Field Investigations to Study the Fate and Transport of Light Non-Aqueous Phase Liquids (LNAPLs) in Groundwater

Report to the
Water Research Commission

by

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Executive Summary

In this report the key features in characterising and evaluating a LNAPL contaminated site is presented. The characteristics which define LNAPLs are expanded on in this report, with special attention to the chemical and physical properties of these compounds. The influence that the local geology has on the distribution of these compounds has been discussed in regards to the type of aquifers present in South Africa. A review of geophysical methods was incorporated in this study to highlight the most effective methods available. To conclude the review of LNAPL contamination at a site, the most important transport and remediation mechanisms were highlighted.

A systematic review of site investigation and characterisation methods is reported, as well as a methodology to construct a site conceptual model. Two main study areas were used, to highlight the difference in applicable methods to characterise a coastal and inland contamination site. Subsequently a conceptual model of each site was constructed incorporating the most significant features that affect remediation options. An estimation of remediation costs were done, although values presented are based on a generalised site with no significant difficulties.

Acknowledgements

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    c. Dr C Mills (Mills & Otten)
    d. Dr E van Wyk (DWA, Hydrogeological Section)

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 NAPLs.
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.
Effective solubility	The aqueous solubility of a compound in (ground)water, where that compound is derived from a multi-component NAPL. The effective solubility is proportional to the molar fraction of that compound in the NAPL 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, NAPLs would be fully miscible (infinitely soluble) in water. The fact that interfacial tension exists between a NAPL and water is a defining feature of a NAPL. 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, NAPL and water, and NAPL and air.

LNAPL (light, non-aqueous phase liquid)	A liquid that is less dense 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 vaporise 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 slower than the groundwater.
Plume	A contiguous region of groundwater containing dissolved contaminants. Plumes are typically formed by the dissolution of NAPL into groundwater and therefore occur hydraulically down-gradient of the NAPL source zone. Plume migration is subject to advection and dispersion, and may be subject to sorption, biodegradation and matrix diffusion.
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).
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 NAPL.
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 NAPL phase to the air phase (often referred to as evaporation). The rate of vaporisation is proportional to the vapour pressure of the NAPL, which in turn is temperature dependent. Highly volatile NAPLs such as some chlorinated solvents will vaporise quicker than low volatility NAPLs such as PCB oils. In a multi-component NAPL, the individual compounds with high vapour pressures will vaporise quicker than those with lower vapour pressures, resulting in an enrichment of the NAPL 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 slower 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, NAPL is wetting with respect to air, and water is wetting with respect to NAPL. 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 NAPL and the chemical composition of the solid surface of interest.

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1 INTRODUCTION

This report introduces the concepts, framework and best practice procedures. It outlines procedures on how to help address water research management issues and will hopefully provide a step-by-step approach in dealing with LNAPL contamination from a South African perspective.

The influence of environmental contaminants is a hot topic in a developing country such as South Africa, specifically LNAPL contamination touches on diverse fields in chemistry, physics and hydrology. It does not exclude surface water and groundwater interactions or the effect of urbanisation. This field of study combines the social, legislative, industrial and scientific fields into a unified management approach to resolve issues emanating from LNAPL contaminants.

1.1 What is Groundwater Contamination from LNAPLs?

The South African mission for groundwater quality 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 approach:

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

Studies on the fate and transport of organic pollutants in groundwater in South Africa have, to date, been done on an ad hoc basis. LNAPLs are organic chemicals that have a lower density than water (i.e. will float on top of water) with an immiscible phase that have been released into the environment. These molecules include a number of organic products and represent some of the most widely used chemicals which can pose a potential environmental threat. LNAPLs are used extensively in industrial, commercial and modern lifestyles. On release to the subsurface environment, an LNAPL will migrate downwards to the water table or until it encounters a low-permeability horizon. Once the water table is encountered, the LNAPL may move laterally as a free-phase layer along the surface of the water table; this migration will generally be in the direction of the groundwater gradient. Components of the LNAPL may dissolve in the groundwater and form a dissolved phase, the movement of which will be controlled by conventional groundwater transport mechanisms (advection, dispersion and diffusion). LNAPL compounds may also migrate in the vapour phase since more volatile LNAPL compounds readily partition into the air phase. Thus LNAPLs pose especially difficult challenges for remediation since it can occur in three distinct phases and the transport mechanism for each scenario is markedly different.

The composition of South African aquifers is considerably unlike the idealized porous media described in literature. South African aquifers are characterised by their fractured or dual porosity nature and tend to have unique transport characteristics. The major aquifer systems such as the Karoo aquifers, Table Mountain Group aquifers and the basement rock aquifers in the northern part of the country are all dominated by fractured features. In contrast Dolomitic aquifers which are Karstic in nature have predominantly channel flow transport systems.

In fracture-flow dominated systems the occurrence, orientation and extent of the fractures will dominate the groundwater flow directions and rates. As such all the soluble/partially soluble phases can only be transported along these fracture zones. Factors such as retardation and the chromatographic effect of separation in the phases according the Raoult’s law are therefore considerably altered. The influences of matrix diffusion upon the LNAPL contaminant migration with in a dual porosity medium also become increasingly important.

The importance of fracture transport of LNAPLs includes:

1. More rapid transport way from the site due to enhanced hydraulic conductivity of the fracture/ fracture zone.
2. Shorter travel times to sensitive receptors (environmental and human).
3. If the depth of the water table/capillary zone coincides with a fracture, the rapid distribution of LNAPL can occur.
4. Enhanced smearing where sub-vertical fractures are encountered.
5. Greater importance of matrix diffusion.

In the subsurface, the general depth at which the potentiometric/water table lays or the presence of sub-vertical fractures also becomes important for the gas transport. Where such a fracture exists a pressure release in the three-phase gas/LNAPL/dissolved phase occurs, which radically changes the mass distribution leading to relative enrichment in the less volatile phases. This has important implications regarding the application of most international methodologies.

A number of groundwater studies on the fate and transport of organic pollutants has been done internationally, i.e. the application of tools/approaches (ASTM, 1994). Many of the assumptions inherent in these approaches are not directly applicable to South African aquifers systems, and although values such as the health hazards remain appropriate when detected, the approach to determine the risk may not always be appropriate. The results from international literature may not be valid to this region as the soil type and climatic conditions are very different. However, international experience does represent an important knowledge base which can be built upon.

1.2 Need for Guidelines

Due to the inherent complexity of South Africa's geology and subsequent geohydrology, guidelines will always be an integral part of any decision support system for the management of water resources. The scarcity and applicability of international guidelines to a South African environment can have significant detrimental effects on the method by which water resources are managed. The development and evaluation of resource management strategies for sustainable and safe water allocation are dependent on the correct characterisation and allocation of possible harmful contaminants in the subsurface. In general LNAPL contamination does not occur on a regional scale but are located on a local scale, i.e. industrial or commercial sites.

The end-user (be it a water resource manager, community representative or regulator) should be able to use this report to launch an investigation into LNAPL contamination on site with adequate background knowledge to assist in further decision making processes. The development and implementation of the LNAPL guidelines and report is designed to reduce the level of uncertainty for decision makers, end-users and the community. This study will hopefully promote transparency in field investigation methodologies and encourage consistency in reporting, which would result in a best practice approach combined with greater confidence in the results obtained. It is expected that the study should provide both non-professionals and professionals with a guideline which can help with site investigations as well as reviewing results obtained from a field investigation.

1.2.1 Analysis Laboratories

During the course of this investigation it became clear that a number of laboratories exist in South Africa that focuses on water analysis. However, a number of the laboratories are only equipped to handle inorganic samples. Secondly, a significant shortage of organic analysis laboratories (TPH, TAME, BTEX, MTBE, dioxane, aromatics, EDCs and POPs) in South Africa exists. Finally, lab accreditation is also an important factor, although duplicate samples should be sent to another accredited laboratory to verify analysis and errors. It is envisaged that the number of accredited organic laboratories in South Africa would dramatically increase in the next few years to assist the regulator in monitoring these sites.

1.3 Stakeholders

The project team has made a conscious effort to involve stakeholders from government and industry with the project. The main stakeholders include DWAF, local municipalities, chemical industry and the oil industry.

1.4 Research Approach

The following is a broad outline of the research approach that will be taken over the four year period of the project. Many of the actions will be done in parallel and outputs will be given according to the deliverable schedule.

1. **Discussions**
    1. Project team and Stakeholders.
2. **Site selection criteria**
    1. Availability/access to the site or information pertaining to the site.
    2. Extent of the contamination and field investigations/rehabilitation activities undertaken at the site.
    3. Age or history of the problem.
    4. Geology/hydrogeology of the site.
    5. Location relative to research partners.
    6. On-going activities on the site.
3. **Literature review**
4. **Data Collection**
    1. Database construction and evaluation/interrogation of data.
5. **Site Assessment/Characterisation**
    1. Preliminary investigations on field sites.
    2. Defining research objectives at each site.
    3. Targeted LNAPL research (rapid methods, microbiology, geophysics, vadose zone characterisation).
    4. Prediction and risk methodologies.
    5. Vulnerability mapping.
6. **Remediation**
    1. The lines of evidence approach to demonstrate that natural attenuation is occurring at a site, will be tested in this project. (MNA)
    2. The different remediation options available will be evaluated in this project by using existing data from sites where remedial actions have taken place.

1.5 Stakeholder Input

The Initial/Launch Workshop series was held early April 2008. These LNAPL workshops were combined with the dissemination of the products of WRC project K5/1501 on DNAPLs (Usher et al., 2008). The intention at these workshops was to get collective buy-in from the industries and oil companies, the regulators and local authorities on the objectives, approach and methodologies planned for the research.

Three workshops were held in three major centres (Pretoria, Durban and Cape Town). Collectively the workshops were attended by approximately 70 delegates from the target groups. The attendees' main comments have been listed below and this report hopefully addresses most of these important issues.

1. Linkage with related research/guideline projects, i.e. remediation project from DWA.
2. NAPL investigations/management should be based on risk principals.
3. Urgent guidance from regulator is requested by industry for management and remediation of contaminated sites.
4. The results of the WRC research projects need to be communicated to DWA.
5. Organic contaminants need to be addressed in DWAF's National Groundwater Strategy.
6. The issue of lack of accredited laboratories for organic water and soil analyses was discussed.
7. Need for guidance and regulations discussed in detail.
8. General consensus that risk based approach is most suitable for these types of sites.
9. Current legislation does not allow for MNA principals to be applied.
10. Remediation targets need to be realistic and achievable.

1.6 Aims and Objectives of the Report

This project needed to consolidate knowledge about the fate and transport of LNAPL pollutants in groundwater in a systematic manner. This project is a follow-on of the WRC project K5/1501 on DNAPLs (Usher et al., 2008). It also intended that this work serves as a document on which the Department of Water Affairs can build their policy on for South Africa. One of the main reasons behind the creation of this document is to describe and assess the impact of LNAPLs on South Africa, since most of South Africa's aquifers are located in low yielding geological formations. This makes South Africa unique as well as the arid climate that dominates most of the country. These two factors results in low recharge values to the aquifer systems and increased vulnerability due to the lack of water resources in the event of a drought.

The following aims and objectives were set for this study**:**

1. Identify flagship field sites for studies to characterise the fate (including attenuation processes) and transport of identified priority LNAPLs (including the importance of preferential flow).
2. Evaluate site assessment techniques (including rapid methods) for the delineation of contaminated zones, to achieve successful remediation.
3. Conduct field based studies to investigate LNAPLs i.e. areas and mechanisms by which LNAPL pollutants enter groundwater flow systems, their fate in the subsurface and the applicability of different remedial techniques in South Africa.
4. Develop reliable predictions of the transport of LNAPLs within the South African flow systems.
5. Develop appropriate guidelines (including monitoring, site assessment and remediation) for LNAPLs which are appropriate to South African conditions.

1.7 Conclusion

In the following chapters a systematic evaluation of the extent and character of LNAPL contamination will be presented. Initially the focus will be on the required background that a person should develop to gain an understanding for the problem. Secondly, the chemical and physical processes which occur during LNAPL transport. Finally, the influence that the setting has on the contaminant distribution in the sub-surface and possible exposure pathways.

Two distinct regional environments will be discussed from a global perspective. The construction of a conceptual model that can be applied to geohydrology as well as remediation. A short discussion on risk, costs and methods that can be applied to a South African environment.

2 BACKGROUND

2.1 Physical, Chemical and Distribution Properties of LNAPLs

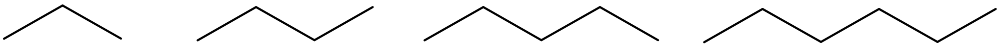
The term LNAPL refers to Light Non-Aqueous Phase Liquids in soils and groundwater. The LNAPL source is typically associated with petroleum products or derived from other chemical industries. In this report the main focus will be on the composition and distribution of LNAPLs from a petroleum source. In broad terms petroleum liquids do not mix with water, this however, is a generalisation since petroleum liquids can contain a certain percentage of water. The production of LNAPL is from crude oil or coal gasification (gas-to-liquid) processes. Common LNAPLs are fuels (petrol, diesel and paraffin), lubricants and chemical feedstock for manufacturing. Thus LNAPLs are typically multi-component organic mixtures of chemicals with varying degrees of water solubility.

2.2 Chemical Properties of LNAPLs

The composition of petroleum fuels is commonly divided into four main categories, i.e. Paraffins, Olefins, Naphthenes and Aromatic components. Additionally, additives are added in varying amounts (ppm or ppb levels), which can include oxygenates and performance enhancers or engine protective compounds. Petroleum products can contain more than 500 hydrocarbon compounds which may have between 3 to 12 carbons in the molecule. Furthermore, these components can have a boiling range from 30 °C to 220 °C at atmospheric pressure. Since such a wide range of chemical compounds exist in petroleum fuels only the most significant components will be discussed below, with the most relevant chemical properties highlighted (CRC, 2003-2004).

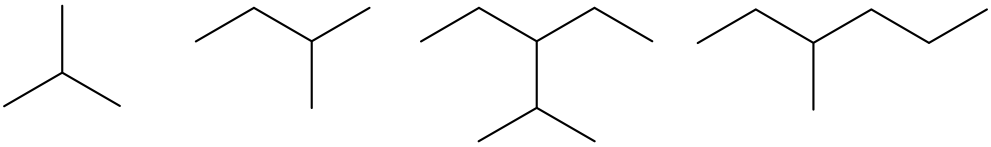
2.2.1 Paraffins

Paraffins are saturated non-cyclic hydrocarbons (alkanes), which can either be straight chains (n-alkanes with a general formula of C_nH_{2n+2}) or branched (iso-alkanes with a general formula of C_nH_{2n+2}). Examples of each group are represented in Figure 2-1 and Figure 2-2, respectively.



propane C_3H_8 butane C_4H_{10} pentane C_5H_{12} hexane C_6H_{14}

Figure 2-1 Straight chain non-cyclic alkanes. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.



isobutane C_4H_{10} isopentane C_5H_{12} 3-ethyl-2-methylpentane C_8H_{18} 3-methylhexane C_7H_{16}

Figure 2-2 Branched chain non-cyclic alkanes. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.

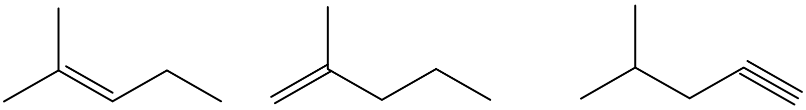
Paraffins form the bulk of petroleum fuels, with branched alkanes, increases the octane number the most in this group. Alkanes are preferred due to their stability and clean conversion during combustion.

2.2.2 Olefins

Olefins are unsaturated non-cyclic hydrocarbons (alkenes, alkynes), which can either be straight chains (n-alkenes or n-alkynes) or branched (iso-alkenes or iso-alkynes). Examples of each group are represented in Figure 2-3 and Figure 2-4, respectively.

pent-2-ene C_5H_{10} pent-1-ene C_5H_{10} pent-1-yne C_5H_8

Figure 2-3 Straight chain non-cyclic alkenes and alkyne. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.



2-methylpent-2-ene C_6H_{12}

2-methylpent-1-ene C_6H_{12}

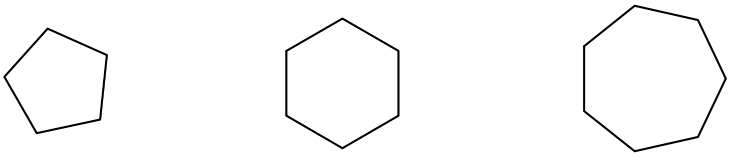
4-methylpent-1-yne C_6H_{10}

Figure 2-4 Branched chain non-cyclic alkenes and alkyne. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.

Olefins tend to be unstable and are usually only present in petroleum fuels as a small percentage of the total bulk.

2.2.3 Naphthenes

Naphthenes are saturated cyclic hydrocarbons (cycloalkanes), which can either be a simple cyclic hydrocarbon (with a general formula of C_nH_{2n}) or derivative with side chains emanating from the ring structure. Examples of each group are represented in Figure 2-5 and Figure 2-6, respectively.

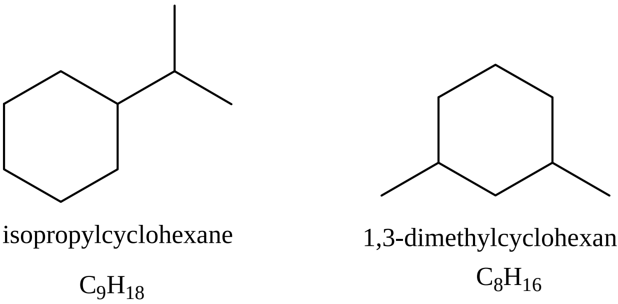


cyclopentane C_5H_{10}

cyclohexane C_6H_{12}

cycloheptane C_7H_{14}

Figure 2-5 Selected cycloalkanes with the chemical symbol, nomenclature and reduced chemical formula given for each molecule.



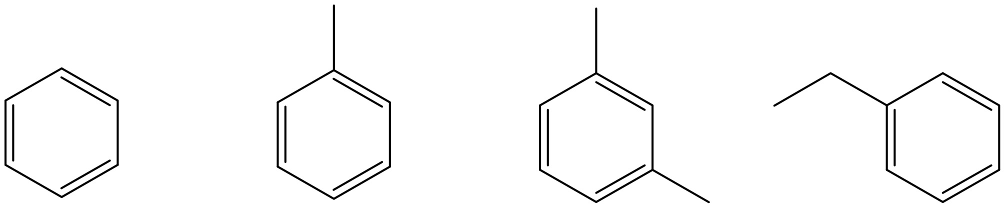
isopropylcyclohexane C_9H_{18}

1,3-dimethylcyclohexane C_8H_{16}

Figure 2-6 Selected branched or derivative cycloalkanes with the chemical symbol, nomenclature and reduced chemical formula given for each molecule.

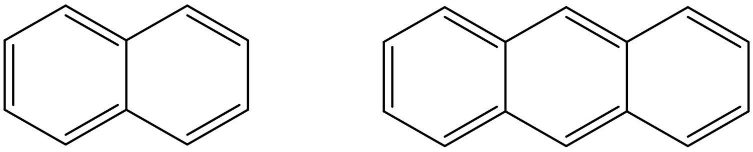
2.2.4 Aromatics

Aromatic compounds are unsaturated aromatic carbon systems (benzene or phenyls), which can either be monomeric (benzene, toluene and xylene) or polymeric (anthracene, napthalene). Examples of each group are represented in Figure 2-7 and Figure 2-8, respectively.



benzene C_6H_6 | toluene C_7H_8 | *m*-xylene C_8H_{10} | ethylbenzene C_8H_{10}

Figure 2-7 Mono-aromatic compounds typically found in petroleum fuels. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.



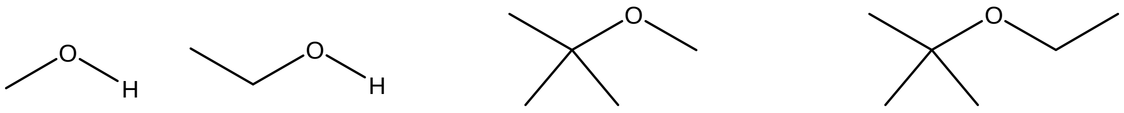
naphthalene $C_{10}H_8$ | anthracene $C_{14}H_{10}$

Figure 2-8 Polymeric aromatic compounds that can be found in petroleum fuels. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.

The aromatic composition of petroleum fuels used to be as much as 40 % but due to the inherent hazards of these compounds the acceptable limits has been reduced to less than 20 %.

2.2.5 Oxygenates

These compounds are used to provide a reasonable anti-knock value to petroleum fuels and contain an oxygen atom in the hydrocarbon structure. Currently, in a South African context these compounds are used as a substitute for aromatics compounds or organic lead products. Examples of oxygenates are methanol (MeOH), ethanol (EtOH), 2-methoxy-2-methylpropane or methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME) and 2-ethoxy-2-methylpropane or ethyl tertiary butyl ether (ETBE). Examples of each group are represented in Figure 2-9.



methanol	ethanol	2-methoxy-2-methylpropane	2-ethoxy-2-methylpropane
CH_4O	C_2H_6O	$C_5H_{12}O$	$C_6H_{14}O$
MeOH	EtOH	MTBE	ETBE

Figure 2-9 Oxygenates commonly found in petroleum products. Chemical symbol, nomenclature, reduced chemical formula and common name given for each molecule.

Oxygenates can be produced from fossil fuels, biomass or industrial synthetic approaches (i.e. Monsanto and Cativa processes)(Jones, 2000). Oxygenates added to petroleum fuels function as an octane booster, reduce the CO emissions or act as an anti-knocking agent, although at a lower power output.

2.2.6 Chemical component mixtures

In each type of petroleum fuel composition only a minimum quality standard is set for each batch. This causes different brands to have varying mixing standards and additive requirements, a typical additive package might containing in various quantities the following components:

1. Octane enhancing additives
2. Anti-oxidants
3. Metal deactivators
4. Deposit modifiers
5. Surfactants
6. Freezing point depressants
7. Corrosion inhibitors

8. Dyes

It is in this regard that not all petroleum products behave in the same method and should usually be considered as a separate instance when a site is characterised. Most components of petroleum fuels are not water soluble (paraffins, naphthenes and some aromatic compounds) while another fraction will dissolve readily into the aqueous phase and these components typically contain hetero-atoms (oxygenates, anti-oxidants, surfactants, dyes and freezing point depressants). A special case is the solubility of oxygenates which can either totally dissolve (methanol or ethanol) or partially (MTBE or ETBE) and the migration path of these two types of oxygenates should be linked to their respective chemical and physical properties in the subsurface zone.

In the following section some of the most important physical properties will be presented with a focus on solubility and transport.

2.3 Physical Properties that Affect LNAPLs

The presence of LNAPLs in a subsurface zone is usually detected by the presence of a layer of LNAPL on the water surface. This is due to the lower density or “buoyancy” of LNAPL, which also prohibits the LNAPL from migrating into the groundwater zone. This however, does not exclude the possibility of a LNAPL spreading through the aquifer but does limit the extent of the movement of the non-aqueous phase. In the contact zone between the LNAPL and water surface, pore spaces can be shared by both components which significantly complicates the removal of the LNAPL. Since a small percentage of the LNAPL component does dissolve in the aqueous phase, areas in close proximity to the contamination source should be evaluated to determine if it exceeds general safety values.

It should be stated that for a LNAPL to penetrate through the vadose zone into the saturated zone, a certain threshold amount should be exceeded. This threshold amount is dependent on the geological structure of the area, water content of the soil and temperature of the surrounding area. If any of the factors are unfavourable the rate of LNAPL penetration into the subsurface zone will be limited.

2.3.1 Temperature effect

Temperature effects can play a significant role in determining the infiltration rate and volume of LNAPL contamination at a site. Since LNAPLs consist of volatile organic compounds, in areas where shallow aquifers are present evaporation of the LNAPL can occur.

One key factor in the susceptibility of LNAPLs to evaporation is the vapour pressure of each component. The vapour pressure can be defined as the pressure of a vapour in equilibrium with its non-vapour phases in the atmosphere. Most liquids and solids tend to evaporate to a gaseous form, and conversely the gases of this compound tend to condensate back into the original form which can either be a liquid or solid. Thus, at any given temperature, for a particular substance, there is a pressure at which the gas of that substance is in dynamic equilibrium with its liquid or solid forms. This is the vapour pressure of that substance at that temperature.

The equilibrium vapour pressure is an indication of a liquid's evaporation rate, which relates to the tendency of molecules and atoms to escape from a liquid or a solid. A substance with a high vapour pressure at normal temperatures is often referred to as volatile, **Table 2-1**. The higher the vapour pressure of a liquid at a given temperature, the lower the normal boiling point of the liquid.

Table 2-1 Vapour pressure and solubility of selected molecules (CRC, 2003-2004).

Compound	Vapour Pressure (mmHg) at 30°C	Solubility in water (mg/l) at 20°C
Benzene	100	1200
Toluene	30	800
Ethylbenzene	13	105
Xylene	11	110
Ethanol	78	900 000
Methanol	163	990 000
Hexane	186	600
1-Hexene	228	1200
MTBE	643	30 000
Water	31	1 000 000

It is clear from Table 2-1 that not all of the organic substances behave in the same manner, with MTBE and 1-hexene having a much higher volatility than the other compounds. This effect has some consequences concerning the type of chemical composition of a LNAPL spill on the surface. If the LNAPL evaporates before it can penetrate into the subsurface zone no significant amount will be observed at the groundwater level. Secondly, if a shallow aquifer exists (less than 2 meters) the likelihood of evaporation into the atmosphere should be considered during the site characterisation phase. Finally, if the surface contains clay layers or any sedimentary deposits which might act as trapping agents for hydrocarbons, i.e. dolomitic structures.

Once the LNAPL has penetrated deep enough into the subsurface, microbial activity and geochemical processes should be considered. Pockets of hydrocarbon vapour can form in karst caverns or natural cave systems, although the ambient temperature in these areas can vary between 10 and 20 °C depending on the season and depth.

2.3.2 Moisture content

Below land surface all geological formations can be considered as porous media. The porous media can consist of two major components if no water moisture is present, i.e. solids and void spaces. In the vadose zone air coexists with water in these pore spaces. Water is attracted to the solids, forming a coating layer around larger particles and fills smaller pore spaces – this is called the wetting phase. The water does not fill all the open pore spaces and the remaining areas are filled with air – the non-wetting phase. These concepts can be illustrated as shown in Figure 2-10.

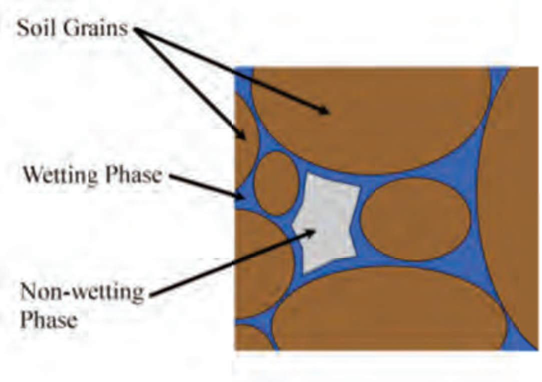


Figure 2-10 Pore spaces in a soil matrix, with a wetting and non-wetting phase.

The release of a LNAPL on the surface or a non-saturated zone below the surface above the groundwater level will cause the LNAPL to flow into the non-wetting phase partially displacing the air. The downward movement of the LNAPL will continue as long as a sufficient pressure or concentration exists at the source to create a gradient which will allow the LNAPL to displace the air. The wetting phase around the particles will remain during this whole process. If enough LNAPL is present the LNAPL will eventually reach the groundwater level. The method of water displacement in the saturated zone by LNAPL is via the larger pore spaces. This effectively creates an interconnected system of pore spaces which contain LNAPLs, subsequently the LNAPL can be distributed in a large area. During the whole process the LNAPL is surrounded by water which forms a thin film around the particles in the matrix. Once enough LNAPL has intruded to the groundwater level, the combined force of the LNAPL will exert enough force to locally displace the water in the aquifer, see Figure 2-11. The movement of the LNAPL is reduced by the pressure required to displace the water in the pores at the edge of the LNAPL plume.

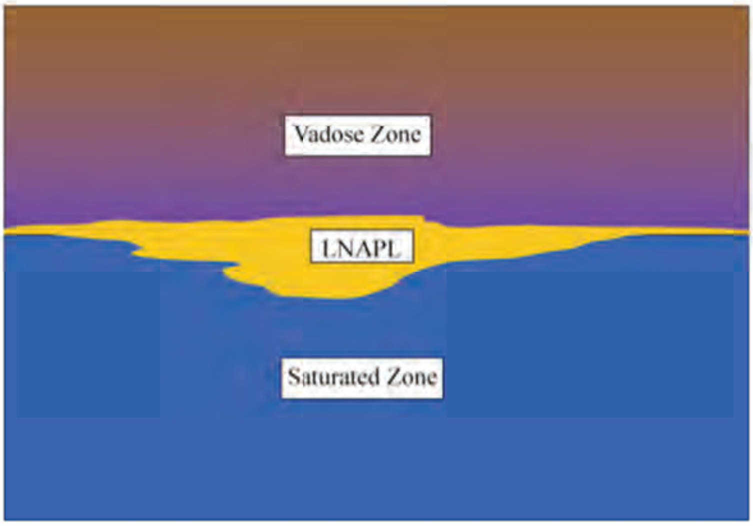


Figure 2-11 LNAPL interaction with the vadose and saturated zones.

If a heterogeneous mixture of particles is present or preferred pathways exist, LNAPLs can pool in selected areas. This can result in LNAPL pockets or lenses forming in the subsurface zone that can remain long after the initial contamination event or clean-up efforts. This has been observed in Bloemfontein area where an underground storage tank caused considerable contamination to an area (Botha, 1996).

The initial clean-up efforts removed most of the perceived LNAPL pollution and activities at the clean-up site were stopped after 11 months. After a good spell of rain the presence of LNAPLs were again observed and the clean-up operation of the area continued for another 4 years. This clearly illustrates the complex behaviour of LNAPLs in the subsurface zone.

