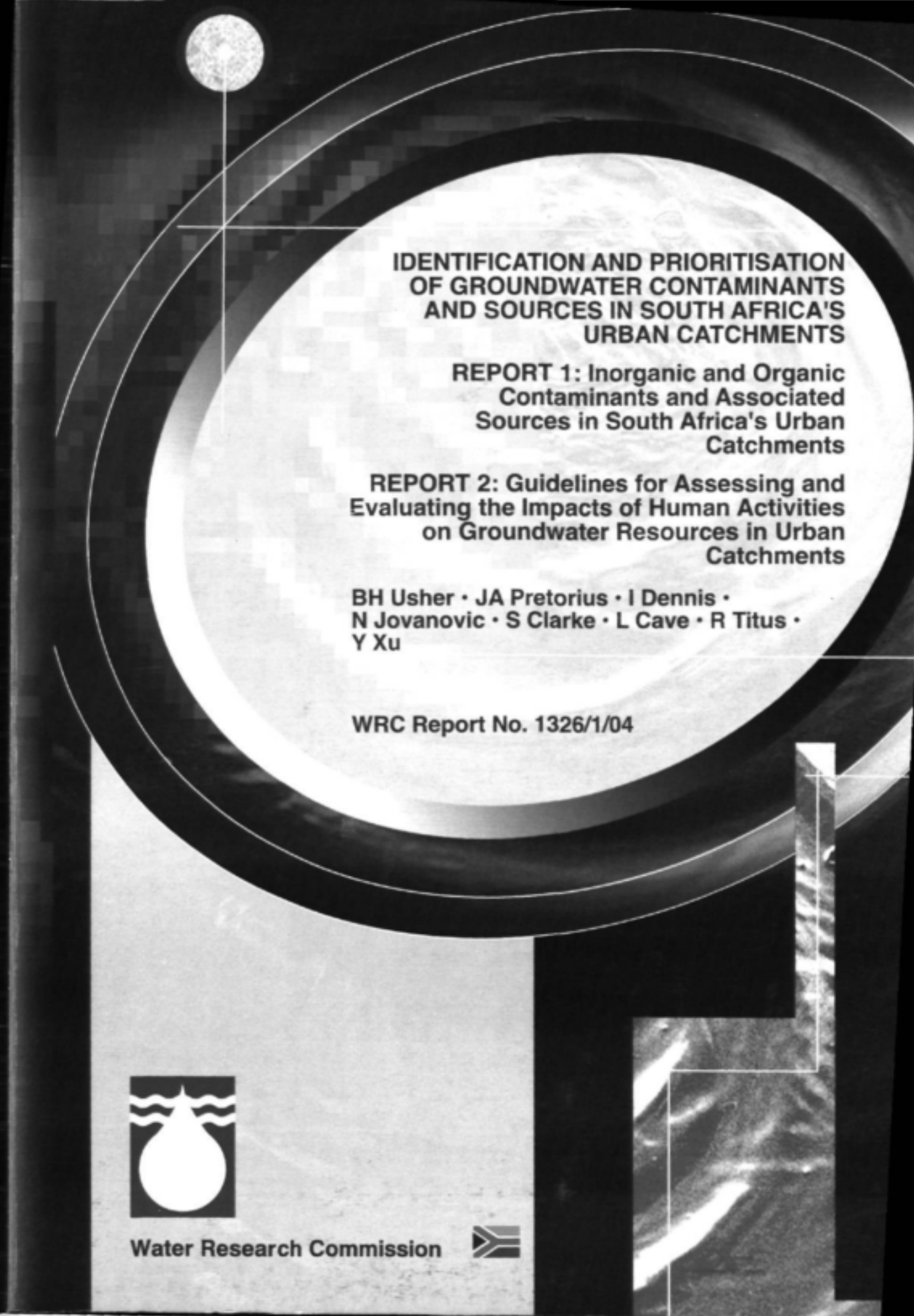

IDENTIFICATION AND PRIORITISATION OF GROUNDWATER CONTAMINANTS AND SOURCES IN SOUTH AFRICA'S URBAN CATCHMENTS

REPORT 1: Inorganic and Organic Contaminants and Associated Sources in South Africa's Urban Catchments

REPORT 2: Guidelines for Assessing and Evaluating the Impacts of Human Activities on Groundwater Resources in Urban Catchments

BH Usher · JA Pretorius · I Dennis ·
N Jovanovic · S Clarke · L Cave · R Titus ·
Y Xu

WRC Report No. 1326/1/04

Water Research Commission

Identification and prioritisation of groundwater contaminants and sources in South Africa's urban catchments

Report 1:	Inorganic and Organic Contaminants and Associated Sources in South Africa's Urban Catchments
Report 2	Guidelines for Assessing and Evaluating the Impacts of Human Activities on Groundwater Resources in Urban Catchments

Report to the

Water Research Commission

by

[1]BH Usher, JA Pretorius, [1]I Dennis, N Jovanovic, [2]S Clarke, L Cave, R Titus and [3]Y Xu

[1]Institute for Groundwater Studies
[2]CSIR, Environmentek and
[3]University of the Western Cape

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EXECUTIVE SUMMARY

GENERAL

In many regions, economic growth is closely linked to the availability of groundwater. In most urban areas in South Africa, groundwater is less utilized than surface water, but often the bulk of water used in rural communities is groundwater. With increasing scarcity of fresh water resources, urban groundwater may be utilized to a greater extent in future.

Contamination of South Africa's urban aquifers presents a threat to the sustainability of this water resource. Man's activities, use of chemicals and generation of wastes tend to concentrate potential sources of contamination in the urban areas. The threat caused by undesirable substances is recognized in this country, but the understanding of the extent of the problem in South Africa's urban catchments is poor (Sililo *et al*., 2001). In their WRC project No. 1008 (Sililo *et al.*, 2001) identified several research priorities for understanding the extent of urban groundwater contamination. This project is therefore geared towards filling the gap in the understanding of groundwater contamination in South Africa's urban environments. By doing so, the principal pollutants can be identified and, based on their risk, prioritised. This will facilitate better management of groundwater quality in South Africa by assisting future land use planning and vulnerability studies.

AIMS OF THIS STUDY

The Institute for Groundwater Studies, entered into a research contract with the Water Research Commission for collaborative research with the CSIR Environmentek and the University of the Western Cape's Groundwater Group to investigate groundwater contaminants and sources in South Africa's urban catchments.

The aims of the investigation are to:

- identify and prioritise the type of contaminants and their associated sources which present a threat to groundwater, the environment and health in South Africa's urban catchments;
- formulate strategies for better understanding the impacts of polluting activities on groundwater resources in urban catchments;
- establish a data information system on South Africa's contaminants.

APPROACH TO STUDY

The initial stages of the project involved the collection of information that would give a general overview of the status of urban groundwater pollution, mainly from textbooks and published international literature. Information on general sources of groundwater contamination and types of groundwater contaminants in the urban environment are summarised. Various approaches that have been used to classify groundwater contaminants and their sources are discussed.

General information on urban groundwater contamination was related to the South African context using information on local urban areas and summary statistics from Statistics South Africa (South African census data); Chamber of Mines (South African mining statistics); State of the Environment Reports (South African Metro Areas); Municipal websites (South African Metro Areas) and Water Research Commission Reports. These were used to identify potential sources of groundwater contamination in South African urban areas.

Case studies of reported contaminated sites were identified from archives of newspaper articles; conference and workshop proceedings (International Association of Hydrogeologists, Water Institute of Southern Africa, Institute of Waste Management) and project reports and monitoring databases, where available. Case studies from literature were intended to provide a baseline of the current level of groundwater contamination in South Africa's urban areas. The availability of published data and information, however, proved to be a major limitation in quantifying groundwater contamination in South Africa's urban areas.

A questionnaire requesting information concerning contaminant sources, activities likely to cause contamination, main contaminants of concern and contaminated aquifers were sent to Water Affairs officials, municipalities and consultants. Unfortunately the response to these questionnaires was poor. The project team then set up meetings with relevant parties such as DWAF, municipalities, water boards and private consulting companies, who could potentially supply information/data on contamination in various areas across the country. Since it was not possible to cover all urban areas within the scope of this project, detailed information and data were only collected for the major urban centres, namely Johannesburg-Pretoria (Gauteng), Durban (Kwa-Zulu Natal), Cape Town (Western Cape) and Port Elizabeth (Eastern Cape), as being the main areas likely to be affected by pollution.

Contamination incident reports and databases supplied by various organizations involved in potentially polluting activities or the monitoring of these activities could then be used to compile the contaminant inventories.

METHODOLOGIES DEVELOPED FOR THE PRIORITIZATION OF SOURCES AND CONTAMINANTS

A risk based prioritization framework

Rating occurs when contaminant sources are given a quantitative or qualitative measure of the potential hazard they pose to groundwater. Prioritisation methods focus on aspects such as contaminant loading, mobility, persistence and risk. A risk analysis estimates the probability and consequences of a contaminant event and usually considers both the properties of the contamination source and the hydrogeological environment.

Based on the amount of data available a tiered approach is followed when considering risk assessments. The first tier (LEVEL 0) is a rapid assessment of sources and contaminants in which minimal data are required and it produces low confidence results. This assessment should be completed within a few minutes. LEVEL 1 is the second tier which is a rapid assessment of contaminants on a local scale. It is intended to give the assessor a guideline of the risks. The assessment should take a couple of hours to complete. The next tier (LEVEL 2) is an intermediate assessment. The first step in the intermediate assessment is to collect all relevant data. Data requirements include aquifer and contaminant parameters, as well as health information. Most of the general information will be obtained from databases, but it is sometimes necessary to have site-specific data. The confidence attached to this assessment should be medium to high.

Level 0 is based on a rating system while LEVELS 1& 2 are based on complete risk assessments.

A fuzzy logic based approach was followed when conducting the risk assessments. The factors taken into account in the risk assessments are:

- Exposure is defined by the frequency, magnitude and duration of contact with the contaminant.
- Aquifer vulnerability, the parameters needed for describing vulnerability are:
    - Depth to groundwater
    - Urban recharge
    - Aquifer media
    - Soil media
    - Topography
    - Impact of the vadose zone

  PLEASE NOTE: Emphasis was not place on aquifer vulnerability due to a current WRC project focusing on vulnerability methods for South Africa.
- Health effects of contaminant.

- Source type
- Physio-chemical aspects of contaminant

Protection zones
A protection zone can be defined as the surface and subsurface area surrounding a borehole or wellfield, supplying water (for example basic human needs), through which contaminants are reasonably likely to move and reach such a borehole or well field. In many cases it is difficult to protect the whole area, therefore various zones are established within the area. These zones have been defined as (Braune, 2000; EPA, 2000 & and Boulding, 1995):

- Zone 1: Highly protected area around the borehole or spring. Its purpose is to protect the borehole or spring from the direct introduction of contaminants into the borehole and its immediate area from spills, surface runoff, or leakage from storage facilities or containers. Potential contaminant sources should be strictly monitored.
- Zone 2: Is established to protect a borehole from contact with pathogenic micro-organisms (e.g. bacteria and viruses) which can emanate from a source (eg septic system) located close to the borehole, as well as to provide emergency response time to begin active cleanup and/or implementation of contingency plans should a chemical contaminant be introduced into the aquifer near the borehole.
- Zone 3: Is designed to protect the borehole from chemical contaminants that may migrate to the borehole; it typically includes a major portion of the recharge area or the capture zone.

Excel-based data information system
The objective of the Excel-based data information system is to provide a user-friendly, easy-to-update inventory on South Africa's groundwater contaminants in urban catchments. The idea originated from the need to capture, store and make information easily accessible, as well as for future linkage with national GIS-database systems. The Excel database includes the following components:

- An inventory of inorganic and organic contaminants and associated sources in major urban areas of South Africa (Gauteng, Durban, Port Elizabeth, Cape Town)
- An inventory of properties of inorganic and organic contaminants
- A simple model for site-specific ranking of priority contaminants

The inventory of inorganic and organic contaminants includes the type of source (urban settlement, agriculture, mining, non-metallurgical industry, metallurgical and metal products manufacturing), expected contaminants, examples and references.

The inventory of properties of inorganic and organic contaminants includes values of properties for about 2500 contaminants. These properties are mainly relevant to groundwater pollution, for example Henry's constant for volatilization, half-life and the organic carbon partitioning coefficient. CAS numbers are available for each contaminant, as well as links to international web sites where properties can be found, in particular those that are variable depending on environmental conditions and are not filled in the Excel-database.

A simple model developed by Rao *et al.* (1982) was included in the Excel database as a tool for prioritisation and site-specific ranking of contaminants. The model of Rao *et al.* (1982) calculates the attenuation and retardation factors of specific contaminants, based on properties of contaminants included in the database (Henry's constant, half-life and organic carbon partitioning coefficient) and user's input of hydrogeological characteristics (groundwater depth and net recharge rate, air-filled soil porosity, volumetric soil water content at field capacity, soil bulk density and organic carbon content in the soil).

RESULTS

The products resulting from this research are:

- A tiered risk based prioritization tool with which both sources and contaminants can be rated.
- An excel-based data information system in which contaminants, associated sources and contaminant properties are stored.

Using the above-mentioned products, contaminants found in the urban environment can be prioritized on a national, regional and local scale. Therefore a source and contaminant prioritization list was established for:

- South Africa
- Gauteng
- Durban
- Cape Town
- Port Elizabeth

These prioritization lists are based on a national inventory, together with inventories for each of the above-mentioned cities.

CONCLUSIONS

Case studies from literature were intended to provide a baseline of the current level of groundwater contamination in South Africa's urban areas. Data that exists is often localised to a particular industry and in most cases no time series data is available. The availability of published data and information, however, proved to be a major limitation in quantifying groundwater contamination in South Africa's urban areas. One of the problems is that under South African law (National Water Act, Act 36 of 1998), monitoring of potential pollution sources is the responsibility of the polluter. This means that any data relating to the impact of polluting activities also resides with the polluter and they may be reluctant to release it to the public domain. Despite this, a large set of representative case studies has highlighted problems and lessons at different urban activities, with regards to groundwater quality.

The reviews of the transport of contaminants has revealed the importance of proper hydrogeological characterisation, as this largely determines the risk that a pollutant holds. The fuzzy logic approach combines the expert knowledge generated in this project with site-specific considerations so that sources and pollutants can be identified and prioritised in any area, at various scales of implementation. Using a multi-tiered approach facilitates management of sources, according to available information and expertise of the user. Through case studies, both real and generic, the methodologies and tools developed in this project have been tested and refined.

The results of this project therefore include:

- A national South African priority list of contaminants and contaminant sources in urban areas has been established.
- Priority lists of contaminants and contaminant sources have been derived for Gauteng, Cape Town, Port Elizabeth and Durban.

The priority lists have shown that several high priority contaminants have not yet received adequate attention in terms of water management in this country.

In conclusion these documents and the associated software should serve as a good guide to expected contaminants associated with different activities. Methodologies have been created whereby a water manager in any urban area can identify and prioritise the potential groundwater contaminants in the area. The software packages should be very useful tools for persons ranging from municipal water mangers to researchers and hydrogeologists with detailed knowledge of a site.

RECOMMENDATIONS FOR FURTHER RESEARCH

Groundwater monitoring in urban areas needs to be addressed as a matter of priority. Based on the research conducted in this project, several sources and contaminants have been highlighted as potential priorities. Of great concern is the fact that for many of these the currently available datasets show that very little attention has been paid to the constituents in most groundwater monitoring programs. The following contaminants of concern are highlighted:

- Petroleum products, industrial thinners and mineral oils and other non-aqueous phase liquids represent a category of potential pollutants that have been largely overlooked by regulatory agencies and legislature, despite their harmful effects at small concentrations. Research in this current project, has shown these contaminants to be of the most problematic in urban groundwater resources. There is an urgent need for published research into NAPL contamination in South Africa.
- Based on the paucity of groundwater-related microbial data encountered in this project, the inclusion of these aspects in urban groundwater management must be regarded as a priority. In order to evaluate the public health threat posed by waterborne micro organisms, rapid and accurate methods for the detection of these organisms within large populations of other bacteria are therefore essential and further research and inclusion in groundwater monitoring should be promoted.
- A general lack of data on groundwater pollution from pesticides is evident. This is due to: i) surface waters are the main source of water supply in the country (little data is available on groundwater pollution); ii) cost and difficulty to measure organic contaminants; iii) private companies are often sensitive to make public data related to pollution problems. There is therefore need to monitor groundwaters and to develop modeling tools for the prediction of the fate and behaviour of pesticides.
- High nitrate concentrations have been found to occur from sources ranging from agricultural fertilizing (especially the application of sludge to land) to pit latrines and explosives companies. There is, no directed programme to monitor nitrate in urban and peri-urban areas and hence the gap in information.

The National Water Act of 1998, provides the framework within which the Department of Water Affairs and Forestry (DWAF) can manage the protection, use, development, conservation and control of South Africa's water resources. In this context groundwater quality can be managed in an integrated and sustainable manner within the context of the National Water Resource Strategy and thereby to provide an adequate level of protection to groundwater resources and secure the supply of water of acceptable quality. In the Policy and Strategy for Groundwater Quality Management in South Africa (DWAF, 2000) DWAF describes the means and measures available to achieve groundwater quality management.

Implementation of the three strategies (source-directed, resource-directed and remediation) must be integrated to achieve the overall objective of sustainable groundwater utilization. Regulatory instruments provide DWAF with the means to intervene and influence the behaviour of the community targeted for regulation. Intervention is intended to ensure that the policy goals are achieved by inducing the desired behaviour from polluters and potential polluters.

In order to implement the Policy and Strategy, DWAF will launch a series of groundwater quality management programmes. These programmes will have a clearly defined objectives, action plans and time frames. The purpose of each programme will be to develop a component of the strategy and to oversee its implementation into the operational part of the regulatory system.

This investigation took a holistic approach and considered all activities that could influence groundwater quality in an urban environment. The issues highlighted in the recommendations must be considered in the implementation of the Policy and Strategy by DWAF, especially in specific groundwater management plans related to the identified activities and contaminants. Of highest importance is a need to develop policy and guidelines for monitoring of groundwater for organic contaminants. Secondly the development of modeling tools for the prediction of the fate and behaviour of NAPLs and pesticides, under South African aquifer conditions are essential in addressing the above issues.

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"Identification and prioritisation of groundwater contaminants and sources in South Africa's urban catchments"

The Steering Committee responsible for this project consisted of the following persons:

Dr K Pietersen	Water Research Commission
Mr JM Nel	Department of Water Affairs and Forestry (Pta)
Mr RI Grose	Johannesburg Water
Ms DM Damon	City of Cape Town
Mr JS Snyman	Tshwane Municipality

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- Mr M Obree and Ms I Murray (GIS) from the City of Cape Town Municipality
- Randwater

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1. Background

Groundwater contamination can occur as a result of various activities of man. With increased human settlement and economic development, a range of undesirable waste products are produced that can end up in the environment. If these waste products are not well handled, they can cause contamination of groundwater. The threat to groundwater caused by undesirable substances has been recognized in South Africa and measures put in place through legislation to protect groundwater from contamination (National Water Act, Act 36 of 1998; National Environmental Management Act, Act 107 of 1998).

Although groundwater contamination incidences have been reported countrywide, we do not have an indication of the extent of the problem (Sililo *et al*., 2001). In their WRC project No. 1008 (Sililo *et al*, 2001) identified several research priorities for understanding the extent of urban groundwater contamination. This project is therefore geared towards filling the gap in the understanding of groundwater contamination in South Africa's urban environments. By doing so, the principal pollutants can be identified and, based on their risk, prioritised. This will facilitate better management of groundwater quality in South Africa by assisting future land use planning and vulnerability studies.

The Institute for Groundwater Studies, entered into a research contract with the Water Research Commission for collaborative research with the CSIR Environmentek and the University of the Western Cape's Groundwater Group to investigate groundwater contaminants and sources in South Africa's urban catchments.

The aims of the investigation are to:

- identify and prioritize the type of contaminants and their associated sources which present a threat to groundwater, the environment and health in South Africa's urban catchments;
- formulate strategies for better understanding the impacts of polluting activities on groundwater resources in urban catchments;
- establish a data information system on South Africa's contaminants.

This report addresses the first aim, by detailing our findings and evaluation of the groundwater contaminants and potential contamination sources in the catchments of South Africa's urban areas. The products of this work include the "Guidelines for strategising, assessing and evaluating impacts of human activities on groundwater resources in urban catchments" and an Excel-based data information system on groundwater contaminants in urban areas of South Africa.

2. Approach to the study

The initial stages of the project involved the collection of information that would give a general overview of the status of urban groundwater pollution, mainly from textbooks and published international literature. Information on general sources of groundwater contamination and types of groundwater contaminants in the urban environment are summarised in Sections 3 and 4. Section 3 also describes various approaches that have been used to classify groundwater contaminants and their sources. Details on the physicochemical behaviour of the contaminants have been documented in the accompanying report "Guidelines for strategising, assessing and evaluating impacts of human activities on groundwater resources in urban catchments"

General information on urban groundwater contamination was related to the South African context using information on local urban areas and summary statistics from Statistics South Africa (South African census data); Chamber of Mines (South African mining statistics); State of the Environment Reports (South African Metro Areas); Municipal websites (South African Metro Areas) and Water Research Commission Reports. These were used to identify potential sources of groundwater contamination in South African urban areas as presented in Section 4.

Case study examples of groundwater pollution in South African urban areas are presented in Section 4.6.1. Case studies of reported contaminated sites were identified from archives of newspaper articles; conference and workshop proceedings (International Association of Hydrogeologists, Water Institute of Southern Africa, Institute of Waste Management) and project reports and monitoring databases, where available.

Case studies from literature were intended to provide a baseline of the current level of groundwater contamination in South Africa's urban areas. The availability of published data and information, however, proved to be a major limitation in quantifying groundwater contamination in South Africa's urban areas. One of the problems is that under South African law (National Water Act, Act 36 of 1998), monitoring of potential pollution sources is the responsibility of the polluter. This means that any data relating to the impact of polluting activities also resides with the polluter and they may be reluctant to release it to the public domain.

Literature searches were therefore followed by contacting individuals at various organizations, such as DWAF, municipalities, water boards and private consulting companies, who could potentially supply information/data on contamination in various areas across the country. Since it was not possible to cover all urban areas within the scope of this project, detailed information and data were only collected for the major urban centres, namely Johannesburg-Pretoria (Gauteng), Durban (Kwa-Zulu Natal), Cape Town (Western Cape) and Port Elizabeth (Eastern Cape), as being the main areas likely to be affected by pollution.

A questionnaire requesting information concerning contaminant sources, activities likely to cause contamination, main contaminants of concern and contaminated aquifers were sent to Water Affairs officials, municipalities and consultants. Unfortunately the response to these questionnaires was poor. The project team then set up meetings with relevant parties to obtain the required information.

Contamination incident reports and databases supplied by various organizations involved in potentially polluting activities or the monitoring of these activities could then be used to compile the contaminant inventories in Section 6 and for the prioritisation of contaminants and sources in Section 7.

It was found that most organizations, including DWAF, collect surface water data, and that only few groundwater analyses are available. Although the effect of surface water pollution on groundwater resources should not be excluded from the analysis in this report, there is a need for increased efforts in groundwater pollution monitoring in the urban areas of South Africa. National groundwater quality monitoring efforts by DWAF are also mainly directed towards groundwater resource evaluation, rather than groundwater pollution monitoring (E. Van Wyk, *pers. comm.*). Section 8 highlights some of the areas, sources and contaminants identified for future investigations, either because of a high priority in terms of contamination potential or because of a lack of existing information.

3. Classification of contaminants and sources

3.1 Definitions

As a starting point, it is necessary to define some of the terms that are used in this project:

Contamination refers to levels of hazardous substances in the environment over and above what would ordinarily be found in the absence of local activities. Groundwater contamination therefore refers to the occurrence of substances (inorganic species, organic compounds or microbial agents) in concentrations above those that would naturally be found in an aquifer. The substances themselves, both chemical and microbial, are called *contaminants*.

It is important to note that there are thousands of contaminants, not all of which can be discussed in this document. Only those for which data is available or those of importance are included in these documents.

Sources, in this context, refer to the origin of the substances (inorganic species, organic compounds or microbial agents) that are causing, or may potentially cause, the contamination. The term is used very broadly over a range of scales and may describe physical entities (e.g. a pond, a tank, a pipeline); human activities (e.g. mining, irrigation, wastewater treatment); the site at which potential contaminants are stored, used or disposed (e.g. wastewater treatment works, cemeteries, fuel filling stations) or even large scale phenomena (e.g. atmospheric deposition).

Pollution refers to an undesirable change in the physical, chemical, or biological characteristics of the natural environment, brought about by man's activities. Pollution may be harmful to humans or the environment. Point source pollution refers to pollution where the source can be easily identified and exists at one location. Non-point sources of pollution refer to diffuse sources over an area, such runoff from farms and city streets and the deposition of pollutants from the air.

Although the term *urban* can refer to any city or town, in this project we have only concentrated on the major metropolitan areas in South Africa with a population of over one million people and area over 1000 km^2.

These areas include the City of Cape Town, Port Elizabeth (Nelson Mandela Metropolitan Municipality), Durban (eThekwini Muncipality) and the urban conglomeration of Gauteng, including the City of Johannesburg, Pretoria (Tshwane Municipality) and the cities of the East and West Rand (Ekhurleni Metro and Mogale City Municipalities).

3.2 Classification of contaminants

There are various ways in which to group or classify groundwater contaminants. Examples of classification systems include those based on chemical type, human health impacts or fate in the environment. Each of these has major classes, which can then be broken down into smaller categories.

The choice of system and level of detail of the classification is dictated by the purpose of the classification. It is important to note that there are many classification systems however only a few will be discussed here.

