THE OCCURRENCE AND EVALUATION OF LNAPLs CONTAMINATION IN URBAN AREAS OF SOUTH AFRICA.

RESEARCH

BY

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DECLARATION

30 November 2004

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ABSTRACT

Petroleum liquids are a basic building block of our modern lives. Uses include fuels, lubricants, and the raw material for manufactured products. The by-product of these uses has been the inadvertent release of petroleum liquids. A result of our utilization of petroleum liquids is a legacy of soil and groundwater impacted by petroleum liquids. The aim of this research is to provide an overview of LNAPLs in South African urban areas, transport mechanism of the LNAPLs in the subsurface, framework for detecting and evaluating LNAPLs under South African conditions.

LNAPL is a convenient label for petroleum liquids in soils and groundwater. The acronym stands for Light Non Aqueous Phase Liquid. *"Light"* highlights the fact that petroleum liquids (i.e., gasoline) are less dense than water; *"Non Aqueous"* highlights the fact that petroleum is not completely miscible in water.

An LNAPL contamination assessment was conducted at a service station after a complaint was raised by a resident who found free product (petrol) in her borehole. A multitude of private boreholes were found during the hydrocensus survey. A petroleum contamination assessment was done through soil vapour survey (SVS), hand auger holes and rotary percussion drilling. No significant petroleum vapours were detected due to clay soil which has low transmission of vapours. Hand auger holes were restricted to shallow depth due to the lack of penetration though the clay soils. Percussion drilling was needed to gather groundwater information (i.e., quality and quantity). Free product (petrol) was found within the percussion and some of the private boreholes. Groundwater samples were collected and analyzed for BTEX (Benzene, Toluene, Ethyl benzene and Xylenes) compounds. No detectable levels of BTEX were found in the soil samples. Risk assessment was done suing the RBCA approach and BP RISC software. BTEX concentrations of groundwater samples have triggered the Tier 1 risk based screening level for the risk values of carcinogenic and non-carcinogenic through groundwater ingestion, indoor and outdoor vapour inhalation exposure pathways. BP RISC was used to conduct Tier 2 evaluation and carcinogenic risk does exist in the receptor borehole through groundwater ingestion risk pathway. AQUA-WIN finite element model was used to determine the abstraction rate that could be used to conduct a pump-and-treat system. Free product could be recovered within two years after commencing with pump and treat system. Due to the lack of South African regulations with regard to petroleum contamination, the pump and treat system was stopped as

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soon as the product was recovered and monitoring of the dissolved phase hydrocarbons was continued.

The establishment of South African guidelines and risk assessment protocols for petroleum hydrocarbons is outlined and strongly recommended for implementation.

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NOTATIONS

P_o: Outward pressure exposed to the atmosphere

P_I: Inward pressure in the aquifer

P_{nw}: Pressure of the non-wetting fluid

P_w: Pressure of the wetting fluid

ΔP: Pressure difference across the interface

σ : Interfacial tension,

r_1, r_2 : Principal radii of curvature of the interface

S_w : Wetting-fluid saturation ratio

S_{wi}: Irreducible wetting-fluid saturation

S_{nwr}: Residual no-wetting fluid saturation

P_d: Displacement pressure

S_m: Maximum water saturation

k_{rw}: The relative permeability of wetting fluid

k_{rnw}: Relative permeability of non-wetting fluid

Q: Volumetric flow rate (m^3/s)

L: Flow path length (m)

A: Flow area perpendicular to L (m^2),

K: Hydraulic conductivity (m/s)

Δh: Change in hydraulic head over the path L(m)

p: Pressure (N/m^2)

ρ: Fluid density (kg/m^3),

g: Acceleration of gravity (m/s^2)

z: Elevation (m)

μ: Dynamic viscosity

k: Intrinsic permeability (m^2)

Φ: Fluid potential

E: force vector (N)

K_{ow}: octanol-water partition coefficient (dimensionless)

K_{oc}: the value that reflects the impact of organic material to adsorb organic compounds out of solution

f_{oc}: the weight fraction of organic carbon in the soil

Rf: Retardation factor (dimensionless)

K_d: sorption coefficient (cm^3/g)

K_H: Henry's Law Constant

V_w: the average velocity of water (cm/sec)

V_c: the average velocity of chemical contaminant (cm/sec)

ρ_b: soil bulk density (g/cm^3)

Θ: soil porosity (dimensionless)

LIST OF ACRONYMS

NAPL: Non Aqueous Phase Liquid

LNAPL: Light Non-Aqueous Phase Liquid

DNAPL: Dense Non-Aqueous Phase Liquid

BTEX: Benzene, Toluene, Ethyl benzene, Xylenes

GRO: Gasoline Range Organic

TPH: Total Petroleum Hydrocarbons

RBCA: Risk Based Corrective Action

MCL: Maximum Contaminant Level

BP RISC: British Petroleum Risk Integrated Software for Cleanups

EPA: Environmental Protection Agencies

DWAF: Department of Water Affairs and Forestry

DEAT: Department of Environmental Affairs and Tourism

CHAPTER 1.   INTRODUCTION

Petroleum liquids are a basic building block of our modern lives. Uses include fuels, lubricants, and the raw material for manufactured products. The by-product of these uses has been the inadvertent release of petroleum liquids. Fortunately, releases represent a very small fraction of total use and the improvements of the infrastructure have dramatically reduced the potential for future releases. Nevertheless, a result of our utilization of petroleum liquids is a legacy of soil and groundwater impacted by petroleum liquids. Over the last 30 years recognition of the need for better environmental stewardship has driven rapid evolution of science and technology associated with managing releases of petroleum liquids. The aim of this dissertation is to provide an overview of LNAPLs in South African Urban areas, transport mechanism of the LNAPLs in the subsurface, framework for detecting and evaluating LNAPLs under South African conditions and through case studies to construct a holistic methodology for the detection and evaluation of LNAPLs in South Africa.

1.1.   Definition of LNAPL's

LNAPL is a convenient label for petroleum liquids in soils and groundwater. The acronym stands for Light Non Aqueous Phase Liquid. *"Light"* highlights the fact that petroleum liquids (i.e., gasoline) are less dense than water, *"Non Aqueous"* highlights the fact that petroleum do not mix with water. LNAPLs are composed of mixtures of organic molecules that are slightly soluble in water. Where LNAPL comes in contact with groundwater, trace to low percent concentrations of the organic compounds dissolve into it. Dissolution of LNAPLs in groundwater often results in the exceedances of water quality close to the releases. A benefit of low solubility is that loading to the environment is typically small and natural processes often attenuate contaminants of concern over small distance. A disadvantage of low solubility is that LNAPL can persist as a source of groundwater contamination for extended periods (www.api.org/lnapl).

1.2. Aims of the project

- To provide an overview of LNAPLs in South African Urban areas
- Discuss relevant concepts relating to transport of LNAPLs in the subsurface environment
- Give a framework for detecting and evaluating LNAPLs under South African conditions
- Through case studies to construct a holistic methodology for the detection and evaluation of LNAPLs in South Africa.

CHAPTER 2. OCCURRENCE AND POTENTIAL SOURCES OF ORGANIC CONTAMINANTS IN URBAN AREAS OF SOUTH AFRICA

2.1. Occurrence of organic contaminants

During the last few decades, urbanization has taken place at an alarming rate, especially in the developing countries. Cities and small country towns have increased in size tremendously and facilities for the disposal of waste, wastewater, stockpiling, etc. have not always been implemented in a satisfactory manner. Therefore, there are numerous known cases of waste, stockpiles, leaking tanks and pipelines, and accidents damaging the urban environment. Not only the urban area itself is threatened, but also the subsurface framework, including the groundwater resources.

This document will concentrate on the occurrence and potential sources of organic contaminants in urban areas of South Africa. South Africa is divided into nine provinces of which the following urban centers appear to be the main areas affected by organic contaminants, thus Johannesburg-Pretoria (Gauteng province), Sasolburg (Free States province), Sasol Synfuels, Secunda (Mpumalanga province), Durban (Kwa-zulu Natal province) and Cape Town (Western Cape province). Based on these urban centers there are six major petrochemical industries (i.e. refineries, such as Natref, Enref, Calref, Secunda, Mossgas and Sapref) and more than 4368 service stations for all the South African Oil Companies, such as, BP, Caltex, Engen, Sasol, Shell, and Total.

2.1.1. Refineries

All South Africa's refineries were built on grass-root sites well away from urban areas. However over time suburbia has spread to the point where the refineries are now surrounded by habitation. Although the refineries have all spent significant sums in recent years to reduce emissions, the issue of refinery pollution has become a popular one with the fledgling environmental groups in South Africa. Oil refineries convert crude oil into fuel products, lubricating oils, bitumen and chemical feedstock.

The *Natref refinery* (**National Petroleum Refiners of SA (Pty) Ltd**) is located in Sasolburg, South Africa. It is a complex processing refinery with a nameplate distillation capacity of 4280 ktonnes per annum (86 tbpd, *thousand barrels per calendar day*). Sasol Oil (Pty) Ltd (63.64%) and Total South Africa (36.36%) jointly own the refinery. The company was founded in 1967 with three shareholders, which included Sasol, Total and the Iranian Oil Company. The Iranian Oil Company sold its shares to Sasol and Total in 1989.

At the Natref refinery, crude oil is refined to produce **petrol, diesel, liquid petroleum, gas, jet fuel, paraffin and bitumen**. Natref is located approximately 500 kilometers inland within a hundred kilometers from Johannesburg. Crude oil is transported to Sasolburg by means of a pipeline, which runs from Durban. In Durban the crude oil is discharged from tankers through an offshore Single Buoy Mooring facility and product is stored at the Sasol owned Natcos crude oil tanker facilities. Kuwait Petroleum Company (KPC) is a major supplier of crude oil to Natref. (http://www.mbendi.co.za/rena.htm and http://www.sasol.co.za/).

The *Enref refinery* (**Engen refinery**) in Durban, South Africa, is a complex refinery with a nameplate distillation capacity of 5250 ktonnes per annum (105 tbpd). The refinery is owned by Engen and was originally opened in 1954 by Mobil. The refinery was upgraded in 1992 and again in 1994. Also located on the Enref site is the **Safor lubricating base oil refinery**, which is jointly owned by Engen, Caltex and Total South Africa. Safor has a capacity of 145 thousand tonnes per year, which contributes, to the base oil production capacity of the South African lubricants industry as well as having an impact on the African product of base oils.

Enref is a complex refinery with a wide product slate. The Enref fuels, lubricants and asphalt product slate are augmented by the production of aliphatic and aromatic solvents, benzene, process oils and sulphur which contribute to the country's chemicals sector (http://www.mbendi.co.za/reen.htm).

The *Calref refinery* (**Caltex refinery**) in Cape Town, South Africa, is a complex refinery with a distillation capacity of 5500 Kitonnes per annum (110tbpd,).

Caltex refinery was commissioned in July 1966 at a cost of R22 million and was designed to run on light Persian Gulf crude. During the 1970s the refinery capacity was upgraded from its original 50tbd capacity to 110tbd by addition of a second crude train.

The additional capacity was subsequently mothballed when the Sasol synfuel plant was streamed at Secunda. In early 1993 the second train was re-commissioned to restore its capacity of approximately 105tbd. Caltex spent almost R1-billion ($289m) in further upgrading and modernising the refinery. Environmental benefits are expected to include curbing of sulphur in diesel and fuel oil. Cracking capacity was increased and unleaded gasoline is now available (http://www.mbendi.co.za/reca.htm).

The *Sapref refinery* (**South African Petroleum Refinery**) in Durban, South Africa, is a complex refinery, the largest in South Africa, having a nameplate distillation capacity of 8250 ktonnes per annum (165 tbpd). Shell SA and BP SA jointly own the refinery. The Sapref site has a fuels refinery as well as a base oil refinery, the **Samco lubricating oil refinery,** which is also jointly owned. The base oil refinery has a capacity of 155 thousand tonnes per year. This is possibly the largest base oils refinery in Africa and it contributes substantially to the production capacity of the South African lubricants industry. Sapref is able to augment its fuels and lubricants and asphalt product slate so that it also contributes some propylene feedstock for the chemical sector as well as producing aliphatic hydrocarbon solvents, industrial processing oils and sulphur.

The Sapref refinery originally opened in 1963 with an integrated unit and associated storage facilities. In the years following, a bitumen high vacuum unit, blowing unit and blending facilities, first crude distillation unit and lube oil plant were added.

Work on upgrading the refinery commenced in 1991 at a total cost of $150 million. Capacity was increased by more than 30% and provided facilities for producing unleaded gasoline and low-sulphur diesel as well as decreasing energy consumption and environmental emissions (http://www.mbendi.co.za/resa.htm). Table 2.1 below presents the capacity of South African Refineries.

Table 2.1: Capacity of South African Refineries

RIFINERIES	Capacity (barrels per day)		
	1992	1997	1998
Sapref	120 000	165 000	180 000
Enref	70 000	105 000	105 000
Calref	50 000	100 000	100 000
Natref	78 000	86 000	86 000
Sasol	150 000	150 000	150 000
Mossgas	45 000	45 000	45 000
Total	**513 000**	**651 000**	**666 000**

These figures reflect the expansion in capacity at the conventional refineries in the early 1990's, whereas the certain additions to capacity occurred in 1998 (http://www.mbendi.co.za/resa.htm).

2.1.2. Service Stations and Depots

TOTAL's marketing assets includes 688 branded service stations, with a network of depots and a fleet of road tankers. The company manufactures and sells the full range of petroleum products including lubricants and greases, kerosene, jet fuel and liquid petroleum gas (http://www.total.com).

BP South Africa has its head office in Cape Town and is one of the major oil companies in South Africa with extensive marketing, refining assets and a product portfolio that comprises a full range of fuels, lubricants, bitumens and solvents. BP's marketing assets include 780 branded service stations which are concentrated in Gauteng (Johannesburg/Pretoria), Durban (Kwa-zulu natal) and Cape Town (Western Cape), a 26 countrywide network of depots and a fleet of road tankers ensuring that its new generation BP petrol and other fuels are available in every part of Southern Africa (http://www.mbendi.co.za/cobpsa.htm) and (http://www.bp.com).

Caltex Oil South Africa has a network of over 1000 service stations with representation at 92 depots (http://www.caltex.com/Africa/about/history.htm).

Engen has the largest network of service stations in Southern Africa with more than 1 300 locations, covering all corners of the country (http://www.engen.com).

Shell is one of the major oil companies in South Africa with extensive marketing and refining assets and a product portfolio that comprises a full range of fuels, lubricants, bitumens, solvents and other chemicals. Shell has a strong position in the Southern African gasoline and automotive diesel sectors, holding a 17.8% share of the market with over **800 retail sites**. These are distributed throughout the region and include sites with convenience stores and several highway site locations. Shell is also active in the marketing of fuel, oil and chemical products. (http://www.mbendi.co.za/coshsa.htm). Table 2.2 below shows the estimated number of fuel service stations in South Africa.

Table 1.2: Estimated number of fuel service stations in South Africa.

South African Oil Company	Estimated number of service stations
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,   www.shell.co.za,   www.bp.com,   www.engen.co.za, www.caltex.co.za

2.2.   Potential sources of organic contaminants

Major sources of organic contaminants are mainly associated with human activities (*i.e. industries and urban settlements*), through these activities; the synthetic organic compounds, *solvents and petroleum hydrocarbons in particular*, may get contact with subsurface, which eventually migrates to groundwater environment.

The petrochemical industries (*refineries, such as Natref, Enref, Calref, Secunda, Mossgas and Sapref*), service stations and petroleum depots (*BP, Caltex, Engen, Sasol, Shell, and Total*) are the main potential urban sources of the organic contaminants, including *Light Non-Aqueous-Phase Liquid (LNAPL) and Dense Non-Aqueous Phase Liquid (DNAPL)* in particular. These contaminants occur through leaking of product storage tanks (*below and above ground*) and pipelines thereby exposing the subsurface to hydrocarbons, which eventually deteriorates the groundwater resources.

2.3.   Polluting activities

Anthropogenic activities such as industrial and urban settlements have the potential of inducing the organic contaminants to the groundwater media. Organic contaminants may reach the groundwater if leakage or spillage occurs from both above and underground product storage tanks.

Groundwater contamination in urban areas may arise from the following activities:

- Production, use and storage of hazardous chemicals
- Accidental spills of chemicals during use and transport
- Transport of chemicals or waste via underground pipelines and

▪ Above and underground petroleum storage tanks and other chemical products

Figure 2.1 below present the recent example of accidental spill of petrol that occurred on the 06 February 2003, 09H19 A.M along the N6 outside MacLean in the Eastern Cape. The tanker, carrying 35 000 liters of petrol, was enroute to Stutterheim when it overturned and immediately caught fire (http://www.sabcnews.com/South Africa). It is therefore evident that the hydrocarbons from the spill site will enter the subsurface and eventually cause groundwater contamination. Table 2.3 below shows the anthropogenic activities and the arising organic contaminants thereof.

Figure 2.1: The tanker overturned and caught fire outside MacLean in the Eastern Cape (Petrol tanker on fire on the N6 February 06, 2003, 09:19 AM, Burnt tanker was carrying 35 000 liters of fuel February 06, 2003, 01:01 PM

Table 2.3: Anthropogenic activities and potential organic contaminants in urban areas of South Africa.

Category	Type	Source type	Organic contaminants	Class of Contaminants
Industries	Petroleum refineries (i.e. Natref, Enref, Calref, and Sapref)	Leak, spill and run off	BTEX, PCE, TCE, DCE, and Chloroform (*gasoline, solvents and degreasing agents*) diesel fuel and Coal tar (*small quantity of BTEX, and predominately PAHs*)	LNAPL&DNAPL
	Dry cleaning	Effluent	TCE, PCE	DNAPL
	Plastic and wood manufacturing	Effluent	Vinyl chloride	DNAPL
	Oil and solvent recycling	Leaking, spill and runoff	BTEX and solvents	LNAPL&DNAPL
	Paint works	Effluent	Methylene chloride (DCM)	DNAPL
Urban settlements	Service Stations	Leaking above and underground petroleum storage tanks, pipelines rupture, runoff	BTEX (Gasoline) and diesel fuel	LNAPL&DNAPL
	Dump sites	Residential disposal, leaching	Commonly cleaning and degreasing agents	DNAPL
	Miscellaneous	Accidents during transport, pipelines	Gasoline and other petroleum products	LNAPL&DNAPL

2.4. Types of organic contaminants

The type of organic contaminants that may be released depends on the nature of the raw materials used and waste generated by the specific petrochemical industrial processes. Most organic pollution in both soil and groundwater results from leaking underground storage tanks for petrol (gasoline) and the use of solvents and degreasing agents in manufacturing (http://mineral.gly.bris.ac.uk/envgeochem/organics.pdf).

Some organic contaminants from common polluting petrochemical industries (*Enref, Calref, Secunda, Mossgas and Sapref*) are cyclic (i.e., aliphatic) hydrocarbons such as *ethylene, propylene, and butylene* and cyclic aromatic hydrocarbons such as *benzene, toluene, styrene, xylene, ethyl benzene*, made from refined petroleum or liquid hydrocarbons. *Aliphatic* is hydrocarbons which do not contain benzene ring, while *aromatic* is hydrocarbons which contain benzene ring (Fetter, 1999). Generally these hydrocarbons are collectively known as Light Non Aqueous Phase liquids (*LNAPLs*) due to their specific density, which is less than the density of water.

The petrochemical industries are also capable of inducing the halogenated solvents, such as, *tricholoroethene (TCE)*, *tetrachloroethene (PCE), 1,1dichloroethene and 1,2 trans-dichloroethene* (DCE) and *chloroethene (vinyl chloride)*, of which are not environmentally friendly. The solvents are commonly known as Dense Non Aqueous Phase liquids (*DNAPLs).* DNAPLS are heavier than water and therefore they sink to the bottom of the water bearing formation (aquifer).

2.4.1. The physicochemical properties of common organic contaminants particularly petroleum hydrocarbons (LNAPLS) and solvents (DNAPLS).

LNAPLs and DNAPLs are the most common organic contaminants, which have potential of causing soil and groundwater pollution (subsurface). All these organic contaminants have been named based on their physical (*i.e. density, viscosity, volatility, solubility, octanol-water partition coefficient "K_{ow}", vapour pressure and Henry's coefficient*) and chemical properties (*i.e. molecular weight and structural complexity*).

2.4.1.1. Light Non Aqueous Phase Liquids (LNAPLs)

LNAPLs (*including petroleum products and other refined hydrocarbons*) have a specific gravity, which is less than water; therefore they tend to form a pool on top of the groundwater table (Hulling et al, 1991). Viscosity of a liquid organic compound is a measure of the degree to which it will resist flow under a given force measured in dyne-seconds per square centimeter (Devitt et al., 1987). Examples of LNAPLs include gasoline, jet fuel and heating oils. Gasoline is made up of mono-aromatic compounds such as benzene, Toluene, Ethyl benzene and Xylenes (*including ortho-Xylenes, meta- and para-Xylenes*), which are collectively called BTEX compounds.

Organic compounds differ widely in their solubility, from infinitely miscible polar compounds, such as methanol, to extremely low solubility nonpolar compounds, such as polynuclear aromatic hydrocarbons (PAHs) (Horvarth, 1982). The Solubility represents the maximum concentration of the compound that will be dissolved in water under equilibrium conditions (Eckenfelder et al, 1993). Solubility is generally increases with temperature (increase of $10^{o}C$, increase in solubility of 5-30%).

Solubility of the organic compounds (LNAPLs and DNAPLs in particular) is controlled by the molecular weight, structural complexity and octanol-water partition coefficient (K_{ow}). The octanol-water partitioning coefficient (K_{ow}) is a measure of the degree to which an organic substance will preferentially dissolve in water or organic solvent (Fetter, 1999). Solubility of organic compounds in water tends to decline as the molecular weight and the K_{ow} of the compound increases. The decrease and increase in K_{ow} determines whether the compound is hydrophilic (*water attracting associated with low K_{ow}*) or hydrophobic (*water repelling, associated with high K_{ow}*), respectively (Riser-Roberts, 1998).

It is generally believed that for hydrophobic compounds, the relationships based on K_{ow} are superior to those based on water solubility. However, for gasoline constituents with low K_{ow} values, solubility based relationships are probably superior to those based on K_{ow} (Lyman, 1992). Figure 2.2 below shows the chemical structure of the mono-aromatic hydrocarbons (BTEX) (http://mineral.gly.bris.ac.uk/envgeochem/organics.pdf).
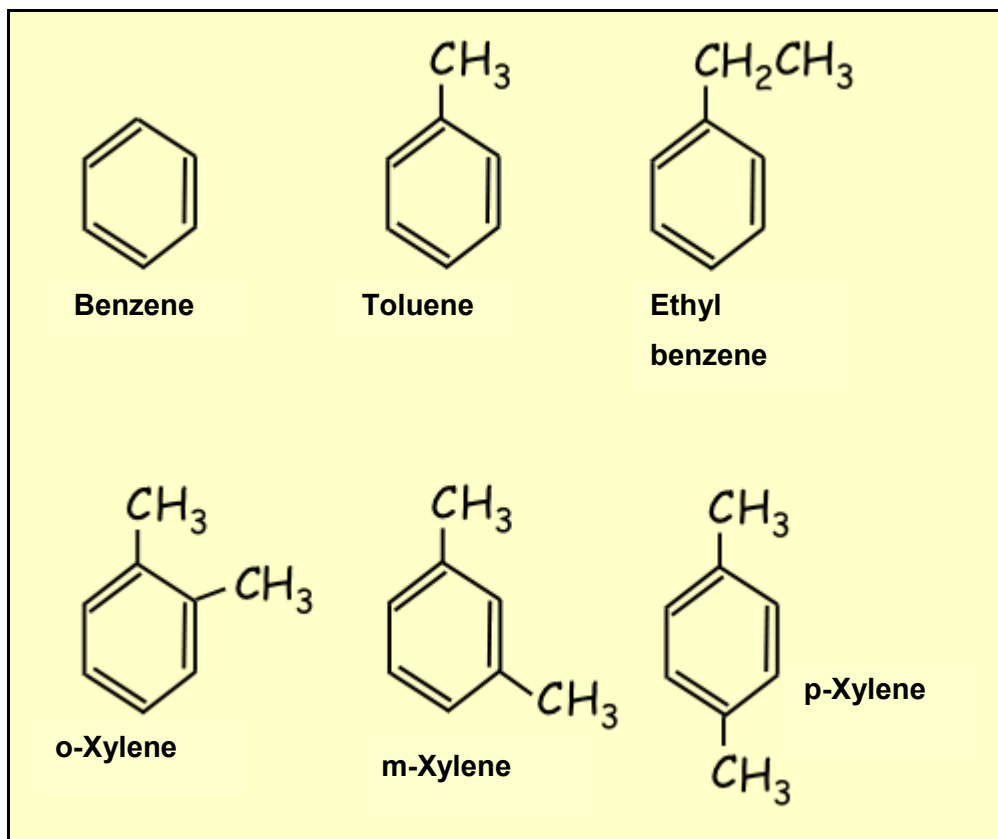
Figure 2.2: The chemical structure of mono-aromatic hydrocarbons.

2.4.1.2.   Dense Non Aqueous Phase Liquids (DNAPLs)

Many organic solvents are denser than water, hence the designation "dense". DNAPLs have a specific gravity which is denser than water, therefore DNAPLs tend sink through the water column and collect in depressions at the base of the aquifer. They flow along the bottom of the water table aquifer and can move in directions that are different than groundwater flow. Flows along open fractures or bore holes downward in response to gravity, not the hydraulic gradient. Some examples of DNAPLs include chlorinated solvents such as, *tricholoroethene (TCE)*, *tetrachloroethene (PCE), 1,1dichloroethene and 1,2 trans-dichloroethene* (DCE) and *chloroethene (vinyl chloride)*, polychlorinated biphenyls (PCBs), creosote, coal tar and some pesticides (Cohen et al, 1993). The physical/chemical properties of selected chlorinated solvents are shown in Table 2.4 below (http://mineral.gly.bris.ac.uk/envgeochem/organics.pdf). Based on the Henry's constants in Table 2.4 below, it is clear that the chlorinated solvents are less volatile. Generally, the transport of a substance in the vapour phase is favored by high vapour

pressure and Henry's law constants (Eckenfelder et al, 1993). Vapour pressure is a measure of the tendency of a substance to pass from a solid or liquid to a vapour phase (Fetter, 1999). The K_{oc} value reflects the impact of organic material to adsorb organic compounds out of solution (Riser-Roberts, 1998). Figure 2.3 below show the chemical structure of chlorinated solvents (http://mineral.gly.bris.ac.uk/envgeochem/organics.pdf).

Table 2.2: physicochemical properties of selected Chlorinated solvents

Compound	Vapor Pressure (mm Hg)	Henry's Law Constant (bar-m^3/mole)	K_{oc}
Trichloroethene ("TCE")	60	0.01	152
Dichloromethane CH$_2$Cl$_2$	349	0.0031	25
1,1-dichloroethene CH$_2$=CCl$_2$	217	0.0043	180
Tetrachloroethene ("PCE") CCl$_2$=CCl$_2$	14	0.0083	303
Tetrachloromethane or Chloroform (Chloroform) CCl$_4$	160	0.023	232
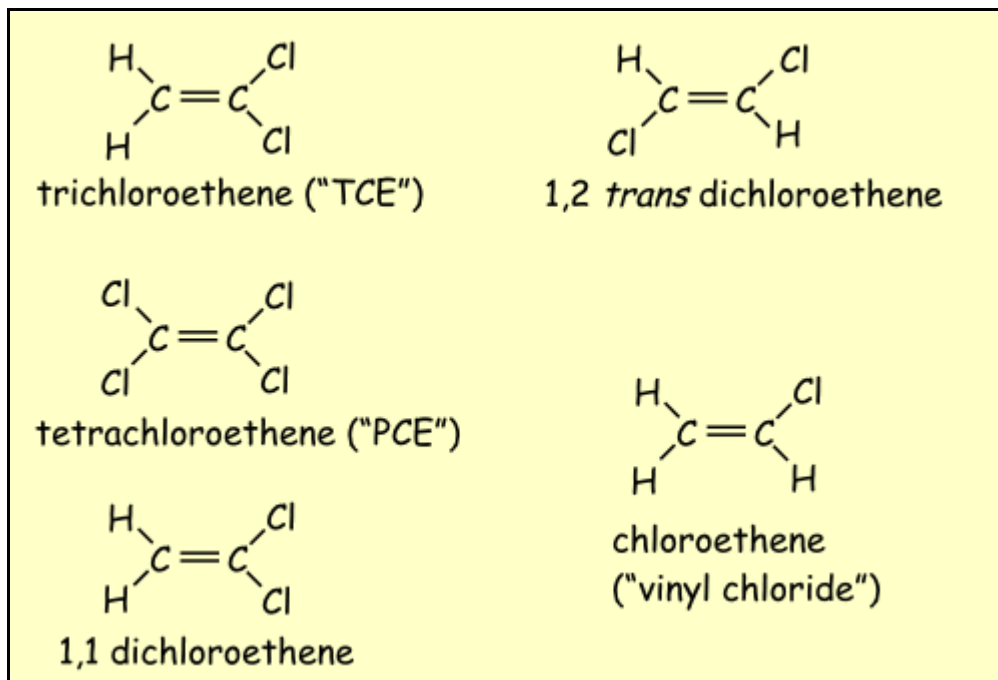
Figure 2.3: The chemical structure of chlorinated solvents .

CHAPTER 3.   MECHANISM OF NAPLS TRANSPORT

3.1.   Multi-phase flow

The gasoline and chlorinated solvents entering the subsurface from a spill, leak release often does so as constituents of a non -aqueous phase liquids (NAPL). They may have densities that are greater than water (dense no aqueous phase liquids, DNAPLs) or densities that are less than water (light non aqueous phase liquids, LNAPLs). LNAPLs and DNAPLs may be partially soluble in water, so that a dissolved phase as well as a non-aqueous phase (free phase) may be present (Schwille, 1981, 1984,1988).

The fundamental principles which are governing the multi-phase flow in porous media include the saturation ratio, interfacial tension, wettability, capillary pressure and relative permeability. Two-phase flow may occur below the water table with water and a DNAPL (McWhorter et al., 1990). Three-phase flow may occur in the vadose zone with air, water and an LNAPL (Abriola et al., 1985a, 1985b).

3.1.1. Saturation ratio, Interfacial tension and Wettability.

Saturation ratio of a fluid is the fraction of the total pore space filled with the specific liquid (i.e. saturation ratio of water or LNAPL). The total of the saturation ratios for all the fluids present in the pore space, including air, add up to 1.0 of which can be also expressed as percent saturation.

Interfacial tension is the forces exerted on the interface of the two immiscible fluids. The tension arises due to the unbalanced cohesion forces on the molecules at the interface. The tension causes the interface between the two fluids to contract and form an area that is as small as possible. Because a tension is force acting over an area, it is customarily measured as force per unit length. A force balanced on a curved interface between two fluids leads to the conclusions that the pressure in the fluids on either side of the interface is not equal, the difference being given by equation

$$\Delta P = \sigma \left[1/r_1 + 1/r_2 \right] \tag{3.1}$$

Where ΔP is the pressure difference across the interface, σ is the interfacial tension, and r_1 and r_2 are the principal radii of curvature of the interface. The fluid on the concave side of the interface is at the higher pressure. If the interface forms a subsection of a sphere, then $r_1 = r_2$ and the equation 3.2 obtained. Therefore interfacial tension is seen to be the property of that permits two fluid to exist in contact at different pressures.

$$\Delta P = 2\sigma/r \qquad (3.2)$$

When two fluids are in contact with a solid, one usually has a great affinity for the solid than the other. Therefore, the fluid with the greater affinity for the solid is said to be the **wetting fluid**, the other being the **non-wetting fluid**. The wetting fluid will preferentially spreads over the solid; however the relative affinity of the two fluids for the solid (**wettability**) is manifested in a **contact angle**. Contact angle is the angle that the fluid-fluid interface makes with the solid. The size of the contact angle is determined mainly determined by the cohesion force between the liquid molecules and the adhesion forces between the liquid, gas and the solid molecules. If the adhesive forces between the solid and liquid are greater than the cohesive forces of the liquid and the adhesive forces between the surface and gas, the angle tends to be acute. A contact angle of zero mean that the drop has spread completely over the solid, while a contact angle of 180° indicates that the surface has completely rejected the drop. Such a drop will retain its spherical shape if the effect of gravity is neglected. Fluids that display acute contact angles are therefore known as **wetting fluids**, and those that display obtuse angles as **non-wetting fluids**. Figure 3.1 below shows a graphical representation of the contact angle and the equilibrium forces at the edge of a liquid drop that is in contact with a solid (Hillel, 1971)
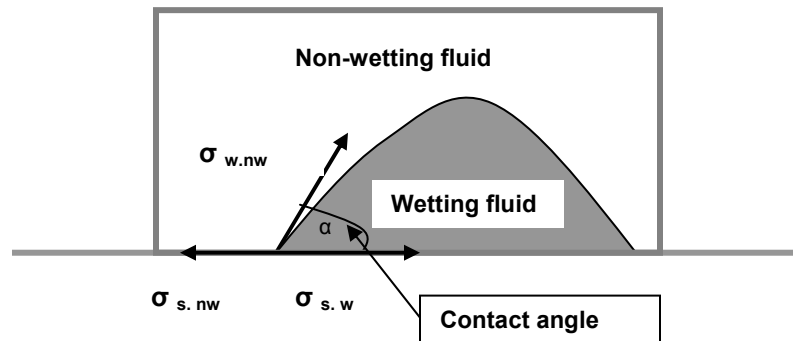
Figure 3.1: Equilibrium of the forces at the edge of a liquid drop that is in contact with a solid surface**.**

The contact angle between the interface of wetting and non-wetting fluid and a solid surface is thus given by

$$\cos \alpha = (\sigma_{s, nw} - \sigma_{s, w}) / \sigma_{w, nw} \qquad (3.3)$$

The wetting angle of pure water upon smooth and clean inorganic surface is usually zero, but it can be considerable larger where the surface is rough with adsorbed hydrophobic surfactants. It is always possible to change the contact angle between a solid and fluid, by changing the $\sigma_{s,\,nw}$ and $\sigma_{w,\,nw}$ in equation (3.3) above. The application of this result in groundwater pollution, is where $\sigma_{s,\,nw}$ (i.e. porous media and NAPL) is increased, by an infiltrating surfactant. This can therefore increase the rate of flow across the solid surface (porous media). This is because the higher the interfacial tension, less likely emulsion will form, and better the phase separation after mixing of the wetting fluid (water) and the non wetting fluid (NAPL) (Mercer, 1989).

Aquifers are naturally water-wet system because they contain water before any NAPLs are discharged to them. The vadose zone may be either water-wet or oil-wet, depending upon whether the soil is moist or dry when the oil is discharged (Fetter, 1999).

3.1.2. Capillary pressure

If two immiscible liquids (water and NAPL) are in contact, a curved surface will tend to develop at the interface. **Capillary pressure** (P_c) is therefore the difference between the non-wetting fluid (NAPL) pressure and the wetting fluid (water) pressure. The capillary pressure in a general two-phase flow wetting and non-wetting fluids can be expressed in the form

$$P_c\,(P_o - P_i) \text{ -= } P_{nw} - P_w \tag{3.4}$$

Where P_o, is the outward pressure exposed to the atmosphere, P_i, is the inward pressure in the aquifer, P_{nw} is the pressure of the non-wetting fluid and P_w is the pressure of the wetting fluid. Note that the inward pressure is greater than the outward pressure. The two fluids that are often encountered in the groundwater investigations are water (as the wetting fluid) and air (as the non-wetting fluid). Since the density of air is smaller than that of water, the custom is to take atmospheric pressure as the reference pressure and to equate it with zero. The capillary pressure in the vadose zone is therefore negative according to equation (3.4) above.

For a given porous medium the relationship of the capillary pressure to the saturation ratio can be determined. Throughout this chapter the water is assumed as wetting fluid

with respect to non-wetting fluid (NAPL). If a porous medium starts off saturated with the wetting fluid and the wetting-fluid is slowly displaced by a non-wetting fluid (NAPL), the wetting-fluid saturation ratio (S_w) decreases and the capillary pressure increased as a result of invasion of NAPL into the previously water saturated media, the end result is known as **drainage**. Drainage corresponds to the field situation in which the DNAPL advances into groundwater from some other type of source. Once the source is exhausted, the DNAPL (non-wetting) will continue to migrate away from the source and will be replaced in source area by water (wetting-fluid), thereby increasing the water saturation ratio and decreasing the capillary pressure, this referred to as **wetting or imbibitions** During drainage and wetting a hysteresis commonly occur where the water saturation at any particular capillary pressure is less during wetting process than during drainage (Fetter, 1999).

The saturation at which the no more wetting fluid is displaced by non-wetting fluid, even with further decrease in capillary pressure is referred to as **irreducible wetting-fluid saturation** (S_{wi}). When the wetting process is completed at a zero capillary pressure, some of the non-wetting fluid will remain in the porous media, this referred to as **residual no-wetting fluid saturation** (S_{nwr}). The residual non-wetting fluid (NAPL) is comprised of blobs and fingers of NAPL that have been cutoff and disconnected from the continuous NAPL body by the invading water. Note that the drainage starts off at a wetting fluid saturation ratio of 1.0 with a nonzero capillary pressure, thus **displacement pressure** or threshold values (P_d). Note that the **maximum water saturation** (S_m) achievable during the wetting process is **<1**. In order for non-wetting fluid (NAPL) to start to displace the wetting fluid (water) the threshold value or displacement pressure must be exceeded (Fetter, 1999).

3.1.3. Relative permeability

During the simultaneous flow of two immiscible fluids (water and NAPL), part of the available pore space will be filled with water and the remainder will be filled with the NAPL. Because the two fluids must compete for space in which to flow, the cross-sectional area of the pore space available for each fluid is less than the total pore space. **Relative permeability** is therefore the ratio of the intrinsic permeability of the fluid at a given saturation ratio of the pore space to the total intrinsic permeability of the rock.

Intrinsic permeability is solely a function of the grain-size distribution of the porous medium defines its ability to transmit a fluid and is generally decreasing from sands to loams to silt to clay soils. Intrinsic permeability is a measure of the resistance of the unsaturated zone to the flow of a liquid and is independent of the physical properties of the liquid (Lyman et al., 1992). A relative permeability exists for both wetting and non-wetting fluids.

The irreducible water saturation is the water content at which no additional water will flow in the pore space until and unless the irreducible wetting-fluid saturation is exceeded. Likewise for the residual non-wetting fluid saturation, NAPL fluid will not begin to flow until the residual non-wetting fluid saturation is exceeded. This implies that if the water content is less than the irreducible water saturation, NAPL can flow but capillary forces will hold the water (**drainage process**). When the NAPL content is less than residual NAPL saturation, water can flow but NAPL cannot (**wetting process**). However the NAPL droplets dispersed in the water cab still migrate (Fetter, 1999).

The relative permeability to the wetting phase (k_{rw}) is thought to be practically free of hysteresis. The saturation at which the relative permeability of non-wetting fluid (k_{rnw}) is zero in a wetting or draining process is not the same because of the entrapment of non-wetting fluid during the wetting process. It is usual to assume that k_{rnw} is greater than zero in a draining process for all water saturation (S_w) is **<1**. Therefore relative permeability of NAPL becomes zero at $S_w = 1 - S_m$. It is also worthwhile to note that the relative permeability to water during wetting process does not become unity (1) because of the presence of residual NAPL (Fetter, 1999).

3.1.4. Darcy's law for multi-phase flow

Darcy's law is the starting point for analyzing both single-phase (water) and multi-phase (water and NAPL) flow. Darcy's law states that the volumetric flow rate through a porous media is proportional to the head loss and inversely proportional to the length of the flow path. Since its discovery, it has been found valid for any Newtonian fluid. Likewise, while it was established under saturated flow conditions, it may be adjusted to account for

multiphase flow. Darcy's law for the steady state saturated single-phase (water) flow is given as

$$Q = -KA \Delta h/ L \qquad (3.5)$$

Where, **Q** is volumetric flow rate (m^3/s), **A** is flow area perpendicular to **L** (m^2), **K** is hydraulic conductivity (m/s), **L** is flow path length (m or ft), **h** is hydraulic head (m), and Δ denotes the change in **h** over the path **L**. Hydraulic conductivity (K) is the rate of flow through a porous media. A negative sign indicates that the flow of fluid (water) is in the direction of decreasing head. Figure 3.2 below shows the pressure distribution and hydraulic head loss in a single-phase flow through a sand column.

Sources: http://biosystems.okstate.edu/Darcy/LaLoi/basics.htm
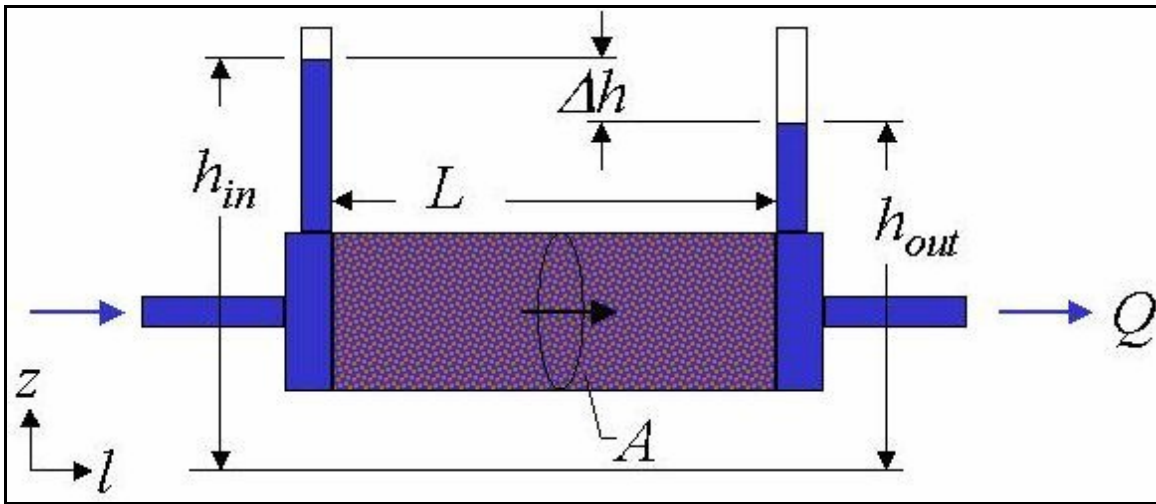
Figure 3.2: Sand column presenting the single-phase flow.

The hydraulic head at a specific point, **h** is the sum of the pressure head and the elevation, expressed as

$$h = (p/\rho g + z) \qquad (3.6)$$

Where, p is the water pressure (N/m^2), ρ is the water density (kg/m^3), g is the acceleration of gravity (m/s^2), and z is the elevation (m).

The Darcy flux is defined as the volumetric flow pr unity area, which is given (David K.T, 1980) as

$$q = Q/A \qquad (3.7)$$

by substituting equation (3.5) into (3.7) **q** becomes,

$$q = -KA \Delta h/ L /A$$

$$= -K \Delta h/ L \tag{3.8}$$

Since Darcy's law is applicable for both single and multi-phase flow, the concept of relative permeability must be considered in order to account for the presence of two fluids (i.e. water and NAPL) in the pore space. Fluid motion in a porous medium is impelled by the gradient of the fluid pressure and the body force due to gravity. Motion is resisted by viscous shear, which in turn depends upon the rate of motion, fluid viscosity, the size, shape and tortuosity of each opening through which the fluid passes. Fluid motion is also governed by the intrinsic permeability (k) of the porous medium when a single fluid is present. Permeability is the property of the medium only and is independent of the fluid properties (Fetter, 1999).

