

**Characterisation and Management of a  
LNAPL Pollution Site Along the Coastal  
Regions of South Africa**

by  
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**Magister Scientiae**

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**Faculty for Natural- and Agricultural Sciences,**

at the  
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November 2009

## **Declaration**

I, Kevin Harry Vermaak, declare that the thesis hereby submitted by me for the Master of Science degree at the University of the Free State. Is my own independent work and has not previously been submitted by me at another university/faculty. I further more cede copyright of the thesis in favour of the University of the Free State.

Kevin Harry Vermaak  
(2004024150)

## **Dedication**

I dedicate this thesis to my Mom, Dianne Bisset Vermaak, who passed away this year. Thank you for the strength I found in you.

“This above all, to thine own self be true” – William Shakespeare.

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- Most of all to the Lord, in whom I found strength and courage.

## **Key Words**

Light Non-Aqueous Phase Liquids (LNAPLs)

Characterisation

Coastal

Hydraulic Parameters

Soil Analysis

Porosity

Vaporisation

Shallow Aquifer

Management

Monitored Natural Attenuation (MNA)

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# 1. Introduction

Petroleum liquids form the basic building blocks of our modern lives. The uses include fuels, lubricants, and the raw material for manufactured products. Current consumption in the United States is estimated at 840 million gallons per day. Total use over the last 100 years is on the order of one million times 10 million gallons (API - May 2003). In order to assist in the development of countries, these products are stored in underground storage tanks (UST) and in huge tanks grouped together on pieces of land called tank farms.

LNAPLs are a concentrated source of chemical mass and generally pose long term impacts on the immediate and adjacent environment. The use of these oil-based petroleum fuels dates as far back as the late 1800's. Due to old technology used in the construction of these tank farms, together with the lack of knowledge concerning the environmental impacts of these fuels, many petroleum sites are severely polluted. The study of LNAPLs forms specialised part of hydrology pollution. Light non aqueous phase liquids are the cause of numerous groundwater contaminations in industrialised countries (Betthar, *et al.*,1998).

A vast amount of Fuel stations and depots spread across the country. Most of these stations and depots are located in the vicinity of an urban area. The main six stakeholders in South Africa's Fuel industry are Total, Engen, Sasol, Caltex, BP and Shell with a total of 5000 fuel stations amongst them. Fuel depots are located in major cities across South Africa with retail fuel stations located in virtually every city suburb. Table 1 shows the estimated number of fuel stations in South Africa.

**Table 1: Estimated number of fuel stations in South Africa**

<b>South African Oil Company</b>	<b>Estimated Number of service stations</b>
Total Oil SA	688
Caltex Oil SA	800
BPSA	780
Engen	More than 1300
Shell Oil SA	800
Total	4368

Sources: [www.total.co.za](http://www.total.co.za), [www.shell.co.za](http://www.shell.co.za), [www.bp.com](http://www.bp.com), [www.caltex.co.za](http://www.caltex.co.za), [www.engen.co.za](http://www.engen.co.za).

The project site is located along the Eastern Cape coast of South Africa. The location of the site is unique because of its proximity to the ocean and an adjacent river. Site specific details cannot be divulged due to confidentiality agreements that have been put in place. The project site has experienced various spills over the last ten years. Data dating back before this period is unavailable.

The site is shared by four separate companies and is divided accordingly. (Figure 1).



**Figure 1: Location of the project site with sub-sections shown in yellow, indicating the different petroleum operation areas.**

All the sites experienced spills at different times.

During March 2005 a product spill of 6900 litres occurred in section 3, when a tank was overfilled. It is reported that approximately 6700 litres were recovered and only approximately 200 litres lost to the environment.

In order to prevent future product losses to the environment the underground lines were pressure tested for duration of one hour and no drop in pressure was experienced and the underground lines were classified as safe.



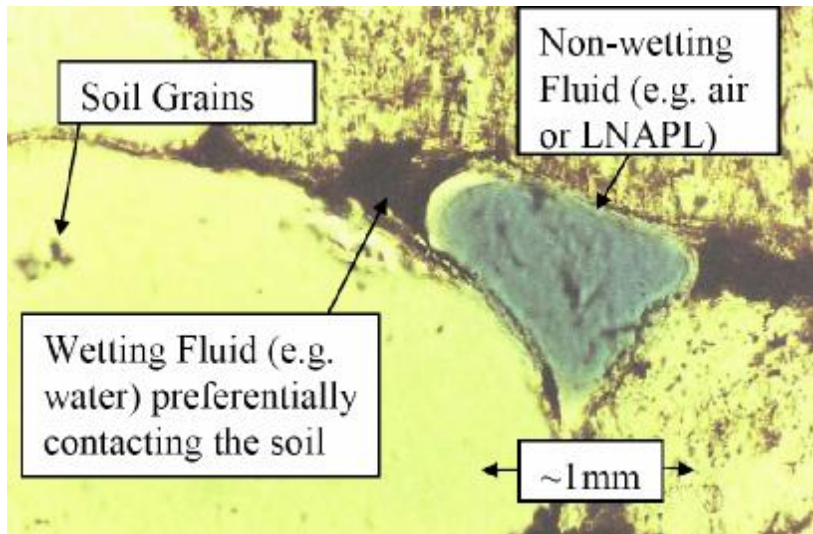
A reported diesel spill of approximately 30 000 litres occurred during September 2005 in Section 1, of which nothing was recovered. No other noteworthy spills or product losses have been reported in the past 7 years. There are no underground pipes in Section 1 that require pressure testing.

### **1.1 Definition of LNAPLs**

The acronym LNAPL stands for Light Non-aqueous Phase Liquid. LNAPLs usually refer to petroleum liquids. The word 'light' suggests that the petroleum (hydrocarbon) compounds have a density less than that of water and thus "float" on water. 'Non-aqueous' implies that the liquid does not mix freely with water, although trace amounts do go into solution with water.

From an environmental perspective, key factors of LNAPLs include:

- LNAPLs are found at the top of groundwater zones, floating on the water's surface. The buoyancy of LNAPL in water thus inhibits LNAPL migration into the groundwater zone.
- The fact that water and LNAPLs are largely immiscible means that water and LNAPLs share pore space in rocks and soils that have been affected by LNAPLs. The sharing of pore space limits the mobility and thus complicates the remediation/recovery of the LNAPL. (Figure 2).



**Figure 2: LNAPL and water sharing pore space**

- The immiscibility of LNAPLs has its advantages and disadvantages. The low solubility implies that less loading on the environment takes place and thus natural processes are able to be more effective over small distances. A disadvantage of low solubility is that LNAPL can persist as a source of groundwater contamination for extended periods. (<http://www.api.org/2009-08-08>).

The project site is located in the coastal regions in South Africa. The area is primarily used for industrial purposes. No borehole water is used for human consumption. The river to the north of the site acts as a natural harbour. See Figure 3.



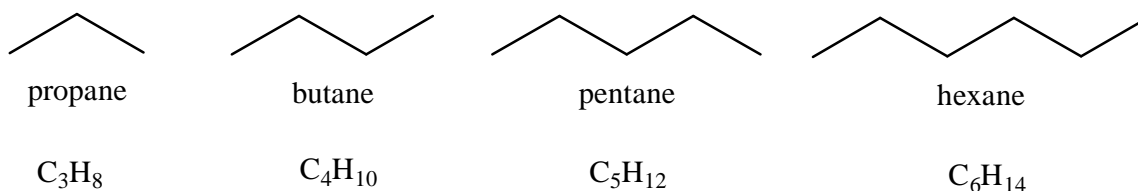
**Figure 3: Location of the project site.**

## ***1.2 Chemical Characteristics***

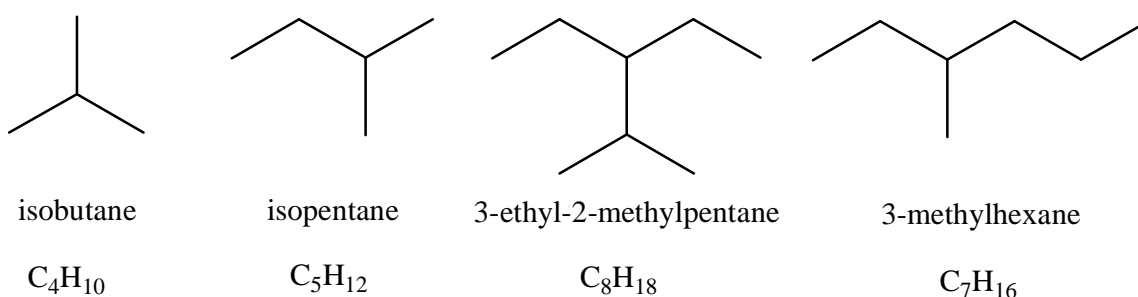
Petroleum fuels contain: Paraffin's, Olefins, Naphthene's and Aromatic components. Different petroleum companies add various additives in various quantities (ppb or ppm). These additives include oxygenates, performance enhancers or engine protective compounds. Petroleum products can potentially contain up to 500 compounds which may contain between 3 and 12 carbons in a molecule. The boiling range varies between 30°C and 220°C at standard atmospheric pressure. Because there is such a wide range of compounds existing in petroleum fuels, only the most important and relevant compounds will be discussed in the following paragraphs. (CRC 2004)

### 1.2.1 Paraffin's

Paraffin's 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 4 and Figure 5:



**Figure 4: Straight chain non-cyclic alkanes. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.**

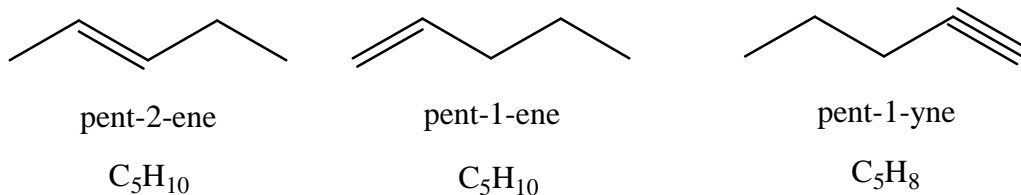


**Figure 5: Branched chain non-cyclic alkanes. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.**

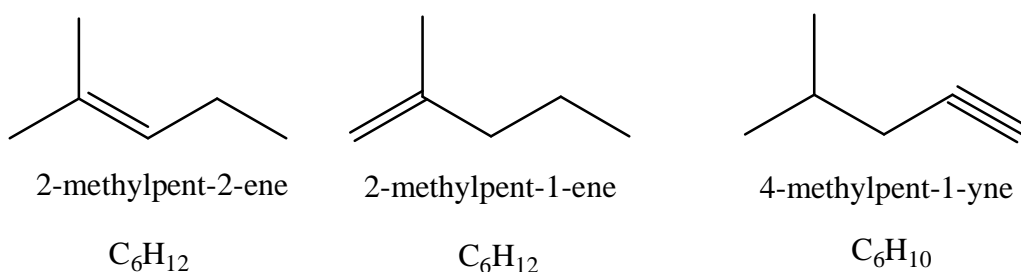
Paraffin's form the majority of petroleum fuels, with branched alkanes increasing the octane number the most significantly in this group. Alkanes are most preferred due to their stability and clean conversion during combustion.

### 1.2.2 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 6 and Figure 7.



**Figure 6: Straight chain non-cyclic alkenes and alkynes. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.**

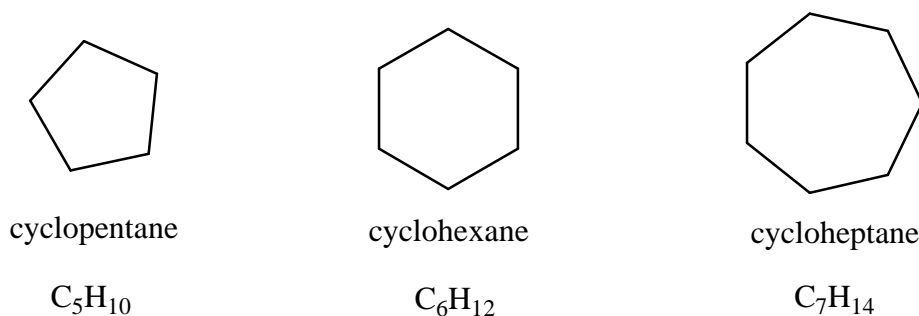


**Figure 7: Branched chain non-cyclic alkenes and alkyne. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.**

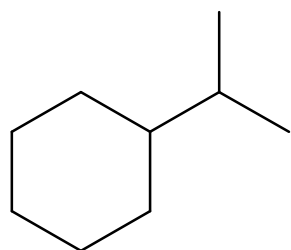
Olefins are greatly unstable and are usually only present in petroleum fuels as a small percentage of the total bulk.

### 1.2.3 Naphthene's

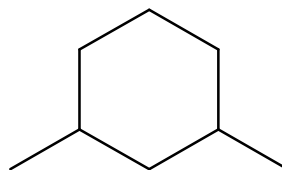
Naphthene's are saturated cyclic hydrocarbons (cycloalkanes), which can either be a simple cyclic hydrocarbon (with a general formula of  $C_nH_{2n}$ ) or derivative with side chains emanating from the ring structure. Examples of each group are represented in Figure 8 and Figure 9.



**Figure 8: Selected cyclohexanes with the chemical symbol, nomenclature and reduced chemical formula given for each molecule.**



isopropylcyclohexane



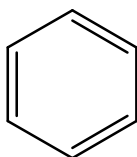
1,3-dimethylcyclohexane



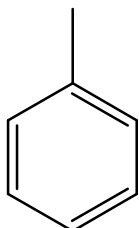
**Figure 9: Selected branched or derivative cyclohexanes with the chemical symbol, nomenclature and reduced chemical formula given for each molecule.**

### 1.2.4 Aromatics

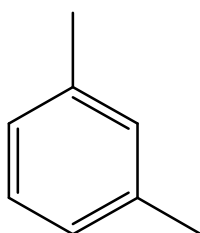
Aromatic compounds are unsaturated aromatic carbon systems (benzene or phenyls), which can either be monomeric (benzene, toluene and xylene) or polymeric (anthracene, naphthalene). Examples of each group are represented in Figure 10 and Figure 11:



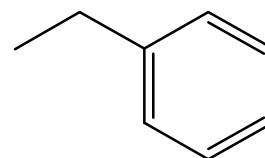
benzene



toluene



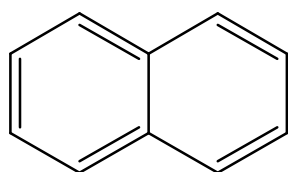
*m*-xylene



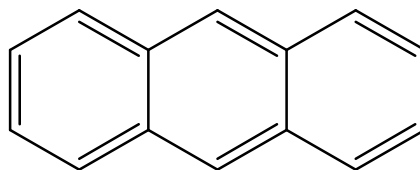
ethylbenzene



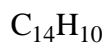
**Figure 10: Mono-aromatic compounds typically found in petroleum fuels. Chemical symbol, nomenclature and reduced chemical formula given for each molecule.**



naphthalene



anthracene

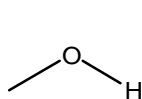


**Figure 11: Polymeric aromatic compounds that can be found in petroleum fuels. Chemical symbol, nomenclature and reduced formula given for each molecule.**

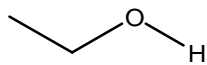
The aromatic composition of petroleum fuels used to be as much as 40 % but due to the inherent hazards of these compounds the acceptable limits has been reduced to less than 20 %.

### 1.2.5 Oxygenates

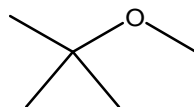
These compounds are used to provide a reasonable anti-knock value to petroleum fuels and contain an oxygen atom in the hydrocarbon structure. Currently, in a South African context these compounds are used as a substitute for aromatics compounds. Examples of oxygenates are methanol (MeOH), ethanol (EtOH), 2-methoxy-2-methylpropane or methyl tertiary butyl ether (MTBE) and 2-ethoxy-2-methylpropane or ethyl tertiary butyl ether (ETBE). Examples of each group are represented in Figure 12:



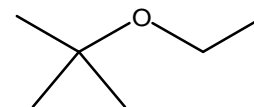
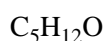
methanol



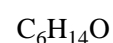
ethanol



2-methoxy-2-methylpropane



2-ethoxy-2-methylpropane



**Figure 12: 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). Oxygenates added to

petroleum fuels function as an octane booster and reduces the CO emissions, although at a lower power output.

### 1.3 General LNAPL Conceptual Model

Once a quantity is released into the vadose zone, it will move downwards under the force of gravity. (Newell *et al.*, 1995). A small fraction will be withheld by capillary forces as residual globules and form a residual deposit, often referred to as a smear zone. If a sufficient amount of LNAPL is spilt, the LNAPL will continue to migrate downward until a barrier such as an aquitard or aquiclude is reached. Because of the difference in buoyancy between the LNAPL and water, water itself would act as a physical barrier. Once the groundwater is reached the LNAPL will move as a function of gravity, capillary force and groundwater gradient. A portion of the LNAPL will dissolve in the water. Some fraction may move in the opposite direction of groundwater flow, this being caused by capillary forces as can be seen in Figure 13 below.

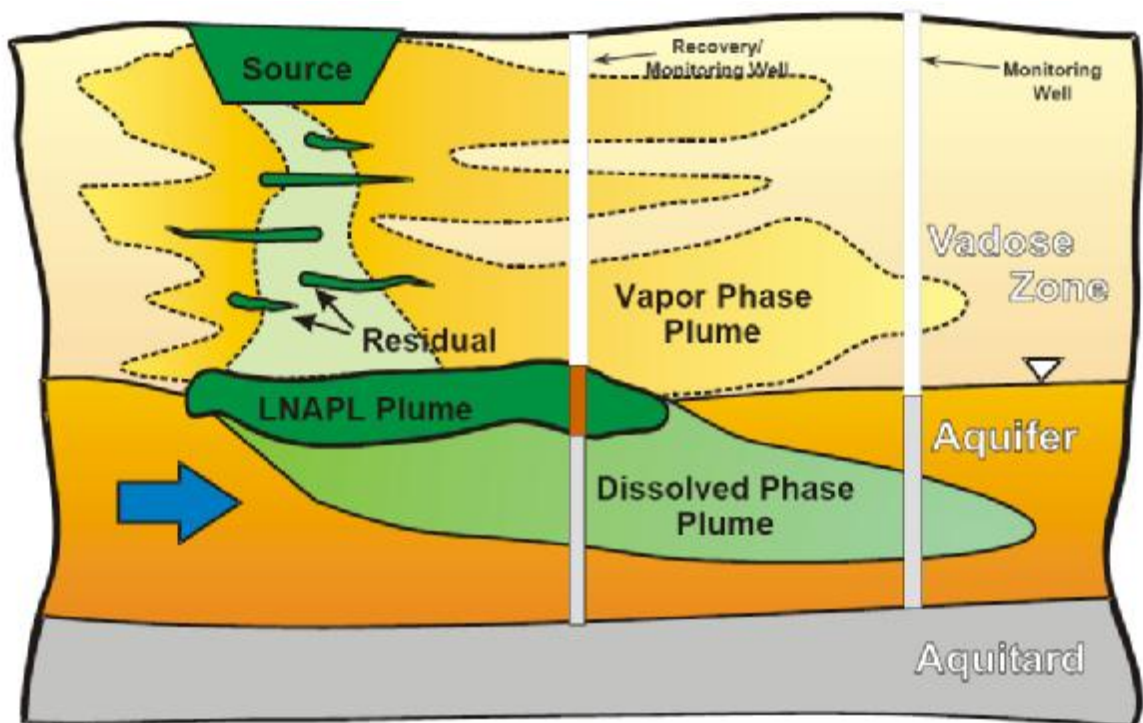


Figure 13: Simplified conceptual model for the release and migration of LNAPL in the subsurface.



## 1.4 Climate of Study Area

In this project climate plays a vital role in the characterisation of the site. Temperature together with humidity and precipitation are the major influences.

The project area experiences a warm climate with temperatures very seldom dropping to low single digits. The summers are warm and humid with most precipitation occurring during the summer months with the average day temperature of 25°C and night temperature of 17°C. The winters are also warm with the average day time temperature being 22°C and the average night time temperature being 12°C. The mean annual precipitation is 921mm.

**Table 2: Climatological information for the study area (weathersa.co.za)**

Month	Temperature (° C)				Precipitation		
	Highest Recorded	Average Daily Maximum	Average Daily Minimum	Lowest Recorded	Average Monthly (mm)	Average Number of days with $\geq$ 1mm	Highest 24 Hour Rainfall (mm)
January	36	26	18	12	69	13	119
February	37	26	19	13	92	12	126
March	36	25	18	10	105	13	217
April	36	24	15	8	83	9	131
May	37	23	13	5	52	8	78
June	32	21	11	3	40	6	101
July	34	21	10	3	47	5	155
August	38	21	11	4	78	7	447
September	42	21	12	5	80	10	91
October	39	22	14	6	102	13	180
November	35	23	16	9	110	13	185
December	38	25	17	8	63	12	80
<b>Year</b>	<b>42</b>	<b>23</b>	<b>14</b>	<b>3</b>	<b>921</b>	<b>121</b>	<b>447</b>

This climatological data are the normal values and, according to World Meteorological Organization (WMO) prescripts, based on monthly averages for the 30-year period 1961 – 1990 (Weathersa.co.za).

### ***1.5 Aims and objectives***

This project considers characterization and management of LNAPL pollution along a coastal region in South Africa with the following aims and objectives:

1. To manage and characterise a pollution site along the coastal regions of South Africa.
2. Determine the fate of LNAPL pollutants in coastal vadose zone aquifers with regard to soil types and composition.
3. Evaluate the major contributing factors to the fate and transport of LNAPL pollutants in specific coastal aquifer conditions.
4. Determine sampling techniques, intervals and methodology for coastal aquifer systems.
5. Explore the role and impact of MNA in the remediation of LNAPL pollution in the vadose zone of a coastal aquifer.
6. Develop, explore and recommend appropriate monitoring and management systems for LNAPL pollution in coastal aquifer systems.
7. To characterize and classify the physical soil properties, soil make-up and conditions present in the vadose zone of the aquifer.
8. Evaluate the relationship between clay content and the expulsion of LNAPLs to the atmosphere by means.

## **1.6 Conclusion**

It is very clear that LNAPL pollution is prevalent at the project site as well as at many fuel depots all over the world.

LNAPLs are clearly defined and their general chemical makeup is briefly discussed. For the purpose of this thesis, a thorough chemical description and analysis is not required.

From the definition of LNAPLs a general conceptual model showing the behavior of LNAPLs in was constructed was constructed.

Given the spills that have occurred at the project site, a clear set of aims and objectives has been set to be achieved in this thesis.

In the following chapter the effect of the physical characteristics effecting the characterization of LNAPLs in the vadose zone will be discussed.

## **2. Physical characteristics to be observed in the characterisation of LNAPLs in the vadose zone environment.**

The physical properties of organic compounds affect their behaviour in the subsurface (Fetter, 1999). The project sites' pollution occurs mainly in the vadose zone. The vadose zone forms the section between the land surface and the water table, which in this case includes the capillary fringe which is the narrow region directly above the water table. Water in this zone is generally under less than atmospheric pressure, and the voids may contain water, air or other gases. Most groundwater recharge pass through this zone and the nature and thickness of this zone plays an important role in preventing contaminants reaching the aquifers.

The site is made unique by its location near to the coast and because of its shallow aquifer with shallow water levels. Due to the fact that the water levels in this particular study are so shallow, the contamination is mostly present in the vadose zone. The environment in the vadose where the LNAPLs occur is of utmost importance to their behaviour in the subsurface and to the characterisation of the site. The main contributing physical factors to the environment in the vadose zone include:

- Temperature,
- Saturated zone,
- Phase distribution,
- Water levels,
- Porosity and
- Hydraulic parameters.

The above factors together with the roles they play will be thoroughly discussed in the following chapter.

## **2.1 Temperature**

Temperature effects can play a significant role in the volatilisation. The fact that LNAPLs consist of a large percentage of volatile constituents will enhance the effects of evaporation in area where the water levels are shallow. Volatilisation is a mass loss mechanism in play at this particular site and plays a huge role in its remediation.

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. The higher the vapour pressures of a liquid at a given temperature, the lower the normal boiling point of the liquid.

**Table 3: Vapour pressures and relative solubilities**

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

From the above table it is made clear that not all the organic compounds behave in the same manner and that the composition of the spill has some consequences. It can be assumed that if the pollution evaporated before most of it descends to the water table, there is a minimal amount of pollution. Secondly, in the case of a shallow aquifer, the likelihood of the evaporation of the contaminant must be considered when doing a site characterisation. Finally, if the surface contains clay layers or any sedimentary layers, these might act as trapping agents for the hydrocarbons and thus keeping the contaminant close to the surface.

As the contaminant descends, microbial activity as well as geochemical processes will take action in the natural remediation. Ambient temperatures vary between 10 and 20 degrees Celsius depending on the seasonal effects and depth.

## **2.2 Porosity**

Porosity is the ratio of the volume of void space to the total volume of the rock or earth material. Porosity is an indication of the amount of water in the subsurface, but does not equate to the volume that can be released from storage. (IGS Groundwater dictionary).

Porosity of soils determines the absorption rate and the transport through the medium. In the case of LNAPLs, movement will be faster through coarse grained medium than a finer grained medium simply because LNAPLs prefer a path of least resistance. If preferred pathways exist in the system the LNAPL transport from the surface zone to the groundwater level will be significantly enhanced.

The average porosity of the soils at the project site is 24 %. This correlates to the grain-size, which will be discussed at a later stage.

## **2.3 Water levels**

Water levels were measured by means of a basic dip-meter; all collar heights were noted and taken into consideration.

The groundwater levels at the East London site are very shallow and vary between 0.3 m and 3.0 m below surface level. A very accurate correlation between the water levels and the surface topography exists. See figure 14. From this accurate correlation, the use of Bayesian interpolation can be used in the construction of an accurate water level contour map.

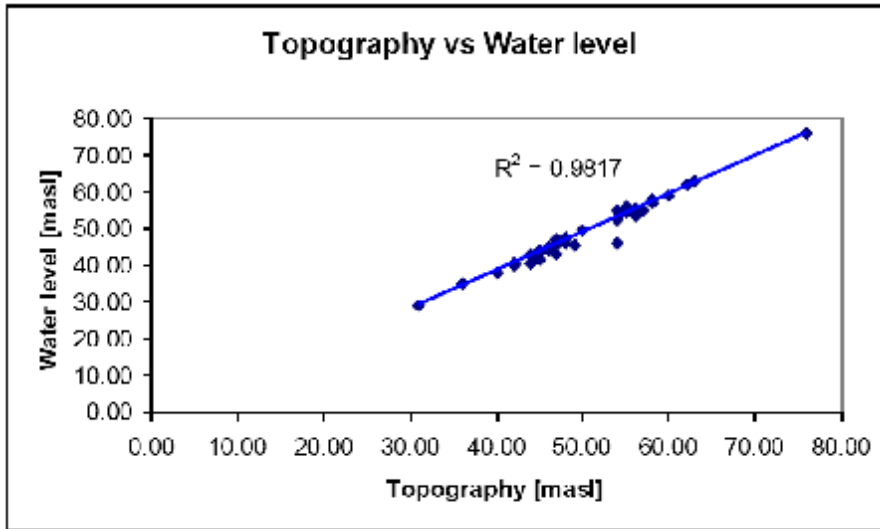


Figure 14: A plot of surface elevation vs. water levels in the East-London study area. A good correlation (98 %) can be observed for the data.

From this accurate correlation, the use of Bayesian interpolation can be used in the construction of an accurate water level contour map.



Figure 15: Borehole with shallow water level (0.3m).



## **2.4 Hydraulic Parameters**

### **2.4.1 Pump Tests**

This test is 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 analyzed to provide information with regard to the hydraulic properties of the groundwater system.

The basic procedure of the pumping tests is as follows:

The pump is installed near the bottom of the borehole so as to achieve maximum drawdown. Once the pump is installed the rest water level is noted. Once pumping has commenced water levels are measured at regular intervals.

An initial pumping rate and duration is decided upon based on the results obtained in the slug tests. In this particular instance it was decided that the borehole should be pumped at a rate of 0.16 l/s for two hours.

The water levels were measured by the use of Solinst levellogger transducers. Hand measurements were also taken. Due to time constraints on this particular project, the recovery could not be measured by hand and this data was acquired from the transducers at a later stage.

Pump tests were only performed on the newly drilled boreholes. Pump tests were not conducted on the pre-existing boreholes due to inadequate borehole construction, which would have had an adverse effect on the integrity of the data acquired.

In some cases the pump tests were not able to be run to completion due to the boreholes not having sufficient yields. In these cases the recovery of the water levels were used for the estimation of their hydraulic parameters. The Cooper-

Jacob as well as the recovery, time versus water level was used to determine the respective T values. FC software was used in the interpretation and fitting of the graphs. These pump test analyses can be seen in the figures below. The data from the boreholes is shown in table 4.

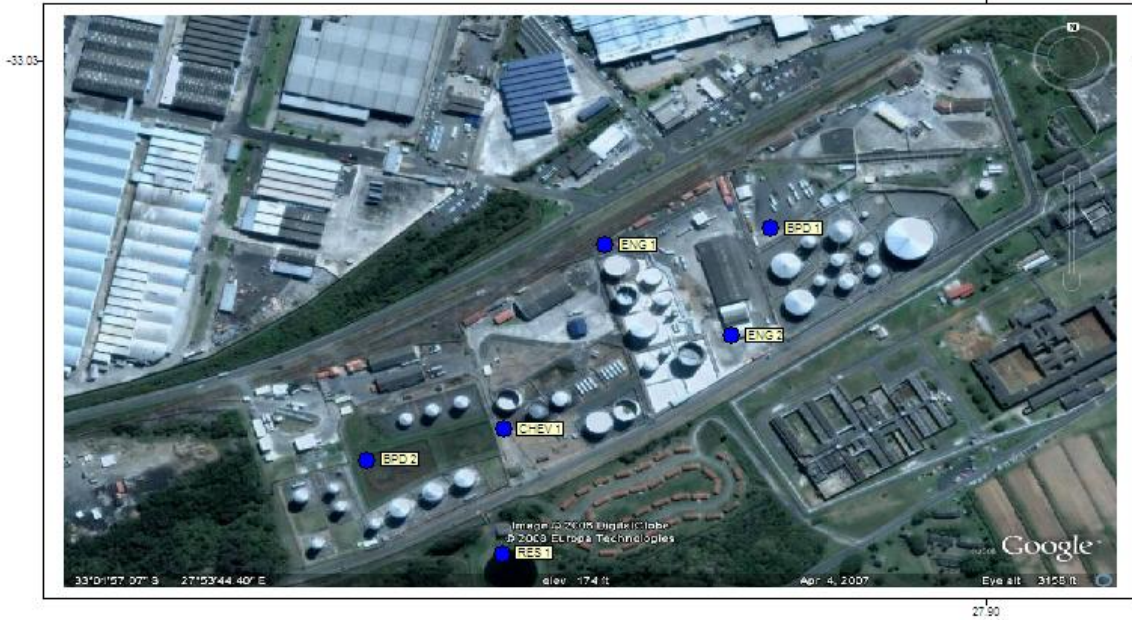


Figure 16: Six new boreholes drilled in October 2008.