Fate in the environment

Contaminants may be classed as:

- **Degradable** contaminants, which can be rendered harmless by natural processes and need therefore cause no permanent harm if adequately dispersed or treated; and
- **Persistent** contaminants, which eventually accumulate in the environment and may be concentrated in food chains.

Contaminants may also be divided by their behaviour in water into:

- **Soluble** contaminants, which includes most inorganic species and some organics.
- **Insoluble** substances, which are small enough to be carried through the aquifer matrix, including microbial contaminants and colloidal inorganic contaminants.
- **Non-aqueous phase liquids** (NAPLs), which are organic compounds that do not dissolve readily in water and remain as a separate liquid phase. These are further subdivided into Light Non Aqueous Phase Liquids (LNAPLs) and Dense Non Aqueous Phase Liquids (DNAPLs).

Human health impacts

Contaminant classes include:

- **Non-harmful** substances, which have no observed effects on human health
- **Toxic** substances, which 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.
- **Pathogenic** substances, which are known to cause diseases in humans.

Contaminant types

There are three major categories of contaminants:

- **Inorganic** contaminants, which include subcategories such as major cations and anions, nutrients, trace metals, radionuclides and other inorganic species.
- **Organic** contaminants, which can be subdivided into natural hydrocarbons and synthetic organic compounds

- **Microbial** contaminants, which include the categories bacteria, viruses and protozoan and metazoan parasites.

Of the **inorganic contaminants**, the major cations and anions are often present in naturally high concentrations, so pollution from a man-made source may sometimes be difficult to distinguish as contamination. The major cations and anions (particularly sodium, chloride and sulphate) are the most common cause of increased salinity, which could be viewed as a class of contamination in groundwater. Nutrients generally refer to inorganic nitrogen and phosphorus species, which are often associated with plant and animal matter. Trace metals can be subdivided into cation-forming (e.g. copper, nickel, cadmium) and oxyanion-forming metals (e.g. arsenic, molybdenum, chromium) and inert (or noble) metals (e.g. gold, platinum). These seldom occur in any significant concentration in groundwater. Radioactive contaminants include many of the heavier elements (e.g. radium, uranium, radon). Among the other inorganic species that may cause groundwater contamination are elements such as strontium, boron and fluoride, which are present in varying amounts in natural groundwater and can provide a useful contamination tracer when background levels are low.

There are a vast number of **organic compounds** which can be further subdivided based on their origin, use, or reactivity, which is related to the organic functional groups on the chemical compound. As noted above, organic contaminants can be classified as synthetic organic chemicals (e.g. pesticides, solvents and pharmaceuticals) and hydrocarbons (e.g. petroleum). Pesticides can be chemically subdivided to include organohalogen, organophosphorus, organonitrogen, organotin and organosulphur compounds. Pharmaceutical compounds are a class of organic contaminant that is causing growing concern in terms of their impact on water resources. Hydrocarbons can be subdivided into two classes, aromatic hydrocarbons, which contain a benzene ring, and aliphatic hydrocarbons, which don't contain a benzene ring (Fetter, 1993). Otherwise hydrocarbons can be classified, as shown in Domenico and Schwartz (1990), to include aromatic hydrocarbons, oxygenated hydrocarbons, hydrocarbons with specific elements (e.g. with N, P, S, Cl, Br, I, F), and other hydrocarbons. Petroleum hydrocarbons are usually present as a mixture of individual organic compounds and are often classed by their separation in the crude oil refining process into categories such as tars & waxes, bitumen, heavy fuel oil, fuel oil, petrol, kerosene and diesel.

Two classes of organic compounds that are often used in groundwater contamination studies are the light nonaqueous phase liquids **(LNAPLs)** and dense nonaqueous phase liquids **(DNAPLs).** A further subdivision of the DNAPL class is shown in Table 1. The chlorinated solvents and pesticides tend to have more information available because of their relatively higher frequency of occurrence and detection, especially at waste disposal sites (Pankow and Cherry, 1996).

Table 1. A list of organic compounds that are DNAPLs (Pankow and Cherry, 1996).

Group	Compound	Group	Compound
Chlorinated solvents	Tetrachloroethylene (PCE)	**Substituted aromatics, phthalates, and miscellaneous organics**	Chloroanilines
	Trichloroethylene (TCE)		Chlorotoluenes
	Dichloromethane		Nitrotoluenes
	1,1,1-Trichloroethane (TCA)		Nitrobenzene
	Chloroform		Benzyl butyl phthalate
	Chlorobenzene		Di-n-butyl phthalate
	Carbon tetrachloride		Diethyl phthalate
	1,2-Dichlorobenzene		o-Anisidine
	1,3-Dichlorobenzene		Phenyl ether
	1,2-Dibromoethane (EDB)		Tri-o-cresol phosphate
	1,1,2-Trichlorobenzene	**[PCB mixtures]**	Aroclor 1221
	1,2,4-Trichlorobenzene		Aroclor 1232
Other halogenated organics	Benzyl chloride		Aroclor 1242
	Bromobenzene		Aroclor 1248
	Bromochloromethane		Aroclor 1254
	Bromodichloromethane	**Pesticides**	Chlordane
	Bromoform		Chloropicrin
	4-Bromophenyl phenyl ether		1,2-Dibromo-3-chloropropane
	bis(2-chloroethyl) ether		1,2-Dichloropropane
	2-Chloroethyl vinyl ether		1,2-Dichloropropylene
	1-Chloro-1-nitropropane		Dichlorvos
	4-Chlorophenyl phenyl ether		Disulfoton
	Dibromochloromethane		Ethion
	1,1-Dichloromethane		Ethylene dibromide
	1,2-Difluorotetrachloroethane		Malathion
	1-Iodopropane		Parathion
	Hexachlorodibutadiene		
	Pentachloroethane		
	1,1,2,2-Tetrabromoethane		
	1,1,2,2-Tetrachloroethane		
	1,2,3-Trichloropropane		
	1,1,2-Trichloro-1,2,2-trifluoroethane		

Organic contaminants can also be subdivided on an operational basis according to the method of chemical analysis e.g. extractable compounds (acid-extractable and base-extractable); volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). Diesel range organics (DRO), gasoline range organics (GRO) and the benzene, toluene, ethylbenzene and xylene compounds (BTEX) are commonly analysed groups of organic groundwater contaminants.

Microbial contaminants can also be classed into subclasses, such as pathogenic (disease-causing) and non-pathogenic micro organisms or faecal and non-faecal micro organisms. They can also be grouped by their biological taxonomy.

3.3 Classification of sources

There are also several existing methods for classifying the sources of groundwater contamination. Broad systems of classification are summarised in Table 2.

Table 2. Systems for classification of groundwater contamination sources (Nonner, 2002; Domenico & Schwartz, 1990)

Classification system based on	**Examples**
Way of release	Discharge sources, transport sources
Loading history	Spill or continuous
Location	Above ground surface, below surface
Degree of localization	Point (or line) and non-point sources
Chemical type	Heavy metals, hydrocarbons, pesticides
Origin	Industrial sources, mining sources

An early classification of groundwater contaminants by **way of release** was established by the US Environmental Protection Agency. Their classification consists of six categories, based on the way in which the contaminants are released into the environment (EPA, 1977):

I. Sources designed to discharge substances: intentional discharge e.g. septic systems, injection boreholes;

II. Sources designed to treat, store and/or dispose of substances: discharge through unplanned releases from storage/treatment/disposal facilities e.g. landfills, cemeteries;

III. Sources designed to retain substances during transport or transmission: discharge from pipelines and transport or transfer operations by accident or negligence;

IV. Sources discharging substances unintentionally as a consequence of other planned activities e.g. fertilizer application, irrigation, urban runoff, mine drainage;

V. Sources providing a conduit or inducing discharge through altered flow patterns e.g. production boreholes or excavations;

VI. Naturally occurring sources, where discharge may be created or exacerbated by human activity e.g. saline intrusion.

The **loading history** of the contaminant source is related to the way of release. This classification system refers to variations in both the concentration of a contaminant and the rate of production of the contaminant as a function of time (Domenico and Schwartz, 1990). The source behaviour can be described as spill or pulse loading, continuous loading or discontinuous emissions.

Under spill or pulse loading conditions the contaminant source produces contaminants at a fixed concentration over a relatively short period, such as a once-off release of contaminants from a ruptured storage tank.

For continuous source loading, the contaminant source produces contaminants over an extended period. Sewage treatment effluent and discharge from a continuous production process are examples of continuous emissions. Three types of continuous loading are identified: (1) contaminant concentration remains constant with time (e.g. small quantities of contaminant is leached from a volumetrically large source); (2) contaminant concentration varies with time (e.g. contaminant concentration can vary due to changes in the manufacturing processes, seasonal or economic factors, dilution, etc.) or (3) contaminant concentration decreases with time due to its decay function or due to varying leaching rates from the source.

Discontinuous emissions show variations in both volume and concentration with time and can be both peak emissions and block emissions. Peak emissions are characterized by relatively large discharges over a short time. The time between peaks and the peak height can vary greatly. Block emissions are characterized by a reasonably constant flow rate over a certain time, but with regular intervals of low or zero emission.

A classification by source **location** refers to the original location of the contaminant source in relation to the groundwater i.e. above ground surface, in the unsaturated zone, or in the saturated zone (Zaporozec, 1981). These may also be suitable for setting sub-classifications for groundwater contamination sources that have been classified according to another system.

The **degree of localization** of a contaminant source refers to point and non-point (diffuse) sources (Domenico & Schwartz, 1990). A point source (or line source) is characterized by a well-defined, small-scale source (e.g. leaking storage tank, a landfill, an unlined stormwater canal etc.) producing a well-defined contaminant plume. Non-point sources are characterized by larger-scale, relatively diffuse contamination emanating from numerous smaller, often poorly defined contaminant sources. Pollution plumes associated with non-point sources are not well-defined with extreme variation in contaminant concentrations (e.g. herbicides and pesticides for farming purposes, acid precipitation, etc.). Contaminant concentrations arising from non-point sources may vary significantly with time and space, reflecting both the seasonal patterns of usage and the various factors that influence the relative contribution of a particular chemical. Sometimes a distinction is made between diffuse and multipoint sources, where several small point sources are spread over an area (e.g. on-site sanitation systems).

Classification of contaminants by **type** was discussed in Section 3.2. It may be the case that a contaminant source releases only one type of chemical or microbial contaminant, e.g. only inorganic contaminants or only pesticides, but often there are several types of contaminants released from the same source. This complicates the use of this classification system for contaminant sources.

Classification by **origin** is possibly the simplest classification method in terms of its practical application. Contaminant sources can be divided in a number of ways, but the broadest level is generally based on economic sector e.g. industrial sources, mining sources, agricultural sources and contamination from urban settlements and related services. Classifications by origin are extensive and sub-classifications, usually by activity within the sector, but also by location, character or type of chemical compound, are common.

In this document the current and potential sources of groundwater contamination have been classified by origin.

Classification by origin is a simple and logical method for organising contamination sources. It is best suited for visual representation in the form of mapping contamination potential. One can easily identify an industry or waste site, and hence the source or potential source of groundwater contamination on a map. If one were trying to map contamination sources using chemical type or source character, for example, questions may arise such as "where do I start looking?" or "can I see chemical type or chemical character if I don't consider the origin?" Classification by origin is also the system, which is most likely to be easily understood and efficiently used by a wide cross section of water managers and technical field staff.

4. Sources of contamination in urban areas

The main sources of groundwater pollution in South African urban areas are associated with three economic sectors: *mining, industry* and *services in urban settlements*. The contamination of groundwater often arises from the inadequate disposal of solid and liquid waste from these sectors. Since *waste disposal* activities may overlap between sectors and waste sites often accept wastes from several sources, we have included waste disposal as a separate category. *Agriculture* is another sector which can result in significant groundwater contamination (Conrad *et al.*, 1999) but this sector is more relevant in rural, rather than urban areas. Some agricultural sources are relevant in the urban context such as the storage and use of fertilizers and pesticides (e.g. in market gardening operations) and intensive animal husbandry, which is practiced within the boundaries of the major metropolitan areas.

Table 3 summarises the various types of groundwater contamination sources, typical contaminant types and potential impacts for the major potential contamination sources in South African urban areas.

Table 3. Classification of groundwater contamination sources as well as the location of the affected area, typical contaminants and potential impacts (adapted from Nonner, 2002 and Sililo *et al.*, 2001)

Category	**Source type**	**Localization**	**Normal location**	**Main contaminant**	**Potential impact**
Urban settlements & services	On-site sanitation	Multipoint	Vadose zone	Nitrate, viruses & bacteria	Health risk / odour & taste / eutrophication of surface water
	Wastewater	Point and line	Surface/vadose zone	Nutrients, salinity, metals, organic, microbial	
	Underground storage tanks	Point	Vadose /saturated zone	Hydrocarbons, trace metals	
	Stormwater runoff	Point and line	Surface/vadose zone	Salinity, viruses & bacteria	
	Accidental leaks & spills	Point	Surface	Various	
	Cemeteries	Point	Vadose /saturated zone	Nutrients, viruses & bacteria	
	Sports grounds*	Non-point	Surface	Salinity, nutrients, pesticides & herbicides	
Mining	Mine tailings	Point	Surface/vadose zone	Acid drainage, sulphate, trace metals	Some metals may reach toxic levels
	Mine water	Point and line	Various	Salinity, sulphate, trace metals	
Industry	Solid waste	Point	Surface/vadose zone	Salinity, nutrients, metals, organic, microbial	Health risk (toxic & carcinogenic eg. As, CN) / odour & taste
	Process water & effluent	Point and line	Surface/vadose zone	Salinity, trace metals, organic compounds	
	Evaporation ponds	Point	Surface/vadose zone	Salinity, trace metals, organic compounds	
	Spills, leaks	Point	Surface	Various	
Waste disposal	Solid waste sites	Point	Surface/vadose zone	Salinity, nutrients, metals, organic, microbial	Health risk (toxic & carcinogenic eg. As, CN) / odour & taste
	Uncontrolled dump sites	Point	Surface/vadose zone	Salinity, nutrients, metals, organic, microbial	
	Effluent disposal ponds	Point	Surface/vadose zone	Salinity, trace metals, organic compounds	
Agriculture	Use of agrichemicals	Non-point	Surface/vadose zone	Salinity, nutrients, pesticides & herbicides	Toxic/Carcinogen health risk / eutrophication of surface water
	Sewage sludge application	Non-point	Surface/vadose zone	Nutrients, metals, microbial	
	Spills of agrichemicals	Point	Surface	Nutrients (N & P), pesticides & herbicides	
	Disposal of animal wastes		Surface/vadose zone	Nutrients, viruses & bacteria	
Miscellaneous	Airborne coal-fired power or vehicle emissions	Non-point	Surface	Acid (sulphate, nitrate), salinity	Acidification, leaching of metals
	Contaminated surface water	Point or line	Vadose/saturated zone	Various	

*Lately the impacts of golf estates on groundwater systems are being investigated. Many developers claim there are few impacts, however if the golf course is irrigated and fertilised there can be impacts on the groundwater system.

4.1 Sources relating to urban settlements and services

Groundwater contamination may arise from the following activities and services associated with dense urban settlements:

- On-site sanitation
- Underground transport of wastewater (sewer pipes)
- Wastewater treatment works and maturation ponds
- Stormwater collection and disposal
- Grey water disposal
- Irrigation and agrichemical application to sports fields and golf courses
- Cemeteries
- Underground storage of petroleum products
- Disturbance or damage to aquifers during construction
- Activities which alter recharge (e.g. hardening of surfaces by construction)
- Excessive or uncontrolled groundwater abstraction

4.1.1 Contaminant sources in urban settlements in South Africa

Sources related to settlement activities, such as cemeteries, stormwater systems and wastewater systems are widespread and are found in all urban centres of South Africa. The size, density and location of a settlement determine the degree or intensity of pollution or potential pollution to that area within the water environment (DWAF, 1999). As settlement density increases, the amount of waste produced per unit area also increases. The natural assimilation of waste during the delivery process then also decreases.

The South African situation is unique in that it is characterised by both formal and informal settlement types, with very different levels of service provision, types of services and potential groundwater impacts in each. Old, leaking sewage pipelines, septic tanks in unsuitable locations, unlined maturation ponds at wastewater treatment works, unlined stormwater basins and leaking underground fuel storage tanks represent groundwater contamination threats from the more formal settlement areas.

Uncontrolled sanitation and waste disposal practices are probably among the greatest threats in terms of groundwater contamination, because of the wide spatial extent across which these activities occur, and the likelihood of occurrence.

On-site sanitation

Under some hydrogeological conditions, notably where fractured bedrock is close to the surface and/or the water table is extremely shallow, the use of on-site sanitation units of standard design results in a high risk of nearby groundwater sources contamination by nitrates and pathogenic bacteria and viruses. Often, in fast growing, informal and unplanned settlements this type of sanitation method is applied by residents themselves and not by the municipal authority, which result in even poorer control over design and siting of the facilities. The main factors determining the severity of such pollution are the non-consumptive per capita water use, the natural infiltration rate and the proportion of the gross nitrogen load that will be leached to groundwater as nitrate. This happens most often in densely populated informal urban settlements, but can also occur in more prosperous urban settings where individual houses have both private shallow boreholes and, septic tanks and soakaways without appropriate siting controls. If correctly installed and managed chemical toilets should have no impact on groundwater systems. Sullage waters (grey water) will also increase the risk of groundwater contamination, because of the widespread use of household products, detergents and chemicals which contain persistent halogenated synthetic organic compounds.

Urban wastewater

In South Africa urban wastewater is generally treated by municipal authorities. Wastewater is collected via a sewer system piped to municipal wastewater treatment works for primary and secondary treatment. Conventional tertiary wastewater treatment (final polishing) is used in most, but not all of South Africa's wastewater treatment works in the major urban areas. Treated wastewater is often retained in shallow oxidation ponds prior to discharge to rivers, to the ground, to marine outfall or for reuse in irrigation. These municipal maturation ponds are often unlined, with high rates of seepage loss, and the leakage of partially treated effluent can significantly affect the quality of local groundwater. Sewage sludge is the residue/product from wastewater treatment works after primary and secondary treatment processes and its disposal poses another potential threat to groundwater quality. The most commonly used procedures to dispose of sewage sludge include incineration, deposition in landfills and application to agricultural land. Geohydrological investigations (for example Parsons and Taljard, 2000) in the vicinity of three wastewater treatment works in the Cape

Metropole have shown that groundwater contamination resulting from these activities are at least comparable to impacts resulting from waste disposal sites.

Underground storage tanks

Petrol stations in South Africa commonly store petroleum products (mostly petrol and diesel) in underground storage tanks, which pose a threat to the groundwater environment if a release occurs. There is an estimated 50 000 underground storage tanks (USTs) in service in South Africa. A study carried out by the South African Oil Industry estimated that approximately 9.6% of the UST's in service are currently leaking. Additionally the survey showed that at least 53% of petrol stations have a history of leaking UST systems. The life expectancy of a UST can range from 8 to 27 years with an average expectancy of 17 years. This however depends on soil conditions, proximity to direct-current traction systems, quality of coating, etc. (Holt, 1996).

Woodford and Chevalier, (2002) provide overviews of case studies of petroleum pollution in Karoo aquifers. One is from a small Karoo town in the Free State is situated on shale of the Volksrust Formation, which is dissected by numerous dolerite dykes and sills. The benzene as dissolved phase was detected in the central part of town, in close proximity of two petrol-service stations and an old depot. Benzene contamination was also found in a borehole some 50m away from the town's production borehole. The boreholes within the affected zone **do not show nonaqueous phase liquid (NAPL)** as a separate phase floating on the top of groundwater table, only dissolved aromatic hydrocarbons. The total petroleum hydrocarbon (TPH) content in the groundwater was **10 times greater than the maximum allowable limi**t of 0.6 mg/l according to the Dutch C levels. The benzene concentrations were up to 170 times greater than the Dutch C maximum allowable limit of 0.03 mg/l. (Dutch C levels were used due to a lack of such standards in South Africa. The Dutch values differ from those developed elsewhere, in that the intention is to allow the return of contaminated land to any potential use, rather than tailoring the level of remediation to the intended use of the land (www.sanaterre.com/guidelines/dutch.htm).) Follow-up monitoring showed that a range of diesel organics eventually contaminated the town's production borehole.

Therefore despite the relatively low permeability of the host rock there is potential for the development of a widespread contaminant plume originating from such fuel leaks.

Based on the number, location and propensity for leakage, groundwater contamination from USTs is a significant problem in **all** urban areas in South Africa.

USTs can result in pools of "free product" becoming trapped in voids. These form underground sources of contamination from which petroleum contaminants are slowly dissolved into the groundwater.

Cemeteries

There are a large number of cemeteries in the country, which pose a threat of groundwater contamination and are not subject to the same level of regulatory control as waste disposal sites (Engelbrecht, 1998).

Irrigation of recreational areas

The semi-arid South African climate requires that intermittent or continuous irrigation be practiced to maintain areas such as parks, gardens, landscaped areas and sports grounds. In these situations there is often excessive use of water, especially if water is applied by flooding from irrigation channels or hose pipes. These areas are irrigated for aesthetic, rather than commercial reasons and the amount of water applied is rarely related to the water needs of plants. Irrigation rates vary widely with water charging policy, the affluence of individual consumers and, in the case of municipal parks, bureaucratic procedures. In urban areas with permeable soils, over-irrigation can result in extremely high rates of local groundwater recharge. While return water from irrigation of recreational areas is normally of relatively good quality, this is not the case where urban wastewater is used for irrigation. Urban wastewater tends to overload the soil with nitrogen and sometimes contaminates groundwater with microbiological and/or organic agents.

4.1.2 *Types of contaminants*

A wide range of potential groundwater contaminants is associated with the activities and services in dense urban settlements, ranging from nutrients and pathogens in human wastes, hydrocarbons from the use and storage of fuels, solvents used for cleaning and agrichemicals (fertilizers and pesticides) used for maintaining sports grounds. Many of these are combined in the stormwater and wastewater streams that collect from urban areas.

Wastewater systems receive inorganic (particularly nutrients), organic, and microbial pollutants from different sources including human excretion products, household disposals, fossil fuel spillages, and urban runoff inputs that flush the contaminants deposited on the ground surface (Rogers, 1996). Physical, chemical and biological treatment can remove some of the contaminants before wastewater is discharged to the environment. Secondary treatment generally lowers the organic load and removes some of the nitrogen and phosphorus species, while tertiary treatment further improves the quality and removes most of the microbial contaminants. The resultant sewage sludge is a mixture of inorganic constituents, organic compounds, microbiological pollutants and pathogens. More than 300 different organic compounds have been identified in wastewater sludges (Duarte-Davidson and Jones, 1996).

Petroleum hydrocarbons are common groundwater contaminants in urban areas from leaking storage tanks, uncontrolled dumping and stormwater runoff from roads and other surfaces where fuels have been spilt (e.g. mechanical workshops). The most water-soluble constituents in common refined petroleum (petrol, diesel, etc.) are aromatic compounds and oxygenation additives, which together comprise <20% of the total material (Fels, 1999). Benzene, toluene, ethylbenzene and total xylenes (BTEX) are the common indicators of dissolved-phase petroleum contamination. Currently there is a move towards out phasing leaded petrol internationally and in South Africa, and according to the most recent legislation, leaded petrol will no longer be in use after 2006 in South Africa. The current market in South Africa is however still geared towards leaded petrol. (Unleaded petrol only has a 30% share in the market.) Tetraethyl Lead is used as an additive in leaded petrol. The two most common additives used to take the place of lead in petrol are MTBE and MMT. Both these additives have a debate raging regarding the health risks related to them. It is claimed that MTBE, is a possible cause of cancer and MMT a suspected neurotoxin. Some oil majors in South Africa are considering the use of MMT (A. Moldan, *pers. comm*). MTBE is currently being phased out in the US, due to the risk that it poses to groundwater. Ethanol is another oxygenate that could be used, which is harmless from a groundwater contamination point of view, however other environmental problems are caused by the large-scale production of ethanol. All of these compounds are volatile and, with the exception of MTBE, tend to partition into the gaseous phase as opposed to being dissolved in water (Fels, 1999).

Table 4 summarises the potential contaminants that may arise from activities and services in urban settlements. The amount and types of potential contaminants vary considerably between formal and informal areas in South Africa.

Table 4. Contaminants associated with potential pollution sources in urban settlements

Source	Nutrients	Trace metals	Salinity/ Acidity	Other inorganic	Hydro-carbons	Synthetic organics	Microbial pathogens
On-site sanitation	NH_4 NO_3 K PO_4 DOC		Salinity Cl	B (tracer)			bacteria viruses & parasites
Wastewater	NH_4 NO_3 K PO_4 DOC	Possibly Cd Cr Cu Pb Ni Zn	Salinity Cl SO_4 HCO_3	B (tracer)		diverse industrial chemicals	bacteria viruses & parasites
Underground storage tanks		Pb			BTEX alcohols	MTBE and other additives	
Stormwater runoff	NH_4 NO_3 K PO_4 DOC	Possibly Cd Cr Cu Pb Ni Zn	Salinity Cl SO_4 HCO_3			diverse industrial chemicals	bacteria viruses & parasites
Cemeteries	NH_4 NO_3 K PO_4 DOC		EC may be higher				bacteria viruses & parasites
Sports grounds*	NH_4 NO_3 K PO_4		EC may be higher			pesticides herbicides	

Data from Dallas & Day 1993; Morris *et al.*, 2003; case studies *Refer to footnote in Table 3

Light shading = possible contaminant/low levels Dark shading = probable contaminant

4.2 Industrial sources

Various industrial activities have the potential to cause groundwater contamination. Contaminants from industry may reach the groundwater (1) if they spill or leak on the surface or underground, (2) if wastes are disposed on land or to surface water bodies or (3) if recharge water is contaminated either by artificial recharge of wastewater or wet or dry deposition of contaminants from atmospheric emissions.