Water and LNAPLs exert different pressures in the pore spaces. This difference in pressure between the wetting and non-wetting phase can be defined as the capillary pressure. It can be stated in a mathematical equation as follows

$$P_c = gh_{NAPL}(\rho_{LNAPL} - \rho_{water})$$

with $P_c$is the Capillary Pressure, g the gravitational constant, $h_{NAPL}$the vertical height of the LNAPL and $(\rho_{LNAPL} - \rho_{water})$ the respective densities for the LNAPL and water. The capillary pressure also plays a significant role in the movement of the LNAPL as well as the distribution area of the contaminant.

Once removal of LNAPL starts the behaviour of the system can be altered quite significantly, as the LNAPL concentration is reduced the fraction of pore spaces occupied is also reduced. Subsequently, the flow paths become smaller and the LNAPL has a higher resistance to move through these reduced pore spaces. This effectively reduces the ease by which an LNAPL contaminant can be removed, breaking up into smaller pools or lenses in the subsurface zone. The point at which a LNAPL is immobile is termed as the residual saturation, after which other remediation options should be considered.

Finally, equilibrium between phases (gas, liquid and solid) can exist for the volatile organic compounds. This is mostly determined by the solubility of the organic substance in the aqueous phase, **Table 2-1**, and the total amount or concentration of the substance (Figure 2-12). Three basic types of solubility scenarios are shown (Figure 2-12), which can affect the concentration of the organic substance. As the LNAPL moves through the subsurface layer it encounters regions with lower concentrations in either the aqueous or gas phase. Using Le Châtelier’s principle which states that a system at equilibrium, when subjected to a perturbation, responds in a way that tends to eliminate its effect.

In short the LNAPL components will always attempt to be in equilibrium with both the liquid and gas phase, but this equilibrium changes with the temperature in the subsurface zone. This effectively increases the problem of remediating LNAPL contamination at a site.

A weakly soluble compound (Figure 2-12 top left) will mostly likely be present in the solid phase since it cannot dissolve into the aqueous phase. At low percentage water saturation and exchange between the gas phase and the LNAPL adsorbed onto the solid phase will occur readily, while at higher percentages of water saturation the exchange into the gas phase will be from the aqueous medium. Removal of this contaminant will be extremely protracted since physical methods would be required to remove the source of the contamination. A steady release of the compound will be observed over time, and most likely can be classified as a continuous low concentration point source. If this source is benzene or toluene, it can pose serious long term health hazards if the concentration is above accepted limits.

In the case of a moderately soluble compound (Figure 2-12 top right), the initial phases at less than 10 % water saturation will be similar to the weakly soluble compound. Subsequently the concentration of the organic compound in solution will be far greater than that observed in either phase, with the aqueous phase playing the major role in determining the mass fraction in either the gas or solid phase.

In the instance of a compound that is highly soluble in the aqueous phase then the remediation of the site is somewhat easier. It will result in the contaminant moving in the direction of the groundwater flow. If mass transport conditions are considered for a single occurring point source, the compound will be washed out over an extended period of time.

Finally, if the compounds are completely soluble in the aqueous phase (Figure 2-12 bottom left) then only the aqueous phase will be considered during the mass transfer since this phase will carry the bulk of the compound in the groundwater flow direction. Over time, if mass transport conditions are considered for a single occurring point source, the compound will be washed out of the matrix or air. If the contaminant is present as a continuous source then a plume in the direction of the groundwater flow will be observed.

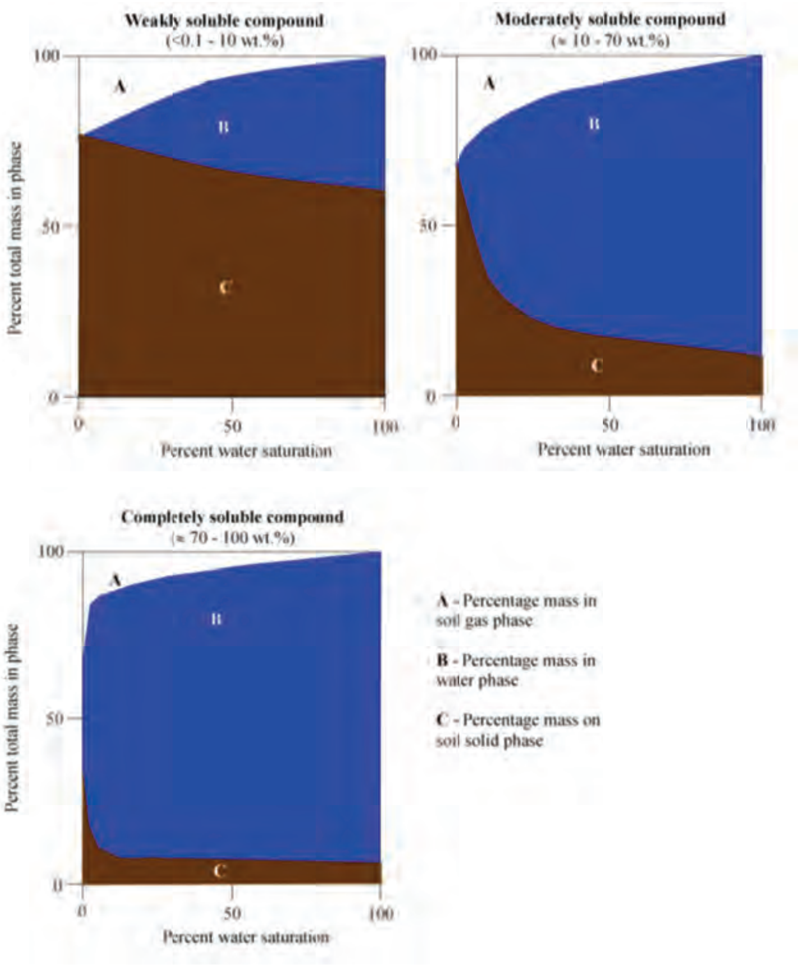


Figure 2-12 Equilibrium partitioning between gas, liquid and solid phase for soluble compounds.

2.3.3 Soil properties and capillary pressure

2.3.3.1 Soil composition and properties

Soil properties can be in part described by the soil texture, composition type and regional occurrence. In this section key features will be highlighted as well as the effect on the capillary pressure which it exerts in the vadose zone. Soil texture is an approximation of the relative quantities of sand, silt and clay particles in any given soil. Soil structure is a measure of the arrangement of these soil particles and the spaces between them and can also be related to packing effects.

Soil texture refers to the relative proportions of sand, silt and clay in a given sample. The sand, silt and clay percentages are also useful because we can use these measurements to classify the soil into general categories, which can then be used to give approximate infiltration rates. In Table 2-2 and Figure 2-13 a general comparison of particle sizes are given.

Table 2-2 Ranges for particle sizes (diameter) of clay, silt and sand.

Material	Particle Size (mm)
Very Coarse Sand	2.00-1.00
Coarse Sand	1.00-0.50
Medium Sand	0.50-0.25
Fine Sand	0.25-0.10
Very Fine Sand	0.10-0.05
Silt	0.05-0.002
Clay	<0.002

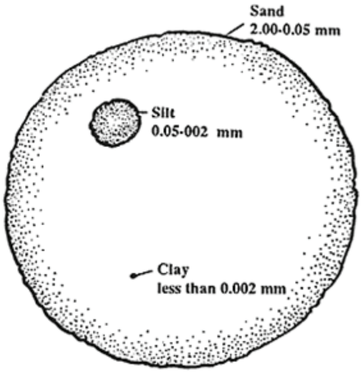


Figure 2-13 A visual comparison of particle sizes for sand, silt and clay units. (Staff, 1993)

A loamy soil contains these three types of soil particles in roughly equal proportions. A sandy loam is a mixture containing a larger amount of sand and a smaller amount of clay, while a clay loam contains a larger amount of clay and a smaller amount of sand (Figure 2-14 for the classification of the different soil types).

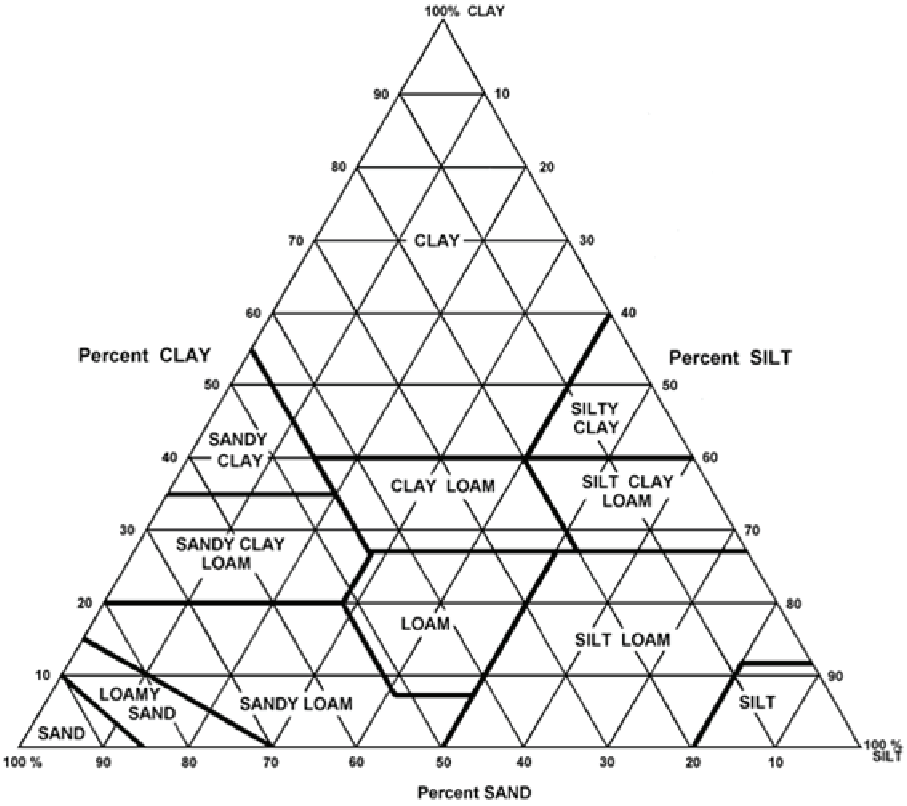
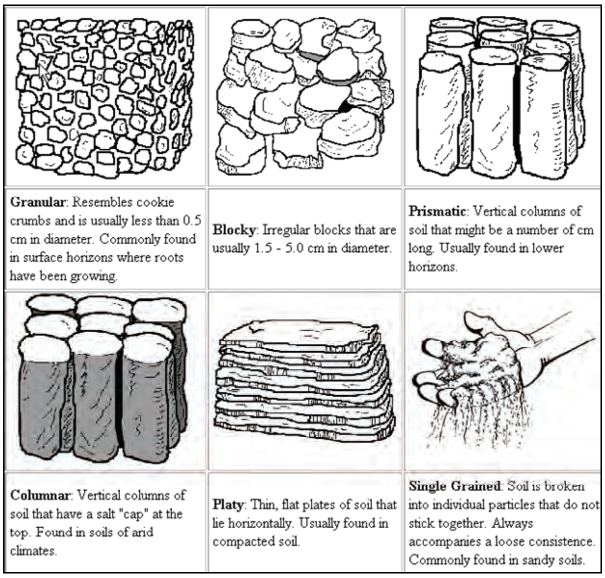


Figure 2-14 Classification of different soil types according to sand, silt and clay composition. (Staff, 1993)

A second fundamental property of soils is the structure, it is described the aggregates in soil in terms of shape. These can be classified into four groups, i.e. spheroidal, platy, prismlike and blocklike (Figure 2-15). The different shapes of aggregates in the soil define the pattern of pores and packing arrangements. This pattern defines the soil structure which greatly influences water movement, heat transfer, aeration and porosity in soils. Agricultural activities on farmlands (disturbed), tillage and liming, impact soils largely through the effect on the soil structure; especially in the surface horizons. The effect of soil structure on the saturated hydraulic conductivity of soils is clearly illustrated in Table 2-3.

To explain the flow-impeding role of clay in soil materials, one can use flow through pipes as an analogy. Narrow diameter pipes will be more restrictive to the flow of water (under the same pressure) than a single large diameter pipe, having the same cross-sectional area as all narrow ones put together. This is basically due to frictional forces, such as capillarity, that tend to impede the flow of water in small diameter pipes (Figure 2-16 illustrates this concept).



Granular: Resembles cookie crumbs and is usually less than 0.5 cm in diameter. Commonly found in surface horizons where roots have been growing.

Blocky: Irregular blocks that are usually 1.5 - 5.0 cm in diameter.

Prismatic: Vertical columns of soil that might be a number of cm long. Usually found in lower horizons.

Columnar: Vertical columns of soil that have a salt "cap" at the top. Found in soils of arid climates.

Platy: Thin, flat plates of soil that lie horizontally. Usually found in compacted soil.

Single Grained: Soil is broken into individual particles that do not stick together. Always accompanies a loose consistence. Commonly found in sandy soils.

Figure 2-15 The primary classification groups of soil structure. (Staff, 1993)

Table 2-3 Range of hydraulic conductivities in different soil types.

Soil Type	Saturated Hydraulic Conductivity, K_s (cm/s)
Gravel	3×10^{-2}-3
Coarse Sand	9×10^{-5}-6×10^{-1}
Medium Sand	9×10^{-5}-5×10^{-2}
Fine Sand	2×10^{-5}-2×10^{-2}
Loamy Sand	4.1×10^{-3}
Sandy Loam	1.2×10^{-3}
Loam	2.9×10^{-4}
Silt, Loess	1×10^{-7}-2×10^{-3}
Silt Loam	1.2×10^{-4}
Till	1×10^{-10}-2×10^{-4}
Clay	1×10^{-9}-4.7×10^{-7}
Sandy Clay Loam	3.6×10^{-4}
Silty Clay Loam	1.9×10^{-5}
Clay Loam	7.2×10^{-5}
Sandy Clay	3.3×10^{-5}
Silty Clay	5.6×10^{-6}
Unweathered marine clay	8×10^{-11}-2×10^{-7}

In Figure 2-16 the flow through a single large pipe is greater than the flow through all the narrow pipes combined. Soils are much more complex than pipes, but the same principle holds true. Flow through soil, as measured by hydraulic conductivity, is affected by the degree of saturation, capillary forces, connection between voids, mineralogical structure and soil texture. Therefore, the reason that clay-rich soils have such low hydraulic conductivities is because there is less connection between the pores and a greater resistance to flow through the narrow passages.

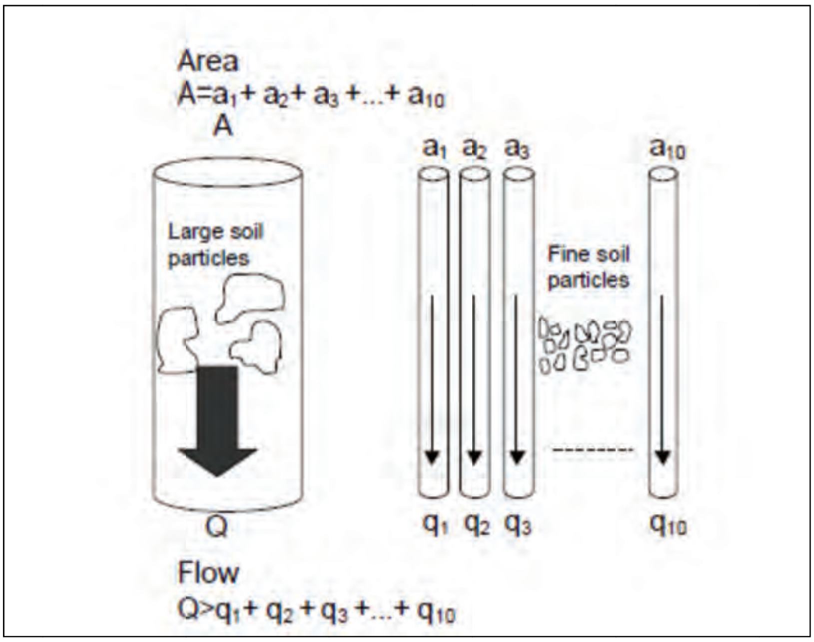


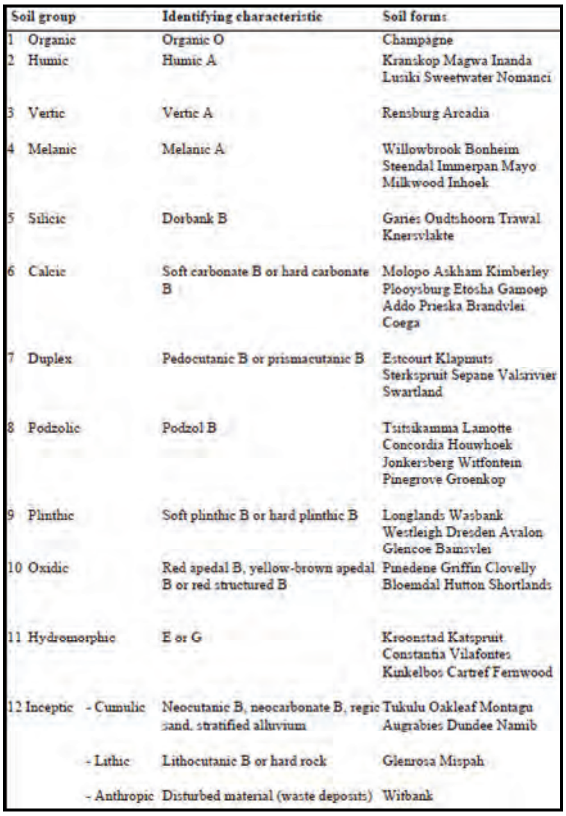
Figure 2-16 Demonstration of the difference in flow through a large and small diameter pipes.

Most soil classification systems are simple to begin with and then become more complex and elaborate as differences which at first were considered inconsequential, assume heightened significance with the expansion of knowledge. The classification of South African soils (Group, 1991) is already quite elaborate, and the seventy three soil forms are too numerous for purposes of broad generalization. Grouping into fewer classes are considered as essential.

The 73 soil forms can be organised into 12 groups based on either a distinctive topsoil (1-4) or, if the topsoil is orthic, a distinctive subsoil horizon or material (5-12). The group to which a soil belongs is arrived at by means of a key which works by elimination, proceeding through the groups until the defining characteristic is encountered (Figure 2-17). As indicated earlier, this key is similar in concept to that used for grouping soils at the highest level in the WRB and USDA (Soil Taxonomy) systems of classification.

It would be helpful at this point to explain how the criteria and their ranking were chosen for the key. All soils have elements of soil forming processes expressed in their make-up. Differing degrees of expression of these processes give rise to different soils

(R W Simonson). There is no single, best method for constructing a key to identification: the precedence given to one criterion over another depends on the perspective of the classifier. As far as possible, however, the criteria for grouping soil forms are given an order of priority Figure 2-17. Grouping of soil forms as an eliminative key to identification based on the presence of specific diagnostic horizons or materials. The first four groups are distinguished by topsoil horizons, and the remainder according to subsurface features.



Soil group	Identifying characteristic	Soil forms
1 Organic	Organic O	Champagne
2 Humic	Humic A	Kranskop Magwa Inanda Lusiki Sweetwater Nomanci
3 Vertic	Vertic A	Rensburg Arcadia
4 Melanic	Melanic A	Willowbrook Bonheim Steendal Immerpan Mayo Milkwood Inhoek
5 Silicic	Dorbank B	Garies Oudtshoorn Trawal Knersvlakte
6 Calcic	Soft carbonate B or hard carbonate B	Molopo Askham Kimberley Plooysburg Etosha Gamoep Addo Prieska Brandvlei Coega
7 Duplex	Pedocutanic B or prismacutanic B	Estcourt Klapmuts Sterkspruit Sepane Valsrivier Swartland
8 Podzolic	Podzol B	Tsitsikamma Lamotte Concordia Houwhoek Jonkersberg Witfontein Pinegrove Groenkop
9 Plinthic	Soft plinthic B or hard plinthic B	Longlands Wasbank Westleigh Dresden Avalon Glencoe Bainsvlei
10 Oxidic	Red apedal B, yellow-brown apedal B or red structured B	Pinedene Griffin Clovelly Bloemdal Hutton Shortlands
11 Hydromorphic	E or G	Kroonstad Katspruit Constantia Vilafontes Kinkelbos Cartref Fernwood
12 Inceptic - Cumulic	Neocutanic B, neocarbonate B, regic sand, stratified alluvium	Tukulu Oakleaf Montagu Augrabies Dundee Namib
- Lithic	Lithocutanic B or hard rock	Glenrosa Mispah
- Anthropic	Disturbed material (waste deposits)	Witbank

Figure 2-17 Soil grouping system for South African conditions. (Group, 1991)

2.3.3.2 Capillary flow basics

Consider for instance, a cylinder of a radius “a”, containing a liquid with a free upper surface (Figure 2-18). The liquid surface meets the wall at a contact angle θ. In this case where the radius is very small, it is clear that the radius of curvature of an axial section of the free surface is approximately uniform and equal to:

$$R = \frac{a}{cos(\theta)},$$

This departure of the free surface from a spherical shape is only created by the relatively small variations of the liquid pressure along the surface due to gravity. The surface tension in this highly curved surface causes a large jump of pressure across the interface and a high column of fluid can be supported in the tube against gravity. Therefore at equilibrium, the height H, of the column of fluid is satisfying the relation:

$$\rho g H = \Delta p = \frac{2\gamma cos(\theta)}{a},$$

This result can be reworked into the following form:

$$H = \frac{2\gamma cos(\theta)}{\rho g a}.$$

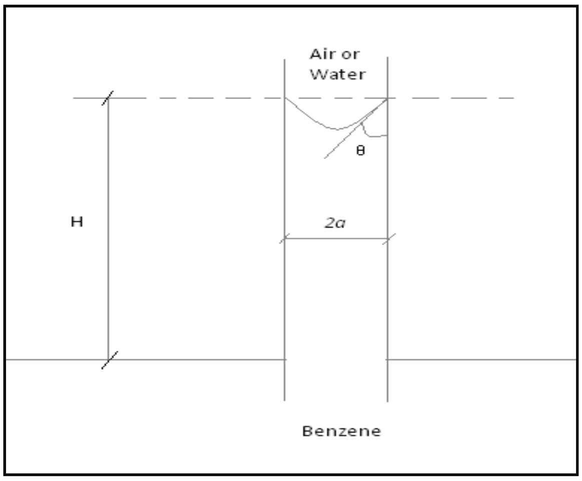


Figure 2-18 Capillary flow model system containing benzene. (Botha, 1996)

If all the parameters are known for the system then the height rise (H) can be calculated. For example, if the capillary rise of benzene is consider in 3 different soil formations, i.e. sand, silt and clay. In either instance the system can be saturated with water or unsaturated. The following data is known for benzene at 20°C, at saturation the surface tension is 35 dyn/cm and under unsaturated conditions it is 29 dyn/cm, in both instances the density is 0.79 g/cm^3. In order to understand the implications of the difference in height two plots are presented, firstly the total effect of grain size (Figure 2-19) and finally a zoomed area showing the drastic effect silt has on capillary rise (Figure 2-20).

In Figure 2-19 and Figure 2-20 the minimum rise (red line) and maximum rise (blue line) are shown as an illustration. The maximum theoretical capillary rise in a system can be as much as a 180 meters, although for benzene in commonly occurring soils (Table 2-2) the maximum expected increase in height would be 9 meters. This would be because there is an interplay between diffusion and capillary action in the vadose zone. Furthermore, since the matrix would most likely be heterogeneous this increase would be further reduced. Considering the capillary rise of water, Figure 2-21 and Figure 2-22, a considerable increase in capillary rise can be observed. This is largely due to the increase in surface tension, 72.8 dyn/cm, which effectively increases the pressure of the system.

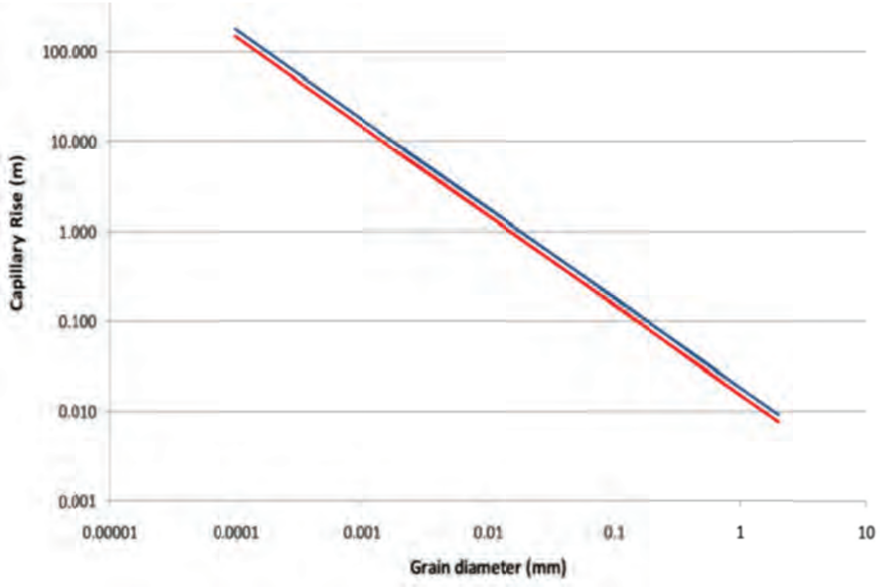


Figure 2-19 Theoretical capillary rise effects for benzene as a result of grain diameter.

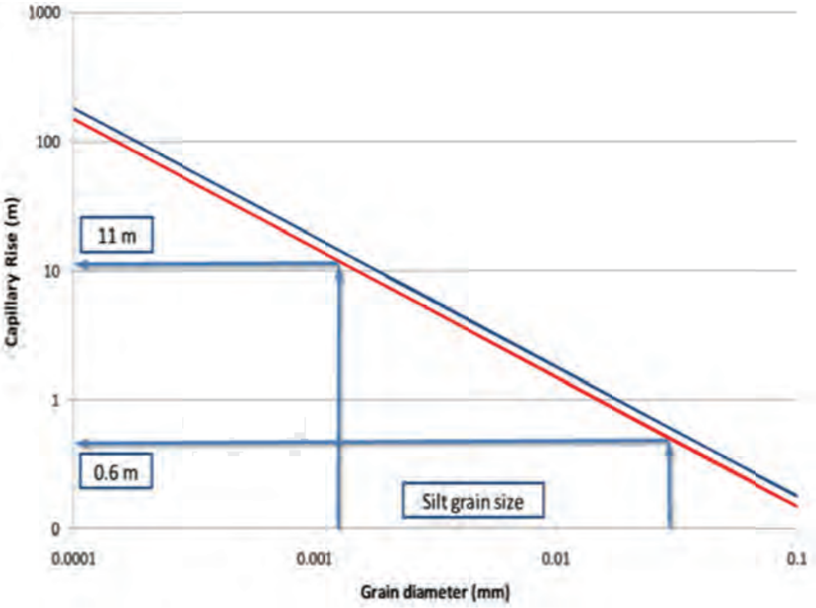


Figure 2-20 Expanded view showing the difference in grain size for silt particles.

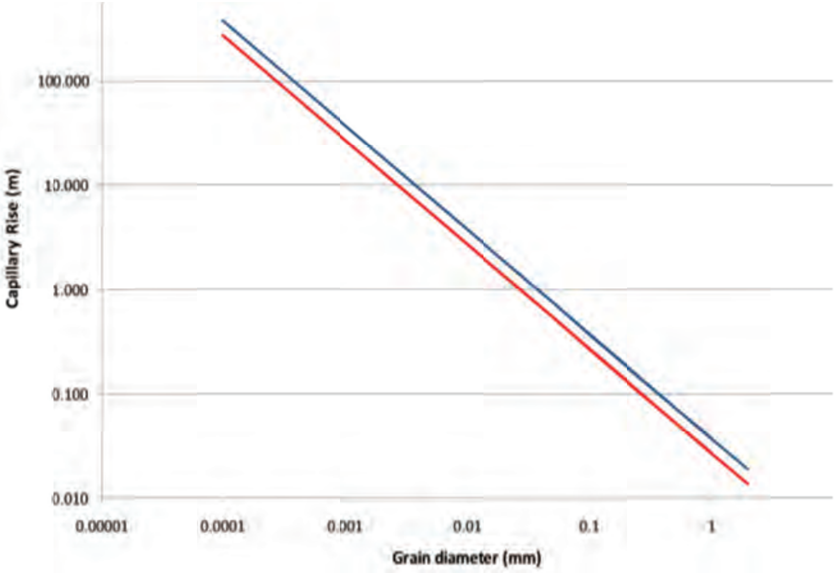


Figure 2-21 Theoretical capillary rise effects for water as a result of grain diameter.

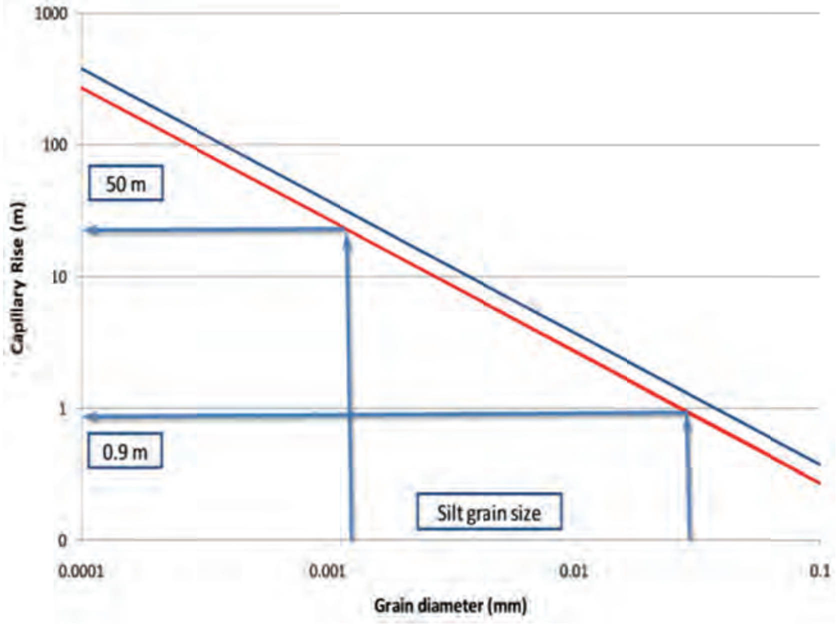


Figure 2-22 Expanded view showing the difference in grain size for silt particles.