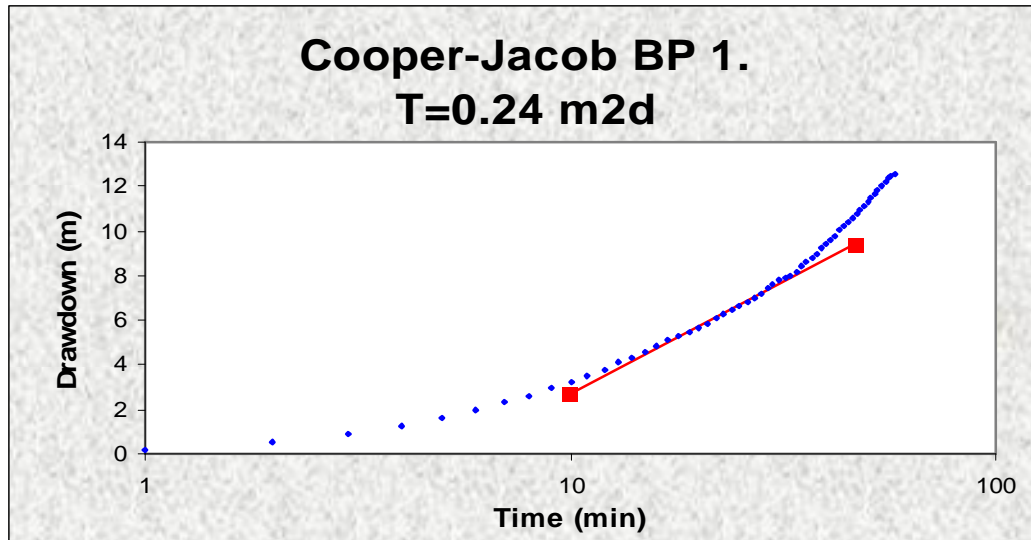


Figure 17: Analysis of pump test data using F-C.

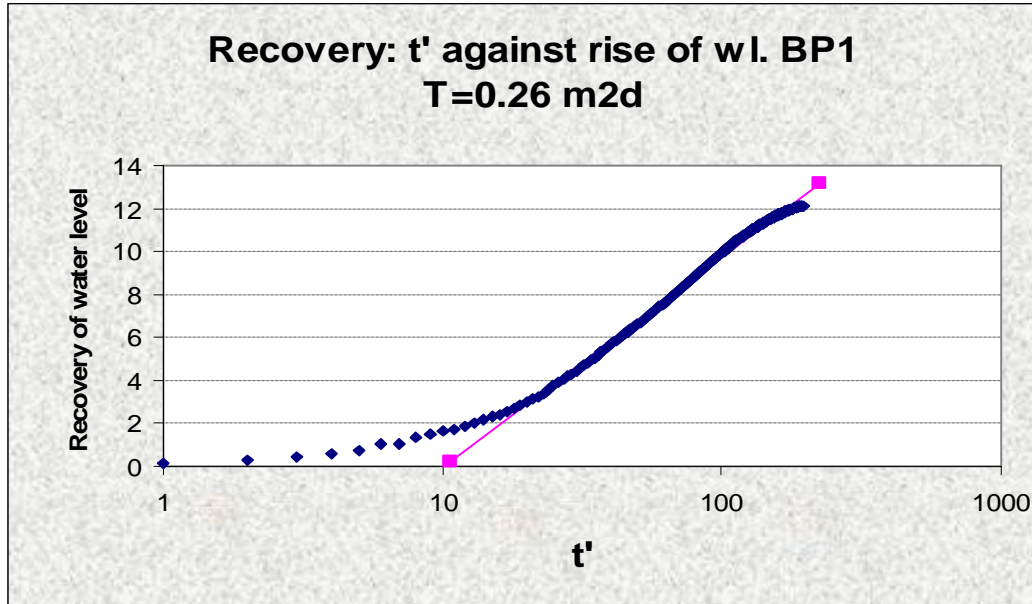


Figure 18: Analyses of pump test data using F-C. Recovery: Time against water level.

Table 4: Transmissivity values for the various new boreholes.

Borehole	T m <sup>2</sup> d (Cooper-Jacob)	Recovery T : ( $t'$ against rise of wl)
BP 1	0.24	0.26
BP 2	0.25	0.24
CHEV 1	0.81	0.88
ENGEN 1	0.31	0.36
ENGEN 2	0.51	0.37
RES 1	0.81	N/A
AVG	0.49	0.422

### 2.4.2 Darcy's Experiment

Darcy's Law states that the rate of flow through a porous medium is proportional to the loss of head and inversely proportional to the length of the flow path and is defined by the following equation:

$$Q = K i A,$$

Where;

Q = Discharge

I = Groundwater gradient

A = Area

K = Hydraulic Conductivity

Hydraulic conductivity is a measure of the ease with which water will pass through the earth's material; defined as the rate of flow through a cross-section of one square meter under a unit hydraulic gradient at right angles to the direction of flow (m/d).

A Darcy Experiment was done using the apparatus seen in Figure 19.



**Figure 19: Apparatus used in the Darcy Experiment.**

The experiment was performed for a duration of 16 hours due to the slow flow velocity. The discharge was measure by collecting the discharged water and weighing it. Readings were taken at 12 hour intervals. The discharge container was sealed so as to prevent any loss due to evaporation. The experiment was repeated twice and similar values were attained. The K value was calculated to be  $3.35 \times 10^{-3} \text{ m.d}^{-1}$ .

### 2.4.3 Groundwater Velocities

An average Transmissivity value  $0.4 \text{ m}^2/\text{d}$  was calculated. If a thickness of 10 meters is used, the hydraulic conductivity (K) for the unconsolidated material is in the order of  $0.04 \text{ m/d}$ . 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  $0.5 \text{ m/a}$ .

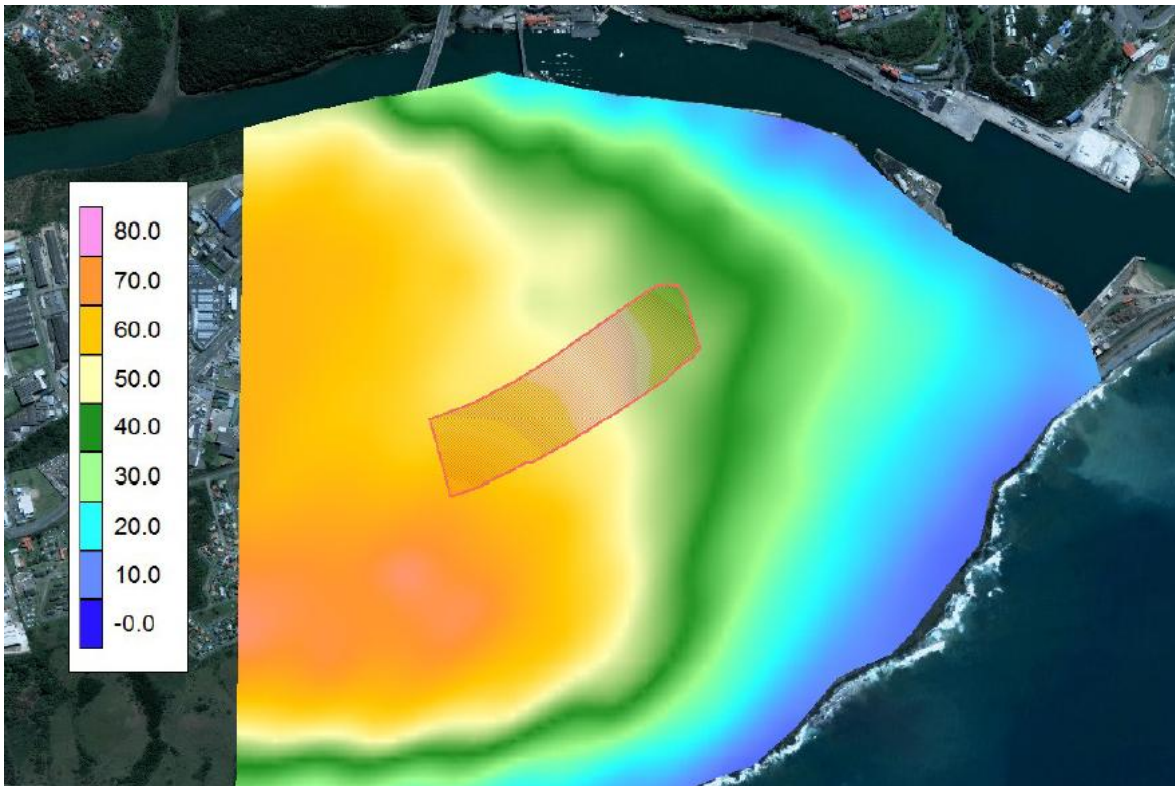


Figure 20: Bayesian water level contour map of the study area.



**Figure 21: Anticipated flow lines of the ground water under natural conditions. The flow lines are constructed from topography.**

## ***2.5 Phase distribution***

LNAPL contaminants generally exist in four phases namely the LNAPL phase, the aqueous phase (dissolved phase), gaseous phase and the solid phase (residual on aquifer material) (Newell, *et al.*, 1995). It is possible that in the unsaturated zone all four phases coexist. In the saturated zone NAPL contaminants coexist in the aqueous phase, solid phase and the NLAPL phase. The constituents may partition into the various phases depending on the environmental conditions (discussed later). See Figure 22: Partitioning of LNAPL in the vadose zone into the four potential phases. Here, Le Châtelier's principle together with Henry's Law constant play a vital role.

Le Châtelier's principle states that a system at equilibrium, when subjected to a perturbation, responds in a way that tends to eliminate its effect. What this

means is that the LNAPL components will always strive to be in equilibrium with the liquid and gaseous phase. For example, at a specific set of temperature and pressure conditions, the components will be in equilibrium but, in the vadose subsurface zone the temperatures are less than stable, thus making the phase distribution more complicated.

Henry's law constant is the partitioning coefficient between water and soil gas. The coefficients show the tendency for a contaminant to partition from one phase to another. These coefficients are dependant on the properties of the LNAPL and the aquifer material.

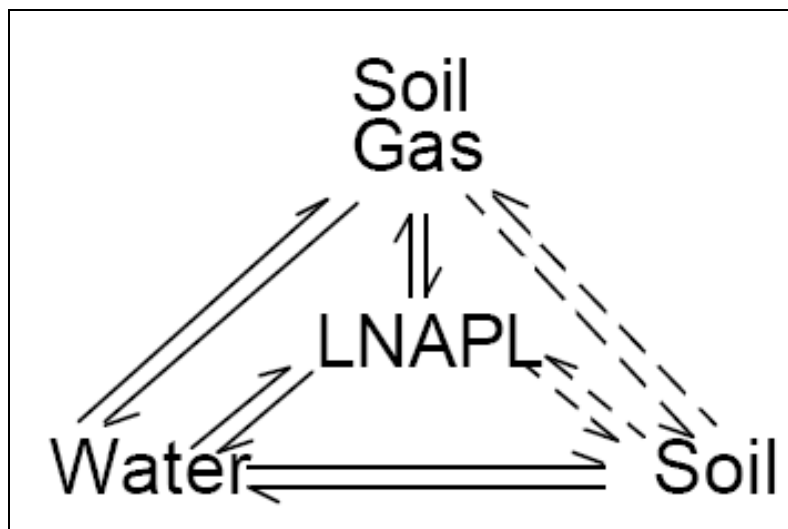


Figure 22: Partitioning of LNAPL in the vadose zone into the four potential phases.



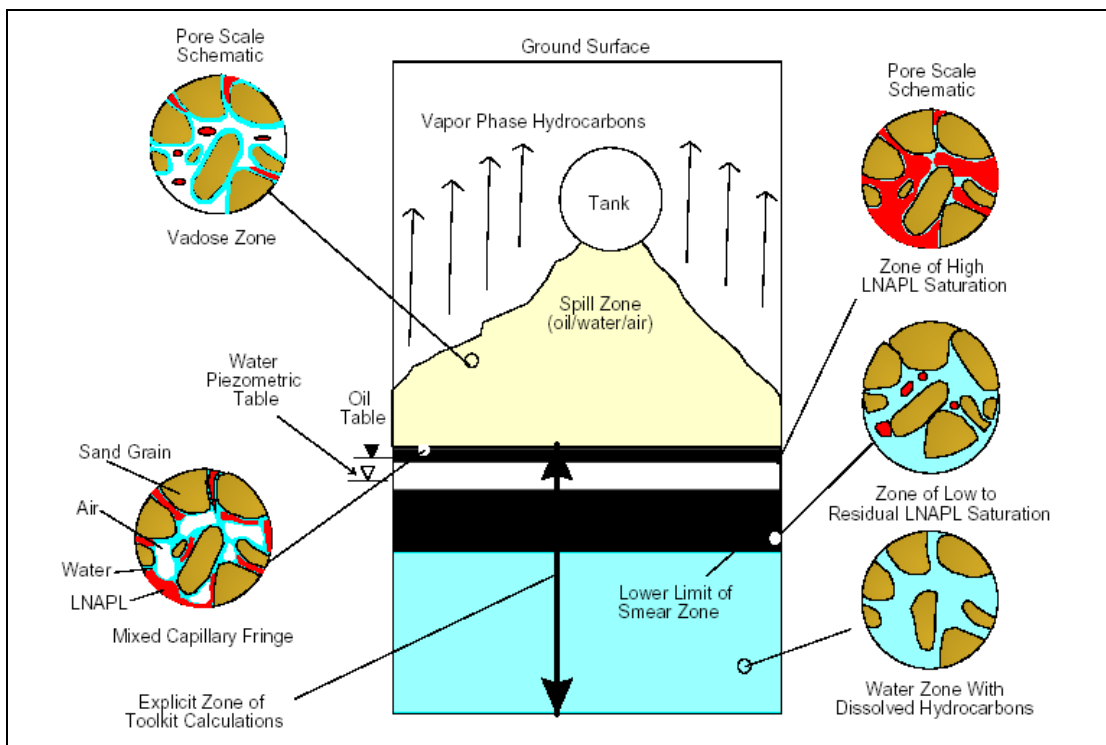
## **2.6 Saturated Zone**

Once the NAPL has been transported through the unsaturated portion below the contaminant source, these NAPL's will interact with the saturated aquifer in different manners depending particularly on the density of the contaminant and the saturation level of the soils.

Huntley and Beckett, 2001 provide the following overview of LNAPL transport processes below the vadose zone:

- If the release is sufficiently big enough in quantity to overcome the capillary forces of the porous media of the vadose zone, the LNAPL will continue to migrate downwards towards the capillary fringe. As the LNAPL encounters partial or completely filled pore spaces, its weight will cause it to displace the pore water until hydraulically the large vertical gradient through the vadose zone dissipates into a lateral gradient in the capillary and water table zones. The lateral movement is often retarded due to the resistance caused by water-wet materials which in turn causes mounding of the LNAPL.
- Once the constant release of LNAPL ceases, the resistive forces in the water wet sediments will equal those of the driving force of the LNAPL. The absolute stop in LNAPL movement will stop when it reaches field saturation, when the hydraulic conductivity of the LNAPL is zero. This leaves a mass of LNAPL that can potentially be further transported by means of secondary dissolved and vapour-phase transport. When the plume is stationary it only poses a threat to the environment only as a source of vapour phase and dissolved phase compounds.
- Over time there may be external factors that disturb the hydraulic equilibrium of the LNAPL. An example of this would be water table fluctuation that would cause a smear zone vertically throughout the hydraulic range.

- As soon as the LNAPL comes into contact with the capillary fringe or water table, certain components enter the water through dissolution, and a plume forms in the direction of the hydraulic gradient.
- For the biodegradable constituents of the plume, the dissolved phase continues to grow until it comes into equilibrium with the rate of biodegradation. At this point the plume stabilizes spatially. The portion of LNAPL that is not biodegradable continues to spread until an equilibrium is reached between the rate of dissolution from the LNAPL source area and rate of dispersion and dilution.
- As dissolution and volatilisation of these compounds continues the LNAPL becomes increasingly depleted in these compounds, resulting in a depletion of the concentration of these compounds at the source, and therefore results in the contraction of the dissolved plume phase. This process continues until the constituents are depleted and the dissolved phase of the plume disappears.



**Figure 23: Schematic of a LNAPL spill showing different zones of impact from the source (modified after White et al., 1996).**

## **2.7 Conclusion**

The project site is unique because of its very shallow aquifers and therefore closeness to the atmosphere. The project sites' pollution occurs mainly in the vadose zone. It was therefore necessary to observe some physical effects prevalent in the vadose zone in order to characterise the LNAPLs in this environment. The most prevalent physical factors discussed included temperature, phase distribution, water levels, porosity and the hydraulic parameters.

It was found that temperature played a major role in the volatilisation of certain constituents of LNAPLs into the atmosphere due to vapour pressure. A contributing factor to temperature playing a major role is the fact that the project site is located in a warm and humid climate area.

The water levels at the project site are very shallow. A correlation between the water levels and the topography exists. With the use of Bayesian interpolation an accurate water level contour map was constructed. This was used in conjunction with the hydraulic testing to produce a map showing the anticipated flow lines of the groundwater.

The effects of phase distribution are dependant on the environmental conditions prevalent in the vadose zone. LNAPL can partition into the vapour phase at the project site given the correct conditions, which are in fact suitable for this partitioning to occur.

The saturation of the vadose zone is a determining factor in the movement of LNAPLS. The more saturated the vadose zone is, the less movement will be possible. This is due to the resistive forces of the wet sediments. The dissolved phase does however continue to move in the direction of the groundwater gradient. Natural biodegradation and volatilisation will continue to deplete the constituents until the plume is immobile and slowly diminishes.

## **3. Soil and Geology Characterisation**

### **3.1 Soils**

Soils form the interface boundary between the atmosphere and the hard rock making up the lithosphere of the earth. The compositions of soils can vary greatly. The composition of soils are influenced by many physical factors, these include factors such as climate, adjacent geology and vegetation.

Soil is a multifaceted combination of eroded rock, mineral nutrients, decaying organic material, water, air and micro organisms. The formation of soils occurs when sediments are deposited, when life forms decay and when rocks crumble due to weathering. As the deposited soils become older they are said to be more 'mature'. Mature soils are arranged in layers formally known as 'horizons', these are different layers or zones each with their own distinct characteristics. A 'cross-sectional view of the soil horizon is known as a profile. Generally speaking, most mature soils have three horizons. (<http://www.deat.gov.za/Enviro-Info/prov/soil.htm>)



**Figure 24: Excavation at the project site showing the unconsolidated layers. Water fingers can be observed on the bottom sand layer.**

Soils' grain sizes vary greatly and the different variances and combinations of grain sizes give rise to different classifications of soils, which in turn have different structures and permeabilities.

Soil type is a factor of remediation. The role the soil plays is integral in the project site. The grain size is the major role player in this situation. The various soil characteristics and their influence will be discussed in the following section.

There are many ways in describing the physical properties of soils, these include:

- texture in general,
- structure,.
- shape of the grains,

- grain size,
- colour and
- mineralogical composition.

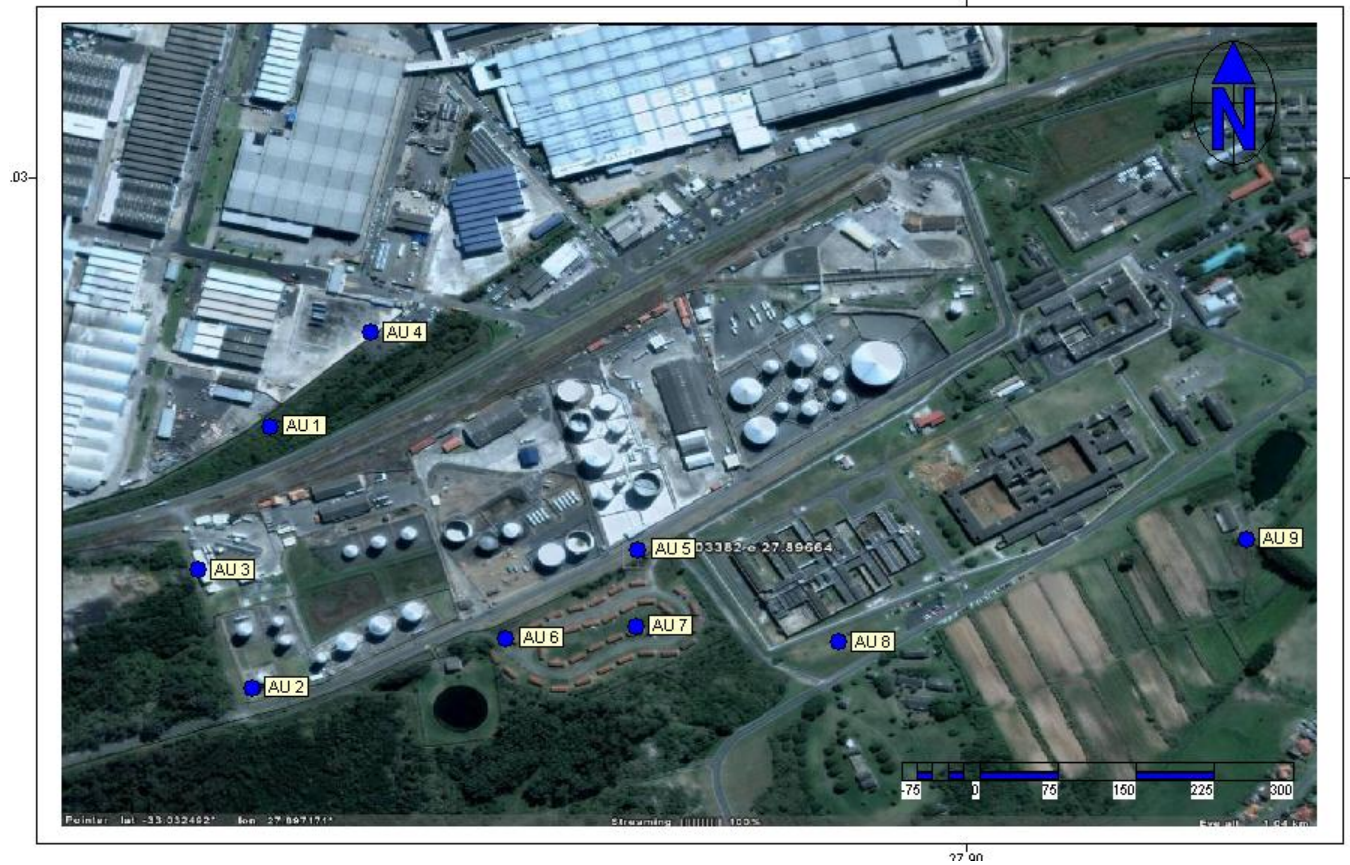
From these physical parameters, a host of deductions can be made. Each of these properties will be described with relevance to the study are in the following section.

Soil samples were taken at various locations around the site. Several analyses were done on the samples; these include XRF (X-Ray Fluorescence), XRD (X-Ray Diffraction) and a soil texture analysis. Due to safety reasons no samples were taken within the boundaries of the project site. Samples were taken at one meter intervals to a depth of three meters. A motorized auger was used for the sampling. See Figure 25.



**Figure 25: Author with removed in-situ sample. Tank farm can be seen in the background.**

A total of ten samples were taken. Samples were placed in marked airtight plastic bags and relevant information was noted. The locations of the auger sampling points can be seen in Figure 26.



**Figure 26: Location of auger sampling points.**



**Figure 27: Samples placed in airtight plastic bags and relevant data noted.**

### **3.1.1 Texture**

Soil texture refers to the term used to assign proportional distributions of grain sizes of mineral sizes in the soil. Organic matter is not included. The mineral or grain sizes vary greatly from those barely distinguishable by the unaided human eye, to those easily seen and distinguished by the unaided human eye. According to their sizes the soils are divided into separates. (Brown, R.B Institute of Food and Agricultural Sciences, University of Florida, Gainesville, FL 32611-0510).

Permeability is affected by soil structure: how the particles are organized and clumped together. Soils vary in their contents of gravel, sand silt and clay. The proportion of the various different sizes of grains is indicative of the texture.



Soils' texture can be described by the use of a soil texture diagram as shown in Figure 28. The soils at the project site are classified as sandy loam or sandy clay loam.

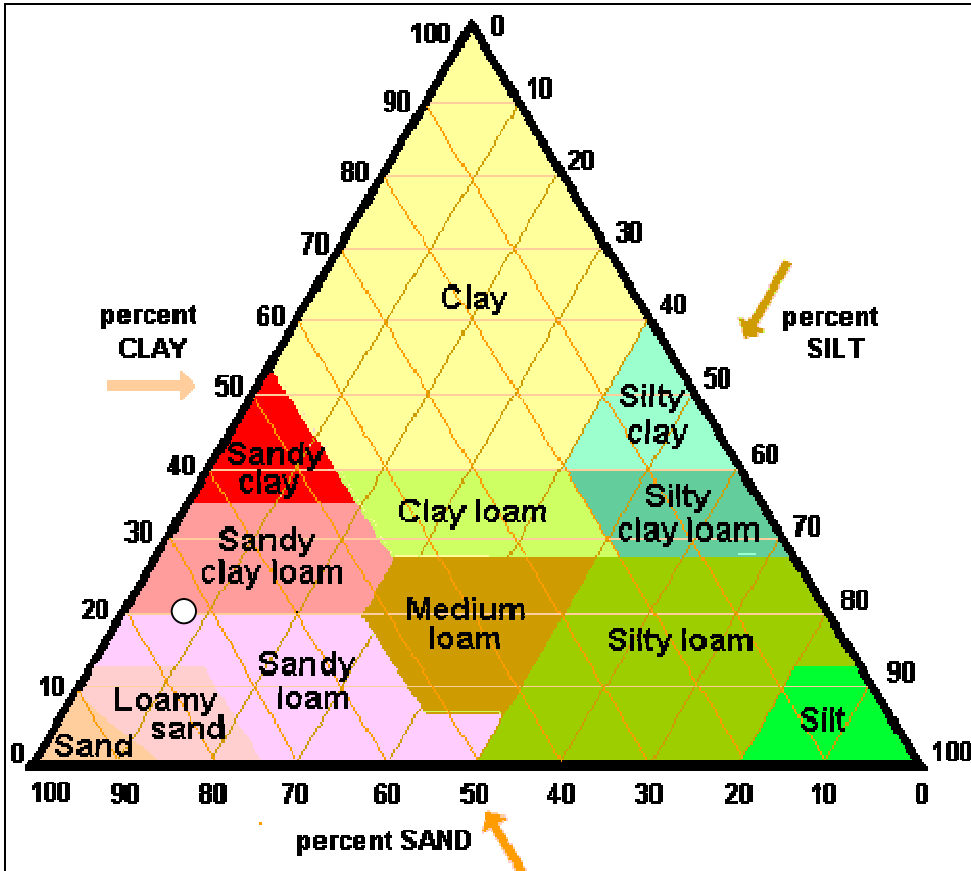


Figure 28: Ternary diagram for soil textures showing the texture of the project site's soil. (<http://www.oneplan.org/Images/soilMst/SoilTriangle.gif>).

The effects of texture on saturated hydraulic conductivities are shown in the Table 4.

**Table 5: Hydraulic conductivities of different soil types. ( Usher, *et al.*,2008).**

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

The results obtained from the soil texture analysis done by the IGS are shown in the table below:

**Table 6: Results of soil texture analysis showing that the soil is classified as a sandy loam.**

Soil Texture Analyses							
Client	Kevin						
Sample nr.	Lab. nr.	4 min.	6 hour	Clay	Silt	Clay Silt	Sand
AU1	1	9	5	4	8	12	88
AU2	2	13	10	14	6	20	80
AU3	3	21	19	32	4	36	64
AU4	4	13	10	14	6	20	80
AU5	5	16	12	18	8	26	74
AU6	6	24	17	28	14	42	58
AU7	7	21	13	20	16	36	64
AU1B	8	15	9	12	12	24	76
AU1C	9	15	12	18	6	24	76
AU2B	10	16.5	14	22	5	27	73
AU2C	11	6	4	2	4	6	94
AU4B	12	7.5	5	4	5	9	91
AU4C	13	21	18	30	6	36	64
AU7B	14	23	20	34	6	40	60
AU7C	T2	11	9	12	4	16	84
AU3B	T3	30	21.5	37	17	54	46
Average				18.8	7.9	26.75	73.25

### 3.1.2 Structure

A fundamental property of soils is the structure, it is described the aggregates in soil in terms of shape. The structure is described in terms of the shape of the soil structures in terms of how the soils are “packed” or the “pattern” they follow. The structure influences many aspects of how the soil will handle various conditions, such as water movement, heat transfer, aeration and porosity. Farming activities greatly influence the structure of soils. The primary soil classifications of soils can be seen in the figure below.

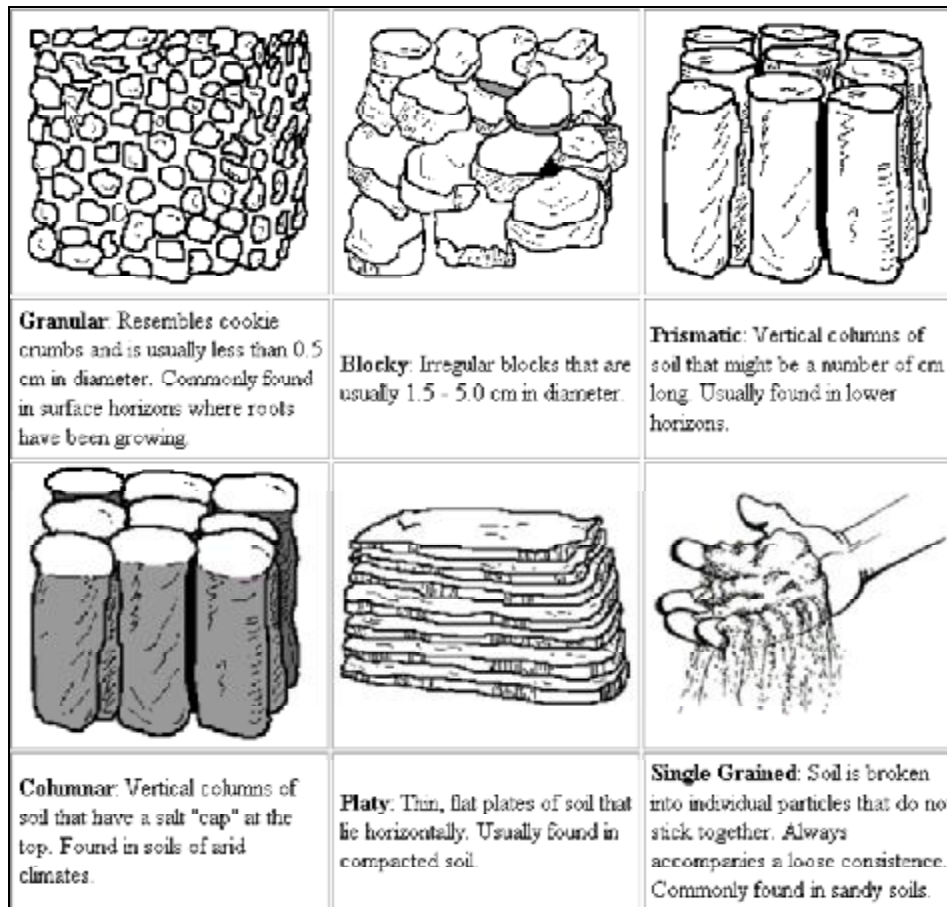


Figure 29: Primary classification groups of soil structure.