Contamination of groundwater may arise from the following industrial activities:

- Production, use and storage of hazardous chemicals
- Accidental spills of chemicals during use and transport
- Transport of chemicals or waste via underground pipelines
- Storage and disposal of solid and liquid wastes
- Underground storage of petroleum and other chemical products
- Disposal of waste ash from power generation
- Hazardous waste disposal by landfill

- Storage of radioactive materials and waste
- Uncontrolled dumping
- Disturbance or damage to aquifers during construction
- Activities which alter recharge (e.g. hardening of surfaces by construction)
- Wet and dry deposition of contaminants from industrial emissions

Of these activities, those linked to the disposal of solid, liquid and hazardous wastes are considered major threats to groundwater quality in urban areas and will be considered separately in one of the following sections.

4.2.1 Contaminant sources in the industrial sector in South Africa

According to the 1996 Census of Manufacturing, there were 25402 factories in South Africa, with a total output of R 331 502 million. Of these factories, 11 534 (45.4%) were situated in Gauteng; 5141 (20.2%) in KwaZulu-Natal, 4 670 (18.4%) in the Western Cape and 1500 (5.9%) in the Eastern Cape (Stats SA, 1998).

Larger industrial plants often use large volumes of process water and commonly use lagoons for handling and concentrating liquid effluents. Large industrial concerns in South Africa include:

- Five oil refineries (Cape Town, Durban (2), Secunda and Sasolburg),
- Large petrochemical industries (Sasolburg, Secunda, Mossel Bay),
- Four steel plants (Vanderbijlpark, Vereeniging, Newcastle and Saldanha),
- Aluminium smelters (Richards Bay)
- Thirteen coal-fired and two gas turbine power stations.

The oil refineries are located within the metropolitan areas of Cape Town and Durban and two steel plants and some of the power stations within the Gauteng area considered in this study. Sugar mills and pulp and paper factories may also generate large quantities of effluents, but these are mostly located outside the urban areas.

Many other industries tend to be located on the fringes of urban areas and are without sewerage cover. Most of these industries generate liquid effluents such as spent lubricants, acidic, metal-rich liquors, solvents and disinfectants, which are often discharged directly to the soil and may represent a serious long-term threat to groundwater quality. These practices were allowed or even encouraged by authorities in the past before there was an understanding of the interactions with groundwater resources.

It is important to note when considering the collected data, that the majority of South African industries have no groundwater monitoring in place or do not report their results.

Exceptions to this occur principally at the larger industrial complexes or at some of the larger industries in the country. The implication is that while suspected contaminants are most likely found in urban catchments, very few reports or data sets are available to verify their presence.

Where groundwater monitoring data are available, the analyses are usually only for macro inorganic parameters and seldom organic contaminants.

This is a major concern for groundwater quality management in South Africa and should receive urgent attention.

4.2.2 *Types of contaminants*

The type of contaminants that may be released depends on the nature of the raw materials used and waste generated by the specific industrial process. Food industries represent the largest contribution to the output of the manufacturing sector in South Africa (14.4% of the total economic value of goods). This is followed by the motor vehicle industry (11.2%); chemical industries (10.7%); basic metals (9.7%); paper (5.1%) and the petroleum products divisions (4.8%) (Stats SA, 1998).

Expected contaminants from common polluting industries are summarised in Table 5. The importance of these contaminants are discussed in Sections 6 & 7.

Table 5. Expected contaminants associated with industrial processes and waste products

Source	Nutrients	Trace metals	Salinity/ Acidity	Other inorganic	Hydro-carbons	Synthetic organics
Adhesives		Al			toluene	acrylates, chlorinated solvents, formaldehyde, isocyanates naphthalene, mineral spirits phenol, phthalates

Source	Nutrients	Trace metals	Salinity/ Acidity	Other inorganic	Hydro-carbons	Synthetic organics
Aluminium smelters		Sn Zn	Salinity	F		
Alkalis, chlorine, inorganic chemicals	NH_4	Cd Cr Fe Pb Hg Sn Zn	Salinity Cl SO_4 Acidity			
Batteries		Cd Cu Pb Ag Zn				
Detergents		As Cd Cr Cu Fe Ni Zn				organophosphates, surfactants
Dry cleaning / laundry						DCE , TCE, PCE, vinyl chloride
Electrical components		Al As Cd Pb Hg Ni Se	Acidity	Be CN		chlorinated solvents
Electroplating		Cd Cr Cu Pb Hg Ni Se Ag	Salinity	CN		chlorinated solvents
Explosives	NH_4 NO_3					ethyl acetate, HMX, methanol, nitrobenzenes, nitroglycerine, nitrotoluenes, PETN, RDX, tetrazene, tetryl, 1,3-DNB
Fertilizer	NH_4 NO_3 PO_4 K	As Cd Cr Cu Fe Pb Mn Hg Ni Zn	Salinity Cl SO_4			
Food processing*	NH_4 NO_3 PO_4 K	Se Ag Zn	Salinity		methane	pesticides, dioxins
Fossil fuels / energy / ash		Cd Cr Pb Hg Ni Se V Zn	Alkaline	Be B		
Glass, cement, asbestos		As Cr Pb				
Inks & dyes	NH_4	As Cd Cr Ni			aromatic hydro-carbons, toluene	acrylates, anthraquinones, benzidene, chlorinated solvents, ethyl acetate, oxalic acid, phenol, phthalates
Leather goods and tanneries		As Cr Cd	Cl SO_4		benzene, toluene	
Metal works (non ferrous)		As Cd Cr Cu Pb Hg Zn	Acidity SO_4	Be		chlorinated solvents, mineral oils
Oil & solvent recycling		As Cr Pb Zn			see petrol refineries	see solvents
Pesticides & herbicides		As Pb		CN	ethyl-benzene toluene xylene	carbamates, chlorinated insecticides, chlorophenols, naphthalene, organo-phosphates, phenols, phthalates
Petrochemical		Cd Cr Fe Pb Hg Sn Zn			alkanes BTEX PAH	phenols

Source	Nutrients	Trace metals	Salinity/ Acidity	Other inorganic	Hydro-carbons	Synthetic organics
Paint & coating works		Al Cd Cr Co Pb Hg Zn		CN	aromatic hydro-carbons, toluene	acetates, acrylates, alcohols, chlorinated solvents, glycol ethers, ketones, mineral spirits, phthalates, styrene, terpenes, 1,4-dioxane
Petroleum refineries		Cd Cr Cu Fe Ni Zn	SO_4		alkanes BTEX PAH	
Pharma-ceuticals		As Cd Cr Cu Pb Hg	SO_4	Bi		alcohols, benzoates, dyes, glycols, mineral spirits
Photographic industries		Cd Se Ag				
Pulp / paper manufacture		Cr Cu Pb Hg Ni Zn	Salinity SO_4			acrylates, chlorinated solvents, dioxins, phenols, styrene
Rubber & plastics		Cd Cr Pb Sb	SO_4		benzene	acrylonitrile, butadiene, chloroform, DCE, phenols, phthalates, styrene, vinyl chloride
Solvents (chlorinated)						carbon tetrachloride, chlorofluoroethanes, DCE, methylene chloride, PCE, TCE, vinyl chloride, 1,1,1-trichloroethane
Solvents (non - chlorinated)					BTEX	acetates, alcohols, ketones
Steel works		Cd Cr Cu Fe Pb Hg Ni Se Sn V Zn				chlorinated sovents, PCB
Textiles	NH_4	Cr Cu Ni				acetic acid, acetone, acrylates, chlorinated solvents, formaldehyde, naphthalene, phenols, phthalates
Timber treatment	NH_4	As Cr Cu			creosote PAH	dioxins, pentachlorophenol, phenol, tri-n-butyl tin oxide

Data from Dallas & Day 1993; Morris *et al.*, 2003; case studies

Light shading = possible contaminant/low levels   Dark shading = probable contaminant

* Note: Food and beverage industries also produce microbial pathogens (viruses, bacteria, protozoan and metazoan parasites) and biogenic organic wastes containing amines.

Key to chemical abbreviations:

BTEX	benzene, toluene, ethylbenzene and xylenes	CN	cyanides
DCE	dicholoroethylene	HMX	high melting explosive
PAH	polyaromatic hydrocarbons	PCB	polychlorinated biphenyls
PETN	pentaerthythritol tetranitrate	PCE	perchloroethylene
TCE	trichloroethylene	1,3-DNB	1,3-dinitrobenzene

4.3 Mining sources

Activities in the mining environment which pose a threat of groundwater contamination include the following:

- Disposal of mining and mineral processing wastes (e.g. tailings, slimes, waste rock dumps)
- Mine wastewater ponds
- Mine de-watering and mine drainage
- Disposal of waste in unused or abandoned mines
- Uncontrolled dumping
- Disturbance or damage to aquifers by quarrying, opencast or underground mining
- Activities which may result in the alteration of recharge

Activities are specific for different types of mines and hence the pollution type and severity will vary depending on the activity and the type of mine.

4.3.1 Contaminant sources from mining activities in South Africa

Mining activity is widespread in South Africa. South African mines produce a variety of ores e.g. chromite, coal, copper, diamonds, fluorspar, gold, iron ore, lead, limestone, manganese, nickel and platinum group metals.

Mines also produce a variety of potential contaminants, depending on the ore deposit type, mining processes and mineral processing activities at specific sites.

Johannesburg is the centre of the gold mining industry and has been for many decades. Active gold mines are located in the West and East Rand areas in Gauteng, Klerksdorp area in the North West Province and in the Free State Goldfields area. Gold mines are the largest employer in the mining sector with 39 operational gold mines in 2001 (Chamber of Mines, 2001). By-products from gold mines, include uranium and acid/pyrite, which are potential sources of groundwater pollution (acid mine drainage).

Coal mines are located in the northern and western parts of South Africa in the major drainage regions of the Vaal River, Olifants River and the northeastern escarpment within which four major rivers flow. The South African Chamber of Mines recorded sixty-two operational coal mines in 2001, the third highest employer in the mining sector. Coal mining's impact on the water resources varies according to the life cycle of the mine. Coal mines may produce large quantities of acid or saline mine drainage.

Diamond mining occurs away from the major urban centres, in Kimberley and surrounding areas and along the West Coast into Namibia. Diamond mining operations are the most common, with 69 mines operating in 2001, but mining occurs on a smaller scale than gold and coal mining. The associated environmental impacts are generally less severe and the potential for groundwater contamination lower than for gold or coal mining, because the gangue minerals in diamond ores are generally less-reactive than those in gold and coal tailings. However it must be noted that alluvial diamond mining can destroy the natural grading of aquifers.

Other ores, including iron ore and base metals, are mined in the Northern Cape (e.g. Hotazel, Sishen, Okiep), North West (Rustenburg) and Mpumalanga (Barberton). Chrome and platinum group metals (PGM) are important mining enterprises in the Bushveld with 12 PGM mines and 13 chrome mines in operation in 2001. PGM's are the most significant growth area in terms of future projects in the mining sector and the second largest employer in the mining industry.

Of the four major metropolitan areas covered in this study, Gauteng is the only region where mining occurs at any significant scale within the urban environment. Small-scale mining activities do occur within the Cape Town, Durban and Port Elizabeth metropolitan areas, but these are usually quarry operations for building materials. Several companies mine sand, dolerite, limestone or granite near urban areas.

The magnitude of the threat from mining activities is dependant on whether precautionary measures are taken to prevent contamination, but in many cases, the scale of mining operations is such that groundwater pollution cannot be completely avoided.

Abandoned mines pose a potentially even larger threat to groundwater resources, since most were operated for decades without any environmental controls. Recorded polluting incidents from mines have occurred primarily in Gauteng and Mpumalanga Provinces, where gold and coal mines produce acidic leachates (Acid Mine Drainage), causing contamination of groundwater systems following infiltration.

4.3.2 *Types of contaminants*

A summary of potential groundwater contaminants occurring in the mining environment along with the polluting activities has been included in Table 6.

Table 6. Contaminants associated with potential pollution sources in the mining sector

Source	**Nutrients***	**Trace metals**	**Salinity/ Acidity**	**Radio-nuclides**	**Other inorganic§**	**Organics#**
Acid mine drainage**		Al Co Cu Fe Mn Ni	Acidity		Na SO_4 F	
Base metal mines		As Cd Cr Co Cu Fe Pb Mn Ni Zn	Acidity		SO_4	
Coal mines		Fe Mn As	Salinity Acidity/HCO_3		SO_4 Na Cl F	
Diamond mines			Salinity		Na Cl	
Gold mines		Al As Cr Co Cu Mn Ni Pb Zn	Acidity (often neutralized) Salinity	^{238}U ^{230}Th ^{226}Ra ^{222}Rn	SO_4	
Platinum Group Metals		from associated sulphides, e.g. Co Cu Cr Ni	Salinity		Na Cl SO_4	
Quarries (sand/stone)			Salinity		Major ions	
Quarries (limestone)			Alkalinity Salinity		Major ions	
Smelting & processing		As Cd Cr Cu Fe Pb Hg Ni Se Sn V Zn	Salinity		Na Cl SO_4 CN Be B	chlorinated solvents, mineral oils

*Nutrients & microbial contaminants may arise from sewage facilities at mines. Explosives used in mining are a potential source of NH_4, NO_3 and synthetic organic chemicals (see Table 5). ** Can be associated with most ore/coal mining activities. §Ions such as Ca and Mg are common but are not considered problematic in general. # Hydrocarbons e.g. lubrication oils are potential contaminants from the use of machinery (underground/surface)

Data from Morris *et al.*, 2003; Rösner *et al.* 2001; case studies

Light shading = possible contaminant/low levels Dark shading = probable contaminant

Coal and gold mines, especially closed and abandoned mining operations, appear to be the most significant threats in terms of potential groundwater contamination from the mining sector in South Africa. Acid generation and decreasing groundwater pH has been noted in some gold and coal mining areas in South Africa, but in many cases, acid drainage is neutralised by reaction with the country rock to produce saline drainage instead.

4.4 Waste disposal

Potential sources of groundwater contamination from waste disposal activities include:

- Leakage of leachate from formal landfill sites
- Infiltration of leachate from informal solid waste dumps
- Infiltration of liquid wastes from industrial effluent lagoons
- Effluent irrigation on land
- Effluent discharge to rivers

Groundwater monitoring data from formal waste disposal sites suggest that where sites are unlined or liners have failed, leachate from the waste site causes groundwater contamination.

Accidents and polluting incidents occur primarily where waste disposal sites are poorly managed and/or not properly lined.

Liquid effluents may leach through the vadose zone into the aquifer undetected and contaminate the groundwater if the site is unlined or if plume migration is not controlled or effectively monitored. Early warning systems as well as controls should be in place to minimize the impacts of pollution and to allow timely control of contamination incidents.

4.4.1 Contaminant sources from waste disposal activities in South Africa

General waste and hazardous waste disposal sites are probably the most intensively monitored sources of potential groundwater contamination in urban environments in South Africa. This is partly due to the regulatory requirements that waste disposal facilities be licensed by the Department of Water Affairs and Forestry. Minimum requirements for water monitoring at waste management facilities were specified by DWAF (1998). In 1998 DWAF initiated a baseline study on waste generation in South Africa in order to review existing classification methodology systems, quantify distribution and amount of waste generated as well as to project waste generation rates for South Africa (DWAF, 1998). The main findings of the project indicated the following:

- There is a lack of reliable data with regard to waste generation rate. Small scale urban and industrial generation, in particular could not be quantified.

- Generation rates of waste per capita differ between regions. Waste generated is believed to be dependant on demographics and socio-economic situation in each region.
- There is a good correlation between waste generated, calculated on the basis of historical generation rates per capita and the volume of waste received at landfill sites at a regional level.
- There is a lack of reliable information on mining and industrial wastes, which are disposed of on site.

Table 7 is a summary of the waste generation rates in million tons per annum, as was calculated in this baseline study.

Table 7. Summary of waste generation rates (million tons/annum) from DWAF 1998

Waste Stream	1992 CSIR	1998 WMB
Mining	378	468.2
Industrial	23	16.3
Power Generation	20	20.6
Agriculture and Forestry	20	20*
Domestic and Trade	15	8.2
Sewage Sludge	12	.3
Total	468	533.6

* Assumed from CSIR study

South Africa has 10 major hazardous waste sites and around 30 large general waste disposal sites located near major urban centres (Table 8). A waste site is classified as "large" if the maximum deposition rate is greater than 500 tons of waste per day.

Table 8. Hazardous waste sites and large general waste disposal sites in South Africa as at 1998 (CSIR database)

Name	Location	Class	Name	Location	Class
Aloes	Port Elizabeth	H:H	Arlington	Port Elizabeth	GLB-
Boipatong	Western Vaal	H:H	Bothaville	Bothaville	GLB-
BulBul Drive	Durban	H:h	Garstkloof	Pretoria	GLB-
Holfontein	Springs	H:H	Linbro Park	Johannesburg	GLB-
Koedoeskloof	Uitenhage	H:H	Luipaardsvlei	Krugersdorp	GLB-
Mossgas Regional	Mossel Bay	H:H	Marie Louis	Johannesburg	GLB-
Shongweni	Shongweni	H:h	New England	Pietermaritzbrg	GLB-
Umlazi	Durban	H:h	Nomonde	Molteno	GLB-
Vissershok - CCC	Cape Town	H:H	Northern	Bloemfontein	GLB-
Vissershok – Private	Cape Town	H:H	Northern Works	Johannesburg	GLB-
Alusaf Industrial	Richards Bay	GLB+	Platkop	Germiston	GLB-
Bellville Park	Cape Town	GLB+	Randburg/Kya Sands	Johannesburg	GLB-
Bisasar Road	Durban	GLB+	Robinson Deep	Johannesburg	GLB-
Chloorkop / WT	Kempton Park	GLB+	Rooikraal	Germiston	GLB-
Coastal Park	Cape Town	GLB+	Scaw Metals	Germiston	GLB-
Goudkoppies	Johannesburg	GLB+	Simmer & Jack	Germiston	GLB-
Nuffield	Springs	GLB+	Southern	Bloemfontein	GLB-
Pinetown (South)	Durban	GLB+	TSB Malelane	Malelane	GLB-
Richards Bay Alton	Richards Bay	GLB+	Waldrift	Eastern Vaal	GLB-
Swartklip	Cape Town	GLB+	Weltevreden	Brakpan	GLB-
Tongaat	Durban	GLB+	West Wits	Krugersdorp	GLB-

Key:

Waste Type:	[G] – general waste, [H] – hazardous waste
Landfill size:	[L] – large
Potential for leachate:	[B-] – no significant leachate produced,
	[B+] – significant leachate produced
Hazardous waste:	[H:H] – landfills that can accept all hazardoes ratings of waste
	[H:h] – landfills that can only accept Hazard Ratings 3 and 4 and general wastes
Hazard Ratings:	1 – Extreme hazard, 2 – High hazard, 3 – Moderate hazard, 4 – Low Hazard

A far greater threat of groundwater contamination is expected to arise from the numerous old and uncontrolled waste sites and dumping grounds than from these formal waste disposal facilities. Liquid effluent lagoons and evaporation ponds are sources with high contamination potential in high aquifer vulnerability areas because of their hydraulic loading.

4.4.2 *Types of contaminants*

The types of groundwater contaminants associated with a particular waste disposal site would be expected to be dictated by the type of waste involved. There are, however, some other factors which may influence the contaminant composition, especially when dealing with a mixture of wastes, as in a landfill site. These include the method of disposal (e.g. dumping, ponding, irrigation, co-disposal, injection); degree of compaction of the waste; the age of waste; the climate and the hydrogeology of the site.

The source of groundwater contaminants at a solid waste disposal site is a concentrated liquid mixture of organic and inorganic species that emanates from the waste, known as leachate. The impacts of groundwater contamination by landfill leachate include significant increases in groundwater salinity (electrical conductivity) and concentrations of organic compounds (dissolved organic carbon or total organic carbon). Landfill leachate typically has a high chemical oxygen demand (COD) and is highly reducing. High concentrations of dissolved ammonium are often detected in monitoring boreholes near leaching landfill sites. Examples of typical leachate compositions from landfill sites are given in Table 9.

Table 9. Concentrations of inorganic parameters, trace metals and bulk organic measurements in various landfill leachates

Parameter (mg/L)	**General leachate**[1]	**UK leachate**[2]	**Brazil leachate**[3]	**SA leachate**[4]
EC mS/m	500 - 3000	2500	-	3090
Na	500 - 2000	2040	-	4880
Ca	500 - 1500	3650	-	240
Mg	-	555	-	210
K	-	1070	-	2280
NH_4 as N	200 - 1200	1400	310 - 1190	1490
NO_3 as N	-	below detection	-	0.3
SO_4	50 - 400	1170	-	970
Cl	1000 - 3000	2700	1470 - 2320	7000
Alkalinity as $CaCO_3$	-	-	4400 - 7400	9040
Fe	200 - 1000	-	5.9 - 10.5	5.9
Cd	10 - 100	-	0.06	<0.01
Cr	20 - 1000	-	0.05	0.8
Cu	10 - 1000	-	0.03 - 0.13	0.1
Mn	-	-	-	3.1
Ni	50 - 2000	-	0.06 - 0.40	3.1
Pb	20 - 1000	-	0.1 - 0.8	0.05
Zn	0.1 - 10	-	0.07 - 0.73	8
B	-	-	-	16
F	-	-	-	3.6
TOC	3000 - 15 000	18 850	-	2320
COD	500 - 30 000	247 700	1670 - 2500	9970

[1] Typical concentrations from Kiely (1996) [2] Thorton, unpublished data from acid phase landfill, *pers. comm.*

[3] Operating landfill sites (Vendrame and Pinho, 1997) [4] CSIR, unpublished data from hazardous waste site.

Heavy metals are not widely reported to occur in high concentrations in contaminated groundwater near waste sites in South Africa. Case studies of waste disposal sites have found that the toxic trace metals, such as cadmium, lead and nickel, are not particularly mobile, probably because the groundwater conditions tend to remain near neutral pH.

The data may be biased in some cases by the fact that heavy metals and other potential contaminants (particularly organics) are less routinely analysed than major ions in pollution studies.

Leachates from domestic and hazardous waste landfills may contaminate groundwater with a variety of organic compounds (Lyngkilde and Christensen, 1992). The organic compounds include natural dissolved organic matter (DOM), such as volatile fatty acids (VFAs) and humic substances, as well as xenobiotic organic micro-pollutants (XOMs) such as chlorinated solvents, petroleum-derived hydrocarbons and pesticides (Volkman *et al*., 1997; Oman and Hynning, 1993; Robinson and Gronow, 1993). Although they represent only a few percent of the organic matter in most leachates, the XOMs are of key concern due to their potential health risks and the low water quality standards enforced for these compounds (Christensen *et al*., 1994).

Fetter (1993) presents a list of nearly 80 organic contaminants found in groundwater at a single hazardous waste disposal site in the United States (Table 10). The compounds shown in **bold** (together with chlorobenzene and naphthalene) are the **20 most abundant organic compounds** found at 183 waste disposal sites in the US (Plumb and Pitchford, 1985).

A large number of the compounds in Table 10 are chlorinated solvents and phenolic compounds. **Chlorinated solvents** such as trichloroethene (TCE) and perchloroethene (PCE) are common groundwater contaminants from industrial applications and waste disposal sites (Pankow and Cherry, 1996). These solvents have been applied to degrease metals or dry-clean textiles since the 1930s. 1,4-Dioxane has also been widely used as a solvent and as a stabilizer for chlorinated solvents, particularly 1,1,1-trichloroethane. **Phenol** and chlorinated phenols are common in contaminated surface and groundwater systems. Chlorophenols are found as groundwater pollutants at numerous sites, due to their presence in creosote, a common wood preservative, (Mueller *et al*., 1989; Pollard *et al*., 1993). Phenol, 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) are listed as EPA priority pollutants (Keith and Telliard, 1979) as a result of extensive contamination (Howard, 1989, 1991; Van Gestel *et al*., 1996) and the associated toxic and carcinogenic effects of this class of chemicals.

Table 10. Organic contaminants found in groundwater at a US hazardous waste site (Fetter, 1993).

Volatile organics		
benzene	2-methyl-2-butanol	**trichloroethene**
chloroform	2-butanol	**methylene chloride**
chloroethane	4-methyl-2-pentanol	dichlorofluoromethane
1,1-dichloroethane	m-xylene	**acetone**
1,1,2-trichloroethane	**toluene**	2-methyl-2-propanol
trans-1,2-dichloroethane	**ethyl benzene**	2-propanol
tetrachloroethene	chloromethane	2-hexanone
vinyl chloride	**1,2-dichloroethane**	ethyl ether
tetrahydrofuran	**1,1,1-trichloroethane**	o-xylene
2-butanone	**1,1-dichloroethene**	p-xylene
Extractable organics		
phenol	3-methylbenzoic acid	3,3,5-trimethylhexanol
2,3,6-trimethylphenol	benzenepropionic acid	2-heptanone
2,3-dimethylphenol	2-ethyl-hexanoic acid	cyclohexanone
3,4-dimethylphenol	octanoic acid	4-hydroxy-4methyl-2-pentanone
2-ethylphenol	hexanoic acid	tri-*n*-propyl-amine
3-methylphenol	nonanoic acid	1,4-dioxane
4-methylphenol	cyclohexanecarboxylic acid	*n,n*-dimethylacetamide
di-*n*-butyl phthalate	1,2'-oxy bis (2-methoxy ethane)	4-methylbenzoic acid
benzo(a)anthracene	2-chlorophenol	3-methyl-butanoic acid
4-methyl-2-pentanone	2,4-dimethylphenol	benzeneacetic acid
2-hexanol	2,6-dimethylphenol	2-ethyl butanoic acid
cyclohexanol	3,5-dimethylphenol	heptanoic acid
2-hydroxy-triethylamine	2-methyl phenol	decanoic acid
alkyl amine	**bis (2-ethylhexyl) phthalate**	pentanoic acid
n,n'-dimethylformamide	isophorone	1-methyl-2-pyrrolidinone
benzoic acid	chrysene	1,2-dichlorobenzene

4.5 Agricultural sources

Agricultural activities have been recognized as a source of potential groundwater contamination in South Africa (Conrad *et al.*, 1999). In the urban areas, agriculture is limited by the availability of land, leading to the adoption of more intensive practices, rather than large-scale crop production or grazing. Examples of agricultural operations within the metropolitan areas include market gardening, nurseries, dairies, piggeries and abattoirs.

