MANUAL FOR SITE ASSESSMENT AT DNAPL CONTAMINATED SITES IN SOUTH AFRICA

Report to the Water Research Commission

by

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Report to the Water Research Commission

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WRC REPORT NO 1501/2/08
ISBN 978-1-77005-662-6
SET NO 978-1-77005-657-2

January 2008

The publication of this report emanates from a project entitled**:** *Field investigations to study the fate and transport of dense non-aqueous phase liquids (DNAPLs) in groundwater* (WRC Project No K5/1501)

Manual for Site Assessment at DNAPL Contaminated Sites in South Africa

The considerations for site assessment and the techniques required at DNAPL sites is often very different to those required for understanding of the majority of contaminated sites. This report's purpose is therefore to document the applicable assessment procedures for a DNAPL contaminated sites. Consideration of the following aspects is given to provide guidance to site owners, regulators en site investigators for South African-specific DNAPL site assessment:

- DNAPL contaminant properties
- South African aquifer characteristics
- Available technology in South Africa
- Innovative and cost-effective assessment methodologies.

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

The documents in this series include:

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

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

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1. INTRODUCTION

The potential for serious long-term contamination of groundwater by some DNAPL chemicals at many sites is largely due to their toxicity, limited solubility (but much higher than drinking water limits) and significant migration potential in soil gas, groundwater, and/or as a separate phase. DNAPL chemicals, especially chlorinated solvents, are among the most prevalent groundwater contaminants identified in groundwater supplies and at waste disposal sites (Cohen and Mercer, 1993).

The South African Department of Water Affairs and Forestry (DWAF) have adopted a risk-based approach to managing contaminated sites. In order to determine the risk that contamination may pose at a site and to manage that risk, it is necessary to have a good understanding of the nature and distribution of contaminants in the subsurface, and to understand how the contaminant will behave within the soil and/or groundwater system.

Collecting environmental data is expensive. Owners of contaminated sites must balance costs against the need for adequate information about the subsurface conditions and contaminant distribution to be able to make informed decisions about whether the contamination represents a threat to human health or the environment. Contamination of fractured rock aquifers by non-aqueous phase liquids (NAPLs), is a worldwide problem. The resulting groundwater contamination is difficult to manage, due in part to the problems associated with collecting the necessary data to understand contaminant behaviour within the system, properly.

The subsurface movement of DNAPL is controlled substantially by the nature of the release, the DNAPL density, interfacial tension and viscosity, porous and/or fractured media capillary properties and usually, to a lesser extent, by hydraulic forces. Below the water table, non-wetting DNAPL migrates preferentially through permeable pathways such as soil and rock fractures, root holes and sand layers that provide relatively little capillary resistance to flow. Visual detection of DNAPL in soil and groundwater samples may be difficult where the DNAPL is transparent, present in low saturation or distributed heterogeneously. These factors confound characterisation of the movement and distribution of DNAPL, even at sites with relatively homogeneous soil and a known, uniform DNAPL source. The difficulty of site characterisation is further compounded by fractured bedrock, heterogeneous strata, multiple DNAPL mixtures and releases, etc.

Obtaining a detailed delineation of subsurface DNAPL, therefore, can be very costly and may be impractical when using conventional site investigation techniques. Although DNAPL may greatly complicate site characterisation, failure to define adequately its presence, fate and transport may result in misguided investigation and remedial efforts. Large savings and environmental benefits can be realised by conducting studies and implementing remedies in a cost-effective manner. Cost-effective DNAPL site management requires an understanding of DNAPL properties and migration processes and of the methods available to investigate and interpret the transport and fate of DNAPL in the subsurface.

This report's purpose is therefore to document the applicable assessment procedures for a DNAPL contaminated site. Consideration was given to the following aspects:

- DNAPL contaminant properties
- South African aquifer characteristics
- Available technology in South Africa
- Innovative and cost-effective assessment methodologies.

2. GENERAL SITE ASSESSMENT

A general assessment of a contaminated site may be made to determine the potential presence of a DNAPL in the groundwater zone. This general assessment is usually made early on in the investigation and use is made of existing information about the site.

The site investigator must consider whether the chemicals found at a site or expected at a site, could comprise DNAPLs and if the activities at the site could have resulted in the release of significant quantities of the DNAPL to the surface.

2.1 Types of chemicals

The first step in the general assessment of a potential DNAPL site is the consideration of the types of chemicals which are found or might be present at the site.

A wide variety of chemical products and wastes may comprise a DNAPL. For a chemical to be regarded as a potential DNAPL in a given circumstance, it must have a fluid density greater than 1.01 g/cm^3, a solubility in water of less than 2% (or about 20 000 mg/l) and a vapour pressure of less than 300 torr. For a potential DNAPL to be an actual DNAPL at a given site, the amount of chemical released to the subsurface will need to be in excess of the total amount that could have dissolved into the water and sorb to the soil materials in the source zone. Compounds which are either more soluble than 2%, lighter than 1.01 g/cm^3 or more volatile than 300 torr would generally not be expected to persist in the DNAPL phases in the subsurface (Pankow and Cherry, 1996).

The major DNAPL types include: halogenated hydrocarbons especially solvents, coal tar and creosote, polychlorinated biphenyls (PCBs), some pesticides and miscellaneous or mixed DNAPLs. Of these types, the most extensive subsurface contamination is associated with halogenated (primarily chlorinated) solvents, either alone or within mixed DNAPL sites, due to their widespread use and properties (high density, low viscosity, significant solubility and high toxicity).

Whenever the past or present use of chemicals is considered, cognisance should be taken of the fact that many chemicals are known by a variety of chemical synonyms and product names. If there are no records or chemical inventories, then the principal use of organic chemicals may be used as a reference to determine the possible use at a site[1].

Furthermore, it is important that site assessors must not only understand the type of chemicals used at a site, but also how these chemicals have been used or are currently being used. It should be considered that some DNAPL releases could have occurred many years before and that the activities contributing to the releases have since ceased. In such cases, records of the chemicals used or disposed of may not exist. Knowledge of the type of business conducted on these sites and the nature of the wastes must be estimated.

Thus, with an appreciation of the varied uses of DNAPL chemicals, a site assessor can identify the activities that should be associated with DNAPL use and disposal.

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[1] Chemical inventory lists for South Africa are given in Usher *et. al.* (2004).

2.1.1 Site operations

For a typical industrial site, a site assessor needs to determine the type of manufacturing operations and the types and quantities of chemicals that have been used at a site. Possible information sources include:

Interviews with present or former employees;

- records of chemical purchases, off-site waste disposal or waste received;
- historical site engineering drawings; and
- archival aerial photographs.

Records of volumes of DNAPLs that were produced, used or disposed of, are often not available, however estimates may be gained from interviews with employees. A common cause of DNAPL contamination is releases of small amounts at off-loading areas, floor drains, sumps, catch basins, septic tanks, lines and sewers and storage tanks.

Locations of any disposal facilities such as landfills or effluent dams need to be determined. At these facilities DNAPLs have a greater potential for migration due to the larger volumes disposed. Examination of aerial photographs may be useful in determining the locations of such areas.

2.2 *Assessment of potential DNAPL migration*

An estimation of the potential depth of DNAPL penetration/migration through the vadose zone and into the groundwater zone is an important component of a site assessment (Pankow and Cherry, 1996).

This estimation is often attempted early on in a site investigation and based on general information about site operations and subsurface conditions.

The depth of the penetration/migration will depend on:
- Properties of the DNAPL;
- Nature of the release;
- Properties and the geological structure within the vadose and groundwater zone.

Although it is not possible to predict precisely the extent or rate of DNAPL migration, it is important to recognise, in general terms, the factors that will influence the depth of DNAPL penetration in the subsurface. These factors are summarised in Table 1.

It has been common practice in the assessment of petroleum hydrocarbons (Pankow and Cherry, 1996) to estimate the depth (D) of penetration of a DNAPL or LNAPL spill through the vadose zone on the basis of volume(V) released, the area (A) of the release and the penetration capacity (R_s) of the soil according to:

$$D = V/AR_s \qquad (1)$$

This equation assumes that the NAPL penetrates directly downward from the release area with negligible lateral spreading and forms a regular prismatic or cylindrical NAPL zone. For sandy aquifer materials residual saturations of 5 to 25% of the pore space (Mercer and Cohen, 1993) were measured in the laboratory. For a total porosity of 30% this range of residual saturations yields retention capacities of 15 to 75 L/m^3 or 1.5 to 7.5%

of the bulk volume of soil. These ranges are typically used to determine the penetration depth of NAPL in the vadose zone.

However, cognisance should be taken of the limitations of this estimation as the equation *assumes homogenous conditions*. Variations in permeability of the vadose zone could cause lateral spreading and thus the NAPL penetration depth may be over- estimated.

Table 1: Factors facilitating or inhibiting DNAPL penetration

(Adapted from Pankow and Cherry, 1996).

Factors facilitating DNAPL penetration	**Typical circumstances**
High DNAPL density	▪ Chlorinated solvents, PCB aroclors
Low interfacial tension	▪ Surfactants or miscible co-solvents e.g. methanol, ketones, acetone in DNAPL ▪ Surfactants or co-solvents in aqueous wastes or groundwater ▪ Complex mixtures
Low viscosity	▪ Chlorinated solvents
Large DNAPL volume release	▪ Disposal in landfill or dams ▪ Catastrophic and/or ongoing spills
Long duration DNAPL release	▪ Disposal in landfill or dams ▪ Catastrophic and/or ongoing spills
High permeability	▪ Sand, gravel and fractured rock
Vertical and sub-vertical geological structures	▪ Angled bedding planes ▪ Fractures and fissures in aquitards ▪ Fractured rocks
Factors inhibiting DNAPL penetration	**Typical circumstances**
Low DNAPL density	▪ Coal tar/ creosote ▪ Chlorinated solvents at low concentrations in petroleum hydrocarbons
High interfacial tension	▪ Relatively pure chemical products
High viscosity	▪ Coal tar/ creosote ▪ PCB aroclors ▪ Mixtures with high concentrations, high molecular hydrocarbons
Small DNAPL volume release	▪ Small spills and leaks
Short duration DNAPL release	▪ Small once–off spills and leaks
Low permeability	▪ Unfractured silt and clay aquitards ▪ Unfractured rock
Horizontal geological structures	▪ Horizontal bedding in sandy aquifers, silt and clay aquitards ▪ Horizontal bedding plane partings in sedimentary rocks

2.3 Initial Site Conceptual Model

The development and utilisation of conceptual models to explain geologic processes and environments has long been the province of geoscientists. Contamination site investigators routinely formulate conceptual models of chemical migration to guide characterisation and clean-up efforts. Although site conditions, DNAPL properties and release characteristics are variable, these parameters generally conform to certain types of hydrogeological environments and releases (Cohen and Mercer, 1993).

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

Schwille (1988) and researchers at the Waterloo Centre for Groundwater Research (WCGR, 1991), have developed and refined general DNAPL conceptual models. Recently the UK Environmental Agency also published (2003) DNAPL conceptual models for UK specific aquifer conditions.

These DNAPL conceptual models are utilised to assess:

- Site characterisation priorities,
- The utility of alternative subsurface characterisation methods,
- Site data,
- The potential for separate phase DNAPL migration,
- The potential for vapour transport of DNAPL chemicals,
- The potential for dissolution of DNAPL chemicals and dissolved chemical transport,
- Chemical distributions associated with these transport mechanisms,
- Cross-contamination risks associated with characterisation and remedial activities, and,
- The potential effectiveness of alternative remedial actions.

Table 2 lists a variety of contaminant characteristics that are useful in establishing a site conceptual model and in selecting a remediation strategy.

Table 2: Contaminant characteristics to establish during site investigations

(From Kueper et al., 2003)

Parameter	Example use of information
DNAPL density	DNAPL mobility and pool height calculations
DNAPL viscosity	Determine if DNAPL could still be moving Design of NAPL recovery system
DNAPL component composition	Effective solubility calculations Predict future composition of plume
DNAPL water interfacial tension	Determine importance of capillary forces Pool height calculations
Organic carbon partition coefficient	Determine degree of aqueous phase sorption and rate of plume migration
Contaminant half-life	Determine degree of degradation and rate of plume migration
DNAPL vapour pressure	Determine if vapour migration is a potential issue; Estimate lifespan of DNAPL above water table
Date and volume of DNAPL release	Estimate of depth of DNAPL migration. Is DNAPL still moving?
Potential DNAPL release locations	Help guide monitoring well placement

Measurement of the DNAPL properties will require the recovery of a sample of DNAPL from the subsurface. If this is not possible, but the composition of the DNAPL is known, its density and viscosity may be estimated from the literature sources.

DNAPL water interfacial tension should not be estimated from handbooks, however, as this is a site-specific parameter which is influenced strongly by even small amounts of impurities. The organic carbon partition coefficient is typically obtained from the literature sources, along with the DNAPL vapour pressure. The contaminant half-life depends on site-specific geochemical conditions and therefore, should not generally be taken from handbooks or the literature; this parameter is typically determined through model calibration.

Table 3 and Table 4 list the properties of the aquifer media, which will be relevant to establishing a conceptual site model and the use of the information during the site assessment. Many of these parameters may be estimated from the literature or ideally, measured during field investigations.

Table 3: Unconsolidated deposit characteristics to determine during site investigations

(From Kueper et al., 2003)

Parameter	Example use of information
Porosity	Plume velocity calculation; Diffusion calculations
Dry bulk density	DNAPL threshold concentration calculation
Fraction organic carbon	Plume velocity calculation; DNAPL threshold calculation
Hydraulic conductivity	Plume velocity calculation; Design of extraction wells
Displacement pressure	Pool height calculations
Bulk retention capacity	DNAPL mass estimate
Contact angle	Refinement of conceptual model on DNAPL mobility
Hydraulic head distribution	Directions of groundwater flow and velocity of groundwater
Bedding structures	Directions of DNAPL migration
Spatial extent of DNAPL source zone	Guide remedy selection and design
Spatial extent of plume	Guide remedy selection; risk analysis

Table 4: Bedrock properties to determine during site investigations

(From Kueper et al., 2003)

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

3. DETERMINING THE PRESENCE OF DNAPL FROM FIELD OBSERVATIONS

3.1 Introduction

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

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

The toolbox approach recognises that all characterisation methods contribute to the conceptual model of the site.

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

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

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

Figure 1 provides a brief summary of the parameters that can be measured at a site during field investigations.

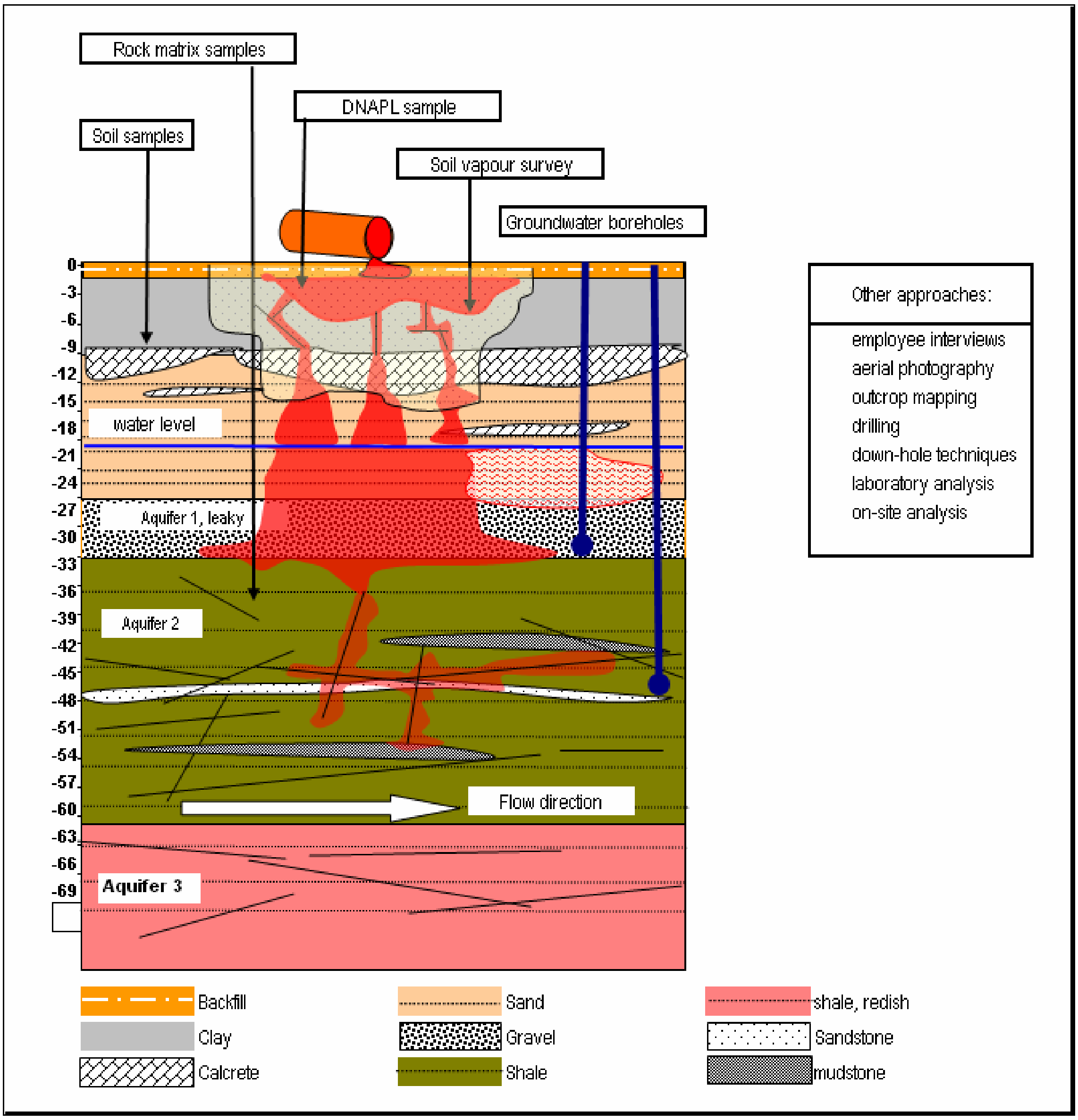

Figure 1: Site assessment techniques

(Adapted from Kueper, et. al., 2003)

3.2 Soil gas surveys

Soil gas analysis is a popular screening tool for detecting volatile organic chemicals in the vadose zone at contamination sites (Cohen and Mercer, 1992). Soil gas surveys generate extensive chemical distribution data quickly at a fraction of the cost of conventional invasive methods and offer the benefits of real-time field data. Consideration should be given to its use during the early phases of site investigation to assist delineation of DNAPL in the vadose zone, contaminant source areas, contaminated shallow groundwater and contaminated soil gas and thereby, guide subsequent invasive field work.

Soil gas surveys measure VOC concentrations in soil gas that arise from the partitioning of contaminated water or non-aqueous phase liquid (NAPL) to the vadose zone air. Surveys typically employ probes that are installed at a depth from 0.3 to 3 metres below the surface. Soil gas samples are captured in suitable containers and may be analysed off-site or with on-site equipment such as a photo ionisation detector (PID) or flame ionisation detector (FID).

Many DNAPLs, including most halogenated solvents, have high vapour pressures and will volatilise in the vadose zone to form a vapour plume around a DNAPL source. Volatile organic compounds (VOCs) dissolved in groundwater may also volatilise at the capillary fringe into soil gas. However, it is important to *discern the origins of VOCs* in soil gas when using surveys to interpret the nature and extent of subsurface contamination.

Multiplicity of sources and paucity of groundwater data at sites usually make the understanding of processes and discernment of soil-gas origins difficult.

Pankow and Cherry (1996) give the following conceptualisation of vapour transport processes as a DNAPL moves downwards towards the saturated zone:

As the DNAPL liquid moves downward, some is immobilised by capillary forces and remains in the pore spaces as residual. Pools of DNAPL may also form on lenses of less permeable media. In the vadose zone the DNAPL from the residual and 'pool' DNAPL will vaporise into the gas phase and migrate by gaseous diffusion in all directions away from the source. Gaseous advection due to pressure or density gradients also plays a role in the transport process. The migration of vapours may be retarded by partitioning into the aqueous and solid phases. Eventually, the contaminants reach the top of the capillary fringe. Contaminants in the dissolved phase are transported into the groundwater by diffusion across the water table, by infiltrating water and as a result of water table fluctuations. At the ground surface, vapours may be lost to the atmosphere if no impermeable cover is present.

The field experiments and modelling (Rivett, 1995) indicate that groundwater plumes originating from sources such as DNAPL pools or residual, located much below the water table are unlikely to give soil-gas signatures, due to the weakness of vertical transverse transport in the groundwater zone. The downward velocity near the water table due to recharge, may often be sufficient to prevent groundwater zone solutes partitioning to the soil gas, unless they originate from less than about a metre below the air-water interface.

Thus, soil-gas signatures from vadose zone DNAPL sources and their associated interface zone groundwater plumes will predominate and mask any signatures from other groundwater zone plumes; only the dissolution of DNAPL in the saturated zone that is within or very close to, the interface zone may contribute to the soil-gas contamination. It is therefore reasonable to interpret from soil-gas plumes that up gradient maxima are indicative of source locations and that the soil-gas plume may approximately define the extent of the very shallow, interface zone ground-water contamination. A discrepancy in plume widths may cause a further problem in delineating groundwater contamination at depth from soil-gas plume data. Soil-gas and interface zone plumes will be tens of metres wider than the source zone, due to vapour transport lateral to the groundwater flow direction; whereas, deeper groundwater plumes will be not much wider than the DNAPL source zone, due to the weakness of transverse horizontal dispersion (Anderson et al., 1992).

Soil-gas data should therefore be used with caution and their limitations recognised. In spite of their limitations, soil-gas surveys may still be a valuable reconnaissance tool to delineate subsurface VOC contamination and facilitate location of monitoring boreholes and soil borings.

3.3 Geophysics

3.3.1 Surface geophysics/ aerial geophysics

One of the aims of the project was to determine if specific geophysical methods could timeously and effortlessly delineate DNAPL plumes or layers within the subsurface. A desk study concluded that most of the methods utilised in Europe and the USA are not suitable for the local conductive overburdened conditions often encountered. The time domain electromagnetic, magnetic, resistivity and airborne geophysics methods were found to be most suitable for South African conditions. Refraction seismics are ruled out due to the cost involved in operation.

The results from the airborne geophysics (magnetic and radiometric) and the frequency domain EM34-3 methodology were overshadowed by cultural noise and results indicated that the noise levels were too high to interpret the data effectively. The time domain EM was applied and some positive results could be inferred. However, some operating restrictions could also see this method rendered ineffective. Some dykes could be inferred from these data and confirmed with additional field observations (CGS, 2006). The results of the investigation thus seem to be inconclusive with only marginal success from a timeous expensive method that occupies a large surface area for operation.

It is realised that most DNAPL contamination sites are likely to be located in heavily constructed industrial sites and that the noise and available size for surveying would be insufficient for geophysical work in general.

Surface geophysics therefore, seems to be effective only as a tool to map variations in geology such as dykes and faults as a reconnaissance exercise, if funding is available and cultural noise at a minimum. It can also be useful in detecting disturbed ground (such as old waste disposal pits) and buried objects (USTs, pipelines or electrical cables). These areas or objects may often be sources or conduits for subsurface contamination.

3.3.2 Down-the-hole geophysics

The physical properties of fractured-rock aquifers are well understood in principle. If the geometry and hydraulic properties of the fracture network are specified, the flow and dispersion in such aquifers may be predicted. Of course, these properties are not known in detail for most fracture-rock aquifers. The obvious recourse is to sample subsurface conditions using boreholes.