### 3.1.3 Shape of grains

The shape of the grains is described according to the relationship between the three axes, as well as the abrasion the grain has experienced. There are two concepts regarding the shape of grains. (Department of Geology, University of the Free State - Advanced Sedimentology notes Mr. L Nel, 2005)

1. Sphericity – Sphericity can best be described as the relationship between the three axes of the grain. Sphericity is dependant on the physical properties of the original material from which it originated and the distance of transportation. The shape of the grains gives to some extent an indication of the depositional environment. Grains from beaches are mainly disc shaped; those from river beds generally rod shaped, whereas

clasts from glacial deposits have a flat-iron shape. (Department of Geology, University of the Free State - Advanced Sedimentology notes Mr. L Nel, 2005).

2. Roundness – The roundness of a grain can be defined as the average ratio between the average radii of the rounding of the corners and the sides and the radius of the contained sphere. A perfectly round grain will thus have a roundness of 1.00 whereas more angular grains will have lower values. Values for roundness are given as rho units. This method is very tedious and roundness of particles as usually estimated. For this purpose five classes were defined: angular, subangular, subrounded, rounded and well rounded.

#### **3.1.4 Grain-size**

Grain size is a function of the transportation process. Grain size analysis can be done where the diameters are measured by means of sieves or direct measuring. In consolidated material the diameter is measured by means of a microscope. Grain size is a direct contributor to capillary rise due to the related pore spaces, and will be discussed in forthcoming sections. Several classifications have been used in the past, the Wentworth scale is still the most universally acceptable and efficient and can be seen in Figure 30.

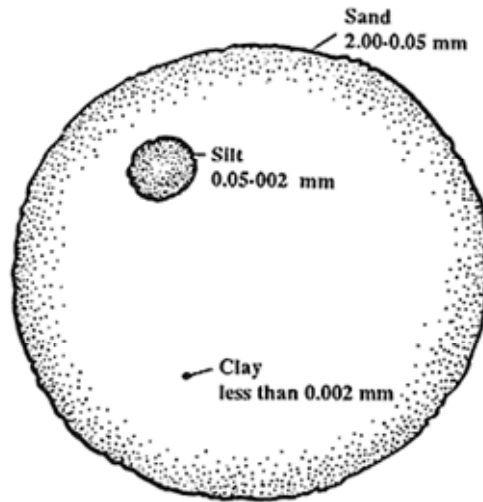
Millimeters (mm)	Micrometers (μm)	Phi (φ)	Wentworth size class	Rock type
4096		-12.0	Boulder	Conglomerate/ breccia
256		-8.0	Cobble	
64		-6.0	Pebble	
4		-2.0	Granule	
2.00		-1.0	Very coarse sand	
1.00		0.0	Coarse sand	Sandstone
1/2	500	1.0	Medium sand	
1/4	250	2.0	Fine sand	
1/8	125	3.0	Very fine sand	
1/16	63	4.0	Coarse silt	
1/32	31	5.0	Medium silt	
1/64	15.6	6.0	Fine silt	
1/128	7.8	7.0	Very fine silt	
1/256	3.9	8.0	Clay	Claystone
0.00006	0.06	14.0		

Figure 30: Udden-Wentworth grain size classification table 1922. ([http://www-odp.tamu.edu/publications/204\\_IR/chap\\_02/c2\\_f2.htm](http://www-odp.tamu.edu/publications/204_IR/chap_02/c2_f2.htm))

The subdivision can be made simplified and refined by using the phi scale. Thereby 4mm has a value of  $-2\phi$  and 1/8mm a value of  $3\phi$ . For the conversion from fractions of a mm to the phi scale the following formula is used:

$$\text{Phi } (\phi) = -\log_2 \text{ diameter (mm)}$$

A histogram of the grain size distribution can show certain characteristics and is the most elementary depiction of grain-size distribution. The classification terms are explained below:



**Figure 31: A visual reference for the relative grain sizes of sand, clay and silt (Nel 2005).**

A grain size analysis was done on the samples collected at the project site. An analysis was done for every depth interval. I.e. 1 meter, 2 meters and 3 meters.

The samples were dried for a period of 16 hours in an oven at 100 degrees Celsius. The samples were then made smaller with the use of a splitter box, see figure below.



**Figure 32: Splitter box used in grain-size analyses.**

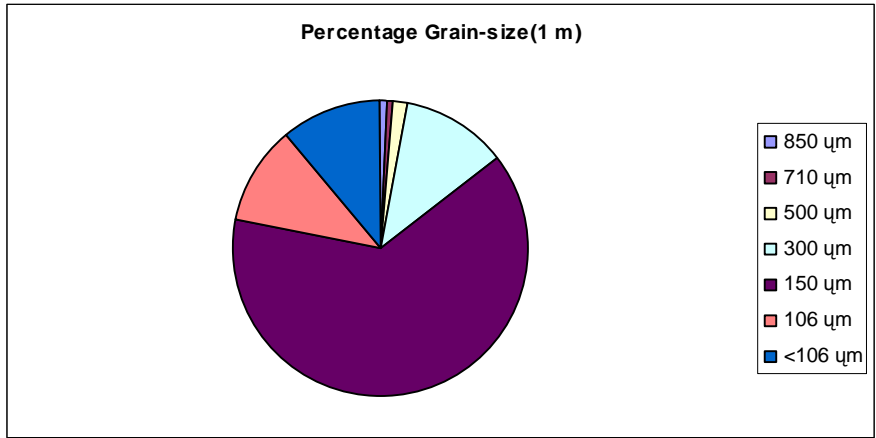
Once the samples were split to a manageable size, the samples were weighed and the mass noted. The sample was then shaken through a series of sieves for duration of 20 minutes. An electrical shaker was used. See Figure 33.



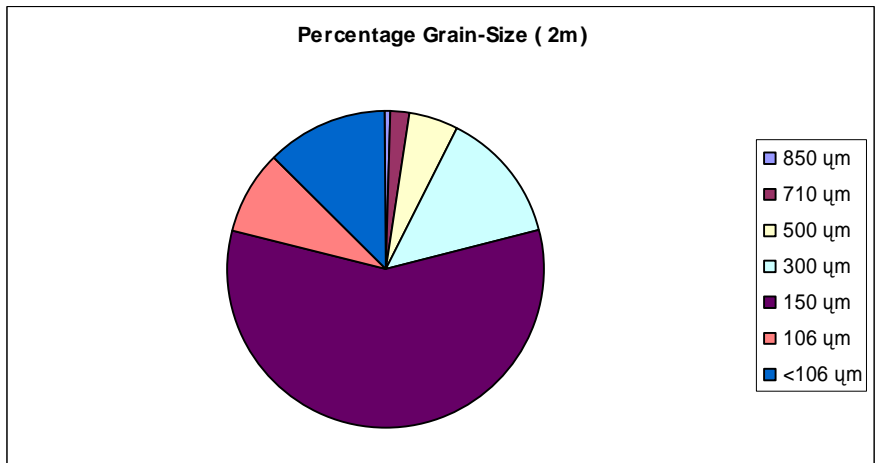
**Figure 33: Sieve shaker used in the grain-size distribution analysis.**

The remaining sample above each sieve as weighed and plotted as a percentage of the original mass. The sieve diameters were as follows: 800 $\mu\text{m}$ , 710 $\mu\text{m}$ , 500 $\mu\text{m}$ , 300 $\mu\text{m}$ , 150 $\mu\text{m}$ , 106 $\mu\text{m}$  and <106 $\mu\text{m}$ . The results can be seen in Figure 34, Figure 35 and Figure 36.

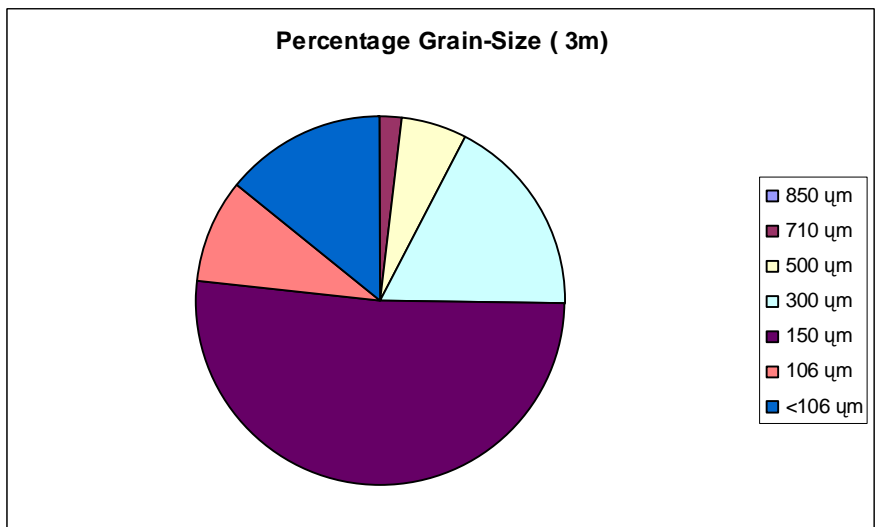




**Figure 34: Grain-Size distribution at 1 meter below the surface.**



**Figure 35: Grain-Size distribution at 2 meters below the surface.**



**Figure 36: Grain-Size distribution at 3 meters below the surface.**

From the figures above it can be seen that the soils can be classified as very fine sand, and that the soils are well sorted.

### 3.1.5 Colour



**Figure 37: Photograph taken at the project site showing red clay.**

The colour of a soil can be primary or secondary. Secondary colours originate by weathering and therefore it is necessary that when the colour of a soil is to be described, fresh samples are to be studied. A colour chart is necessary to ensure uniformity in the description. The colour is described by the use of a colour chart.

The most important pigments in soils are the oxides of iron and organic matter. The colour of soil containing Fe oxides, depends on the oxidation condition of the Fe and not necessarily on the amount of Fe in the soil. The amount of organic

material in a soil is largely dependant on the depositional environment. It is only the preservation of the organic matter during and after the deposition that contributes to the dark colour of sediment. At this site, the red condition indicates oxidizing conditions in the depositional environment. The climate can vary from humid and warm to warm arid.

Oxygen is used as an electron acceptor by aerobic organisms in aerobic soils, as it releases the most energy. When the soil is saturated with water moist air is expelled from the soil. Aerobic bacteria will die due to the lack of O<sub>2</sub> but facultative and obligatory bacteria can use other electron acceptors. These electron acceptors release increasingly less energy to micro organism and therefore is a strict sequence in which electron acceptors are reduced in the absence of O<sub>2</sub> (Van Huyssteen, 2008). This sequence can be seen in Table 7.

The specific sequence of Redox reactions described in Table 7, result in a unique soil morphological indicators developing in the soil due to the prevalent soil water regime during soil formation. For example, soil that never or seldom saturates with water will never be reduced (Van Huyssteen, 2008).

**Table 7: Order of utilization of electron half-reactions in soils and associated potentials (Bohn et al., 2001).**

Reduction half reaction	Redox potential (mV)
$O_2 + 4e^- + 4H^+ = 2H_2O$	600 to 400
$2NO_3 + 10e^- + 12H^+ = N_2 + 6H_2O$	500 to 200
$MnO_2 + 2e^- + 4H^+ = Mn^{2+} + 2H_2O$	400 to 100
$Fe(OH)_3 + e^- + 3H^+ = Fe^{2+} + 3H_2O$	
$FeOOH + e^- + 3H^+ = Fe^{2+} + 2H_2O$	300 to 100
$Fe_2O_3 + 2e^- + 6H^+ = 2Fe^{2+} + 3H_2O$	
$SO_4 + 8e^- + 10H^+ = H_2S + 4H_2O$	0 to -150
$2CO_2 + 8e^- + 8H^+ = CH_4 + 2H_2O$	-150 to -220
$2H^+ + 2e^- = H_2$	-150 to -220

### 3.1.6 Mineralogical Composition

Grains consist of mineral particles (quartz, feldspar, clay, carbonate), and lithic and organic fragments. (GLG 224 notes - Advanced Sedimentology Mr. L Nel)

The mineralogical composition of a soil is dependant on the source rock, depositional environment and current physical conditions. The table below shows the mineralogical compositions of samples taken around the project site. The locations of the sampling positions can be seen in Figure 26. The analyses as done by means of XRD .The raw data can be seen in appendix A.

**Table 8: Mineralogical compositions of Augured Samples**

	Quartz	Montmorillonite	Hornblende	Plagioclase
AU2A	XX			
AU3A	XX			
AU3B	XX	x		
AU4A	x	XX	X	XX
AU4B	x	XX	X	XX
AU4C	x	XX	X	XX
AU5A	XX			
AU5B	XX	x		
AU8A	XX			
AU8B	XX	x		
AU9A	XX			
AU9A1	XX			
AU9B	XX			
AU9C	XX			

**Table 9: Reference table for mineralogical compositions above.**

Dominant	XX	>40%
		10 -
Major	X	40%
Minor	x	2 - 10%
Accessory	<x	1 - 2%
Rare	<<x	<1%

From the data obtained from the XRD and XRF analyses it is clear that the soils are dominated by Quartz, which is indicative of typical sand.

### **3.2 Capillary Rise in Soils**

Capillary flow in soils is the primary mode of water movement. Capillary pressure is the pressure difference across the interface between the wetting and non-wetting phases and is often expressed as the height of an equivalent water column. It is a measure of the relative attraction of the molecules of a liquid (cohesion) for each other and for a solid surface (adhesion). The capillary pressure of the largest pore spaces must be exceeded before the non-wetting fluid (generally NAPL) can enter the porous medium. The minimum pressure required for the NAPL to enter the medium is termed the entry pressure. (Newell, *et al.*, 1995).

Capillary pressure increases with decreasing pore size and increasing interfacial tension. Capillary forces that hold residual LNAPL are relatively strong, although they can be overcome to some degree by viscous forces applied by groundwater flow. Complete mobilisation by the sole use of groundwater flow is almost impossible. The Hydraulic gradient is so high that it becomes unreasonable to attempt to “flush” and residual LNAPL. (Newell, *et al.*, 1995).

The table below shows the capillary rise for benzene at 20°C as given for particles with various diameters in saturated and unsaturated conditions.

**Table 10: Theoretical Capillary rise for benzene at 20 °C in saturated and unsaturated conditions.**

Condition	Surface Tension	Particle diameter		Density	Grav. Const.	Capillary Height Rise	
		Min (mm)	Max (mm)			Min (m)	Max (m)
	$\gamma$ (dyn/cm)			(g/cm <sup>3</sup> )	(m/s <sup>2</sup> )		
Saturated	35	1	2	0.79	9.80665	0.018	0.009
	35	0.5	1	0.79	9.80665	0.036	0.018
	35	0.25	0.5	0.79	9.80665	0.072	0.036
	35	0.1	0.25	0.79	9.80665	0.181	0.072
	35	0.05	0.1	0.79	9.80665	0.361	0.181
	35	0.002	0.05	0.79	9.80665	9.035	0.361
	35	0.0001	0.002	0.79	9.80665	180.709	9.035
Unsaturated	29	1	2	0.79	9.80665	0.015	0.007
	29	0.5	1	0.79	9.80665	0.030	0.015
	29	0.25	0.5	0.79	9.80665	0.060	0.030
	29	0.1	0.25	0.79	9.80665	0.150	0.060
	29	0.05	0.1	0.79	9.80665	0.299	0.150
	29	0.002	0.05	0.79	9.80665	7.487	0.299
	29	0.0001	0.002	0.79	9.80665	149.730	7.487

In Figure 38 and Figure 39, 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 180 meters, although for benzene in commonly occurring soils the maximum expected increase in height would be 9 meters. This would be because there is interplay between diffusion and capillary action in the vadose zone. Another factor is that most soils are not homogeneous and therefore the rise will be further reduced.

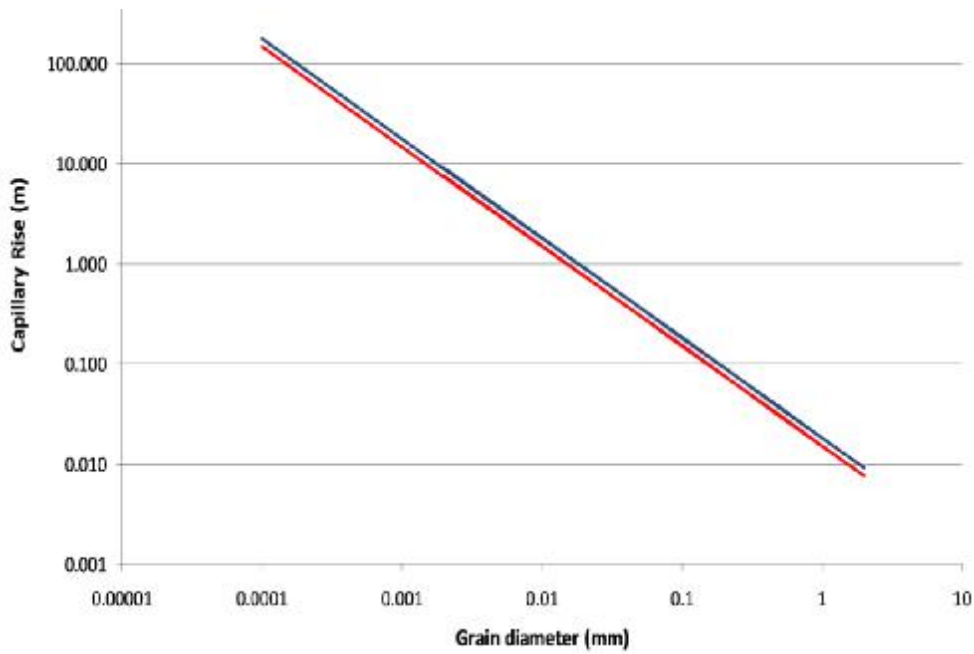


Figure 38: Theoretical capillary rise as an effect of grain size diameter and pore size.

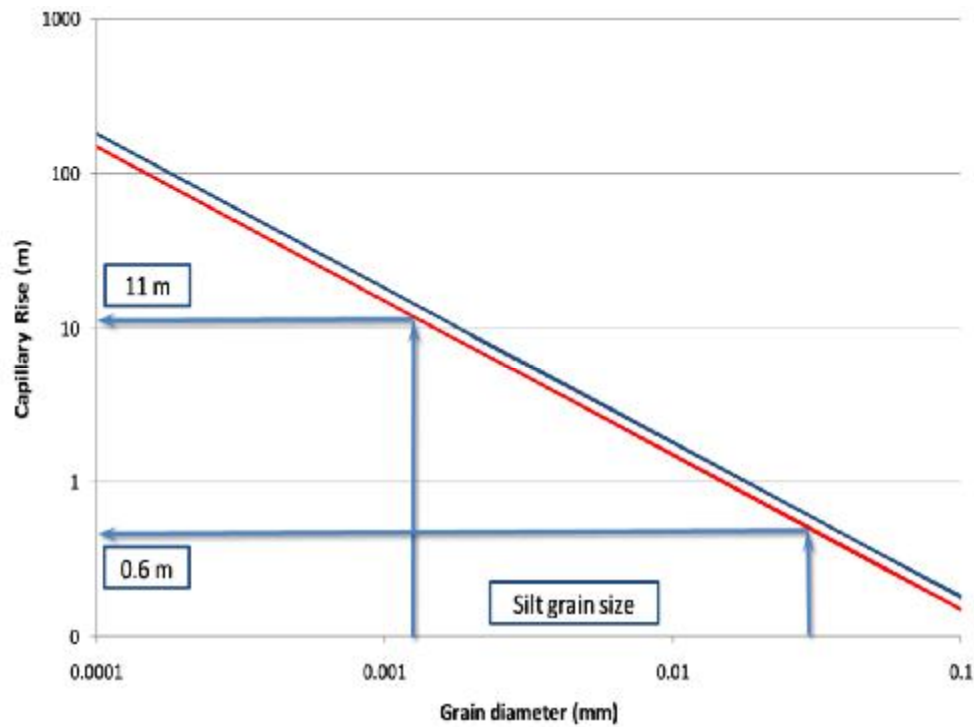


Figure 39: Magnified view showing capillary rise for the various grain sizes.

### **3.3 Geology**

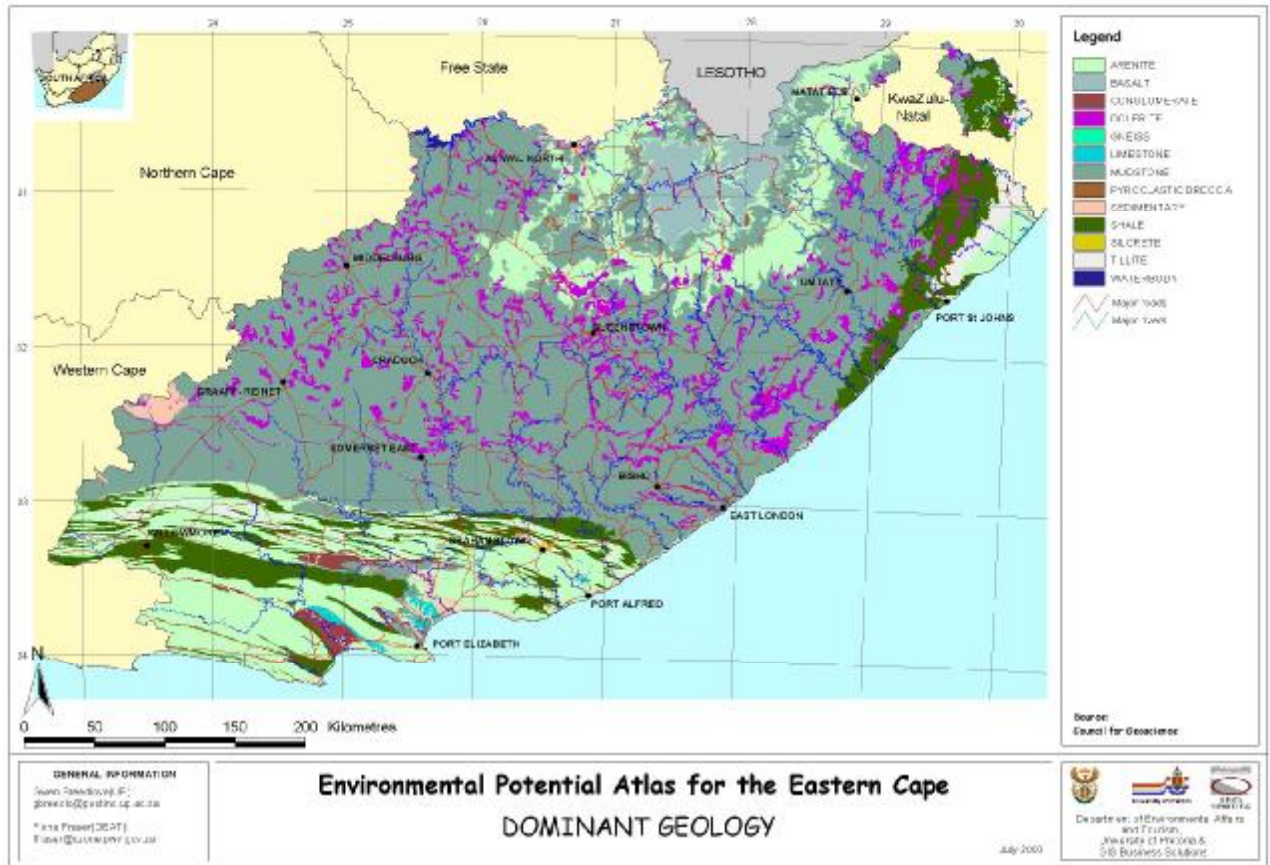
Geological mapping was done as part of requirements for a report to the Water Research Commission for the Initial Field Results during October 2008. Relevant data will be discussed and illustrated. The geological survey was done by Mr. Brent Cock of SRK Consulting.

The underlying geology is characterised by alternating grey, moderately to well sorted, fine to very fine-grained, ultralithopathic 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 (Council for Geoscience, Geological Survey of South Africa: The Geology of the Grahamstown area. Johnson et al.,1994) The geology as seen from across the river can be seen in Figure 40 below:





**Figure 40: Geology below the project area. Tank farm can be seen in the background.**



**Figure 41: Map showing the generalised geology of the Eastern Cape coastline.**

A geological mapping exercise was carried out in order to determine the orientation of the dominant joint sets that may have a potential influence on the preferred groundwater flow direction. Outcrop was minimal and could only be done to the north of the site on road cuttings. Structural geology data was gathered at 8 locations, four road cuttings and outcrop along the coastline below the West Bank Golf club.

Figure 42, Figure 43 and Figure 44 show the locations of where the geological mapping and investigations were done.

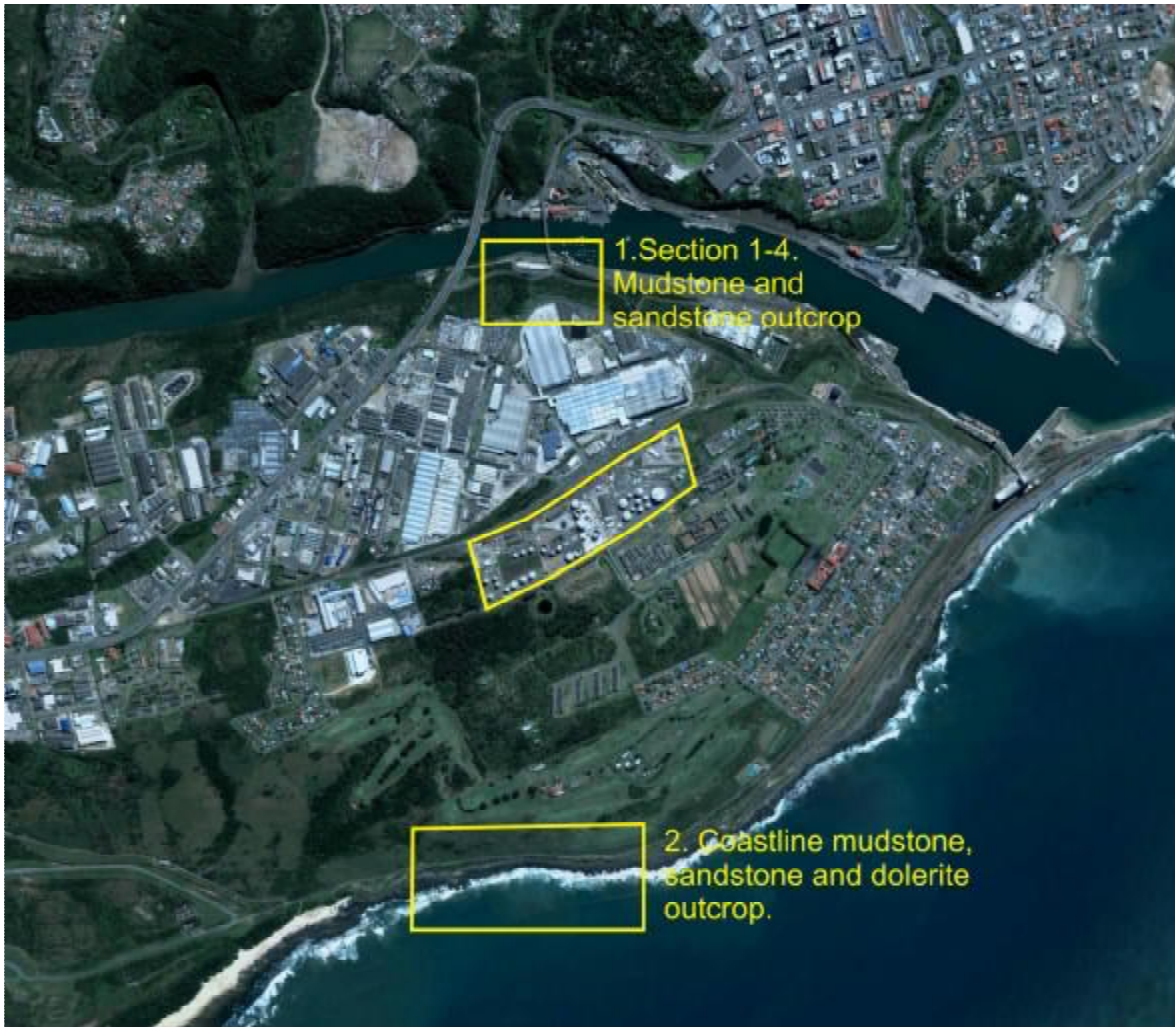


Figure 42: Satellite image showing the locations of where geological mapping was done.



Figure 43: Section 1 to 4 of geological mapping/ sections.



Figure 44: Location of coastline outcrop.

### **3.3.1 Geological Sections**

- The dominant joint orientations dip at subvertical inclinations towards the east, south and southwest;
- The subordinate joint sets dip at subvertical inclinations towards the north, northeast, southeast, west-northwest and northwest;
- A steep north-northeast dipping joint set is present in the sandstone unit but absent in the mudstone;
- A similar trend is applicable to the mudstone where steeply-dipping south-southwest and north-northwest joint sets are present but absent in the sandstone units; and
- Two fault planes, one cutting through a sandstone unit, with prominent yet weathered lineations were measured in Section 1. The fault planes dip towards the northeast ( $51^{\circ}$ ) at shallow angles ( $29^{\circ}$ ). The lineations plunge towards the northeast at shallow angles – the sense of movement is difficult to determine due to the weathered nature of the slickensides. (Usher et al.,2008).



Figure 45: Section 4 – Contact between mudstone and cross bedded sandstone (insert).

### 3.3.2 Coastline Geology

- The dominant joint orientations dip at subvertical inclinations towards the northeast, south, southwest and west.
- The subordinate joint sets dip at subvertical inclinations towards the north, east, southeast, south-southwest and northwest;
- A steep north-northwest dipping joint set is present in the sandstone unit but not in the mudstone;
- Steep north-northeast, south-southeast and south-southwest dipping joints measured within the dolerite sill are absent in the mudstone/sandstone sequence;
- The dolerite sill is interpreted to have a thickness in excess of 200 m.

