Dense Non-Aqueous Phase Liquids in South Africa: A COMMUNITY GUIDE

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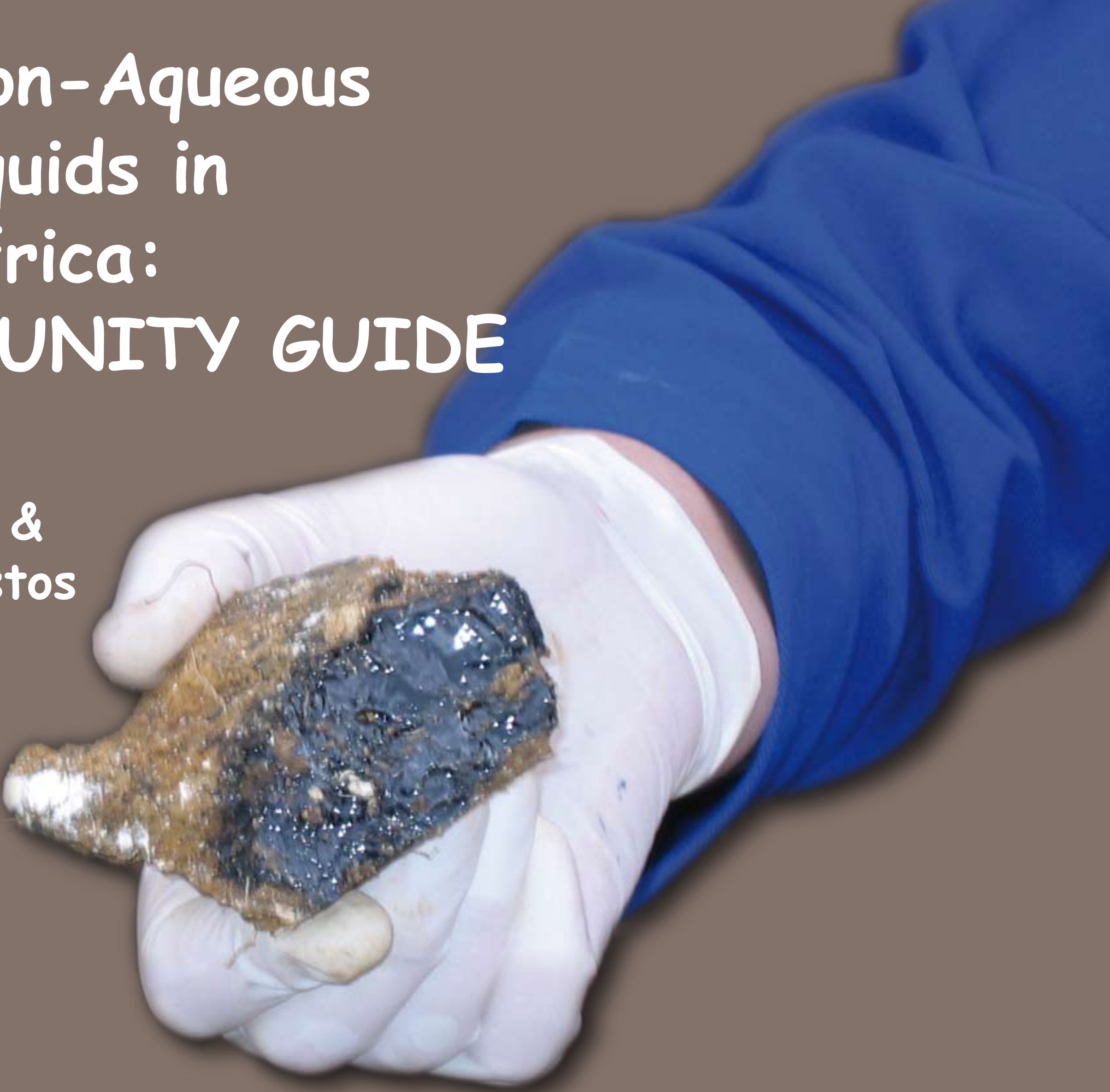

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Water Research Commission

An Introduction to Dense NON-AQUEOUS Phase Liquids (DNAPLs) in South Africa:

A Community Guide

Report to the Water Research Commission

by

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An Introduction to DNAPLs in South Africa

This document gives a brief summary of important considerations for DNAPLs in South Africa. The document provides key information on the sources and occurrence of DNAPLs in South Africa, appropriate site characterisation approaches, application of Monitored Natural Attenuation (MNA), and expected DNAPL migration in the major South African aquifer systems is provided. More detailed information is given in one of the accompanying reports emanating from this project (see details below).

This report is aimed at the general public, site owners, and interested and affected parties.

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

The documents in this series include:

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

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

Glossary

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

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

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

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1. INTRODUCTION

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

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

This report is one of a series of documents produced as part of the project. The purpose of this handbook is to provide a user-friendly overview of the nature of DNAPL contamination in a South African context. It is intended to assist non-specialists in understanding the basic concepts of DNAPLs in groundwater.

A more detailed handbook providing a user-friendly overview of the nature of DNAPL contamination to assist site investigators, site owners and regulators in evaluating site investigations and making informed decisions, forms part of this series. Detailed guidance on site assessment, monitoring at DNAPL contaminated sites and monitored natural attenuation can be found in other documents in this series.