Capillary suction diagrams can also be used, which result a similar type of behaviour as capillary rise. These results are indicated in Figure 2-23 for the most prominent soil types. The influence of water saturation (as a percentage of the bulk) clearly follows a non-linear pattern, with clays exhibiting the most linear increase.

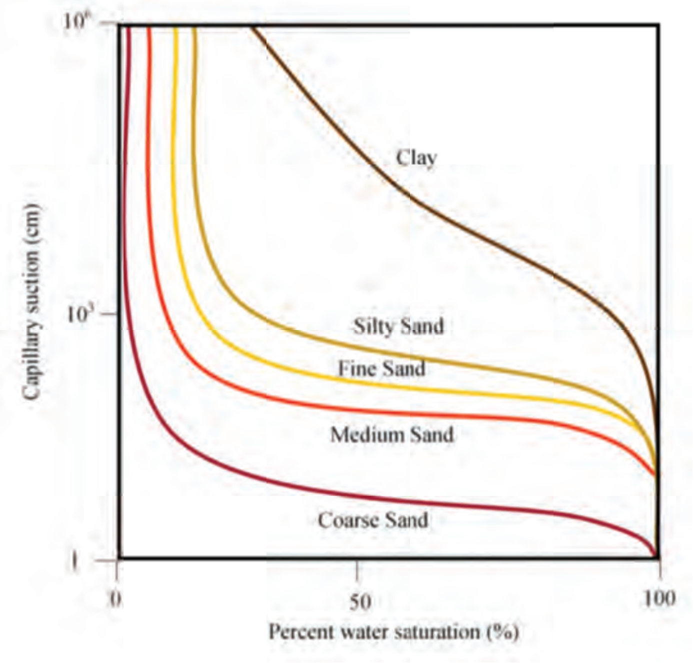


Figure 2-23 Characteristic capillary suction curves for different soil types as a function of water saturation percentage.

2.3.4 Lithology effects

The layering of the subsurface zone, or the lack of it, can play an important role in the distribution of an LNAPL plume.

Firstly, the porosity of the medium can determine the absorption rate and transport through the medium. Considering only the porosity of a system LNAPL movement will be much higher in coarse media than fine grained particles. As noted previously in 2.3.2: “The method of water displacement in the saturated zone by LNAPL is via the larger pore spaces. This effectively creates an interconnected system of pore spaces which contain LNAPLs, subsequently the LNAPL can be distributed in a large area.” Similarly to the behaviour of water, LNAPLs prefers to path of least resistance. Furthermore, if preferred pathways exist in the system the LNAPL transport from the surface zone to the groundwater level will be significantly enhanced.

Secondly, the local water level gradient in the area in combination with the lithology of the subsurface can either act as a barrier or a preferential pathway. If weakly soluble LNAPL components are considered (Table 2-1), the bulk of these compounds will be present at the contact between the water level and the vadose zone. This would localise the movement of the weakly soluble component to areas which can be accessed due to gradient flow in the vadose zone. In contrast miscible components would move in the direction of groundwater flow and would experience typical hydrodynamic dispersion and eventually occur in low concentrations in the down gradient areas of the aquifer.

Finally, the homogeneity of the subsurface will also play an important role in the movement of the LNAPL. Considering the type and extend of no-flow boundaries and aquitards in an area can have a significant effect on the distribution of LNAPL contaminant. In the Karoo Supergroup the presence of dolerite dykes and sills are common while in primary porous aquifer systems clay layers might exists. In the following section an overview of the major types of aquifers in South Africa will be presented.

2.4 Typical Aquifer Systems in South Africa

2.4.1 Introduction

In the South African context four major aquifers systems exists, which can be used to conceptually describe most of the possible aquifers that could be encountered while doing a site characterisation. These aquifer systems are porous media, fractured rock, fractured porous rock and karst type aquifers. Since LNAPLs will behave differently in each of these aquifer systems a brief conceptualised summary of the LNAPL behaviour will be presented in the follow sections.

2.4.2 Porous media aquifers

2.4.2.1 Coastal aquifers and Kalahari sands

In most coastal aquifers groundwater levels are generally shallow giving rise to several fresh water surface lakes (Miller, 2001). In shallow water table aquifers the interaction between the atmosphere and near-surface LNAPLs can create a negative pressure in the soil, due to capillary action, causing LNAPLs to evaporate into the atmosphere. Coastal aquifers are also characterised by groundwater level fluctuations due to tidal effects. The rising and falling water table can create pockets of LNAPLs which are trapped under the groundwater level, Figure 2-24. This substantially increases the difficulty of site remediation, since over abstraction of an aquifer might cause saline intrusion into the freshwater system. In order to survey the coastal regions, volatile organic vapours should initially be detected with the use of a PID (Photo Ionic Detector readings) and subsequently by chromatographic methods.

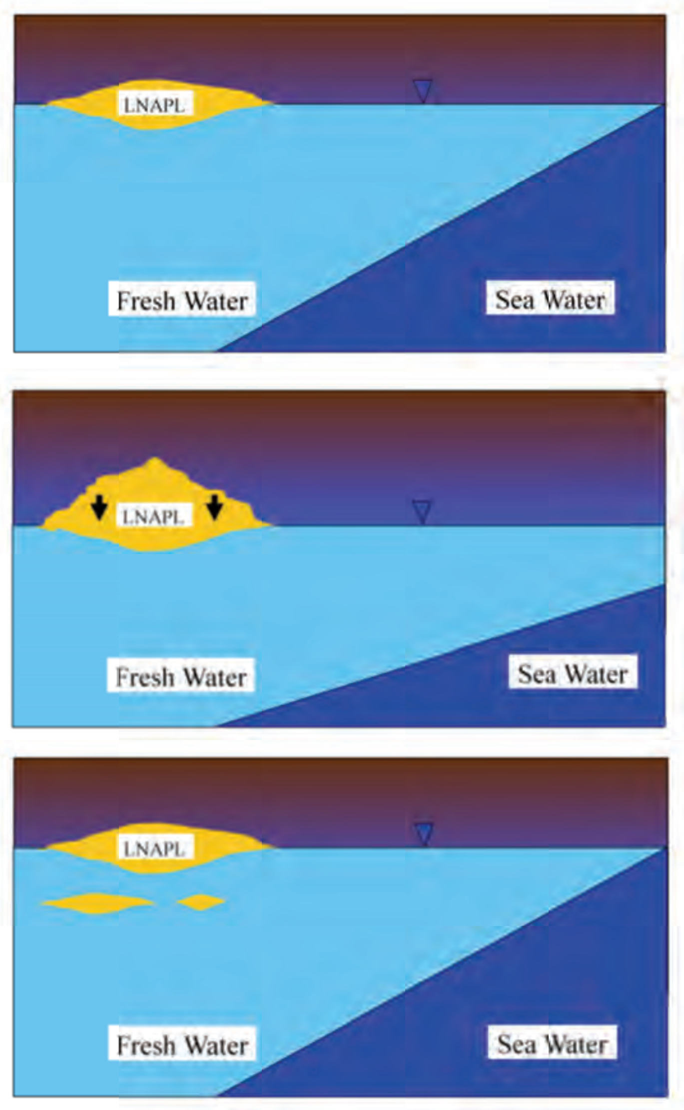


Figure 2-24 Tidal movement and LNAPL intrusion into a porous media aquifer. Top indicates starting level of LNAPL, middle LNAPL moving downwards at low tide and bottom section as high tide returns.

In the Kalahari sands LNAPLs behaviour is affected by two parameters. Firstly, the groundwater level in the area is substantially deeper. The shallowest sections at ca. 50 meters while in deeper areas it can go down in excess of a 150 meters. Secondly, the Kalahari sands have medium to small grain sizes. This effectively increases the penetration rate of the LNAPL to deeper zones. Although it should be noted that the temperatures in this area are moderate to high, and the LNAPL evaporation rates would be significantly increased. The most likely result would be that the LNAPL is baked out of the first 2-3 meters within hours in the summer months. During the winter this process might be prolonged but the depth of the water table and reduced moisture levels protect the groundwater from LNAPL contamination.

Recharge of the Kalahari sands aquifer is very low, due to the thickness of the vadose zone in the area and as such would require careful monitoring. In order to contaminate the groundwater resource, significant volumes of LNAPL should be released at the surface. Remedial action on the Kalahari sands aquifer would also be less strenuous due to the grain size which reduces capillary pressure. This would result in less LNAPL (per volume) being trapped, which in turn results in less energy being expended to clean the Kalahari sands of petroleum contaminants.

2.4.2.2 Limpopo river alluvial aquifer

The Limpopo river alluvial aquifer occupies the northern part of South Africa and is shared by another two countries (Botswana and Zimbabwe) as trans-boundary aquifers. In general alluvial is composed of alluvial deposits consisting of poorly sorted sand, gravel, cobbles and thin beds of silt and or clay.

Recharge of the alluvial aquifers is generally excellent and is derived principally from river flow. The seasonal flow regime of the Limpopo River is characterised by wet season runoff that recharges the alluvial aquifer. The seasonal water table fluctuation in the Limpopo unconsolidated alluvial aquifer has the potential to cause vertical smearing of the mobile LNAPL contamination zone (Figure 2-25). This effect is similar to tidal effects but on a longer time cycle (see 2.4.2.1).

In this instance it would be a greater challenge to remediate the site since the alluvial material consists of smaller particles which increases the capillary pressure within the system. This in turn would increase the persistence of the contamination in the aquifer as well as increasing the distribution of LNAPL sections. In some case it can also result in disappearance of free mobile LNAP after entrapment below the water table which might create the impression that the LNAPL plume has disappeared. The net result would be that treatment of the area would cease although the LNAPL is only trapped in the subsurface and would resurface after some time or continually dissolve into the groundwater aquifer. If this is the final result the contamination would spread over a larger area but with concentration levels below that of the original site.

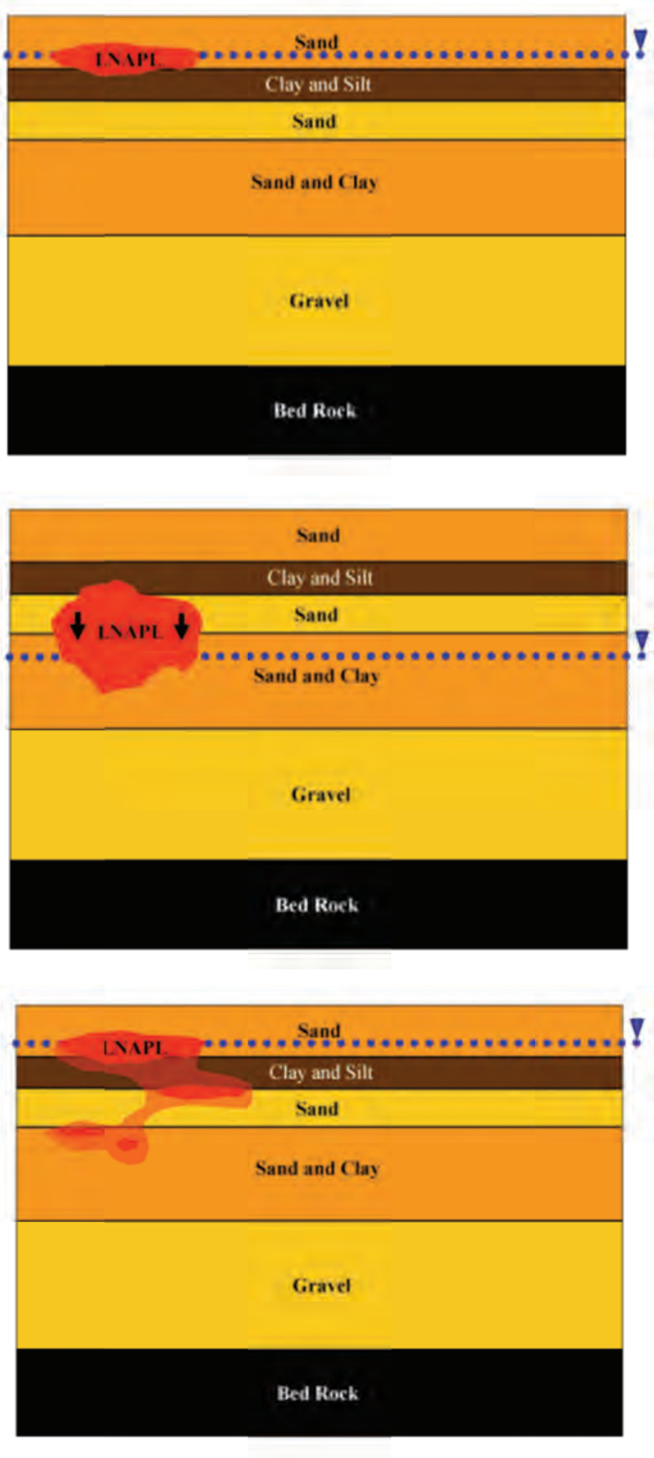


Figure 2-25 Smearing of a LNAPL in an alluvial aquifer. Top section shows the starting level, middle the downward movement of the LNAPL and the bottom section localisation and smearing of LNAPL.

The potential for contamination in the Limpopo river alluvial aquifer is quite high, due to human activities in the area. The persistence of LNAPL residue in this aquifer system would also be significant since high capillary pressure is present. The dominance of unconsolidated sediments in the area up to a thickness of 24 meters (Busari, 2007), can significantly impair remediation actions. The need Volatile Organic Carbon (VOC) analysis during site characterisation in the Limpopo river alluvial aquifer should be given priority.

Where perched aquifer systems exist in the Limpopo river alluvial aquifer, the potential for increasing the vertical extent of contamination should be considered. This might be due to clays or other non-porous barriers, which should be kept in mind when evaluating drilling and well installation programs. Drilling operations could further distribute mobile LNAPL (e.g. liquids perched on low permeability units above the water table) by means of puncturing aquitard layers and creating preferred pathways to the main aquifer system. This would result in contaminating deeper sections, which would increase the probability of LNAPL contamination over a larger area.

2.4.3 Fractured rock aquifers

South Africa also contains aquifer systems which could be classified as pure fractured rock aquifers, i.e. the Lebombo and Drakensberg group. In these systems a preferred flow path exists, these fractures are interconnected and can either be formed along horizontal fault or vertical vault lines (Figure 2-26). In either situation these fractured systems can have a high transmissivity, which would significantly increase the transport of LNAPL contamination. Identification of inter connected fracture networks is crucial for LNAPLs contamination in typical pure fractured rock aquifer. An investigation on this scale would require the application of various geological, geophysical and hydraulic complementary tools.

A secondary property of fractured rock aquifers that should be kept in mind is that localisation of LNAPLs readily occur in the vadose zone (Figure 2-26). This is usually associated with dead-ending of fractures in which the LNAPL can localise. The movement of the water table in the area can mobilise these trapped LNAPLs over time to penetrate into the groundwater of the area.

Fractured rock aquifers can be classified as secondary aquifers, which require constant recharge due to the high transmissivity of the system. This has an inherent advantage since the mobilization of the mobile LNAPL would require less head and energy as there is very little entrapment of residual LNAPLs in pure fractured aquifer due to capillary pressure.

Entrapment of LNAPLs can occur at deeper groundwater levels, as a result of seasonal or fluctuating pumping rates.

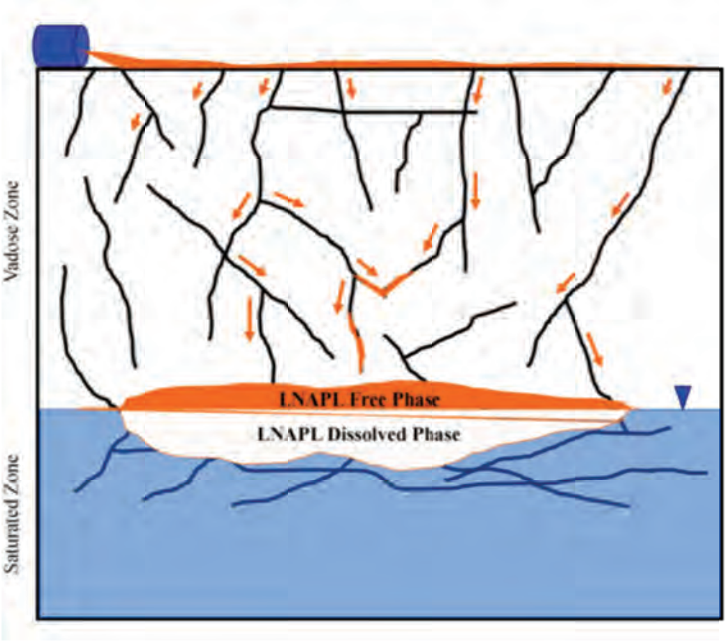


Figure 2-26 A conceptual model of the LNAPL intrusion pathways into a pure fractured rock aquifer. Both the free phase and dissolved phase are shown as an illustration.

2.4.4 Fractured porous rock aquifers

In a pure fractured rock aquifer, interconnected fractures create a preferential flow path which contributes significantly to flow to the groundwater level. The inclusion of a porous media component in this system allows for matrix diffusion to also play an important role in the contaminant migration. In the following section this type of formation will be discussed under the heading of the Karoo Supergroup formations aquifer.

2.4.4.1 Karoo fractured rock aquifer

Karoo fractured rock aquifers, which are the most extensive group of aquifer system present in South Africa, occurs within the Karoo Supergroup. This Karoo Supergroup consists of different groups of sediments, with each sediment group having its own physical and hydrogeological properties. In the current context these different properties will not be discussed. A major characteristic of the Karoo Supergroup, which mainly consists of sandstone, mudstone, shale and siltstone, is their low permeability.

Sedimentary layering creates contact areas which present an opportunity for the creation of water bearing bedding plane fractures. The bedding plane fractures can act as preferential pathway to highly mobile LNAPL, while matrix diffusion occurs in the sedimentary deposits hosting the fractures. The behaviour of the LNAPL within the fractured rock mass is a function of the properties of the immiscible fluid, the geometry of the fracture network, rock matrix properties, and the groundwater regime. In other words their behaviour is completely different in fractured rocks as compared to porous media.

Hardisty (Hardisty and Ozdemiroglu, 2004) noted the potential of relatively small volumes of LNAPL within vertical or sub-vertical fractures to produce significant LNAPL pressure heads, resulting in LNAPL penetration into the saturated zone and such penetration can be significantly deeper than predicted by porous medium models.

Advection plays an important role in both groundwater and LNAPL flow through these fractures. Groundwater flow in a fractured aquifer is mainly dependent on the fracture density, orientation, effective aperture width and nature of the matrix. Mercer and Spalding (Mercer and Spalding, 1991) noted the tendency of LNAPLs to be transported in the same general direction as the groundwater flow direction.

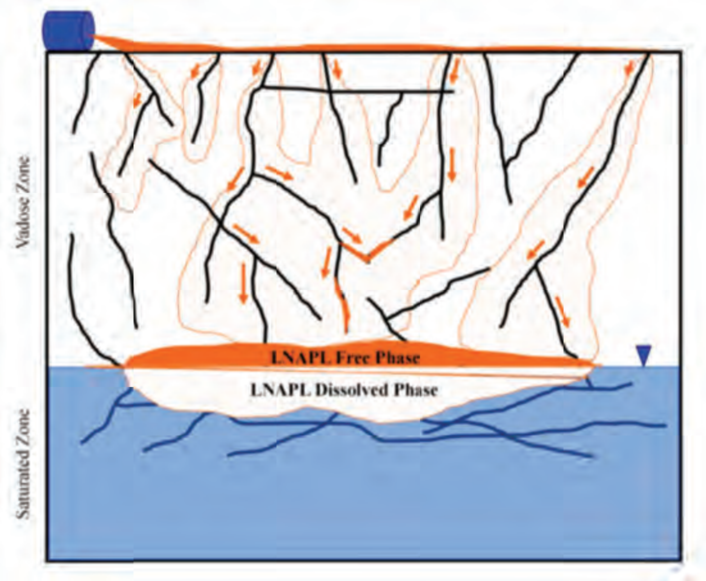


Figure 2-27 A conceptual model of the LNAPL intrusion pathways into a porous fractured rock aquifer. Matrix diffusion is shown along the fracture zone. Both the free phase and dissolved phase are shown as an illustration.

In a fractured aquifer LNAPL contamination characterisation is focused on identifying and locating fracture preferential flow pathways. Determination of preferential flow pathway properties is also of vital importance in understanding the migration and distribution of both free phase LNAPLs and dissolved phase LNAPLs. Such an exercise will call for the use of range of complimentary tools; include core and percussion drilling, borehole geophysics, tracer and aquifer testing to name only a few.

Nevertheless, conventional site investigation techniques developed for porous media aquifers tend to be used when characterizing LNAPL spills in fractured rock environments. This is partly due to a lack of established field methods for the investigation of LNAPL-contaminated fractured systems (Mercer and Cohen, 1990). Accordingly, there is little in the literature describing the economic costs and benefits of various remedial options for LNAPLs in fractured rocks (Hardisty and Ozdemiroglu, 2004), or specifically on remediation methods for dealing with LNAPL intrusion in fractured systems. As a result the need to unveil site characterisation tools, their applicability in typical Karoo fracture aquifer remains a research priority.

The nature and properties of the rock matrix plays an important role in the movement of water and contaminants through fractured porous rock aquifers. The study area is dominated by coarse grained sandstone which is characterised by high primary porosity and permeability. Though fractures serve to convey the bulk of the groundwater fluids, matrix diffusion has strong implications for dissolving LNAPL contaminants. The occurrence of chemical concentration gradients between the fractures and the rock matrix will result in mass transfer of contaminants from the flowing groundwater in the fractures into the relatively immobile groundwater in the rock matrix (Feenstra et al., 1984). Due to matrix diffusion effect the contamination concentrations in the fracture preferential flow pathway are bound to diminish rapidly into the matrix resulting in the contaminant plume moving at slower rate than the groundwater, thus causing the contaminant to persist long after the initial contamination event.

2.4.5 Dolomitic aquifers

Dolomitic aquifers are dominated by caverns and karst-like features; this is due to the dissolution of the carbonate ($CaCO_3$/$MgCO_3$) in these formations. These cavities and karsts usually become water bearing features as time passes and is commonly used as groundwater abstraction points. Normally, the karst systems can be divided into compartmental or free standing units. In either case the water levels in these systems can change significantly with recharge events or abstraction from human activities. In the larger systems a water level drop can be observed in the order of 2-25 meters per day depending on the stress which the dolomitic aquifer experiences.

During the intrusion of LNAPLs into a dolomitic aquifer, the behaviour of the LNAPL can be characterised as a major component (free phase) floating on water surface within the dolomitic system with the bulk of water soluble components dissolved into the groundwater. Additionally, the temperature in these caverns and volume available will also contain the equilibrium fraction as a gas vapour.

During site characterisation the location and distribution of the dolomitic aquifers should be determine and if possible quantified by sampling procedures. The top layer covering the karst system should also be defined since sand and clay particles will influence the penetration tempo of the LNAPL into these aquifer systems.

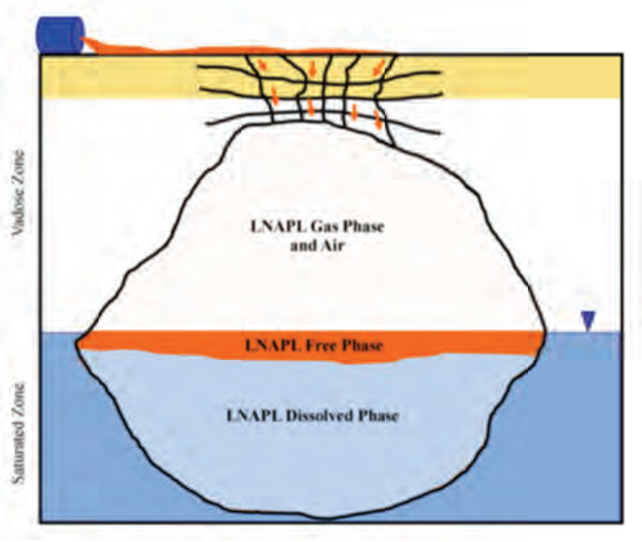


Figure 2-28 A conceptual model of the LNAPL intrusion pathways into a dolomitic (karst) aquifer. LNAP intrusion is shown through fractures, with an equilibrium state between gas, free and dissolved phases.

2.5 Geophysical Methods to Characterise an Aquifer System

In this section methods to determine the extent and location of an aquifer will be briefly discussed. **Most of the geophysical methods as such are not tuned to locating LNAPL contamination sources**, and for these studies it is best to use boreholes to monitor the movement and quantity. **It is the recommendation of this report that at least a resistivity survey of the site should be conducted to determine the geological units present in the investigation area.** The resistivity survey should be conducted by a specialist to avoid field and interpretation errors. Each of the four major aquifer systems will be discussed in regard to surveying techniques, although it should be kept in mind that this is only a summary of techniques that could be applied and is only a recommendation.

2.5.1 Limpopo River alluvial aquifer

In general alluvial aquifers consist of fine river sand, beds of silt and or clay. In such environments Electromagnetic (EM) methods are more applicable to obtain geological and hydrogeological information. This is based on the premise that EM methods uses conductivity contrasts to distinguish between subsurface materials. In general clays and silts typically exhibit higher conductivity values because they contain a relatively large number of ions, while sand and gravel exhibiting less conductivity. In other words in the Limpopo River alluvial aquifer, clays, silt and river depositional fine sand mainly constitute the aquifer material and they can be easily detected with EM.

Resistivity can be used to distinguish between loose sand and clay/silt formations, which at times occur together in alluvial aquifers. Ground penetrating radar (GPR) are of limited use in this environment as clay, silt and fine sand attenuated high frequency electromagnetic waves emitted by the equipment antenna, thus limiting the amount of reflected waves, and consequently affect the output results.

2.5.2 Kalahari sands

Resistivity method is useful as sands offer good resistance, thus enhancing distinguishable features which results in a good resolution for the aquifer materials. Ground penetrating radar (GPR) is applicable in this environment as sands have good reflective capacity on high frequency electromagnetic waves emitted by the equipment antenna, thus good resolution.

2.5.3 Karoo fractured aquifer

A major characteristic of the Karoo Supergroup, which consists mainly of sandstone, mudstone, shale and siltstone, is the low permeability. The contacts or bedding planes between sedimentary layers as well as joints and fractures in the bedrock can acts as preferential flow paths. Resistivity geophysical characterisation can be used to identify water bearing fractures. Water filled fractures are more likely to conductive due to the availability of ions in the aqueous phase. The methods efficacy also depends on the total dissolved solid in the groundwater aquifer. However, on the other extreme open faults and fractures can be also distinguishes on being more resistivity as compared surrounding areas.

The existence of sandstone as part of the quaternary deposits in the typical Karoo basin makes the application of resistivity more applicable as it can distinguish between hard quartz based sand from shale and mudstone formations. Above all the success of the resistivity method depends on the natural occurring minerals in the aquifer formation.

It is important to highlight the possibility of iron rich red sandstones which are more conductive and would effectively be delineated using EM methods. EM methods are also applicable in detecting water filled fractures and faults, since these structures would be more conductive and distinguishable from the host rock.

2.5.4 Dolomite aquifers

Dolomitic aquifers are dominated by cavity and karst features due dissolution calcium and magnesium carbonate based formations. Cavities and karsts usually become water bearing features for groundwater, and abstraction of these areas are viable if the system receives enough recharge to maintain a sustainable water level. The gravimetric geophysical method is more applicable to locating water bearing cavities in dolomitic aquifers, which are based on density differences between the water filled underground cavities.

These systems can also be detected by EM based methods, due to the difference in conductivity between the water bearing feature and the surrounding rocks. Furthermore, resistivity should also be able to distinguish between the less resistive underground water filled cavities or karst aquifers from the host rock. However, cavities are not always totally filled with water, and can be a combination of partially filled cavern or an empty cavern which is disconnected from the surface or groundwater.

2.5.5 Dolerite intrusions

In the instance of dolerite intrusions, the use of magnetic methods should be more reliable in mapping the subsurface. The reason for using the magnetic methods is that dolerite intrusions consist of magnetic minerals. The application of resistivity methods would also yield favourable results due to the iron content of the rock. Ground penetrating radar (GPR) should also be of great use considering the hardness of dolerite, which would increase the potential of high frequency electromagnetic waves to be reflected back to the recording system. In dolerite intrusion areas the use of seismic methods would prove useful, since this method can provide stratigraphic information by measuring how acoustic waves travel through the subsurface.

2.6 Fate of LNAPLs in the Subsurface

Condensing all the previous sections findings, the following generalised model can be proposed for the fate of LNAPLs in the subsurface.

2.6.1 Vaporisation of organic compounds

Considering that water and the LNAPL is in equilibrium (Le Châtelier’s principle), either Henry’s Law or Raoult’s Law can be used to determine the partitioning ratio between water and LNAPL for a system. It should be kept in mind that these calculations are at equilibrium and under ideal conditions for which rarely exist in the subsurface zone.

The best procedure in these instances is to evaluate the VOC of the soil at different levels to get the best practical solution.

2.6.2 Solubility of organic compounds

LNAPLs are a complex mixture of organic compounds which differ not only in content but also in blending process used at the time of constituting the petroleum fuel. The solubility of these compounds is governed by temperature effects and to a lesser extent in shallow aquifers the effect of pressure. The organic compounds contained in an LNAPL might consist of different solution properties and will be in equilibrium with the free phase as well as the aqueous phase. Finally, concentration effects should not be ignored which can be a function of the groundwater velocity as well as the extent of the aquifer.

2.6.3 Adsorption of organic compounds

The surface of a solid or liquid is potentially an active site for adsorption of LNAPLs this would include both water and the subsurface media. Adsorption is most noticeable when porous solids are considered with LNAPLs. In this instance the LNAPL first adsorbs onto the surface of the liquid and subsequently does the same process to adsorb onto the subsurface media. Following this process the LNAPL becomes imbedded into the matrix which significantly reduces the remediation of these sites – although it might only represent a small fraction of the total aquifer.