In order to avoid confusion with hydraulic conductivity, which includes the properties of groundwater, an intrinsic permeability can be expressed as

$$k = K\mu / \rho g \tag{3.9}$$

Where $\mathbf{K}$ is the hydraulic conductivity, $\boldsymbol{\mu}$ is dynamic viscosity, $\boldsymbol{\rho}$ is the fluid density and $\mathbf{g}$ is acceleration of gravity.

The coexistence another fluid in the pores space reduces the area available for flow of either fluid and increases the tortuosity of the flow path which fluid elements must traverse. As discussed in section **3.1.3** the existence of two fluids in the pore space is incorporated in the relative permeability to each fluid and is strong functions of the fluid saturation.

By taking the intrinsic permeability of the medium, the Darcy's law for the saturated flow of water in the presence of a non-aqueous phase liquid (multi-phase flow) is give as

$$Q_w = -KA\, dh_w/dl \tag{3.10}$$

By solving equation (3.9) for intrinsic permeability, equation (3.10) can be expressed as

$$Q_w = -\, k_{rw}k_i\, \rho_w/\, \mu_w.\, A\, dh_w\, /dl \tag{3.11}$$

Where $\mathbf{k_{rw}}$ is the relative permeability of water in the presence of the non-wetting fluid, the other parameters were defined in equation (3.5 and 3.9).

A similar expression for the no-wetting fluid (NAPL) is given (Schwille 1984) as

$$Q_{nw} = -\, k_{rnw}k_i\, \rho_{nw}/\, \mu_{nw}.\, A\, dh_{nw}\, /dl \tag{3.12}$$

3.1.5. Fluid potential and head

Fluid potential (Φ) is defined as the amount of work needed to move a unit mass of fluid from some standard position and condition to a different position and condition. Position of a fluid represents the potential energy (energy at rest) of the fluid or elevation above the standard datum. The condition can be represented by the difference in the pressure between the position under consideration and the standard pressure. The fluid potential is thus defined (Hubbert, 1953) as

$$\Phi = g\,(z - z_s) + (P - P_s)\,v_m \tag{3.13}$$

Where **g** is the acceleration of gravity, **z** is the elevation; z_s is the standard elevation, **P** is the pressure, P_s is the standard pressure and V_m is the volume per unit mass.

Since volume per unit mass is the reciprocal of the density (ρ) equation (3.13) can be expressed as

$$\Phi = g\,(z - z_s) + (P - P_s) / \rho \tag{3.14}$$

If the standard pressure is taken as atmospheric pressure and **z** is define as elevation above a convenient datum, such as sea level, the equation 3.14 becomes

$$\Phi = gz + P/\rho \tag{3.15}$$

If a pipe with an opening bottom is inserted into an aquifer to a point at distance **z** above the sea level (datum), the fluid pressure at that location will cause the fluid in the aquifer to rise to a height **h** above the sea level. The fluid pressure is equal to the weight of the fluid in the pipe per unit cross-sectional area:

$$P = \rho g\,(h - z) \tag{3.16}$$

Equation 3.16 can be substituted into equation 3.15 to give

$$\Phi = gz + \rho g\,(h - z) / \rho$$
$$\Phi = gz + g\,h - gz$$

$$\Phi = gh \tag{3.17}$$

Where **h** is the total head.

Therefore fluid will flow from an area of higher fluid potential (**Φ + ΔΦ**), to an area of lower fluid potential (**Φ**). The force per unit mass exerted on the fluid by its environment is a vector, **E**. This force vector is perpendicular to the equipotential surfaces and in the direction of decreasing potential as shown in Figure 3.3 below. It has a magnitude equal to the change in potential (ΔΦ), divided by the distance over which the change in potential is measured (Δ**n**).
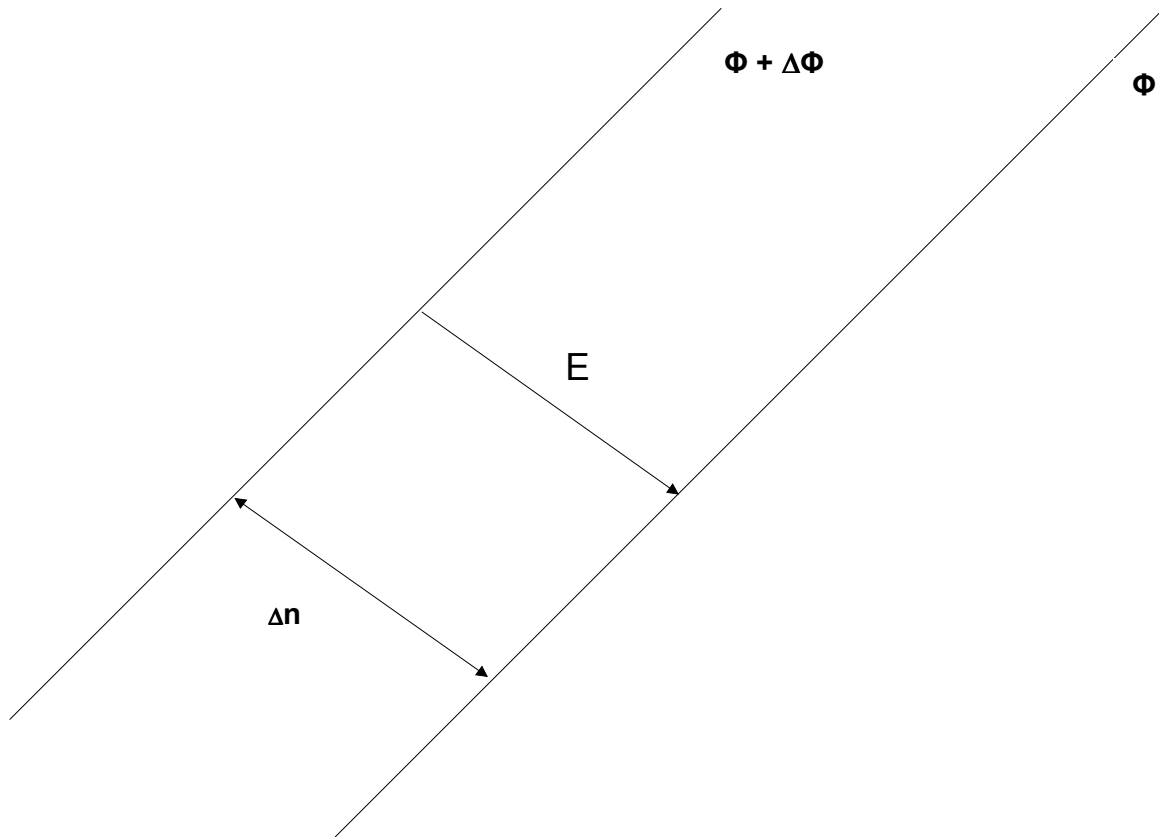
Figure 3.3: Relation between force field and potential gradient (Hubbert, 1953)

$$E = - \Delta\Phi / \Delta n \qquad (3.18)$$

The force vector **E** can be expressed in other way:

$$E = g - 1/\rho . \text{ gradient } P \qquad (3.19)$$

Equation 3.19 shows that at a point a unit mass of a fluid will be acted upon by a force **E**, which is the vector sum of gravity and the negative gradient of the pressure divided by the fluid density. It also shows that the direction of the force vector is a function of the fluid density. Thus for the point in the aquifer, different fluids will have different force vectors, and hence different flow directions in the same potential field. Figure 3.4 below shows a force vector for water (E_w), force vector for an LNAPL (E_{LNAPL}) and a force vector for a DNAPL (E_{DNAPL}). The water is shown to be flowing horizontally, that is, the force vector E_w, although it could be going in any direction. Since the density of the LNAPL is less than the density of water, the vector –grad P/ ρ_{LNAPL} is longer than vector

-grad P/ ρ_w and the resulting vector $\mathbf{E_{LNAPL}}$ angle upward compared with $\mathbf{E_w}$. The vector $\mathbf{E_{DNAPL}}$ is angled downward because the vector –grad P/ ρ_{DNAPL} is shorter than the vector –grad P/ ρ_{LNAPL}. Figure 3.4 illustrates why a DNAPL will sink and LNAPL will rise with respect to the direction of groundwater flow in the same potential field (Fetter, 1999).

The fluid potential of non-wetting fluid, either an LNAPL or a DNAPL is given by

$$\Phi_{nw} = gz + P/\rho_{nw} \tag{3.20}$$

The fluid potential for wetting fluid (water) is given by

$$\Phi_w = gz + P/\rho_w \tag{3.21}$$

By solving equation 3.21 for P and substitute it into 3.20, the following equation can be obtained

$$\Phi_{nw} = \rho_w.\ \Phi_w\ /\ \rho_{nw} - (\rho_w - \rho_{nw})\ gz\ /\ \rho_{nw} \tag{3.22}$$

Equation 3.22 relates the fluid potential of a non-wetting fluid to the fluid potential of water at the same location.

From equation 3.17, equation 3.20 and 3.21 can be expressed as $\Phi_{nw} = gh_{nw}$ and $\Phi_w = gh_w$, therefore equation 3.22 can be written as

$$h_{nw} = \rho_w.\ h_w\ /\ \rho_{nw} - (\rho_w - \rho_{nw})\ z\ /\ \rho_{nw} \tag{3.23}$$

Where $\mathbf{z}$ is the elevation of the point in the aquifer, $\mathbf{h_w}$ is the height above the datum that water would stand in an open pipe terminating at the point, and $\mathbf{h_{nw}}$ is the height that a non-wetting fluid of density $\boldsymbol{\rho_{nw}}$ would stand.

Figure 3.5 below illustrates the relationships between $\mathbf{h_w,}$ $\mathbf{h_{LNAPL}}$ and $\mathbf{h_{DNAPL}}$. The fluid elevation in the pipe filled with LNAPL will be higher than the pipe filled with water, whereas the fluid elevation of the pipe filled with DNAPL will be lower. This illustration again corresponds with the field situation where DNAPL sink and the LNAPL rise with respect to the direction of groundwater flow (Fetter, 1999).

-gradP
ρ_{LNAPL}

-gradP
ρ_w

-gradP
ρ_{DNAPL}

E_LNAPL

E_W

E_DNAPL

g
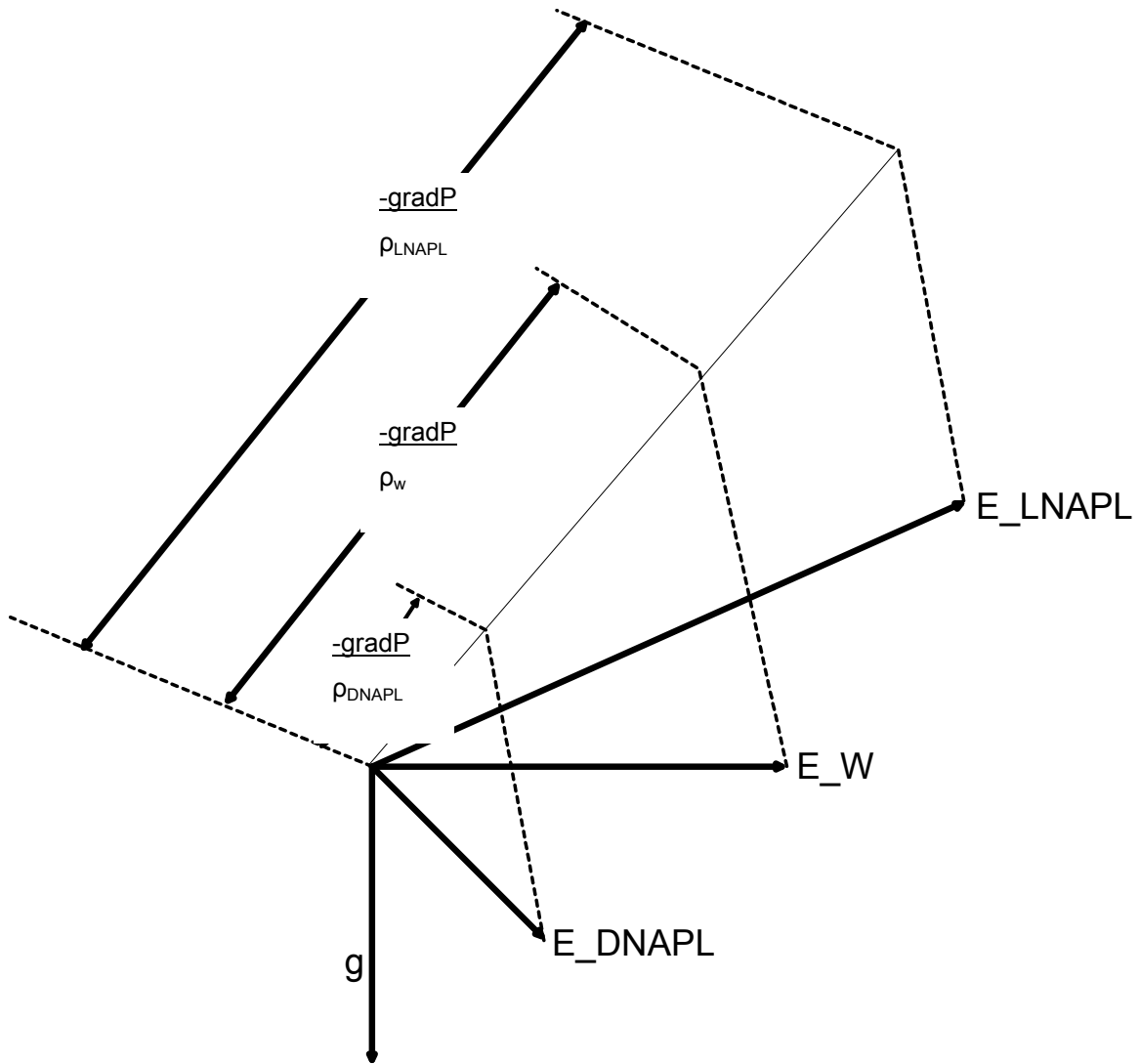
Figure 3.4: Force vectors of DNAPL, water and an LNAPL in the same potential field (Hubbert, 1953).

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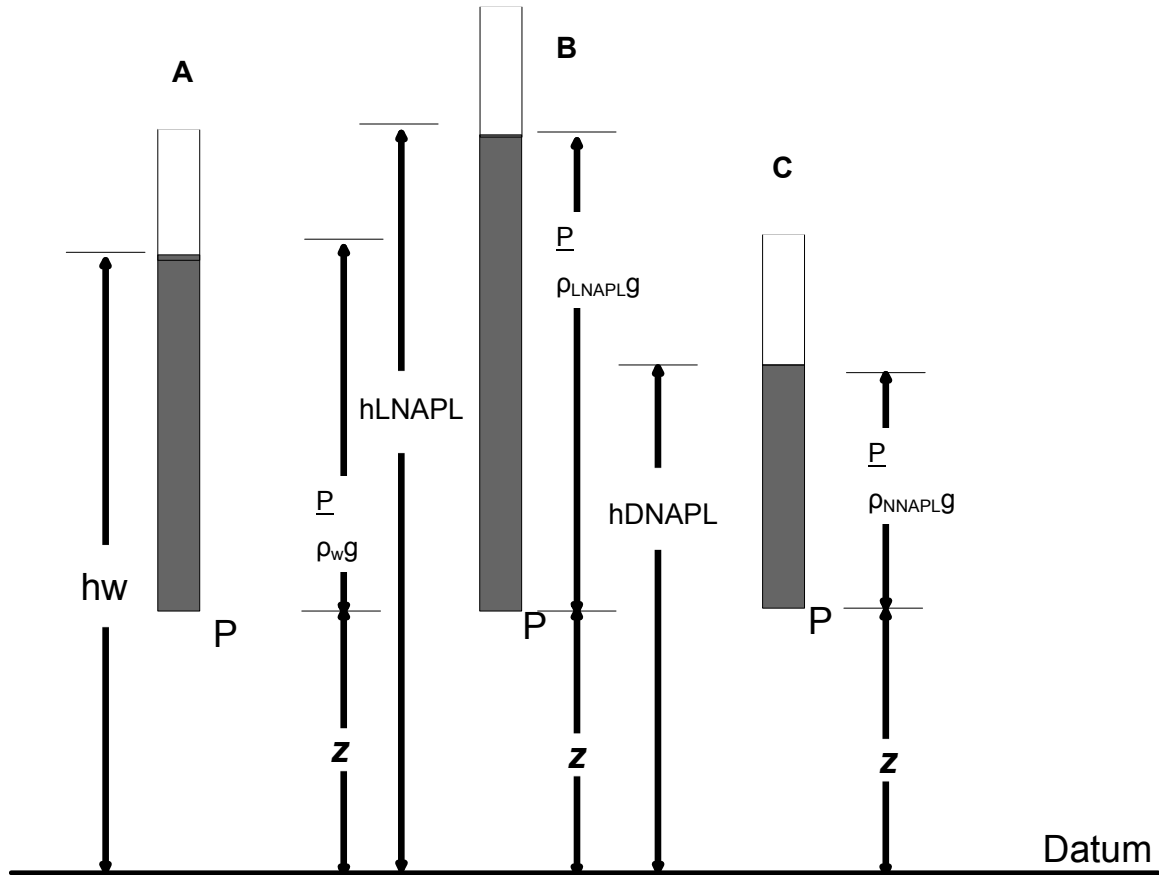
Figure 3.5: Total head (h), pressure head (p/ρg) and elevation head (z) with (**A**) water, (**B**) an LNAPL and (**C**) DNAPL. All the pipes have the same pressure at the open end.

3.2. Mobility of Light Non-Aqueous Phase Liquids (LNAPLs)

This study will focus on the mobility of LNAPLs instead of the DNAPLs. Light Non-Aqueous Phase Liquids are less dense than water. If small volumes of a spilled gasoline (LNAPL) enter the vadose zone (unsaturated zone), the LNAPL will flow through the central portion of the unsaturated pores until residual saturation is reached (Palmer, et al, 1989b). Residual saturation is the volume of discontinuous immobile liquid contaminant per unit void volume (Mohanty, et al., 1980: Chatzis, et al., 1983). A three-phase system consisting of water, LNAPL, and air is formed within the vadose zone. Infiltrating water dissolves the constituents within the LNAPL (e.g., benzene, ethyl benzene, xylene, and toluene) and transports them to the water table. These dissolved contaminants form a contaminated plume radiating from the area of the residual product. Most of the constituents found in LNAPLs are volatile and can partition into soil air and

be transported by molecular diffusion to other parts of the aquifer. As these vapors diffuse into adjoining soil areas, they may partition back into the water phase and transfer contamination over wider areas. If the soil surface is relatively impermeable, vapors will not diffuse across the surface boundary and concentrations of contaminants in the soil atmosphere may build up to equilibrium conditions. However, if the surface is not covered with an impermeable material, vapors may diffuse into the atmosphere.

If large volumes of LNAPL are spilled, the LNAPL flows through the pore space to the top of the capillary fringe of the water table. Dissolved constituents of the LNAPL precede the less soluble constituents and may change the wetting properties of the water, causing a reduction in the residual water content and a decrease in the height of the capillary fringe.

Since LNAPLs are lighter than water, they will float on top of the capillary fringe. As the head formed by the infiltrating LNAPLs increases, the water table is depressed and the LNAPLs accumulate in the depression. If the source of the spilled LNAPLs is removed or contained; LNAPLs within the vadose zone continue to flow under the force of gravity until reaching residual saturation. Figure 3.6 below shows the behaviour of LNAPLs and DNAPLs in the subsurface (http://mineral.gly.bris.ac.uk/envgeochem/organics.pdf).
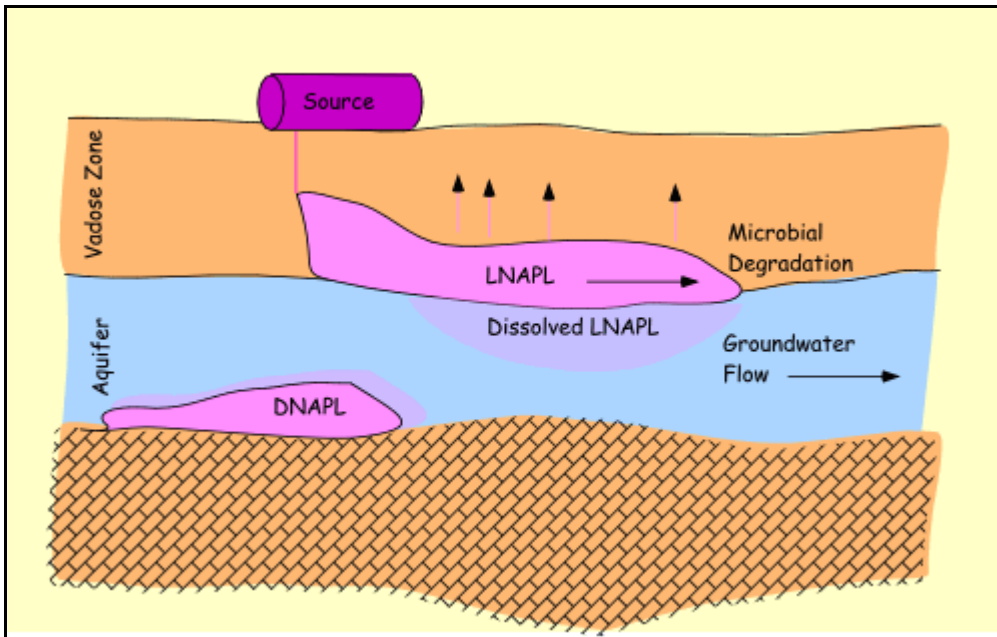
Figure 3.6: Behaviour of LNAPL and DNAPLs in the subsurface environment.

As the LNAPLs continue to enter the water table depression, they spread laterally on top of the capillary fringe. The draining of the upper portions of the vadose zone reduces the total head at the interface between the LNAPLs and the ground water, causing the water table to rebound slightly. The rebounding water displaces only a portion of the LNAPLs because some of the LNAPLs remain at residual saturation. Ground water passing through the area of residual saturation dissolves constituents of the residual LNAPLs, forming a contaminant plume. Water infiltrating from the surface also can dissolve the residual LNAPLs and add to the contaminant load of the aquifer.

Decrease in the water table level from seasonal variations or groundwater pumping also causes dropping of the pool of LNAPLs. If the water table rises again, part of the LNAPLs may be pushed up, but a portion remains at residual saturation below the new water table. Variations in the water table height, therefore, can spread LNAPLs over a greater thickness of the aquifer, causing larger volumes of aquifer materials to be contaminated (Palmer, et al, 1989b).

3.2.1. Physical processes that control the migration rate of LNAPLs in the subsurface

The migration of LNAPLs is governed by the following physical properties, namely *Density, viscosity, water solubility, octanol-water partition coefficient (K_{ow}), vapour pressure and Henry's law constant*.

3.2.1.1. Density

The density of an organic compound refers to the amount of substance per unit volume (g/cm^3). The difference in density between the contaminant and groundwater is the most important parameter in determining the contaminant migration relative to the aquifer (Schwille, 1984). Density differences of about 1% can significantly affect fluid movement, and the density differences between organic liquids (LNAPLs) and water are in excess of 1 and often 10%. When organic liquids reaches an aquifer, its density will determine where it will most likely be concentrated (Mackay et al., 1985). Since LNAPLs have the density which is less than the density of water it is associated with the solubilities of less than 1% and is referred to as floaters. (New York State Department of Environmental

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Conservation, 1983). Therefore an LNAPL such as gasoline which is immiscible and with less dense than water, would migrate vertically through the soil (unsaturated zone) to the water table (saturated zone) and then float on the surface, spreading out down gradient direction (Mackay et al., 1985).

3.2.1.2. Viscosity

The viscosity of the liquid organic compound is the measure of the degree to which it will resist flow under a given force measured in dyne-seconds per square centimeter (Devitt et al 1987). The viscosity of an organic fluid such gasoline will affect the flow velocity (Schwille, 1984). The combination of density and viscosity will govern the migration of an immiscible organic liquid in the subsurface (Mackay, et al, 1985). For example, about four times the volume of a light fuel oil in the high viscosity range would be retained by the average soil, as compared with gasoline, a distillate with a lower viscosity (Noel, et al, 1983). Gasoline would spread over a wider area of an aquifer than a light fuel oil.

3.2.1.3. Water solubility

Water solubility is referred to as the extent to which an organic compound dissolves in water (Devitt et al 1987). Organic compounds with high water solubility partitions primarily into the liquid water phase. The rate at which these compounds move through the unsaturated zone is, therefore, controlled to a great extent by the unsaturated hydraulic conductivity of the water in porous medium.

Organic compounds with high water solubility would have shorter downward travel times. For gasoline spills, the hydrocarbons constituents (benzene, toluene, Ethyl benzene and Xylenes) will dissolve out differently and produce a simultaneous aging and leaching effect on the spill (Pfannkuch, 1985). The solubility represents the maximum concentration of the compound that will be dissolved in water under equilibrium conditions (Eckenfelder et al., 1993). Water solubilities of the selected gasoline constituents are presented under section 2.4.1.1.

3.2.1.4. Octanol-water partition coefficient

The octanol-water partitioning coefficient (K_{ow}) is a measure of the degree to which an organic substance will preferentially dissolve in water or organic solvent. The organic compound is shaken with a mixture of n-octanol and water and the proportion dissolving into each phase is measured. The octanol-water partition coefficient is the ration of the concentration in the octanol to the concentration in the water, and can be expressed (Fetter, 1999) as

$$K_{ow} = C_{octanol} / C_{water} \qquad (3.24)$$

The K_{ow} values of the organic compounds play an important role in terms of water solubility of a compound. The organic compounds with low K_{ow} are referred to as hydrophilic (water attracting) while compounds with high K_{ow} are referred to as hydrophobic (water repelling). It is generally believed that for hydrophobic compounds, the relationships based on K_{ow} are superior to those based on water solubility. However, for gasoline constituents with low K_{ow} values, solubility based relationships are probably superior to those based on K_{ow} (Lyman, 1992).

Table 3.1 below shows the physical/chemical properties of selected gasoline constituents. Based on physical/chemical properties presented in Table 3.1 below, it is evident that benzene is moderately hydrophobic as compared to toluene, ethyl benzene and Xylenes. The Log K_{ow} is a measure of the tendency of a compound to dissolve in hydrocarbons, fats, or organic components of soil rather than in water (Nash, 1987).

Table 3.1: physicochemical properties of selected gasoline compounds (Lyman et al., 1992).

Gasoline Component	Log K_{ow}	Selected conc. in Gasoline (Mol.Fr)	Water solubility at 25°C(mg/L)	K_{ow}
n-Butane	2.89	0.0163	61.4	490
Isobutane	2.76	0.0326	48.9	420
n-Pentane	3.39	0.0394	41.2	910
n-Hexene	4.00	00.0990	12.5	1900
1-Hexene	3.39	0.0169	50.0	910
2-Methyl pentane	3.80	0.0880	14.2	1500
Benzene	2.13	0.0364	1780	190
Toluene	2.69	0.0515	537	380
Ethyl benzene	3.15	0.0179	167	680
m-Xylene	3.20	0.0625	162	720
2,2,4Trimethylhexane	5.23	0.0148	0.8	8700
2,2,5,5-Tetramethylhexane	5.64	0.0100	0.13	14000
1,4-diethylbenzene	4.35	0.0353	15.0	2900

3.2.1.5.   Vapour pressure

Vapour pressure is a measure of the tendency of an organic contaminant to pass from a solid or liquid to a vapour phase. The BTEX compounds normally regarded as volatile, however they have quite low vapour pressures relative to the other gasoline constituents. Table 3.2 below shows the values of vapour pressure for selected gasoline constituent. Vapour pressure is strongly temperature-dependant, for example, vapour pressure of benzene rises from 45.53mm Hg to 75.20mm Hg as the temperature changes from 10°C to 20°C (Lyman et al., 1992).

3.2.1.6. Henry's law constant

Henry's law constant (K_H) states that there is a linear relationship between the vapour pressure of an organic contaminant above its aqueous solution and the concentration in solution (Fetter, 1999).

$$K_H = \text{con. of a compound in the vapour phase/ con. in aqueous phase} \qquad (3.25)$$

BTEX compounds are relatively volatile mono-aromatic hydrocarbons, which are commonly found together in crude petroleum and gasoline. The volatilization of BTEX from gasoline-contaminated groundwater is controlled by Henry's Law constants (H). Compounds with higher Henry's constants (H) tend to volatilize more readily. The Henry's law constants have a tendency to increase with increasing molecular weight (Devitt, et al., 1987). Based on the Henry's constant values as shown in Table 3.2 below it suggests that benzene would volatilize to a lesser extent than xylene, toluene and ethyl benzene, respectively.

Table 3.2: Estimated properties for a synthetic gasoline and its constituent at 10°C and 20°C (Lyman et al., 1992).

Gasoline Component	Vapour Pressure (as mm Hg) at 10°C	Vapour Pressure (as mm Hg) at 20°C	Henry's law Constant at 10°C (dis.)	Henry's law Constant at 20°C (dis.)
n-Butane	1112.75	1555.33	2521.65	3404.37
Isobutane	1647.77	2252.75	3259.64	4304.39
n-Pentane	283.84	424.38	2977.29	4299.67
n-Hexane	75.70	121.24	3661.34	5663.95
1-Hexane	94.87	149.97	917.75	1401.18
2-Methylpentane	109.55	171.50	3785.69	5724.28
Benzene	45.53	75.20	11.32	18.07
Toluene	12.43	21.84	12.60	21.38
Ethyl benzene	3.77	7.08	13.65	24.76
Xylene	3.26	6.16	11.83	21.60

3.2.2. Chemical processes that control the migration rate of LNAPLs in the subsurface

If contaminants undergo chemical reactions while being transported through an aquifer, their movement rate may be less than the average ground-water flow rate; this effect is called **Retardation** (Palmer, 1989a). Such chemical reactions that slow movement of contaminants in an aquifer include sorption (i.e. *adsorption, ion exchange, and partitioning into organic matter or organic solvents*). *Adsorption* includes the processes by which a solute clings to a solid. *Iron exchange* is when the cation/anion are attracted to the region close to a positively/negatively charge clay-minerals surface and held there by electrostatic forces. *Partitioning into organic matter or organic solvents* in the process by which an organic compound which was originally in solution, becomes distributed between the solution and the solid phase.

3.2.2.1. Retardation

Retardation is simply the ratio of the velocity of a dissolved contaminant plume in relation to the bulk velocity of the groundwater. It can be described by the conventional retardation equation (Lyman et al., 1992):

$$R_f = V_w/V_c = 1 + K_d\rho_b/\Theta \qquad (3.26)$$

Where,

R_f = the retardation factor (dimensionless)

V_w = the average velocity of water (cm/sec)

V_c = the average velocity of chemical contaminant (cm/sec)

K_d = sorption coefficient (cm^3/g)

ρ_b = soil bulk density (g/cm^3)

Θ = soil porosity (dimensionless)

$$K_d = K_{oc} \times f_{oc} \qquad (3.27)$$

Where,

K_{oc} = the value that reflects the impact of organic material to adsorb organic compounds out of solution

f_{oc} = the weight fraction of organic carbon in the soil

Equation 3.26 shows that the retardation factor moves inversely to the porosity. That is, at low porosity values the retardation increases, while it decreases as the porosity if the medium increases. The species in a mixture of reactive contaminants that are dissolved in groundwater will travel at different rates depending on their retardation factors. Thus, the contaminant plume will exhibit a chromatographic effect over time.

Retardation is strongly affected by the subsurface carbon content. The effect on retardation differs, however based on the phase of the carbon. Dissolved organic carbon (DOC) (i.e. *high soluble organic compounds such as methyl tertiary butyl ether (MTBE) and tertiary butyl alcohol (TBA) and colloidal particles of humic and fulvic acids*) may significantly lower retardation. Organic matter in the solid phase increases sorption and hence retardation.   Garret et al., 1986 report on how the presence of MTBE in gasoline spills affects the movement of the plume and the detection of a release. MTBE has multiple effects related to retardation and movement.

MTBE, which may comprise up to 11% by volume of gasoline, is soluble in water to 43,000mg/L (Garret et al., 1986), about 25 times more soluble than benzene, otherwise the most soluble gasoline constituent at 1,780mg/L. Generally sorption of organic compounds is inversely proportional to their solubility. Thus MTBE is likely to be minimally retarded, allowing it to travel faster than other gasoline constituents.

MTBE also decreases the retardation of the other gasoline constituent by increasing their dissolved concentrations in the groundwater. Benzene, toluene, ethyl benzene and xylenes (BTEX) are more soluble in ether than in water. When MTBE is present in the gasoline plume, the BTEX concentrations in the groundwater are higher. Since the BTEX compounds are more soluble, they are likely to be more mobile (less retarded) in the groundwater. Therefore, for groundwater that contain significant dissolved organic carbon (DOC), the conventional retardation equation (3.26) can be modified to reflect the effect that DOC has:

$$R_f = 1+(K_d\rho_b/\Theta) / 1+ K_{DOC} (DOC) 10^{-6} \qquad (3.28)$$

Where,

K_{DOC} = sorption constant for compound in DOC (L/kg) (~K_{oc})

DOC = dissolved organic carbon concentrations (mg/L), and the other parameters described in equation 3.26 above.

Equation 3.28 presumes that the solid organic matter is less than 0.1%, so the K_d-type constants may replace K_{oc} constants. Higher levels of organic carbon in the solid matter can increase sorption and elevate retardation effects. Table 3.3 below shows the retardation factors ranging over two orders of magnitude. The higher molecular weight aliphatic compounds are most strongly retarded (Lyman et al., 1992).

Table 3.3: Estimated retardation factors for hydrocarbon gasoline constituents (Lyman et al., 1992)

Gasoline Component	Sorption constants[a] K_{oc} (L/kg)	Sorption constants[a] K_d f_{oc}= 0.1%	Retardation factors (R_f)[b]
n-Butane	490	0.49	4.5
Isobutane	420	0.42	4.0
n-Pentane	910	0.91	7.6
n-Hexane	1900	1.90	14.7
1-Hexene	910	0.91	7.6
2-Methylpentane	1500	1.50	11.8
Benzene	190	0.19	2.4
Toluene	380	0.38	2.7
Ethyl benzene	680	0.68	5.9
m-Xylene	720	0.72	6.2

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

b. Using equation 3.26, a bulk density of 1.8L/kg and soil porosity of 0.20

CHAPTER 4.   DETECTION METHODS AND EVALUATION OF METHODS OF LNAPLS IN THE SUBSRUFACE ENVIRONMENT

4.1.   Detection of LNAPLs in the subsurface environment

Current methods of assessment of hydrocarbon-contaminated sites are the result of a gradual evolution of techniques which have been adapted from applications that were primarily exploratory in their scope. None of the techniques presently in use resulted from major technological breakthrough, but rather are the products of innovation and adaptation to the specific demands of growing field of hydrocarbon contamination assessment.

Hydrocarbon site assessment methods can be categorized broadly into those that merely attempt to detect the presence or absence of contamination and those that attempt to quantify the magnitude and extent of contamination. Pedestrian survey and soil gas/vapour surveys fall into qualitative category, while soil and groundwater sampling have a quantitative goal (Calabrese et al, 1991).

The detection of organic contaminants such as Light Non-Aqueous Phase Liquids (LNAPL) in the sub-surface has been the subject of considerable interest among earth-scientists in recent years (www.rsdynamics.com).

LNAPL contamination may differentiate into at least four distinct forms, each of which has unique chemical and geophysical characteristics (Figure 4.1). There is a free product, which is mobile or free to migrate under gravitational pull. Secondly, the residual phase is that portion which is left behind after the free product has migrated. Thirdly, volatile LNAPLs may have developed a vapor phase plume in the space above the free product and the residual product. Finally, small amounts of hydrocarbon may enter the aquifer as a dissolved phase. A brief description of principal hydrocarbon assessment methods described below:
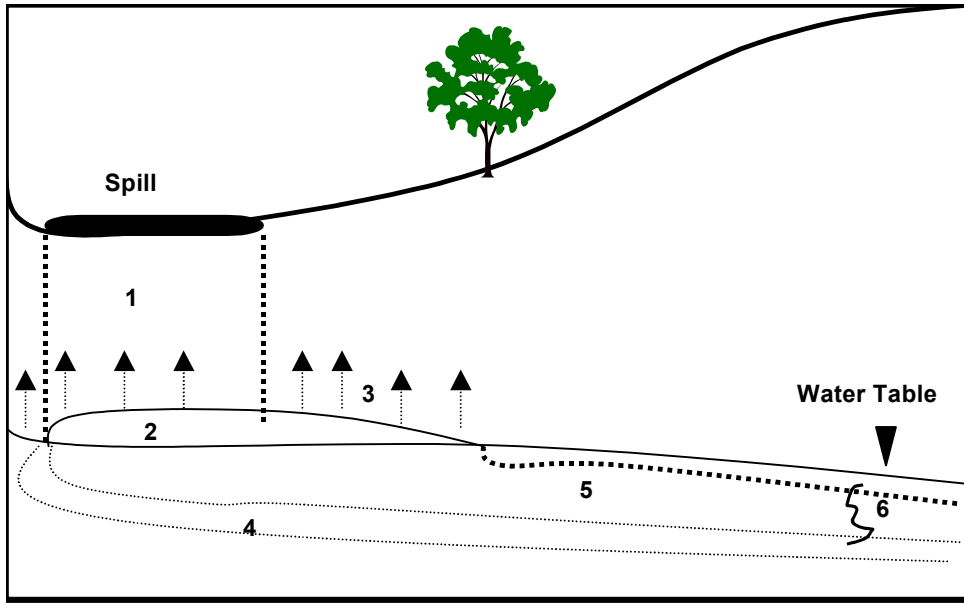
Figure 4.1: Cross-section diagram of zones around an LNAPL spill site, static water table case : **1** – vadose zone directly beneath the spill, **2** – free (mobile) product and residual product zone, **3** – vadose zone directly above the free/residual product, **4** – reactive fringe around the dissolved plume, **5** – anaerobic core of the dissolved plume, **6** – distal end of the dissolved plume.

4.1.1. Pedestrian survey

Certainly the most common of all the assessment technique is the pedestrian survey in which the investigator walks a site looking for visual signs of contamination or indicators of hydrocarbon presence. This type of assessment does not claim to be a rigorous scientific technique, but proves to actually be a quick and inexpensive approach. While "nasal appraisals" cannot be recommended due to health concerns associated with inhalation of volatile organic compounds, the incidental detection of such odours is a clear indication of contamination. Visually, hydrocarbon stained soils and pavements are often readily apparent even to the untrained observer. The appearance of an oily film on water surfaces is also an obvious sign of hydrocarbon contamination. Seldom will a pedestrian survey be sufficient for site assessment, but it offers valuable guidance for planning of subsequent work (Calabrese et al, 1991).

4.1.2. Geophysical survey

Several geophysical site assessment techniques have been attempted on an experimental basis. One of these is ground penetrating radar. In theory this technique can identify free product plumes based upon the characteristics of return radar signals. Another geophysical method that has been explored is induced polarization. When a current is applied to a conductive media it alters the distribution of negative and positive ions, creating a gradient effect. When the current is terminated the gradient relaxes, resulting in a current flow and measurable voltage termed the induced polarization effect. In theory and experimentally there is evidence that the presence of relatively large non-polar organic molecules will reduce the induced polarization effect (Calabrese et al, 1991).

Electrically resistivity surveys are commonly used to identify contamination by inorganic materials that cause an increase in the electrical conductivity of soils. This techniques has been applied in attempting to define the extent of hydrocarbon contamination by searching for areas of reduced conductivity that might be characteristic of organic contamination. In general, geophysical methods are at present, very limited in application to the assessment of hydrocarbon contamination, due to the difficulty in separating the subtle response of dissolved or sorbed hydrocarbon material from the natural variable background responses of native soils (Calabrese et al, 1991).

4.1.3. Soil Vapour Survey

A basic knowledge of certain closely related disciplines is essential for the successful planning, execution and interpretation of in-situ investigation of subsurface contamination by liquid hydrocarbons. The relevant aspects include:

- Physico-chemical properties of hydrocarbons (i.e. Henry's law, vapour pressure, etc.)
- Partitioning of a contaminant in the subsurface environment
- Subsurface migration of liquid hydrocarbons (i.e., LNAPL)
- Subsurface behaviour of the vapour phase
- Geohydrology
- Geology and pedology

Gas from the pore space in soil and rock formations is commonly known as a soil vapour. The composition of this phase, in particular the presence and concentration of

organic compounds, reveals vital information about pollution of the subsurface environment. Organic compounds constitute a group of contaminants which impact severely on groundwater resources. The presence and distribution of such pollutants can be detected by an established technique known as a *Soil Vapour Analysis (SVA) or Soil Vapour Survey (SVS)*. The following types of contaminants are addressed:

- Liquid organic materials including hydrocarbons (mainly petroleum products) and
- Organic vapours from landfills and gas leaks.

Once the hydrocarbons contaminant have penetrated the soil it will break down into free, adsorbed, dissolved and vapour phase. The hydrocarbon vapor phase and its distribution are of particular interest, because the various characteristics of this phase have a direct bearing on SVS method. The main sources of hydrocarbon vapour are:

- The vadose zone where an effluent petroleum product breaks down into a vapour phase that mixes with natural soil gas.
- Free substance floating on groundwater and
- Dissolved contaminant in soil moisture and in groundwater.

4.1.3.1. Factors affecting in-situ soil vapour measurements

Under natural conditions, transport of the subsurface vapour phase is mainly by diffusion, which is primarily the result of a concentration gradient. The most important subsurface factors that affect in-situ soil vapour measurements are (George et al, RS Dynamics Ltd):

1. **Soil permeability:** soils with different properties of permeability create different soil vapor evaporation conditions. Due to their inner structure, relatively impermeable soils such as clay produce soil vapors for much shorter periods of time compared to highly permeable soils such as sand.

2. **Presence of Methane of natural origin:** as a product of natural biodegradation, Methane occurs in varying concentrations everywhere in the sub-soil environment, this may cause misinterpretation of all total-based in-situ measurements.

3. **Type of contaminant:** for the SVS method to be applied successfully, the contaminant of interest must yield sufficient vapour phase (i.e. some compounds

like transformer oils, PCB and certain phenols create very low vapour phase and require a special sampling technique).

4. **Age of contaminant:** all petroleum products experience some degree of natural biodegradation process in the subsurface environment. LNAPLs hydrocarbons are more readily degraded than the DNAPLs hydrocarbons. After a lapse of time the spectral composition of contaminants will dramatically change, moreover, some contaminants may become morphologized, which is composed of non-toxic aromatic compounds which are out of basic hydrocarbon spectrum.

5. **Zoning and age of a contaminant:** differences in several physical properties of the compounds present in a complex contaminant e.g. vapour pressure, solubility in water, diffusion/mobility, resistance to degradation/oxidation in subsurface environment, etc. constitute some of the factors which may contribute towards the heterogeneous character of a contamination plume. A well studied incident of diesel and kerosene spills from the above ground storage tanks onto unconsolidated dune sand in Perth, Western Australia, indicated strongly developed zonation of benzene, toluene and Tertiary Methyl benzene in the contamination plume.