Intensive agriculture in urban areas tends to use increased quantities of fertilizers (including sewage sludge and treated wastewater available from urban wastewater treatment plants) and pesticides/herbicides or to produce concentrated streams of animal wastes in comparison with rural operations.

Agricultural activities which may cause groundwater contamination in the urban environment include:

- Application of inorganic fertilizers
- Application of sewage sludge as a soil amendment
- Irrigation with wastewater
- Application of pesticides and herbicides
- Storage and disposal of animal wastes from dairies/feedlots/piggeries
- Disposal of wastewater from abattoirs
- Accidental spills of agrichemicals

4.5.1 Contaminant sources from agricultural activities in South Africa

A study of the impact of agricultural activities on groundwater quality in South Africa identified five activities that affect South African groundwater resources. These are fertilizer application, sludge application, feedlots, pesticide application and irrigation (inducing salination) (Conrad *et al.*, 1999).

Within the urban areas, increased groundwater nitrate concentrations have been reported in the Philippi Horticultural Area on the Cape Flats and the Elspark/Rondebult area in Johannesburg (Alberton). These are important market gardening areas making use of fertilizers. Sewage sludge is used as a soil conditioner at Philippi, while treated wastewater is used to irrigate non-food crops (turf and fodder) at Elspark/Rondebult. The use of nitrogen as fertilizer in sugarcane plantations in Durban peri-urban areas could pose a threat to urban groundwater, although no reports are available. Intensive stock farming in the Durbanville/Milnerton area of Cape Town poses a potential pollution threat due to contaminated runoff from the feedlot pens. In some dryland catchments in the Western Cape (e.g. Berg river), salination of waters was reported as salt decantation occurred from naturally saline soils due to changes in land use from extensive pastoral to intensive cropping over the last century or so (Fey, 2004).

The inappropriate use of pesticides in vineyards and orchards in Cape Town urban areas poses a threat to groundwater. Although most of the research was done on surface waters, there are a number of reports on detected pesticides in groundwater (Dalvie *et al.*, 2003; Solomons *et al.*, 2003; London *et* *al*., 2000). An indication of possible threats of specific pesticides to groundwater can also be obtained from their sale and usage figures (Jovanovic and Maharaj, 2004). The causes of pollution can be due to normal usage via direct applications to agricultural land, as well as incorrect usage, handling, storage and disposal of current and obsolete pesticides. Obsolete chemicals include those that have been banned, discarded and expired such as DDT and dieldrin, amongst others (Naidoo and Buckley, 2003).

4.5.2 *Types of contaminants*

The potential groundwater contaminants associated with agricultural activities are predominantly nutrients, microbial pathogens and synthetic organic pesticides. These are summarized in Table 11.

Table 11. Contaminants associated with potential pollution sources from urban-based agriculture

Source	**Nutrients**	**Trace metals**	**Salinity/ Acidity**	**Synthetic organics**	**Other organic**	**Microbial pathogens**
Inorganic fertilizers	NO_3 NH_4 K PO_4 DOC	As Cd Cr Cu Fe Pb Mn Hg Ni Zn	Salinity SO_4 Cl			
Sewage sludge	NO_3 NH_4 K PO_4 DOC	Possibly Cd Zn	EC may be higher	traces of industrial chemicals e.g. PAH		bacteria viruses & parasites
Wastewater irrigation	NO_3 NH_4 K PO_4 DOC	Possibly Cd Cr Cu Pb Ni Zn	Salinity Cl SO_4 HCO_3	traces of industrial chemicals		bacteria viruses & parasites
Pesticide & herbicide application		As Pb		carbamates, chlorinated insecticides, chlorophenols, naphthalene, organo-phosphates, phenols, phthalates		
Animal wastes	NO_3 NH_4 K PO_4 DOC		EC may be higher		hormones & steroids	bacteria viruses & parasites
Abattoirs	NO_3 NH_4 K PO_4 DOC		EC may be higher	pesticides	biogenic amines	bacteria viruses & parasites

Data from Conrad *et al.* 1997; Morris *et al*., 2003; case studies

Light shading = possible contaminant/low levels   Dark shading = probable contaminant

4.6 Miscellaneous sources

4.6.1 Contaminant sources from airborne coal-fired power generation and from vehicle emissions in South Africa

Some 90% of South Africa's emissions of pollutants and chemicals such as sulphur dioxide are generated on the Highveld in Gauteng, much of it by refineries, power stations, large factories - and township kitchens. As reported in the Sunday Times (2003), Dr Tal Freiman of the Climatology Research Group at Wits University identifies, the biggest culprits as:

- The burning of fossil fuels by motor vehicles;
- The burning of wood and smoky low-grade coal in homes;
- Dust from mine dumps and slime dams; and
- Chemical emissions from heavy industry and farming.

4.6.2 Types of contaminants

Several contaminants can result from combustion processes, which can have a potential influence on the groundwater quality in urban areas. It is however difficult to quantify the effect on the groundwater quality from this source. The most common contaminants found are:

- Nitrogen dioxide (NO_2), a toxic, irritating gas,
- Sulphur dioxide (SO_2), a colourless gas which can be chemically transformed into acidic pollutants such as sulphuric acid and sulphates. The main sources of airborne SO_2 are coal-fired power generating stations and smelters,
- Carbon monoxide (CO) a colourless, odourless and tasteless gas that comes primarily from vehicle emissions,
- Lead from emissions from vehicles still using leaded fuel. New legislation will ensure that leaded fuel will no longer be in use from 2006
- Acid rain is the result of chemical reactions of nitrogen and sulphur in the atmosphere. The resulting acidic water droplets can be carried long distances by prevailing winds, returning to earth as acid rain, snow, or fog. Acid rain is not only damaging to aquatic and terrestrial ecosystems but also to human health.

4.6.3 Contaminant sources from contaminated surface water

Contamination of groundwater sources from contaminated surface water is possible where there is a direct connection between the resources. The connection to these surface water bodies, contributing to this type of groundwater contamination, can either be natural or man-made. In urban areas the surface water sources are often man made or affected by human activities. Some examples of such interaction in South Africa is noted below:

- Wherever there are grazing animals (e.g. feedlots, small-holdings), pets, and birds, faecal coliforms are deposited in faecal matter. Surface water (storm run-off) running over lands with faecal matter becomes contaminated. Where such water enters groundwater directly without filtration through soil, as it does where the water table is shallow, it contaminates the groundwater.
- Pumpage from mines into surface water. An example of this is the Stilfontein Gold Mine water which is pumped from Margaret shaft into the Koekemoer spruit (Klerksdorp Goldfields). Winde (2001) explains in detail how the pumping influences the flow, temperature, and hydrochemical interactions and consequent contaminant transport within this spruit. He goes on to show that in times of higher surface water flow and groundwater abstraction, flow reversals could occur. The interaction between the hydrology of the two systems is thus clearly illustrated here.
- Decant from coal and gold mines. Several of the gold mines on the West Rand (Gauteng) and coal mines in Mpumalanga Province will decant poor quality water post –closure (Hodgson *et al.*, 2000; Grobbelaar *et al.*, 2002)
- Localized salination of alluvial aquifers can occur adjacent to the Vaal River as a result from the high salt load (contributed by effects from urbanization and mining activities) in the river.
- Re-circulation of water from sources such as slimes dams, evaporation dams, etc, at the mines overlain by dolomite can lead to heightened salination and increase in the dissolution of subsurface dolomites and subsequent sinkhole formation.
- Where polluted streams (flowing through densely populated informal settlements (e.g. south of Johannesburg) converge with natural springs or "eyes" (where underlain by dolomite), groundwater contamination can be the result.
- In heavy industrialized areas (e.g. Sasolburg, Modderfontein) discharges from factories into channels, streams and ponds can result in contamination of the aquifers directly below these sources.

The number and types of sources in this category is thus numerous and will vary according to the contamination load and type/intensity of the groundwater/surface water interaction.

4.6.4 *Types of contaminants*

The types of contaminants resulting from contaminated surface water resources will vary according to the original source of the contamination. The main contaminants are however microbial contaminants (e.g. faecal coliforms) and inorganic contaminants. The inorganic contaminants contributed mainly to the salt and nutrient levels in the groundwater. For example streams containing discharge from sewage plants and/or mine water. Organic contamination can be the result from sludge lagoons/ponds channels and streams which are used as discharge points for heavy and chemical industries.

5. Examples of existing groundwater contamination in South Africa's urban catchments

Reference has already been made to the paucity of published data or reports on groundwater contamination in South Africa's urban areas.

The case studies discussed in the sections which follow therefore provide **some examples** of available case histories; **several other** areas/potential problems are known to exist.

5.1 Case studies relating to settlements and services

Title:	Cape Flats Cemeteries
Urban area:	Cape Town
Source:	Cemeteries
Major contaminants:	Nutrients (e.g. nitrate, phosphate, potassium), bacteria.
Aquifer type:	Cape Flats - unconfined, primary sand aquifer
General findings:	The groundwater table rises during the wet winter season and graves become water logged. Nutrients are released and bacteria thrive in this environment.
Lessons learnt:	Cemeteries should be sited taking into account the geology and water table depth and groundwater quality should be monitored.
References:	Gosling (2001). Engelbrecht (1998) Engelbrecht and Cavé (1997).

Title:	Cape Flats Wastewater Treatment Works
Urban area:	Cape Town
Source:	Unlined sewage sludge drying ponds
Major contaminants:	Phosphorus (>7.5mg/l), ammonium (200mg/l as N).
Aquifer type:	Cape Flats - unconfined, primary sand aquifer
General findings:	Concentrations of contaminants were higher in the vicinity of the unlined sludge ponds, hence leakage/seepage into the aquifer is suspected.
Lessons learnt:	Sludge ponds should be located on impermeable geologies or lined. If not, they should be effectively monitored.
Reference:	City of Cape Town

Title:	Zandvliet Wastewater Treatment Works
Urban area:	Cape Town
Source:	Unlined sewage sludge drying ponds
Major contaminants:	Potassium (>80 mg/l), total nitrogen (>160 mg/l), mostly ammonium.
Aquifer type:	Cape Flats - unconfined, primary sand aquifer
General findings:	A sludge spill in 1996 had a significant, but localised impact on groundwater quality. Nitrate contamination was detected from nearby agricultural activities (septic tanks and livestock), but contamination of groundwater from informal settlements was not detected.
Lessons learnt:	Prompt remediation of spills was effective in minimising the effect on groundwater. Significant pollution arose from past unremediated spills.
Reference:	Parsons and Taljard (2000)

5.2 Case studies of industrial contamination

Title:	Metal plating industry
Urban area:	Cape Town
Source:	Leaks and spills in storage and production areas, improper treatment and disposal of wastes.
Major contaminants:	Cyanide (15-210 mg/kg in soils), and trichloroethene (TCE, 6-4089µg/l). Chromium, nickel, cadmium and zinc are also potential contaminants.
Aquifer type:	Unconfined primary sand aquifer.
General findings:	Removal of contaminated soil and pump-and-treat programme (to control the contamination plume) were successful in decreasing TCE concentrations.
Lessons learnt:	Potentially toxic metal ions react with ligands and alter their behaviour in the subsurface.
Reference:	Morris *et al.* (2000)

Title:	Metal plating industry
Urban area:	Cape Town
Source:	Unlined effluent disposal ponds.
Major contaminants:	Nickel (27.8 mg/l) and copper (21.4 mg/l). Soils are also contaminated with chromium.
Aquifer type:	Weathered and fractured shale.
General findings:	Groundwater contamination was found in the weathered zone near the disposal ponds. Heap leaching was attempted to remove metals from soils.
Lessons learnt:	The clay layer beneath the ponds was not as effective a barrier to groundwater contamination as initially thought.
Reference:	Eichstadt (2000)

Title:	Umbogentweni Industrial Complex
Urban area:	Durban
Source:	Seepage from unlined slimes dams, mercury ponds and buried drums (containing tar and chlorinated hydrocarbons).
Major contaminants:	Chlorinated hydrocarbons (100 mg/l), including 1,2-dichloroethane, tetrachloroethene, trichloroethene, cis-1,2-dichloroethene & vinyl chloride. Sulphate, chloride, ammonium, mercury (<3 µg/l) and high salinity.
Aquifer type:	Shallow primary and deeper weathered secondary aquifers.
General findings:	Both inorganic and organic contamination occur.
Lessons learnt:	Hydraulic containment had to be implemented to avoid plume from reaching an informal settlement close by.
Reference:	Palmer *et al.* (2000)

Title:	Wood treatment plant
Urban area:	Kynsna, outside major metro areas
Source:	Seepage of leachate
Major contaminants:	Arsenic, chromium, copper and phenolic compounds.
Aquifer type:	Unconfined, coastal, primary aquifer.
General findings:	Data indicate that contamination occurred in the immediate surroundings of the poleyard. Chromium and copper had little effect on groundwater, but arsenic concentrations were unacceptable in 9 out of 10 samples.
Lessons learnt:	Creosote is the main contaminant from the pole yard, while metal contamination is less severe.
References:	Parsons (1995) Gibb Africa (1999) Eichstadt (2000)

Title:	Shell Sapref Refinery
Urban area:	Durban
Source:	Underground pipelines that deliver the refinery's finished products to nearby industrial complex.
Major contaminants:	Alkanes and BTEX
Aquifer types:	Shallow primary and deeper weathered secondary aquifers.
General findings:	Noted as the largest petrol spill in the history of South Africa more than 1 million litres of petrol has been recovered from remediation site up to date (ongoing to 2004). Five residences had to be evacuated due to fumes from contaminated soil.
Lessons learnt:	Sound inspections and maintenance techniques are a necessity with regard to underground pipelines
Reference:	Verweij (2003)

Title:	Dow Sentrachem
Urban area:	Chloorkop industrial suburb of Ekurhuleni Metro
Source:	Seepage from wastewaters discharged to a channel from the production facility to the nearby evaporation ponds
Major contaminants:	Chloroform, tetrachloromethane, di-, tri- and tetra-chlorinated benzenes and chlorinated alkanes, hexachlorocyclohexane (HCH), nickel, cobalt, DDT and degradation products (DDD and DDE), 2,4-dichlorophenol, chlorpyrifos ("Dursban"), isomers of the pesticide HCH.
Aquifer type:	Shallow primary and deeper weathered secondary aquifers.
General findings:	Surface and groundwater, as well as soil and sediment, have been contaminated with the contaminants emanating from the discharge channel.
Lessons learnt:	Organophosphates and their degradation products can be very persistent in soil and groundwater even years after the original source was removed.
Reference:	Santillo, *et al.* (2002)

5.3 Case study of petroleum contamination

Title:	Hydrogeology of the Main Karoo Basin
Urban area:	Free State Towns
Source:	Leakage from petrol stations and fuel depots
Major contaminants:	Benzene, Toluene, Ethylbenzene-Xylenes.
Aquifer type:	Weathered fractured rock aquifers.
General findings:	Concentrations several orders above suggested limits. Dissolved phase contamination severe even where no free phase was detected
Lessons learnt:	Low permeability rocks can still cause widespread contaminant plumes. Absence of free phase does not indicate there is no pollution. Even in small towns NAPL pollution can be very problematic.
Reference:	Woodford and Chevalier (eds). (2002)

5.4 Case studies of mining contamination

Title:	Assessment and rehabilitation of reclaimed gold tailings dams areas
Urban area:	Gauteng
Source:	Leakage from tailings dams and waste rock dumps
Major contaminants:	Copper, cobalt, nickel and zinc.
Aquifer type:	Weathered fractured rock aquifers.
General findings:	Tailings dams can contain 10-30kg/ton of sulphide minerals which are prone to generate acid mine drainage.
Lessons learnt:	Acidic conditions mobilize the Cu, Co, Ni, and Zn
Reference:	Rösner *et al.* (2000)

Title:	Current legislation to manage the impacts of mining on groundwater
Urban area:	General overview – not specific to one area
Source:	Waste rock dumps and tailings dams
Major contaminants:	Metals e.g. cobalt, zinc, nickel and copper; other ions (e.g. fluoride) and radioactive elements.
Aquifer type:	Weathered fractured rock aquifers.
General findings:	Waste rock dumps and tailings form an acid generating environment.
Lessons learnt:	Both gold and coal mining contribute to the acid mine drainage by generating an acidic leachate.
Reference:	Cameron-Clarke (1997)

5.5 Waste disposal site case studies

Title:	Vissershok Hazardous Waste Site
Urban area:	Cape Town
Source:	Unlined disposal areas under old evaporation ponds.
Major contaminants:	Sodium (4750 mg/l), chloride (3470 mg/l), sulphate (1530 mg/l), ammonium (1400 mg/l) and potassium (360 mg/l).
Aquifer type:	Shallow, seasonal, unconfined water table in discontinuous sandy layer.
General findings:	Contamination is limited to the shallow aquifer. The deeper confined fractured shale aquifer that is present in the area is not affected by the contamination.
Lessons learnt:	Aquifer vulnerability and groundwater potential should be taken into account before siting such activities.
References:	Tredoux and Cavé (2001)

Title:	Swartklip General Waste Site
Urban area:	Cape Town
Source:	Unlined general waste disposal area.
Major contaminants:	Sodium (410 mg/l), magnesium (70 mg/l), chloride (630 mg/l), nitrate (2.2 mg/l), bicarbonate (2120 mg/l), calcium (240 mg/l), sulphate (50 mg/l), potassium (240 mg/l), boron (0.7 mg/l), total chromium (0.05 mg/l).
Aquifer type:	Cape Flats – unconfined, primary sand aquifer
General findings:	Elevated major ion concentrations and salinity.
Lessons learnt:	The location of this waste disposal site is not suitable as it is contaminating a major aquifer system.
References:	City of Cape Town Cavé (2000)

Title:	Paarl Waste Site
Urban area:	Paarl, outside major metro areas
Source:	Hazardous industrial and domestic waste
Major contaminants:	Potassium (400 mg/l) and ammonium (240 mg/l) near the toe of the landfill.
Aquifer type:	Shallow, unconfined alluvium (Berg River) and deep (25 -30 m), confined, low-yielding aquifer.
General findings:	A groundwater pollution plume is moving towards the Berg River. Contaminant concentrations are low towards the edges of the plume. Groundwater monitoring is continuing.
Lessons learnt:	Problems arose when a housing development was allowed to be situated within 15 m of the closed landfill site.
References:	Eichstadt (2000)

Title:	Leachate from landfill sites
Urban area:	Durban
Source:	4 hazardous waste sites and 16 municipal waste sites.
Major contaminants:	Leachates from old landfills contain high levels of COD and ammonium. Some also have high sulphate and phosphate. No data given for groundwater.
Aquifer types:	Various fractured rock and unconsolidated sand and clay.
General findings:	Major polluting potential arises from COD and ammonium. Heavy metals and cumulative toxins are insignificant.
Lessons learnt:	The landfill engineering and age affect the leachate composition.
Reference:	Ntsele *et al.* (2000)

5.6 Case studies of agricultural contamination

Title:	The quality of surface and groundwater in the rural Western Cape with regard to pesticides
Urban area:	Hex River Valley, Piketberg, Grabow, outside major metro areas
Source:	Agriculture (predominantly vineyards and orchards)
Major contaminants:	Azinphos-methyl, chlorpyrifos, deltamethrin, endosulfan, iprodione, penconazole, prothiofos, simazine, vanmidothion
Aquifer types:	Table Mountain Group
General findings:	Several pesticide species were detected in both surface and groundwaters in the peri-urban agricultural areas around Cape Town metro.
Lessons learnt:	Monitoring of groundwater for pesticides is required, as well as improved management at field level.
Reference:	London *et al.* (2000), Dalvie *et al.* (2003), Solomons *et al.* (2003)

Title:	A preliminary survey of pesticide levels in groundwater from a selected area of intensive agriculture in the Western Cape
Urban area:	Hex River Valley, Western Cape, outside major metro areas
Source:	Agriculture (predominantly vineyards and orchards)
Major contaminants:	Aldicarb, bromopropylate, chlorpyrifos, copper oxychloride, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, dichlorovos, dimethoate, dinocap, diquat, endosulfan, fenamiphos, fenthion, fenvalerate, folpet, glyphosate, hexaconazole, iprodione, mancozeb, MCPA, metaldehyde, methidathion, nuarimol, oryzalen, paraquat, penconazole, pirifenox, propetamphos, propoxur, prothiofos, simazine, vinclozolin
Aquifer types:	Table Mountain Group
General findings:	The preliminary survey did not indicate groundwater contamination, despite high usage of pesticides.
Lessons learnt:	Monitoring with state-of-the-art equipment is required in order to detect low pesticide concentrations in groundwater.
Reference:	Weaver (1993)

Title:	Wheat cultivated lands
Urban area:	Free State
Source:	Agricultural
Major contaminants:	Nitrate
Aquifer type:	Confined, fractured rock aquifer with 3-4m alluvium cover with 30-40m deep boreholes. Shale and dolerite are the main lithological units intersected.
General findings:	Nitrogen from fertilizer is leached to water table. Natural nitrogen is released during ploughing.
Lessons learnt:	The rate of application of fertilizer is not high, but the timing of application was more crucial.
Reference:	Conrad and Colvin (2000)

Title:	Intensive animal husbandry
Urban area:	Cape Town
Source:	Agricultural: vineyards, wheat farming, 1200 cows.
Major contaminants:	Pesticides, fertilizers, nitrate, ammonia, potassium, microbial
Aquifer type:	Shallow, unconfined, occurring within the weathered zone of the cape granite
General findings:	Waste management is not practised efficiently at this site. Breakdown of solid waste separator resulting in excess solid waste in effluent dams and flooding of down slope area resulted from waste slurry overflow.
Lessons learnt:	Farmers should employ proper waste management strategies to avoid unnecessary incidents leading to contamination.
Reference:	Conrad *et al.* (1999)

6. Inventory of potential sources of groundwater contaminants in major urban areas of South Africa

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:

I. 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;

II. Identify the locations of activities and operations that pose the greatest risks to the water supply; and

III. Educate managers and the public about the potential threats to the water supply posed by various activities.

A typical approach to a contaminant inventory will be iterative, starting simple and moving to more complex methods as experience and resources grow. The first step will be to identify the most significant or serious sources of contamination. Activities and land uses that manufacture, produce, store, use, dispose or transport these regulated contaminants within the area will be identified.

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 everything from septic tanks, dry cleaners and underground storage tanks to landfills, urban runoff 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 a complete listing** of all potential sources, since virtually anything spilled or placed on the ground has the potential to leach to groundwater.

The approach taken to compile a groundwater contaminant inventory for South Africa's urban areas was similar to that described in several US regulatory publications. The first step was to identify all possible sources and activities which can pose a threat to groundwater resources in South Africa. Then all *expected/ potential contaminants* (chemicals) *were identified that would result from these* sources. The result was a generic contaminant inventory (or baseline) from which the individual urban centers' inventories were compiled (See sections 6.2-6.5).

The applicable information that was taken from the generic table was verified by means of real data or case studies. A column was added in the tables for specific reference sources. The data used to verify the contaminants were typical from literature searches, which was followed by contacts of individuals at various organizations, such as DWAF, municipalities, water boards and private consulting companies. Contamination incident reports, databases, DWAF publications, consultant reports, internet searches and other relevant publications were typical examples of data used to verify the information. Since it was not possible to cover all urban areas within the scope of this project, detailed information and data were only collected for the major urban centres, namely Johannesburg-Pretoria (Gauteng), Durban (Kwa-Zulu Natal), Cape Town (Western Cape) and Port Elizabeth (Eastern Cape), as being the main areas likely to be affected by pollution.