The inherent complexity of fractured aquifers and the dependence of hydraulic properties in these aquifers on the scale of investigation, mean that it is impractical to expect complete characterisation by borehole investigations alone. Effective characterisation of fractured bedrock aquifers depends on the integration of different kinds of data at different scales of investigation, so as to:

1) determine the relation between aquifer properties and the scale of the investigation by comparing measurements spanning the spatial scale of interest; and
2) relate the geophysical and hydraulic properties of the aquifer through empirical or model-based relationships, by comparing geophysical and hydraulic data at borehole locations (Paillete, 2004).
3) Borehole geophysical surveys involve lowering a logging tool, also known as a sonde, down a borehole to make physical measurements as a function of depth. A sensing element within the sonde measures the property of interest and converts it into electrical signals. These signals are transmitted to the surface through a cable and recorded digitally or by using an analogue strip chart. Several types of geophysical logs may be made, sometimes simultaneously, in the same borehole.

Figure 2: Geophysical logging of boreholes at research site - Test Site 1.

Borehole geophysical surveys are conducted to:

- characterise lithologies,
- correlate stratigraphy between boreholes,
- identify fracture zones, estimate formation properties (e.g. porosity and density),
- identify hydraulically active fractures,
- identify fractures that do not intersect the hole,
- determine ambient flow in the borehole,
- design well completion method, and
- identify intervals containing conductive dissolved contaminants.

A wide variety of geophysical borehole-logging techniques is available to the practising geohydrologist, as well as to researchers. Most of the techniques have been developed for the oil exploration industry and adapted for geohydrological applications. The most common techniques applied in the groundwater industry, with their field application, are listed in Table 5. These methods provide continuous high resolution measurements of subsurface conditions. As such, they can be used to distinguish thin layers and subtle stratigraphic features which may influence contaminant movement.

Table 5: Geophysical borehole logging tools and their fields of application

(Adapted from Woodford and Chevalier, 2000)

Technique	Types of Log	Field of Application
Radioactivity	Natural gamma Gamma-gamma Neutron	Clay content; rock structure and lithology Rock density; porosity; fracturing Porosity
Resistivity	Normal (multiple array). Focused Induction	Rock or formation resistivity; lithology; detection of thin (clay) layers
Caliper	Caliper log	Borehole or casing diameter
Temperature (water)	Temperature	Ground water temperature; fracture location; geothermal gradient
Conductivity (water)	Conductivity	Ground water conductivity; water quality stratification (pollution investigations)
Sonic	Acoustic Televiewer (ATV)	Fracture and structural orientations Borehole deviation Only in water- filled holes
Optical	Borehole-Wall Imaging Optical Televiewer (OTV)	Oriented digital video image Conventional fisheye Air- and water- filled holes (clear) Virtual Core image Fracture and structural orientations Borehole deviation
	Borehole or TV camera	Casing attributes (Damage, clogging); fracture position; visual inspection of borehole sides
Borehole orientation	Dipmeter Deviation	Dip and strike of penetrated layers, fractures and fissures. Spatial course of borehole

Although frequently used elsewhere, geophysical borehole logging not been widely used in the Karoo environments. Resistivity logs (normal) have been used with good results in assisting with the calibration of sounding curves, whereas natural gamma logs were used in the case of surveys at Beaufort West and are invaluable in the construction of complex geohydrological models (Vandoolaeghe, 1978).

Fractures identified in boreholes have often been mechanically enlarged by drilling and flow-conducting passages embedded in the fracture face represent only a small proportion of the fracture zone volume as imaged by geophysical methods. Lateral continuity of individual fractures may be verified by GPR imaging from the surface and cross-hole hydraulic testing (Romanowicz et al*.,* 2004).

Identifying the fracture locations with the caliper probe is an important first step in modelling the transmissive response of boreholes, but the presence of fractures and their size at the wall of the borehole is not indicative of the magnitude of the transmissivity of the fracture (Rickert et al., 2004).

Overall, the potential value of using borehole geophysical surveys to delineate NAPL presence and saturation is poorly defined (Cohen and Mercer, 1993).

From the field data collected during this project, the down-hole geophysics proved to be of limited use for DNAPL site assessment. Geological features such as more permeable zones or fracture zones may be delineated with the some of the probes. However, finer detail such as fracture aperture and orientation (which is important for determination of exact flow paths), could not be determined. A cost benefit analysis should be used to determine whether it is worthwhile to perform down-hole geophysics for its applicability at a DNAPL site assessment.

3.3.3 Flow logging

Without understanding the flow regime within open bedrock boreholes, sampling programmes may not adequately characterise the distribution of contamination in an aquifer. Vertical flow within open boreholes in fractured bedrock aquifers may cause cross-contamination, mixing or the dilution of water samples. By understanding the flow patterns within the borehole, a sampling strategy may be designed to obtain more meaningful data.

Several new high-resolution flow logging techniques such as heat-pulse (Hess, 1986) and electromagnetic (Molz et al., 1994) flowmeter logging and borehole dilution methods (Tsang et al., 1990), provide more cost-effective and flexible methods for putting the hydrology into the geophysical investigation. One of the most important attributes of high-resolution borehole flow logging is that all logs may be run as part of the same operation. This avoids the possibility of trying to compare straddle-packer measurements made using one hydraulic condition with geophysical logs run at another time under other conditions. Geophysical measurements in boreholes may characterise fractures in detail, but only adjacent to individual boreholes, while hydraulic measurements in boreholes may be used to generate direct relationships between geophysical and hydraulic properties (Paillet, 2001).

Flowmeter logs collected under ambient and stressed conditions along with fluid and televiewer logs are valuable for identifying ambient vertical flow and the most transmissive fractures that intersect the borehole. Under ambient conditions, flowmeter logs are used to identify the direction and magnitude of vertical flow within boreholes. Under stressed (pumping) conditions, flowmeter logs are used to identify the transmissive fractures within the borehole by measuring the rate of water entering the borehole at each fracture, while simultaneously pumping from or injecting into the top of the borehole at a low rate.

Collectively, these data are critically important for assessing the flow regime; determining the location, transmissivity and hydraulic head of fractures in the borehole; designing well completions to minimise cross contamination; and planning water quality sampling strategies (Johnson et al., 2004).

A major task in the characterisation of fractured aquifers and the prediction of contaminant migration is the identification of fracture flow paths in situ and the specification of their hydraulic properties.

The possibility of multiple flow paths intersecting a single borehole indicates that boreholes in fractured bedrock aquifers should be treated as observation boreholes, intersecting multiple confined or partially confined aquifers.

3.3.4 Video logging

Down-the-hole video logging is often utilised during a site investigation, together with the other methods described in Sections 3.3.2 and 3.3.3, with the purpose of enhancing these methods for the identification of fracture flow paths *in situ.*

The method typically involves the lowering of the borehole camera down the borehole, similar to the other geophysical probes described above.

The advantages of the method include:

- Determination or confirmation of well construction (depth, casing type, etc)
- Inspection of casing attributes (e.g. damage, clogging)

- Determination of fracture positions and orientation
- Geological profiling

Orientation may be determined by the use of a compass attached to the camera. Borehole videos can confirm the presence of vertical fractures in boreholes, which can not be detected by use of other geophysical methods (except with optic televiewer). Detection of vertical fractures at a site is very important as these fractures may greatly influence the depth of DNAPL penetration and can explain dissolved concentration found at great depth in the aquifer system.

3.4 Invasive Methods

During the intrusive investigation, samples of soil, rock, groundwater and soil gas may be taken from pit excavations, auger holes or boreholes. These samples may either be analysed *in situ* (soil gas), at the site (mobile GCMS or SiteLab) or preserved and shipped to an appropriate laboratory for chemical analysis.

It is important to log all relevant information when carrying out an intrusive investigation. Such information consists of, as a minimum:

- Location of excavation
- Site number/identification
- Type of excavation
- Depth of excavation
- Date and time of excavation
- Field measurements (soil gas, pH, etc)
- Descriptions of soil/lithology with depth
- Backfilling/construction details
- Photographs

During excavation, cross contamination of samples should be minimised by selecting appropriate investigation and sampling techniques and the decontaminating of equipment between sample locations.

3.4.1 Test pits

Excavating test pits and/or trenches may be a very rapid and cost-effective means to (Cohen and Mercer, 1993):

- Characterise the nature and continuity of shallow overburden stratigraphy, including the macropore distribution;
- Identify, delineate, and characterise waste disposal and grossly contaminated areas;
- Help determine the horizontal and vertical extent of shallow contamination;
- Locate and examine buried structures, tanks, pipelines, etc. and their bedding/backfill that may act as contaminant reservoirs or preferential pathways; and
- Acquire soil samples for chemical and physical analyses.

Figure 3: Example of variation in soil layers in test pit.

Limitations and/or disadvantages of excavation as a site characterisation tool include:

- The limited depth of exploration;
- The diminished view of excavation sidewalls with depth due to shadows, viewing angle and distance (binoculars may enhance sidewall viewing);
- Potential sidewall stability problems, of particular concern near structures, utilities, and roads;
- Potential airborne release of contaminated vapours and dust;
- Potential creation of a preferential pathway for contaminant transport along a trench;
- Potential increased waste handling requirement; and
- Potential subsidence problems after the excavation has been backfilled.

The main advantage of excavation for site characterisation is that it provides an opportunity to examine a large, continuous subsurface section. As a result, excavations may reveal conditions such as soil vapour plume, subtle or complex stratigraphic relations, soil fracture patterns, heterogeneous NAPL distributions and irregular disposal areas that can be difficult to characterise by examining drill cuttings or samples. The potential risk of causing DNAPL migration is limited by the relatively shallow depth of excavation. Cross contamination of samples may be avoided by taking large bucket scoops of soil with the excavator and then taking a sample from the centre of the bucket where the soil has had no contact with the sides of the bucket.

3.4.2 Drilling

Boreholes are installed to evaluate subsurface stratigraphic, hydrogeologic and contaminant conditions. Selection of drilling locations, depths and methods must be based on available information regarding site conditions.

The number of boreholes available to a site assessor is often limited due to cost constraints by site owners. Drilling of boreholes is an iterative process, whereby more than one drilling event will be required to characterize a site. The knowledge gained through such successive drilling events, is used to continually update the site conceptual model.

The potential for causing DNAPL migration by drilling through a barrier layer should be considered before and during drilling and thus minimised. Conventional drilling methods have a high potential for promoting downward DNAPL migration. For example, DNAPL trapped in structural or stratigraphic lows may be mobilised by site characterisation activities for example, drilling through a DNAPL pool, (Cohen and Mercer, 1993). The type of drilling used must cause as little disturbance as possible to the aquifer, producing minimal modification to the qualitative characteristics of the subsurface water. Depending on the lithological characteristics of the subsurface and the depth to read, the commonly used methods (CGR, 2000) are rotary or roto-percussion drilling with compressed air with water or mud, percussion drilling and auger drilling (or temper screw) with hallow or full shafts.

Several guidelines for drilling at DNAPL sites are available (e.g. Milan, (2000); Pankow and Cherry (1996); Aller et al. (1989); Millison et al. (1989); and Cohen and Mercer, (1993). The following is a summary from these references:

1) Avoid unnecessary drilling within the DNAPL zone and an **outside-in approach is advised**. The first boreholes are installed on the perimeter of the site (in less contaminated areas or uncontaminated areas). The initial boreholes may be drilled up gradient of the DNAPL source (and/or dissolved-phase plume) and through any possible confining layer to characterise the geology of the site. The appropriateness of this approach must be evaluated on a site-specific basis.
2) **Utilise knowledge** of site stratigraphy and chemical distribution and carefully examine subsurface materials brought to the surface as drilling proceeds, to **avoid drilling through a confining layer** beneath DNAPL. In some situations, it may be necessary to drill through actual or possible confining layers at a site. Special precautions should be taken when investigators believe they may encounter a confining layer during drilling. Moreover, if field personnel suspect they may have encountered a possible confining layer while drilling a borehole and an approved plan for drilling through confining layers does not exist, drilling should be stopped immediately and the borehole should be decommissioned.
3) **Minimise the time and the length of hole, which is open at any time**. Any borehole that is not completed as a monitoring borehole should be properly decommissioned.
4) A **"telescoped casing drilling technique"** is advised to isolate shallow contaminated zones from deeper zones. Such techniques typically involve drilling an initial borehole partially into the possible confining layer, installing (grouting in) an exterior casing, emplacing grout in the cased portion of the borehole and after flushing the interior of the casing, drilling a smaller diameter hole through the cased off/grouted portion of the borehole (i.e., telescoping casing) through the confining layer. The appropriateness and actual design of telescoping borings and casings should be determined on a site-specific basis. Telescoping boreholes may be completed as boreholes or piezometers.
5) **Select optimum construction materials** and grouting methods based on consideration of site-specific chemical compatibility (Section 3.4.3).
6) The drilling method should allow for the **collection of representative samples** of rock, unconsolidated materials and soil. Temporary casings may be used to isolate different soil layers for sampling during drilling.
7) The drilling and sampling method should allow the geologist to determine where an **appropriate location for the screened interval** exists.
8) If drilling in a suspected DNAPL 'pool', consider the use of dense drilling mud to prevent DNAPL from sinking down the borehole during drilling.
9) **Drilling fluids** (including air) should be used only **when minimal impact** to the surrounding formation and groundwater can be ensured.

10) The drilling techniques using the auger bit cause fewer risks of cross- contamination between the various levels of the aquifer and do not require the introduction of drilling fluids. However, it is not able to drill very durable rock formations of loose ones with large fragments and could influence the local permeability; thus significantly reducing the efficacy of the operation.
11) To prevent surface contamination, **sheeting may be placed** on the surface to collect any contaminated sludge at the top of the borehole. After drilling is completed the sheeting together with the contaminated sludge should be properly disposed of.

3.4.2.1 Drilling techniques

From the available drilling techniques, the following were selected to be recommended as suitable techniques for the installation of boreholes on DNAPL contaminated sites in South Africa. Utilisation of different drilling techniques (auger, core and air percussion), provide the site assessor with valuable information regarding the subsurface. However, due to high costs and limited availability of specialized (e.g. diamond core and direct push auger) drilling rigs, these techniques are often neglected in site assessments in South Africa.

3.4.2.1.1 Air Percussion drilling

Percussion drilling methods operate by pulverising material at the bottom of a hole by dropping or pounding a bit. This type of drilling involves crushing by impact of the teeth of the drill bit. Most percussion drills are actuated by compressed air (pneumatic percussion). Percussion drills are best suited for drilling brittle, moderately soft to hard rock. In hard rock with percussion drills, you can drill faster and more economically than with other drilling methods. The air blows the cuttings from under the bit and up the annulus to the surface. The air's ability to carry the rock chips depends primarily on high air velocity. An up-hole velocity of about 4,000 fpm is required to remove cuttings.

Advantages of air percussion drilling include the speed of drilling through most semi- to well-consolidated formations and no water is required. The use of drilling fluids may be minimised when required. The technique is relatively inexpensive, but the equipment is expensive and has a high maintenance cost. It is also the most widely used drill technique for groundwater investigations in South Africa.

Disadvantages of air percussion drilling include the difficulty in defining precisely the boundaries between geologic layers. Due to the high air pressure applied during drilling, loss of VOCs by volatilization can occur.

3.4.2.1.2 Auger drilling

Hollow-stem augers are widely used in drilling and sampling at contaminated sites. The auger stem is hollow and may be used to sample the formation for geophysical logging and for well completion procedures while the formation is stabilised by the outside of the auger flights. Drilling with hollow-stem augers is similar to solid-flight augers. The augers are rotated into the ground using a rotary drive head on the drill rig. Sampling may be achieved at any depth if a pilot bit is used inside the hollow stem. The pilot bit and rods are withdrawn and a sampling device inserted. This may be either a split-spoon sampler driven into the formation beneath the bottom of the augers to obtain a disturbed core or a thin wall tube pushed beyond the base of the augers to collect an undisturbed sample.

When drilling into an aquifer that is under even low to moderate confining pressure or drilling far beneath the water table, the sand and gravel will frequently ‘heave’ upward into the hollow stem. If a centre plug is used during drilling, then flow of the aquifer material frequently occurs as the rods are pulled back. When this problem occurs, the bottom of the augers must be cleaned out before further sampling or progress can occur.

Unfortunately, the removal of material from the base will normally induce further material to flow up into the augers, thus compounding the problem. Sampling of running sands (or heaving sands) is very complicated.

Figure 4: Caking of sand and clay slurry during auger drilling.

The advantages of auger drilling include: minimal damage to aquifer, no drilling fluids are required; auger flight acts as temporary casing, stabilising hole for well construction; good technique for unconsolidated deposits; collection of relative undisturbed *in situ* soil samples at greater depth than is possible with test pits; and a continuous core can be collected hollow-stem method.

The disadvantages of auger drilling include: sand and clay may form a slurry which can cake the outside of the formation (this can be difficult to remove later and may prevent contamination from being detected in lower hydraulic conductivity layers); contaminants may be smeared down the formation, which leads to bias and inaccuracy in later sampling; cannot be used in consolidated deposits; sampling of running sands (or heaving sands) is very complicated; limited to boreholes less than approximately 50 m in depth; and possible abandonment of holes if boulders are encountered.

3.4.2.1.3 Core drilling

Diamond core drilling is the most versatile of all the methods and it is designed specifically for the resource exploration industry. In diamond drilling, the sample is cut by a diamond-armoured drill bit, stored in the inner barrel of a drill pipe. Then the pipe is brought to the surface and the core removed. In wire line diamond drilling, the most widely used and time effective method, the inner tube is hoisted to the surface through the drill rods without the need to remove them from the hole.

The advantages of this technique include: its versatility allows it to be done at most surface and underground locations; **it is the only method available that provides a core, a complete record of geological structure and rock texture; and it is the only commonly used method that provides reliable samples for accurate**

geochemical testing. It is recommended that DNAPL site assessments require the drilling of at least one core borehole during investigations.

Figure 5: Diamond drilling at UFS Campus Research Site. Note the temporary sump used for circulation of drill fluids.

During bedrock drilling and coring, DNAPL will usually be forced out of fractures during core recovery; however, more viscous DNAPLs may be recovered. During visual inspection of cores, DNAPL staining at fracture surfaces may be seen, but staining is not conclusive evidence of the presence of DNAPL. The physical properties of the core (porosity, diffusion, carbon on fracture surfaces, etc.) may be determined.

Extraction of pore fluid from sections of core, results in significant higher concentrations than measured *in situ* in the borehole. Sections of the core (preferably adjacent to fractures), are crushed and then methanol is added in a container and stored for several months before analysis. The samples should be collected and isolated from the atmosphere in less than 5 minutes after exposure at land surface (Shapiro, 2006). The measured contaminant concentrations in samples are often several orders higher than the contaminant levels measured in the borehole.

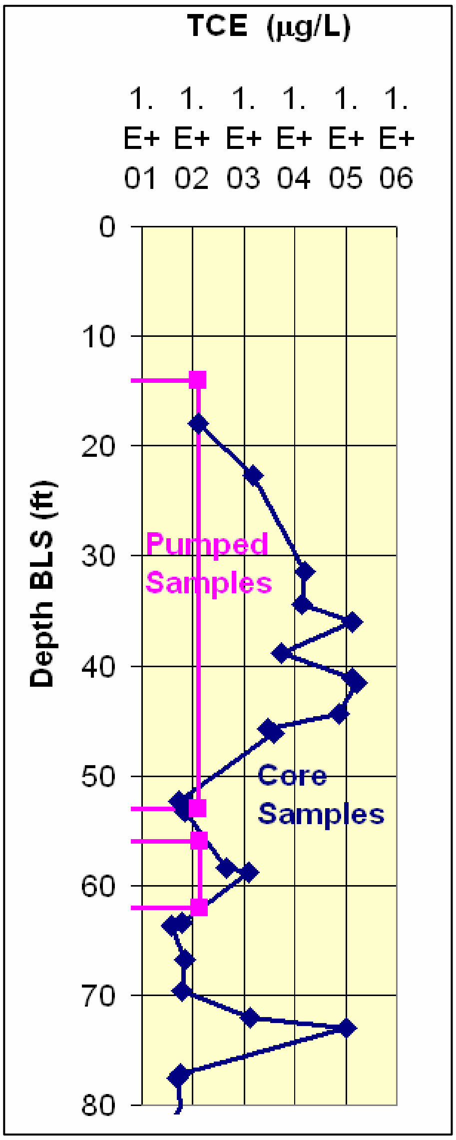

Figure 6: Comparison of measured TCE concentrations from pumped borehole samples and extracted core samples

(From Shapiro, 2006).

Disadvantages are however, that the technique is the **most expensive** of all the drilling techniques and the drill rigs are often not available for contamination investigations. Some types of broken and abrasive rock are nearly impossible to core at a reasonable cost (these lithologies literally fall apart during transport up the drill string), but special methods of recovery for these soft lithologies have been designed using tubes and protective sheaths, but the recovery is still generally poor.

Some fractures may be the result of mechanical breaks from the coring and the log should therefore be correlated with borehole wall imaging (afterwards) and other down-hole geophysics.

It is not possible to restrict the use of drill fluids during core drilling. Many of the fluids used are organic based surfactants. It is advisable that the type and quantity of fluid used during the drill process be recorded and that a temporary sump be used for drill fluid circulation on surface (Figure 5).

3.4.3 Borehole construction

The monitoring of boreholes is necessary to characterise flow directions and rates, groundwater quality, NAPL fluid distributions and media hydraulic properties. Pertinent data are acquired by conducting fluid thickness and elevation surveys, fluid sampling surveys, hydraulic tests and down-hole surveys. The locations and design of the boreholes are selected based on consideration of the site conceptual model and specific data collection objectives (Cohen and Mercer, 1993).

The design and construction of boreholes at DNAPL sites require special consideration of:

- The effect of borehole design and location on NAPL movement and distribution within the borehole and the surrounding environment;
- The compatibility of construction materials with NAPLs and dissolved chemicals; and
- Borehole development options.

Inadequate design may increase the potential for causing vertical DNAPL migration and misinterpretation of fluid elevation and thickness measurements and aqueous concentrations. It is recommended that “borehole nests” of varying depths (and correct construction), be installed at a DNAPL sites. Multiple piezometer installations in single boreholes often fail to separate aquifer systems and could cause migration (and therefore misinterpretation of results) of DNAPL and aqueous phase between systems.

Table 6 lists the relationship between borehole construction to the mobile DNAPL phase and capillary barriers. From this, it is clear that the construction may influence direct measurements of DNAPL in boreholes and cause potential vertical DNAPL migration in the borehole environment.

A borehole that is completed to the top of a capillary barrier and screened from the capillary barrier surface to above the DNAPL water interface, is most likely to provide DNAPL thickness and elevation data that are representative of formation conditions.

It is therefore very important to record all observations during drilling in order to select the correct construction method for the borehole.

Furthermore, it is important to note that most of these observations noted above and in Table 6 are relevant to unconsolidated media. Pankow and Cherry (1996) observe that the only conclusion that may be drawn from the observation of DNAPL in a borehole in fractured media, is the presence of DNAPL at the site.