DNAPLs in Groundwater

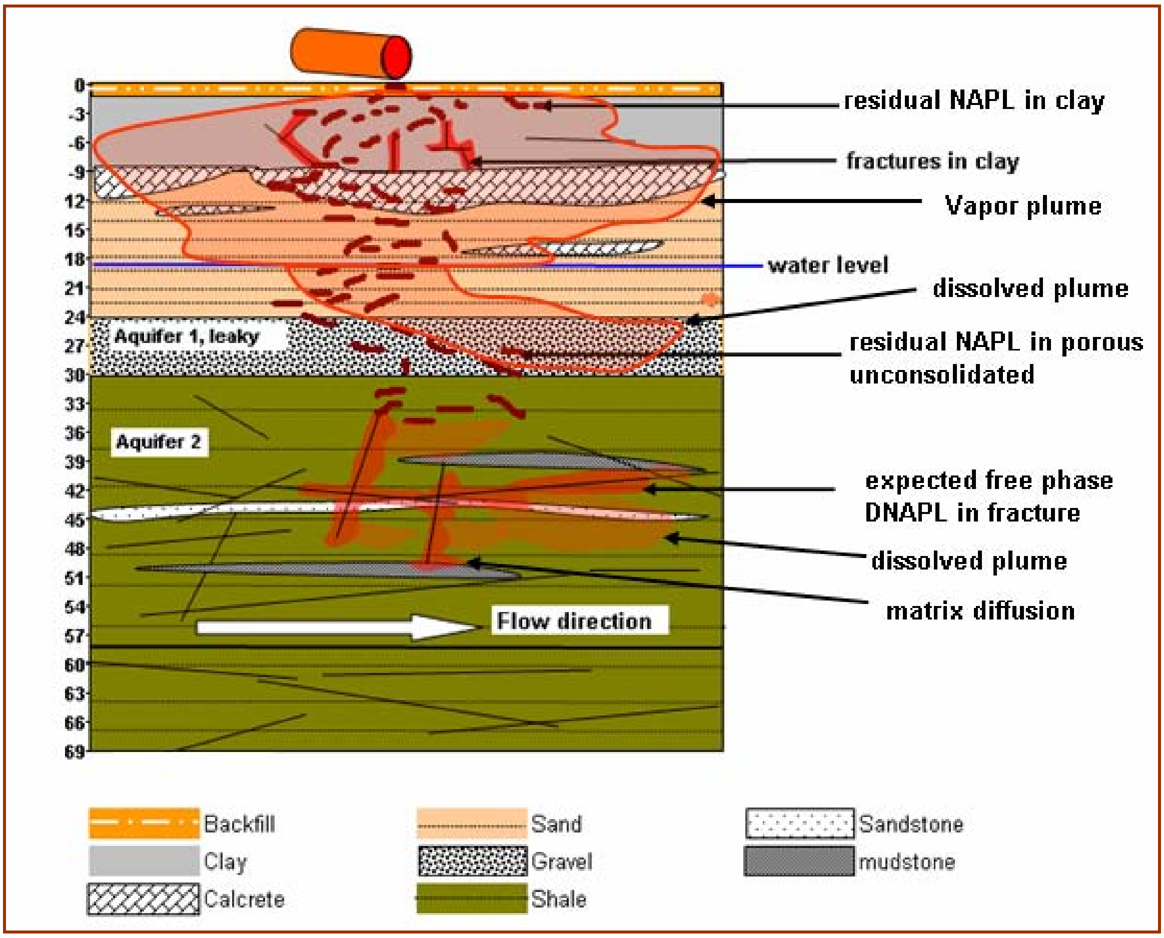
DNAPLs in Groundwater

What are DNAPLs?

DNAPLs are Dense Non-Aqueous Phase Liquids. These liquids are denser than water and only slightly soluble in water. DNAPLs exist in the subsurface as a separate fluid phase in the presence of either air or water, and can both vapourise into air and slowly dissolve into flowing groundwater.

Where do DNAPLs occur?

The potential for the widespread contamination of groundwater by DNAPLs is substantial, because of the extensive production, transport, utilisation, and disposal of large volumes of DNAPL chemicals. There are thousands of potential sites in South Africa, as elsewhere in the world, where DNAPLs may have been released to the subsurface in varying quantities. Examples include chlorinated solvents (degreasers and drycleaning fluids), creosote, coal tar and Polychlorinated Biphenyls (PCBs) in dielectric oils.



Why are DNAPLs of concern to us?

Many of these chemicals are very toxic and carcinogenic. Several DNAPL chemicals are very persistent in the environment, and very small amounts of these can pollute very large volumes of groundwater resources due to their high toxicity, even at very low concentrations. DNAPLs are not often released into the environment as pure chemicals, but are often discharged as used solvents that contain varying amounts of other organic chemicals. These other components can significantly influence the overall properties of the DNAPL, and both aid detection and complicate remediation. DNAPL that is trapped in the subsurface acts as a continuing source of dissolved contaminants to groundwater, and their removal from aquifers is very difficult and costly. Due to this, DNAPL contaminants have been classified as high priority groundwater pollutants in several countries, including South Africa (Usher *et al*., 2004, WRC Report No. 1326/1/04).