6. **Surface contamination:** a pollutant occurring in the surface layer as a result of either having being transported by storm water or generated in situ, will seriously affect the distribution and concentration patterns of an underlying, deep source of contamination. The resulting false configuration could be analyzed through profiling to determine the vertical distribution of contamination.

7. **Soil moisture:** since the transport of soil vapour through the soil depends upon the porosity of the medium, it follows that the presence of water will reduce the effective porosity which in turn, will negatively affect the migration and ultimately the volume of soil vapour available for investigation.

8. **Soil temperature:** for a given amount of contaminant in the soil, the vapour density and vapour diffusion will increase significantly with increasing temperature. Although fluctuations in soil temperature are generally seasonal, they may show daily variations which are however, restricted to the top one to two meters of the soil cover

4.1.3.2.   Soil vapour survey using ECOPROBE 5 technique

Previously, Soil Vapor Survey methods did not reflect natural subsurface conditions and interpretations often yielded unreliable results. This fact caused the Soil Vapor Survey to be wrongfully left behind other methods. RS DYNAMICS has been developing the ECOPROBE method since 1989. The improved instrument ECOPROBE 5 is based upon the most advanced technology and extensive field experience, providing flexibility, convenience and quality for the in-situ detection and analysis of VOC's. This is the result of its unique combination of a Photo Ionize Detector (PID) analyzer for measurement of total soil gas concentration and a selective Infrared (IR) analyzer for the separate measurement of Methane, Petroleum Hydrocarbons and Carbon Dioxide. The resulting set of parameters is further complemented by temperature, pressure and oxygen measurement (www.rsdynamics.com).

Long-standing surface hydrocarbon contamination has been usually changed into aromatic compounds which do not show any readings on the instrument screen as volatile vapor phase has already evaporated. Aromatic hydrocarbons smell intensively and very dark colour of the contaminated soil give an impression of a large contamination. Usually regular measurement from 1meter deep hole shows Methane and/or Total Petroleum readings, depending on the age of contamination. The vapor phase caused by hydrocarbon contamination exists under different weather conditions, with higher volatility in sunny weather. Temperatures below the freezing point represent the only limitation since the vapor phase shows almost no volatility when temperatures are low. It is easy to distinguish between a recent and a long-standing contamination, *the long-standing contamination shows up mostly as Methane due to natural bioremediation activity (www.rsdynamics.com)*.

ECOPROBE 5 instruments have been used for many pipeline rupture assessments, where petroleum hydrocarbon products were leaking into the ground. Leaking pipelines usually cause large fresh hydrocarbon contaminants, which give out huge amounts of hydrocarbon vapours, easily detectable on the surface without the necessity of making sampling holes into the ground. Fresh pipeline leakage contamination is characterized by no Methane readings (bacterial activity has not yet started). Large pipeline contaminations are most common, very easily detectable by the Infra-Red Total

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petroleum channel. Small ruptures and leakages or deep contaminations are detectable by PID analyzer, providing identification of even minimal contamination levels.

4.1.4. Soil sampling

The collection and analysis of soil samples has become a standard practice in site assessment and along with groundwater sampling, one that has gained the wide acceptance of regulatory agencies. Physical access to the soil may be provided in a variety of ways, from hand tools to truck mounted drill rigs. The method depends almost entirely upon site conditions and investigation goals. The sampling plan may be equally varied. Due to the cost involved in analysis of soil samples, it is also to screen samples in the field for evidence of contamination, using organic vapour analyzers. Samples showing positive indicators of contamination are then submitted for laboratory analysis (Calabrese et al, 1991).

4.1.5. Groundwater sampling

Groundwater sampling is one of the most widely practiced methods of assessment because of the immediate threat of contamination of drinking water and the resulting public health concerns. Groundwater samples may be sampled through existing water supply boreholes, or most commonly from especially constructed monitoring boreholes. Monitoring boreholes for hydrocarbon assessment require screening above the water table to be able to adequately detect free-phase product, but in construction are otherwise similar to small, shallow domestic water boreholes (Calabrese et al, 1991).

4.2. Evaluation of methods

An unbiased evaluation of assessment techniques must consider multiple factors ranging from site limitations to amount of money and time available for the survey. Seldom, if ever, does the investigator have an ideal site or infinite resources to commit to a site assessment, so ultimately every assessment is somewhat of a compromise that hopefully yields reliable and accurate results. The experience and wisdom of the investigator is by far the most significant factor in a site assessment. It is the investigator who decides which technique is applicable, how that technique is applied, the level of effort appropriate, and who interprets the results. The following evaluation is presented

with the recognition that there are many varied approaches to each method, some of which effectively overcome limitations, however, most methods have the following characteristics:

4.2.1. Pedestrian survey

- Positives Aspects

Inexpensive, rapid, good gross integration of many variables, no permits, unobtrusive, provides good guidance for future work.

- Limitations

Depends upon experience of investigator, subjective, limited to surface assessment, personal protective equipment may limit sensitivity.

The pedestrian survey is of limited value in making absolute measurements of concentration and extent of hydrocarbon contamination. As a result, it will seldom satisfy the requirement of regulators or potential purchases of property if there is any site history of petroleum use or storage. The value of pedestrian survey is that in a short period of time and with little expense, an experienced investigator can develop an opinion regarding potential areas of contamination which should be targets for future investigation. During the pedestrian survey the investigator can assess hydrocarbon storage and housekeeping practices, identify utility trench locations which may be possible conduits for contamination migration, assess proximity of any sensitive neighbors, and examine any open excavations, manholes, or utility vaults, on-or offsite, to gain insight into subsurface condition. Because this is qualitative approach that relies on human sensory abilities and the judgment of the individual in the field, there is no way to critically assess this method other than to recognize that it cannot provide the type of data typically necessary to reach conclusions about the magnitude and extent of hydrocarbon contamination (Calabrese et al, 1991).

4.2.2. Soil vapour survey

▪ Positives Aspects

Inexpensive, rapid, quantitative, immediate results, limited regulatory permitting, minimal disruption to operating facilities, low public visibility, does not generate waste, excellent guidance for further investigation.

▪ Limitations

Does not work well in wet or clayey soil, limited depth penetration, not accepted by regulatory agencies, requires experienced field personnel, results can be over interpreted, usually requires soil or water sampling to confirm results, quality control often lacking.

The accuracy and value of soil gas/vapour sampling as a site assessment for hydrocarbon contamination has been the subject of recent reviews. The technique has proven to be reliable in determining the presence or absence of contamination in groundwater on the basis of a whole site survey with an accuracy of approximately 80%. That is, when groundwater is contaminated with hydrocarbons, eight out of ten times it will be detected in a soil gas/vapour survey regardless of the site variables. When individual soil vapour sampling points are correlated with nearby groundwater samples, the influence of site variables is revealed.

Correlation of soil type and the distance between the vapour samples are taken as close to the potential source of hydrocarbon vapours as possible and when soil are porous enough to result in good gas transport. Analysis of field data and observations by investigator indicate that water saturated and clay soils are not adequately sampled with this method, primarily due to lack of good vapour transport (Calabrese et al, 1991).

4.2.3. Soil sampling

▪ Positives Aspects

Quantitative, direct measurement of contaminants of concern, generally accepted by regulatory agencies.

▪ Limitations

Sample collection and analysis can be expensive; sample numbers typically low due to cost per sample; spatial distribution of contaminants in soils causes high sample variability; may require special regulatory permits; generates waste soil necessitating special handling and disposal.

Soil sampling may be accomplished using a variety of methods ranging from simple hand augers to drill rigs. It is commonly viewed as a definitive method of characterizing magnitude and extent of contamination; however, it has some significant and often overlooked limitations. Most notable is the fact that only a very small fraction of the total volume of soil at a site is sampled and an even smaller portion is actually analyzed.

4.2.4. Groundwater sampling

▪ Positives Aspects

Quantitative, direct measurement of contaminants of concern; provides essential data for risk assessment; can also incorporate soil sampling; accepted by regulatory agencies; monitoring may be continued over time to evaluate trends.

▪ Limitations

Expensive, so a limited number of boreholes usually installed; analytical costs high; special permits required, generates waste for disposal; time required for permits, drilling, analyses; long-term monitoring commitment may be necessary; highly visible to public; may be disruptive to operating facilities, access for drill equipment may limit use.

4.3. The petroleum analytical process: from sample collection to measurement.

This study focuses on three types of petroleum analytical methods:

- Method that measure a TPH concentration
- Method that measure a petroleum group type concentration and
- Method that measure individual petroleum constituent concentrations.

These three types of methods measure different petroleum hydrocarbons that might be present in the petroleum contaminated environmental media. TPH methods generate a single number that represents the combined concentrations of all petroleum hydrocarbons in a sample, which are measurable by a particular method. Petroleum group type method separate and quantify different categories of hydrocarbons (e.g., saturates, aromatics, and polars/resins). The results for petroleum group type analyses can be useful for product identification because different products (e.g., gasoline, fuel oil and jet fuel) can have characteristic levels of various petroleum groups. Individual constituent methods quantify concentrations of specific compounds that might be present in petroleum-contaminated samples, such as benzene, ethyl benzene, toluene and xylenes (BTEX) as well as polycyclic aromatic hydrocarbons (PAHs). Concentration data for individual petroleum constituents can be used to evaluate human health risk, provided that the necessary toxicity data are available (Total Petroleum Hydrocarbon Criteria Working Group Series, 1998).

Although these three method types measure different petroleum hydrocarbon categories, there are several basic steps that are common to the analytical processes for all methods, no matter the method type or environmental matrix. Most of the common analytical steps are related to the separation of analytes of interest from a sample matrix prior to their measurement. In general, these steps are the following:

- Collection and preservation – requirements specific to environmental matrix and analytes of interest.
- Extraction – separate the analytes of interest from the sample matrix.
- Concentration – enhances the ability to detect analytes of interest.
- Cleanup – may be necessary to remove interfering compounds
- Measurement – quantifies the analytes.

4.3.1. Collection and preservation of environmental samples

The ability to collect and preserve a sample that is representative of the site is a critically important step. Obtaining representative environmental samples is always a challenge due to the heterogeneity of different sample matrices. Additional difficulties are encountered with petroleum hydrocarbons due to the wide range in volatility, solubility, biodegradation and adsorption potential of individual constituents.

Most site investigations for assessment of petroleum hydrocarbon contamination in the environment are regulated by the states. However, sample collection and preservation recommendations follow the U.S.EPA guidelines. A summary of the most commonly used guidelines is included in Appendix A. It should be noted that there might be additional requirements in given states. Before sample is collected the particular state requirements must be investigated. Because of holding time consideration, the laboratory must be selected and notified prior to the collection of the samples (Total Petroleum Hydrocarbon Criteria Working Group Series, 1998).

4.3.2. Sample extraction

For most analyses, it is necessary to separate the analytes of interest from matrix (i.e., soil, sediment, and water). Extraction of analytes can be performed using one or more of the following methods:

- Extracting the analytes into a solvent
- Heating the sample (used in the analyses of volatile compounds)
- Purging the sample with an inert gas (used in the analyses of volatile).

There are a variety of common sample extraction techniques. Soxhlet, sonication, supercritical fluid, sub critical or accelerated solvent, and purge and trap extraction have been promulgated by the U.S.EPA as soil extraction methods. Headspace is recommended as a screening method. Environmental laboratories also generally perform matrix spikes (addition of target analytes) to determine if the soil or water matrix retains analytes.

Solvents have different extraction efficiencies. Methylene chloride has been the solvent of choice for many semi-volatile analyses due to its high extraction efficiency, low cost and specification by many state regulatory methods. Methanol is the most common solvent used to preserve and extract volatiles such as BTEX in soil (Total Petroleum Hydrocarbon Criteria Working Group Series, 1998)

4.3.2.1. Water samples

Water extraction methods in common use include the following:

For volatiles:

- Purge and trap
- Headspace

Volatile compounds (gasoline, solvents) in water are generally separated from the matrix by purging with an inert gas and trapping the compounds on a sorbent (EPA 5030, purge and trap analysis). The sorbent is later heated to release the volatile compounds and a carrier gas sweeps the compounds into a gas chromatograph.

Headspace analysis is considered as a screening method by EPA (Methods 3810, and 5021), although it performs well in particular situations, especially field analysis. In this method water sample is placed in a closed vessel with a headspace and heated to drive volatiles into the gas phase. Addition of salts or acids may enhance this process. In a headspace analysis, instrument contamination is minimized because only volatile compounds are introduced into the instrument. Samples containing heavy oils and high analyte concentrations can severely contaminate purge and trap instrumentation (Total Petroleum Hydrocarbon Criteria Working Group Series, 1998).

4.3.2.2. Soil samples

Soil extraction methods in common use include the following:

For volatiles:

- Purge and trap
- Headspace

Volatile compounds (e.g., BTEX and gasoline) may be solvent-extracted from soil. EPA method 5035, purge and trap analysis, specifies a methanol extraction, which is usually done by mechanical shaking of the soil with methanol. A portion of the methanol extract is added to a purge vessel and diluted in reagent grade water. The extract in purged similar to a water sample.

Headspace analysis, (EPA Methods 3810 and 5021), also works well for analyzing volatiles in soils. The soil is placed in a headspace vial and heated. Salts can be added

to more efficiently drive out the volatiles from the sample into the headspace of the sample container. Similar to water headspace analysis, the soil headspace technique is useful when heavy oils and high analyte concentrations are present which can severely contaminate purge and trap instrumentation. Detection limits are generally higher for headspace analysis than for purge and trap analysis (Total Petroleum Hydrocarbon Criteria Working Group Series, 1998).

4.3.2.3. Free Phase Hydrocarbon Samples

In some releases of petroleum products to the environment where free phase product is found, hydrocarbon material can be collected directly for characterization. The ability to analyze free product greatly aids the determination of product type and potential source. The samples may be diluted prior to analysis. EPA Method SW-846 3580, waste dilution, gives some guidelines for proper dilution techniques.

4.3.3. Concentration of sample extract

Extracts are generally filtered, dried with desiccant, and concentrated before analysis. Concentration of the extract may allow for lower sample detection limits. Frequently, sample extracts must be concentrated to obtain detection limits low enough to meet regulatory action limits. Concentration may be achieved by:

For volatiles:
- Sorbent trapping
- Cryogenic trapping

The trapping steps in a purge and trap analysis is essentially a concentration step. Analytes are purged from the matrix into a gas stream and captured on a sorbent trap. The analytes are released by heating the trap. Some laboratories use cryogenic trapping in place of sorbent trapping. A very cold material such as liquid nitrogen surrounds a sample loop. As analytes are purged and swept through the sample loop, they free in the sample loop. The analytes are released when the trap is heated.

4.3.4. Cleanup of sample extract

Cleanup steps can be an important component of infrared (IR) –based and gravimetric methods because these methods are very sensitive to non-petroleum hydrocarbon interferences. Cleanup steps are less commonly utilized for gas chromatography (GC)-based methods because experienced GC analysts can recognize the presences of interfering compounds (e.g., animal and vegetable derived hydrocarbons).

Cleanup steps are not always a part of the petroleum analytical process, but when they are necessary, the goals of extract cleanup steps typically include one or more of the following:

- Removal of non-petroleum compounds
- Isolation of a particular petroleum fraction
- Concentration of analytes of interest.

The techniques employed to extract the analytes of interest can frequently extract interfering compounds. Polar compounds such as animal and plant fats, proteins, and small biological molecules may be improperly identified as petroleum constituents. Extract cleanup techniques can be used to remove them. In an ideal situation, only interfering compounds are removed. In reality, some polar petroleum constituents can also be removed.

Two techniques are used to clean petroleum extracts. In one technique, interfering compounds are removed by passing the extract through a glass column filled with sorbent. A second technique is to swirl the extract with loose sorbent, then remove the sorbent by filtration. Three of the EPA-promulgated cleanup techniques involve trapping the interfering compounds on a sorbent column. EPA SW-846 3611 is an alumina cleanup designed to remove interfering compounds and to fractionate petroleum wastes into aliphatic, aromatic and polar fractions. The fractions can be analyzed separately or combined for a total TPH measurement. EPA SW-846 3630, silica gel cleanup, is the most common cleanup technique used on extracts designated for PAHs and phenol analyses.

EPA method SW-846 3660 is used for sulfur removal. This technique uses copper, mercury, and tetrabutylammonium sulfite as desulfurization compounds. Sulfur is a common interfering compound for petroleum hydrocarbon analysis, particularly for sediments. Sulfur containing compounds are very common in heavy fuels and crudes

and on refinery sites. Elemental sulfur is often present in anaerobically biodegraded fuels. High levels of sulfur may be measured as "TPH" by some techniques if the cleanup technique is not used.

4.3.5. Measurement

Once the sample preparation is complete, there are several approaches for detecting and quantifying petroleum hydrocarbons:

- Total petroleum hydrocarbon (TPH) measurement
- Petroleum group type
- Individual component measurement

4.3.5.1. Total petroleum hydrocarbon (TPH) measurement

Total petroleum hydrocarbon (TPH) measurements are conducted to determine the total amount of hydrocarbon present in the environment. There are a wide variety of TPH methods. In practice TPH is define by the method used to analyze it. Different methods often give different results because they are designed to extract and measure slightly different subsets of petroleum hydrocarbons. No single method gives a precise an accurate measurement of TPH for all types of contamination. The four most commonly used TPH testing methods include gas chromatography (GC), Infrared spectrometry (IR), gravimetric analysis and immunoassay.

4.3.5.2. Petroleum group type measurement

Petroleum group type measurements are conducted to determine amounts of various petroleum compounds classes (e.g., saturates, aromatics, and polars/resins) present in petroleum-contaminated samples. This type of measurement is sometimes used to identify fuel type or to tract plumes. It may be particularly useful for heavier hydrocarbons such as tar and asphalt. Group type test methods include multidimensional gas chromatography, high performance liquid chromatography (HPLC), and thin layer chromatography (TLC).

4.3.5.3. Petroleum constituent measurement

Methods that analyze individual compounds (e.g., BTEX and PAHs) are generally run to detect the presence of an additive or to provide concentration data needed to estimate human health risk associated with individual compounds. Common constituent measurement techniques include gas chromatography with second column confirmation, gas chromatography with multiple selective detectors and gas chromatography with mass spectrometry detection (GC/MS).

CHAPTER 5.   HEALTH RISK ASSESSMENT

5.1.   Risk Based Corrective Action

5.1.1. Overview of Risk Based Corrective Action

Risk Based Corrective Action (RBCA) is a decision-making process for assessment and response to subsurface contamination associated with petroleum hydrocarbon releases. The guidelines for RBCA are published in American Society for Testing Materials (ASTM E-1739-95), thus "*Standards Guide for Risk Based Corrective Action applied at Petroleum Releases Sites"*. RBCA integrates Environmental protection Act (EPA) risk assessment practices with traditional site investigation and remedy selection activities in order to determine the cost-effective measures for protection of human health and environmental resources.

Under this integrated approach, petroleum release sites are characterized in terms of sources, transport mechanism and receptors (Figure 5.1). Remedial measures are then applied as needed to prevent human health or environmental exposure to harmful levels of site constituent. Risk Based Corrective Action can be used by addressing any step in the exposure process such as (Connor et al, 1995):

i.   Removing or treating the source
ii.   Interrupting contaminant transport mechanism or
iii. Controlling activities at the point o exposure.
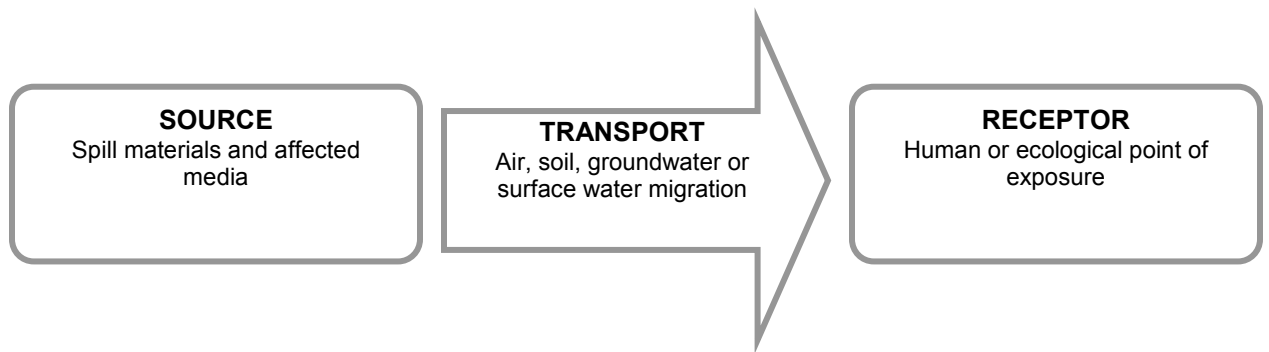
Figure 5.1: Conceptual Exposure Model

Under RBCA, risk management strategies are developed and implemented in accordance with the process flowchart as shown in Figure 5.2 below. Based on the available site information, a site classification step is completed to characterize the relative magnitude and immediacy of site risks and prescribe immediate response actions (Step2 on figure 5.2). After any acute or near-term hazards have been properly addressed, risk-based cleanup standards are developed to protect against potential chronic health or environmental impacts associated with long-term exposure to low levels of contaminants   (Step3-7 on Figure 5.2). To achieve the final risk management goals, the remedial action program may involve:

  i.   Source removal/treatment
 ii.   Containment measures
iii.   Institutional controls and
iv.   Some combination thereof.

| | **1** | **Initial Site Assessment**
 ▪ Conduct site investigation and complete Tier 1 Summary Report to organize available site information regarding principal contaminants, presence of affected environmental media, and potential migration pathways and receptors. |

| **SCOPE OF TIER 1 GUIDANCE MANUAL** | **2** | **Site Classification and Initial Response Action**
 ▪ Classify site per specified scenarios implement appropriate initial response action.
 ▪ Reclassify site as appropriate following initial and interim response actions or additional data collection. | **Interim Corrective Action**
 ▪ Conduct partial source removal or other action to reduce risk(s) and adjust site classification. |

3 **Tier 1 Evaluation**
▪ Identify reasonable potential sources, transport pathways, and initial response action.
▪ Reclassify site as appropriate following initial and interim response actions additional data collection.

4 Contaminant concentrations exceed RBSLs? → Remediation to Tier 1 SSTLs practicable? → Interim Corrective Action appropriate?

Tier 2 Evaluations
▪ Collect additional site data as needed.
▪ Conduct Tier 2 assessment per specified procedures. Compare Tier 2 Site-Specific Target (SSTLs) with site conditions.

5

Contaminant concentrations exceed RBSLs? → Remediation to Tier 2 SSTLs practicable? → Interim Corrective Action appropriate?

6

Tier 3 Evaluations
▪ Collect additional site data as needed.
▪ Conduct Tier 3 assessment per specified procedures. Compare Tier 3 Site-Specific Target (SSTLs) with site conditions.

7

Contaminant concentrations exceed RBSLs? → Interim Corrective Action appropriate?

8

Remedial Action Program
▪ Identify cost-effective means of achieving final corrective actions goals, including combinations of remediation, natural attenuation, and institutional controls. Implement the preferred alternative.

9

Continued monitoring required

10 **Compliance monitoring**
▪ Conduct monitoring program as needed to confirm that corrective action goals are satisfied.

No Further Action

SCOPE OF TIER 2 GUIDANCE MANUAL

SCOPE OF TIER 1 GUIDANCE MANUAL

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Figure 5.2: ASTM RISK-BASED CORRECTIVE ACTION (RBCA) FLOWCHART (Connor et al, 1995)

Further discussion of the underlying concepts of the RBCA process, as well as the specific tasks involved in site classification and development of risk-based remediation goals are provided below.

5.1.2. Hazard characterization and response under RBCA.

Release of petroleum products or other chemical substances can results in an *acute* (i.e., immediate) or a *chronic* (i.e., long-term) hazard to life or health. In general, chronic hazards are associated with long-term exposure to relatively low levels of the site constituents, whereas acute hazards involve high concentrations sufficient to pose an immediate risk of fire, explosion, or health impairment. The presence of an acute hazard can be ascertained based on established threshold criteria (e.g., lower explosive limit, vapour IDLH). However, chronic health effects are not immediately evident and therefore require a more careful evaluation of long-term, future exposure patterns in order to establish appropriate site cleanup (Connor et al, 1995).

Consistent with EPA risk assessment protocol, the RBCA Tier1, 2, and 3 evaluations address source zone cleanup standards that will protect against chronic health or environmental impacts, i.e., carcinogenic or toxic effects caused by long-term exposure to low level of contaminants. Such analysis is appropriate only after any and all acute hazards associated with the site have been identified and properly controlled. For this purpose, the RBCA evaluation process requires site classification and implementation of appropriate interim response actions (see step2 on figure 5.2) prior to analysis of media cleanup standards. Types of acute hazards to be addressed in the site classification-response phase include explosive vapour levels, utility impacts, or the presence of free phase hydrocarbon liquid in the groundwater. In addition, interim stabilization measure may be applied to prevent incidence of short-term chronic impacts.

Following completion of step1 to 4 of RBCA process (Figure 5.2), the procedures outlined in this ASTM Risk Based Corrective Action guidelines can be used to define site-specific soil and groundwater cleanup levels necessary to protect against future health impacts. The general sequence of hazard characterization and response under

RBCA is illustrated on Figure 5.2. As shown, in some applications, other non-aesthetic consideration (i.e., odour, appearance and taste) may affect the future use of a property or resources even after constituent concentrations have been reduced to levels posing no further health concern (Connor et al, 1995).

5.1.3. RBCA Site Classification

Under the RBCA planning process, sites are first classified with regard to the current magnitude and immediacy of human health and environmental risks. Appropriate emergency actions are then implemented without delay to address acute hazards or near term-term impacts. Under the classification scheme outlined in ASTM E-1739, applicable exposure scenarios are reviewed to match the site with one of the four qualitative risk categories indicated in Table 5.1 below. For each classification, an appropriate response action is prescribed to effectively manage the potential site hazards as the site evaluation and remediation process. As shown on Table 5.1, remedial actions are expected at near-term high-risk sites, while interim monitoring system are required to long term, low-risk sites. This site classification represents a "snapshot" in time, addressing hazards associated with current site conditions and land use.

Table 5.1: RBCA site classification and response actions (Connor et al, 1995)

Current Hazard	Site Classification	Initial Response Action
Acute	Class1:Immdiate Threat	Abate release
Chronic	Class2: Near- Term Threat (0-2years)	Monitor/Remediate
	Class3: Future Threat (>2years)	Monitor/Investigate
Aesthetic	Class4: No Current Demonstrate Risk	Monitor only

5.1.4. Tiered Evaluation of Risk-Based Standards

To address chronic human health or environmental hazards, site remediation requirements are evaluated on the basis of risk-based soil and groundwater clean-up goals, developed in accordance with U.S.EPA risk assessment guidelines. To provide an economical use at both small and large facilities, the RBCA process has been designed to match the site evaluation effort to the relative risk or complexity of each site. For this purpose, a tiered approach is employed for determination of risk-based cleanup goals, involving increasingly sophisticated levels of data collection and analysis (Figure 5.3). Upon completion of each sequential tier, the user reviews the results to determine whether further data collection and evaluation is warranted. For purpose of efficiency, the site investigation steps and decisions involved in this process are indicated on the RBCA flowchart (Figure 5.2). The scope of Tiers 1, 2, and 3 are as follows (Connor et al, 1995):

5.1.4.1.   Tier 1: Generic Screening-Level Corrective Action Goals

Tier 1 of the RBCA process involves comparison of site constituent concentration to generic Risk Based Screening Levels (RBSLs) to determine whether further evaluation is required. RBSL values are derived from standard exposure equations and reasonable maximum exposure (RME) estimates per U.S.EPA guidelines. As shown on Figure 5.3, RBSL concentration limits are designed to be protective of human health even if exposure occurs directly within the on-site area of affected soil or groundwater (i.e., the "source zone").

If Tier 1 limits are not exceeded, the user may proceed directly to compliance monitoring and/or no further action (see Figure 5.2). However, if these generic levels are exceeded, the affected media may be addressed by:

  i.   Remediating to the generic Tier 1 limits, if practicable
  ii.   Conducting a Tier 2 evaluation to develop site-specific remediation goals
  iii. Implementing an interim action to abate risk "hot spots".

In general, the Tier 1 evaluation serves to identify   sites requiring no further action. For most sites exceeding Tier1 limits, a Tier 2 analysis will provide a more cost-efficient basis for evaluation of appropriate remedial measures.

5.1.4.2.   Tier 2: Site-Specific Corrective Action Goals

Under Tier2, Site-Specific Target Levels (SSTLs) for soil and groundwater cleanup goals are determined on the basis of site-specific information and/or points of exposure. Simple analytical models are employed in conjunction with additional site data to calculate Tier 2 SSTL values in a manner consistent with EPA-recommended practices. Modeling and calculation procedures are streamlined so as to represent a minor incremental effort relative to Tier 1. Both the Tier 1 RBSL and Tier 2 SSTL values represent concentration limits for constituents within the source zone. However, SSTLs differ from RBSLs in three significant ways:

i.   Site-specific data are used to calculate risk-based cleanup goals

ii.   Human exposure to affected media may be assumed to occur not at the source zone, but at a separate "point of exposure" (POE) and

iii.   The effects of natural attenuation of constituent concentration during lateral transport from the source to an off-site POE may be considered in the SSTL calculation (Figure 5.3).

If site constituent concentrations exceed SSTL values, subsequent actions may involve the following:

i.   Remediation to site specific Tier 2 cleanup goals

ii.   Further evaluation per Tier 3 of the RBCA process

iii.   Interim response measures targeted at principal risk sources (see Step 6 on Figure 5.2)

5.1.4.3.   Tier 3: Site-Specific Corrective Goals

If Tier 2 results are judged inappropriate or impracticable, a Tier 3 evaluation can be conducted to refine Tier 2 corrective action goals on the basis of a more complex risk and exposure assessment, involving more detailed site information, probabilistic data analysis, and/or numerical fate and transport modeling. Such Tier 3 evaluation will typically entail significant additional data and expense relative to Tiers 1 and 2 should therefore be reserved for highly complex, cost-significant sites. Tier analysis may be warranted at sites for which Tier 2 modeling methods are non-conservative or detailed ecological impact assessment are required.

Similar to Tier 2, the Tier 3 evaluation provides source zone cleanup levels designed to protect against health or environmental impacts at a site-specific POE (Figure 5.3). The

tiered evaluation process concludes upon derivation of applicable and remediation standards. It should be noted that the soil and groundwater standards developed under Tier1, 2, and 3 are equally protective of human health and the environment, based on applicable target risks and exposure criteria (Figure 5.4). However, with each tier upgrade, the degree of uncertainty and conservation involved in the cleanup standard calculation is reduced based upon a more detailed characterization of actual site condition. As indicated on the RBCA process flowchart (Figure 5.2), the user reviews the results of each tier to determine if further evaluation is necessary (Connor et al, 1995).
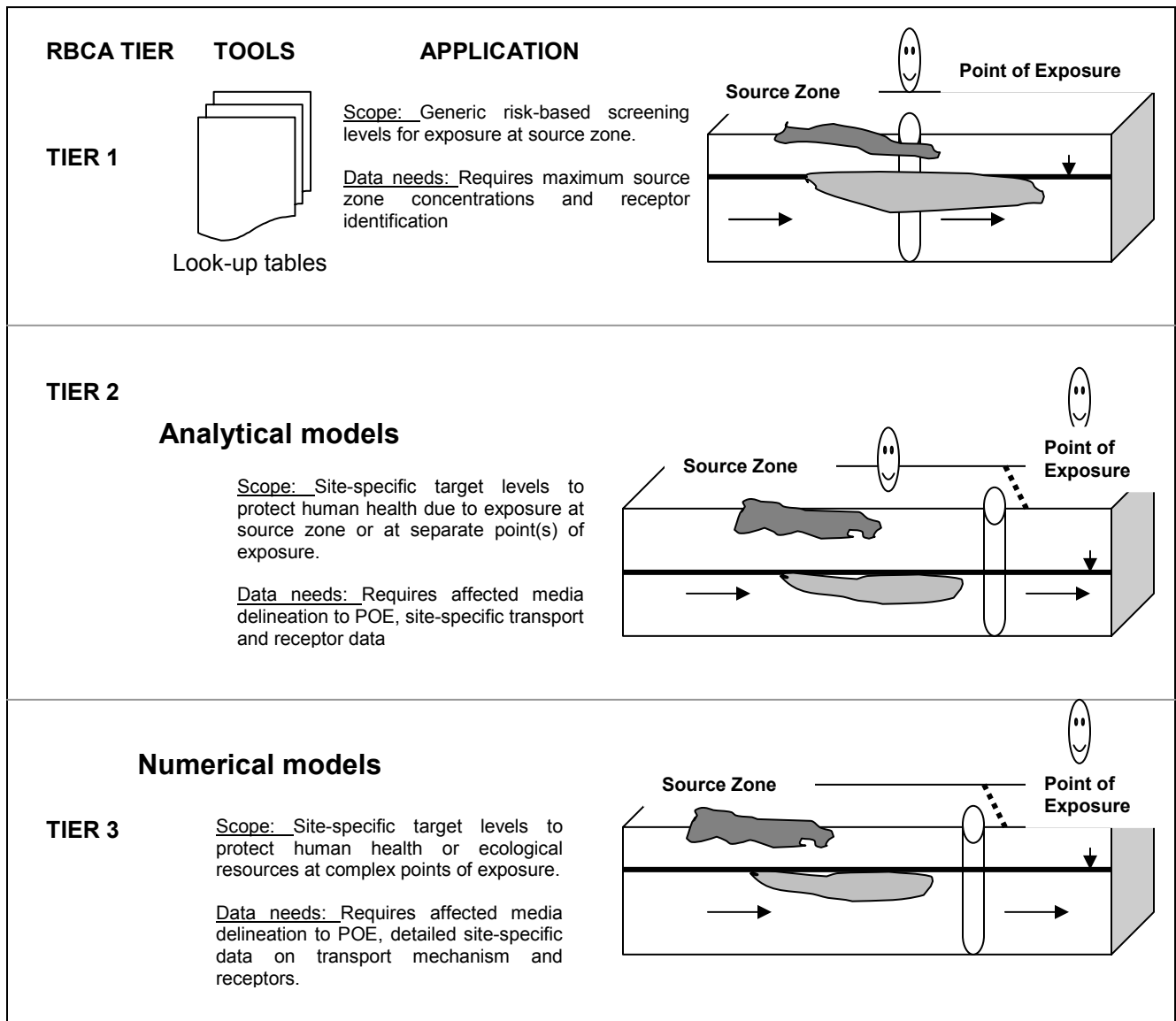
Figure 5.3: Overview of Tiered Process for Cleanup Goal Calculation.
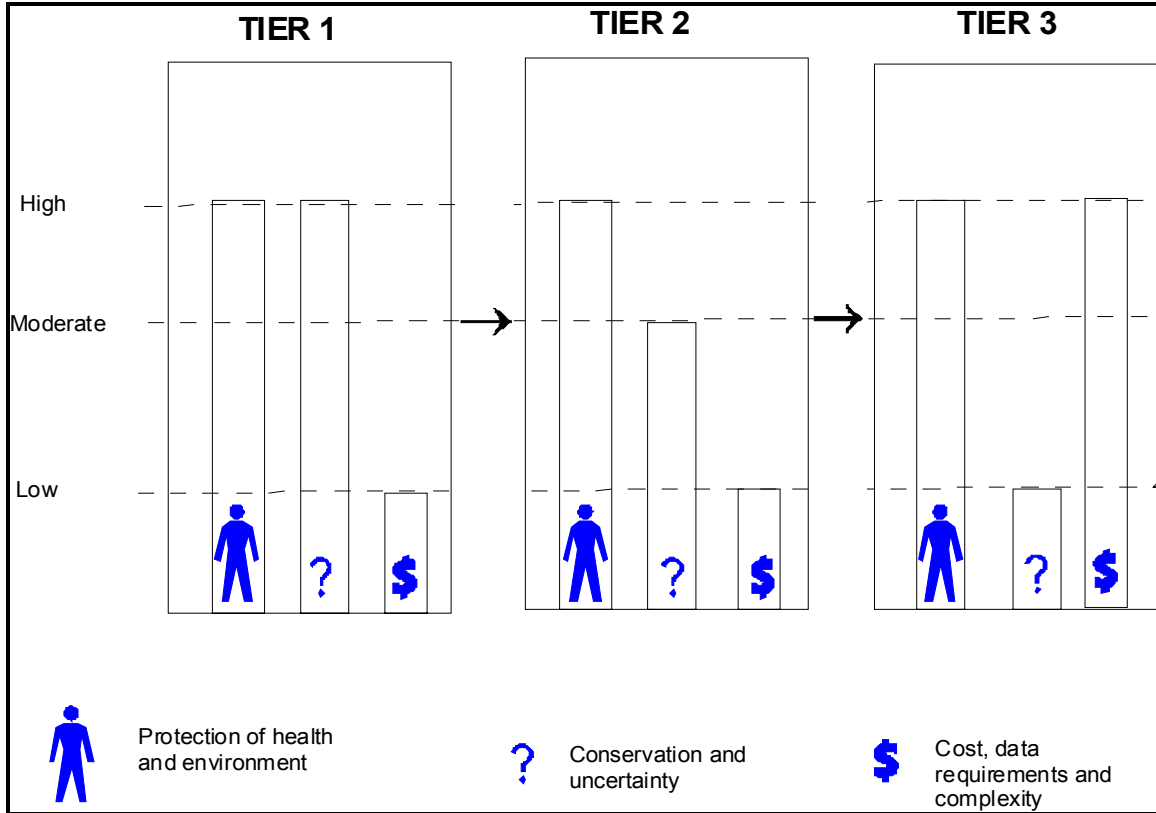
Figure 5.4: Comparison of RBCA TIER1, 2, and 3 evaluations (Connor et al, 1995).

5.2. Overview of Tier 2 Evaluation Process

5.2.1. Tier 2 Information Requirements

Prior to commencing the Tier 2 evaluation, the user should complete all tasks required for site classification and the Tier 1 analysis (i.e., Steps 1-4 on Figure 5.2). The results of the Tier 1 evaluation should identify the source zone media and exposure pathways to be addressed under Tier 2. If the Tier 1 screening levels are exceeded and remediation to these limits is impracticable, Tier 2 evaluation should be conducted to develop Site Specific Target Levels (SSTLs) for relevant site constituent and exposure pathways.

Under RBCA, the site investigation proceeds in a just-in-time approach, addressing only the immediate data needs of each tier. Tier 1 data requirements may be limited to characterization of on-site land use and determination of maximum constituents

concentrations in source zone media. For Tier 2, site data must be sufficient Connor et al, 1995):

   i.   Complete the Tier 2 SSTL calculation and

  ii.   Confirm the exceedance or non-exceedance of these risk-based cleanup goals throughout the full area of affected soil and groundwater.

The additional site information required for the Tier 2 evaluation may include:

    i.   Source Zone Characterization: lateral and vertical limits of affected soil and groundwater zones; representative concentrations of constituents of concern.

   ii.   Hydrogeologic Site Conditions: Site stratigraphy, surface soil conditions, rate and direction of groundwater flow, attenuation factors etc.

 iii.   Relevant Points of Exposure: Distance from source zone(s) to potential receptors (i.e., likely point of contact with affected soil, water, or air), receptor type and applicable exposure factors.

 iv.   Applicable Risk Goals: Human health protection criteria for individual and cumulative effects of exposure to site constituents applicable regulatory exposure limits and ecological protection standards.

The goal of the Tier 2 evaluation is to determine whether or not remedial measures will be required to meet target risk limits at relevant points of exposure. For this purpose, site constituent concentrations in affected soil and groundwater are compared to SSTL values for applicable exposure pathways. To develop the SSTL value for each pathway, site-specific data must be obtained to characterize current or potential constituents transport from the source to the relevant receptor. Data regarding constituent concentrations below Tier 1 RBSL levels or constituent transport beyond relevant points of exposure are not required for the immediate purpose of the Tier 2 evaluation. The minimum data requirements for Tier 2 evaluation are summarized on Table 5.2 below.

Table 5.2: Minimum Site-Specific Data Requirements For Tier 2 Evaluation (John, et al, 1995)

SOURCE ZONE CHARATERISTICS	
i. Surface soils	▪ Dimensions of affected soil zone (depth interval, length, width) ▪ Constituents o Concerns (COCs) ▪ Representative COC concentrations
iii. Subsurface Soil Zone (e.g. >3ft Below Ground Surface)	▪ Dimension of affected, unsaturated soil zone (depth interval, length, width) ▪ Constituents o Concerns (COCs) ▪ Representative COC concentrations
iii. Subsurface fluids	▪ Dimension of affected groundwater and/or NAPL zone (depth interval, length, width). ▪ Constituents o Concerns (COCs) ▪ Representative COC concentrations
EXPOSURE PATHWAY INFORMATION	
i. Air Pathway	▪ Area of affected surface soils ▪ Depth interval of affected subsurface soils ▪ Thickness and soil type of unsaturated soil zone ▪ Downwind distance to vapor/dust receptor (s) ▪ Average annual climatic conditions (typical wind speed, etc.)
ii. Groundwater Pathway	▪ Depth to uppermost water-bearing unit with potentially usable groundwater ▪ Leachate potential through overlying soil zone (rainfall infiltration, etc.) ▪ Hydraulic conductivity of water-bearing unit ▪ Groundwater flow gradients, seepage velocity, and flow direction ▪ Attenuation factors (electron acceptors, retardation factors, decay-rate coefficients for COCs)

	▪ Distance from plume source point to groundwater receptor (s)
iii. Soil Pathway	▪ Lateral limits of affected surface soil area ▪ Surface soil type
iv. Soil Water Pathway	▪ Storm water drainage pathway from affected surface soil zone to surface water body and estimated COC loading rate ▪ Groundwater water to surface water discharge and estimated COC loading rate ▪ Harmonic mean flow in surface water body ▪ Surface water body quality and use classification
RECEPTOR INFORMATION	
i. Land Use Characterization	▪ Land use on-site (current and future) ▪ Land use at off-site points of exposure (current and future)
ii. Receptor Characterization	▪ Anticipated type* and location of receptor (s) for each pathway ▪ Applicable exposure factors at each Point of Exposure.

5.2.2. Tier 2 SSTL Calculation Options

In the Tier 2 evaluation, Site Specific Target Levels (SSTLs) for affected soil and groundwater are developed through application of relatively simple analytical tools. The SSTLs represent upper bound constituent concentrations that, if achieved throughout the source zone, will present exceedance of applicable risk limits at potential points of exposure. Tier 2 SSTL values can be derived by any of the three methods summarized on Table 5.3 below.

