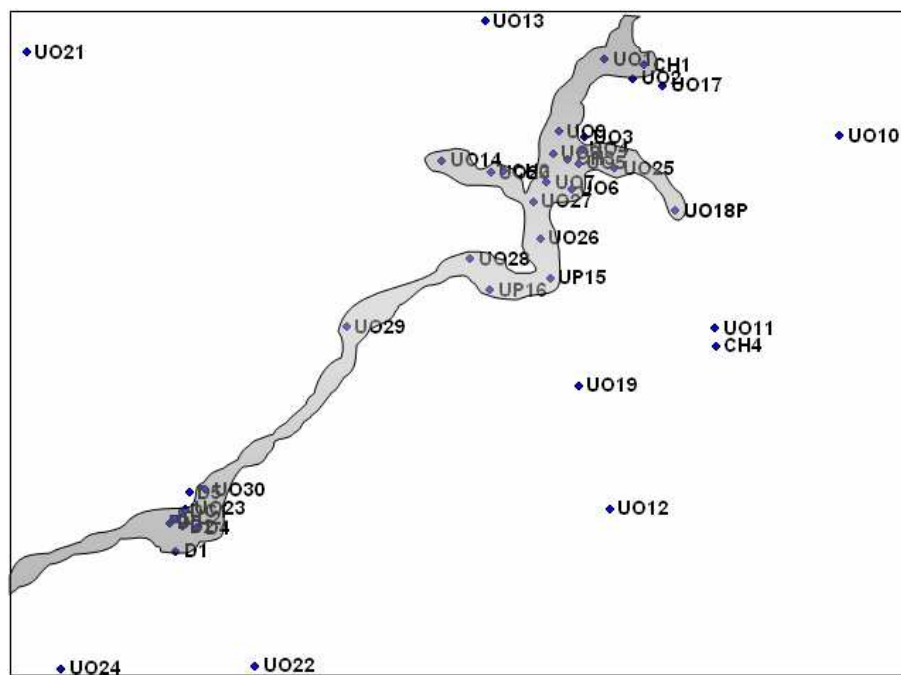


Figure 6-91: A conservative estimate of the fracture (shaded) connectivity.

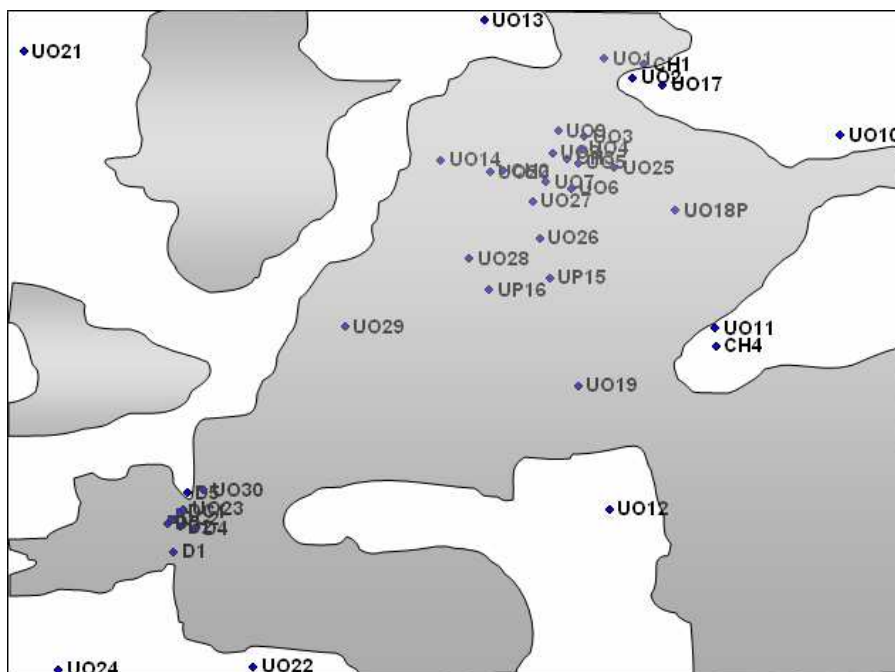


Figure 6-92: An exaggerated estimation of the fracture (shaded) connectivity.

6.9.3 Apparent Fracture Aperture

Various geophysical loggings and borehole video camera were employed to evaluate the aperture of the fracture in the Campus Test Site. However, it was not possible to assess the exact aperture of the fracture in the aquifer, and the estimated aperture is the exposed fracture on the borehole walls. This aperture is generally bigger than the true aperture as it is enlarged during drilling; therefore, it is termed as **apparent aperture**.

6.9.3.1 Borehole-video Cameras

Borehole video pictures were taken in various boreholes to characterise the position and apparent aperture of the fracture precisely. A measuring tape was inserted in the borehole so that the positing of the video camera can be located on a millimetre scale. A compass was attached below the televiewer of the video camera so that the direction at which the picture was taken could be assessed (Figure 6-93). Measurement of the direction of the fracture aperture is important in determining the direction of DNAPL and groundwater movement, as they are the preferential pathways.

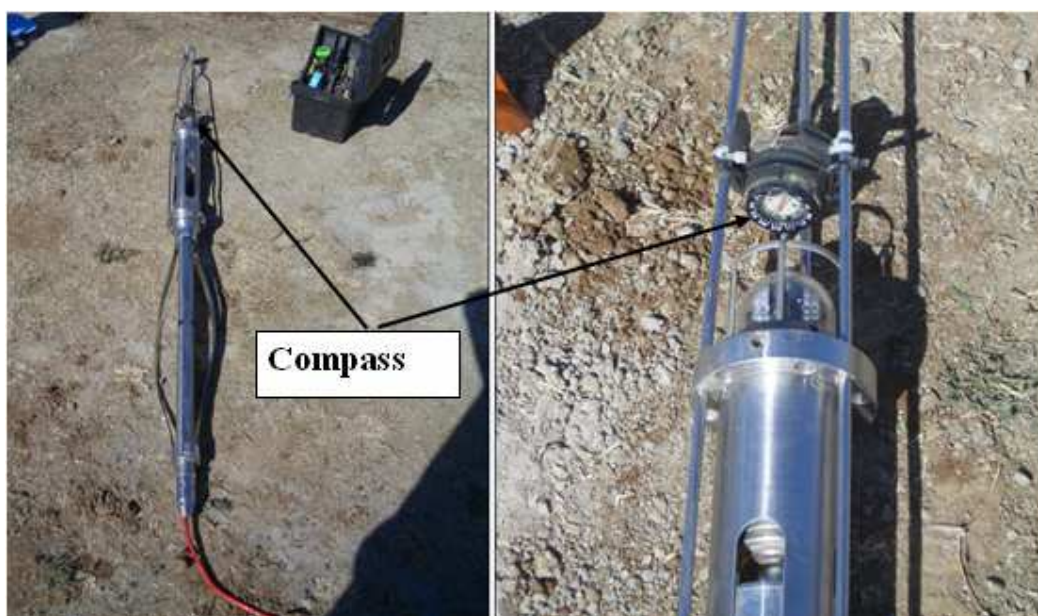


Figure 6-93: Video camera used to log the Campus Test Site boreholes. A compass was attached to the base of the televiewer to position the direction of the fracture apertures.

With the video camera, it was possible to locate the fracture position and apparent aperture of the fracture more precisely and easily. However, it was not possible to evaluate the connectivity and transmissivity of the fracture with the video camera. Figure 6-94 shows a video log of Borehole D3 with an apparent aperture of about 1 cm at a depth of 21.29 m from the collar height.



Figure 6-94: Video camera of Borehole D3 with accurate depth measurement and aperture of the fracture.

6.9.3.2 Apparent Aperture

The apparent aperture of the fracture was found to be extremely heterogeneous, changing with direction and distance in a small scale. As an example, Boreholes UO23, D3 and D2 are used to plot the apparent apertures of the fracture. The distribution of the boreholes is given in Figure 6-83. Boreholes D3 and D2 are less than 4 m away from UO23, and D2 and D2 are 2.5 m apart. Although they are closely spaced, the fracture aperture was found to vary considerably.

Figure 6-95 shows the apparent aperture in Borehole UO23, and can be seen that the fracture is locally dipping from south to north. The fracture runs across three cobbles and the maximum aperture has a thickness of 1.2 cm, facing N45°E.

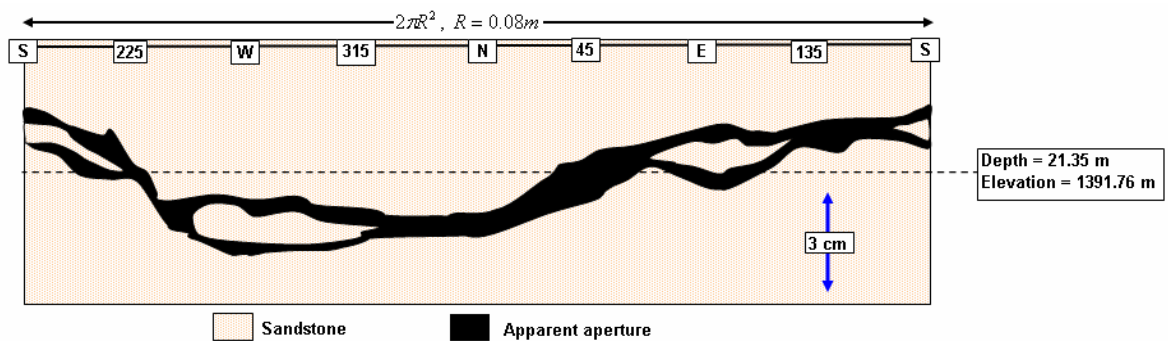


Figure 6-95: Apparent fracture aperture in Borehole UO23.

Figure 6-96 shows the apparent aperture in Borehole D2. The fracture is horizontal in this borehole and the maximum thickness is about 1.2 cm facing in the north and south directions. A zone of dense small-aperture fractures is common in most of the boreholes, indicated by green colour in the figure. The fracture zone of Borehole UO23 (Figure 6-95) was relatively compact and the dense small-aperture fracture zone was not observed.

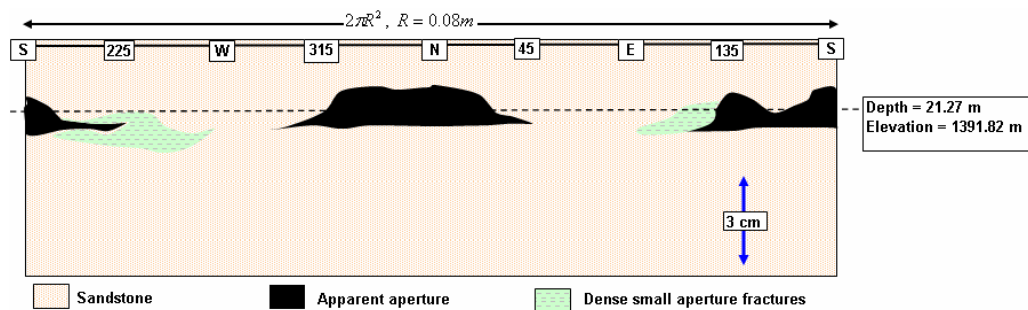


Figure 6-96: Apparent fracture aperture in Borehole D2.

Figure 6-97 shows the apparent aperture in Borehole D3 which is very different to the others. Two fracture holes were observed that are 25 cm apart. The upper fracture was smaller than the lower fracture, which has a maximum aperture of 1.5 cm facing to

N45°W. As confirmed by tracer test conducted in each fracture separately, both fractures are connected with the main horizontal fracture in the aquifer system. The Darcy velocities in the upper and lower fractures were estimated as 2.01 and 3.05 m/d. The dense small-aperture fracture zone is predominant in the upper fracture but less common in the lower fracture.

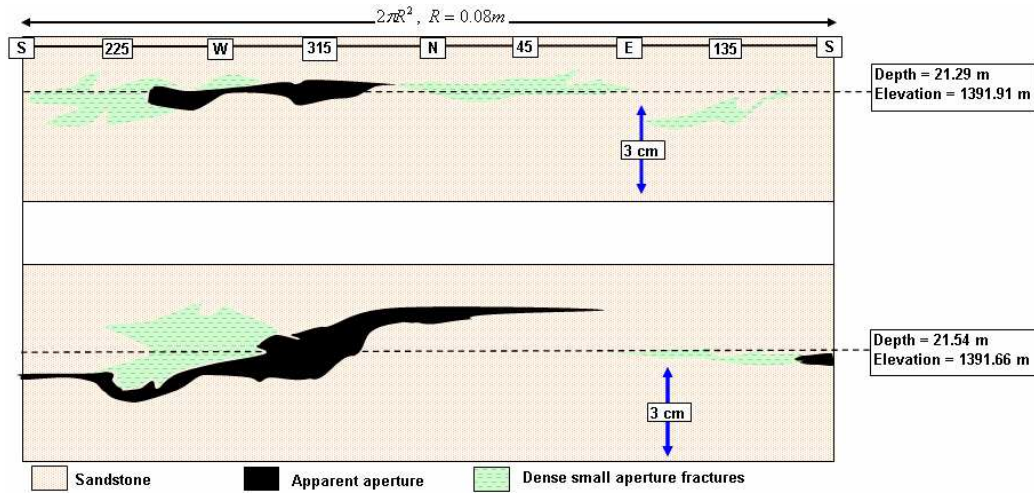


Figure 6-97: Apparent fracture aperture in Borehole D3.

6.9.4 Fracture Orientation (Dip, Strike and Depth)

6.9.4.1 Depth of the fracture

In addition to the pumping tests, borehole video camera, and geochemical loggings, various geophysical methods were applied to locate the positions of the fracture in different boreholes. Examples of geophysical (caliper, full wave sonic (FWS) and natural neutron (NN)) profiles of Borehole UO23 is provided in Figure 6-98. All the geophysical techniques show anomalies at depths of 21.2 and 26.1 m. The first anomaly is the horizontal fracture that this research is intending to characterise, while the second fracture is a subvertical fracture which is insignificant to the hydrogeology of the aquifer system. These anomalies were later confirmed by core holes DC1 and DC2 drilled 0.60 and 2.7 m away from UO23, respectively.

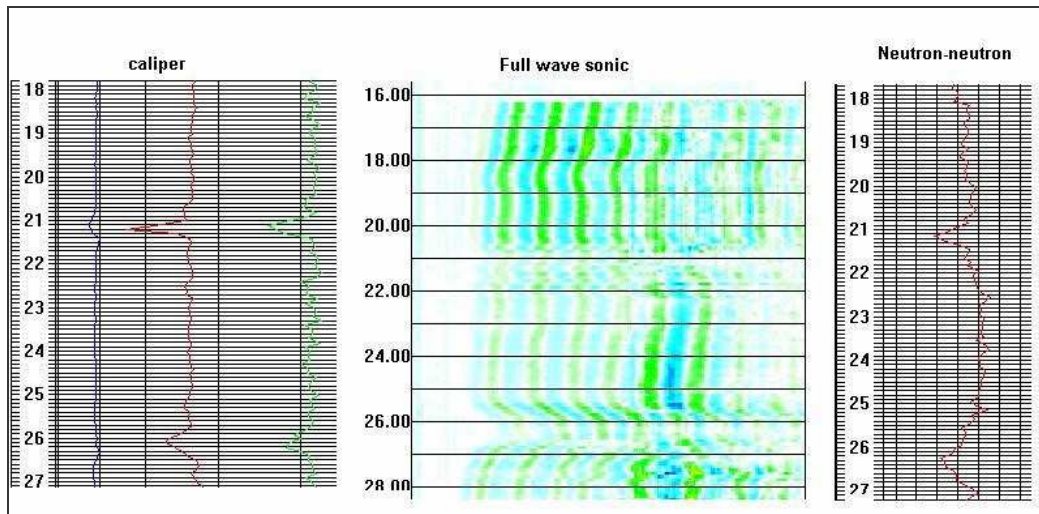


Figure 6-98: Caliper, FWS and NN logs of Borehole UO23.

Figure 6-99 shows the geologic and EC profile of UO23; where the fracture anomaly was peaked at a depth of 21.35 m. The red and blue lines in the figure are EC-profiles taken at different times.

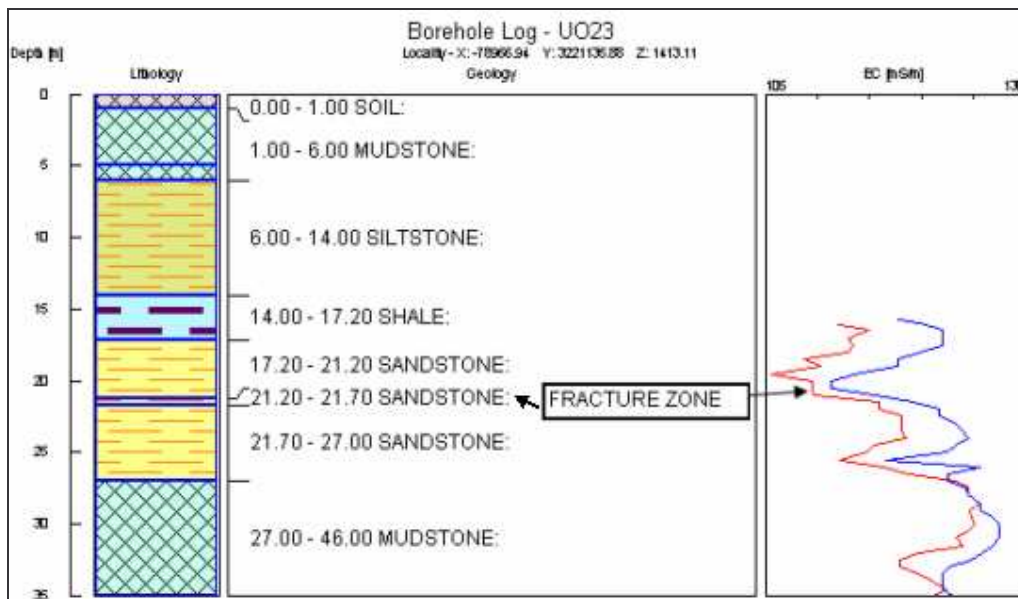


Figure 6-99: Geologic log and EC profile of Borehole UO23.

