Handbook for DNAPL Contaminated Sites in South Africa

JA Pretorius, BH Usher & RA Gebrekristos

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Handbook for DNAPL Contaminated Sites in South Africa

Report to the Water Research Commission

by

B.H. Usher, J.A. Pretorius and R.A. Gebrekristos

Institute for Groundwater Studies
University of the Free State
Bloemfontein 9300

Project Leader: B.H. Usher

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Handbook for DNAPL Contaminated Sites in South Africa

This document provides an overview of the most important considerations for DNAPLs in South Africa. The document discusses the sources and occurrence of DNAPLs and the most important factors controlling the migration and fate of DNAPLs and dissolved organics. A brief overview of appropriate site characterisation in South Africa is provided in this document, but more detailed information is given in one of the accompanying reports emanating from this project (see details below). Discussion of the expected behaviour of DNAPL contaminants in the major South African aquifer systems is provided in a separate section, which highlights the differences between the types of aquifer, and the implications these differences have on migration, understanding and assessment. For each of these a generalised conceptual model of DNAPL contamination is provided as a first step toward understanding these interactions in local aquifers.

This report is aimed at site investigators, geohydrologists, site-owners and regulators (DWAF and local authorities).

This document forms part of a series of documents, produced by Water Research Commission project K5/1501 "*Field investigations to study the fate and transport of dense non-aqueous phase liquids (DNAPLs) in groundwater*".

The documents in this series include:

- Executive Summary of the Project
- Manual for Site Assessment at DNAPL Contaminated Sites in South Africa
- Groundwater monitoring guidelines for DNAPLs in South African Aquifers
- Guidelines for the acceptance of Monitored Natural Attenuation processes in South Africa
- *Handbook for DNAPL Contaminated Sites in South Africa*
- An Introduction to DNAPLs in South Africa: A Community Guide
- Field and laboratory investigations to study the fate and transport of DNAPLs in groundwater

All these documents are contained on the CD included with this report.

Glossary

Biodegradation	The degradation of contaminants in either the unsaturated or the saturated zones as a result of biological activity. The rate of biodegradation depends on factors such as the presence of micro-organisms capable of degrading the contaminant(s), availability of electron acceptors, temperature and the specific contaminant of interest. Biodegradation typically results in the formation of daughter products, which may or may not biodegrade in the system of interest. Biodegradation manifests itself as lower contaminant (parent) concentrations in groundwater and a shorter steady-state plume. If oxygen is the primary electron acceptor, the degradation process is referred to as aerobic. Anaerobic degradation occurs when oxygen has been depleted and other electron acceptors such as nitrate, sulphate, iron or manganese facilitate degradation.
Capillary pressure	The pressure difference between the non-wetting fluid and the wetting fluid. Capillary pressure arises because of interfacial tension. The capillary pressure is directly proportional to the interfacial tension, and inversely proportional to the radius of curvature of the fluid-fluid interface. Usually expressed in Pascals (Pa).
Density	Mass per unit volume. Usually expressed in kg/m^3 for liquids such as DNAPLs.
Dispersion	The spreading of aqueous phase contaminants due to small-scale velocity variations in both porous and fractured media. Because of dispersion, concentrations decrease towards the leading and side edges of a plume.
DNAPL (dense non-aqueous phase liquid)	A liquid that is denser than water and only slightly soluble in water. DNAPLs exist in the subsurface as a separate fluid phase in the presence of either air or water, and can both vaporise into air and slowly dissolve into flowing groundwater. Examples include chlorinated solvents, creosote, and coal tar and PCB oils.
DNAPL component composition	The composition of a DNAPL. The various components that combine to form the DNAPL phase are each present at a specific mass fraction. In some cases, the DNAPL of interest may be a single component liquid (for example, pure trichloroethene) and in other cases it may be composed of many different chemical constituents (for example, creosote).
DNAPL dissolution	The transfer of components present in the DNAPL to the water phase. Over time, the DNAPL composition will change as certain components dissolve out of the DNAPL earlier than other components. The effective solubility of these other components will therefore increase later.
Effective solubility	The aqueous solubility of a compound in (ground)water, where that compound is derived from a multi-component DNAPL. The effective solubility is proportional to the molar fraction of that compound in the DNAPL and the compound's single component solubility (as described by Raoult's law).
Fracture entry pressure	The threshold capillary pressure required for a non-wetting fluid to enter a wetting-fluid saturated fracture. Fracture entry pressures are directly proportional to the interfacial tension and inversely proportional to the fracture aperture. Usually expressed in Pascals (Pa).
Fracture porosity	Volume of open fractures per unit volume of bulk rock. Typical values range between 0.001 and 0.01 (that is, 0.1-1 percent).

Interfacial tension	A tensile force that exists in the interface between immiscible fluids. Without interfacial tension, DNAPLs would be fully miscible (infinitely soluble) in water. The fact that interfacial tension exists between a DNAPL and water is a defining feature of a DNAPL. Interfacial tension can be measured in the laboratory; typical units are N/m and dynes/cm (1,000 dynes/cm = 1 N/m). Interfacial tension exists between any pair of immiscible fluids such as air and water, DNAPL and water, and DNAPL and air.
LNAPL (light, non-aqueous phase liquid)	A liquid that is denser than water and only slightly soluble in water. LNAPLs exist in the subsurface as a separate fluid phase in the presence of either air or water, and can both vapourise into air and slowly dissolve into flowing groundwater. Examples include fuel oils such as diesel, petrol and heating oil.
Matrix diffusion	The transfer of contaminants dissolved in groundwater from open fractures to the rock or clay matrix. If concentrations are higher in the open fractures, diffusion will occur into the rock or clay matrix (forward diffusion). If concentrations are higher in the matrix, diffusion will occur out of the rock or clay matrix into water in the fractures (back-diffusion). As a consequence of matrix diffusion, contaminants in fractures will migrate more slowly than the groundwater.
Plume	A contiguous region of groundwater containing dissolved contaminants. Plumes are typically formed by the dissolution of DNAPL into groundwater and therefore occur hydraulically down-gradient of the DNAPL source zone. Plume migration is subject to advection and dispersion, and may be subject to sorption, biodegradation and matrix diffusion.
Pooled DNAPL	A continuous distribution of DNAPL in either porous media or fractures. DNAPL pools in porous media form above capillary barriers and typically range in both length and thickness from several centimeters to several metres. Pooled DNAPL is potentially mobile and is relatively easy to mobilise through increases in the hydraulic gradient (for example, as brought about by groundwater pumping). DNAPL pools in fractured media tend to form in horizontal and sub-horizontal fractures rather than vertical or steeply dipping fractures.
Porous media displacement pressure	The threshold capillary pressure required for a non-wetting fluid to enter a wetting-fluid saturated porous medium. Lower permeability media such as silts and clays exhibit higher displacement pressures than more permeable media such as coarse sands and gravels. Usually expressed in Pascals (Pa).
Residual DNAPL	Disconnected blobs and ganglia of organic liquid (DNAPL) trapped by capillary forces in either porous or fractured media. Residual DNAPL forms at the trailing ends of a migrating DNAPL body because of pore-scale hydrodynamic instabilities. Residual DNAPL saturations are typically between 5 percent and 20 percent of pore space for both porous media and fractures. Residual DNAPL is difficult to mobilize through increases in the hydraulic gradient (for example aggressive groundwater pumping).
Sorption	The transfer of contaminants dissolved in water to the solid phase (typically fracture walls, the surfaces of sand/silt/clay grains or the surfaces of the solid portion of the rock matrix). Sorption is typically higher for more hydrophobic contaminants and higher where greater amounts of naturally occurring organic carbon are present on the solid surfaces of interest.
Source zone	That region of the subsurface containing residual and/or pooled DNAPL.
Steady-state plume	The term applied to a contaminant plume that is no longer advancing in flowing groundwater. The time required to reach a steady-state configuration and the resulting length of the steady-state plume depend on factors such as groundwater velocity and the degree of dispersion, sorption and biodegradation occurring.

Vaporisation	The transfer of mass from the DNAPL phase to the air phase (often referred to as evaporation). The rate of vaporisation is proportional to the vapour pressure of the DNAPL, which in turn is temperature dependent. Highly volatile DNAPLs such as some chlorinated solvents will vaporise quicker than low volatility DNAPLs such as PCB oils. In a multi-component DNAPL, the individual compounds with high vapour pressures will vaporise more quickly than those with lower vapour pressures, resulting in an enrichment of the DNAPL in the low vapour pressure compounds over time (referred to as weathering).
Viscosity	The shear resistance to flow of a fluid. Higher viscosity (thicker) fluids migrate more slowly in the subsurface than lower viscosity (thinner) fluids. Viscosity is temperature-dependent and should be measured in the laboratory at the subsurface temperature of interest. Typical units include Pascal seconds (Pa s), centipoises (cP), and centistokes (cSt).
Volatilisation	The transfer of contaminants dissolved in water to the air phase. Volatilisation is characterised by the Henry's law constant of the dissolved contaminant of interest.
Wettability	Describes the affinity of one fluid for a solid surface in the presence of a second fluid. The fluid that preferentially wets the solid surface is referred to as the wetting fluid and the other as the non-wetting fluid. A perfectly wetting fluid spreads spontaneously to coat the solid surface. A perfectly non-wetting fluid repels the solid surface and typically forms a spherical (beaded) shape on the solid surface. In many subsurface systems, water is wetting with respect to air, DNAPL is wetting with respect to air, and water is wetting with respect to DNAPL. Wettability is quantified by the contact angle, which is the angle measured between the fluid-fluid interface and the solid surface at the point of contact with the solid. Wettability is dependent on the chemical composition of the groundwater, the chemical composition of the DNAPL and the chemical composition of the solid surface of interest.

List of Abbreviations

Abbreviations	**Definition**
CF	Chloroform
CHC	Chlorinated Hydrocarbons
DCA	Dichloroethane
DCE	Dichloroethene
DNAPL	Dense Non-aqueous phase liquid
DO	Dissolved Oxygen
EC	Electrical Conductivity
foc	Fraction of organic carbon in solid material
LNAPL	Light Non-aqueous phase liquid
mbgl	meters below ground surface
NAPL	Non-aqueous phase liquid
ORP	Oxidation/Reduction Potential
PAH	Polyaromatic hydrocarbons
PCE	Perchloroethene/Perchloroethylene/Tetrachloroethene
PCR	Polymerase Chain Reaction
PID	Photoionisation detector
PVC	Polyvinylchloride
TCE	Trichloroethene/Trichloroethylene
TPH	Total Petroleum Hydrocarbons
VC	Vinyl Chloride
VOC	Volatile Organic Compounds

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1. INTRODUCTION

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

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

Research support for the above-mentioned strategy was given through a WRC funded research programme, which focuses mainly on urban areas (Usher *et al.*, 2004), where intensive land-use as a consequence of increased human settlement and economic development, can have serious impacts on groundwater quality. The programme outputs were to establish an improved understanding of the origin of pollutants, the pathways which these pollutants could follow into the environment and the ultimate fate of these pollutants. One of the findings of this project was the urgent need for research into the fate and transport of Non-Aqueous Phase Liquids (NAPLs), as these are the most widespread groundwater contaminants found in urban aquifers.

DNAPL contamination is a worldwide phenomenon which has been thrust upon developing countries during recent years. Much of this type of contamination has taken place during the industrial development following World War II. These organic contaminants are found in a wide range of industrial manufacturing and operational processes. Recognition of the halogenated solvent (or DNAPL) problem in the United States did not come until the early 1980's. The lateness of the recognition was due to a lack of monitoring of organic compounds in groundwater (Schwille, 1988). In South Africa the monitoring of organic contaminants does not yet take place on a wide scale. Increase in the awareness of the problem is needed in South Africa and the implementation of appropriate monitoring systems.

This report is one of a series of documents produced as part of the project. The purpose of this handbook is to provide a user-friendly overview of the nature of DNAPL contamination in a South African context. It is intended to assist site investigators, site owners and regulators in evaluating site investigations and making informed decisions with regard to mitigation and management options at DNAPL contaminated sites.

2. TYPES AND OCCURRENCE OF DNAPL CONTAMINANTS

2.1 General

In general, a DNAPL is defined as a heavier-than-water organic liquid that is only slightly soluble in water. The potential for widespread contamination of groundwater by DNAPLs is substantial because of the extensive production, transport, utilization, and disposal of large volumes of DNAPL chemicals. There are thousands of potential sites in South Africa, as elsewhere in the world, where DNAPLs may have been released to the subsurface in varying quantities. DNAPL chemicals are frequently detected in groundwater at contaminated sites even where DNAPL presence has not been determined.

All DNAPLs can be characterised by their physical properties such as: density, viscosity, and interfacial tension with water, component composition, and solubility in water, vapour pressure and wettability. The most prevalent DNAPL types are outlined in Table 5 in Appendix A, with summary information on DNAPL density and viscosity, appearance, and usage.

The first step in the assessment of a potential DNAPL site is the consideration of the potential chemicals that might be present at the site. A wide variety of chemical products and wastes may comprise a DNAPL.

For a chemical (or chemical mixture) to be considered as a DNAPL, it must have a fluid density greater than 1.01g/cm^3, a solubility in water of less than 2% (or 20000 mg/ℓ) and a vapour pressure of less than 300 torr (Pankow and Cherry, 1996).

Thus, the amount of chemical released had to be in excess of the total amount that could have dissolved or be sorbed on the soil materials in the source zone.

The major DNAPL types include: halogenated hydrocarbons, especially *solvents, coal tar and creosote, Polychlorinated Biphenyls (PCBs), some pesticides, and miscellaneous or mixed DNAPLs.* Of these types, the most extensive subsurface contamination is associated with halogenated (primarily chlorinated) solvents, either alone or within mixed DNAPL sites, due to their widespread use and properties (high density, low viscosity, significant solubility, and high toxicity). Appendix A gives a list of selected DNAPLs with their viscosity and density values. The appearance, occurrence, and uses are also given.

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

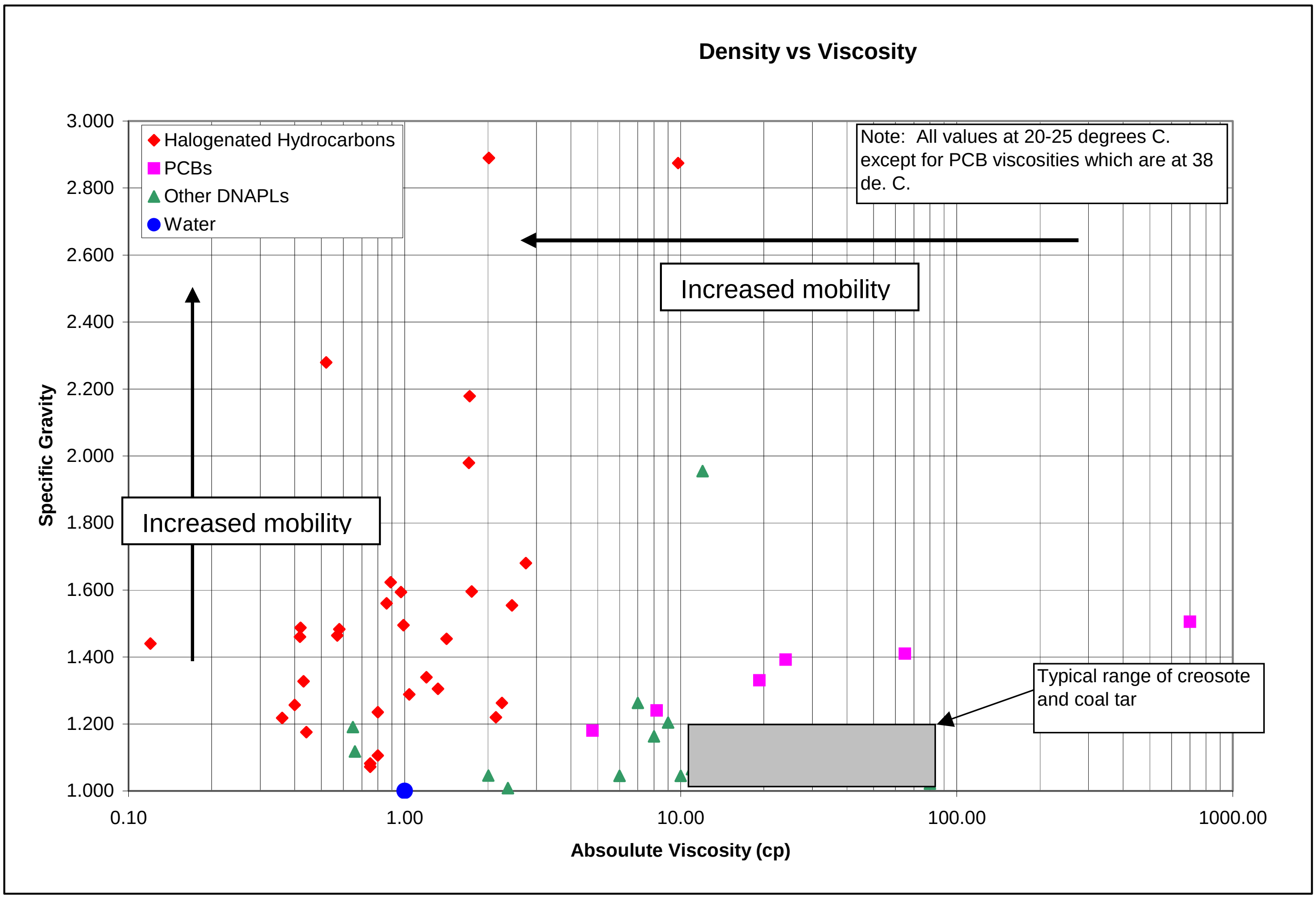


Figure 1: Density versus absolute viscosity for some DNAPLs.

(Adapted from Cohen and Mercer, 1993)

An increase in Density:Viscosity ratio also relates to increased mobility of a DNAPL (Figure 2).