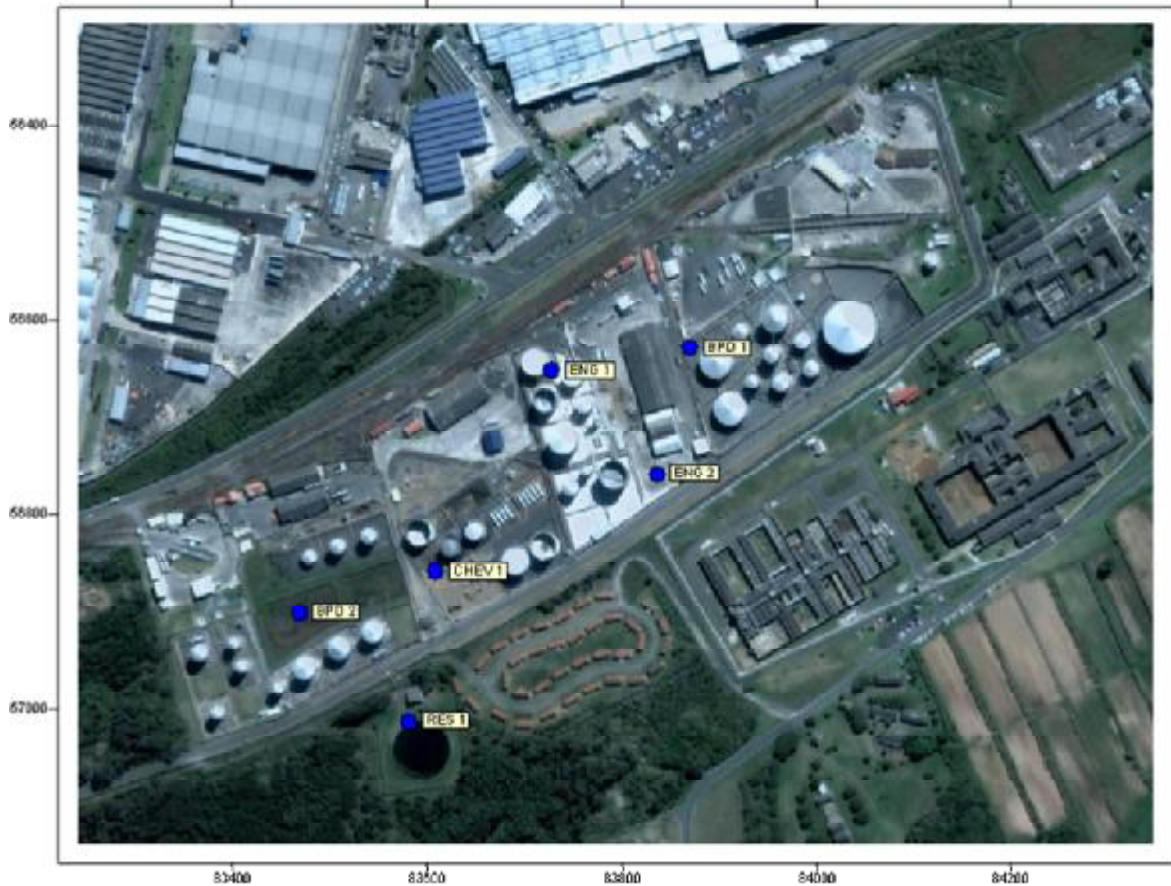


**Figure 46: Coastline -Contact between mudstone and sandstone with rounded to subrounded dolerite boulders in the foreground.**

### ***3.3.3 Percussion Drilling***

The air percussion drilling method was used to drill six new boreholes within the site area. The percussion drilling technique utilizes the method of pulverizing the material at the bottom of the hole by means of a specialised bit. Most percussion drills are powered by compressed air. Percussion drills are best suited for moderate to hard rock. The advantage of percussion drilling is that the method is relatively fast, no water is required and relatively inexpensive. The running costs are inexpensive, although the parts are expensive. The disadvantages are that the boundaries between geological layers cannot be precisely located. The fact that percussion drilling makes use of high pressure air jets in the hole, the majority of VOC's are lost due to vaporisation,

As part of the invasive part of the investigation it was decided to have 6 new boreholes drilled in and around the site. Boreholes are installed to evaluate subsurface stratigraphic, hydrogeologic and contaminant conditions.



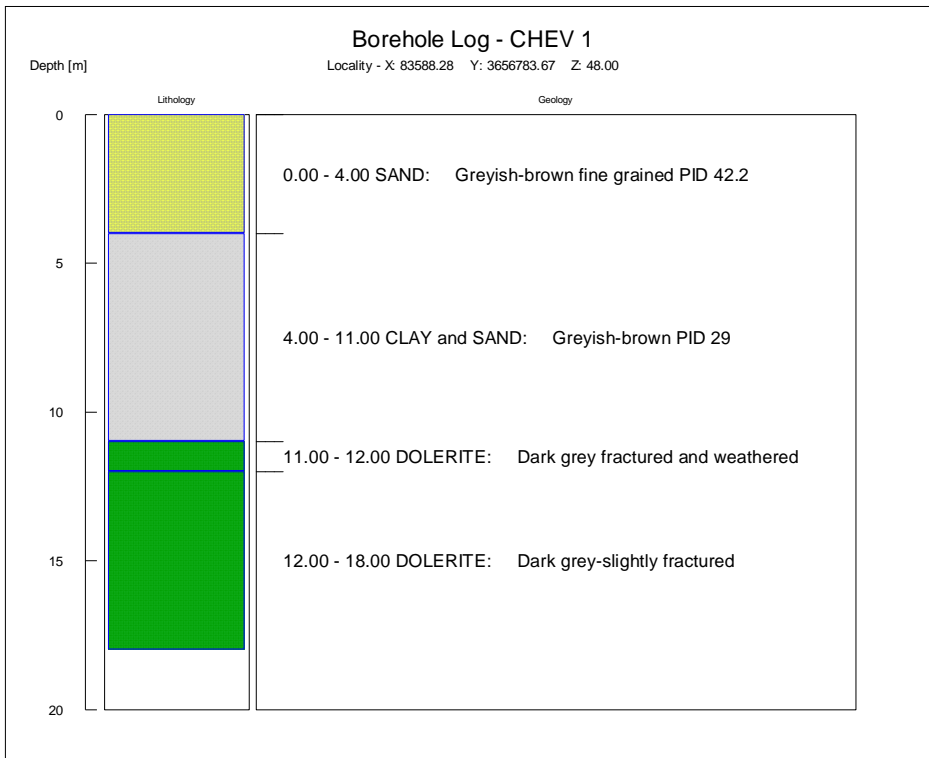
**Figure 47: Location of new boreholes drilled additional to the pre-existing boreholes.**

The boreholes were drilled to depths of between 14 and 30 meters. All boreholes were cased down to bedrock with perforated casing, either PVS or steel. All boreholes were capped and given a sanitary seal on the surface. Generally the lithologies consisted of a sandy/clayey layer on top followed by fresh dolerite. Water strikes were encountered at the upper clay layer and the contact with the bedrock.



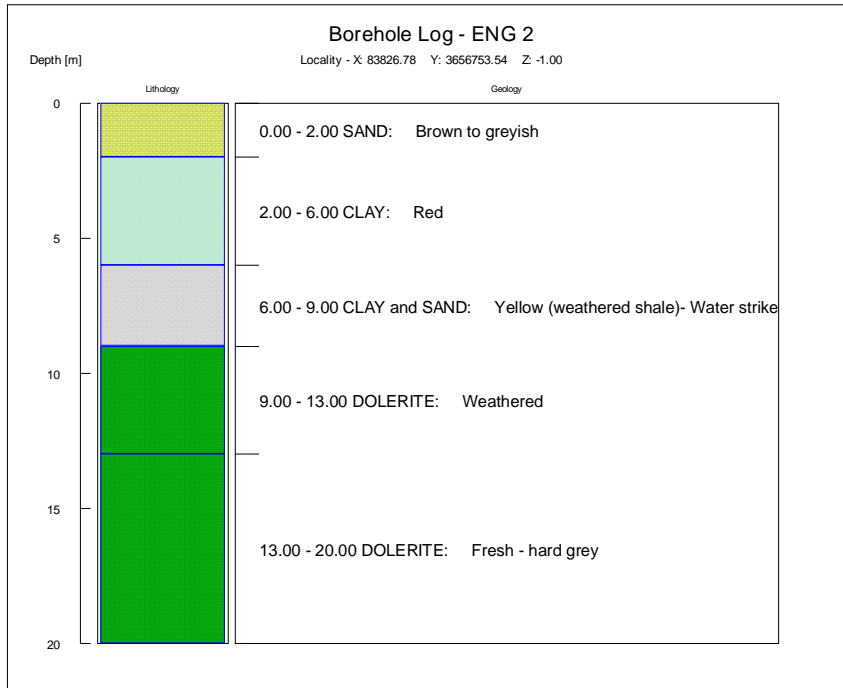


**Figure 48: Percussion method used at the site.**



**Figure 49: Borehole log for CHEV 1.**

Borehole CHEV1 was drilled adjacent to borehole ELD 18 because ELD 18 was the only borehole containing free phase. After some time, free phase was also apparent in borehole CHEV 1.



**Figure 50: Borehole log for ENF 2.**

Borehole ENF2 was drilled to the south of ENO1. This is the only borehole where the samples, although very weathered, showed evidence of the underlying shale formation between 6 and 9 meters below surface.



**Figure 51: Drill samples at ENO 2, samples taken at 1m intervals.**

### ***3.4 Geophysics***

The geophysical technique used at this site was the ERT (Electrical Resistivity Tomography).

The primary use of geophysics at this particular site was to substantiate the results obtained from the drilling and to attempt to detect the LNAPL plume. The geophysical technique used was not able to delineate the LNAPL plume due to the fact that LNAPL simply distorted the data due the LNAPL being a good conductor.

It was found that the overburden was made of sand (Resistive layer  $> 200 \Omega\text{m}$ ), with sand-clay or clay (conductive layer  $< 40 \Omega\text{m}$ ) overlaying. The

sedimentological sequence is underlain by a fractured dolerite sill (Resistive layer > 200  $\Omega$ m).

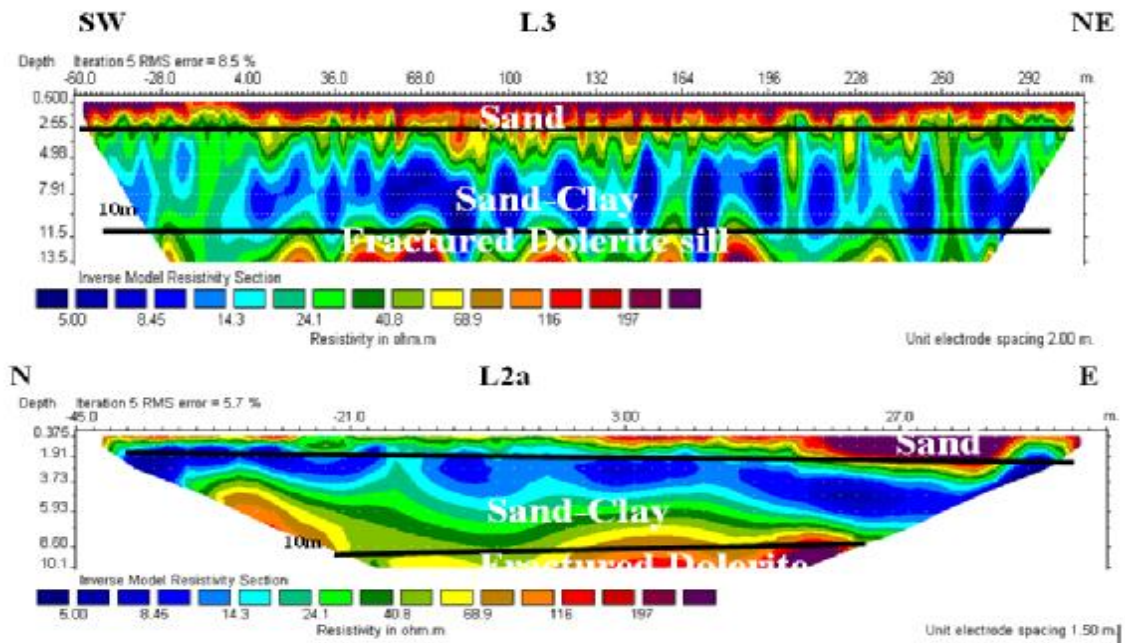


Figure 52: Example of the geophysical results obtained from the project site.

### **3.5 Conclusion**

In order for a complete geological and soil classification of the project site, it was necessary to drill numerous auger holes and percussion boreholes.

Soil samples were analysed in terms of texture, grain size, structure, grain-shape, colour and mineralogical composition. The soils texture is classified as sandy loam. According to grain size classification the soils are classified as well-sorted very fine sand. Due to the fact that the soils consist of a large amount of very fine sand, the capillary rise should be big. It must be noted that the capillary rise shown in the text is a theoretical portrayal. The XRF and XRD analysis show that the soil is made up generally of quartz and minor amounts of clay minerals such as montmorillonite, hornblende and plagioclase.

Six boreholes were drilled additional to the pre-existing boreholes. Borehole logs were constructed for these holes. From these it was found that the geology at the site consists of interbedded sandstones and mudstones underlain by a dolerite sill. Additional to the percussion drilling a detailed mapping exercise was carried-out on outcrops in the vicinity where the orientations of the structures were noted.

The ERT method of geophysics was used at the project site. The geophysics substantiated the geological model.

## **4. Site Pollution Characterisation**

### **4.1 *Pollution Status of the Project Site***

Various sampling runs have been carried out at the project site. The sampling runs included samples for organics, inorganics as well as a Soil Vapour Survey. The main aim of the various forms of sampling runs is to delineate potential contaminated zones. The results of the sampling data will determine what steps are to be taken in parallel to the RBCA ( Risk Based Corrective Action) procedure of remediating and assessing the situation at the project site.

The results of each type of sampling run will be shown and discussed in detail below.

#### **4.1.1 SVS**

A Soil Vapour Survey (Photo Ionization Detector) was done throughout the site. The survey was done by Mr. Steven Fonkem of the IGS and Mr. Johan du Plooy of SRK consulting.

The figure below shows the proposed sampling locations. Due to infrastructure on the sites, the grid had to be modified.



**Figure 53: Proposed SVS sampling grid.**

A soil vapour survey relies on the volatile nature of contaminants such as petrol and diesel. 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). A Photo-Ionization Detector (PID) is a sensor that measures VOC's and other toxic gases in low concentrations from ppb (parts per billion) up to 10,000 ppm (parts per million or 1% by volume). By measuring the VOC's at various points in the near surface soils the extent of the plume can be mapped.

In order to meet the goals for this project, the Multi Rae Plus (MRP) and MiniRae 3000 were used. The MRP has five gas sensors;

- VOC,
- Carbon Monoxide (CO),

- Lower Explosive Limited (LEL) Detector, (this describes the gas mixture with the smallest fraction of combustible gases),
- Oxygen (OXY) Detector, and
- Hydrogen Sulphide (H<sub>2</sub>S) Detector.

The MiniRae 3000 has one sensor that only measures total VOC's. The survey was done on a grid spacing of between 5 and 20 meters. A small diameter hole of about 30 cm was drilled into the upper soil surface, and the probes were inserted to measure the released soil gasses.



**Figure 54: The Mini Rae Plus 3000 used in the soil vapour survey.**



Using WISH software, the data obtained from the SVS was used to construct a contour map of the site. The contour maps can be seen in the figures below.

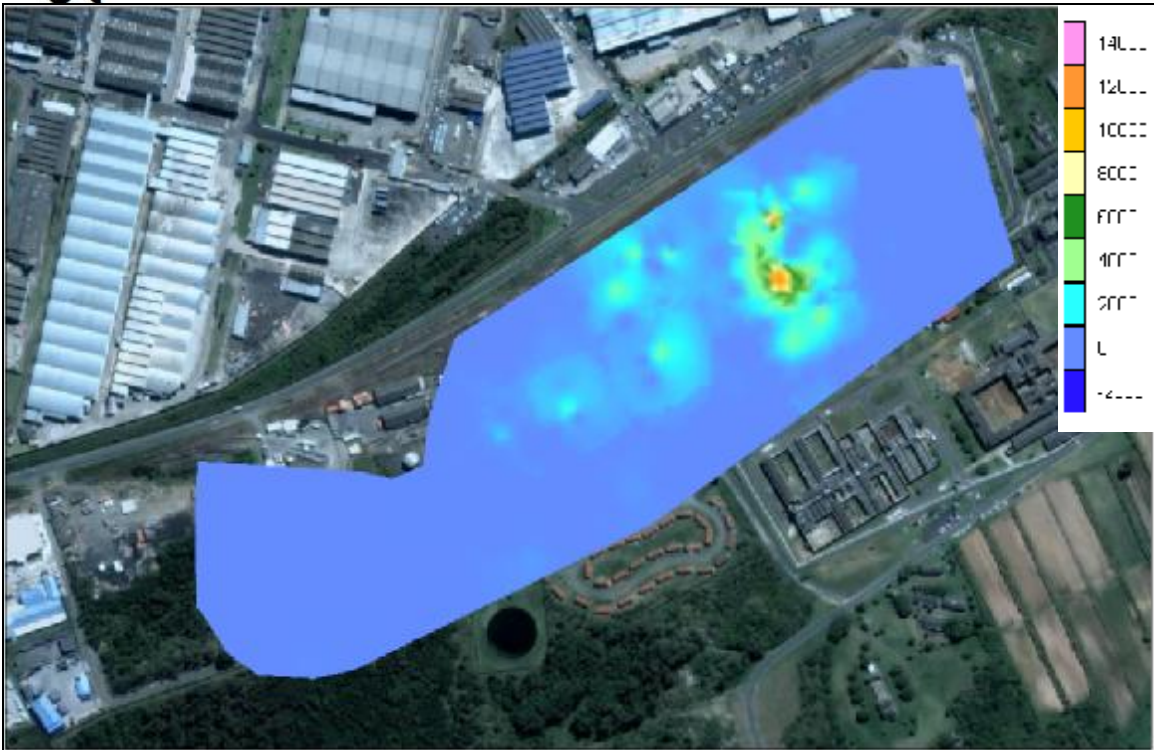
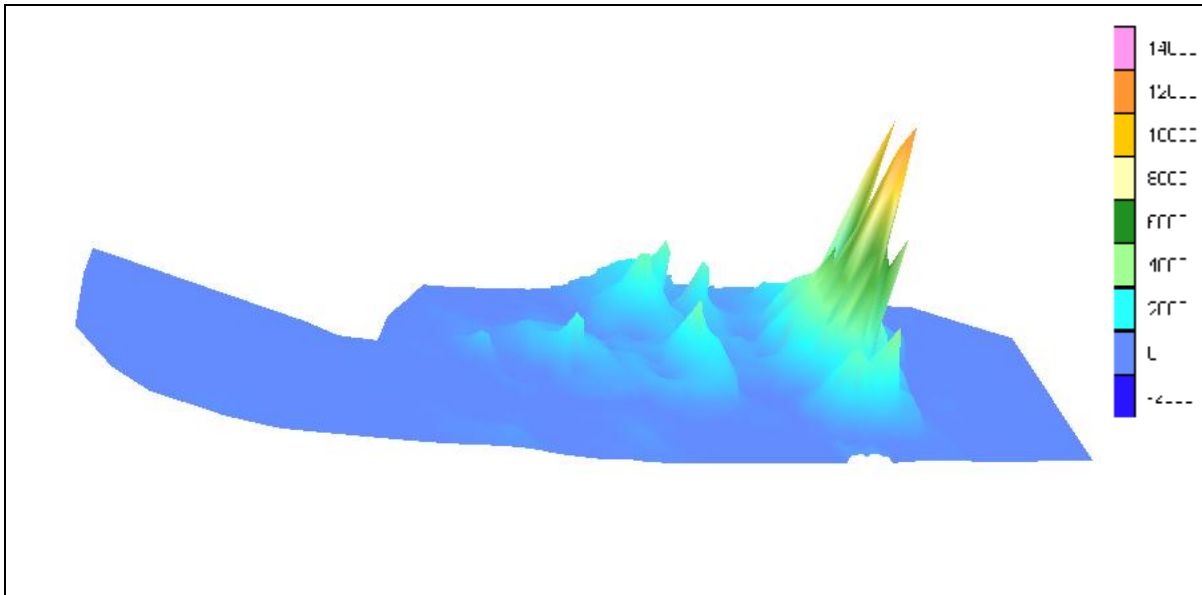


Figure 55: Contour map of the SVS data. Units in parts per million.



**Figure 56: Contour map of the SVS data shown in 3 dimensions. Units in parts per million.**

From the contour maps of the SVS a clear anomaly can be seen with values peaking at 1200 ppm. The overlay map clearly shows the high soil gas values in the north eastern part of the site. The vast high value in the north eastern part of the overlay distorts the lesser values obtained to the south-western section. The anomalies are related to the spill that occurred in section 3 during 2005.

#### **4.1.2 Water Sampling**

The main aim of water sampling is to obtain samples that are representative of the water in the given aquifer and to minimize as far as possible any alterations to the chemical properties during the sample collection and handling. It is often noted that sampling and handling procedures are the source of any discrepancies in the water-qualities. These differences may be due to differences in sampling personnel or the inconsistency of procedures and improper use of equipment.

There are various procedures that are able to be used. The main criterion used in determining which procedure is appropriate is knowing when the sample is representative of the groundwater conditions.

There is no single sampling procedure that is universally acceptable and used. Different procedures are used in different conditions, depending on site- specific conditions. These conditions include factors such as the sampling objectives, equipment availability, site location, and physical and financial constraints.

For the project site two sampling events took place. The first was done during October 2008 and the second in January 2009.

During the first sampling event 20 existing boreholes and piezometers were sampled to obtain a baseline organic water quality. During the second event the new boreholes were sampled in addition to the existing boreholes. In addition to the organic analysis, inorganic and microbial analysis were also performed on selected samples. The purpose of these was to assess the viability of the use of the MNA (Monitored Natural Attenuation) as a possible remediation method.

The sampling protocol followed, involved the following steps:

- A low flow pump was installed at an identified depth (from geochemical logging).
- The boreholes were purged until the geochemical parameters (Temp, EC, Redox, and pH) stabilised.
- Generally the volume of water discharged did not exceed 120 L.
- Samples were taken in sterilised dedicated bottles.
- Samples were stored in cooled boxes at approximately 5°C.
- All equipment was decontaminated between boreholes with a detergent and deionised water
- In boreholes with free phase water was bailed from below the free phase, with a depth specific bailer.

#### **4.1.2.1 Chemical Results**

##### **4.1.2.1.1 Inorganic Analysis**

One of the major factors in the site characterization of groundwater is the presence of organics together with inorganic contaminants. Because the two contaminants behave so differently, investigations, have to a large extent, focused on the characterization and management of either the organic part or the inorganic part, rather than mixed waste. In most instances organic waste will be present at any LNAPL site. It is therefore important to investigate both the inorganic as well as the organic contamination.

It is useful to have inorganic parameters at a site not only to determine the inorganic pollution, but from these parameters we could be able to deduce the subsurface geochemical conditions. The inorganic parameters are also useful in classifying the type of groundwater in order to determine the origin, recharge conditions and the type of aquifer system. In some cases the inorganic parameters are important indicators of the extent of natural attenuation at a site, especially when MNA is being considered as a possible remedy at the site.

The first step in the analysis of inorganic data is by making use of diagrams such as the Durov, Expanded Durov and stiff diagrams. These help in gaining a general classification of the water.

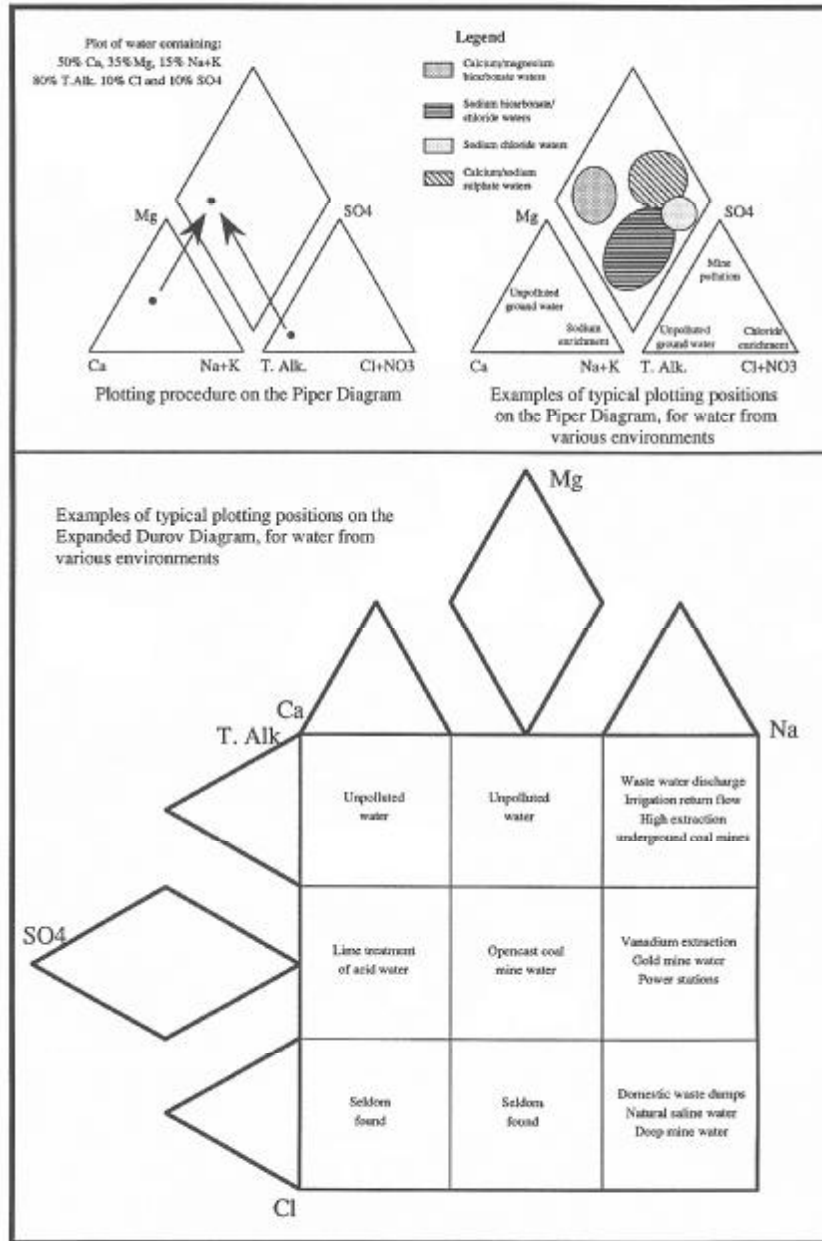


Figure 57: Diagram used for the interpretation of Durov and Expanded Durov diagrams.

From Figure 58 it can be seen that the groundwater quality generally increase in salinity with an increase in chloride content. This is generally to be expected in coastal regions.

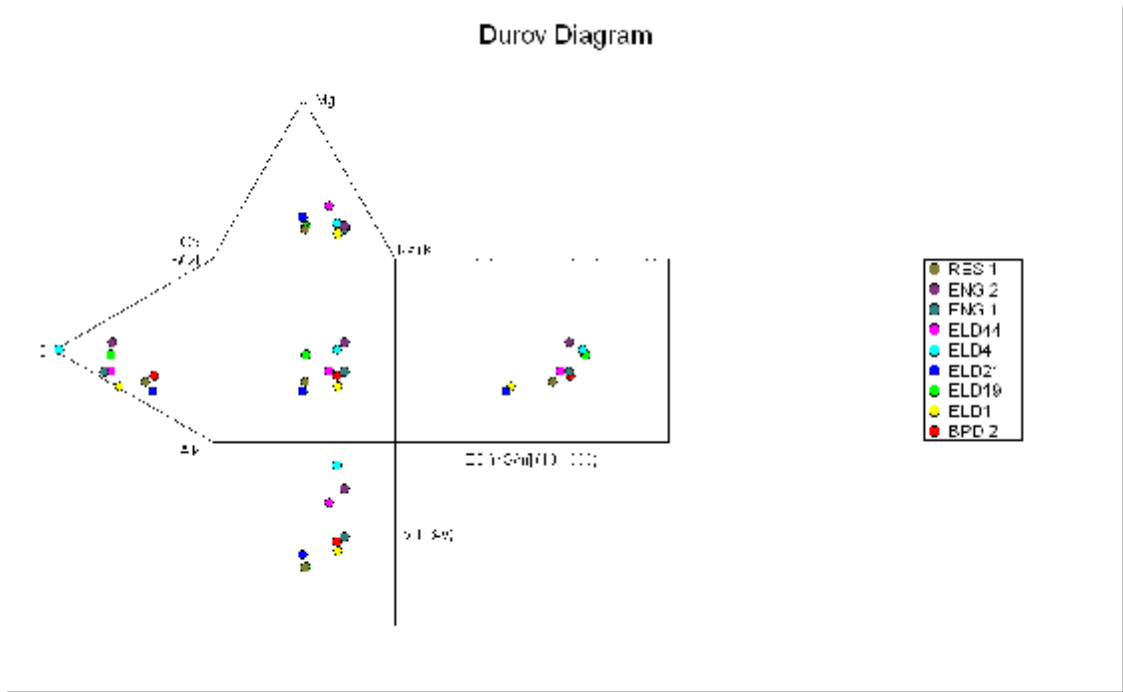


Figure 58: Durov diagram for the boreholes sampled.

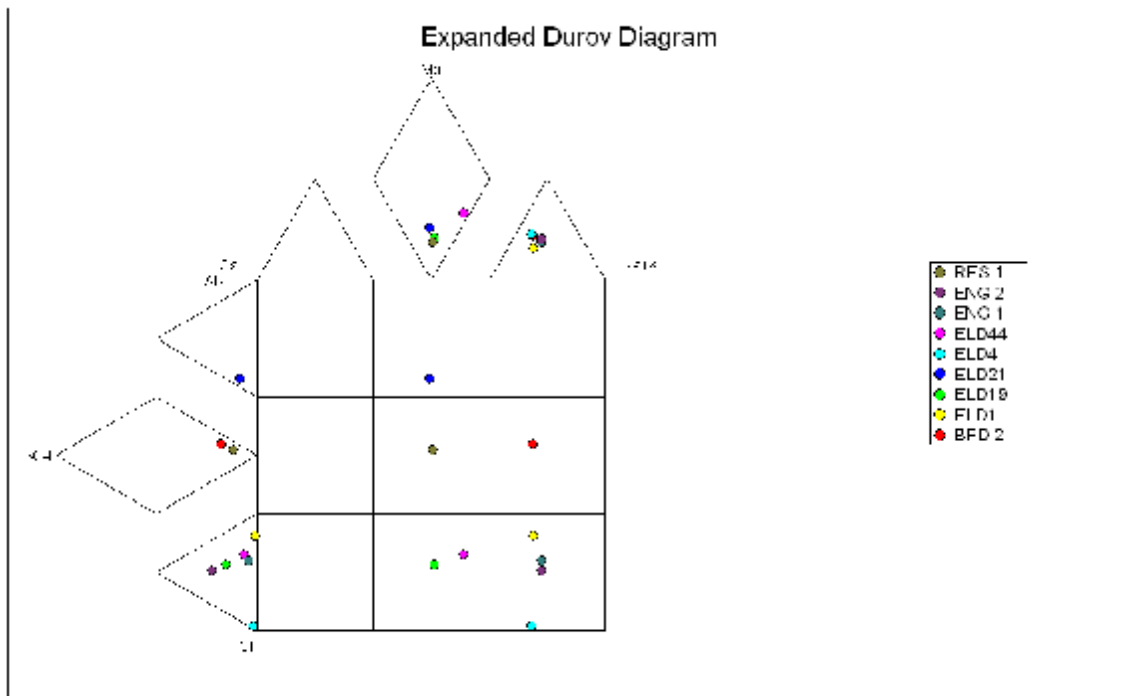
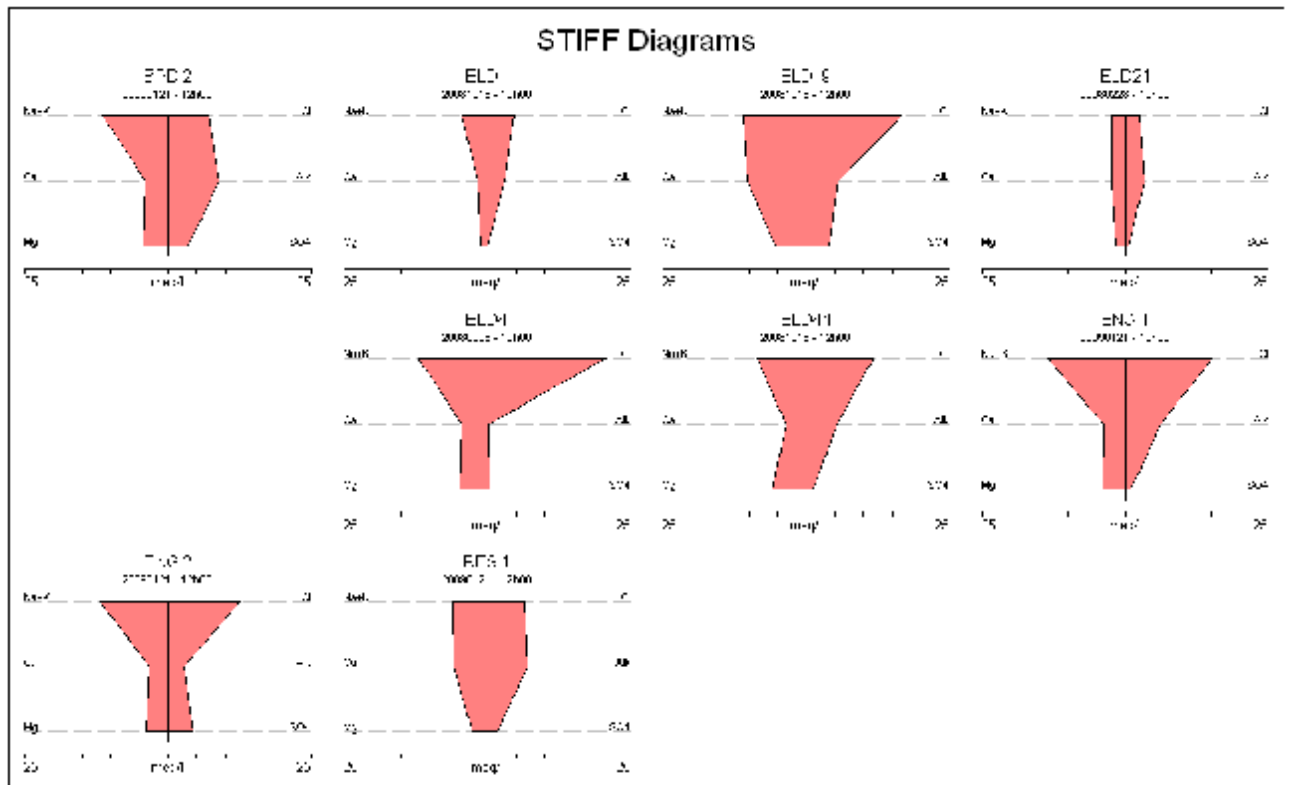


Figure 59: Expanded Durov diagram of the boreholes sampled.