A pumping test was also conducted in the boreholes to locate the fracture. An example is given in Figure 6-100 where UO23 was pumped with a rate of 3.5 L/s, the drawdown increased suddenly after about two hours. This sudden increase happened at a depth of 21.74 m and is due to the dewatering of the fracture which is the main conduit of water in the aquifer.

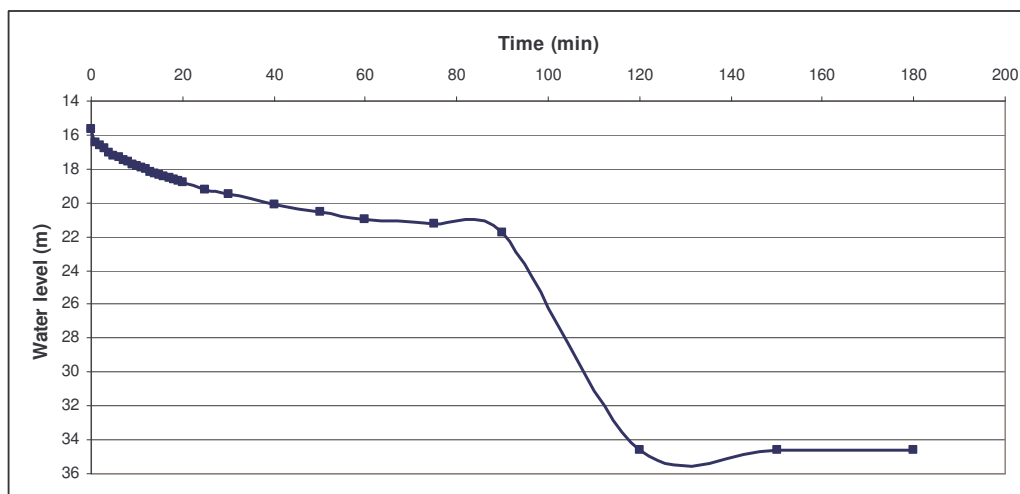


Figure 6-100: Drawdown versus time graph of UO23.

After evaluating the different techniques and correlating for a better location of the fracture, a summary of the fracture positions in all the boreholes that intersect it is given in Table 6-26.

Table 6-26: Borehole coordinates and fracture depth (from the collar height) and elevation (from mean annual sea level) at the Campus Test Site.

Borehole	fracture depth (m)	fracture elevation (m)		Borehole	fracture depth (m)	fracture elevation (m)
D2	21.27	1391.82		UO26	23.92	1387.74
D3	21.29	1391.91		UO27	20.91	1390.55
D3	21.54	1391.663		UO28	20.2	1391.56
D4	21.04	1391.99		UO29	21.17	1391.66
DC1	21.04	1391.91		UO4	22.95	1387.95
DC2	20.92	1391.98		UO5	23.03	1388.08
UO1	23.2	1387.88		UO6	22.62	1388.41
UO14	22.7	1388.72		UO7	22.8	1388.47
UO18	23.08	1387.61		UO9	22.66	1388.23
UO20	21.85	1389.44		UP15	20.96	1390.45
UO23	21.35	1391.76		UP16	20.75	1390.66
UO25	23.44	1387.68				

6.9.4.2 Dip and Strike of the Fracture

Although fractures are usually undulating, a rough estimate of the depth, dip and strike can be done by assuming as planar bodies. This estimate is helpful in characterising the migration pathways of DNAPLs. The estimation of dip and strike is not restricted to fractures only, but can be applied to water table gradient and other planar features such as dykes.

Using basic trigonometric relationships, if the elevation of a planar body is known at three points, the dip and strike of the plane joining the three points can be evaluated.

After identifying the highest and lowest points, a plane can be plotted as shown in Figure 6-101.

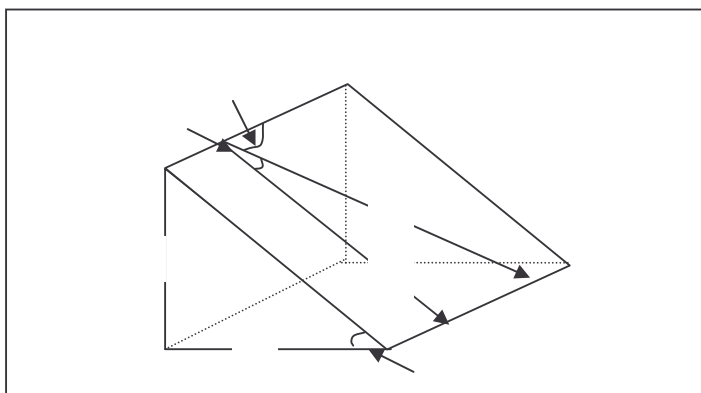


Figure 6-101: Relationship between true dip and apparent dip.

The angle of dip of the plane can then be evaluated as follows:

$$\sin \theta = \frac{\sin \varphi}{\sin \alpha}$$

Equation 6-7

where

θ = angle of dip

φ = apparent dip (any angle on the plane formed by the three points)

α = angle between the direction of apparent dip and direction of true dip

The tangent of the angle of dip gives the gradient of the plane. That is,

$$\text{gradient} = \tan \theta$$

Equation 6-8

Using Equation 6-7 and Equation 6-8, the dip and dip direction of the fracture in the DNAPL boreholes is calculated as listed in Table 6-27. Although the fracture is undulating locally, generally it is a horizontal fracture plane slightly dipping to the N15°W direction (Figure 6-102). However, this orientation is local, only in the DNAPL boreholes. If other combination of borehole points from the entire site are taken, a slightly different dip and dip direction is expected. It is worth noting that borehole logs show that the fracture in Borehole UO20 is abruptly higher than the surrounding boreholes by about 1 m (Table 6-26).

Table 6-27: Dip and dip direction of the fracture in the DNAPL Boreholes.

Borehole Points	Dip °	gradient	Dip direction °
D3,D4,UO23	3.67	0.064	N 21.24 W
D3,D2,UO23	2.65	0.046	N 11.13 W
D4,D2,UO23	3.62	0.063	N 38.66 W
D3,D4,D5	4.96	0.087	N 14.24 W
D3,D2,D5	4.38	0.077	N 14.24 W
D3,D4,UO30	4.97	0.087	N 18.81 W

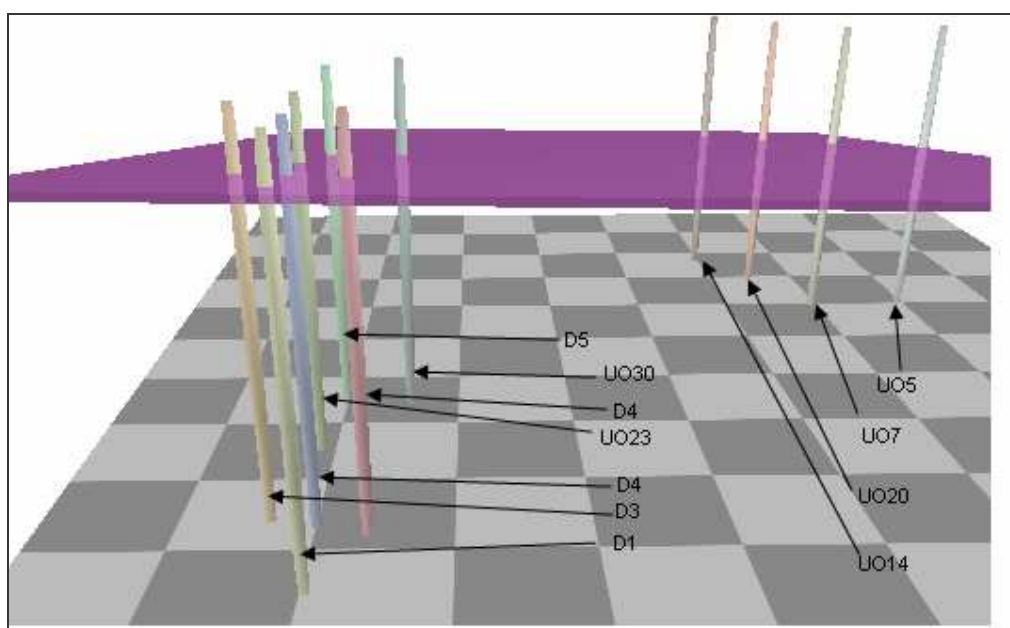


Figure 6-102: A simplified conceptual model of the fracture in the Campus Test Site.

7 Proposed Methodology for South African Conditions

In the previous chapters, the behaviour of DNAPLs and migration patterns in various geologic media were discussed. Research undertaken on site characterisation in two South African aquifers and the laboratory investigations were also addressed. It is evident from this research that detailed site characterisation extending beyond the usual inorganic contaminated site is essential in understanding DNAPL sites, and that where fractured aquifers are encountered, they must be well-defined to construct credible conceptual models of DNAPL contaminated sites. The aim of this chapter is to document the site characterisation methodologies that can be applied to South African DNAPL-contaminated sites more effectively. The approaches and technologies applied to DNAPL site characterisation in fractured aquifers will be evaluated, focusing on their advantages and disadvantages in South African cases. This way, innovative and cost-effective assessment methodologies will be identified.

It is the general experience that DNAPL presence is established on the basis of converging lines of evidence rather than direct visual observation. The tortuous and sparse nature of DNAPL migration through fractures and porous pathways, together with the fact that boreholes and other invasive procedures typically only physically access a minute fraction of the subsurface, result in a low probability of actually encountering DNAPL in South African aquifer investigations. During DNAPL characterisation, the overall extent of the source zone should therefore be delineated at a site, rather than the specific locations of individual DNAPL pools and zones of residual DNAPL within the overall source.

7.1 Non-invasive Characterisation Methodologies

DNAPL contamination spreading due to inefficient site characterisation techniques should be avoided at all times. Drilling on a DNAPL pool and improper borehole construction are some of the processes that could result in further DNAPL migration. Generally, site assessment should start from the non-invasive approach. After collecting the available and relevant data, a conceptual model should be developed of the site and invasive techniques should proceed for further improvement of the conceptual model. Under this section, the proposed non-invasive methodologies, as evaluated in Chapter 6, will be addressed. Some techniques, such as soil gas survey and enhanced visual analysis using UV and Sudan IV dye, can be applied in combination with the non-invasive as well as invasive techniques. In this chapter they will be treated with the non-invasive techniques.

7.1.1 General Site Assessment

A general assessment of the contaminated site should be made to determine the potential presence of a DNAPL in the groundwater zone depending on the historical use of the site. This should be done early in the investigation by using 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 DNAPLs to the surface.

7.1.1.1 Types of Chemicals

The first step in the general assessment of a potential DNAPL site is the consideration of the types of chemicals found or possibly present at the site. A wide variety of chemical products and wastes may comprise a DNAPL. For a potential DNAPL to be an actual DNAPL at a given site, the amount of chemical released to the subsurface will need to be in excess of the total amount that could have dissolved into the water and sorb to the soil materials in the source zone.

Whenever the past or present use of chemicals is considered, cognisance should be taken of the fact that many chemicals are known by a variety of chemical synonyms and product names. If there are no records or chemical inventories, then the principal use of organic chemicals may be used as a reference to determine the possible use at a site.

Furthermore, it is important that site assessors not only understand the type of chemicals used at a site, but also how these chemicals have been used or are currently used. It should be considered that some DNAPL releases could have occurred many years before and that the activities contributing to the releases have since ceased. In such cases, records of the chemicals used or disposed of may not exist. Knowledge of the type of business conducted on these sites and the nature of the wastes must be estimated. Thus, with an appreciation of the varied uses of DNAPL chemicals, a site assessor can identify the activities that could be associated with DNAPL use and disposal.

7.1.1.2 Site Operations

For a typical industrial site, a site assessor needs to determine the type of manufacturing operations and the types and quantities of chemicals that have been used at a site. Possible information sources include:

- Interviews with present or former employees;
- Records of chemical purchases, off-site waste disposal or waste received;

- Historical site engineering drawings; and
- Archival aerial photographs.

Records of DNAPL volumes produced, used or disposed of may not be available; however, estimates may be made from interviews with employees. A common cause of DNAPL contamination is releases of small amounts at off-loading areas, floor drains, sumps, catch basins, septic tanks, lines and sewers and storage tanks. Locations of any disposal facilities such as landfills or effluent dams need to be determined. At these facilities, DNAPLs have a greater potential for migration due to the larger volumes disposed. Examination of aerial photographs may be useful in determining the locations of such areas.

7.1.1.3 Assessment of Potential DNAPL Migration

An estimation of the potential depth of DNAPL penetration/migration through the vadose zone into the groundwater zone is an important component of site assessment (Pankow and Cherry, 1996). The depth of the penetration/migration will depend on:

- Properties of the DNAPL;
- Nature of the release;
- Properties and the geological structure within the vadose and groundwater zone.

Although it is not possible to precisely predict the extent or rate of DNAPL migration, it is important to recognise, in general terms, the factors that will influence the depth of DNAPL penetration in the subsurface. These factors are summarised in Table 7-1.

Table 7-1: Factors facilitating or inhibiting DNAPL penetration (adapted from Pankow and Cherry, 1996).

Factors facilitating DNAPL penetration	<i>Typical circumstances</i>
High DNAPL density	<i>Chlorinated solvents, PCB aroclors</i>
Low interfacial tension	<i>Surfactants or miscible co-solvents e.g. methanol, ketones, acetone in DNAPL</i> <i>Surfactants or co-solvents in aqueous wastes or groundwater</i> <i>Complex mixtures</i>
Low viscosity	<i>Chlorinated solvents</i>
Large DNAPL volume release	<i>Disposal in landfill or dams</i> <i>Catastrophic and/or ongoing spills</i>
Long duration DNAPL release	<i>Disposal in landfill or dams</i> <i>Catastrophic and/or ongoing spills</i>

Factors facilitating DNAPL penetration	Typical circumstances
High permeability	<i>Sand, gravel and fractured rock</i>
Vertical and sub-vertical geological structures	<i>Angled bedding planes</i> <i>Fractures and fissures in aquitards</i> <i>Fractured rocks</i>
Factors inhibiting DNAPL penetration	Typical circumstances
Low DNAPL density	<i>Coal tar/ creosote</i> <i>Chlorinated solvents at low concentrations in petroleum hydrocarbons</i>
High interfacial tension	<i>Relatively pure chemical products</i>
High viscosity	<i>Coal tar/ creosote</i> <i>PCB aroclors</i> <i>Mixtures with high concentrations, high molecular hydrocarbons</i>
Small DNAPL volume release	<i>Small spills and leaks</i>
Short duration DNAPL release	<i>Small once-off spills and leaks</i>
Low permeability	<i>Unfractured silt and clay aquitards</i> <i>Unfractured rock</i>
<i>Horizontal geological structures</i>	<i>Horizontal bedding in sandy aquifers, silt and clay aquitards</i> <i>Horizontal bedding plane partings in sedimentary rocks</i>

7.1.2 Aerial Photo and Map Interpretations

Aerial photos and maps should be evaluated during the initial phases of a site characterisation study to facilitate analysis of waste disposal practices and locations, drainage patterns, geologic conditions, signs of vegetative stress, and other factors relevant to contamination site assessment. Additionally, aerial photos and satellite images could be informative in fracture tracing at sites where bedrock contamination is a concern.

7.1.3 Surface and Airborne Geophysics

One of the aims of the research was to determine if specific geophysical methods could time-effectively and effortlessly delineate DNAPL plumes or layers within the subsurface. Refraction seismic is ruled out due to the cost involved in the operation. The time-domain and frequency-domain electromagnetic, magnetic, resistivity and airborne geophysical methods were applied for site characterisation and some positive

results could be inferred in delineating geological features. However, most DNAPL contamination sites are likely to be located in heavily constructed industrial sites in South Africa, and that the noise and available size for surveying would be insufficient for geophysical work in general.

Surface geophysics therefore seems to be effective only as a tool to map variations in geology such as dykes and faults as a reconnaissance exercise, if funding is available and cultural noise at a minimum. It can also be useful in detecting disturbed ground (such as old waste disposal pits) and buried objects (underground storage tanks, pipelines or electrical cables). These areas or objects may often be sources or conduits for subsurface contamination.

7.1.4 Initial Site Conceptual Model

As discussed in Section 5.2.3, the development and utilisation of conceptual models to explain geologic processes and environments have long been the province of geoscientists. Schuille (1988) and researchers at the Waterloo Centre for Groundwater Research (WCGR, 1991) have developed and refined general DNAPL conceptual models, which may be applied to South African aquifers. Recently the UK Environmental Agency (Kueper *et al.*, 2003) also published DNAPL conceptual models for UK-specific aquifer conditions. These DNAPL conceptual models are utilised to assess:

- Site characterisation priorities,
- The utility of alternative subsurface characterisation methods,
- Site data,
- The potential for separate phase DNAPL migration,
- The potential for vapour transport of DNAPL chemicals,
- The potential for dissolution of DNAPL chemicals and dissolved chemical transport,
- Chemical distributions associated with these transport mechanisms,
- Cross-contamination risks associated with characterisation and remedial activities, and
- The potential effectiveness of alternative remedial actions.

Table 7-2 lists a variety of contaminant characteristics that are useful in establishing a site conceptual model and in selecting a remediation strategy.