2.6.4 Biodegradation of organic compounds

The presence of LNAPLs in the subsurface in some respects is agreeable with naturally occurring microorganisms. However, biodegradation should be divided into the free phase and the dissolved aqueous phase. If the free phase is considered, the naturally occurring microorganisms have substantial difficulty in maintaining an environment, which is appropriate for the degradation process. In contrast, dissolved phase biodegradation is more likely under both aerobic and anaerobic conditions. It should be kept in mind that aerobic degradation usually occurs at a much faster rate than anaerobic degradation.

2.6.5 Aquifer composition and extent

The type of aquifer plays a significant role in determining the methodology by which an LNAPL site would be remediated. In South Africa we have four basic types of aquifer systems, which can be located at different depths and experience different hydrogeological conditions. Understanding the mass transport of LNAPLs in these environments is critical in developing an efficient strategy in counteracting LNAPL contamination.

3 FIELD SITES CHARACTERISATION AND RESULTS

In this section field site characterisation will be presented in conjunction with data obtained from the selected study sites. The objective of the investigation was to determine the influence that different geological and climatic conditions would have on the LNAPL movement. With this in mind, the first site was located near the coastline while the second site was situated far inland with a predominantly semi-arid environment.

3.1 LNAPL Site Characterisation

The site characterisation of LNAPL contaminated sites is a scientific and an engineering challenge. The focus of this subsection is to present a general introduction into site characterisation with the objective of creating a fundamental set of parameters which can be useful in determining the geographical extent of an LNAPL contamination site. Basic concepts that have been discussed in the previous section will be used to characterise the subsurface processes and conditions that influence the movement and retention of the LNAPL in the subsurface. These processes require the use of experts in the fields of chemistry, geology, geohydrology and soil sciences. These guidelines will attempt to address the effects of sources, pathways and possible receptors, although these parameters have been approached in a generalised method due to the complexity of LNAPL contamination at a site.

3.1.1 Explorative site investigation

During the explorative phase of an LNAPL contamination site characterisation the following general guidelines should adhered to:

3.1.1.1 Historical data

In order to get an initial assessment of the site all possible sources of contamination should be identified.

1. This would include obtaining information on the location of possible above ground storage units and/or below ground storage areas.
2. Time period that each of these areas were in use.

3. Size of storage unit (tanks or large reservoirs).
4. Contents of storage units (Oil, Diesel, Petrol or Paraffin).
5. Decommissioning time or period of storage units.
6. First incident report (LNAPL).
7. Rehabilitation procedures of the decommissioned areas.

3.1.1.2 Site safety

Before a site can be inspected, assure that the site complies with basic safety regulations. Prepare required safety documentation to enter the site and obtain written permission to enter the area. If possible coordinate a meeting with the site manager, safety officer and plant engineer to discuss any possible hazards and restricted areas.

3.1.1.3 Area of contamination

The procedure for determining the area of contamination should be pre-empted by a basic hydrocensus of the area. This will assist in determining possible areas which might be affected outside (down gradient) of the contamination site. Locate any boreholes which might be on the site or in close proximity to it. If boreholes are sealed with a metal screw cap or any type of device which might cause a spark, be aware that hydrocarbon gas build-up can occur and an explosion might be possible. Setup a geographical database with the most relevant sites logged and hydrocensus data.

3.1.1.4 Site inspection

The first site inspection can be the most informative part of the initial phase.

1. On entering the site, can any volatile components of LNAPLs be detected by smell?
2. Are there any clear signs of LNAPL spillage on the site? Drums leaking, oily patches or small LNAPL ponds. This might indicate a continuous source of contamination.
3. If the site has vegetation on it, does it seem to be normal or are there dead patches or dead trees around?
4. Has the site been sealed off from the local populace?
5. Talk to as many people on site as possible to determine if LNAPL spillage events could be identified.
6. Determine if the boreholes were constructed from the correct material. Plastic linings should not be used on these sites, since certain components of LNAPLs dissolve

plastic or the linings should be constructed of chemically inert materials. Stainless steel and/or concrete construction methods are preferred.

7. Identify any hotspots which might be a direct source of LNAPL intrusion into the subsurface.
8. Try and obtain initial samples from boreholes with a bailer for analysis to determine what kind of LNAPL might be present (major component analysis).
9. Discuss follow-up visit time-schedules and access to the site.

3.1.1.5 Initial conceptual model

Construct an initial conceptual model for the area as this would allow you to quickly assess possible gaps in your assessment method.

3.1.2 Comprehensive site characterisation

During the comprehensive phase of an LNAPL contamination site characterisation, the following general guidelines should be followed, in addition to the data gathered in the exploratory phase.

3.1.2.1 Borehole construction

It is important that no boreholes should be drilled until a good fundamental understanding of the types of aquifers in the area has been established. Puncturing of a confining layer that prohibits LNAPL movement deeper into the main aquifer system can significantly increase clean-up costs.

Borehole construction is most likely the single most significant aspect of monitoring and evaluation of LNAPL contamination sites. Two possibilities exist for borehole construction at an LNAPL site. Firstly, if severe contamination is observed a solid lining of stainless steel would be required to ensure safe operations. Secondly, if the contamination is less severe, a chemical resistant material can be used above the LNAPL zone of influence. In all instances pumping equipment should be chemically resistant to function in these boreholes. All boreholes should be sealed with a non-metallic cap with a pressure equalizing valve to prevent gas build-up in the well.

During site selection of boreholes, the geology of the area should be considered. If possible, drilling of boreholes should be setup in groups of three (to determine groundwater flow direction) and at groundwater watershed areas. The well screens should be setup in such a method to be compatible with the particle size of the formation and allow affective monitoring of the LNAPL contaminant.

3.1.2.2 Sampling intensity (loggers and sniffers)

Sampling intensity is a direct function of available funds, if possible all wells in an area should be sampled in each of the three phases (gas phase, free phase and dissolved phase). In the field PID (Photo Ionic Detector) readings should be gathered for the gas phase and subsequently analysed by chromatographic methods in a recognised analytical lab. Standard sampling techniques should be used to determine EC, pH, redox potentials and temperature at each well site. Samples should be taken and stored in the correct procedure for lab analysis for both macro inorganic and organic components. Loggers can be installed at the site, although a stainless steel cable should be used to insert these loggers.

3.1.2.3 Aquifer parameters

3.1.2.3.1 Geology

The geology of the site should be characterised to determine the transport parameters in both the vadose and saturated zones. Important features such as fault or shear zones, dolerite dikes and aquitards should be identified. Borehole logs should be examined for any possible structures which might act as preferred pathways such as horizontal and vertical fractures or porous media such as sandstones. Down the hole geophysics should also be attempted since these methods can highlight fracturing patterns in an aquifer area. Understanding the geological effects on the groundwater movement can also assist in determining the receptors which might be at risk and if the LNAPL will daylight at another position.

Areas which might pose significant difficulty in site characterisation are:

1. Fine grained sediments – LNAPL distribution tends to be scant along secondary features. These features also tend to be poorly connected which makes LNAPL recovery difficult.
2. Complex geological areas – These areas increase the difficulty of finding the main source of LNAPL contamination.
3. Manmade obstructions can hamper LNAPL location – built-up areas and industrial zones.

3.1.2.3.2 Vadose zone

The vadose zone can play the most critical role in the study of a LNAPL contamination site, since it is this zone that affects the mass transport of the LNAPL to the groundwater table. At a LNAPL site an assessment of the influence of the vadose zone should be made. Firstly, did the intrusion originate from the surface or is it an underground storage unit that leaked into the subsurface. Secondly, a vapour analysis of the vadose zone should be done to determine if the LNAPL vapour is present, two sampling areas should be tested. The top 2 meters and the remaining section of the characterisation site area. The presence of LNAPL vapour in the top soil might indicate that the LNAPL has an interaction with the atmosphere; this is especially relevant in humid or coastal climates. Below 2 meters it becomes less likely that an interaction with the atmosphere is possible and the LNAPL plume might be moving downwards to the groundwater level. These influences are also a function of the quantity of LNAPLs present and are only a guide to estimate the vadose zone impact.

3.1.2.3.3 Depth of water level and groundwater level gradient

Three types of aquifer systems will be classified for this discussion in this section. Firstly, shallow aquifers which have water level less than 4 meters below the surface. Secondly, intermediate aquifers with water levels which range from 4-10 meters below surface. Finally, deep aquifers which are any aquifer system with water level greater than 10 meters below the surface. The reason behind this classification is to assist in defining the interaction between the three phases which exist in any LNAPL system, i.e. gas, liquid and solid phase. In South Africa typical temperatures at depths greater than 10 meters ranges in the area of 10-20°C, while in the first 10 meters a significant difference can be observed which is determined by seasonality.

In South Africa shallow aquifers have a high probability that the LNAPL might evaporate into the atmosphere since these systems are usually unconfined. At greater depths, intermediate or deep aquifer systems confining or semi-confining conditions might prevail trapping the LNAPL in the subsurface. In the latter instance LNAPL migration usually occurs through preferred pathways to the groundwater level, and LNAPL contamination might be spread through a larger area.

To effectively determine the LNAPL distribution area, a careful study of the general region groundwater levels around the investigation site should be conducted. To effectively study an area, pumping rates from residence and industrial (agriculture, mining or development) activities should be known. Quantity of abstraction should be determined for each of the active sites as well as pumping frequencies.

The abstraction characteristics of an area are fundamental in determining the movement of the LNAPL plume. One specific example is the presence of fractured rock aquifers in the Karoo Supergroup. Consider the scenario where an individual abstracts enough water in an aquifer system to allow the LNAPL to move into the fracture zone at a nearby site. Through this type of action the LNAPL is drawn into the fracture zone and transported at high transmissivity rates through the aquifer system, this would effectively inject LNAPL into the whole aquifer down gradient from this site.

3.1.2.3.4 Hydraulic parameters of the LNAPL

Sampling of the LNAPL can be a valuable tool in determining the effect of the contaminant in a specific site. LNAPL component mixtures can be analysed to determine the main organic components; and with the use of evaporation rates, mixing volumes and solvation properties a good estimate can be made on the available contaminant at a site.

3.1.3 Methodology of Constructing a Site Conceptual Model

One common problem in evaluating LNAPL contamination at a site is the assumption that it only occurs in one phase, i.e. a pure geohydrological problem or a gas phase only problem. The subtleties involved in the study and clean-up of an LNAPL site is the presence of a three phase system, i.e. gas, liquid and solid. The LNAPL can be distributed in both the vadose and saturated zone and this should be incorporated into the conceptual model. In the instance of Mandle (2002) the focus for the construction of a conceptual model is solely based on the aquifer system, during the research phase the conceptual model will be constructed using the following guiding principles:

1. Determine the approximate depth of the aquifer system
    a. Shallow aquifer systems
    b. Deep aquifer systems
2. Geology of the area
    a. Alluvial deposits
    b. Bedding plane fractures
    c. Hard rock fractured systems
    d. Dolomitic areas
3. Vadose zone interactions
    a. Significant contact with the atmosphere
    b. Moderate contact with the atmosphere
    c. Reduced contact with the atmosphere
4. Aquifer parameters
    a. Hydraulic conductivity
    b. Gradient of aquifer system
    c. Storativity of the system with respect to LNAPL and water
5. Human interaction
    a. Pumping activities in the area
    b. LNAPL source type – continuous, accidental spillage (once-off)

A short discussion of each point will be presented below, highlighting the main points which should be considered.

3.1.3.1 Determine the approximate depth of the aquifer system

This is one of the most important factors in determining the proportions of an LNAPL contaminant site. If the aquifer system is shallow, i.e. less than 5 meters below surface; an interaction with the atmosphere is highly possible and careful consideration should be given to vadose zone interactions. Deeper than 5 meters it is highly unlikely that rapid transport to the surface will be observed. In deep aquifer systems the geology of the area will contribute more to the LNAPL source distribution and transport.

3.1.3.2 Geology of the area

The geology of the study area contributes significantly to the behaviour of the LNAPL. The presence of fractured hard rock or bedding planes in a study area considerably affects the movement of the LNAPL as compared to alluvial or dolomitic systems.

In most fractured rock aquifer systems the presence of preferred pathways complicates the construction of a conceptual model. In this instance an average value should be used to determine the percentage of connected fractures in an aquifer system (tracer tests). Furthermore, the movement and distribution of LNAPL in these fractures should also be scaled. The presence of bedding plane fractures can be determined from pump tests, but it should be kept in mind that the bedding plane fracture in the system is not of constant aperture neither at constant depth.

Dolomitic systems can be approximated with an interconnected “pipe” system in which free phase can flow from one compartment to another. The presence of dolerite intrusions into karst systems should also be included in the conceptual model to reduce the conceptual model size.

Alluvial aquifer systems are quite common along coastal areas, river systems and arid regions. Depth of the aquifer system and LNAPL quantities in the subsurface will dominate in the construction of the conceptual model.

3.1.3.3 Vadose zone interactions

The role of the interaction of the unsaturated zone in the distribution of the LNAPL in the subsurface should not be underestimated since this could be the single most important factor in shallow aquifer systems. In order to successfully evaluate the influence of the vadose zone; the average grain size, sorting of the material and humidity should be known.

If significant contact with the atmosphere is suspected in a shallow aquifer system, the conceptual model should incorporate evaporation rates. Climatic conditions such as high humidity and windy areas could have higher rates of evaporation and thus decrease the amount of LNAPL in the aquifer by a substantial amount.

Moderate contact with the atmosphere could imply that evaporation as well as bioactivity of micro-organisms can play a role in the removal of LNAPL in the system. The interaction between the LNAPL present in the subsurface and the aquifer could be substantial. In this regard aquifer parameters should be investigated to determine if the vadose zone would be a major role in the LNAPL contaminant distribution.

In the instance in which reduced contact with the atmosphere is suspected, the vadose zone would not contribute significantly to the construction of the conceptual model.

3.1.3.4 Aquifer parameters

The determination of aquifer parameters for an aquifer is critical in understanding the behaviour of a study site. However, it should be kept in mind that LNAPLs does not share the same physical properties. The hydraulic conductivity of the aquifer will only indicate the flow properties of the water in the system. These values could give a good indication of the movement of the LNAPL dissolved phase in the aquifer system, but not the free-phase which is located at the piezometric level.

To determine the flow direction of the free-phase in the study area, the hydraulic gradient is required. If it is assumed that no geological formations prohibit the movement of the free-phase a good estimate can be derived as to the spread of the LNAPL in the study area.

LNAPLs can also adhere to soil or rock particles in the subsurface and this should also be considered in the construction of the conceptual model. The influence of piezometric fluctuations in an aquifer can contribute to the distribution of the LNAPL in the miscible areas.

3.1.3.5 Human interaction

The role of human activities at a site should never be neglected, since pumping activities can significantly increase the movement of LNAPLs in the subsurface. In bedding plane fractured systems the introduction of LNAPL into the fracture is typically associated with over abstraction.

3.2 Study Areas

As noted earlier in this section, results obtained from the study sites will be presented to illustrate the effect that different geological and climatic regions will have on LNAPL contaminant distribution.

3.2.1 Case Study: Coastal Field Site

The first site is located along the coast and underlain by typical fractured Karoo aquifer material. The site consists of various storage facilities and the investigation was launched to determine if there is a potential source of free phase contamination on the terrain.

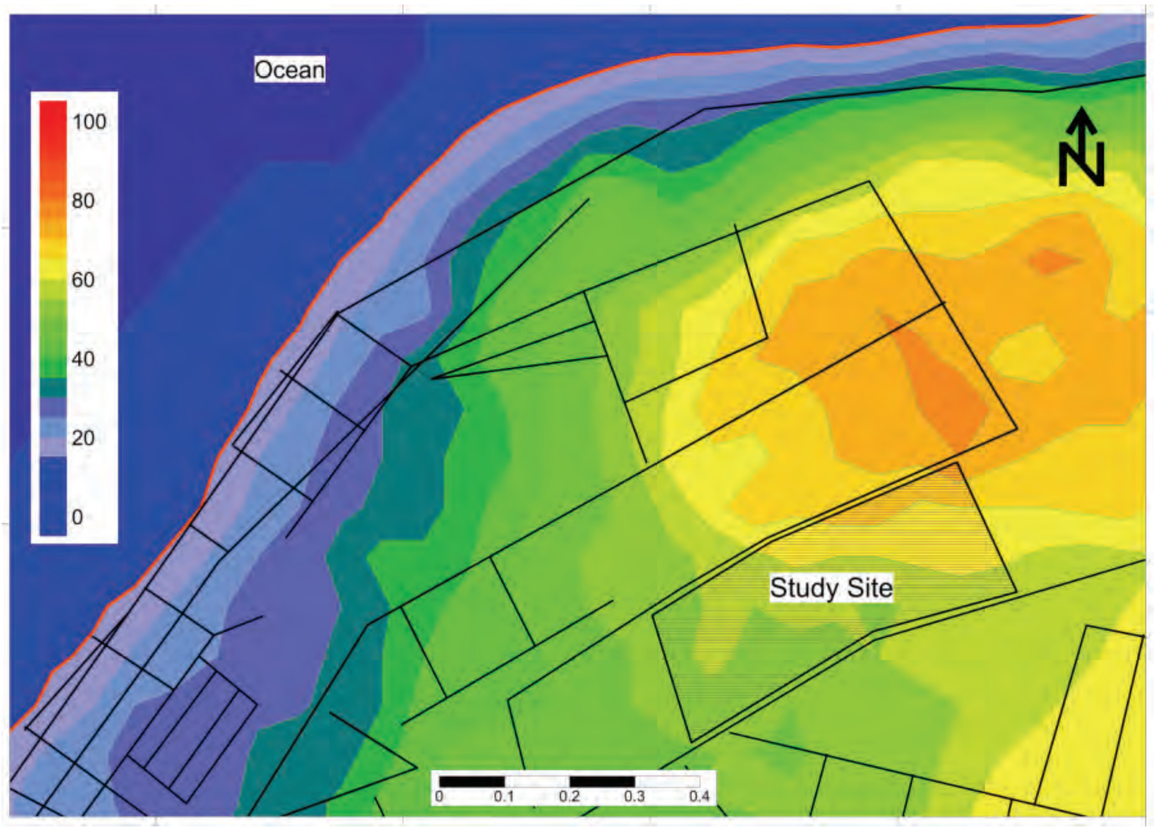


Figure 3-1 A topographic illustration of the coastal study site. The study site is indicated on the figure and the scale is in kilometers.

The study at the site was systematically conducted with the following main points in mind:

1. Non-invasive geological mapping.
2. Soil vapour survey of the area.
3. Geophysical methods – resistivity.
4. Soil sampling.
5. Percussion drilling and auguring.
6. Pump testing and hydrological evaluation.
7. Geochemical evaluation.

3.2.1.1 Assessment methodology

The first phase of the proposed site assessment was a desktop review of all relevant information. The intention was to gain a better understanding of site history, site contamination profile, geology and geohydrology. After the desktop review, a site walk over was conducted to get a better understanding of site conditions. Some field work, such as measuring product thickness and water levels in existing boreholes, was performed during the site walkover. A hydrocensus was initially suggested but due to access restriction of the surrounding properties, this was replaced by a geological mapping exercise.

The first step in the site assessment was a non-invasive phase, comprising of soil vapour and geophysical surveys. A soil vapour survey was completed over the site using Two PID instruments, a MiniRae 3000 and a Multi Rae. A two dimensional resistivity survey was proposed to map the thickness of the weathered material on top of the underlying hard rock aquifer. Geological structures like fractures and contact zones can also be mapped with this method.

3.2.1.2 Non-invasive investigation

3.2.1.2.1 Geological mapping

A geological mapping was done to determine the orientation of the dominant joint sets which may affect the direction of groundwater movement through the study site. Outcrops were minimal in the area and the study was confined to road cuttings and the coastline outcrop near the site.

The underlying geology is characterised by alternating grey, moderately to well sorted, fine to very fine-grained, ultralithospathic sandstones and bluish grey, greenish-grey or greyish-red mudstones of the Middleton Formation – Adelaide Subgroup – Beaufort Group. The Beaufort strata have been intruded by doleritic sills of Jurassic age at various angles to bedding. The Middleton Formation and associated dolerite sills are unconformably overlain by aeolian deposits of the Nanaga Formation (Johnson and Le Roux, 1994).

The dominant joint orientations dip at sub-vertical inclinations towards the west, north and northeast. The subordinate joint sets dip at sub-vertical inclinations towards the south, southwest, northwest, east-southeast and southeast. A steep south-southwest dipping joint set is present in the sandstone unit but absent in the mudstone. Similarly, the mudstone where steeply dipping north-northeast and south-southeast which are absent in the sandstone units. The dominant joint sets indicate that groundwater movement will follow the joints and be directed northwards to the coastal zone.

3.2.1.2.2 *Soil vapour survey*

A soil vapour survey relies on the volatile nature of contaminants such as petroleum products. The volatile fraction of the contaminants equilibrates with the soil gas in the unsaturated zone and can be detected with hand held instruments such as a PID (Photo Ionisation Detector). By measuring the VOCs at various points in the near surface soils the extent of the plume can be mapped. It can be observed from Figure 3-2 that the western and southern sections showed an elevated soil gas value, while the northern and eastern sections had results which were acceptable.

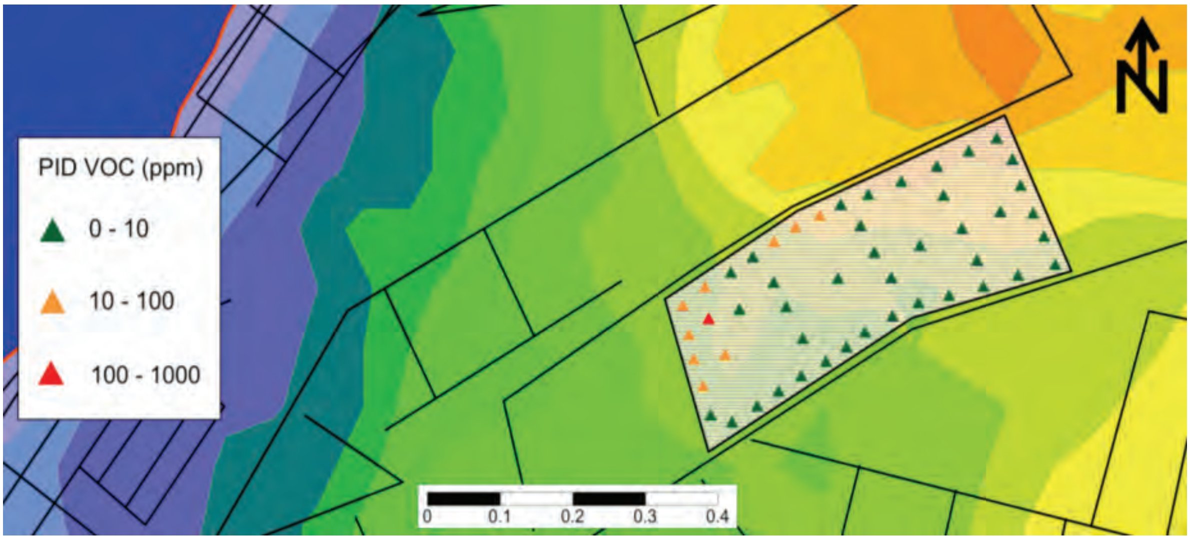


Figure 3-2 PID measurement points and results from soil survey (ppm).

3.2.1.2.3 *Geophysical survey*

The use of geophysical methods to characterise the subsurface materials and to detect LNAPL product flow pathways and contaminants plumes has been applied at this site. The geophysics included Electrical Resistivity Tomography (ERT), Induced Polarization (IP) and Electromagnetic (EM) surveys.

This section presents the results of the ERT experiment at the coastal study site. In general, aquifers in the Adelaide subgroup are multi-layered and multi-porous with variable thickness (Botha et al., 1998). As part of the Karoo bedding, parallel fractured formations, groundwater in the Beaufort formation occurs in joints and fractures of dolerite contact zones with country rock, in decomposed dolerites and in the semi-weathered zones between decomposed and solid dolerite (Bordy et al., 2004). The geophysical survey lines are classified in two groups. The first includes four traverses chosen outside the study site (Figure 3-3), which will be used to characterise the geology and hydrogeology of the general area. The second set includes four traverses inside the study site to locate or to detect the remnants of LNAPL degradation (Figure 3-3).

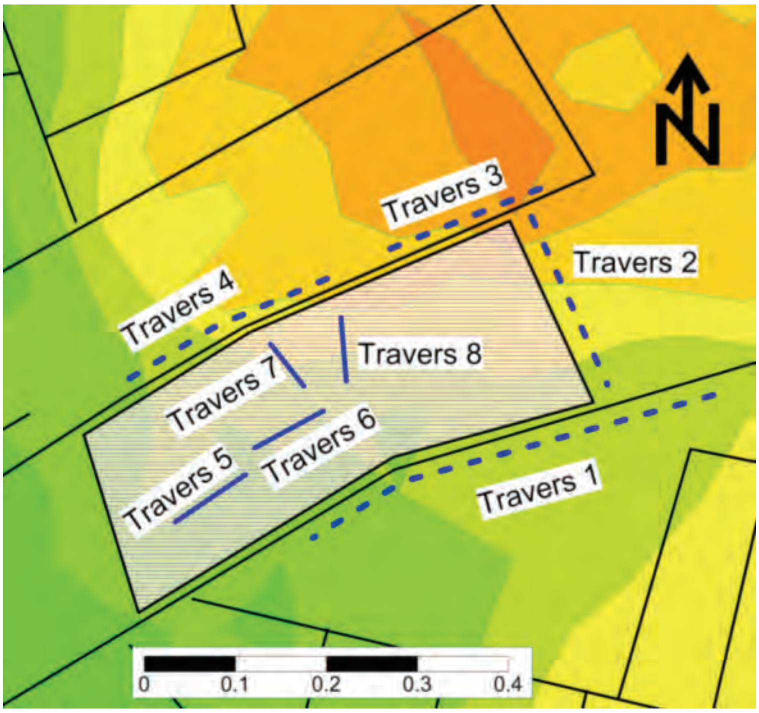


Figure 3-3 ERT survey traverse inside and along the border of the study site.

The Wenner protocol of measurement was chosen because of its ability to discriminating noise. The electrode spacing was chosen as 2 m for the external traverses and 0.5 m for traverses inside the site. A roll-along technique was used for lateral data coverage by moving the first cable to the fourth one, repeatedly. GPS reading were taken using the differential GPS with a 2 cm precision. The data obtained from all survey transects were analyzed using the RES2DINV program which makes use of the smoothness-constrained least-squares method and automatically determines a 2-D resistivity/chargeability model of the subsurface.

3.2.1.2.3.1 ERT survey results

In order to characterise the geological and hydrological condition of the study site, four traverses were used in the ERT survey. For each traverse two or three 2D resistivity sections are presented. The first section without topography data gives the true depth of the different layers. The second section with topography data, gives the true lateral lengths of the geological features. In general most of the ERT images present similar results and only a few traverses will be shown to illustrate the main geometry at the study site.

1. **Traverse 1**

This ERT image presents essentially three resistivity contrasts including a very conductive layer from 0.5 to 5 m and a second layer more resistive which could be a fractured bedrock which goes from 8 m to the base of the survey extent (Figure 3-4). An intermediate layer from 5 m to 8 m could be weathered material.

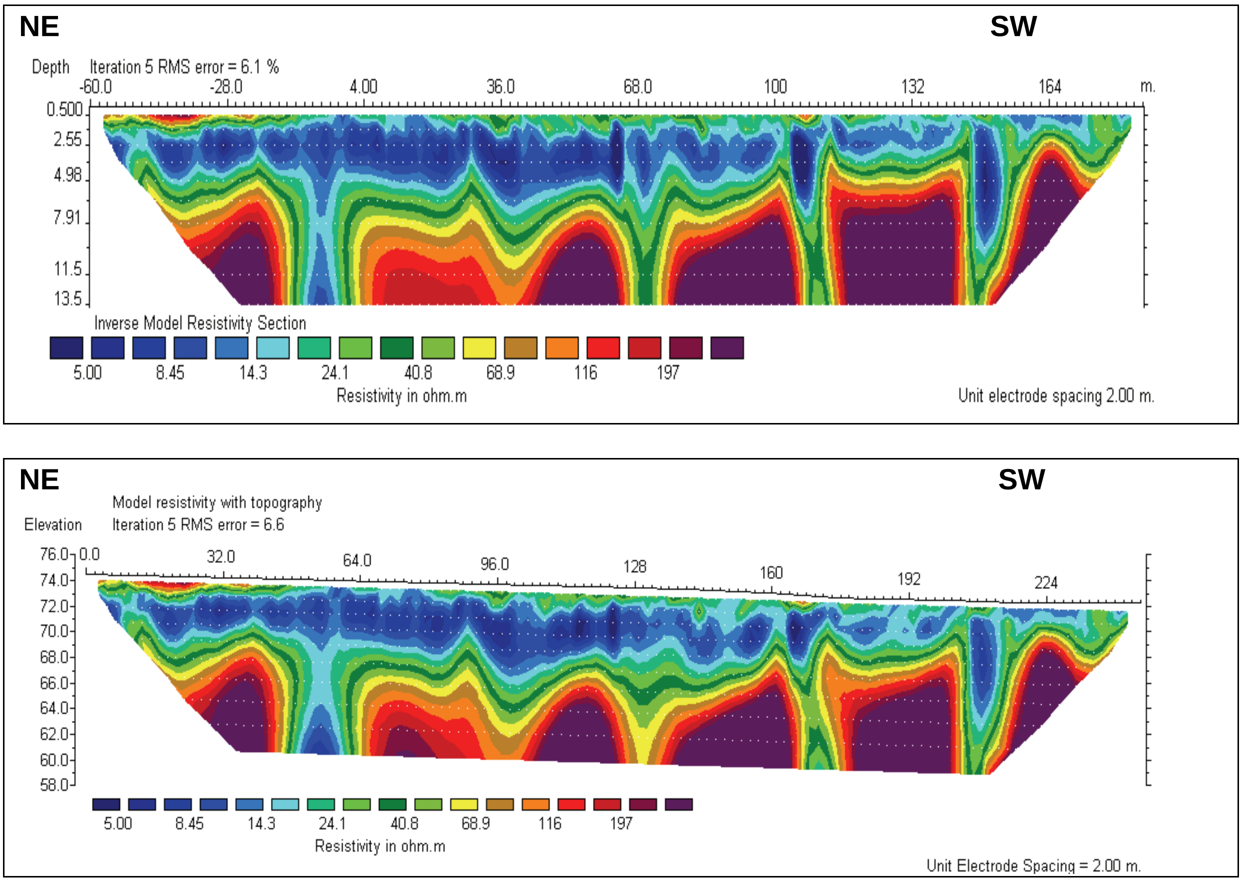


Figure 3-4 Resistivity results of traverse 1.