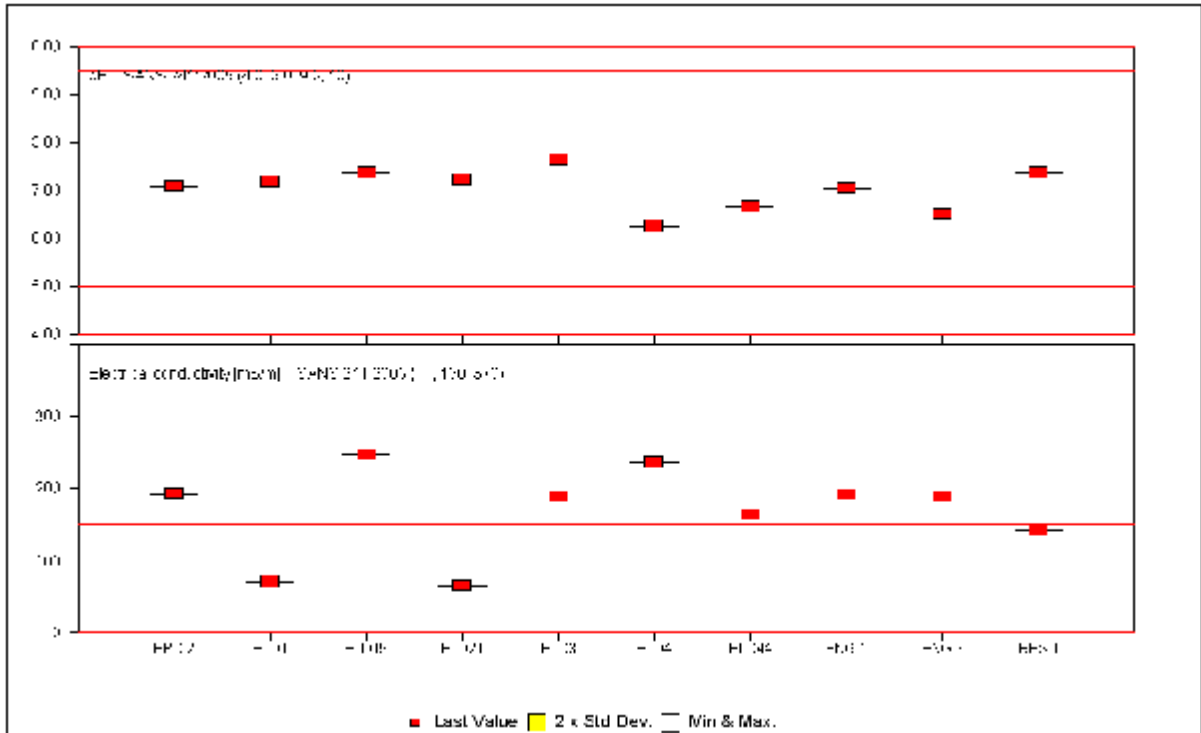
The Expanded Durov diagram does not show a specific type of water, it does however; show that the water can be classified as Na-Cl-type water.



**Figure 60: Stiff diagrams for water sampled.**

The amount of Ca and Mg cations in the samples vary across the site. This is likely to be contributed by the weathering of the dolerite formations, and will thus vary according to the degree of weathering of the dolerite at that point in the subsurface. The content of anions such as sulphate and nitrate also seem to vary, and could be an indication of degradation of contaminants occurring

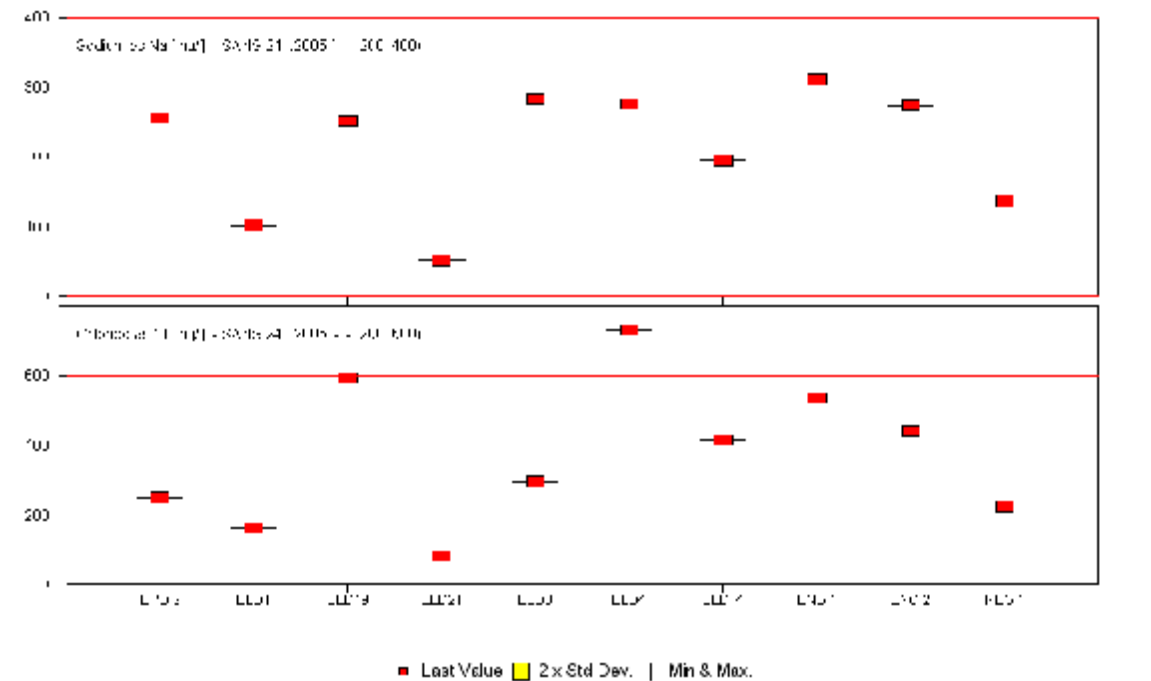
Generally if salinity is considered, the inorganic water quality is good at the site. The salinity (measured in Electrical conductivity – EC, unit ms/m) and pH plot within or below maximum allowable drinking water standards. See figure below.



**Figure 61: EC (mS/m) and pH of sampled boreholes.**

From the sodium and chloride values it can be seen that these parameters are exceeded in some of the boreholes. This is typical of coastal aquifer systems. Refer to Figure 62.





**Figure 62: Sodium and chloride of sampled boreholes.**

#### 4.1.2.1.2 Organic water quality

Figure 65, Figure 66, Figure 67, Figure 68, Figure 69 and Figure 70 give the spatial distribution of selected organic parameters measured in the groundwater across the site. The results will be discussed according to NR 140 which can be found on the attached CD.

The sampling procedure entailed the following:

1. Installation of low-flow pump at depth determined by multi-parameter logging.
2. Purging borehole until conditions became stable (EC, pH and ORP).
3. Once all conditions stabilised samples boreholes were sampled.
4. Samples kept on ice and shipped for analysis.

Examples of the stabilisations can be seen in Figure 63 and Figure 64. The remainder of the stabilization plots can be found in Appendix D.

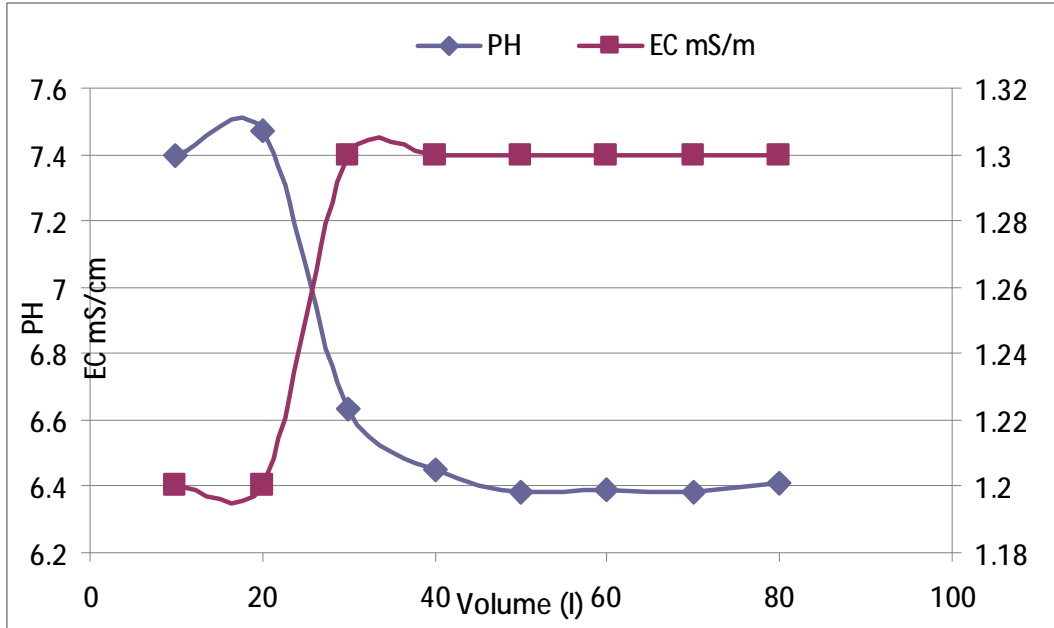


Figure 63: EC and pH plotted against time.

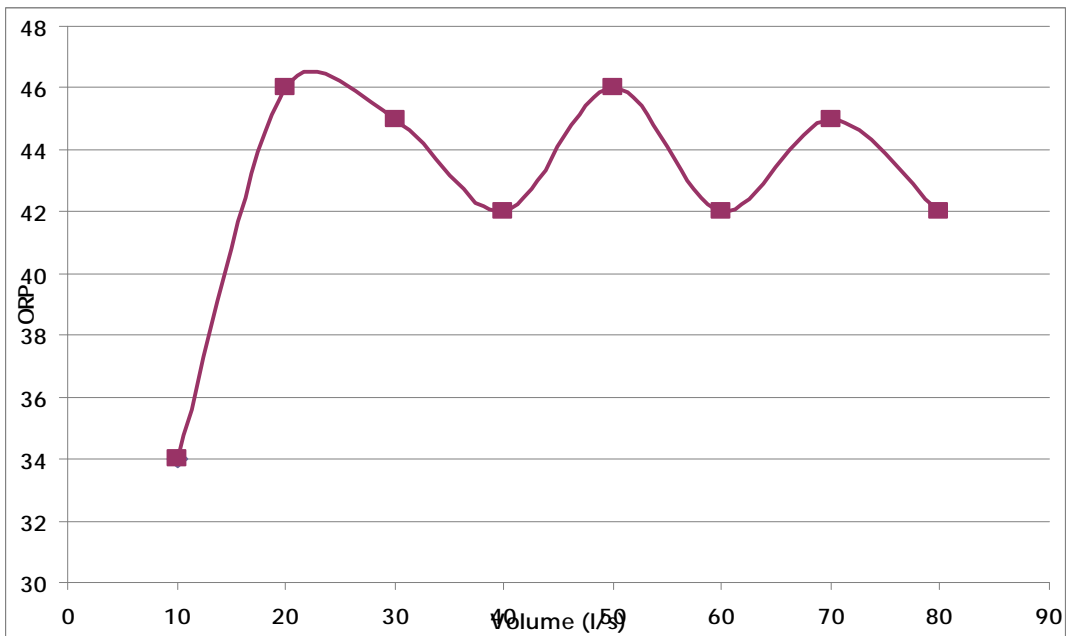


Figure 64: ORP plotted against time



Ethylbenzene's toxicity is low and there is no evidence that it causes cancer. EPA drinking water and OSHA occupational exposure limits are set at 7mg/l and 100ppm ( 8h/day per 40 h/week), respectively.

Like toluene, high concentration exposures to xylene can cause death, while moderate exposure can effect the brain. No evidence for the carcinogenicity of xylene is found. EPA drinking water and OSHA occupational exposure limits are set at 10 and 100ppm ( 8h/day per 40 h/week), respectively.



Figure 66: MTBE µg/L in boreholes.

#### 4.1.2.1.2.2 MtBE Exposure Limits

MtBE is generally unpleasant in taste and odor. Studies have been conducted on the concentrations of MtBE in drinking water at which individuals can detect the odor or taste of the chemical. This U.S. EPA recommends that keeping levels of contamination in the range of 20 to 40 µg/L or below to protect consumer acceptance of the water resource would also provide a large margin of exposure (safety) from toxic effects.(EPA, 1997-Drinking Water Advisory).



Figure 67: TPH (C10 – C16) µg/L in boreholes.



Figure 68: TPH (C16- C22) µg/L in boreholes.



Figure 69: TPH (C22 – C30)  $\mu\text{g/L}$  in boreholes.



Figure 70: TPH (C22 – C30)  $\mu\text{g/L}$  in boreholes.

What can be seen from the figures above is the following:

- ELD 18 is clearly the most polluted borehole, obviously due to the presence of free-phase in the borehole.
- The more mobile fractions of the contaminants (BTEX and MTBE) are the most widespread of all the constituents.
- 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.
- A good correlation can be made between the SVS data and the organic water quality data, thus substantiating the use of the SVS method.

## ***4.2 Risks Associated with Organic Pollution***

### **4.2.1 MTBE**

Methyl Tertiary-Butyl Ether. MTBE is a chemical compound manufactured by means of the chemical reaction between methanol and iso-butane. MTBE is produced in very large quantities and is almost exclusively used as a fuel additive. MTBE is part of a group of chemicals commonly known as oxygenates simply because they raise the oxygen content of the given fuel. MTBE is an extremely volatile substance that is highly flammable and dissolves relatively easily in water. (<http://www.epa.gov/MTBE/gas.htm>).

#### **4.2.1.1 MTBE Health Effects**

The majority of human health risk research associated with MTBE has been related to the inhalation of the chemical. When research animals inhaled MTBE, some developed cancers and non-cancer illnesses. Independent research groups have not concluded that the inhalation of MTBE poses a serious risk to

human health. Researchers have limited data pertaining to the swallowing (ingesting) of water containing MTBE. However data does support that exposure to MTBE has a high potential of being a human carcinogen. Recent work done by the EPA researchers is expected to help determine more precisely the potential for health effects from MTBE in drinking water.

#### 4.2.2 BTEX

The abbreviation BTEX is used for four compounds found in petroleum liquids. The compounds are toluene, ethylbenzene, benzene and xylenes. Benzene toluene's and xylenes are found naturally in products such as diesel and crude oil. *Ethylbenzene* is an additive to petrol, diesel and jet fuel. *Benzene* is often used in the manufacturing of synthetic materials such as plastics, rubber, nylon and various paints. *Toluene* is mostly used as a solvent for paints, gums, oils and resins. *Ethylbenzene* is often apparent in commercial products such as paints, inks, plastics and pesticides. Xylenes are mostly used as a solvent in printing, rubber and leather industries. (TOSC Environmental Briefs for Citizens).

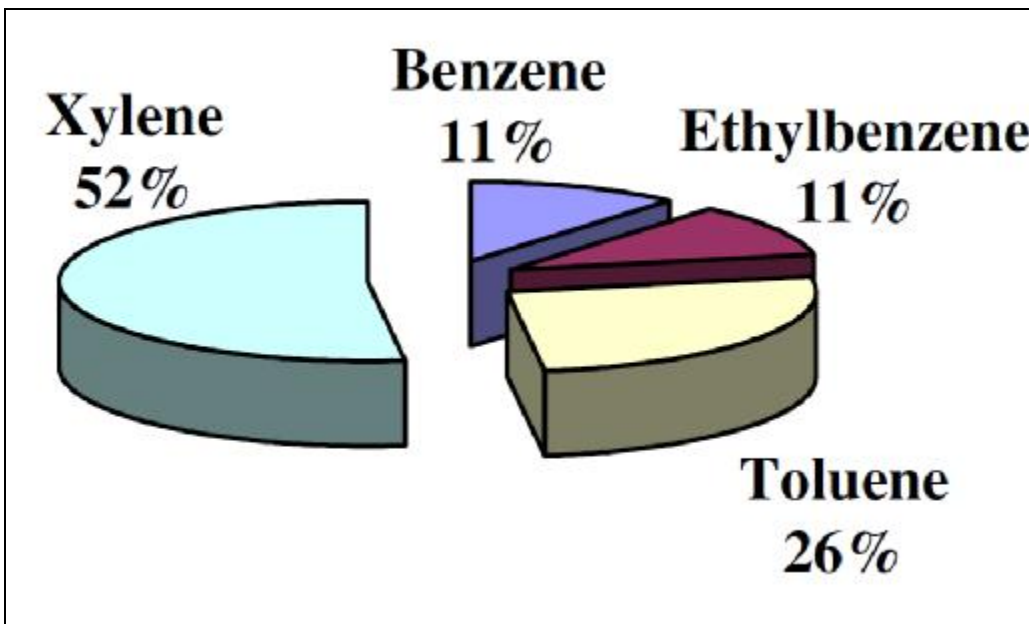


Figure 71: BTEX components of Diesel and Petrol fuels (%weight). (TOSC Environmental Briefs for Citizens).



#### **4.2.2.1 BTEX Health Effects**

Exposure to BTEX can occur in three ways; by ingestion (drinking of polluted water), inhalation (exposure to BTEX in the air) or absorption through the skin. Acute exposure to BTEX has been linked to skin and sensory irritation, central nervous system depression, and effects on the respiratory system. Extended exposure to the BTEX compounds has similar effects. The liver, kidney and blood systems are also adversely affected. According to the U.S. EPA (U.S. Environmental Protection Agency) there is enough evidence from both human and animal studies that benzene is a human carcinogen. Subjects that have undergone extended exposure to an elevated level of benzene were found to have an increased incidence of leukemia. (TOSC Environmental Briefs for Citizens).

#### **4.2.3 TPH**

Total Petroleum Hydrocarbons is a family name used to describe several hundred hydrocarbon compounds ranging from light, volatile, short-chained organic compounds to heavy, long-chained, branched compounds. The exact composition of petroleum products varies depending on: (Toxicology Profile for Hydrocarbons -<http://www.atsdr.cdc.gov/toxprofiles/tp123.html>).

1. The source of the crude oil (crude oil is derived from underground reservoirs which vary greatly in their chemical composition).
2. The refining practices used to produce the product.

Given the vastness of different chemicals found in crude oils, it is not practical to measure each one separately.

#### 4.2.3.1 TPH Health Effects

TPH can enter the body through inhalation of its fumes or through the ingestion. Some TPH compounds are widely distributed throughout the body but are easily broken down into less harmful chemicals. Others may be broken down into more harmful chemicals.

Some of the TPH compounds such as benzene, toluene, and xylene can affect the human nervous system and can even cause death when high enough concentrations are ingested. Breathing toluene at concentrations higher than 100ppm can cause fatigue, headache, and nausea and vomiting for several hours. When exposure is stopped the symptoms will fade away. However, exposure for a long time may cause permanent neurological damage. One TPH compound (n-hexane) can affect the central nervous system in a different way, causing a nerve disorder called "peripheral neuropathy" characterized by numbness in the feet and legs and, in severe cases, paralysis. (Public Health Statement for Total Petroleum Hydrocarbons.

<http://www.atsdr.cdc.gov/toxprofiles/phs123.html>).

Benzene has shown to cause cancer (leukemia) in people. The International Agency for Research on Cancer (IARC) has determined that benzene is carcinogenic to humans (Group 1 classification). Some of the other TPH compounds are considered to be probably and possibly carcinogenic to humans (IARC Groups 2A and 2B, respectively) based on cancer studies in people and animals. Most of the other TPH compounds and products are considered not classifiable (Group 3) by IARC. (Public health Statement for Total Petroleum Hydrocarbons. (<http://www.atsdr.cdc.gov/toxprofiles/phs123.html>)).

### **4.3 Conclusion**

A thorough sampling of the project site was done. Various samples including SVS, inorganics and organics were sampled.

From the Soil Vapour Survey, high soil gas values were found in the north-eastern parts of the project site.

Water sampling included sampling for inorganics and organics. The inorganic data revealed typical values for a coastal aquifer. The inorganic results are of no cause for concern.

The BTEX concentrations in the boreholes achieved acceptable limits. Three boreholes(BPD2, ELD4 and ELD44) showed unacceptably high concentrations of MtBE. These boreholes should be monitored.

The TPH values were all within acceptable limits, with the exception of the borehole containing free-phase. This borehole should be closely monitored.

In the following chapter the implementation of risk-based corrective action will be discussed.

## **5. Implementation of Risk-based Corrective Action**

The RBCA process is designed to facilitate the efficient allocation of corrective action resources based upon site-specific evaluation of human health and environmental risks (Groundwater Services, Inc). The main aim of the RBCA process is to close down a site in an expedient, protective and cost-effective manner and most importantly, to reduce the potential effect on humans and the environment to acceptable limits.

Requirements for the investigation and remediation of LUST site and other sources of release are specified in Chapters NR 140 and NR 700-726 of the Wisconsin Administrative Code.

### **5.1 RBCA Risk Management Objectives**

The main objective of the RBCA planning process is the remediation and closure of sites where contamination is present. The process must be done in a practical, cost-effective and protective manner. The fundamental risk assessment objectives to be taken into account in the development of a RBCA program are as follows:

- *Site Prioritization and Immediate Response* - The site is classified with regard to the magnitude of the threat existing to human health as well as risk of potential harm to the environment. The necessary immediate emergency response actions are to be implemented as soon as possible. The greatest risks are dealt with immediately.
- *Protection of Public Health and the Environment* – According to the RBCA approach, human and ecological exposure must be avoided. It is therefore necessary that potential pathways must be identified and remedial actions must be developed.

- Streamlined Application and Review procedures – it is imperative that the final corrective measures are implemented timeously.
- *Site-Specific Risk Characterization* – when the RBCA process is being used, the usual soil and groundwater standards are no longer mandated and standards to be achieved at every site. Instead every site is classified and the risk calculated according to the site specific risks posed to human health and the environment. This reduces the need to remediate sites that are of little or no risk. Remediation is therefore focused on sites where is absolutely necessary.
- *Technical Practicability* – The standard must be able to be achieved by methods available. The physical limitations of the site must be taken into account. If remediation of a contaminated site is not achievable, alternative methods or a more detailed analysis is required.
- *Risk Management Options* – The RBCA objectives are unlike other site remediation programs, the key objective under RBCA is not mass reduction but risk reduction. That is the reduction of the risk posed by the contaminant to humans and the environment.
- *Cost Effective Resource allocation* - Under the RBCA approach, financial and administrative resources must be effectively allocated according to the immediacy and importance of the risk posed.

## **5.2 Overview of RBCA Planning Process**

The RBCA process is an efficient approach to the assessment and response to pollution associated with LNAPL release. The RBCA is a combination of EPA risk assessment practices with traditional site investigation techniques that are used to determine cost effective measures to protect human health and the environment.

With the use of this approach, LNAPL release sites are characterised in terms of *sources, transport mechanisms, and receptors*. (See Figure below)



Figure 72: Conceptual Exposure Model (Groundwater Services, Inc.).

Remedial action is implemented so as to prevent human and environmental exposure to harmful levels of the site pollutants. This type of risk-based corrective action is easily achieved by addressing any step of the exposure process: i) removing or treating the source, ii) interrupting transport mechanisms, or iii) controlling the activities at the point of exposure. The main elements of the process are shown and discussed below.

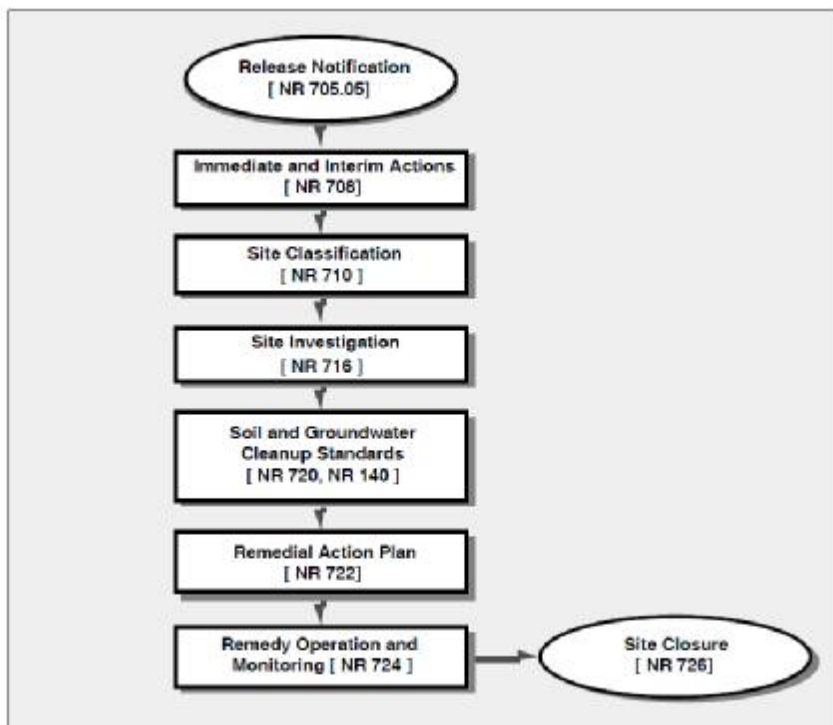


Figure 73: Wisconsin Corrective Action Program (NR 140 and NR 700 Series) (Groundwater Services, Inc.).

### **5.2.1 Immediate and Interim Actions**

After the release or spill of LNAPL, the relevant authorities are to be immediately notified. If the discovered release/spill poses an imminent threat to the public health/safety or the environment, the party responsible must conduct immediate actions to remove any sources of acute hazard. Interim actions may be required during early stages of release to stabilize the release and spread of the LNAPL. If the release has caused levels in the groundwater to exceed relevant public health standards, the responsible party must continue with a relevant site investigation and take remedial action. (Groundwater Services, Inc).

### **5.2.2 Site Classification**

A site classification is always completed to assess the magnitude and the urgency of the site risks and suggest immediate response actions. After any acute or blatantly obvious (free- phase being spilled) have been properly addressed, risk-based cleanup standards are developed to protect against any potential chronic health or environmental impacts that are associated with the long time exposure to the given levels of remaining contamination.

According to NR 710 (See attached CD), sites are classified as high medium or low priority, based on the risk posed to public health or the environment. A site qualifies as high priority if the groundwater below it contains substances that are of public concern and exceed the applicable standards. Site may be further sub-classified within the original classification using the LUST site scoring sheet, which assigns a numerical rating based on various factors including environmental media, hydrogeologic setting, and product type. (Groundwater Services, Inc).

### **5.2.3 Site Investigation**

Sites where the soil and/or groundwater have been directly affected by a release event, it is of utmost importance that the site be investigated in order to define

the full extent of soil and groundwater containing constituents in excess of applicable standards. Site investigation protocols are described under NR 716 and relevant DNR documents. The assessment must provide sufficient data to characterize the potential rate of and direction of pollution migration and assess the viability of potential remedial procedures, including monitored natural attenuation. (Groundwater Services, Inc).

#### **5.2.4 Soil and Groundwater Cleanup Standards**

The soil and groundwater remediation standards for remediation of hazardous spills are shown in Sections NR 720 and NR 140. Exceedance of any of these standards will trigger the need for remedial action.

According to NR 140 there are two levels of groundwater standards, these are commonly known as Enforcement Standards and Preventative Standards. The Enforcement Standards are derived from or related other existing regulatory standards the presence of contaminants in the groundwater exceeding the applicable ES level will require remediation. The Preventative Action Limit (or PAL) is a percentage of the enforcement standard, with the toxicity, carcinogenic and tetra-carcinogenic properties determining the exact fraction. The aim of the PAL is i) to serve as a means to inform regulatory agencies of potential problems, ii) to establish a trigger level of groundwater impacts requiring control action, and iii) to provide a basis for design and performance standards. (Groundwater Services, Inc).

Soil remediation standards, as specified by NR 720 are derived on various criteria, i) protection of groundwater qualities to PAL levels and, ii) protection of human health impacts due to direct contact. Only under certain conditions (i.e. that the investigation has been completed and the only concerns are petrol-range or diesel-range contaminants and that the subsurface has been adequately characterised) may the responsible party apply generic residual contaminant



levels listed on tables 1 and 2 of NR720 (See Attached CD) (Groundwater Services, Inc).

As an alternative to soil treatment or removal to site specific concentration limits, the responsible party may opt to implement a long-term engineering control subject to an applicable performance standard. In the case of MNA, the soil performance standard could correspond to a target level concentration at the source zone which prevents exceedance of relevant groundwater enforcement standards at the downstream site property line. (Groundwater Services, Inc).

The responsible party may be authorized to perform a site-specific risk evaluation and cleanup standard calculation under two circumstances: i) the remediation standards specified under NR 720, NR 140 and NR 722.09 are deemed not protective of human health or ii) remediation to the soil standards of NR 720 is technically impracticable. The provision concerning non-protective standards is intended to address those cases in which the additive or synergistic effects of exposure to multiple constituents could result in excessive cumulative risk levels (Groundwater Services, Inc).