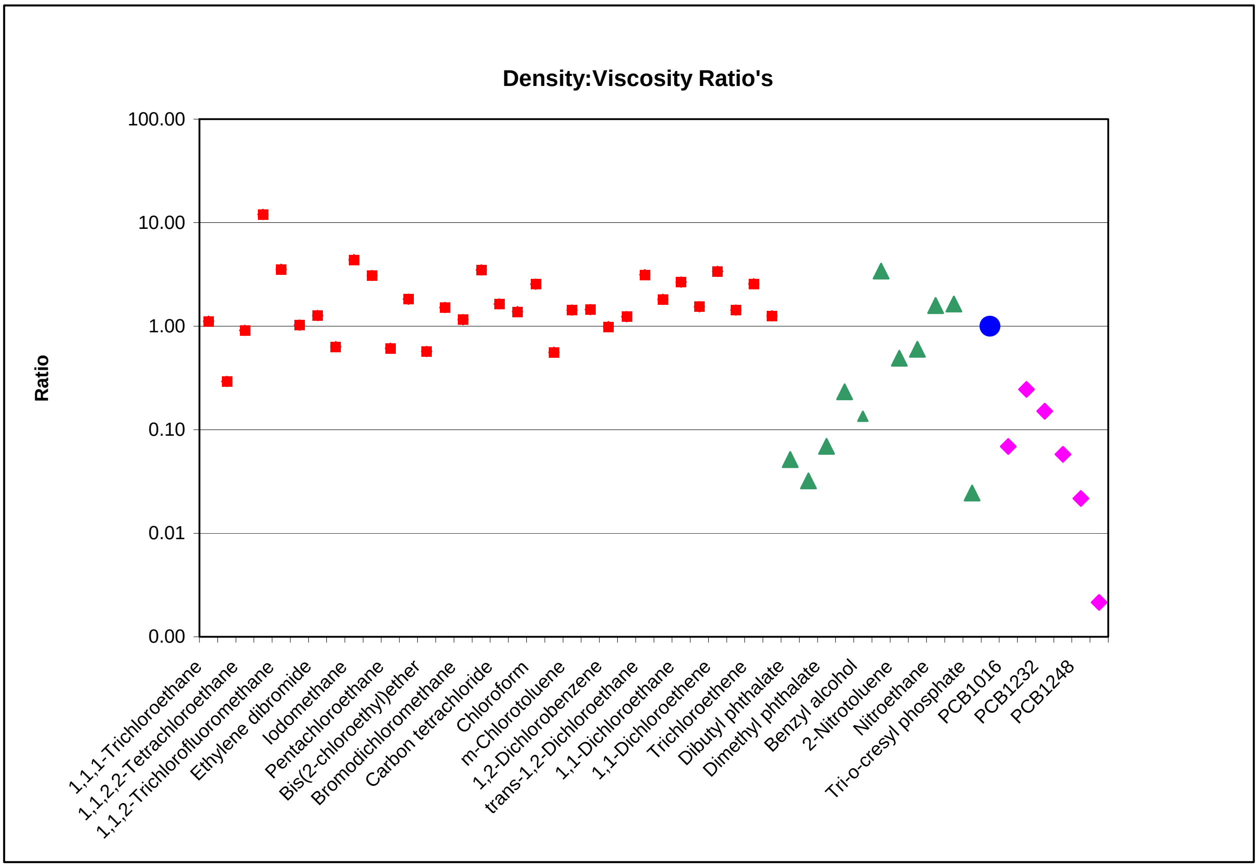


Figure 2: Density:Viscosity ratios for selected DNAPL contaminants, mobility increases with increased ratio. (Squares- Halogenated hydrocarbons, triangles-PAHs, diamonds-PCBs, circle-water)

2.2 *Inventory of potential sources of DNAPL contaminants in major urban areas of South Africa*

From the project undertaken by the WRC into groundwater contaminants in urban catchments of South Africa (Usher *et al.*, 2004, WRC Report No. 1326/1/04) a contaminant inventory and priority list of all possible groundwater contaminants in these environments was compiled for urban related activities. All possible sources (activities) were identified within the urban environment and expected contaminants assigned to each source. These were prioritized according to set criteria.

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

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

- Educate managers and the public about the potential threats to the water supply posed by various activities.

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

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

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

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

Appendix A, is an adapted version of the contaminant inventory as was compiled by Usher *et al*. (2004). Only organic contaminants are included in the list. It must be noted that some contaminants listed (e.g. petroleum hydrocarbons), can rather be classified as Light Non Aqueous Phase Liquids (LNAPLs), thus implying a density or specific gravity less than that of water. The reason for inclusion can be attributed to the complex behaviour of NAPLs and the changes that take place when contaminant mixtures are considered, as opposed to single component contaminants. These mixtures would more often than not, rather behave as a DNAPL than as a LNAPL. (This behaviour will be discussed in detail in a later section.)

2.3 Prioritisation of DNAPL contaminants and sources in major urban areas of South Africa

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

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

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

Out of the 50 possible sources, 36 are sources of DNAPL contamination (see Table 1 and Table 7). Out of the top ten ranked sources only on-site sanitation, cemeteries and feedlot/poultry farms are excluded from this list. From this prioritization, a picture of the widespread occurrence and extent of the DNAPL problem in South Africa is emerging.

Table 7 is also adapted from Usher *et al*. (2004). Only the NAPL type contaminants with their ranking are included. Out of the 121 contaminants listed in the national prioritization list, 64 can be considered to be DNAPL contaminants. However, not all the contaminants listed have the physical properties of a DNAPL. Many of the contaminants listed are often either used as intermediates to synthesize compounds with DNAPL properties, or are found at sites often associated with the better known and more common DNAPL contaminants (e.g. solvent use). The properties of the contaminant mixture found in the aquifer, will determine the behaviour of the NAPL source.

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

Table 1/…

Table 1: Prioritisation list of sources of possible DNAPL groundwater contamination in urban environments

(Adapted from Usher et al., 2004).

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

Table 2/…

Table 2: Contaminant Prioritisation – NAPL contaminants with ranking

(Adapted from Usher et al., 2004).

Contaminant prioritisation (from highest to lowest risk)			
1	Chlordane	46	Ethylene oxide
2	HCH	47	Ethylene Dibromide
3	Lindane	48	Dioxane 1,4
4	DDD	49	Chlorine Dioxide
5	Butadiene	50	Carbon Tetrachloride
6	Trichloroethylene	52	Benzidine
8	Dichloromethane	53	Trichlorobenzene
9	Tetrachloromethane	54	Toluene
10	Phenol	56	Dichloroethylene
11	Atrazine	57	DDE
12	TCA	59	Chloroform
13	Formaldehyde	61	Diuron
14	Creosote	62	Heptane
15	Dichlorobenzene	63	Chlorobenzene
16	MEK	66	Tetrachlorobenzene
19	Acrylonitrile	72	Ethylbenzene
20	Vinyl Chloride	73	Ethyl Alcohol
22	Trichlorophenol 2,4	74	Ethyl Acetate
23	Dichloropropane 1,2	79	Tri-n-Nutyltin Oxide
24	Dichlorophenol 2,4	81	Styrene
28	Benzene	88	Perchloroethylene
29	Arsenic	91	Naphthalene
30	Methylene Chloride	94	Glycol
31	Tebuthiuron	95	Fluorocarbon 113
33	Monosodium-Methyl Arsenate	96	Floridebenzene
34	Isopropanol	97	Chloropyrifos
35	Acetone	98	Chlorofluoroethane
41	Aldicarb	101	Butane
42	Xylene	103	Acetylene
43	Trichloroethane 1,1,1,-	104	Phthalates
44	Pentachlorophenol		

2.3.1 DNAPL pollution in Africa

As is the case in South Africa, very few published cases of NAPL contamination is available for the rest of the continent. In a book on Groundwater Pollution in Africa published in 2006 (Editors Xu and Usher), the following remarks are made by the editors:

"There are a multitude of well-documented potential sources of groundwater pollution and this section shows that these also exist in the African continent.

The anthropogenic sources include discussions on pollution caused by sewerage and petrol station leakage and acid mine drainage. While these are largely point sources, the ubiquity of these problems across Africa merits discussion. …

It is important to note that this book is not comprehensive in terms of all the types of groundwater pollution. In urban areas, Africa should take cognizance of the priority pollutants and sources from North America and Europe. Potential sources should be identified, and proactive measure implemented to prevent contamination of the groundwater resources by toxic, carcinogenic and recalcitrant chemicals. It is with a note of caution that the absence of case studies on non-aqueous phase liquids (NAPLs) and groundwater remediation in this section is highlighted, with a view to pointing out the challenges ahead and the mistakes Africa should avoid.

The value of groundwater in Africa can not be overemphasized, and raising awareness to communities and decision makers regarding pollution sources, particularly those that may lead to more persistent groundwater quality degradation, should form an integral part of the landuse planning and regulation in this continent."

On the Blacksmith Institute's web page (http://www.blacksmithinstitute.org/about.php) several cases of sites polluted from industrial chemicals are listed in Africa. In November of 2003, Blacksmith Institute launched the "Polluted Places Initiative" to address severely polluted sites throughout the world. By identifying polluted sites directly through an on-line nomination process, researching each site and publishing dossiers online, and conducting site assessments to consult with local stakeholders, Polluted Places seeks to streamline and target the way in which Blacksmith addresses pollution in the developing world.

One of the worst cases listed is in Baie de Hanne, Senegal. Potentially 2 million people are affected by pollutants such as PCB, Heavy Metals, Chemicals, Tannery Waste, Sewage, and Solid Waste. PCB's are also listed as a major problem in Guinea, Tanzania and Zambia.

2.4 Halogenated Solvents

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

Although most chlorinated solvents were first synthesized during the 1800s, large-scale production generally began around the middle of the 1900s. Typical uses of these chemicals include dry cleaning, metal degreasing, pharmaceutical production, pesticide formulation and chemical intermediates. Chlorinated solvents typically enter the subsurface as a result of past disposal directly onto land, storage and disposal into unlined evaporation ponds and lagoons, leaking storage tanks and vapour degreasers, leaking piping and accidental spills during handling and transportation. Chlorinated solvents can be encountered as single component DNAPLs or as part of a multi-component DNAPL containing other organic compounds such as PCB oils, mineral oils and fuels. The four principal chlorinated solvents are: perchloroethylene (PCE), trichloroethylene (TCE) 1,1,1-trichloroethane (1,1,-TCA) and dichloromethane (DCM).

Fluorocarbons were discovered in the search for improved refrigerants in 1930. Fluorocarbon is used as refrigerants, foam blowing agents, solvents, fluoropolymers (such as teflon), and as aerosol propellants. Prior to 1974, when concerns arose regarding atmospheric ozone depletion, aerosol propellants were the main end use of fluorocarbons.

Most of domestic bromine output is used to manufacture ethylene dibromide (EDB) for use in engine fuel antiknock fluids to prevent lead oxide deposition. Use of EDB for this purpose, will diminish with the phase out of leaded petrol internationally. Brominated hydrocarbon DNAPLs are also used as fire retardants and fire extinguishing agents, and in a variety of other products.

The halogenated solvents present an extremely high contamination potential due to their extensive production and use, relatively high mobility as a separate phase (high density:viscosity ratio), significant solubility and high toxicity (Cohen and Mercer, 1993). Most of the chlorinated solvents have densities that range from 1.1 g/cm^3 to 1.63 g/cm^3. Viscosities are less than or similar to water. The solubilities are as much as a hundred thousand times higher than the respective drinking water standards (USEPA).

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

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

Limited published data is available in South Africa on DNAPL contamination from solvent mixtures. Morris *et al*. (2000) describes 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. A pump and treat system was used as containment and rehabilitation method. Total chlorinated hydrocarbon concentrations of 100 000 ppb at a depth of 30 meters below surface was measured at an industrial hazardous waste site in Durban (Palmer and Cameron-Clarke, 2000). Modelling and field trials was developed as part of the rehabilitation strategy. In a high profile court case, subsistence farmers alleged that a steel works has poisoned their water, harming their health and that of their livestock by pumping harmful industrial effluent into the environment. The farmers' lawyers argue that the primary cause of the pollution lies in the plant's vast "evaporation" and furnace sludge dams that cover an area of about 140ha. The dam closest to the applicants' properties receives dangerous contaminants including benzene, toluene and xylene. The borehole water has at times given off a strong smell of naphthalene, which is toxic and can cause cancer, respiratory depression and lung tumours (DEAT, 2003).

2.5 Coal tar and Creosote

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

Coal tar was historically produced as a by-product of manufactured gas operations up until approximately 1950, and is currently still produced as a by-product of blast furnace coke production. The tars are made up of 500 to 3000 different compounds, typically toxic to humans, mammals, and plant life. Tar is not to be considered equivalent to asphalt, which is a residual of natural petroleum deposits and of oil refineries. Also associated with gas manufacturing were captured impurities such as ammonia, cyanide, sulphur and heavy metals, particularly arsenic. Coal tar contains hundreds of hydrocarbons, including light oil fractions, middle oil fractions, heavy oil fractions, anthracene oil and pitch. The density of coal tar typically ranges from 1,010 to 1,100 kg/m^3 and the viscosity from 20 to 100 cP. The relatively low density and high viscosity of coal tar implies that it may still be migrating as a DNAPL at sites where it was introduced to the subsurface many years earlier. With respect to the impact on groundwater, most investigators typically select a subset of compounds to assess the impact on water quality. These may include the suite of BTEX compounds (benzene, toluene, ethylbenzene and xylenes), as well as PAHs including benzo[a]pyrene, naphthalene and phenanthrene (Kueper *et al.,* 2003).

Creosote is composed of various coal tar distillates and was commonly used to treat wood products such as railway sleepers and telegraph poles. It is still used today in certain timber-treating operations and as a component of roofing and road tars. Creosote contains many hydrocarbons, primarily, polycyclic aromatic hydrocarbons (PAHs) and phenolic compounds. Creosote may be blended, however, with up to 50% of a carrier fluid such as diesel fuel prior to use. The density of creosote typically ranges between 1,010 and 1,130 kg/m^3, depending on the amount and type of any carrier fluid. Creosote is therefore one of the least dense DNAPLs of environmental interest. It often takes a long time for movement to cease following initial release into the subsurface because creosote is only slightly denser than water and has a relatively slow downward (gravity-driven) migration. The relatively high viscosity of creosote, which typically ranges between 20 and 50 cp, also facilitates the long migration timescale (Kueper *et al.*, 2003).

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

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

2.6 Polychlorinated biphenyls (PCBs)

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

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

PCBs were frequently mixed with carrier fluids prior to use. For example, PCBs were typically diluted with 0% to 70% carrier fluid, usually chlorobenzenes or mineral oil, in askarel (Askarel is a generic name for fire-resistant dielectric fluids). The mix of Aroclor and carrier fluid type and content, therefore, determines the physical properties of the PCB fluid, including its density, viscosity, solubility and volatility. Depending on the particular combination of congeners present and the type of carrier fluid, the density of most PCB oils encountered in practice ranges from approximately 1,100 to 1,500 kg/m^3, while the viscosity ranges from approximately 10 to 50 cP (Kueper *et al.*, 2003). The relatively high density of PCB oils indicates that the timescale of migration may be relatively short, but their relatively high viscosity results in an intermediate range of timescales of migration.

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

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

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

2.7 *Miscellaneous and Mixed DNAPLs*

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

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

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

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

3. BEHAVIOUR OF DENSE NON-AQUEOUS PHASE LIQUIDS IN THE SUBSURFACE

3.1 Introduction

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

In this section the factors controlling the behaviour of DNAPLs will be discussed as well as the distinctive behaviour in different aquifer types, including porous media, fractured media and porous fractured media. It is especially the latter two types of aquifer media, which are applicable in South Africa, and thus the focus of this handbook will be on these types of aquifers.

3.2 Physical Properties related to DNAPL Migration

The physical properties of the organic compounds affect their behaviour in the subsurface (Fetter, 1999). Some of these physical properties are, for example, interfacial tension and wettability, density, viscosity, solubility, Henry's law constants, capillary pressure, and relative permeability. Table 3 summarises some of the important physical properties of DNAPL compounds and how these affect their behaviour as groundwater contaminants.

Table 3: Physical properties of DNAPLs affecting their behaviour

(Adapted from Fetter, 1999).

Parameter [and Units]	Derivation	Behaviour
Melting Point [˚C] or Boiling Point [˚C] at 1 atm.	Specific phase dependant on temperature	Compound will be present as gas, liquid or vapor as a function of temperature
Specific Gravity	Ratio of weight of a given volume of a substance (at 20°C) to weight of same volume of water (at 4 °C)	Substance will float on water if specific gravity of pure substance < 1. Substance will sink in water if specific gravity of pure substance > 1
Water Solubility [ppm or ppb]	A measure of how readily a substance will dissolve in water. Liquids: solubility is a function of the temperature of the water and the nature of the substance. Gases: water solubility must be measured at a given vapor pressure.	More soluble substances have a greater potential mobility. The solubilities of organic compounds can range from being completely miscible with water to being totally immiscible (insoluble) with water.
Octanol-Water Partition Coefficient (K_{ow})	A measure of the degree to which an organic substance will preferentially dissolve in water or an organic solvent. The coefficient is the ratio of the equilibrium concentrations of the substance in two immiscible fluids, water and octanol.	The greater the coefficient, the greater the tendency for the substance to dissolve in an organic liquid/solvent and the less mobile the free phase substance will be in the aqueous environment.
Distribution Coefficient (K_d)	A measures of how strongly a substance adheres to soil as opposed to remaining dissolved in water or the ratio of the mass of a substance adsorbed per unit mass of soil to the mass of the substance remaining in solution at equilibrium.	Substances with high K_d values are not very water soluble and will preferentially adhere to soils. Such substances are unlikely to be transported as dissolved constituents but rather transported adhered to sediment particles.
Vapor Pressure [Pa or mm Hg or psi or atm]	The pressure of the gas in equilibrium with the liquid or solid at a given temperature. A measure of the tendency of a substance to pass from solid or liquid states to a vapor state (i.e. a measure of how readily a substance will evaporate).	The greater the vapor pressure, the more volatile the substance.
Vapor Density (of a gas)	The vapor density is related to the equilibrium vapor pressure, the gram molecular weight of the gas and the temperature.	Indicates whether a gas will rise (i.e. gas lighter than air) or sink (i.e. gas denser than air) in the atmosphere.
Henry's Law Constant	Relates to a linear relation between the partial pressure of a gas above a liquid and the mole fraction of the gas dissolved in the liquid. Can also be applied to organic compounds that are volatile liquids when dissolved in water	The greater the Henry's Law constant, the greater the rate of volatilization from soil or water.