The Problem of DNAPL Spreading

When released in sufficient quantities in soil and rock above the water table or into the saturated zone, DNAPLs will actively spread, mostly due to gravity, until the free phase (undissolved oil fraction) is distributed in discontinuous beads of DNAPL. This is commonly called residual saturation, or residual. The spread and distribution of residual DNAPL is not uniform or easy to predict in the subsurface, due to the small variations in pore size and fractures in the subsurface. The residual DNAPL is immobile under normal conditions, but it can act as a long-term source of contaminants to groundwater.

Major factors controlling DNAPL migration in the subsurface:

- The volume of DNAPL released
- Area of infiltration at the DNAPL entry point to the subsurface
- Duration of release
- Properties of the DNAPL (such as density, solubility, viscosity and interfacial tension)
- Properties of the soil/aquifer material such as pore sizes, fracturing, permeability and susceptibility to matrix diffusion processes
- General stratigraphy such as the location and orientation of low permeability layers
- Other features such as sizes, orientation and connectivity of fractures

Implication for site characterisation at DNAPL sites:

- “Standard” approaches do not yield answers required
- In South Africa, with predominantly fractured aquifers, detailed fracture characterisation is required
- Drilling and borehole construction considerations are very different to Minimum Requirements
- Contaminant-specific sampling and analytical techniques are required
- International case studies show that successful remediation of NAPLs depends on a proper understanding of the site through **very detailed** site characterisation

DNAPLs as Priority Contaminants in Groundwater in South Africa

Potential Sources of DNAPL Contaminants in Major Urban Areas of South Africa

A project undertaken by the Water Research Commission, focusing on groundwater contaminants in the urban catchments of South Africa (Usher *et al*., 2004, WRC Report No. 1326/1/04), resulted in a contaminant inventory and priority list of possible groundwater contaminants in these environments. All possible sources (activities) were identified within the urban environment and expected contaminants assigned to each source. These were then prioritised according to set criteria.
The contaminant source inventory is one of the most important elements in water resource assessment. It identifies potential sources of contamination associated with specific activities, industries, and land uses located within an area. The contaminant inventory should serve three important functions:

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

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

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

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

Table 1 is an adapted version of the contaminant inventory compiled by Usher *et al.*, (2004). Only organic contaminants are included in the list. It must be noted that some contaminants listed (e.g. petroleum hydrocarbons), can be classified as Light Non Aqueous Phase Liquids (LNAPLs), thus implying a density or specific gravity less than that of water. The reason for inclusion can be attributed to the complex behaviour of NAPLs and the changes that take place where contaminant mixtures are concerned, as opposed to single component contaminants. These mixtures would more often than not behave as a DNAPL than as an LNAPL.

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

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

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

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

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

Of the 121 contaminants listed in the national prioritisation list, 64 are considered to be DNAPL contaminants. However, not all the contaminants listed have the physical properties of a DNAPL. Many are often either used as intermediates to synthesise compounds with DNAPL properties, or are found at sites often associated with the better-known and more common DNAPL contaminants (e.g. solvent use). The properties of the contaminant mixture in the aquifer will determine the behaviour of the NAPL source.

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

Table 1: Prioritisation list of sources of possible DNAPL groundwater contamination in urban environments (Adapted from Usher et al., 2004).

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

Table 2: Contaminant Prioritisation – NAPL contaminants with ranking (Adapted from Usher et al., 2004).

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

DNAPL Site Characterisation

DNAPL Site Characterisation

1.1 Introduction

In most groundwater systems, there is significant variability. This makes the delineation and detection of these sparingly soluble, dense contaminants very difficult. Several techniques can be applied for the characterisation of a site contaminated with dense non-aqueous phase liquids (DNAPLs). Detailed site characterisation methods are described in an accompanying report "*Field investigations to study the fate and transport of dense non-aqueous phase liquids (DNAPLs) in groundwater: Manual for Site Assessment at DNAPL Contaminated Sites*."

Despite the very different nature of DNAPL pollutants, and due to the wider experience in dealing with investigations aimed at delineating the nature and extent of a dissolved plume, environmental professionals will often attempt to apply flow and transport principles developed for dissolved contaminants to multi-phase DNAPL water-air-soil systems, where different or additional principles apply.

The following investigative methods are typically employed in establishing the DNAPL presence at a site.