Table 7-2: Contaminant characteristics to establish during site investigations (Kueper *et. al.*, 2003)

Parameter	Example use of information
DNAPL density	<i>DNAPL mobility and pool height calculations</i>
DNAPL viscosity	<i>Determine if DNAPL could still be moving</i> <i>Design of NAPL recovery system</i>
DNAPL component composition	<i>Effective solubility calculations</i> <i>Predict future composition of plume</i>
DNAPL water interfacial tension	<i>Determine importance of capillary forces</i> <i>Pool height calculations</i>
Organic carbon partition coefficient	<i>Determine degree of aqueous phase sorption and rate of plume migration</i>
Contaminant half-life	<i>Determine degree of degradation and rate of plume migration</i>
DNAPL vapour pressure	<i>Determine if vapour migration is a potential issue;</i> <i>Estimate lifespan of DNAPL above water table</i>
Date and volume of DNAPL release	<i>Estimate of depth of DNAPL migration.</i> <i>Is DNAPL still moving?</i>
<i>Potential DNAPL release locations</i>	<i>Help guide monitoring well placement</i>

7.2 Invasive Methods

During the intrusive investigation, samples of soil, rock, groundwater and soil gas may be taken from pit excavations, auger holes or boreholes. These samples may either be analysed *in-situ* (soil gas), at the site (mobile GCMS or SiteLab) or preserved and shipped to an appropriate laboratory for chemical analysis. It is important to log all relevant information when carrying out an intrusive investigation. Such information consists of, at the minimum:

- Location of excavation
- Site number/identification
- Type of excavation
- Depth of excavation

- Date and time of excavation
- Field measurements (soil gas, pH, etc)
- Descriptions of soil/lithology with depth
- Backfilling/construction details
- Photographs

During excavation, cross-contamination of samples should be minimised by selecting appropriate investigation and sampling techniques, and the decontaminating of equipment between sample locations. Unnecessary invasive techniques should be avoided, as they could create DNAPL migration where conditions were initially stable (short circuiting). Invasive investigations should generally be started on the border of the site (in less contaminated areas) and proceed towards the source zone after the conceptual model is improved, as discussed in Section 5.2.3.3.

7.2.1 Visual and Visual-Enhanced Examination of Soil/Rock Samples

Evidence of the presence and distribution of DNAPLs may be obtained by careful observation and field testing during drilling or the collection of soil and rock samples. Significant cost savings are possible during site investigation if DNAPL presence can be determined directly by a visual 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. This is often true for coal tar or creosote when released in large quantities (Figure 6-25(B)). It is less common to visually identify DNAPLs such as chlorinated solvents, because of the nature of the liquid and its variability in source zones. The integrity of the sample (e.g. core samples from hollow-stem technique), will also influence the visual identification of possible DNAPL presence.

Visual identification of DNAPLs may be enhanced by using methods such as ultraviolet (UV) fluorescence and soil-water shake tests (with or without dye). The UV fluorescence method involves the examination of soil samples under a portable UV light. Many of the aromatic and polycyclic aromatic hydrocarbons (PAHs) and unsaturated aliphatic hydrocarbons (e.g. TCE and PCE) fluoresce (Pankow and Cherry, 1996). Examination by UV fluorescence may be accomplished in transparent plastic bags or bottles so that the samples can be manipulated without excessive loss of volatiles. Soil samples of uncontaminated soil should also be examined under UV light as controls, since some minerals could fluoresce. This method proved to be a cost-effective first-order screening of soil samples, and provides guidance for either

further detailed laboratory analyses of soil samples, or indicates where more detail assessment techniques should be focused on the site.

Soil-water shake tests involve the transfer of a soil sample to a clear, sealed container (tube) with an equal amount of water. The container is then shaken by hand and/or centrifuged and then inspected for DNAPL at the bottom of the container. The test may be enhanced by the addition of a hydrophobic dye such as Sudan IV. Sudan IV is a relatively inexpensive (100 g costs R180-00 from Aldrich Chemical Co.), reddish-brown powder that dyes organic fluids red upon contact, but is practically insoluble in water at ambient temperatures. This method may be used on site during drilling and sampling exercises. Cohen and Mercer (1992) recommend that dye shake tests be conducted in plastic containers (e.g., polypropylene tubes), because hydrophobic NAPLs generally wet plastic better than glass, thereby enhancing NAPL detection on the container wall. Visual and enhanced visual identification (especially UV fluorescence) may be recommended as first-order screening methods, but consideration has to be given to the limitations of the tests poor colour contrast.

7.2.2 Test Pits

Excavating test pits and/or trenches may be a very rapid and cost-effective means, as stated by Cohen and Mercer (1993) to:

- Characterise the nature and continuity of shallow overburden stratigraphy, including the macropore distribution;
- Identify, delineate, and characterise waste disposal and grossly contaminated areas;
- Help determine the horizontal and vertical extent of shallow contamination;
- Locate and examine buried structures, tanks, pipelines, containers (Figure 7-1), etc. and their bedding/backfill that may act as contaminant reservoirs or preferential pathways; and
- Acquire soil samples for chemical and physical analyses.



Figure 7-1: Example of excavated container with organic contaminants in a test pit at Test Site 1.

Limitations and/or disadvantages of excavation as a site characterisation tool include:

- The limited depth of exploration;
- The diminished view of excavation sidewalls with depth due to shadows, viewing angle and distance (binoculars may enhance sidewall viewing);
- Potential sidewall stability problems, of particular concern near structures, utilities, and roads;
- Potential airborne release of contaminated vapours and dust;
- Potential creation of a preferential pathway for contaminant transport along a trench;
- Potential increased waste handling requirement; and
- Potential subsidence problems after the excavation has been backfilled.

The main advantage of excavation for site characterisation is that it provides an opportunity to examine a large, continuous subsurface section. As a result, excavations may reveal conditions such as soil vapour plume, subtle or complex stratigraphic relations, soil fracture patterns, heterogeneous DNAPL distribution and irregular disposal areas that can be difficult to characterise by examining drill cuttings or samples. The potential risk of causing DNAPL migration is limited by the relatively shallow depth of excavation. Cross-contamination of samples may be avoided by taking large bucket scoops of soil with the excavator and then taking a sample from the centre of the bucket where the soil has no contact with the sides of the bucket.

7.2.3 Drilling

Boreholes are installed to evaluate subsurface stratigraphic, hydrogeologic and contaminant conditions. The selection of drilling locations, depths and methods must be based on available information regarding site conditions.

The number of boreholes available to a site assessor is often limited due to cost constraints by site owners. Drilling of boreholes is an iterative process, whereby more than one drilling event will be required to characterise a site. The knowledge gained through such successive drilling events is used to continually update the site conceptual model.

The potential for causing DNAPL migration by drilling through a barrier layer should be considered before and during drilling, so that the danger can be minimised. Conventional drilling methods have a high potential of promoting downward DNAPL migration. The type of drilling used must cause as little disturbance to the aquifer as possible, producing minimal modification to the qualitative characteristics of the subsurface water. Depending on the lithological characteristics of the subsurface and the depth to reach, the commonly used methods (Rosti *et al.*, 2000) are rotary or roto-percussion drilling, with compressed air with water or mud, percussion drilling and auger drilling (or temper screw), with hallow or full shafts.

Several guidelines for drilling at DNAPL sites are available (e.g. Pankow and Cherry, 1996; Aller *et al.*, 1989; Millison *et al.*, 1989; and Cohen and Mercer, 1993. The following is a summary from these references:

- Avoid unnecessary drilling within the DNAPL zone. The first boreholes are installed on the perimeter of the site (in less contaminated or uncontaminated areas). The initial boreholes may be drilled up-gradient of the DNAPL source (and/or dissolved-phase plume) and through any possible confining layer to characterise the geology of the site. The appropriateness of this approach must be evaluated on a site-specific basis.
- Utilise knowledge of site stratigraphy and chemical distribution and carefully examine subsurface materials brought to the surface as drilling proceeds to avoid drilling through a confining layer beneath DNAPL. In some situations, it may be necessary to drill through actual or possible confining layers at a site. Special precautions should be taken when investigators believe that they may encounter a confining layer during drilling. Moreover, if field personnel suspect a possible confining layer while drilling a borehole, and an approved plan for drilling through confining layers does not exist, drilling should be stopped immediately and the borehole decommissioned.

- Minimise the time and the length of hole that is open at any time. Any borehole that is not completed as a monitoring borehole should be properly decommissioned.
- A “telescoped casing drilling technique” is advised to isolate shallow contaminated zones from deeper zones. Such techniques typically involve drilling an initial borehole partially into the possible confining layer, installing (grouting in) an exterior casing, placing grout in the cased portion of the borehole and after flushing the interior of the casing, drilling a smaller diameter hole through the cased-off/grouted portion of the borehole (i.e., telescoping casing) through the confining layer. The appropriateness and actual design of telescoping borings and casings should be determined on a site-specific basis. Telescoping boreholes may be completed as boreholes or piezometers.
- Select optimum construction materials and grouting methods based on a consideration of site-specific chemical compatibility .
- The drilling method should allow for the collection of representative samples of rock, unconsolidated materials and soil. Temporary casings may be used to isolate different soil layers for sampling during drilling.
- The drilling and sampling method should allow the geologist to determine where an appropriate location for the screened interval exists.
- If a drilling site is a suspected DNAPL ‘pool’, consider the use of dense drilling mud to prevent DNAPL from sinking down the borehole during drilling.
- Drilling fluids (including air) should be used only when minimal impact to the surrounding formation and groundwater can be ensured.
- Drilling techniques using the auger bit entail fewer risks of cross-contamination between the various levels of the aquifer and do not require the introduction of drilling fluids. However, it is not able to drill through very durable, loose rock formations with large fragments, and could influence the local permeability; thus significantly reducing the efficacy of the operation.
- To prevent surface contamination, sheeting may be placed on the surface to collect any contaminated sludge at the top of the borehole. After drilling is complete, the sheeting, together with the contaminated sludge, should be properly disposed of.

7.2.3.1 Drilling Techniques

From the available drilling techniques, the following was selected and recommended as suitable techniques for the installation of boreholes on DNAPL-contaminated sites in South Africa. The utilisation of different drilling techniques (auger, core and air

percussion), provide the site assessor with valuable information regarding the subsurface. However, due to the high costs and limited availability of specialised (e.g. diamond core and direct push auger) drilling rigs, these techniques are often neglected in South African site assessments.

7.2.3.1.1 Air Percussion drilling

Percussion drilling methods operate by pulverising material at the bottom of a hole by dropping or pounding a bit. This type of drilling involves crushing by the impact of the drill bit teeth. Most percussion drills are actuated by compressed air (pneumatic percussion). Percussion drills are best suited for drilling brittle, moderately soft to hard rock. In hard rock, percussion drills work faster and more economically than other drilling methods. The air blows the cuttings from under the bit and up the annulus to the surface. The ability of the air to carry the rock chips depends primarily on high air velocity. An up-hole velocity of about 1,200 m/min is required to remove cuttings.

The advantages of air percussion drilling include the speed of drilling through most semi- to well-consolidated formations, and no water is required. The use of drilling fluids may be minimised when required. The technique is relatively inexpensive, but the equipment is expensive and has a high maintenance cost. It is also the most widely used drilling technique for groundwater investigations in South Africa.

The disadvantages of air percussion drilling include the difficulty in defining precisely the boundaries between geologic layers. Due to the high air pressure applied during drilling, loss of VOCs by volatilisation can occur.

7.2.3.1.2 Auger drilling

Auger drilling is widely used not only for drilling but also for sampling at contaminated sites. In this research, the hollow-stem, direct push, and solid-stem auger drillings were attempted. Hollow- and solid-stem augers operate by rotating into the ground, using a rotary drive head on the drill rig. Sampling may be achieved at any depth if a pilot bit is used inside the hollow stem. As the name implies, direct push drilling is achieved by pushing the rig using high pressure without the rotation of the stem.



Figure 7-2: Caking of sand and clay slurry during auger drilling.

The advantages of auger drilling include: minimal damage to aquifer, no drilling fluids are required; auger flight acts as temporary casing, stabilising hole for well construction; good technique for unconsolidated deposits; collection of relative undisturbed *in-situ* soil samples at greater depth than is possible with test pits; and a continuous core can be collected from the hollow-stem method.

The disadvantages of auger drilling include: sand and clay may form a slurry that can cake the outside of the formation, as shown in Figure 7-2 (this can be difficult to remove later and may prevent contamination from being detected in lower hydraulic conductivity layers); contaminants may be smeared down the formation, which leads to bias and inaccuracy in later sampling; it cannot be used in consolidated deposits; sampling of running sands (or heaving sands) is very complicated; it is limited to boreholes less than approximately 50 m in depth; and holes may need to be abandoned if boulders are encountered.

As observed in some South African aquifers, the hollow-stem is not effective in clay layers. The clay layer expands when moistened and becomes impermeable. The direct push was ineffective in calcrete layers because of the soil hardness. Due to the high friction between the auger stem and soil material during drilling, the temperature of the soil samples could be so high that VOCs could be lost due to volatilisation.

7.2.3.2 Core Drilling

Diamond core drilling is the most versatile of all the methods, and is designed specifically for the resource exploration industry. In diamond drilling, the sample is

cut by a diamond-armoured drill bit, and stored in the inner barrel of a drill pipe. Then the pipe is brought to the surface and the core removed.

The advantages of this technique include: its versatility allows it to be used at most surface and underground locations; it is the only method available that provides a core, a complete record of geological structure and rock texture; and it is the only commonly used method that provides reliable samples for accurate geochemical testing. It is recommended that DNAPL site assessments require the drilling of at least one core borehole during investigations.

During bedrock drilling and coring, DNAPL will usually be forced out of fractures during core recovery; however, more viscous DNAPLs may be recovered. During visual inspection of cores, DNAPL staining at fracture surfaces may be observed, but staining is not conclusive evidence of DNAPLs. The physical properties of the core (porosity, diffusion, carbon on fracture surfaces, etc.) may be determined.

The extraction of pore fluid from the sections of a core results in significantly higher concentrations than measured *in-situ* in the borehole. Sections of the core (preferably adjacent to fractures), are crushed and methanol added in a container and stored for several months before analysis. The samples should be collected and isolated from the atmosphere in less than 5 minutes after exposure at land surface (Shapiro, 2006). The measured contaminant concentrations in samples are often several orders higher than the contaminant levels measured in the borehole.

Disadvantages are however that the technique is the most expensive of all the drilling techniques, and that the drill rigs are often not available for contamination investigations. Some types of broken and abrasive rock are nearly impossible to core at a reasonable cost (these lithologies literally fall apart during transport up the drill string). While special methods of recovery for these soft lithologies have been designed using tubes and protective sheaths, the recovery is still generally poor.

Some fractures may be the result of mechanical breaks from the coring, and the log should therefore be correlated with borehole wall imaging (afterwards) and other down-the-hole geophysics. It is not possible to restrict the use of drill fluids during core drilling. Many of the fluids used are organic based surfactants. It is advisable that the type and quantity of fluid used during the drill process be recorded and that a temporary sump be used for drill fluid circulation on surface.

7.2.3.3 Borehole Construction

Monitoring boreholes are necessary to characterise flow directions and rates, groundwater quality, DNAPL fluid distributions and media hydraulic properties. Constructing monitoring boreholes on a multi-level and use of packers in fractured media helps not only to collect discrete data, but also understand the hydraulic

parameters of the aquifer. Pertinent data are acquired by conducting fluid thickness and elevation surveys, fluid sampling surveys, hydraulic tests and down-the-hole surveys. The locations and design of the boreholes are selected based on consideration of the site conceptual model and specific data collection objectives (Cohen and Mercer, 1993).

The design and construction of boreholes at DNAPL sites require special consideration to:

- The effect of borehole design and location on DNAPL movement and distribution within the borehole and the surrounding environment;
- The compatibility of construction materials with DNAPLs and dissolved chemicals; and
- Borehole development options.

Table 7-3 lists the relationship between borehole construction with the mobile DNAPL phase and capillary barriers. From this, it is clear that the construction may influence direct measurements of DNAPL in boreholes and cause potential vertical DNAPL migration in the borehole environment. A borehole completed to the top of a capillary barrier and screened from the capillary barrier surface to above the DNAPL water interface, is most likely to provide DNAPL thickness and elevation data representative of formation conditions

7.2.3.4 Compatibility of Construction Materials

The compatibility of borehole construction materials with DNAPL contamination should also be evaluated during borehole design. Borehole construction materials (e.g. screens, casings, sealants) are subject to degradation or corrosion in the natural environment. Materials exposed to DNAPLs 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. Detailed discussion on the construction materials is provided by Pretorius (2007).

Table 7-3: Well (borehole) construction design and the effect it has on DNAPL thickness in borehole (adapted from Cohen and Mercer, 1993).