Figure 7 shows that the height of DNAPL measured in the borehole may be misleading. The same height of DNAPL in the borehole may be measured for two different scenarios: either the presence of DNAPL corresponds with the general same elevation of DNAPL in the formation or the height of DNAPL measured in the borehole is from accumulation of DNAPL from a higher elevation in the formation. The borehole may also act as a conduit and DNAPL can short-circuit to the formation below the borehole if the capillary pressure exceeds the entry pressure for a fracture below the borehole. It is therefore very important to ensure that boreholes in fractured media are adequately sealed (with e.g. bentonite) at the bottom and the screen intervals selected, according to the geological log and with the purpose of preventing the downward mobilisation of DNAPL.

Table 6: Well (borehole) construction design and the effect it has on measured DNAPL thickness in well (borehole).

Adapted from Cohen and Mercer 1993.

Well construction	**Measurement/observation of DNAPL in well**
If the well screen or casing extends below the top of a DNAPL barrier layer	DNAPL thickness > pool thickness Exceed by the length of the well below the barrier layer surface
If the well bottom is set above the top of a DNAPL barrier layer	Measured DNAPL thickness < pool thickness By the distance separating the well bottom from the capillary barrier layer upon which DNAPL pools
If the well connects a DNAPL pool above a barrier layer to a deeper permeable formation and the well will cause DNAPL to short-circuit the barrier layer and contaminate the lower permeable formation	DNAPL elevation and thickness in the well are likely to be erroneous The height of the DNAPL column at the well bottom will tend to equal or be less than the critical DNAPL height required to overcome the capillary resistance offered by the sandpack and/or of the less permeable formation
NAPL which enters a coarse sandpack may sink to the bottom of the sandpack rather than flow through the well screen	Small quantities of DNAPL may elude detection by sinking down the sandpack and accumulating below the base of the well screen
The bottom of the well screen is set above the bottom of the sand pack and there is no casing beneath the screen	Small quantities of DNAPL may elude detection by sinking out the base of the screen and into the underlying sandpack
Sand packs generally should be coarser than the surrounding media	Screen or sandpack openings that are too small may act as a capillary barrier to DNAPL flow and DNAPL will not be able to enter the well
If the well screen is located entirely within a DNAPL pool and water is pumped from the well	DNAPL will upcone in the well to maintain hydrostatic equilibrium causing the DNAPL thickness in the well to exceed that in the formation
If the top of the DNAPL pool is under drainage conditions	The elevation of DNAPL in a well may exceed that in the adjacent formation by a length equivalent to the DNAPL-water capillary fringe height

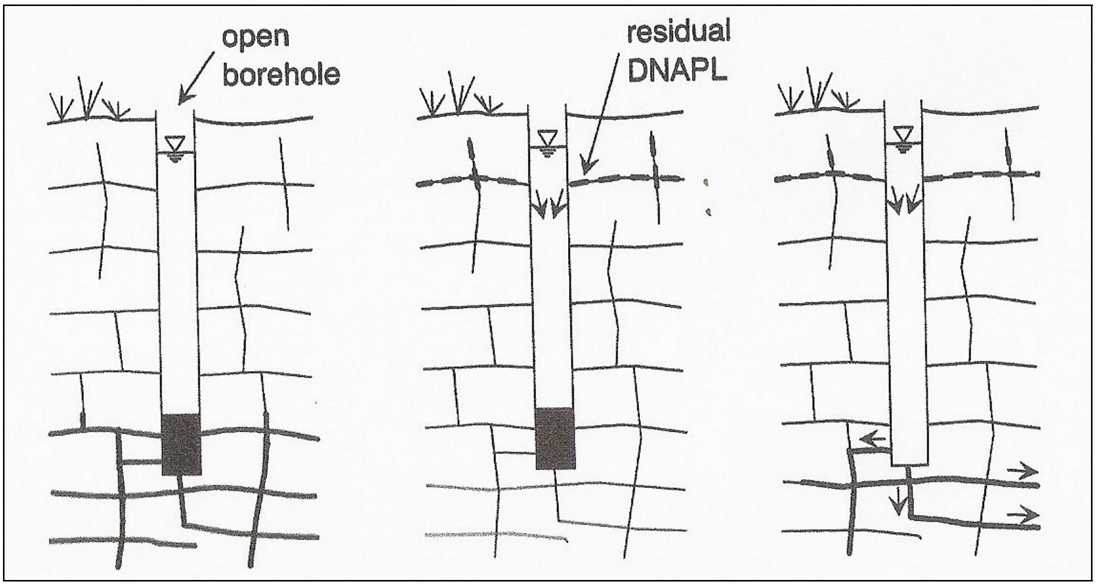

Figure 7: Height of DNAPL in a well in fractured media

(From Pankow and Cherry, 1996).

3.4.3.1 Compatibility of construction materials

The compatibility of borehole construction materials with NAPLs and highly contaminated groundwater should also be evaluated during borehole design. Borehole construction materials (e.g. screens, casings, sealants) are subject to degradation or corrosion in the natural environment. Materials exposed to NAPLs may also be degraded or corroded, which may lead to structural failure. This vulnerability applies to materials exposed to these chemicals in both the subsurface and above ground. The EPA, (1995) recommends that at sites where the presence of NAPLs is suspected, a materials' compatibility review should be conducted. Since the time requirements for either monitoring (or subsurface remediation systems) at contaminated sites are usually long-term, it is economically and technically important that these systems be constructed of materials with known chemical resistance qualities to provide reliable service over many years.

There are two types of effects that NAPLs have on materials used in borehole construction (sampling and remediation): firstly, the structural integrity of a material may be compromised by corrosion or solvation. Secondly, dissolved groundwater contaminants from NAPLs can sorb to or leach from monitoring materials, which affect groundwater quality measurements. Another way of viewing these two effects is from a concentration perspective. Sorption to monitoring surfaces may have the greatest effect on water quality measurements when contaminants are present at low dissolved concentrations. Conversely, sorption of contaminants present as NAPLs or in high dissolved concentrations, may have a minimal effect on water quality measurements, while the effects on the structural integrity of the materials may be at a maximum.

McCaulou et al. (1995) published a "Chemical Compatibility Table". The compatibility in this paper is defined as "a material's ability to withstand corrosion or degradation under specific experimental conditions". This refers to the effects that NAPLs and high concentrations of dissolved organic compounds have on the structural integrity of materials.

During this project commonly used (in South Africa), borehole construction materials were tested with various TCE concentrations for a period of 18 months. Bentonite was tested as a sealant of a borehole bottom. It was found that under the correct application (the bentonite must be submersed in water), the integrity of the bentonite is not affected by a NAPL such as TCE. However, if the bentonite is not correctly applied, cracks may develop which cause preferential pathways for the NAPL to migrate downwards.

The following photograph shows how the TCE (dyed red with Sudan IV) has sorbed to the PVC and after 18 months, the PVC has become completely plasticised. TCE concentrations also increased the corrosion of the steel casing material and where NAPL was present, it sorbed to the steel casing material to some extent; however, not as strongly as to the PVC.

Figure 8/…

Figure 8: Effect of TCE (dyed red) on PVC material after 11 months of exposure.

HDPE, (which was inspected by means of UV fluorescence in order to determine the extent of sorption and/or corrosion) showed no signs of sorption or corrosion. Therefore, from the results of these simple experiments it is evident that care should be taken to select the correct construction material to ensure long-term stability and to prevent water quality errors during sampling.

It is recommended that the selection of construction materials be done on a site-specific basis. Once the contaminants of concern are known, the Chemical Compatibility Table of McCaulou et al. (1995) may be used to select suitable materials. A copy of this table is in Appendix A.

3.5 Pumping Tests

The principle of a pumping test is that if water is pumped from a borehole and the discharge and the drawdown of the borehole is measured in the borehole and in observation boreholes at known distances from the borehole, the measurements may be substituted into an appropriate well-flow equation. These may used to calculate the hydraulic characteristics of the aquifer (Kruseman and De Ridder, 1994).

Pumping tests are important tools that provide information on the hydraulic behaviour of a borehole, the reservoir and the reservoir boundaries. All this information is essential for efficient aquifer and well field management. In general, the objectives of a pumping test are (Van Tonder et al., 2001):

- to obtain an understanding of the aquifer;
- to quantify the aquifer's hydraulic and physical properties; and
- to determine the sustainable yield and efficiency of a borehole.

The interpretation of pumping test data is based on mathematical models that relate drawdown response to discharge in the abstraction and/or monitoring borehole. The results obtained from these short duration tests may then be used to project the borehole's performance over a long period of time. In fractured-rock aquifers, the geometry and permeability of the system have a large influence on the drawdown. The scale of heterogeneity in a fractured-rock system may be large in relation to the scale of the test. Therefore, conventional models developed for homogeneous porous aquifers might not be viable in fractured-rock systems.

Specific methods and software developed to analyse pumping tests conducted in fractured-rock systems should be used when considering the estimation of hydraulic parameters in these fractured systems.

Estimation of the correct aquifer parameters is used for the construction of the correct conceptual model in combination with the geological set-up. In cases of contaminated groundwater, the aquifer parameters are important for planning and management during risk assessments and/or groundwater remediation. Depending on the objectives, several observation boreholes and piezometers at different depths may be used for measurements.

From the above-mentioned points, it is clear that the principles for conducting and analysing pumping tests depend on the objectives of the investigation. During DNAPL investigations, pumping tests are used to estimate the hydraulic parameters and for finding the principal hydraulic features of the system. Pumping tests are rarely used in isolation for aquifer parameter estimation and the use of a suite of aquifer testing methods, such as slug testing, pumping tests, flow logging, and tracer testing is preferred by site investigators (Cohen and Mercer, 1993; Pankow and Cherry, 1996; Sara, 2003).

However, when pumping tests are used at a suspected DNAPL site, pumping boreholes and pump rates should be carefully selected in order to prevent DNAPL pool mobilisation.

If DNAPL is pooled on an aquitard layer, an increase in hydraulic gradient from groundwater pumping may mobilise the pool (Pankow and Cherry, 1996).

If the objective of the pumping test is to estimate aquifer parameters that are to be used in e.g. a numerical management model, the constant rate test is the most important test and is set as a minimum requirement for parameter estimation. Although a slug test and step drawdown (or multi-rate) test may also be conducted, it is of not much practical value. If the interest is setting up a 3D numerical model, a number of piezometers or well-nests must be installed (to measure pressure heads and vertical K-values of each layer). One of the most important factors of a constant rate test in this case is selecting the abstraction rate during the test. The abstraction rate must be chosen in such a way that no main water-yielding structures will be dewatered during the test.

Aquifer parameters, which are typically estimated from the pumping tests, are hydraulic conductivity or transmissivity, specific yield (unconfined aquifers) and storativity (confined aquifers). Pumping test results could also be evaluated using methods such as the Flow Characteristics (FC) methodology to locate fracture zones and highly transmissive units that would control DNAPL movement.

3.6 Tracer Testing

3.6.1 Conventional Tracer Testing

Understanding the processes controlling subsurface transport is a key element in the demonstration of the safe disposal of hazardous wastes, as well as the design and implementation of effective contaminant remediation. Subsurface transport is complex, controlled by the transport parameters such as groundwater velocity, kinematic porosity and dispersion. According to Riemann (2002), these parameters normally have to be analysed from field tests, known as tracer tests. Conventional field methods such as pumping tests are adequate for most water supply investigations, but do not yield sufficient information for modelling aqueous mass transport.

Field-scale tracer testing is a highly effective technology for determining controlling transport processes, as well as important transport parameter values used in risk assessment and remediation design.

3.6.1.1 Tracers

Tracers are identifiable substances, which may be used to infer the general behaviour of a flowing medium. An ideal groundwater tracer has the following characteristics:

- it is conservative and will follow the movement of the water without loss from flow due to physical or chemical processes, like adsorption on sediment or equipment;
- be safe in drinking water;
- it is detectable with a high sensitivity and can be measured accurately *in situ*;
- it does not contaminate the terrain of investigation and does not affect results of further tests; and
- it is inexpensive and available.

Since there is no ideal tracer, the selection of the tracer should be based on the most important considerations, which will depend on the nature of the investigation. For instance, if the advective properties of a medium are investigated, care should be taken that the tracer is physically compatible with the fluid, while a study of the diffusive flow through a porous medium will require attention to the diffusion constants and the molecular size of the tracer.

Tracers may be classified as environmental and artificial, depending on their origin. Substances normally present in the medium are environmental, while those deliberately introduced into the medium for the purpose of the study, are termed artificial tracers. The use of artificial tracers for parameter estimation requires special equipment for introducing, mixing and sampling, but the tests may be carried out on a local scale with low time consumption and costs. In most cases conducting tracer tests with artificial tracers is sufficient for the purpose of the study and is more applicable to South Africa (Riemann, 2002).

Artificial tracers may be categorised by their mode of analysis and include: radioactive tracers; activated tracers; chemical tracers; and particulate tracers. All radioactive tracers are subjected to legislation in most countries and the disadvantage of a negative general public reaction to the use of radioactivity limits their applicability. Activated tracers are stable elements, which are capable of neutron irradiation over a short term during activation to produce a radioactive isotope and they are generally used as anionic complexes. These tracers present no radioactive hazard to natural waters and no authorisation is required for use. High levels of sensitivity are reached, but the costs of analyses are very high. Elements applied as activated tracers are indium, bromide and iodine. Chemical Tracers have the advantage that they may be used without authorisation and that field detection equipment is readily available (especially for the dyes). For some tracers, such as many salt tracers, analysis requires sample treatment and has to be carried out in the laboratory. Inorganic salt tracers, such as the anions Cl^- (NaCl) and Br^- (NaBr, KBr), are commonly used to trace groundwater movement, while the cations are often lost by ion exchange. The most commonly used salt tracers are NaCl and NaBr.

Organic dyes are frequently used as groundwater tracers, since the sensitivity of fluorometric analysis is very high and dye tracers are detectable in very low concentrations compared to salt tracers. The main advantage is that field measurements may be performed with filter fluorometers. The sensitivity of the analysis depends on the efficiency of the dye to convert the excitation energy into fluorescence and the transmission of the filter combination in the fluorometer. The delectability depends on the background fluorescence value. Rhodamine B and Rhodamine WT have the lowest level of sensitivity and delectability, while the sensitivity of Fluorescein is about ten times higher.

Some dyes, however, are not conservative and are influenced by water quality. Temperature variations may affect the measured concentration of the dye tracer. During the measurement process, non-adsorptive dye loss may happen due to chemical reactions and decay under light. Adsorption onto sediment surfaces is another disadvantage of some tracers such as Rhodamine B and Rhodamine WT, for instance. Rhodamine B is toxic to aquatic organisms and therefore should not be used as a water tracer. The toxicity of Fluorescein, Eosin and Photine is relatively low.

Taking all this information into account, and comparing the properties of the different dye tracers, Fluorescein and inorganic salt tracers are recommended for use if tracer testing is to be conducted at a DNAPL contaminated site. The tracers may be detected in the field with a Fluorometer and EC meter, respectively, which avoids sampling and chemical analysis in the laboratory. It is further recommended that after a tracer test has been performed, investigators should ensure that recovery of the tracer was adequate in order not to contribute to the contaminant load in the groundwater system.

3.6.1.2 Tracer Tests

Tracer tests aim to relate the concentration of chemical, biological or solid substances measured in observation boreholes to the flow velocity. A variety of single-well and multiple-well tracer tests with their analysing methods, are available for use at NAPL contaminated sites. In the following, a brief summary of some of these methods is given:

As the name indicates, single-well tracer tests are conducted in one borehole only, meaning that injection of the tracer and measurement of the concentration take place in the same borehole. Conducting and measuring types vary for the different test types. Common methods used are the single-well point dilution test method and the single well injection-withdrawal test.

Multiple-well tracer tests under natural gradient are usually conducted with one injection borehole and one or more observation boreholes. When conducting a natural flow tracer test, one borehole is used for the injection of the tracer, while several boreholes downstream of the source borehole are used for observing the concentration of the tracer at different times. The analysing methods for this type of tracer test may also be applied to natural conditions with environmental tracers, such as pollutants at contaminated sites, if measurements of the concentration at different times are available.

The transport and spread of the tracer plume is controlled by advection (i.e. flow velocity) and longitudinal and transversal dispersion, while the certain concentration at time t and position (x,y) is also a function of matrix diffusion, retardation due to non-ideal tracing behaviour and decay (Fetter, 1999).

The disadvantages of this test are the time necessary to carry out the test and the difficulties in measuring the tracer concentration in the observation boreholes. The measurement tool should not disturb the natural flow field. On the other hand, the real concentration in the flow path (i.e. the fracture zone) is required, which cannot be realised properly in open boreholes. Another practical problem related to this test is the position of the boreholes, which are often not located exactly in the flow direction. Moreover, the flow direction is often not known exactly or may change along the flow path.

Some of these difficulties were overcome during the research project by the determination of fracture orientations (and therefore flow paths) where information was available.

The most common methods in conducting tracer tests are multiple-well tracer tests, where a specific flow field is created by recharging and/or abstracting water at different boreholes, called a ***multiple-well tracer test, forced gradient.*** Injection and observation of the tracer will then take place at specific points in the created flow field. The tests and the analysis methods differ according to the created flow field.

Pumping a well until steady state conditions are reached creates a radial convergent flow field (Riemann, 2002). A tracer is then quickly introduced in an injection well located in the vicinity of the pumping well, in such a way that a minimum disturbance of the flow field is caused, while the tracer breakthrough curve is monitored at the pumping well. Analyses of the resulting breakthrough curves yield estimates of the kinematic porosity, aquifer dispersivity and groundwater velocity. The ***radial convergent test*** is attractive because it is theoretically possible to recover the tracer from the aquifer completely. Furthermore, it most closely represents reality as groundwater pollution often occurs in the vicinity of pumping wells, where radial flow fields are present. The convergent tracer test, in combination with the borehole dilution test, has proved to be a powerful hydrogeological tool for measuring groundwater velocity and kinematic porosity.

A combination of radial convergent and point-dilution tests may be used to estimate the Darcy velocity $q_{f.}$ The radial convergent test yields independently a value for the flow velocity. The analysing procedure stays the same for each part of the test. This opens new possibilities of parameter estimation, especially for the flow dimension and flow domain and the kinematic porosity.

Thus, the single-well tests, mainly the point-dilution and injection-withdrawal, may be easily performed to evaluate the Darcy and natural-flow velocities, respectively. Since they are done under natural groundwater flow, they do not require specific and expensive equipment that is difficult to handle. To save time and costs, both the tests may be done in one experiment but at different steps. The injection part of the injection-withdrawal test may be used as a point-dilution test. Data are then analysed independently for each test. Radial-convergent tests are recommended to provide reliable results of dispersivity, kinematic porosity and groundwater velocity. Only two pairs of boreholes, which are closely spaced, are required for the injection and abstraction of the tracer.

As discussed above, the aim of a tracer test is to estimate transport parameters of the aquifer. Although the movement of DNAPL through a geologic medium depends on the density and viscosity of the DNAPL, the transport parameters also play a vital role in the extent of DNAPLs in the subsurface and their study is important in the site characterisation and fate of the DNAPLs.

3.6.2 Partitioning Interwell Tracer Tests (PITTs)

The Partitioning Interwell Tracer Test (PITT) approach has been used to determine the distribution and volume of DNAPL (Pope et al., 1994, Jin et al., 1995). Accurate evaluations of contaminant transport, effective risk assessments and successful remediation for NAPL-contaminated sites requires knowledge of the occurrence and distribution of NAPL and its dissolution behaviour. The availability of such information is limited by current site characterisation techniques. A major limitation of these methods is that they provide data at discrete points, in such a way that the probability of sampling a zone of localised NAPL is quite small. In addition, the use of point-sampling methods for characterising large domains is constrained by sample-size limitations (Brusseau et al., 2000).

Because the subsurface distribution of immiscible-liquid saturation is complex, the use of point-sampling methods is often problematic. This has created interest in the use of partitioning tracer tests for characterising the occurrence, quantity and distribution of immiscible-liquid saturation in subsurface systems. The use of partitioning tracer tests to measure immiscible organic-liquid saturation in the subsurface was developed by the petroleum industry in the 1970s as a means to determine residual oil saturation in oil fields. Since then, numerous partitioning tracer tests have been conducted, as reviewed by Tang, 1995. PITTs are designed to measure the volume and saturation of residual DNAPL in the test zone and the presence of free-phase DNAPL reduces their accuracy (Jin et al., 1997).

The main purpose in conducting these experiments is to determine whether naturally occurring organic matter would interfere with the accuracy of DNAPL measurement by partitioning tracers. If the tracer response curve shows any retardation of the partitioning tracer with respect to the conservative tracer, there is sedimentary organic carbon in the aquifer sediments.

Successful implementation of a PITT requires the development of an engineering design based on careful and systematic simulations. A good design should minimise the risk of failure, optimise the information collected and save time and money. Simulation modelling before field test implementation can provide valuable insight into pertinent design parameters that affect the outcome of the tracer test.

It should however be considered that use of PITT techniques for DNAPL assessment is a time- and cost-intensive exercise and with available technology only applicable to shallow, porous aquifer systems. The advantages of the information gained during such a test needs to be considered. Before implementation, a site assessor needs to be certain that the DNAPL residual source zone is significant enough in extent to warrant such a test.

3.7 Visual examination of soil/rock samples

Evidence of the presence and distribution of DNAPLs may be obtained by careful observation and field testing during drilling or the collection of soil and rock samples. Significant cost savings may be realised during a site investigation if DNAPL presence can be determined directly by visual examination of soil and groundwater samples, rather than indirectly by more costly chemical analyses (Section 4.1). In certain circumstances, DNAPL in soil or rock is obvious. Abundant dark-coloured DNAPL at high residual saturation or in layers and pools is usually readily visible in soil cores (Pankow and Cherry, 1996). This is often true for coal tar or creosote when released in large quantities (Figure 9). It is less common to identify visually DNAPLs such as chlorinated solvents, because of the nature of the liquid and the variability in source zones. The integrity of the sample, (e.g. core samples from hollow-stem technique) will also influence visual identification of possible DNAPL presence.

Figure 9: Coal tar visible on soil sample from test pit.

Visual identification of DNAPLs may be enhanced by using methods such as ultraviolet (UV) fluorescence and soil-water shake tests (with or without dye). The UV fluorescence method involves the examination of soil samples under a portable UV light. Many of the aromatic and polycyclic aromatic hydrocarbons (PAHs) and unsaturated aliphatic hydrocarbons (e.g. TCE and PCE) fluoresce (Pankow and Cherry, 1996). Examination by UV fluorescence may be accomplished in transparent plastic bags or bottles so that the samples can be manipulated without excessive loss of volatiles. Soil samples of uncontaminated soil should also be examined under UV light as controls, since some minerals could fluoresce. This method proved to be a cost-effective first order screening of soil samples and provides guidance for either, further detailed laboratory analyses of soil samples or indicates where more detail assessment techniques should be focused on the site.

Soil water shake tests involve the transfer of a soil sample to a clear, sealed container (tube) with an equal amount of water. The container is then shaken by hand and/or centrifuged and then inspected for DNAPL at the bottom of the container. The test may be enhanced by the addition of a hydrophobic dye such as Sudan IV. Sudan IV is a relatively inexpensive (100 g costs R180-00 from Aldrich Chemical Co.), reddish-brown powder that dyes organic fluids red upon contact, but is practically insoluble in water at ambient temperatures. This method may be used on site during drilling and sampling exercises. Cohen et al. (1992) recommend that dye shake tests be conducted in plastic containers (e.g., polypropylene tubes) because hydrophobic NAPLs generally wet plastic better than glass, thereby enhancing NAPL detection on the container wall.

Visual and enhanced visual identification (especially UV fluorescence) may be recommended as first order screening methods, but consideration has to be taken of the limitations of the tests.