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

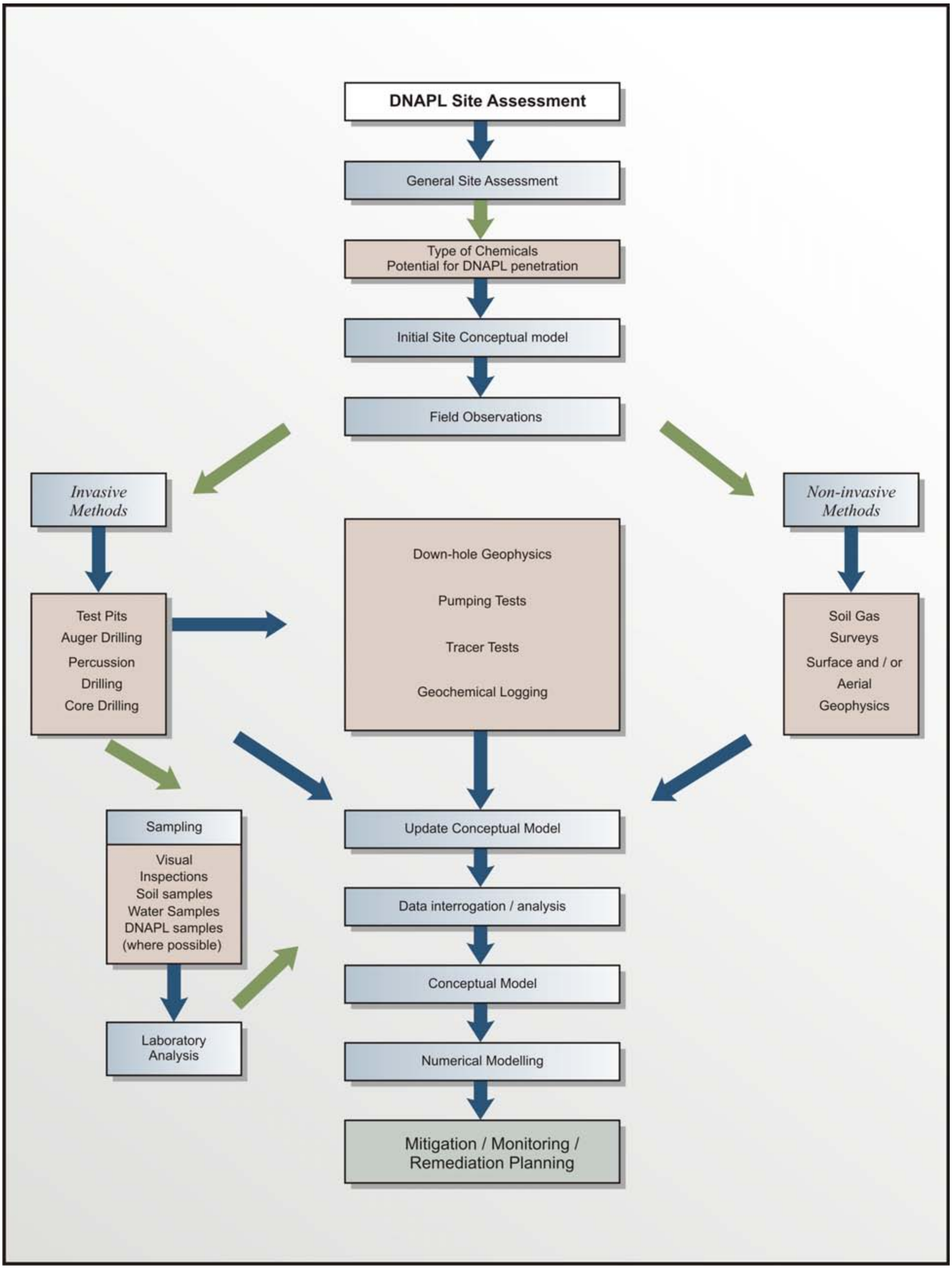
1. The behaviour of subsurface DNAPL cannot be defined adequately by *investigating dissolved contaminants* due to differences in properties and principles that govern DNAPL and solute transport;
2. DNAPL can *persist for decades or centuries as a significant source* of groundwater and soil vapour contamination;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

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

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

The overall objectives of a 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. The delineation of subsurface geologic conditions is critical to site evaluation, because DNAPL movement can largely be 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 process, whereby each phase of investigation and remediation is used to define the conceptual understanding of the site, and the future steps to follow. 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 throughout the investigation.