Well construction	Measurement/observation of DNAPL in well
If the well screen or casing extends below the top of a DNAPL barrier layer	<i>DNAPL thickness > pool thickness</i> <i>Exceed by the length of the well below the barrier layer surface</i>
If the well bottom is set above the top of a DNAPL barrier layer	<i>Measured DNAPL thickness < pool thickness</i> <i>By the distance separating the well bottom from the capillary barrier layer upon which DNAPL pools</i>
If the well connects a DNAPL pool above a barrier layer to a deeper permeable formation and the well will cause DNAPL to short-circuit the barrier layer and contaminate the lower permeable formation	<i>DNAPL elevation and thickness in the well are likely to be erroneous.</i> <i>The height of the DNAPL column at the well bottom will tend to equal or be less than the critical DNAPL height required to overcome the capillary resistance offered by the sandpack and/or of the less permeable formation</i>
NAPL that enters a coarse sandpack may sink to the bottom of the sandpack rather than flow through the well screen	<i>Small quantities of DNAPL may elude detection by sinking down the sandpack and accumulating below the base of the well screen</i>
The bottom of the well screen is set above the bottom of the sand pack and there is no casing beneath the screen	<i>Small quantities of DNAPL may elude detection by sinking out the base of the screen and into the underlying sandpack</i>
Sand packs generally should be coarser than the surrounding media	<i>Screen or sandpack openings that are too small may act as a capillary barrier to DNAPL flow and DNAPL will not be able to enter the well</i>
If the well screen is located entirely within a DNAPL pool and water is pumped from the well	<i>DNAPL will upcone in the well to maintain hydrostatic equilibrium, causing the DNAPL thickness in the well to exceed that in the formation</i>
<i>If the top of the DNAPL pool is under drainage conditions</i>	<i>The elevation of DNAPL in a well may exceed that in the adjacent formation by a length equivalent to the DNAPL-water capillary fringe height</i>

7.2.4 Soil Gas Surveys

Although soil gas surveys are not applicable to the saturated zone, it is a popular screening tool for detecting volatile organic chemicals in the vadose zone at contamination sites (Cohen and Mercer, 1993). Soil gas surveys generate extensive chemical distribution data quickly at a fraction of the cost of conventional invasive methods and offer the benefits of real-time field data. Consideration should be given to its use during the early phases of site investigation to assist delineation of DNAPL

in the vadose zone, contaminant source areas, contaminated shallow groundwater and contaminated soil gas, and thereby guide subsequent invasive field work. The multiplicity of sources and sparsity of groundwater data at sites may make the understanding of processes and discernment of soil gas origins difficult.

Many DNAPLs, including most chlorinated solvents, have high vapour pressures and will volatilise in the vadose zone to form a vapour plume around a DNAPL source. Volatile organic compounds (VOCs) dissolved in groundwater may also volatilise at the capillary fringe into soil gas. However, it is important to discern the origins of VOCs in soil gas when using surveys to interpret the nature and extent of subsurface contamination.

It is reasonable to interpret from soil gas plumes that up-gradient maxima are indicative of source locations and that the soil gas plume may approximately define the extent of the very shallow, interface zone groundwater contamination. A discrepancy in plume widths may cause a further problem in delineating groundwater contamination at depth from soil gas plume data. Soil gas and interface zone plumes will be tens of metres wider than the source zone due to vapour transport lateral to the groundwater flow direction; whereas deeper groundwater plumes will not be much wider than the DNAPL source zone, due to the weakness of transverse horizontal dispersion (Anderson *et al.*, 1992).

Soil gas data should therefore be used with caution and their limitations recognised. In spite of their limitations, soil gas surveys may still be a valuable reconnaissance tool to delineate subsurface VOC contamination and facilitate the location of monitoring boreholes and soil samples.

7.2.4.1 Vapour analyses of soil samples

By performing vapour ‘head space’ tests on soil samples as they are collected during the drilling, a further distribution of soil vapours in the subsurface may be obtained and the testing used as a field screening test to assist in deciding which samples should be submitted to the laboratory for chemical analysis.

During drilling, samples of soil and rock (*of a fixed volume*) may be collected in sealable plastics bags. After a few minutes, a PID (‘sniffer’) is inserted into the head space of the bag to measure the concentrations of VOCs (Volatile Organic Compounds) over a 1 minute logging period. It is recommended that the average and peak PID levels be recorded on the soil sampling field sheet.

However, from the field experience during this research, it was found that the results from the headspace tests often did not correlate with the chemical analyses of the soil samples. This may be attributed to loss of VOCs during the sample collection or incorrect calibration standards for the particular on-site contaminants. The

concentration measured is also dependent on the sample size, i.e., the bigger the soil sample in the plastic container, the higher is the reading. If samples are exposed to high temperatures, sorbed DNAPLs will escape from the matrix and higher readings will be obtained than in cold temperatures.

More sophisticated soil gas samples are commercially available, which will yield more accurate results. However, these are often expensive, and soil gas measurements should rather be used as a screening method for possible source zones and not as a quantitative measurement at DNAPL sites. Soil gas surveys should also be associated with test pits and borehole drilling.

7.2.5 Soil samples

Chemical analyses of soil samples may be useful in determining the presence and distribution of DNAPLs in the porous and fractured media. However, such analyses may be ineffective if the soil sampling and analysis methods are not suitable for the purpose of investigation. The following sections provide guidance on sample collection, analysis and indirect calculations to determine DNAPL presence.

7.2.5.1 Sample collection

Soil samples may be collected during the site investigation from above or below the water table. For shallow soil profiling, samples are often taken from test pits (Section 7.2.2). For deeper profiling, samples may be taken during auger, air percussion or core drilling (Section 7.2.3).

During drilling operations, soil samples may be taken and subjected to visual examination in order to determine the presence of DNAPLs. If DNAPL is present at high saturations it will probably be readily noticeable. If DNAPLs are present at low saturations, enhanced techniques such as UV and dye testing may be used (Section 7.2.1). Soil samples are however not only used to determine DNAPL presence, but should be submitted for chemical analysis to determine the presence of contaminants in the sorbed, aqueous and vapour phases. Pankow and Cherry (1996) list the critical issues to be considered related to any soil sampling as:

1. The lateral and vertical spacing of the samples,
2. Cross-contamination during sample collection,
3. The selection of sub-sample portions for analysis, and
4. Loss of volatiles during sample collection, handling and storage.

Since the migration pathways of DNAPLs are strongly influenced by heterogeneities in the media, both on small and larger scales, the spatial distribution of DNAPL in the subsurface will be highly variable. It is recommended where possible, that vertically continuous samples (e.g. with hollow-stem auger) be collected in order to reliably

identify the variability throughout the soil profile. If this method is not possible at a site, either collecting samples through test pit or normal auger drilling may provide similar results, if the spatial distribution of the sample points is carefully selected. Cross-contamination during sampling may be prevented by using dedicated sampling tubes (hollow-stem auger) or by decontaminating sampling equipment (e.g. spoons, shovels, drill bits) in-between sampling points. Some cross-contamination between layers of variable permeability may also take place within the tubing of the continuous samples. The NAPL may find a pathway along the tube wall and collect at a different layer than originally found in the soil profile.

Soil gas measurements (Section 7.2.4) offer an economic and rapid screening method at some sites, but soil gas concentrations cannot be used to predict the total concentration of soil VOCs (vapour, sorbed, dissolved and NAPLs). In contrast, soil samples, if properly sealed and preserved, may be used to measure VOCs in all phases. However, unquantifiable VOC losses may occur during sampling and during sample transfer prior to analysis (Siegrist and Jenssen, 1990).

The preservation of soil samples with methanol (1:1 ratio soil to extraction solvent) is recommended by the US EPA for VOC sampling. Several references regarding the method and precautions are available on their website <http://www.epa.gov>. This method was tested during this research. However, no conclusions could be drawn. The analytical results from the methanol preserved samples were similar to those of the non-preserved samples taken.

Once samples are collected and sealed in suitable containers, they should be labelled, logged and handled correctly, with the appropriate chain-of-custody documentation included. Samples should be kept in temperatures of no more than 4°C. Transport of samples to the designated analytical laboratory should be completed well before the holding times expire. It is preferable that samples be shipped or delivered daily to the analytical laboratory, in order to maximise the time available for the laboratory to perform the analysis.

7.2.6 Borehole logging

7.2.6.1 Geophysical Borehole Logging

The physical properties of fractured rock aquifers are well understood in principle. If the geometry and hydraulic properties of the fracture network are specified, the flow and dispersion of DNAPLs in such aquifers may be predicted. Of course, these properties are not known in detail for most fractured rock aquifers. The obvious recourse is to sample subsurface conditions by means of boreholes.

Borehole geophysical surveys involve lowering a logging tool, also known as a sonde, down a borehole to make physical measurements as a function of depth (an example

is shown in Figure 7-3). A sensing element within the sonde measures the property of interest and converts it into electrical signals. These signals are transmitted to the surface through a cable, and recorded digitally or by using an analog strip chart. Several types of geophysical logs may be made, sometimes simultaneously, in the same borehole.



Figure 7-3: Geophysical logging of boreholes at research site - Test Site 1.

Borehole geophysical surveys are conducted to:

- characterise lithologies,
- correlate stratigraphy between boreholes,
- identify fracture zones, estimate formation properties (e.g. porosity and density),
- identify hydraulically active fractures,
- identify fractures that do not intersect the hole,
- determine ambient flow in the borehole,
- design well completion methods, and
- identify intervals containing conductive dissolved contaminants.

A wide variety of geophysical borehole logging techniques is available to the practicing geohydrologist, as well as to researchers. Most techniques have been developed for the oil exploration industry and adapted for geohydrological applications. The most common techniques applied in the groundwater industry, with their field application, are listed in Table 7-4. These methods provide continuous high resolution measurements of subsurface conditions. As such, they can be used to distinguish thin layers and subtle stratigraphic features that may influence contaminant movement.

Although frequently used, geophysical borehole logging techniques have had limited application in Karoo environments. Resistivity logs (normal) have been used with good results in assisting with the calibration of sounding curves, whereas natural gamma logs were used in the case of surveys at Beaufort West and are invaluable in the construction of complex geohydrological models (Vandoolaeghe, 1978).

Fractures identified in boreholes have often been mechanically enlarged by drilling and flow conducting passages embedded in the fracture face represent only a small proportion of the fracture zone volume as imaged by geophysical methods. Lateral continuity of individual fractures may be verified by ground penetrating radar (GPR) imaging from the surface and cross-hole hydraulic testing (Romanowicz *et al.*, 2004). Identifying the fracture locations with the caliper probe is an important first step in modelling the transmissive response of boreholes, but the presence of fractures and their size at the wall of the borehole are not indicative of the magnitude of the transmissivity of the fracture (Rickert *et al.*, 2004).

From the field data collected during this research, down-the-hole geophysics proved to be of limited use for DNAPL site assessment. Geological features such as more permeable zones or fracture zones may be delineated with some of the probes. However, finer detail such as fracture aperture and orientation (important for determination of exact flow paths), could not in general be determined. A cost-benefit analysis should be used to determine whether it is worthwhile to perform down-the-hole geophysics for its applicability at a DNAPL site assessment.

Table 7-4: Geophysical borehole logging tools and their fields of application (adapted from Woodford and Chevalier, 2000)

Technique	Types of Log	Field of Application
Radioactivity	Natural gamma	Clay content; rock structure and lithology
	Gamma-gamma	Rock density; porosity; fracturing
	Neutron	Porosity
Resistivity	Normal (multiple arrays). Focused Induction	Rock or formation resistivity; lithology; detection of thin (clay) layers
Caliper	Caliper log	Borehole or casing diameter
Temperature (water)	Temperature	Groundwater temperature; fracture location; geothermal gradient
Conductivity (water)	Conductivity	Groundwater conductivity; water quality stratification (pollution investigations)
Sonic	Acoustic Televiwer (ATV)	Fracture and structural orientations
		Borehole deviation
		Only in water-filled holes
Optical	Borehole-Wall Imaging Optical Televiwer (OTV)	Oriented digital video image Conventional fisheye Air- and water-filled holes (clear) Virtual core image Fracture and structural orientations Borehole deviation
	Borehole or TV camera	Casing attributes (damage, clogging); fracture position; visual inspection of borehole sides
Borehole orientation	Dipmeter deviation	Dip and strike of penetrated layers, fractures and fissures. Spatial course of borehole

7.2.6.2 Flow logging

Without understanding the flow regime within open bedrock boreholes, sampling programmes may not adequately characterise the distribution of DNAPL contamination in an aquifer. Vertical flow within open boreholes in fractured bedrock aquifers may cause cross-contamination, mixing, or dilution of water samples. By understanding the flow patterns within the borehole, a sampling strategy may be designed to obtain more meaningful data.

Several new high-resolution flow logging techniques such as heat-pulse (Hess, 1986) and electromagnetic (Molz *et al*, 1994) flowmeter logging and borehole dilution

methods (Tsang *et al.*, 1990), provide more cost-effective and flexible methods for addressing hydrology in the geophysical investigation. One of the most important attributes of high-resolution borehole flow logging is that all logs may be run as part of the same operation. Geophysical measurements in boreholes may characterise fractures in detail, but only adjacent to individual boreholes, while hydraulic measurements in boreholes may be used to generate direct relationships between geophysical and hydraulic properties (Paillet, 2001).

Flowmeter logs collected under ambient and stressed conditions along with fluid and televiwer logs are valuable for identifying ambient vertical flow and the most transmissive fractures that intersect the borehole. Under steady state conditions, flowmeter logs are used to identify the direction and magnitude of vertical flow within boreholes. Under stressed (pumping) conditions, flowmeter logs are used to identify the transmissive fractures within the borehole by measuring the rate of water entering the borehole at each fracture, while simultaneously pumping from or injecting into the top of the borehole at a low rate.

7.2.6.3 Video logging

Down-the-hole video logging should be utilised during a DNAPL site investigation, together with the pumping test and other down-the-hole techniques with the purpose of enhancing these methods for the identification of fracture flow paths *in-situ*. The method typically involves lowering the borehole camera down the borehole, similar to the other geophysical probes described above. The advantages of the method include:

- Determination or confirmation of well construction (depth, casing type, etc)
- Inspection of casing attributes (e.g. damage, clogging)
- Determination of fracture positions and orientation
- Geological profiling
- Inspection of any visible DNAPL residual or flow through fracture openings

Orientation may be determined with a compass attached to the camera. Borehole videos can confirm the presence of vertical fractures in boreholes, which cannot be detected by other geophysical methods (except the optic televiwer). 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 concentrations found at great depths in the aquifer system.

7.2.6.4 Geochemical logging

Geochemical profiling is an inexpensive, yet effective tool for site assessment at DNAPL-contaminated sites. The advantages of this type of profiling include the

determination of hydraulic variation within the vertical profile of the subsurface and the identification of important features in the system. By using this, features such as fractures or layers, which transport different salinity groundwater, may be identified. As stand-alone measurements, these observations have limited value; however, when viewed in conjunction with the geological logs or other down-the-hole measurements, a far more detailed conceptual understanding of the most important geohydrological features may be obtained. These features are important for the dissolved phase plumes from NAPLs and also for the NAPL transport itself, since they identify the stratigraphic horizons along which these are most likely to be transported.

When considering the degradation of organic contaminants, chemical parameters such as redox potential and dissolved oxygen may provide information on the indication of aerobic or anaerobic conditions in the subsurface. The main parameters considered of importance at DNAPL sites are conductivity (EC), pH, temperature, chloride, redox potential and dissolved oxygen (DO). Several multi-parameter probes are available for this purpose. Another down-the-hole probe that is inexpensive and easy to use, is the Solinst TLC Meter, which measures EC and temperature.

7.2.6.5 Interface meter

Under ideal conditions, a DNAPL thickness of about 2 mm or greater can be detected. However, a DNAPL is difficult to detect by these means when mixed with fine sediment at the bottom of the well, when it is conductivity, or when it preferentially wets the probe materials (Pankow and Cherry, 1996). The presence or absence of DNAPL is determined by lowering the probe to the bottom of a borehole. If a steady tone and light is activated, it indicates a non-conductive liquid. Then the probe is lowered until it touches the bottom of the borehole and the tape becomes slack. The thickness of the DNAPL layer is determined by subtracting the first reading from the second.

At some sites, DNAPL will be observed in the observation boreholes. Although this will confirm the presence of DNAPL at a site, the thickness in the borehole cannot be related to the thickness of DNAPL in the subsurface, as discussed in Section 3.3.6. The presence of DNAPL in the boreholes cannot be related to the vertical distribution of DNAPL in the subsurface. The only circumstances under which the thickness may be related to the subsurface, is in the case of large discrete pools in granular media (Pankow and Cherry, 1996).

The reason for this discrepancy is often that it is very difficult to know where the borehole is installed within the pool. The only time the thickness may be determined from the borehole, is when the capillary properties of the formation, the borehole construction material, together with the properties of the DNAPL, are known.

7.2.7 Pumping Tests

The principle of a pumping test is that, if water is pumped from a borehole and the discharge and the drawdown of the borehole 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 be used to calculate the hydraulic characteristics of the aquifer (Kruseman and De Ridder, 1994).

Pumping tests are important tools that provide information on the hydraulic behaviour of a borehole, the reservoir and the reservoir boundaries. All this information is essential for efficient aquifer and borehole field management. In general, the objectives of a pumping test are (Van Tonder *et al.*, 2001):

- to obtain an understanding of the aquifer;
- to quantify the aquifer's hydraulic and physical properties; and
- to determine the sustainable yield and efficiency of a borehole.

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 pumping tests conducted in fractured rock systems should be used when considering the estimation of hydraulic parameters in these fractured systems.

An 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 above-mentioned points, it is clear that the principles for conducting and analysing pumping tests depend on the objectives of the investigation. During DNAPL investigations, pumping tests are used to estimate the hydraulic parameters and for finding the principal hydraulic features of the system (Cohen and Mercer, 1993; Pankow and Cherry, 1996; Sara, 2003).

However, when pumping tests are used at a suspected DNAPL site, pumping boreholes and pump rates should be carefully selected in order to prevent DNAPL pool mobilisation as discussed in Section 3.3.3.

7.2.8 Tracer Tests

Understanding the processes controlling subsurface transport is a key element in the understanding of the dissolved DNAPL movement. 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 tracer tests. Conventional field methods such as pumping tests are adequate for most water supply investigations, but do not yield sufficient information for modelling aqueous mass transport.

Field-scale tracer testing is a highly effective technology for determining controlling transport processes, as well as important transport parameter values used in risk assessment and remediation design. A detailed discussion on the type of tracers and tracer test experiments can be found in Riemann (2002).