6.1 Generic Inventory

Type of source	**Expected contaminants**	**Comment**
Urban settlement (Domestic/ Commercial):		
Wastewater treatment	Ammonium, nitrate, potassium, phosphate, chloride, sulphate, COD, diverse industrial chemicals, faecal pathogens, metals	Depending on the type of water treatment process and management of the system, the likelihood of groundwater contamination may increase.
Stormwater/ sewer systems	Ammonium, nitrate, potassium, chloride, sulphate, DOC, hydrocarbons, faecal pathogens, diverse industrial chemicals	Likelihood of groundwater contamination dependant on the type and integrity of the network
On-site sanitation	Nitrate, potassium, chloride, COD, faecal pathogens, phosphate, boron	Present in all urban areas where rapid urbanisation / informal settlement takes place, typical of SA conditions
Cemeteries	Ammonium, potassium, microbial pathogens	Often located on outskirts of urban area
Transport	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH, any other chemicals transported resulting from accidents or spills	Accidents and spills in urban area often cleaned up quickly after reporting
Marine maintenance industry	Solvents; paints; cyanide; acids; VOC emissions; heavy metal sludge; degreasers	Only relevant to coastal urban centers with large port facilities
Railroad yards	Petroleum hydrocarbons; VOCs; BTEX; solvents; fuels; oil and grease; lead; PCBs	Widespread, with long histories
Electricity generation	Sulphate, metals (iron, chromium, manganese, lead, nickel), alkali, salinity, PCBs, PAHs	Widespread, with long histories
Hospitals / Health Care	Formaldehyde; radionuclides; photographic chemicals; solvents; mercury; ethylene oxide; chemotherapy chemicals	Waste often not disposed of or incinerated on site
Incinerators	Dioxin; various municipal and industrial waste	Most incinerators are permitted and strict compliance to storage of waste and ash must be followed
General/ Domestic waste sites	Ammonium, salinity (sodium, chloride, sulphate), DOC, methane, lead, mercury	Most legal domestic waste sites are located on outskirts of urban area due to aesthetic reasons, groundwater contamination will vary with size, type and management of each site

Type of source	**Expected contaminants**	**Comment**
Hazardous waste sites	Ammonium, salinity, DOC, heavy metals, methane	Only 6 H:H sites in SA, all permitted. There are however private H:H sites.
Workshops (Mechanical and electrical)	Polyaromatic hydrocarbons, diesel, benzene, alkanes, acids, aluminum, arsenic, beryllium, cadmium, lead, mercury, nickel, chlorinated solvents	Spills and wash water directed to sewers or stormwater drains
Petrol Service Stations (Underground Storage Tanks)	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH	Leakage from UST common due to corrosion of systems
Photographic manufacturing and uses	*Silver bromide; methylene chloride; solvents; photographic products*	*Chemicals flushed to sewer network*
Research and educational institutions	Inorganic acids; organic solvents; metals and metal dust; photographic waste; waste oil; paint; heavy metals; pesticides	Chemicals flushed to sewer network
Printing industry	Silver; acids; waste oils; toluene; MEK; xylene, TCE	Very common industry widely distributed throughout urban area but often chemicals are flushed to sewer network
Dry cleaning activities	VOCs such as chloroform and tetrachloroethane; various solvents; spot removers; fluorocarbon 113	Spills often occur at chemical storage area and below machinery.
Agriculture:		
Agriculture (General and crop cultivation)	Volatile organic compounds (VOC); arsenic, copper, carbon tetrachloride, ethylene dibromide, and methylene chloride; pesticides; insecticides; herbicides; grain fumigants	Activities mostly irrigation crop cultivation, some vineyards (Cape Town) but not common within urban boundaries
Abattoir	DOC, nutrients, bacterial pathogens	Located on outskirts of urban area due to aesthetic reasons.
Feedlot/ poultry farms	DOC, nutrients (organic nitrate), bacterial pathogens	Located on outskirts of urban area due to aesthetic reasons.
Mining:		
Metal (predominately gold) and coal mining	Sulphate, acid, metals (iron, chromium, manganese, lead, nickel, uranium), salinity, radioactivity, petroleum hydrocarbons, chemicals/ reagents used in benefiaction processes	Potential for groundwater contamination high but not often found within urban area (except Gauteng)
Diamond, sand, calcrete and gravel	Petroleum hydrocarbons, oil and greases	Located on outskirts of urban areas.
Non-metallurgical Industries:		
Adhesives and sealants	Benzene, toluene, methyl-ethyl ketone (MEK)	Most of these types of industries are relative small.

Type of source	Expected contaminants	Comment
Agricultural Chemicals (fertilizers, herbicides, pesticides)	Ammonia, arsenic, chlorides, lead, phosphates, potassium, nitrates, sulphur; Arsenic, carbamates, chlorinated insecticides, cyanides, ethylbenzene, lead, naphthalene, organophosphates, phenols, phthalates, toluene, xylene, Dioxin; metals; herbicides	Not a common industry, limited to large industrial premises, but mobility and type of contaminants pose a great contaminant risk to groundwater.
Food and beverage manufacturing	Chlorine, chlorine dioxide, nitrate/nitrite, pesticides, biogenic amines, methane, dioxins, bacteria, lead	Very common type of industry but only certain types pose groundwater contamination risk (e.g. breweries, dairies).
Leather manufacturing	Toluene; benzene; arsenic, chromium, cadmium, sulphate	Very few large tanneries in SA, number of small-scale operations, but due to nature of chemicals used the risk for groundwater contamination is great.
Pharmaceuticals and cosmetics manufacturing	Alcohols, benzoates, bismuth, dyes, glycols, mercury, mineral spirits, sulphur, dichlorobenzene, methylene chloride, nitrate	Most of this type of industries are relative small and does not manufacture own base chemicals.
Non-metallic Mineral products	Asbestos	Not common type of industry.
Paint/ink manufacturing and coatings	Acetates, acrylates, alcohols, aluminum, cadmium, chlorinated solvents, chromium,cyanides, glycol ethers, ketones, lead, mercury, methylene chloride, mineral spirits,nickel, phthalates, styrene, terpenes, toluene, 1,4-dioxane, ammonia, anthraquinones, arsenic, benzidine, chromium, ethyl acetate, hexane, nickel, oxalic acid, phenol	Industries vary between small-scale to very large scale. Larger manufacturing (opposed to "mixing") industries will pose greater threat to groundwater.
Rubber and plastics	Acrylonitrile, antimony, benzene, butadiene, cadmium, chloroform, chromium, dichloroethylenes, lead, phenols, phthalates, styrene, sulphur, vinyl chloride, toluene, heptane, formaldehyde	Industries vary between small-scale to very large scale. Rubber conversion industry pose greater threat than plastic conversion.
Paper/ pulp industry	Acrylates, chlorinated solvents, dioxins, mercury, phenols, styrene, sulphur; furans; chloroform, mercury, sulphate, potassium dichromate	Industries vary between small-scale to very large scale. Paper mills pose greater threat to groundwater but often located on outskirts of urban area due to aesthetic reasons.
Textile manufacture	Ammonium, arsenic, cadmium, chromium, ethyl acetate, nickel, hexane, oxalic acid, phenols, phthalates, toluene, lead	Common industry varying in type and size. Some more likely to cause groundwater contamination (e.g. wool washing)
Wood processing and preserving	Ammonia, arsenic, chromium, copper, creosote, dioxins, polyaromatic hydrocarbons, pentachlorophenol, phenol, tri-n-butyltin oxide, PCB; PAHs; beryllium	Spills and accidents more likely the greater the operation.

Type of source	Expected contaminants	Comment
Manufacturing - Chemicals	VOCs (Acetylene, Benzene, Butane, Chloroform, Ethyl Alcohol, and Methane), PAHs, ammonia, chloroform, tetrachloromethane, di-, tri- and tetra-chlorinated benzenes, chlorinated alkanes, hexachlorocyclohexane (HCH), cobalt, nickel, DDT (DDD and DDE), 2,4-dichlorophenol, HCH, ketones, toluene, xylene; carbon tetrachloride, chlorofluoroethanes, dichloroethylene, methylene chloride, PCE, TCE, vinyl chloride, 1,1,1-trichloethane	Usually large industrial premises, variety of base and more complex chemicals (used and produced), often have own waste disposal areas/ponds, which pose great contaminant risk to groundwater.
Munitions manufacturing	Nitrate, sulphate, chromium, copper, boron, lead, antimony and phosphate	Not a common industry, limited to large industrial premises, but mobility and type of contaminants pose a great contaminant risk to groundwater.
Glass manufacturing	Arsenic; lead	Not a common industry, with limited contaminant risk to groundwater.
Metallurgical and Metal Products Manufacturing:		
Metallurgical	Acids, mineral oils, sulphur, cyanide, metals (including aluminum, beryllium, cadmium, chromium, cobalt, iron, strontium, tin, titanium, vanadium, lead, copper, mercury, nickel, zinc and arsenic); dioxins and furans; organic solvents; chlorobenzenes; PCBs, asbestos, flouride	Usually large industrial premises, variety chemicals used, often have own waste disposal areas/ ponds which pose great contaminant risk to groundwater.
Electrical and electrical products manufacturing	Petroleum hydrocarbons, isopropanol, methanol, salinity, trichloroethylene, arsenic, silane, metals	Most of these types of industries are relative small.
Other metal product manufacturing	Various metals such as cadmium, beryllium chromium, cyanide, copper, silver, tin, zinc and nickel; benzene, trichloroethane and trichloroethylene, VOCs; dioxin; degreasing agents; waste oils	Diverse
Automotive manufacturing	Various metals such as cadmium, beryllium chromium, cyanide, copper, silver, tin, zinc and nickel, hydrocarbons, solvents, paints (see above)	Little waste generation of groundwater importance; spillage, accidents, illegal disposal
Auto Salvage/Metal Recyclers	Metals, asbestos, PCBs, hydraulic fluids and lubricating oils, fuels, and solvents	Most of these types of industries are relative small.
Automotive refinishing and repair	Paint; scrap metal; waste oils; toluene, acetone, perchloroethylene, xylene, gasoline and diesel fuel, carbon tetrachloride, and hydrochloric and phosphoric acid	Spills and wash water directed to sewers or stormwater drains

6.2 Gauteng

Type of source	Expected contaminants	Examples/ Comments	Reference
Urban settlement (Domestic/ Commercial):			
Wastewater treatment	Ammonium, nitrate, potassium, phosphate, chloride, sulphate, COD, diverse industrial chemicals, faecal pathogens, metals	No figure is available on the number of waste water works in Gauteng. 345,000 cubic meters of effluent is treated daily at several water treatment works in Pretoria	http://www.tshwane.gov.za/ http://www.statssa.gov.za/
Stormwater/ sewer systems	Ammonium, nitrate, potassium, chloride, sulphate, DOC, hydrocarbons, faecal pathogens, diverse industrial chemicals		
On-site sanitation	Nitrate, potassium, chloride, COD, faecal pathogens, phosphate, boron	About 88% of Gauteng households used a flush/chemical toilet in 1999, with 10% using a pit latrine and 1% using a bucket or other system. (In 1996, 83% used a flush toilet in Gauteng.) The bucket system will be eradicated by 2007 in the whole of Gauteng. 13% of Pretoria have on-site sanitation.	http://www.tshwane.gov.za/ http://www.statssa.gov.za/
Cemeteries	Ammonium, potassium, microbial pathogens	No numbers available.	
Transport	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH, any other chemicals transported resulting from accidents or spills	Several airports commercial and freight, incl. Johannesburg International (busiest in Africa)	
Railroad yards	Petroleum hydrocarbons; VOCs; BTEX; solvents; fuels; oil and grease; lead; PCBs		
Electricity generation	Sulphate, metals (iron, chromium, manganese, lead, nickel), alkali, salinity, PCBs, PAHs	Kelvin Power Station (Kempton Park)	
Hospitals / Health Care	Formaldehyde; radionuclides; photographic chemicals; solvents; mercury; ethylene oxide; chemotherapy chemicals	No numbers available.	
Incinerators	Dioxin; various municipal and industrial waste	Eleven incinerators proposed/ commissioned varying from rubber, medical and toxic waste incinerators	http://www.groundwork.org.za
General/ Domestic waste sites	Ammonium, salinity (sodium, chloride, sulphate), DOC, methane, lead, mercury	Twelve landfills located in the City of Johannesburg	

Type of source	**Expected contaminants**	**Examples/ Comments**	**Reference**
Hazardous waste sites	Ammonium, salinity, DOC, heavy metals, methane	Only one site classified as H:H located on the East Rand - Holfontein	
Workshops (Mechanical and electrical)	Polyaromatic hydrocarbons, diesel, benzene, alkanes, acids, aluminium, arsenic, beryllium, cadmium, lead, mercury, nickel, chlorinated solvents	Many located within semi-residential areas as well as in the industrial area	
Petrol Service Stations (Underground Storage Tanks)	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH	Approximately 900 service stations in Vaal triangle; 1300 in greater Johannesburg	Randwater (1998)
Photographic manufacturing and uses	Silver bromide; methylene chloride; solvents; photographic products	No numbers available.	
Research and educational institutions	Inorganic acids; organic solvents; metals and metal dust; photographic waste; waste oil; paint; heavy metals; pesticides	Many educational facilities (e.g. schools, technikons, universities) 207 research laboratories and 45 industrial research facilities	Randwater (1998)
Printing industry	Silver; acids; waste oils; toluene; MEK; xylene, TCE	More than 400 printing industries in Gauteng	
Dry cleaning activities	VOCs such as chloroform and tetrachloroethane; various solvents; spot removers; fluorocarbon 113	Approximately 3000 in Gauteng	www.serviceseta.org.za
Agriculture:			
Agriculture (General and crop cultivation)	Volatile organic compounds (VOC); arsenic, copper, carbon tetrachloride, ethylene dibromide, and methylene chloride; pesticides; insecticides; herbicides; grain fumigants	Twenty two percent of the province is used to produce crops such as maize, sorghum, sunflowers, beans and deciduous fruit; 19% is grazing land for dairy cattle and sheep. Approximately 200 nursery/ vegetable producers in Gauteng	www.nbi.ac.za/landdeg, Randwater (1998)
Abattoir	DOC, nutrients, bacterial pathogens	Three abattoirs identified in Vaal triangle; 10in Johannesburg and East Rand	Randwater (1998)
Feedlot/ poultry farms	DOC, nutrients (organic nitrate), bacterial pathogens	Three livestock feedlots and 8 poultry farms identified in Vaal triangle, 20 in greater Johannesburg, 31 in Pretoria	Randwater (1998)
Mining:			
Metal (predominately gold) and coal mining	Sulphate, acid, metals (iron, chromium, manganese, lead, nickel, uranium), salinity, radioactivity, petroleum hydrocarbons, chemicals/ reagents used in benefiaction processes	One hundred and fifty nine mines (some still active) in City of Johannesburg	www3.iclei.org

Type of source	Expected contaminants	Examples/ Comments	Reference
Diamond, sand, calcrete and gravel	Petroleum hydrocarbons, oil and greases	Approximately. 10 quarries/ crushers in Vaal Triangle, 47 in greater Johannesburg, 30 in Pretoria, Premier Diamond Mine	Randwater (1998)
Non-metallurgical Industries:			
Adhesives and sealants	Benzene, toluene, methyl-ethyl ketone (MEK)	Thirty six manufacturers identified in Gauteng	DWAF (1998)
Agricultural Chemicals (fertilisers, herbicides, pesticides)	Ammonia, arsenic, chlorides, lead, phosphates, potassium, nitrates, sulphur; Arsenic, carbamates, chlorinated insecticides, cyanides, ethylbenzene, lead,naphthalene, organophosphates, phenols, phthalates, toluene, xylene, Dioxin; metals; herbicides	Approximately 31 pesticide/ herbicide manufacturers in Gauteng (e.g. I C I Kynoch Agrochemicals (Sandton); 3 historical fertiliser manufacturers associated with explosive manufacturing (Chloorkop and Modderfontein), 9 smaller fertiliser companies located on the East Rand, Organic fertiliser: Atlas misstowwe (Meyerton)	DWAF (1998); Randwater (1998)
Food and beverage manufacturing	Chlorine, chlorine dioxide, nitrate/nitrite, pesticides, biogenic amines, methane, dioxins, bacteria, lead	Breweries (approximately 20 in Gauteng), ice cream manufacturers (23 in greater Johannesburg) and dairy producers (64 in greater Johannesburg) are among the highest waste generators in this sector; 20 dairy producers and 8 breweries and soft drink manufactures in Vaal triangle. 30 soft drink producers in greater Johannesburg, 6 in Pretoria, 20 dairy producers and 8 breweries in Pretoria,	DWAF (1998); Randwater (1998)
Leather manufacturing	Toluene; benzene; arsenic, chromium, cadmium, sulphate	Six major leather tanneries identified in Gauteng	DWAF (1998)
Pharmaceuticals and Cosmetics manufacturing	Alcohols, benzoates, bismuth, dyes, glycols, mercury, mineral spirits, sulphur, dichlorobenzene, methylene chloride, nitrate	Gauteng is the major producer of cosmetics (approximately 65) and pharmaceuticals (approximately 67)	DWAF (1998)
Non-metallic Mineral products	Asbestos	Everite building materials	DWAF (1998)
Paint/ink manufacturing and coatings	Acetates, acrylates, alcohols, aluminium, cadmium, chlorinated solvents, chromium, cyanides, glycol ethers, ketones, lead, mercury, methylene chloride, mineral spirits, nickel, phthalates, styrene, terpenes, toluene, 1,4-dioxane, ammonia, anthraquinones, arsenic, benzidine, chromium, ethyl acetate, hexane, nickel, phenol	Approximately 150 producers in Gauteng	DWAF (1998); Randwater (1998)

Type of source	Expected contaminants	Examples/ Comments	Reference
Rubber and plastics	Acrylonitrile, antimony, benzene, butadiene, cadmium, chloroform, chromium, dichloroethylenes, lead, phenols, phthalates, styrene, sulphur, vinyl chloride, toluene, heptane, formaldehyde	Approximately 120 producers of rubber products and 550 producers of plastic products in Gauteng. Polifin and Dow Sentrachem are dominant producers of primary feedstock chemicals for this sector. 10 plastic product manufactures in Vaal triangle.	DWAF (1998); Randwater (1998)
Paper/ pulp industry	Acrylates, chlorinated solvents, dioxins, mercury, phenols, styrene, sulphur; furans; chloroform, mercury sulphate, potassium dichromate	Approximately 70 located in Gauteng, mainly consists of packaging and wrapping manufactures e.g. Crystal Paper Mill in Heidelberg	DWAF (1998); Randwater (1998)
Textile manufacture	Ammonium, arsenic, cadmium, chromium, ethyl acetate, nickel, hexane, oxalic acid, phenols, phthalates, toluene, lead	Activities include the production of synthetic fibres and yarns (especially polyester, nylon and acrylic), the manufacture of home textiles, automotive textiles, apparel textiles and technical/industrial textiles. Approximately 20 companies in Gauteng; 10 textile industries in Vaal triangle	DWAF (1998); Randwater (1998)
Wood processing and preserving	Ammonia, arsenic, chromium, copper, creosote, dioxins, polyaromatic hydrocarbons, pentachlorophenol, phenol, tri-n-butyltin oxide, PCB; PAHs; beryllium	Small portion of the section is represented in Gauteng (approximately 40 companies mostly located on the East Rand)	DWAF (1998); Randwater (1998)
Manufacturing - Chemicals	VOCs(Acetylene, Benzene, Butane, Chloroform, Ethyl Alcohol, and Methane), PAHs, and semi-volatile organic compounds, Ammonia,Chloroform, tetrachloromethane, di-, tri- and tetra-chlorinated benzenes, chlorinated alkanes, hexachlorocyclohexane (HCH), cobalt, nickel, DDT (DDD and DDE), 2,4-dichlorophenol, HCH, chlorpyrifos ("Dursban")	Kynoch, NCP, Henkel, Trochem, Rolfes, Reef Chemicals, Sanachem, Dow Sentrachem (Chloorkop); aprox. 300 companies located in (respectively in abundance) East Rand, Johannesburg, Alberton, West Rand (Champdor). Twenty five in Pretoria	Santillo (2002); DWAF (1998); Randwater (1998)
Solvents (nonchlorinated)	Acetates, alcohols, benzene, ethylbenzene, ketones, toluene, xylene	Dow Sentrachem (Chloorkop)	
Solvents, chlorinated	Carbon tetrachloride, chlorofluoroethanes, dichloroethylene, methylene chloride, PCE, TCE, vinyl chloride, 1,1,1-trichloethane	Dow Sentrachem (Chloorkop)	
Munitions manufacturing	Nitrate, sulphate, chromium, copper, boron, lead, antimony and phosphate	Lion Match (Isando), AEL (Modderfontein)	DWAF (1998)
Glass manufacturing	Arsenic; lead	Glass South Africa (GSA) (Edenvale)	
Non-metallic Mineral products - Cement	Salinity, sodium, calcium, dioxins	PPC cement factory (There is a threat of incorporating waste burning in the process, irresponsible handling of the waste could lead to groundwater pollution)	http://www.earthlife.org.za/index.html

Type of source	Expected contaminants	Examples/ Comments	Reference
Metallurgical and Metal Products Manufacturing:			
Metallurgical	Acids, mineral oils, sulphur, cyanide, metals (including aluminium, beryllium, cadmium, chromium, cobalt, iron, strontium, tin, titanium, vanadium, lead, copper, mercury, nickel, zinc and arsenic); dioxins and furans; organic solvents; chlorobenzenes; PCBs, asbestos, fluoride	Included in this group of industries are several battery manufacturers, steel producers and various other metal producers. Many of these are located on the East Rand (Benoni, Boksburg) or in the Vaal Triangle (Vanderbijl, Meyerton) for example Metalloys and Iscor	DWAF (1998)
Electrical and electrical products manufacturing	Petroleum hydrocarbons, isopropanol, methanol, salinity, trichloroethylene, arsenic, silane, metals	More than 250 companies in Gauteng	DWAF (1998)
Other metal product manufacturing	Various metals such as cadmium, beryllium chromium, cyanide, copper, silver, tin, zinc and nickel; benzene, trichloroethane and trichloroethylene, VOCs; dioxin; degreasing agents; waste oils	This group include galvanising, electroplating, engineering works and manufacturing of all steel/ metal products, machinery, etc. Several hundred of these industries are located in Gauteng, many of which is located in the Vaal triangle close to the Iscor Steel plant in Vanderbijl.	DWAF (1998)
Automotive manufacturing	Various metals such as cadmium, beryllium chromium, cyanide, copper, silver, tin, zinc and nickel, hydrocarbons, solvents, paints (see above)	NissanSA (Pty) Ltd (Rosslyn, Pretoria); Ford Motor Company of South Africa (Silverton, Pretoria); BMW SA (Pty)Ltd (Rosslyn, Pretoria)	
Auto Salvage/Metal Recyclers	Metals, asbestos, PCBs, hydraulic fluids and lubricating oils, fuels, and solvents	No numbers available.	
Automotive refinishing and repair	Paint; scrap metal; waste oils; toluene, acetone, perchloroethylene, xylene, gasoline and diesel fuel, carbon tetrachloride, and hydrochloric and phosphoric acid	Many located within semi-residential areas as well as in the industrial area	

6.3 Durban

Type of source	Expected contaminants	Examples/ Comments	Reference
Urban settlement (Domestic/ Commercial):			
Wastewater treatment	Ammonium, nitrate, potassium, phosphate, chloride, sulphate, COD, diverse industrial chemicals, faecal pathogens, metals	Up to 420,000 cfu 100 ml-1 of E. coli, 200 mg l-1 COD and 42 mg l-1 PV4; pH between 6.6 and 10.1 in Durban surface waters.	Rutter *et al.* (2003)
Stormwater/ sewer systems	Ammonium, nitrate, potassium, chloride, sulphate, DOC, hydrocarbons, faecal pathogens, diverse industrial chemicals		
On-site sanitation	Nitrate, potassium, chloride, COD, faecal pathogens, phosphate, boron		
Cemeteries	Ammonium, potassium, microbial pathogens		
Transport	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH, any other chemicals transported resulting from accidents or spills	Airport commercial and freight, Durban International	
Railroad yards	Petroleum hydrocarbons; VOCs; BTEX; solvents; fuels; oil and grease; lead; PCBs	Spoornet dominant role in sourcing traffic in and out of the Port of Durban, 2000 kms of railway line between Durban and Gauteng. Traffic conveyed consists of liquids, agricultural products, timber, cement, metals and minerals, as well as coal and ore.	http://www.kzn-deat.gov.za/pub/kzn_review.doc
Marine maintenance industry	Solvents; paints; cyanide; acids; VOC emissions; heavy metal sludge; degreasers	Internationally acclaimed harbour facilities	
Hospitals / Health Care	Formaldehyde; radionuclides; photographic chemicals; solvents; mercury; ethylene oxide; chemotherapy chemicals	See incinerators.	
Incinerators	Dioxin; various municipal and industrial waste	Medical waste incinerated from over 70% of the hospitals in KwaZulu Natal, clinics and veterinary clinics. Located in Prospecton and Ixopo. 135 t/ month. Some hospitals have medical incinerators on site.	www.ceroi.net/reports/durban/index.htm
General/ Domestic waste sites	Ammonium, salinity (sodium, chloride, sulphate), DOC, methane, lead, mercury	Four (Bisasar Road (monitoring committee for impacts from this site), Mariannhill, Mpumalanga and La Mercy) 1.4 million tonnes of waste is landfilled annually	www.ceroi.net/reports/durban/index.htm

Type of source	Expected contaminants	Examples/ Comments	Reference
Hazardous waste sites	Ammonium, salinity, DOC, heavy metals, methane	Hazardous wastes generated in the DMA are landfilled in low hazard (H:h) landfill sites. No high hazard (H:H) site in the DMA or province, small quantity of high hazard waste (approx 200 tonnes per annum) is exported to high hazard (H:H) landfill sites in Gauteng and the Eastern Cape.	www.ceroi.net/reports/durban/index.htm
Workshops (Mechanical and electrical)	Polyaromatic hydrocarbons, diesel, benzene, alkanes, acids, aluminium, arsenic, beryllium, cadmium, lead, mercury, nickel, chlorinated solvents	No numbers available.	
Petrol Service Stations (Underground Storage Tanks)	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH	No numbers available.	
Photographic manufacturing and uses	Silver bromide; methylene chloride; solvents; photographic products	No numbers available.	
Research and educational institutions	Inorganic acids; organic solvents; metals and metal dust; photographic waste; waste oil; paint; heavy metals; pesticides	Many educational facilities (e.g. schools, technikons, universities) No figures available on number of laboratories	
Printing industry	Silver; acids; waste oils; toluene; MEK; xylene, TCE		
Dry cleaning activities	VOCs such as chloroform and tetrachloroethane; various solvents; spot removers; fluorocarbon 113	Estimated 2000 companies in the KwaZulu Natal	www.serviceseta.org.za
Agriculture:			
Agriculture	Volatile organic compounds (VOC); arsenic, copper, carbon tetrachloride, ethylene dibromide, and methylene chloride; pesticides; insecticides; herbicides	About 6% of the Durban Bay catchment was under agriculture, comprising mostly subsistence farming, commercial sugar cane, commercial forest, and improved grasslands	www.environment.gov.za/soer/estuary/catch/durbanbay.html
Abattoir	DOC, nutrients, bacterial pathogens	No numbers available.	
Feedlot/ poultry farms	DOC, nutrients (organic nitrate), bacterial pathogens	No numbers available.	
Mining:			
Shale, sandstone and granite	Petroleum hydrocarbons, oil and greases	No numbers available.	