The following sections give a brief overview of some of the properties listed in the table above, and how this relates to the physical concepts of DNAPL migration.

3.2.1 Density and Viscosity

Density, defined as mass per unit volume, is closely related to specific gravity, which is the ratio of a substance's density to that of water.

Mercer and Cohen (1990) state that density differences of ~ 1%, can influence fluid movement in the subsurface, in many situations NAPL densities differ from that of water by 10-50%.

The relatively high density of chlorinated solvents means that they may penetrate the water table and flow downward, directed by paths of least capillary resistance, even possibly against the direction of groundwater flow.

Viscosity is a measure of a liquid's internal resistance to flow. Lower DNAPL viscosity results in deeper penetration of an aquifer in a given time. Coal tars and creosote (See Figure 1 and Figure 2) are examples of DNAPLs with high viscosities and thus lower mobility rates as opposed to the halogenated solvents (with low viscosities).

3.2.2 Solubility

When organic chemicals are released into the environment from a mixture like a petroleum hydrocarbon fuel, the water solubilities of the chemicals are typically far lower than their published solubilities. For example, the solubility of benzene is around 1750 mg/ℓ, but typical maximum benzene concentrations resulting from equilibrium between petrol and water is only 20 to 40 mg/ℓ. This occurs because the concentration (or effective solubility) depends on the relative abundance of the chemical in the fuel. This behaviour is based on an extension of Raoult's Law and is related to the relative mole fraction of the contaminant within the total spill or release of organics (Schwarzenbach *et al.*, 1993). This can be calculated as:

$$C_W = x_o S \qquad \textit{Equation (1)}$$

where C_W is the effective solubility, x_o is the mole fraction (of the organic compound in the mixture) and S is its solubility. The mole fraction is calculated from:

$$x_o = MF_x \, MW_o / MW_x \qquad \textit{Equation (2)}$$

where MF_x is the mass fraction of the selected organic compound in the mixture, MW_o is the average molecular weight of the mixture and MW_X is the molecular weight of the selected compound.

In many studies, the octanol-water partition coefficient, K_{ow}, is used to describe the degree to which an organic substance will preferentially dissolve in water or an organic solvent. The substance is mixed with equal amounts of two immiscible fluids, water and octanol. The coefficient is given by the ratio:

$$K_{ow} = C_{octanol} / C_{water} \qquad \textit{Equation (3)}$$

where $C_{octanol}$ is a measure of the equilibrium concentration of the substance in octanol and C_{water} the equilibrium concentration in water. K_{ow} is usually reported as a logarithm. The greater the value of log K_{ow}, the greater the tendency of the organic substance to dissolve in the organic liquid, rather than in the water. Thus, the larger the octanol-water partition coefficient, the less mobile the compound is in the environment (Fetter, 1999).

3.2.3 Volatility

The pure phase of each contaminant will have its own specific capacity to mobilise from the liquid to gaseous phase. The Henry's Law constant of a compound defines the partitioning of that compound between the air and water phases:

$$K_h = C_a / C_w \qquad \text{Equation (4)}$$

where K_h is the dimensionless Henry's constant, C_w and C_a are the concentration in mass per volume units in water and air, respectively. This law can be applied to organic compounds that are volatile liquids when they are dissolved in water. The greater the Henry's law constant is, the greater the rate of volatilisation from soil to air (Fetter, 1999).

3.2.4 Interfacial tension

Interfacial tension is a representation of the co-existence of liquids at different pressures. This is the most important physicochemical property controlling multiphase fluid migration in the subsurface.

At the interface between two liquid phases, the cohesive forces acting on the molecules in either phase are unbalanced: this exerts tension on the interface - similar to that on a stretched membrane - causing the interface to contract to as small an area as possible. A force balanced on a curved interface between two fluids leads to the conclusions that the pressure in the fluids on either side of the interface is not equal, the difference being given by equation:

$$\Delta P= 2\sigma/r \qquad \text{Equation (5)}$$

Where ΔP is the pressure difference across the interface, σ is the interfacial tension, and r is the radius of curvature of the interface (Pankow and Cherry, 1996).

Interfacial tension is seen to be the property that permits two fluids to exist in contact at different pressures. Values of interfacial tension range from about 20 to 50 dynes/cm for most water-DNAPL pairs (Mercer and Cohen, 1990).

It is important to remember that DNAPLs at field sites have often undergone changes or are found in complex mixtures, thus the interfacial tension of the DNAPL found at the site should be measured.

3.2.5 Wettability

Wettability is a measure of a liquid's relative affinity for a solid. Where two liquid phases are present, the 'wetting' fluid will preferentially spread over the solid surface at the expense of the 'non-wetting' fluid. Wettability is depicted by the concept of a contact angle, the angle subtended by the liquid-liquid interface and the solid surface. Since wettability conventionally refers to the non-aqueous phase, the angle is measured through the aqueous phase as seen below:

It is commonly the case that DNAPLs are non-wetting relative to water; this relationship is illustrated by the fact that although both fluids are in contact with the solid, the water has a greater affinity for the surface (wetting), which produces a contact angle of less than 90°. This implies that, the majority of DNAPL contaminants will rather be restricted to the larger openings, while water occupies the smaller pore spaces and preferentially spreads across solid surfaces.

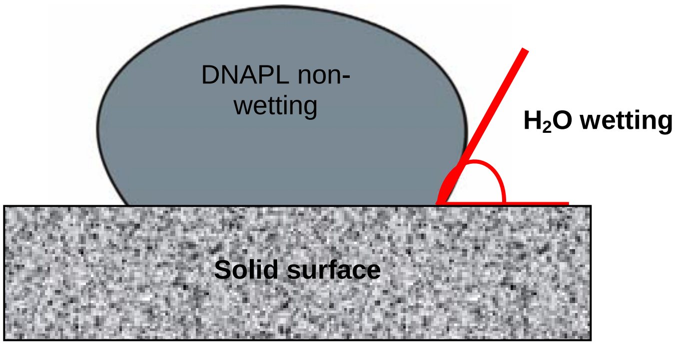


Figure 3: Wettability: Contact angle < 90° then DNAPL equals non-wetting fluid, water equals wetting fluid.

In the rarer case of a DNAPL having greater affinity for a solid (wetting) than water (non-wetting), the contact angle is will be greater than. This is often referred to as an oil-wet surface.

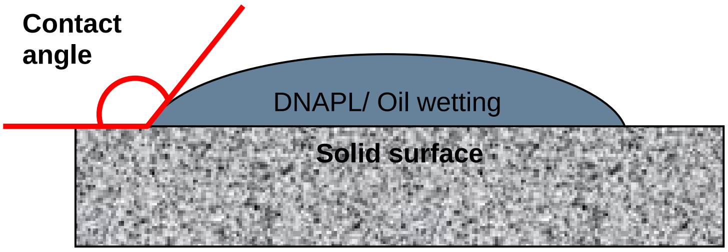


Figure 4: Wettability: Contact angle > 90°, DNAPL equals the wetting phase.

From the above cases, it follows that it should be theoretically possible to attain a contact angle of 90°. This neutral condition is approached by mixtures such as crude oil & water and coal-tar & water in which the NAPL can be termed 'neutrally wetting'. In actual fact, phases with contact angles ranging between 75° and 105° are considered neutrally wetting.

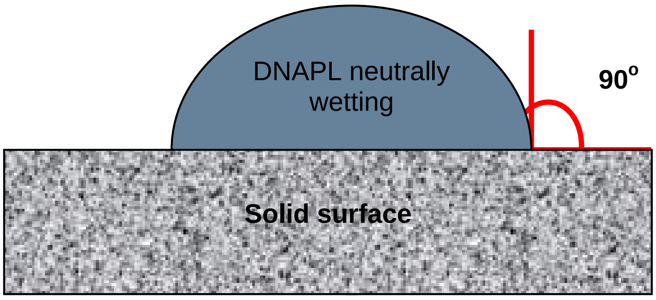


Figure 5: Wettability: Contact angle = 90°, DNAPL is considered neutrally wetting

Although most DNAPLs are non-wetting, taking into account the variation of groundwater composition, DNAPL composition and the characteristics of the solid surfaces, the possibility of complex wettability relationships must be considered at actual field sites.

3.2.6 Capillary Pressure

As explained above, DNAPLs tend to be the non-wetting fluid in aquifers. The curved interface between two fluid phases, DNAPL and water, is determined by the difference in fluid pressure between the wetting and non-wetting phase, and this difference in pressure is termed the capillary pressure (Pc):

$$P_c = \Delta P = P_{nw} - P_w \text{ Equation}$$ *Equation (6)*

where Pnw is the pressure of the non-wetting fluid (DNAPL) and Pw is the pressure of the wetting fluid (water) (Pankow and Cherry, 1996).

Capillary pressure is related to interfacial tension, pore size and contact angle by the following equation:

$$(Pc) = (2\ \sigma \cos \theta)/r$$ *Equation (7)*

where σ is the interfacial tension, r is the radius water-filled pore and θ is the contact angle (Mercer and Cohen, 1990).

The geometry of the interstitial pore space is highly complex. If the network of interstitial spaces is seen to be connected by pore throats of smaller dimension, equation (7) would predict the threshold value of the capillary pressure that must be exceeded for DNAPL to pass through a pore throat of radius. There will be no DNAPL access to an interstitial pore until the capillary pressure exceeds the threshold value associated with the largest throat already in contact with the DNAPL. The water-DNAPL interface will then migrate across regions of pore space that support radii of curvature consistent with the prevailing capillary pressure. If the capillary pressure is increased, successively smaller pore throats will be invaded by DNAPL (Pankow and Cherry, 1996).

Equation (7) can be adapted for parallel flat plates (or a fracture plane) to the following:

$$Pc = \sigma\ (1/r_1 + 1/r_2) \quad (8)$$ *Equation (8)*

If it assumed that $r_2 = \infty$ then:

$$r_1 = e/2$$ *Equation (9)*

Where e is the fracture aperture and then:

$$Pc = (2\sigma \cos \theta)/e$$ *Equation (10)*

(Thomson, 2004).

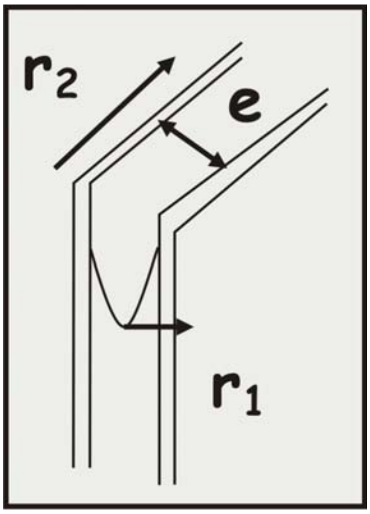


Figure 6: Explanation of capillary pressure between parallel plates/ fracture plane

3.2.6.1 Capillary pressure, Saturation and Hysteresis

The above equations describe capillary pressure for ideal homogenous porous media or flat parallel plates. Geologic media however is made up of various interface geometrics and radii of curvature at each pore or pore throat. The macroscopic average capillary pressure is needed to describe the relationship between DNAPL invasion and the water saturation in the media. This relationship is known as the capillary pressure-saturation function or sometimes as the capillary pressure curve (Pankow and Cherry, 1996).

The fluid contents are expressed in terms of the fraction of the total interstitial void volume occupied by each fluid. If V_v is the void volume in a representative element of bulk porous medium, then:

$$S_w = V_w/V_v \quad \text{Equation (11)}$$

$$S_{nw} = V_{nw}/V_v \quad \text{Equation (12)}$$

$$S_w + S_{nw} = 1 \quad \text{Equation (13)}$$

Where V_w and V_{nw} are the volumes of wetting and non-wetting fluids, respectively, and S_w and S_{nw} are the relative volumes of wetting and non-wetting fluids expressed as a fraction of the pore volume. These relative volumes are referred to as saturations (Pankow and Cherry, 1996).

The capillary pressure saturation function $P_c(S_w)$ is measured in experimental cells, where a NAPL source is allowed to invade a saturated porous medium (at incremental increased NAPL pressures) and the subsequent volume of displaced water is measured at these pressure intervals. Capillary pressure-saturation curves can then be derived for different media and DNAPL components.

Figure 7 is an example of such a curve.

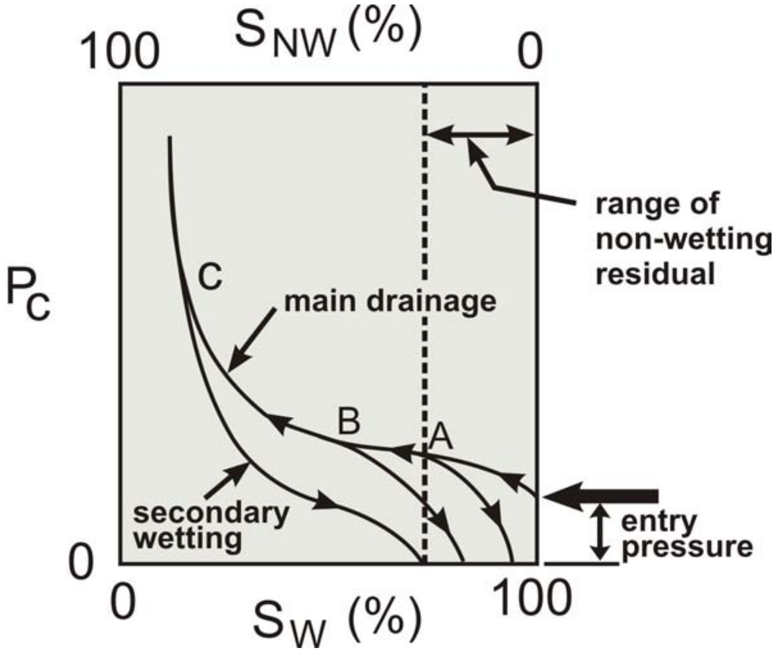


Figure 7: Capillary pressure-saturation curve

(From Thomson, 2004).

From the derived curves, it was found that as was previously stated by equation (7), the DNAPL would only start to invade the media continuously once the threshold value has been reached. This capillary pressure is known as the *entry pressure*. For most materials entry pressure corresponds to a water saturation in the range 0.8 to 0.95 (Pankow and Cherry, 1996).

These curves have been derived under conditions where the water saturation first has decreased and the capillary pressure increased as a result of the DNAPL invasion, this process is known as drainage. Once the source of DNAPL is exhausted, the DNAPL will continue to migrate away from the source and will be replaced by water in that zone. The situation has now changed from one of increasing water saturation to decreasing capillary pressure, known as wetting. The capillary pressure is less during the wetting process than during the drainage. The relationship between drainage and wetting is however not equal, which leads to a type of hysteresis.

This results in what is known as residual DNAPL saturation ($1-S_m$) where S_m is the maximum water saturation achievable during the wetting process. Residual DNAPL is blobs and fingers of DNAPL which has been cut off and disconnected from the continuous DNAPL body by invading water (Figure 8).

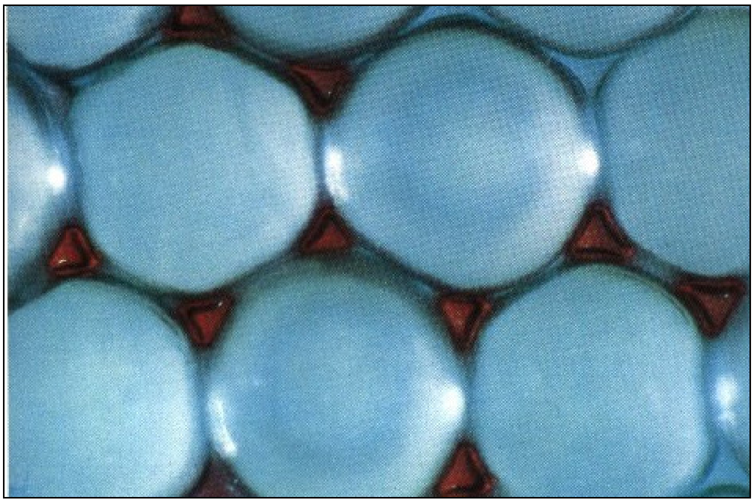


Figure 8: Residual DNAPL (red) entrapped between water-wet glass beads

(From Schwille, 1988).

*Based on the understanding of these **pore level processes**, estimations of hydrostatic conditions in actual field investigations can be made. Such invasion relationships will include the DNAPL pool heights required for invasion across a capillary barrier, or fracture aperture required to stop downward migration.*

These relationships will be discussed in more detail in the following sections.

3.2.7 Influence of Chemical complexity on DNAPL behaviour

The discussion above has focused on the behaviour of pure phase organic fluids. However, many DNAPL wastes that are produced in manufacturing and industrial operations are complex mixtures of organic compounds. The behaviour of such chemically complex mixtures of organic compounds can vary significantly from the single component DNAPLs and, consequently, should be considered when assessing or remediating sites with complex, multi-component DNAPLs. The following sections describe some of the impacts of complex chemical composition on DNAPL transport and distribution in the subsurface.

The presence of polar or ionisable compounds in DNAPLs can significantly affect NAPL-water interfacial tension and the wetting character of the DNAPL (Dawson and Illangasekare, 1999). As shown before, these parameters are integral to the definition of capillary pressure. Lower DNAPL-water interfacial tension will lead to a greater degree of miscibility between the fluids and therefore a greater potential for DNAPL to enter into smaller pore spaces. Significant reduction in interfacial tension occurs as a function of increasing ionic strength. This phenomenon presumably occurs because an increase in the concentration of aqueous ions promotes stronger interactions with the functional groups of polar constituents in the NAPL phase (Dawson and Illangasekare, 1999).