### **5.2.5 Remediation Action Plan**

After appropriate cleanup standards have been set, remedial measures must be set in order to identify the most cost effective manner in which the remediation goal can be achieved. According to NR 722, active engineering methods may involve source removal or treatment, long-term engineering plans (capping, containment) or some combination thereof. Passive remedial methods such as MNA are highly encouraged. An amendment is being made to NR 722 that the remedy selection process includes a completion of a 'siting criteria form' to assess the need for an engineering-based remedy in place of the favored MNA. If the engineering option is taken, the system is required to be evaluated twice a year in order to check its operation and effectiveness. The NR 140 regulations are

also to be adjusted to identify MNA as a viable long term response to ES or PAL exceedance, under certain conditions. The responsible party will retain the option on which method to use, be it MNA or engineering methods. The lower cost method will be the popular choice. (Groundwater Services, Inc).

### **5.2.6 Remedy operation and Monitoring**

The performance and completion of the remedial action effort must be demonstrated on the basis of actual site monitoring data. Site monitoring requirements are clearly specified under NR 724. Once the remedial programmed has been completed, the duration of monitoring required to verify compliance with the set goals will be determined on a site specific basis. It is recommended that the monitoring of MNA be done on a regular basis. (Groundwater Services, Inc).

### **5.2.7 Site Closure**

Once the remediation techniques have been applied correctly the responsible party may apply for site closure once the monitoring data suggests that sufficient remediation standards have been met. Only if the contaminant concentrations do not exceed the applicable NR 140 groundwater standards or NR 720 RCL's, the DNR can issue a "no further action letter" imposing no restrictions on the future land use. If the standards exceed the standards of NR140, closure of sites may take place if: i) adequate source control measures have been met, ii) MNA is reducing the concentrations enough that the NR 140 standards will be attained "within a reasonable time period" iii) NR 140n standards are not exceeded off-site, and iv) a groundwater restriction in place on the property deed. (Groundwater Services, Inc).

### **5.2.7 Application and Review Procedures**

The nature of the release determines what reporting and approval requirements for the corrective action process, and are characterised under NR 700 and NR 710. In NR 700, separate reporting/approval steps are established for “simple” and “complex” sites. For simple sites, the responsible party may proceed with corrective action and submit only a final report documenting completion of the remedy. Complex sites may be subject to up to 6 agency review steps prior to final approval site closure.

For RBCA to be economically viable at a big and small sites, the RBCA process has been designed to be able to adapt to the complexity of each specific site. For this purpose, a tiered approach is implemented for the calculation of risk-based cleanup levels, each step in involving increasingly sophisticated levels of data collection and analysis. In South Africa however, the use of the most state of the art equipment and techniques is not an option. The costs involved in these techniques are out of most companies’ range. It is therefore required that innovative ideas and concepts are applied to sites in South Africa. Once each tier has been completed the user reviews the results and decides if further analysis is required base on the recommendations made in the first tier. The tiered approach can be seen in the figure below.



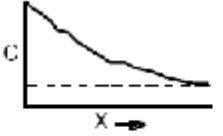
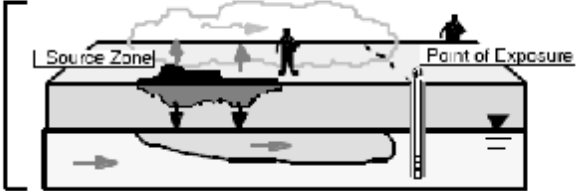

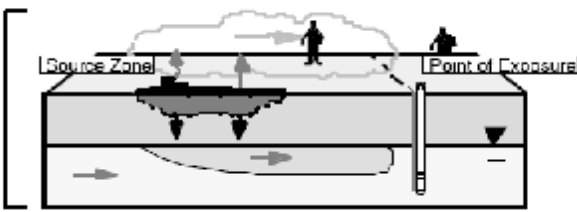
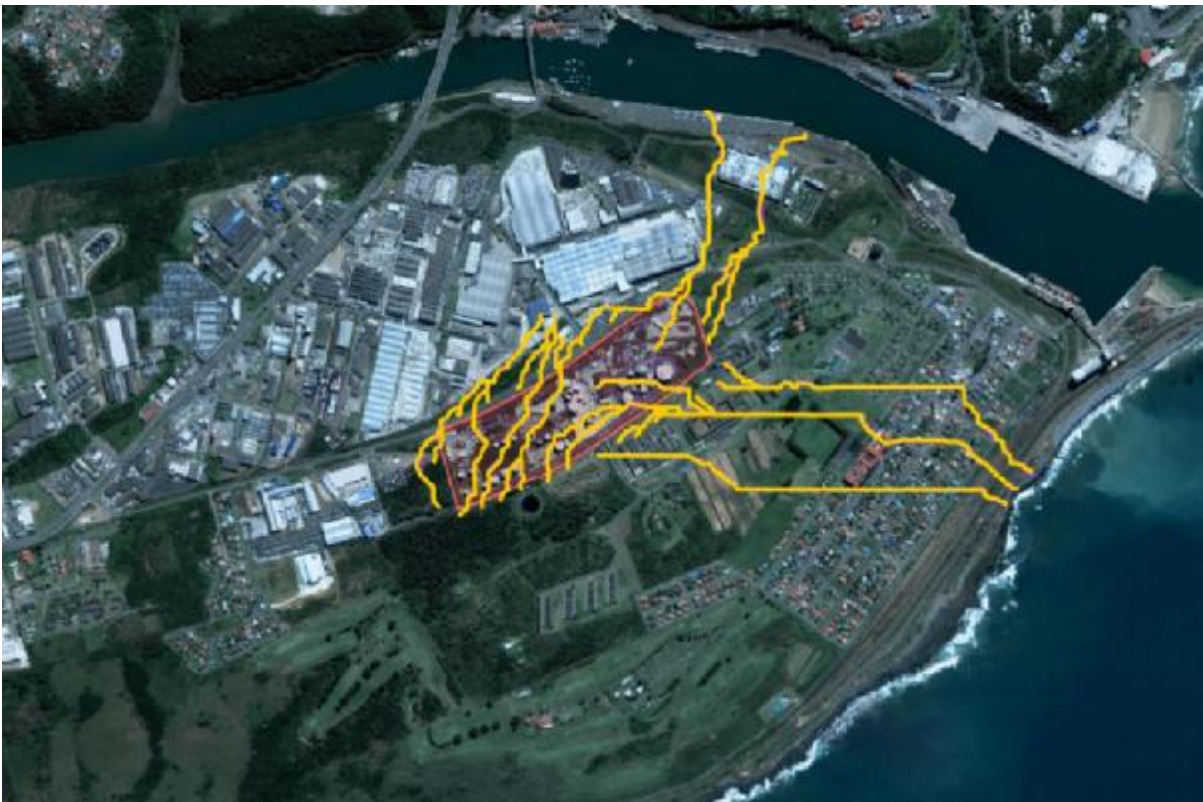
RBCA TIER	TOOLS	APPLICATION
Tier 1	 Look-Up Tables	
Tier 2	 Analytical Models	
Tier 3	 Numerical Models	

Figure 74: Overview of Tiered RBCA Evaluation Process.

## 6. Management of the Project Site

The management of the project site will follow a RBCA (Risk-Based Corrective Action) format.

At present there are no known existing water supply wells in the close vicinity of the project site. However, from the digital water and terrain elevations and predicted groundwater flow directions, contaminants could potentially flow into the adjacent river or ocean. See figure below:



**Figure 75: Predicted groundwater flow directions.**

It must be noted that the spillages occurred during the year 2005 and that the author could not gain access to any older data. The RBCA process will be adapted where possible at this late stage and present data will be used to make necessary conclusions and management suggestions.

## **6.1 Immediate and Interim Actions**

A product spill of 6900 litres occurred in section 3, when a tank was overfilled. It is reported that approximately 6700 litres were recovered and only approximately 200 litres lost to the soil. This product spill occurred during March 2005. The underground line was pressure tested for a duration of one hour and no drop in pressure was experienced.

A reported diesel spill of approximately 30 000 litres occurred during September 2005 in section 1. See figure 2. No other spills or product losses have been reported in the past 7 years. There are no underground pipes that require pressure testing. No further details were available to access.

In the first case the responsible part acted speedily and recovered a large percentage of the spillage. No further details were accessible on what actions were taken concerning the spillages.

## **6.2 Site Classification**

It must be emphasised that in this study that the risk will be specified according to different receptors, that being human risk, environmental risk and financial risk.

Under NR 170, sites are classified as high, medium or low priority based on the relative threat to public health or the environment.

### **6.2.1 Public Health Risk**

Human exposure can occur through the consumption of contaminated groundwater or through the inhalation of vapours expelled from the site. The threats from groundwater consumption and inhalation will be discussed separately.

### **6.2.1.1 Groundwater Threat**

Although the groundwater qualities at the site are not within the groundwater quality standards it is important to note that there are no abstraction boreholes in the vicinity of the site. thus the human aspect of the groundwater consumption and impact is low. There are several contributing factors to this observation:

- Absence of abstraction boreholes in the vicinity – no consumption risk.
- Slow movement of the constituents due to hydrologic conditions.
- No abstraction – no groundwater gradient created .
- Physical conditions at the site aid in the expulsion of constituents through vapourisation.

Contribution of MNA to the site's "self-remediation" (Discussed in next chapter).

### **6.2.1.2 Vapour Threat**

The SVS shows the presence of vapours across the site, with some distinct anomalies. The risk posed by vapours to humans is high. This is due to the constant vapourisation of LNAPL constituents from previous spills. The vapours are not aesthetically noticeable but still pose a risk when inhaled.

## **6.2.2 Environmental Risk**

The importance of environmental risk is not as large as human risk although the ecology may be adversely affected.

### **6.2.2.1 Groundwater Threat**

Given that the groundwater is above accepted for human consumption, it can be assumed that the levels of contamination will also surpass the levels tolerable by various aspects of the environment. If the pollution were to migrate as far as the adjacent river or sea, the threat would be high. In this situation however, the site

is located in an industrial area and contaminants are relatively immobile and are not in contact with any natural ecosystems. The environmental impact is thus low.

#### **6.2.2.2 Vapour Threat**

Due to the project site's location in an industrial area, the effect due to vapour release will be minimal. Any vapours release will be diffused and dispersed into the atmosphere relatively quickly and will have little or no effect on the environment.

### **6.3 Site Investigation**

The site investigation will be based only on data attained during the author's time-span of involvement with the project.

A complete site investigation and site characterisation was done on the site. All data can be seen in chapter 4. The investigation included:

- Organics sampling
- Inorganics sampling
- Slug testing
- Pump testing
- Soil Vapour Survey
- Auger drilling and Soil Analyses
- Borehole drilling
- Geophysics

All results and interpretation thereof can be seen in chapter 4.



## **6.4 Soil and Groundwater Cleanup Standards**

The South African National Standards were used for the interpretation of the inorganic data. No South African standards are available for the interpretation of the organic data. It was therefore necessary to use the standards provided under NR 140. (See attached CD).

## **6.5 Remedial Action Plan**

When commencing with the remedial action plan, it is important to identify the most practical and cost-effective alternative for achieving the remediation goal. The remediation plan will be divided in to two sections:

1. Engineered remedies
2. Monitored Natural Attenuation

### **6.5.1 Engineered Remedies**

The majority of LNAPL spills take place at loading and receiving bays, each loading bay's drainage system is accompanied by an oil separator to prevent LNAPL run-off and contamination. (See Figure 76).



**Figure 76: Oil separator and run-off collection pit.**

Free phase product is only found in two boreholes which are adjacent to each other. It is advisable to install a low-flow pump-and-treat system in one of these boreholes.

The project site area is approximately 30% covered by reinforced concrete which is no more than 20cm thick. The concrete layer was laid for obvious structural and logistical reasons.

### **6.5.2 Monitored Natural Attenuation**

MNA is becoming a commonly accepted method of non-invasive remediation of LNAPL contamination sites. MNA has a great advantage of adaptability and cost-effectiveness. MNA is highly prevalent at the project site and will be thoroughly discussed in chapter 7.

### **6.6 Remedy Operation and Monitoring**

It is the duty of all companies located on the project site to maintain a suitable monitoring program. Site monitoring requirements are specified under NR 724 (see attached CD).

Monitoring at the project site can take two forms:

1. The monitoring of one borehole on each company's premises. It is important that the borehole being monitored be located on the down-gradient of the site. When implementing this strategy, the concentrations will be monitored and will be representative of the section. Any drastic fluctuations will act as a trigger response to a more detailed investigation.
2. The monitoring of up to 5 or 6 boreholes per premises in order to delineate a plume. These boreholes will be strategically chosen in order to get the best representation of the site and enough data will be available to delineate a plume if one exists.

At this specific site the second method will be applied and the following boreholes will be monitored at the project site:



**Figure 77: Locations of boreholes to be monitored.**

The duration of the monitoring should be continuous, with sampling intervals being bi-annually. It is important that all the companies located on the site use the same contractor so as to avoid discrepancies in the data.

MNA packages should also be analysed on a yearly basis. Care must be taken to be consistent in the time of year of sampling, as seasonal variations may have effects on the vadose zone environment and thus affect the microbial activity.

## **6.7 Site closure**

Given that that the project site is a working depot, no site closure can be implemented. Although certain aspects of the site can gain a no further action letter imposing the shut down of certain engineering remedies where the minimum acceptable standards have been reached.

## **6.8 Application and Review Procedures**

It is necessary that the appropriate reporting procedures are followed and that the site be continuously be monitored and the database be updated. All companies located on the site must use the same consultants to do the reporting and review procedures.

## **6.9 Conclusions**

The fact that there are no abstraction boreholes in the vicinity of the project site, the risk to humans is minimal. There is a high risk factor posed to employees working on the project site by vapours emanating from the soils at certain places on the project site.

The ecology at the project site may be adversely affected but the risk is not noteworthy.

All drainage systems and run-off spillage tanks and oil separators are to be regularly inspected. It is recommended that a pump and treat system be installed where free-phase is apparent.

The site's groundwater is to be monitored as advised in the chapter.

## 7 Monitored Natural Attenuation as a Remedy for LNAPL Site

### 7.1 What is Monitored Natural attenuation?

Natural attenuation (NA) processes such as biodegradation, dispersion, sorption and volatilisation affect the fate and transport of NAPL's in all hydraulic systems. When these processes are shown to be capable of attaining site-specific remediation objectives in a time period that is reasonable compared to other alternatives, they may be selected alone or in combination with other more active remedies as the proffered remedial alternative. Monitored Natural Attenuation (MNA) is a term that refers specifically to the use of natural attenuation processes as part of overall site remediation. The United States Environmental Protection Agency (U.S. EPA defines monitored natural attenuation as (OSWER Directive 9200.4-17, 1999) :

*“The term “monitored natural attenuation”, as used in this Directive, refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The “natural attenuation processes” that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilisation, transformation, or destruction of contaminants. When relying on natural attenuation processes for site remediation, EPA prefers those processes that degrade or destroy contaminants. Also, EPA generally expects that MNA will only be appropriate for sites that have a low potential for contaminant migration.”*

The definition of Natural Attenuation (NA) in groundwater is (WRC1501/4/08):

*“ The effect of naturally occurring physical, chemical and biological processes, or any combination of those processes to reduce the load, concentration, flux, or toxicity of pollution substances in groundwater. For natural attenuation to be effective as remedial action, the rate at which those processes occur must be sufficient to prevent polluting substances entering the identified receptors and to minimize the expansion of pollutant plumes into currently unpolluted groundwater. Dilution within a receptor, such as in a river or borehole, is not natural attenuation”*

The definition of Monitored Natural Attenuation (MNA) is (WRC1501/4/08):

*“Monitoring of groundwater to confirm whether NA processes are acting at a sufficient rate to ensure that the wider environment is unaffected and that remedial objectives will be achieved within a reasonable timescale; this will typically be less than one generation, or 30 years”*

Natural attenuation processes typically occur at all contamination sites, but to varying degrees of effectiveness, depending on various contributing factors such as the type of contaminant, concentration, and the physical, biological and chemical characteristics of the groundwater.

## **7.2 Microbial Physiology**

Although bacteria are unicellular, they share characteristics similar to most other living organisms. Information is encoded in DNA (deoxyribonucleic acid) and is transferred to the RNA (ribonucleic acid) to ribosomes to manufacture proteins or enzymes which in turn are used to operate the systems within the organism. For the purpose of this study, enzymes are responsible for the degradation of organic carbon, which is used by the bacteria to produce the building blocks of life and

energy in general. In order for this to happen the efficient use of these enzymes is necessary. In many cases the degradation is merely a process involving oxidation/reduction reactions. The reducing equivalents (hydrogen or electron-transferring molecules) produced must be transferred to a terminal electron acceptor (TEA). During the process of electron transfer, energy is released and is used by the cell. (Azadpour-Keeley et al.1999).

When concerning TEA's, the bacteria can be grouped into three categories:

1. Aerobic bacteria – in this case the bacteria can only make use of molecular oxygen as a TEA. Without oxygen these bacteria are not capable of degradation.
2. Facultative aerobes/anaerobes – bacteria that can use oxygen when oxygen concentrations are extremely low or non-existent. These may switch to nitrate, manganese oxides or iron oxides as electron acceptors.
3. Anaerobes – bacteria that does make use of oxygen in the breakdown of organic carbon and for which oxygen is toxic. Anaerobes make use of nitrates or other electron acceptors, although it can be generally be said that they mainly make use of carbon dioxide and sulphate as electron acceptors.

It is of utmost importance to know the Redox conditions in the sub-surface in order to know what bacteria are active in the subsurface. In some cases where the type of conditions is known the type of bacteria can be inferred and the bacteria can be supplemented with whatever TEA is required. If a contaminant provides the only source of carbon and energy, the conditions must be within acceptable pH, Eh and temperature limits and the appropriate TEA must be available. The rate of degradation will be determined by the rate of dissolution of toxic end products away from the microbial population and the rate at which the TEA is replenished. (Azadpour-Keeley et al.1999).



In addition to organic carbon and a TEA, bacteria require macronutrients and micronutrients for the production of DNA and RNA as well as other cellular requirements. These take the form of Nitrogen and Phosphorus. (Azadpour-Keeley et al.1999).

### **7.3 MNA at the Project Site**

This study focused on the different microbial populations found in the LNAPL polluted soils and groundwater at the site. Specific targeted sampling sites were identified.

#### **7.3.1 Sample Collection**

Thie samples were taken at the same time as the organics samples. The samples were immediately put on ice. Once the samples had reached the laboratory, a constant temperature of 4 degrees was maintained until the DNA could be extracted.

**Table 11: Description of samples taken for DNA analysis.**

DNA number	Sample description	Sample type
1	CHEV new 21/01/09	Water
2	EN new 01 22/01/09	Water
3	TOT 02 22/01/09	Water
4	ENNEWZ 22/01/09	Water
5	BP 03 21/01/09	Water
6	RES 1 22/01/09	Water
7	TOTAL 1	Soil
8	BP Trench	Soil
9	ENGEN1	Soil
10	CHEV 1	Soil
11	BP2	Soil
12	MMW75	Soil
13	MMW90 (mna)	Soil
14	115 (mna)	Soil

### **7.3.2 DNA Extraction**

The DNA extraction was carried out by Dr. A.K.J. Surridge. DNA extraction was performed using the BIO101 Fast DNA Spin kit (Soil) (Qbiogene Molecular Biology products, IEPSA, South Africa) as follows:

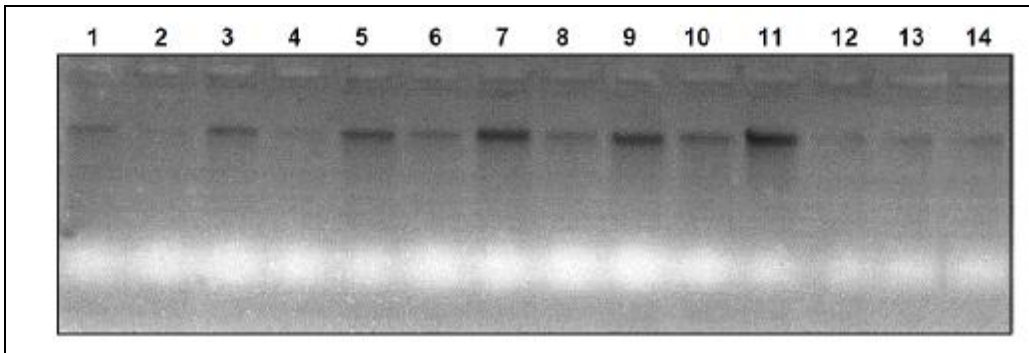
- Pre extraction sample preparation of the liquid samples was necessary, thus ca. 50ml of each sample was filtered through a 0.22µm bacterial filter. Once clogged the filter was aseptically opened and the paper placed into the lysing matrix tube.
- 0.5g of the samples was added to the Lysing Matrix E tube.

- 978µl Sodium Phosphate Buffer and 122µl MT Buffer was added to the sample in the Lysing Matrix E tube.
- Tubes were shaken on the Disruptor Genie (Inqaba Biotec, Pretoria, South Africa) for 2- 5min.
- Tubes were centrifuged at 14000 rpm for 10 min.
- The supernatant was transferred to a clean tube and 250µl PPS reagent was added, this was mixed by inverting 10 times.
- Tubes were centrifuged at 14000 rpm for 5 minutes to pellet the precipitate. The supernatant was transferred to a clean tube and 1ml of Binding Matrix suspension was added.
- These tubes were inverted by hand for 2 min allowing binding of the DNA to the matrix. Tubes were then allowed to stand for 3 min to allow the settling of the silica matrix.
- 500µl of the supernatant was removed and discarded being careful to avoid the settled Binding Matrix. The Binding Matrix was resuspended in the remaining amount of supernatant and 600 µl of the mixture was transferred to a SPIN™ Filter and centrifuged at 14000 rpm for 1 minute. The catch tube was emptied and the remaining supernatant was added to the SPIN™ Filter and spun again.
- 500µl SEWS-M was added to the SPIN™ Filter and centrifuged at 14 000 rpm for 1 minute. The flow-through was decanted and the SPIN™ Filter replaced in the Catch tube. Filters were centrifuged at 14000 rpm for 2 minutes to dry the matrix of residual SEWS-M wash solution.
- SPIN™ Filters were removed and placed in a fresh Catch tube where they were allowed to air dry for 5 minutes at room temperature.
- 50µl DES (DNase/Pyrogen Free water) was added to the matrix and gently stirred on filter membrane with a pipette tip to resuspend the silica for efficient elution of the DNA. Tubes were centrifuged at 14000 rpm for 1 minute to transfer the eluted DNA to the catch tube. The DNA was application ready.

### 7.3.3 Results

#### 7.3.3.1 DNA Extraction

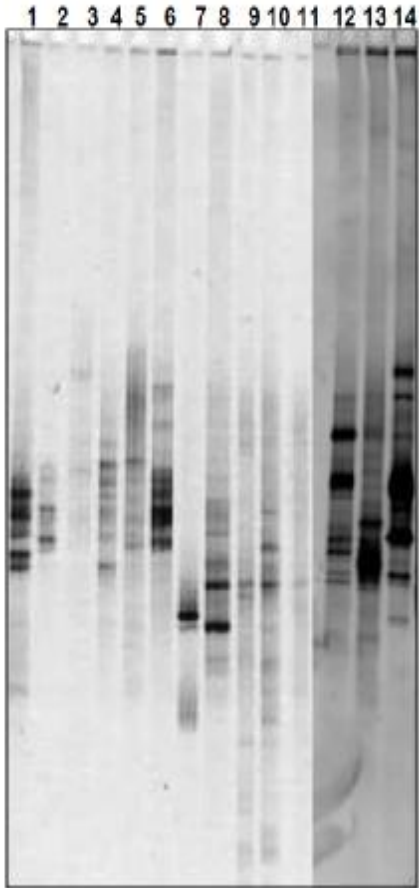
DNA was successfully extracted from all samples collected. No evidence of RNA or protein contamination that could inhibit further application of DNA is visible either below the lanes or in the wells of the gel, respectively. It is important to note that although some of the DNA appears to be of low concentration, this is still application ready DNA and will still yield a PCR product for further analysis.



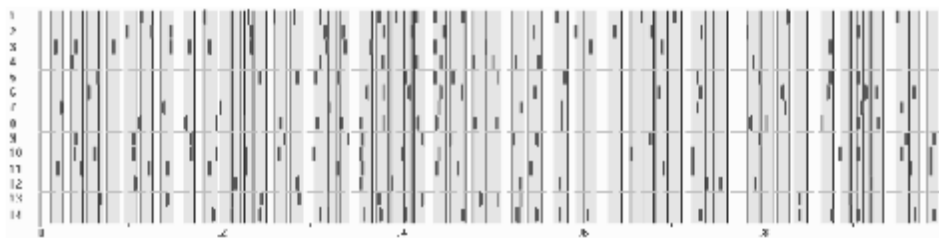
**Figure 78: 1.5% TAE agarose gel showing high-quality, clean genomic DNA extracted from soil and ground water samples (Table 1), by means of the BIO101 Fast DNA Spin Kit for soil.**

#### 7.3.3.2 DGGE

DGGE yielded gels showing clear multiple banding, forming a fingerprint in each lane (Figure 79). These gel images were loaded and a graphical image of the gel was produced for further species diversity bioinformatics analysis. Dominant species per lane are indicated as dark prominent bands across the lane (Figure 80).



**Figure 79: DGGE gel showing species diversity of bacteria from soil and water samples, run at 30-60% denaturants. PCR product is separated according to base-pair sequence differences to determine community richness and diversity of microorganisms based on these fingerprints.**



**Figure 80: Graphic representation of the DGGE gels in Figure 79 depicting the band pattern, indicating species diversity within the bacterial population, produced by each of the samples.**

## **7.4 Discussion – MNA**

Water and soil sampled were screened for bacterial diversity. The DGGE technique proved to be an appropriate means of assessing the bacterial diversity in environments polluted by LNAPLs and that a diversity of microbes occurs at the project site in the soils and in the groundwater. It has been globally shown that the mere presence and diversity of these microbes directly improve LNAPLs in polluted soil (Glick 2003).

Studies taking place on the microbial diversity at the project site should be ongoing and a more comprehensive understanding of the microbial population dynamics is expected to emerge over time. It seems that the microbial populations within the project LNAPL site are very diverse, considering the stress placed on microorganisms living and growing in such polluted sites. Given the diversity of the organisms it can be safely said that the microbial action is very present and active in the remediation of the site.

## 8 Conclusions

### 8.1 *Characterization of the Project Site*

Given the financial constraints experienced in South Africa, the characterization of the site was successful.

It was necessary to drill 6 monitoring boreholes additional to the existing boreholes in order to gain a better understanding of the underlying geology. The initial model of the geology was confirmed.

The ERT method of geophysics was used to attempt to delineate the pollution plume. This was not able to be done due to the ERT method not being able to 'pick up' the LNAPL due to distortion of the signal as explained in the text. The ERT method did, however, compliment the geological model.

Hydraulic testing (slug tests, pump tests, Darcy tests) was done on selected boreholes in order to assign values to the hydraulic parameters. The groundwater velocities were also calculated. A digital terrain vs. elevation map was created using WISH software, this gave an approximation of the groundwater flow directions.

Soil samples were taken at various points surrounding the site and were used to do various tests (grain-size analysis, structure, texture, porosity mineralogical composition).

A thorough chemical characterisation was undertaken. In fulfilling this, various sampling procedures had to be carried-out. A soil vapour survey of the entire site was done. Water samples included samples for; organics, inorganics and MNA packages. Based on these results, a management plan for the site was devised.

## **8.2 Conceptual Model of the Project Site**

The aim of this conceptual model is to attempt to explain and understand what has happened to the spilled LNAPL at the project site and how the site is remediating itself. The conceptual model will be explained by means of Figure 81 and the following text.

It was found that a fraction LNAPL was being vaporized into the atmosphere by a combination of physical factors including; capillary rise, shallow aquifers, phase distribution, temperature effects, porosity effects and humidity effects. All the LNAPL is not able to be vaporized to the atmosphere due to a limiting factor “holding” a portion of the LNAPL by a means of adsorption. The remaining portion of the LNAPL in the soil is degraded by means of microbial action, the proof of the existence of a variety of microbial populations. The mere existence of a variety of thriving populations of microbes is a strong line of evidence showing that the microbial organisms are improving the quality of the soils and groundwater. A diagram showing the conceptual model can be seen in Figure 81.



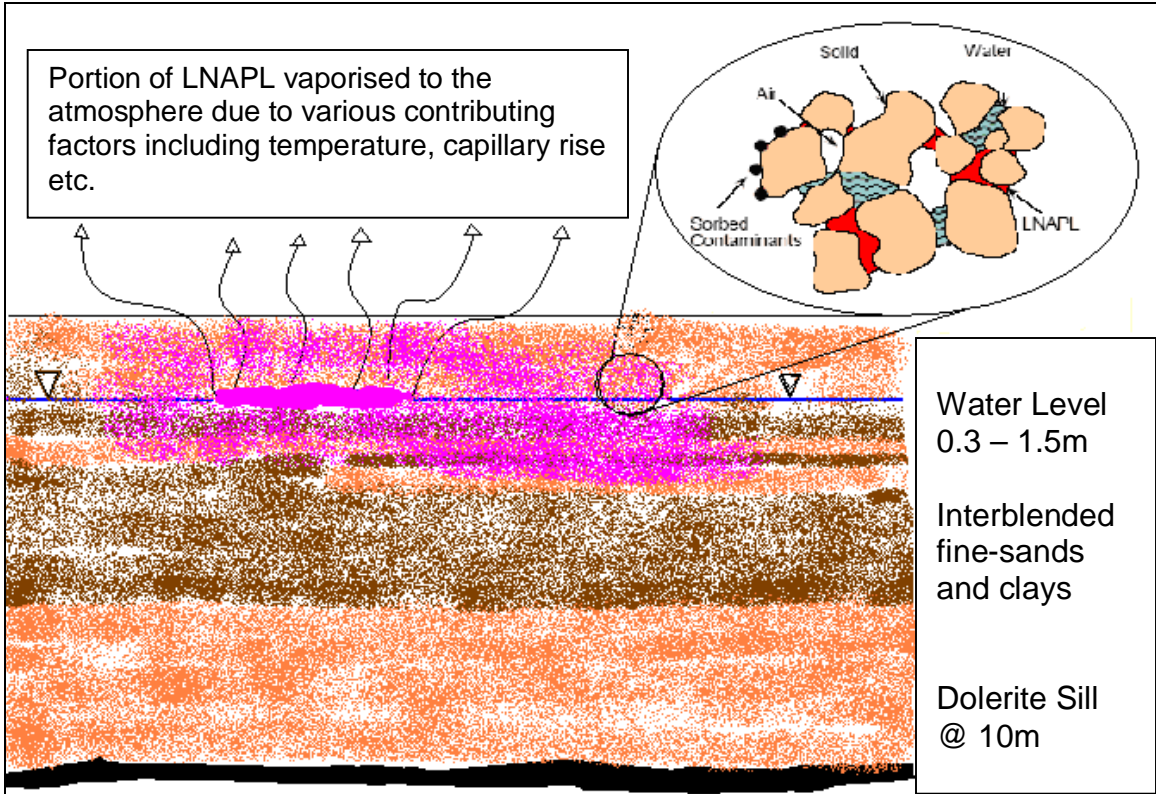


Figure 81: Conceptual model of the project site.