Type of source	**Expected contaminants**	**Examples/ Comments**	**Reference**
Non-metallurgical Industries:			
Petroleum refining and reuse. Also Enref refiniry	Petroleum hydrocarbons; benzene, toluene, ethylbenzene, xylene (BTEX); fuels; oil and grease	There have been 23 major incidents at the South Durban Sapref plant in less than four years, including the world's largest underground oil spill (more than 1 mil litres, 6 houses evacuated). Many spills from 6 underground pipelines that run underground through residential areas and industrial parks. Also Enref (connected to Sapref with pipelines), FSS Refiners (liquid heating fuel products)	Gravelet-Blondin (2003); www.foenl.org
Adhesives and sealents	Benzene, toluene, Methyl-Ethyl Ketone (MEK)	Twelve companies located in KwaZulu Natal	DWAF (1998)
Agricultural Chemicals (fertilisers, herbicides, pesticides)	Ammonia, arsenic, chlorides, lead, phosphates, potassium, nitrates, sulphur; Arsenic, carbamates, chlorinated insecticides, cyanides, ethylbenzene, lead, naphthalene, organophosphates, phenols, phthalates, toluene, xylene, Dioxin; metals; Tebuthiuron, Monosodium-methyl arsenate, Diuron, Aldicarb, Carbamates	Fertiliser number unknown - E.g. Neutrog (process poultry manure); Sanachem - Dow Agrichemicals,	
Food and beverage manufacturing	Chlorine, chlorine dioxide, nitrate/nitrite, pesticides, biogenic amines, methane, dioxins, bacteria, lead	Several breweries (incl. SAB), dairies (incl. Clover, Dairybelle), centre of national sugar industry - 18% of manufacturing in DMA (Illovo, Hullet)	DWAF (1998); www.durban.gov.za/
Leather manufacturing	Toluene; benzene; arsenic, chromium, cadmium, sulphate	Small scale operations associated with footwear manufacturing	www.ceroi.net/reports/durban/index.htm
Pharmaceuticals and Cosmetics manufacturing	Alcohols, benzoates, bismuth, dyes, glycols, mercury, mineral spirits, sulphur, dichlorobenzene, methylene chloride, nitrate	Approximately 20 companies e.g. Unilever, Smith and Nephew, Pfhizer	
Paint/ink manufacturing and coatings	Acetates, acrylates, alcohols, aluminum, cadmium, chlorinated solvents, chromium, cyanides, glycol ethers, ketones, lead, mercury, methylene chloride, mineral spirits, nickel, phthalates, styrene, terpenes, toluene, 1,4-dioxane, ammonia, anthraquinones, arsenic, benzidine, chromium, ethyl acetate, hexane, nickel, oxalic acid, Perchloroethylene (PCE); Trichloroethylene (TCE); Dichloromethane; 1,1,1Trichloroethane (TCA); 1,4-Dioxane; 2,4,6-trichlorophenol and pentachlorophenol	Approximately 30 companies in KwaZulu Natal e.g. Plascon, Dulux, Solchem	Fennemore (2003); DWAF (1998)
Rubber and plastics	Acrylonitrile, antimony, benzene, butadiene, cadmium, chloroform, chromium, dichloroethylenes, lead, phenols, phthalates, styrene, sulphur, vinyl chloride, toluene, heptane, formaldehyde	Approximately 37 companies E.g. Industrial Urethanes, Dunlop, Trentyre	DWAF (1998)

Type of source	Expected contaminants	Examples/ Comments	Reference
Paper and cardboard industry	Acrylates, chlorinated solvents, dioxins, mercury, phenols, styrene, sulphur; furans; chloroform, mercury sulphate, potassium dichromate	More than 40 companies including packaging manufacturers and mills - e.g. Sappi, Mondi, Nampak	DWAF (1998)
Textile manufacture	Ammonium, arsenic, cadmium, chromium, ethyl acetate, nickel, hexane, oxalic acid, phenols, phthalates, toluene, lead	Hammersdale cross-sectional waste mininmisation club, with mainly textiles, chemical manufacturers, the Hammarsdale Wastewater Treatment Works and a chicken abattoir	www.nu.ac.za/wasteminclubs/
Wood processing and preserving	Ammonia, arsenic, chromium, copper, creosote, dioxins, polyaromatic, hydrocarbons, pentachlorophenol, phenol, tri-n-butyltin oxide, PCB; PAHs; beryllium	Approximately 40 companies but mostly located on outer skirts of the industrial areas	DWAF (1998)
Manufacturing - Chemicals	VOCs (Acetylene, Benzene, Butane, Chloroform, Ethyl Alcohol, and Methane). PAHs, and semi-volatile organic compounds, Ammonia, Chloroform, tetrachloromethane, di-, tri- and tetra-chlorinated benzenes, chlorinated alkanes, hexachlorocyclohexane (HCH), cobalt, nickel, DDT (DDD and DDE), 2,4-dichlorophenol, HCH, mercury	Comprises 20% of all manufacturing in DMA for example AECI complex Umbogintwini (several specialised chemical producers); Thor Chemicals (Cato Ridge) houses more than 3 500 tons of mercury-containing wastes.	www.greenpeace.org; DWAF (1998); www.durban.gov.za/; Gravelet-Blondin (2003)
Solvents (nonchlorinated)	Acetates, alcohols, benzene, ethylbenzene, ketones, toluene, xylene		
Solvents, chlorinated	Carbon tetrachloride, chlorofluoroethanes, dichloroethylene, methylene chloride, PCE, TCE, vinyl chloride, 1,1,1-trichloethane		
Munitions manufacturing	Nitrate, sulphate, chromium, copper, boron, lead, antimony and phosphate	At the AECI complex explosives used to be manufactured	
Metallurgical and Metal Products Manufacturing:			
Metallurgical and Metal Products Manufacturing:	Acids, mineral oils, sulphur, cyanide, metals (including aluminium, beryllium, cadmium, chromium, cobalt, iron, strontium, tin, titanium, vanadium, lead, copper, mercury, nickel, zinc and arsenic); dioxins and furans; chlorobenzenes; PCBs, asbestos, flouridebenzene, trichloroethane and trichloroethylene, VOCs; dioxin; degreasing agents; waste oils	Twenty nine members in a waste minimisation club, 23 of which are electroplaters; 3, galvanisers; and 3, powder coaters.	www.nu.ac.za/wasteminclubs/
Automotive manufacturing	Various metals such as cadmium, beryllium chromium, cyanide, copper, silver, tin, zinc and nickel, hydrocarbons, solvents, paints	Several truck and bus assembly companies (e.g. Serco) and Toyota SA	DWAF (1998)
Automotive parts manufacturing	Various metals such as cadmium, beryllium chromium, cyanide, copper, silver, tin, zinc and nickel, hydrocarbons, solvents	Many companies in support of the automotive manufacturing	

Type of source	Expected contaminants	Examples/ Comments	Reference
Auto Salvage/Metal Recyclers	Metals, asbestos, PCBs, hydraulic fluids and lubricating oils, fuels, and solvents	No numbers available.	
Automotive refinishing and repair	Paint; scrap metal; waste oils; toluene, acetone, perchloroethylene, xylene, gasoline and diesel fuel, carbon tetrachloride, and hydrochloric and phosphoric acid	Many located within semi-residential areas as well as in the industrial area	

6.4 Cape Town

Type of source	Expected contaminants	Examples/ Comments	Reference
Urban settlement (Domestic/ Commercial):			
Wastewater treatment	Ammonium, nitrate, potassium, phosphate, chloride, sulphate, COD, diverse industrial chemicals, faecal pathogens, metals	Twenty one treatment plants in CMC	www.capetown.gov.za
Stormwater/ sewer systems	Ammonium, nitrate, potassium, chloride, sulphate, DOC, hydrocarbons, faecal pathogens, diverse industrial chemicals	Estimated 7200 dwellings without operational stormwater drainage	www.capetown.gov.za
On-site sanitation	Nitrate, potassium, chloride, COD, faecal pathogens, phosphate, boron	10.5% of dwellings have no waterborne sanitation	www.capetown.gov.za
Cemeteries	Ammonium, potassium, microbial pathogens	No numbers available.	
Transport	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH, any other chemicals transported resulting from accidents or spills	Airport commercial and freight, Cape Town International	
Railroad yards	Petroleum hydrocarbons; VOCs; BTEX; solvents; fuels; oil and grease; lead; PCBs		
Marine maintenance industry	Solvents; paints; cyanide; acids; VOC emissions; heavy metal sludge; degreasers	International acclaimed harbour facilities	
Electricity generation	Radioactive waste, salinity, PCBs	Radioactive fuels for Koeberg nuclear power plant are stored on-site. In 1996/97, 1045 m^3 of low-level waste and 515 m^3 of inter-mediate level waste, were generated. High level waste is stored on site in pools. Acacia provides back-up electrical supply to Koeberg.	www.capetown.gov.za

Type of source	Expected contaminants	Examples/ Comments	Reference
Hospitals / Health Care	Formaldehyde; radionuclides; photographic chemicals; solvents; mercury; ethylene oxide; chemotherapy chemicals	Quantity incinerated estimated at 1700 t/a. Estimated 30% of medical waste not disposed of at permitted medical waste incinerators.	www.capetown.gov.za
Incinerators	Dioxin; various municipal and industrial waste	Two medical waste incinerators, Enviroserv (Vissershok) and BCL (Delft). Other medical waste incinerators are linked to hospitals. (See Hospitals/ health care)	www.capetown.gov.za
General/ Domestic waste sites	Ammonium, salinity (sodium, chloride, sulphate), DOC, methane, lead, mercury	Seven general sites; 37 known closed landfill sites throughout the CMC	www.capetown.gov.za
Hazardous waste sites	Ammonium, salinity, DOC, heavy metals, methane	Two sites at Vissershok H:H	www.capetown.gov.za
Workshops (Mechanical and electrical)	Polyaromatic hydrocarbons, diesel, benzene, alkanes, acids, aluminium, arsenic, beryllium, cadmium, lead, mercury, nickel, chlorinated solvents	No numbers available.	
Petrol Service Stations (Underground Storage Tanks)	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH	No numbers available.	
Photographic manufacturing and uses	Silver bromide; methylene chloride; solvents; photographic products	No numbers available.	DEAT (2003)
Research and educational institutions	Inorganic acids; organic solvents; metals and metal dust; photographic waste; waste oil; paint; heavy metals; pesticides	Many educational facilities (e.g. schools, technikons, universities)	
Printing industry	Silver; acids; waste oils; toluene; MEK; xylene, TCE	86% of all book printers and 35% of the total printing industry are located in the Cape	
Dry cleaning activities	VOCs such as chloroform and tetrachloroethane; various solvents; spot removers; fluorocarbon 113	Estimated 750 companies in the Western Cape	www.serviceseta.org.za
Agriculture:			
Agriculture	Volatile organic compounds (VOC); arsenic, copper, carbon tetrachloride, ethylene dibromide, and methylene chloride; pesticides; insecticides; herbicides	Vineyards, fruit and vegetable production common. Agricultural land is concentrated to north-east along the Tygerberg Hills and to south-east around the Helderberg Mountains and to south around Constantia and Hout Bay. The Philippi horticultural area situated to the south of the City of Cape Town. Viticulture contributes some 30% to the region's horticultural income and about 3% to its Gross Regional Product.	DEAT (2003); www.capetown.gov.za

Type of source	**Expected contaminants**	**Examples/ Comments**	**Reference**
Abattoir	DOC, nutrients, bacterial pathogens	Unsuitable slaughtering facilities are posing potential health risks and are a public nuisance. Meat production includes the slaughter, dressing and packing of animals, as well as smoking, drying and pickling.	www.capetown.gov.za
Feedlot/ poultry farms	DOC, nutrients (organic nitrate), bacterial pathogens	No numbers available.	
Mining:			
Shale, sandstone and granite	Petroleum hydrocarbons, oil and greases	Building sand from dunes on the Cape Flats; clay in Bellville, Brackenfell and south of Atlantis; Table Mountain sandstone in Camps Bay; hornfells from the Tygerberg; and, large quantities of high grade silica sand from the Phillippi area on the Cape Flats.	www.capetown.gov.za
Non-metallurgical Industries:			
Petroleum refining and reuse	Petroleum hydrocarbons; benzene, toluene, ethylbenzene, xylene (BTEX); fuels; oil and grease	Caltex refinery (Calref) has a distillation capacity of 100 000 barrels per day	DEAT (2003); www.wesgro.org.za
Adhesives and sealants	Benzene, toluene, Methyl-Ethyl Ketone (MEK)	Twelve manufacturers in Western Cape	DWAF (1998)
Agricultural fertiliser	Ammonia, arsenic, chlorides, lead, phosphates, potassium, nitrates, sulphur	Kynoch Fertilisers produce ammonia and nitrogen fertilisers	www.wesgro.org.za
Food and beverage manufacturing	Chlorine, chlorine dioxide, nitrate/nitrite, pesticides, biogenic amines, methane, dioxins, bacteria, lead	Four hundred companies contribute 18% to the country's total food manufacture. Dairy products - Clover-Danone; Parmalat; Nestlé and DairyBelle. Canning industry - Langeberg Foods, Del Monte and Ashton Canning. Fish processing (salting, drying, dehydrating, smoking, pickling, canning, and quick-freezing) Irvin & Johnson (I&J), Sea Harvest, Oceana and Lusitania, Dried fruit production - SA Dried Fruit. Production of edible oils - Cape Oil ; 5 breweries (SAB Claremont)	www.wesgro.org.za
Leather manufacturing	Toluene; benzene; arsenic, chromium, cadmium, sulphate	Richard Kane Hides & Skins, Sheepskin	DWAF (1998)
Pharmaceuticals and Cosmetics manufacturing	Alcohols, benzoates, bismuth, dyes, glycols, mercury, mineral spirits, sulphur, dichlorobenzene, methylene chloride, nitrate	Ten pharmaceutical companies e.g. SmithKline-Beecham. 15 cosmetic manufactures (e.g. Wella, Yardley)	www.wesgro.org.za; DWAF (1998)

Type of source	Expected contaminants	Examples/ Comments	Reference
Paint/ink manufacturing and coatings	Acetates, acrylates, alcohols, aluminum, cadmium, chlorinated solvents, chromium, cyanides, glycol ethers, ketones, lead, mercury, methylene chloride, mineral spirits, nickel, phthalates, styrene, terpenes, toluene, 1,4-dioxane, ammonia, anthraquinones, arsenic, benzidine, chromium, ethyl acetate, hexane, nickel, oxalic acid, phenol	Approximately 50 companies	DWAF (1998)
Rubber and plastics	Acrylonitrile, antimony, benzene, butadiene, cadmium, chloroform, chromium dichloroethylenes, lead, phenols, phthalates, styrene, sulphur, vinyl chloride, toluene, heptane, formaldehyde	Produce no monomers but SA Nylon Spinners (SANS), one of only two PET (polyethylene terephthalate) producers are located in CMC. Additional there is 220 plastic converters companies. 15 rubber products related small size industries	www.wesgro.org.za; DEAT (2003); DWAF (1998)
Paper and cardboard industry	Acrylates, chlorinated solvents, dioxins, mercury, phenols, styrene, sulphur; furans; chloroform, mercury sulphate, potassium dichromate	Forty four companies associated with paper wrapping, etc.	DEAT, 2003
Textile manufacture	Ammonium, arsenic, cadmium, chromium, ethyl acetate, nickel, hexane, oxalic acid, phenols, phthalates, toluene, lead	Hoechst, produces polyester stable fibre, and SA Nylon Spinners (See plastics). Cape Town Central Business District, Woodstock/Salt River, Maitland, Parow Industrial, Parow East, Mitchell's Plain, Beaconvale, Epping, Elsies River Industrial, Landsdowne, Primrose Park and Atlantis. E.g. Levi Strauss; Novel (spinning, weaving and dyeing operations); Herdmans;, House of Monatic, SA Fine Worsteds, SANS, Court Fabrics, Berg River Textiles.	www.wesgro.org.za
Wood processing and preserving	Ammonia, arsenic, chromium, copper, creosote, dioxins, polyaromatic hydrocarbons, pentachlorophenol, phenol, tri-n-butyltin oxide, PCB; PAHs; beryllium	Approximately 25 timber processing plants	DEAT (2003); DWAF (1998)
Solvents (nonchlorinated)	Acetates, alcohols, benzene, ethylbenzene, ketones, toluene, xylene		
Solvents, chlorinated	Carbon tetrachloride, chlorofluoroethanes, dichloroethylene, methylene chloride, PCE, TCE, vinyl chloride, 1,1,1-trichloethane		
Munitions manufacturing	Nitrate, sulphate, chromium, copper, boron, lead, antimony and phosphate	AECI (Somerset West), now only depot but part sold to Somchem, which still produces explosives on small scale for the defence industry.	
Non-metallic Mineral products	Asbestos	Everite building materials	DWAF (1998)

Type of source	**Expected contaminants**	**Examples/ Comments**	**Reference**
Metallurgical and Metal Products Manufacturing:			
Metallurgical and Metal Products Manufacturing:	Acids, mineral oils, sulphur, cyanide, metals (including aluminium, beryllium, cadmium, chromium, cobalt, iron, strontium, tin, titanium, vanadium, lead, copper, mercury, nickel, zinc and arsenic); dioxins and furans; chlorobenzenes; PCBs, asbestos, flouridebenzene, trichloroethane and trichloroethylene, VOCs; dioxin; degreasing agents; waste oils	Saldanha Steel (carbon steel as ultra-thin hot rolled coil), CISCO (carbon steel) and Hulett (aluminium). 500 supporting firms - automobile manufacturing, building and construction, consumer appliances, domestic and professional catering, machinery manufacturing, packaging, shipping, transport and winemaking.	www.wesgro.org.za
Automotive parts manufacturing	Various metals such as cadmium, beryllium chromium, cyanide, copper, silver, tin, zinc and nickel, hydrocarbons, solvents	The sector comprises some 30 small and medium-sized firms. No automobile assembly companies but component producers. Components are produced in the following areas Montague Gardens, Epping, Parow, Maitland (Airport Industria) and Atlantis. These include Atlantis Foundries; Gabriel Arvin; Grapnel; Bosal; Arvin Exhausts; Safety Transport, TRW; Cape Manufacturing Engineering; Laingsdale Engineering and 16 truck, trailer and bus builders.	www.wesgro.org.za
Auto Salvage/Metal Recyclers	Metals, asbestos, PCBs, hydraulic fluids and lubricating oils, fuels, and solvents	No numbers available.	
Automotive refinishing and repair	Paint; scrap metal; waste oils; toluene, acetone, perchloroethylene, xylene, gasoline and diesel fuel, carbon tetrachloride, and hydrochloric and phosphoric acid	Many located within semi-residential areas as well as in the industrial area	

6.5 Port Elizabeth

Type of source	Expected contaminants	Examples/ Comments	Reference
Urban settlement (Domestic/ Commercial):			
Wastewater treatment	Ammonium, nitrate, potassium, phosphate, chloride, sulphate, COD, diverse industrial chemicals, faecal pathogens, metals	Uitenhage, Despatch, KwaNobuhle sewage works (86% of city waterborne sewage system - 193 600 households); Buckets - 23000 in PE, 1400 in Uitenhage.	Devey (2003)
Stormwater/ sewer systems	Ammonium, nitrate, potassium, chloride, sulphate, DOC, hydrocarbons, faecal pathogens, diverse industrial chemicals	Kat Canal, Uitenhage	Devey (2003)
On-site sanitation	Nitrate, potassium, chloride, COD, faecal pathogens, phosphate, boron	Estimated number of unofficial pit latrines in urban area = 3500 Pit latrines is not allowed in PE	Devey (2003)
Cemeteries	Ammonium, potassium, microbial pathogens	No numbers available.	Baron (2003)
Transport	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH, any other chemicals transported resulting from accidents or spills	Airport commercial and freight, Port Elizabeth International	
Railroad yards	Petroleum hydrocarbons; VOCs; BTEX; solvents; fuels; oil and grease; lead; PCBs		
Marine maintenance industry	Solvents; paints; cyanide; acids; VOC emissions; heavy metal sludge; degreasers	Third largest port in SA and new Coega deepwater harbour development	www.ehso.com/contents.php; www.cimec.co.za
Hospitals / Health Care	Formaldehyde; radionuclides; photographic chemicals; solvents; mercury; ethylene oxide; chemotherapy chemicals	Waste disposed with hazardous waste, e.g. Aloes	Baron (2003)
Incinerators	Dioxin; various municipal and industrial waste	3 waste incinerators proposed (Aloes, Pelts Products and regional waste facility as part of Coega development)	www.groundwork.org.za
General/ Domestic waste sites	Ammonium, salinity (sodium, chloride, sulphate), DOC, methane, lead, mercury	Municipal waste sites, e.g. KwaNobuhle (closed); commercial waste, building rubble, e.g. Arlington (south of PE)	Baron (2003)
Hazardous waste sites	Ammonium, salinity, DOC, heavy metals, methane	Hazardous waste sites, e.g. Ibayi (closed), Koedoeskloof (closed, liquid cells), Aloes (in operation, licensed)	Baron (2003)
Workshops (Mechanical and electrical)	Polyaromatic hydrocarbons, diesel, benzene, alkanes, acids, aluminium, arsenic, beryllium, cadmium, lead, mercury, nickel, chlorinated solvents	No numbers available.	Baron (2003)

Type of source	**Expected contaminants**	**Examples/ Comments**	**Reference**
Petrol Service Stations (Underground Storage Tanks)	Benzene, toluene, xylenes (BTEX), oxygenates (alcohols, MTBE), metals (lead, nickel), sulphur, alkanes, TPH, PAH	Filling stations, fuel storage depot (no refinery in PE), airport	Baron (2003); Morris *et al*., (2003)
Photographic manufacturing and uses	Silver bromide; methylene chloride; solvents; photographic products	No numbers available.	DEAT (2003)
Research and educational institutions	Inorganic acids; organic solvents; metals and metal dust; photographic waste; waste oil; paint; heavy metals; pesticides	Many educational facilities (e.g. schools, technikons, universities) No figures available on number of laboratories	
Printing industry	Silver; acids; waste oils; toluene; MEK; xylene, TCE	Approximately 280 businesses in PE. (Waltons)	DWAF (1998)
Dry cleaning activities	VOCs such as chloroform and tetrachloroethane; various solvents; spot removers; fluorocarbon 113	Estimated 450 companies in the Eastern Cape	www.serviceseta.org.za
Agriculture:			
Agriculture	Volatile organic compounds (VOC); arsenic, copper, carbon tetrachloride, ethylene dibromide, and methylene chloride; pesticides; insecticides; herbicides	Very little farming within urban boundaries. Some general crop and citrus cultivation close to Uitenhage upstream in the Swartkops River basin.	
Abattoir	DOC, nutrients, bacterial pathogens		
Feedlot/ poultry farms	DOC, nutrients, bacterial pathogens	Rocklands, Graham's Poultry	Baron (2003); Morris *et al*, (2003)
Mining:			
Sand, calcrete and gravel	Petroleum hydrocarbons, oil and greases	PPC limestone mine (Grasslands) Open cast, sand, gravel, calcrete	Baron (2003)
Non-metallurgical Industries:			
Adhesives and sealants	Benzene, toluene, methyl-ethyl ketone (MEK)	Five companies listed for the Eastern Cape	DWAF (1998)
Food and beverage manufacturing	Chlorine, chlorine dioxide, nitrate/nitrite, pesticides, biogenic amines, methane, dioxins, bacteria, lead	SAB breweries, SABCO (soft drinks), Cadbury, Bonnita and Parmalat	www.cimec.co.za/
Leather manufacturing	Toluene; benzene; arsenic, chromium, cadmium, sulphate, lead, zinc, titanium, manganese, strontium, copper and tin	Three tanners: East Cape Tanners, African Hide Tanning (Exotan) & Mario Levi - Leather Processing factory	Baron (2003); Binning and Baird (2001)