Table 5.3: Summary of Tier 2 SSTL Calculation Options

OPTION	ASSUMED	APPLICATION	SSTL CALCULATION METHOD
▪ **Option1** Site-Specific Screening Levels	At source zone	Develop site-specific screening levels for affected soil and groundwater.	Revise tier 1 RBSL calculation using site specific input values
▪ **Option2** Individual Constituent SSTLs	At site-specific distance from source zone	Develop soil and groundwater cleanup levels to prevent exceedance of individual constituent risk limits at POE.	Use contaminant transport model and/or site data to define Natural Attenuation Factor (NAF) SSTL= NAF x risk-based exposure limit for each constituent at POE (i.e. RBSL).
▪ **Option3** Cumulative/Individual Constituent SSTLs	At site-specific distance from source zone.	Develop soil and groundwater cleanup levels to prevent exceedance and cumulative constituent risk limits at POE.	Use contaminant transport model and/or site data to predict potential exposure concentrations and baseline risks at POE SSTL = Lower of: ▪ NAF x risk-based exposure limit for each constituent at POE or ▪ C_s x Cumulative Risk Goal/ Cumulative Baseline Risk Where Cs = source concentration for each COC.

5.2.3. Potential pathway of chronic exposure

To develop risk-based cleanup goals, the user must first identify the reasonable mechanism for contaminant transport from the source zone to a point of contact with a human population or ecological resource. For this purpose, the RBCA evaluation considers several exposure pathways for contaminant migration from the source to the receptor through air, soil, groundwater or surface water. To pose an actual risk to human health or the environment, all three components of an exposure pathway must be present at a site: *an affected source medium, a mechanism for contaminant transport, and a current or potential receptor.*

For a given site, the applicability of each exposure pathway is therefore a function of the physical site conditions, the presence and proximity of potential receptors, and the mobility and concentration of the constituents of concern. Two types of exposure are identified:

i. Direct exposure pathways, in which the receptor comes in direct contact with the affected source medium (i.e. soil ingestion), and

ii. Indirect exposure pathways, in which exposure occurs at a different medium that the source (i.e. soil-to-air volatilization).

Under a Tier 1 evaluation, the receptor is assumed to be located on-site, in immediate proximity to the source zone, and may therefore be subject to both direct and indirect pathways of exposure. Under Tier 2, actual or potential receptors (i.e. groundwater users) may be determined to be off-site, at some measurable distance from the zone of affected media. Such off-site receptors will be subject only to indirect exposure pathways (Connor et al, 1995)

5.2.4. Source Zone Characterization

5.2.4.1.   Definition of Source Materials

The source zone consists of both primary sources (waste materials, spilled product, etc.) and secondary sources (affected media) that can serve as a continuing source of contaminant release to the environment. Prior to the Tier 2 evaluation, the primary

source of release should have been terminated under the site classification/response phase of the RBCA process (Figure 5.2). Tier 2 SSTL are therefore directed toward remediation of secondary source materials. For the purpose of the SSTL calculation, secondary source materials can be grouped into three principal areas.

 i. **Surface materials:** Affected surface soils (e.g., <0.9144m below ground surface)
 ii. **Subsurface Soils:** Affected subgrade soils (e.g., >0.9144m below ground surface) above water bearing material.
 iii. **Subsurface** fluids: Affected groundwater and nom-aqueous phase liquids (NAPLs) in saturate, water bearing material.

5.2.4.2.   Physical Dimensions of Affected Media

For each of the source materials identified above, site investigation data should be reviewed to define the lateral and vertical extent of affected media. For the immediate purpose of the Tier 2 evaluation, this delineation effort may be limited to:

 i. The area between the source point and applicable POE (s) (Table 5.4) and
 ii. COC concentrations in excess of Tier 1 RBSL values.

Analytical methods used to measure COC concentrations must have detection limits that are less than the corresponding Tier 1 RBSL value for each constituent. Test results for each sampling location should be plotted on scaled site plans and on stratigraphic cross-sections to define "clean lines" for affected soil and groundwater (e.g., COC concentrations < Tier 1 cleanup goals). Isopleths contours can be drawn when feasible to identify constituent "hot spots".

5.2.4.3.   Representative COC Source Concentrations

Under Tier 2, any site constituent detected at concentrations in excess of the Tier 1 RBSL value should be considered as a constituent of concern (COC). The user must select representative source concentration values for each COC in source material (e.g., surface materials, subgrade soils, subgrade fluids). This representative concentration will be used to calculate baseline risk levels and/or evaluate exceedance or non-exceedance of SSTL values.

The source concentration value must be representative of the capacity of the source medium to release COCs to the environment. The source term should therefore be matched to COC measurements in the central mass of the affected zone, using an appropriate statistical method. Options include the maximum concentrations, the mean concentrations, or the upper 90% or 95% confidence limit (UCL) on the mean source concentration, as determined from the analytical database.

5.2.5. Risk Characterization

Human health risk associated with exposure to COCs can be quantified on the basis of average daily intake rates and the correspondence toxicological parameters for carcinogenic and non-carcinogenic effects. Guidelines for calculation of health risks for:
  i.   Individual constituents
  ii. Multiple constituents and
  iii. Multiple exposure pathways are provided below.

5.2.5.1.   Individual Constituents Risks

Based on toxicological data, each COC can be classified as a carcinogen (Class A, B, or C), a systemic toxicant, or both. Corresponding carcinogenic and toxic effects are calculated as follows:

  i. **Carcinogenic Risk:** The excess lifetime cancer risk (R) due to chronic exposure to a COC is estimated as:

$$R = CDI \times SF$$

  where CDI = chronic daily intake for carcinogens (i.e., intake averaged over 70 years period) in mg/kg-day

  SF = slope factor for COC, in $(mg/kg\text{-}day)^{-1}$

  The excess risk value represents an upper bound estimate of the added probability of exposure to the COC.

  ii. **Hazard Quotient:** The hazard quotient (HQ) associated with exposure to a systematic toxicant is calculated as:

$$HQ = I/RfD$$

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where I = chemical intake for toxicants, averaged over exposure period, in mg/kg-day

RfD = reference dose, in mg/kg-day

The hazard quotient is not a probability value. Rather, the HQ value represents the ratio of the actual exposure level to the threshold level for non-carcinogenic effects. If HQ ≥ 1, non-carcinogenic effects could potentially occur in sensitive populations. Toxicological parameters must be matched to the route exposure. Oral values (SF$_o$, RfD$_o$) are used for soil and groundwater ingestion pathways, and inhalation values (SF$_i$, RfD$_i$) are for air exposure pathways. For dermal exposure routes, oral toxicity values, adjusted by an appropriate absorption factor, can be used to estimate health effects (except skin cancer). Reference dose values must furthermore be matched to the exposure duration, with chronic values used for lifetime exposure and sub chronic or short-term values used for short-term exposure (John et al, 1995).

5.2.5.2. Multiple Constituents Risks

The toxicological effects of exposure to multiple constituents have not been established. However, as a conservative measure, the cumulative effect of exposure to multiple constituents can be estimated by summing individual constituents values within each separate pathway, as follows:

i. **Cumulative Carcinogenic Risk:** For each pathway, total excess lifetime cancer risk (R$_T$) due to multiple constituent exposures can be estimated.

$$R_T = \Sigma R_i$$

where R$_i$ = individual risk for Ith COC

Individual cancer risk values based upon slope factors (i.e., 95% confidence limits on dose-response curve) are not strictly addictive; consequently, the user should note that summation of individual risks (in the absence of synergistic effects) typically overestimates the actual cumulative risk associated with exposure to multiple constituents.

ii. **Hazard Index:** For each pathway, the hazard index (HI) for non-carcinogenic effects of exposure to multiple constituents is calculated as:

$$HQ = \Sigma HQ_i$$

Where HQ_i = hazard quotient for I^{th} COC

A hazard index greater that 1.0 suggest that the threshold for non-carcinogenic effects could be exceeded due to the additive dose of multiple constituents. Direct summation of HQ values, regardless of the type of effect or mechanism of action associated with each COC, is likely to overestimate actual cumulative effects. Consequently, if the HI for all COCs in a given pathway is found exceed 1.0, the user can segregate COCs by target organs, etc., and recalculate separate organ-specific HI values for a more accurate assessment of cumulative hazards. Information regarding the organ-specific effects of various constituents can be found in IRIS and HEAST (Table 5.4). Available information for selected hydrocarbons is provided on Table 5.4. As shown target organ information is not available for many common constituents.

Table 5.4: Reported Organ-Specific Effects of Selected Hydrocarbons (John, et al, 1995)

CONSTITUENT	TARGET ORAGN FOR NON-CARCINOGENIC EFFECTS	REFERENCE
Volatile Organics		
Ethyl benzene	NA	-
Toluene	Liver (oral), Kidney (oral)	IRIS, HEAST
Xylene-m	Nervous System (oral), Whole Body (oral)	HEAST
Xylene-o	Nervous System (oral), Whole Body (Oral)	HEAST
Xylene-p	NA	-
Xylene- Total	NA	-
Semi-Volatile Organics		
Naphthalene	NA	-
Pyrene	Kidney (oral)	IRIS, HEAST

Notes:
  a) Human target organs for non-carcinogenic effects of selected compounds based on current information reported in IRIS and HEAST.
  b) NA = Not available. Target organs have not been identified in available toxicological references.
  c) (Oral) = Target organ specified for intake via oral ingestion.

5.2.5.3.   Multiple Exposure Pathways

Risk from separate exposure should be combined only if the same individual or group of individuals is likely to be consistently exposed at the critical POE of more than one pathway. As noted above, exposure concentrations from pathways affecting the same medium of exposure should be summed to calculate total chemical intake (e.g., sum intakes through surface soil to air and subsurface soil to air as shown in Figure 5.5). However, a single receptor will not typically contact more than one medium of exposure. For example, on a routine basis, a down gradient well user (groundwater exposure pathway) will not likely be located at the nearest downwind point from the source area (air exposure pathway).

Should pathway combinations be appropriate, the user may wish to modify standard exposure factors to avoid significant overestimation of cumulative effects. For example, exposure frequency and duration factors may be modified to reflect the reduced time period during which the receptor would be exposed to both pathways. In addition, for non-carcinogenic COCs, research indicates that chemical intakes through different portals of entry (e.g., inhalation vs. ingestion) may not be strictly additive, therefore, mechanisms of action and organ-specific effects should be considered in interpreting the significance of baseline risk values estimated for exposure pathway combinations (Connor et al, 1995).
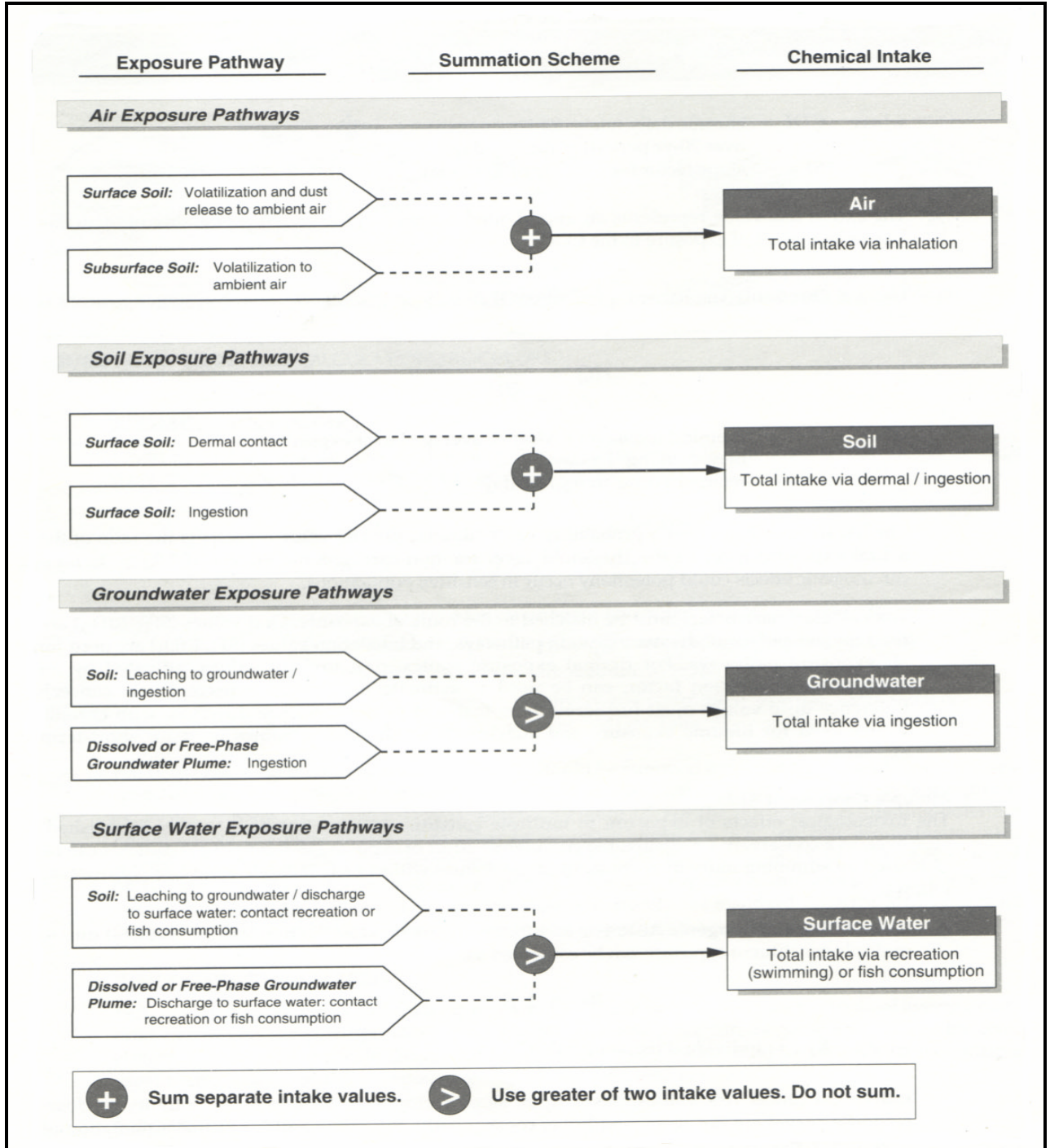
Figure 5.5: Exposure Pathway for Chemical Intake (Connor et al, 1995)

5.2.6. Comparison to Applicable Risk Goals

The baseline risk values calculated for each separate pathway (or combination of pathways, if appropriate) should be compared to applicable human health or environmental protection criteria to determine the need for remedial measures, as follows:

5.2.6.1. Human Health Risk Goals

Human health protection standards specified under state or federal regulations commonly include the following criteria:

i. **Carcinogenic Risk Goals:** Upper bound excess lifetime risk from chronic exposure to individual constituents (e.g., 10^{-6} to 10^{-4}) and multiple constituents (e.g., 10^{-4}).

ii. **Hazard Threshold Limits:** Maximum hazard quotient (e.g., 0.2 to 1.0) for individual constituents and maximum hazard index (e.g., 1.0) for multiple constituent exposures.

iii. **Exposure Limits:** Maximum concentration limits for exposure to individual constituents in air or water (e.g., PEL or TLV limits for ambient vapours; surface water quality criteria for human consumption of fish).

For each pathway, the individual and cumulative baseline risk values (or exposure concentrations) predicted for the POE must be compared to the applicable limits. Pathways exceeding specified risk limits by the greatest margin would be the critical pathways for determination of source medium clean-up requirements.

5.2.6.2. Ecological Exposure Limits

Due to very limited information regarding exposure mechanisms and dose-response characteristics, potential impacts on ecological resources (fish, wild life, sensitive habitats, etc.) are not readily amenable to quantitative risk assessments, as defined herein. However, for certain and locations, recommended exposure limits for site constituents can be defined through applicable regulatory guidelines or research literature. For example, for surface waters classified as high quality aquatic habitats, state and federal water quality criteria have been established for protection of fresh and salt-water fish. Is such data are available for those pathways presenting a risk of

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ecological exposure (e.g., soil, surface water), the measured or predicted COC concentrations at the relevant ecological POE can be compare to the applicable ambient exposure limits.

5.2.7. Tier 2 Response Options.

Upon completion of the Tier 2 SSTL evaluation, four optional actions are available to the user, as indicated under Step 6 of the overall RBCA planning process (Figure 5.2):

5.2.7.1. No Action

If COC concentrations in the source media (soil and groundwater) do not exceed the applicable risk-based cleanup value, no further action may be required. Compliance monitoring may be conducted, as indicated under Step 10 of the RBCA process (Figure 5.2), to confirm that current source concentrations are stable or diminishing with time.

5.2.7.2. Final Corrective Action

If source concentrations exceed the applicable cleanup values, a remedial action program can be implemented to reduce COC concentrations in soil and groundwater to the specified levels. Alternatively, containment measures or institutional controls can be used to prevent exposure in excess of allowable limits at the PE. In all cases, the remedial action should be targeted to those exposure pathways and media found to exceed allowable risk limits in the Tier 2 evaluation (i.e., pathways for which COC concentrations exceed applicable risk-based cleanup goals). Such actions correspond to Step 9 of the RBCA process (see Figure 5.2).

5.2.7.3. Interim Corrective Action

If full remediation of the source area is impracticable due to technology or resource limitations or if prompt action is required to prevent a near-term impact, an Interim Corrective Action can address a principal risk sources. Such actions may include removal or treatment of "hot spots" or prevention of off-site contamination release. Completion of the interim action may affect the site priority classification and the

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baseline risk characterization, requiring reassessment of the applicable cleanup standards (Step 2 on Figure 5.2).

5.2.7.4. Tier 3 Evaluation

If remediation to the Tier 2 SSTL values is judged to be impracticable or overly conservative, Tier 3 evaluation can be conducted to refine the baseline risk and SSTL estimates, based on additional site information and/or more complex modeling efforts (see Step 7, on Figure 5.2). Such Tier 3 analyses would typically be restricted to complex, cost significant sites for which Tier 2 calculation methods may be inappropriate (Connor et al, 1995).

CHAPTER 6.   LNAPL CONTAMINATION CASE STUDY

An overfill of a Premium Petrol in a Service Station

6.1.   Background

Petroleum pollution assessment was conducted at a service station after a complaint was raised by a resident who found free product (petrol) in her borehole. The contaminated borehole was located down gradient at a distance of approximately 100m southwest of the service station. The underground fuel storage tanks and associated infrastructure were pressure tested and no obvious leaking tanks were found. Reconciliation records of the service station did not show any significant losses. It was then found that the source of the free product was due to the overfill that took place during the filling of the existing underground premium petrol storage tank at the service station.

Early in 1998 the underground fuel storage tanks were removed and contamination of the soil by petroleum contamination was observed during the lifting of the tanks. Due to the old age of the tanks it was then decided to remove the other existing tanks of the same age with those that have been removed early 1998. The detailed information about the contamination assessment is depicted below.

6.2.   Topography and geological settings of the investigated site.

The service station is located in a town which is situated at the foot of the mountains. A stream was found at the eastern direction of the site with an approximate distance of 1km. The surface drainage direction from the site is to the southeast. Gentle undulating hills can be found in the immediate vicinity of the site towards the town. According to the 1:250 000 geological map the site is situated on basalt of the Sibasa Formation which is part of the Soutpansberg Group. Rocks of this group occupy a wedge-shaped, mountainous area which stretches from the Kruger National Park in the east, where it is at its widest, up to the Blouberg in the west, where the rocks wedge out against a fault on the northern side. The strike of the rock beds is east-west and the dip moderate to steep and to the north. The group is classified into seven formations and they are affected by a various number of faults of various geological ages.

6.3. Geohydrological settings and hydro census survey

The aquifer in the investigated site can be classified as a fractured/secondary aquifer. This means that the water bearing features of these rocks were developed through faulting, fracturing and weathering of the solid, consolidated mother rocks. Due to the latter the flow patterns in these geological units are irregular, complex and difficult to predict. Although the larger fractures, the so called preferred pathways, act as conduits along which most of the flow takes place, the smaller cracks, fissures and openings in the matrix rocks are where the bulk of the water is stored in the aquifer.

A hydro census survey was conducted in a one-kilometer radius of the site. The purpose of a hydro census is generally to find boreholes and gather information on the depth to groundwater, groundwater quantity and quality and possibly drilling data that can help in describing the aquifer.

A multitude of private boreholes were found during the survey as indicated in Figure 6.1 below. Short interviews were held with those residents who were available during the borehole census. One of the residents who reside down gradient of the service station at a distance of approximately 100m found petrol inside the borehole. The ground water level in the identified boreholes was ranging from 15m.b.g.l (meter below ground level) to 24m.b.g.l. Groundwater samples were collected for Gasoline Range Organic (**B**enzene, **T**oluene, **E**thylene benzene and **X**ylenes (meta+ para - and ortho-Xylenes)). The chemical results of the groundwater samples are discussed in section 6.4.5 below. The typical compounds in gasoline are listed in Table 3.1 above, however, in this case study only BTEX were analyzed.
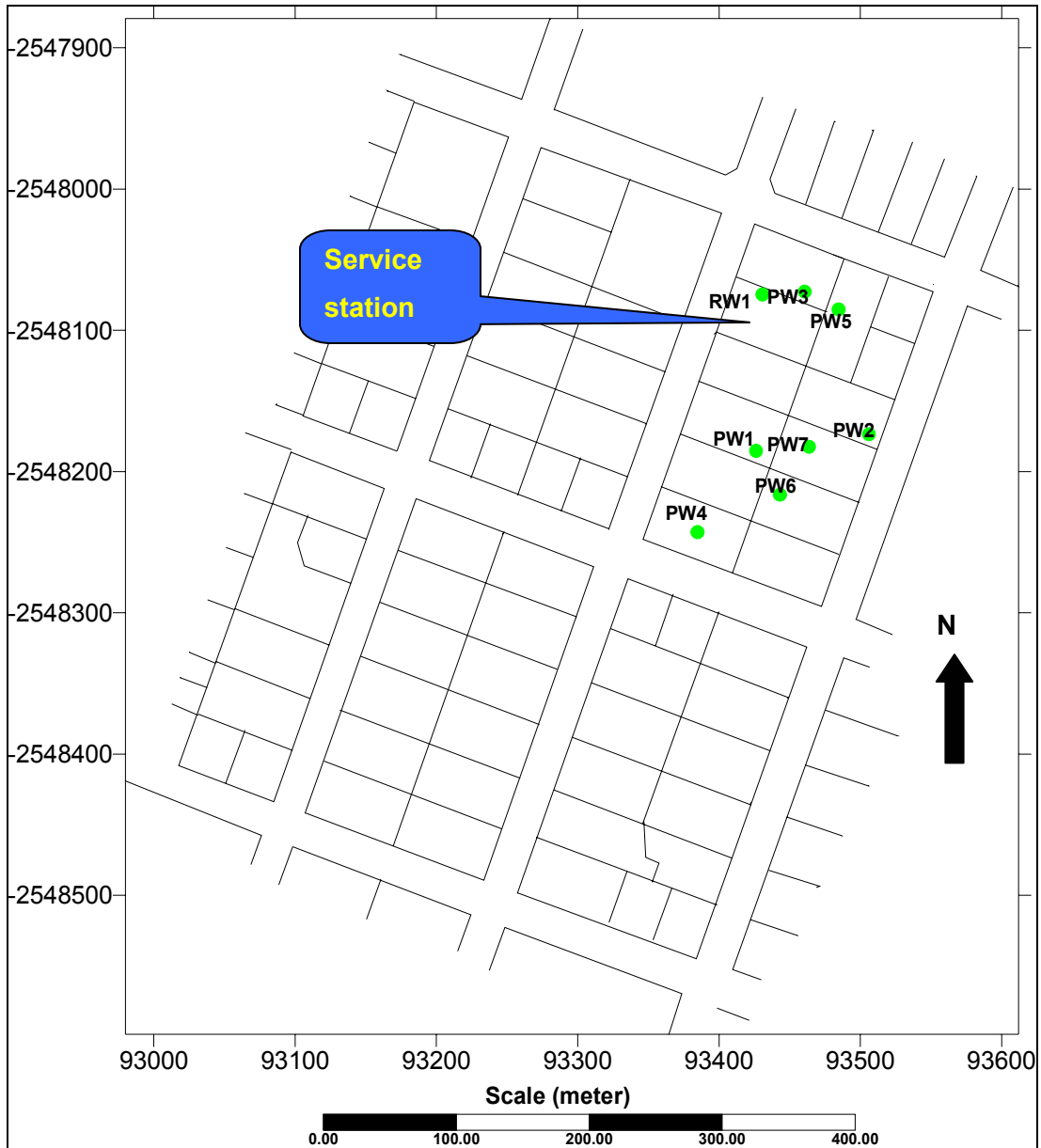
Figure 6.1: Boreholes that were found during hydro census except borehole RW1

6.4. Fieldwork and discussion of the results

This section is describing the steps that were followed in order to determine the lateral and vertical extent of petroleum contamination.

6.4.1. Soil Vapour Survey

Soil vapour survey (SVS) was conducted at the service station by making use of Ecoprobe 4 PID instrument in order to:

- ▪ Determine the lateral extent of the Volatile Organic Compounds (in vapour phase) contamination and
- ▪ Outlining the areas where the vertical distribution of petroleum contamination has to be determined (See chapter 4 section 4.1.3 for a detailed description of SVS technique).

The soil vapour survey contour map is shown in Figure 6.2. The highest vapour VOC reading of 7ppm was detected down gradient of the dispensers. The rest of the detected VOC readings were insignificant. Based on the geology of the site, which comprised of predominantly clay as the residual soil resulting from the chemical weathered basalt, it is evident why not much of the VOC were detected during the soil vapour survey. Note that impermeable soils such as clay are not adequately sampled with this method, primarily due to lack of good vapour transport as compared to highly permeable soils such as sand (Calabrese et al, 1991). Therefore it is clear that geological formation in the unsaturated zone of the investigated site act as limiting factor during the soil vapour survey. Detailed description of the factors affecting the efficiency of soil vapour survey method is listed in chapter 4, section 4.1.3.1 and 4.2.2.

Figure 6.2: Soil vapour contour map

VOC Concentrations (ppm)
(In Vapour Phase)

	0 to .5
	.5 to 1
	1 to 1.5
	1.5 to 2
	2 to 2.5
	2.5 to 3
	3 to 3.5
	3.5 to 4
	4 to 4.5
	4.5 to 5
	5 to 5.5
	5.5 to 7

0   4   8
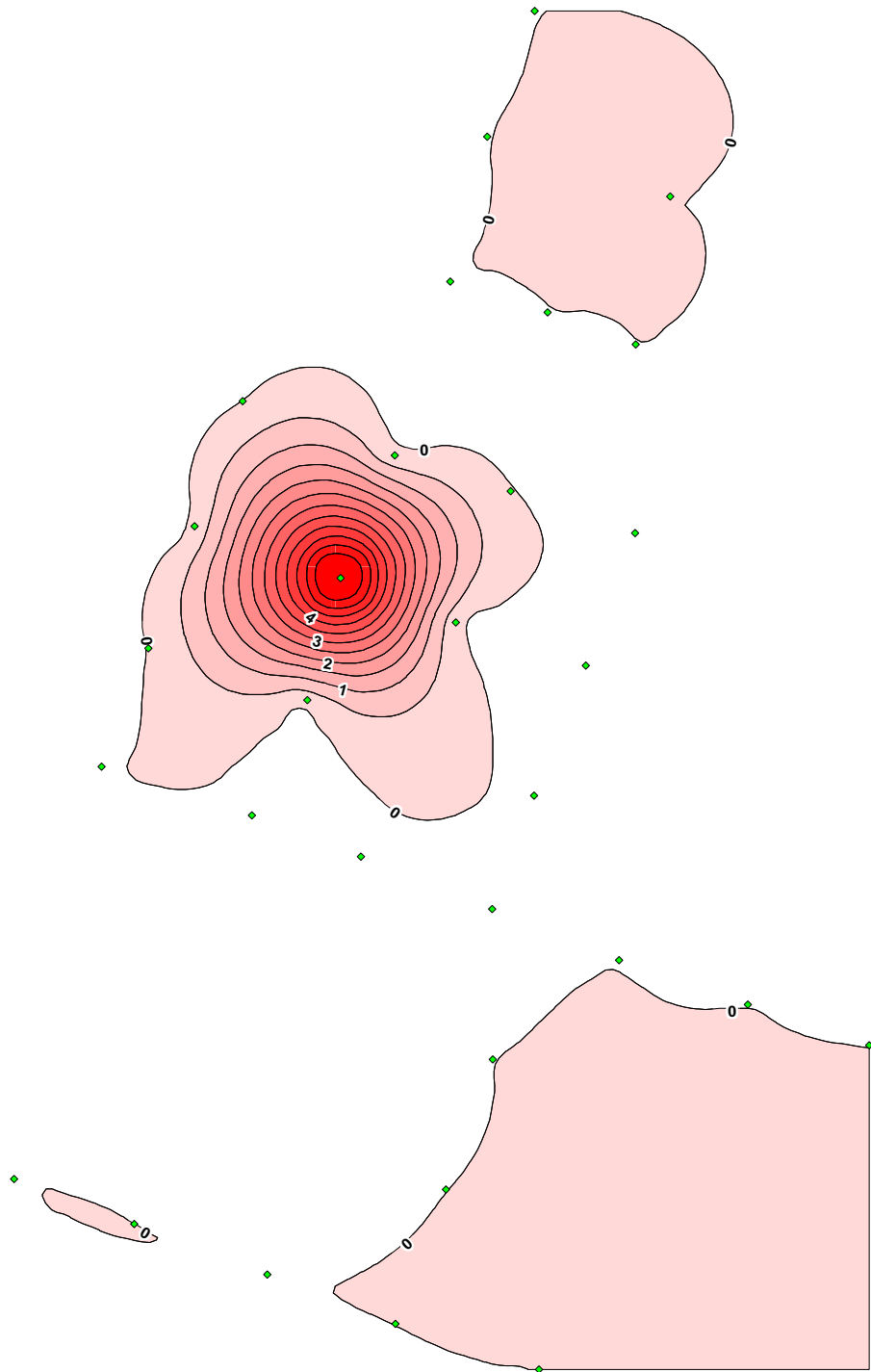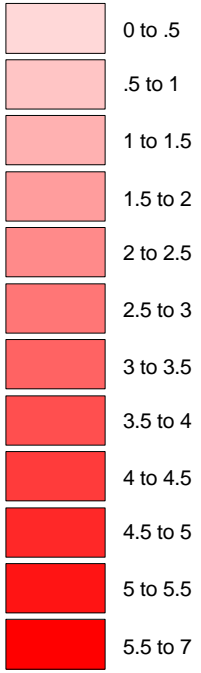
INFERRED
GROUNDWATER FLOW
DIRECTION

0   5   10
metres
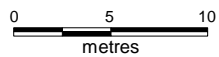
6.4.2. Hand auger drilling

Four hand auger holes were drilled at the positions determined by the soil vapour survey results (Figure 6.3). The main aim was to determine the soil profile and shallow petroleum contamination. The deepest hand auger was drilled to the refusal depth of 2.56m.b.g.l (meters below ground level) due to the clay which inhibits the penetration of the auger. No petroleum smell was detected in any of the holes. All the holes were comprised of clay soil up to the depth of refusal.
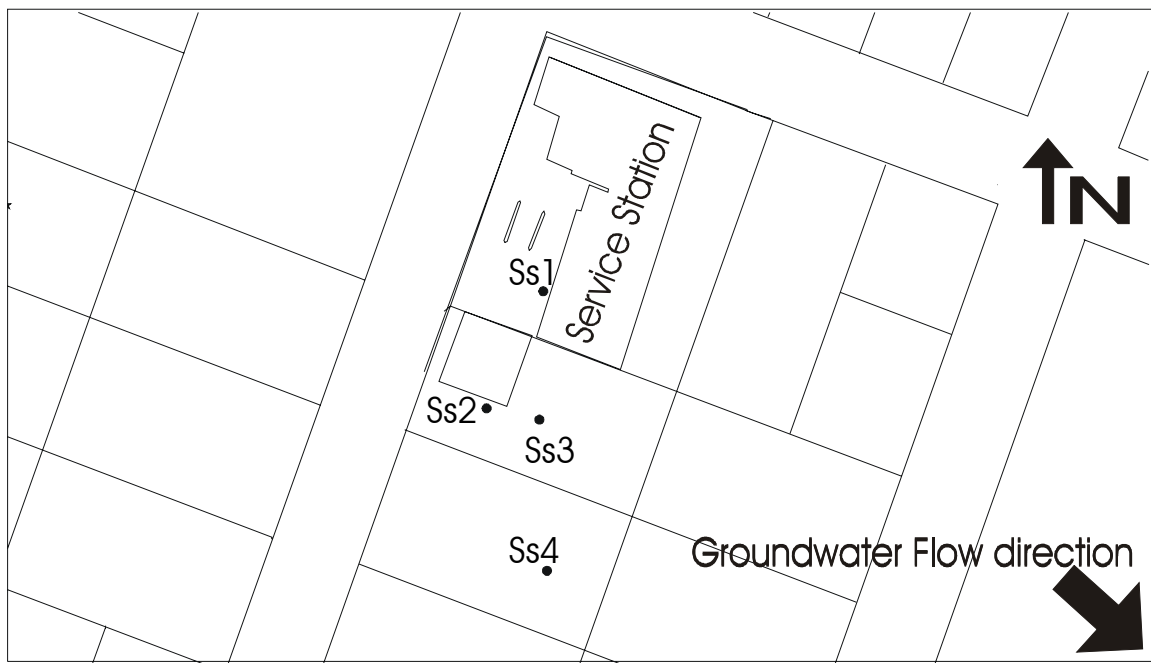
Figure 6.3: Positions of hand auger holes

6.4.3. Rotary percussion drilling

Due to the deep water level that was established during the hydro census survey it was then decided to drill a rotary percussion borehole in order to investigate the vertical extent of petroleum contamination. This borehole was also drilled to be used for recovery purposes should there be any free product. Usually the soil vapour survey results are used as a guideline for drilling positions, but in this case no high VOC readings were detected during the survey. The position of the percussion borehole is shown in Figure 6.4. The considerations were to drill in close proximity to the tank pit

that was allegedly contaminated during the tank removal as well as having a borehole between the potential source area (tank pit) and the contaminated private borehole down gradient of the service station. Finally it was decided to drill the borehole as close as possible to the tank pit (potential source).

No petroleum contamination was detected in the borehole from surface (0.0m) up to the depth of 18m.b.g.l based on visual and olfactory observation. A slight petroleum smell was detected from the depth of 19m.b.g.l up till the final borehole depth of 55m.b.g.l. The borehole log is attached under Appendix B. It must be noted that a percussion drilling is not the optimum means of collecting soil samples, because during drilling soil is carried from the borehole with pressurised air. In this process petroleum hydrocarbons that are mostly volatile are evaporated from the contaminated soil. The first and second water strike was intercepted at the depth of 27m.b.g.l and 48m.b.g.l, respectively. The borehole was equipped with a 1 meter plain PVC casing (**P**oly-**V**inyl-**C**hloride), 54m perforated PVC casing, bentonite seal around the plain casing as well as gravel around the perforated casing. The PVC casing was used because of the following merits:

- It is resistant to alcohols, aliphatic hydrocarbons, weak and strong alkalies, oils, strong mineral acids, mineral acids, and oxidizing acids.
- It is completely resistant to galvanic and electrochemical corrosion and
- High strength to weight ratios and resistant to abrasion.

In contrast the steel casing is capable of catalyzing some organic chemical reactions. Steel casing may corrode if exposed to long-term corrosive conditions and leach chromium (Cohen et al, 1993). Even though PVC is poorly resistance to some of the aromatic hydrocarbons it was still decided to be used as compared to the disadvantages of the steel casing.

Immediately after drilling a floating groundwater sample was taken from the borehole and a layer of free product was observed. Floating groundwater sample is a sample which is collected by making use of transparent bottom-loading PVC bailers. A 90 cm meter bailer was used in order to make sure that its top is in the air when its check valve is in the water. Transparent bottom-loading bailer help to estimate the thickness of the floating product (petrol) thereby measuring the LNAPL (petrol) column height in the

bailer. Care was always taken in order to ensure that an equilibrium height of LNAPL has entered the bailer before lowering into the water and LNAPL interface.
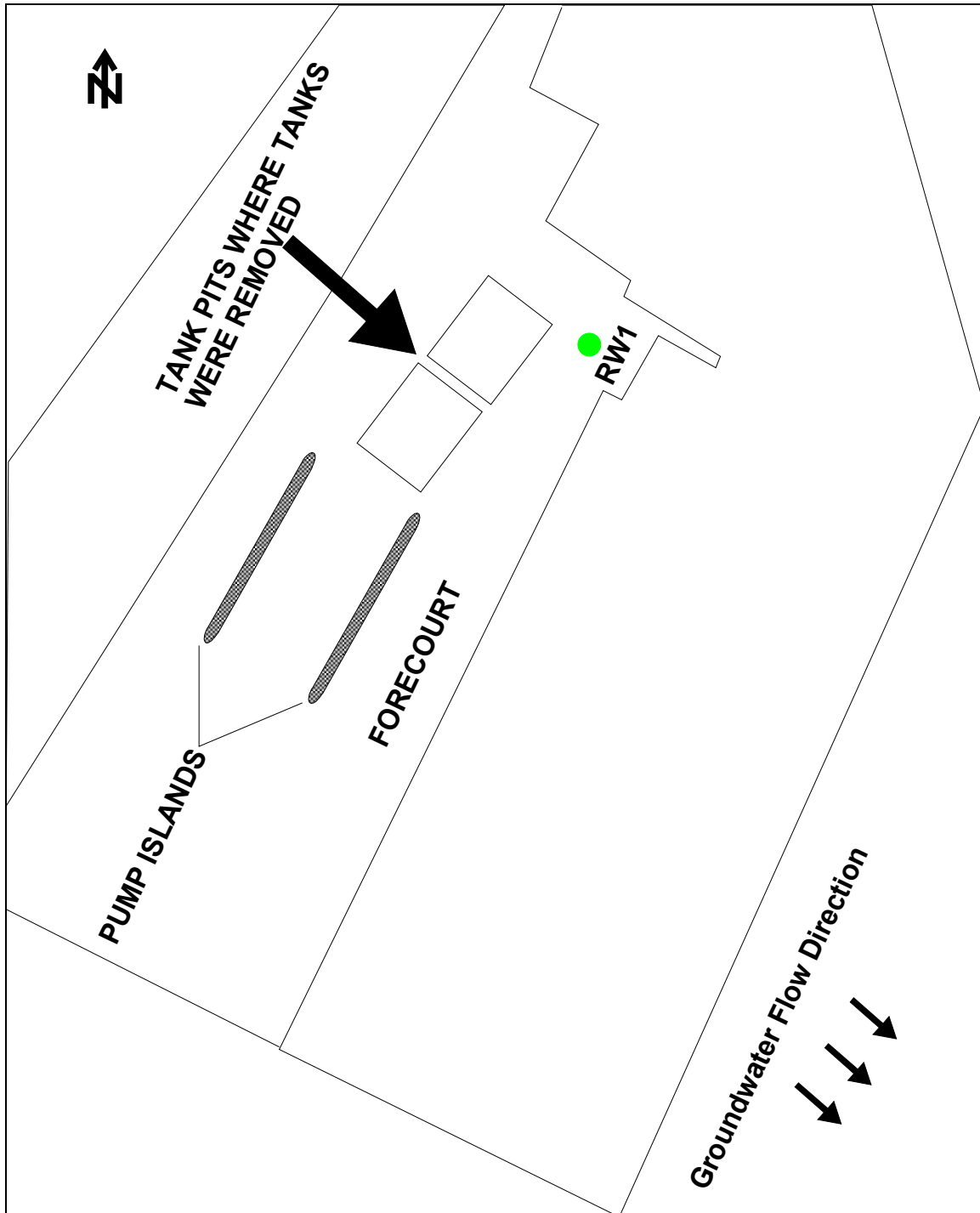
Figure 6.4: Position of a percussion borehole

6.4.4. Groundwater and soil sampling

Groundwater samples were collected from borehole *PW1, PW2, PW3, and PW4* that were identified during the hydro census survey. The samples were analysed for Gasoline Range Organic (GRO), such as Benzene, Toluene, Ethyl benzene and Xylenes. Sampling routine from these private production boreholes have started immediately after a complaint was raised by a resident who smelled petroleum hydrocarbons in the water. The floating groundwater samples were collected with a transparent bottom-loading PVC bailer in order to have an estimate of the free product thickness in the borehole. A true thickness of free product in the aquifer can be obtained by conducting a bailing down test. This involves bailing the free product completely and measures its recovery rate in the borehole. The boreholes were also purged in order to have a representative groundwater sample. Purging protocol is necessary because a groundwater sample must be representative of the Formation (aquifer) water. This is because water that has been standing is the borehole above the borehole screen is:

- Not free to interact with formation water
- In contact with borehole construction material (i.e., casing) for long period of time.
- In direct contact with atmosphere which is then subject to different chemical equilibria.

Volatile Organic Compounds (VOC) and dissolved gases in stagnant water column in the borehole may volatilize in as few as two hours (Nielsen, et al 1991). Furthermore, the boreholes were purged at very low rate in order to avoid:

- Cone of depression (*caused by lowering the water table*)
- Turbulence that would cause dilution in the water and then mask the presence of contamination.
- Exposure of portion of formation (aquifer) materials to air and other gases, product floating on top of water table if present.
- Drawing of contamination to boreholes which do not intersect contamination plume, since this cause wide spreading of contamination.

In contrast, float sampling (bailing) may cause aeration, degassing and turbulence while lowering the bailer through the water column or while transferring the sample from the bailers to the sample bottle. It may also be difficult to determine the point within the water column that the sample represents. Bailer check valves may not operate properly under certain conditions (e.g., high suspended solids content and freezing temperature).

Groundwater samples were stored in the glass vial bottles with Teflon seals and cooled to a temperature of below 4°C. This sampling procedure was done in order to comply with the U.S.EPA recommended sampling protocols (detailed in chapter 4). No free product (Petrol) was found in borehole *PW1, PW2, PW3 and PW4* during August 95, Feb 96 and June 96 sampling periods.

Seven soil samples were taken and submitted for sieve, pH, carbon fraction and moisture content analyses. Three samples were collected from the hand auger holes and another four samples from the percussion borehole. The soil samples from the percussion borehole were collected at horizons where drilling, although disturbing the samples, did not crush it. Another three soil samples were also collected at the depth of 18, 21 and 26m.b.g.l for Gasoline Range Organic (GRO) in order to determine the vertical extent of petroleum contamination. The GRO results of the soil samples are presented in Table 6.1 under section 6.4.5 below. The results of sieve, pH, carbon fraction and moisture content will be discussed under section 6.5 for developing the risk conceptual model of the site.

A floating groundwater sample was collected from the percussion borehole (RW1) during April 1999 and visually inspected. Free product (Petrol) with the thickness of 3 meters was measured in borehole RW1 during April 1999 by making use of Solinst interface instrument. Free product (Petrol) was also found in borehole PW2 and PW5 which is located at a distance of approximately 200m and 60m down gradient of the service station, respectively. The presence of free product in these boreholes confirmed the down gradient migration of contamination plume from the service station. No groundwater samples were collected from the borehole because of the known risk associated with free phase.

6.4.5. Results of Gasoline Range Organic in both soil and groundwater samples

Table 6.1 below presents petroleum hydrocarbon chemical results for groundwater samples (mg/L) while Table 6.2 presents the chemical results for soil samples (mg/kg). Note that some of the private boreholes could not be sampled during the sampling series due to the absence of the owners. The sampling series were done in a frequency of a three monthly basis.

Table 6.1: Analytical results for petroleum hydrocarbons in the groundwater samples (mg/L).