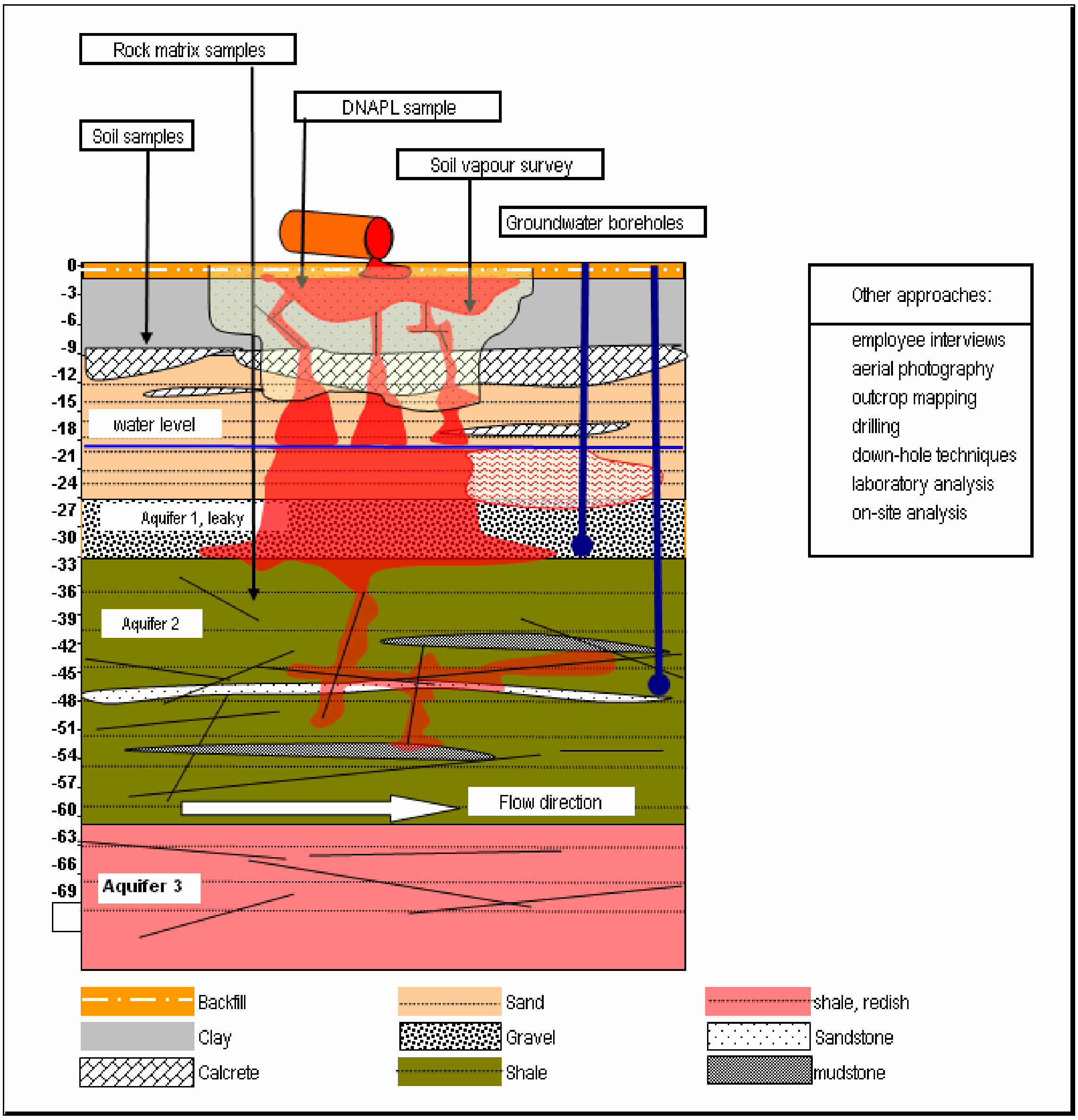

DNAPL Site Assessment
General Site Assessment
Type of Chemicals
Potential for DNAPL penetration
Initial Site Conceptual model
Field Observations
Invasive Methods
Non-invasive Methods
Test Pits
Auger Drilling
Percussion Drilling
Core Drilling
Down-hole Geophysics
Pumping Tests
Tracer Tests
Geochemical Logging
Soil Gas Surveys
Surface and / or Aerial Geophysics
Sampling
Visual Inspections
Soil samples
Water Samples
DNAPL samples (where possible)
Laboratory Analysis
Update Conceptual Model
Data interrogation / analysis
Conceptual Model
Numerical Modelling
Mitigation / Monitoring / Remediation Planning

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. These innovative methods indicate significant advances over conventional sampling-based approaches, but the true 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.

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

The figure below provides a brief summary of the parameters that can be measured at a site during field investigations.



DNAPL in South African Aquifer Systems

DNAPLs in South African Aquifer Systems

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

South African Aquifer Systems

South African aquifers can be broadly divided into four groups, according to the dominant flow mechanism (Pietersen, 2004).

Flow mechanisms of the main aquifer systems in South Africa.

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

Only the intergranular and fractured aquifer type is provided here as an example, due to its predominance. Details of all four major types can be found in the accompanying document.

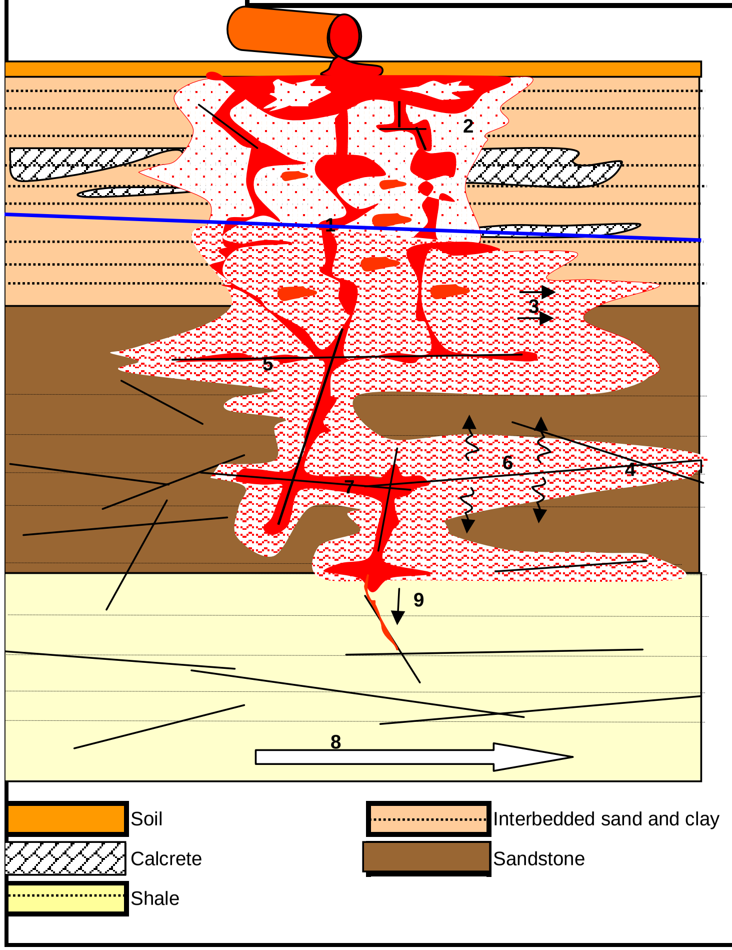
The two most studied and utilised intergranular and fractured (or dual porosity) aquifer systems in South Africa are the Karoo and Table Mountain Group (TMG) aquifers.