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(2009-09-23 ) TOSC ENVIRONMENTAL BRIEFS FOR CITIZENS

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<http://www.bp.com>,

<http://www.caltex.co.za>,

<http://www.engen.co.za>

## **ABSTRACT**

The project site experienced LNAPL spills in the recent past. In the characterisation of the site it was necessary to investigate the physical properties of the vadose and saturated zones. It was found that temperature, saturation, phase-distribution, the hydraulic properties and water levels contributed to the LNAPL being vaporised. The attributes of the soils substantiated the vaporisation model. The geology was found to be dominated by interbedded sandstones and mudstones, underlain by a dolerite sill. The pollution plume was delineated at the study area and an appropriate management plan was proposed for the site. MNA was shown to be an effective management option.

## **OPSOMMING**

Die projek area het verskillende fases van LNAPL besoedeling ondervind. Die ondersoek van die area het beide n studie van onversadigte en versadigte sones geveerg. Die rol van temperatuur, water inhoud, fase verspruiding, hidroliese eienskappe en watervlakke dra by tot die diffusie van die petoleum produk na die atmosfeer. Die grond samestelling het die verdampings-model be vestig. Die geologie van die area is saamgestel uit sandsteen en moddersteen wat rus op 'n doleriet plaat. Gemoniteerde natuurlike verval proses in die studie area het 'n beduidende rol en kan as bekampingsmateriaal oorweeg word.'n Bestuursplan vir die besoedelde area is voorgestel.

## Appendix A: XRD and XRF data

Analysis Kevin Vermaak. Major elements in wt% and trace elements in ppm.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Total
AU2A	93.07	0.63	2.52	0.04	0.65	0.17	0	0.02	1.9	0.03	99.03
AU3A	89.63	3.35	3.82	0.03	0.32	0.25	0.08	0.17	1.79	0.01	99.45
AU3B	85.96	5.11	5.42	0.03	0.37	0.25	0	0.24	1.77	0.01	99.16
AU4A	62.07	13.76	13.68	0.08	1.72	3.95	1.97	0.79	1.61	0.07	99.7
AU4B	55.19	15.83	16.49	0.08	1.68	5.08	2.59	0.98	1.79	0.09	99.8
AU4C	53.75	15.73	16.82	0.15	2.09	5.88	2.76	0.91	1.7	0.15	99.94
AU5A	93.98	0.49	2.6	0.04	0.09	0.08	0.43	0.03	2.03	0	99.77
AU5B	84.06	6.64	5.88	0.05	0.5	0.19	0.07	0.3	1.75	0.01	99.45
AU8A	94.58	0.49	2.29	0.03	0.14	0.08	0.07	0	1.69	0.01	99.38
AU8B	80.39	8	7.16	0.03	1.88	0.2	0.03	0.38	1.67	0.01	99.75
AU9A	87.93	4.58	4.15	0.04	0.37	0.4	0.01	0.32	1.28	0.02	99.1
AU9A1	90.69	3.35	3.06	0.03	0.25	0.13	0.13	0.13	1.5	0.01	99.28
AU9B	86.92	5.5	4.76	0.03	0.46	0.48	0.05	0.42	1.07	0.01	99.7
AU9C	84.66	8.02	3.93	0.02	0.4	0.12	0	0.35	0.96	0.01	98.47

Trace elements

Sc	V	Cr	Co	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	U
1.8	42	50	5	7	6	22	0	5	14	10	1725	13	27	21	0	2
6.3	69	96	4	10	5	62	0	20	17	16	1342	12	46	7	1	1
9.5	87	156	4	16	4	34	0	28	18	19	1251	12	50	9	1.5	0
23.9	345	130	32	51	54	59	8	29	136	41	455	8	389	10	4	2
31	434	91	37	48	77	73	0	31	156	51	219	8	390	8	4	0
21.3	375	78	44	48	97	82	1	27	163	48	170	8	423	6	4	1
2.4	40	47	5	5	3	4	0	6	12	10	1828	14	34	5	0	4
14.8	93	137	12	19	7	13	1	34	15	18	1316	14	75	10	4	1
2.1	39	42	3	5	5	5	0	5	9	9	1516	11	18	4	0	2
23.1	131	223	7	26	3	18	8	40	18	25	874	13	91	11	5	2
11	79	200	8	18	4	14	1	30	29	16	871	9	69	8	2	2
7.1	53	58	5	9	4	7	3	20	12	12	1214	11	43	6	0	2
10.3	95	294	6	18	5	15	4	31	29	11	679	8	69	8	2	1
13.3	76	145	4	15	5	13	4	34	14	15	534	8	72	11	4	1



## Appendix B: Pump test data

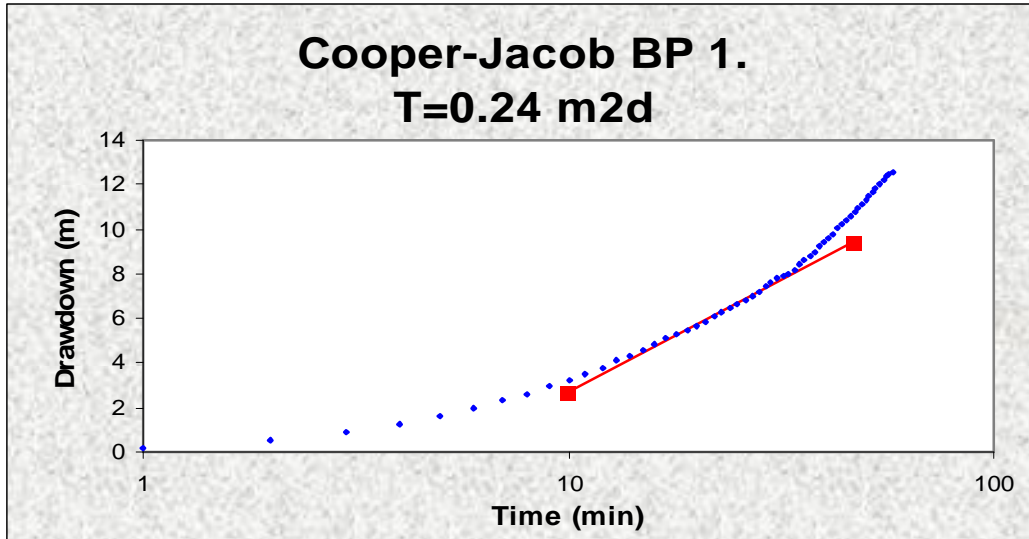


Figure 82: Analyses of pump test data using F-C. Recovery: Time against water level.

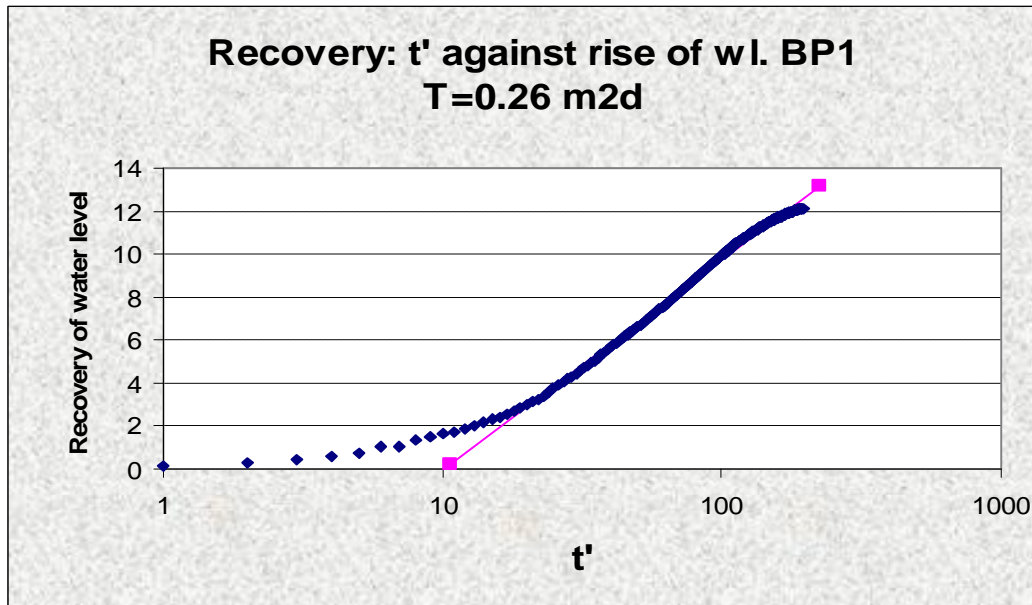


Figure 83: Analyses of pump test data using F-C. Recovery: Time against water level.

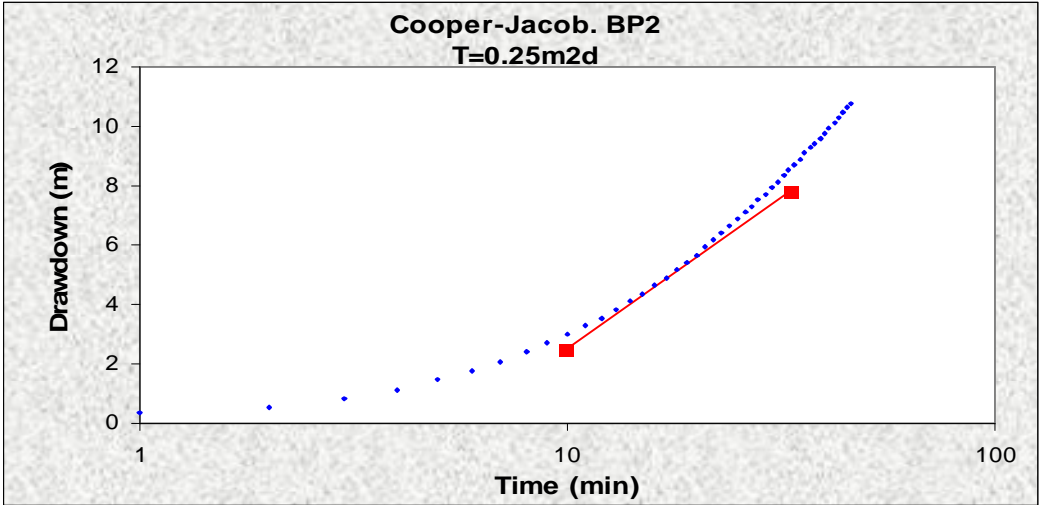


Figure 84: Analyses of pump test data using F-C. Recovery: Time against water level.

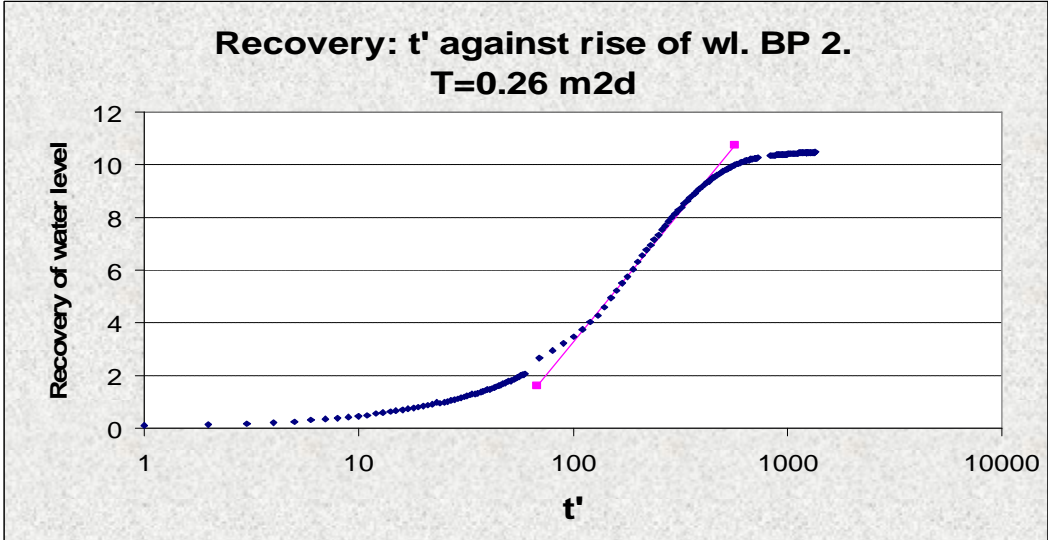


Figure 85: Analyses of pump test data using F-C. Recovery: Time against water level.

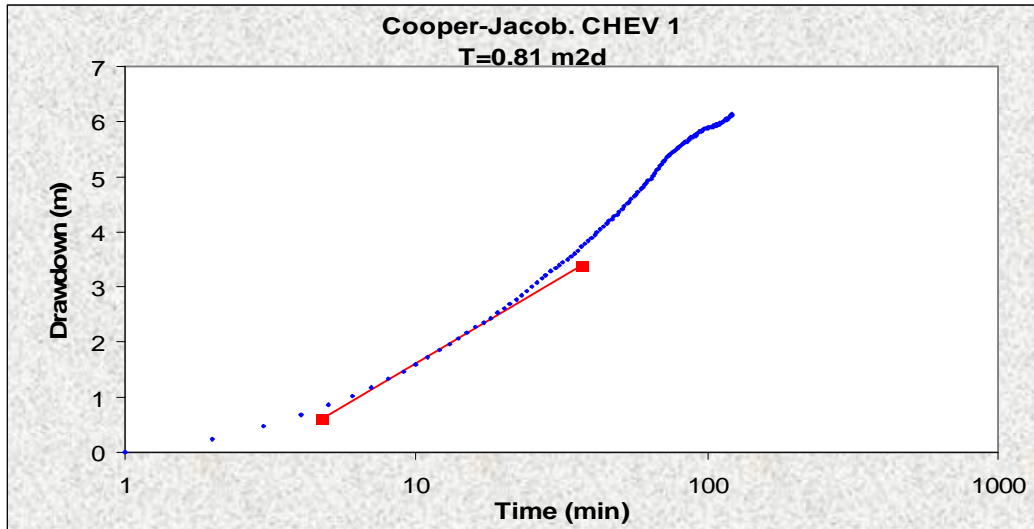


Figure 86: Analyses of pump test data using F-C. Recovery: Time against water level.

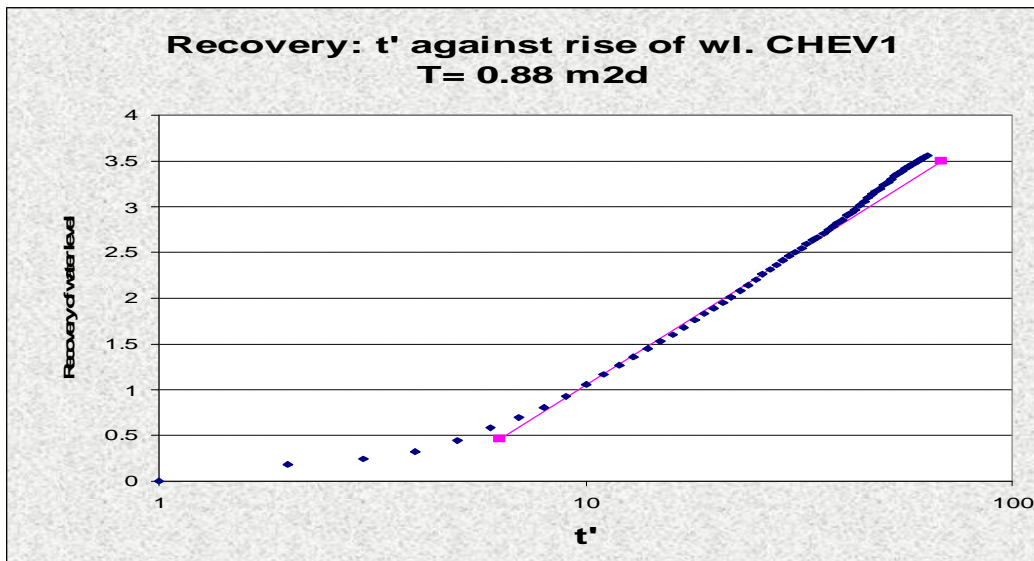


Figure 87: Analyses of pump test data using F-C. Recovery: Time against water level.

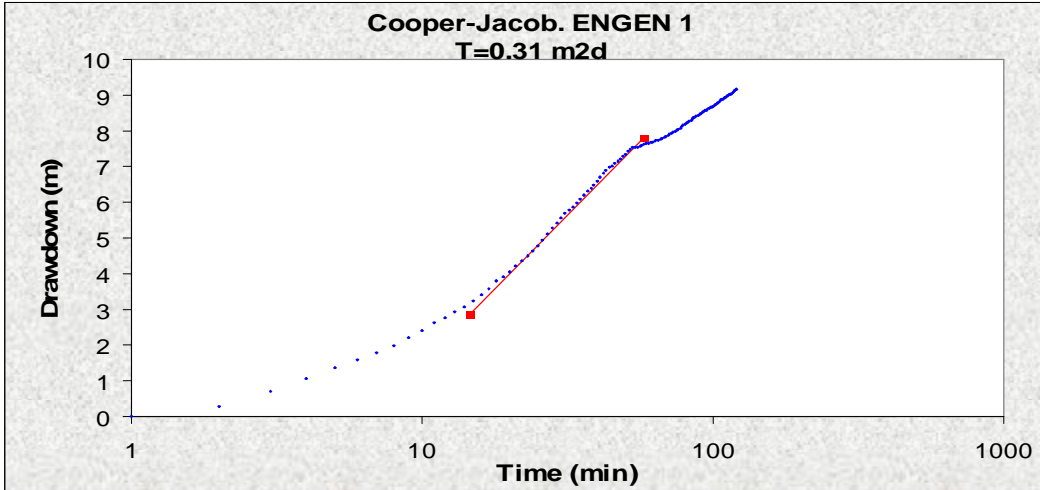


Figure 88: Analyses of pump test data using F-C. Recovery: Time against water level.

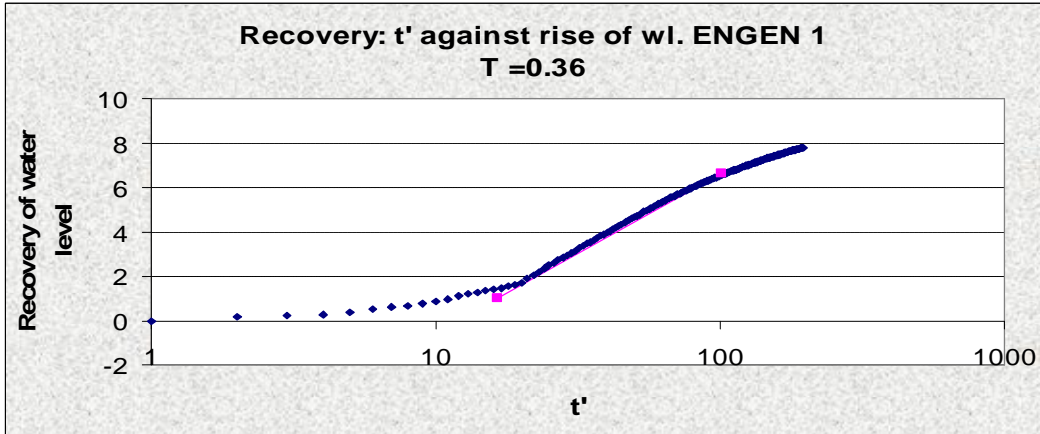


Figure 89: Analyses of pump test data using F-C. Recovery: Time against water level.

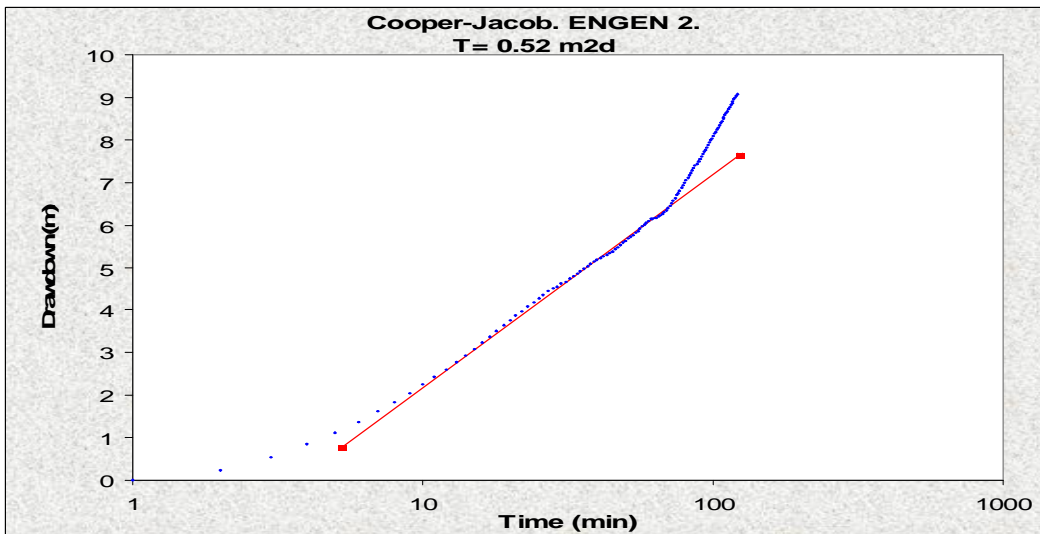


Figure 90: Analyses of pump test data using F-C. Recovery: Time against water level.

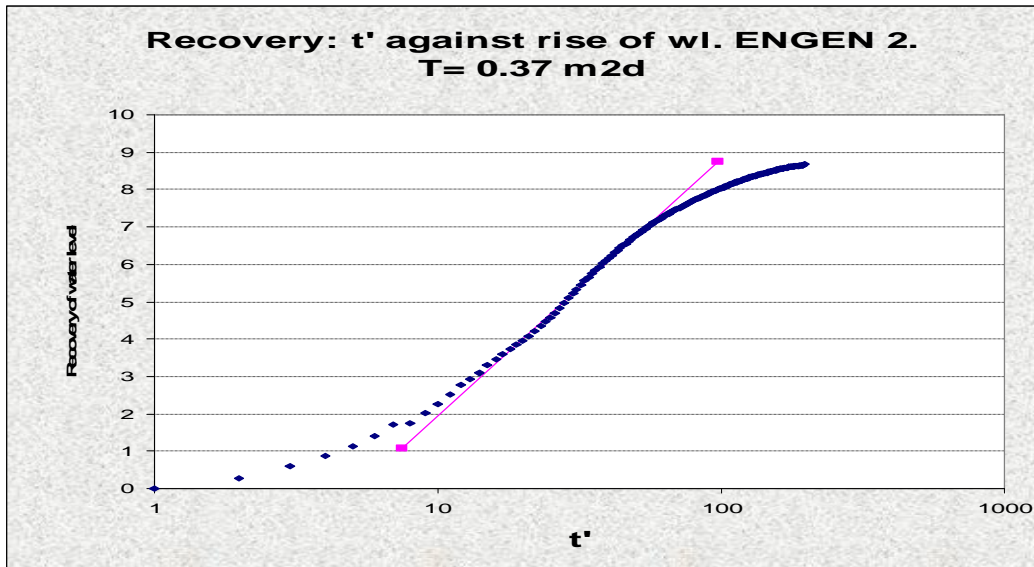


Figure 91: Analyses of pump test data using F-C. Recovery: Time against water level.

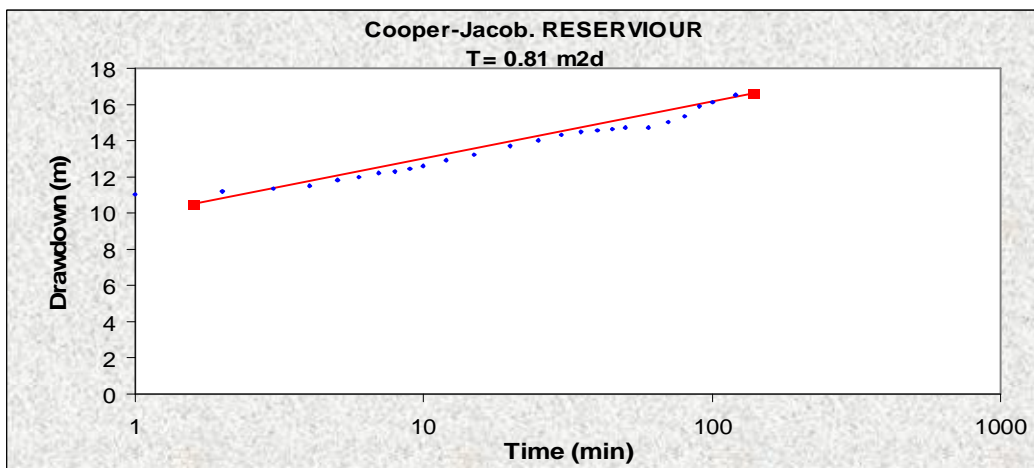


Figure 92: Analyses of pump test data using F-C. Recovery: Time against water level.

# Appendix C: Borehole Logs

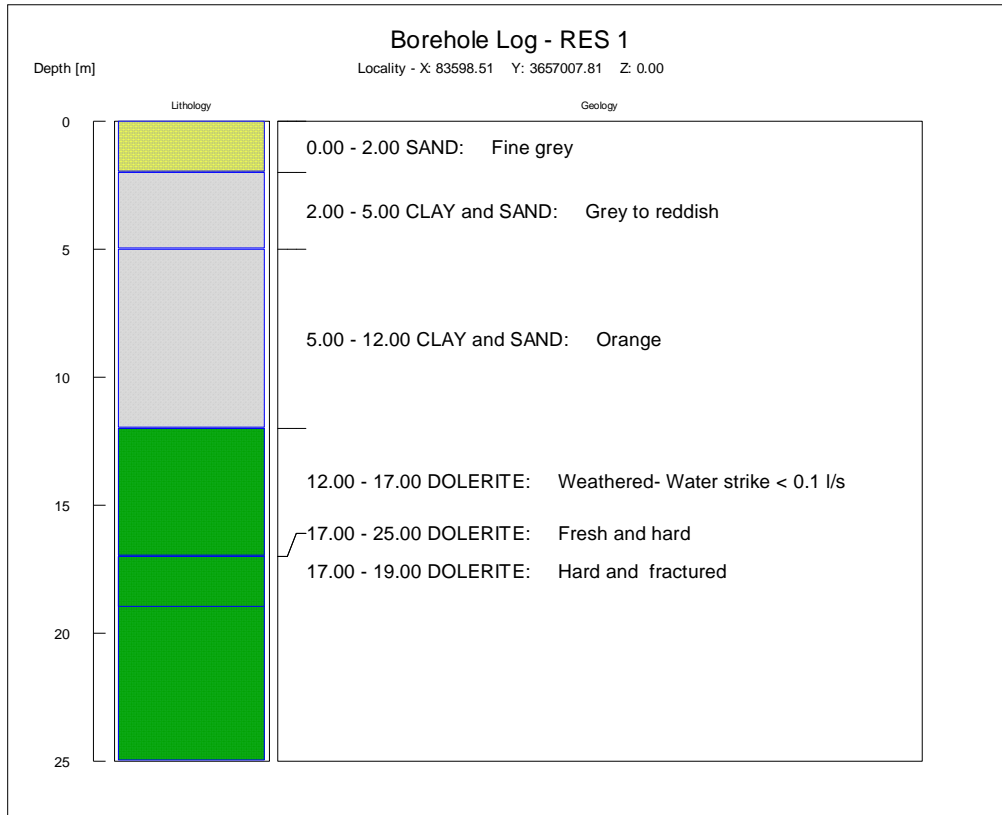
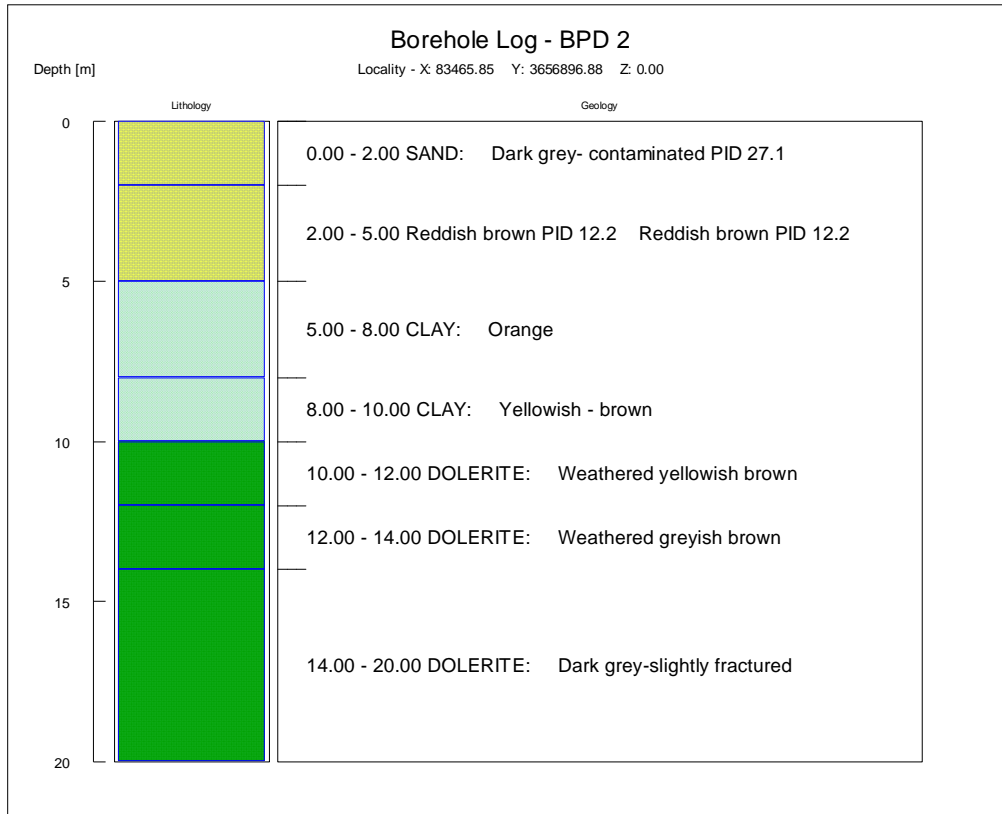
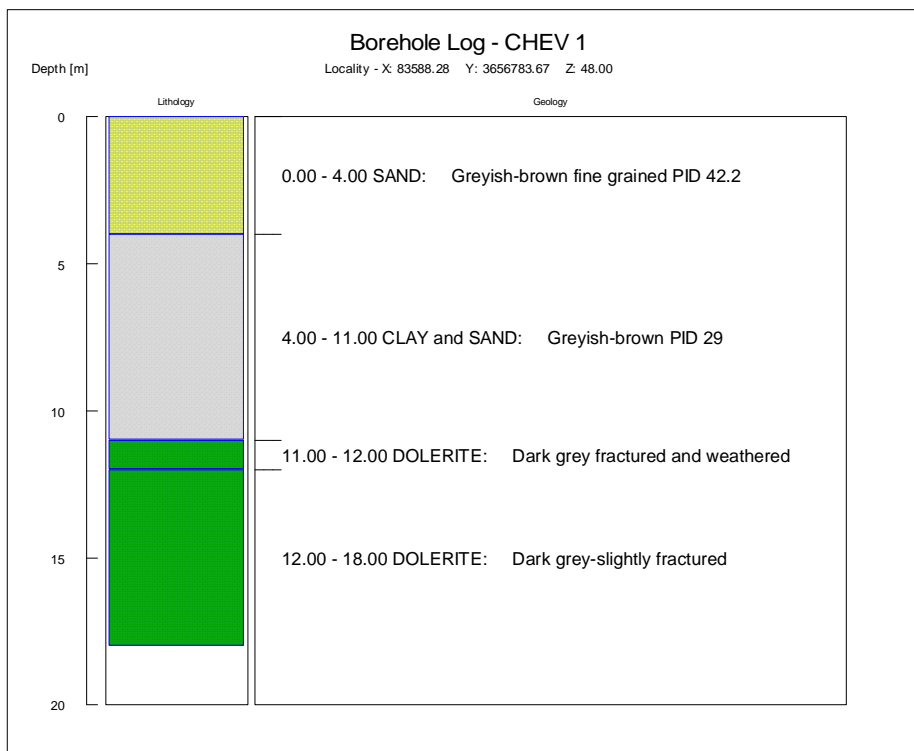