Type of source	Expected contaminants	Examples/ Comments	Reference
Pharmaceuticals and Cosmetics manufacturing	Alcohols, benzoates, bismuth, dyes, glycols, mercury, mineral spirits, sulphur, dichlorobenzene, methylene chloride, nitrate	Two major pharmaceutical manufacturers but no known cosmetic manufacturers for example Intramed, Aspen Pharmacare Lennon	DWAF (1998)
Paint/ink manufacturing and coatings	Acetates, acrylates, alcohols, aluminum, cadmium, chlorinated solvents, chromium, cyanides, glycol ethers, ketones, lead, mercury, methylene chloride, mineral spirits, nickel, phthalates, styrene, terpenes, toluene, 1,4-dioxane, ammonia, anthraquinones, arsenic, benzidine, chromium, ethyl acetate, hexane, nickel, oxalic acid, phenol	Four companies listed for the Eastern Cape for example Dulux and Plascon	DWAF (1998)
Rubber and plastics	Acrylonitrile, antimony, benzene, butadiene, cadmium, chloroform, chromium, dichloroethylenes, lead, phenols, phthalates, styrene, sulphur, vinyl chloride, toluene, heptane, formaldehyde	Continental tyres, Firestone and Gentyre. More than 30 manufacturers of plastic products and a plastics cluster process in Port Elizabeth-Uitenhage. Algorax produces carbon black for rubber industry.	Baron (2003)
Paper and cardboard industry	Acrylates, chlorinated solvents, dioxins, mercury, phenols, styrene, sulphur; furans; chloroform, mercury sulphate, potassium dichromate	Approximately 7 companies based in Port Elizabeth mainly manufacture paper/ cardboard packaging for example Mondipak, Nampak One paper mill - Sappi	DWAF (1998)
Textile manufacture	Ammonium, arsenic, cadmium, chromium, ethyl acetate, nickel, hexane, oxalic acid, phenols, phthalates, toluene, lead	Industex (2 plants), Cape Mohair Spinners (CMS), Umbala Dyers SA , Colibri Towels Also footwear manufacturers e.g. Bagshaw	Baron (2003); DWAF (1998)
Wool processing	Potassium, COD, grease, arsenic, atrazine, lindane, chrome, lead, zinc, titanium, manganese, strontium, copper and tin	Port Elizabeth is the main centre for wool and mohair processing in SA, e.g. Gubb & Inggs, CGH Woolcombers, Perseverance Woolpullery, Cape Mohair Spinners (CMS)	Baron (2003); Binning and Baird (2001)
Wood processing and preserving	Ammonia, arsenic, chromium, copper, creosote, dioxins, polyaromatic hydrocarbons, pentachlorophenol, phenol, tri-n-butyltin oxide, PCB; PAHs; beryllium	Six manufacturers based in the Eastern Cape forestry industry (5 sawmills and one chipboard manufacturer).	
Solvents (nonchlorinated)	Acetates, alcohols, benzene, ethylbenzene, ketones, toluene, xylene		

Type of source	Expected contaminants	Examples/ Comments	Reference
Solvents, chlorinated	Carbon tetrachloride, chlorofluoroethanes, dichloroethylene, methylene chloride, PCE, TCE, vinyl chloride, 1,1,1-trichloethane		
Glass manufacturing	Arsenic; lead	Shatterprufe SA	www.cimec.co.za/
Non-metallic Mineral products - Cement	Salinity, sodium, calcium, dioxins		
Metallurgical and Metal Products Manufacturing:			
Metallurgical and Metal Products Manufacturing:	Acids, mineral oils, sulphur, cyanide, metals (including aluminium, beryllium, cadmium, chromium, cobalt, iron, strontium, tin, titanium, vanadium, lead, copper, mercury, nickel, zinc and arsenic); dioxins and furans; chlorobenzenes; PCBs, asbestos, flouridebenzene, trichloroethane and trichloroethylene, VOCs; dioxin; degreasing agents; waste oils	Steel recycling, steel wire manufacturing, electroplating, supporting industries for automotive plants and battery manufacturing e.g. Duracell, Willard Batteries, Murray and Roberts Alucast Foundry	www.cimec.co.za/
Automotive manufacturing	Various metals such as cadmium, beryllium chromium, cyanide, copper, silver, tin, zinc and nickel, hydrocarbons, solvents	Volkswagen, General Motors (Delta); Ford (Samcor)	www.cimec.co.za/economy.htm
Automotive parts manufacturing	Various metals such as cadmium, beryllium chromium, cyanide, copper, silver, tin, zinc and nickel, hydrocarbons, solvents	Makes up a large portion of the industrial sector in support of the three major automotive manufacturers. For example Dorbyl Automotive Group, Armstrong Hydraulics, Gemtec, Bosal, Dorbyl, Gillet Tenneco	www.cimec.co.za/
Auto Salvage/Metal Recyclers	Metals, asbestos, PCBs, hydraulic fluids and lubricating oils, fuels, and solvents	No numbers available.	
Automotive refinishing and repair	Paint; scrap metal; waste oils; toluene, acetone, perchloroethylene, xylene, gasoline and diesel fuel, carbon tetrachloride, and hydrochloric and phosphoric acid	Many located within semi-residential areas as well as in the industrial area	

7. Prioritisation of contaminants and sources

This section deals with prioritising the contaminant inventories discussed in Section 6. The methods and software used to prioritise both sources and contaminants are documented in *Guidelines for assessing and evaluating impacts of human activities on groundwater resources in urban catchments.* It is important to note there is no information on many of the contaminants and therefore they are not included in the listed presented in the following sub-sections.

7.1 Generic priority of contaminants and sources for South Africa

Figure 1 is the land use map of South Africa. In this section a generic national priority list of contaminants and sources is presented for South Africa (see Table 12 & Table 13).

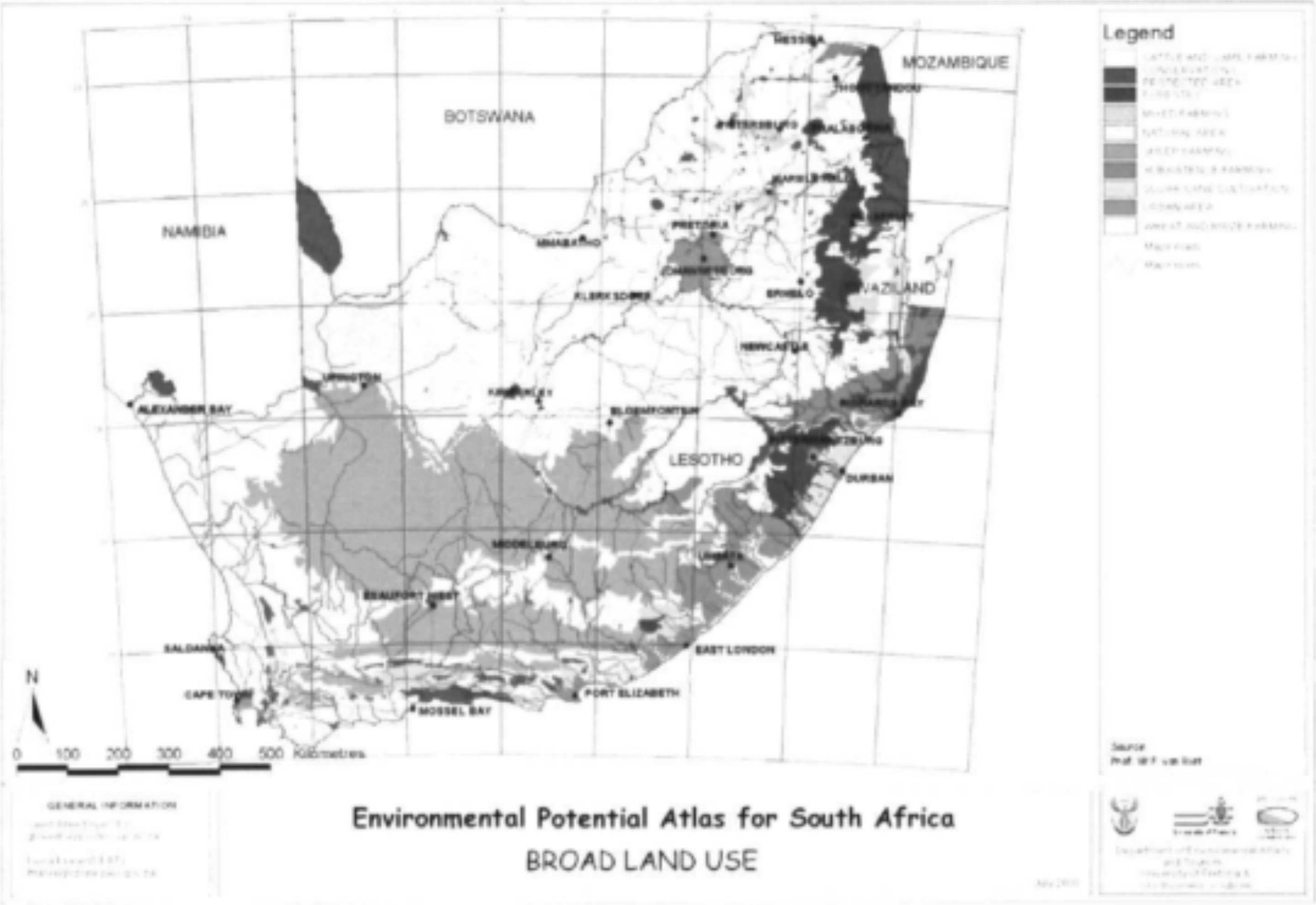

Figure 1. South African land use map (*taken from http://www.ngo.grida.no/soesa/nsoer/general/map.htm*)

Table 12. National prioritisation of sources

Source prioritisation (from highest to lowest risk)	
1	On-site sanitation
2	Agricultural Chemicals (fertilisers, herbicides, pesticides)
3	Cemeteries
4	Metallurgical
5	Metal (predominately gold) and coal mining
6	Transport
7	Petrol Service Stations (Underground Storage Tanks)
8	Wood processing and preserving
9	Feedlot/poultry farms
10	Manufacturing - Chemicals
11	Workshops (Mechanical and electrical)
12	Stormwater/ sewer systems
13	Automotive refinishing and repair
14	Other metal product manufacturing
15	Railroad yards
16	Non-metallic Mineral products
17	Abattoir
18	Agriculture (General and crop cultivation)
19	Paper/pulp industry
20	Research and educational institutions
21	Petroleum refining and reuse
22	Solvents, chlorinated
23	Solvents (nonchlorinated)
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
32	Non-metallic Mineral products - Cement
33	Leather manufacturing
34	Food and beverage manufacturing
35	Printing industry
36	Diamond, sand, calcrete and gravel
37	Shale, sandstone and granite
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 sealents
45	Automotive parts manufacturing
46	Automotive manufacturing
47	Wool processing
48	Hospitals / Health Care
49	Glass manufacturing
50	Incinerators

Table 13. National prioritisation of contaminants*

Contaminant prioritisation (from highest to lowest risk)		Contaminant prioritisation (from highest to lowest risk)	
1	Chlordane	59	Chloroform
2	HCH	60	Antimony
3	Lindane	61	Diuron
4	DDD	62	Heptane
5	Butadiene	63	Chlorobenzene
6	Trichloroethylene	64	Dioxin
7	TCE	65	Hexane
8	Dichloromethane	66	Tetrachlorobenzene
9	Tetrachloromethane	67	Sulphate
10	Phenol	68	Nickel
11	Atrazine	69	Methanol
12	TCA	70	Manganese
13	Formaldehyde	71	Fluoride
14	Creosote	72	Ethylbenzene
15	Dichlorobenzene	73	Ethyl Alcohol
16	MEK	74	Ethyl Acetate
17	Ammonium	75	Cobalt
18	Ethanol	76	Chromium III
19	Acrylonitrile	77	Ammonia
20	Vinyl Chloride	78	Vanadium
21	Uranium	79	Tri-n-Nutyltin Oxide
22	Trichlorophenol 2,4	80	Titanium
23	Dichloropropane 1,2	81	Styrene
24	Dichlorophenol 2,4	82	Sodium
25	Cyanide	83	Silver Bromide
26	Chromium VI	84	Silane
27	Chlorine	85	Potassium Dichromate
28	Benzene	86	Potassium
29	Arsenic	87	Phosphate
30	Methylene Chloride	88	Perchloroethylene
31	Tebuthiuron	89	PCE
32	Phosphoric Acid	90	Oxylic Acid
33	Monosodium-Methyl	91	Naphthalene
34	Arsenate	92	Methane
35	Isopropanol	93	Iron
36	Acetone	94	Glycol
37	Strontium	95	Fluorocarbon 113
38	Mercury	96	Floridebenzene
39	Cadmium	97	Chloropyrifos
40	Nitrite	98	Chlorofluoroethane
41	Nitrate	99	Chloride
42	Aldicarb	100	Calcium
43	Xylene	101	Butane
44	Trichloroethane 1,1,1,-	102	Bismuth
45	Pentachlorophenol	103	Acetylene
46	Lead	104	Phthalates
47	Ethylene oxide	105	Aluminium
48	Ethylene Dibromide	106	Zinc
49	Dioxane 1,4	107	Tin
50	Chlorine Dioxide	108	Silver
51	Carbon Tetrachloride	109	Selenium
52	Beryllium	110	Hydrochloric acid
53	Benzidine	120	Copper
54	Trichlorobenzene	121	Boron
55	Toluene		
56	Sulphur		
57	Dichloroethylene		
58	DDE		

*The relative ranking of the contaminant is of greater importance than the absolute value

7.2 Priority contaminants and sources in Gauteng

Figure 2 is a land use map for the Gauteng area. The list of priority sources and contaminants is documented in Table 14 & Table 15.

Table 14. Prioritisation of sources for Gauteng

Source prioritisation (from highest to lowest risk)	
1	On-site sanitation
2	Cemeteries
3	Metallurgical
4	Agricultural Chemicals (fertilisers, herbicides, pesticides)
5	Workshops (Mechanical and electrical)
6	Stormwater/ sewer systems Abattoir Other metal product manufacturing Automotive refinishing and repair
7	Agriculture (General and crop cultivation)
8	Transport Petrol Service Stations (Underground Storage Tanks)
9	Wood processing and preserving Auto Salvage/Metal Recyclers
10	Manufacturing - Chemicals
11	Paper/pulp industry
12	Wastewater treatment General/ Domestic waste sites Dry cleaning activities
13	Rubber and plastics Textile manufacture
14	Research and educational institutions Printing industry Food and beverage manufacturing
15	Electrical and electrical products manufacturing
16	Adhesives and sealents Pharmaceuticals and Cosmetics manufacturing Paint/ink manufacturing and coatings
17	Metal (predominately gold) and coal mining
18	Diamond, sand, calcrete and gravel
19	Non-metallic Mineral products - Cement
20	Leather manufacturing
21	Railroad yards
22	Solvents, chlorinated Solvents (nonchlorinated) Munitions manufacturing
23	Hospitals / Health Care Incinerators Non-metallic Mineral products - Cement
24	Electricity generation
25	Paint/ink manufacturing and coatings
26	Automotive manufacturing
27	Glass manufacturing
28	Hazardous waste sites

Table 15. Prioritisation of contaminants for Gauteng

Contaminant prioritisation (from highest to lowest risk)	
1	Chlordane
2	HCH
3	Asbestos
4	DDD
5	Butadiene Trichloroethylene
6	Arsenic Cyanide
7	TCE
8	Benzene Dichloromethane Phenol
9	Dichloropropane 1,2 Trichlorophenol 2,4
10	Creosote Monosodium-Methyl Arsenate
11	Nitrate
12	Acrylonitrile Ammonium Cadmium Chlorine Mercury Strontium Vinyl Chloride
13	Dichlorobenzene Formaldehyde TCA Uranium
14	Tetrachloromethane
15	Beryllium Trichloroethane 1,1,1,-
16	Aldicarb Ethanol Xylene
17	Carbon Tetrachloride Dioxane 1,4 MEK Pentachlorophenol Sulphur
18	Ethylene Dibromide Methylene Chloride Toluene
19	Acetone Chloroform Phosphoric Acid
20	Chlorobenzene Nitrite
21	Chlorine Dioxide Cobalt DDE Nickel Trichlorobenzene

Contaminant prioritisation (from highest to lowest risk)	
22	Ammonia Chloride Ethylbenzene Hexane Phosphate Potassium
23	Antimony Benzidine Dioxin Ethyl Acetate Isopropanol Sulphate
24	Manganese
25	Floridebenzene Iron Titanium Vanadium
26	Ethyl Alcohol Ethylene oxide Heptane Naphthalene Tetrachlorobenzene
27	Diuron PCE
28	Methanol Oxylic Acid Perchloroethylene
29	Acetylene Aluminium Butane Chloropyrifos Methane Tri-*n*-Nutyltin Oxide
30	Phthalates Potassium Dichromate Styrene
31	Fluorocarbon 113 Sodium
32	Bismuth Glycol Silane
33	Boron
34	Calcium
35	Chlorofluoroethane Chromium III Copper Tin Zinc

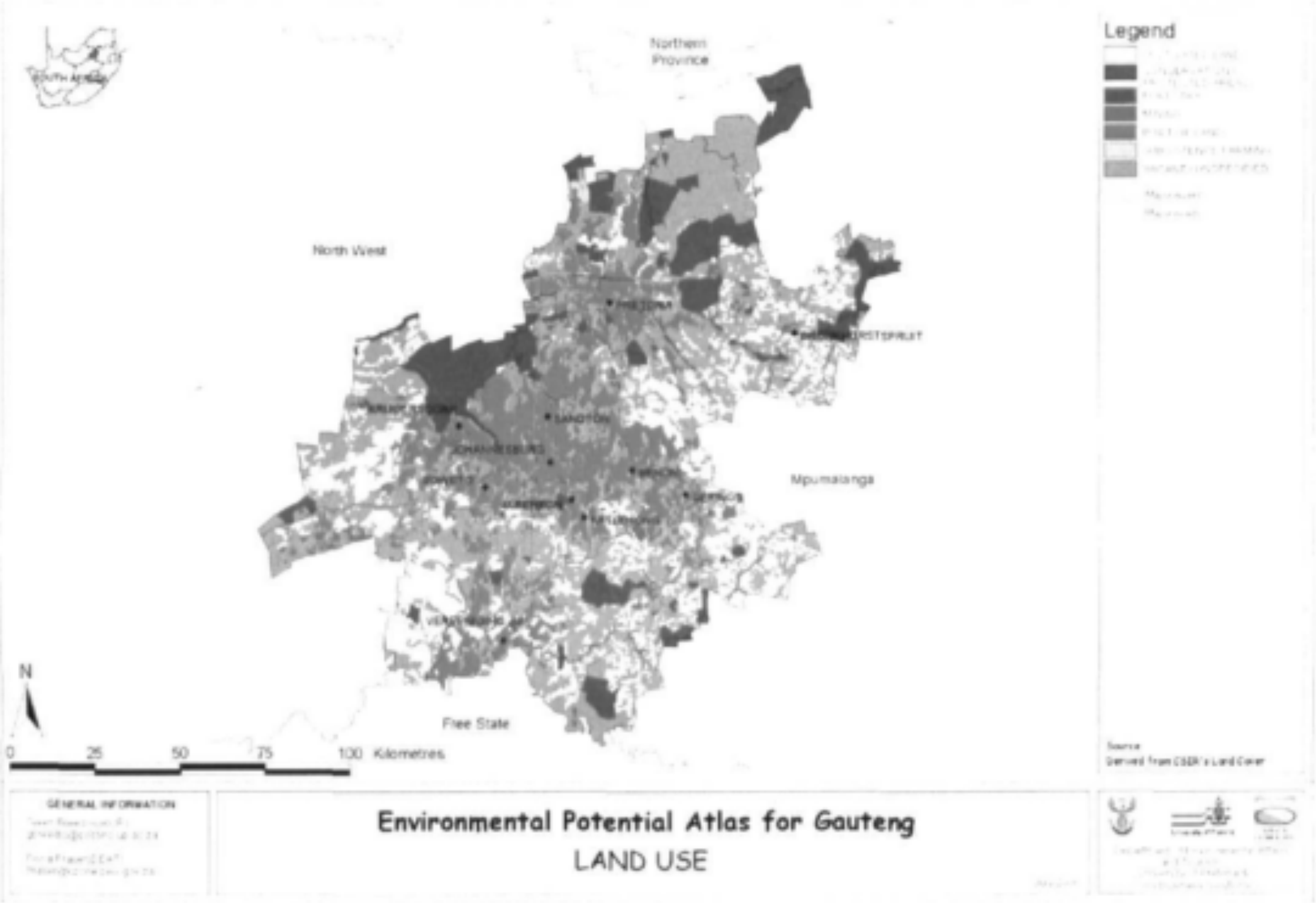

Figure 2. Land use map for Gauteng (*taken from http://www.johannesburg.gov.za/csoe*)

7.3 Priority contaminants and sources in Durban

Figure 3 is a land use map for the Durban area. The list of priority sources and contaminants is documented in Table 16 & Table 17.

Table 16. Source prioritisation for Durban

Source prioritisation (from highest to lowest risk)	
1	On-site sanitation
2	Workshops (Mechanical and electrical)
3	Stormwater/ sewer systems Cemeteries Automotive refinishing and repair
4	Agriculture (General and crop cultivation)
5	Metallurgical
6	Petrol Service Stations (Underground Storage Tanks) Printing industry Agricultural Chemicals (fertilisers, herbicides, pesticides)
7	Feedlot/poultry farms Wood processing and preserving Auto Salvage/Metal Recyclers
8	Automotive parts manufacturing
9	Abattoir
10	Paper/pulp industry
11	Dry cleaning activities
12	Rubber and plastics Textile manufacture
13	Transport Shale, sandstone and granite
14	Pharmaceuticals and Cosmetics manufacturing Paint/ink manufacturing and coatings
15	Railroad yards
16	Wastewater treatment General/ Domestic waste sites
17	Research and educational institutions Food and beverage manufacturing
18	Photographic manufacturing and uses Manufacturing - Chemicals Automotive manufacturing
19	Adhesives and sealants
20	Petroleum refining and reuse Solvents, chlorinated Solvents (nonchlorinated) Munitions manufacturing
21	Hospitals / Health Care Incinerators Leather manufacturing
22	Marine maintenance industry
23	Hazardous waste sites

Table 17. Prioritisation of contaminants for Durban

Contamination prioritisation (from highest to lowest risk)	
1	Chlordane
2	HCH
3	Butadiene
4	TCE
5	DDD Trichloroethylene
6	Arsenic Benzene Dichloromethane
7	Cyanide Dichloropropane 1,2 Trichlorophenol 2,4
8	Phenol
9	Creosote
10	Nitrate
11	Acrylonitrile Vinyl Chloride
12	Formaldehyde Monosodium-Methyl Arsenate TCA
13	Ammonium Cadmium Mercury
14	Chlorine MEK Strontium
15	Dichlorobenzene
16	Ethanol
17	Beryllium Carbon Tetrachloride Dioxane 1,4 Lead Pentachlorophenol Trichloroethane 1,1,1,- Xylene
18	Ethylene Dibromide Methylene Chloride
19	Acetone Aldicarb Chloroform Phosphoric Acid
20	Sulphur Tetrachloromethane Toluene
21	Chlorobenzene Hexane Nitrite Phosphate Potassium
22	Antimony Benzidine Ethyl Acetate Nickel Sulphate

Contamination prioritisation (from highest to lowest risk)	
23	Chlorine Dioxide Cobalt Manganese
24	Ammonia Ethylbenzene
25	Dioxin Ethylene oxide Heptane
26	DDE Naphthalene PCE Trichlorobenzene
27	Dichloroethylene Floridebenzene Iron Oxylic Acid Perchloroethylene Titanium Vanadium
28	Diuron Tri-n-Nutyltin Oxide
29	Ethyl Alcohol Potassium Dichromate Styrene Tetrachlorobenzene
30	Aluminium Fluorocarbon 113
31	Bismuth Glycol
32	Boron Phthalates
33	Methane Sodium

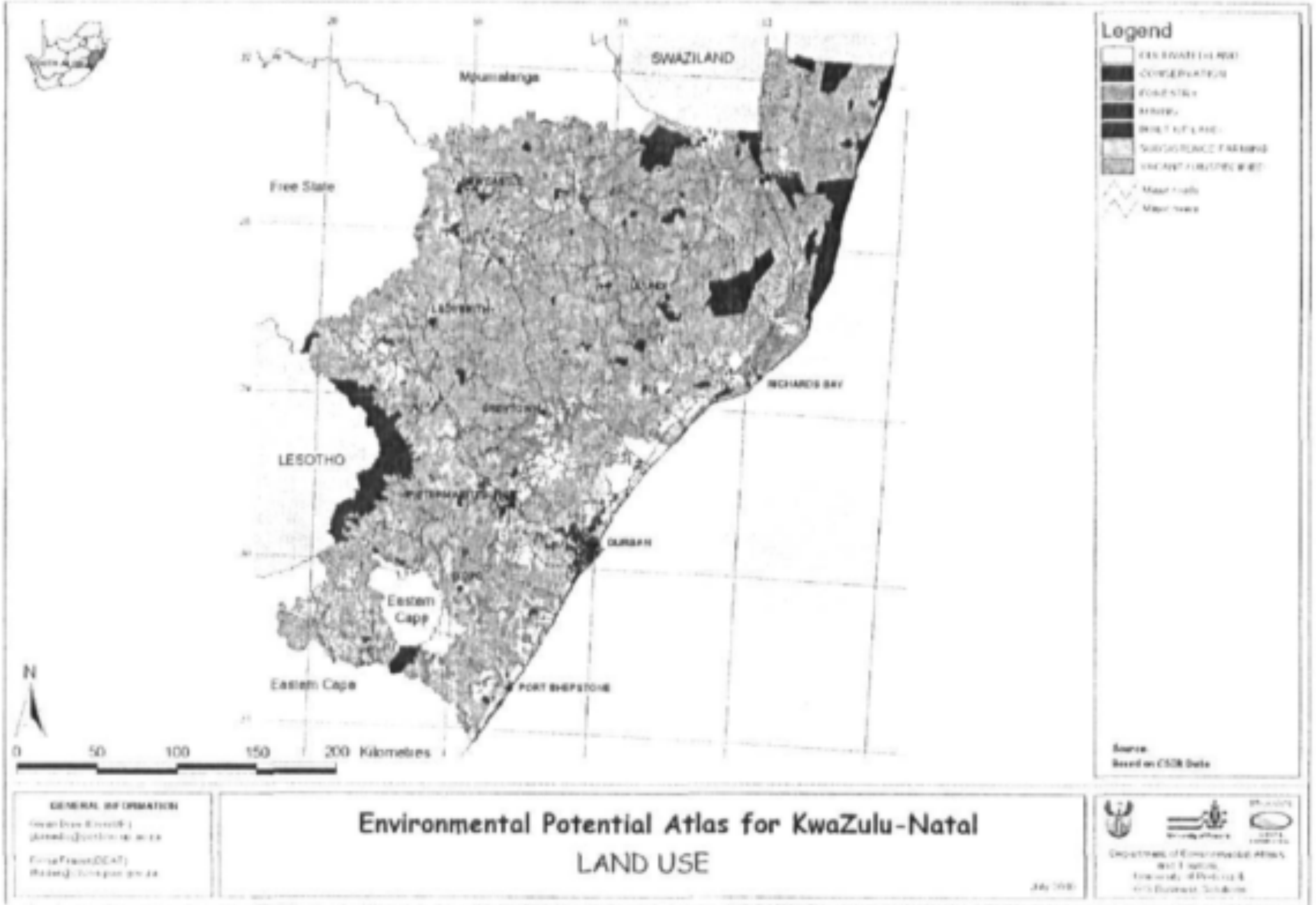

Figure 3. Land use map for Durban (*taken from http://www.environment.gov.za/Maps/*)

7.4 Priority contaminants and sources in Cape Town

Figure 4 is a land use map for Cape Town. The list of priority sources and contaminants is documented in Table 18 & Table 19.