3.8 Vapour analyses of soil samples

By performing vapour ‘head space’ tests on soil samples as they are collected during the drilling, a further distribution of soil vapours in the subsurface may be obtained and the testing may also be used as a field screening test to assist the sampler in deciding which samples should be submitted to the laboratory for chemical analysis.

During drilling, samples of soil and rock (*of a fixed volume*) may be collected in sealable plastics bags. After a few minutes, a PID (‘sniffer’) is inserted into the head space of the bag to measure the concentrations of VOCs

(Volatile Organic Compounds) over a 1 minute logging period. It is recommended that the average and peak PID levels be recorded on the soil sampling field sheet.

However, from the field experience during this project, it was found that the results from the headspace tests often did not correlate with the chemical analyses of the soil samples. This may be attributed to loss of VOCs during the sample collection or incorrect calibration standards for the particular onsite contaminants. The concentration measured is also dependent on the sample size, i.e., the bigger the soil sample in the plastic container, the higher is the reading. At times of higher temperatures, a sample in a container will volatilize VOC's and will have higher "concentration" than in colder temperatures.

More sophisticated soil gas samples are commercially available, which will yield more accurate results. However, these are often expensive and soil gas measurements should rather be used as a screening method for possible source zones and not as a qualitative measurement at DNAPL sites (see also Section 3.2).

3.9 Water and fluid sampling

Water samples may be collected during the drilling of boreholes. It is not recommended that these samples be used for chemical analysis, but rather in screening for further sampling and chemical analysis (Section 4.3). During drilling, there are several factors which could influence chemical results. The most important are the possible presence of drill fluids and/or oils from the drilling process. VOCs are also unlikely to be detected in water samples during drilling, in the case where the drill method involves air flushing (e.g. air percussion).

Samples may be used to perform screening tests such as a dye shake test and even field measurement of geochemical parameters such as EC and pH.

In the event of drilling through a suspected DNAPL, a 'pool' collection of a sample of the NAPL fluid should be done. This might be the only opportunity of collecting an NAPL sample, as it is possible that the NAPL will not collect any further within the borehole. NAPL samples may be used to test for the physical properties and chemical composition.

3.10 Borehole logging

3.10.1 Geochemical logging

Geochemical profiling is an inexpensive, yet effective tool for site assessment at DNAPL contaminated sites. The advantages of this type of profiling include the determination of hydraulic variation within the vertical profile of the subsurface and the identification of important features in the system. By using this, features such as fractures or layers which transport different salinity groundwater may be identified. As stand-alone measurements, these observations have limited value; however, when viewed in conjunction with the geological logs or other down-hole measurements, a far more detailed conceptual understanding of the most important geohydrological features may be obtained. These features are important for the dissolved phase plumes from NAPLs and also for the NAPL transport itself, since they identify the stratigraphic horizons along which these are most likely to be transported.

When considering the degradation of organic contaminants, chemical parameters such as redox potential and dissolved oxygen may provide information on the indication of aerobic or anaerobic conditions in the subsurface.

The main parameters considered to be of importance at DNAPL sites are conductivity (EC), pH, temperature, chloride, redox potential and dissolved oxygen (DO). Several multi-parameter probes are available on the market for this purpose. Another down-hole probe which is inexpensive and easy to use, is the Solinist TLC Meter, which measures EC and temperature. The Solinist TLC Meter displays accurate measurements of conductivity and temperature on an LCD display. Water level and probe depth measurements are read off the accurate flat-tape, marked in millimetres. The tape is housed on a standard reel. These features make the TLC Meter ideal for profiling conductivity and temperature in wells and open water.

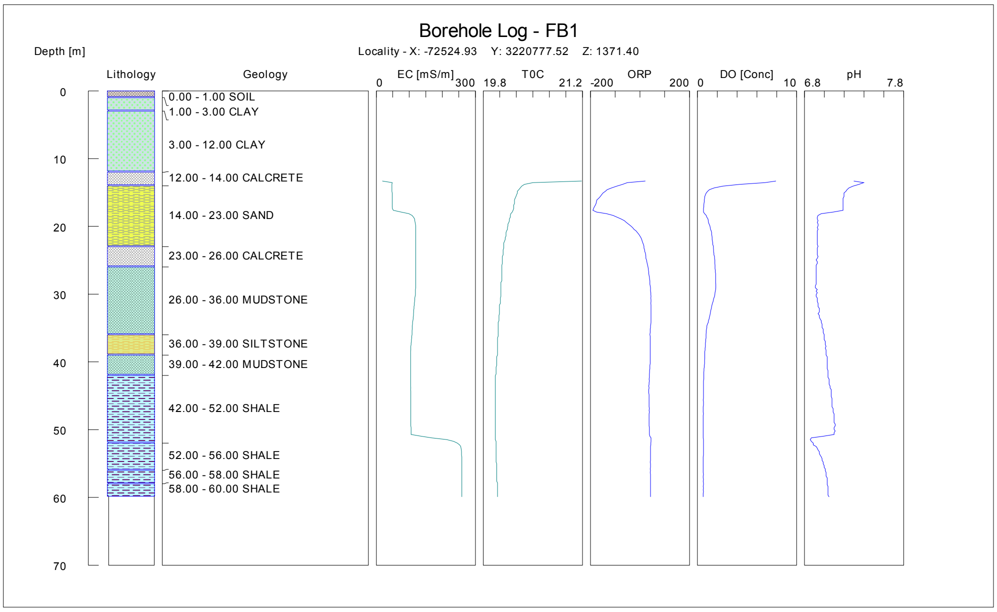

Figure 10: Multi-parameter log of Borehole FB1.

3.10.2 Interface meter

The accumulation of DNAPL in the bottom of a monitoring well may be determined effectively by the use of interface probes or by sampling at the bottom of the well. Interface probes are down-hole sensors on a graduated cable or tape. They commonly use an optical sensor for detecting the air-water interface and a conductivity sensor for detecting a water/DNAPL interface. (In boreholes that also contain an LNAPL, the optical sensor would detect the air/LNAPL interface and the conductivity sensor would detect the LNAPL/water interface.)

Under ideal conditions, a DNAPL thickness of about 0.5 cm or greater can be detected. However, a DNAPL is difficult to detect by these means when it is mixed with fine sediment at the bottom of the well, when it is conductive, or when it preferentially wets the probe materials (Pankow and Cherry, 1996).

The presence or absence of DNAPL is determined by lowering the probe to the bottom of a borehole. If a steady tone and light is activated, it indicates a non-conductive liquid. Then the probe is lowered until the probe touches the bottom of the borehole and the tape goes slack. The thickness of the DNAPL layer is determined by subtracting the first reading from the second.

At some sites, DNAPL will be observed in the observation boreholes. Although this will confirm the presence of DNAPL at a site, the thickness in the borehole cannot be related to the thickness of DNAPL in the subsurface. The presence of DNAPL in the boreholes cannot be related to the vertical distribution of DNAPL in the subsurface. The only circumstances under which the thickness may be related to the subsurface, is in the case of large discrete pools in granular media (Pankow and Cherry, 1996).

The reason for this discrepancy is often that it is very difficult to know where the borehole is installed within the pool. The only time the thickness may be determined from the borehole, is when the capillary properties of the formation, the borehole construction material, together with the properties of the DNAPL, is known.

4. ANALYSIS OF DNAPL, SOIL AND WATER

Chemical and physical properties of contaminants and media are measured to evaluate chemical migration and remediation alternatives at DNAPL contaminated sites. These chemical and physical properties are defined and their significance with regard to DNAPL contamination is discussed in Progress Report 1 for this project. Methods used to determine DNAPL composition, aquifer media (soil) properties and water chemistry are described briefly in this section.

4.1 NAPL samples

The first step in determining the type of contaminant at a site and the properties of such contaminants is to determine the contaminant source. Therefore, it is important to obtain a representative sample of the (D)NAPL contaminating the site.

As discussed in previous sections, it is not always possible to collect a sample of the NAPL as it will be found in the subsurface. In this case, knowledge of the suspected chemicals (and impurities/mixtures that are caused by the site activities) used at the site is required and the contaminant properties estimated from the literature. In the case where NAPL contamination is still visible at the surface, a sample may be collected from this source (e.g. spill sites or in disposal dams/areas). However, cognisance should be taken, when determining NAPL properties in this manner, of changes due to dissolution, weathering and degradation that could change the properties of the DNAPL in the subsurface.

If NAPL 'pools' were intersected during invasive methods, such as test pits or drilling, a sample of the NAPL may be collected directly from the subsurface from sampling the borehole or test pit and the properties thereof, determined.

4.2 Soil samples

Chemical analyses of soil samples may be useful in determining the presence and distribution of DNAPL in the vadose and saturated zones. However, such analyses may be ineffective if the soil sampling and analysis methods used are not suitable for the purpose of the investigation. The following sections give guidance on sample collection, analysis and indirect calculations to determine DNAPL presence.

4.2.1 Sample collection

Soil samples may be collected during the site investigation from above or below the water table. For shallow soil profiling, samples are often taken from test pits (Section 3.4.1). For deeper profiling, samples may be taken during auger drilling (Section 3.4.1) or during air percussion drilling (Section 3.4.2.1.1). Each of these sample collection methods has its own advantages and disadvantages.

During drilling operations, soil samples may be taken and subjected to visual examination, in order to determine the presence of DNAPL. If DNAPL is present at high saturations it will be probably be readily noticeable. If the DNAPL is present at low saturations, enhanced techniques such as UV and dye testing may be used (see Section 3.7). Soil samples are however, not only used to determine DNAPL presence, but should be submitted for chemical analysis to determine the presence of contaminants in the sorbed, aqueous and vapour phases.

Pankow and Cherry, (1996) list the critical issues related to any soil sampling as:

1) The lateral and vertical spacing of the samples,
2) Cross-contamination during sample collection,
3) The selection of sub-sample portions for analysis, and
4) Loss of volatiles during sample collection, handling and storage.

These critical issues need to be considered, regardless of the sampling method.

Because the migration pathways of DNAPL are strongly influenced by heterogeneities in the media, both on small and larger scales, the spatial distribution of DNAPL in the subsurface will therefore be highly variable. It is recommended where possible, that vertically continuous samples (e.g. with hollow-stem auger) be collected in order to reliably identify the variability throughout the soil profile. If this method is not possible at a site, either collecting samples through test pit or normal auger drilling may provide similar results, if the spatial distribution of the sample points is carefully selected.

Cross-contamination during sampling may be prevented by using dedicated sampling tubes (hollow-stem auger) or by decontaminating sampling equipment (e.g. spoons, shovels, drill bits) in between sampling points. Some cross contamination *between layers* of variable permeability may also take place within the tubing, of the continuous samples. The NAPL may find a pathway along the tube wall and collect at a different layer than originally found in the soil profile.

The selection of sub-samples for analysis must be performed carefully to obtain a representative sample. Concentrations may be found to be too high, if for example, a nodule of soil, coated in NAPL is included in a sub-sample, but this is not necessarily representative of the contaminant concentrations at that level in the soil profile.

Loss of volatiles during soil sampling, collection and storage, is often a problem. It has been repeatedly stated that 80% of the total errors occur in the field for the more stable contaminants (e.g., metals, PCBs and pesticides) and up to 99% of the total errors occur in the field for non-stable contaminants (e.g. volatile organic compounds; VOCs) (http://www.epa.gov).

Soil gas measurements (Section 3.8) offer an economical and rapid screening method at some sites, but soil gas concentrations cannot be used to predict the total concentration of soil VOCs (vapour, sorbed, dissolved and NAPLs). In contrast, soil samples, if properly sealed and preserved, may be used to measure VOCs in all phases. However, unquantifiable VOC losses may occur during sampling and during sample transfer steps prior to analysis (Siegrist and Jenssen, 1990).

Studies have shown that large VOC losses occur if samples are not collected and handled prudently (Siegrist and Jenssen, 1990). A comparison of in-house purge-and-trap analysis vs. contractor-analysed collected samples has shown that preservation and transfer steps were responsible for the loss of one to three orders of magnitude (Hewitt, 1994). Prudent handling is generally described as:

1) Sampling by a limited disruptive method or one that limits exposure of soil surfaces;
2) A quick transfer into the sample container taking care to provide a complete seal between lid, liner and container (avoid contact of soil particles with the sealing surfaces of the container); and
3) The use of either methanol extraction or a container/analytical system that requires no further atmospheric exposure during transfer steps.

Preservation of soil samples with methanol (1:1 ratio soil to extraction solvent) is recommended for VOC sampling by the US EPA. Several references regarding the method to be used and precautions to be taken are available on their website http://www.epa.gov. This method was tested during the project. However, no conclusions could be made with regard to the method. The analytical results from the methanol preserved samples were similar to those of the non-preserved samples taken.

Once samples are collected and sealed in suitable containers, the samples should be labelled, logged and handled correctly, with the appropriate chain-of-custody documentation included. Samples should be kept in temperatures of no more than 4°C. Transport of samples to the designated analytical laboratory should be completed well before the holding times expire. It is preferable that samples be shipped or delivered daily to the analytical laboratory, in order to maximise the time available for the laboratory to do the analysis.

4.2.2 Sample analysis and calculations

Soil characterisation programmes typically involve sending discrete soil samples to the laboratory for quantitative analysis of contaminant composition. The analysis provides a measure of total chemical mass in the soil. The results of the soil analysis may be used in a quantitative manner to assess the possible presence of DNAPL contamination when there is no visual evidence of the presence of DNAPL.

The analysis of a soil sample generally provides a measure of the total amount of the chemical of interest in the sample, expressed as the mass chemical per unit dry weight of soil. The result will include the chemical that is dissolved in pore water, sorbed to the soil, in the soil gas and in any NAPL phase.

If there is no DNAPL present, there is a maximum amount of chemical, which may be contained in a sample of soil that contains soil solids, pore water and gas. This maximum total soil concentration is determined by the maximum solubility concentration S_w of the chemical in water; the concentration in the soil gas that would be in equilibrium with S_w; and the concentration sorbed to the solids that would be in equilibrium with S_w. The only way for DNAPL phase ('free phase') to be present is, if the value of C_w (or the pore-water concentration) is greater than S_w. (Pankow and Cherry, 1996).

All the parameters for the calculation of C_w (dry bulk density, water filled porosity, air-filled porosity, partitioning coefficient between pore water and soil solids, fraction organic carbon, organic portioning coefficient and Henry's constant) may either be determined by relatively simple measurements in the field and laboratory or alternatively, values are available in the literature.

The presence of NAPL in a soil sample may be evaluated using the following equation (Keuper et al., 2003):

$$C^T_i = Ci/Pb\ (K_dP_b + \theta_w + H'\theta_a)\ (1)$$

Where:
C^T_i is the concentration of an organic substance at or above that which may be present in a non-aqueous phase (mg/kg);
C_i is the effective solubility of the substance in groundwater (mg/l);
P_b is the dry soil bulk density (kg/l);
K_d is the soil-water partition coefficient (l/kg);
θ_w is the water-filled porosity (dimensionless);
H' is the dimensionless Henry's law constant;
θ_a is the air-filled porosity.

The soil-water partition coefficient is often approximated by:

$$K_d = K_{oc}f_{oc}\ (2)$$

Where:

K_{oc}	is the organic carbon-water partition coefficient (l/kg);
f_{oc}	is the fraction organic carbon present in the soil (dimensionless).

The effective solubility, C_i, of any component in a in a multicomponent NAPL, may be estimated using:

$$C_i = m_i S_i \quad (3)$$

Where:
C_i is the effective solubility of component i;
m_i is the mole fraction of component i in the NAPL;
S_i is the single component solubility of component i.

Equation 1 represents the maximum amount of contaminant that can be present in a soil sample in the sorbed, aqueous and vapour phases, without a NAPL phase being present. If reported soil concentrations exceed $C^T{}_i$, it may be concluded that a NAPL phase was present in the sample. This calculation procedure assumes that the composition of the DNAPL is known, *a priori*, such that the required mole fractions can be determined. If the DNAPL is known to be composed of primarily one component, the mole fraction of that component may be assumed to be one. At sites where a multi-component DNAPL is suspected and a DNAPL sample has not been obtained for component composition analysis, the required mole fractions will not be known. In such cases, this calculation procedure may still be employed, but with a slight modification.

For a multi-component DNAPL of unknown composition, the sum of the mole fractions must equal one. DNAPL will therefore be present in a soil sample, if the following condition is met:

$$\sum_{i=1}^{n} \frac{C_{obs}^{T}}{C_{S}^{T}} \geq 1 \qquad (4)$$

Where:

C_{obs}	is the reported concentration of component i;
$C_S{}^T$	is the single component soil concentration of component i;
n	is the total number of components observed in the soil sample.

4.2.2.1 NAPLANAL

Mariner et al. (1997) also presented an algorithm for the estimation of a NAPL saturation and composition from typical soil analyses. From this, a PC software program, NAPLANAL, was developed. This model may be used to make similar calculations as above, if the composition of the NAPL is known.
NAPLANAL is distributed as freeware. The advantages of the program are:

- Supports All Windows Platforms (Windows 3.1/95, Win NT 3.5/4.0)
- Easy to use with simple User Interface
- Free of charge
- The physical properties of most common chemicals are attached as a database

Two files are needed to run the program, an input file (*.inp) and a database file (*.dbs). There are several options to select for the input. Samples may either be entered as from the saturated, vadose zone or as ‘liquid only’ samples. When the calculations are completed, NAPLANAL writes a summary of the input and output in an ASCII file.

The output file summarises the input and output for each sample on a single page. The type of model used (saturated vs. unsaturated, porosity known vs. water content known, etc.) and the values of input parameters except for the chemical concentrations, are displayed in the first several lines for verification. The following columns give the results of the calculations and if NAPL is present, the NAPL saturation (volume of NAPL per volume of pore space) is presented as a percentage. If no NAPL is present in the sample, a dilution factor is given. This dilution factor provides a measure of how much more concentrated the chemicals in the sample must be before NAPL would be able to be calculated to exist in the sample.

Overall, the NAPLANAL model was found to be user-friendly and should provide accurate answers to residual NAPL presence, if the input data is correct.

4.3 Water samples

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

Several different groundwater sampling procedures may be used, which vary primarily through the criteria used to determine when a sample is representative of the groundwater conditions.

No single method or procedure is universally applicable to all types of groundwater sampling programmes; therefore, consideration should be given to a variety of factors when determining which method is best suited to site-specific conditions.

These site-specific conditions include sampling objectives, equipment availability, site location and physical constraints.

(See also the accompanying report “Groundwater Monitoring Guidelines for DNAPL Contaminated Sites.”).

4.3.1 Sampling objectives

The objective of a good sampling programme should be the collection of a ‘representative’ sample of the current groundwater conditions over a known or specified volume of aquifer. Ideally, to meet this objective, sampling equipment, sampling method, monitoring borehole construction, monitoring borehole operation and maintenance and sample handling procedures should not alter the chemistry of the sample. A sample that is obtained from a poorly constructed well, using improper sampling equipment, using poor sampling techniques or preserved improperly, may bias the sampling results. Unrepresentative samples can lead to misinterpretations of groundwater quality data. Generally, the costs of obtaining representative groundwater samples are insignificant when compared to potential remedial responses that may be implemented based on erroneous data or when considering the overall monitoring programme costs, over the life of the programme (Nielson, 1991).

The objectives of the sampling programme should be thoroughly developed, presented and understood by the site assessor. The purpose of the sampling effort and data use(s) should be clearly defined. Examples of these purposes include site assessment, contaminant detection, site characterisation, remediation, corrective action or compliance monitoring. For each purpose, the objectives may vary. These variables would include sample depths, length of screened intervals, number and type of chemical parameters tested for, etc. These differences may dictate the type of sampling equipment used, the type of information collected and the sampling protocol.

4.3.2 Sampling Conceptual Model

In order to develop objectives, a site conceptual model should be developed. However, at this stage of the site assessment, the Initial Site Conceptual Model (Section 2.3) should be updated with substantial information that was collected during the field observation phases of the assessment.

The focus of the conceptual model, as it applies to the sampling event, should focus on contaminant fate and transport processes, such as contaminant pathways, how the geologic materials control the contaminant pathways, types of contaminants present and the processes that influence concentrations of the contaminants present, such as dilution, biodegradation, dispersion.

The detail of the conceptual model will depend largely on the availability of information and the amount of existing analytical data. Specific parameters that a conceptual model should describe that may impact on the design of a groundwater sampling programme include:

a) The thickness, lateral extent, vertical and horizontal flow direction and hydraulic conductivity contrasts of the geologic materials controlling contaminant transport from the site (thick units versus thin beds versus fractures, etc.)
b) The types of contaminants to be sampled (volatile organic compounds, semi-volatile organic compounds, metals, etc.) and factors that could bias sampling results (turbidity for metals, co-solvation effects on PCBs, etc.)
c) Lateral and vertical distribution of contamination (contaminants distributed throughout an entire unit being monitored versus localised distribution controlled by small scale features, etc.)

In order to construct the appropriate conceptual model and ensure that the appropriate methodology is used during sampling, the following information should be obtained prior to the start of field activities:

Background Data:
These include: borehole casing diameter, diameter of the borehole, type of casing material, lock number and keys, physical access to boreholes, length of and depth to screening. This information is used to select the correct equipment and technique for purging and sampling.

The length and depth of each screen and depth to water is important when placing a sampling device's intake at the proper depth for purging and sampling, and for choosing a sampling device. If previous sampling information is available it must be used to evaluate and determine the nature and concentrations of expected contaminants. When evaluating previous sampling information, consideration should be given to the amount of time that has expired between the last sampling effort and the planned sampling effort. If this time exceeds one year, the need for the redevelopment of the monitoring boreholes should be evaluated. The necessity of redevelopment may be evaluated by measuring the total depth and comparing it to construction logs. If the depth measurement indicates siltation or clogging, the borehole should be redeveloped prior to sampling. This assessment of the condition of the boreholes should be completed several weeks prior to the commencement of sampling activities, in order to allow the proper recovery of the developed boreholes, prior to sampling.

Determination of the screened intervals or, in the case of open boreholes in hard rock, the fractured zones, is important when the appropriate sample depth is selected. This information may be gained from construction logs or from down-hole logging (See Sections 3.3.2, 3.3.3, 3.3.4 and **Error! Reference source not found.**).

Reference Point:

Each borehole should have a reference point from where all measurements must be taken. This will ensure consistency of data collected from the borehole. It is recommended that the collar height to be taken as a point of reference.

The elevation of this reference point should be known and clearly marked at the site.

Total borehole depth:

The depth of each borehole is required in order to calculate the volume of standing water in the borehole and to document the amount of siltation that may have occurred. Moreover, measuring the depth to the bottom provides checks for casing integrity and for siltation of the screens. Corrosion may cause leaking or the collapse of the well casing, which could lead to erroneous or misleading water level measurements. Corrosion, silting, and biofouling may clog well screens and result in a sluggish response or no response to water level changes, as well as to changes in groundwater chemistry. Borehole re-development or replacement may be needed to ensure the accurate collection of a representative water-quality sample.

Water level depth

All water levels should be measured from the reference point by the use of a water level device. The water level measurement must be made in all boreholes to be sampled prior to activities in any single borehole, which may change the water level, such as bailing, pumping and hydraulic testing.

Water sampling methods

The groundwater sampling methods to be employed at a site should be dependent on site-specific conditions and requirements, such as data objectives and borehole accessibility. Groundwater sampling methods vary based on the type of device used, the position of the sampler intake, the purge criteria used and the composition of the groundwater to be sampled (e.g., turbid, containing high volatile organics, etc.).