2. Traverse 2

This traverse 2 has been surveyed in two parts because of the presence of a fence dividing it in the middle. A space of about 20 m separated the two sections. Figure 3-6 below present the two parts side by side as they are located on the site.

The first and resistive layer completely covers the south part but not toward the north. The subsequent layer has four separated conductive pockets which overlay the fractured bedrock with intermediate zones which represents the weathered zone between 2 and 5 m.

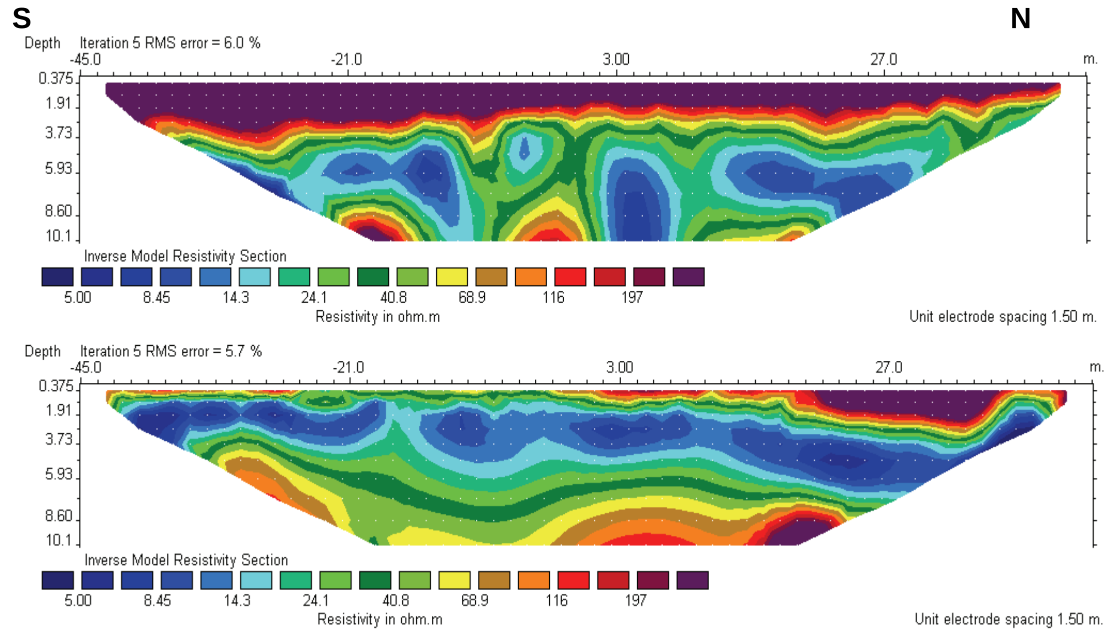


Figure 3-5 Resistivity section for traverse 2

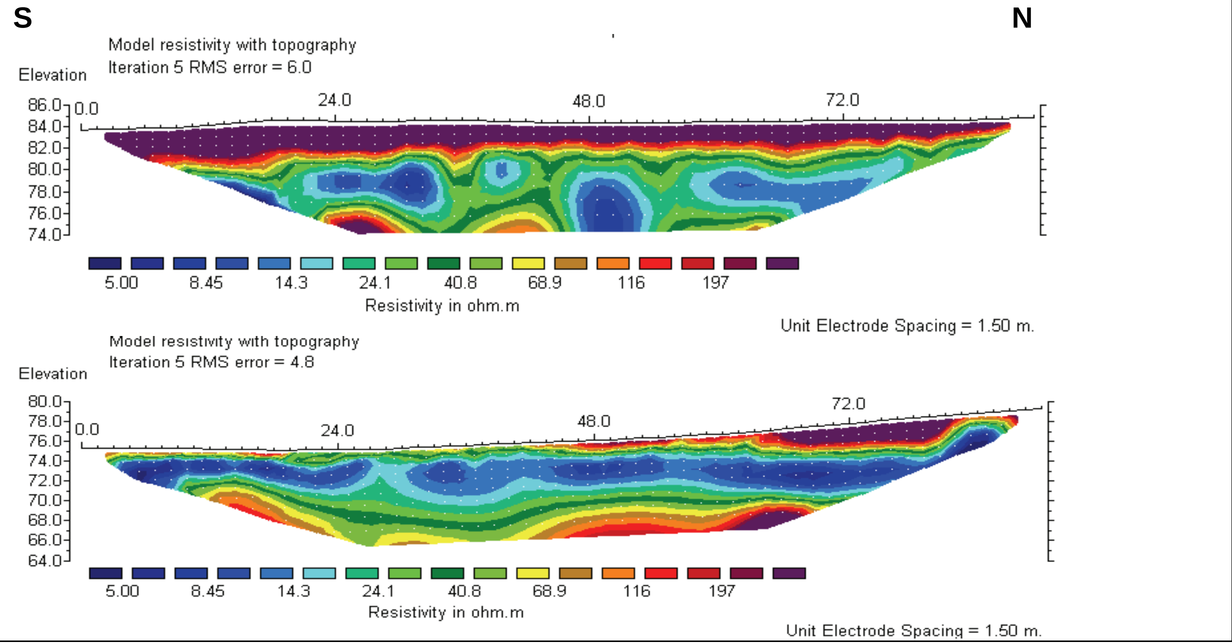


Figure 3-6 Resistivity section for traverse 2

The detection of a possible LNAPL contaminant plume in the subsurface with 2D resistivity survey is possible, if these results are used to compare with that observed inside the study site, i.e. a background system. A second indication of LNAPL presence can be identified by noting anomalously high or low resistivity values. High anomalous resistivity values for fresh LNAPL spills and low anomalous resistivity values for old LNAPL spills that have been biodegraded over time, hence accumulation of salts and heavy metal ions.

3. Traverse 5

A resistant layer is found near the surface followed by five conductive pockets which are separated by less conductive intrusions which bound what could likely be the perched aquifer system. The first and highly resistive layer could be the presence of a clay layer which impacts heavily on the ERT measurements. The spatial distribution can be observed in Figure 3-7.

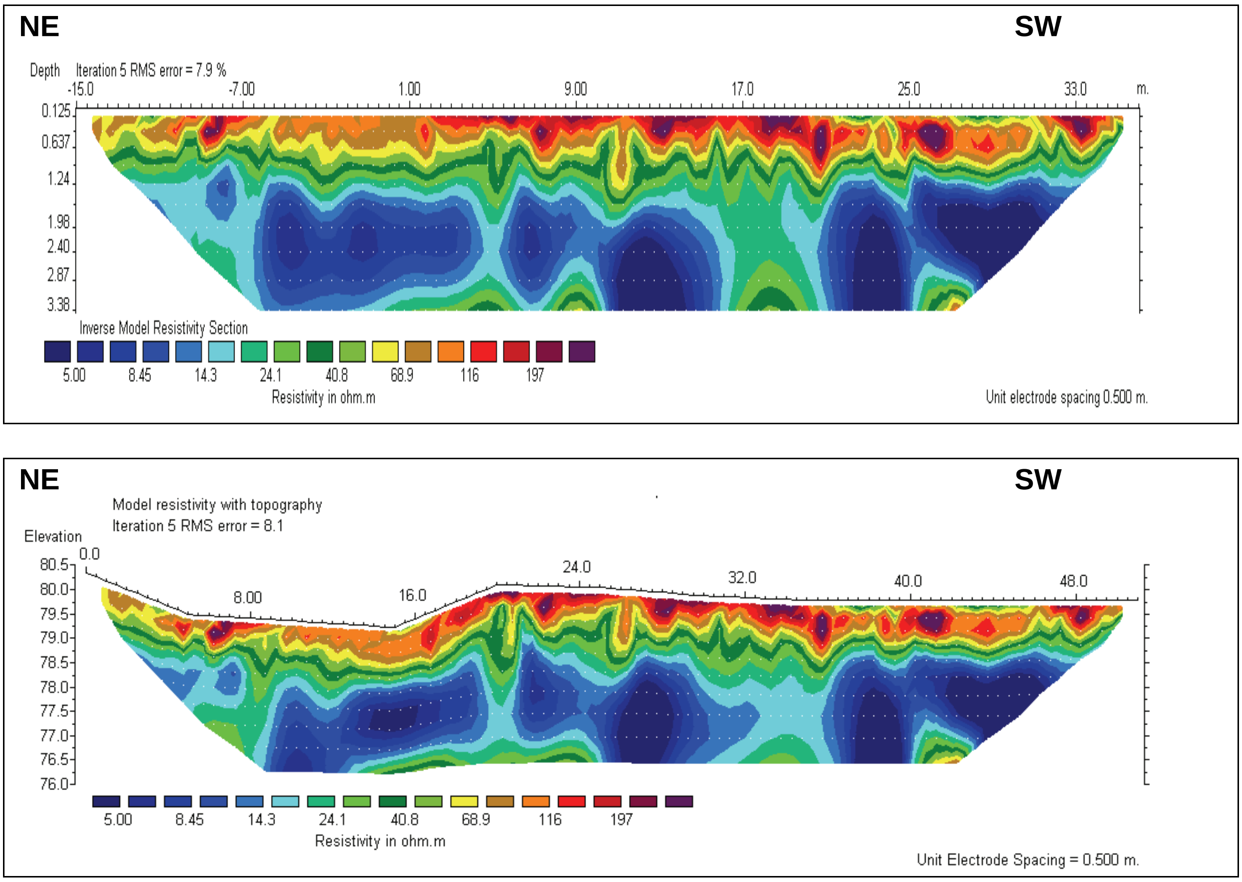


Figure 3-7 Resistivity section of traverse 5.

4. Traverse 7

This line passes near a borehole located in the study site and in which 2.9 cm of free phase have been found during the team visit. The borehole is situated about 9 m off the section line. The ERT diagrams reveal a resistive layer at about 1.5 m depth (Figure 3-8); this could be because of the LNAPL present in the area, creating a high resistive zone.

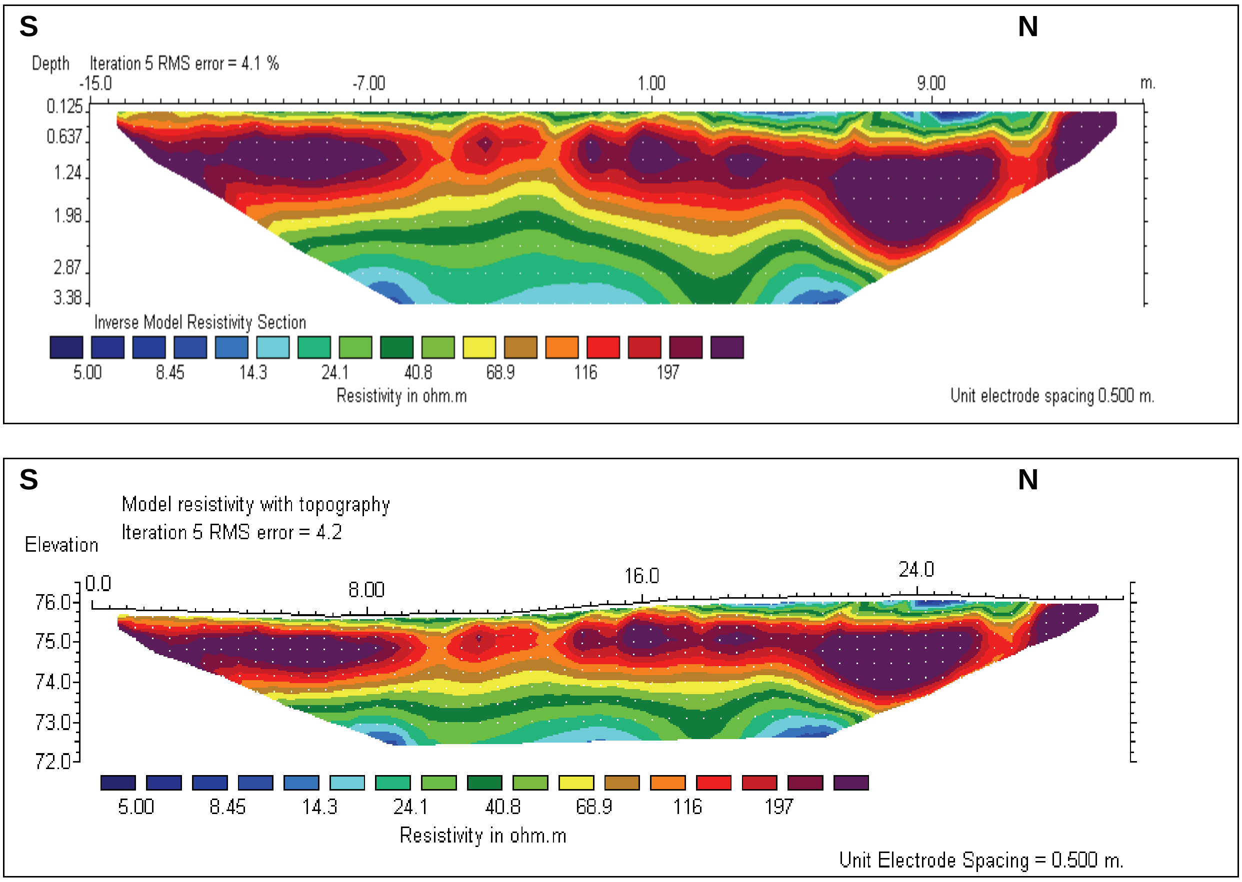


Figure 3-8 Resistivity section of traverse 7.

3.2.1.3 Invasive

3.2.1.3.1 Auger drilling and soil sampling

Auguring was done on all the boundaries of the site with 20 m spacing between each evaluation point. The depth of the sample holes varied from 1 to 4 meters below surface, depending on the subsurface material.

Where access was gained within the individual properties a series of holes was also drilled with the hydraulic rig. Both the core and auger methods were used to collect soil samples at different depths on site. The core method involves pressing a thin walled cylinder into the soil and withdrawing it with a relatively undisturbed sample. Some core samples were extracted from excavated trench sites. The augured samples were bagged and sealed to serve as samples for describing the profile and for conducting textural analyses.

In the laboratory three different tests have been completed on the soil samples returned from the field study site:

1. Initial gravimetric water content was estimated by weighing, oven drying at 105°C for 24 hours and weighing again.
2. Descriptions of the soil profiles at each sampling depth which comprised texture and colour estimates.
3. Particle size analysis by hydrometer and sieving methods.

From the particles size analysis of the soil sample taken at 1.5 m, the soil can be classified as loamy sand (LmSa) and is well graded (Figure 3-9).

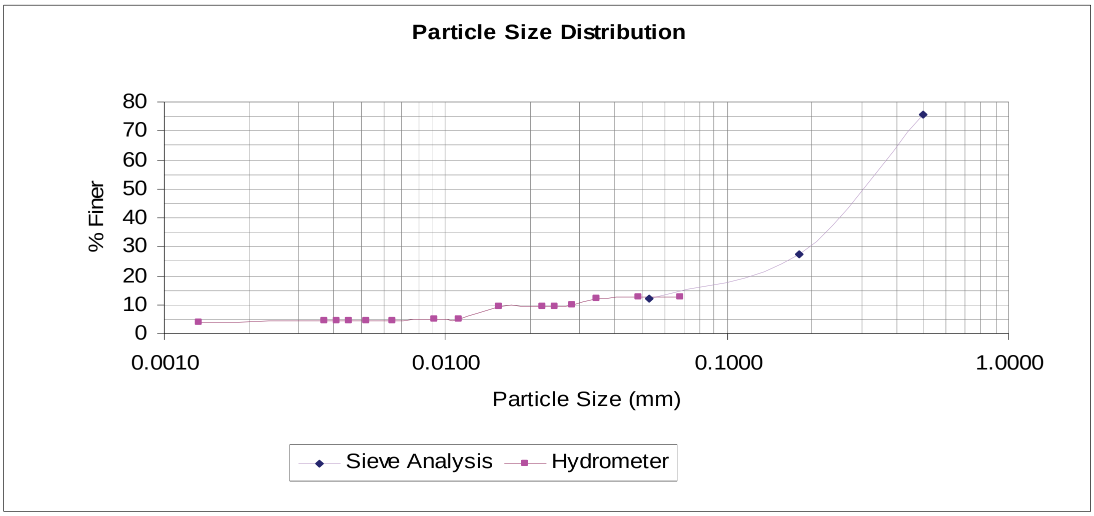


Figure 3-9 Particle size distribution curve for the samples taken at the study site

3.2.1.3.2 Percussion drilling

As part of the invasive phase six new percussion boreholes were installed. Boreholes were installed to evaluate subsurface stratigraphic, hydrogeologic and contaminant conditions. Selection of drilling locations, depths and methods were based on available information regarding site conditions. The knowledge gained through such successive drilling events, is used to construct and update the site conceptual model.

The air percussion drilling method was selected. The advantage of air percussion drilling is the speed of drilling through most semi- to well-consolidated formations. The technique is relatively inexpensive. It is also the most widely used drill technique for groundwater investigations in South Africa. Disadvantages of air percussion drilling include the difficulty in defining precisely the boundaries between geologic layers. Due to the high air pressure applied during drilling, loss of VOCs by volatilization can also occur.

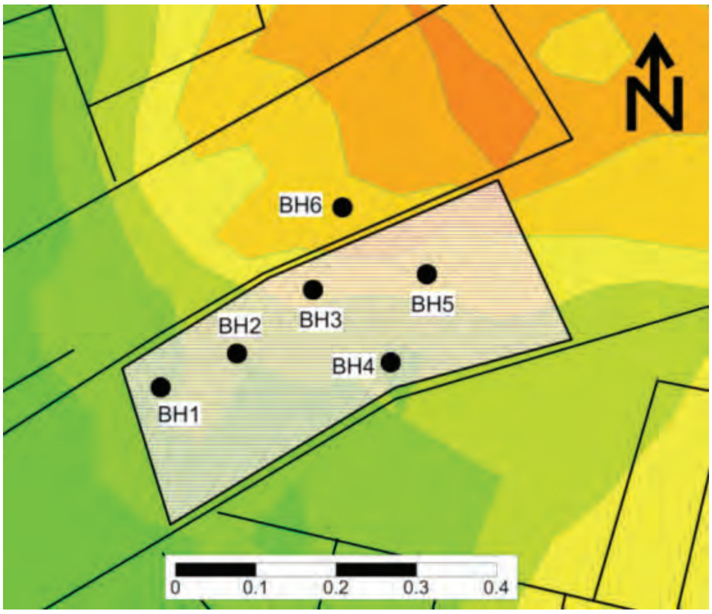


Figure 3-10 Location of drilled boreholes on or near the study site.

The boreholes were drilled to a depth of 14 to 30 meters below surface. The construction of all holes was similar, since the boreholes were cased down to bedrock with perforated casing, either UPVC or steel. All boreholes were capped and given a sanitary seal on surface. Generally the lithologies consisted of a sandy clayey layer on top, followed with various layers of clayey material before reaching the bedrock, which consisted of fresh dolerite.

Water strikes were generally found on the upper contact of the clay layer and again at the contact zone with the bedrock. However, the borehole blow yields were all low (<0.1 l/s).

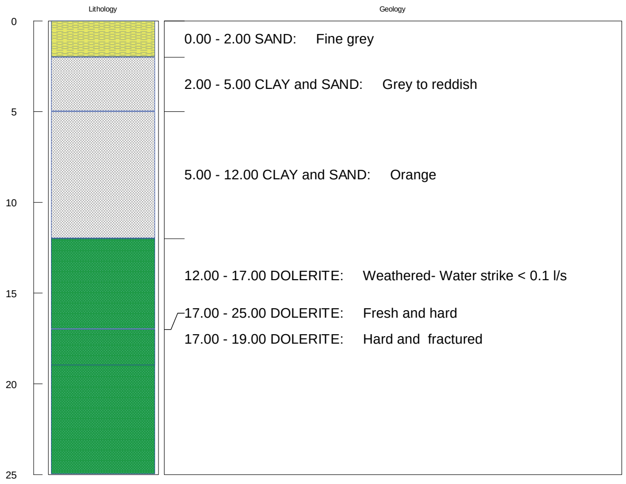


Figure 3-11 Borehole log of BH6 showing three definite lithologies.

Borehole BH6 was drilled off site and topographically upstream from the site. The purpose of this hole was to be used as a background observation borehole. Bedrock was located at 12 meters below surface. Slight fracturing was observed at approximately 12 to 17 meters below surface.

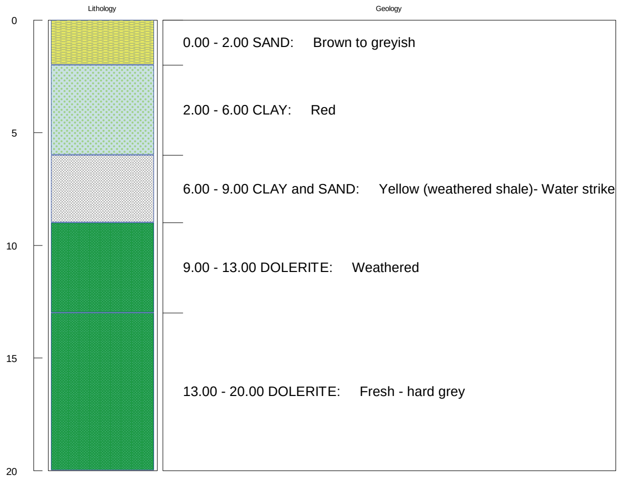


Figure 3-12 Borehole log of BH4 showing four distinct lithologies.

Borehole BH4 was drilled to the south and similar geology was intersected for most of the other borehole sites. However, this was the only borehole where the samples, although weathered, showed evidence of the underlying shale formation between 6 and 9 meters below surface.

3.2.1.3.3 Pump tests and measured water levels

Pump tests are performed to assess the productivity of the aquifer according to its response to the abstraction of water, and/or to determine the transmissivity of the aquifer. This response can be analysed to provide information with regard to the hydraulic properties of the groundwater system.

Slug test data were only used as estimates for pump rates during the pump tests. The data were not further interpreted. The reason for this is that the Bouwer and Rice method requires that the extent of the fracture be known. The extent of the fracturing is not known in this scenario. However, the K value can be calculated relative to the T value, this k value will not be of strong enough integrity for scientific use.

Table 3-1 Transmissivity values for the coastal field study site.

Borehole	T (m^2d) (Cooper-Jacob)	Recovery T (t' against rise of wl)
BH1	0.24	0.26
BH2	0.25	0.24
BH3	0.81	0.88
BH4	0.31	0.36
BH5	0.51	0.37
BH6	0.81	N/A
AVG	0.49	0.42

The depth to the groundwater levels varies from 0.6 to 3.0 meters below surface level, and is a good indication of a shallow unconfined aquifer system. A very good correlation of 98 % exists between topography and water levels as indicated by Figure 3-13. This implies that the Bayesian method of interpolation can be used to construct a reliable water level contour map of the coastal study area.

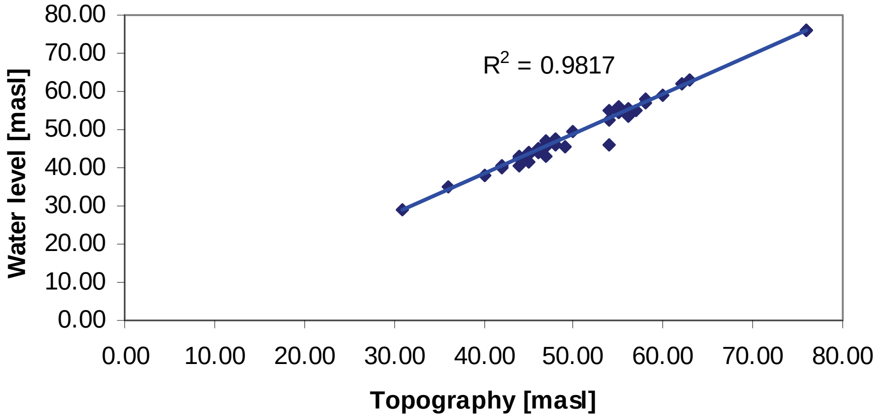


Figure 3-13 A plot of surface elevation versus water levels at the coastal study area. A good correlation (98 %) can be observed for the data.

The general direction of groundwater movement in the area can be illustrated using a vector map constructed from the Bayesian interpolated water levels (Figure 3-14). It can be clearly observed that if the contaminant should move in the direction of steepest gradient, then it would move in a north westerly direction.

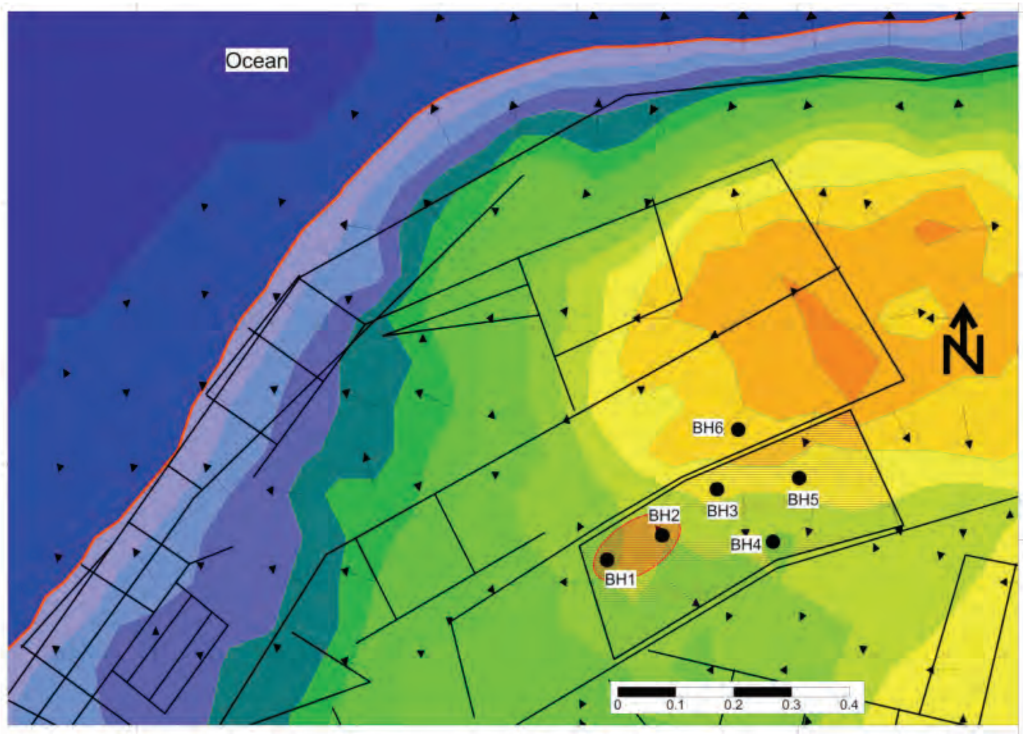


Figure 3-14 Vector diagram showing steepest gradients in the coastal study area.

3.2.1.3.4 Water sampling

The goal of groundwater sampling is to collect samples which are ‘representative’ of *in situ* groundwater conditions and to minimise changes in groundwater chemistry during sample collection and handling. Experience has shown that groundwater sample collection and handling procedures may be a source of variability in water-quality concentrations, due to differences in sampling personnel, sampling procedures and equipment (EPA, 1995).

3.2.1.3.4.1 Inorganic analysis

One of the major challenges in site characterisation (or remediation) of soil and groundwater, is the presence of mixed organic and inorganic contaminants. Inorganic contaminants will usually be present at any NAPL contaminated site. Measurements of inorganic parameters at a NAPL site will thus be used not only to determine if there is any inorganic contamination present, but some of these parameters are important indicators of subsurface geochemical conditions. The inorganic parameters are also used to classify the type of groundwater in order to determine the origin, recharge conditions and type of aquifer system. The first step in evaluating inorganic parameters at a site is to use diagnostic diagrams such as the Durov, Expanded Durov or Stiff diagrams. These diagrams help the site assessor to classify the general water types of the samples.

The Durov diagram (Figure 3-15) shows a steady increase in salinity with an increase in chloride content. This result is not unexpected since the study site is located close to the coast. No significant trends can be observed although the amount of Ca and Mg cations in the samples vary across the site. This could be because of recharge that is occurring creating dominant hydrofacies of Ca(Mg)Cl and $NaHCO_3$ waters due to cation exchange in the subsurface.

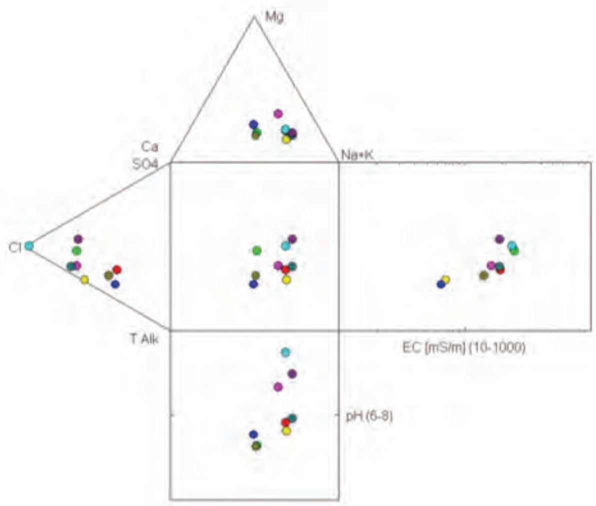


Figure 3-15 Durov diagram for boreholes sampled.