Borehole number	PW1	PW1	PW2	PW3	PW4
Type of sample	Water	Water	-	Water	-
Sampling method	Pump	Float	-	Pump	-
Free product thickness (m)	0.00	0.00	-	0.00	-
Sampling date	Series 1	Series 1	Series 1	Series 1	Series 1
Benzene	5.9	4.8	n.s[1]	1.8	n.s
Toluene	2.5	0.3	n.s	0.8	n.s
Ethyl benzene	0.2	0.0	n.s	0.0	n.s
m+p-Xylene	1.2	0.2	n.s	0.3	n.s
o-Xylene	0.7	0.1	n.s	0.3	n.s
TPH	10.5	5.4	n.s	3.2	n.s

[1] n.s: not sampled

Borehole number	PW1	PW1	PW2	PW3	PW4
Type of sample	Water	Water	-	Water	-
Sampling method	Pump	Bailer	-	Pump	-
Free product thickness (m)	0.00	0.00	-	0.00	-
Sampling date	Series 2	Series 2	Series 2	Series 2	Series 2
Benzene	14.8	12.8	n.s	7.8	n.s
Toluene	4.5	2.8	n.s	2.6	n.s
Ethyl benzene	0.4	0.2	n.s	0.3	n.s
m+p-Xylene	0.9	0.6	n.s	0.4	n.s
o-Xylene	1.0	0.7	n.s	0.5	n.s
TPH	21.6	17.1	n.s	11.6	n.s

Borehole number	PW1	PW1	PW2	PW3	PW4
Type of sample	Water	Water	-	Water	-
Sampling method	Pump	Bailer	-	Pump	-
Free product thickness (m)	0.00	0.00	-	0.00	-
Sampling date	Series 3	Series 3	Series 3	Series 3	Series 3
Benzene	15.2	0.8	n.s	11.2	BDL[2]
Toluene	4.2	0.3	n.s	1.8	BDL
Ethyl benzene	0.2	0.0	n.s	0.2	BDL
m+p-Xylene	0.0	0.0	n.s	0.5	BDL
o-Xylene	0.6	0.0	n.s	0.4	BDL
TPH	20.2	1.1	n.s	14.1	BDL

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[2] BDL: Below Detection Limit

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Borehole number	PW1	PW1	PW2	PW3	PW4
Type of sample	Water	Water	-	Water	-
Sampling method	Pump	Bailer	-	Pump	-
Free product thickness (m)	0.00	0.00	-	0.00	0.00
Sampling date	Series 4	Series 4	Series 4	Series 4	Series 4
Benzene	1.0	0.8	n.s	1.8	BDL
Toluene	BDL	0.3	n.s	0.9	BDL
Ethyl benzene	BDL	BDL	n.s	BDL	BDL
m+p-Xylene	BDL	BDL	n.s	0.4	BDL
o-Xylene	BDL	BDL	n.s	0.2	BDL
TPH	1.0	1.1	n.s	3.3	BDL

Borehole number	PW1	PW1	PW2	PW3	PW4
Type of sample	Water	Water	-	Water	-
Sampling method	Pump	Bailer	-	Pump	-
Free product thickness (m)	0.00	0.00	-	0.00	0.00
Sampling date	Series 5	Series 5	Series 5	Series 5	Series 5
Benzene	13.0	BDL	n.s	9.0	BDL
Toluene	1.0	BDL	n.s	1.0	BDL
Ethyl benzene	BDL	BDL	n.s	BDL	BDL
m+p-Xylene	BDL	BDL	n.s	BDL	BDL
o-Xylene	BDL	BDL	n.s	BDL	BDL
TPH	14.0	BDL	n.s	10.0	BDL

Table 6.2: Analytical results for petroleum hydrocarbons in the soil samples (mg/kg).

Borehole number	RW1	RW1	RW1
Depth of sample	18m	21m	26m
Type of sample	Soil	Soil	Soil
Petroleum smell	Slight	Slight	Slight
Benzene	BDL	BDL	BDL
Toluene	BDL	BDL	BDL
Ethyl benzene	BDL	BDL	BDL
m+p-Xylene	BDL	BDL	BDL
o-Xylenes	BDL	BDL	BDL
Naphthalene	BDL	BDL	BDL
Total hydrocarbons	BDL	BDL	BDL

Based on the chemical results in Table 6.1 above it is evident that borehole PW1 and PW3 were found contaminated with significant concentrations of the dissolved phase petroleum hydrocarbons such as benzene, toluene during *Series 1, Series 2, Series 3, Series 4 and Series 5* sampling events. Low levels of BTEX were detected during *Series 4* because it was sampled during wet season (rainfall). This means the sampled groundwater was the mixture of the freshly recharged rainwater and the old contaminated groundwater which then resulted in the dilution of the hydrocarbon contamination.

High concentration levels of BTEX were found in the pumped sample than in the float sample. The cause of the differences in the BTEX levels of the float (Bailing method) and pumped (purge method) sample within the same borehole is due to the following reason:

- ▪ The bailing method (float sampling) mostly sampled the stagnant water, which is not interacting with the formation, which is in contact with the borehole construction material (e.g. casing) for long period of time, which is in direct contact with the atmosphere.

In contrast, the pumped sampling (purging) is a sampling method which tapped the groundwater which is representative of the formation water quality.

Based on the chemical results in Table 6.2 above it is evident that no detectable levels of petroleum hydrocarbons were found in soil samples that were collected from the percussion borehole that was drilled at the service station.

This section identified secondary sources of pollution in the form of **affected surface soils** (soil vapour survey), **affected subsurface soils** (soil sampling), a **dissolved groundwater plume** (groundwater sampling) and a **free phase plume** at the service station and the neighboring borehole.

6.5. Risk assessment

6.5.1. Development of risk conceptual model

Conceptual models are generally developed and used iteratively in the remedial investigation and feasibility studies. Conceptual models should be presented for the current case and for any credible future cases that could results in increased risk. All the conceptual models for the contaminated sites begin with **sources,** followed by the **routes** by which the contaminants in the sources are transferred to the ambient media, and finally the endpoint **receptors** which should be presented as those that, have been proposed to be or designated as an assessment endpoint receptors (detailed description in chapter 5, Figure 5.1).

6.5.1.1. Source characterization

The primary source at the service station was addressed by testing the fuel storage tanks and its infrastructure, through removing the old aged fuel storage tanks and replaced with the ones. Soil vapour survey, soil and groundwater sampling was conducted in order to identify the secondary sources at the site. The secondary sources in the service station were found to be the following:

- Affected surface soil (<1m.b.g.l)
- Affected subsurface soil (>1m.b.g.l)
- Dissolved groundwater plume and
- Free phase plume

6.5.1.2.   Potential transport mechanism

Having identified secondary sources the next step was to determine the different transport mechanisms at the service station and its surrounding.

Based on the soil samples that were collected from the percussion borehole no detectable levels of GRO compounds were found. However, the absence of petroleum contamination in the soil samples was caused by pressurized air induced during drilling which then volatilized the absorbed contamination from the soil. No groundwater sample was collected from the newly drilled borehole, because of the known risk associated with free product that was measured in this borehole. Significant petroleum contamination was found from the borehole collected from the private boreholes (Table 6.1). Thus potential transport media (detailed description in section 3.2 above) for the contaminants at the site are soil (through *leaching to groundwater*) and groundwater (through *dissolved or free phase plume migration*).

6.5.1.3.   Exposure pathways

Four possible pathways are defined by the RBCA methodology, i.e. soil, air, groundwater and surface water. The relevant pathway in the investigated site is soil, air and groundwater.

6.5.1.3.1.   Air

Air is a potential pathway through inhalation of vapours from the dissolved phase plume and free phase plume. However, its significance in this case study is limited due the thickness of the clay soil in the unsaturated zone and a deep groundwater level (refer to Chapter 5, Table 5.2). The property of this pathway was then not investigated further.

6.5.1.3.2.   Soil

The soil characteristics determine the transport and degradation rate of the petroleum contamination. Soil samples were analyzed for particle size and carbon content. Below is the discussion of some of the soil characteristics.

6.5.1.3.2.1. Unsaturated and saturated hydraulic conductivity

Seven soil samples were collected and submitted for sieve, pH, organic carbon fraction and moisture content analyses. Three soil samples were collected from the hand auger holes and the rest from the rotary percussion borehole. The samples from the percussion well were collected at horizons where drilling, although disturbing the samples, did not crush it. The **Walkley Black, 122.5 soil water ratio, 105°C drying and fraction pipette method** were used to analyze the foc, soil pH, moisture content and particle size, respectively.

An approximate hydraulic conductivity for the unsaturated zone could be calculated from the sieve analyses (see Appendix C). Table 6.3 below lists the granulometric data and the carbon content.

Table 6.3: Granulometric results and carbon content.

Sample no and sampling depth	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Unsaturated Hydraulic Conductivity (m/d)	Organic Carbon fraction (%)	pH of the soil sample	Moisture Content in the soil sample (%)
SS1 (2.5m)	2.2	12.4	28.1	57.3	8.32E-8	0.47	5.84	21.6
SS2 (1m)	2.3	20.3	16.5	60.9	4.66E-8	0.52	5.36	18.9
SS4 (2.25m)	2.1	14.5	25.2	58.2	6.58E-8	0.40	6.08	20.8
RW1 (10m)	1.4	29.5	42.9	26.2	1.17E-3	0.00	4.01	19.1
RW1 (12m)	0.7	18.4	27.6	53.3	4.79E-7	0.05	5.34	20.3
RW1 (17m)	1.3	44.8	38.8	15.1	1.56E-2	0.00	4.64	13.4
RW1 (21m)	1.2	67.5	21.4	9.9	1.45E-1	0.02	5.21	8.0

The subsurface migration is of contaminant is dependent on the hydraulic conductivity of the underlying formation. The unsaturated zone at the service station consists of layers with different hydraulic conductivity (K). The samples from the hand auger holes have very low K-values, while deeper samples show considerably higher conductivities. These values are calculated for groundwater, which is generally accepted to approximate the worst-case scenario. The travel time of a leachate through the unsaturated zone can be approximated by the following formula:

$$T_t = \frac{di}{\left[K / (n/100) \right]}$$

where T_t = travel time (days),

K = hydraulic conductivity (m/day),

i = the hydraulic gradient,

n = porosity (%),

d = thickness of the barrier between the contaminant and groundwater resources.

The hydraulic gradient of the site was calculated by using the difference of groundwater levels (above mean sea level [a.m.s.l]) in borehole PW5 and RW1 divided by the distance between them.

$I = h_1 - h_2$ (a.m.s.l) /distance m)

= 961.3105a.m.s.l -959.8508a.m.s.l /80.6

=2.0E-02

Where **I** is the hydraulic gradient, h_1 and h_2 is the groundwater level in borehole PW5 (961.3105a.m.s.l) and RW1 (959.8508a.m.s.l) and distance (80.6m)

Under conditions of vertical flow the hydraulic gradient approaches unity, and can therefore be disregarded in the calculations. Using the highest value found for hydraulic conductivity (K=1.45E-1m/day) and assuming a porosity of 40% (typical porosity range for residual soil of basalt formation, Freeze, et al, 1979), and with d taken as the thickness of the unsaturated zone (~20m), the travel time is found to be about 55 days **assuming that no preferential flow paths exist**.

It is very important to note that these calculations are based on sieve analyses only. The swelling and contraction of soils, especially where high clay content is found, facilitate the forming of open spaces that act as preferential flow paths.

A constant rate test was performed in borehole RW1 with an abstraction rate of 0.33L/s for the duration of more than ten hours. The main aim of the test was to obtain the hydraulic parameters such as transmissivity of which the saturated hydraulic conductivity was then calculated from the estimated transmissivity value and the assumed aquifer thickness of 30m. The late transmissivity value of 14.49m^2/d was estimated from the pump test data that were captured into the **Flow Characteristic Method** (Van Tonder et al 2001) (see Appendix D). The saturated hydraulic conductivity was then calculated as follows:

Transmissivity (**T** in m^2/d) = **H**ydraulic conductivity (**K** in m/d) multiply by the **A**quifer thickness (**D** in m) (Kruseman et al 1991).

$$T = KD$$
$$K = T/D$$
$$K = 14.49 \ m^2/d \ /30m$$
$$K = 4.83E\text{-}01m/d$$

6.5.1.3.2.2. *Organic carbon non aqueous phase liquids (NAPLs) partitioning*

NAPL partitioning is a complex process involving several different phenomena including hydrogen bonding and hydrophobic forces. In the case of hydrocarbons, due to their non-polar nature, sorption most often occurs through hydrophobic bonding to organic matter. Hydrophobic bonding often is an important factor influencing the fate of dissolved phase hydrocarbons in the subsurface. The sorption coefficient of an organic compound in soil generally is empirically related to the organic content of the soil and the octanol/water-partitioning coefficient of the compound.
Sorption isotherm generally follow one of three shapes; Langmuir, Freundlich, or linear.

The Langmuir isotherm describes the sorbed contaminant concentrations as increasing linearly with total contaminant concentration, then leveling off as the numbers of sites

available for sorption are filled. This isotherm accurately describes the situation near the contaminant source where concentrations are high. The Freundlich isotherm assumes an infinite number of sorption sites, which would accurately describe an area at some distance from the contaminant source where concentrations are dilute. The linear isotherm is relatively simple and is valid for dissolved compounds at less than one-half of the solubility. The linear isotherm is typically valid to describe hydrocarbon sorption, (Lyman et al, 1992)

The linear isotherm is expressed mathematically as

$$C_s = K_d.C_w$$

Where C_w is the *volumetric concentrations of contaminant in the aqueous phase* (g/L$_{aqueos}$), C_s is the *quantity of contaminant sorbed to the soil* (g/g$_{soil}$) and K_d is the *sorption coefficient*.

Non-polar organic compounds sorbed on soil usually are held by hydrophobic interactions resulting in weak non-specific sorption forces. The sorption coefficient is a function of the hydrophobic character of the compound and the amount of organic matter present and may be expressed as.

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

Where K_{oc} is the *chemical-specific organic carbon-partitioning coefficient*, f_{oc} is the *fraction of organic carbon in the soil.*

The K_{oc} is often estimated as being equal to the K_{ow}. Hydrocarbons tend to become more hydrophobic with increasing carbon number, so larger hydrocarbons tend to sorb more strongly in comparison to smaller hydrocarbon (BTEX).

 (*See chapter 3, section 3.2.1.4 and 3.2.2.1 for detailed description about octanol-water partition coefficient*):

Based on the obtained sorption coefficients (Table 6.4 below) it is clear that sorption of the hydrocarbon compounds increase with an increase in the hydrophobic of the compound. This implies that the sorption rate of **B**enzene should be less than the sorption rate of **T**oluene. On the other hand the sorption rate of **T**oluene should be less than that of Xylene. Generally, the sorption rate of the hydrocarbons increases with an increase in the carbon content of the soil media.

Table 6.4.: The K_d, K_{oc} and f_{oc} dependence.

Selected samples	Typical K_{oc}[3] values of the selected hydrocarbons	Average site-specific f_{oc} values	Average Sorption coefficient ($K_d = K_{oc}.f_{oc}$)
SS1 (2.5m.b.g.l)			
SS2 (1m.b.g.l)	Benzene (K_{oc} = 190)	0.0035	0.665
RW1 (12m.b.g.l)			
SS1 (2.5m.b.g.l)			
SS2 (1m.b.g.l)	Toluene (K_{oc} = 380)	0.0035	1.33
RW1 (12m.b.g.l)			
SS1 (2.5m.b.g.l)			
SS2 (1m.b.g.l)	m-Xylene (K_{oc} = 720)	0.0035	2.52
RW1 (12m.b.g.l)			

The net effect of adsorption is to retard the migration of hydrocarbons. If the local equilibrium between hydrocarbon and passing water is maintained, the hydrocarbon stays on the surface of the particle. High velocity flow can cause desorption, because the local equilibrium is disrupted to such an extent that adsorption forces are not strong enough to keep a contaminant at site (**detailed description in chapter 3, section 3.2.2.1**).

The measure of retardation is quantified as the retardation factor, R_f, which determines the relative velocity of the contaminant migration as a multiple of the intrinsic flow velocity. It is defined as follows:

$$R_f = 1 + K_d\rho_b/\Theta$$

where ρ_b is the bulk soil density of the dark reddish brown clay (**1800kg/m^3** ,*Brink, 1981*) and Θ = soil porosity (**dimensionless**).

The following table provides retardation for typical organic carbon fractions.

Table 6.5. : Retardation factors.

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[3] (The source of the K_{oc} values is Lyman et al, 1992),

Selected samples	Typical K_{oc} values of the selected hydrocarbons	Average site-specific f_{oc} values	Average Sorption coefficient (K_d = $K_{oc}.f_{oc}$) in (L/kg)	Porosity value for the unconsolidated material at the site (Clay)	Retardation factors (R_f = 1+ $K_d\rho_b$/Θ)
SS1 (2.5m.b.g.l) SS2 (1m.b.g.l) RW1 (12m.b.g.l)	Benzene (K_{oc} = 190)	0.0035	0.665	0.4[4]	3.99
SS1 (2.5m.b.g.l) SS2 (1m.b.g.l) RW1 (12m.b.g.l)	Toluene (K_{oc} = 380)	0.0035	1.33	0.4	6.985
SS1 (2.5m.b.g.l) SS2 (1m.b.g.l) RW1 (12m.b.g.l)	m-Xylene (K_{oc} = 720)	0.0035	2.52	0.4	12.34

Based on the calculated sorption coefficient (Table 6.4 above) and the retardation factors (Table 6.5 above) it is clear that sorption and retardation of the petroleum hydrocarbons is expected to occur at the investigated site. This implies that the benzene will migrate faster than toluene and toluene is expected to migrate faster than xylenes. This means that the down gradient boreholes are expected to have high concentrations of benzene as compared to those of toluene and xylenes. Based on the chemical results of BTEX in Table 6.1 above, it is evident that benzene concentrations were always higher in the down gradient boreholes during sampling series 1 up till series 5 as compared to the concentrations of toluene and xylenes.

6.5.1.3.3. Groundwater

The groundwater environment of the investigated site is contaminated with both free phase and the dissolved phase petroleum hydrocarbons.

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[4] The source of range of values of porosity is Freeze, et al, 1979

6.5.1.4. Potential receptors and complete pathways

Table 6.6 below presents the sources, pathways/routes and receptors, which exist at the service station.

Table 6.6: Presents the sources, pathways/routes and receptors of concern at the service station.

Sources	Primary sources *(underground fuel storage tanks, pipelines and dispensers)* Secondary sources *(affected subsurface soils*, a *dissolved groundwater plume* and a *free phase plume).*
Exposure Pathways	The relevant exposure pathways at the site are soil (*leaching to groundwater*) and groundwater (*dissolved or free phase*). Note that air (*though volatilization*) is also an exposure pathway in the petroleum-contaminated sites, however, its significant in this case study is limited due the thickness of the clay soil in the unsaturated zone and a deep groundwater level (refer to section 5, Table 5.2). Air will only be regarded as a complete pathway in the cases where water from the contaminated boreholes is used for irrigation because vapours may be present.
Receptors	Some of the residents surrounding the service station are regarded as the complete receptors of petroleum contamination because they are using groundwater for drinking and gardening (domestic purpose).

6.5.2. Risk Based Corrective Action (RBCA) and BP RISC

RBCA was used to quantify the risk associated with petroleum hydrocarbons. Risk Based Corrective Action (RBCA) is a decision-making process for assessment and response to subsurface contamination associated with petroleum hydrocarbon releases. The guidelines for RBCA are published in American Society for Testing Materials (ASTM E-1739-95), thus "*Standards Guide for Risk Based Corrective Action applied at Petroleum Releases Sites".* RBCA integrates Environmental protection Act (EPA) risk assessment practices with traditional site investigation and remedy selection activities in

order to determine the cost-effectives measures for protection of human health and environmental resources. The detailed description of RBCA is under Chapter 5 above.

6.5.2.1. Tier 1 analysis: (Generic Screening- Level Corrective Action Goals)

Generally, Tier 1 evaluation serves to identify sites requiring no further action. For most sites exceeding Tier 1 limits, a Tier 2 analysis will provide a more cost-efficient basis for evaluation of appropriate remedial action (refer to chapter 5, section 5.1.4.1 for detailed description).

The chemical results of pumped groundwater sample PW1 and PW3 (Table 6.1 above) that were collected during sampling series2 and series3 were entered into the RBCA look up tables in order to assess the worst case risk scenario at the investigated site. The chemical results of water sample PW1 and PW3 have triggered the Tier 1 Risk Based Screening Levels (RBSLs) for risk exposure pathways of:

- *Groundwater Ingestion*
- *Volatilization to Indoor Air Inhalation and*
- *Volatilization to Outdoors Air Inhalation.*

The risk values that were triggered through the above mentioned exposure pathways are the following (see Appendix E):

- Carcinogenic risk (10^{-06} to 10^{-04}) which is the excess risk value of an upper bound estimate of the added probability of incurring cancer as a result of exposure to the carcinogenic hydrocarbon compound (***e.g. benzene***)
- Hazard Quotient (HQ) which is associated with non-carcinogenic compounds (***e.g., Toluene, Ethyl benzene and Xylenes***) and
- MCL which is acronym for Maximum Contaminant Level.

Based on the fact that the petroleum hydrocarbons pose risk to the pathways of concern at the investigated site, it was therefore imperative to conduct a Tier 2 evaluation to develop site specific remediation goals.

6.5.3. BP RISC (British Petroleum Risk Integrated Software for Cleanups)

BP RISC was also used in order to conduct the Tier 2 evaluation to develop the site-specific remediation goals. BP RISC package was specifically developed to assist in the evaluation of potential human health risks, associated with contaminated sites. It is used to estimate the potential for adverse human health impacts (both carcinogenic and non-

carcinogenic) from up to nine exposure pathways. It also contains unsaturated zone, saturated zone, and air fate and transport models for estimating receptor point concentrations.

Human health risk can be defined as the characterization of the potential adverse effects on human life or health. The US EPA's Risk Assessment Guidance for Superfund, or the RAGS manual, characterizes the risk assessment process by dividing it into four basic steps:

1. Data collection
   a. Gather and analyze relevant site data
   b. Identify potential chemicals of concern

2. Exposure assessment
   a. Analyze contaminant releases
   b. Identify exposed populations
   c. Identify potential exposure pathways
   d. Estimate exposure concentrations for pathways
   e. Estimate contaminant intakes for pathways

3. Risk characterization
   a. Characterize potential for adverse health effects to occur
   b. Estimate cancer risk
   c. Estimate non-cancer hazard quotient
   d. Evaluate uncertainty
   e. Summarize risk information.

The RISC software was used for steps 2 through 3 of the risk assessment, while step 1 was done during the site investigation.

Table 6.7 below presents the input summary of the fate and transport model. The BP RISC output summary results are presented under section 6.6 below.

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Table 6.7: Summary of the input parameters for fate and transport model.

FATE AND TRANSPORT MODEL INPUT SUMMARY	
Model Description:	Saturated zone model
Simulation time (years).	70
SATURATED ZONE MODEL SOURCE	
Length of pulse (yr).	10.
Total thickness of source or free product (m)	3.
Length of source (m).	30.
Width of source (m)	20.
AQUIFER PROPERTIES	
Effective porosity (cm3/cm3)	0.30
Fraction organic carbon (gram of organic carbon/gram of soil).	3.53E-03
Hydraulic conductivity (m/d)	0.48
Soil bulk density (g/cm3).	1.8
Hydraulic gradient (m/m)	2.0E-02
RECEPTOR WELL LOCATION	
Distance down gradient (m).	60.
Distance cross gradient (m).	0.0
Depth to top of well screen (m).	Unknown
Depth to bottom of well screen (m).	Unknown
Number of points used to calc. conc.	4
CHEMICAL DATA FOR BENZENE (default values)	
Diffusion coefficient in air (cm2/s)	8.80E-02
Diffusion coefficient in water (cm2/s)	9.80E-06
Solubility (mg/l)	1.75E+03
Vapor pressure (mmHg)	95.
KOC (L/kg).	59.
Henry's Law coefficient (-).	0.23
Molecular weight (g/mol).	78.

Degradation rate, saturated zone (1/d).	9.60E-04
SOURCE CONCENTRATIONS FOR BENZENE (LABORATORY RESULTS)	
Average source conc. for groundwater model (mg/l)	12.25
CHEMICAL DATA FOR ETHYL BENZENE (default values)	
Diffusion coefficient in air (cm2/s)	7.50E-02
Diffusion coefficient in water (cm2/s)	7.80E-06
Solubility (mg/l)	1.69E+02
Vapor pressure (mmHg)	9.6
KOC (L/kg).	3.60E+02
Henry's Law coefficient (-).	0.32
Molecular weight (g/mol).	1.06E+02
Degradation rate, saturated zone (1/d).	3.00E-03
SOURCE CONCENTRATIONS FOR ETHYL BENZENE (LABORATORY RESULTS)	
Source conc. for groundwater model (mg/l)	0.28
CHEMICAL DATA FOR TOLUENE (default values)	
Diffusion coefficient in air (cm2/s)	8.70E-02
Diffusion coefficient in water (cm2/s)	8.60E-06
Solubility (mg/l)	5.26E+02
Vapor pressure (mmHg)	28.
KOC (L/kg).	1.80E+02
Henry's Law coefficient (-).	0.27
Molecular weight (g/mol).	92.
Degradation rate, saturated zone (1/d).	2.50E-02
SOURCE CONCENTRATIONS FOR TOLUENE (LABORATORY RESULTS)	
Source conc. for groundwater model (mg/l)	3.3
CHEMICAL DATA FOR XYLENES (default values)	
Diffusion coefficient in air (cm2/s)	7.20E-02
Diffusion coefficient in water (cm2/s)	8.50E-06
Solubility (mg/l)	1.98E+02
Vapor pressure (mmHg)	8.8
KOC (L/kg).	2.40E+02

Henry's Law coefficient (-).	0.29
Molecular weight (g/mol).	1.06E+02
Degradation rate, saturated zone (1/d).	1.90E-03
SOURCE CONCENTRATIONS FOR XYLENES (LABORATORY RESULTS)	
Source conc. for groundwater model (mg/l)	1.1

Note that the vapour model could not be done since there were no detectable levels of petroleum hydrocarbons in soil samples.

6.5.4. Groundwater flow and transport modeling for conducting Tier 3 analysis

The Tier 3 evaluation was done using the AQUAWIN (Van Tonder,1996) finite element model in order to refine the Tier 2 corrective action goals on. This involved more detailed site information and numerical modeling. Note that the Tier 3 evaluation provides the source zone cleanup levels designed to protect against health or environmental impacts at a site-specific POE (point of exposure).

6.5.4.1. Modus Operandi

The following modus operandi was followed:

- A dynamic groundwater flow model was constructed using as input (1) storativity values and (2) hydraulic conductivity values (K-values) using all the available groundwater flow information.
- A mass transport model was constructed using as input the determined water levels obtained from the groundwater flow model.
- The constructed flow model was calibrated using the available water level values.
- The resulting mass transport model was used to predict the migration of polluted water to the surrounding fractured aquifer. A constant source with 100% concentration was accepted for the time period over which the model was run. The 100% source concentration was assumed due to unknown lateral extent of LNAPL contamination.

6.5.4.2. Groundwater levels

It can be assumed that the groundwater level distribution generally emulates the surface topography. It is further reasonable to assume that polluted groundwater will flow from a topographic high to a topographic low. The Bayesian interpolation technique, which uses the possible relationship between the topography and groundwater levels, was used to interpolate groundwater levels and therefore the groundwater flow directions. Figure 6.5 is presenting the topography against the groundwater elevation.
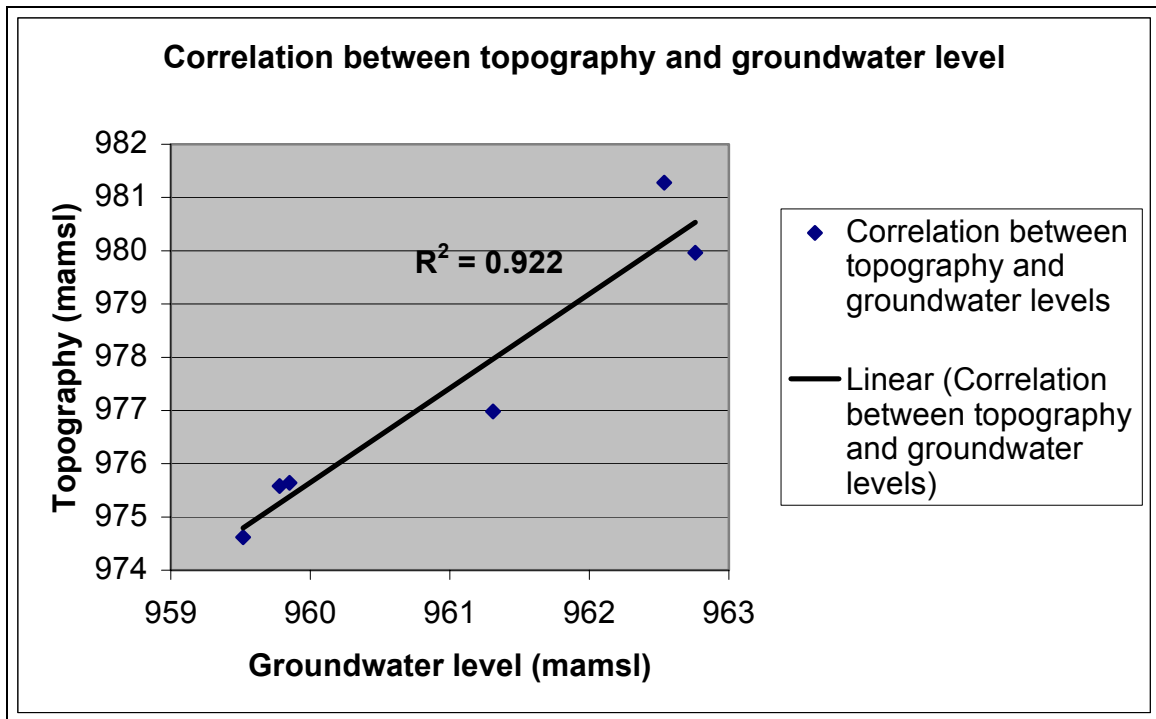
Figure 6.5: Correlation between the topography and groundwater level

6.5.4.3.   Conceptual model

The first step in the procedure of modeling is the construction of a conceptual model of the problem and the relevant aquifer domain. The conceptual model consists of a set of assumptions that reduce the real problem and the real domain to simplified versions that are acceptable in view of the objectives of the modeling and of the associated management problem.

As hydro geological data are scarce the following list of assumptions will be presented, which constitutes the conceptual model:

- As limited water levels are available in the immediate proximity of the site it is assumed that currently groundwater flow below the site conforms to the topography.
- It is assumed that a groundwater boundary conforms to topographical basin boundaries.
- In areas where preferential flow paths like fractures are present, it is assumed that groundwater flow takes place in a porous, heterogeneous and anisotropic medium.
- In areas where fractures are not present, groundwater flow takes place in a porous, homogeneous and isotropic medium.
- As the geometry of the aquifer is such that it is thin relative to its horizontal dimension, horizontal two dimensional flow conditions were assumed.

Note that the aim of the model was to determine the abstraction rate that could be used to run the pump and treat system in order to contain the free phase in the groundwater environment.

6.5.4.4.   Limitations of the model

The modeling exercise was based on limited information. The results obtained from this exercise model should be viewed carefully with the assumptions made. It must also be emphasized that the modeling done in this investigation is conservative not taking the retardation, sorption into account.
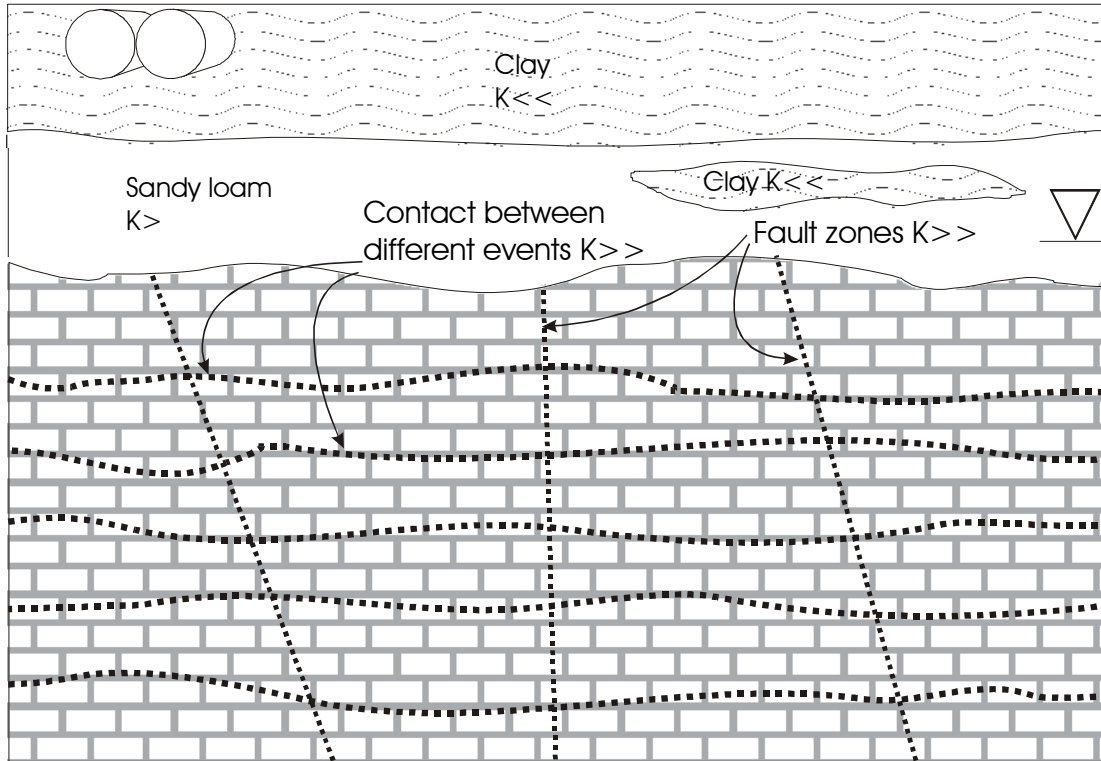
Figure 6.6: Refined conceptual model of the subsurface at the Service Station

6.5.4.5. Mass transport simulation for different scenario

By making use of the available chemistry the mass transport model was calibrated. Figure 6.7 shows the situation at the time the modeling was done. A number of scenarios were executed using the concentration levels in Figure 6.7 as input concentrations, to determine the optimum pumping sequence and pumping rates for the different boreholes with the aim of plume containment.
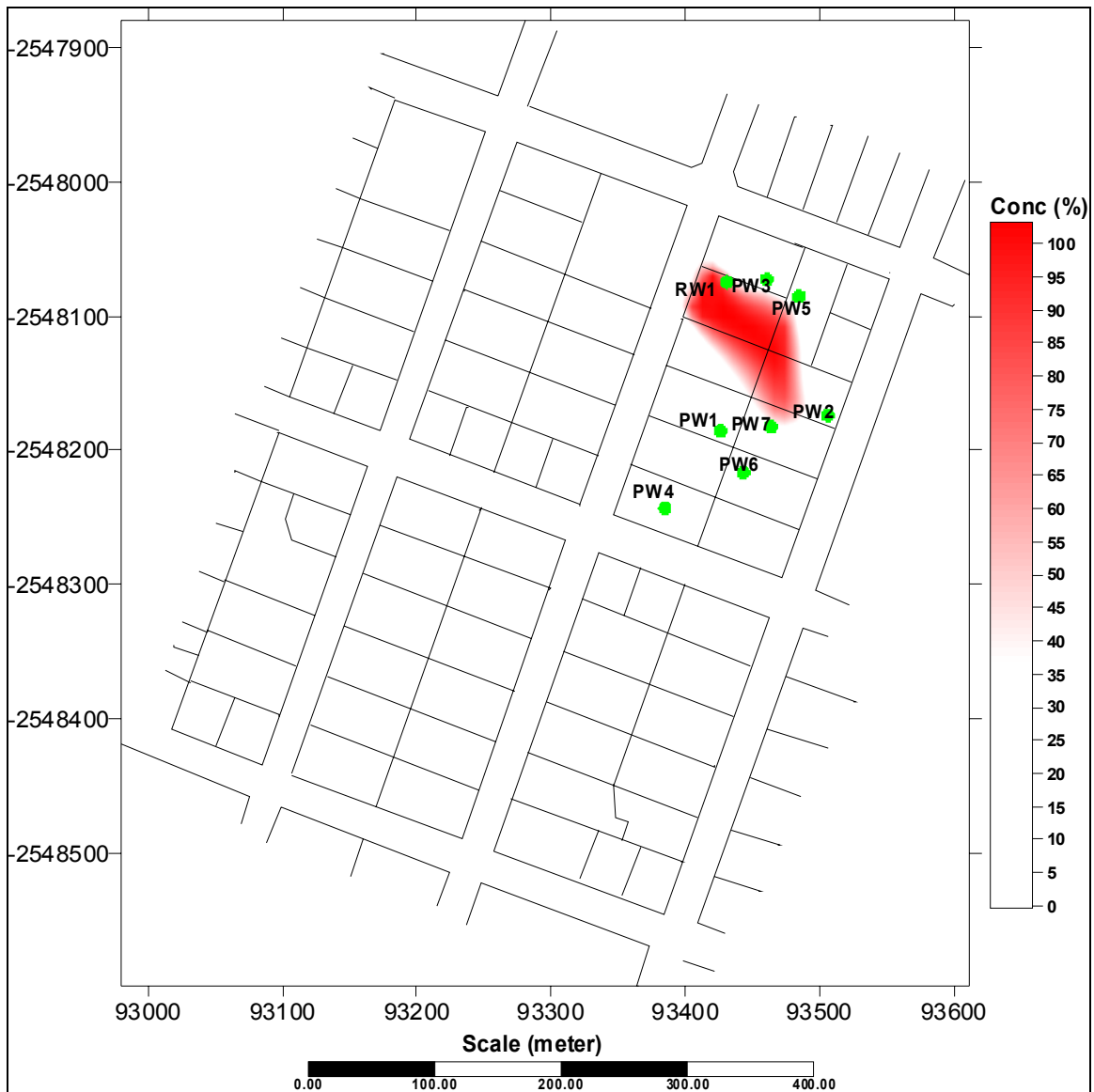
Figure 6.7: Concentrations used as input before model was run.

6.5.4.5.1.   Scenario 1

This scenario was set as follows:

- Pumping borehole PW 1, PW 2 and PW 3 at an abstraction rate of 0.5 l/s.
- A constant concentration at the source of 100 %.
- Input concentrations as seen in Figure 6.7.
- The model was simulated for a period of 10 years

Figure 6.8 shows the concentrations after 10 years.
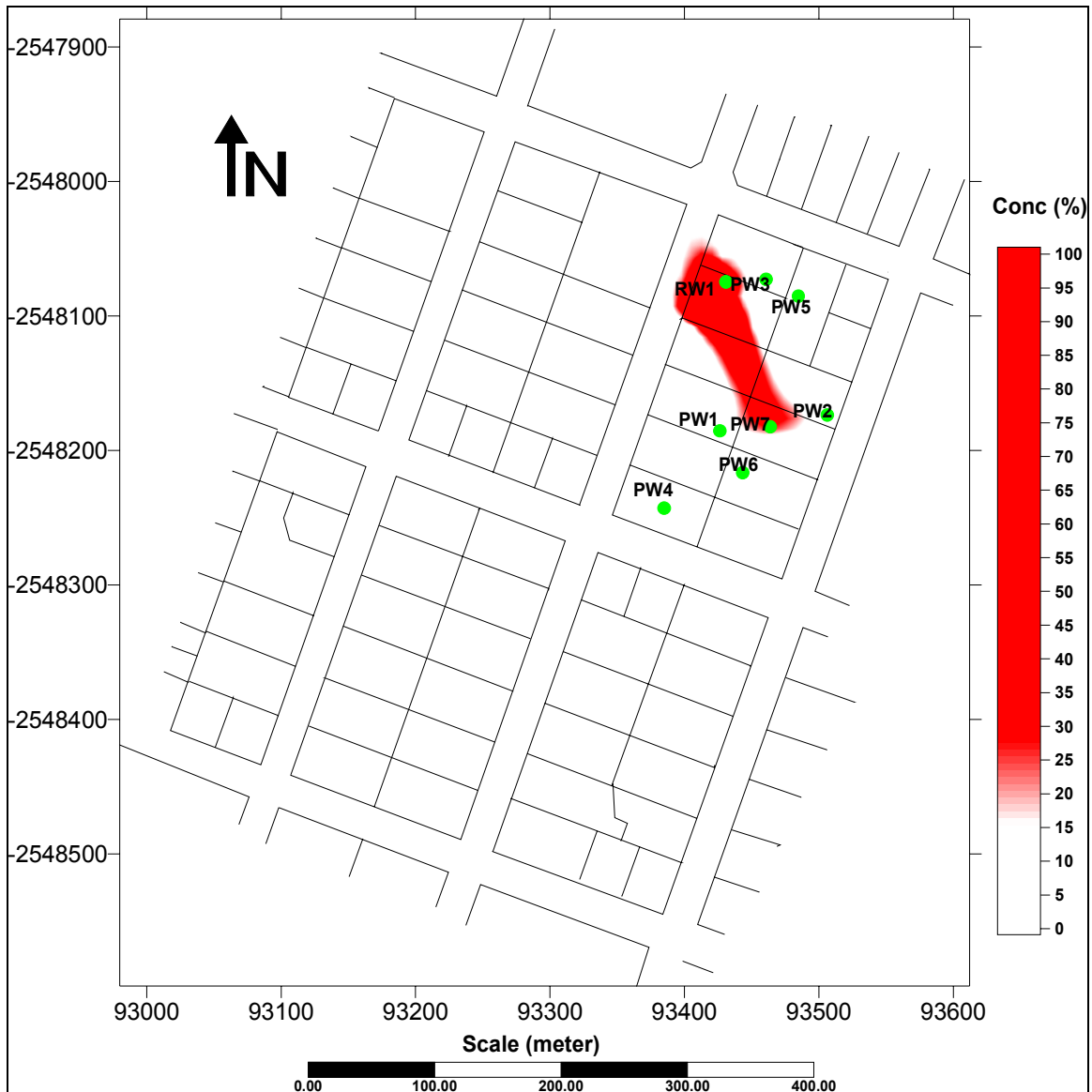
Figure 6.8: Concentration migration for scenario 1 after 10 years

It can be seen from this scenario that the pumping of PW 1, PW 2 and PW 3 at this rate will not contain the plume within 10 years.

6.5.4.5.2.   Scenario 2

This scenario was set as follows:

- Pumping borehole RW 1(0.75 l/s), PW 2 (0.2 l/s) and PW 3 (0.3 l/s).
- A constant concentration at the source of 100 %.