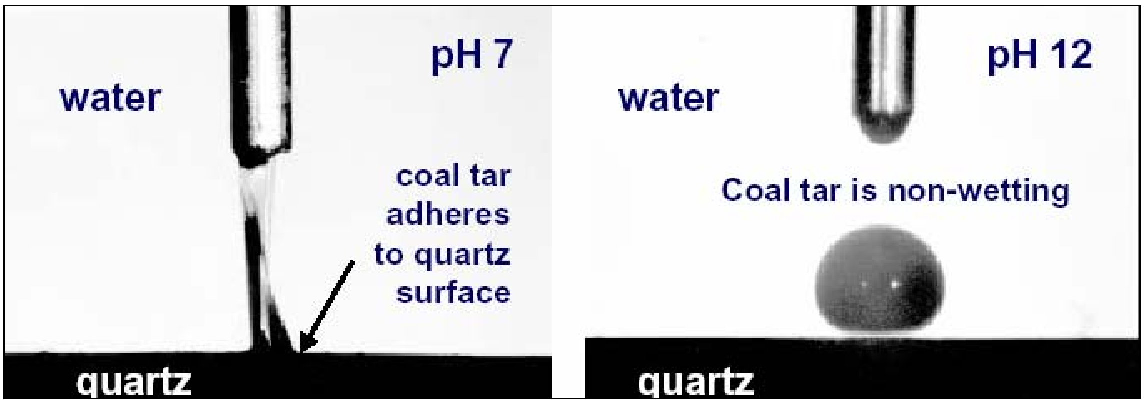


Figure 9: Photomicrographs of a coal tar-water system and aqueous pH 7 and pH 12. (Needle size for scale: o.d. = 0.52 mm).

(Barranco and Dawson, 1998)

As described earlier, contact angles less than 90° generally indicate that water is the wetting phase relative to the DNAPL, whereas contact angles greater than 90° indicate the DNAPL is the wetting phase relative to water. In general, the wetting fluid will tend to coat mineral surfaces and occupy the smaller pore openings in porous media. Many factors influence the wettability of a system, including DNAPL and aqueous-phase composition, presence of organic matter, mineralogy, and saturation history (Dawson and Illangasekare, 1999). Changes in wettability, will affect a number of properties that influence multiphase flow, including capillary pressure, relative permeability, and residual saturation.

Strong water wetting conditions exist for most aquifers containing DNAPLs composed of non-polar (e.g. saturated hydrocarbons) or relatively non-polar constituents (e.g. chlorinated organic hydrocarbons) (Barranco *et al.*, 1997). This condition exists because interaction between non-polar, hydrophobic DNAPL constituents and hydrophilic minerals (e.g. quartz) is energetically unfavourable. However, wetting behaviour that deviates from that observed for non-polar DNAPLs has been observed for systems containing polar or ionisable organic compounds. These include high-molecular-weight compounds found in mixtures with coal tar, creosote, and some fuel oils (Barranco and Dawson, 1998). The wettability of systems containing water and NAPLs with ionisable organic constituents is dependent upon the type and concentration of the ionisable constituents as well as the aqueous chemistry. (Dawson and Illangasekare, 1999). Wettability is also dependent on aqueous pH, since pH influences the speciation of ionisable organic constituents as well as the charge of the mineral surfaces present. Figure 9 shows that quartz wettability changes from coal tar-wet to water wet as pH is varied from 7 to 12 (Barranco and Dawson, 1998).

DNAPL wastes may exhibit a range of properties, depending on the mix of constituents that comprise the DNAPL. The composition can vary due to the altering of pure chemical substances by industrial processes, prior to disposal. Degradation and transport processes will also cause changes to the chemical structure and character of the DNAPL over time and space in the subsurface.

The combination of higher molecular weight constituents, with lower molecular weight components can cause an increase in the bulk density of a DNAPL. Coal tar has a density slightly greater than 1 gm/cm^3 as a result of a number of high-molecular weight, asphaltenic constituents, even though most coal tars are composed predominantly of low density mono-aromatic hydrocarbons (EPRI, 1993).

Viscosity can also vary considerably among constituents of DNAPLs. As with density, the viscosity of multi-component DNAPLs increases with increasing content of higher molecular-weight constituents in the mixture.

For example, coal tar has a significantly higher viscosity (approximately 20 cP;) than its mono-aromatic hydrocarbon constituents (e.g. benzene: 0.65 cP) (EPRI 1993).

Mixing of such NAPLs in the subsurface, due to repeated spills of different NAPLs or both LNAPLs and DNAPLs, can significantly alter the character of the NAPL over time and space. The multi-component nature of complex NAPL wastes may result in changes in their properties over time or as the NAPL migrates due to differential volatilization, dissolution, sorption and degradation of constituents (Cohen and Mercer, 1993). For example, lighter, more volatile components of fuels may volatilize over time, leaving a heavier, less volatile NAPL in the subsurface. This process is referred to as weathering (or degradation).

The weathered product may have transport characteristics that are considerably different than the original product. Awareness of the possible changes to the character and migration properties of a DNAPL is very important when decisions regarding site characterization or remediation options are made.

3.2.8 Transport and Fate of DNAPLs in the Subsurface

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

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

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

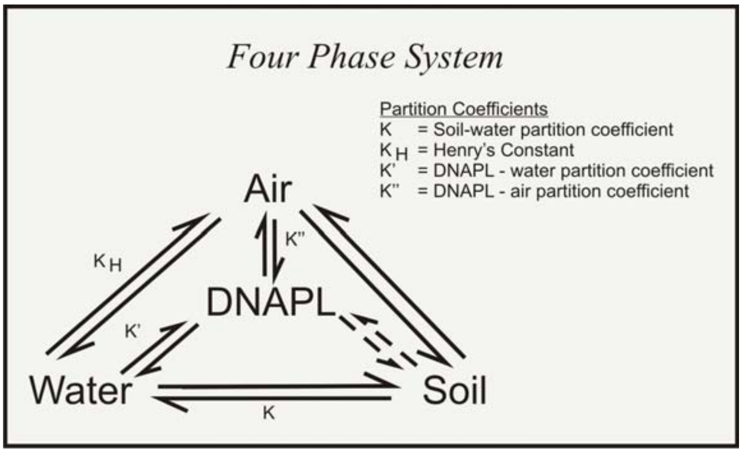


Figure 10: Distribution of DNAPL between the four phases found in the vadose zone

(From Huling and Weaver, 1991).

The concept of phase distribution is critical in all decision making. Understanding the phase distribution of a DNAPL introduced into the subsurface provides significant insight in determining which tools are viable options with respect to site characterization and remediation. DNAPL represented by residual saturation in the four-phase diagram (Figure 10) is largely immobile under the usual subsurface pressure conditions and can migrate further only:

1. In water according to its solubility; or
2. In the gas phase of the unsaturated zone.

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

3.2.8.1 DNAPLs in the Vadose Zone

Studies at most industrial sites show that DNAPLs will tend to penetrate through the vadose zone into the groundwater zone where most of the DNAPL mass will accumulate and then cause persistent contamination (Pankow and Cherry, 1996). It is however possible where the water table is exceptionally deep or where the volume is small that the entire mass of DNAPL may reside within the vadose zone.

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

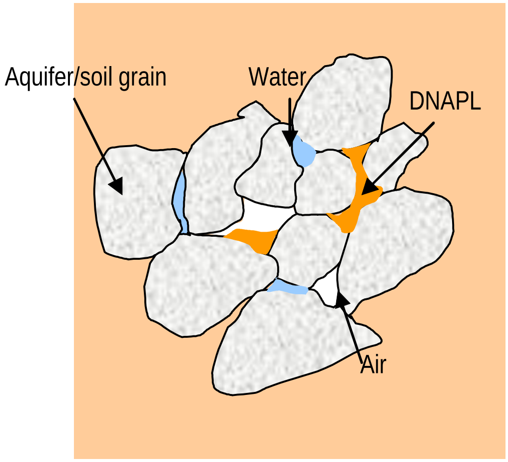


Figure 11: Residual DNAPL in the unsaturated or vadose zone

(From Kueper et al., 2003)

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

Because the vapour pressure of many DNAPL compounds is relatively high, the lifespan of residual DNAPL in the unsaturated zone can be much less than the lifespan of residual DNAPL below the water table. This will not eliminate the presence of vapour phase, absorbed phase and aqueous phase contamination in the unsaturated zone, but it can lead to an absence of the DNAPL phase. The vaporisation process can deplete residual chlorinated solvent DNAPLs such as TCE and PCE within 5-10 years in relatively warm and dry climates (Kueper *et al*., 2003).

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

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

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

3.2.8.2 DNAPLs in the Groundwater (Saturated) Zone

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

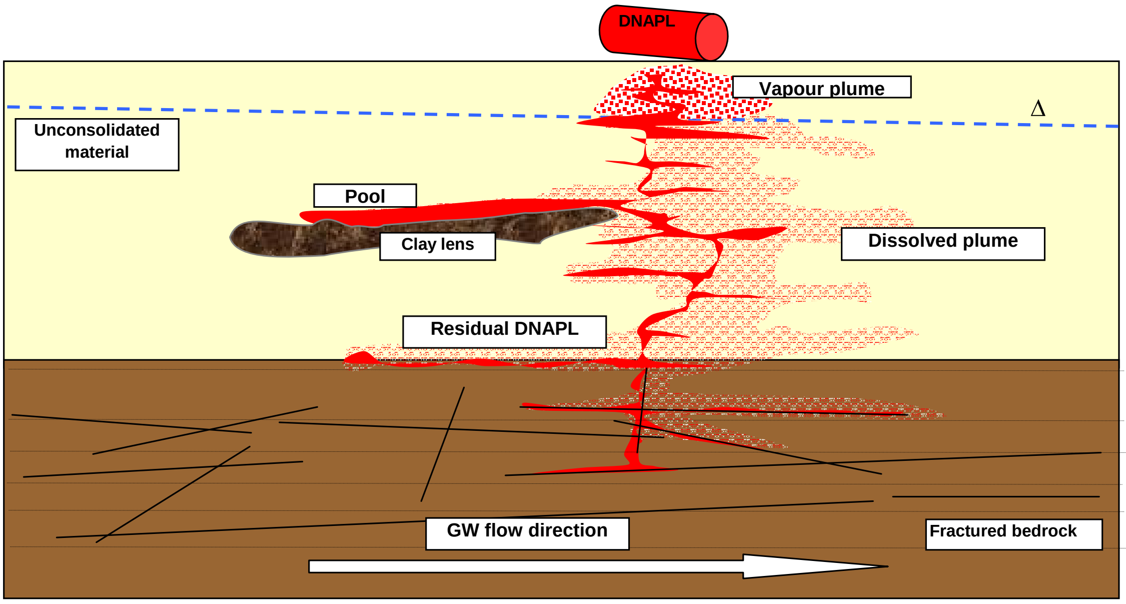


Figure 12: DNAPL distributions in unconsolidated deposits and fractured bedrock

Due to the lack of air (or gaseous phase), the saturated zone containing DNAPL is considered a three-phase system consisting of the solid (soil), water, and immiscible fluid (DNAPL). Figure 13 indicates the three phases and the transfer of the mass of contaminant between the phases. There are therefore only three pathways of phase distribution in the saturated zone, except at the water table.

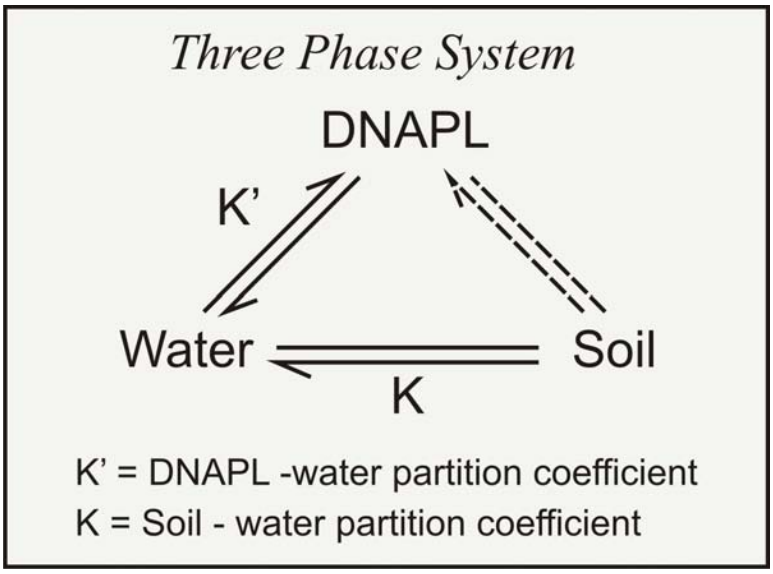


Figure 13: Distribution of DNAPL between the three phases found in the saturated zone

(From Huling and Weaver, 1991).

3.2.8.2.1 Porous Media

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

The DNAPL phase will be distributed in porous media depending on the layering or bedding planes. As the DNAPL moves downwards, some residual DNAPL will be entrapped on the pathway downwards. Any contrast in grain size distribution (permeability) will cause a change in entry pressure (Pankow and Cherry, 1996). A higher entry pressure will be encountered at any change to a smaller grain size and, this will cause lateral spreading of the DNAPL phase. The DNAPL will accumulate (pool) on the finer grained layer and continue to spread laterally until the height of the layer (pool) exceeds the entry pressure for the layer (Figure 14).

Residual and pooled DNAPL collectively form what is referred to as the DNAPL source zone. It is within the DNAPL source zone that dissolution into groundwater occurs and aqueous phase plumes originate. The DNAPL migration along these multiple pathways, in a very tortuous manner; is sometimes referred to as dendritic form (Figure 14) due it its resemblance to the branches of a tree (Kueper *et al*., 2003). The specific migration pathways will be governed by the bedding structure of the porous medium, with migration occurring along pathways on the scale of millimetres to metres. In horizontally bedded media, significant amounts of lateral spreading can be expected, including in directions not coincident with the direction of groundwater flow.

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

Figure 14: Example of a two-layer bead medium, initially saturated with water. Entry of smaller pore space by DNAPL only after sufficient pressure as result from pool height

(From Schwille, 1988).

Figure 15 illustrates maximum pool heights for different DNAPL types perched above a variety of capillary barriers. The height of DNAPL that can accumulate above a capillary barrier below the water table can be estimated using Equation 8 (Kueper *et al*., 1993):

$$H = (P_c'' - P_c')/(P_D - P_W)g \qquad \textit{Equation (14)}$$

where:

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

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

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

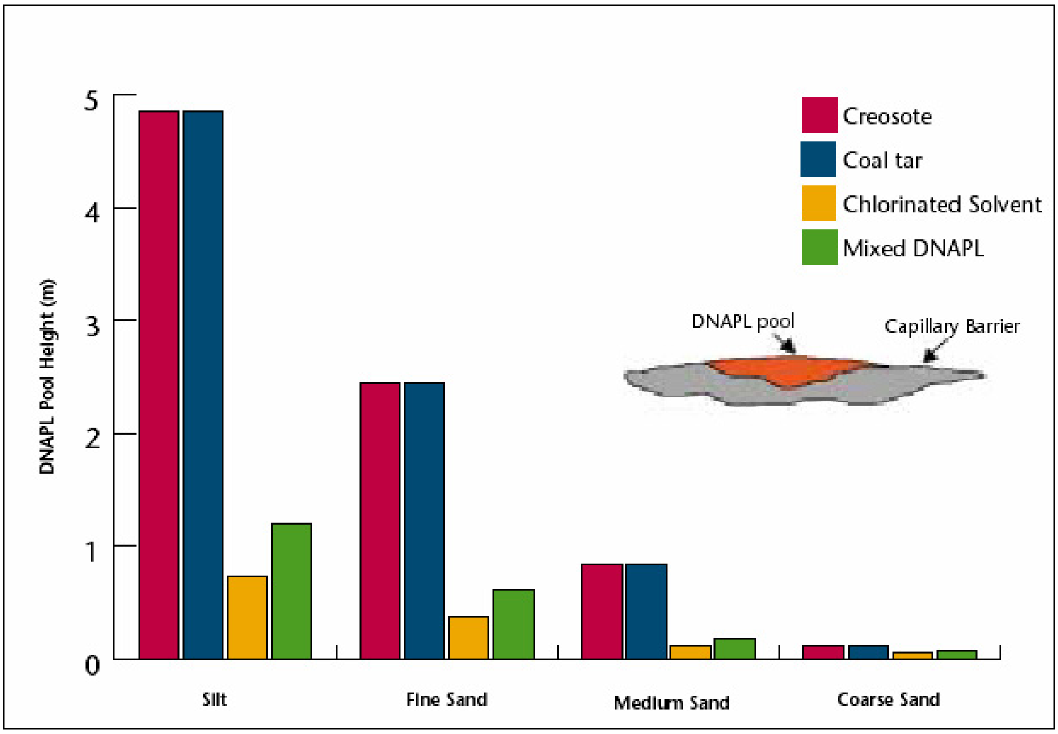


Figure 15: Maximum DNAPL pool height above various capillary barriers

(From Kueper et al., 2003).

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

3.2.8.2.2 Fractured Non-Porous Media

The pattern of DNAPL migration in a fractured media will be controlled by the orientation and interconnection of the fractures. DNAPL will move laterally along horizontal fractures and downward along vertical fractures.
DNAPL will enter fractures in bedrock both above and below the water table. Analogous to unconsolidated deposits, both residual DNAPL and pools will form in rock fractures, with a higher likelihood of pool formation in horizontal to sub-horizontal features. Fracture entry pressures are directly proportional to interfacial tension and inversely proportional to fracture aperture (Kueper *et al.,* 2003). This results in preferential DNAPL migration through the larger aperture fractures of a fracture network. Once DNAPL enters a fracture network, it is likely that downward and lateral migration will occur until the DNAPL source is exhausted.

The scenario that DNAPL will pool on top of a fractured formation is unlikely and it would rather continue the downward migration through the fracture system (Figure 16). The reason being, that capillary pressure increases linearly with depth in a hydrostatic system, which implies that a fracture aperture would need to be extremely small to support the overlying distribution of DNAPL. The fracture aperture required to stop migration denotes the largest aperture that can exist at a corresponding depth such that DNAPL migration is arrested.

For chlorinated solvents such as TCE, fracture apertures need to decrease quickly with depth in order to prevent further downward migration. Even a 1m accumulation of TCE in fractured rock would require apertures to be no larger than 9 µm at the base of the accumulation in order to prevent further downward migration (Kueper *et al*., 2003). Experience has shown 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.

It is calculated for less dense DNAPLs such as creosote and coal tar that a less drastic reduction in fracture aperture with depth is required to arrest downward migration, but that significant reductions are still required to support an accumulation of DNAPL. 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 (Kueper *et al*., 2003). It is therefore very likely that by the time a site investigation has started that a more dense and less viscous DNAPL (e.g. solvents) would have stopped downward migration, as opposed to a less dense, more viscous DNAPL (creosote or coal tar).