The water in the screen and filter pack (or in the case of an open borehole in hard rock, at a fracture site), is generally in a constant state of natural flux as groundwater passes in and out of the borehole. However, water above these sections remains relatively isolated and becomes stagnant. Stagnant water is subject to physio-chemical changes and may contain foreign material, which may be introduced from the surface or during construction, resulting in non-representative sample data. To safeguard against collecting a sample biased by stagnant water, specific borehole purging guidelines and techniques should be followed.

A non-representative sample also may result from excessive pumping of the monitoring well. Stratification of the contaminant concentrations in the aquifer may occur or heavier-than-water compounds may sink to the lower portions of the aquifer. Excessive pumping may dilute or increase the contaminant concentrations from what is representative of the sampling point.

4.3.3 Purging and Sampling Devices

The device used to purge and sample a borehole depends on the inner casing diameter, water level depth, volume of water in the borehole, accessibility and types of contaminants to be sampled.

The types of equipment available for groundwater sampling include hand-operated or motor-driven suction pumps, peristaltic pumps, positive displacement pumps, submersible pumps, various *in situ* devices and bailers made of various materials, such as PVC, stainless steel and Teflon.

Some of these devices may cause volatilisation and produce high-pressure differentials, which could result in variability in the results of pH, dissolved oxygen concentrations, oxidation-reduction potential, specific electrical conductance, metals, volatile organics and dissolved gases. Therefore, the device chosen for purging and sampling should be evaluated for the possible effects it may have on the chemical and physical analyses.

In general, the device used for purging and sampling should not change geochemical and physical parameters and/or should not increase turbidity.

For this reason, low-flow submersible or positive displacement pumps that can control flow rates, are recommended for purging boreholes. Dedicated sampling systems are greatly preferred since they avoid the need for decontamination of equipment and minimise turbulence in the borehole. If a sampling pump is used, the pump should be lowered into the borehole as slowly as possible and be allowed to sit as long as possible, before pumping commences. This will minimise turbidity and volatilisation within the borehole.

Sampling devices (bladders, pumps, bailers and tubing) should be constructed of stainless steel, Teflon, glass and other inert materials to reduce the chance of these materials altering the groundwater in areas where concentrations of the site contaminants are expected to be near detection limits. The sample tubing thickness should be maximised and the tubing length should be minimised, so that the loss of contaminants through the tubing walls may be reduced and the rate of stabilisation of groundwater parameters is maximised. The tendency of organics to sorb into and out of many materials makes the appropriate selection of sample tubing materials critical for these trace analyses. McCaulou et al., (1995) gives specific guidelines on the compatibility of materials used during sampling with DNAPL chemicals (see also Appendix A).

Preferably, boreholes should be purged and sampled using a positive pressure pump or a low-flow submersible pump with variable controlled flow rates and constructed of chemically inert materials. If a pump cannot be used because the recovery rate is so slow and the volume of the water to be removed is minimal, then a bailer may be used to obtain the samples.

Bailers are best suited for purging shallow or narrow diameter monitoring boreholes. Deeper and larger in diameter, and boreholes generally require mechanical pumps to evacuate a large volume of water. For VOC analysis, a positive-displacement volatile sampling bailer is most effective. Bottom-fill bailers which are more commonly used, are suitable provided that care is taken to preserve volatile constituents. Sample containers must be filled directly from the bailer and those for VOC analysis should be filled first.

A number of alternative sampling devices are also available, including passive diffusion samplers and other *in situ* sampling devices. However, these devices are often expensive and difficult to obtain. The advantages of use and compatibility with the parameters tested for, should be evaluated before a decision is made to select such a sampler.

Generally, the more complicated the sampling equipment is, the greater the chance of some form of failure in the field.

Utilise the simplest and most effective sampling devices available. Adequate training in equipment safety and use is critical to personnel safety, as well as to sample representativeness. Consider ease of decontamination when using non-dedicated equipment.

4.3.4 Purging methods

One of two approaches is recommended when purging a borehole for sampling. The first is the '*Low-Stress Approach*', which requires the use of a variable-speed, low-flow-sampling pump. The second approach is the '*Well-Volume Approach* ', which is based on proper purging of the stagnant water above the screened interval and the stabilisation of water-quality-indicator parameters prior to sampling.

The low-stress method offers the advantage that the amount of water discharged will be minimised. The low-stress method is based on the assumption that pumping at a low rate by a pump within the screened zone will not pull stagnant water down, as long as drawdown is minimised during pumping. Drawdown should not exceed 0.1 m (Yeskis and Zavala, 2002). The water-quality-indicator parameters pH, EC, DO, ORP, temperature and turbidity are monitored at specific intervals. The intervals will depend on the volume within the tubing, pump rate and drawdown; usually every three to five minutes. Once three successive readings of the water-quality-indicator parameters have stabilised, the sampling may begin. Continuous water-level measurements must also be taken regularly at 30-second to five-minute intervals (depending on the hydraulic conductivity of the aquifer, diameter of the borehole and pumping rate) to document the amount of drawdown during purging.

During the second approach, the pump rate during sampling should produce a smooth, constant (laminar) flow rate and should not produce turbulence during the filling of bottles. The stabilisation criteria for a 'well-volume approach' may be based on the stabilisation of water-quality-indicator parameters or on a pre-determined well volume. The parameters should be recorded approximately every well volume and when three successive readings have reached stabilisation, the sample(s) are taken.

If a groundwater monitoring borehole has been sufficiently sampled and characterised (at least several rounds of water-quality samples obtained, including the field parameters, during several seasonal variations),and if water-quality-indicator parameters are no longer needed as a part of site characterisation and/or monitoring, then samples may be obtained, based on a specific number of well volumes at the previous pumping rates.

4.3.5 Decontamination

Although decontamination procedures vary considerably in their methodology, most utilise some type of aqueous cleaning method and often use solvent cleaning as a final or additional rinse.

A typical protocol for decontaminating groundwater sampling devices that has been used to sample organic solutes is as follows: wash with detergent, rinse with tap water, rinse with (high quality) organic solvents, rinse with some type of high quality water (e.g. distilled, deionised, organic-free reagent water) and air dry.

This methodology is recommended as it is a simple and practical method of decontaminating stainless steel bailers between boreholes in the field.

In addition, steam cleaners or high-pressure washing systems are sometimes recommended for decontaminating sampling devices, especially for removing gross contamination such as dirt and oils. However, these methods are not always practical in the field and require a lot of time between sampling events.

Aqueous cleaning is used to first remove gross contamination and particles. Water acts as a solvent medium for contaminants that are soluble in water and as a dispersal medium for substances that do not dissolve in water, but may be carried in suspension. A surface active agent (or surfactant), such as detergent, is commonly added to improve the wetting ability of the cleaning solution and aid cleaning by separating the contaminant from the solid surface and then keeping the contaminants in suspension, thus preventing re-deposition.

Organic solvent rinses are used to remove any residual contaminants by dissolving them. Generally, dissolvers such as polar solvents, dissolve polar contaminants and non-polar solvents dissolve non-polar contaminants. Because water is a very polar solvent, non-polar solvents are typically used to remove non-polar organic contaminants (e.g., oils, tars) that have not been removed previously by aqueous cleaning. Recommended organic solvents vary with the particular protocol, but typically include acetone, hexane or methanol. In most protocols, these solvents are recommended without regard to the type of contaminants and it should be noted that among the three solvents mentioned, only hexane is relatively non-polar. Obviously, any organic solvent that is used as a rinsing agent should not be one of the target analyses or interfere with the chemical analyses. There are however, a number of problems associated with using organic solvents. These can include flammability, toxicity, disposal (although recycling can reduce this problem) and spillage, and degradation of, and sorbtion to some polymers (e.g., thermoplastics).

For more detail on more intensive decontamination procedures including steam cleaning and pressurised water washing systems, refer to Parker and Ranney (1997). A number of publications was published with regard to decontamination procedures and the effects on both the sampling devices and the analytical results.

4.3.6 Sample preservation

Field samples must be transferred from the sampling equipment to the container that has been specifically prepared for that given parameter.

Samples should not be composited in a common container in the field and then split in the lab.

Specific containers are almost always available from the laboratory where the analysis is performed. Amber glass bottles with Teflon cap liners are preferable for sampling organic contaminants.

Samples should be labelled, logged and handled correctly, with the appropriate chain-of-custody documentation included.

Samples should be placed in coolers and the temperature maintained at 4°C.

Ship samples to arrive at the designated analytical laboratory well before their holding times have expired. It is preferable that samples be shipped or delivered daily to the analytical laboratory, in order to maximise the time available for the laboratory to do the analysis.

4.4 Sample analysis

DNAPL chemicals in the subsurface may migrate as volatiles in soil gas, dissolve in the groundwater or exist as a mobile, separate phase. This migration is governed by several factors and principles, some of which differ from those controlling miscible contaminant transport (Cohen and Mercer, 1993). In order to characterise a DNAPL site, it therefore important to determine the correct properties/parameters of all the phases that are applicable to the site and the associated transport mechanisms. In the previous sections, the correct sampling procedures to collect representative samples of all the phases were discussed and in this section, the properties of fluid and media associated with DNAPL flow that need to be analysed for, are listed.

4.4.1 Physical parameters

The physical properties of the organic compounds and the aquifer media affect their behaviour in the subsurface. Table 7 summarises some of the important physical properties of DNAPL compounds and how these affect their behaviour as groundwater contaminants. Many of these parameters may be measured in the laboratory or field derived from the literature or calculated by means of simple equations and mathematical relationships.

However, it is important to remember that DNAPLs at field sites have often undergone changes (due to weathering, dissolution, and mixing) or are found in complex mixtures and these parameters of the DNAPL (a representative sample) found at the site, should be measured when possible.

Table 7: Physical properties of DNAPLs affecting their behaviour

(Adapted from Fetter, 1999).

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

Parameter	Derivation	Behaviour
Interfacial Tension	A force balanced on a curved interface between two fluids leads to the conclusion that the pressure in the fluids on either side of the interface is not equal; the difference being given by equation: $\Delta P = 2\sigma/r$ Where ΔP is the pressure difference across the interface, σ is the interfacial tension and r is the radius of curvature of the interface (Pankow and Cherry, 1996).	Interfacial tension which is a representation of the co-existence of liquids at different pressures, is the most important physicochemical property controlling multiphase fluid migration in the subsurface.
Wetability/ contact angle	Wetability is a measure of a liquid's relative affinity for a solid. Where two liquid phases are present, the 'wetting' fluid will preferentially spread over the solid surface at the expense of the 'non-wetting' fluid. Wetability is depicted by the concept of a contact angle, the angle subtended by the liquid-liquid interface and the solid surface.	Although most problematic, DNAPLs are non-wetting, taking into account the variation of groundwater composition, DNAPL composition and the characteristics of the solid surfaces, the possibility of complex wetability relationships must be considered at actual field sites.
Saturation relationships/ capillary pressure	The saturation of a fluid is the volume fraction of the total void volume occupied by that fluid. The capillary pressure saturation function Pc(Sw) is measured in experimental cells, where a NAPL source is allowed to invade a saturated porous medium (at incremental increased NAPL pressures) and the subsequent volume of displaced water is measured at these pressure intervals. Capillary pressure-saturation curves may then be derived for different media and DNAPL components.	Saturations range from 0 to 1 and the saturations of all fluids sum to one. Saturation is important because it is used to define the volumetric distribution of DNAPL, and because other properties, such as relative permeability and capillary pressure, are functions of saturation.

4.4.1.1 Density

There are several methods for determining the density (and/or specific gravity) of liquids and solids, as described by Cohen and Mercer (1993):

- In the **displacement method**, a solid sample is weighed to determine its mass and then immersed in a graduated cylinder containing a known volume of water. Density is calculated by dividing the mass of the object by the change in volume in the graduated cylinder.
- Density of Liquids by the **Westphal Balance Method** may be determined by employing Archimedes' principle that the mass of a floating object is equal to the mass of the liquid it displaces. Based on this principle, Westphal and chain balances are used to determine the volume displacement of liquids by an object of known, constant mass. If one of the liquids is water, the density and/or specific gravity may be determined.
- Hand-held portable **densitometers** are available that give direct LCD readouts of specific gravity and temperature.
- Use of a **hydrometer** (calibrated, weighted, glass float), thermometer and cylinder, is perhaps the simplest and least expensive for field use. After the cylinder is filled with sufficient NAPL to allow the hydrometer to float, it is placed in the NAPL and allowed to come to rest without touching the walls of the cylinder. The liquid specific gravity is read from the graduated scale on the hydrometer stem at the liquid-air interface and the temperature recorded.

- The density of a liquid at a measured temperature may be determined by **weighing the mass** of a known volume of liquid in a container of known mass. The mass of the empty container is subtracted from the mass of the full container and the resultant liquid mass is divided by its volume.
- If certifiable and high precision measurements are required, a sample may be submitted to a **laboratory for analysis**.

4.4.1.2 Viscosity

Methods of viscosity measurement include the following (Cohen and Mercer,1993):

Falling ball method: A ball falling through a viscous liquid will accelerate until it attains a constant velocity that is inversely proportional to fluid viscosity. The amount of time required to fall a known distance can be measured using a stopwatch. The apparatus used is called a "falling ball viscometer" and is easy to use and convenient for field measurements.

An adaptation of the falling ball method uses **glass needles** of varying density. This method was designed to reduce wall interferences and eddy currents possible in falling ball units. Other instruments include the **rotating disc viscometer and viscosity cups**. Samples may also be submitted to certified **laboratories** for high precision analysis.

4.4.1.3 DNAPL solubility

DNAPLs are soluble to a variable degree in water and will be leached to the groundwater. The dissolved chemistry derived from water contact with DNAPL may be assessed directly by analysis of DNAPL-contaminated groundwater samples and indirectly by equilibrium calculation methods or laboratory dissolution studies.

The equilibrium aqueous concentrations of DNAPL components in groundwater may be assessed by placing DNAPL and (real or simulated) groundwater in a closed jar at the prevailing groundwater temperature. After four hours of contact, samples of water, excluding DNAPL, may be taken for chemical analysis to determine the dissolved phase composition.

Simple leaching experiments (column tests) may also be conducted, in which water is passed through a sample of DNAPL contaminated porous media to simulate vadose zone or saturated conditions. The experiments can be designed to represent various field conditions (e.g., DNAPL pools or ganglia, variable flow rates and variable background groundwater chemistry).

When organic chemicals are released into the environment from a mixture, the water solubilities of the chemicals are typically far lower than their published solubilities. This occurs because the concentration (or effective solubility) depends on the relative abundance of the chemical in the mixture. This behaviour is based on an extension of **Raoult's Law** and is related to the relative mole fraction of the contaminant within the total spill or release of organics (Schwarzenbach et al., 1993). This may be calculated as:

$$C_w = x_o S \qquad (2)$$

where **C_w is the effective solubility**, x_o is the mole fraction (of the organic compound in the mixture) and S is its solubility.

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

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

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

4.4.1.4 Volatility

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

$$K_h = C_a / C_w \qquad (4)$$

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

4.4.1.5 Interfacial Tension

Interfacial tension, a representation of the co-existence of liquids at different pressures, is the most important physicochemical property controlling multiphase fluid migration in the subsurface and therefore accurate measurements are required during any site assessment. Methods to determine surface tension and interfacial liquid tension are described below (Cohen and Mercer, 1993):

Surface Tension Determination by Capillary Rise: The wetting force of a liquid is equal to the gravitational force on a liquid that has risen in a capillary tube. After measuring the capillary rise of a fluid sample in a tube, surface tension can be calculated by:

$$\sigma = (rh\rho g)/(2\cos\theta) \qquad (5)$$

Where, σ is the surface tension in dynes/cm, ρ is the density of the liquid in g/mL, h is the height of the capillary rise in cm, r is the internal radius of the tube in cm, θ is the contact angle and g is the acceleration due to gravity (980 cm/s^2).

To measure capillary rise, gentle suction is applied to raise the fluid sample to the top of the capillary tube and then released to allow the fluid to decline to an equilibrium position. This measurement should be repeated several times to provide reliable data. The presence of air bubbles within the liquid column will result in inaccurate data. Between samples, the capillary tube should be cleaned and dried and accuracy checks should be made periodically using a liquid of known surface tension (such as water). The temperature of samples should be maintained and documented, because surface tension decreases with rising temperature.

Du Nouy Ring Tensiometer Method: Surface or liquid interfacial tension may be determined directly using a tensiometer employing the du Nouy ring method in accordance with ASTM D971 and D1331. The force necessary to separate a platinum-iridium ring from the liquid's surface (either at a liquid-air or liquid-liquid interface), is measured to the nearest +/- 0.25 dynes/cm.

Interfacial tension determinations can also be made by a testing laboratory.

4.4.1.6 Wettability

Wettability is a measure of a liquid's relative affinity for a solid. Where two liquid phases are present, the 'wetting' fluid will preferentially spread over the solid surface at the expense of the 'non-wetting' fluid. Wettability is depicted by the concept of a contact angle; the angle subtended by the liquid-liquid interface and the solid surface. It is therefore common that the **'contact angle method'** is used to determine the wettability.

Using the sessile drop contact angle method, a drop of DNAPL is formed at the end of a fine capillary tube and brought in contact with the smooth surface of a porous medium under water within a contact angle cell (Cohen and Mercer, 1993). The drop of DNAPL is allowed to age on the medium surface and the contact angle can be measured and documented by taking photographs, preferably with enlargement using a special photomacrographic apparatus. For application to DNAPL-groundwater-media systems, the smooth surface used must be a thin section of rock, clay smeared on a glass slide, the top of a cohesive soil sample that has been sliced with a knife or a relatively flat surface of silt or sand. The water should be actual or simulated groundwater. Water advancing and water receding contact angles typically vary due to hysteresis and may be measured by using the capillary tube to expand and contract the volume of the DNAPL drop. Alternatively, a **modified sessile drop** method may be used in which the drop of DNAPL is positioned between two flat substrates that are mounted parallel to each other on adjustable posts in the contact angle cell.

NAPL wetting has been shown to increase with ageing (contact time) during contact angle studies. Thus, an assessment of the significance of ageing should be considered and the contact duration associated with each measurement noted.

The representativity of contact angle measurements is uncertain and cannot take into account the effects of media heterogeneity, roughness and complex pore geometry.

4.4.1.7 (NAPL)Saturation

Saturation relationships are used to define the volumetric distribution of DNAPL and several other properties are functions of the saturation. NAPL saturation may be measured directly from soil samples for porous media. Several laboratory methods for this determination are described in Cohen and Mercer (1993), to determine the saturation directly from a sample containing NAPL phase. Care should be taken that the samples submitted for this analysis are representative of the DNAPL zone that is being investigated.

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

Figure 11 shows a schematic outlay of the apparatus used and Figure 12 is an example of a $P_c(S_w)$ curve. These curves have been derived under conditions where the water saturation first has decreased and the capillary pressure increased as a result of the DNAPL invasion; this process is known as drainage. Once the source of DNAPL is exhausted, the DNAPL will continue to migrate away from the source and will be replaced by water in that zone. The situation has now changed from one of increasing water saturation to decreasing capillary pressure, known as wetting. The capillary pressure is less during the wetting process than during the drainage. The relationship between drainage and wetting is however not equal, which leads to a type of hysteresis.

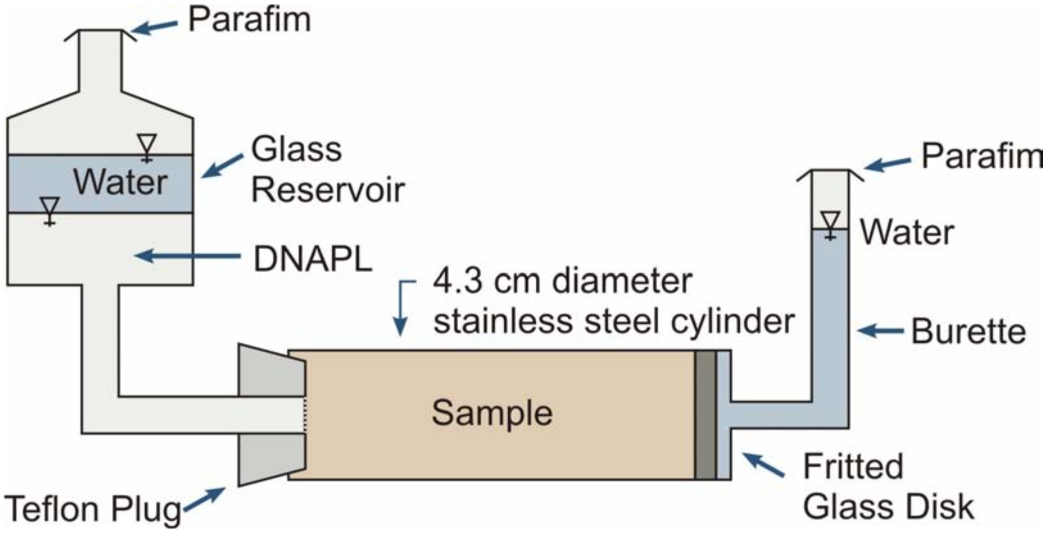

Figure 11: Schematic outlay of apparatus to determine $P_c(S_w)$ (Cohen and Mercer, 1993).

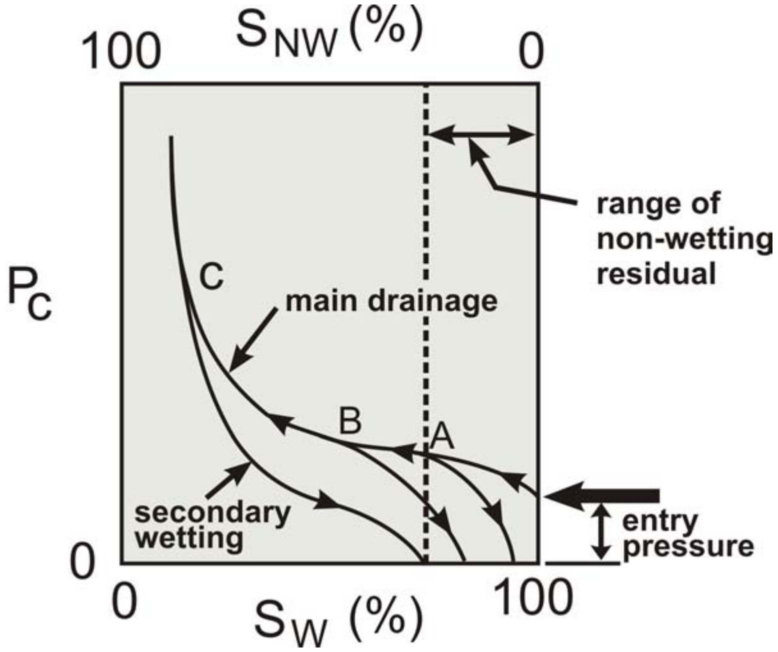

Figure 12: Capillary pressure-saturation curve

(From Thomson, 2004).

From these derived curves, it was found that the DNAPL would only start to invade the media continuously once the threshold value has been reached.

This capillary pressure is known as the ***entry pressure****. For most materials, entry pressure corresponds to a water saturation in the range 0.8 to 0.95 (Pankow and Cherry, 1996).*

Many literature sources of these saturation relationships are available. Diomampo et al. (2002) derived several curves for fractured media and listed the circumstances for when the flow relationships differ from those in porous media.