- Input concentrations as seen in Figure 6.7.
- The model was simulated for a period of 10 years

Figure 6.9 shows the concentrations after 5 years
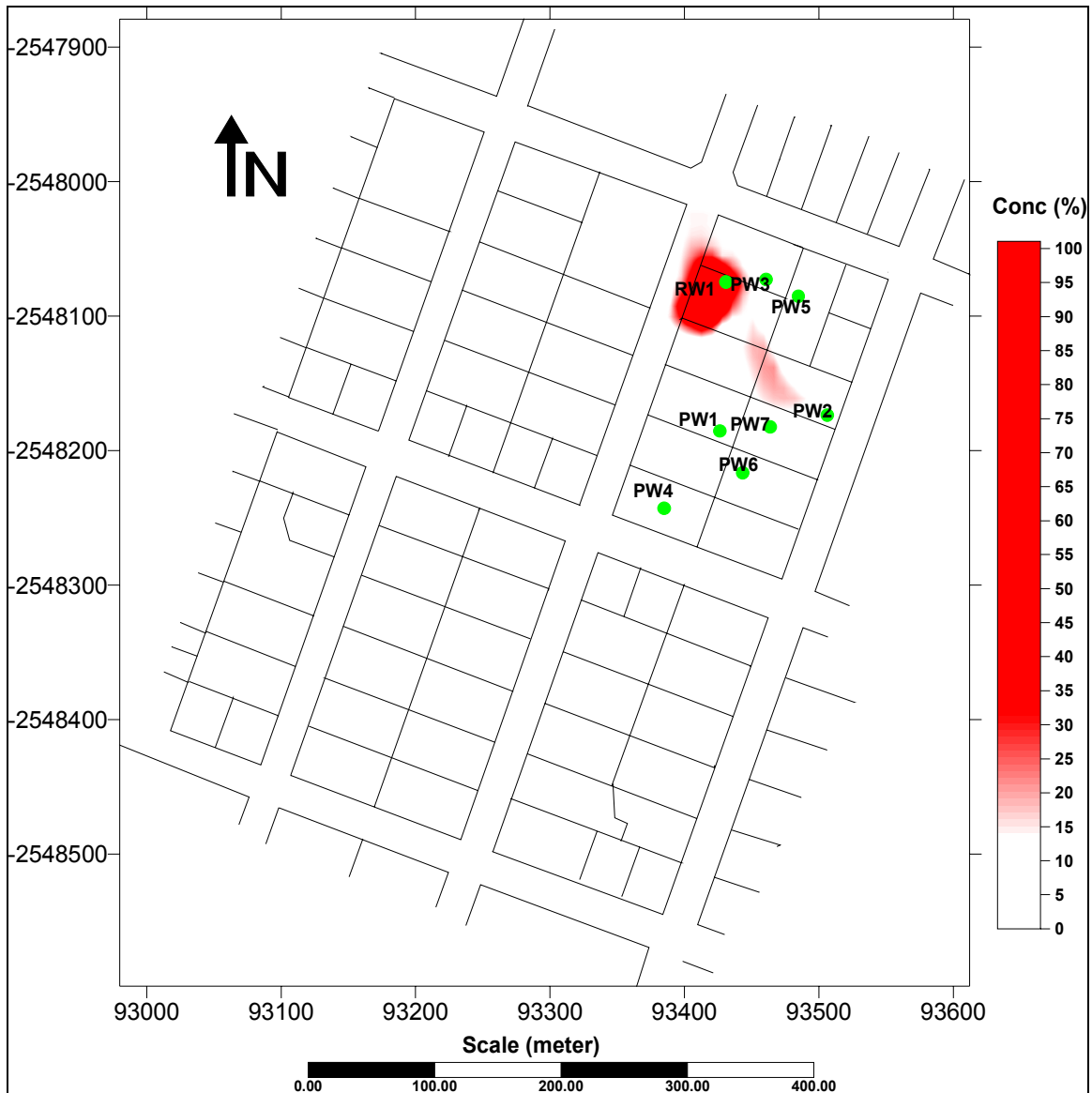
Figure 6.9: Concentration migration for scenario 2 after 5 years

It can be seen from this scenario that the pumping of RW 1 at a rate of 0.75 l/s, PW 2 at a rate of 0.2 l/s and PW 3 at a rate of 0.3 l/s will contain the plume within 5 years. This seems to be the optimum pumping rate for the plume containment assuming that no other boreholes are pumped in the residential block.

6.5.4.5.3. Scenario 3

This scenario was set as follows:

- Pumping borehole RW 1(0.75 l/s)
- A constant concentration at the source of 100 %.
- Input concentrations as seen in Figure 6.7
- The model was simulated for a period of 10 years

Figure 6.10 shows the concentrations after 5 years. It can be seen from this scenario that the pumping of only borehole RW 1 at a rate of 0.75 l/s will not contain the plume within 5 years.

From the modeling scenarios it is evident that the optimum pumping schedule and rate will be as in scenario 2.
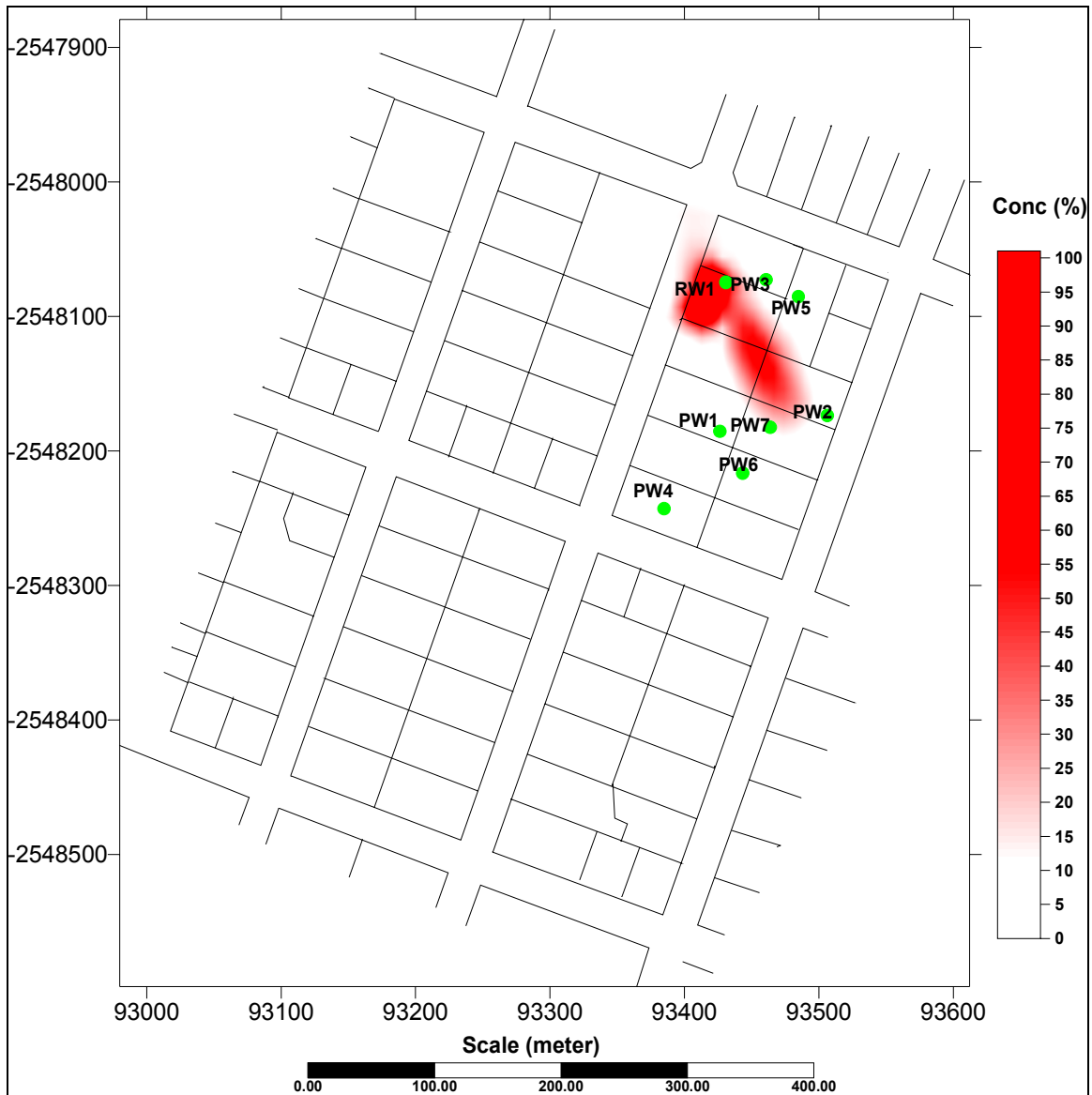
Figure 6.10: Concentration migration for scenario 3 after 5 years

Note that the results obtained from this exercise model should be viewed carefully with the assumptions made. The model was conservative not considering the sorption and retardation of the petroleum contamination. However, the obtained results form the model scenario 2 were then used to run a pump and treat system with the aim of free phase plume containment (*detailed description of the pump and treat system in section 6.4.2.1*).

6.6. Interpretation of the risk posed by LNAPL contamination in groundwater environment.

6.6.1. Tier 1 RBSL analysis

One can never have a no-risk situation when dealing with contaminated sites .The risk can rather be expressed as an acceptable or non-acceptable risk. Carcinogenic risk in the range of 1 in 1000 000 are generally seen as acceptable, while risks greater than 1 in 1000 000 population are deemed unacceptable in countries like Australia and New Zeeland. The potential for non-carcinogenic effects is evaluated by comparing an exposure level over the exposure duration with a reference dose derived for a similar exposure period. This ratio of exposure to toxicity for an individual pathway and chemical is called a hazard quotient. The hazard quotients are usually added across all chemicals and routes to estimate a hazard index. The hazard quotient assumes that there is a level of exposure (reference dose) below which it is unlikely that even sensitive populations would experience adverse health effects. The reference dose (RfD) is therefore a toxicity value for evaluating non-carcinogenic effects and it is assumed that if the intake is below RfD (hazard quotient <1) no adverse health effects should occur.

Table 6.8 Below present the environmental media affected by contamination, risk pathways, receptors and the risk values posed by the dissolved phase petroleum hydrocarbons (BTEX). The chemical results of water sample PW1 and PW3 have triggered the Tier 1 Risk Based Screening Levels (RBSLs) for risk exposure pathways of:

- *Groundwater Ingestion*
- *Volatilization to Indoor Air Inhalation and*
- *Volatilization to Outdoors Air Inhalation.*

The risk values that were triggered through the above mentioned exposure pathways are the following (*Detailed description of human health risk goals is presented in chapter 5, section 5.2.6.1*):

- Carcinogenic risk (10^{-06} to 10^{-04}) which is the excess risk value of an upper bound estimate of the added probability of incurring cancer as a result of exposure to the carcinogenic hydrocarbon compound (***e.g. benzene***)

- Hazard Quotient (HQ) which is associated with non-carcinogenic compounds (*e.g., Toluene, Ethyl benzene and Xylenes*) and
- MCL which is acronym for Maximum Contaminant Level.

Table 6.8: Presents the environmental media, risk pathways, receptors of concern and risk values posed by petroleum hydrocarbons.

Environmental media	Risk pathways	Receptors	Risk values	PW1 (Series 2)	PW1 (Series 3)	PW3 (Series 2)	PW3 (Series 2)
Groundwater	Ingestion of Groundwater	Residential	10^{0-6} to 10^{-04}	✔	✔	✔	✔
			HQ	✔	✔	✔	✔
		Commercial/ Industrial	10^{0-6} to 10^{-04}	✔	✔	✔	✔
			HQ	·	·	·	·
	Inhalation of Indoor Air Vapours	Residential	10^{0-6} to 10^{-04}	✔	✔	✔	✔
			HQ	·	·	·	·
		Commercial/ Industrial	10^{0-6} to 10^{-04}	✔	✔	✔	✔
			HQ	·	·	·	·
	Inhalation of Outdoor Air Vapours	Residential	10^{0-6} to 10^{-04}	·	·	·	·
			HQ	·	·	·	·
		Commercial/ Industrial	10^{0-6} to 10^{-04}	✔	✔	·	·
			HQ	·	·	·	·
			MCL	✔	✔	✔	✔

Ticked block present the specific risk value which is triggered by the concentration level of both carcinogenic and non-carcinogenic compounds

6.6.2. BP RISC (Tier 2 analysis through analytical modeling)

Based on the site specific data available Tier 2 analysis was conducted by making use of BP RISC software. Figure 6.11 below and Appendix F present the output of fate and transport model for BTEX compounds. The maximum groundwater concentration of 4.52E-01mg/L was modeled to occur in the receptor borehole after 70 years. The summary of carcinogenic and hazardous risk in the saturated zone (aquifer) is presented in Figure 6.12, 6.13 and Table 6.9 below. The calculated carcinogenic risk in groundwater is above the range of 1 in 1000 000, it is then obvious that carcinogenic risk does exist through groundwater ingestion pathway and identified receptors. The calculated hazard quotient is also below 1 and it is therefore expected that a non-carcinogenic risk does not exist through the identified pathways and receptors.
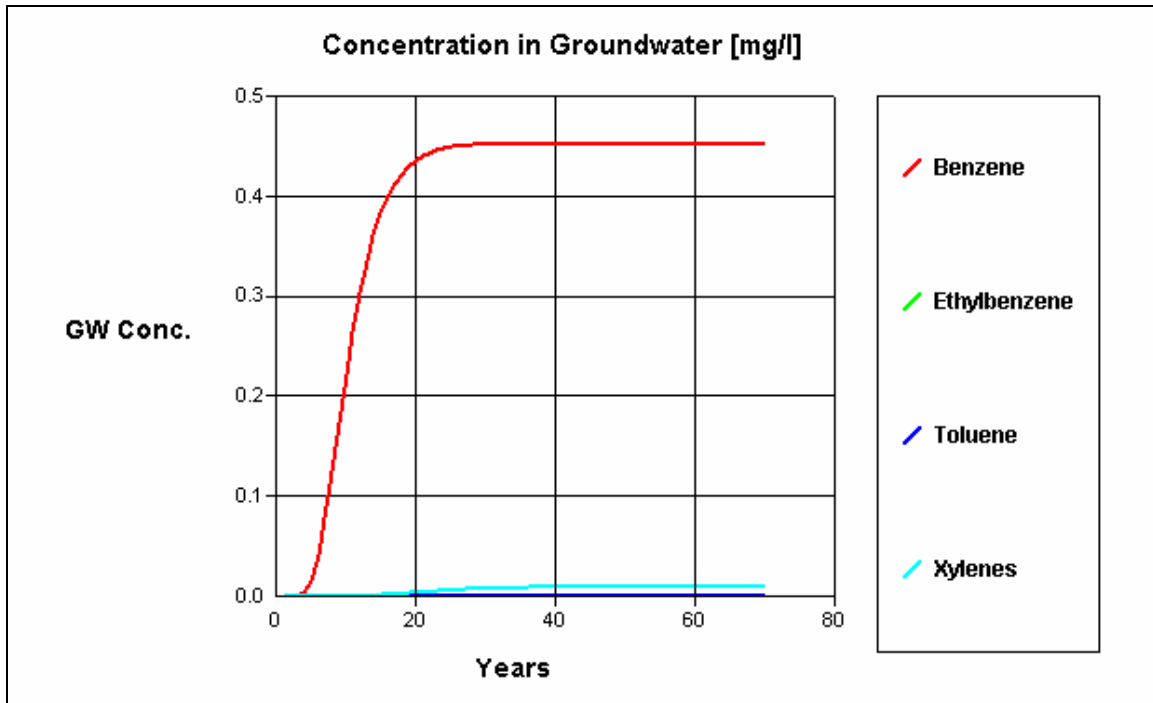
Figure 6.11: Groundwater concentration (mg/L) in the receptor borehole after 70 years

Based on the results of Figure 6.11 above, it confirms the fact that benzene is less retarded in the soil media as compared to toluene and xylenes. The figure above shows that in 20 years time the receptor borehole would still have insignificant concentrations of toluene and xylenes as compared to benzene concentrations at that time. The model output results in a table format are attached in Appendix F.
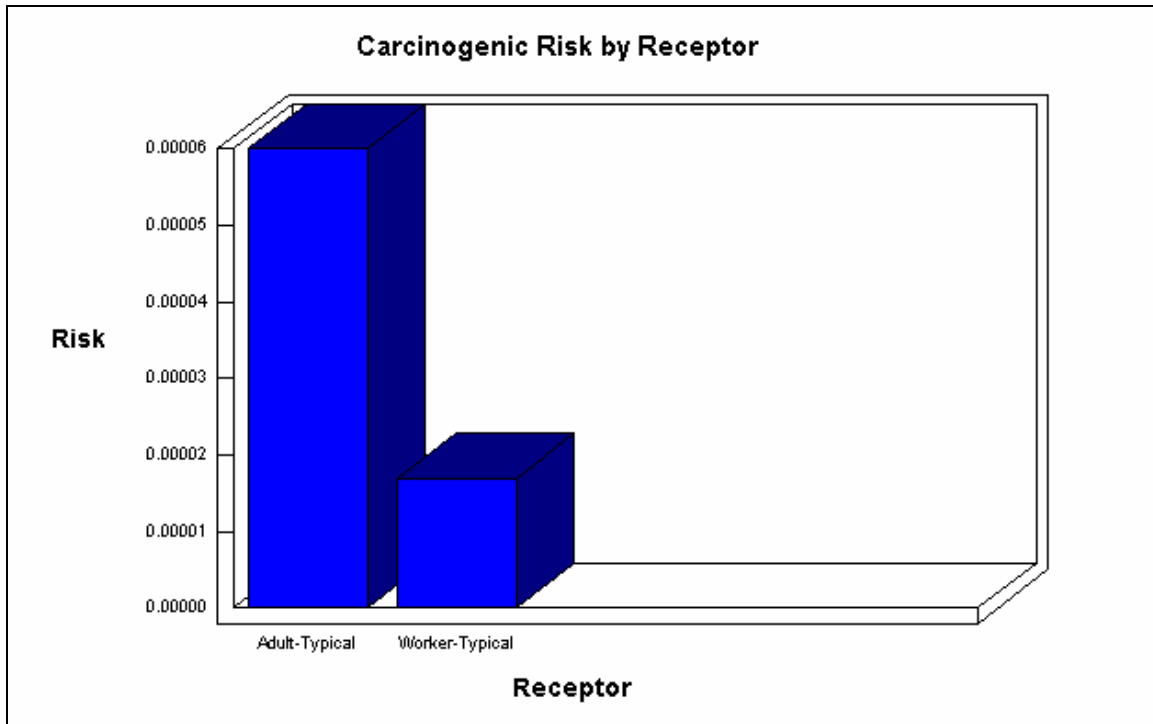
Figure 6.12: Carcinogenic risk by the receptor
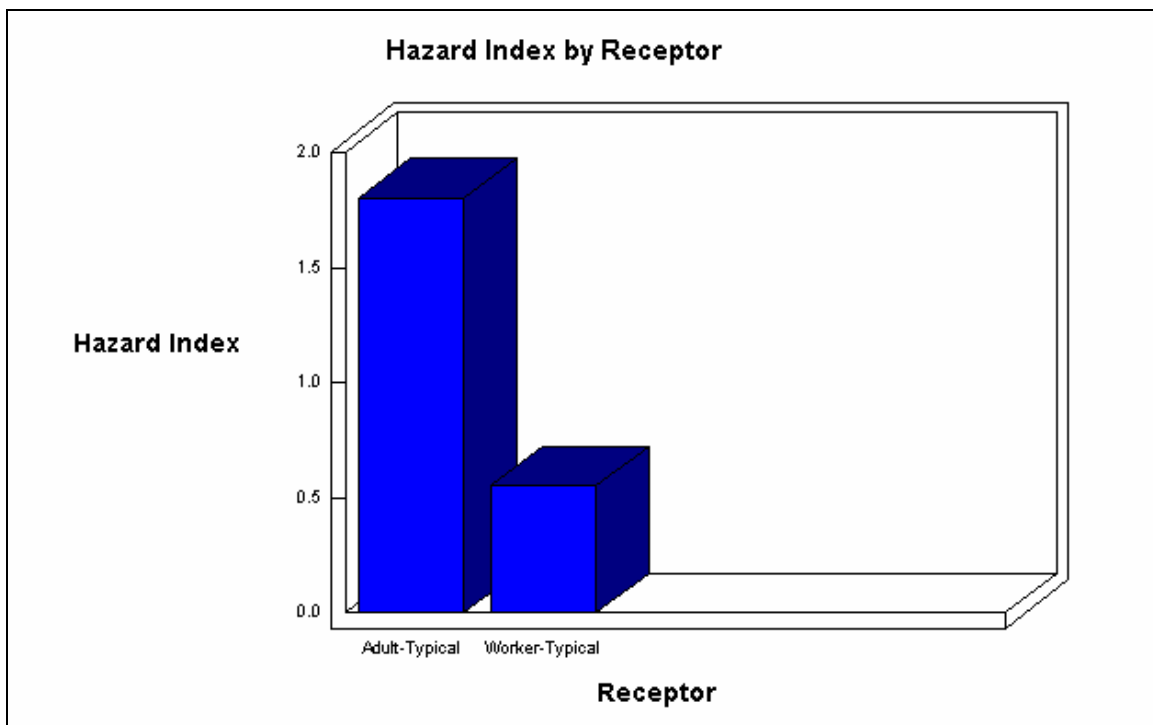
Figure 6.13: Hazard Index by receptor

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Table 6.9: Summary of carcinogenic and hazardous risk in the saturated zone (aquifer).

SUMMARY OF CARCINOGENIC RISK *For Saturated Zone Source*						
RECEPTOR 1: ADULT RESIDENT						
Compound	*RISK PATHWAYS*					
	Ingestion of groundwater	Dermal contact in shower	Ingestion of irrigation spray	Ingestion of irrigation water	Dermal contact with irrigation water	Ingestion of vegetables
Benzene	5.6E-07	2.4E-06	5.9E-08	5.8E-09	2.3E-07	7.3E-07

SUMMARY OF CARCINOGENIC RISK *For Saturated Zone Source*						
RECEPTOR 2: WORKER						
Compound	*RISK PATHWAYS*					
	Ingestion of groundwater	Dermal contact in shower	Ingestion of irrigation spray	Ingestion of irrigation water	Dermal contact with irrigation water	Ingestion of vegetables
Benzene	1.7E-05	0.0E-00	0.0E-00	0.0E-00	0.0E-00	0.0E-00

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SUMMARY OF HAZARD QUOTIENTS (NON-CARCINOGENIC COMPOUNDS)						
For Saturated Zone Source						
RECEPTOR 1: ADULT RESIDENT						
Compounds	**RISK PATHWAYS**					
	Ingestion of groundwater	Dermal contact in shower	Ingestion of irrigation spray	Ingestion of irrigation water	Dermal contact with irrigation water	Ingestion of vegetables
Toluene	1.3E-09	1.1E-10	1.3E-12	2.4E-13	1.1E-11	7.2E-11
Ethyl benzene	9.5E-05	1.4E-05	9.9E-08	3.3E-09	1.4E-06	8.4E-06
Xylenes	7.2E-04	1.2E-04	7.5E-07	5.0E-07	1.1E-05	7.6E-05

SUMMARY OF HAZARD QUOTIENTS (NON-CARCINOGENIC COMPOUNDS)						
For Saturated Zone Source						
RECEPTOR 2: WORKER						
Compounds	**RISK PATHWAYS**					
	Ingestion of groundwater	Dermal contact in shower	Ingestion of irrigation spray	Ingestion of irrigation water	Dermal contact with irrigation water	Ingestion of vegetables
Toluene	4.1E-10	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Ethyl benzene	3.1E-05	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Xylenes	2.4E-04	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00

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6.6.3. Flow and mass transport modeling (Tier 3 evaluation)

Based on the results arise from the flow and mass transport modeling, it was predicted that the contamination plume could be contained after 5years when borehole RW1, PW2 and PW3 are pumped at a rate of 0.75L/s, 0.2L/s and 0.3L/s, respectively. This was done on the assumption that no other borehole must be pumped in the resident block except RW1, PW2 and PW3.

6.7. Groundwater mitigation plan based on the findings

Due to the presence of free product in the private boreholes PW1 , PW2 and PW5 as well as the percussion borehole (RW1) that was drilled at the service station the following mitigation strategies were selected and evaluated for cleaning up the contaminated site.

- Vacuum Enhance Recovery and
- Pump and treat system

These two remedial techniques were evaluated based on the site-specific condition in order to get the suitable technique that would be conducive for the problem in question.

6.7.1. Single –pump Dual-Phase Extraction (DPE)

Single -pump Dual-phase extraction also known as Vacuum-enhanced Recovery, is an in-situ technology that uses pumps to remove various combinations of contaminated groundwater, separate-phase petroleum product and hydrocarbon vapour from the subsurface. Extracted liquids and vapour are treated and collected for disposal. DPE system can be effective in removing separate-phase product from the subsurface, thereby reducing concentrations of petroleum hydrocarbons in both saturated and unsaturated zones of the subsurface. High hydraulic gradients enhance the recovery rates of both water and LNAPL (Bruce et al 1992). The depressed groundwater table that results from these high recovery rates serves both to hydraulically control groundwater migration and to increase the efficiency of vapour extraction.

Single pump-DPE technology is best suited to sites with intrinsic permeability ranging from 10^{-9} to 10^{-11} cm^2. High moisture content in the unsaturated zone soils can reduce soil permeability as well as the effectiveness of DPE in removing hydrocarbons from the

unsaturated zone. Generally, with water saturation levels equal to or greater than 85% of field capacity, airflow is blocked because the effective air permeability is essentially zero. DPE is difficult to apply at the sites where the water table is located less than 1meter below ground level due to high potential for airflow short circuiting due to the large vertical airflow rates in the immediate vicinity of the extraction borehole within high permeable soils. The *radius of influence* (ROI) depends on the soil moisture content, intrinsic permeability and the desired remediation time. Radius of influence is the maximum distance of from a vapour extraction borehole at which sufficient airflow can be induced to sustain acceptable rates of remediation. Generally, the design ROI can range from 1.5m (for fine grained soils) to 30meters (for coarse grained soils) for a single borehole operating alone.

DPE system is typically designed to maximize extraction rates; however, the technology also stimulates biodegradation (**natural attenuation**) of petroleum constituents in the unsaturated zone by increasing the supply of oxygen, in a manner similar to **bio venting** (USEPA, 1995).

This is because DPE works on the principle that a vacuum is generated which is transplanted to the unsaturated zone. In permeable soils air is sucked out which has to be replaced by air which comes from other parts in the unsaturated zone, and ultimately from the air (*atmosphere*). By injecting a vacuum on the unsaturated zone air flow is then enhanced which then take part in the natural degradation of the dissolved phase petroleum hydrocarbons.

Positive aspects about DPE technique

- Proven performance in low permeability soils. Requires no downhole pump.
- Can be applied at site with floating product, and can be combined with other technologies, such as air sparging and bioremediation.
- Intercept free product at higher recovery rate than pump and treat system (P&T).
- Can reduce the cost of groundwater treatment through air striping within the vacuum extraction tube.
- Removes free product, vapours and groundwater from the subsurface.

- Vent the soil and increase the percentages of oxygen in the subsurface resulting in the enhancement of biodegradation.
- Can be used under buildings and other locations that cannot be excavated.

Limitations of DPE technique

- Not efficient in low permeable soils (i.e. clay) due to low transmission of air.
- Difficult to apply to sites where water table fluctuates.
- Can extract a large volume of water that may require treatment.
- Requires specialized equipment with sophisticated control capabilities.
- Requires complex monitoring and control during operation.
- Treatment may be expensive for extracted vapours and for oil-water separation.
- Mostly efficient when dealing with petrol, diesel and jet fuel product due their significant volatility.

Generally, the efficiency of DPE depends on the geologic and hydraulic parameters (i.e. type of formation on both saturated and unsaturated zone, permeability of the soil, the hydraulic conductivity of the formation) as well as the type of product at the site of concern.

6.7.2. Pump and treat system (P&T)

When contaminated groundwater is removed from the subsurface by pumping, it is often treated before it is discharged. Hence this method is referred to as pump and treats system. This is the most common form of groundwater remediation (USEPA,1996). Sites where the contaminants are in a mobile, dissolved state and less sorption occur, are ideal for pump and treat remediation. The well design, pumping system, and treatment are dependent on the site characteristics and contaminant type. It is not uncommon to find many boreholes extracting groundwater at the same time. These boreholes may be screened at different levels to maximize effectiveness. A major component of any groundwater extraction system is a ground water monitoring program to verify its

effectiveness. Monitoring the cleanup allows the operator to make adjustments to the system in response to changes in subsurface conditions.

A major component of a pump and treat system is determining when to turn the system off. For contaminants regulated by the EPA, levels established under the Safe Drinking Water Act are usually the prevailing levels that groundwater has to meet. Termination requirements are based on the cleanup objectives combined with site-specific aspects revealed during remedial operations (http://www.cpeo.org/techtree/ttdescript/pumtre.htm.

Positive aspect of P&T system

- It is the optimum tool for plume and hydraulic gradient control.

Limitations of P&T system

- Pump-and-treat systems often take a very long time (e.g., 50 -100 years) to meet cleanup goals.

- Pumping depresses the groundwater level, leaving residuals sorbed to the soil. After the groundwater level returns to its normal level, contaminants sorbed onto soil become dissolved. This phenomenon is called "rebound". Rebound tests should be performed frequently in the first few years after the system is turned off, and after major precipitation or flooding events.

- Generation of substantial amounts of secondary wastewater, high energy costs for pumping and moving large volumes of water, indiscriminate removal of all groundwater components, potential impacts on groundwater resources, and slow progress toward terminal regulatory goals due to technical limitations (Looney, 1994).

By considering the site-specific parameters of the service station as well as the positive aspects and limitation of the two remedial techniques (DPE and P&T system) a pump and treat system was employed to cleanup the contaminated subsurface environment. DPE technique was not used because of a the following:

- Deep groundwater level which was established during hydrocensus survey.

- Thick unsaturated zone (~20m), which is comprised of clay. Clay is a fine-grained soil, which is less permeable and hence low transmission of air during the vapour extraction.

- The unknown construction information of the private boreholes particularly PW1, PW2 and PW5, which were contaminated with free product.

6.7.2.1. The Implementation of the pump and treat system at the investigated site.

Firstly the pump and treat system was conducted in borehole PW1 during 1997 to 1998 as an immediate response. This was done before the detailed investigation including SVS and drilling of percussion boreholes was done. The main aim was to contain the product in this borehole. Tables 6.10 below present the chemical analysis of water sample that were collected form the inlet and outlet of the separator during the monitoring events. Free product was recovered in borehole PW1 during September 1998. Pump and treat system was then stopped and start with monitoring of the dissolved phase petroleum hydrocarbons.

Table 6.10: Results of petroleum hydrocarbons during monitoring of pump and treat system.

Borehole number	PW1	PW1	PW3	PW4	PW1	PW1
Depth of sample	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Type of sample	Water	Water	Water	Water	Water	Water
Sampling date	19.03.97	19.03.97	19.03.97	19.03.97	12.09.97	12.09.97
Benzene	1.3	0.8	1.9	BDL	3.34	2.71
Toluene	0.1	0.1	0.4	BDL	0.43	0.27
Ethyl benzene	0.0	0.0	0.0	BDL	0.03	0.0
m+p-Xylene	0.1	0.1	0.1	BDL	0.43	0.32
o-Xylene	0.1	0.1	0.1	BDL	0.25	0.21

Borehole number	PW1	PW1	PW1	PW3	PW4
Depth of sample	Inlet	Pumped	Pumped	Pumped	Outlet
Type of sample	Water	Water	Water	Water	Water
Sampling date	07.01.98	07.01.98	06.10.98	06.10.98	06.10.98
Benzene	3.02	BDL	0.58	2.19	BDL
Toluene	0.52	BDL	0.1	0.33	BDL
Ethyl benzene	0.18	BDL	0.04	0.07	BDL
m+p-Xylene	0.80	BDL	0.25	0.29	BDL
o-Xylene	0.41	BDL	0.12	0.15	BDL

Pump and treat system resumed during 1999 up to 2003 where the AQUAWIN (Van Tonder, 1996) abstraction rates that were determined from the numerical model were used to run pump and treat system in borehole RW1, PW2 and PW3. Borehole RW1, PW2 and PW3 were pumped at the rate of 0.75L/s, 0.2L/s and 0.3L/s, respectively (*section 6.5.4.4.2 above*). Borehole RW1, PW2 and PW3 were installed with submersible pumps that could handle abstraction rate of 0.75L/s, 0.2L/s and 0.3L/s, respectively. The pumps were installed at the depth of 30m.b.g.l, 22m.b.g.l and 27m.b.g.l in borehole RW1, PW2 and PW3, respectively. A bigger separator was build to handle a flow of 1L/s. Borehole RW1 and PW3 used the same separator, while PW2 used the separator that was moved from PW1.

6.7.2.1.1. Monitoring results

Groundwater levels and free product was monitored on a monthly basis and the following results were obtained (Figure 6.14, 6.15, 6.16, 6.17 below):

- High groundwater recharge occurred during February 2000 due to the floods, which then caused a rise in groundwater level. Most of the free product that was still retained in the formation was then desorbed and leached into groundwater. An increase in free product was evident in borehole RW1 during June 2000 after the floods (Figure 6.14).
- Free product was recovered in borehole PW2 and PW5 during January 2000 (Figure 6.16).
- Free product was recovered in borehole RW1 during October 2002 (Figure 6.16).

- No free product was found in borehole PW1 and PW3 during November 1998 up till October 2003 (Figure 16.17).
- No detectable levels of the dissolved phase hydrocarbons were found in borehole PW1, PW2, and PW3 during Jan 00, Oct 01, Mar 02, Oct 02, Mar 03 and Oct 03 (see Appendix G).
- The absence of the dissolved phase petroleum hydrocarbons in borehole PW1, PW2 and PW5, which are located down gradient of the service station, confirm that the contamination plume was contained through pump and treat system.
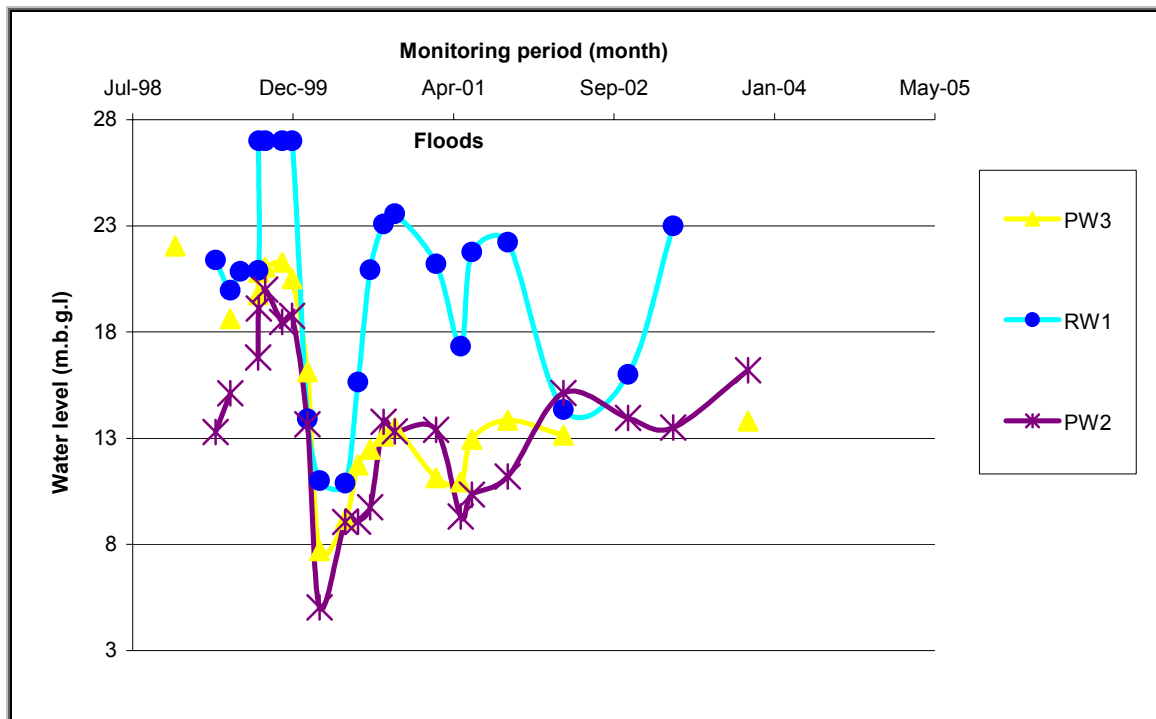
Figure 6.14: Groundwater levels in the pumping boreholes (RW1, PW2 and PW3)

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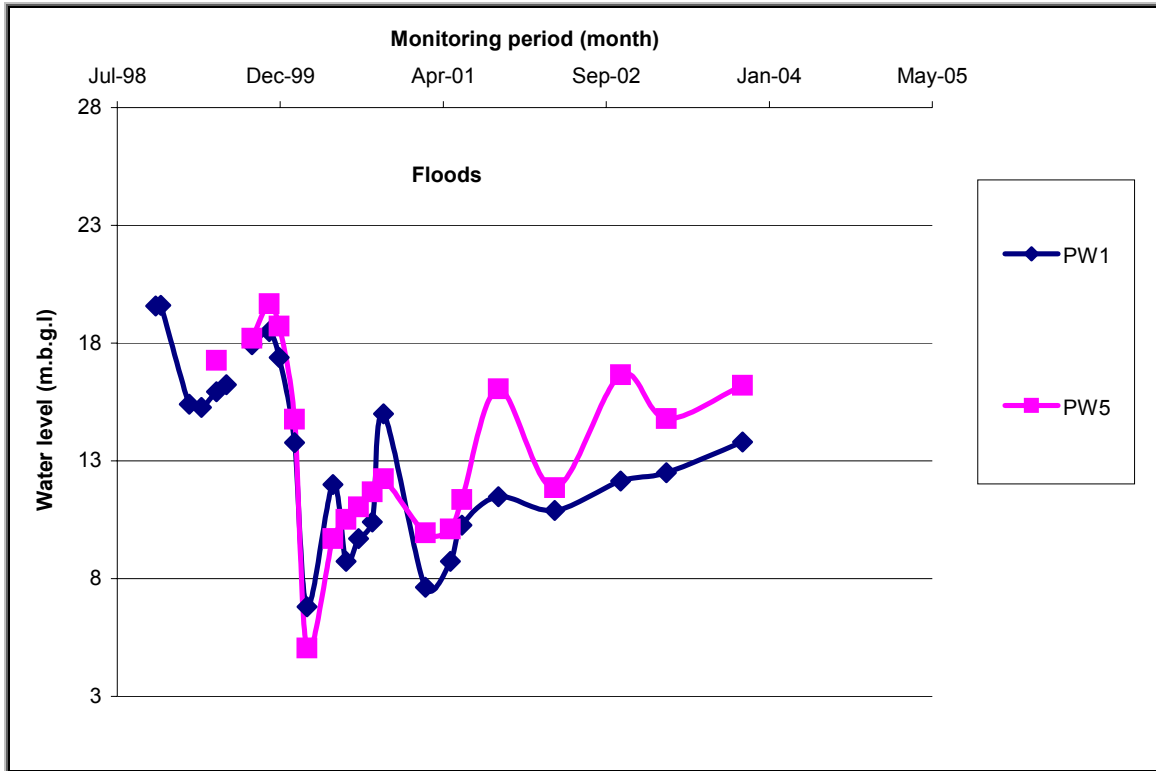
Figure 6.15: Groundwater levels in the monitoring boreholes (PW1 and PW5).
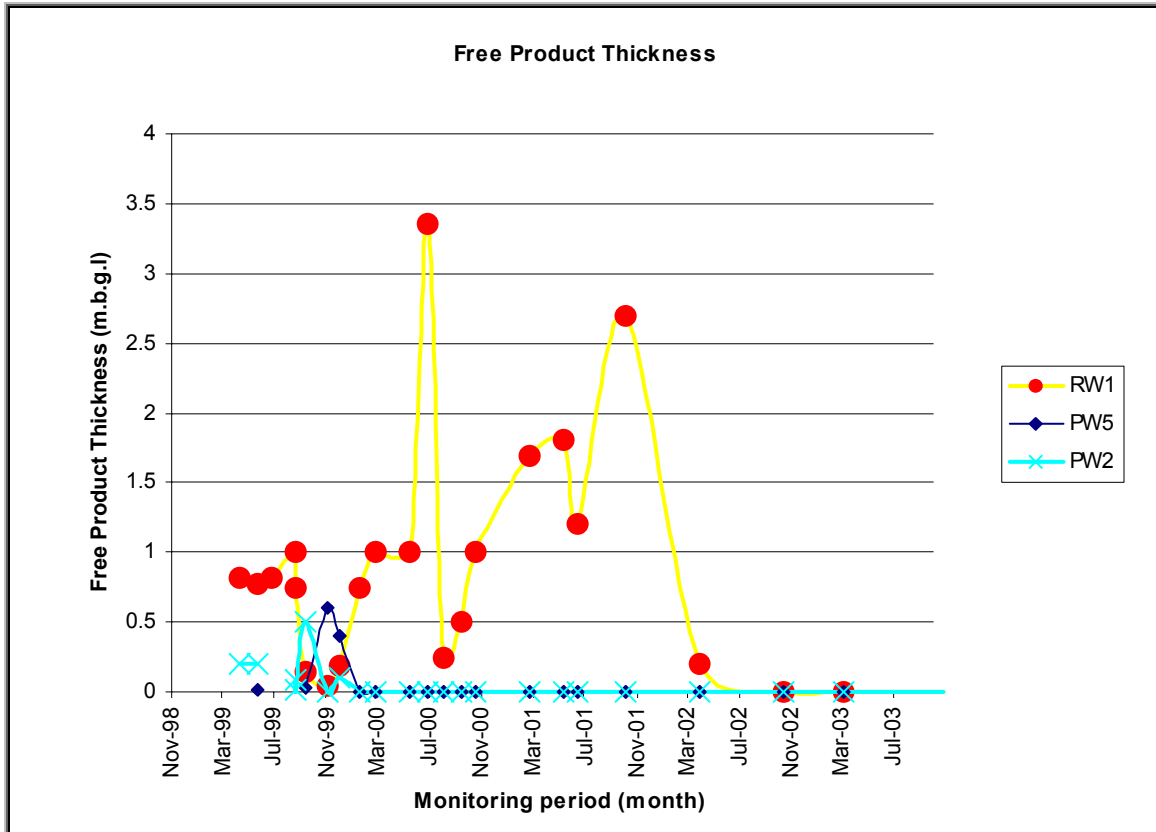
Figure 6.16: Free product (petrol) thickness in borehole RW1, PW2 and PW5.
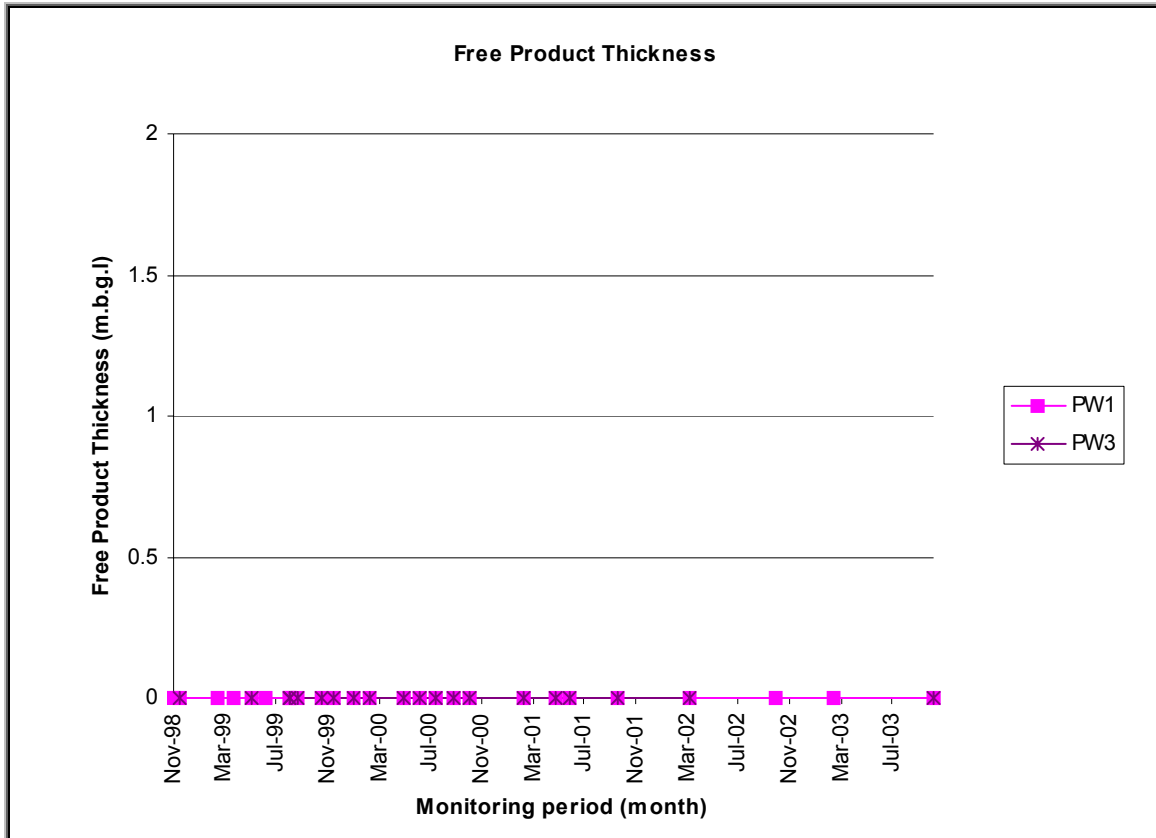
Figure 6.17: Free product (petrol) thickness in borehole PW1 and PW3.