It should however be considered that all fractures are rough walled and exhibit a range of apertures within a fracture plane. This is analogous to the concept of pore throat in a porous medium, and the DNAPL will enter only the fracture aperture (or pore throat) large enough to support the required entry pressure.

The overall ability of fractured bedrock to retain residual and pooled DNAPL is relatively small given the low fracture porosity of most rock types. A typical fractured rock, for example, may exhibit fracture porosities in the range of 0.001 to 0.01. Assuming that DNAPL will occupy on average 20 percent of the fracture pore space, this range of fracture porosities corresponds to bulk retention capacities ranging from 0.0002 m^3 DNAPL per m^3 of bedrock to 0.002 m^3/m^3 (that is, between 200 ml and 2 litres of DNAPL per m^3 of rock) (Kueper *et al*., 2003).

This implies, for example, that one drum of DNAPL containing 205 litres (0.205 m^3) of product will occupy a bulk bedrock volume of 103 -1025 m^3. From this it is clear that relatively small volumes of DNAPL have the potential to impact relatively large volumes of bedrock. This conclusion holds for many of the hard rock aquifer types in South Africa.

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

3.2.8.2.3 Fractured Porous Media

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

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

If concentrations are higher in the open fracture, the diffusion process will result in dissolved contaminants moving into the matrix (forward diffusion). If concentrations are higher in the matrix, dissolved contaminants will move out of the matrix and into water in the open fractures (back diffusion) (Kueper *et al.,* 2003). Matrix diffusion will occur in all rock types exhibiting matrix porosity. This process of forward and backward diffusion can lead to persistence of contaminants in an aquifer long after the DNAPL source has disappeared.

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

A second manifestation of the matrix diffusion process is that the timescale of remediation in fractured rocks is often controlled by the back diffusion process and not by the presence of DNAPL in fractures. *Even for relatively short initial exposure times, the back diffusion process can continue for many decades.* The concentration gradient driving back-diffusion is typically less than the initial concentration gradient driving forward-diffusion into the matrix while residual DNAPL is present in the fracture. In fractured environments exhibiting matrix diffusion, conventional technologies such as pump-and-treat should be viewed as either a source zone containment technology, or a plume interception technology, not as a technology capable of restoring groundwater to near-pristine quality within short periods. The effectiveness of many remedial techniques is diffusion limited and this process needs to be considered during development of a remedial strategy, and selection of a remedial technique (Kueper *et al*., 2003).

In fractured porous media the volume of pore space available for contaminant mass is measured as, the total fracture porosity, plus the matrix porosity. In situations where DNAPL in the fracture network continues (e.g. continues source), the maximum storage capacity is attained when all the pore water in the matrix is at solubility limit (Pankow and Cherry, 1996).

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

Once DNAPL enters a fracture network, it is probable that continued downward and lateral migration occurs until the source of DNAPL to the bedrock is exhausted (Kueper *et al.*, 2003). It is unlikely in that the DNAPL can come to rest as a continuous vertical distribution in the overburden once the fractured bedrock reached. This is because capillary pressure increases linearly with depth in a hydrostatic system; this means that the fracture aperture at that point would *need to be extremely small to support the overlying distribution of pooled DNAPL.*

Van Tonder and Shapiro (2006) calculated the relationship between fracture aperture, transmissivity and the required entry pressure (in mm head), that needs to be overcome, to enter the fracture for TCE. The graph below shows this relationship.

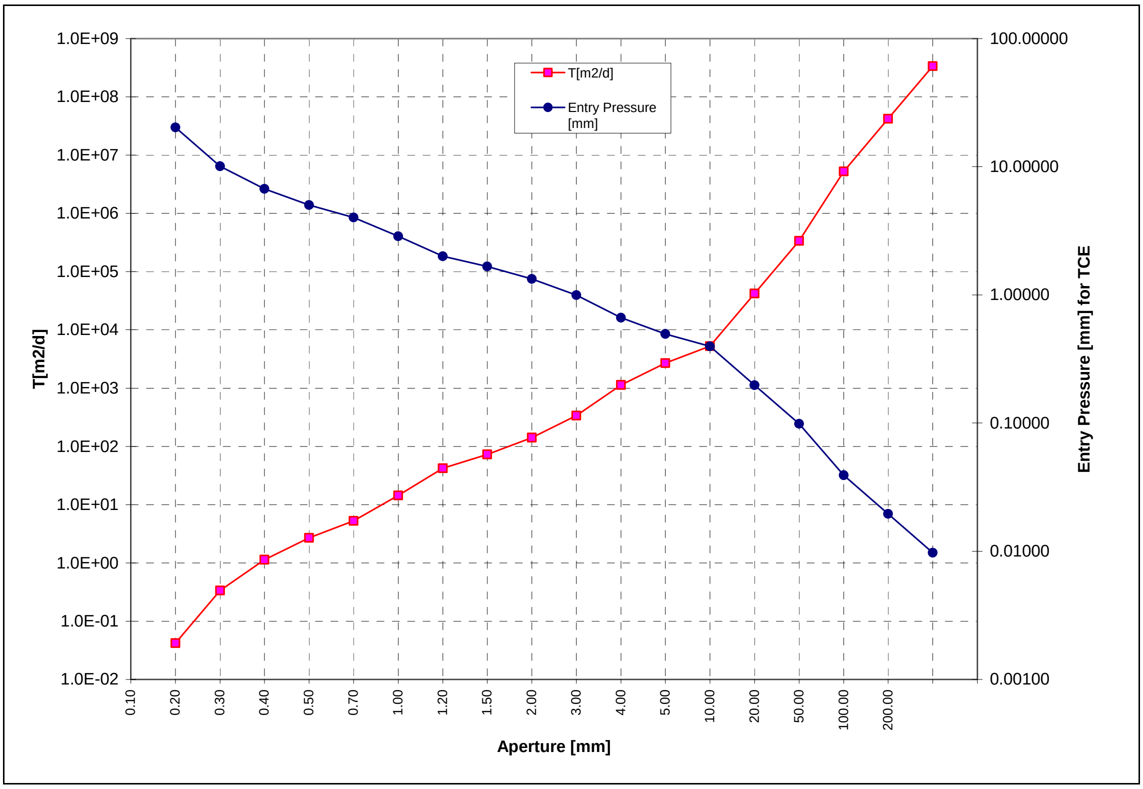


Figure 16: Entry pressure and transmissivity vs. Fracture aperture

The implication from this relationship is clear, in that greater apertures lead to higher transmissivities, which will lead to more rapid transport of both the NAPL and the dissolved species, and also that greater apertures lead to lower entry pressures. This latter point reiterates the fact that larger fractures will allow entry of lesser heads of TCE and that these two factors combined will lead to significant transport of DNAPLs and plume development on such sites. It is also clear that as fracture apertures decrease in size downward migration of DNAPLs can be halted.

3.2.8.3 Plumes from DNAPLs

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

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

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

In-borehole dilution can lead to the measuring of lower concentrations than actually concentrations in the aquifer. This refers to the fact that pumping the monitoring borehole draws in both the local contaminant plume as well as surrounding uncontaminated water. The result is a mixing of clean and contaminated water in the monitoring well, and a resulting lowering of concentrations in the obtained sample relative to what may be present in the aquifer immediately adjacent to the borehole. In addition to mixing during purging, this in-borehole dilution effect can occur naturally if vertical flow gradients exist within the borehole (Kueper *et al*., 2003).

Biotic and abiotic degradation can also result in the lowering of concentrations in the down-gradient direction within a contaminant plume.

The net effect of hydrodynamic dispersion, in-borehole dilution, monitoring borehole placement and potential degradation processes is that contaminant concentrations in a sample obtained from a monitoring borehole downstream of a DNAPL source zone may be significantly less than the aqueous solubility of the DNAPL of interest (Kueper et al., 2003).

Experience has shown that a DNAPL source may be present upstream of a monitoring borehole, if the water sample concentrations exceed 1 percent of the effective solubility of the component of interest (US EPA, 1992). The 1 percent ‘rule of thumb’ has been criticised because it does not provide guidance on how far upstream the DNAPL source zone is located. It is clear that a variety of site-specific factors influence the magnitude of sampled contaminant concentrations and that some of these factors cannot be determined. The 1 percent ‘rule of thumb’ should be used as a means of establishing that DNAPL may be present upstream of the monitoring point in question, and therefore as a means of justifying the use of additional site investigation techniques to confirm or refute the presence of DNAPL (Kueper *et al.,* 2003).

If the DNAPL of interest is composed of a variety of components, these components will not dissolve into groundwater at their single component, textbook solubility values. Rather, the various components may compete for the dissolution process. The dissolution of a multi-component NAPL can be described using Raoult’s law (See section 0).

The dissolution of a multi-component DNAPL into groundwater will be characterised by the preferential depletion of the higher effective solubility components at an early time. The lower effective solubility components will display slower rates of concentration decrease with time; with some components displaying moderate increases in concentration with time. The total concentration of all components will decrease with time. This is not an indication that DNAPL is not present. In addition, DNAPL mass will decrease fastest at an early time (after DNAPL entry), showing increasingly slower rates of mass depletion as time progresses from the initial entry of DNAPL into the groundwater (Kueper *et al.*, 2003).

Once DNAPL is present in a fractured aquifer, it will also slowly dissolve into groundwater flowing through open fractures, giving rise to aqueous phase plumes. The plumes will generally migrate in the hydraulically down-gradient direction subject to advection, dispersion, sorption to fracture walls, possible biodegradation and matrix diffusion (Kueper *et al.,* 2003). As with plume migration in unconsolidated deposits, the chemical composition of the plume will be a function of the chemical composition of the DNAPL.

Like plumes in unconsolidated deposits, all plumes in fractured media will eventually reach a steady-state configuration where the leading and side edges of the plume (as defined by a specific concentration level) are no longer expanding. One objective of many site investigations is to determine whether the aqueous phase plume has reached its steady-state configuration.

The concept of a steady-state plume is applicable to both porous and fractured media, and can result from the dispersion process alone. As a result, all plumes reach a steady-state configuration at some point in time where the leading and side edges of the plume are stable as defined by a specified concentration contour and ultimately, once the source zone is exhausted, will shrink. Generally, plumes reach steady-state concentrations first near the source and last at the leading edge. The precise time interval is site-specific and is influenced by a number of factors including hydraulic conductivity, hydraulic gradient, source zone concentration, sorption and degradation. In general, degradation will lead to shorter steady-state plumes than those arrived at by dispersion alone. Whether a plume has reached steady-state is typically determined through several years of groundwater quality monitoring and/or the use of numerical simulation.

4. DNAPL SITE CHARACTERIZATION

4.1 Introduction

In natural subsurface systems dominated by heterogeneity, the delineation and even the detection of sparingly soluble, dense contaminants can be extremely difficult. Several techniques can be applied for the characterization of a site contaminated with dense non-aqueous phase liquids (DNAPLs). Detailed site characterization methods are described in the accompanying report "*Field investigations to study the fate and transport of dense non-aqueous phase liquids (DNAPLs) in groundwater: Manual for Site Assessment at DNAPL Contaminated Sites."*

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

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

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

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

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

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

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

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

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

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

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

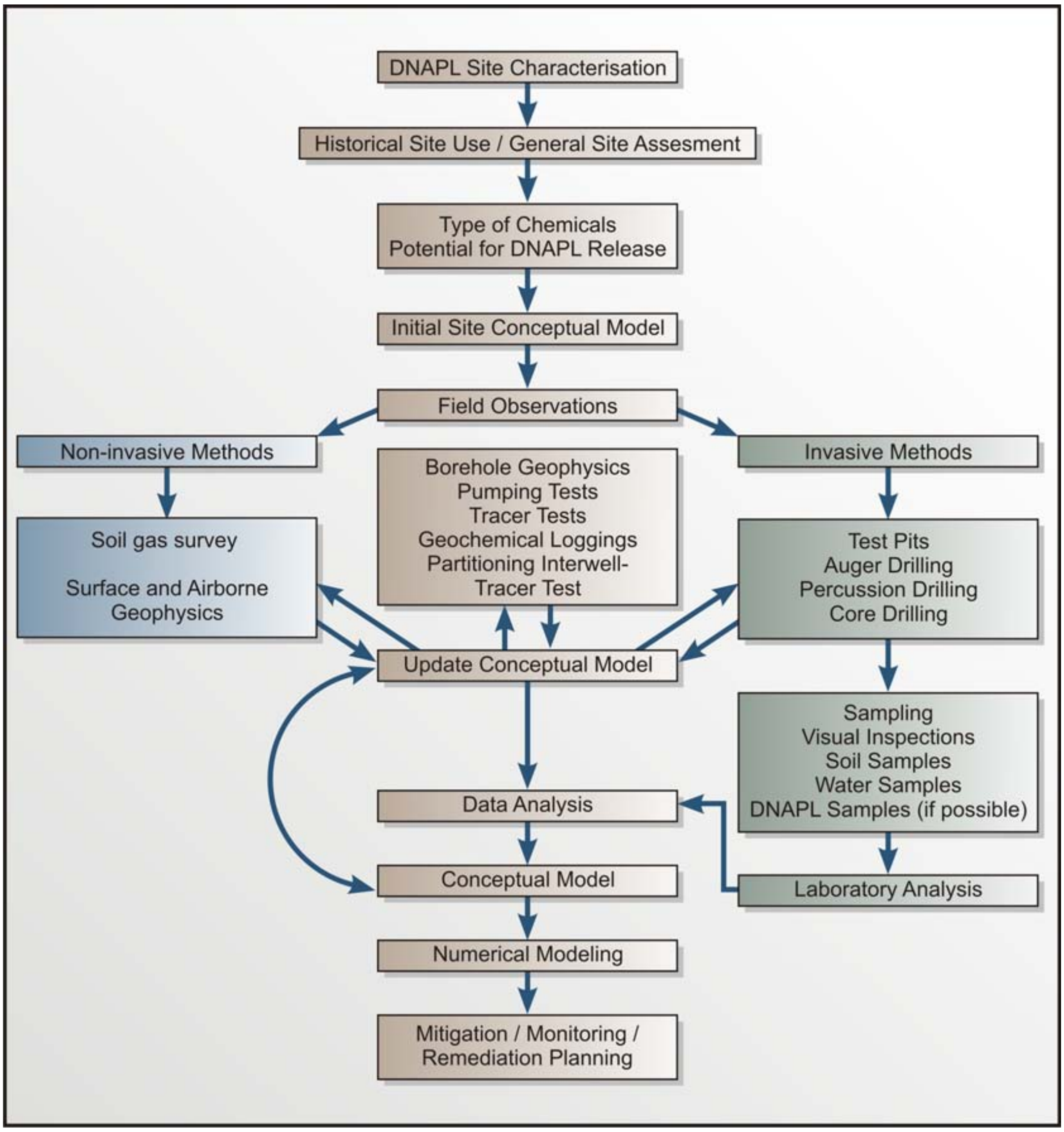


Figure 17: Framework for DNAPL site assessment.

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

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

The toolbox approach recognizes that all characterization methods contribute to the conceptual model of the site.

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

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

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

More than 90% of South African aquifers are fractured, and research from this project has shown that very detailed fracture characterization is required at DNAPL contaminated sites.

Figure 18; provide a brief summary of the parameters that can be measured at a site during field investigations.

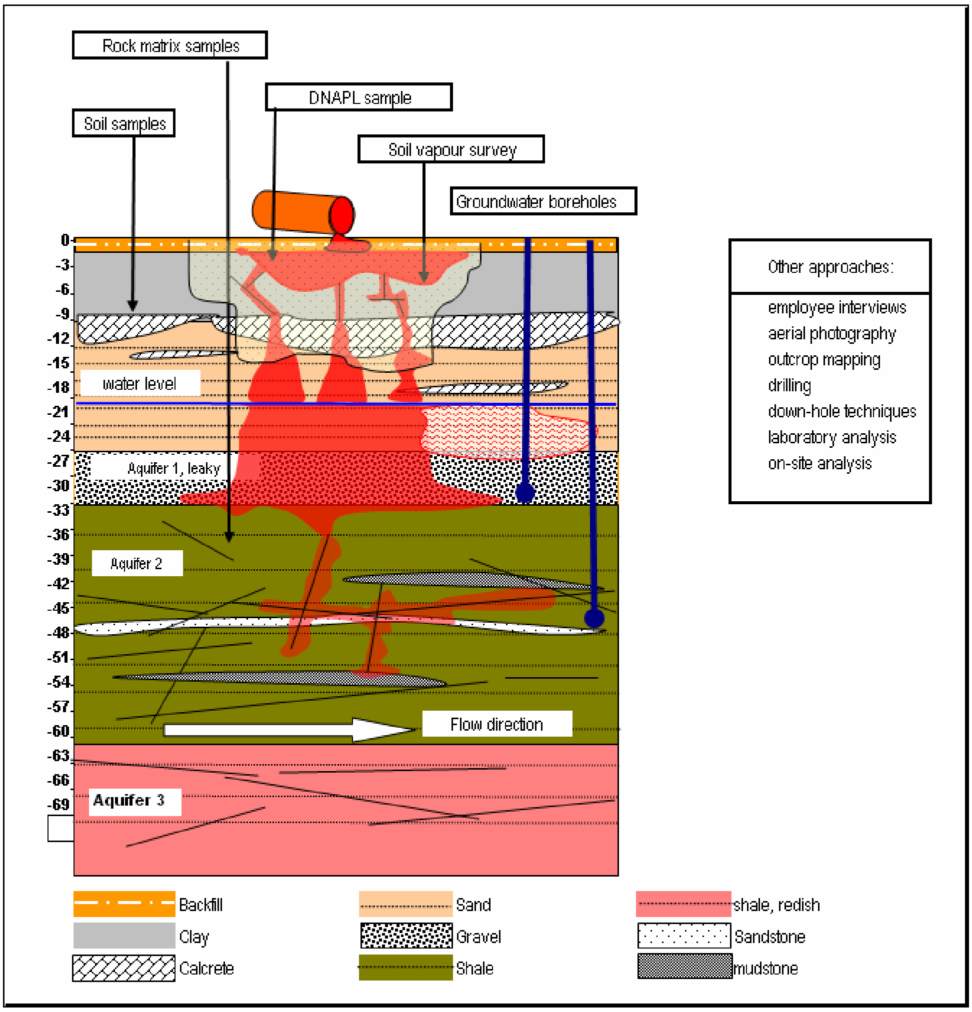


Figure 18: Site assessment techniques

(Adapted from Kueper et al., 2003)

5. DNAPLS IN SOUTH AFRICAN AQUIFER SYSTEMS

5.1 Introduction

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

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

The properties of selected South African aquifers are shown in the following section, related to the dominant flow mechanisms, flow characteristics and the implications for DNAPL contaminant fate and transport.