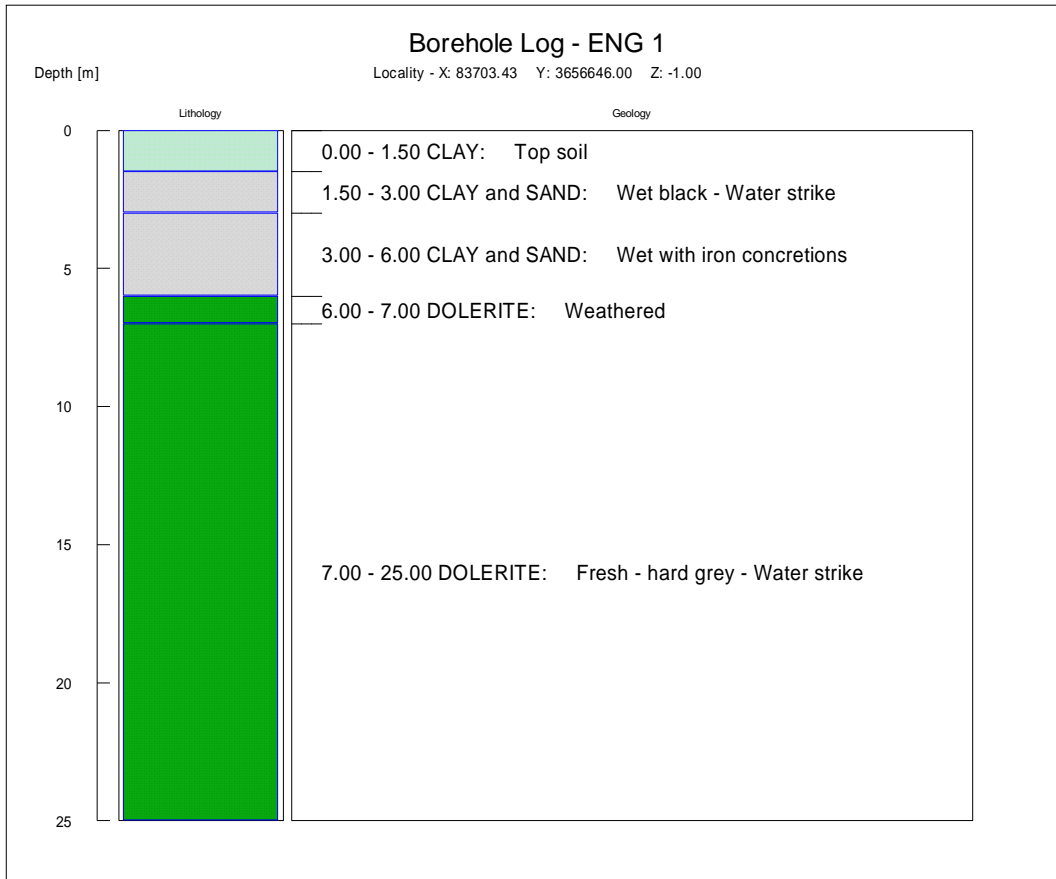
Figure 93: Borehole log for RES 1



**Figure 94: Borehole log for BPD2**

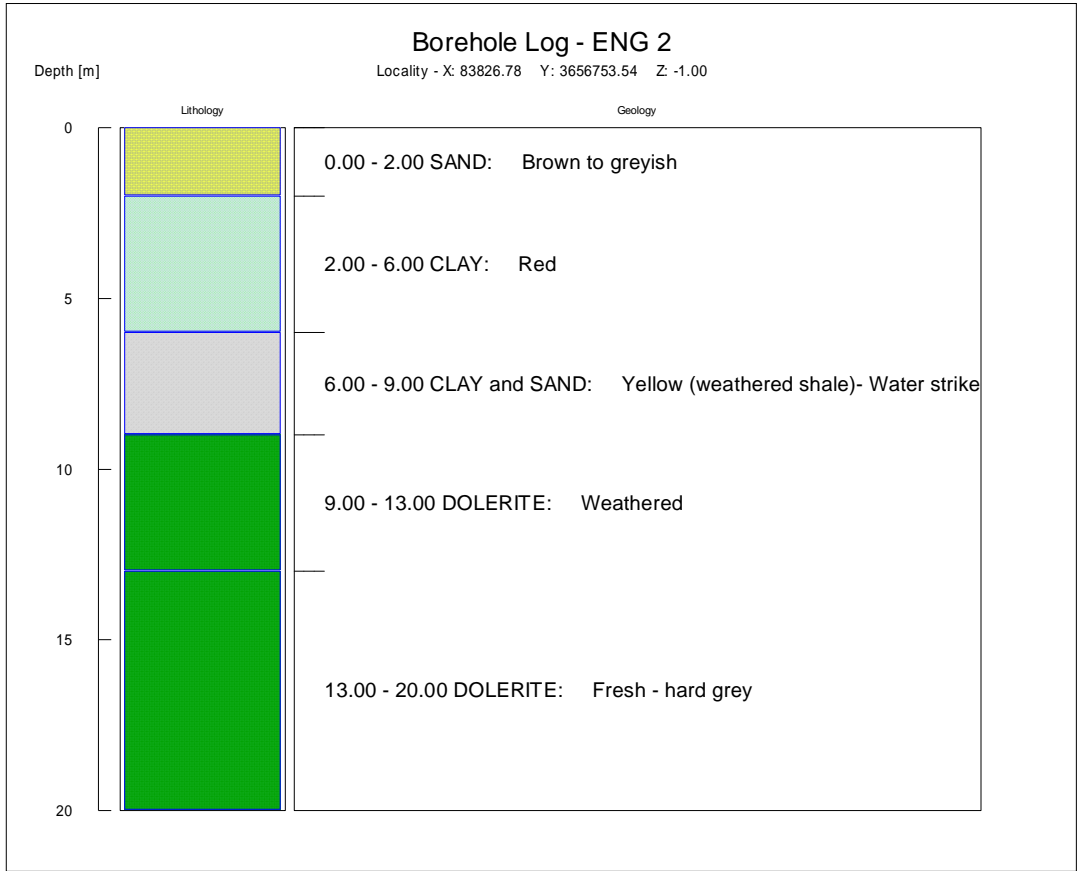


**Figure 95: Borehole log for CHEV1**

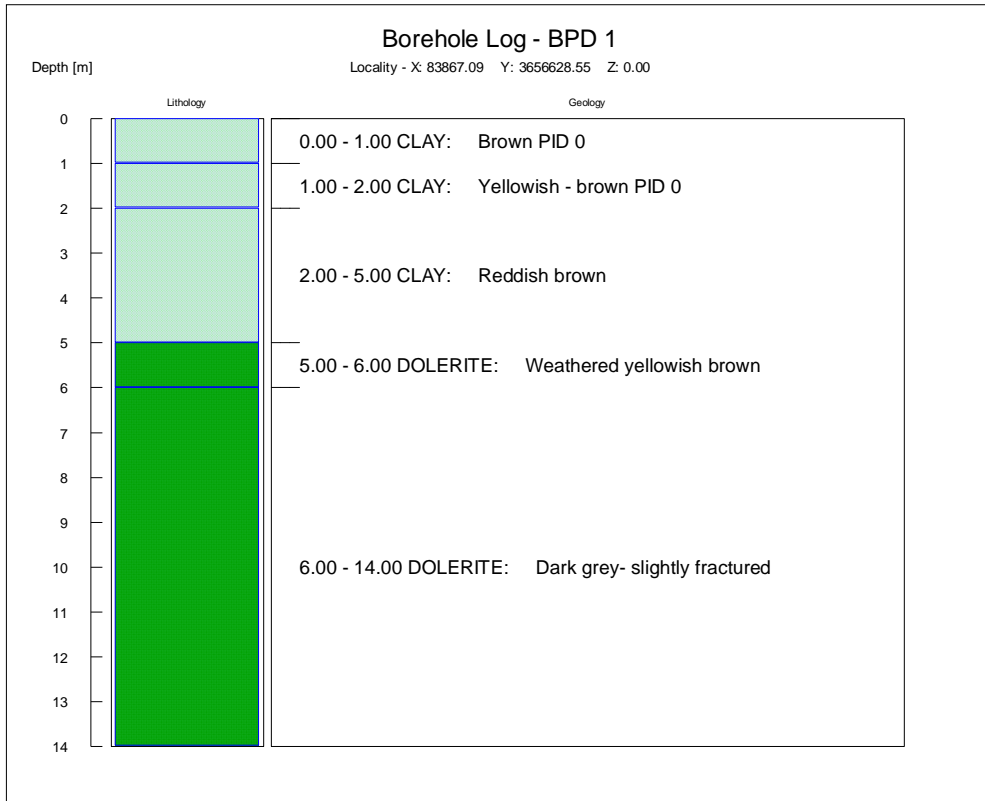


**Figure 96: Borehole log for ENG1**





**Figure 97: Borehole log for ENG2**



**Figure 98: Borehole log for BPD1**

## Appendix D: SAMPLING STABILIZATION CURVES

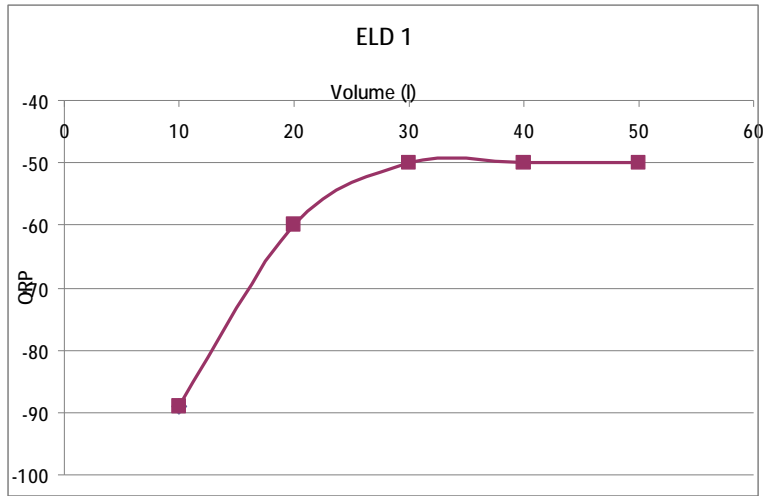


Figure 99: Stabilization of ORP

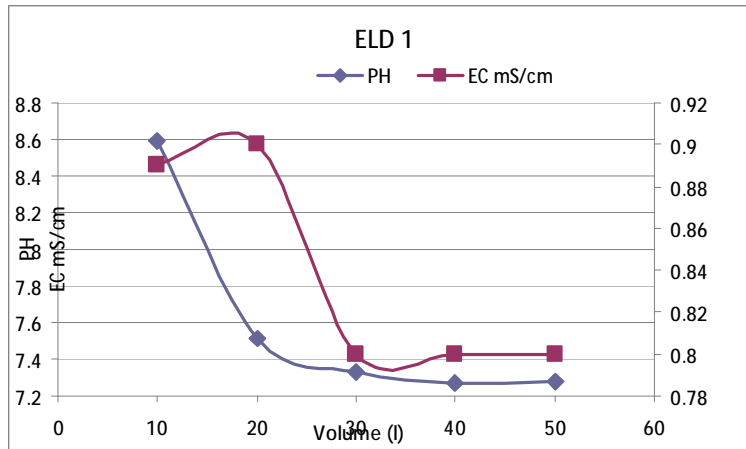


Figure 100: Stabilization of pH and EC

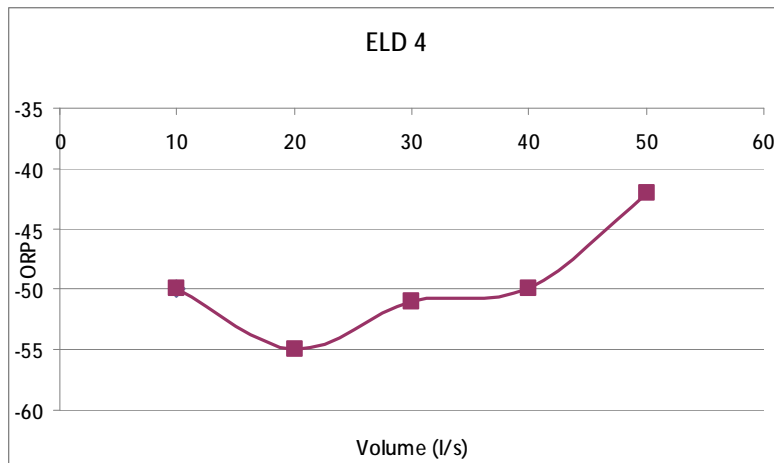


Figure 101: Stabilization of ORP

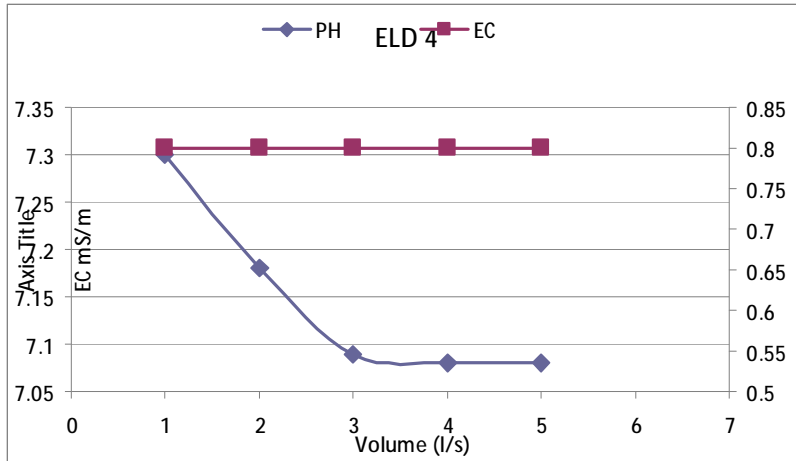


Figure 102: Stabilization of pH and EC

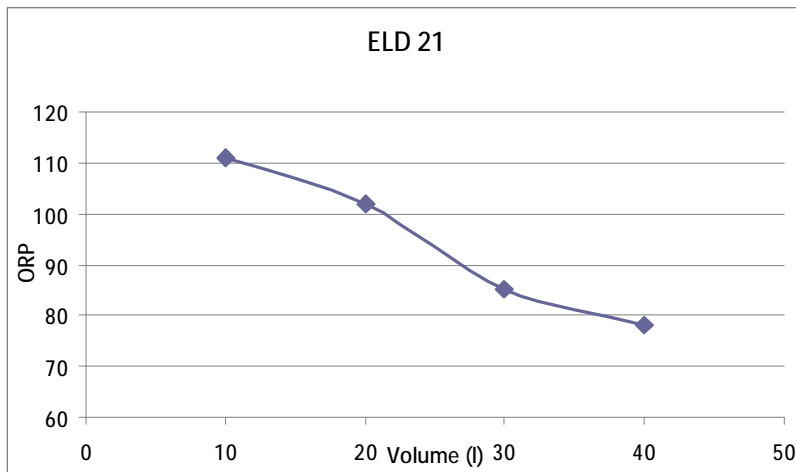


Figure 103: Stabilization of ORP

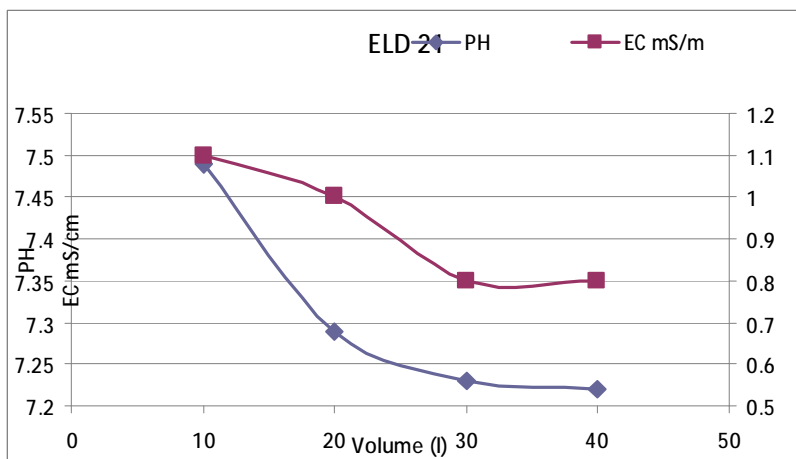


Figure 104: Stabilization of pH and EC

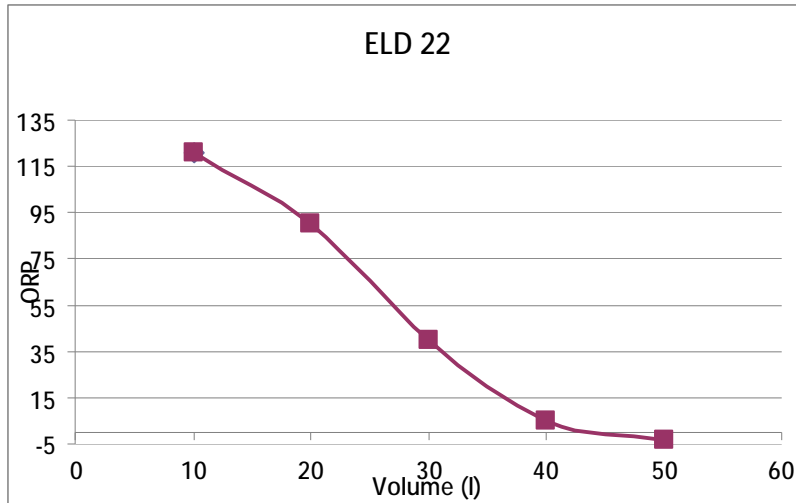


Figure 105: Stabilization of ORP

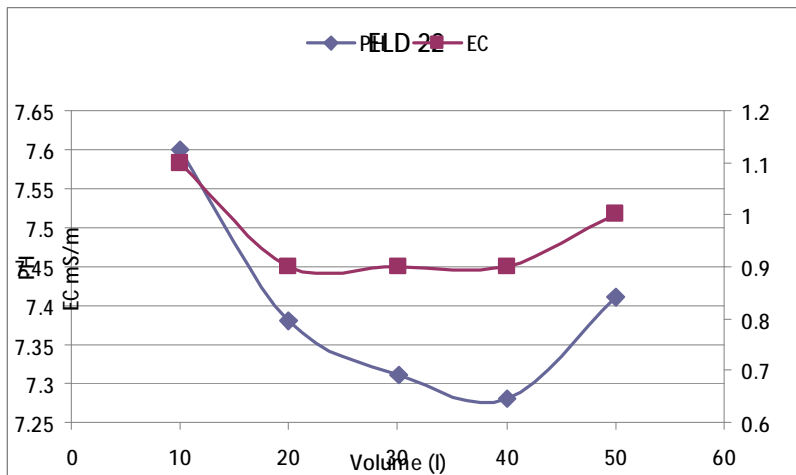


Figure 106: Stabilization of pH and EC

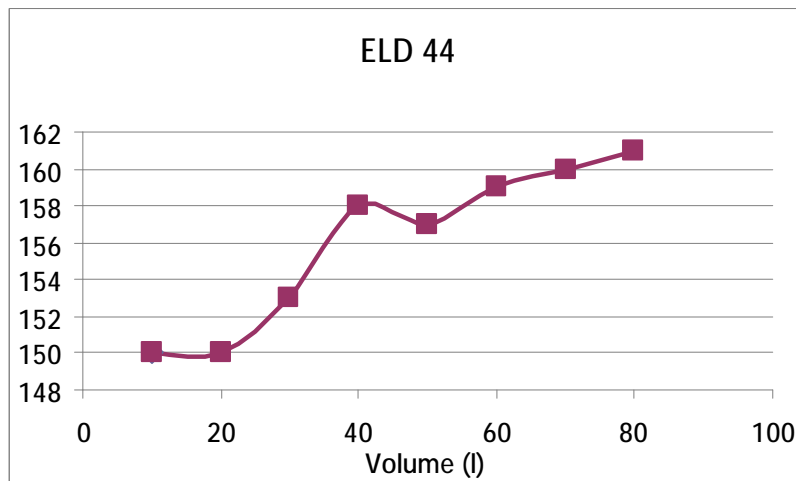


Figure 107: Stabilization of ORP

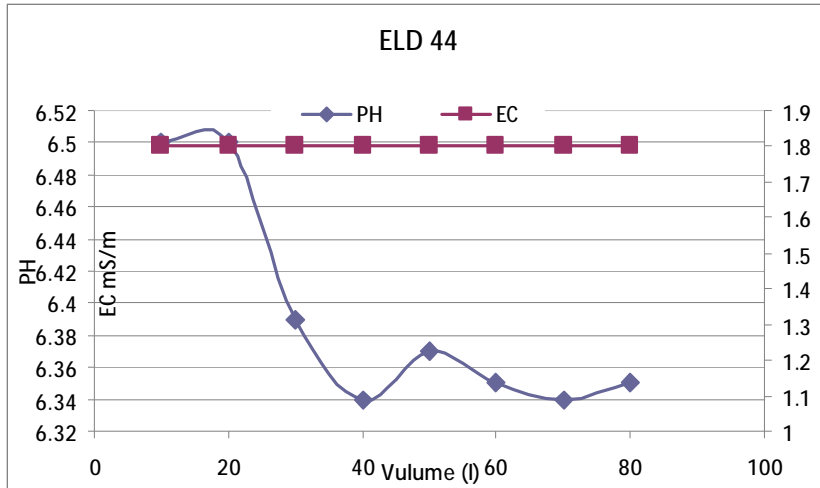


Figure 108: Stabilization of pH and EC

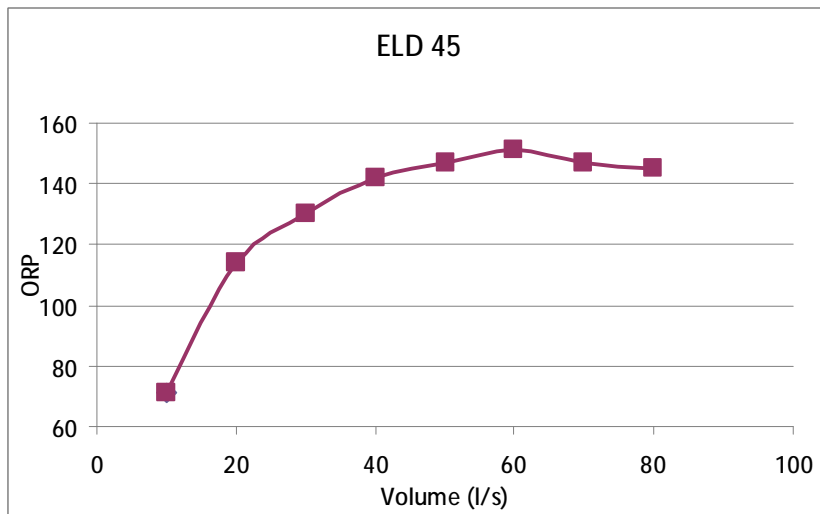


Figure 109: Stabilization of ORP

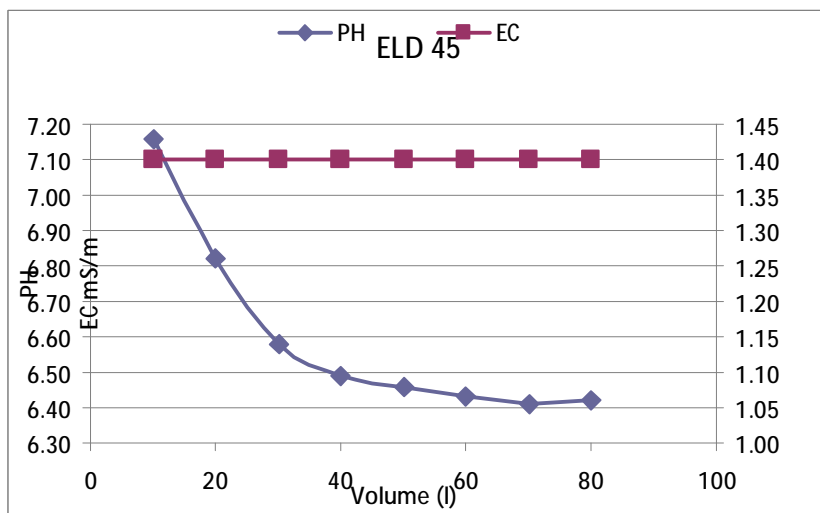


Figure 110: Stabilization of pH and EC

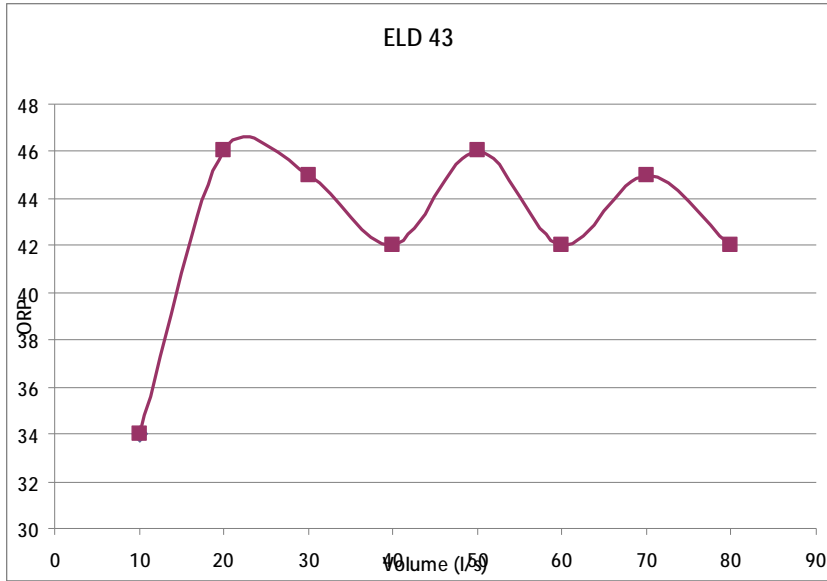


Figure 111: Stabilization of ORP

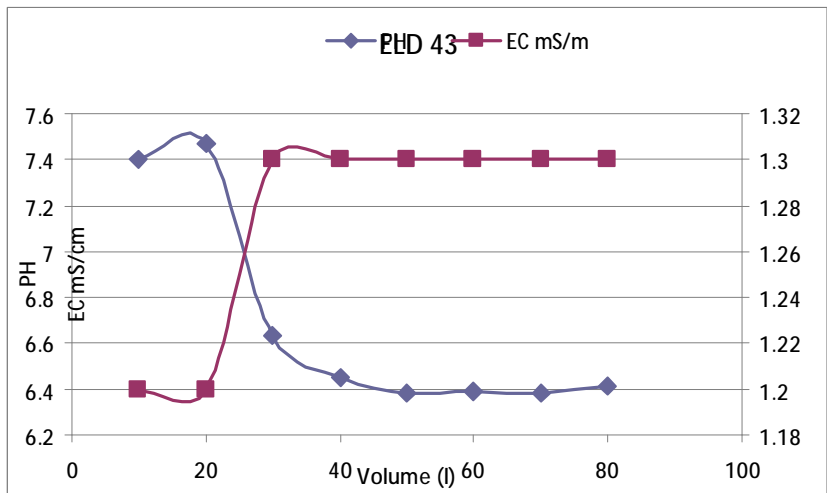
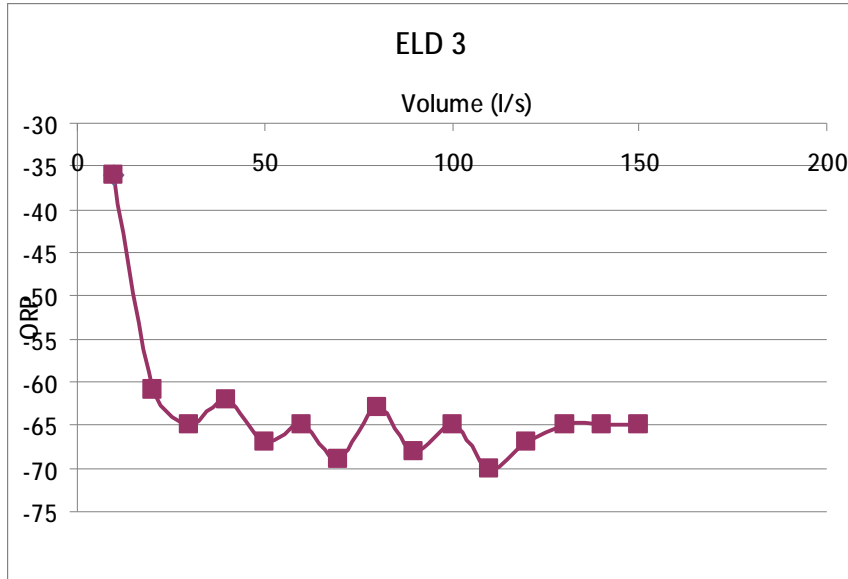
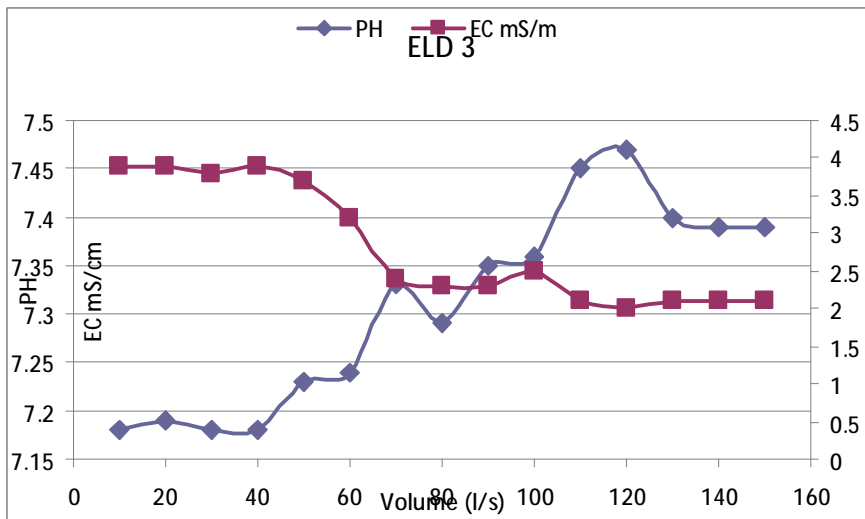


Figure 112: Stabilization of pH and EC



**Figure 113: Stabilization of ORP**



**Figure 114: Stabilization of pH and EC**