4.4.1.7.1 Height of accumulation above a capillary barrier (porous media)

Kueper et al. (2003) uses these saturation relationships to determine the height of DNAPL that may accumulate above a capillary barrier below the water table. Thus, the circumstances under which the threshold (entry) pressure of the barrier layer will be overcome, may be estimated using the following equation:

$$H = P_c'' - P_c' / (P_D - P_W)\, g \qquad (6)$$

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

Larger pool heights may form for higher DNAPL-water interfacial tension, lower DNAPL density and lower capillary barrier permeability. For chlorinated solvent and PCB DNAPLs, pool heights typically range from a few centimetres to several tens of centimetres. Chlorinated solvent pools as thick as 2m have been reported at sites in the USA, but this is a relatively rare occurrence. For creosote and coal tar, DNAPL pool heights are generally larger than those associated with PCB and chlorinated solvent DNAPLs because of the lower density of these compounds (Kueper et al., 2003). The calculations used to create the following figure are:

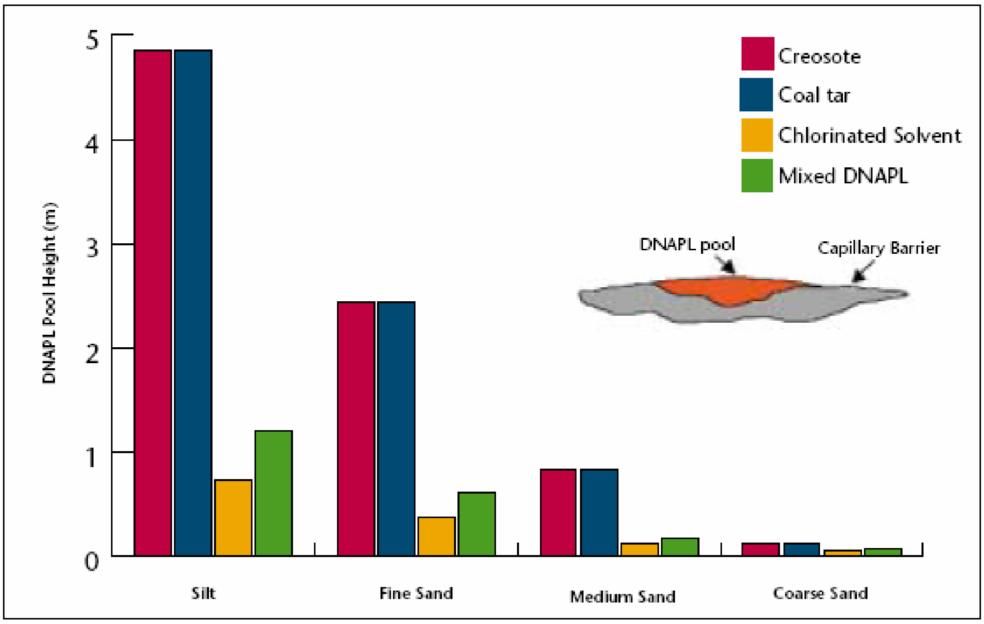

Figure 13: Maximum DNAPL pool height above various capillary barriers

(From Kueper et al., 2003).

4.4.1.7.2 Fracture aperture required to stop migration in bedrock

Similar to the above section, DNAPL will also 'pool' on fractured bedrock. It is assumed that there are no vertical components to groundwater flow and that the DNAPL has come to rest because of a narrowing of fracture apertures in the vicinity of point A. The narrowing of fracture aperture provides the capillary resistance to support the overlying distribution of DNAPL. The threshold (entry) pressure that is required to enter the fracture system will thus depend on the fracture aperture.

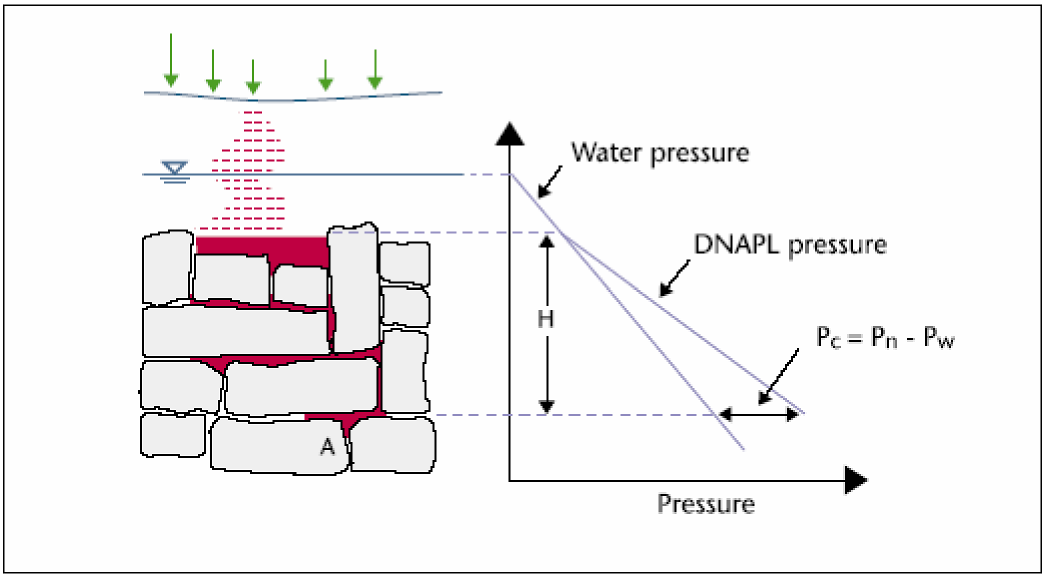

Figure 14: Vertical accumulation of DNAPL in a fracture network. Assuming a hydrostatic system, capillary pressure increases linearly with depth

(From Kuepe, et al., 2003).

Figure 14 shows that both the groundwater and DNAPL pressures increase linearly with depth; thus, the capillary pressure also increases linearly with depth. The relationship between the vertical height of accumulated DNAPL (H) and the fracture aperture at A required to support the accumulation of DNAPL is given by:

$$H = 2\ \sigma\cos\theta / (P_N - P_W)ge \quad (7)$$

Where:
H is the vertical height of accumulated DNAPL;
σ is the DNAPL-water interfacial tension;
θ is the contact angle;
P_N is the DNAPL density;
P_W is the groundwater density;
g is the acceleration due to gravity;
e is the fracture aperture.

Kueper et al. (2003) compiled a table with accumulation of height required versus the supporting fracture aperture. The corresponding fracture aperture at which the entry pressure will be overcome, is approximately ten times smaller for TCE (a chlorinated solvent) than for a coal tar or creosote mixture.

4.4.1.8 Aquifer Media Parameters

Table 3 and Table 4 list a variety of parameters that may be needed at the various stages of site investigation, risk assessment and in the selection of remedial or management options and may be defined during the investigation. Many of the methods for determining these parameters are described in previous sections.

The **porosity, dry bulk density and fraction organic carbon** are tests that may be conducted on samples of retrieved core. Each major rock type should be sampled as these parameters exhibit spatial variability. Although no specific number of samples may be dictated, a general rule of thumb is that 5-10 samples should be obtained during a site investigation (Kueper et.al., 2005).

Hydraulic conductivity is typically determined on a field-scale using pumping tests and slug tests. The displacement pressure of capillary barriers is usually not measured on a site-specific basis, but may be estimated from values of interfacial tension and hydraulic conductivity (see Sections 4.4.1.7.1 and 4.4.1.7.2).

The **hydraulic head distribution** is typically determined through quarterly water level measurements in piezometers and monitoring boreholes. Bedding structures are determined from test pits or down-hole techniques, while the spatial extent of the DNAPL source zone and plume are determined using the techniques discussed early in this report.

The **orientation of major fracture** sets is typically determined through outcrop mapping and down-hole geophysical surveys. The fracture spacing is typically determined using the results of down-hole hydraulic testing in conjunction with core logs, acoustic televiewer (virtual core) and an optical (video) televiewer. It should be noted that core may contain mechanical breaks that may be difficult to distinguish from natural fractures. However, it should be noted that fracture patterns may be variable and often unpredictable over short distances at any site and caution must be used when applying extrapolation techniques such as fracture pattern generation.

The **fracture porosity** is typically determined from estimates of fracture spacing and estimates of fracture aperture, determined from hydraulic testing. The bulk hydraulic conductivity is generally determined through pumping tests and slug tests, as well as hydraulic testing using straddle packer assemblies. The bulk retention capacity of the rock mass for DNAPL is typically estimated from fracture porosity.

4.4.2 Organic Parameters

4.4.2.1 DNAPL composition

The organic content of soils or groundwater at contamination sites is often a complex mixture of chemicals. Immiscible fluid samples may be fractionated or split into several portions, using a separator funnel or a centrifuge (Cohen and Mercer, 1993). For NAPL organic samples, the customary methods of analysis are infrared (IR) spectrometry, high resolution nuclear magnetic resonance (NMR) spectrometry, gas chromatography (GC), high performance liquid chromatography (HPLC) and mass spectrometry (MS).

Composition analyses may be either qualitative or quantitative or both. A qualitative analysis will only identify a compound’s presence and will not determine the purity or percentage composition of a mixture. Preliminary site investigations may focus on a qualitative analysis to indicate the constituents of concern. Quantitative analyses identify a compound’s presence and determine the purity or the percentage composition of each component of a mixture. Quantitative analyses are usually required to provide data for site characterisation, feasibility, risk assessment and treatability studies (Cohen and Mercer, 1993).

4.4.2.2 Soil/core analysis

Soil characterisation programmes typically involve sending discrete soil/core samples to the laboratory for quantitative analysis of contaminant composition. In Section 4.2.1 the importance of correct sampling technique and preservation was described. However, cognisance should be taken that the chosen analysis technique may also influence chemical results. Laboratories often use one of three techniques:

1) purge and trap,
2) direct headspace measurement or
3) methanol extraction.

VOC (volatile organic carbon) analysis was found to be especially sensitive to the different methods. Pankow and Cherry (1996) conclude that the analysis method is more effective for some chemicals. Therefore, it is recommended that if the investigation requires a high level of confidence in specific parameters, it is advisable to use the analytical method best suited for those parameters.

It must be noted though, that organic analyses are expensive and target contaminant groups should be chosen carefully, with enough background information on the suspected contaminants present at a site. To reduce costs, it is recommended that some type of screening be performed prior to submission of samples for analysis. Section 3.7 describes some of these techniques. From experience in this project, it was found that UV testing is a fast cost-effective method for screening soil/core samples for analysis.

Selection of the parameters to analyse for, is site-specific and dependent on the composition of suspected NAPL source.

The following table lists the general groups of organic contaminants for which soil samples should be tested at a DNAPL site. (The complete target compound lists are included in Appendix B). *Included in the list, are contaminants which are generally described as L(light)NAPLs, but often these contaminants are found in association with DNAPLs. Depending on the composition and the ratios of the contaminants in the NAPL mixture, the properties (i.e. density) will determine whether the NAPL is light or dense.

Other parameters that may also be tested for, if contaminants are suspected, are the groups of pesticides and phenols. These analyses are also available as total values or as separate components.

4.4.2.3 Dissolved Phase Composition

The characterisation of the distribution and extent of dissolved plumes at any DNAPL contaminated site are important for long-term management, monitoring and remediation plans. The site assessor therefore needs to have a clear understanding (with help from the conceptual model), of what the suspected contaminants could be at a site, before samples are submitted for analysis. Often water analyses are only performed after extensive soil sampling and analysis. The soil sample results should thus be used as a guideline for water analysis.

Analytical methods are well developed for most of the parameters required. Knowledge of the various analytical methods and the *associated parameter target lists* are important and should be cleared with the laboratory prior to submission of samples. The sample objectives (i.e. quality monitoring, investigation of attenuation) should guide the investigator to which parameters should be chosen.

The analytical target groups for water samples are similar to the ones listed in the previous section.

Table 8: Analytical target groups for organic soil analysis.

Target group	**(Commonly used) Analysis method**	**Comment**
Volatile Organic Carbons (VOC)	US EPA 8260	Various target lists for VOCs. Any method that uses 'purge and trap' is recommended. Many of the halogenated volatile solvents are found in this group.
Semi-volatile organic carbons(SVOC)	US EPA 8270	Various target lists for SVOCs. Many of the components of coal tars/creosote are found in this group.
Polycyclic aromatic hydrocarbons (PAH)	US EPA 8270	Often, if a full suite of SVOCs and VOCs was done, the target list for PAHs may be calculated from these results. Thus, a separate PAH analysis will not be required. A Total (PAH) analysis may also be performed as a screening test. Many of the components of coal tars/ creosote are found in this group. **This group of contaminants is often found in high(er) concentrations in soil than in the groundwater, as it tends to be strongly attenuated by soil particles.**
Polychlorinated biphenyls (PCB)	Various methods	Depending on the suspected PCB, either one or more of the Aroclors may be used as standards. Most common used is Aroclor 1254.
Total organic halogens (TOX)	US EPA 8260 & 8270	In this suite, the PCH (Polychlorinated hydrocarbons) is also analysed for. Many of the chlorinated solvents are in this group. (Can calculate TOX from VOC and SVOC analyses)
BTEX (Benzene, toluene, ethylbenzene, and xylene)	Various methods	Volatile portion of gasoline (petrol) range chemicals. Often used as first screening to determine if any petroleum hydrocarbon spillage has occurred.
DRO	Various methods	**Diesel range hydrocarbons (nC10-nC24).** When mineral oils are included in analysis, the longer chains (up to nC35) are included.
GRO	Various methods	**Gasoline range hydrocarbons (nC5-nC10).**
TPH*	Various methods	**Total petroleum hydrocarbons.** Methods may vary between only a total value (used for screening) or split in aliphatic, aromatic and BTEX, ranges.

Table 9: Analytical target groups for organic soil analysis

Target group	(Commonly used) Analysis method	Comment
Volatile Organic Carbons (VOC)	US EPA 8260	Various target lists for VOCs. Any method that uses "'purge and trap' is recommended. Many of the halogenated volatile solvents are found in this group.
Semi-volatile organic carbons(SVOC)	US EPA 8270	Various target lists for SVOCs. Many of the components of coal tars/creosote are found in this group.
Polycyclic aromatic hydrocarbons (PAH)	US EPA 8270	**A Total (PAH) analysis is recommended as a screening test.. These chemicals have low solubility and are therefore not expected to be present in high concentrations in the water.** Often, if a full suite of SVOCs and VOCs was done, the target list for PAHs may be calculated from these results. Thus, a separate PAH analysis will not be required. Many of the components of coal tars/creosote are found in this group.
Polychlorinated biphenyls (PCB)	Various methods	Depending on the suspected PCB, either one or more of the Aroclors may be used as standards. Most common used is Aroclor 1254.
Total organic halogens (TOX)	US EPA 8260 & 8270	In this suite, the PCH (Polychlorinated hydrocarbons) are also analysed for. Many of the chlorinated solvents are in this group. (May calculate TOX from VOC and SVOC analyses.)
BTEX (Benzene, toluene, ethylbenzene, and xylene)	Various methods	Volatile portion of gasoline (petrol) range chemicals. Often used as first screening to determine if any petroleum hydrocarbon spillage has occurred.
DRO	Various methods	**Diesel range hydrocarbons (nC10-nC24).** When mineral oils are included in analysis, the longer chains (up to nC35) are included.
GRO	Various methods	Gasoline range hydrocarbons (nC5-nC10).
*TPH**	*Various methods*	**Total petroleum hydrocarbons.** Methods may vary between only a total value (used for screening) or split in aliphatic, aromatic and BTEX, ranges.

Analysing for other specific indicator organic species (e.g. DCA, methane, ethane, ethane) and microbial species are additional parameters that need to done when investigating MNA. These parameters are however, very site specific and in the accompanying report "Guidelines for the acceptance of Monitored Natural Attenuation processes in South Africa", they are discussed in more detail.

4.4.2.4 Inorganic Parameters

One of the major challenges in site characterisation (or remediation) of soil and groundwater, is the presence of mixed organic and inorganic contaminants. Due to their very different behaviour, research and investigations have, to a large extent, focused on the characterising (remediation) of either organic or inorganic contaminants, rather than **mixed waste**. However, inorganic contaminants will usually be present at any NAPL contaminated site. It is therefore important to investigate not only the organic contamination, but also any possible inorganic contamination.

Measurement of inorganic parameters at a DNAPL site will thus be used not only to determine if there is any inorganic contamination present, but some of these parameters are important indicators of subsurface geochemical conditions. The inorganic parameters are also used to classify the type of groundwater in order to determine the origin, recharge conditions and type of aquifer system. Table 10 below, indicates parameters that need to be analysed in water and soil and their relevance to the site assessment. Many of these parameters are important indicators (lines of evidence) of the extent of natural attenuation at a site, when considering monitored natural attenuation (MNA) as a remedy at a site.

Table 10: Inorganic parameters for analyses during site assessment of a DNAPL contaminated site

Parameter	Soil	Water	MNA	Relevance to site assessment
TDS		√	√	Total dissolved solids in water; first indicator if water is contaminated (with possible dissolved (inorganic)contaminants.
Conductivity (EC)	√	√	√	If no TDS determination, EC is indication of TDS content of water or soil.
pH	√	√	√	Reflects the degree of acidity or alkalinity in water/soil. Chemical reactions very dependant on pH changes, e.g. dissolution reactions.
Total Alkalinity as $CaCO_3$		√	√	Increased alkalinity may be indicative of microbial activity (increase in CO_3).
Chloride as Cl	√	√	√	Increase in Cl may be indicative of dechlorination reactions of CHCs.
Calcium as Ca Magnesium as Mg Sodium as Na Potassium as K	√	√	√	As part of macro analyses, explain general chemistry and type.
Manganese as Mn Iron as Fe	√	√	√	Indicator of redox state, depletion and accumulation rates may be used to infer biodegradation.
Fe II ;Fe III; Mn II			√	Indicator of redox state, depletion and accumulation rates may be used to infer biodegradation.
NH_4 as N	√	√	√	Indicator of redox state, depletion and accumulation rates may be used to infer biodegradation.
SO_4 Nitrate as N Nitrite as N Phosphate as PO_4 or P		√	√	Act as nutrient sources for biodegradation.
H_2S			√	Indicator of reducing conditions
Trace metals	√	√		Indicator of metal contamination in soil/water
Cyanide (total/ free)	√	√		Indicator of cyanide contamination in soil/water
BOD		√	√	Gross indicator of organic/microbial content
COD		√	√	Gross indicator of organic/microbial content and of redox state
TOC		√	√	Gross indicator of dissolved organic carbon
DO		√	√	Oxygen content which can indicate changes in redox state and microbial activity
Redox potential		√	√	Redox state indicator
Mineralogy	√			Determine the clay content and nature of retardation
Dissolved CO_3 and H				Redox state and microbial degradation indicators

4.4.2.5 Lethality, Inflammatory, Mutagenicity and Modulating Potential

While it is possible to test for the presence of DNAPL in groundwater by chemical analysis, this does not provide answers on potential health effects on humans that may consume such waters. It is therefore important to consider testing water, polluted by DNAPL, for its potential to affect human health.

Several techniques are available to test potential effects on a human system after exposure to contaminated water namely:

- Lethal effects;
- Inflammatory effects;
- Modulating effects and
- Mutagenic effects.

Human cells can be exposed in-vitro to the various contaminated water to emulate human cell reactivity associated with all four effects. In the more “known” area of toxicity testing i.e. lethal effects and mutagenicity testing, conventional test kits can be used as supplementary (confirmatory) tests, assessing reactions of non-human cells (bioindicators) to the exposure.

Testing is done **in-vitro**. This means using human cells and the relevant biomarkers, as well as non-human cells as bioindicators at laboratory scale:

- The human cells are lymphocytic white blood cells isolated from human whole-blood;
- The non-human bioindicators can be bacteria species or higher order organisms.

Lethal effects are marked and indicated by cell reactions measured as:

- Changes in general human cell viability;
- Apoptosis and necrosis for human cells;
- Mortality / inhibition of the non-human bioindicators;

Inflammatory effects are measured by the cytokine response of the human cells;

Modulation effects are measured by oestrogenic activity as a biomarker of human endocrine system disruption.

Mutagenicity is measured using DNA damage to human cells as a biomarker;
Highly variable results are obtained during toxicity testing of DNAPL contaminated water in this project. This high variability indicated that the test techniques, especially those used to measure with the human cells (PBMC) under high test concentrations, were not yet suited for application in this field and that more work needs to be done before these tests can be commercially applied.
The tests based on microorganisms are more stable and in some areas the results concurred with the results obtained from human cell reactions. Another drawback of these microorganism based tests would be that results cannot be extrapolated to predict potential human effects.

As a screen, the test array shows promise for showing that water can put a human system under pressure.

The test array cannot detect any activity that could be related to specific DNAPL contamination. The issue of “mixed” groundwater contamination needs to be highlighted here. All of these tests will detect the overall toxicity effects of the contaminants in the water and not only that of the DNAPL contaminants. Therefore the test array can point out that some boreholes are “more” contaminated than the others.

The array in its current format is cumbersome, but this type of testing may form an important part of future DNAPL toolboxes.

4.4.2.6 Molecular Microbiology to Determine Microbial Diversity

Monitored Natural Attenuation (MNA) or Bioremediation relies upon the enzymatic activities to transform or degrade the offending contaminants. Bioremediation is a cost effective means of removing many chemical pollutants that can adversely impact human health or environmental quality – "*a green solution"* (Philip et al., 2005). To develop this strategy as a cost effective solution that can successfully be applied at a site, the microbial diversity and machinery should be understood. Advances in molecular techniques have made the study of molecular diversity and genetic machinery a lot easier.

Using molecular approaches it is possible to determine whether a certain bacteria may be in the environment by looking for certain distinctive genes that can be detected by means of Polymerase chain reaction (PCR) This technique can also be applied and using universal primers recognising the conserved 16SrDNA sequence of bacteria, and by means of screening and sequencing of a variety of clones one can determine the microbial diversity at the site.

Using these techniques to support geochemical characterisation of a site has a numerous advantages.

Determining which microbes are present in the groundwater could help indicate what geochemical processes are present in the system and even be indicative of the possible contaminants that may be present. These tests are important for MNA and can be used to explain the presence and absence of selected degradation products on a site.

5. CONCEPTUAL SITE MODEL

As discussed in Section 2.3, the construction of a site conceptual model is an integral part of any DNAPL site assessment. The conceptual model is the 'snapshot' or realisation of the site at a particular time. It is optimally constructed through historical information, the complete set of physical, chemical, geologic and hydrogeologic data and understanding of the dynamic processes, experiential knowledge of similar sites, the risk scenarios related to the site and its contaminants and the type and scope of remediation envisioned. The model is updated and refined by subsequent data and information and the process is iterative.

At first, the initial conceptual model will be based on assumptions of what is 'expected' at the site, later refined with data collected through field observation/ testing and finally through analytical results. The following sections describe the type of information/data that may be used to construct the final site conceptual model in terms of the geology/geohydrology and the DNAPL and dissolved phase distribution. Key features of the conceptual model include the descriptions of the geology/geohydrology, contaminant source, the pathway to the receptor and the physical, chemical and biological processes that may significantly affect contaminant movement.

5.1 Geology and geohydrology

From the initial conceptual model, the site assessor needs to have a clear understanding of what processes/factors will influence the transport and migration of the DNAPL and dissolved phases in the subsurface. These processes are controlled mainly by the DNAPL's and aquifer media's physical parameters, discussed in previous sections. For the final conceptual model, these physical parameters are used to describe the geology and geohydrological environment and the effects that it will have on the transport and migration of the contaminants during the model construction.