5.2 South African Aquifer Systems

Most South African aquifers occur in fractured rock ranging in age from earliest Pre-Cambrian to Jurassic. Aquifers consisting of recent to Tertiary formations are restricted to coastal dune belts and unconsolidated deposits associated with rivers and Aeolian sands. Characterisation of these fractured rock resources has been limited. The dominant occurrence of groundwater in fractured rocks implies that these aquifer systems are more difficult to manage and to protect (Pietersen, 2004).
Vegter (1995) has divided South African aquifers according to:

- Type of opening – primary or secondary
- Lithostratigraphy
- Physiography, and
- Climate

This resulted in the groundwater regions map (Vegter, 2000) in which 64 groundwater regions were delineated.

Most of the research on groundwater in South Africa has been focused on the main Karoo Basin. This is to a large degree understandable because of the Karoo Basin being the largest aquifer system in areal extent in South Africa. The aquifers support the domestic and agricultural needs of a number of small towns and rural communities. The dolomite and Table Mountain Group (TMG) aquifers have also been studied in some detail.

The key challenge for the dolomite aquifer system relates to the management of the resource which is threatened by various land use impacts and the protection of aquifer integrity. This will require an integrated aquifer management arrangement. The rest of the hydrogeological domains have been investigated in lesser detail (Pietersen, 2004).

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

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

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

5.2.1 Intergranular flow systems

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

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

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

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

Little is known regarding true riverbed sand aquifers in South Africa. General characteristics of riverbed aquifers can be summarized as:

- Coarse gravels and sands are more typical of alluvial deposits. However, flood plains consist mainly of fine silt. Towards the end of a river's course, the river slows down dumping some of the heavier materials on these flood plains. Boreholes drilled into these types of formations normally have higher yields. It is important to note that borehole design is plays an important role in the yield of boreholes drilled into riverbed aquifers.
- Alluvial deposits' grain size varies considerably; fine and coarse materials are intermixed. The hydraulic conductivities vary between 10^{-3} to 10^{3} m/d and their porosities vary between 25 – 70%. However, flood plain porosities usually range 35 – 50% and the hydraulic conductivities vary between 10^{-8} – 10^{-1} m/d.
- In general riverbed aquifers are high recharge areas and often recharge deeper underlying aquifers and are unconfined in nature.

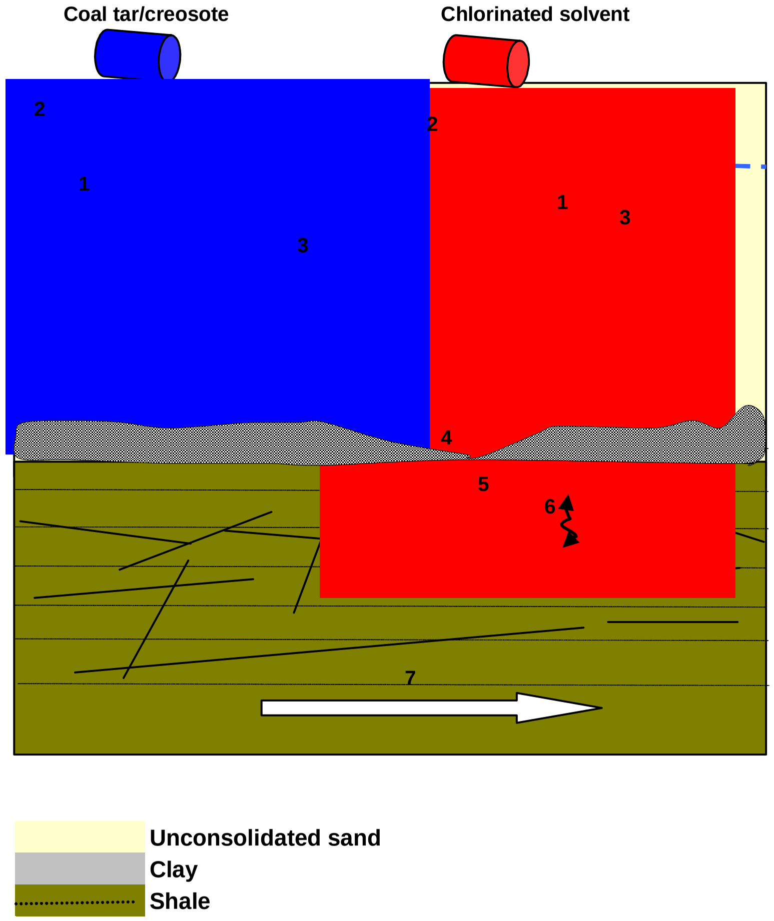
The surface-water groundwater interaction is often intermittent (depending on the elevation of the water level, groundwater may recharge the surface water body or the surface water may recharge groundwater). This is normally dependent on the rainfall cycle (Pretorius & Dennis, 2004).

The issues and implications with regard to DNAPL fate and transport are as listed below, and illustrated in the conceptualisation in Figure 19.

1. **Primary aquifer systems are often "thin" aquifers with shallow water tables** - This implies that the aquifer is highly susceptible to contamination. However, due to this characteristic, site characterization and remediation techniques are easiest translated from US and other international experiences. A wide range of well established techniques are available to the site assessor.
2. **Thin unsaturated zone** allows for easy access to contaminated zone and less chances for vapour plume development and transport.
3. **High porosity** – implies higher groundwater velocities and larger dissolved plumes.
4. **High organic and clay content** of these systems allows for higher attenuation, nutrient availability, and thus degradation rates when considering monitored natural attenuation (MNA) as a remedy.
5. **Variable lithology and permeability** –heterogeneity of the system will cause a tortuous and varied pathway for the vertical and sub-vertical flow of the DNAPL phase.

In Figure 19 the difference between a coal tar/creosote vs. chlorinated solvent contaminated `system is shown. From this it can be seen due to the difference in physical properties (density and viscosity) of the contaminant, the transport processes will differ. The free phase of solvents, are more likely to migrate deeper but less horizontal in the source zone, than the coal tar/creosote mix. The source zone area containing residual and pooled DNAPL at the coal tar/creosote spill tend to be more spread out horizontally.

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



Features

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

Issues and implications

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

Figure 19: Conceptualisation of DNAPL fate and transport in intergranular flow systems.

5.2.2 Intergranular and fractured

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

The main Karoo Basin encompasses an area of approximately 630 000 km^2. A major characteristic of the Karoo Supergroup, which consists mainly of sandstone, mudstone, shale and siltstone, is the low permeability. The Dwyka diamictite and shale have very low hydraulic conductivies, and virtually no primary voids. Water is confined to within narrow discontinuities like jointing and fracturing. The Dwyka Group is not considered an ideal unit for large-scale development of groundwater. The Ecca Group consists mainly of shales, with thicknesses varying from 1 500 m in the south to 600 m in the north. Significant tracts of land are irrigated from groundwater found in the Ecca shales. This is surprising because this formation is considered dense. Aquifers in the Beaufort Group are multi-layered and multi-porous with variable thickness. The characteristics and depositional history of the Molteno Formation would indicate better groundwater potential. The sediment bodies are more persistent than those of the Beaufort Group. The Elliot Formation consists mostly of red mudstone. This Formation thus presents more of an aquitard than an aquifer. The Clarens Formation consists almost entirely of well-sorted, medium- fine-grained sandstones, deposited as thick consistent layers. Although the Formation has a relatively high and uniform porosity (average 8.5%), it is poorly fractured and has a very low permeability. The formation may therefore be able to store large volumes of water, but is unable to release it quickly (Woodford *et al*., 2002).

Dolerite intrusives are prevalent throughout the Karoo Basin. The country rock is often fractured during and after dyke emplacement. These discontinuities represent zones of relatively higher permeability which act as conduits for groundwater flow within the aquifer. Most successful boreholes show some relationship with the dolerite intrusives. (Woodford *et al*., 2002).The aperture and areal extent of water-yielding fractures in Karoo Formations are limited, and therefore unable to store large quantities of water (Botha *et al*., 2002). The rock matrix is considered as the main storage units for water in Karoo aquifers. Major flow in Karoo aquifers occurs from the rock matrix to the fracture, which supplies the borehole with water. A highly permeable fracture quickly dewaters when pumped unless recharged through its surfaces. The recharge rate depends on the rate at which the water can leak from the surrounding rock matrix to the fracture. The immediate yield of a borehole is not limited by the amount of water stored in Karoo aquifers but more so by the finite rate at which water leaks from the matrix to the fracture (Woodford *et al*., 2002).

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

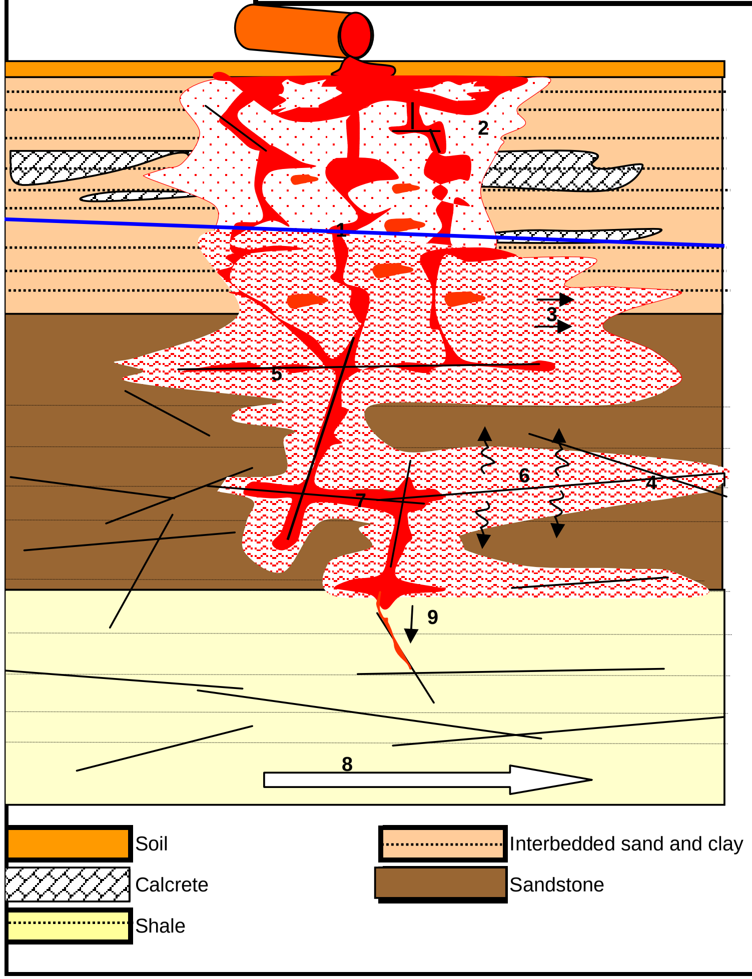
a) Fractures and
b) Inter-fracture blocks or rock matrix.

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

The issues and implications with regard to DNAPL fate and transport in dual porosity systems are as listed below, and illustrated in the conceptualisation in Figure 20.

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

Dual porosity, intergranular and fractured flow systems e.g. Table Mountain Group, Karoo Group (Sandstones, shales, arenites)



Features

1 Residual and pooled DNAPL in weathered clay/sand
2 Vapour plume
3 Aqueous phase plume migration
4 Aqueous phase plume migration in fracture
5 Residual DNAPL in fracture
6 Matrix diffusion from aqueous phase and DNAPL
7 Pooled DNAPL in fractures
8 Groundwater flow direction
9 DNAPL migration to depth

Issues and implications

High fracture porosity, low matrix porosity

Fracture/pore water interaction

Fracture aperture determines entry pressure into fractures

Density driven flow through vertical fractures

Multi-layered aquifer due to presence of hydraulic variance in horizons - construction of boreholes should reflect this

Horizontal and vertical flow important

Generally “deep” aquifers with "thick" unsaturated zone - High cost of investigation in thick aquifers/ deep unsaturated zones

Layering may limit vertical dispersion

Matrix diffusion - cause contamination to be persistent makes remediation difficult

Slow groundwater velocities- smaller aqueous plumes than in porous systems

Figure 20: Conceptualisation of DNAPL fate and transport in intergranular and fractured (dual porosity) flow systems.

5.2.3 Fractured Flow

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

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

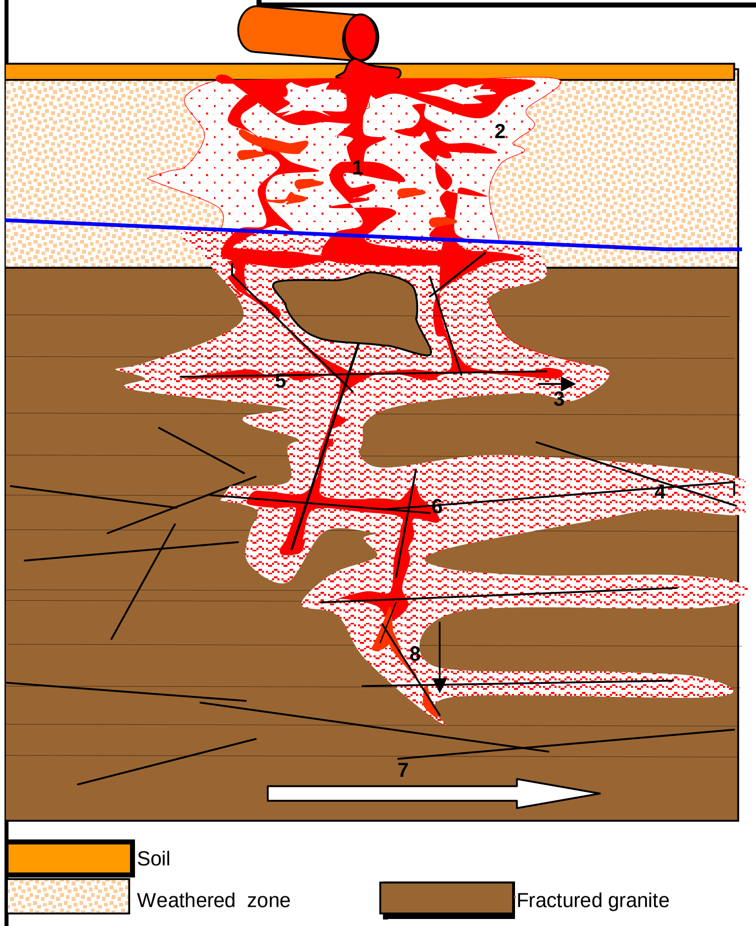
The occurrence of groundwater depends on the existence in the rock formation of a thick weathered zone (the uppermost 10 – 30 m) or the occurrence of deeper fracture zones (MacDonald *et al.*, 2002). Lloyd (1999) concludes the following about igneous and metamorphic basement rocks:

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

The issues and implications with regard to DNAPL fate and transport in fractured systems are as listed below, and illustrated in the conceptualisation in Figure 21.

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

Fracture flow systems e.g. Intrusive and extrusive rock regions West Rand Group, Basement Granites (crystalline metamorphic and igneous rocks)



Features

1 Residual and pooled DNAPL in weathered zone
2 Vapour plume
3 Aqueous phase plume migration
4 Aqueous phase plume migration in fracture
5 Residual DNAPL in fracture
6 Pooled DNAPL in fractures
7 Groundwater flowdirection
8 DNAPL migration to depth

Issues and implications

Fracture flow
Preferential flow paths
Fracture aperture determines entry pressure into fractures
Density driven flow through (sub)vertical fractues
Rapid flow
Variability in vertical and horisontal permeability
Borehole location in relation to fracture positions important
Variability in sample results due to erratic flowpath
Low matrix porosity - Aqueous plumes confined to fractures and "matrix" around fractures

Figure 21: Conceptualisation of DNAPL fate and transport in fractured flow systems.

5.2.4 Karst Flow

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

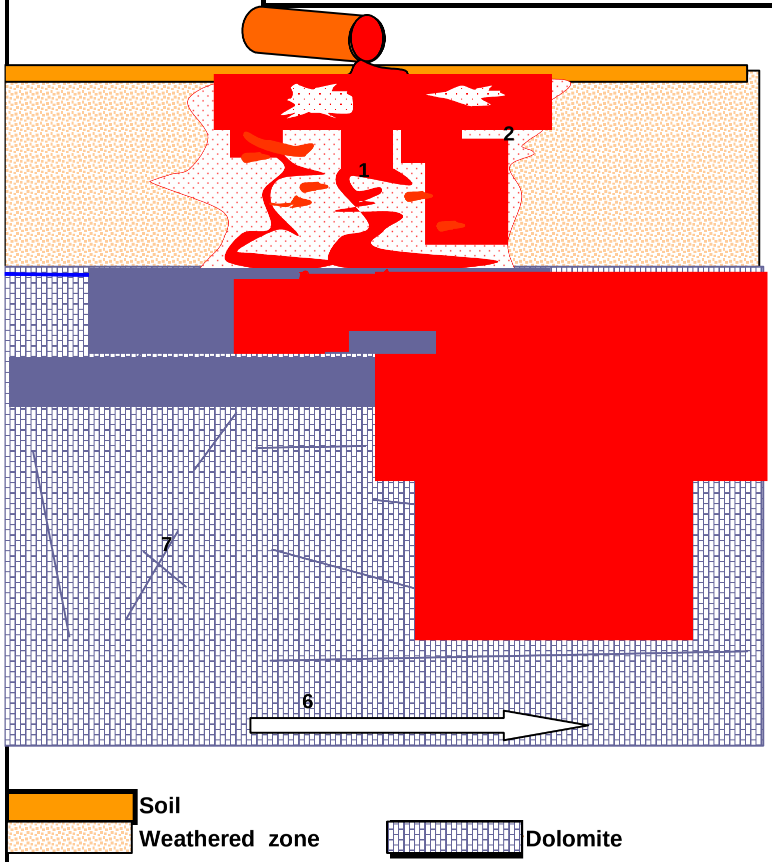
The dolomite aquifers cover an area of about 5000 km^2, with storage estimated at 5000 million m^3 (Bredenkamp, 2002). It is estimated that available groundwater resources are 300 million m^3.