In general the water quality is good at the field study site. The salinity (EC) and pH are within the maximum allowable drinking water standards. However, the sodium and chloride content in some of the boreholes exceed national standards but this can be ascribed to the proximity to the coast line.

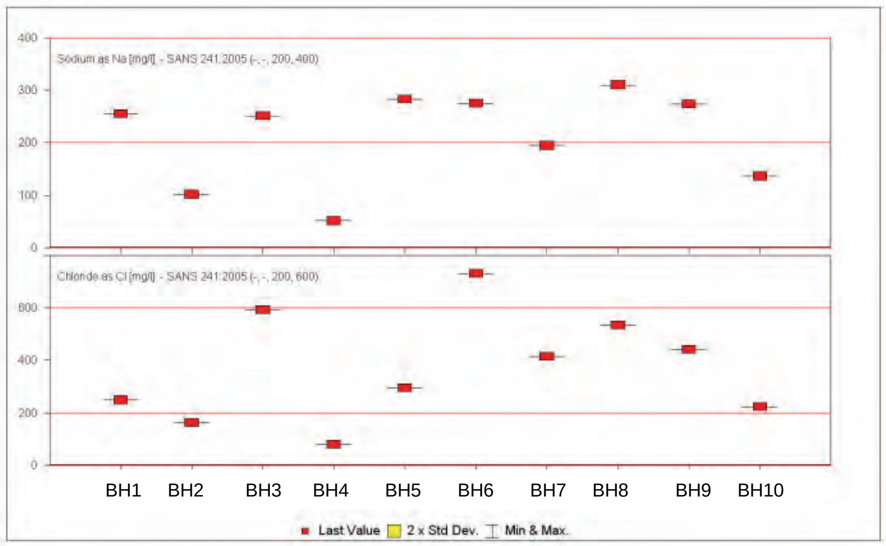


Figure 3-16 Sodium and chloride of sampled boreholes.

3.2.1.3.4.2 Organic analysis

The more mobile fractions of the contaminants (BTEX and MTBE) are the most widespread of all the constituents. However, the concentrations are relatively low compared to the TPH content. Borehole BH2 had the highest values, which was to be expected since free phase was detected in the borehole. There are fewer of the heavier fractions of TPH in the groundwater than in the soils, this is due to the presence of clays in the surface zone. From the organic results it is evident that more than one type of fuel/product (from more than one event) has contributed to the contamination in the subsurface. The elevated levels of contaminant concentration are shown in Figure 3-17.

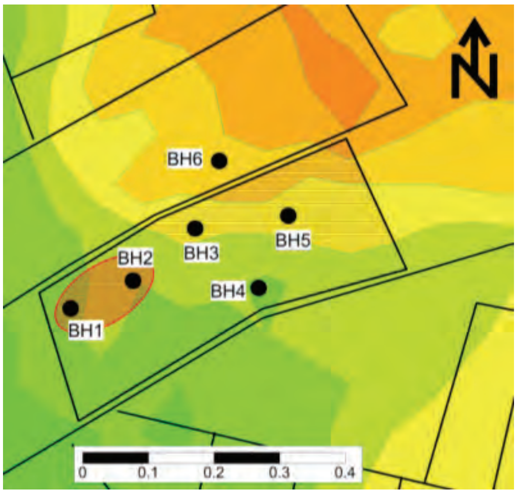


Figure 3-17 Distribution of organic contaminants on site from borehole water sample analysis.

Analysis for BTEX (Total), TPH (C10-C16), TPH (C16-C22), TPH (C22-C30) and TPH (C22-C30), in each instance elevated levels were observed in borehole BH2. Lab results for MTBE at the study site indicated that borehole BH1 had elevated concentrations compared to the other monitoring sites. It is due to this that the organic contaminant plume is shown as a red ellipse in Figure 3-17.

3.2.2 Case Study: Inland Field Site

The second site comprised a number of boreholes located close to a small town in Karoo sediments (Figure 3-18). This area had a high probability of LNAPL contamination due to suspected leakages from underground storage tanks/bunkers. The aim of the fieldwork was first to characterise the fracture network and determine the potential LNAPL contaminant fate and transport pathways.

The aim of the suggested field work at the field site was to initially characterise the fracture network to determine the potential LNAPL contaminant fate and transport pathways. Based on previous work the aquifer could be conceptualised as a dual-porosity system, with transport occurring primarily in fractured sandstone with high transmissivity and the bulk of groundwater being stored in the low transmissivity alluvial-sedimentary deposit matrix.

Characterisation of fracture network plays a pivotal role in understanding the flow process and its related processes. According to Wealthall (Wealthall et al., 2001), LNAPL contaminant fate and transport is controlled significantly by the fracture network, contaminant properties and recharge events.

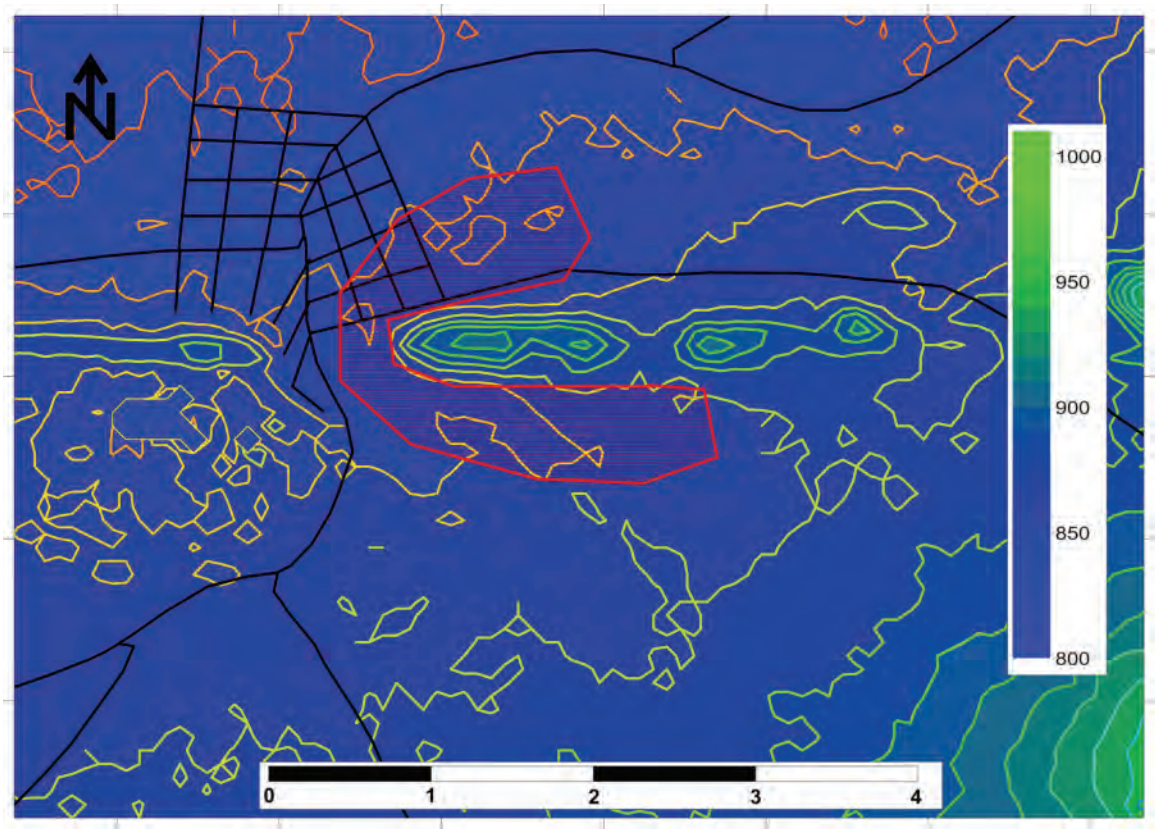


Figure 3-18 A topographic illustration of the inland study site. The study site is indicated on the figure in red and the scale is in kilometers.

The study at the site was systematically conducted with the following main points in mind:

1. Geology and Geohydrology.
2. Percussion drilling and auguring.
3. Pump testing and hydrological evaluation.
4. Geochemical evaluation.

3.2.2.1 Assessment methodology

The first phase of the proposed site assessment was a desktop review of all relevant information. The intention was to gain a better understanding of site history, site contamination profile, geology and geohydrology. After the desktop review, a site walk over was conducted to get a better understanding of site conditions. Some field work, such as measuring product thickness and water levels in existing boreholes, was performed during the site walkover. A hydrocensus was initially suggested but due to access restriction of the surrounding properties, however from previous studies the geological mapping of the area was known. Additional reports were also found but were mostly focused on water supply and bulk hydrogeological properties of the study site.

The study area is characterised by generally flat topography which drains into a north to north west direction. The average elevation of the study area is approximately 840 mamsl. Typical trellis drainage pattern which is mainly attributed to flat topography dominates the study area. Hot wet summers and relatively dry cold winters characterises the region. The area is generally dry, receiving on average about 240 mm/year.

3.2.2.2 Non-invasive investigation

3.2.2.2.1 Geological mapping

The area under investigation falls under the Beaufort group of the main Karoo Supergroup. The Karoo Supergroup mainly consists of sandstone, mudstone, shale and siltstone. Teekloof formation dominated by red mudstone characterises the Adelaide Subgroup in the study area. The sandstones of the southern Karoo basin have extremely low primary porosity and permeability (Woodford and Chaevallier, 2002). In general this impacts groundwater abstraction in that aquifers have low yields.

The Adelaide Subgroup attains a maximum thickness of about 5000 m in the southeast, which decreases rapidly to about 800 m in the center of the Karoo Basin and thereafter more gradually to around 100-200 m in the extreme north. In the southern and central parts of the basin the Adelaide Subgroup consist of alternating bluish-grey, greenish-grey or grayish red – mudstone and grey, very fine to medium grained, lithofeldspathic sandstone. In the northern part of the basin coarse to very coarse sandstone, or even gluestone, are also common in the Normandien formation (Woodford and Chaevallier, 2002).

According to Woodford (Woodford and Chaevallier, 2002), Quaternary deposits are a major characteristic along major rivers in the Karoo basin. Deposits on the bed of braided streams consists mainly of coarse sediments, conglomerates and patches of finer material on their banks while meandering streams deposit mainly fine-grained sand, mudstone and siltstone with little or no conglomerates (Visser, 1989). These deposits mainly constitute of gravels, comprising well-rounded cobbles and boulders, sometimes cemented by calcrete.

Vegter (Vegter, 1992) stated that porosity of Karoo sediments appears higher close to the surface and this has implications for both groundwater yield and contamination flow in the catchment. The high porosity sediments are important as they present potential for high recharge along major rivers of the Karoo basin. High recharge waters have great implications for hydrocarbon biodegradation as they aid to replenish groundwater oxygen which serves as the first electron acceptor during microbial consumption of organic carbon.

The aquifer types in this area are dominated by irregular fracturing. It is the existence of such hydraulically conductive zones that might facilitate and accelerated petroleum hydrocarbon movement between the surface/subsurface and receptors in the environment. In contrast the thickness and associated indurations of the sill intrusions are considerably large and this result in the contact zones near the sill or sheet-like intrusions being thoroughly metamorphosed. Good storage properties or low transmissivity ranges are however sometimes provided by the clayey product of dolerite weathering. The regional hydraulic gradient is directed south to north, with the gradient being high in all localities.

3.2.2.3 Invasive investigation

3.2.2.3.1 Percussion and core drilling

Six new boreholes were drilled in the study area, i.e. BH1-BH6 over a period of two years (Figure 3-19). The main objective in drilling the wells was to gain a better understanding of the underlying geological formations as well as to perform test and measurements on the newly constructed boreholes (Table 3-2). This allowed for aquifer parameters to be investigated and to observe if any hydrocarbon movement would eventually take place in the boreholes. At each site a dual pair was drilled, one percussion and one core borehole in close proximity to one another. This enabled a comparison to be made of the two different sample logs. The two core boreholes were BH4 and BH6 while the two percussion wells were BH3 and BH6, respectively.

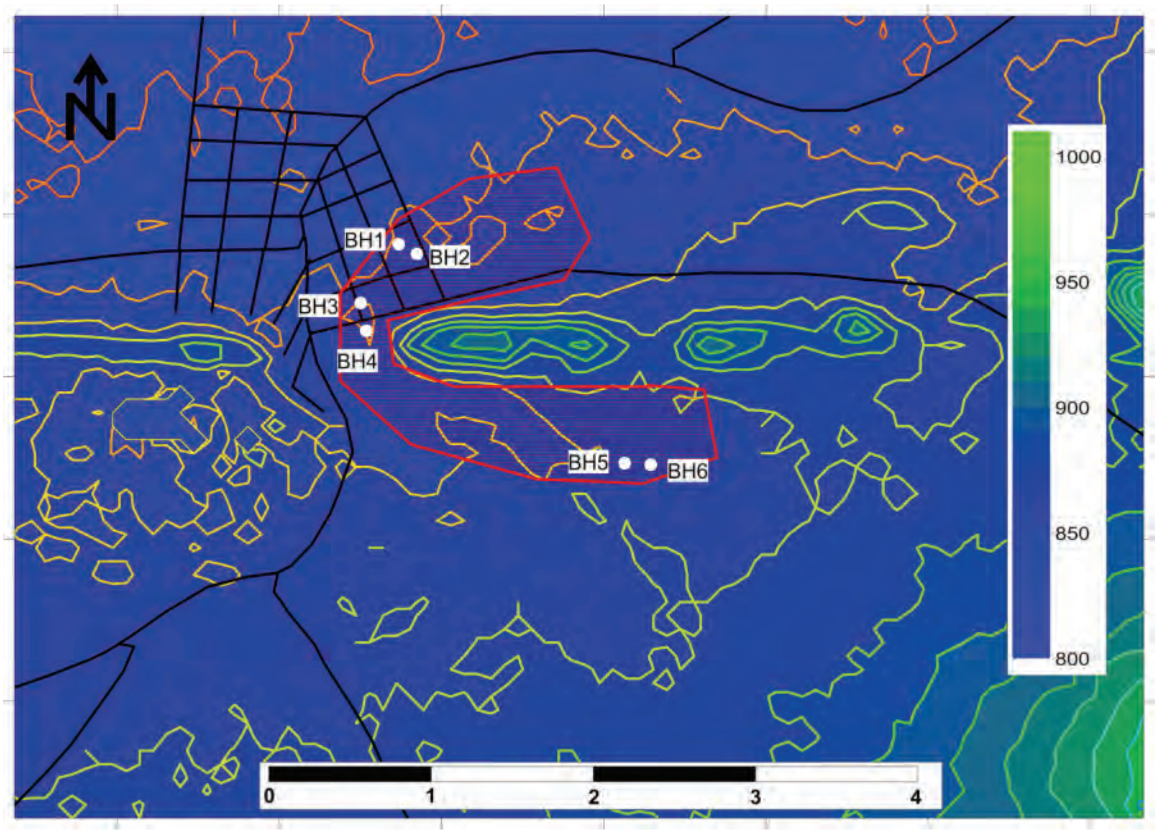


Figure 3-19 Location of drilled boreholes on the study site.

Table 3-2 Borehole depths, water levels and water strikes.

Site name	End of hole (m)	Water level (m)	Water Strike (m)
BH3	45	9.72	16-17, 24-26, 29-30, 40-42
BH4	45.59	10.9	
BH5	45	15.20	25-26
BH6	46.60	11.82	

The core drilling results also reveals the presents of a dolerite intrusion at depths 5.15-5.99 m and 31.40-34.40 m in BH4. The contact between the intrusion and other geological layers has great potential for generating fracture zones during the magma cooling. It is the presence of fractured zones which has great implications for groundwater flow and contamination given the associated high hydraulic conductivities. Figure 3-20 shows core picture of possible fractured positions between 13-8.5 m depth.

Figure 3-20 Fractured zone (13-18.5 m) in borehole BH4

The strike of the fractures shown is not clear and this can be attributed to disorientation of cores during drilling and core placement. It is however possible identify the fracture strike direction, dip and other features through the use of additional fracture characterisation tools such as borehole camera and acoustic viewing, thus the application of such tools is recommended as part of this investigation. The core borehole logs are shown in Figure 3-21.

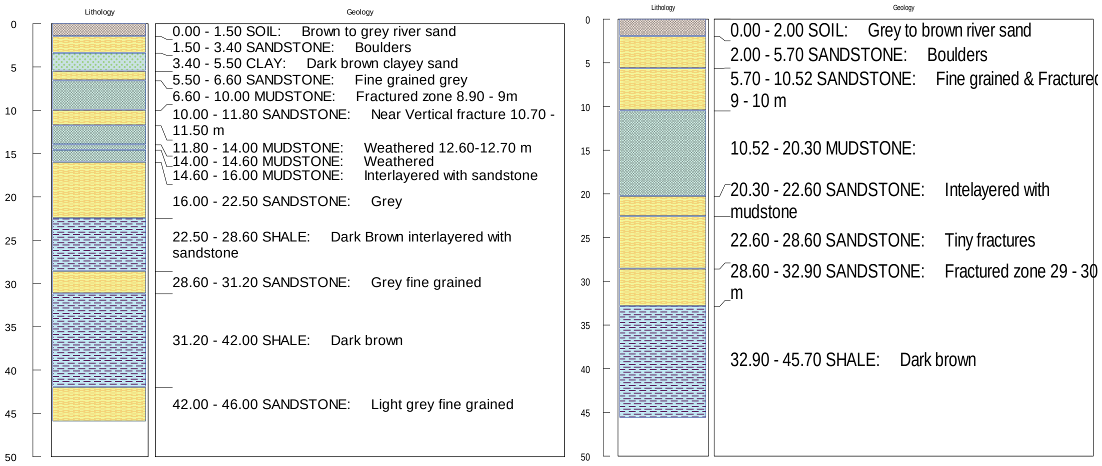


Figure 3-21 Borehole log of both cores from BH4 and BH6, respectively.

One of the major challenges experienced during the drilling exercise was a series of borehole wall collapses, which resulted in the drill being stuck on a number of occasions. The wall collapse can be mainly attributed to the existence of loose boulders of river depositional material. Considering the valuable information obtained from this exercise, the need for more core drilled holes on the site cannot be overemphasized.

The drilling of the percussion boreholes allowed for larger diameter boreholes and also the possibility of performing pump tests to evaluate aquifer parameters.

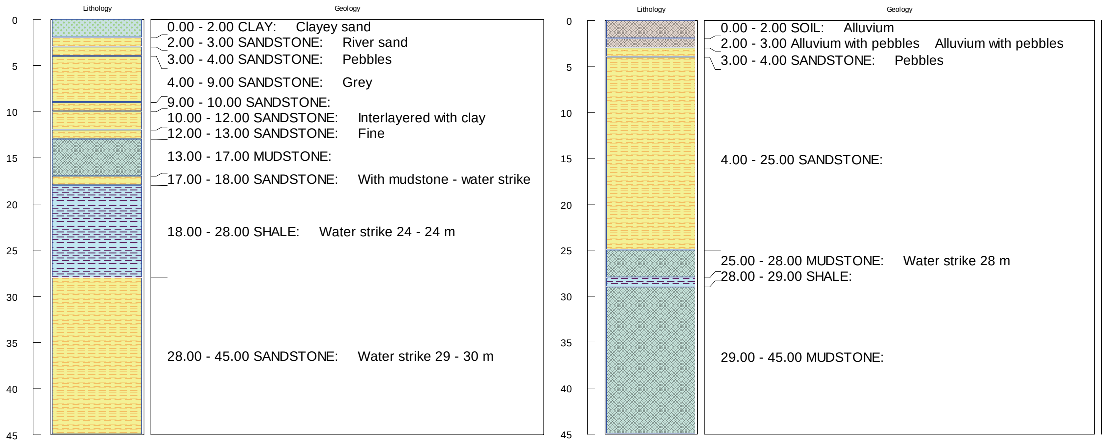


Figure 3-22 Borehole logs of both percussion boreholes from BH3 and BH5, respectively.

In each instances a significant difference can be observed in the lithology. In the instance of the core boreholes much more detail could be observed, however minimal correlation could be detected between core and percussion boreholes.

3.2.2.3.2 Pump tests and measured water levels

A number of constrains were faced during the aquifer testing phase and it is noteworthy to mention this before detailed description of the test. Three of the four tests were conducted on existing private boreholes without information of the drilling details such as: water strikes, geological logs, borehole depth and date of drilling. The missing geohydrological information is important for preparation of an aquifer test.

Bearing in mind that the area is characterised as an arid to semi-arid environment, water abstraction in the area is for domestic use. The community relies heavily on groundwater with most of the houses having private boreholes. Such a large number of boreholes in use equate to a pumping well field. This has the added drawback that during aquifer testing, it is difficult to distinguish between the effects of the pump test and the surrounding pumping well field.

Slug tests are usually single-well tests that give estimates of hydraulic conductivity near the bore or screen of the test well but studies by (Belitz and Weston, 1999) revealed that water levels can be monitored in observation well located in porous media and has the potential to improve aquifer parameter estimation. In further studies (Gonthier and Mayer, 2003) presents an example on the usefulness of monitoring water levels in nearby wells during slug tests performed in fractured crystalline rock. The study has great implications in the current investigation as area is located in a typical Karoo fractured aquifer which usually host fractured zone as groundwater preferential pathway.

Table 3-3 Slug test results for selected boreholes in the study area.

Name	Water Level (mbgl)	d (m)	b (m)	r_w (m)	T (m^2/d)	K (m/d)
BH1	11.89	8	30.00	0.08	3.14	0.105
BH2	10.89	3	34.11	0.08	0.03	0.009
BH8	11.82	8	33.18	0.06	0.01	0.001
BH3	14.43	15	30.47	0.08	0.01	0.001
BH5	11.89	8	30.00	0.08	3.14	0.105

The estimated T for BH1 is high in comparison to the remainder of the boreholes. This is mainly attributed to the fact that the borehole has been a production boreholes for the past 8 years, thus the borehole should be fully developed with very little skin effects. As for BH2-BH8 these were newly drilled or still to be developed boreholes, the low T results are most likely due to skin effects in the vicinity of the borehole. Slug tests were also performed on three other boreholes but the interference from external effects rendered the results useless.

Aquifer pump testing is essential for providing information on aquifer properties, which has great implications for groundwater flow, mass transport and fate of contaminants. With regard to mass transport and fate of contaminants, aquifer pump test can yield important information such as showing the existence of hydraulic connectivity between contaminant sources and receptors as is the case in the current study. As per minimum requirement of aquifer parameter estimation (Van Tonder et al., 2001) an 8.4 hours duration constant rate pump test has been performed for the study area. BH3 was used as the pumping well at an abstraction rate of 0.78 l/s, with BH1, BH2 and BH4 serving as observation boreholes. All boreholes were allowed to fully recover during a 12 hour monitored recovery period. Transducers were installed in each well about 3 hours before the test to monitor the water levels prior, during and after stopping of pump (recovery). Flow Characteristic (FC) method (Verwey et al., 1995) was used to identify flow regimes and estimate aquifer parameters. Typical transmissivity values for the boreholes located in the study site ranged from 0.2 to 4 m^2/d.

The depth to the groundwater level varied from 10 to 14 meters below surface level, and is a good indication of a shallow aquifer system. A good correlation exists (97 %) between topography and water levels as indicated by Figure 3-23. This implies that the Bayesian method of interpolation can be used to construct a reliable water level contour map of the study area.

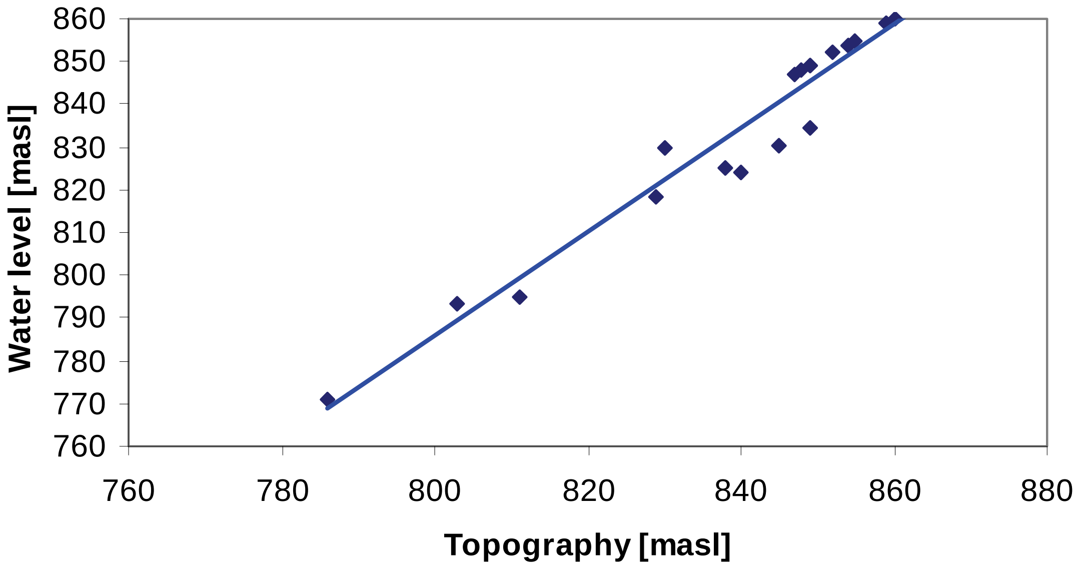


Figure 3-23 A plot of surface elevation versus water levels in the study area. A good correlation (97 %) can be observed for the data.

The anticipated direction of movement of groundwater in this area under natural conditions is shown in Figure 3-24. It is clear that groundwater moves towards the river which is located to the north-west of the study area.

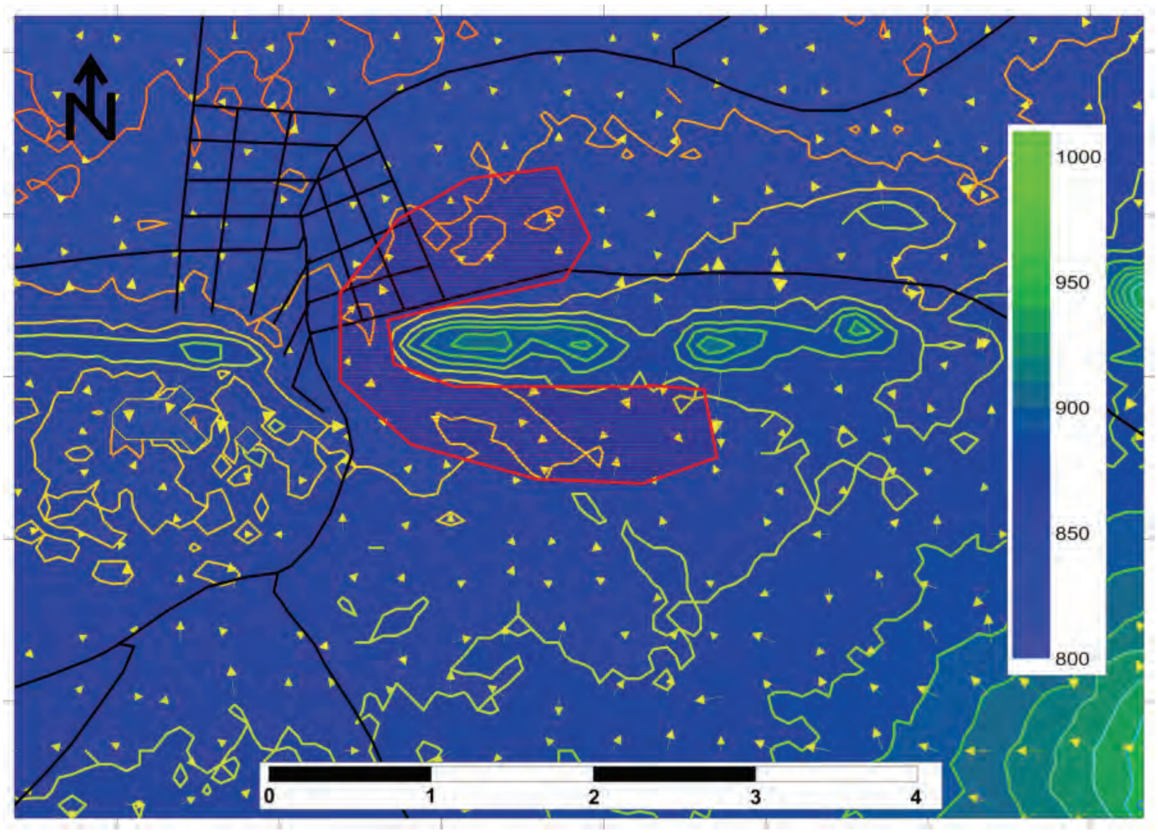


Figure 3-24 Vector diagram showing steepest gradients in the inland study area.

3.2.2.3.3 Water sampling

The goal of groundwater sampling is to collect samples which are 'representative' of *in situ* groundwater conditions and to minimise changes in groundwater chemistry during sample collection and handling. Experience has shown that groundwater sample collection and handling procedures may be a source of variability in water-quality concentrations, due to differences in sampling personnel, sampling procedures and equipment (EPA, 1995).

3.2.2.3.3.1 Inorganic analysis

The ion balance error for the analyses varied from -4.64 to +4.68 % and this falls within the accepted range of -5 to +5 %. The water chemistry appears to evolve along two lines; one from a calcium/magnesium rich groundwater towards a sodium rich type and the other from carbonate/bicarbonate to SO_4. However, as shown in the piper diagram, Figure 3-25, the evolving from carbonate/bicarbonate system to SO_4 is more pronounced.