The main Karoo Basin encompasses an area of approximately 630 000 km^2 in the central portion of the country. The Karoo Supergroup consists mainly of sandstone, mudstone, shale and siltstone. The Table Mountain Group (TMG) is found between the west and south coasts of South Africa. The issues and implications with regard to DNAPL fate and transport in dual porosity systems are listed below, and illustrated in the figure that follows.

1. **Generally "deep" aquifer systems with thick unsaturated zone** – This makes translating US and other international experiences with regard to site assessment and characterisation difficult. Many of these methodologies cannot be applied to hard rock and/or at great depths. Also, high costs of investigation in thick aquifers/deep unsaturated zones.
2. **High fracture porosity, low matrix porosity** – Slow groundwater velocities in matrix but localised high flow in preferred pathways (fractures). This gives rise to smaller dissolved plumes than in porous media.

3. **Multi-layered aquifer due to presence of hydraulic variance in horizons** – The resulting contaminated zones will be strongly influenced by the hydraulic variance leading to irregular distribution of NAPL and dissolved plumes. This is important for the construction of boreholes and interpreting sample results. Layering may also limit vertical dispersion
4. **Fracture aperture, strike, and dip** - Fracture entry pressures are directly proportional to interfacial tension and inversely proportional to fracture aperture. This results in preferential DNAPL migration through the larger aperture fractures of a fracture network. The strike and dip of the more permeable fractures will therefore control the primary directions of DNAPL migration in a fracture network.
5. **Horizontal and vertical flow** must be considered, but density-driven flow through vertical fractures will result in the deep penetration of DNAPL.
6. **Matrix diffusion** refers to the process whereby solutes dissolved in groundwater diffuse into and out of the rock matrix. If concentrations are higher in the open fracture, the diffusion process will result in dissolved contaminants moving into the rock matrix (forward diffusion). If concentrations are higher in the rock matrix, dissolved contaminants will move out of the rock matrix and into water in the open fractures (back diffusion). Matrix diffusion will occur in all rock types exhibiting matrix porosity. This process causes the contamination to be persistent over time and makes remediation techniques such as “pump-and-treat” unfeasible in dual porosity systems in the long term.

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



Features

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

Issues and implications

High fracture porosity, low matrix porosity

Fracture/pore water interaction

Fracture aperture determines entry pressure into fractures

Density driven flow through vertical fractures

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

Horizontal and vertical flow important

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

Layering may limit vertical dispersion

Matrix diffusion - cause contamination to be persistent makes remediation difficult

Slow groundwater velocities- smaller aqueous plumes than in porous systems

Figure 1: Conceptualisation of DNAPL fate and transport in intergranular and fractured (dual porosity) flow systems.

Monitored Natural Attenuation

Monitored natural attenuation

What is natural attenuation?

Natural attenuation makes use of natural processes to contain the spread of contamination from chemical spills and reduce the concentration and amount of pollutants at contaminated sites. Natural attenuation means that environmental contaminants remain in place while natural attenuation works on them. Natural attenuation is often used as one part of a site clean-up that also includes the control or removal of the contamination source.

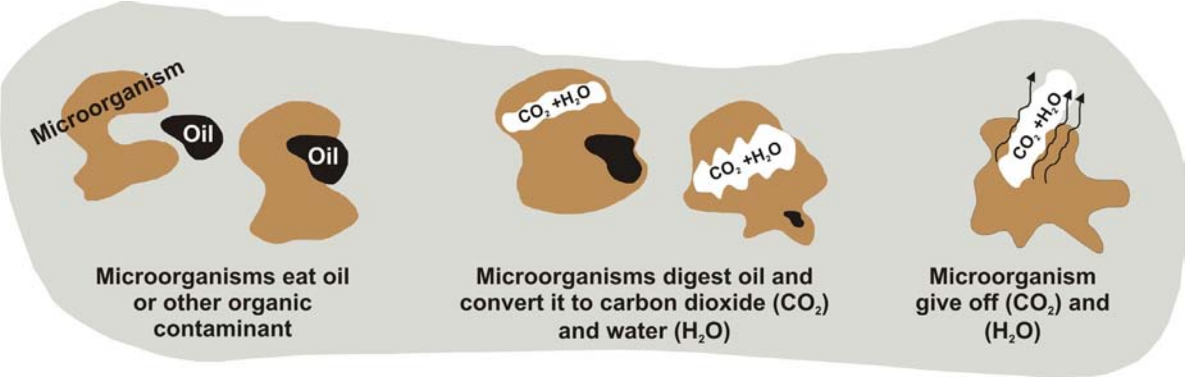
The 'natural attenuation processes' at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favourable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilisation, and chemical or biological stabilisation, transformation, or destruction of contaminants.