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

The issues and implications with regard to DNAPL fate and transport in fractured systems are as listed below, and illustrated in the conceptualisation in Figure 21.

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

Karstic flow systems e.g. Karst Belt, Ghaap plateau (dolomite)



Features

1 Residual and pooled DNAPL in weathered zone
2 Vapour plume
3 Aqueous phase plume migration
4 Aqueous phase plume migration in solution cavity
5 Residual and pooled DNAPL in fracture
6 Groundwater flow direction
7 Unconnected fractures

Issues and implications

Fracture and Karst flow - regional variations in behaviour of the aquifer (e.g. solution features)

Preferential pathways - Borehole location in relation to preferential pathways

Rapid flow - Variable and rapid travel times need to be taken into account in assessing viability of attenuation and frequency of monitoring

Low matrix porosity

Fracture/pore water interaction

Significant variation in vertical and horizontal permeability

Large seasonal water table variation - Short-circuiting of normal flow regime at times of high water table

Thick aquifers and deep unsaturated zones may result in high cost of investigation

Figure 22: Conceptualisation of DNAPL fate and transport in karst flow systems.

6. CONCLUDING REMARKS

This document has provided an overview of DNAPL contaminants and their properties, the impact of these properties on the fate and transport of DNAPLs in South African aquifers, and generalized conceptual models of DNAPL contaminants in most common type of aquifers in the country.

The following general issues regarding DNAPL contaminated sites need to be considered in the South African context:

1. Utilisation of different drilling techniques (auger, core and air percussion), provide the site assessor with valuable information regarding the subsurface. However, due to high costs and limited availability of specialized (e.g. diamond core and direct push auger) drilling rigs, these techniques are often neglected in site assessments in South Africa.
2. 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 characterize 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 characterization* in order to successfully plan and implement (costly) mitigation and/or remediation.
3. Many problem DNAPLs are volatile organic compounds. Therefore, analyzing soil or water samples during a site investigation on site will yield the better analytical results than costly and time consuming laboratory analysis. Many innovative "on-site" analytical techniques which yield accurate results have been developed e.g. Mobile Gas Chromatograph. However, availability of such equipment is scarce and costly in South Africa.
4. 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. Due to firm regulation of organic contamination in European countries, the European laboratories provide their clients with a number of 'environmental analysis packages". These "packages" targets specific contaminant groups or required lines of evidence (e.g. for monitored natural attenuation) which are more cost effective than analysis of separate contaminants. It is recommended that these practices be adopted by South African laboratories.
5. Although the National Water and Environmental Acts of South Africa are very clear on prevention of pollution to, and management of water resources, no guidelines exists on how to deal with NAPL contaminated sites. Guidelines which are required would include, water quality standards, site assessment guidelines, and monitoring and sampling guidelines.

7. REFERENCES

Adelana S.M.A. and Xu, Y. (2006). Contamination and protection of the Cape Flats Aquifer, South Africa. Published in Xu and Usher (eds) "Groundwater Pollution in Africa". Published by Taylor and Francis/Balkema, The Netherlands. ISBN 13:978-0-415-41167-7 P. 279-288.

Barranco, F.T., and Dawson, H.E. (1998). "Influence of aqueous pH on the interfacial properties of coal tar." Accepted for publication in Environ. Sci. & Tech.

Barranco, F.T., Dawson, H.E., Christener, J.M., and B.D. Honeyman, (1997). Influence of Aqueous pH and Ionic Strength on the Wettability of Quartz in the Presence of Dense Non- Aqueous-Phase Liquids, Environ. Sci. & Tech., Vol. 31(3), pp. 676-681.

Botha, J.F., Verwey, J.P., Van der Voort, I., Vivier, J.J.P., Buys, J., Colliston, W.P and Loock, J.C. (1998). Karoo aquifers: Their geology, geometry and physical properties. WRC Report 487/1/98. Water Research Commission,Pretoria.

Bredenkamp D.B. (2002). Phase 1: Situation Analysis – Technical Assessment. In Stephens and Bredenkamp (2002). Institutional arrangements for groundwater management in dolomitic terrains: Situation analysis. WRC Report KV 140/02. Water Research Commission, Pretoria.

De Beer, C.H. (2002). The stratigraphy, Lithology and Structure of the Table Mountain Group. In Pietersen and Parsons (eds) A synthesis of the hydrogeology of the Table Mountain Group – Formation of a research strategy. WRC Report TT 158/01. Water Research Commission, Pretoria: 9-18

Department of Environmental Affairs and Tourism (DEAT). (2003). Compilation of the South African National Chemicals profile (Draft Report). Project No. J22044A Pretoria, South Africa. Available at: http://www.environment.gov.za/Documents/Documents/2003Jun9_1/Chapt-05_Draft%202.doc

DWAF. (2000). Policy and strategy for groundwater quality management in South Africa - First Edition 2000. Water Quality: Waste Management Subseries, published by Department of Water Affairs and Forestry, Pretoria, South Africa, ISBN 0-620-23789-9.

EPRI. (1993). Chemical and Physical Characteristics of Tar Samples from Selected Manufactured Gas Plant (MGP) Sites; EPRI Tech. Rep. 102184; Project 2879-12; EPRI: Palo Alto, CA, 1993.

Fetter, C.W. 1999. Contaminant Hydrogeology. 2nd edition. Prentice Hall. Upper Saddle River, New Jersey.

Huling, S.G. and Weaver, J.W. (1991). Dense Nonaqueous Phase Liquids. Ground Water Issue, Published by the United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Office of Research and Development. EPA/540/4-91-002, March 1991.

Kueper B.H. ,Wealthall G.P., Smith J.W.N., Leharne S.A., Lerner D.N. (2003). An illustrated handbook of DNAPL transport and fate in the subsurface. Environment Agency, Bristol United Kingdom. ISBN 1844320669

Lloyd, J. W. (1999). Water Resources of hard rock aquifers in arid and semi-arid areas. In Lloyd, J. E. (ed), 1999.Water Resources of hard rock aquifers in arid and semi-arid areas. Unesco Publishing, Studies and Reports in Hydrology. 58, 13-19.

Mercer, J.W. and Cohen R.M. (1990). A Review of immiscible fluids in the subsurface: Properties, models, characterization and remediation, Journal of Contaminant Hydrology, 6:107-163.

Morris R.D., Allerton H.G. and Van der Westhuysen J.P.W. (2000). Practical and responsible approaches to soil and groundwater contamination management at a South African metal plating factory. Published proceedings of the XXX IAH Congress on Groundwater, held in Cape Town, South Africa. A.A. Balkema Publishers.

Palmer J.A. and Cameron-Clarke I.S. (2000). Modelling and field trials for the development of a rehabilitation strategy for an existing hazardous waste site. Published proceedings of the XXX IAH Congress on Groundwater, held in Cape Town, South Africa. A.A. Balkema Publishers.

Pankow, J.F. and Cherry, J.A. (1996). Dense Chlorinated Solvents and other DNAPLs in Groundwater. Waterloo Press, Ontario, Canada.

Pietersen, K.C. (2004). A decision-making framework for groundwater management in arid zones (with a case study in Namaqualand). A thesis submitted in fulfilment of the requirements for the degree of PhD in the Faculty of Natural Sciences, Department of Earth Sciences, University of the Western Cape, Bellville, South Africa.

Pretorius, J.A., and Dennis, I. (2004). Groundwater Overview for Lower Vaal Water Management Area. Prepared for the Directorate Water Resource Planning, DWAF, Pretoria.

Rosewarne, P. (2002). Hydrogeological characteristics of the Table Mountain Group Aquifers. In Pietersen and Parsons (eds) A synthesis of the hydrogeology of the Table Mountain Group – Formation of a research strategy.WRC Report TT 158/01. Water Research Commission, Pretoria: 33-44

Rossabi J., Looney B.B., Eddy-Dilek C.A., Riha B.D., and Jackson D.G. (2000). DNAPL Site Characterization: The Evolving Conceptual Model and Toolbox Approach, U.S. Department of Energy, No. DE-AC09-96SR18500.

Schwarzenbach, R.P, Gschwend, P.M and Imboden, D.M. (1993). Environmental Organic Chemistry. John Wiley & Sons Inc., New York.

Schwille, F. (1988). Dense Chlorinated Solvents in Porous and Fractured Media – Model Experiments, translated from the German by J. F. Pankow, Lewis Publishers, Boca Raton, Florida.

Thomson, R. 2004. DNAPLs in Porous and Fractured Media. Notes presented at a Short Course on the Migration, Characterization and remediation of Non-aqueous Phase Liquids in the subsurface. University of Sheffield, 9-11 March 2004.

Usher B.H., Pretorius J.A., Dennis I., Jovanovic N., Clarke S., Cave L., and Titus R. (2004). Identification and Prioritisation of Groundwater Contaminants in South Africa's Urban Catchments. Published by the Water research Commission, Pretoria, South Africa, WRC Report No. 1326/1/04. ISBN 1-77005-196-1

Van Wyk, E. (2002). Pers. Comm. From Pietersen (2004) "A decision-making framework for groundwater management in arid zones (with a case study in Namaqualand)." A thesis submitted in fulfilment of the requirements for the degree of PhD in the Faculty of Natural Sciences, Department of Earth Sciences, University of the Western Cape, Bellville, South Africa.

Vegter, J.R. (1995). An explanation of a set of National Groundwater Maps. WRC Report TT 74/95. Water Research Commission, Pretoria.

Vegter, J.R. (2000). Groundwater development in South Africa and an introduction to the hydrogeology of groundwater regions. WRC Report TT 134/00. Water Research Commission, Pretoria.

Woodford, A.C. (2002). Interpretation and applicability of pumping tests in Table Mountain Group Aquifers. In Pietersen and Parsons (eds) A synthesis of the hydrogeology of the Table Mountain Group – Formation of a research strategy. WRC Report TT 158/01. Water Research Commission, Pretoria: 71-84.

Wright, E. P. (1992). The hydrogeology of crystalline basement aquifers in Africa. Wright, EP and Burgess, WG(eds.) The hydrogeology of crystalline basement aquifers in Africa. Geological Society Special Publication 66, 1-27

Xu, Y. and Usher, B.H. (eds) (2006). Groundwater Pollution in Africa. Published by Taylor and Francis/Balkema, The Netherlands. ISBN 13:978-0-415-41167-7

Websites:

http://www.blacksmithinstitute.org/about.php

http://www.epa.gov

Appendix A

Table 5: Selected DNAPLs with Viscosity (cp) and Specific Gravity Appearance/occurrence and uses.

(Sources: Cohen & Mercer, 1993, www.epa.gov/safewater/contaminants/; www.epa.gov/iris/; www.chemicalland21.com/; www.eco-usa.net/toxics/; www.atsdr.cdc.gov/ and www.speclab.com/)

DNAPL	Acronym	Absolute viscosity	Specific Gravity	Appearance and Use
Halogenated Hydrocarbons				
1,1,1-Trichloroethane	1,1,1-TCA, Methyl chloroform	1.20	1.339	It is a colorless liquid with a sharp, sweet odor and does not occur naturally in the environment. It is found in many common products such as glue, paint, industrial degreasers, and aerosol sprays.
1,1,2,2-Tetrabromoethane	Acetylene tetrachloride	9.79	2.875	Clear to pale yellow liquid with pungent odour. It is used as a flame retardant/fire extinguishing ingredient, solvent for fats, oils, greases, and a chemical intermediate. It is also used in separating minerals.
1,1,2,2-Tetrachloroethane	Acetylene tetrabromide	1.75	1.595	It is a manufactured, colorless chemical and has a sweet odor. It does not burn easily but is volatile. In the past, it was used in large amounts to produce other chemicals and as a solvent, to clean and degrease metals, and in paints and pesticides. It presently is used only as a chemical intermediate in the production of other chemicals.
1,1,2-Trichloroethane	1,1,2-TCA	0.12	1.440	It is an organic liquid with a chloroform-like odor. It does not burn easily, can be dissolved in water, and evaporates easily. It is used as a solvent and as an intermediate in the production of the chemical, 1,1-dichloroethane. Major Industries where it can be found: Alkalies, chlorine, photograph equipment, meat packing plants, petroleum refining, blast furnaces, and steelworks.
1,1,2-Trichlorofluoromethane	Freon 11	0.42	1.487	It is used as a solvent, chemical intermediate, blowing agent for polyurethane foams and polymeric foams, dry cleaning agent, aerosol propellant and in fire extinguishers. It is also used in the manufacturing of aerosol sprays, commercial refrigeration equipment, as an "inert" ingredient in pesticides and cleaning compounds. Very resistant to chemical and biological degradation and likely to be a persistent contaminant if it reaches groundwater.
1,2,4-Trichlorobenzene	1,2,4-TCB	1.42	1.454	It is an aromatic, colorless organic liquid. The greatest use of 1,2,4-trichlorobenzene is primarily as a dye carrier. It is also used to make herbicides and other organic chemicals; as a solvent; in wood preservatives; and in abrasives. It was once used as a soil treatment for termite control. Major environmental releases of 1,2,4-trichlorobenzene are due to its manufacture and use as a dye carrier from textile finishing industries.

DNAPL	Acronym	Absolute viscosity	Specific Gravity	Appearance and Use
Ethylene dibromide	EDB	1.72	2.179	EDB is a colorless liquid with a mild sweet odor, like chloroform. It is used as an additive to leaded petrol; as a fumigant to protect against insects and pests in a number of crops and on turf; spot treatment of milling machinery; and is also used as an intermediate for dyes, resins, waxes, and gums.
Hexachlorobutadiene	HCBD	2.45	1.554	Hexachlorobutadiene is a colorless liquid with a turpentine-like odor. It is mainly used to make rubber compounds. It is also used as a solvent, and to make lubricants, in gyroscopes, as a heat transfer liquid, and as a hydraulic fluid.
Iodomethane	Methyl iodide	0.52	2.279	It is a colourless liquid with a sweet, pungent odour. The primary use is as a chemical intermediate in the manufacture of certain pharmaceuticals and pesticides. It is also used in methylation processes and in the field of microscopy. To a lesser extent, it has been used in fire extinguishers and as an insect fumigant.
Methylene chloride	Dichloromethane	0.43	1.327	Methylene chloride is a colorless liquid with a mild, sweet odor. It is used as an industrial solvent and as a paint stripper. It may also be found in some aerosol and pesticide products and is used in the manufacture of photographic film.
Pentachloroethane	Ethane pentachloride	2.75	1.680	Colourless liquid with chloroform smell. Used as solvent for oil and grease in metal cleaning; separation of coal from impurities, dry cleaning; in soil sterilisation; in organic synthesis as a drying agent for timber immersed in it at temperatures greater than 100 deg C. Also is used as a solvent for cellulose acetate, certain cellulose ethers, resins and gums.
Tetrachloroethene	Perchloroethylene, PCE	0.89	1.623	It is a nonflammable, colorless liquid at room temperature which readily evaporates into air and has an ether-like odor. It is a manufactured chemical that is widely used in the dry-cleaning of fabrics. It is also used for degreasing metal parts and in manufacturing other chemicals. It is found in consumer products, including some paint and spot removers, water repellents, brake and wood cleaners, glues, and suede protectors.
Bromochloromethane	Chlorobromoethane	0.99	1.495	Clear colourless to pale yellow liquid, with sweet chloroform like odour. As a chemical intermediate and limited use as fire extinguishing agent.
Bis(2-chloroethyl)ether		2.14	1.220	It is a colorless, nonflammable liquid with a strong unpleasant odor. It dissolves easily in water, and some of it will slowly evaporate to the air and does not occur naturally. Most of it is used to make pesticides. Some of it is used as a solvent, cleaner, component of paint and varnish, rust inhibitor, or as a chemical intermediate to make other chemicals.