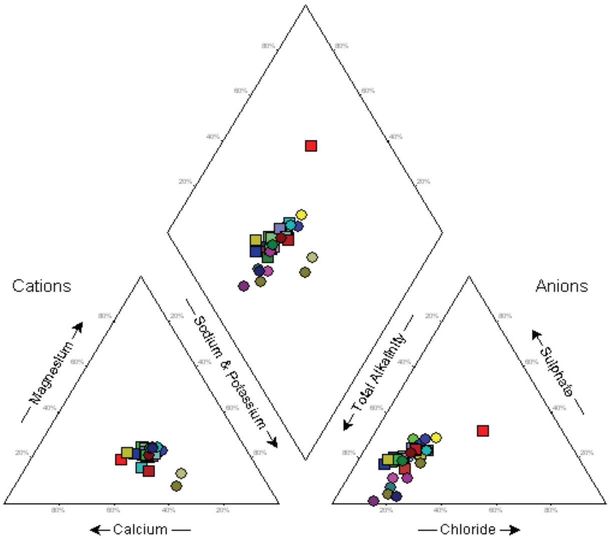


Figure 3-25 Piper diagram illustrating sampled borehole water quality.

The groundwater can be classified as (Ca+Mg)-(Na+K)-(CO_3+HCO_3). The presents of Ca and HCO_3 recharge waters in the near surface environment results most likely from two closely related processes; carbonate dissolution and plagioclase weathering. The study area is underlined by dolerite intrusions which have plagioclase minerals as one of its main constituents. Plagioclase weathering produces calcite that precipitates mostly in the fractures and cavities and may be the source of Ca+HCO_3 waters for a new generation of meteoric surface water (Stober and Butcher, 1998). Na concentrations in the range of 44.8-212 mg/l can be mainly attributed to cation exchange of calcium and magnesium ions in aqueous solution with sodium ions on clay laminating the shale geological formation in the study area.

Total dissolved solids ranged from 195.84-1090.84 mg/l, and this concentration according to South African Water quality guidelines (1996) does not have any likely health effects. The alkalinity dominance is also evident by the slightly high pH range varying from 6.8-8.1.

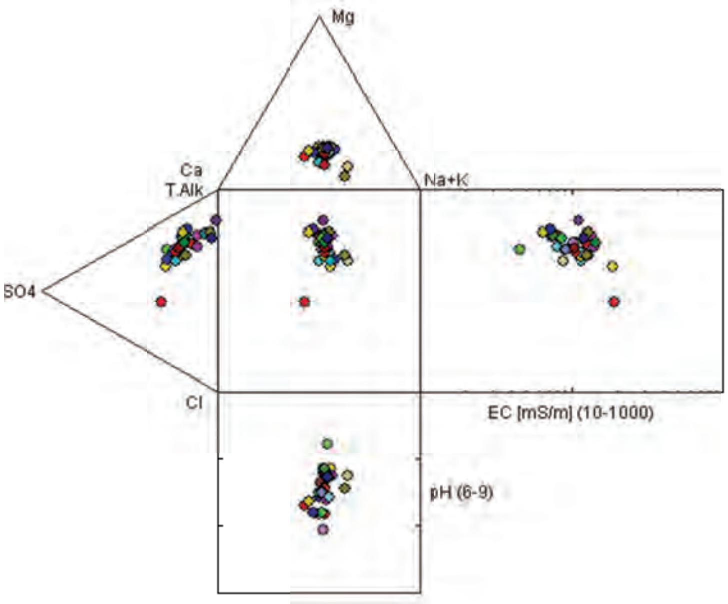


Figure 3-26 Durov diagram illustrating sampled borehole water quality.

SO_4 ranges from 5.84-325 mg/l with the highest concentration being also recorded in the municipal boreholes. The presence of SO_4 ions, though in low concentration, is most likely due to oxidation of sulphide minerals contained shale formation underlying the study area. The relatively low SO_4 concentrations can be attributed to microbial hydrocarbon degradation which utilizes electron acceptors and SO_4 is no exception. Silicon concentration ranges from 2.74-20.2 mg/l and its presents is explained by the quarts in the sandstone formation underlying the study area. Water passing through or over the earth dissolves silica from sands, rocks and minerals as one of the impurities it collects.

Iron total (as Fe) and manganese are the only trace metals present of note in the study area. Fe is relatively low in all samples except for BH1 and BH6 in which 1.2 mg/l and 13.9 mg/l were measured respectively exceeding the SANS (Standards, 2006) of 2 mg/l. Compared with the drinking water guidelines South Africa, Mn-concentrations exceeded the guidelines of 1 mg/l in 9 wells (64 % of samples). The occurrence of elevated concentrations of Fe and Mn can be attributed to industrial effluent, sewage and landfill leachate. However, in this situation elevated Fe and Mn concentrations can be attributed to increased levels of electron acceptors reaction products thus providing secondary evidence of hydrocarbon biodegradation.

3.2.2.3.3.2 Organic analysis

Organic chemistry analysis gives an indication of the hydrocarbon contamination constituents on the site. The research focus was on 16 boreholes located within the field site are and samples were sent for analysis to a laboratory in the Netherlands.

The more mobile fractions of the contaminants (BTEX and MTBE) are the most widespread of all the constituents. However, the concentrations are relatively low compared to the TPH content. Borehole BH2 had the highest values, which was to be expected since free phase was detected in the borehole. There are fewer of the heavier fractions of TPH in the groundwater than in the soils, due to the presence of clays and the depth of the water table. From the organic results it is evident that more than one type of fuel/product (from more than one event) has contributed to the contamination in the subsurface. The elevated levels of contaminant concentration are shown in Figure 3-17 (yellow ellipses).

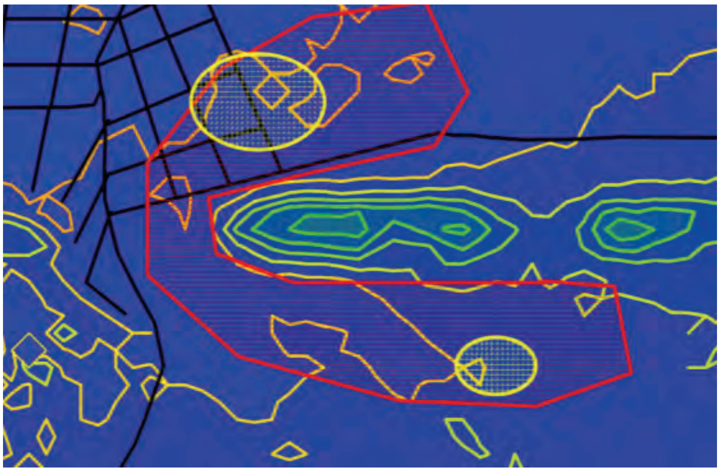


Figure 3-27 Distribution of organic contaminants (yellow ellipses) on site from borehole water sample analysis.

Analysis for BTEX (Total), TPH (C10-C16), TPH (C16-C22), TPH (C22-C30) and TPH (C22-C30), in each instance were conducted, elevated levels were observed in borehole BH2 and BH6. Lab results for MTBE at the study site indicated that borehole BH2 and BH6 had elevated concentrations compared to the other monitoring sites. It is due to this that the organic contaminant plume is shown as yellow ellipses in Figure 3-17.

4 CONCEPTUAL MODEL

The construction of a conceptual model for a field site is one of the most important and fundamental precepts in LNAPL site remediation. The inclusion of various principles in this model phase will determine if an effective remediation option can be constructed and applied to a field site. In short the following key concepts should be taken into account, see Figure 4-1.

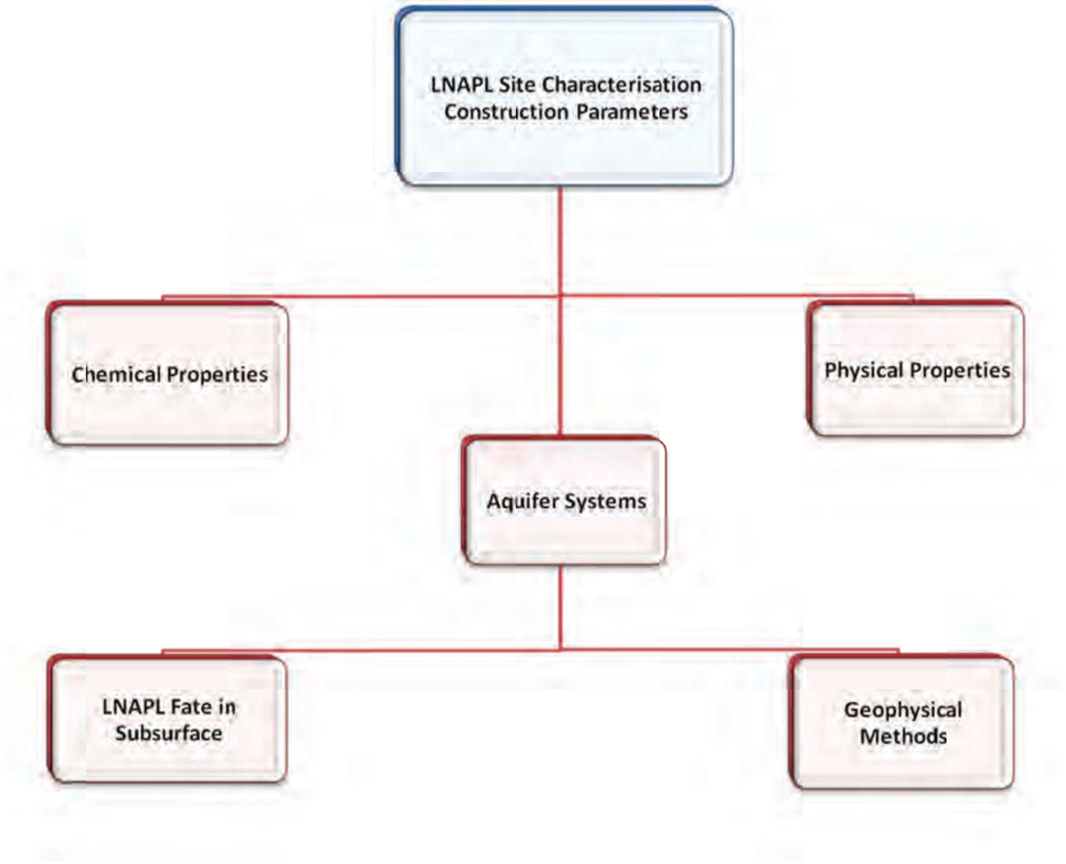


Figure 4-1 A general review of methods and parameters in the construction of a conceptual model for a site.

In order to determine these parameters a step-wise investigation of each site should be conducted, as guided by the geology, hydrology and chemical properties of the LNAPL being explored. This aspect of the study has been covered in the previous section.

Model conceptualization is the process in which data describing field conditions are assembled in a systematic methodology to describe groundwater flow and contaminant transport processes at a site.

In the construction of a conceptual model the following general key points should be kept in mind:

1. The conceptual model is an idealisation of a natural system.
2. Relevant geohydrological units must be defined in the model.
3. Boundary and initial conditions should be specified for the area.
4. The controlling processes in each system have to be identified, i.e. flow, capillarity, gravity, transport and chemical reactions which include biochemical systems.

In the following sections case studies of the field sites will be presented to illustrate the application of the previously described methodology to construct a conceptual model for an aquifer contaminated by LNAPL.

4.1 Case Studies of Selected Field Sites

Each of the selected field sites in this section was chosen to illustrate the significant differences in the study of coastal and inland regions have on the fate of LNAPL contaminated sites. Firstly, the inland area site was selected since it is underlain by Karoo formations which represent a large section of South Africa’s aquifer systems. Secondly, a coastal region site was selected to indicate the influence of water table aquifers on the transport and remediation pathways of an LNAPL contaminant.

4.1.1 Inland Study Site

In order to construct a conceptual model for the site, use was made of the following information reported previously in Chapter 3; drilling logs, geophysics, borehole video, core drilling, groundwater levels and digital terrain elevations, pumping tests and tracer tests. The main location of the LNAPL site investigation area is indicated in Figure 4-2.

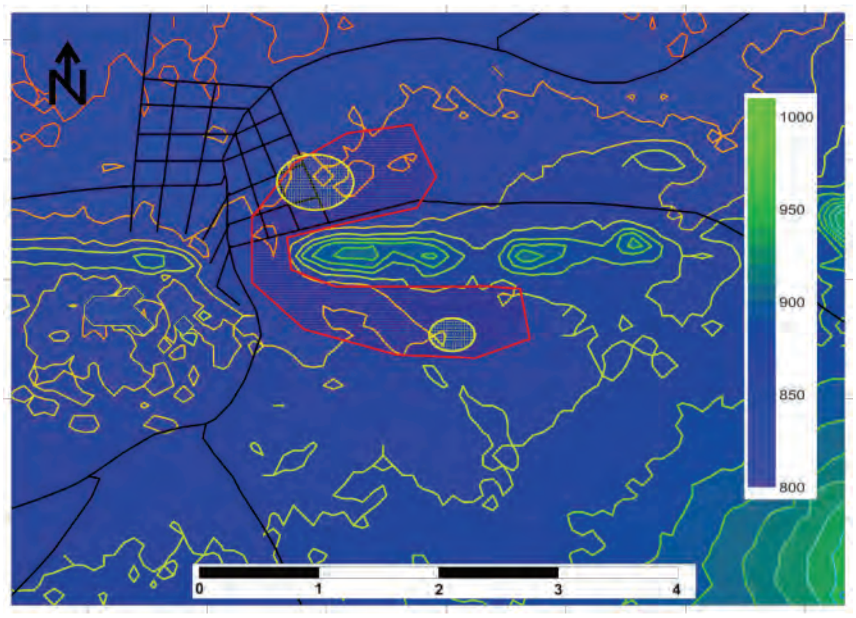


Figure 4-2 Investigation area of the inland site. Yellow ellipses indicate the main sources of contaminants.

4.1.1.1 Geology

The geology of the area is typical of the Karoo Formations of South Africa. Water strikes of the boreholes drilled are between 16 and 42 meters below surface and are correlated with both horizontal and vertical fractures in the sandstone, mudstone and shale. Shale/dolerite contacts are also an important feature for good water strikes in the area.

4.1.1.1.1 Conceptually the main important structures below the LNAPL sites are:

1. Riverbed pebbles in the unsaturated zone with a very high porosity value and vertical hydraulic conductivity (large K-values).
2. Vertical fractures in LNAPL transport.
3. Horizontal fractures for the areal extent of LNAPL.
4. Dolerite intrusions.

4.1.1.2 Pumping tests

In order to determine the aquifer parameters of the inland study site, pumping and tracer tests were conducted in the area. Typical transmissivity values for boreholes drilled during the field investigation phase ranged from 0.2 to 4 m^2/d.

4.1.1.3 Groundwater levels

The depth to the groundwater levels varies from 10 to 14 meters below surface level, and is a good indication of a shallow aquifer system. A very good correlation of 97 % exists between topography and water levels. This implies that the Bayesian method of interpolation can be used to construct a reliable water level contour map of the study area in the inland region.

To assist in the construction of the conceptual model, a smaller area was selected from the total inland study region. An enlarged section of this area is shown in Figure 4-3. The water level contours are depicted in Figure 4-3 as a colour map image. The anticipated direction of movement of groundwater in this area under natural conditions is shown in Figure 4-3. It is clear that groundwater moves towards the river systems.

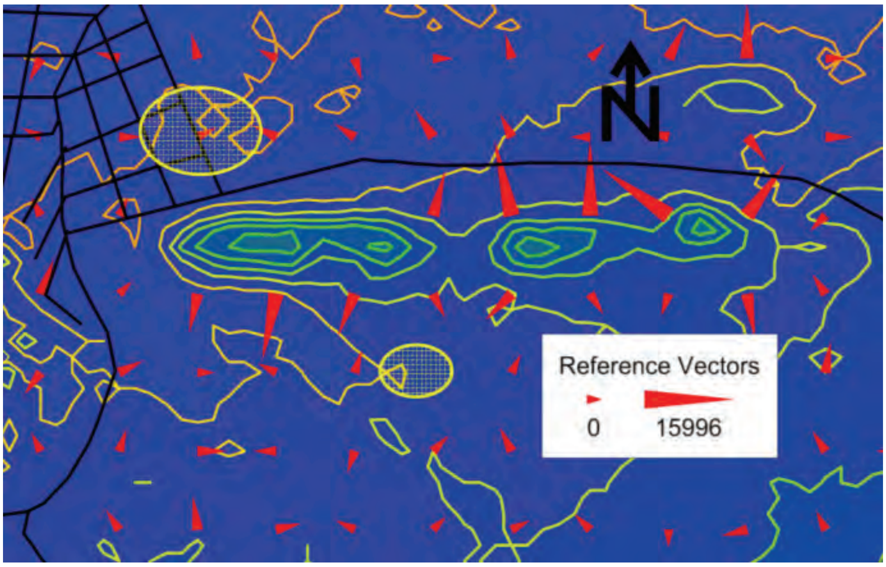


Figure 4-3 A close-up of the smaller selection area in inland study zone for Bayesian interpolation of water levels. Flow direction is illustrated as red arrow heads.

4.1.1.4 Groundwater velocities

It is expected that the kinematic porosity of the formations at the inland area could be between 0.03-0.07, as obtained from a large number of tracer tests conducted by the IGS in the Karoo Formations. As a result of the possible kinematic porosity values, a seepage velocity of the area can be estimated to be in the order of 1 to 3 meters per annum under normal conditions. These values were calculated using a flow zone thickness of 2 m and a gradient of 0.005.

Using a forced gradient tracer tests between two boreholes at the test site, which are ca. 5 m apart, a flow velocity of 70 meters per day was observed. This is significantly higher than the natural seepage velocity of the area and can only be attributed to the presence of fractures between the two boreholes.

4.1.1.5 LNAPL movement at inland area

At the inland study area the aquifer can be regarded as a semi-confined aquifer and/or a water table aquifer, see Figure 4-4.

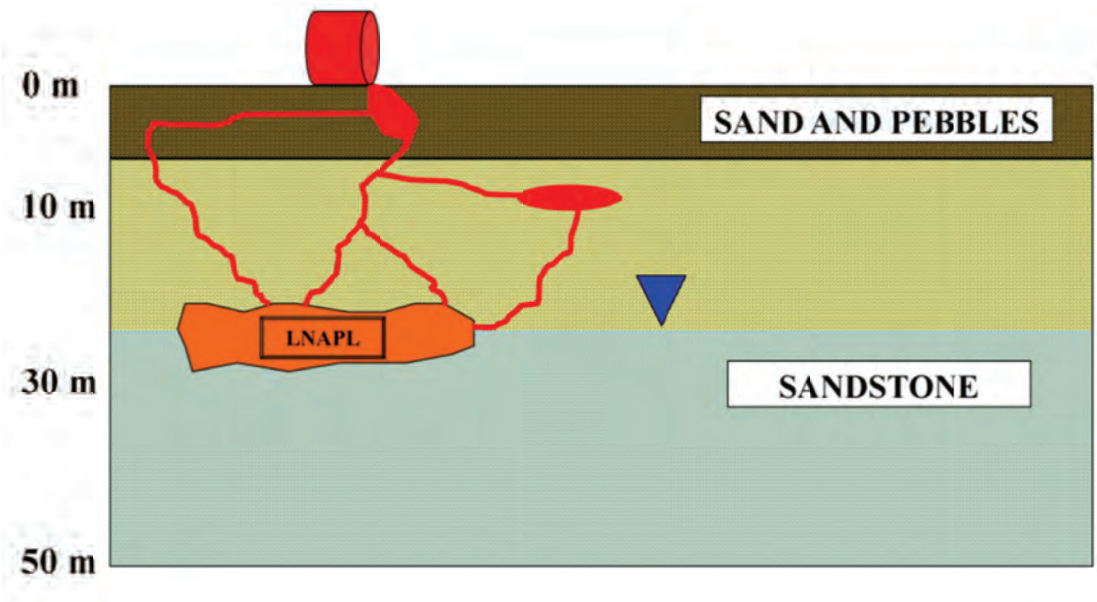


Figure 4-4 Conceptual representation of LNAPL intrusion at the inland site. Preferred pathways and infiltration along horizontal and vertical fracture zones are apparent. Approximate depth and composition of each layer is also included with the water level.

The movement of the LNAPL would be influenced by the dissolved phase in the groundwater and the free-phase lying on top of the water level. The dissolved phase will naturally move in the direction of groundwater flow and with the same velocity as that of the groundwater. In contrast the free-phase, which is floating on the water, will also move in the direction of the groundwater flow but the velocity will be a function of the thickness and gradient of the free-phase and the geological structure present in the aquifer. A further complication is the equilibrium between the dissolved and free-phase in the system. If enough dissolved phase is present in an area without free-phase, Le Chateliers principle might cause the dissolved phase to form a free-phase layer (equilibrium between phases). This will effectively spread the LNAPL over a larger area through various mechanisms which can include perched LNAPL sources.

4.1.1.5.1 Influence of abstraction on the movement of LNAPL

The inland aquifer area is a typical fractured rock Karoo aquifer. There are a number of boreholes at the LNAPL site that are constantly being used for irrigation purposes and domestic use. This variable pumping of the aquifer considerably complicates matters regarding the movement of the LNAPL plumes in the area, since there are always water table fluctuations.

The following are the most important parameters in the determination of LNAPL movement:

1. Position of the water strikes in each abstraction borehole.
2. Abstraction rate of the borehole and duration of pumping.
3. Drawdown in water level at the borehole.

For example, two abstraction boreholes that are situated close to each other but have different yields will have a different influence on the LNAPL movement. If the water level drops [in the weaker borehole] below the water strike, the LNAPL will enter the fracture while the neighbour’s borehole will not experience the same level of LNAPL intrusion. Thus over abstraction in one area could result in massive LNAPL intrusions while a few meters away none is observed.

4.1.2 Coastal Study Site

In order to construct a conceptual model for the site, use was made of the following information reported previously in Chapter 3; drilling logs, geophysics, borehole video, core drilling, groundwater levels and digital terrain elevations, pumping tests and tracer tests. The main location of the LNAPL site investigation area is indicated in Figure 4-5.

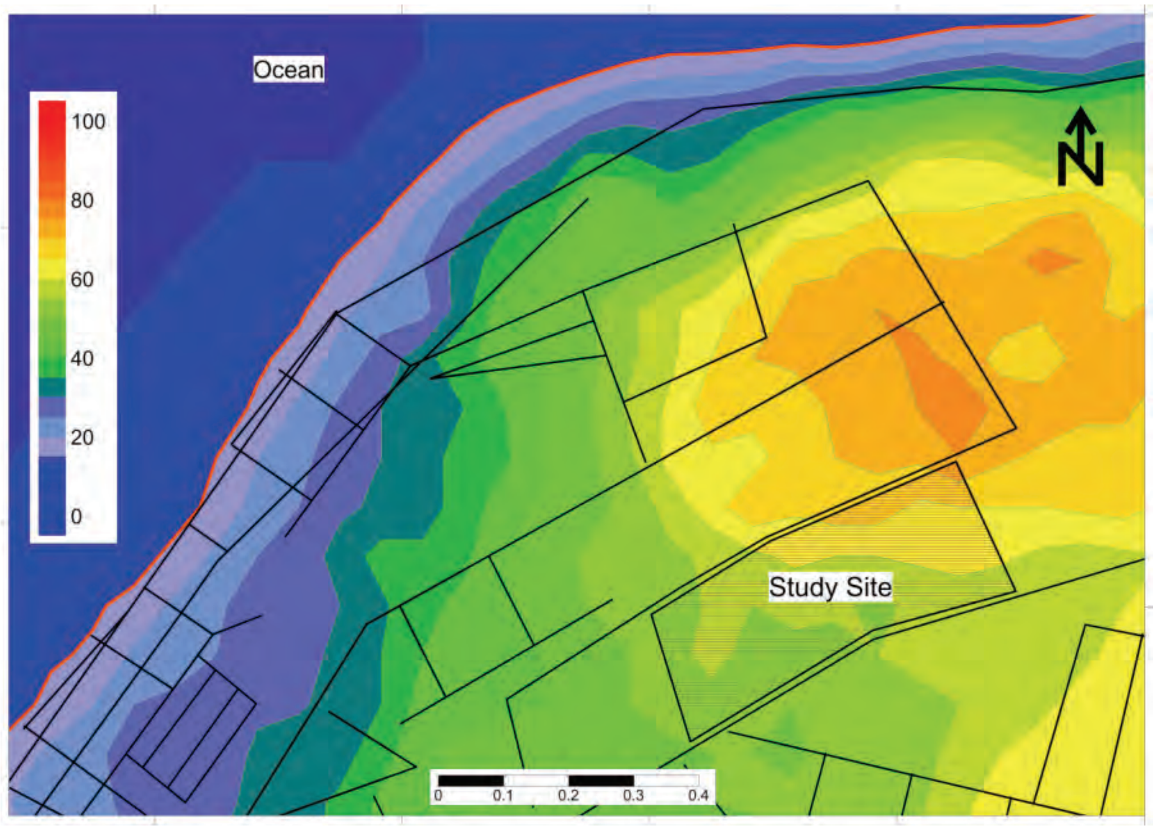


Figure 4-5 A topographic illustration of the coastal study site. The study site is indicated on the figure and the scale is in kilometers.

In order to construct a conceptual for the site, use was made of the following information; drilling logs, geophysics, groundwater levels and digital terrain elevations and pumping tests.

4.1.2.1 Geology

The coastal site is underlain by a 10 meter layer of unconsolidated clay and sand. The unconsolidated layer is in turn underlain by a dolerite sill. The area has a typical geology associated with the Beaufort group which forms part of the Karoo Supergroup.

4.1.2.2 Pumping tests

Pumping tests were conducted on six boreholes that were drilled during the month of October 2008. Transmissivity values for these boreholes ranged from 0.2 to 0.5 m^2/d.

4.1.2.3 Groundwater levels

The depth to the groundwater levels varies from 0.6 to 3 meters below surface level, and is a good indication of a shallow unconfined aquifer system. A very good correlation of 98 % exists between topography and water levels. This implies that the Bayesian method of interpolation can be used to construct a reliable water level contour map of the study area.

The water level contours are depicted in Figure 4-6 as a colour map image with the test site outlined in red. The anticipated direction of movement of groundwater in this area under natural conditions is shown in Figure 4-6. It is clear that groundwater moves towards the sea.

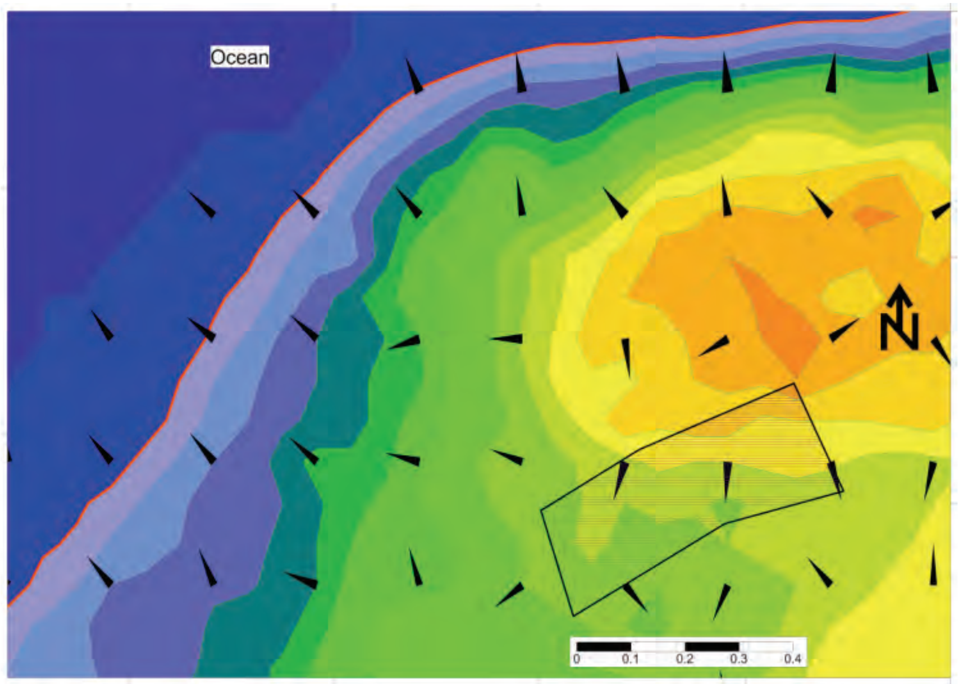


Figure 4-6 Coastal area showing the area for Bayesian interpolation of water levels. Flow direction is illustrated as black arrow heads.

4.1.2.4 Groundwater velocities

Pumping tests conducted on the site yielded an average transmissivity value of 0.4 m^2/d. If a thickness of 10 meters is used, the hydraulic conductivity (K) for the unconsolidated material is in the order of 0.04 m/d. In order to determine the groundwater velocity a water level gradient of 0.005 and a kinematic porosity of 0.15 was used to give an average groundwater velocity of 0.5 m/a.

4.1.2.5 LNAPL movement at the coastal site

At the coastal study area the aquifer can be regarded as a water table aquifer, which rests on top of a dolerite sill. The dolerite sill can be described as a fractured aquifer with a weathered zone, see Figure 4-7.

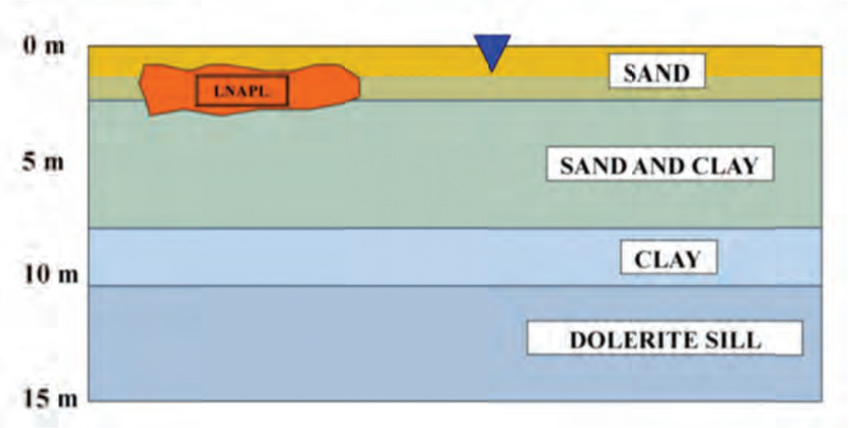


Figure 4-7 Conceptual representation of LNAPL intrusion at the test site. Approximate depth and composition of each layer is also included with the water level.