The single-well tests, mainly the point-dilution and injection-withdrawal, may be easily performed to evaluate the Darcy and natural-flow velocities, respectively. Since they are done under natural groundwater flow, they do not require specific and expensive equipment that is difficult to handle. To save time and costs, both tests may be done in one experiment, but in different steps. The injection part of the injection-withdrawal test may be used as a point-dilution test. Data are then analysed independently for each test.

Radial-convergent tests are recommended to provide reliable results of dispersivity, kinematic porosity and groundwater velocity. Only two pairs of boreholes, which are closely spaced, are required for the injection and abstraction of the tracer.

As discussed above, the aim of a tracer test is to estimate the transport parameters of the aquifer. 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 dissolved DNAPLs in the subsurface and their study is important in the site characterisation and fate of the DNAPLs.

7.2.9 Partitioning Interwell Tracer Tests (PITTs)

The Partitioning Interwell Tracer Test (PITT) approach has been used to determine the distribution and volume of DNAPL (Pope *et al.*, 1994, Jin *et al.*, 1995). Accurate evaluations of contaminant transport, effective risk assessments and successful remediation for NAPL-contaminated sites requires a knowledge of the occurrence and distribution of NAPL and its dissolution behaviour. The availability of such information is limited by current site characterisation techniques. A major limitation of these methods is that they provide data at discrete points, in such a way that the probability of sampling a zone of localised NAPL is quite small. In addition, the use of point-sampling methods for characterising large domains is constrained by sample-size limitations (Brusseau *et al.*, 1999).

Since the subsurface distribution of immiscible-liquid saturation is complex, the use of point-sampling methods is often problematic. In a column experiment with a

controlled release of DNAPL residual, it was possible to estimate the saturation of the DNAPL with an accuracy of $\pm 95\%$.

The successful implementation of a PITT in the field-scale requires the development of an engineering design based on careful and systematic simulations. A good design should minimise the risk of failure, optimise the information collected and save time and money. A simulation modelling before field test implementation can provide valuable insight into pertinent design parameters that affect the outcome of the tracer test.

It should however be considered that use of PITT techniques for DNAPL assessment is a time- and cost-intensive exercise and only applicable to shallow, porous aquifer systems, with available technology. The advantages of the information obtained during such a test needs to be considered. Before implementation, a site assessor needs to be certain that the DNAPL residual source zone is significant enough in extent to warrant such a test.

7.3 Site Conceptual Model

As discussed in Section 5.2 and Section 7.1.4, the construction of a site conceptual model is an integral part of any DNAPL site assessment. At first, the initial conceptual model will be based on assumptions of what is expected at the site, later refined with data collected through field observation/testing and finally through analytical results. The following sections describe the type of information/data that may be used to construct the final site conceptual model in terms of the geology/hydrogeology and the DNAPL and dissolved phase distribution. Key features of the conceptual model include the descriptions of the geology/hydrogeology, contaminant source, the pathway to the receptor and the physical, chemical and biological processes that may significantly affect contaminant movement.

7.3.1 Geology and Hydrogeology

From the initial conceptual model, the site assessor needs to have a clear understanding of what processes/factors will influence the transport and migration of the DNAPL and dissolved phases in the subsurface. These processes are mainly controlled by the DNAPL's and aquifer media's physical parameters, discussed in previous sections. For the final conceptual model, these physical parameters are used to describe the geology and hydrogeological environment, and the effects that they have on the transport and migration of the contaminants during model construction. For this purpose, the following type of data representations/interpretations may be used to construct the hydrogeological conceptual model:

- Borehole geological logs (show lithological or aquifer differences and water strikes with estimated or measured yields within the borehole)

- Geological cross-sections (show lithological or aquifer type differences across a site)
- Aquifer delineation in three dimensions (consider boundary conditions caused by geological structures, topography or surface water bodies)
- Water level/elevation contour maps and/or cross-sections (show correlation with topography)
- Aquifer parameters must be assigned to aquifer(s) (when dual porosity system, parameters must be assigned to both matrix and fractures)
- Define preferred pathways such as fracture systems (fracture aperture, orientation and connectivity must be considered, data interpretation of geophysical investigation is important)

The site assessor should now have an understanding of possible factors that will influence the contaminant migration and transport at the site.

7.3.2 Characterisation of DNAPL Source Zone and Dissolved Plume

Once the hydrogeological conceptual model is complete, the extent of the DNAPL source zone and the dissolved plume within the aquifer system needs to be characterised. Interpretation of the following data, summarised from the previous discussions, can be used for the contaminant characterisation:

- Vapour phase composition, distribution/contours in soil profile (from soil gas measurements during drilling or digging) or on surface (surface soil gas survey)
- DNAPL composition and physical properties,
- DNAPL phase (if any evidence was found), distribution in the soil profile, from direct or indirect methods)
- Dissolved phase composition and distribution and plume extent

This conceptualisation of the distribution of the contaminant phases may now be used to plan any further actions such as site assessment (if required), monitoring, management and/or remediation.

7.3.3 Flowchart for DNAPL Site Characterisation

The previous discussions in this chapter can be schematically presented in a flowchart. First, the discussions are summarised as follows:

- The ultimate goal of site characterisation is the absolute knowledge of the contamination at the site. This, of course, may never be reached, but with the

right suite of tools and a comprehensive integration of the data, the most accurate understanding is obtained.

- Following the development of the initial site conceptual model, based on available information collected during historical site use, a combination of non-invasive and invasive field methods/techniques will generally be required to advance site characterisation and enable the investigator to conduct risk and remedy assessments.
- Non-invasive methods may often be used during the early phases of field work to optimise the cost-effectiveness of a DNAPL site characterisation programme. Specifically, surface geophysical surveys, soil gas analysis and photo interpretation can facilitate the characterisation of contaminant source areas, geologic controls on contaminant movement and the extent of subsurface contamination. Conceptual model refinements derived with these methods reduce the risk of spreading contaminants during subsequent invasive fieldwork.
- Invasive methods employ various subsurface exploration techniques to observe and measure subsurface materials and conditions directly and indirectly. 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 and borehole geophysical surveys.

Figure 7-4 shows a flowchart 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 is updated throughout the investigation.

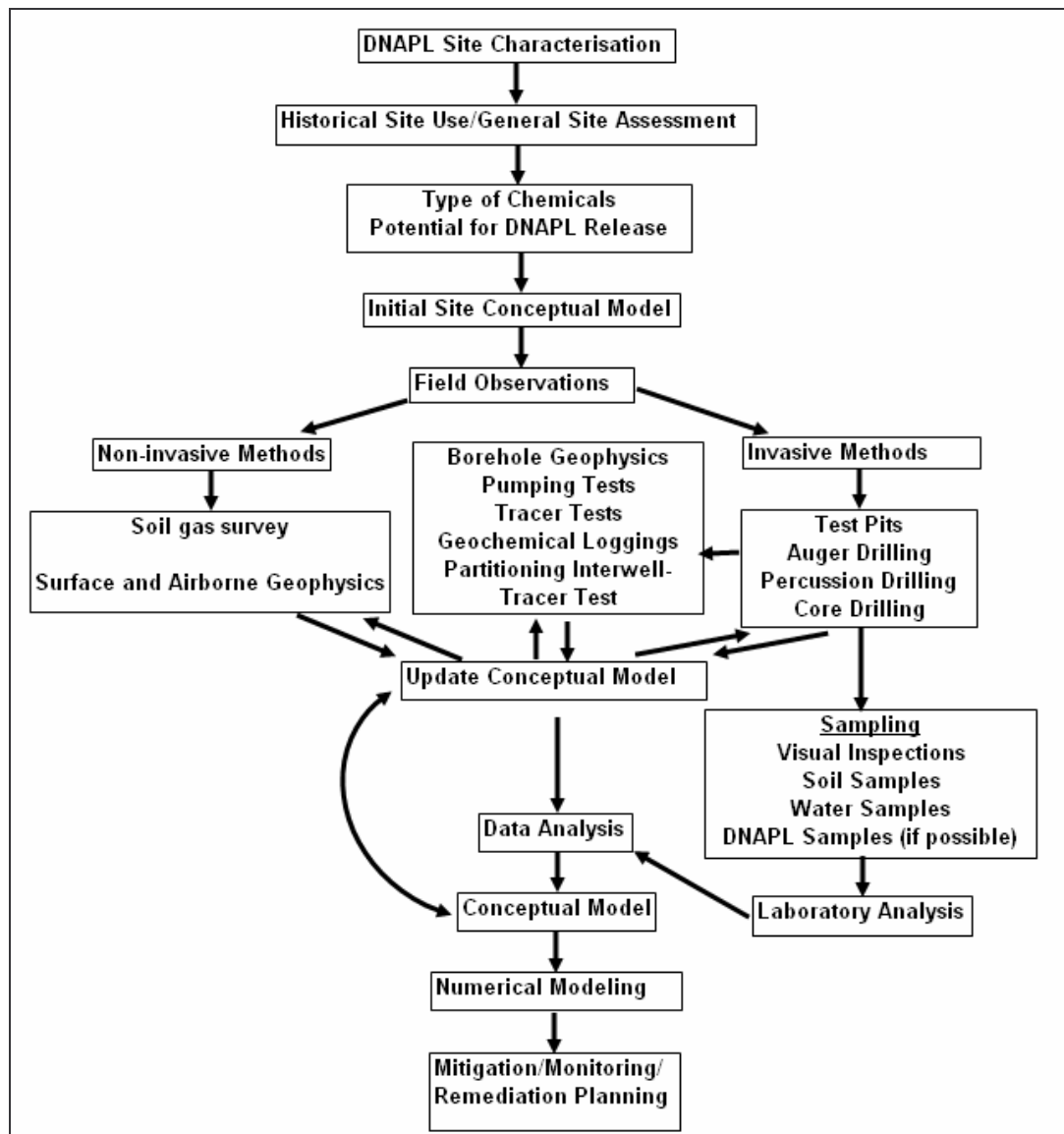


Figure 7-4: Flowchart for DNAPL site characterisation.

8 Conclusions and Recommendations

8.1 CONCLUSIONS

From this research, several important findings on DNAPL site characterisation in fractured aquifers were obtained. These findings can be summarised as follows:

- The DNAPL migration and fate are mainly controlled by fractures, and behave differently from LNAPLs and dissolved contaminants. The field investigations in this research showed that a markedly different approach is needed, and that a 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.
- A 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 yield excellent results in terms of identifying potential groundwater contaminants, for example on Test Site 1, an old dumping area and areas of transport spills were identified through interviews. This step is vital in successfully targeting the main DNAPL release zones and identifying the most likely groundwater contaminants, and forming the initial site conceptual model. From this, the decision can be made whether the site is a potential DNAPL site, and the results can be used to guide the early stages of site assessment.
- Test pits were found to be effective in assessing a DNAPL site in three dimensions. Although limited to the shallow and unconsolidated zones only, they proved to be cost-effective methods for understanding the shallow subsurface in this research. They can also be used to identify additional source zones by determining the properties of backfill or the location of buried waste on sites.
- Soil gas surveys can provide very useful information if used as an initial surveying tool. The greatest value lies in determining multiple volatile species, which allows an understanding of different contaminant zones and identifying biodegradation. The findings in this research suggest that hand-held PID values provide a very coarse guide to the VOC concentrations, as limited success was obtained in assessing contamination quantitatively. The combination of these surveys with other rapid methods such as UV fluorescence, shows a good correlation, which can be used for the selection of samples to be submitted to the laboratory.

- UV fluorescence proved to be a very effective investigation tool. This is related to the fact that PAHs were a major source of organic contamination, but in cases where high VOC values were obtained by PID and UV fluorescent values were high, a 90% success rate was obtained in identifying organic contaminants in soils and aquifer material. A technique of mapping the site using relative UV fluorescence yielded a good comparison to later laboratory observations for the soil material. This provides a useful, cost-effective tool for understanding the distribution of organic contaminants in the shallow zones on a site. However, the fluorescence capacity of the uncontaminated soil should be evaluated in advance, as some inorganic minerals may fluoresce.
 - The findings in this research were that hydrophobic dyes are not effective in coloured soil, and since the probability of encountering free phase DNAPL in water is low, these dyes are unlikely to be useful in groundwater. In cases where evidence points to free-phase DNAPL being present in soils or aquifer material, these dyes may be of use.
- For the specific delineation of DNAPL zones, surface geophysical techniques used in this research did not prove to be successful. Indications are that the techniques available for this would not be applicable in most South African aquifers or are prohibitive in terms of cost. Surface geophysical investigations are appropriate for understanding subsurface conditions but the experience in this research suggests that they are severely limited on most industrial sites due to the very high signal interference from cultural signatures. Geophysics could still be valuable where sites are less influenced with cultural noise and off-site where geological subsurface information lacks. This research did not yield a rapid or cost-effective geophysical method for the delineation of DNAPL contamination under South African conditions.
- The results from field investigations showed that geophysical borehole techniques can provide excellent information of fracture depths and orientations. It was also shown that no single technique provides an unequivocal indication of fracture position and orientation, but that best results were obtained when several techniques are used conjunctively. These tools are most appropriate when used in conjunction with hydraulic testing methods. There are several geophysical techniques for borehole logging, from which several conclusions for their application could be drawn:
 - EC logging
 - Sensitive to the fracture, and some geologic boundaries
 - Anomaly curves not sharp and not easy to precisely locate the fracture
 - One-arm caliper

- Good method if fracture apertures are large
 - May be helpful in borehole construction evaluation
 - Casing structure could be identified
 - Borehole diameter changes can be determined
 - Difficult to differentiate eroded borehole caving from fractures
 - Measurement is only in one dimension. Three-arm caliper could be more informative.
- Natural gamma
 - Was helpful in locating stratigraphic boundaries
 - Was not sensitive to the fracture positions
- Spontaneous potential
 - Showed small anomaly around the fracture positions
- Resistivity probe
 - Good to locate the fracture
 - There must be an ionic water quality difference between the fracture zone and the rest of the borehole.
- Full wave sonic
 - Very sensitive to the fracture
 - Sensitive in locating lithologic boundaries
 - Difficult to locate fracture precisely because of wide anomaly
- Acoustic televiewer
 - Very sensitive to fracture like the full wave sonic.
- It was found that geochemical logging was an easy and cost-effective way of identifying fracture positions. These profiles are also important in investigating chemical activities taking place in the borehole. If borehole water is representative of the aquifer, they can be used to investigate biochemical conditions in the aquifer.
 - EC logging often provides a good initial guide of flow zones or fracture positions, but this may be a very coarse indication, and where there is limited associated inorganic contamination, it may not be appropriate for the identification of these hydraulically active areas. Multi-parameter logging proved to be useful for fracture confirmation and for the understanding of redox conditions, which are important for degradation. These tools are suggested as integral cost-effective tools in the South African DNAPL toolbox
- It is very important to approach drilling at a DNAPL site as an iterative process. This allows improvements in borehole design, materials, and locations and depths of boreholes. A once-off drilling programme 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. Several very innovative techniques used overseas are not capable of drilling in hard or consolidated material, as was found in testing direct push methods at Test Site 1. Solid-stem auger drilling was found to be very useful for unconsolidated materials, and the direct push method appears to have a lot of potential, but is not suitable when a competent layer is encountered. Hollow-stem auger drilling can provide *in-situ* samples, but it was found that this technique struggles in swelling clay and the heat generated may volatilise VOCs in such samples.
- 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 the volatilisation of VOCs.
- It was also found in this research that samples obtained immediately after or during drilling could lead to false positive organic analysis results. This is due to the lubricants or drill fluids used in the processes and cognisance should be taken of this when such samples are taken.
- Although core drilling is a more expensive technique, the results obtained under controlled and industrial site conditions show that it provides vital information for detailed fracture characterisation. Core drilling is especially important for vertical fractures and identification of potential preferential flow zones. It allows the accurate delineation of different magnitudes of fractures and this information will lead to improved conceptual models for DNAPL sites in this country. The extraction of organic contaminants from core using methanol will also provide a better quantification of the NAPL mass distribution in the matrix material than can be obtained by any other testing.
- Laboratory and field observations showed that the material for casing is very important and consideration must be given to inertness in terms of NAPLs. Multiple boreholes drilled to different depths were found to be more effective than piezometer installation. The position of casings and screens is very important; otherwise the measurements do not reflect the true concentrations within a plume.
- This research indicated that fracture “hunting” is extremely difficult with the current technology, which implies that DNAPL migration in the subsurface is also difficult. However, by integrating the different available techniques could result in a better site characterisation. 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. 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 the regional and local dip of fracture. The research also showed the importance of scale issues 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 results on both test sites have shown slug tests to provide a good first-order indication of the hydraulic properties. A comparison of results from different durations of pumping indicates that longer duration tests provide better information on the fracture connectivity across the study area. The Fracture Characteristics (FC) method of analysis indicated that the fracture identification through derivative plots corresponds well with point-dilution tests and visual observations.
 - Riemann (2002) explained that early time drawdown data could be used to estimate the T-value of the fracture zone with the Cooper-Jacob 2 (CJ2) method. However, in this experiment, estimated T-values using CJ2 did not have any physical meaning.
 - Due to changes in hydraulic pressure during pumping, DNAPLs that were initially immobile could start to migrate to the initially uncontaminated zone. Therefore, pumping in DNAPL source areas should be restricted to avoid the spread of contamination to a larger area.
- Tracer tests are found to be cost-effective and fairly rapid methods of determining major flow zones in an 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. As examples, the Darcy velocity and seepage velocity in a fracture of UO23 are 4.70 and 10.50 m/d respectively, while that of D3 is 5.30 and 11.70 m/d respectively. These high values correspond well with the estimated fracture transmissivity values of 150 and 180 m²/d for each of these boreholes.
- The two test sites showed that the orientation and aperture of fractures vary within a short distance. At the campus site for example, the fracture dips slightly in the northeast direction, but on a scale of around 200 m², this dip can vary locally in all directions. Both sites show that the fractures are locally undulating. On the campus site the dip was generally less than 2°. An estimation of the spatial extent of fractures showed that the boundaries of fractures terminate very irregularly. An example of this is shown by the fact

that UO23 intersects the fracture while D5, less than 3.5 m from this borehole, does not. This shows that the location of fractures requires a very detailed site characterisation.