6.8. Lessons learned from the results of the case study

Based on the results that obtained from the case study the following under-mentioned lessons were learned:

- It is very crucial to know the date in which the LNAPL was spilled and or leaked as well as the volume and type of product that spilled and or leaked.

- The complexity of the natural geologic settings can cause substantially different chemical conditions from the boreholes which are drilled only few meters away from each other. It was also learned that the site complexity which is further increased by the surface structures (i.e., Buildings, underground tanks, underground pipelines, utilities and or roadways) often limit access for investigating the extent of contamination and construction of recovery systems.

- The type of the geological formation in the unsaturated zone (soil, air and moisture) plays an important role in terms of the migration rate and the volatility of the petroleum constituents. In this case study the lateral extent of the contamination plume could not be determined because the unsaturated zone of the site is underlain by clay (residual soil from the chemical weathered basalt Formation), which then inhibits the volatilization of the Volatile Organic Compounds.

- It is very important to know the lateral extent of the petroleum contamination plume. This is because the absence of this information poses difficulties in terms of placing the boreholes for recovering the free product and monitoring the dissolved phase petroleum hydrocarbons. The lateral extent of contamination can be attained by conducting the soil vapour survey where the petroleum vapour plume in the unsaturated zone is mapped. Drilling of many hand and mechanical auger holes at different positions of the site also help in the determination of both lateral and vertical extent of contamination. Based on the results of these two methods a broader picture of the extent of contamination can be achieved.

- It is very important to know the construction information about the private boreholes which identified during the hydro census survey. In

this case study, there is borehole PW3 which was found onsite, which is at a distance of approximately 20m down gradient of, but no free product was ever found in borehole PW3 throughout the investigation. Borehole PW3 was only contaminated with low level of the dissolved phase hydrocarbons. It was then difficult to know if the absence of the free product was due to the fracture networks of the site's aquifer or is due to the way in which the hole was constructed. The lack of information about the borehole construction also poses difficulties in terms of determining the hydraulic parameters (saturated hydraulic conductivity and Transmissivity) of the aquifer. In this case study, it has been very cumbersome to conduct slug test and pump test in the private boreholes due to the unknown information about the borehole construction.

▪ Based on the chemical results of the case study, it was evident that very poor chemistry data was collected. This resulted in the lack of chemical trend analysis. This is because the sampling runs were not done according to the recommended sampling schedule due to the lack funds. This implies that the petroleum industries should allocate enough budget for conducting the pollution assessments and remediation thereof.

Based on the results of the pump and treat system which was implemented at the site it was clear that free product was addressed within two years after the commencement of this remedial technique. The reason behind this speedy recovery was probably due to the fact:

▪ It was a once off overfill of product at the site resulting in a relatively small volume that could infiltrate the subsurface.

▪ Borehole RW1, PW2 and PW5 are fully penetrated through the fracture networks of the Sibasa basalt formation of which was then the preferential pathways of free product.

As seen in the preceding discussions, petroleum contamination assessment was done through soil vapour survey (SVS), hand auger holes and rotary percussion drilling. It could be seen that SVS did not reveal much in terms of the petroleum vapour plume in the unsaturated zone and this was due to the clay soils which is commonly associated with low transportation of vapours. It was then difficult to position the hand auger holes

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for determining the absorbed petroleum hydrocarbons through soil sampling. Furthermore, hand auger holes were restricted to a shallow depth due to clay soil. In that case a mechanical auger holes should have been drilled in order to investigate the petroleum contamination in a greater depth of the unsaturated zone. Through percussion drilling no contamination was found in the soil which was still not a true picture of the site. The absence of contamination in the percussion hole was caused by volatilization of the petroleum hydrocarbons which occurred during the drilling process. Therefore, it is clear that SVS, hand auger and percussion holes failed to reveal the extent of petroleum hydrocarbons in the unsaturated zone.

By looking at the failure of the above mentioned methods used during the investigation, drilling of several solid flight auger holes at different positions of the site would have been a better way of determining the vertical distribution of the petroleum contamination in the vadose zone. This is because solid flight auger does not require any fluid or compressed air which commonly alters the chemical condition in a soil media during drilling process. Solid flight auger is also easier to decontaminate which then avoid cross contamination when more than one hole is to be drilled.

Percussion drilling was needed to get the groundwater information (i.e., hydraulic parameters and quality). This is because the solid flight auger would not be able to penetrate through the basalt of the investigated site. A deep water table which was established during hydrocensus survey also necessitated a deep borehole at the site.

By considering a pump and treat system which was selected as a remedial technique at the site, it is clear that better results were obtained. Pump and treat system was compared with the VER or DPE (Vacuum Enhance Recovery or Dual Phase Extraction) method considering the site conditions. It was then found that VER could not work due to a deep clay in the vadose zone as well as deep water table, and this showed that a pump and treat system was the best method to be used for remediation purpose.

Based on the experience of petroleum contamination assessments a soil vapour survey is mostly the first method to be employed in order to map the petroleum vapour plume in the subsurface. However, this method depends on the type of product and permeability of the underlying soils. Out of 20 service stations where petroleum contamination assessments were conducted a soil vapour survey method could provide 95% of the true

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picture of the contamination in the unsaturated zone. The reason behind this might be the fact that:

- Investigations were done in a petrol contaminated sites which is associated with high volatile hydrocarbons.
- The investigation was restricted to the forecourt where the underlying material is mostly backfill which is then conducive for high vapour transportation.

By considering the SVS results from the case study it is clear that only one significant reading was mapped close to the underground petrol storage tank. This shows that the forecourt of the investigated site was composed of the clay soil which transports the vapours in a very low rate.

When it comes to remediation it is always a matter of looking at the site conditions more especially when dealing with petrol contamination. Based on the experience, it can be said that VER is mostly applicable in the areas where there is a shallow water table and high permeable geological formation. This is because in the process a vacuum which is injected in the subsurface is conducive for air flow through the geological formations. In general, there are a lot of remedial techniques that can be used for cleaning up the petroleum contaminated sites, but, they are all depending on the geological and geohydrological conditions of the sites as well as the physical and chemical composition of the contaminants.

Based on the preceding theory of multi-phase flow it can be seen from the case study that it was a petrol release which is less dense than water and is collectively named as LNAPL. The fact that LNAPL (petrol) is partially soluble in water it was seen from the case study where a dissolved phase concentration and free phase was measured in groundwater. In this case a three-phase flow occurred at the site namely, petroleum vapours in the unsaturated zone, free phase (petrol) floating on groundwater table as well as dissolved phase in the groundwater. Free product was measured in borehole RW1 using the Solinst interface instrument. Solinst interface meter uses an infra-red beam and detector in order to distinguish liquids.

Chapter 7 below outlined the steps that can be used to conduct petroleum contamination assessments in the geological conditions of South Africa.

CHAPTER 7. OUTLINE FOR THE DETECTION AND EVALUATIONS OF LNAPL'S UNDER SOUTH AFRICAN GEOLOGICAL CONDITIONS

Generally, the aquifers in most of the inland parts of South Africa can be classified as a fractured/secondary aquifer. This means that the water-bearing features of these rocks were developed through faulting, fracturing, mechanical and chemical weathering of the solid, consolidated parent rocks. Due to the latter the flow patterns in these geological units are irregular, complex and difficult to predict. Although the larger fractures, the so called preferred pathways, acts as conduits along which most of the flow takes place, the smaller cracks, fissures and openings in the matrix rocks are where the bulk of the water is stored in the aquifer.

At this stage the Department of Water Affairs and Forestry (DWAF) does not have a regulatory principles and frameworks for assessing the petroleum contamination in South Africa. There is currently a newly launched project which is focusing in the "*Remediation of the Contaminated Land and Water Resources-Policy and strategy*". This is a joint venture project between Water Affairs and Forestry and the South African Remediation Consortium (SARC). The Remediation Project is a Department of Water Affairs and Forestry (DWAF) initiative to develop a holistic and integrated approach to remediation with appropriate management tools in the form of policy, strategies, assessment methodologies, procedural guidelines and appropriate legislative and financial tools to facilitate proper and consistent remediation of contaminated land and degraded water resources in terms of the appropriate legislation (www.sa-remediation.co.za). The findings of this dissertation can contribute to the formulation of guidelines for South African conditions.

The other ways of keeping track of the extent of petroleum contamination in South Africa may be to set regulations where all the petrochemical industry and other potential occurrences of LNAPL submit an incident report to DWAF and DEAT (Department of Environmental Affairs and Tourism). This is because these two departments mostly get involved during the Environmental Impact Assessment (EIA) process for the proposed developments (i.e. Tank installations, building of services station etc.) and never keep track on the progress of those development after an EIA is approved. In other words

monitoring of the approved developments of which sometimes they are potential sources of LNAPL contamination is not taking place from the regulatory side at this stage. Therefore, if the petrochemical industries and service stations are forced to supply the department with the incident report and their monitoring program if available it will then help to locate areas where there is potential of groundwater contamination by the petroleum hydrocarbons.

The incident report should include and not limited to the following:

- The type of incident (i.e., overfill, leakage from under and above ground product storage tanks etc.)
- Date, volume and type of product lost
- Date that the incident was reported to the authorities (i.e., DWAF and DEAT)
- The name of the regulatory officer allocated to be responsible for the reported incident
- Mitigation strategies taken to mitigate the problem in question
- Name of the consulting firm if there was any hired to assess the extent of the problem in question.

In the case where a consulting firm is hired to conduct an assessment of the LNAPL contamination, there should be a close relationship with the officer allocated for the incident. In other words all the progress and pitfalls during the project should be reported to the officer in the form of report.

A detailed steps which may be used as a framework by both consulting firm and authorities (DWAF,DEAT) when detecting and evaluating the LNAPL contamination in the South African geological conditions are depicted in section 7.1 and 7.2 below.

7.1. Steps to be followed for detecting and evaluating the LNAPL contamination in the South African geological conditions

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┌─────────────────────────────────────────────────────┐
│              INITIAL SITE ASSESSMENT                  │
│ - Product and Infrastructure Information              │
│ - Interim Response                                    │
└─────────────────────────────────────────────────────┘
                          │
┌─────────────────────────────────────────────────────┐
│              ENVIRONMENTAL MEDIA                      │
│ -Geological and geohydrological information           │
└─────────────────────────────────────────────────────┘
                          │
┌─────────────────────────────────────────────────────┐
│              RBCA ASSESSMENT                          │
│ -Conducting Tier 1 analysis                           │
└─────────────────────────────────────────────────────┘
                          │
┌─────────────────────────────────────────────────────┐
│              DETAILED SITE ASSESSMENT                 │
│ -Soil vapour survey                                   │
│ -Drilling (hand and mechanical auger holes,           │
│  percussion holes)                                    │
│ -Sampling                                             │
└─────────────────────────────────────────────────────┘
                          │
       ┌──────────────────────────────────────┐
       │           RBCA ASSESSMENT            │
       │ -Conducting Tier 2 and Tier3 analysis │
       └──────────────────────────────────────┘
                          │
              ┌────────────────────┐
              │    REMEDIATION     │
              └────────────────────┘
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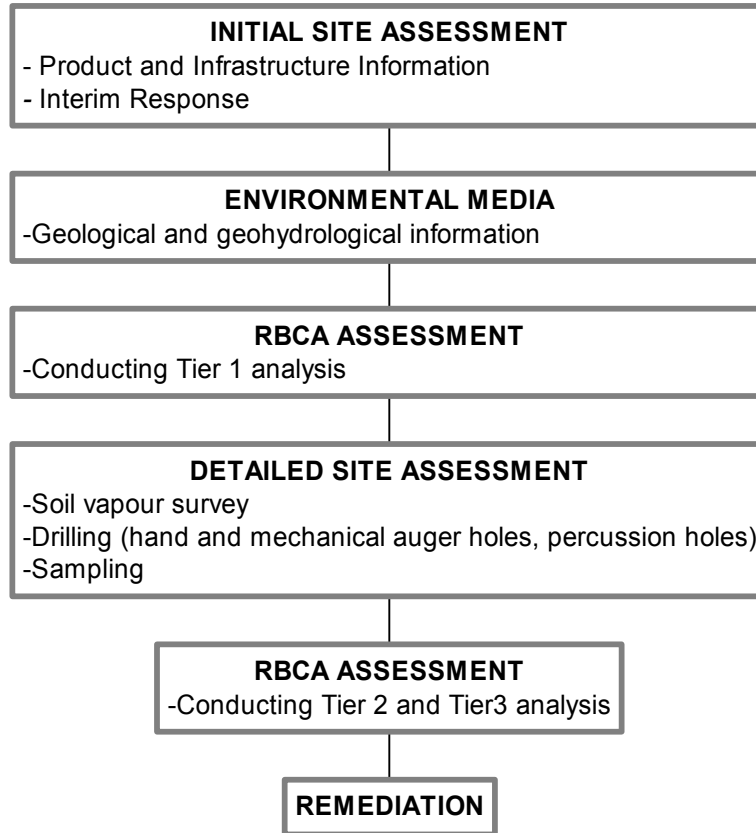
7.2. Detailed steps to be followed for detecting and evaluating the LNAPL contamination in the South African geological conditions.

INITIAL SITE ASSESSMENT

PRODUCT AND INFRASTRUCTURE INFORMATION

- Date, volume and type of product spilled and or leaked
- Description of the site (i.e., forecourt conditions, surface stains etc)
- History of the site
- Information about the tank installation (i.e., age, above or underground tanks, installed depth of the tanks, tank manholes, filler points, pipelines, dispensers, secondary containment and the type of pumps used).
- Local infrastructure (i.e., Telkom lines, sewer lines, water reticulation, power lines and storm water system)
- Interim Response (*i.e., if the leakage occurred at the site where there are basements and lifts in the vicinity, it is therefore important to measure the explosive level of the vapours. Should the vapours in the lifts exceed the maximum allowable explosive level the lifts should be stopped and make use of the stairs, which are available to cater the emergency cases*).

ENVIRONMENTAL MEDIA (i.e., Soil, Air and Water)

- Local geological and the geohydrological information.
- Topography and the drainage direction at the site
- Conducting the hydro census survey within one to two kilometer radius of the investigated site in order to identify the nearby boreholes (i.e., position, water use and water level) and surface water bodies.
- Groundwater sampling from the identified boreholes and analysis for the constituents of concern depending on the type of product released at the site.
- Conducting the intrusive investigation in the unsaturated zone (near surface zone) through hand auger drilling at the identified source. This helps to determine the vertical extent of petroleum contamination at the source.
- Soil and groundwater sampling if groundwater intercepted during hand auger drilling and analysis for the constituents of concern. Soil and water samples should be representative of the source.

RISK ASSESSMENT

- Risk Based Corrective Action can be used to assess the risk at the site, which is associated with the absorbed (soil) and dissolved (water) phase petroleum hydrocarbons.
- The source (i.e., leaking underground tank), risk exposure pathways (air, soil and groundwater) and receptors (residents, workers, river etc) should be well defined in order to be able to assess the risk. Example, if there are no receptors at the site, it then means that the risk level is acceptable at that time (in other words the *source*, *risk exposure risk pathway* and *receptors* should be defined in order to have representative risk assessment).
- Although the EPA calls for the average exposure, the highest concentrations of both soil and water samples collected at the source have to be entered into the Tier 1 Risk Based Screening Level (RBSL) in order to determine the worst case risk scenario at the site. If the Tier 1 level is exceeded by the petroleum constituents of concern, more detailed site assessment (Tier2) is then the second option in order to gather the site specific parameters at the site. Note that all the tiers (i.e., tier 1, tier 2 and tier 3) should achieve the same level of the protectiveness. The protective level refers to the level, which is between the acceptable and non-acceptable risk.

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DETAILED SITE ASSESSMENT

- Conducting Soil Vapour Survey (SVS) in order to determine the lateral extent of petroleum contamination and using the SVS results to decide on the drilling positions.
- The non-intrusive technique like geophysical survey (Magnetic and Electro magnetic method) can be conducted depending on the site conditions (i.e., Geophysical survey is not feasible in urban areas or at the site which is enclosed by the building, and other related infrastructures). The purpose of geophysical survey is to determine the geological structures at the site (i.e. dyke, sills and fault), which can be regarded as the preferential pathways (fractures at the contact zone of the dyke and the intruded formation) or barrier (i.e. fresh dolerite dykes) of the contamination.
- Conducting the unsaturated and saturated intrusive investigation through drilling at the positions determined by the soil vapour and geophysical survey results.
- Soil sampling at different depth in order to determine the vertical extent of the petroleum contamination.
- Conducting slug and pump test in order to determine the hydraulic parameters, such as, the saturated hydraulic conductivity and transmissvity etc.
- Groundwater sampling for the analysis of the petroleum constituents of concern (i.e., Gasoline Range Organic, Diesel Range Organic).
- Gathering the site-specific parameters of the site (i.e. porosity of the formation, hydraulic gradient, velocity of the groundwater, the chemical and physical properties of the contaminant), which play a role in the transportation of the contaminant to a point of exposure.

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DETAILED SITE ASSESSMENT (CONTINUE)

- Conducting the Tier 2 risk assessment in order to protect the human health due to the exposure at the source zone or at separate points of exposure. If the concentration levels of both soil and water sample still exceed the Tier 2 RBSL, then Tier 3 have to be done using the detailed site specific data on transport mechanism and receptors.

- The Tier 3 evaluation is usually done in order to refine the Tier 2 corrective action goals on. This involved more detailed site information and numerical modeling. Note that the Tier 3 evaluation provides the source zone cleanup levels designed to protect against health or environmental impacts at a site-specific POE (point of exposure).

- Design remedial technique in order to cleanup the LNAPL contamination in question. Note that the remedial techniques have to be selected based on the type of chemical properties of the product and the physical environment (i.e., geohydrological condition at the site. For example, a "*Soil Vapour Extraction*" (SVE) cannot be conducive in a predominantly clay environment simply because the clay soil is less permeable).

- The *pump and treat*, *bioventing*, *vacuum enhanced recovery* (VER), *natural attenuation* (in situ clean up technique), *soil washing* and *soil excavation* and *land farming* (ex situ clean up technique) is some of the remedial technique that can be used to address the LNAPL contamination.

- Long term monitoring network should be in place in order to monitor both free product and the dissolved phase petroleum hydrocarbons overtime. The monitoring network should be set in such a way that the source, up and down gradient information regarding the contamination is gathered. Monitoring should continue up till the groundwater concentrations levels are not harmful to the receiving environment. At this stage DWAF do not have the water quality standards for the petroleum hydrocarbons. Therefore, this necessitated a need to research on the water quality standards for human consumption, aquatic and associated ecosystem in South Africa with regard to the petroleum hydrocarbons.

RBCA approach is currently allowed by DWAF to be used in assessing the petroleum contamination until they develop their own risk assessment protocols (Naidoo, 2004. Personal communication).

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In order to avoid and/or minimize the LNAPL groundwater contamination in South Africa there should be:

- An inter-departmental collaboration as well as reporting incidents and progress reports to both DWAF and DEAT. This means that there should be a close relation between the departments as well as the consistency when it comes to the frameworks of assessing the groundwater contamination. Petrochemical industries and consultants should supply the authorities with the incident report (i.e., leaking underground petrol tank etc.) which include all the actions taken to mitigate the problem in question. The progress and pitfalls should be forwarded to the authorities in the form of report.

- An acceptance of some interim standard/approach for evaluating and monitoring the contamination. Consultants should always keep in touch with the authorities in order to be able to know if there is any interim approach developed to be used for conducting contamination assessments.

- A long-term formulation of guidelines for South Africa (i.e., minimum requirements or best practice guidelines for dealing with LNAPL contamination). DWAF should develop guidelines for assessing LNAPL contamination, risk assessment protocols as well as the water quality standards with regard to the petroleum contamination. As soon as these guidelines are developed the consultants should then conduct their investigation in line with the guidelines.

CHAPTER 8.   CONCLUSIONS AND RECOMMENDATIONS

8.1. Conclusions

Based on the theoretical research the following conclusions can be made:

- The petroleum refineries, oil and solvent recycling, miscellaneous and service stations are the occurrence and main potential sources of LNAPL contamination in urban areas of South Africa.

- Groundwater contamination in urban areas arise from the production, use and storage of hazardous chemicals, accidental spill of chemicals during use and transportation, transportation of   chemicals through underground pipelines and leakage and or spillage of product from the above and underground petroleum storage tanks.

- Some of the organic contaminants from common polluting petrochemical industries (*Enref, Calref, Secunda, Mossgas and Sapref*) are aliphatic hydrocarbons such as *ethylene, propylene, and butylene* and aromatic hydrocarbons such as *benzene, toluene, styrene, xylene, ethyl benzene*, made from refined petroleum or liquid hydrocarbons. Generally these hydrocarbons are collectively known as Light Non Aqueous Phase liquids (*LNAPLs*) due to their specific density, which is less than the density of water.

- The fundamental principles which are governing the multi-phase flow in porous media include the saturation ratio, interfacial tension, wettability, capillary pressure and relative permeability. Two-phase flow may occur below the water table with water and a DNAPL while Three-phase flow may occur in the vadose zone with air, water and an LNAPL.

- Light Non- Aqueous Phase Liquids (LNAPL) are less dense than water, If small volumes of a spilled gasoline enter the vadose zone (unsaturated zone), the LNAPL will flow through the central portion of the unsaturated pores until residual saturation is reached. Residual saturation is the volume of discontinuous immobile liquid contaminant per unit void volume.

- If large volumes of LNAPL are spilled, the LNAPL flows through the pore space to the top of the capillary fringe of the water table. Dissolved constituents of the LNAPL precede the less soluble constituents and may

change the wetting properties of the water, causing a reduction in the residual water content and a decrease in the height of the capillary fringe.

- Since LNAPLs are lighter than water, they will float on top of the capillary fringe. As the head formed by the infiltrating LNAPLs, the water table is depressed and the LNAPLs accumulate in the depression. If the source of the spilled LNAPLs is removed or contained; LNAPLs within the vadose zone continue to flow under the force of gravity until reaching residual saturation.

- The migration of LNAPLs is governed by the physical Properties (i.e. *Density, viscosity, water solubility, octanol-water partition coefficient (K_{ow}), vapour pressure and Henry's law constant).*

- The LNAPL migration rate can also be governed by the chemical reactions which slow movement of contaminants in an aquifer (i.e. *adsorption, ion exchange and partitioning into organic matter or organic solvents*.); and this effect is termed *Retardation*.

- LNAPL contamination can be detected and evaluated by using the pedestrian survey, geophysical survey, Soil Vapour Survey, soil and groundwater sampling method.

- Under natural conditions, transport of the subsurface vapour phase is mainly by diffusion, which is primarily the result of a concentration gradient. Therefore, the most important subsurface factors which affect in-situ soil vapour measurements are *soil permeability, presence of methane of natural origin, type of contaminant, age of contaminant, zoning and age of contaminant, surface contamination, soil moisture and soil temperature*.

- Risk Based Corrective Action (RBCA) is a decision-making process for assessment and response to subsurface contamination associated with petroleum hydrocarbon releases.

- Risk Based Corrective Action can be used by addressing any step in the exposure process such as removing or treating the source, interrupting contaminant transport or controlling activities at the point of exposure.

- To provide an economical use at both small and large facilities, the RBCA process has been designed to match the site evaluation effort to the relative risk or complexity of each site. For this purpose, a tiered approach (tier1, 2 and 3) is employed for determination of risk-based cleanup goals, involving increasingly sophisticated levels of data collection and analysis. Upon

completion of each sequential tier, the user reviews the results to determine whether further data collection and evaluation is warranted.

- Tier 1 of the RBCA process involves comparison of site constituent concentration to generic Risk Based Screening Levels (RBSLs) to determine whether further evaluation is required. Under Tier2, Site-Specific Target Levels (SSTLs) for soil and groundwater cleanup goals are determined on the basis of site-specific information and/or points of exposure. If Tier 2 results are judged inappropriate or impracticable, a Tier 3 evaluation can be conducted to refine Tier 2 corrective action goals on the basis of a more complex risk and exposure assessment, involving more detailed site information, probabilistic data analysis, and/or numerical fate and transport modeling.

Based on the results of the case study the following conclusions can be made:

- Petroleum pollution assessment was conducted at a service station after a complaint was raised by a resident who found free product (petrol) in her borehole. The contaminated borehole was located down gradient at a distance of approximately 100m southwest of the service station. The underground fuel storage tanks and associated infrastructure were pressure tested and no obvious leaking tanks were found. The source of the free product was due to an overfill that took place during the filling of the underground premium petrol storage tank.

- A hydro census survey was conducted in a one-kilometer radius of the site in order to find boreholes and gather information on the depth to groundwater, groundwater quantity and quality and possibly drilling data that could help in describing the aquifer system of the site.

- Soil vapour survey (SVS) was conducted at the service station by making use of Ecoprobe 4 PID instrument in order to determine the lateral extent of the volatile organic compounds (in vapour phase) and outlining the areas where the vertical distribution of petroleum contamination has to be determined.

- The highest vapour VOC concentration of 7ppm was detected down gradient of the dispensers. Based on the geology of the site, which comprised of predominantly clay (*residual of chemical weathered basalt*) it is therefore evident why not much of the VOC were. This is because clay soils are less permeable resulting in low transportation rate of petroleum vapours.

- Hand auger and percussion holes were drilled at the site in order to determine the vertical distribution of contamination. Slight petroleum smell was observed from the hand auger holes, while slight to no smell was observed in the percussion hole. This was probably due to the volatilization of hydrocarbons during the percussion drilling process. The percussion borehole was comprised of clay in the first 18m and weathered basalt up till 55m. Groundwater was struck at the depth of 27m.b.g.l and 48m.b.g.l, respectively. Percussion hole was equipped with a 1 meter plain PVC casing (**P**oly-**V**inyl-**C**hloride), 54m perforated PVC casing, bentonite seal and gravel pack.

- Immediately after drilling a percussion borehole a groundwater sample was taken using a transparent PVC bailer and a layer of free product was observed. Groundwater samples were also collected from borehole *PW1, PW2, PW3, and PW4* that were identified during the hydro census survey for the dissolved phase hydrocarbons (Gasoline Range Organic) analyses and free product measurements. No free product (Petrol) was found in borehole *PW1, PW2, PW3 and PW4* during sampling series 1,2,3,4 and 5.

- Significant benzene and toluene concentrations were found in water sample PW1 and PW3 during sampling series 1, 2, 3, 4 and 5. Seasonal effect was observed in sampling series 4 which was done during wet season and this caused the dilution of the contamination.

- No detectable levels of petroleum hydrocarbons were found in any of the soil samples taken at the site.

- Free product (Petrol) with the thickness of 3 meters was measured in borehole RW1 using Solinst interface meter three months after the hole was drilled. Free product (Petrol) was also found in borehole PW2 and PW5 which is located at a distance of approximately 200m and 60m down gradient of the service station, respectively. The presence of free product in these boreholes confirmed the down gradient migration of contamination plume from the service station.

- Based on the results of SVS, groundwater sampling and free product measurements it is clear that a three-phase flow occurred at the site namely, a petroleum vapours in the unsaturated zone, free phase (petrol) floating on groundwater table as well as dissolved phase in the groundwater.

- Purged samples showed high levels of BTEX as compared to the bailing sample. This was due to the fact that a purged sample is representing the formation water while bailing only tap the stagnant water in the borehole.

- As part of the risk assessment the primary source at the service station was addressed by removing the old aged fuel storage tanks and replaced with the new ones. Soil vapour survey, soil and groundwater sampling was conducted and revealed the secondary sources to be the *affected surface soils (<1m), affected subsurface (>1m), dissolved groundwater plume and free phase plume*. The potential transport media for the contaminants at the site were found to be the soil (through *leaching to groundwater*) and groundwater (through *dissolved or free phase plume migration*).

- The exposure pathway of concern in the investigated site was soil, air and groundwater. The late transmissivity value of 14.49m^2/d was estimated from the pump test data that were captured into the **Flow Characteristic Method.** The saturated hydraulic conductivity was then calculated from the assumed aquifer thickness of 30m.

- Based on the calculated sorption coefficient and the retardation factors it is clear that sorption and retardation of the petroleum hydrocarbons was expected to occur at the investigated site. Based on the laboratory results of the samples that were collected from the down gradient boreholes it was evident that benzene was the least compound to be retarded as compared to the concentration levels of toluene and xylene. This is because high concentration of benzene was detected in the down gradient holes during all the sampling series as compared to toluene and xylenes.

- A Tier 1 Risk Based Screening Levels was triggered by the chemical results of water sample PW1 and PW3 for the risk values of *carcinogenic, hazard quotients and maximum contaminant level* through the a risk exposure pathways of *groundwater ingestion, volatilization to indoor and outdoor inhalation*.

- BP RISC software was used as an alternative method for conducting Tier 2 analysis. The maximum groundwater concentration of 4.52E-01mg/L was modeled to occur in a receptor borehole after 70 years. The calculated carcinogenic risk in groundwater is above the range of 1 in 1000 000, it is then obvious that carcinogenic risk does exist through the groundwater

ingestion pathway and identified receptors. The calculated hazard quotient is also below 1, it is therefore expected that a non-carcinogenic risk does not exist through the identified pathways and receptors.

- Pump and treat system was implemented in borehole RW1, PW2 and PW3 pumping at a rate of 0.75L/s, 0.2L/s and 0.3L/s, respectively.

- Free products was recovered in one year in borehole PW2 and PW5 after commencing with a pump and treat system, while in borehole RW1 it was recovered in two years time.

- No detectable levels of the dissolved phase hydrocarbons were found in borehole PW1, PW2, and PW3 during Jan 00, Oct 01, Mar 02, Oct 02, Mar 03 and Oct 03.The absence of the dissolved phase petroleum hydrocarbons in borehole PW1, PW2 and PW5, which are located down gradient of the service station confirm that the contamination plume was contained through pump and treat system.

- Due to the lack of South African regulations with regard to petroleum contamination, pump and treat system has been stopped as soon as the product was recovered within the boreholes and commence with monitoring of the dissolved phase hydrocarbons.

- Based on the results of the case study it was learnt that information about the volume, period and type of product that spilled and/or leaked should be available in order to have a good approach of assessing the LNAPL contamination. The site condition, physical and chemical properties of the contaminants is also some of the governing factors when it comes to the selection of the approach of assessing the petroleum contamination. It was also learned that enough budget should always be available in order to be able to gather representative information of the contamination in question.

8.2. Recommendations

Based on the findings of this research, the results of the case studies and theoretical models it becomes obvious that there is a need for further research, as recommended below:

- From the launched project Department of Water Affairs and Forestry have to establish the guidelines of assessing the petroleum contamination, formulation of the water quality standards with regard to petroleum hydrocarbons and finally generate the law which will then enforce the petroleum industry to allocate enough budgets for environmental management in South Africa.

- The authorities (i.e. DWAF, DEAT) have to be fully involved during the investigation of the petroleum contamination since their involvement can then help in the disclosure of the research findings to the interested and affected parties. This is because most of the contamination which induced in the groundwater environment ends up with the negative impacts to the public.

- An environmental awareness should be implemented in order to make the public aware of the petroleum contamination in the subsurface environment. The public should know where to report whenever they notice petroleum contamination in their boreholes, more especially those who depends on groundwater for domestic and other use. This awareness can be done through workshops, by simply inviting the public as wells as knowledgeable people who can then discuss the issue of petroleum contamination in the subsurface focusing on its detrimental consequences to the environment.

- In terms of risk-based approach, DWAF accepts RBCA until South African risk assessment protocols are developed (*Naidoo, 2004, Personal Communication*). This should be communicated to all officials likely to deal with petroleum risk assessment. Eventually, DWAF should write an official protocol about the acceptance of RBCA so that there is consistency until South African risk-based approach has been established.

In order to avoid and/or minimize the LNAPL groundwater contamination in South Africa there should be:

- An inter-departmental collaboration as well as reporting incidents and progress reports to both DWAF and DEAT. This means that there should be a close relation between the departments as well as the consistency when it comes to the frameworks of assessing the groundwater contamination. Petrochemical industries and consultants should supply the authorities with the incident report (i.e., leaking underground petrol tank etc.) which include all the actions taken to mitigate the problem in question. The progress and pitfalls should be forwarded to the authorities in the form of report.

- An acceptance of some interim standard/approach for evaluating and monitoring the contamination. Consultants should always keep in touch with the authorities in order to be able to know if there is any interim approach developed to be used for conducting contamination assessments.

- A long-term formulation of guidelines for South Africa (i.e., minimum requirements or best practice guidelines for dealing with LNAPL contamination). DWAF should develop guidelines for assessing LNAPL contamination, risk assessment protocols as well as the water quality standards with regard to the petroleum contamination. As soon as these guidelines are developed the consultants should then conduct their investigation in line with the guidelines.

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APPENDICES

Appendix A: U.S.EPA-Recommended Sampling Protocols

Appendix B: Borehole Log

Appendix C: Unsaturated hydraulic conductivity

Appendix D: FC- Method (Data sheet and T-value estimation)

Appendix E: Tier 1 Risk Based Screening Levels (RBSLs)

Appendix F: Summary of output of fate and transport model for benzene

Appendix G: Results of petroleum hydrocarbons during monitoring of pump and treat system (mg/L)

APPENDIX A

U.S.EPA-Recommended Sampling Protocols

| Analytical Parameter | Analytical Method (s) | Media | Sample container[a] | | Preservatives[c] | Holding time |
			Volume	Type		
TPH[b]	EPA 418.1 (IR)	Water	1 liter	Glass jar with Teflon lined cap	Acid fix pH<2; Cool to 4°C	Extract in 7 days; analyse in 40 days
	GC/FD	Soil	125 mL	Wide mouth glass with Teflon lined cap	Cool to 4°C	Extract in 7 days; analyse in 40 days
Volatile Petroleum Hydrocarbons (VPH)[d]	Various	Water	40 mL	Glass vial with Teflon lined septum	Acid fix pH<2; Cool to 4°C	14 days
		Soil	40 mL	Glass vial with Teflon lined septum	Cool to 4°C[e]	14 days
Extractable Petroleum Hydrocarbons[f]	Various	Water	1 liter	Glass jar with Teflon lined cap	Acid fix pH<2; Cool to 4°C	Extract in 7 days; analyse in 40 days
		Soil	60 mL	Wide mouth glass with Teflon lined cap	Cool to 4°C	Extract in 7 days; analyse in 40 days

BTEX	EPA 8240/8260[h]	Water	40 mL	Glass vial with Teflon lined septum	Acid fix pH<2; Cool to 4°C	14 days
	EPA 624[g], EPA 602[g]	Soil	40 mL	Glass vial with Teflon lined septum	Cool to 4°C	14 days
PAHs	EPA 8270[h] EPA 8310[h]	Water	1 liter	Glass vial with Teflon lined septum	Acid fix pH<2; Cool to 4°C	Extract in 7 days; analyse in 40 days
	EPA 8100[h]	Soil	60 mL	Wide mouth glass with Teflon lined cap	Cool to 4°C	Extract in 7 days; analyse in 40 days

[a] Minimum sampling volume may vary depending on specific method.

[b] Refers to extractable hydrocarbons only

[c] ACID FIXATION: use 1:1 HCL to adjust pH of aqueous samples to less than 2. Add approximately 2-4 drops to 40 mL aqueous sample vials; 5 mL to 1 liter aqueous sample jars. Add cid to vials before collecting sample. Other preservative, such as sulfuric acid or sodium bisulfate may also be used for this purpose.

[d] Generally C_5 through C_{10} hydrocarbons detectable through purge and trap or headspace analytes; includes most "Gasoline Range Organics" (GRO) methodologies.

[e] Some methodologies require field preservation of soil samples methanol. In such cases, methanol must be purge and trap grade; typically, add 20mL methanol to vials prior to sample collection. Use gloves and eye protection when sampling.

[f] Generally; C_9 through C_{28} hydrocarbons detectable through a solvent extraction process; includes most "Diesel Range Organics" (DRO) methodologies.