The movement of LNAPL would be influenced by:

1. The dissolved phase in the groundwater.
2. The free-phase lying on top of the water level.

The dissolved phase will naturally move in the direction of groundwater flow and with the same velocity as that of the groundwater. In contrast the free-phase, which is floating on the water, will also move in the direction of the groundwater flow but the velocity will be a function of the thickness and gradient of the free-phase and the geological structure present in the aquifer.

The movement of the LNAPL at the study site would be significantly influenced by the presence of the clay layer, which would act as an aquitard. Since the coastal site is a water table aquifer, an appreciable volume of the LNAPL would be confined to the surface layer of the aquifer. Thus, the combination of the presence of a clay layer (most likely swelling clay) and shallow water table aquifer significantly reduces the complexity of the system and LNAPL movement can be investigated in the surface layers of the area.

A further complication is the equilibrium between the dissolved and free-phase in the system. If enough dissolved phase is present in an area without free-phase, the dissolved phase might reform as a free-phase layer (equilibrium between phases). This will effectively spread the LNAPL over a larger area through various mechanisms which can include perched LNAPL sources.

4.2 Conclusion

In this section the methodology for the construction of a conceptual model for field sites were proposed. Key elements in the construction procedure were highlighted and compared to previously reported methods. Two field sites were discussed which included a coastal area aquifer system as well as a typical Karoo type aquifer. The methodology for the construction of the conceptual model indicated in the preliminary section of the report was used to construct a clear conceptual model of each site.

5 RISKS, COSTS AND METHODS

5.1 Introduction

The government of South Africa is in the process of drafting the National Framework for the Management of Contaminated Land that provides norms and standards to guide remediation activities. This will be based on a tiered approach that focuses on reducing the risk associated with contamination (DEA, 2010). The risk that contamination poses is quantified by reviewing the source of contamination, the pathways by which such contamination can be released to environmental media and the receptors that can be adversely affected by contamination. This process is also referred to as Risk-Based Corrective Action, which is detailed in an ASTM International method (Materials, 2004).

In essence the methodology determines that when all three elements are present, there is a high potential risk that needs to be addressed. This would mean that there is a source of contamination that can impact on receptors through one or more pathways. One example of such a situation in the case of LNAPL would be where an underground storage tank at a filling station leaks product into the subsurface. This leaked product becomes a source of contamination that might migrate with the groundwater to nearby residences where people are using groundwater to irrigate their gardens. In such a case a high risk situation would exist and remediation would be required. The reader is referred to the framework for more detail on how the risk assessment works. In the case where an unacceptable risk exists, remediation is required. The exposure scenario is not specifically addressed in this document and the reader is referred to documents pertaining to this aspect.

Remediation can focus on any of the three elements of the risk model. In order to reduce the risk to receptors the following actions can be taken, see Table 5-1. The application of risk reduction can have significant impacts on the efficacy of remediation and careful consideration should be given to the model applied.

Table 5-1 Risk model actions and illustrative examples.

Action	Example
Destroy or remove the source zone	Excavation is an example of removing the source zone.
Remove or intercept the pathway	Soil vapour extraction (SVE) is an example of intercepting contaminated air before it can impact on a receptor
Remove or change the way receptors are exposed	An example is providing residents with impacted boreholes with an alternative source of water
A combination of the above	Often contamination is found in complex situations where a combination of technologies is required.

Subsequently, the application of a specific risk model should be associated with a remedial method that is appropriate. In Table 5-2 a list of possible methods are reported with a general description, furthermore the application of the specific method can be combined to enhance or expedite the removal of the risk from the environment.

Table 5-2 Remedial method, description and combinatorial application.

Remedial method	*How it works*	*Discussion*	*Often combined with*
Pump & treat	Simple systems would have one pump that is used to remove water from the aquifer and then the effluent is treated before disposal. Thus Pump and Treat. More sophisticated systems would have several pumps.	This method is frequently used in the industry to contain contaminant plumes in fractured aquifers. These kind of projects tend to be long, since the method is not very efficient in reducing the contaminant mass (Van der Linde and Van Biljon, 2000). In fact a common misconception is that the method is used for remediation, while the main aim with P&T should always be containment. It is aimed specifically at preventing contaminants to spread in fractured aquifers. It is not very good at preventing an impact through the pathway of air, except if it can prevent a plume from spreading into an area where the vapour pathway might be relevant. If the vapour pathway is already relevant where the plume is situated, P&T will not address the vapour intrusion pathway. Generally the small gradient formed towards the hole by pumping is not sufficient to facilitate significant recovery of free phase product (NAPL).	This method of addressing the risk that contamination poses
Excavation	Contaminated material	Removal of contaminated soil is often demanded by affected	Remedial technologies that

Remedial method	*How it works*	*Discussion*	*Often combined with*
	is removed and treated off-site, ex-situ or dumped at hazardous waste facility. Sometimes only a portion of the affected material can be removed and then this process needs to take place along with other remedial technologies or at least monitoring.	parties or authorities as it seems to be an obvious answer to address contamination. A positive aspect to the responsible party is that the timeframe of the project can be determined with little uncertainty. In the case of LNAPLs the excavation of soil containing residual product can greatly reduce even groundwater contamination issues. It is not practical to excavate extended plumes of free product or dissolved phase, because of the overlying clean material. Sometimes it might form part of a remedial strategy where excavation removes as much of the affected material as possible, while in-situ methods might have to be used for those portions underneath buildings, for example. For the costing it has been assumed that excavation would take place followed by monitoring once or twice. It has also been assumed that the treatment/disposal of soil takes place locally. Transport costs form a considerable part of such a project, because of the large volumes of soil involved. Generally excavation is not very effective in fracture rock aquifers, due to the difficulty in excavating rock and the large area over which such plumes migrate along fractures.	would remove or address the pathway are often favoured above source destruction, otherwise the whole area would have been excavated in the first place. An example is a forecourt of a filling station where the soil underneath the forecourt is excavated, but the portion of the plume that is situated underneath the building, is treated by other means.

Remedial method	*How it works*	*Discussion*	*Often combined with*
VER (Vacuum Enhanced Recovery)	A mobile unit with either a blower or a liquid ring pump is used to extract liquids and vapour from recovery holes on an intermittent basis.	Because the application is intermittent this method is not suitable to contain plumes. It works best on small areas or pockets of stable free phase (Van Biljon and Van der Linde, 2000). Even in fractured aquifers it can deliver fair results, provided the extent of the problem is limited to a few meters radius around the recovery hole and the hole intersects the most affected fractures. Recovery of NAPL is also much enhanced due to the negative pressure gradient towards the hole. The major advantage from a management point of view is that the method does not need permanent installation of equipment other than recovery holes. One concern with this method is off-gas treatment when significant NAPL is available for capture.	Mostly used in conjunction with monitoring or MNA (monitored natural attenuation) to determine effectiveness.
SVE (Soil Vapour Extraction)	A series of extraction holes is connected via a manifold to a blower or sets of blowers. The holes are installed in	Because this method only focuses on the vadose zone, it is not really suitable for treating a dissolved phase plume. Free phase NAPL cannot be treated with SVE (USEPA, 1994a). It is often used to intercept vapours that might impact on	Often used with Air Sparging to increase evaporation of contamination. MNA or general groundwater monitoring might also be used to determine

Remedial method	*How it works*	*Discussion*	*Often combined with*
	the unsaturated zone only. The extraction of the soil gas leads to the removal of volatile and the slow diffusion of oxygen into the subsurface that aids in biodegradation.	receptors. Due to its limited application in fractured rock settings, it is not frequently used in South Africa. Provided it is used in the correct setting, it has the ability to reduce the source zone, but it cannot contain plume migration or address the groundwater pathway	efficiency.
Bioslurping	This is basically a VER system that is permanently installed. Managing the disposal of captured liquid becomes problematic, since remedial systems usually have to operate at remote locations.	The major advantage of this system is that it operates permanently or on a short cycle, which enables it to contain plumes. This is in contrast with the VER where the intermittent nature of the application does not allow containment. The negative pressure enhances the recovery of NAPL as opposed to pumping only (USEPA, 1995). The major practical obstacle to overcome with this method is to have efficient treatment of the waste streams.	Not frequently used with other active methods. MNA or general groundwater monitoring might also be used to determine efficiency.
MNA (Monitored Natural Attenuation)	Conducting groundwater monitoring for the	This method can only be applied to stable plumes and usually where there is no NAPL. All plumes are finite in length and depending on the risk situation it might be	Could be used in conjunction with any of the other remedial methods. Often would take the

Remedial method	*How it works*	*Discussion*	*Often combined with*
	presence of contaminants as well as the secondary lines of evidence of biodegradation.	feasible to look for signs of degradation rather than to actively pursue source destruction. Changes in the inorganic groundwater chemistry, like the reduction in dissolved oxygen, nitrate and sulphate levels, as well as the increase in dissolved iron and manganese, can be used to infer biodegradation. Such data together with the changes in dissolved concentrations of compounds associated with NAPL can be used to construct an argument on why plumes are stable and possibly shrinking (Van Biljon et al., 2006).	form of groundwater monitoring focussed on contaminant monitoring only and not with the additional component of finding the secondary lines of evidence for biodegradation.
ISCO (In-Situ Chemical Oxidation)	Involves the injection of a chemical that is likely to oxidise the contaminants. A number of holes are used to deliver the oxidants.	Destruction of the source can be achieved if the oxidant can be brought into contact with the hydrocarbons. Timeframes can be short and monitoring that is required can also be wrapped up quickly (USEPA, 2004). A variety of chemicals and trademarked products are available for use. With this approach a proper understanding of the hydrogeology, geology, geochemistry and contaminant makeup is required (ITRC, 2001). Safety issues are also important to consider. The effectiveness of using this method in a fractured aquifer is questionable. This method is	Mostly short term follow up monitoring is conducted.

Remedial method	*How it works*	*Discussion*	*Often combined with*
		regarded as applicable to addressing the air and groundwater pathways by removing the source, provided it is applied to relevant situations.	
AS (Air Sparging)	Air is blown into the aquifer in a series of holes to strip volatiles from the soil and groundwater.	It can be a fairly effective system to reduce the source of contamination over time (USEPA, 1994b). Usually not very effective if NAPL is present and the method cannot contain any groundwater movement. Mostly suited to primary aquifer settings and not deemed to be very effective in a fractured aquifer. Because AS releases more vapour from the source, it is not a method that is suitable to address the air pathway. It can be effective in removing the groundwater pathway if dissolved contamination is treated before groundwater migrates to the receptor.	Often used with SVE to increase efficiency.
Cut-off trench	Installation of a cut-off trench involves digging a trench perpendicular to the flow path and to a depth below that of the groundwater. A pump is then installed on the	This method is very effective in containing plumes as it forms a physical barrier to movement, if correctly installed and pumped continuously. Recovery of free phase is also much more effective than pumping from a single hole as with P&T, mostly due to the enlarged surface area formed on the side of the trench (API, 2004). A cut-off trench cannot address the air pathway, except by preventing the spreading of a plume. Mostly trenches are not installed in bedrock	Monitoring of contaminants over the lifetime of the trench.

Remedial method	*How it works*	*Discussion*	*Often combined with*
	one end to remove any liquid that might collect in the drainage pipes installed in the trench.	aquifers due to the expense of installation in bedrock. This is a fairly long term remedial method, as it is usually installed downstream of a source zone.	

5.2 Costs

In order to give some idea of the costs involved in remediation it is necessary to start with a conceptual model that represents a general scenario. When considering LNAPL contamination, the most frequently encountered situation is a filling station or related site where an underground tank or pipeline has leaked. There are other ways that LNAPL contamination can result like when tanks overturn in vehicle accidents, or at depot where large volumes are handled and tanks leak or spills occur. But the largest number of storage sites where leaks can go unnoticed even for a short while are underground installations. Therefore the cost predictions presented here represent what one would typically find on a filling station or underground storage tank site.

Obviously the cost is absolutely determined by the situation in which such a leak or spill takes place. The more complex the hydrogeology and the more sensitive the receptors, the more expensive remedial actions will be. It is not necessarily a function of the size of the spill, since large spills can sometimes be cleaned without too much effort if the setting allows it. The table below attempts to give a typical cost for the different technologies. Often it is not possible to just apply just one method and there might be a combination, which would result in an increased cost. Sometimes remedial methods are too hastily applied without proper characterisation and they fail. It also happens that subsequent leaks or spills take place reversing most of the progress of remediation and the process has to start over.

For each method a view of the frequency of use is given. The expected timeframe is the time that it would take to complete the remediation process, provided all the right conditions are in place. Each cost consists of three elements. The first is the capital cost to procure the equipment and install the system. The next column provides an indication of the operation and maintenance of such a system. This cost is frequently overseen, since team members expect to install a uniquely designed system to operate without any input or adjustment. These systems usually have pumps or other mechanical equipment that need to operate. Failure to maintain remedial systems is a frequent source of failure of the remedial effort. Another important part of remedial costing is the monitoring that will be required to check that the system is operating as intended. This monitoring will focus on the source and on the receptors as a minimum. Depending on the kind of system and the setting in which it operates, the level and frequency of monitoring also differs. Using these costs and expected timeframes for remediation it is possible to come up with an estimated life cycle cost per

technique. In those cases where more than one technique is applied, it might be possible to save some costs on O&M and monitoring and would it not always be purely added.
No inflation was included in the O&M and monitoring costs and therefore the costs represent a net present value of the life cycle costs.

To give some idea of the applicability of the different methods a rating is supplied in the table below the costs. It is assumed that the methods are applied in the correct setting as far as possible to generate the ratings, because in an obviously incorrect application the method will fail (Table 5-3). As an example consider the pump and treat method where it can be seen that the efficiency of removal or destruction of the source is very poor, but the method is very good in preventing spreading of a plume in a fractured or primary aquifer, then it is possible to form an idea of the applicability of the method (Table 5-4).

Table 5-3 Remedial method, operational time and median costs for a median sized site.

Remedial method	Use	Expected timeframe (yrs)	Capital cost	O&M (per yr)	Monitoring (per yr)	Estimated lifetime cost*
Pump & treat	Frequently	10	R 500 000.00	R 115 000.00	R 112 000.00	R 2 800 000.00
Excavation	Frequently	1	R 1 500 000.00	R -	R 64 000.00	R 1 600 000.00
VER	Frequently	4	R -	R 80 000.00	R 64 000.00	R 600 000.00
SVE	Infrequently	5	R 250 000.00	R 60 000.00	R 50 000.00	R 800 000.00
Bioslurping	Infrequently	5	R 800 000.00	R 115 000.00	R 64 000.00	R 1 700 000.00
MNA	Infrequently	10	R -	R -	R 112 000.00	R 1 200 000.00
ISCO	Infrequently	1	R 500 000.00	R -	R 32 000.00	R 600 000.00
AS	Rarely	4	R 150 000.00	R 60 000.00	R 50 000.00	R 600 000.00
Cut-off trench	Frequently	7	R 500 000.00	R 115 000.00	R 112 000.00	R 2 100 000.00

* No inflation included, therefore represents NPV

\# Provided the technique is applied in the correct setting

- Estimated remedial costs assuming a monitoring system has been installed

Table 5-4 Remedial method, efficiency and application possibilities.

Remedial method	Use	Efficiency of removal/destruction	Ability to prevent plume spreading	Applicability - Fractured Aquifer	Applicability - Primary Aquifer	Applicability to Air pathway	Applicability to GW pathway
Pump & treat	Frequently	Very poor	Very good	Very good	Very good	Poor	Good
Excavation	Frequently	Very good	Good	Very poor	Very good	Good	Good
VER	Frequently	Good #	Poor	Good	Good	Good	Poor
SVE	Infrequently	Good #	Poor	Poor	Very good	Very good	Poor
Bioslurping	Infrequently	Good #	Good	Good	Very good	Poor	Good
MNA	Infrequently	Poor	N/A	Good	Good	N/A	Poor
ISCO	Infrequently	Good #	Good	Poor	Very good	Good	Good
AS	Rarely	Good #	Poor	Very poor	Very good	Poor	Good
Cut-off trench	Frequently	Good #	Very good	Poor	Very good	Poor	Good

 # Provided the technique is applied in the correct setting.

5.3 Optimisation

Experience in the United Stated of America has found that significant costs savings are possible on long term remedial projects when monitoring and evaluation data is gathered during the remedial project and then used to reassess the remediation strategy and methods (ITRC, 2001). Seen in the context of the Waste Act (Act 59 of 2008) where remediation orders will be issued by the authorities, it is important to take into consideration that significant knowledge about the response of the system will be gained during remediation. Remediation orders therefore have to allow sufficient flexibility for remediation strategies to be adapted, because such changes could also encourage more efficient remediation.

5.4 Conclusion

Various methodologies and combinations of methodologies have been presented with the associated costs of each method in field scale systems. The usage of a single or a combination of methods is possible however in this report a single method costing was applied. Due to the number of combinations that are possible, a costing matrix was not constructed. Neither a projection of estimated costs if one method should be replaced due to failure of remediation objectives.

6 SUMMARY OF INVESTIGATION

In this report an attempt has been made to illustrate the context in which LNAPL contaminants should be viewed and investigated. Results obtained in this study indicate that a thorough investigation into all possible contaminants should be conducted extending from water samples (analysis of inorganic and organic), aquifer settings to remediation options. The construction of a plausible site conceptual model could not be stressed enough since it lays the foundation for the successful characterisation, management and remediation of an LNAPL contaminant site.

The following key features and findings of the current study will be highlighted in the subsequent paragraphs.

6.1 The Occurrence of LNAPL

The presence of LNAPLs in modern society is prevalent, since it forms the foundation of our modern lifestyle. Thus from literature and field sites it was confirmed that LNAPLs pose a contaminant risk to the environment and exposure in urban settings is common. The physical and chemical characteristics of LNAPLs were discussed to give a new insight into the possible environment in which LNAPLs could be detected. Most interestingly is the presence of a threefold system, i.e. aqueous phase, free phase (pure LNAPL) and a gaseous phase. The resources (monitoring and compliance) required evaluating LNAPL exposure in South Africa is still in its infancy and major hurdles include legislation and cost effective (laboratories) monitoring programs for organic contaminants.

6.2 Site Assessment

Due to the complex nature of LNAPL contamination, no single method of analysis can be used to evaluate the extent of the plume. Both invasive and non-invasive methods are required, especially if the LNAPL composition is not known. Since LNAPLs are in contact with the vadose zone unsaturated flow paths and chemical sorption should be considered when evaluating the free phase. The miscibility of the LNAPL with the water source also plays a role in the transport of the dissolved phase. In a South African context the fractured character of the aquifer plays an important role with the presence of preferred pathways which could exaggerate the spread of the LNAPL in the aquifer system.

Evaluating the history of a site and conducting interviews with people which are associated with the site can deliver surprisingly good results, however it should be noted that the likelihood of establishing a continuous time line will be difficult due to the low priority LNAPLs were given in the past. As an initial springboard for a site investigation this data can assist in constructing an initial conceptual model.

During the examination of the study sites it became evident that the type of investigative process is whole determined by the site itself. Two sites were evaluated in this study and the methodology of investigation differed due to the geological and geohydrological properties of each area.

6.2.1 Initial Guidance on Site Assessment

The four primary parameters which affected the study sites were:

6.2.1.1 Geology

The geology of the site should be characterised to determine the transport parameters in both the vadose and saturated zones. Important features such as fault or shear zones, dolerite dikes and aquitards should be identified. Borehole logs should be examined for any possible structures which might act as preferred pathways such as horizontal and vertical fractures or porous media such as sandstones. Down the hole geophysics should also be attempted since these methods can highlight fracturing patterns in an aquifer area. Understanding the geological effects on the groundwater movement can also assist in determining the receptors which might be at risk and if the LNAPL will daylight at another position.

6.2.1.2 Vadose zone composition and thickness

The vadose zone can play the most critical role in the study of LNAPL contamination sites, since it is this zone that affects the mass transport of the LNAPL to the groundwater table. At a LNAPL site an assessment of the influence of the vadose zone should be made. The presence of LNAPL vapour in the top soil might indicate that the LNAPL has an interaction with the atmosphere; this is especially relevant in humid or coastal climates.

6.2.1.3 Depth to water level and gradient

Three types of aquifer depths are generally considered during an investigation, i.e. shallow (< 4 m), intermediate (< 10 m) and deep (> 10 m). The classification of depth is to assist in defining the interaction between the three phases which exist in any LNAPL system, i.e. gas, liquid and solid phase. In South Africa typical temperatures at depths greater than 10 meters ranges in the area of 10-20°C, while in the first 10 meters a significant difference can be observed which is determined by seasonality. This would effectively increase evaporation in shallow aquifers if a non-confining layer is absent. At greater depths, intermediate or deep aquifer systems confining or semi-confining conditions might prevail trapping the LNAPL in the subsurface. In the latter instance LNAPL migration usually occurs through preferred pathways to the groundwater level, and LNAPL contamination might be spread through a larger area.

To effectively determine the LNAPL distribution area, a careful study of the general region groundwater levels around the investigation site should be conducted. The abstraction characteristics of an area are fundamental in determining the movement of the LNAPL plume.

6.2.1.4 Hydraulic parameters of the LNAPL

Sampling of the LNAPL can be a valuable tool in determining the effect of the contaminant in a specific site. LNAPL component mixtures can be analysed to determine the main organic components; and with the use of evaporation rates, mixing volumes and solvation properties a good estimate can be made on the available contaminant at a site.

6.2.2 Assessment Methodology

6.2.2.1 Non-invasive techniques

The application of hydrocensus, geological mapping, soil vapour surveys and geophysical methods are highly recommended since it reduces costs of the study and impacts on the environment. Geophysics to a certain extent has limited applicability to LNAPL contaminant plume delineation however it can yield valuable results on geological formations and flow paths.

6.2.2.2 Invasive techniques

The use of invasive techniques should be carefully. Auguring is a relatively low cost solution which can yield results on LNAPL contamination and remediation at a site. Furthermore, soil profiles and organic carbon content can be established which could indicate susceptibility of the soils to LNAPL infiltration. The use of percussion drilling or coring should be evaluated against intended use of the borehole during the post drilling phase. In either instance the borehole should be adequately cased to present dissolved or free phase from entering deeper aquifer systems. Secondly, if monitoring is to be conducted from the borehole that chemically resistant material (UPVC or Steel) is used during the construction and that borehole sealants are not susceptible to LNAPL degradation or solvation. Water strikes and lithology must be recorded by a competent person who enters the data into a suitable database.

6.2.2.3 Pump testing and water levels

Pump tests are performed to assess the productivity of the aquifer according to its response to the abstraction of water, and/or to determine the transmissivity of the aquifer. This response can be analysed to provide information with regard to the hydraulic properties of the groundwater system and give an estimate of the rate of contaminant spread throughout the aquifer. Use of water levels can assist in evaluating the direction of LNAPL movement and the location of possible observation wells.

6.2.2.4 Water sampling

Groundwater sampling is to collect samples which are “representative” of *in situ* groundwater conditions and to minimise changes in groundwater chemistry during sample collection and handling. Experience has shown that groundwater sample collection and handling procedures may be a source of variability in water-quality concentrations, due to differences in sampling personnel, sampling procedures and equipment. Analysis should be conducted for both inorganic and organic components. The measurement of inorganic components is a key indicator of subsurface geochemical processes such as degradation. In the instance of organic components a general list should be analysed for that includes BTEX (Total), TPH (C10-C30) and MTBE/TAME.

6.3 Conceptual Model

The construction of a conceptual model for a field site is one of the most important and fundamental precepts in LNAPL site remediation. The inclusion of various principles in this model phase will determine if an effective remediation option can be constructed and applied to a field site. One common problem in evaluating LNAPL contamination at a site is the assumption that it only occurs in one phase, i.e. a pure geohydrological problem or a gas phase only problem. The subtleties involved in the study and clean-up of an LNAPL site, can be described as a three phased system, i.e. gas, dissolved and free phase. The LNAPL can be distributed in both the vadose and saturated zone and this should be incorporated into the conceptual model. The geology of the site also plays an important role in that fractures or confining layers might be present which dramatically affects the movement and degradation of the LNAPL. Additionally, the role of anthropogenic activities should be included in the final conceptual model since it can act as a vehicle for LNAPL transport in the subsurface as well as a receptor source.

6.4 Risks, Costs and Methods of Remediation

A wealth of methods exists in the remediation of LNAPL contamination and most of the methods have been highlighted in this report. However, there are inherent risks in choosing a specific method and has associated costs. In general pump-and-treat methods are used although this method might actually decrease the probability of remediating a site due to an incorrect conceptual model. Each method discussed in this report has a special place in site remediation and all risks and disadvantages should be first analysed before using the method to ensure effective remediation of a site. Changing of remediation methods partially through a project can have severe cost implications and can impact on the remediation of a site. Thus it is better to build a correct conceptual model of the site before remediation starts, than changing midway through the project. The costing structures presented in this section focused on the application of a single method per site, however some methods can be used in combination but the permutations made it difficult to estimate costs involved.

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8 APPENDIX GENERALISED SITE INVESTIGATION METHOD

8.1 LNAPL Site Characterisation

The site characterisation of LNAPL contaminated sites is a scientific and an engineering challenge. The focus of this subsection is to present a general introduction into site characterisation with the objective of creating a fundamental set of parameters which can be useful in determining the geographical extent of an LNAPL contamination site.

8.1.1 Explorative site investigation guidelines

8.1.1.1 Historical data

1. Obtain information on the location of possible above ground storage units and/or below ground storage areas.
2. Time period that each of these areas were in use.
3. Size of storage unit (tanks or large reservoirs).
4. Contents of storage units (Oil, Diesel, Petrol or Paraffin).
5. Decommissioning time or period of usage for the respective storage units.
6. First incident report (LNAPL).
7. Rehabilitation procedures of the decommissioned areas.

8.1.1.2 Site safety

1. Before a site can be inspected, assure that the site complies with basic safety regulations.
2. Prepare required safety documentation to enter the site and obtain written permission to enter the area.
3. Coordinate a meeting with the site manager, safety officer and plant engineer to discuss any possible hazards and restricted areas.

8.1.1.3 Area of contamination

1. A basic hydrocensus of the area.
2. Locate any boreholes which might be on the site or in close proximity to it.
3. If boreholes are sealed with a metal screw cap or any type of device which might cause a spark, be aware that hydrocarbon gas build-up can occur and an explosion might be possible.
4. Setup a geographical database with the most relevant sites logged and hydrocensus data.

8.1.1.4 Site inspection

The first site inspection can be the most informative part of the initial phase.

1. On entering the site, can any volatile components of LNAPLs be detected by smell?
2. Are there any clear signs of LNAPL spillage on the site? Drums leaking, oily patches or small LNAPL ponds. This might indicate a continuous source of contamination.
3. If the site has vegetation on it, does it seem to be normal or are there dead patches or dead trees around?
4. Has the site been sealed off from the local populace?
5. Talk to as many people on site as possible to determine if LNAPL spillage events could be identified.
6. Determine if the boreholes were constructed from the correct material. Stainless steel and/or concrete construction methods are preferred.
7. Identify any hotspots which might be a direct source of LNAPL intrusion into the subsurface.
8. Try and obtain initial samples from boreholes with a bailer for analysis to determine what kind of LNAPL might be present (major component analysis).
9. Discuss follow-up visit time-schedules and access to the site.
10. Construct an initial conceptual model for the area as this would allow you to quickly assess possible gaps in your assessment method.

8.1.2 Comprehensive site characterisation

8.1.2.1 Borehole construction

1. It is important that no boreholes should be drilled until a good fundamental understanding of the types of aquifers in the area has been established.
2. Borehole construction is most likely the single most significant aspect of monitoring and evaluation of LNAPL contamination sites.
3. Pumping equipment should be chemically resistant to function in LNAPL boreholes.
4. All boreholes should be sealed with a non-metallic cap with a pressure equalizing valve to prevent gas build-up in the well.
5. During site selection of boreholes, the geology of the area should be considered.
6. Drilling of boreholes should be setup in groups of three (to determine groundwater flow direction) and at groundwater watershed areas.
7. The well screens should be setup in such a method to be compatible with the particle size of the formation and allow affective monitoring of the LNAPL contaminant.

8.1.2.2 Sampling intensity

1. Sampling intensity is a direct function of available funds, if possible all wells in an area should be sampled in each of the three phases (gas phase, free phase and dissolved phase).
2. In the field PID (Photo Ionic Detector) readings should be gathered for the gas phase and subsequently analysed by chromatographic methods in a recognised analytical lab.
3. Standard sampling techniques should be used to determine EC, pH, redox potentials and temperature at each well site.
4. Samples should be taken and stored in the correct procedure for lab analysis for both macro inorganic and organic components.
5. Loggers can be installed at the site, although a stainless steel cable should be used to insert these loggers.

8.1.2.3 Aquifer parameters

8.1.2.3.1 Geology

1. The geology of the site should be characterised to determine the transport parameters in both the vadose and saturated zones.
2. Delineate important features such as fault or shear zones, dolerite dikes and aquitards.
3. Borehole logs should be examined for any possible structures which might act as preferred pathways such as horizontal and vertical fractures or porous media such as sandstones.
4. A resistivity survey of the area should be conducted to investigate the subsurface.
5. Down the hole geophysics should also be attempted since these methods can highlight fracturing patterns in an aquifer area.

8.1.2.3.2 Vadose zone

1. The vadose zone can play a critical role in the study of a LNAPL contamination site.
2. At a LNAPL site an assessment of the influence of the vadose zone should be made.
3. The presence of LNAPL vapour in the top soil might indicate that the LNAPL has an interaction with the atmosphere.

8.1.2.3.3 Depth of water level and groundwater level gradient

1. Classification of aquifers
    a. Shallow aquifers which have water level less than 2-4 meters below the surface.
    b. Intermediate aquifers with water levels which range from 4-10 meters below surface.
    c. Deep aquifers which are any aquifer system with water level greater than 10 meters below the surface.

2. Pumping rates from residential and industrial (agriculture, mining or development) activities should be known.
3. Quantity of abstraction should be determined for each of the active sites as well as pumping frequencies.

The abstraction characteristics of an area are fundamental in determining the movement of the LNAPL plume.