Natural attenuation processes typically occur at all contamination sites, but to varying degrees of effectiveness, depending on the types and concentrations of contaminants and the physical, chemical, and biological characteristics of the soil and groundwater.

Where conditions are favourable, natural attenuation processes may reduce contaminant mass or concentration at sufficiently rapid rates and therefore achieve remediation objectives at some sites without the aid of other (active) remedial measures.

Biodegradation, also called bioremediation, is a process in which naturally occurring micro-organisms (often bacteria) break down or degrade hazardous substances such as dissolved solvents at DNAPL sites into less toxic or non-toxic substances. Micro-organisms consume organic substances for nutrition and energy. Certain micro-organisms consume organic substances such as fuels or solvents that are hazardous to humans. Biodegradation reactions are possible both with oxygen present (aerobic conditions) or without oxygen (anaerobic conditions).

The micro-organisms break down the organic contaminants into harmless products; mainly carbon dioxide and water. In the case of chlorinated solvents and other DNAPLs, it is important that the degradation be complete, because some products of the breakdown process can be more toxic than the original compounds. Schematically this process can be represented as follows:



Schematic representation of aerobic biodegradation (US EPA, 1996)

What is Monitored Natural Attenuation (MNA)?

“Monitoring of groundwater to confirm whether natural attenuation processes are acting at a sufficient rate to ensure that the wider environment is unaffected and that remedial objectives will be achieved within a reasonable timescale and are fast enough to limit risks to potential receptors.

What is not MNA?

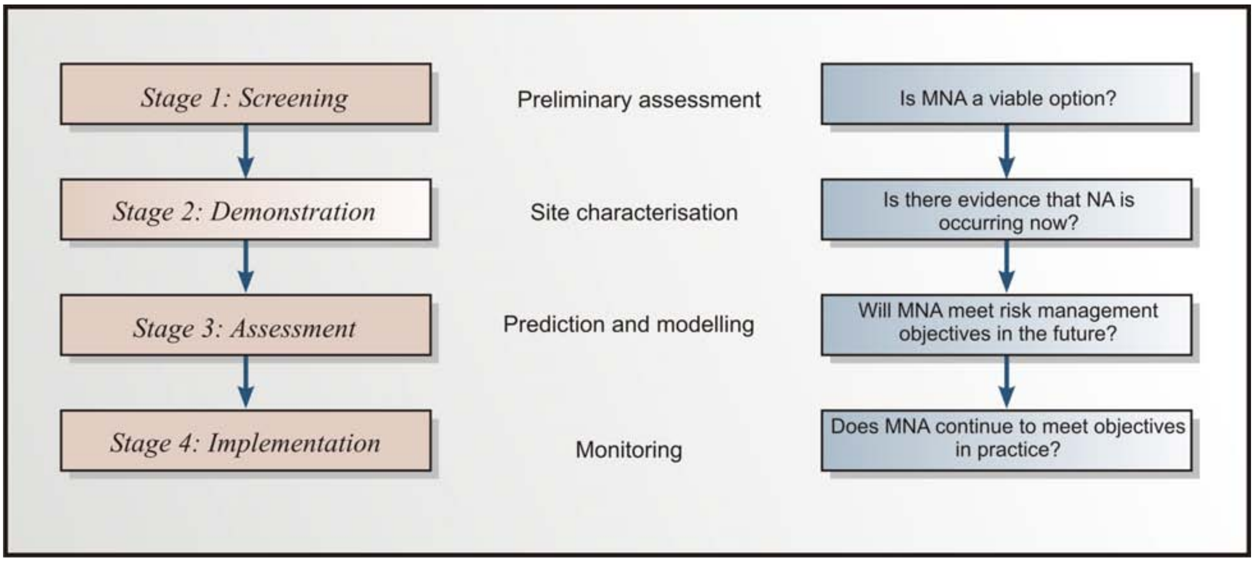
Natural attenuation occurs to some degree at every site; however, depending on site conditions, there may be definite limits to its effectiveness as an interim or long-term solution, because natural attenuation does not necessarily imply that contaminants are removed. Furthermore, the site-specific conditions that often limit the effectiveness of natural attenuation as a contaminant removal/destruction process are rarely properly evaluated.

It is very important to note that MNA IS NOT A ‘DO NOTHING’ APPROACH.

Indeed, the evidence required to select it as a mitigation strategy and to prove that it occurs to the required degree, shifts the onus squarely onto the site owner to show that the risks associated with allowing natural attenuation are acceptable. It follows that detailed monitoring is an integral part of successfully applying MNA at a site.

Suggested Process

It is recommended that the approach for assessing and implementing monitored natural attenuation in South Africa be a risk-based management strategy. The methodology should be based on a multi-stage process, involving structured decision-making and iterative data collection and analysis. The key steps are summarised in the flow chart below.



The initial stage will be to determine whether natural attenuation is likely to occur at sufficient rates on the site under investigation. After reviewing screening factors to determine the viability of MNA, a detailed site characterisation should be performed as part of the next stage.