[g] 40 CFR Part 136

[h] SW-846 methodology

APPENDIX B

Borehole Log

Borehole Construction and Geological Log

Date compiled: 04/10/22

BASIC SITE INFORMATION: *Site Identifier:*   **Number:** RW1   *Site type:* Borehole
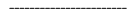
Distr./Farm No.:	*Site Name/Des.:*
Region Type:	*Region Descr.:*

Y Coord. [m]:	-37583.95	*Reg./BB.:*	*Topo-set.:*	*Depth [m]:* 55.00
X Coord. [m]:	2863039.87	*G-Nr.:*	*Site status:*	*Col. ht. [m]:*
Altitude [m]:			*Site purp.:*	*Diam. [mm]:* 165
Coord. acc.:	Accurate to within 10 000 units		*Use applic.:*	*Drain. reg.:*
Coord. meth.:			*Equipment:*	*Rep. inst.:*

Coordinate System: South African LO Transverse Mercator, WGS 1984

Construction and Geohydrological Legend

Hole	165 → Hole diameter [mm]		Bentonite or clay
Casing(plain /perforated, sloted)	← 152 Casing diameter [mm]		Gravel (> 2mm)
Screen/ Mesh Screen	▼ Waterlevel with date meas.		
Piezometer	0:50 → Piezometer (Nr. & Diameter [mm])		

Construction

Lithology

CLAY: Brownish, Red; CLAY;

SAND AND SILT: Light, Brown; SILTY SAND;

BASALT: Green, Weathered, Weathered; WEATHERED BASALT;
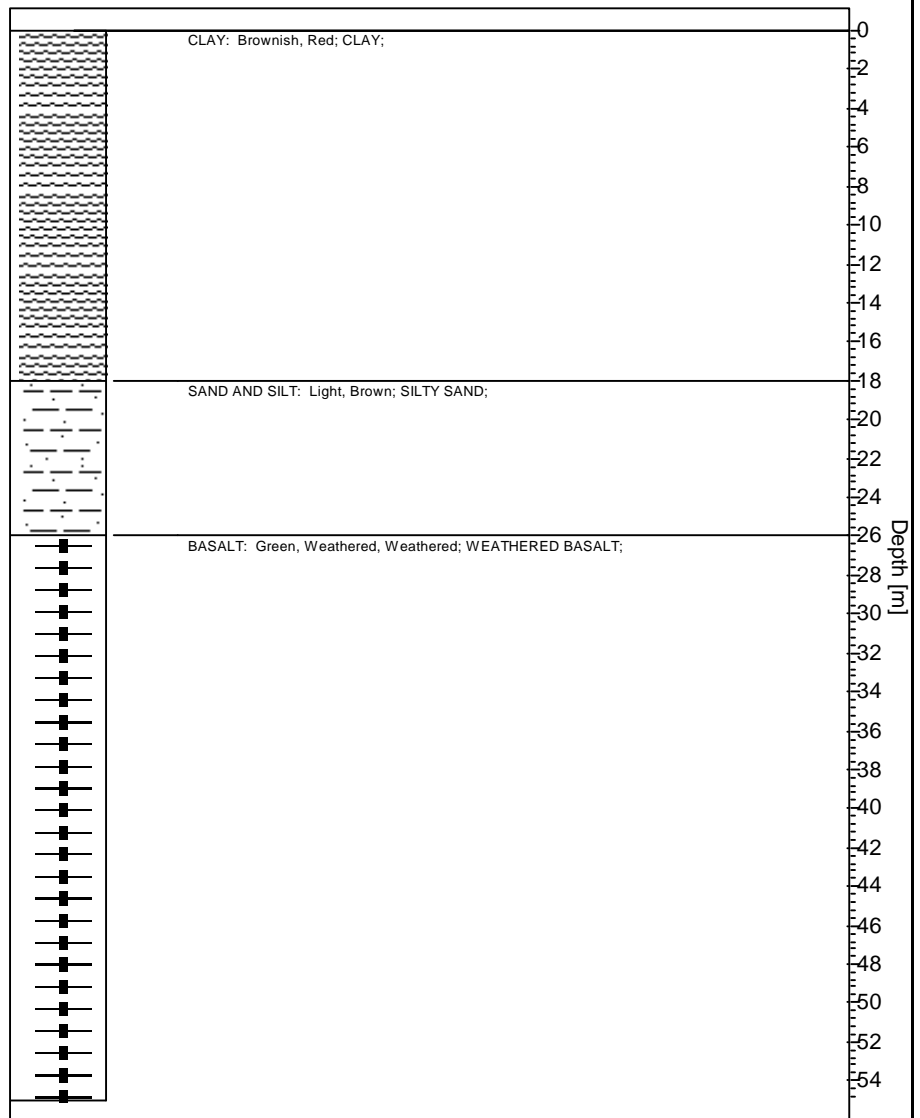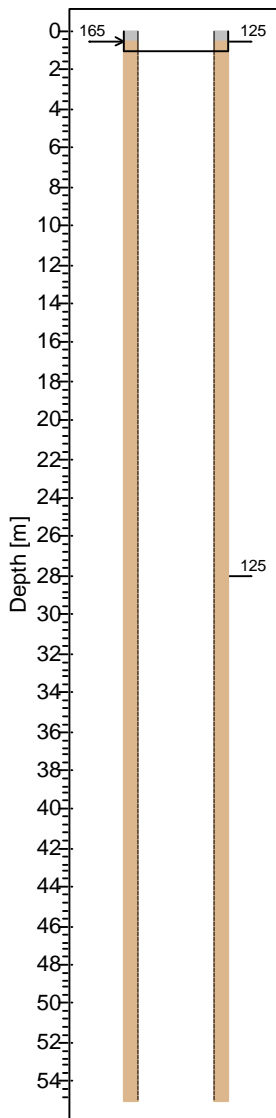
COMMENT:

User name and adress

Page 1

APPENDIX C

Unsaturated hydraulic conductivity

DETERMINATION OF SOIL HYDRAULIC PARAMETERS

d10	0.060	Temperature [ºC]	20		d[mm]	sum %
d20	0.015	Sample No.	SS1		4.750	100
d30	0.200	Depth of sample	2.5m		2.000	97.8
d40	0.280				0.500	94.4
d50	0.320				0.250	91.8
d60	0.400	Gravel (%)	2.2		0.106	88.1
d70	0.480	Sand (%)	12.4		0.050	85.4
d80	0.700	Silt (%)	28.1		0.020	77.8
d90	1.200	Clay (%)	57.3		0.002	57.3
d100	2.000					

USDA Classification   **Clay**
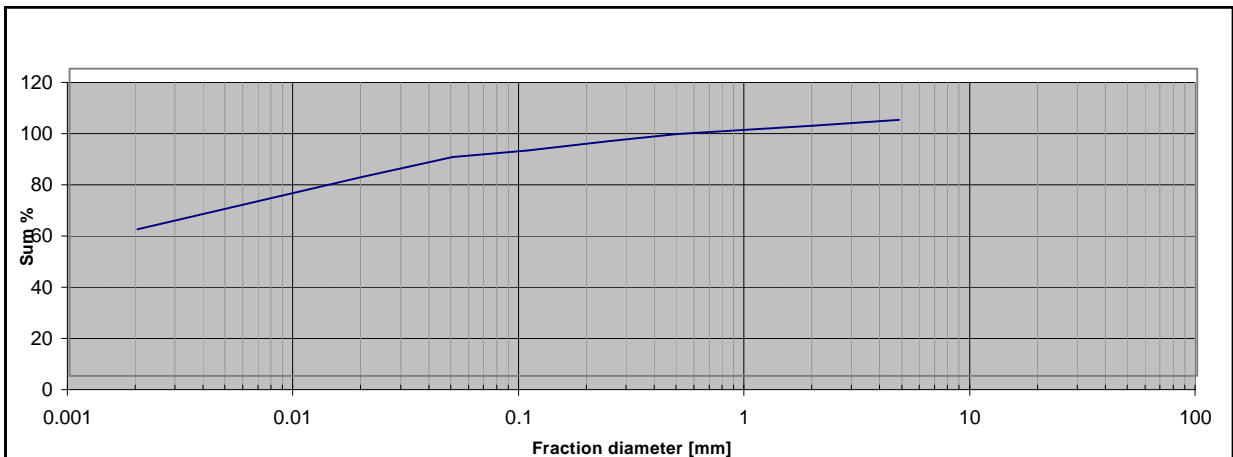
Compaction	Porosity	K [m/day]	Swr	Hce	Pore size distr.
Medium	0.3	8.32E-08	7.50E-02	5.634	2.08E-02

Swr   *Residual water saturation*
Hce   *Air entry head*

DETERMINATION OF SOIL HYDRAULIC PARAMETERS

d10	0.060	Temperature [ºC]	20			
d20	0.015	Sample No.	SS2		d[mm]	sum %
d30	0.200	Depth of sample	1m		4.750	100
d40	0.280				2.000	97.7
d50	0.320				0.500	93.5
d60	0.400	Gravel (%)	2.3		0.250	86.8
d70	0.480	Sand (%)	20.3		0.106	80.3
d80	0.700	Silt (%)	16.5		0.050	77.4
d90	1.200	Clay (%)	60.9		0.020	72.3
d100	2.000				0.002	60.9

USDA Classification   **Clay**
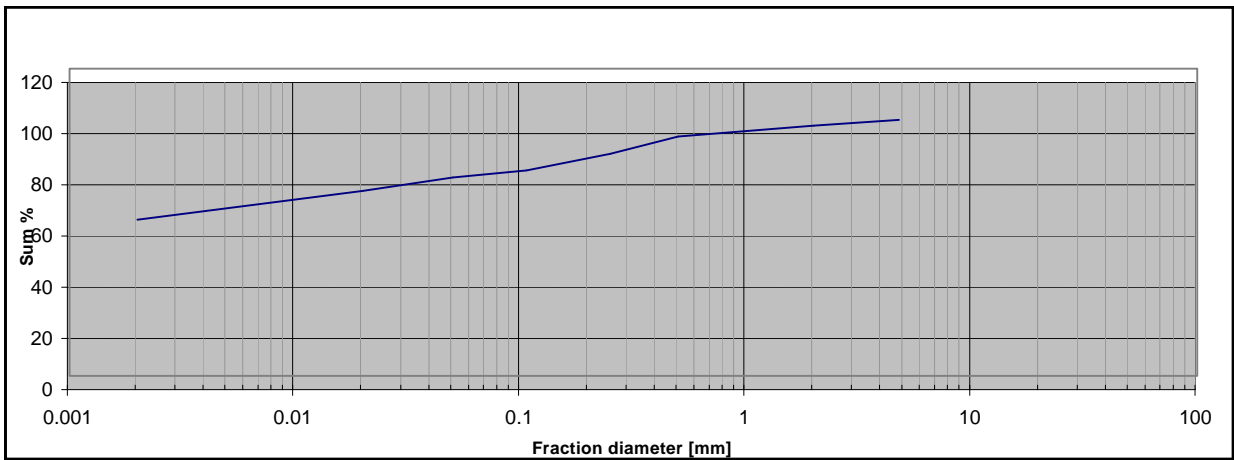
Compaction	Porosity	K [m/day]	Swr	Hce	Pore size distr.
Medium	0.3	4.66E-08	5.12E-02	5.067	1.60E-02

Swr   *Residual water saturation*
Hce   *Air entry head*

DETERMINATION OF SOIL HYDRAULIC PARAMETERS

d10	0.060	Temperature [ºC]	20		
d20	0.015	Sample No.	SS4	d[mm]	sum %
d30	0.200	Depth of sample	2.25m	4.750	100
d40	0.280			2.000	97.9
d50	0.320			0.500	93.3
d60	0.400	Gravel (%)	2.1	0.250	90.6
d70	0.480	Sand (%)	14.5	0.106	86.9
d80	0.700	Silt (%)	25.2	0.050	83.4
d90	1.200	Clay (%)	58.2	0.020	76.1
d100	2.000			0.002	58.2

USDA Classification   **Clay**
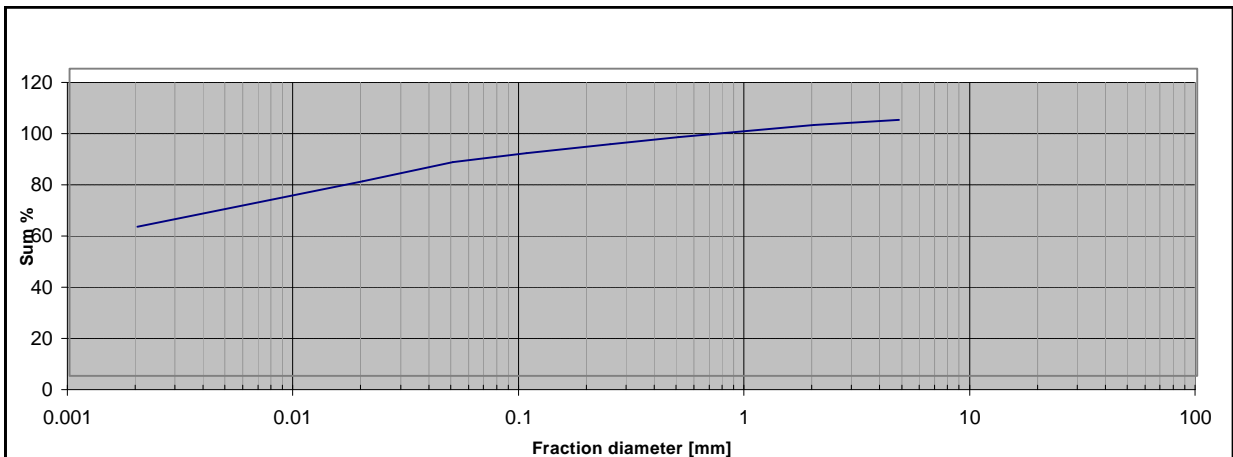
Compaction	Porosity	K [m/day]	Swr	Hce	Pore size distr.
Medium	0.3	6.58E-08	6.65E-02	5.554	1.91E-02

Swr   *Residual water saturation*
Hce   *Air entry head*

DETERMINATION OF SOIL HYDRAULIC PARAMETERS

d10	0.060	Temperature [ºC]	20		d[mm]	sum %
d20	0.015	Sample No.	RW1		4.750	100
d30	0.200	Depth of sample	10m		2.000	98.6
d40	0.280				0.500	98.5
d50	0.320				0.250	96.9
d60	0.400	Gravel (%)	1.4		0.106	82.7
d70	0.480	Sand (%)	29.5		0.050	69.1
d80	0.700	Silt (%)	42.9		0.020	53.2
d90	1.200	Clay (%)	26.2		0.002	26.2
d100	2.000					

USDA Classification   **Loam**

Compaction	Porosity	K [m/day]	Swr	Hce	Pore size distr.
Meduim	0.3	1.17E-03	0.2733	1.422	2.33E-01

Swr   *Residual water saturation*
Hce   *Air entry head*

DETERMINATION OF SOIL HYDRAULIC PARAMETERS

d10	0.060	Temperature [ºC]	20		
d20	0.015	Sample No.	RW1	d[mm]	sum %
d30	0.200	Depth of sample	12m	4.750	100
d40	0.280			2.000	99.3
d50	0.320			0.500	92.9
d60	0.400	Gravel (%)	0.7	0.250	89.6
d70	0.480	Sand (%)	18.4	0.106	85.2
d80	0.700	Silt (%)	27.6	0.050	80.9
d90	1.200	Clay (%)	53.3	0.020	72.9
d100	2.000			0.002	53.3

USDA Classification   **Clay**
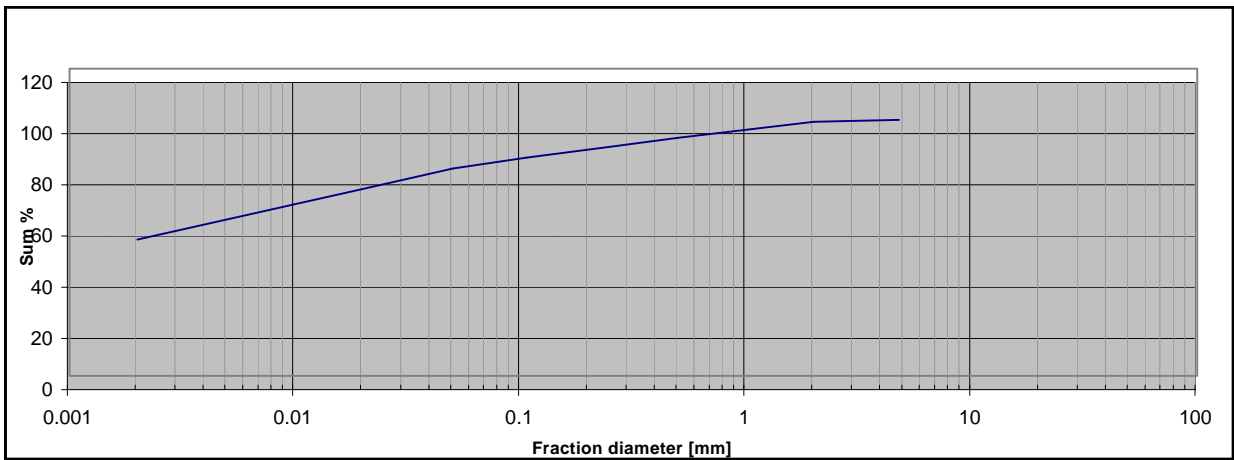
Compaction	Porosity	K [m/day]	Swr	Hce	Pore size distr.
Medium	0.3	4.79E-07	0.1357	4.478	3.16E-02

Swr   *Residual water saturation*
Hce   *Air entry head*

DETERMINATION OF SOIL HYDRAULIC PARAMETERS

d10	0.060	Temperature [ºC]	20	
d20	0.015	Sample No.	RW 1	d[mm] sum %
d30	0.200	Depth of sample	17m	4.750 100
d40	0.280			2.000 98.7
d50	0.320			0.500 97.3
d60	0.400	Gravel (%)	1.3	0.250 89.2
d70	0.480	Sand (%)	44.8	0.106 66.7
d80	0.700	Silt (%)	38.8	0.050 53.9
d90	1.200	Clay (%)	15.1	0.020 36.6
d100	2.000			0.002 15.1

USDA Classification   Loam
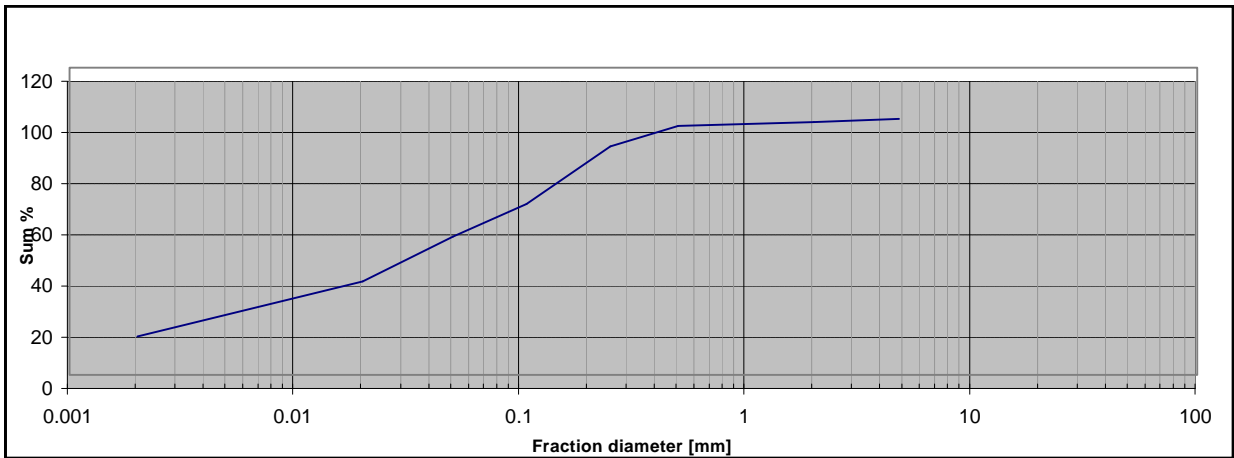
Compaction	Porosity	K [m/day]	Swr	Hce	Pore size distr.
Medium	0.3	1.56E-02	0.2387	0.6136	3.81E-01

Swr   *Residual water saturation*
Hce   *Air entry head*

DETERMINATION OF SOIL HYDRAULIC PARAMETERS

d10	0.060	Temperature [ºC]	20		d[mm]	sum %
d20	0.015	Sample No.	RW 1		4.750	100
d30	0.200	Depth of sample	21m		2.000	98.8
d40	0.280				0.500	86.8
d50	0.320				0.250	61.3
d60	0.400	Gravel (%)	1.2		0.106	40.1
d70	0.480	Sand (%)	67.5		0.050	31.3
d80	0.700	Silt (%)	21.4		0.020	23.1
d90	1.200	Clay (%)	9.9		0.002	9.9
d100	2.000					

USDA Classification   **Medium Sandy Loam**
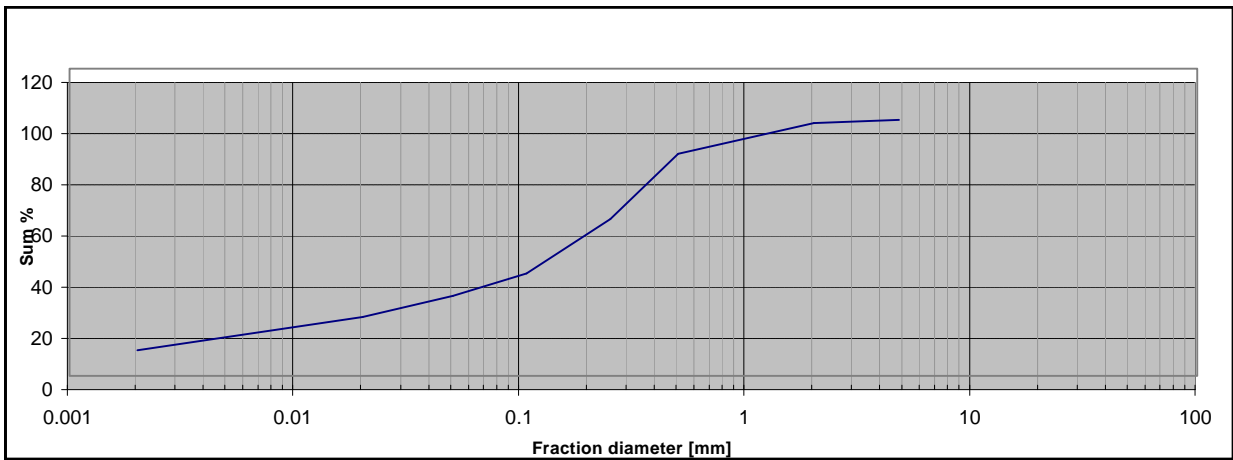
Compaction	Porosity	K [m/day]	Swr	Hce	Pore size distr.
Medium	0.3	1.45E-01	0.2287	0.2416	4.67E-01

Swr   *Residual water saturation*
Hce   *Air entry head*

APPENDIX D

FC- Method (Data sheet and T-value estimation)

Country:	SA		Geology:	Basalts
Region:	North		Depth of BH:	55
Owner:	Service Station		Water strikes:	48
X-coord:			Date of Test:	1999
Y-coord:			Contractor:	

CONSTANT RATE TEST DATA :enter values in cells which are coloured light yellow

Borehole:	RW1										Other info:
Distance from Rest WL to main water strike (m) =	27	S_{max}=	1.33	Recom. AD =	6.0						
Q (l/s)=	0.33			Recovery data							T (m^2/d) : Logan eq.
t (min)	s (m)	avg s'	avg s''	avg T	avg S	Time t'	Res_s	t/t'	WI rise	s'	Rec_T	26.2
1.00	0.31							#####	#####		
2.00	0.43							#####	#####	######	
3.00	0.51	0.55	-0.83					#####	#####	######	
4.00	0.53	0.39	-0.56	13.39	1.41E-03			#####	#####	######	#DIV/0!
5.00	0.6	0.38	-0.06	13.73	1.41E-03			#####	#####	######	#DIV/0!
11.00	0.72	0.38	-0.04	13.63	1.41E-03			#####	#####	######	#DIV/0!
19.00	0.8	0.37	-0.07	14.37	1.41E-03			#####	#####	######	#DIV/0!
27.00	0.86	0.35	-0.13	14.51	1.41E-03			#####	#####	######	#DIV/0!
34.00	0.89	0.34	-0.29	15.28	1.41E-03			#####	#####	######	#DIV/0!
46.00	0.94	0.31	-0.96	16.25	1.41E-03			#####	#####	######	#DIV/0!
54.00	0.955	0.25	-0.09	16.25	1.41E-03			#####	#####	######	#DIV/0!
60.00	0.97	0.28	1.45	16.25	1.41E-03			#####	#####	######	#DIV/0!
70.00	0.97	0.36	0.63	11.61	3.30E-03			#####	#####	######	#DIV/0!
80.00	0.99	0.33	-1.78	9.17	3.30E-03			#####	#####	######	#DIV/0!
90.00	1.1	0.16	-3.37	9.17	3.30E-03			#####	#####	######	#DIV/0!
124.00	1.04	0.09	-0.29	9.17	3.30E-03			#####	#####	######	#DIV/0!
150.00	1.03	0.12	2.39	9.17	3.30E-03			#####	#####	######	#DIV/0!
180.00	1.08	0.22	2.96	9.17	3.30E-03			#####	#####	######	#DIV/0!
210.00	1.09	0.35	2.09	9.17	3.30E-03			#####	#####	######	#DIV/0!
260.00	1.125	0.47	1.29	9.17	3.30E-03			#####	#####	######	#DIV/0!
316.00	1.14	0.62	#NUM!	7.14	3.30E-03			#####	#####	######	#DIV/0!
450.00	1.33	#####	#NUM!	7.14	3.30E-03			#####	#####	######	#DIV/0!
491.00	1.3	#####	#NUM!	7.14	3.30E-03			#####	#####	######	#DIV/0!
608.00	1.29	#####	#NUM!	7.14	3.30E-03			#####	#####	######	#DIV/0!

FC-METHOD : Estimation of the sustainable yield of a borehole
RW1

Extrapolation time in years = (enter)	2	1051200	Extrapol.time in minutes	
Effective borehole radius (r_e) = (enter)	1.47	1.47	← Est. r_e	From r(e) sheet
Q (l/s) from pumping test =	0.33	3.30E-03	← S-late ←	Change r_e
s_a (available drawdown), sigma_s = (enter)	6.0		← Sigma_s from risk	
Annual effective recharge (mm) =		5.99	s_available working drawdown(m)	
t(end) and s(end) of pumping test =	608	1.33	End time and drawdown of test	
Average maximum derivative = (enter)	0.4	0.6	Estimate of average of max deriv	
Average second derivative = (enter)	1.3	0.0	Estimate of average second deriv	
Derivative at radial flow period = (enter)	0.38	0.33	Read from derivative graph	

T and S estimates from derivatives	T-early[m²/d] =	13.73	Aqui. thick (m)	30
	T-late [m²/d] =	14.49	Est. S-late =	1.65E-03
(To obtain correct S-value, use program RPTSOLV)	S-late =	3.30E-03	S-estimate could be wrong	

BASIC SOLUTION

(Using derivatives + subjective information about boundaries)   Maximum influence of boundaries at long time
(No values of T and S are necessary)

	No boundaries	1 no-flow	2 no-flow	Closed no-flow
sWell (Extrapol.time) =	9.26	10.42	11.59	15.09
Q_sust (l/s) =	0.21	0.19	0.17	0.13
	Best case		→	**Worst case**

Average Q_sust (l/s) =	**0.17**
with standard deviation=	0.03

(If no information exists about boundaries skip advanced solution and go to final recommendation)

ADVANCED SOLUTION

(Using derivatives+ knowledge on boundaries and other boreholes)

(Late T-and S-values a priori + distance to boundary)

T-late [m²/d] = (enter) →	14.49			
S-late = (enter) →	1.00E-03			
1. BOUNDARY INFORMATION (choose a or b)		(Code =9999 = dummy value if not applicable)		
(a) Barrier (no-flow) boundaries →	Closed Square	Single Barrier	Intersect. 90°	2 Parallel Barriers
Bound. distance a[meter] : (enter)	9999	9999	9999	9999
Bound. distance b[meter] : (enter)			9999	9999
s_Bound(t = Extrapol.time) [m] =	0.00	0.00	0.00	0.00
(b) Fix head boundary + no-flow →	Closed Fix	Single Fix	90°Fix+no-flow	// Fix+no-flow
Bound. distance to fix head a[meter] : (enter)	9999	9999	9999	9999
Bound. distance to no-flow b[meter] : (enter)			9999	9999
s_Bound(t = Extrapol.time) [m] =	0.00	0.00	0.00	0.00
2. INFLUENCE OF OTHER BOREHOLES →	Q (l/s)	r (m)	u_r	W(u,r)
BH1			0.00E+00	#NUM!
BH2			0.00E+00	#NUM!
s_(influence of BH1,BH2) =	0.00	0.00	5.13E-08	16.21
SOLUTION INCLUDING BOUNDS AND BH's				
Fix head + No-flow : Q_sust (l/s) =	9999.00	9999.00	9999.00	9999.00
No-flow : Q_sust (l/s) =	9999.00	9999.00	9999.00	9999.00
Enter selected Q for risk analysis = (enter) →		Sigma_s =	0.000	

(Go to Risk sheet and perform risk analysis from which sigma_s will be estimated : only for barrier boundaries)

FINAL RECOMMENDED ABSTRACTION RATE

Abstraction rate (l/s) for 24 hr/d = (enter)	
Total amount of water allowed to be abstracted per month (m³) =	0

COMMENTS

Q_sust with 68% safety =
Q_sust with 95% safety =

FC-Method (Version 2.0): Developed by Gerrit van Tonder, Harald Kunstmann and Yongxin Xu

APPENDIX E

Tier 1 Risk Based Screening Levels (RBSLs)

RBCA SITE ASSESSMENT

Worksheet 1.9 GW

SITE NAME:
SITE LOCATION:

ANALYTICAL SUMMARY - GROUNDWATER CONCENTRATIONS - Groundwater Ingestion

											Summary of Test Results									Tier 1 Exposure Scenario													

specified exposure scenario: groundwater ingestion — land use: residential / specified exposure scenario: groundwater ingestion — land use: commercial/industrial

note	CAS No.	chemicals detected	Sample number	QA/QC	no. of samples	typical detect. limit (mg/L)	detect freq.	sampling date (d/m/y)	sample depth (m)	hydro unit	location of maxima	max. conc. (mg/L)	■ Tier 1 RBSL exceeded / no. exceeded 1 E-6	1 E-4	HQ=1	MCL	point of departure relevent RBSL (mg/L) 1 E-6	1 E-4	HQ=1	MCL	■ Tier 1 RBSL exceeded / no. exceeded 1 E-6	1 E-4	HQ=1	MCL	point of departure relevent RBSL (mg/L) 1 E-6	1 E-4	HQ=1	MCL
	71-43-2	BENZENE	PW1	□	1	0.01		11-Aug-95	Pumped			14.80	■	■	□	■	2.94E-03	2.94E-01	NA	5.00E-03	■	■	□	■	9.87E-03	9.87E-01	NA	5.00E-03
	108883	TOLUENE		□								4.50	□	□	□	■	NA	NA	7.30E+00	1.00E+00	□	□	□	■	NA	NA	2.04E+01	1.00E+00
	100414	ETHYLBENZENE		□								0.40	□	□	□	□	NA	NA	3.65E+00	7.00E-01	□	□	□	□	NA	NA	1.02E+01	7.00E-01
	108303	XYLENE, m-		□								0.90	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	95476	XYLENE, o-		□								1.00	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	1330207	XYLENE (mixed isomers)		□								1.90	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	91-20-3	NAPHTHALENE		□								0.00	□	□	□	□	NA	NA	1.46E-01	NA	□	□	□	□	NA	NA	4.09E-01	NA
				□									□	□	□	□					□	□	□	□				
	71-43-2	BENZENE	PW3	□	1	0.01		11-Aug-95	Pumped			7.80	■	■	□	■	2.94E-03	2.94E-01	NA	5.00E-03	■	■	□	■	9.87E-03	9.87E-01	NA	5.00E-03
	108883	TOLUENE		□								2.60	□	□	□	■	NA	NA	7.30E+00	1.00E+00	□	□	□	■	NA	NA	2.04E+01	1.00E+00
	100414	ETHYLBENZENE		□								0.30	□	□	□	□	NA	NA	3.65E+00	7.00E-01	□	□	□	□	NA	NA	1.02E+01	7.00E-01
	108303	XYLENE, m-		□								0.40	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	95476	XYLENE, o-		□								0.50	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	1330207	XYLENE (mixed isomers)		□								0.90	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	91-20-3	NAPHTHALENE		□								0.00	□	□	□	□	NA	NA	1.46E-01	NA	□	□	□	□	NA	NA	4.09E-01	NA
				□									□	□	□	□					□	□	□	□				
	71-43-2	BENZENE	PW1	□	1	0.01		9-Nov-95	Pumped			15.20	■	■	□	■	2.94E-03	2.94E-01	NA	5.00E-03	■	■	□	■	9.87E-03	9.87E-01	NA	5.00E-03
	108883	TOLUENE		□								4.20	□	□	□	■	NA	NA	7.30E+00	1.00E+00	□	□	□	■	NA	NA	2.04E+01	1.00E+00
	100414	ETHYLBENZENE		□								0.20	□	□	□	□	NA	NA	3.65E+00	7.00E-01	□	□	□	□	NA	NA	1.02E+01	7.00E-01
	108303	XYLENE, m-		□								0.00	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	95476	XYLENE, o-		□								0.60	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	1330207	XYLENE (mixed isomers)		□								0.60	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	91-20-3	NAPHTHALENE		□								0.00	□	□	□	□	NA	NA	1.46E-01	NA	□	□	□	□	NA	NA	4.09E-01	NA
				□									□	□	□	□					□	□	□	□				
	71-43-2	BENZENE	PW3	□	1	0.01		09-Nov-95	Pumped			11.20	■	■	□	■	2.94E-03	2.94E-01	NA	5.00E-03	■	■	□	■	9.87E-03	9.87E-01	NA	5.00E-03
	108883	TOLUENE		□								1.80	□	□	□	■	NA	NA	7.30E+00	1.00E+00	□	□	□	■	NA	NA	2.04E+01	1.00E+00
	100414	ETHYLBENZENE		□								0.20	□	□	□	□	NA	NA	3.65E+00	7.00E-01	□	□	□	□	NA	NA	1.02E+01	7.00E-01
	108303	XYLENE, m-		□								0.50	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	95476	XYLENE, o-		□								0.40	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	1330207	XYLENE (mixed isomers)		□								0.90	□	□	□	□	NA	NA	7.30E+01	1.00E+01	□	□	□	□	NA	NA	S<	1.00E+01
	91-20-3	NAPHTHALENE		□								0.00	□	□	□	□	NA	NA	1.46E-01	NA	□	□	□	□	NA	NA	4.09E-01	NA

Notes (where applicable):

The 10-6 and 10-4 risks refer to carcinogens, which is the excess risk value of an upper bound estimate of the added probabily of incurring cancer as a result of exposure to the contaminant of concern. The Hazard Quotient (HQ) is associated with non-carcinogenic compounds which build up over time and might affect sensitive populations. MCL is the acronym for maximum contaminant level.

Completed by: **Mr T.S Phophi**   Revision Date: **11-Apr-2004**

RBCA SITE ASSESSMENT	Worksheet 1.9 GW

SITE NAME:
SITE LOCATION:

ANALYTICAL SUMMARY - GROUNDWATER CONCENTRATIONS - Volatilization to Indoor Air Inhalation

			Summary of Test Results										Tier 1 Exposure Scenario															
													specified exposure scenario: vapor intrusion to buildings, inhalation								specified exposure scenario: vapor intrusion to buildings, inhalation							
													land use: residential								land use: commercial/industrial							
					no. of	typical detect. limit	detect	sampling date	sample depth	hydro unit	location of	max. conc.	■ Tier 1 RBSL exceeded / no. exceeded				point of departure relevent RBSL (mg/L)				■ Tier 1 RBSL exceeded / no. exceeded				point of departure relevent RBSL (mg/L)			
note	CAS No.	chemicals detected	Sample number	QA/QC	samples	(mg/L)	freq.	(d/m/y)	(m)		maxima	(mg/L)	1 E-6	1 E-4	HQ=1	other	1 E-6	1 E-4	HQ=1	other	1 E-6	1 E-4	HQ=1	other	1 E-6	1 E-4	HQ=1	other
	71-43-2	BENZENE	PW1	□	1	0.01		11-Aug-95	Pumped			14.80	■	■	□	□	2.33E-02	2.33E+00	NA		■	■	□	□	7.35E-02	7.35E+00	NA	
	108883	TOLUENE		□								4.50	□	□	□	□	NA	NA	3.14E+01		□	□	□	□	NA	NA	8.25E+01	
	100414	ETHYLBENZENE		□								0.40	□	□	□	□	NA	NA	7.38E+01		□	□	□	□	NA	NA	Rs	
	108303	XYLENE, m-		□								0.90	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	95476	XYLENE, o-		□								1.00	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	1330207	XYLENE (mixed isomers)		□								1.90	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	91-20-3	NAPHTHALENE		□								0.00	□	□	□	□	NA	NA	5.43E+00		□	□	□	□	NA	NA	1.42E+01	
				□										□	□	□						□	□	□				
	71-43-2	BENZENE	PW3	□	1	0.01		11-Aug-95	Pumped			7.80	■	■	□	□	2.33E-02	2.33E+00	NA		■	■	□	□	7.35E-02	7.35E+00	NA	
	108883	TOLUENE		□								2.60	□	□	□	□	NA	NA	3.14E+01		□	□	□	□	NA	NA	8.25E+01	
	100414	ETHYLBENZENE		□								0.30	□	□	□	□	NA	NA	7.38E+01		□	□	□	□	NA	NA	Rs	
	108303	XYLENE, m-		□								0.40	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	95476	XYLENE, o-		□								0.50	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	1330207	XYLENE (mixed isomers)		□								0.90	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	91-20-3	NAPHTHALENE		□								0.00	□	□	□	□	NA	NA	5.43E+00		□	□	□	□	NA	NA	1.42E+01	
				□										□	□	□						□	□	□				
	71-43-2	BENZENE	PW1	□	1	0.01		9-Nov-95	Pumped			15.20	■	■	□	□	2.33E-02	2.33E+00	NA		■	■	□	□	7.35E-02	7.35E+00	NA	
	108883	TOLUENE		□								4.20	□	□	□	□	NA	NA	3.14E+01		□	□	□	□	NA	NA	8.25E+01	
	100414	ETHYLBENZENE		□								0.20	□	□	□	□	NA	NA	7.38E+01		□	□	□	□	NA	NA	Rs	
	108303	XYLENE, m-		□								0.00	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	95476	XYLENE, o-		□								0.60	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	1330207	XYLENE (mixed isomers)		□								0.60	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	91-20-3	NAPHTHALENE		□								0.00	□	□	□	□	NA	NA	5.43E+00		□	□	□	□	NA	NA	1.42E+01	
				□										□	□	□						□	□	□				
	71-43-2	BENZENE	PW3	□	1	0.01		9-Nov-95	Pumped			11.20	■	■	□	□	2.33E-02	2.33E+00	NA		■	■	□	□	7.35E-02	7.35E+00	NA	
	108883	TOLUENE		□								1.80	□	□	□	□	NA	NA	3.14E+01		□	□	□	□	NA	NA	8.25E+01	
	100414	ETHYLBENZENE		□								0.20	□	□	□	□	NA	NA	7.38E+01		□	□	□	□	NA	NA	Rs	
	108303	XYLENE, m-		□								0.50	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	95476	XYLENE, o-		□								0.40	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	1330207	XYLENE (mixed isomers)		□								0.90	□	□	□	□	NA	NA	Rs		□	□	□	□	NA	NA	Rs	
	91-20-3	NAPHTHALENE		□								0.00	□	□	□	□	NA	NA	5.43E+00		□	□	□	□	NA	NA	1.42E+01	

Notes (where applicable):

The 10-6 and 10-4 risks refer to carcinogens, which is the excess risk value of an upper bound estimate of the added probability of incurring cancer as a result of exposure to the contaminant of concern. The Hazard Quotient (HQ) is associated with non-carcinogenic compounds which build up over time and might affect sensitive populations. MCL is the acronym for maximum contaminant level.

Completed by: **Mr T.S Phophi**   Revision Date: **11-Apr-2004**

RBCA SITE ASSESSMENT | **Worksheet 1.9 GW**

SITE NAME:
SITE LOCATION:

ANALYTICAL SUMMARY - GROUNDWATER CONCENTRATIONS - Volatilization to Outdoor Air Inhalation

												Tier 1 Exposure Scenario												
												specified exposure scenario: ambient vapor, inhalation						specified exposure scenario: ambient vapor, inhalation							
												land use: residential						land use: commercial/industrial							
					no.	typical detect.		sampling	sample	hydro	location	■ Tier 1 RBSL exceeded / no. exceeded				point of departure relevent RBSL (mg/L)			■ Tier 1 RBSL exceeded / no. exceeded				point of departure relevent RBSL (mg/L)		
note	CAS No.	chemicals detected	Sample number	QA/ QC	of samples	limit (mg/L)	detect freq.	date (d/m/y)	depth (m)	unit	of maxima	max. conc. (mg/L)	1 E-6	1 E-4	HQ=1	other	1 E-6	1 E-4	HQ=1	other	1 E-6	1 E-4	HQ=1	other	1 E-6	1 E-4	HQ=1	other
	71-43-2	BENZENE	PW1	☐	1	0.01		11-Aug-95	Pumped			14.80	■	☐	☐	☐	1.10E+01	1.10E+03	NA		☐	☐	☐	☐	1.85E+01	NA	NA	NA
	108883	TOLUENE		☐								4.50	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	100414	ETHYLBENZENE		☐								0.40	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	108303	XYLENE, m-		☐								0.90	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	95476	XYLENE, o-		☐								1.00	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	1330207	XYLENE (mixed isomers)		☐								1.90	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	91-20-3	NAPHTHALENE		☐								0.00	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
				☐									☐	☐	☐	☐					☐	☐	☐	☐			
	71-43-2	BENZENE	PW3	☐	1	0.01		11-Aug-95	Pumped			7.80	☐	☐	☐	☐	1.10E+01	1.10E+03	NA		☐	☐	☐	☐	1.85E+01	NA	NA	NA
	108883	TOLUENE		☐								2.60	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	100414	ETHYLBENZENE		☐								0.30	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	108303	XYLENE, m-		☐								0.40	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	95476	XYLENE, o-		☐								0.50	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	1330207	XYLENE (mixed isomers)		☐								0.90	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	91-20-3	NAPHTHALENE		☐								0.00	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
				☐									☐	☐	☐	☐					☐	☐	☐	☐			
	71-43-2	BENZENE	PW1	☐	1	0.01		9-Nov-95	Pumped			15.20	■	☐	☐	☐	1.10E+01	1.10E+03	NA		☐	☐	☐	☐	1.85E+01	NA	NA	NA
	108883	TOLUENE		☐								4.20	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	100414	ETHYLBENZENE		☐								0.20	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	108303	XYLENE, m-		☐								0.00	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	95476	XYLENE, o-		☐								0.60	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	1330207	XYLENE (mixed isomers)		☐								0.60	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	91-20-3	NAPHTHALENE		☐								0.00	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
				☐									☐	☐	☐	☐					☐	☐	☐	☐			
	71-43-2	BENZENE	PW3	☐	1	0.01		9-Nov-95	Pumped			11.20	■	☐	☐	☐	1.10E+01	1.10E+03	NA		☐	☐	☐	☐	1.85E+01	NA	NA	NA
	108883	TOLUENE		☐								1.80	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	100414	ETHYLBENZENE		☐								0.20	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	108303	XYLENE, m-		☐								0.50	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	95476	XYLENE, o-		☐								0.40	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	1330207	XYLENE (mixed isomers)		☐								0.90	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA
	91-20-3	NAPHTHALENE		☐								0.00	☐	☐	☐	☐	NA	NA	NA		☐	☐	☐	☐	NA	NA	NA

Notes (where applicable):

The 10-6 and 10-4 risks refer to carcinogens, which is the excess risk value of an upper bound estimate of the added probability of incurring cancer as a result of exposure to the contaminant of concern. The Hazard Quotient (HQ) is associated with non-carcinogenic compounds which build up over time and might affect sensitive populations. MCL is the acronym for maximum contaminant level.

Completed by: **Mr T.S Phophi**   Revision Date: **11-Apr-2004**

Summary of output of fate and transport model for benzene

FATE AND TRANSPORT MODEL OUTPUT FOR BENZENE	
GROUNDWATER MODEL CALCULATIONS	
Initial mass input to bring source area up to the required concentration in GW (mg/d)	1.49E+07
Mass input rate for pulse source in GW (mg/d)	7.10E+03
Mass input rate = (Darcy flux) x (Source concentrations) = K-value x gradient x (Source concentration)	
CONTAMINANT VELOCITY IN SATURATED ZONE	
Aquifer gradient	2.00E-02
Hydraulic conductivity (m/d)	0.48
Koc (m3/kg)	5.90E-02
Foc (g/g)	3.53E-03
Retardation coefficient	1.9
Seepage velocity (m/d)	2.41E-02
Retarded seepage velocity (m/d)	1.25E-02
DISPERSION CALCULATIONS IN SATURATED ZONE	
Distance used for dispersion calculations (m).	75
Distance = (Distance. to well) + (Source Length)/2	
Calculated longitudinal dispersivity (m)	8.4
Calculated transverse dispersivity (m)	2.8

Calculated vertical dispersivity (m)	3.21E-02
GROUNDWATER CONCENTRATION (ANNUAL AVERAGE) OF BENZENE	
The maximum groundwater concentration (mg/l):	4.52E-01 (Occurred after 70 years)
Benzene concentrations overtime	
Time (yrs)	Concentrations (mg/L)
1	1.82E-11
2	3.43E-06
3	3.31E-04
4	3.72E-03
5	1.60E-02
6	4.11E-02
7	7.85E-02
8	1.24E-01
9	1.73E-01
10	2.20E-01
11	2.64E-01
12	3.02E-01
13	3.34E-01
14	3.61E-01
15	3.82E-01
16	3.99E-01
17	4.12E-01
18	4.22E-01
19	4.29E-01
20	4.35E-01
21	4.39E-01
22	4.43E-01
23	4.45E-01

24	4.47E-01
25	4.48E-01
26	4.49E-01
27	4.50E-01
28	4.50E-01
29-32	4.51E-01
33-70	4.52E-01

NB! the model output results for TEX were not reported because they are insignificant

APPENDIX G

Results of petroleum hydrocarbons during monitoring of pump and treat system (mg/L)

Sample date:	24 October 2003					
Sample no	PW1	PW2	PW3	PW5	RW1	AFTER SEP
Benzene	BDL	BDL	BDL	BDL	n.s	1.6
Toluene	BDL	BDL	BDL	BDL	n.s	0.93
Ethyl benzene	BDL	BDL	BDL	BDL	n.s	0.24
Xylenes	BDL	BDL	BDL	BDL	n.s	2.63

Sample date:	04 March 2003				
Sample no	PW1	PW2	PW3	PW5	RW1
Benzene	BDL	BDL	n.s	0.03	1.83
Toluene	BDL	BDL	n.s	BDL	1.11
Ethyl benzene	BDL	BDL	n.s	BDL	0.22
Xylenes	BDL	BDL	n.s	BDL	2.57

Sample date:	15 October 2002				
Sample no	PW1	PW2	PW3	PW5	RW1
Benzene	BDL	BDL	n.s	BDL	2.19
Toluene	BDL	BDL	n.s	BDL	1.6
Ethyl benzene	BDL	BDL	n.s	BDL	0.35
Xylenes	BDL	BDL	n.s	BDL	3.48

Sample date:	27 March 2002				
Sample no	PW1	PW2	PW3	PW5	RW1
Benzene	BDL	BDL	BDL	0.12	3.05
Toluene	BDL	BDL	BDL	BDL	2.44
Ethyl benzene	BDL	BDL	BDL	BDL	0.5
Xylenes	BDL	BDL	BDL	0.02	2.16

Sample date:	05 October 2001			
Sample no	PW1	PW2	PW3	PW5
Benzene	BDL	0.1	BDL	0.54
Toluene	BDL	BDL	BDL	BDL
Ethyl benzene	BDL	BDL	BDL	BDL
Xylenes	BDL	BDL	BDL	0.05

Sample date:	19 January 2000			
Sample no	PW1	PW2	PW3	PW5
Benzene	BDL	BDL	n.s	0.55
Toluene	BDL	BDL	n.s	1.68
Ethyl benzene	BDL	BDL	n.s	1.61
Xylenes	BDL	BDL	n.s	14.85