For this purpose, the following type of data representations/interpretations may be used to construct the geohydrological conceptual model:

- Borehole geological logs (shows lithological or aquifer differences and water strikes with estimated or measured yields within the borehole)
- Geological cross sections (shows lithological or aquifer type differences across a site)
- Aquifer delineation in three dimensions (consider boundary conditions caused by geological structures, topography or surface water bodies)
- Water level/elevation contour maps and/or cross-sections (show correlation with topography)
- Aquifer parameters must be assigned to aquifer(s) (when dual porosity system, parameters must be assigned to both matrix and fractures)
- Define preferred pathways such as fracture systems (fracture aperture, orientation and connectivity must be considered, data interpretation of geophysical investigation is important)

The site assessor should now have an understanding of possible factors which will influence the contaminant migration and transport at the site. Figure 15 is an example of a simplified geological and geohydrological conceptualisation for the research site, Test Site 1.

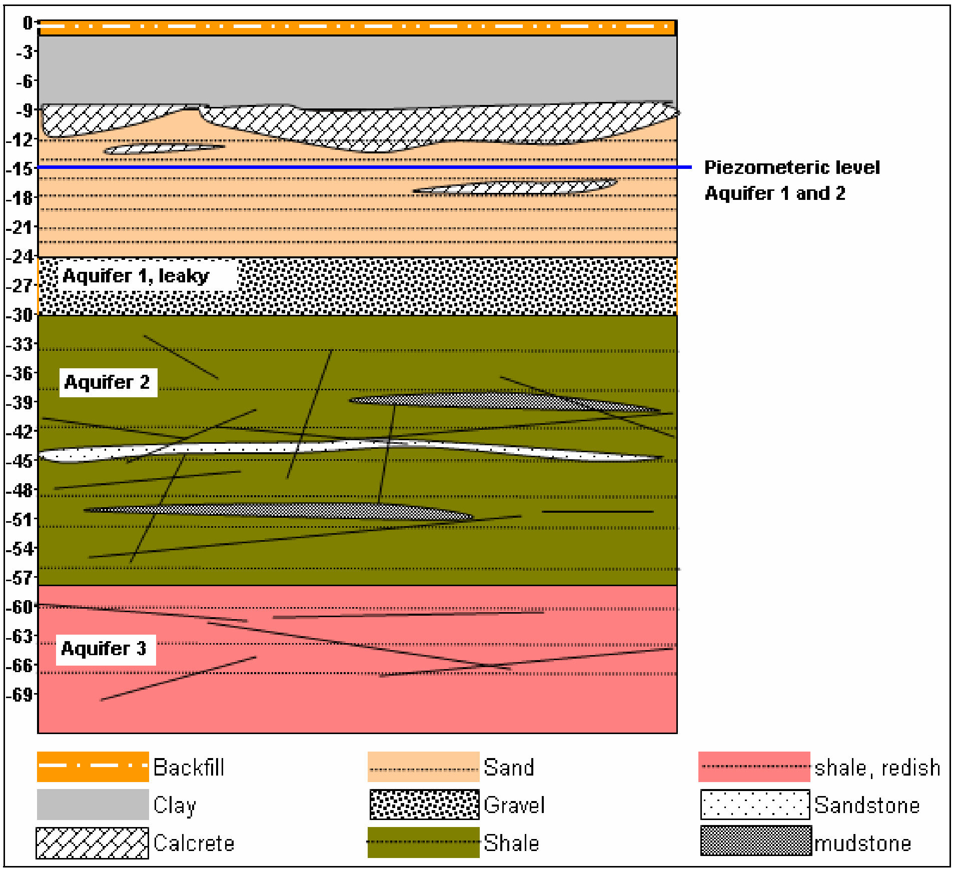

Figure 15: Example of the geological and geohydrological conceptualisation of Test Site 1.

5.2 Characterisation of DNAPL source zone and dissolved plume

Once the geohydrological conceptual model is complete, the extent of the DNAPL source zone and the dissolved plume within the aquifer system, needs to be characterised. Interpretation of the following data, collected during the site assessment, is used for the contaminant characterisation:

- Vapour phase composition, distribution/contours in soil profile (from soil gas measurements during drilling or digging) or on surface (surface soil gas survey)
- DNAPL composition and physical properties (see Section 4.4.1),
- DNAPL phase (if any evidence was found), distribution in the soil profile, from direct or indirect methods (Sections 3.7 and 4.2.2)
- Dissolved phase composition and distribution and plume extent (Sections **Error! Reference source not found.**, 4.3 and 4.4.2.3)

This conceptualisation of the distribution of the contaminant phases may now be used to plan any further actions such as site assessment (if required), monitoring, management and/or remediation.

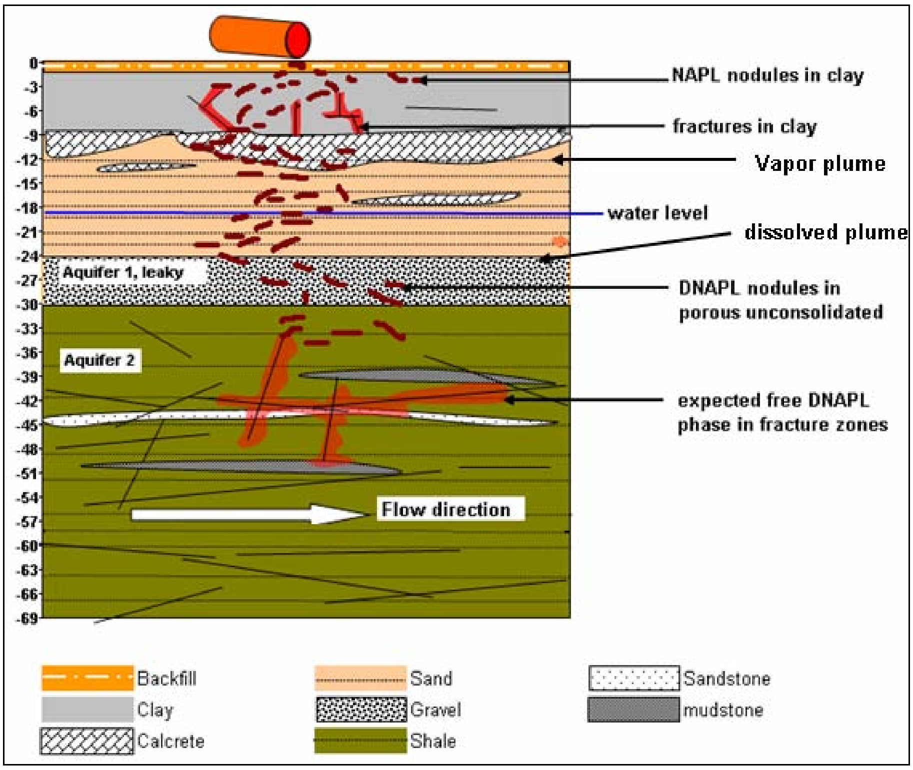

Figure 16: Conceptualisation of DNAPL phase at Test Site 1.

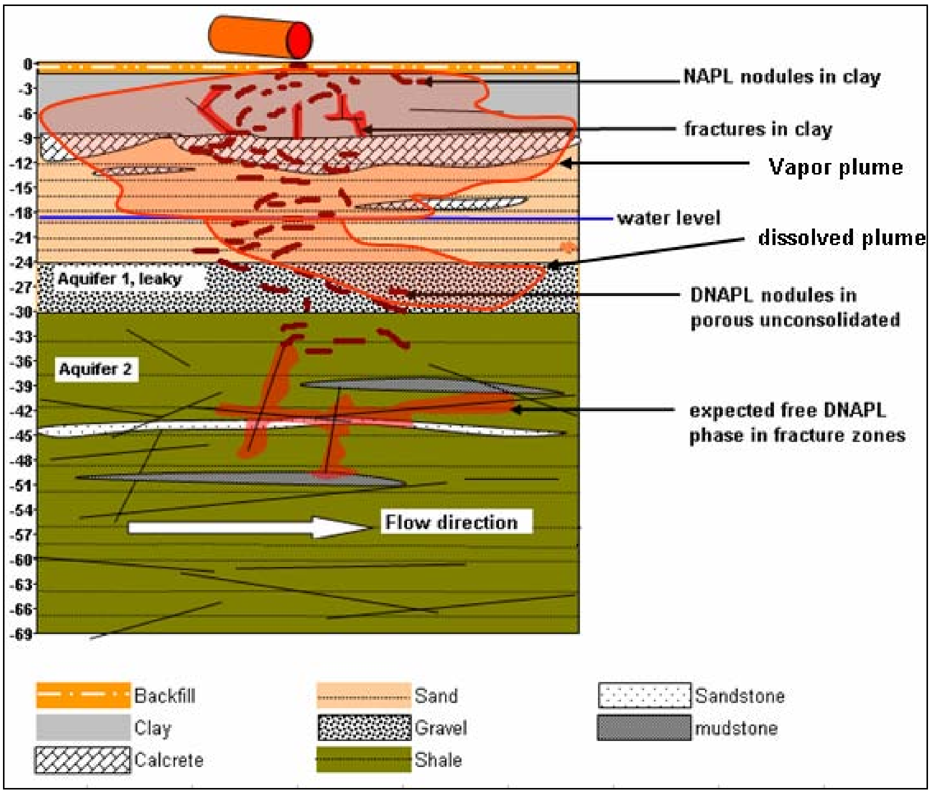

Figure 17: Conceptualisation of vapour and dissolved phases at Test Site 1.

6. MULTI-PHASE MODELLING

Multi-phase modelling is a very important consideration in DNAPL assessment. Due to the complexity of these multi-phase interactions, the models which deal with these problems in a quantitative manner are, of necessity, therefore also generally very complex. For these models to have relevance, the data requirements of such models are also extensive.

Models have several limitations, of which users must be aware when embarking on these modelling exercises, and of which regulators, site owners and other decision- makers should consider when taking action based on numerical or analytical models. Lichtner (1996) puts it as follows:

> *Computer models can provide, if not a direct quantitative description, at least a far better qualitative understanding of the geochemical and physical processes than might otherwise be possible.*

It is important to note that the uncertainties related to multiphase models are not unique in the groundwater environment. Any model is a simplified version of reality, based on various assumptions. Apart from the assumptions made to construct the conceptual model, there is major uncertainty with several input parameters and the results should always be interpreted with these considerations.

6.1 Data requirements

The data requirements for such models would include the following parameters (Pope (UTCHEM) and Reynolds and Kueper, 2004):

- Dimensions
- Mesh size
- Pore volume
- Boundary conditions
- Initial pressure
- Initial DNAPL saturation
- Aquifer pore volume
- Total aquifer DNAPL volume
- List of Reactive Species
- Capillary pressure endpoint
- Concentration: Water, DNAPLs
- Density of fluids
- Diffusion coefficient (m^2/d)
- Dispersivity (m)
- Soil/Aquifer/Bulk density (g/cc)
- Interfacial tension (dyne/cm)
- Permeability (m/d)
- Aquifer dip angles
- Saturation fraction
- Temperature (^oC)
- Viscosity of wetting and non-wetting phases
- Phase Behaviour
- Phase Saturations
- Capillary Pressure
- Relative Permeability Curves
- Trapping Number
- Pore size distribution index (porous media and fractures)
- Residual wetting phase saturation (porous media and fractures)

6.2 Outline of methodology for NAPL modelling

Modelling multiphase flow and transport requires a similar rationale to groundwater reactive mass transport modelling. As such, the guidance provided for codes such as MT3D and MT3D-MS (Zheng, 2004), is an applicable approach to follow. As highlighted in many documents providing guidance on modelling, the proper conceptualisation of the problem, as achieved with a detailed conceptual model of the aquifer, the source of DNAPLs, their properties and the likely interactions expected, will hold the key to the successful modelling of a multiphase transport model of DNAPL.

In every model study the natural system is represented by a conceptual model (see also Sections 2.3 and 4.4.2.4). A conceptual model includes designing and constructing equivalent but simplified conditions for the real-world problem that is acceptable in view of the objectives of the modelling and the associated management problems. Converting the real-world situation into an equivalent model system, which may then be solved using existing programme codes, is a crucial step in groundwater and multiphase flow and transport modelling in aquifers.

A critical and cost-effective use of modelling lies in understanding and evaluating the analysis of proposed or alternative future conditions i.e., the model is used as a management or decision-making tool to help answer “what if" questions (Donagian and Rao, 1986). Models also may be used to approximate and estimate the rates and extent of migration that may be expected at the field-scale under varying conditions. Attempting to answer such questions through data collection programmes would be expensive and very difficult in many situations. For example, information can be generated to evaluate the effects of differing hydraulic, NAPL or microbial activity properties for the site.

Therefore, modelling may be used to assist in the design of the field characterisation, ensuring that the most important factors are included and evaluated adequately and therefore, to assist in focusing available resources (time and money). A suggested flow path for such modelling has been suggested by Carey et al., 1995.

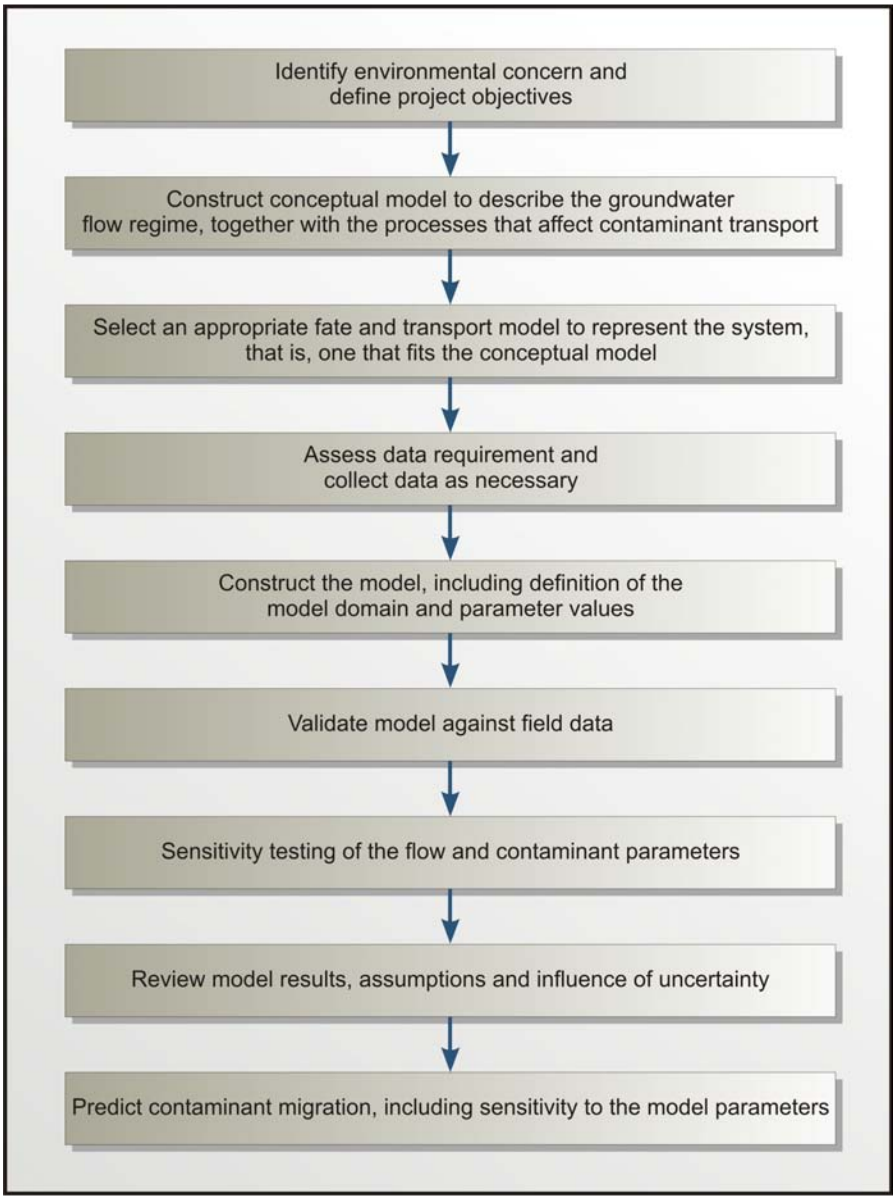

Figure 18: Suggested outline of approach

Anderson et al., 1992 suggests that concentration distributions in the groundwater zone may be highly spatially variable. In addition to dispersion, vertically-averaged sampling from conventional monitoring wells may lead to observed concentrations which are substantially below the maximum values present in the aquifer. Unless caution is observed when those averaged results are being interpreted, incorrect conclusions about the distribution of organic contaminants in the subsurface may be drawn.

6.3 Limitations

As analogues to the real-life situation, multiphase models are due to their inherent nature very limited in what may be achieved. There is a wide range of complexity from simple approaches which make several simplifying assumptions or corrections (and are consequently easier to populate, construct and simulate), to detailed models which attempt to be more comprehensive (requiring far more data, expertise, computing power and time for simulation). While the simpler models are attractive for the ease of use and simplicity, unfortunately, it appears that they can be very misleading.

Gerhard and Kueper, 2003 developed a comprehensive multiphase model and compared these results to simpler methods. Some of their findings include:

- None of the simpler or more conventional constitutive models employed was able to reproduce, within ±10%, the spatial and temporal migration of the non-wetting fluid body at late time predicted by the base case.
- Not accounting for hysteresis functions in the constitutive model demonstrated a relatively small effect on the spatial distribution of non-wetting fluid, but significantly influenced imbibition rates and total growth cessation times.
- Not accounting for non-wetting phase trapping, even when the maximum non-wetting phase residual value is less than 10%, is found to increase the mobility of the non-wetting fluid profoundly, resulting in a wider and deeper extent of DNAPL predicted to occur over a time-frame order of magnitude greater than when trapping is incorporated.
- The non-wetting fluid distribution is tortuous and highly sensitive to the order of the encounter of permeability and capillary properties, with this sensitivity increasing upon termination of the source.
- Not accounting for the abrupt extinction of imbibition, caused the time predicted for the cessation of non-wetting fluid migration to approximately double.
- Typical hysteretic constitutive models based on the van Genuchten function appear to be unsuitable for simulating DNAPL migration in heterogeneous media below the water-table.

The conclusion from the research on multiphase flow modelling by Gerhard and Kueper is very sobering to all practitioners in this field. This conclusion reads as follows:

> *"The practical implication of this study is that in addition to fluid and porous media properties, source characteristics, and the specific distribution of permeability beneath a release location, all of the examined constitutive model hysteresis and trapping phenomena may need to be incorporated, and appropriate values for the corresponding function parameters may need to be known, in order to accurately simulate the redistribution and immobilisation of a non-wetting fluid release below the water table in both space and time."*

The above discussions highlight the difficulties and uncertainties of multi-phase modelling in porous media. In factured media all of the above difficulties similarly apply, but the fractures add an order of the magnitude of complexity and uncertainty in the simulations. Groundwater flow modelling in fractured media is in its infancy and whereas for many applications on a larger scale, the effects of individual fractures may be averaged out in the equivalent porous media; the REV in fractured flow of NAPLs does not allow such an approach. The consequence of this is that the models must explicitly accommodate fractures and the current conundrum is that the select few models that can accommodate fractured flow, do not coincide with the few codes that properly consider multiphase flow. The modelling attempts must therefore be done on only very well characterised sites or considered as alternative scenarios used to highlight critical factors that must be quantified.

6.3.1 UTCHEM

UTCHEM, the University of Texas Chemical Compositional Simulator (copyright owned by The University of Texas, Austin), is a three-dimensional, multiphase, multicomponent, compositional, variable temperature, finite-difference numerical simulator. UTCHEM for can be used to simulate the following groundwater related situations:

- Infiltration and migration of NAPLs in both saturated and unsaturated zones
- Partitioning interwell tracer tests in both saturated and unsaturated zones
- Remediation using surfactants and/or polymers, surfactant foam, or cosolvents
- Bioremediation
- Geochemical reactions

There are other multi-phase codes, but this is the most widely code for NAPL transport in groundwater, probably due the fact that it is available in the public domain.

6.4 Dissolved phase and degradation modelling

It is again emphasised that the dissolved phases can only be accurately modelled if the NAPL transport is considered. They can however be used if the NAPL sources have been accurately determined in the aquifer.

6.4.1 Codes

The question is often posed: “Which is the best modelling tool/package for prediction?” The answer to this is none; each modelling code or method has particular advantages and disadvantages as far as availability, cost, ease of use and inherent assumptions and weaknesses. The only answer is that the appropriate code or method must be used based on the type of answer required. By highlighting the usefulness of these models and their basic data requirements, along with the uncertainties involved in reactive transport or multiphase flow models, the user/researcher will hopefully, be in a position to select an appropriate modelling method and modelling code.

Carey et al., 1995 gives an overview of some available codes. Descriptions of these and other codes are given in Appendix A.

6.5 Uncertainty in multiphase or reactive transport modelling.

The amount of detailed information required on a heterogeneous site to describe the system accurately would be impossible to gather and thus attempts to quantify these flows accurately are fraught with uncertainty. Thompson and Jackson (1996) put it as strongly as this: “From the perspective of contaminant hydrology, the impact of geologic heterogeneity is difficult to consider in practice,” and “(Therefore) oversimplified conceptualisations of system behaviour are used." Thus, through no fault of modellers or modelling codes, which would need to be too complex to be practical if such heterogeneities were incorporated, oversimplifications usually occur.

The problem with codes that can accommodate these features, is that they cannot be verified. It is somewhat paradoxical that as more and more sophisticated representations of heterogeneous porous media are developed, it becomes increasingly difficult to compare the resulting calculations with experimental or field observations to validate model predictions. This is because of the greater burden placed on the detail of observation required to compare with the model calculations (Lichtner, 1996).

Where several interactions are considered and the sequential differentiation of the plume or NAPL occurs along the flow path, the uncertainties are likely to increase. Research on geochemical kinetics has revealed a wealth of possible mechanisms and rates by which minerals, organisms and aqueous species may interact (Steefel and MacQuarrie, 1996). Thus, in the best-case situation, even by adopting the best-constrained independent input parameters, one must accept at least one order of magnitude uncertainties in each parameter. It follows *that the results of reactive transport calculations performed using independently constrained parameters, will also most likely have uncertainties of several orders of magnitude, at best* (Oelkers, 1996).

The cumulative error or uncertainty propagation from the detailed model formulation, added to the uncertainties associated with proper fracture characterisation, make it self-evident that multiphase reactive transport modelling in heterogeneous fractured media must be inherently low in confidence. This is not fault of the modelling codes or the modellers, but merely due to the complexity of the situation. Despite this, models may still be regarded as useful tools, provided the results are presented and evaluated with these factors clearly reported and understood.

7. WATER QUALITY STANDARDS AND GUIDELINES

The need for South African-specific guidelines for dealing with DNAPLs should be a high priority. Currently, for organic groundwater contaminants, consultants and researchers use a multitude of different quality guidelines and standards. Guideline concentrations and maximum contaminant levels from several other countries are often referred to, which has led to an *ad hoc* approach to appropriate trigger concentrations for actions.

There is an urgent need for a consistent approach to allow the groundwater community, the regulators and the site owners to apply the same rationale consistently and be subjected to the same expectations for acceptable concentrations.

In view of this, it is recommended that a common framework with a systematic methodology be applied. In a country such as South Africa, such a framework must be flexible, pragmatic, consistent and cost-effective. It is therefore considered appropriate that a risk-based approach be followed, with a set of screening trigger values for different common groundwater contaminants. This approach is consistent with the methodologies recommended by the USEPA, the UK Environmental Agency, Australian regulations and the trend in much of the rest of the world.