The purpose of the demonstration stage is to show quantitatively that natural attenuation is occurring at a rate that will achieve the objectives in a reasonable time frame. Demonstrating effectiveness involves obtaining data to test and calibrate the conceptual model. The process is iterative, in which data are used to refine the model that in turn guides any necessary additional site characterisation.

The key to MNA demonstration in South Africa is a ‘lines of evidence’ approach.

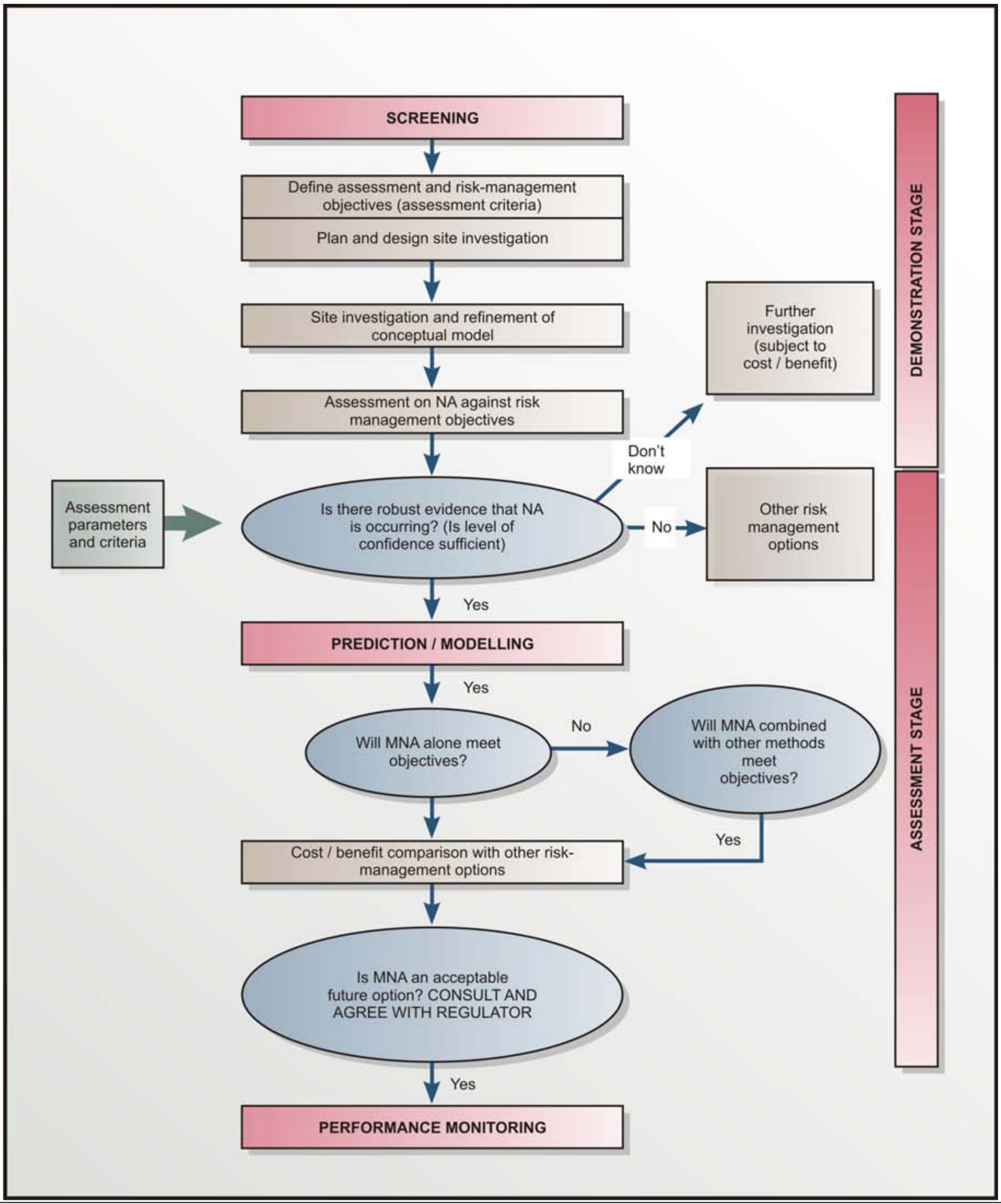
Lines of Evidence

Primary lines of evidence involve the use of historical monitoring data to demonstrate a trend of reduced pollutant *concentrations* down-gradient of the source, along the groundwater flow path.

Secondary lines of evidence involve measuring changes in chemical and geochemical analytical data to prove a loss of contaminant *mass*.

Tertiary lines of evidence use data from laboratory microbiological testing to show that on-site bacteria are capable of degrading site contaminants.

The suggested approach in a South African context is summarised by the figure below:



Will natural attenuation always be appropriate?

For MNA to be considered, a detailed study of the contaminated site is required. Natural attenuation is not an appropriate option at all sites. The rates of the attenuation processes may be too slow to meet the objectives, and in certain cases, the incomplete degrading of pollutants may increase potential risks. It is also important to note that, in more complex environments such as the aquifer conditions common in much of South Africa, where geological formations such as fractured rock aquifers or dolomite occur, these areas will be less likely candidates for natural attenuation. This is because groundwater conditions often have great subsurface variability that makes the prediction of groundwater flow and the associated migration of contamination difficult.