- Laboratory testing showed that PITT is a good method for evaluating the saturation of NAPL residuals, preferable in homogenous unconsolidated aquifer. In principle, the experiment can be performed by one conservative and one partitioning tracers, but for a better estimation, at least two partitioning tracers are recommended with different partitioning coefficients. In a controlled release, it was possible to estimate DNAPL saturation in a column with an accuracy of 95%. The method may therefore be applicable as part of the site characterisation in unconsolidated aquifers. With the current technologies available, the method is believed to have limited applicability in fractured rock aquifers.
- An *in-situ* method of estimating the effective diffusion coefficient associated with intact rock was designed and implemented in borehole completed in a mudstone on the Campus Test Site. The values were estimated at depths of 27 and 36 m and were found to be 3.4×10^{-6} and 7.8×10^{-6} m²/day, respectively. As compared to the literature of similar geology, these values were found to be high. Although the values were estimated for chloride, it is indicative that mass loss for dissolved DNAPL to the matrix porosity due to diffusion to the mudstone to be relatively high.
 - Pump-and-treat can effectively remove DNAPLs from the fractures but due to reverse diffusion, dissolved DNAPLs are expected to contaminate the water, making the site difficult to be remediate.
 - The effective matrix diffusion coefficient was found to be sensitive to the effective porosity and borehole radius. Usually the borehole radius is constant in South African cases; however, the effective porosity may vary significantly on a small scale. Therefore, the effective diffusion coefficient in heterogeneous aquifers is expected to vary considerably.
 - The effective diffusion coefficient is a product of the free-water diffusion coefficient for the constituent under consideration and a formation factor. The formation factor scales the free-water diffusion coefficient to account for diffusion through the highly tortuous void space of the rock matrix. Identifying the formation factor is important in extending the results of the *in-situ* diffusion experiment to other dissolved constituents. Using values of the free-water diffusion coefficient for chloride, the formation factor was estimated to range from 0.027 to 0.062 for the rock matrix mudstone for an assumed matrix porosity of 0.04.

- The tracer test was also applied to evaluate the effective porosity of fracture zones or other areas of interest in the aquifer, which is almost impossible to measure *in situ*. It is of interest that the estimated porosity of the fractured zones shows tremendous variations on the field sites, showing that the fractured transport is not governed by typical parallel plate transport. 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.
- The development of conceptual models through detailed site characterisation is key to the successful management of DNAPL sites. The field investigations showed the integration of results from the different techniques is needed to develop a conceptual model for different aspects of DNAPL site investigation. The most important aspects would include the determination of preferred DNAPL pathways and the size, orientation and density of the fracture network. The work on both field sites showed that this is a continuous process of improvement in complete site characterisation.

The conclusions on the various non-invasive and invasive site characterisation techniques can be summarised based on the test sites assessed during this research, as listed in Table 8-1.

Table 8-1: Applicability of the various characterisation techniques for different sites.

Methods of DNAPL Characterisation	Regional Study	Site Study	Borehole and surrounding area	Applicability to Fractures
Historical site use	NA	HA	FA	NA
Hydrocensus	HA	HA	HA	FA
UV and dye tests	NA	HA	FA	NA
Soil gas survey	NA	HA	HA	NA
Surface and airborne geophysics	HA	FA	FA	HA
Test pits	NA	HA	FA	FA
Drilling	FA	HA	HA	HA
Soil chemical analysis	FA	HA	HA	NA
Water chemical analysis	FA	FA	HA	HA
Borehole geophysical logging	NA	FA	HA	HA
Borehole Geochemical logging	NA	FA	HA	HA
Aquifer test	NA	FA	HA	HA
Tracer test	NA	FA	HA	HA
PITT	NA	HA	HA	NA

Techniques marked with blue are non-invasive Techniques marked with brown are invasive
 NA = not applicable, FA = fairly applicable, HA = highly applicable

8.2 Recommendations

- 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 characterisation, since the benefits should greatly exceed the increased costs.
- Apart from directly drilling into source zones, it is recommended that several other precautions need to be taken during drilling. The drilling showed the importance of limiting the type and quantity of lubricants and drill fluids used, the importance of having lined ponds for circulation of drilling fluids during core drilling and the importance of proper disposal of contaminated water and soil to prevent secondary contamination.
- The DNAPL issue is a relatively new field of science and it is possible that new innovative technologies that enhance non-invasive or invasive site assessment be available with time. It is highly recommended that characterisation should not be restricted to those proposed in this research, but that innovative technologies be incorporated within the site characterisation toolbox.
- Site characterisation should proceed with adequate safety measures. Exposure to DNAPL can occur through inhalation. Site investigators and the people in the areas of contamination should be informed during assessment so that excavation or drilling in these areas can be completed with careful air monitoring and proper protective clothing.
- The cost of site characterisation (especially in fractured aquifers) and cleaning up of DNAPLs contaminants can greatly exceed the value of the contaminated property. It is recommended that the South African government pass strict, comprehensive and long-term legislation on DNAPL release controls such as storage tanks, buried transmission piping, sumps, floor drains, disposal pits, and other sources.
- Although guidelines of water quality standards are similar all over the world, and quality standards can be referred from other institutes, such as the EPA, it is recommended that South Africa implement enforceable and non-enforceable levels of DNAPL concentration limits. In this way, a potentially contaminated site can be identified according to the standards and further site characterisation can proceed.
- The number of boreholes available to a site assessor is often limited due to cost constraints by site owners. Borehole drilling is an iterative process, whereby more than one drilling event will be required to characterise a site.

The knowledge gained through such successive drilling events is used to continually update the site conceptual model. Therefore, site owners in South Africa need to be convinced that a DNAPL assessment requires intensive site characterisation in order to successfully plan and implement (costly) mitigation and/or remediation.

- Water and soil samples are analysed for organic contaminants, using EPA protocols, and employing gas chromatography-mass spectrometry methods. There are only a few laboratories equipped for specialised environmental analysis in South Africa. Generally it was found that European laboratories were more cost effective and turnover time for results was shorter than for local laboratories. It is recommended that these practices be adopted by South African laboratories.

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Abstract

The objective of this research is to characterise fractured aquifers contaminated with DNAPLs in South Africa. The site characterisation approach is conducted in two case studies by integrating a range of site assessment techniques. It started with the non-invasive methodologies that provide rapid and cost-effective ways for screening. After developing the initial conceptual model, the investigation proceeded to invasive techniques that provide more information on DNAPLs and fractures on a local scale.

This research indicated that fracture “hunting” is extremely difficult with the current technology, making DNAPL characterization very challenging. It also indicated that no single technique provides an unequivocal indication of fracture position and orientation, but that best results were obtained when several invasive techniques were used in a toolbox approach. These tools were most appropriate when integrated with hydraulic testing methods. The site characterisation was done in a continuous and iterative process, and each phase of investigation was used to refine the conceptual model of the site.

The non-invasive techniques applied included:

- General assessment of Test Site 1 by site inspection, interviewing employees, documentation studies and aerial photo analysis.
- Hydrocensus
- Direct observing for DNAPL contamination using UV light and Sudan IV shake tests.
- Soil gas surveys by using various models of PIDs to delineate the organic vapour plumes.
- Surface and airborne geophysics for outlining major structures that may play an important role for DNAPL migration pathways. This did not yield useful results at Test Site 1 due to noise interference from industrial activities and infrastructure.

The non-invasive techniques were not applicable for direct evaluation of DNAPLs migrating in fractured aquifers; however, they were essential in understanding DNAPL-release zones and vapour plumes. They were also found to be relatively cost and time efficient.

The invasive techniques applied include:

- Test pits (excavations on the top 3 m soil)

- Drilling using augur, percussion and coring methods. (An outside-in approach was followed during the drilling to avoid unnecessary DNAPL mobilisation).
- Several different borehole geophysical and geochemical logging methods.

Results from this diverse range of activities were integrated to construct conceptual models of the preferential fracture pathways of the two test sites.

Riemann (2002) found that early time drawdown data could be used to estimate the T-value of the fracture zone with the Cooper-Jacob 2 method. However, in this research, the method did not yield results that were consistent with other observations.

The tracer experiment was extended to evaluate the effective matrix diffusion coefficient of the mudstone in the Campus Test Site. The values at depths of 27 and 36 m were estimated as 3.4×10^{-6} and $7.8 \times 10^{-6} \text{ m}^2/\text{day}$, respectively. This means that the rate of dissolved mass disappearance from the fracture to the matrix is relatively high compared to other geologic formations.

An in situ method of effective porosity estimation using tracer tests was employed instead of the traditionally measurements on rock/soil samples from the aquifer. In this way, uncertainty in porosity estimation due to the inherent alteration during sampling was eliminated.

Column experiments were conducted to evaluate the accuracy of PITT for residual DNAPL saturation estimation. The saturation was estimated with an accuracy of 95%. However, the experiment was conducted in unconsolidated, homogenous sand and the experiment may not be accurate as such when applied to heterogeneous aquifer systems usually encountered in South Africa. With the current technologies available, PITT is believed to have limited applicability in fractured rock aquifers.

Finally, based on the findings, a methodology has been proposed for the characterisation strategy of DNAPL contaminated sites in fractured South African aquifers.

Opsomming

Die doelwit van hierdie navorsing is om Suid Afrikaanse fraktuurakwifere, wat besoedel is met DNAPLs, te karakteriseer. Die terrein karakterisering is benader deur die integrasie en toepassing van verskillende ondersoek metodes by twee gevalle studies. Eerstens is nie-binnedringend en vinnige, effektiewe ondersoek tegnieke gebruik. Nadat die aanvangs konseptuele model gekonstrueer is, is daar voort gegaan met binnedringende tegnieke om meer inligting te verskaf oor DNAPLs en frakture op 'n lokale skaal.

Hierdie navorsing het gewys dat fraktuur opsporing baie moeilik is met beskikbare tegnologie, wat DNAPL karakterisering baie uitdagend maak. Dit het ook bewys dat geen enkele tegniek die fraktuur posisie en oriëntasie kan aandui nie, en dat binnedringende tegnieke wat saam gebruik word, die beste resultate gelewer het. Hierdie tegnieke is mees geskik as dit geïntegreer word saam met hidroliese toets metodes. Die terrein karakterisering was gedoen as 'n aaneenlopende en herhalende proses, waar die konseptuele model tydens elke fase opgedateer is.

Die nie-binnedringende tegnieke wat toegepas is sluit die volgende in:

- Algemene ondersoek tegnieke soos terrein inspeksie, onderhoude met werknemers, dokument studies en lugfoto interpretasie.
- Hidrosensus
- Direkte obserwering van DNAPL besoedeling met die hulp van UV-lig en Sudan IV kleurstof skud toetse, van die boonste grondlaag.
- Die organiese gas pluim is gedelineër, deur grond gas opnames met verskillende modelle "PIDs".
- Grond en lug geofisika is gebruik om belangrike geologiese strukture en kenmerke op te spoor wat 'n rol kan speel in die beweging van DNAPLs. (Hierdie tegnieke was egter nie suksesvol op Toets Terrein 1 nie, aangesien daar baie agtergrond geraas was weens die industriële aktiwiteite en infrastruktuur.)

Die nie-binnedringende tegnieke was nie toepasbaar vir direkte evaluering van DNAPL migrasie in die gefraktureerde akwifere nie, maar het bygedra tot die insig in die DNAPL bron areas en die gepaardgaande gas pluime. Dit was ook bevind dat dit koste en tyd effektief is.

Die binnedringende tegnieke wat toegepas is sluit in:

- Toets gate (tot 3 m diep)

- Boor van gate met verskillende tegnieke ('n Buite-na-binne metodiek is gevolg om onnodige mobilisering van DNAPL bron areas te verhoed.)
- Verskillende boorgat geofisika en geochemiese opnames is gebruik.

Riemann (2002) het verduidelik dat vroeë tyd watervlak afname data, gebruik kan word om die T-waarde van die fraktuur sone te bepaal met die “Cooper-Jacop 2” metode. Hierdie navorsing het egter bewys dat die T wat bepaal word op hierdie manier, geen fisiese waarde het nie.

'n Spoorder eksperimente is uitgebrei om die effektiewe matriks diffusie koëffisiënt van die modderstene op die Kampus terrein te bepaal. Die waardes by dieptes 27 and 36 m, was bepaal as 3.4×10^{-6} and 7.8×10^{-6} m²/dag, onderskeidelik. Dit impliseer dat die tempo waarteen opgeloste massa verdwyn uit die fraktuur na die matriks is heelwat hoër as voorheen bepaal vir ander gesteentes volgens literatuur.

Die effektiewe porositeit word tradisioneel gemeet deur rots of grond monsters te neem van die akwifer. Tydens hierdie navorsing is *in-situ* effektiewe porositeit bepaal deur punt verdunning spoorder eksperimente. Op hierdie manier is die porositeit bepaal sonder om die monster bloot te stel aan verandering tydens monsterneming.

Kolom eksperimente was gedoen om die akkuraatheid van PITT vir die bepaling van residuele DNAPL versadiging te bepaal. Die versadiging was bepaal tot 'n akkuraatheid van 95%. Die eksperiment is egter in homogene ongekonsolideerde sand gedoen. Dus mag dit nie toepasbaar wees of dieselfde resultate lewer, indien dit toegepas word in tipiese heterogene akwifere van Suid Afrika, nie. Dus met die huidige beskikbare tegnologie word daar nie geglo dat PITT toepasbaar is in fraktuur akwifere nie.

Deur die bevindinge van hierdie navorsing is daar 'n strategie voorgestel vir karakterisering van DNAPL besoedelde terreine in Suid Afrikaanse fraktuurakwifere.

Appendix A

Table A 1: Numerical model input parameters for fractured clay aquitard, used to generate Figure 3-16 (after Harrison *et al.*, 1992)

Parameter	Aquitard	Aquifer	Waste zone	Cap
Matrix porosity (ϕ_m)	0.05	0.35	0.40	0.50
Hydraulic conductivity (K), cm/s	1.0×10^{-8}	1.0×10^{-2}	1.0×10^{-6}	1.0×10^{-8}
Longitudinal dispersivity, (α_l), m	0.0	1.0	1.0	0.0
Transverse dispersivity (α_t), m	0.0	0.02	0.02	0.0
Tortuosity (τ)	0.2	0.7	0.7	0.2
Effective diffusion coefficient (D_e), cm^2/s	1.49×10^{-6}	5.22×10^{-6}	5.22×10^{-6}	1.49×10^{-6}
Distribution coefficient ¹ (K_d), mL/g	1.26	0.025	1.26	1.26
Retardation factor ² (R)	4.2	1.12	5.5	4.2
Fraction of organic carbon (f_{oc})	0.01	0.0002	0.01	0.01

$$^1 K_d = f_{oc} K_{oc}; K_{oc} = 126 \text{ mL/g} \quad ^2 R = 1 + \rho_b K_d / \phi_m$$

Table A 2 General Information of the hydrocensus boreholes

Site Name	Owner's Name	Adress	Industry type	Contact no.	GPS Co-ordinate S	GPS Co-ordinate E	Depth of borehole (mbs)	Collar Height (m)	Casing (m)	Rest Waterlevel (mbs)	Waterlevel (mbs)	Date drilled	Water potability	Water Use
B1	Heuwelkor Twee (Pty) Ltd	PO Box 3574, Bfn, 9300	Feedlot/Abattoir	051-4332991/4332957 (fax)	29.11159	26.26277	80	0	Steel		#REF!	>20yrs		Wash of feeding pens
B4	Cold Chain/Veekeor		Meat packing/abbatoir		29.11159	26.26.277		0.28	Steel	6.1	5.82	>20yrs		Garden/wash of meat stores
B5	Mr Brink	Hooflaan 8	General Repair Shop	051-4332881	29.09332	26.26058	30	0	Steel	19.4	19.4	>20yrs	Hard	Garden
B6	Mr Steenkamp/Jet Park Driving Range	Lessing Str 10	Driving range	082-4602594	29.0933	26.26058	44	0	Steel	16.6	16.6	>20yrs	Good	Irrigation of greens
B7	Mr Meyers	Lessing Str 20	Engineering Company		29.10239	26.26477		0	Steel			>30yrs		Household/Industry
B8	Mr ECV van Pletzen	San Du Plessis In No. 51	Private house	051-4332148	29.09564	26.26571	30	0.4	Plastic (6)	17.9	17.5	>30yrs	Good	House/Garden
B9	Mr HP Botha	San Du Plessis In No.6	Private house	051-4333607	29.09567	26.26573		0	Steel		>50	>30yrs		Garden
B10	Transwerk	Schoemanpark Golfbaan	Golf course	0828249563 (Jan Smit)	29.11786	26.25375	54	-0.3	Steel		#REF!	1999	Good	Filling of dams
B11	Transwerk	Schoemanpark Golfbaan	Golf course	0828249563 (Jan Smit)	29.1189	26.24494		0	Steel			>30yrs	Good	Filling of dams
B12	Transwerk	Schoemanpark Golfbaan	Golf course	0828249563 (Jan Smit)	29.11937	26.24329		0.3	Steel		#REF!	>30yrs	Good	Irrigation of sportsfield

Table A 3: Inorganic water quality of the hydrocensus boreholes.