7.1 Risk-Based Approaches

A risk assessment is an analysis that uses information about toxic substances at a site to estimate a theoretical level of risk for people/receiving environments potentially exposed to these substances. The information comes from scientific studies and environmental data from a site. A risk assessment provides a comprehensive scientific estimate of risk to persons who could be exposed to these hazardous materials (ATSDR, 2004).

The UK approach is outlined in the following steps:

- Prioritisation of sites and contaminants on site with screening methods
- Quantification of potential risk, using simple analytical methods, advanced analytical equations and detailed numerical modelling
- Identification and implementation of appropriate actions

Such an approach is in line with the widely used Risk-Based Correction Action used widely internationally. Discussions with various DWAF officials have indicated the increasing acceptability of risk-based approaches, provided that they are supported by a high quality scientific and consistent methodology. The common approach in all these methods is the ‘Source-Pathway-Receptor’ philosophy. Such an approach will allow each aquifer to receive the appropriate protection and result in the site investigation, mitigation and remediation being funded, requisite with the risks posed to the receiving environment (users and water resources) and the importance of the resource as a supply or as a strategic reserve.

A typical implementation framework for the implementation of such a methodology is provided by below:

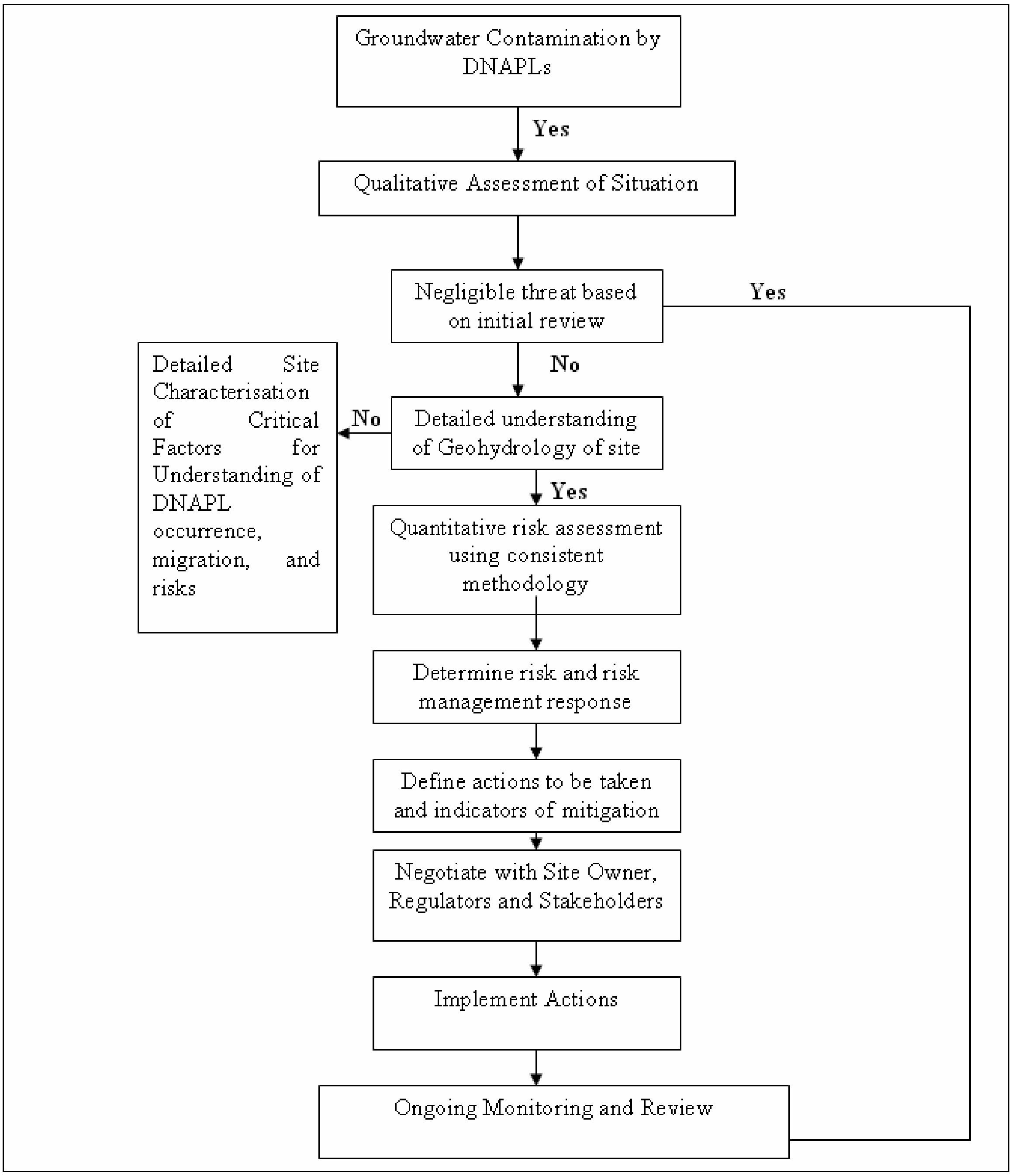

Figure 19: Proposed methodology for setting and implementing groundwater standards for organic contaminants in South Africa

(From Carey et al., 1995)

It is critical to have conservative safety margins as an integral component of the accepted risk assessment analysis to ensure adequate protection of the receptors. Each risk assessment prepared in support of decision-making should include a risk characterisation that follows the principles and reflects the values outlined in South African policy.

A risk characterisation should be prepared in a manner that is clear, transparent, reasonable and consistent with the relevant regulations available to the regulator for enforcement and environmental, water resource or public health protection. Furthermore, discussion of risk in all reports, presentations, decision packages and other documents should be substantively consistent with the risk characterisation. The nature of the risk characterisation will depend upon the information available, the regulatory application of the risk information and the resources (including time) available. In all cases, however, the assessment should identify and discuss all the major issues associated with determining the nature and extent of the risk and provide commentary on any constraints limiting fuller exposition (US EPA, Science Policy Council, 1995).

In all cases, the process should include risk assessment and risk management, discussion of uncertainties/confidence level of the risk determination, a full conceptual model of the site with available information, full disclosure of results and risk perspectives. As part of this Hazard Identification, Dose Response Assessment and Exposure Assessment must be provided in the context of the 'Source-Pathway-Receptor' paradigm.

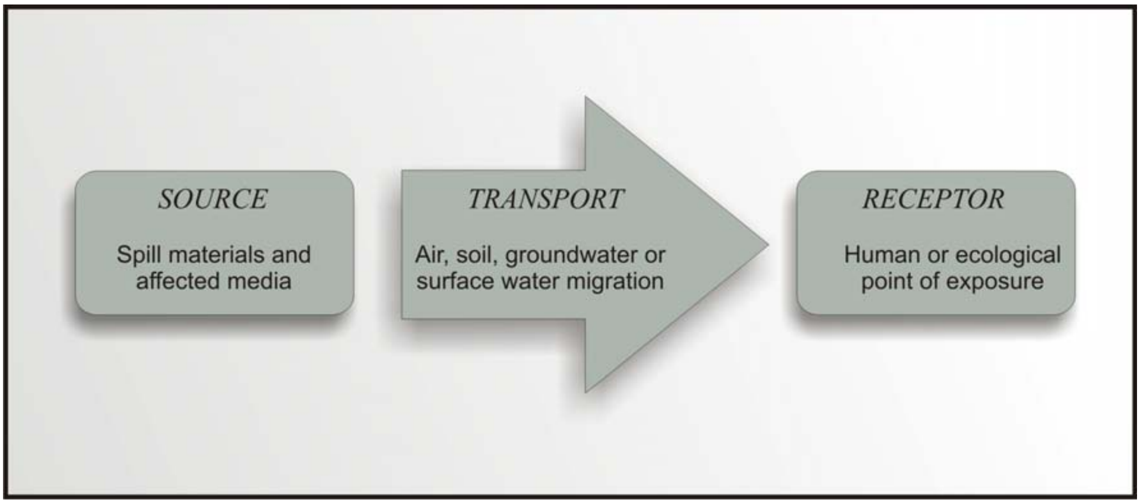

Figure 20: Risk Assessment Overview

While the general approach and procedures should be similar to the well established methodologies such as those described in the ASTM Risk-Based Corrective Action procedure, it is important that the method is focused on the protection of water resources and specifically recognises the statutory responsibilities of DWAF and other agencies as a function of South African legislation.

7.2 Trigger values for action

A difficulty for regulators and site owners is the initial decision of whether action should be taken. It is suggested that an initial screening methodology be established. Such a methodology could follow several approaches. The simplest, but not necessarily the most effective, would be to follow an ultraconservative approach. Such an approach would include listing tables of common organic contaminants and the associated guideline values from different countries. The difficulty here lies in selecting the most appropriate value for each parameter. This is not as easily achieved as might be expected, as indicated by the comparison between different guideline concentrations (Appendix C) from the Dutch and EPA groundwater guidelines (two of the most common references used in South Africa).

In the table, the big differences between two equally well respected and widely used guidelines may be seen for various parameters. This understandably leads to inconsistent application. It is suggested that the Intervention Value of the Dutch guidelines be used where available, due to the more extensive nature of the available list and that as a precaution, a trigger value of 0.01% of maximum solubility of any contaminant not found on the list, be used. Solubility data for a vast range of organics are available in the public domain, including in the URA software developed for the WRC as part of the Identification and Prioritisation of Groundwater Contaminants in South African urban environments (Usher et al., 2004). This trigger value could be used as a first level of action, but risk-based decisions are more appropriate and therefore recommended.

8. SUMMARY

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

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

Standard approaches to site assessment to site assessment as undertaken at most contaminated sites, will not yield the required results in the case of DNAPLs. The field investigations in this project showed a markedly different approach is needed, and that detailed and accurate understanding of the fractures and their influence on the flow and transport of DNAPLs and their dissolved constituents is required. This can be achieved by using a toolbox of diverse techniques to obtain the required information.

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

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

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

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

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

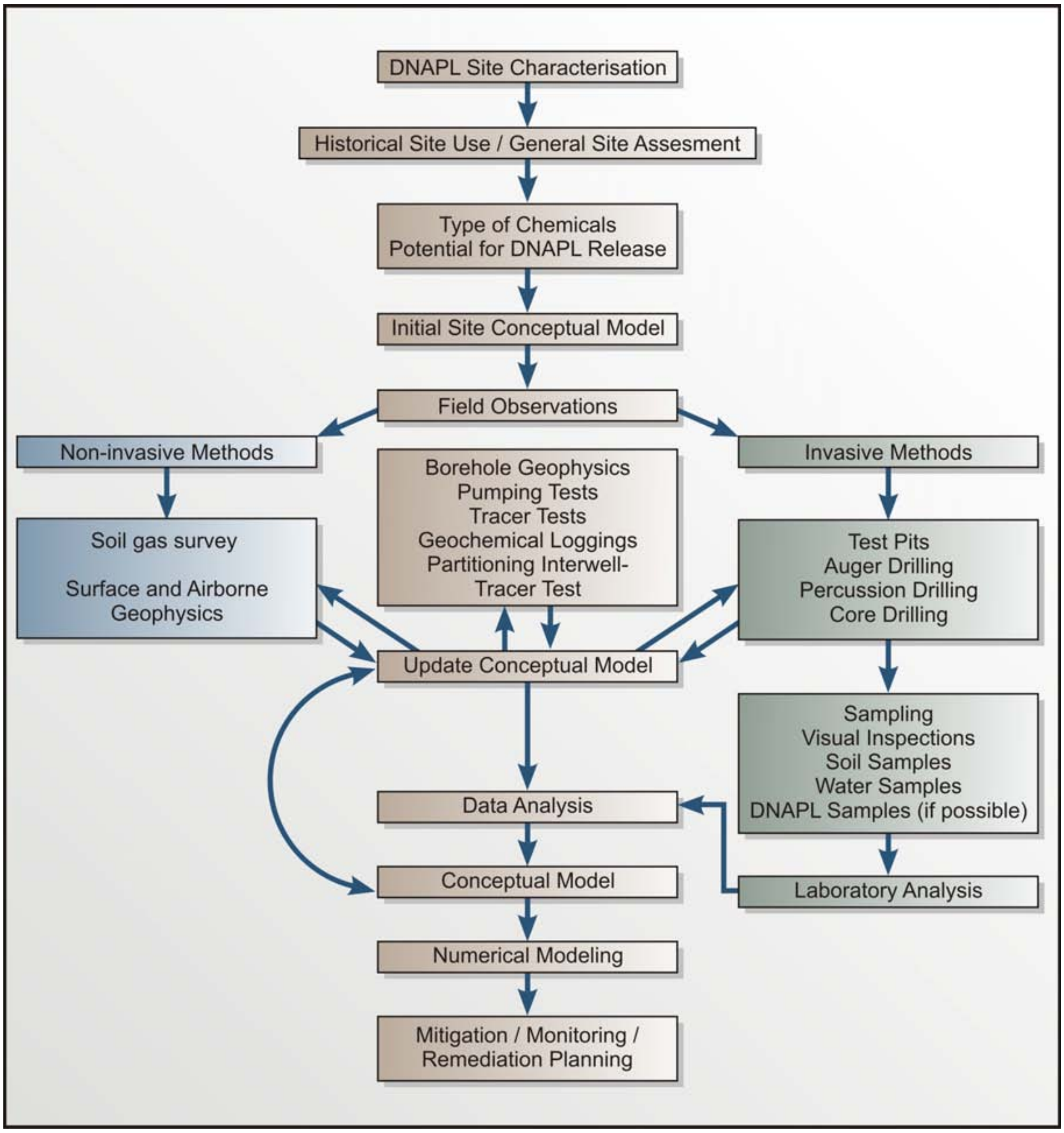

Figure 21: Framework for DNAPL site assessment.

9. CONCLUDING REMARKS

This document has provided an overview of site assessment techniques applicable (and available) to South African site owners, site investigators and Regulators. This document forms part of a series of documents, produced by Water Research Commission project K5/1501 "Field investigations to study the fate and transport of dense non-aqueous phase liquids (DNAPLs) in groundwater". More detail on specific issues such as monitoring and sampling techniques as well as MNA guidance are provided in the accompanying documents.

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

1) Utilisation of different drilling techniques (auger, core and air percussion), provide the site assessor with valuable information regarding the subsurface. However, due to high costs and limited availability of specialized (e.g. diamond core and direct push auger) drilling rigs, these techniques are often neglected in site assessments in South Africa.

2) The number of boreholes available to a site assessor is often limited due to cost constraints by site owners. Drilling of boreholes is an iterative process, whereby more than one drilling event will be required to characterize a site. The knowledge gained through such successive drilling events, is used to continually update the site conceptual model. Therefore, site owners in South Africa need to be convinced that a DNAPL assessment requires *intensive site characterization* in order to successfully plan and implement (costly) mitigation and/or remediation.

3) Many problem DNAPLs are volatile organic compounds. Therefore, analyzing soil or water samples during a site investigation on site will yield the better analytical results than costly and time consuming laboratory analysis. Many innovative "on-site" analytical techniques which yield accurate results have been developed e.g. Mobile Gas Chromatograph. However, availability of such equipment is scarce and costly in South Africa.

4) Water and soil samples are analysed for organic contaminants, using EPA protocols, and employing gas chromatography-mass spectrometry methods. There are only a few laboratories equipped for specialised environmental analysis in South Africa. Generally it was found that European laboratories were more cost effective and turnover time for results was shorter than for local laboratories. Due to firm regulation of organic contamination in European countries, the European laboratories provide their clients with a number of 'environmental analysis packages". These "packages" targets specific contaminant groups or required lines of evidence (e.g. for monitored natural attenuation) which are more cost effective than analysis of separate contaminants. It is recommended that these practices be adopted by South African laboratories.

5) Although the National Water and Environmental Acts of South Africa are very clear on prevention of pollution to, and management of water resources, no guidelines exists on how to deal with NAPL contaminated sites. Guidelines which are required would include, water quality standards, site assessment guidelines, and monitoring and sampling guidelines.

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Appendix A

- AT123D

AT123D is based on an analytical solution for transient one-, two- or three-dimensional transport in a homogeneous isotropic aquifer with uniform regional flow. AT123D computes the spatial-temporal concentration distribution of wastes in the aquifer system and predicts the transient spread of a contaminant plume through a groundwater aquifer. The fate and transport processes accounted for in AT123D are advection, dispersion, adsorption and biological decay. AT123D estimates all the above components on a monthly basis for up to 99 years of simulation time.

- BIOSCREEN

Based on the Domenico analytical solute transport model, BIOSCREEN is a screening model which simulates remediation through natural attenuation of dissolved hydrocarbons at petroleum fuel release sites. (Available at http://www.epa.gov/ada/csmos/models/bioscrn.html) The software, programmed in the Microsoft Excel spreadsheet, has the ability to simulate advection, dispersion, adsorption and aerobic decay, as well as anaerobic reactions that have been shown to be the dominant biodegradation process at many petroleum release sites. It includes three different model types: (1) solute transport without decay, (2) solute transport with biodegradation modelled as a first-order decay process (simple, lumped-parameter approach) and (3) solute transport with biodegradation modelled as an instantaneous biodegradation reaction with multiple soluble electron acceptors, including dissolved oxygen, nitrate and sulphate. The model is designed to simulate biodegradation by both aerobic and anaerobic reactions.

- BIOPLUME II & III

BIOPLUME II is a two-dimensional, finite difference, two-dimensional model for simulating transport of a single dissolved hydrocarbon species under the influence of oxygen-limited biodegradation, first order decay, linear sorption, advection and dispersion. The aquifer may be heterogeneous and anisotropic.

The BIOPLUME III model simulates both aerobic and anaerobic biodegradation processes in addition to advection, dispersion, sorption and ion exchange. BIOPLUME III simulates the biodegradation of organic contaminants using a number of aerobic and anaerobic electron acceptors: oxygen, nitrate, iron (III), sulphate,and carbon dioxide. BIOPLUME III is based on the U.S. Geologic Survey (USGS) Method of Characteristics Model (MOC) dated July 1989 (Konikow and Bredehoeft).

- FATE 5

A new groundwater attenuation modelling tool (FATE 5) has been developed to assist users with determining site-specific natural attenuation rates for organic constituents dissolved in groundwater. FATE 5 is based on and represents an enhancement to the Domenico analytical groundwater transport model (Domenico, 1987). These enhancements include use of an optimisation routine to match results from the Domenico model to actual measured site concentrations, an extensive database of chemical property data and the calculation of an estimate of the length of time needed for a plume to reach steady state conditions. FATE 5 was developed in Microsoft ® Excel and is controlled by means of a simple, user-friendly graphic interface.

- MODFLOW: MT3D/ MT3DMS

MT3D is a transport model that is used in conjunction with any block-centred finite difference flow model, such as MODFLOW. MT3D is a three-dimensional transport model for simulation of advection, dispersion and chemical reactions of dissolved constituents in groundwater systems. It includes linear or non-linear sorption and first-order irreversible decay or biodegradation. (See also Progress Report 3.)

A later version of MT3D, MT3DMS (where MT3D stands for the Modular 3-Dimensional Transport model, while MS denotes the Multi-Species structure), is also now available. MT3DMS has a comprehensive set of options and capabilities for simulating advection, dispersion/diffusion and chemical reactions of contaminants in groundwater flow systems under general hydrogeologic conditions. MT3DMS is unique in that it includes three major classes of transport solution techniques in a single code, i.e.:

- The standard finite difference method;
- The particle-tracking-based Eulerian-Lagrangian methods; and
- The higher-order finite-volume TVD method.

Since no single numerical technique has been shown to be effective for all transport conditions, the combination of these solution techniques, each having its own strengths and limitations, is believed to offer the best approach for solving the most wide-ranging transport problems with the desired efficiency and accuracy.

- RT3D

RT3D is based on MT3D and is used for simulating three-dimensional, multi-species, reactive transport in groundwater. RT3D can accommodate multiple sorbed and aqueous phase species with user-defined reaction frameworks. It allows instantaneous biodegradation, kinetically limited reaction, non-equilibrium sorption/desorption, NAPL dissolution, dual porosity, anaerobic and aerobic biodegradation.

As part of a natural attenuation evaluation, RT3D may be used to predict the fate and transport of groundwater plumes. A sensitivity analysis may be performed to evaluate the range of potential outcomes. Such predictions may be used to define a long-term monitoring programme that will feed back into future reactive transport simulations and model refinement.

Active remediation may also be simulated, whether it be air sparging, chemical oxidation or accelerated bioremediation. The key is understanding the reaction kinetics of the remediation process and applying that knowledge in a user-defined reaction module. Reactive transport simulations could potentially be applied to scenarios involving contaminants such as heavy metals, explosives, petroleum hydrocarbons, and/or chlorinated solvents.

- PHT3D

PHT3D is a multi-component transport model for three-dimensional reactive transport in saturated porous media. The model incorporates the codes MT3DMS for the simulation of three-dimensional advective-dispersive, multi-species transport and the geochemical model PHREEQC-2 for the quantification of reactive processes. PHT3D uses PHREEQC-2 database files to define equilibrium and kinetic (e.g., biodegradation) reactions.

PHT3D has been applied to a number of (bio)geochemical transport modelling studies:

- Natural attenuation of hydrocarbons
- *In situ* remediation of metal-contaminated groundwater
- Artificial recharge and aquifer storage and recovery
- Transport of chlorinated solvents in a permeable Fe(0)-filled reactive barrier
- Natural attenuation of landfill leachates
- Transport and attenuation of ammonium-contaminated groundwater

- SUTRA

SUTRA simulates fluid movement and transport of either energy or dissolved substances in a variably saturated system environment. Solute transport is restricted to a single reacting species and accounts for solute sorption (linear, Freundlich or Langmuir equilibrium isotherm), zero and first-order decay and zero-order production, hydrodynamic dispersion (including corrections for anisotropy) and molecular diffusion.

SUTRA employs a two-dimensional hybrid finite-element and an integrated finite-difference method to approximate the governing equations that describe the two interdependent processes that are simulated: (1) fluid density-dependent saturated or unsaturated ground water flow and either (2a) transport of a solute in the groundwater, in which the solute may be subject to equilibrium adsorption on the porous matrix and both first-order and zero-order production or decay; or (2b) transport of thermal energy in the ground water and solid matrix of the aquifer.

- BIOCHLOR

BIOCHLOR is a screening model that simulates remediation by natural attenuation of dissolved solvents at chlorinated solvent release sites. BIOCHLOR may be used to simulate solute transport without decay and solute transport with biodegradation modelled as a sequential first-order process within one or two different reaction zones.

BIOCHLOR simulates remediation by natural attenuation (RNA) of dissolved solvents at chlorinated solvent release sites. The software, programmed in the Microsoft Excel spreadsheet environment and based on the Domenico analytical solute transport model, has the ability to simulate 1-D advection, 3-D dispersion, linear adsorption and biotransformation via reductive dechlorination (the dominant biotransformation process at most chlorinated solvent sites). Reductive dechlorination is assumed to occur under anaerobic conditions and dissolved solvent degradation is assumed to follow a sequential first-order decay process. BIOCHLOR includes three different model types:

- Solute transport without decay
- Solute transport with biotransformation modelled as a sequential first-order decay process
- Solute transport with biotransformation modelled as a sequential first-order decay process with two different reaction zones (i.e., each zone has a different set of rate coefficient values).

(Available at: http://www.epa.gov/ada/csmos/models/biochlor.html)