DNAPL	Acronym	Absolute viscosity	Specific Gravity	Appearance and Use
Bromodichloromethane	Dichlorobromomethane	1.71	1.980	It is a colorless, nonflammable liquid. Algae in the oceans form small amounts naturally. The small quantities that are produced are used in laboratories or to make other chemicals. However, most bromodichloromethane is formed as a by-product when chlorine is added to drinking water to kill bacteria.
Bromoethane	Ethyl bromide	0.42	1.460	Colorless to yellow liquid with ether like odor. Ethyl bromide is used as a solvent, as an anesthetic in medicine, as a refrigerant, as a fumigant. It is an ethylating agent in organic synthesis and is used in petrol.
Carbon tetrachloride	Tetrachloromethane	0.97	1.594	It does not occur naturally. It is a clear liquid with a sweet smell that can be detected at low levels. It is most often found as a colorless gas. It is not flammable and does not dissolve in water very easily. It was used in the production of refrigeration fluid and propellants for aerosol cans, as a pesticide, as a cleaning fluid and degreasing agent, in fire extinguishers, and in spot removers. Because of its harmful effects, these uses are now banned and it is only used in some industrial applications.
Chlorobenzene	Benzene chloride	0.80	1.106	It is a colorless, flammable liquid with an aromatic, almond-like odor. Some of it will dissolve in water, but it readily evaporates into air. It does not occur naturally in the environment. It was used in the past to make other chemicals, such as phenol and DDT. The greatest use of chlorobenzene is in the manufacture of other organic chemicals, dyestuffs, and insecticides. It is also a solvent for adhesives, drugs, rubber, paints and dry-cleaning, and as a fiber-swelling agent in textile processing.
Chloroform	Trichloromethane	0.58	1.483	Chloroform is a colorless liquid with a pleasant, nonirritating odor and a slightly sweet taste. It was used in the past as an inhaled anesthetic during surgery. Today, chloroform is used to make other chemicals and can be formed in small amounts when chlorine is added to water.
m-Chlorotoluene		0.75	1.072	Clear liquid slightly soluble. It is used as a solvent and as an intermediate for organic synthesis especially for dyes.
o-Chlorotoluene	2-Chloro-1-methylbenzene	0.75	1.082	Clear liquid slightly soluble. It is used as a solvent and as an intermediate for organic synthesis especially for dyes.
1,2-Dichlorobenzene	o-Dichlorobenzene	1.32	1.305	It is a colorless to pale yellow liquid with a pleasant odor. Dichlorobenzenes belong to the group of organic halogen compounds replacing two hydrogen atoms in benzene by chlorine

DNAPL	Acronym	Absolute viscosity	Specific Gravity	Appearance and Use
1,3-Dichlorobenzene	m-Dichlorobenzene	1.04	1.288	atoms. There are three isomers. It is used as a solvent, a chemical intermediate to manufacture dyes, agrochemicals, pharmaceuticals, and other organic synthesis. It is an insecticide and a fumigant. The effluents from industrial and sewage treatment plants; pulp and paper mill effluents; effluents from iron and steel manufacturing, and petroleum refinery effluents have been identified a sources to the environment of this chemical.
trans-1,2-Dichloroethane	trans-1,2-DCE	0.40	1.257	It is a colorless liquid with a sharp, harsh odor. It is used to produce solvents and in chemical mixtures. Also solvent; degreasing agent; paint remover ingredient; aerosol products ingredient; blowing agent in foams; refrigerant.
1,2-Dichloropropane	Propylene dichloride	0.86	1.560	It is a colorless, flammable liquid with a chloroform-like odor. It was used in the past as a soil fumigant, chemical intermediate, and industrial solvent and was found in paint strippers, varnishes, and furniture finish removers. Most of these uses were discontinued. Today, almost all of the 1,2-dichloropropane is used as a chemical intermediate to make perchloroethylene and several other chlorinated chemicals.
1,1-Dichloroethane	1,1-DCA	0.44	1.176	Industrial chemical that is not found naturally in the environment. It is a colorless liquid with a mild, sweet smell. It is used to make certain plastics, such as flexible films like food wrap, and in packaging materials. It is also used to make flame retardant coatings for fiber and carpet backings, and in piping, coating for steel pipes, and in adhesive applications.
1,2-Dichloroethane	Ethylene dichloride; 1,2-DCA	0.80	1.235	It is a clear liquid and has a pleasant smell and sweet taste. The most common use is in the production of vinyl chloride which is used to make a variety of plastic and vinyl products including polyvinyl chloride (PVC) pipes, furniture and automobile upholstery, wall coverings, housewares, and automobile parts. It is also used to as a solvent and is added to leaded petrol to remove lead.
1,1-Dichloroethene	Vinylidene chloride; 1,1-DCE	0.36	1.218	Colourless liquid, with chloroform like smell.(spacing required)Virtually all it produced is used in the production of copolymers with vinyl chloride or acrylonitrile. A small percentage (4%) is used as chemical intermediates. It is used to make certain plastics, such as flexible films like food wrap, and in packaging materials. It is also used to make flame retardant coatings for fiber and carpet backings, and in piping, coating for steel pipes, and in adhesive applications.

DNAPL	Acronym	Absolute viscosity	Specific Gravity	Appearance and Use
Bromoform	Tribromomethane	2.02	2.890	It is colorless to yellow, heavy, nonflammable, liquid with a sweet odor. Plants in the ocean form small amounts naturally. They are somewhat soluble in water and readily evaporate into the air. Most of it that enters the environment is formed as byproducts when chlorine is added to drinking water to kill bacteria. Only small quantities are produced, it was used in the past as solvents and flame retardants, or to make other chemicals, but now it is used mainly as laboratory reagents. Also used in synthesis of sedative, antitussive and antiseptic medication; as a heavy liquid floatation agent in mineral separation, sedimentary petrographical surveys, and purification of materials such as quartz; as an industrial solvent in liquid-solvent extractions, in nuclear magnetic resonance studies; as a catalyst, initiator, or sensitizer in polymer reactions, and in vulcanization of rubber.
Trichloroethene	TCE	0.57	1.464	Trichloroethylene is a heavy, stable, toxic, nonflammable liquid with a chloroform aroma. Because of concerns about its toxicity, the use is declining. It is prohibited to use in food, drugs and cosmetics. It is now mainly used in vapor degreasing of fabricated or assembling metal parts. It is also used as an industrial solvent in extraction processes, as a diluent in paints and adhesives, in textile processing, and other ways. It is used as a chain terminator for PVC production. It is also used as a refrigerant, as a heat exchange liquid, as a chemical intermediate or raw material in the production of chloroacetic acid, pesticides, gums, resins, tars, paints and varnishes. It is used in dry cleaning operations.
Other (incl. components of coal tar and creosote)				
Dibutyl phthalate	Dibutyl-n-phthalate; DBP	20.30	1.046	Clear liquid, slight odor, slightly soluble. DBP, a member of the phthalic acid ester plasticizer, imparts flexibility and impacts strength of plastics. It is used as an ingredient of insect repellent, a solvent in lacquer and perfume fixative, a dye carrier, and as a textile lubricating agent and solid rocket propellant.
1-Nitropropane	UN 2608	0.80	1.008	Almost colorless liquid with a mild, fruity odor. Solvent for cellulose acetate, vinyl resins, lacquers, synthetic rubbers, fats, oils, dyes and protective coatings; rocket propellant; organic intermediate for agrochemicals and pharmaceuticals; solvent-extraction processes; and fuel additive.
Diethyl phthalate	DEP	35.00	1.118	It is a colorless liquid that has a bitter, disagreeable taste. This synthetic substance is commonly used to make plastics more flexible. Products in which it is found include toothbrushes, automobile parts, tools, toys, and food packaging. It can be released fairly easily from these products, as it is not part of the chain of chemicals (polymers) that makes up the plastic. It is also used in cosmetics, insecticides, and aspirin.

DNAPL	Acronym	Absolute viscosity	Specific Gravity	Appearance and Use
Dimethyl phthalate	DMP	17.20	1.191	It is clear oily liquid, slightly soluble. It is used as an ingredient of insect repellent. It is used as a solvent in lacquer and paint and as a dye carrier. It is used as a textile lubricating agent and solid rocket propellant. Also cosmetic ingredient, fluidized bed coating in manufacture of poly(vinylidene fluoride); plasticizer in cellulose acetate and nitrocellulose and plastics, resins, rubber; constituent of rubber.
Aniline	Benzenamine	4.40	1.022	It is a pale brown liquid with a characteristic odor, is slightly soluble in water, and mixes readily with most organic solvents. It is obtained commercially from chlorobenzene by heating with ammonia in the presence of copper catalyst or from a product of coal tar (nitrobenzene) through the reduction reaction. It is the starting material in the dye manufacturing industry and as in the manufacture of others. Aniline is converted into sulfanilic acid which is the parent compound of the sulfa drugs. It is also important in the manufacture of rubber-processing chemicals, antioxidants and varnishes. Amines take part in many kinds of chemical reactions and offer many applications include in agrochemicals, dyestuffs (the best known being aniline), pharmaceuticals, and corrosion inhibitors.
Benzyl alcohol	Benzenemethanol	7.76	1.045	It is a clear, colorless liquid with a mild pleasant aromatic odor. Benzyl alcohol, featuring good solvency, low toxicity, and low vapor pressure, is used as a general solvent for inks, paints, lacquers, and epoxy resin coatings. It is also used as a raw material of various esters, used in the soap, perfume, and flavor industries. It is also used as a photographic developer and in perfumes, flavor industries, pharmaceuticals as a bacteriostatic.
Carbon disulfide	Carbon disulfide	0.37	1.263	Pure carbon disulfide is a colorless liquid with a pleasant odor that is like the smell of chloroform. The impure carbon disulfide that is usually used in most industrial processes is a yellowish liquid with an unpleasant odor, like that of rotting radishes. It is prepared from preheated hydrocarbons (natural gas) with vaporized sulfur in the presence of a catalyst. One of the most important uses is in the production of viscose rayon fibers, which are used to produce rayon filament yarn, rayon tire yarn, rayon stable fibre and Cellophane film. It is widely used as a solvent in the industrial fields of refining rubber.
2-Nitrotoluene	1-Methyl-3-nitrobenzene	2.37	1.163	Yellowish liquid at ordinary temp, weak aromatic odor. Production of toluidine, tolidine, fuchsine and various dyes.
Nitroethane	UN2842	0.66	1.045	Clear liquid with a mild fruity odor. It is a suitable solvent in coatings and inks. It is used as an extraction solvent of rosin and some inorganic materials such aluminum chloride used as a Friedel-Crafts reaction catalyst.

DNAPL	**Acronym**	**Absolute viscosity**	**Specific Gravity**	**Appearance and Use**
Nitrobenzene	Nitrobenzol	2.01	1.204	Nitrobenzene is an industrial chemical. It is an oily yellow liquid with an almond-like odor. It is produced in large quantities for use in industry. Most of the nitrobenzene is used to manufacture a chemical called aniline. Nitrobenzene is also used to produce lubricating oils such as those used in motors and machinery. A small amount of nitrobenzene is used in the manufacture of dyes, drugs, pesticides, and synthetic rubber.
Thiophene	Thiacyclopentadiene	0.65	1.065	Clear to yellow liquid, slightly soluble. It is used as a solvent and chemical intermediate. Its derivatives are widely used in manufacturing dyes, aroma compounds and pharmaceuticals. They are used as monomers to make condensation copolymers. 2-Thiophene Ethanol is used as an intermediate of such as antiplatelet drugs (Clopidogrel, Ticlopidine) used to lessen the chance of heart attack or stroke.
Tri-o-cresyl phosphate	o-Creasyl phosphate	80.00	1.955	Clear liquid, slightly soluble. Tricresyl Phosphate is used as a plasticizer for PVC, rubber and plastics. It is used as an ingredient for flame-retardant in plastics, rubbers and in hydraulic systems. It is used as a heat exchange medium. It is used a solvent and thinner for nitrocellulose, paints and varnishes. It is also used as an additive in high-pressure cooling lubricants and a lead scavenger in petrol.
Polychlorinated Biphenyls				
PCB1016	Aroclor 1016	19.30	1.330	Polychlorinated biphenyls are mixtures of up to 209 individual chlorinated compounds (known as congeners). There are no known natural sources of PCBs. PCBs are either oily liquids or solids that are colorless to light yellow. PCBs are mixtures of synthetic organic chemicals with the same basic chemical structure and similar physical properties ranging from oily liquids to waxy solids. Due to their non-flammability, chemical stability, high boiling point and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics and rubber products; in pigments, dyes and carbonless copy paper and many other applications.
PCB1222	Aroclor 1222	4.80	1.180	
PCB1232	Aroclor 1232	8.20	1.240	
PCB1242	Aroclor 1242	24.00	1.392	
PCB1248	Aroclor 1248	65.00	1.410	
PCB1254	Aroclor 1254	700.00	1.505	

Appendix B

Table 6: Prioritisation list of sources of possible DNAPL groundwater contamination in urban environments

(Adapted from Usher et al., 2004).

Ranking	Type of source	Expected contaminants	Comment
2	Production of agricultural chemicals (fertilizers, herbicides, pesticides)	Chlorinated insecticides, ethylbenzene, naphthalene, organophosphates, phenols, phthalates, toluene, xylene, other herbicides	Not a common industry, limited to large industrial premises, but mobility and type of contaminants pose a great contaminant risk to groundwater.
4	Metallurgical	Mineral oils, organic solvents; chlorobenzenes; PCBs, coal tars	Usually large industrial premises, variety chemicals used, often have own waste disposal areas/ ponds which pose great contaminant risk to groundwater.
5	Metal (predominately gold) and coal mining	Petroleum hydrocarbons, chemicals/ reagents used in benefiaction processes, PCBs, PAHs	Potential for groundwater contamination high but not often found within urban area (except Gauteng)
6	Transport	Benzene, toluene, xylenes (BTEX), alkanes, TPH, PAH, any other chemicals transported resulting from accidents or spills	Accidents and spills in urban area often cleaned up quickly after reporting. Wide variety of chemicals
7	Petrol Service Stations (Underground Storage Tanks)*	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), alkanes, TPH, PAH any other chemicals stored in USTs	Leakage from UST common due to corrosion of systems
8	Wood processing and preserving	Creosote, PAHs, pentachlorophenol, phenol, PCB	Spills and accidents more likely the greater the operation.

Ranking	Type of source	Expected contaminants	Comment
10	Manufacturing - Chemicals	VOCs (Acetylene, Benzene, Butane, Chloroform, Ethyl Alcohol, and Methane), PAHs, chloroform, tetrachloromethane, di-, tri- and tetra-chlorinated benzenes, chlorinated alkanes, hexachlorocyclohexane (HCH), DDT (DDD and DDE), 2,4-dichlorophenol, HCH, ketones, toluene, xylene; carbon tetrachloride, chlorofluoroethanes, dichloroethylene, methylene chloride, PCE, TCE, vinyl chloride, 1,1,1-trichloethane, PCBs, PAHs, coal tars	Usually large industrial premises, variety of base and more complex chemicals (used and produced), often have own waste disposal areas/ponds, which pose great contaminant risk to groundwater.
11	Workshops (Mechanical and electrical)	PAHs, diesel, benzene, alkanes, chlorinated solvents	Spills and wash water directed to sewers or stormwater drains
12	Stormwater/ sewer systems	Hydrocarbons, diverse industrial chemicals	Likelihood of groundwater contamination dependant on the type and integrity of the network
13	Automotive manufacturing	Hydrocarbons, solvents, paints	Little waste generation of groundwater importance; spillage, accidents, illegal disposal
13	Automotive refinishing and repair	Paint; waste oils; toluene, acetone, perchloroethylene, xylene, gasoline and diesel fuel, carbon tetrachloride	Spills and wash water directed to sewers or stormwater drains
14	Other metal product manufacturing	Benzene, trichloroethane and trichloroethylene, other VOCs; degreasing agents; waste oils	Diverse
15	Railroad yards	Petroleum hydrocarbons; VOCs; BTEX; solvents; fuels; oil and grease; lead; PCBs	Widespread, with long histories
18	Agriculture (General and crop cultivation)	Volatile organic compounds (VOC); carbon tetrachloride, ethylene dibromide, and methylene chloride; pesticides; insecticides; herbicides; grain fumigants	Activities mostly irrigation crop cultivation, some vineyards (Cape Town) but not common within urban boundaries

Ranking	Type of source	Expected contaminants	Comment
19	Paper/ pulp industry	Acrylates, chlorinated solvents, mercury, phenols, styrene, chloroform	Industries vary between small-scale to very large scale. Paper mills pose greater threat to groundwater but often located on outskirts of urban area due to aesthetic reasons.
20	Research and educational institutions	Organic solvents; photographic waste; waste oil; paint, pesticides	Chemicals flushed to sewer network
24	Munitions manufacturing	Solvents	Not a common industry, limited to large industrial premises, but mobility and type of contaminants pose a great contaminant risk to groundwater.
25	Hazardous waste sites	Various chemical mixtures	Only 6 H:H sites in SA, all permitted. There are however many private H:H sites.
26	Marine maintenance industry	Solvents; paints; VOC emissions; heavy metal sludge; degreasers	Only relevant to coastal urban centers with large port facilities
27	Dry cleaning activities	VOCs such as chloroform and tetrachloroethane; various solvents; spot removers; fluorocarbon 113	Spills often occur at chemical storage area and below machinery.
28	General/ Domestic waste sites	Various chemicals	Most legal domestic waste sites are located on outskirts of urban area due to aesthetic reasons, groundwater contamination will vary with size, type and management of each site
29	Wastewater treatment	Diverse industrial chemicals	Depending on the type of water treatment process and management of the system, the likelihood of groundwater contamination may increase.
30	Textile manufacture	Ammonium, arsenic, cadmium, chromium, ethyl acetate, nickel, hexane, oxalic acid, phenols, phthalates, toluene, lead	Common industry varying in type and size. Some more likely to cause groundwater contamination (e.g. wool washing)
31	Rubber and plastics	Acrylonitrile, antimony, benzene, butadiene, cadmium, chloroform, chromium, dichloroethylenes, lead, phenols, phthalates, styrene, sulphur, vinyl chloride, toluene, heptane, formaldehyde	Industries vary between small-scale to very large scale. Rubber conversion industry pose greater threat than plastic conversion.

Ranking	Type of source	Expected contaminants	Comment
33	Leather manufacturing	Toluene; benzene; solvents	Very few large tanneries in SA, number of small-scale operations, but due to nature of chemicals used the risk for groundwater contamination is great.
35	Printing industry	Waste oils; toluene; MEK; xylene, TCE	Very common industry widely distributed throughout urban area but often chemicals are flushed to sewer network
38	Auto Salvage/Metal Recyclers	CBs, hydraulic fluids and lubricating oils, fuels, and solvents	Most of these types of industries are relative small.
39	Electrical and electrical products manufacturing	Petroleum hydrocarbons, isopropanol, methanol, salinity, trichloroethylene, arsenic, silane, metals	Most of these types of industries are relative small.
40	Electricity generation	PCBs, PAHs	Widespread, with long histories
41	Photographic manufacturing and uses	Solvents; photographic products	Chemicals flushed to sewer network
42	Paint/ink manufacturing and coatings	Chlorinated solvents, glycol ethers, ketones, methylene chloride, mineral spirits,phthalates, styrene, terpenes, toluene, anthraquinones, benzidine, ethyl acetate, hexane, oxalic acid, phenol	Industries vary between small-scale to very large scale. Larger manufacturing (opposed to "mixing") industries will pose greater threat to groundwater.
43	Pharmaceuticals and cosmetics manufacturing	Dyes, glycols, mineral spirits, dichlorobenzene, methylene chloride	Most of this type of industries are relative small and does not manufacture own base chemicals.
44	Adhesives and sealants	Benzene, toluene, methyl-ethyl ketone (MEK)	Most of these types of industries are relative small.
48	Hospitals / Health Care	Formaldehyde;photographic chemicals; solvents; mercury; chemotherapy chemicals	Waste often not disposed of or incinerated on site
49	Glass manufacturing	Arsenic; lead	Not a common industry, with limited contaminant risk to groundwater.
50	Incinerators	Dioxin; various municipal and industrial waste	Most incinerators are permitted and strict compliance to storage of waste and ash must be followed

Table 7: Contaminant Prioritisation – NAPL contaminants with ranking

(Adapted from Usher et al., 2004).

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