SiteName	B1	B4	B5	B6	B8	B9	B10	B11	B12
pH	7.7	7.87	7.68	7.43	7.78	7.8	7.23	7.24	7.77
EC mS/m	50.3	37.4	114	134	113	125	152	137	136
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
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	140	395	379	370	304	366	326	325
Cl mg/l	22	25	110	163	124	140	150	102	90
SO4 mg/l	18.1	15.15	45.9	116	79	150	260	265	295
N NO3mg/l	0.09	0.41	11.12	10.14	0.02	12.46	15.84	22.1	17.7
F mg/l	0.5	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	2.2	0.28	0.66	0.2	0.3

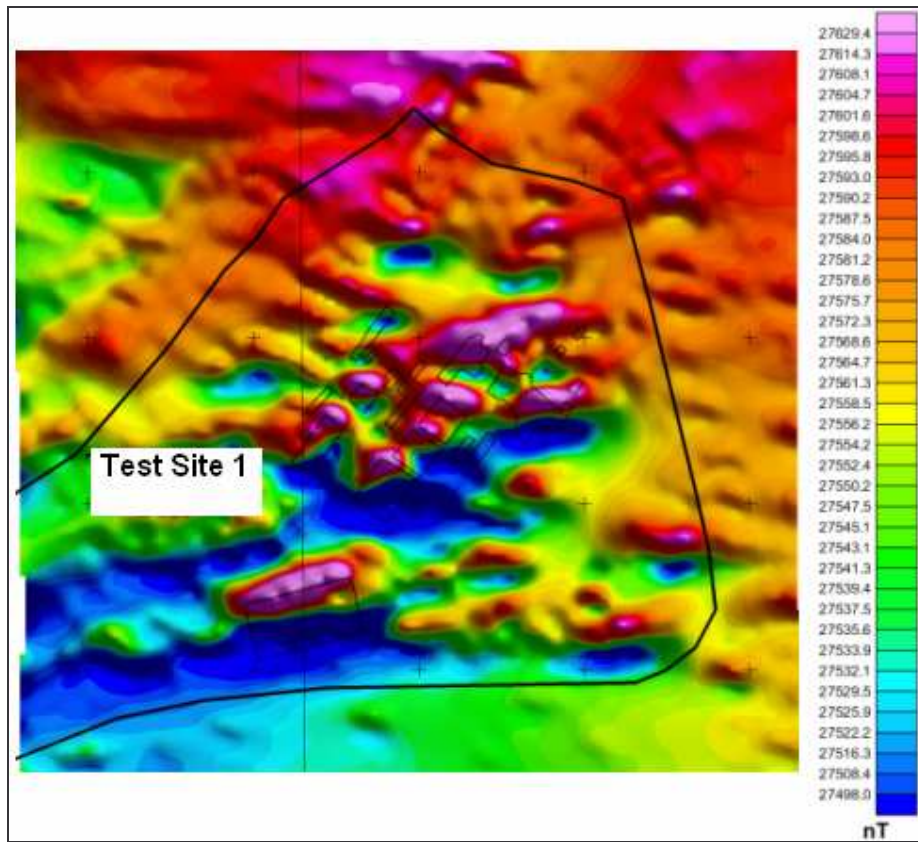


Figure A 1: Total field aeromagnetic map of Test Site 1.

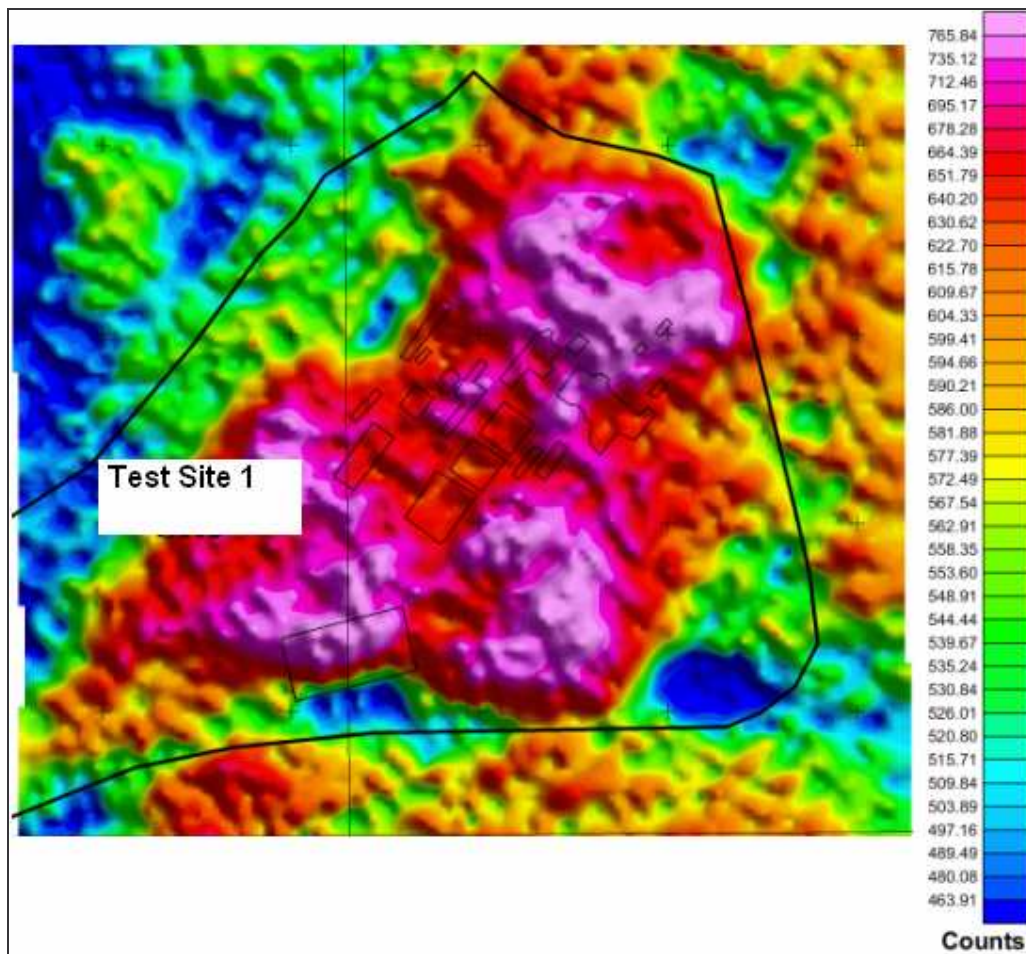


Figure A 2: Total field radiometric map of Test Site 1.

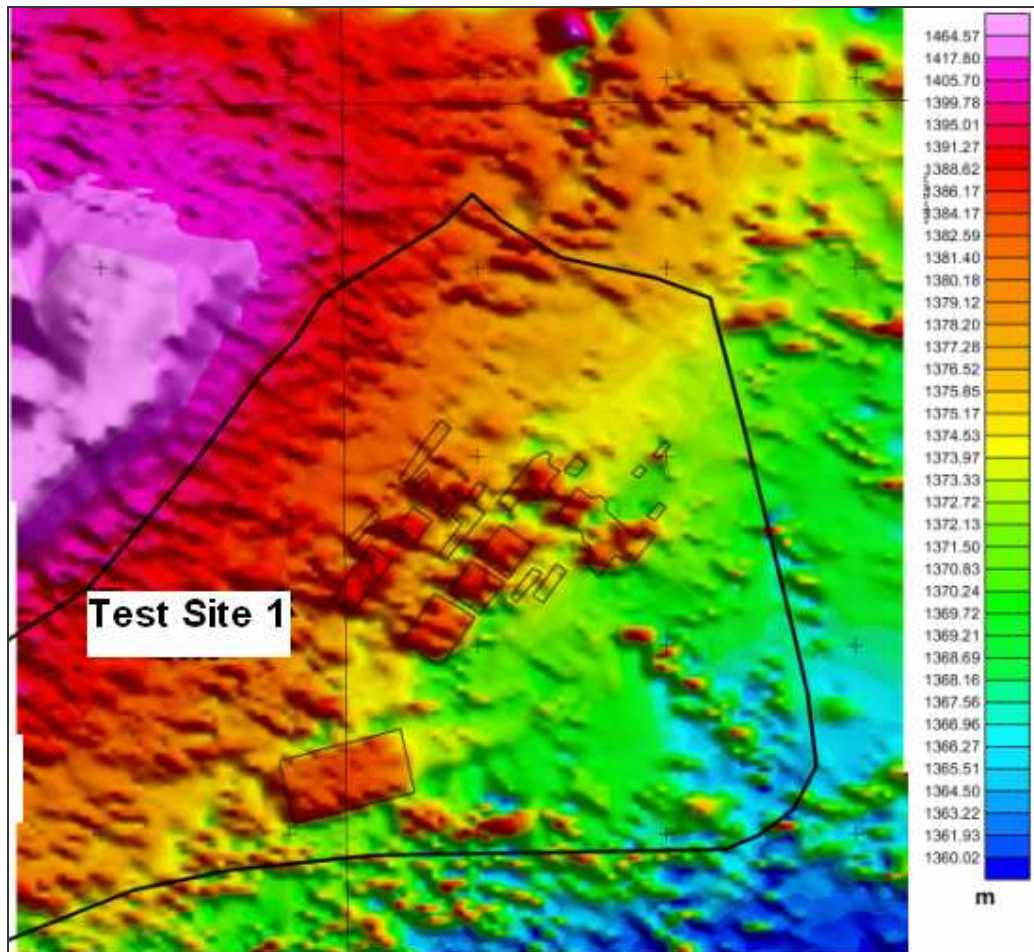


Figure A 3: Digital terrain model from airborne geophysics.

Table A 4: Test Site 1 boreholes, their drilling dates, depths and collar heights.

Borehole	Date Drilled	Depth (m)	Collar Height (m)
GB1	2004/09/10	30.0	0.30
GB2	2004/09/10	30.4	0.14
GB3	2004/12/06	59.8	0.32
EB1	2004/12/06	49.0	0.23
EB2	2005/03/30	36.5	0.37
GB4	2005/04/11	38.8	0.31
GB5	2005/04/12	23.1	0.43
GB6	2005/04/12	8.0	0.32
GB7	2005/04/14	39.3	0.52
GB8	2005/04/15	24.7	0.33
GB9	2005/04/18	39.1	0.27
EB3	2005/04/19	27.0	0.33
FB1	2005/04/21	61.1	0.33
VB1	2005/08/08	30.0	0.15
VB2	2005/08/08	30.0	0.17
SB1	2006/11/21	36.16	0.40
NB1	2006/11/21	41.71	0.40

Table A 5: Piezometer construction information.

Piezometer	Date Drilled	Depth (m)	Collar Height (m)	Un slotted length (m)	Slotted length (m)
GS2	2005/11/08	20	0	3.70	16.30
GS3	2005/11/08	18	0	1.80	16.20
GS5	2005/11/08	19	0.4	2.25	16.75
FS1	2005/11/08	20	0	4.4	15.6

Table A 6: Mineralogy of selected samples from Test Site 1 borehole drilling.

Sample no.	Quartz	Montmorillonite	Illite	Calcite	Albite	Orthoclase	Kaolinite
ES1-9m	XX	x		X	x	x	
ES1-11m	XX	X	x	X		<x	
ES1-13m	XX	X		X		x	
FS1-8m	XX	X	x			x	
GB3-57m	XX	x	X	x		X	x

Sample no.	Quartz	Montmorillonite	Illite	Calcite	Albite	Orthoclase	Kaolinite
GB9-25m	XX	XX			X		<X
GB7-33m	XX	X	x			x	X
GB7-37m	XX	x	x		X		x
GB9-37m	XX	X	x			x	X
GS1-2m	XX	x				x	
GS1-12m	XX	x		X		<X	
SG5-6m	XX	XX	x	x		<X	
SG5-8m	XX	X		<X		<X	
GS5-12m	XX	x		<X		x	
GS5-15m	XX	X		x		x	
EB1-14m	XX	X				x	
EB1-20m	XX	X				x	
EB2-10m	XX	X	x	XX	<x		
EB3-4m	XX	XX				x	

Dominant mineral is represented by XX and constitutes more than 40% of the sample

Major mineral is represented by X and constitutes 10 – 40%

Minor mineral is represented by x and constitutes 2 – 10%

Accessory mineral is represented by <x and constitutes 1 – 2%

Rare mineral is represented by <<x and constitutes <1%

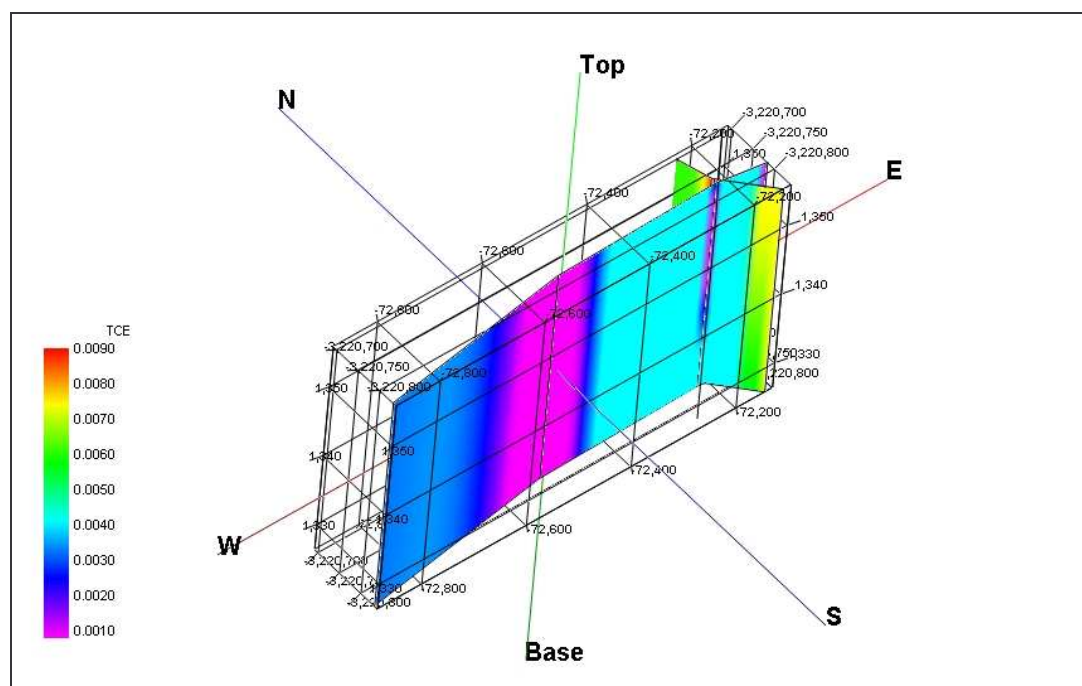


Figure A 4:TCE distribution across Test Site 1

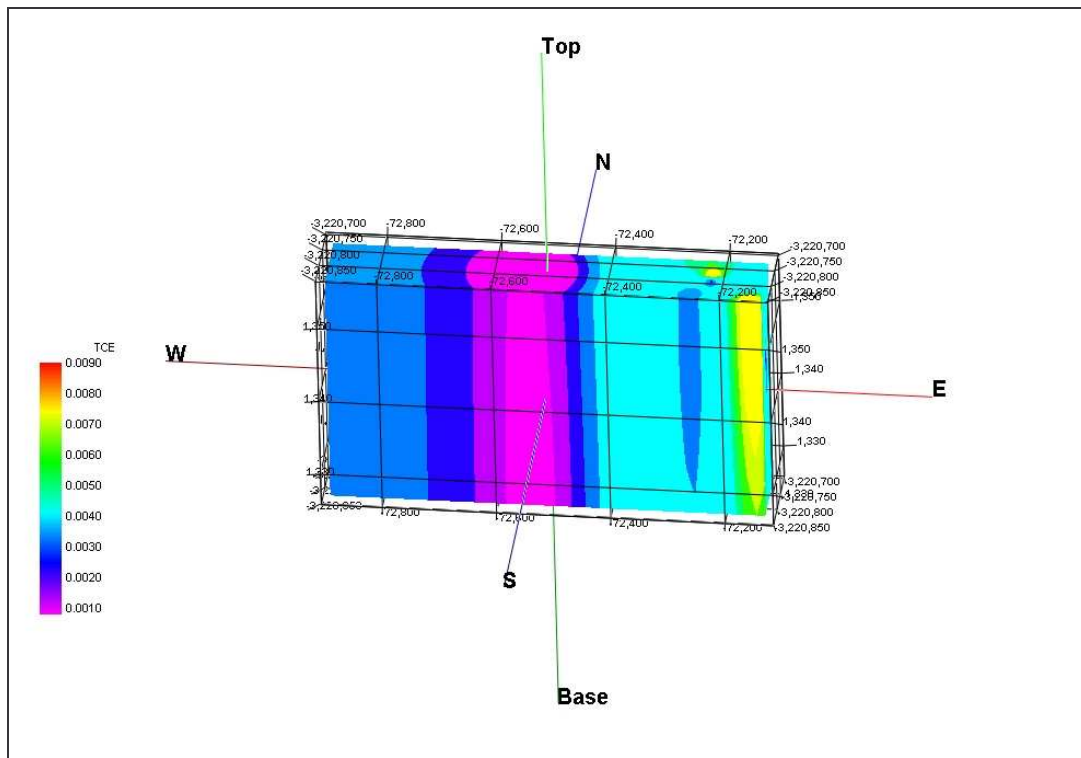


Figure A 5:TCE distribution across Test Site 1

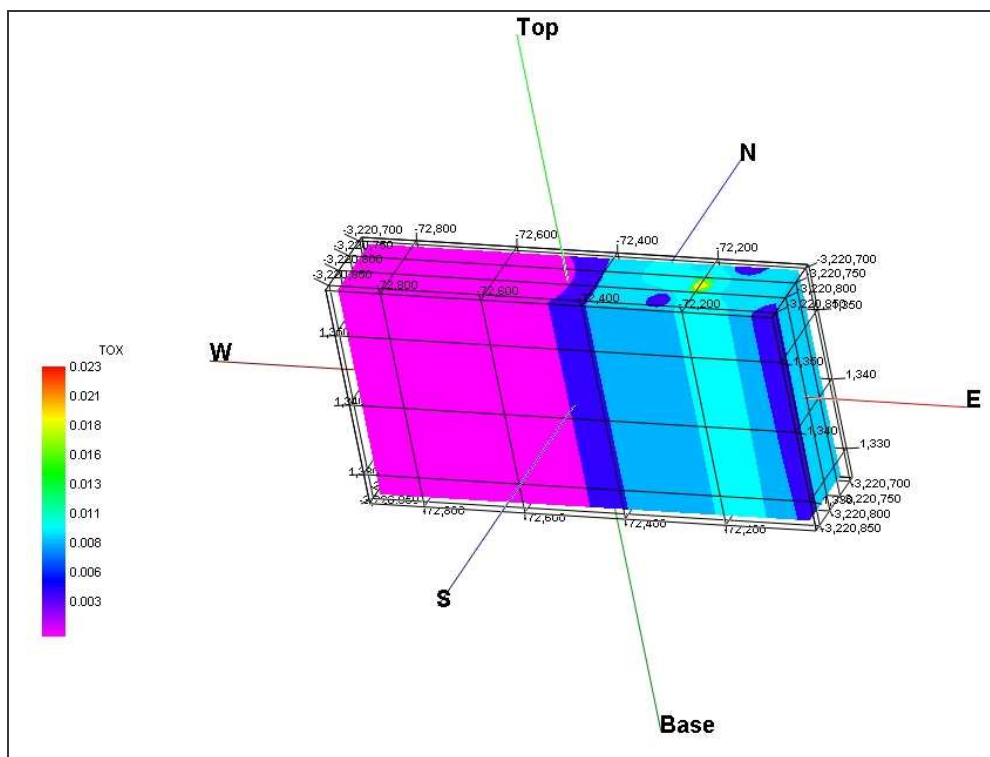


Figure A 6:TOX distribution across Test Site 1

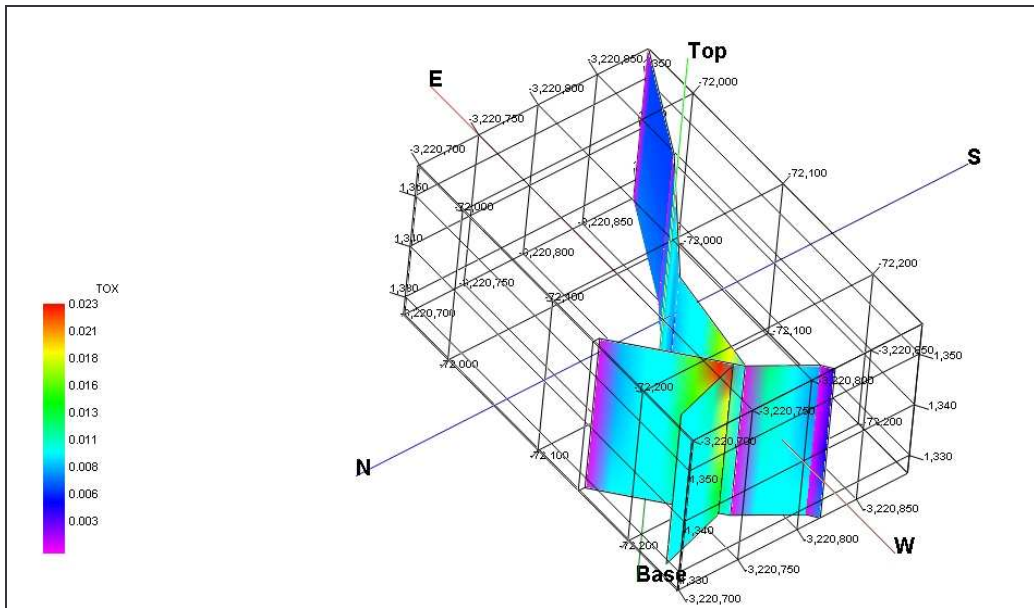


Figure A 7:TOX distribution at the gasworks

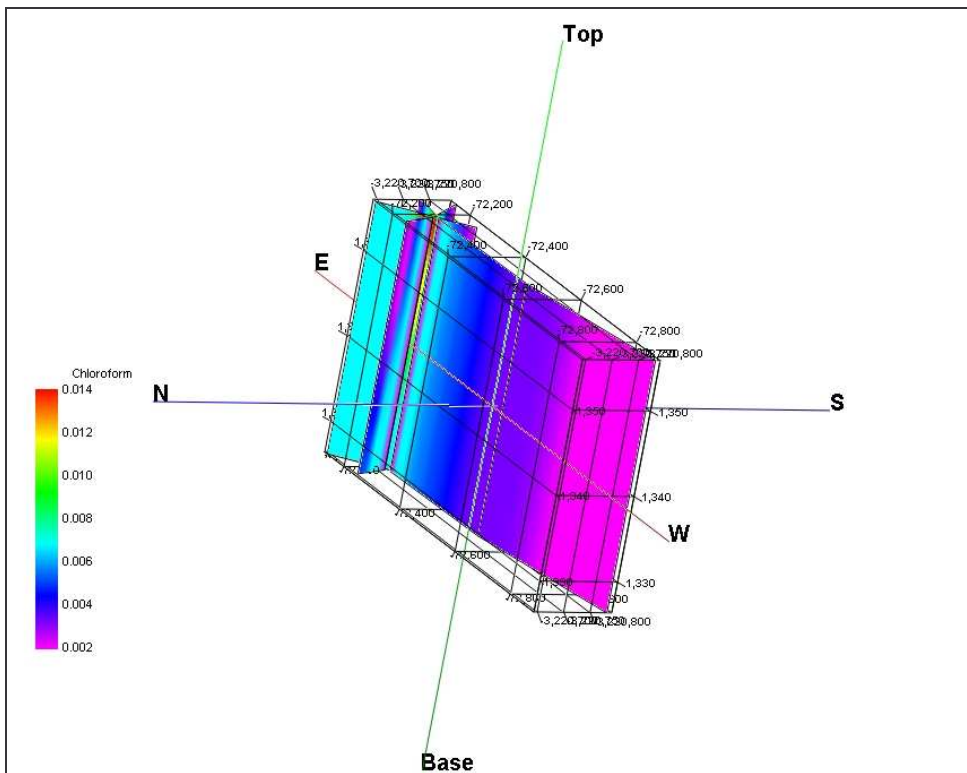


Figure A 8:Chloroform distribution across Test Site 1

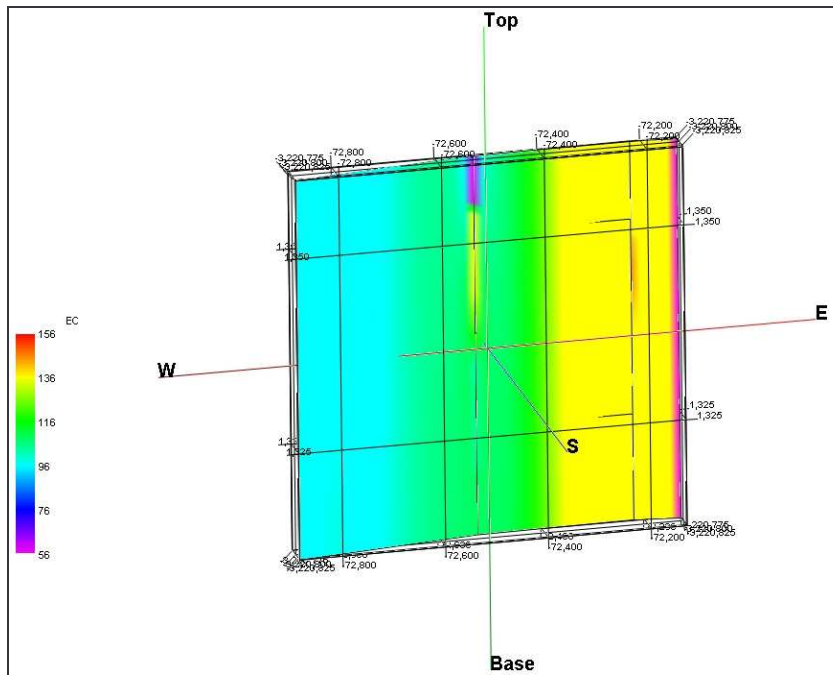


Figure A 9: EC variation on the site

Table A 7: Summary of fracture positions in EC1 and GC1.

Core hole	Depth (m)	Description
EC1	32.39 - 33.69	highly weathered
EC1	33.69 - 33.83	fractured zone
EC1	34.94	large fracture
EC1	36.11	large fracture
EC1	36.3	small fracture
EC1	38.17	large fracture (weathered zone of 1.14 m). Shale very soft. .
EC1	38.91	vertical fracture that runs for 22cm.
EC1	42.1	Small fracture
EC1	45.3	small fracture filled with calcite vein
EC1	49	small fractures with veins
EC1	51.95	large fracture with a zone of 15 cm
EC1	53.77	weathered zone of 5 cm. Partially filled with calcite vein
GC1	29.25 - 30.88	highly weathered
GC1	30.88 - 45.00	randomly scattered, some of them filled with calcite
GC1	48.37	weathered zone of 7 cm
GC1	51.18	Slickensides
GC1	53.5	Slickensides

Appendix B

The solution for the radial diffusion of a nonreactive solute from the rock matrix to a borehole follows the methodology given by Novakowski and van der Kamp (1996). The mass balance equation for radial diffusion in the porous rock matrix is given by:

$$\frac{\partial c}{\partial t} - D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) = 0 \quad (\text{A.1})$$

where r is the radial coordinate measured from the centre of the borehole, c is the aqueous concentration (per unit fluid volume) in the porous matrix, t is time, D is the effective diffusion coefficient in the porous matrix for the chemical constituent under consideration, which is the product of the free-water diffusion coefficient for the constituent under consideration and a formation factor, which is inversely proportional to the tortuosity of the porous matrix, $D = \frac{1}{\tau} D_d$, where D_d is the free-water diffusion coefficient and τ is the formation factor.

The initial and boundary conditions associated with (A.1) are

$$c(r, t = 0) = C_m \quad (\text{A.2})$$

$$c(r \rightarrow \infty, t) = C_m \quad (\text{A.3})$$

$$c(r = R, t) = C_w(t) \quad (\text{A.4})$$

where R is the radius of the borehole, C_m is the concentration in the porous matrix, which is assumed to be spatially uniform, and C_w is the concentration in the fluid column of the borehole, which is also assumed to be well mixed and uniform over the length of the borehole. Equation (A.2) defines the initial concentration in the porous matrix; (A.3) states that at large distances from the borehole, the concentration is unchanged; and (A.4) states that the concentration in the formation at the borehole wall is equal to the concentration in the fluid column of the borehole.

The concentration in the borehole, C_w , is governed by the following balance equation for the mass of the chemical constituent in the borehole:

$$V \frac{dC_w}{dt} = AnD \left. \frac{\partial c}{\partial r} \right|_{r=R} \quad (\text{A.5})$$

where A is the surface area of the borehole through which there is diffusion, V is the volume of the fluid in the borehole, and n is the porosity of the porous matrix. Equation (A.5) is subject to the following initial condition,

$$C_w(t=0) = C_B \quad (\text{A.6})$$

where C_B is the initial concentration of the chemical constituent in the borehole.

To solve equations (A.1)-(A.6), the following change in variables is applied,

$$c'(r,t) = c(r,t) - C_m \quad (\text{A.7})$$

$$C_w' = C_w - C_m \quad (\text{A.8})$$

which yields the following set of governing equations,

$$\frac{\partial c'}{\partial t} - D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c'}{\partial r} \right) = 0 \quad (\text{A.9})$$

$$c'(r,t=0) = 0 \quad (\text{A.10})$$

$$c'(r \rightarrow \infty, t) = 0 \quad (\text{A.11})$$

$$c'(r = R, t) = C_w'(t) \quad (\text{A.12})$$

$$V \frac{dC_w'}{dt} = AnD \frac{\partial c'}{\partial r} \Big|_{r=R} \quad (\text{A.13})$$

$$C_w'(t = 0) = C_B - C_m \quad (\text{A.14})$$

Equations (A.9)-(A.14) are solved by taking the Laplace transformation, and solving the resultant ordinary differential equation and boundary. The Laplace transformation of (A.9)-(A.14) is

$$p\bar{c}' - D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \bar{c}'}{\partial r} \right) = 0 \quad (\text{A.15})$$

$$\bar{c}'(r \rightarrow \infty) = 0 \quad (\text{A.16})$$

$$\bar{c}'(r = R) = \bar{C}_w' \quad (\text{A.17})$$

$$V(p\bar{C}_w' - C_B + C_m) = AnD \frac{\partial \bar{c}'}{\partial r} \Big|_{r=R} \quad (\text{A.18})$$

where p is the Laplace transform variable, and $\bar{c}'$ and $\bar{C}_w'$ are the Laplace transforms of c' and C_w' , respectively.

The solution to (A.15) is

$$\bar{c}'(r) = \bar{C}_w' \frac{K_0\left(\left(\frac{p}{D}\right)^{\frac{1}{2}} r\right)}{K_0\left(\left(\frac{p}{D}\right)^{\frac{1}{2}} R\right)} \quad (\text{A.19})$$

where the boundary conditions given in (A.16) and (A.17) have been applied, and K_0 is the modified Bessel function of the second kind of order 0.

In (A.19), $\bar{C}_w'$ is the Laplace transform solution for the concentration in the borehole, which is defined by (A.18). Introducing (A.19) into (A.18) yields

$$\bar{C}_w' = \frac{V(C_B - C_m)K_0\left(\left(\frac{p}{D}\right)^{\frac{1}{2}} R\right)}{pVK_0\left(\left(\frac{p}{D}\right)^{\frac{1}{2}} R\right) + An(Dp)^{\frac{1}{2}} K_1\left(\left(\frac{p}{D}\right)^{\frac{1}{2}} R\right)} \quad (\text{A.20})$$

and introducing (A.20) into (A.19) yields the solution for the concentration in the formation at any radial distance from the borehole,

$$\bar{c}'(r) = \frac{V(C_B - C_m)K_0\left(\left(\frac{p}{D}\right)^{\frac{1}{2}} r\right)}{pVK_0\left(\left(\frac{p}{D}\right)^{\frac{1}{2}} R\right) + An(Dp)^{\frac{1}{2}} K_1\left(\left(\frac{p}{D}\right)^{\frac{1}{2}} R\right)} \quad (\text{A.21})$$

The Laplace transform for $\bar{C}_w$ and $\bar{c}$, rather than $\bar{C}_w'$ and $\bar{c}'$, are obtained by taking the Laplace transform of (A.7) and (A.8) and introducing the results into the above equations to yield

$$\bar{C}_w = \frac{C_m}{p} + \frac{V(C_B - C_m)K_0 \left(\left(\frac{p}{D} \right)^{\frac{1}{2}} R \right)}{pVK_0 \left(\left(\frac{p}{D} \right)^{\frac{1}{2}} R \right) + An(Dp)^{\frac{1}{2}} K_1 \left(\left(\frac{p}{D} \right)^{\frac{1}{2}} R \right)} \quad (\text{A.22})$$

$$\bar{c}(r) = \frac{C_m}{p} + \frac{V(C_B - C_m)K_0 \left(\left(\frac{p}{D} \right)^{\frac{1}{2}} r \right)}{pVK_0 \left(\left(\frac{p}{D} \right)^{\frac{1}{2}} R \right) + An(Dp)^{\frac{1}{2}} K_1 \left(\left(\frac{p}{D} \right)^{\frac{1}{2}} R \right)} \quad (\text{A.23})$$

From the solution given in (A.23), the mass flux entering or leaving the borehole can also be calculated. The mass flux into or out of the borehole at a given time is defined by (A.5). Integrating (A.5) over time yields the total mass flux into or out of the borehole during the experiment,

$$F(t) = \int_{\tau=0}^{\tau=t} \left(AnD \frac{\partial c(\tau)}{\partial r} \Big|_{r=R} \right) d\tau \quad (\text{A.24})$$

where F is the total mass into or out of the borehole from the start of the test to time t. Taking the Laplace transformation of (A.24) yields

$$\bar{F} = AnD \frac{1}{p} \frac{\partial \bar{c}}{\partial r} \Big|_{r=R} \quad (\text{A.25})$$

where $\bar{F}$ is the Laplace transformation of F at time t. Introducing (A.23) into (A.25) yields

$$\bar{F} = - \frac{AnV(C_B - C_m)K_1 \left(\left(\frac{p}{D} \right)^{\frac{1}{2}} R \right)}{\left(\frac{p}{D} \right)^{\frac{1}{2}} pVK_0 \left(\left(\frac{p}{D} \right)^{\frac{1}{2}} R \right) + pAnK_1 \left(\left(\frac{p}{D} \right)^{\frac{1}{2}} R \right)} \quad (\text{A.26})$$

The solutions for C_w , c , and F are obtained by performing the inverse Laplace transformation to (A.22), (A.23), and (A.26), respectively. A numerical algorithm for performing the inversion of the Laplace transformation solution was implemented (see, e.g., Crump, 1976) to identify $C_w(t)$, $c(t)$, and $F(t)$.