Table 18. Source prioritisation for Cape Town

Source prioritisation (from highest to lowest risk)	
1	On-site sanitation
2	Cemeteries
3	Feedlot/poultry farms Wood processing and preserving
4	Workshops (Mechanical and electrical)
5	Stormwater/ sewer systems Automotive refinishing and repair
6	Agriculture (General and crop cultivation)
7	Metallurgical
8	Petrol Service Stations (Underground Storage Tanks)
9	Auto Salvage/Metal Recyclers
10	Automotive parts manufacturing
11	Abattoir
12	Paper/pulp industry
13	Dry cleaning activities Agricultural Chemicals (fertilisers, herbicides, pesticides) Wastewater treatment
14	Rubber and plastics Textile manufacture
15	Transport Research and educational institutions Printing industry Food and beverage manufacturing
16	Railroad yards Adhesives and sealents Pharmaceuticals and Cosmetics manufacturing Paint/ink manufacturing and coatings
17	Hospitals / Health Care
18	Incinerators
19	General/ Domestic waste sites
20	Photographic manufacturing and uses
21	Shale, sandstone and granite Non-metallic Mineral products
22	Petroleum refining and reuse Solvents, chlorinated Solvents (nonchlorinated) Munitions manufacturing
23	Leather manufacturing
24	Marine maintenance industry Hazardous waste sites
25	Electricity generation

Table 19. Prioritisation of contaminants for Cape Town

Contamination prioritisation (from highest to lowest risk)	
1	Chlordane
2	Butadiene
3	TCE
4	Trichloroethylene
5	Arsenic Benzene Creosote Dichloromethane
6	Cyanide Dichloropropane 1,2 Phenol Trichlorophenol 2,4
7	Nitrate
8	Acrylonitrile Ammonium Chlorine Vinyl Chloride
9	Formaldehyde TCA
10	Cadmium Mercury
11	Strontium
12	Dichlorobenzene Monosodium-Methyl Arsenate
13	Beryllium Ethanol Pentachlorophenol
14	Carbon Tetrachloride Dioxane 1,4 Lead MEK Trichloroethane 1,1,1,- Xylene
15	Ethylene Dibromide Methylene Chloride
16	Acetone Chloroform Phosphoric Acid
17	Nitrite Sulphur
18	Aldicarb
19	Chlorine Dioxide
20	Ammonia Chloride Chlorobenzene Ethylene oxide Hexane Phosphate Potassium
21	Antimony Benzidine Ethyl Acetate Nickel Sulphate

Contamination prioritisation (from highest to lowest risk)	
22	Cobalt Manganese
23	Heptane
24	Ethylbenzene Naphthalene PCE Tri-n-Nutyltin Oxide
25	Dichloroethylene Dioxin Floridebenzene Iron Oxylic Acid Perchloroethylene Titanium Vanadium
26	Potassium Dichromate Styrene
27	Aluminium Diuron Fluorocarbon 113 Methane
28	Bismuth Glycol
29	Boron Sodium
30	Phthalates Silver Bromide
31	Chlorofluoroethane
32	Chromium III Copper
33	Hydrochloric acid
34	Tin Zinc
35	Silver

7.5 Priority contaminants and sources in Port Elizabeth

Figure 5 is a land use map for Port Elizabeth. The list of priority sources and contaminants are documented in Table 20 & Table 21.

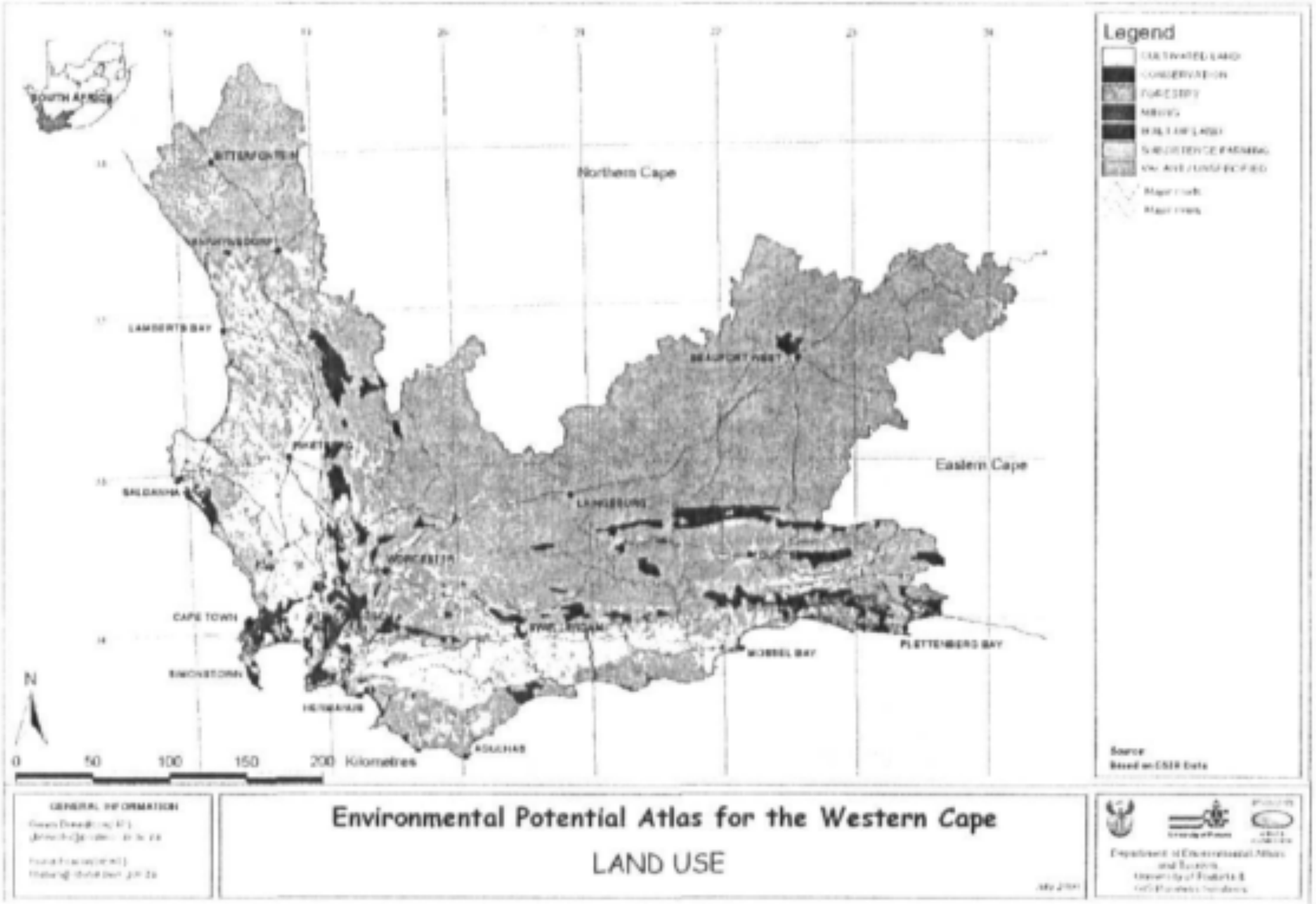

Figure 4. Land use map for Cape Town (*taken from http://www.environment.gov.za*)

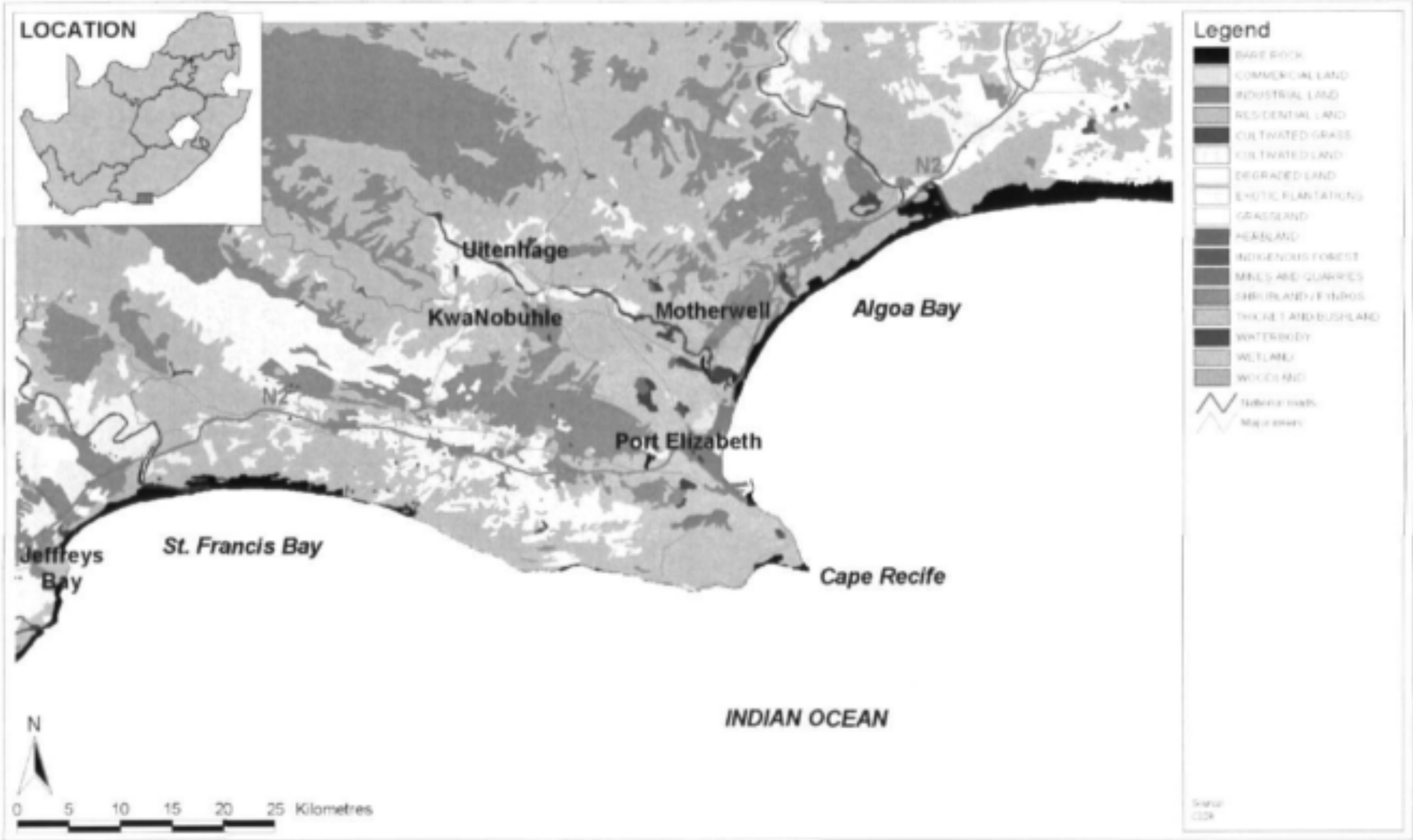

Figure 5. Land use map for Port Elizabeth (*taken from http://www.environment.gov.za*)

Table 20. Source prioritisation for Port Elizabeth

Source prioritisation (from highest to lowest risk)	
1	On-site sanitation
2	Metallurgical
3	Workshops (Mechanical and electrical)
4	Stormwater/ sewer systems Automotive refinishing and repair
5	Agriculture (General and crop cultivation)
6	Petrol Service Stations (Underground Storage Tanks)
7	Feedlot/poultry farms Wool processing Wood processing and preserving Auto Salvage/Metal Recyclers
8	Cemeteries
9	Automotive parts manufacturing
10	Wastewater treatment Dry cleaning activities
11	Rubber and plastics
12	Printing industry Shale, sandstone and granite
13	Railroad yards
14	Hospitals / Health Care Abattoir
15	Incinerators
16	Paper/pulp industry
17	Transport
18	Textile manufacture
19	Food and beverage manufacturing Research and educational institutions
20	Photographic manufacturing and uses
21	Adhesives and sealents Pharmaceuticals and Cosmetics manufacturing
22	Non-metallic Mineral products
23	Marine maintenance industry General/ Domestic waste sites Hazardous waste sites Solvents, chlorinated Solvents (nonchlorinated)
24	Leather manufacturing
25	Paint/ink manufacturing and coatings
26	Automotive manufacturing
27	Glass manufacturing

Table 21. Prioritisation of contaminants for Port Elizabeth

Contamination prioritisation (from highest to lowest risk)	
1	Chlordane
2	Butadiene Lindane Trichloroethylene
3	Arsenic Cyanide TCE
4	Benzene Dichloromethane
5	Dichloropropane 1,2 Trichlorophenol 2,4
6	Phenol
7	Creosote
8	Nitrate
9	Acrylonitrile Cadmium Mercury Strontium Vinyl Chloride
10	Formaldehyde TCA
11	Ammonium Atrazine
12	Chlorine
13	Beryllium Lead Trichloroethane 1,1,1,-
14	Ethanol
15	Carbon Tetrachloride Dioxane 1,4 MEK Pentachlorophenol Sulphur Xylene
16	Dichlorobenzene Ethylene Dibromide Methylene Chloride
17	Acetone Chloroform Phosphoric Acid
18	Chlorobenzene Toluene
19	Cobalt Nickel
20	Chloride Ethylene oxide Hexane Nitrite Phosphate Potassium
21	Antimony Ethyl Acetate Sulphate
22	Chlorine Dioxide Manganese

Contamination prioritisation (from highest to lowest risk)	
23	Ammonia Floridebenzene Iron Titanium Vanadium
24	Heptane
25	Naphthalene PCE
26	Dichloroethylene Oxylic Acid Perchloroethylene
27	Benzidine
28	Aluminium Dioxin Tri-n-Nutyltin Oxide
29	Fluorocarbon 113 Styrene
30	Ethylbenzene
31	Boron Methane Potassium Dichromate Sodium
32	Bismuth Glycol Silver Bromide
33	Chlorofluoroethane Chromium III Copper Tin Zinc
34	Hydrochloric acid
35	Silver

8. Priority contaminants and sources requiring further study

Based on the research conducted in this project, several sources and contaminants have been highlighted as potential priorities. The following contaminants of concern are highlighted:

- **Petroleum products, industrial thinners and mineral oils and other non-aqueous phase liquids (NAPLs)** represent a category of potential pollutants that have been largely overlooked by regulatory agencies and legislature, despite their harmful effects at small concentrations. (Woodford and Chevalier, 2002). Research in this current project, has shown these contaminants to be of the most problematic in urban groundwater resources. There is an urgent need for published research into NAPL contamination in South Africa. The regulatory agencies and water managers should also be urged to consider NAPL contamination when prescribing parameters to be monitored for or when assessing any urban area for contamination. Based on the body of research in this report, NAPLs as potential groundwater contaminants cannot be stressed enough.

- Du Preez *et al.*, (2003), make several recommendations regarding the monitoring of **microbial contaminants**. Based on the paucity of groundwater-related microbial data encountered in this project, the inclusion of these aspects in urban groundwater management must be regarded as a priority. In order to evaluate the public health threat posed by waterborne micro organisms, rapid and accurate methods for the detection of these organisms within large populations of other bacteria are therefore essential and further research and inclusion in groundwater monitoring should be promoted.

- Few data are available on pollution from **pesticides** in urban areas, in particular concerning groundwater contamination. In general, the most commonly detected and/or studied pesticides in South Africa were chlorpyrifos, endosulfan, azinphos-methyl, atrazine, deltamethrin and penconazole (Jovanovic and Maharaj, 2004). Most studies were done in the Cape, namely in the Lourens river (Schulz *et al.*, 2001) and Hex river valley (Weaver, 1993). Grange *et al.* (2003) identified a large number of pesticide species and other organic compounds in surface water samples collected near Johannesburg. Naidoo and Buckley (2003) also carried out a comprehensive Water Research Commission project on pesticide wastes in South Africa and treatment options.

  The priority pesticides can be deduced from sales figures, as it can be assumed that the largest portion of pesticides purchased is eventually used and represents a threat to the environment. According to sales figures from 1994 to 2000, there was a tendency of high sale and usage of organophosphates (e.g. azinphos-methyl, chlorpyrifos and prothiofos), organochlorines (e.g. endosulfan), carbamates, hydrocarbons, triazines (e.g. atrazine), amilime/acetamilide and phenolics).

- High **nitrate** concentrations have been found to occur from sources ranging from agricultural fertilizing (especially the application of sludge to land) to pit latrines and explosives companies. There are some areas with high nitrate values, which could be due mainly to point sources such as pit latrines and other activities polluting unconfined aquifers by direct infiltration of polluted water. Monitoring takes place at waste disposal sites, wastewater treatment works, and other point sources and are recorded in the DWAF Wastebase.

Furthermore, a limited amount of monitoring of groundwater quality takes place in major urban centres/catchments by DWAF. There is, however, no directed programme to monitor nitrate in urban and peri-urban areas and hence the gap in information. In the urban context, nitrate pollution has only been studied in the Cape flats aquifer. It is evident that the need to report nitrate concentrations in other urban areas is important to have a fuller understanding of its nature and extent.

Of the above contaminants identified, least is known of NAPLs and pesticides, in groundwater. This can be ascribed to several factors:

- Surface waters are the main source of water supply in the country and water quality monitoring efforts in urban areas are focused on these resources.
- The number of laboratories available in South Africa that could analyse for these parameters is scarce and analyses are costly.
- Sampling methods for these organic parameters is often difficult and costly.
- There are no guidelines from DWAF on specific sampling methodologies for most organic parameters and no maximum allowable limits in the water quality guidelines.
- Where monitoring of these parameters do take place through private companies own initiative, they are often sensitive to make public, data related to this type of pollution problems.

The National Water Act of 1998, provides the framework within which the Department of Water Affairs and Forestry (DWAF) can manage the protection, use, development, conservation and control of South Africa's water resources. In this context groundwater quality can be managed in an integrated and sustainable manner within the context of the National Water Resource Strategy and thereby to provide an adequate level of protection to groundwater resources and secure the supply of water of acceptable quality. In the Policy and Strategy for Groundwater Quality Management in South Africa (DWAF, 2000) DWAF describes the means and measures available to achieve groundwater quality management.

The functional approach that DWAF adopted in order to achieve its policy goals is:

- source-directed approach to impact prevention and minimisation (authorisations; licenses, standards; and requirements for on-site management, impacts of water use, and clean-up and remediation);

- resource-directed approach to groundwater quality management (national classification system; management classes; determining the "Reserve," which includes the basic human needs reserve and the ecological reserve; and setting of resource-quality objectives); and
- site-specific, needs-based approach to remediation of degraded groundwater (prioritisation and evaluation; clean-up of abandoned sites; and emergency action procedures or plans for accidental spills)

Implementation of the three strategies (source-directed, resource-directed and remediation) must be integrated to achieve the overall objective of sustainable groundwater utilization. Regulatory instruments provide DWAF with the means to intervene and influence the behaviour of the community targeted for regulation. Intervention is intended to ensure that the policy goals are achieved by inducing the desired behaviour from polluters and potential polluters.

In order to implement the Policy and Strategy, DWAF will launch a series of groundwater quality management programmes. These programmes will have a clearly defined objectives, action plans and time frames. The purpose of each programme will be to develop a component of the strategy and to oversee its implementation into the operational part of the regulatory system.

This investigation took a holistic approach and considered all activities that could influence groundwater quality in an urban environment. The issues highlighted in the recommendations must be considered in the implementation of the Policy and Strategy by DWAF, especially in specific groundwater management plans related to the identified activities and contaminants. Of highest importance is a need to develop policy and guidelines for monitoring of groundwater for organic contaminants. Secondly the development of modeling tools for the prediction of the fate and behaviour of NAPLs and pesticides, under South African aquifer conditions are essential in addressing the above issues.

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Identification and prioritisation of groundwater contaminants and sources in South Africa's urban catchments

Guidelines for Assessing and Evaluating the Impacts of Human Activities
on Groundwater Resources in Urban Catchments

Report 2 of 2

Report to the

Water Research Commission

by

Institute for Groundwater Studies
CSIR, Environmentek and
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1. Background

A reliable assessment of exploitable resources is essential for management of groundwater resources (Bredenkamp *et al.*, 1995). In many regions, economic growth is closely linked to the availability of groundwater. In most urban areas in South Africa, groundwater is less utilized than surface water, but often the bulk of water used in rural communities is groundwater. With increasing scarcity of fresh water resources, urban groundwater may be utilized to a greater extent in future (for example the Table Mountain Group aquifers). In most large cities in South Africa, groundwater is abstracted by private landowners, mainly for irrigation of gardens (Verhagen *et al.*, 1995).

Contamination of South Africa's urban aquifers presents a threat to the sustainability of this water resource. Man's activities, use of chemicals and generation of wastes tend to concentrate potential sources of contamination in the urban areas. The threat caused by undesirable substances is recognized in this country, but the understanding of the extent of the problem in South Africa's urban catchments is poor.

The Institute for Groundwater Studies, entered into a research contract with the Water Research Commission for collaborative research with the CSIR Environmentek and the University of the Western Cape's Groundwater Group to investigate groundwater contaminants and sources in South Africa's urban catchments.

The aims of the investigation are to:

- identify and prioritize the type of contaminants and their associated sources which present a threat to groundwater, the environment and health in South Africa's urban catchments;
- formulate strategies for better understanding the impacts of polluting activities on groundwater resources in urban catchments;
- establish a data information system on South Africa's contaminants.

This report addresses the second aim, by documenting guidelines for assessing and evaluating impacts of human activities on groundwater resources in urban catchments. The report specifically addresses risk assessments and associated risk-based software developed during this project and an Excel-based data information system.

2. Approach and outline

These guidelines are intended to help groundwater practitioners and water authorities in assessing the likely transport, fate an impact of contaminants in the subsurface in an urban environment. Much of the information presented has been collected from a review of the international literature.

The characteristics of urban recharge and mechanisms of groundwater contamination are presented in Section 3. This is supported by a detailed review of the physicochemical properties of inorganic and organic pollutants commonly encountered in urban catchments in Appendix A. The review places a strong emphasis on organic compounds, particularly dense non-aqueous phase liquids, in an attempt to address the need for improving knowledge of organic groundwater contaminants in South African aquifers.

Risk assessment provides a tool for facilitating integrated decision-making in a complex environment.

Section 4 outlines a risk assessment framework for assessing high priority contaminants and sources in urban catchments. Section 5 focuses on the Excel-based data information system. Sections 4 & 5 are supported by the information in Appendix B. Appendix B discusses several approaches that are used to prioritise contaminants or sources of contamination in the urban environment at various scales, from site-specific studies to catchment or regional scale. These may provide useful tools for deciding where to focus attention on groundwater contaminants in an urban catchment.

3. Characteristics of urban contamination of groundwater

3.1 Recharge in urban areas

Recharge in urban areas is a potential source of contamination to aquifers. In general, groundwater recharge estimation is a very complex process and even more so in urban environment.

Rapid urbanisation has profound impacts on the hydrological cycle, including major changes in groundwater recharge (Lawrence *et al*., 1998). Existing infiltration mechanisms are radically modified, and new ones introduced, with evidence of an overall increase in recharge rates. These significant impacts on groundwater can affect the quantity, flow and quality. Changes in groundwater levels, both reductions and increases, can also pose engineering problems for infrastructure and facilities (Chilton, 1998).

3.1.1 *Sources and pathways for urban groundwater recharge*

The sources and pathways for groundwater recharge in urban areas are more numerous and complex than in rural environments (Lerner, 2002). Buildings, roads, and other surface infrastructure combine with man-made drainage networks to change the pathways for precipitation. The large amount of water that is imported into cities for supply and distributed through underground pipes is collected again in sewers or septic tanks. Leaks from these pipe networks often provide substantial recharge. Furthermore, there are major differences in development sequence between higher-income areas, where the process is normally planned in advance, and lower-income areas, where informal settlements are progressively consolidated into urban areas. South African cities are characterized by a combination of formal and informal areas.

These effects of urbanisation on recharge are summarised by Lawrence *et al.* (1998) in Table 1. It must be kept in mind that the impact of any given process will vary significantly with climatic regime, hydrogeological environment, and with the pattern of urban development itself.

Table 1. Effects of urbanisation on subsurface recharge (Lawrence *et al.*, 1998)

Process	**Infiltration Rates**	**Infiltration Area**	**Infiltration Time base**	**Implications for quality**	**Principal contaminants**
MODIFICATIONS TO NATURAL SYSTEMS – DRAINAGE & HARDENED SURFACES					
Roofs & paved areas	Reduction	Extensive	Permanent	Minimal	None
Stormwater soakaways	Increase	Extensive	Intermittent	Marginal negative	Cl, HC, CHC
Mains water drainage	Reduction	Extensive	Continuous	None	None
Surface water canalisation	Marginal reduction	Linear	Variable	Variable	None
Irrigation of recreational areas	Increase	Restrictive	Seasonal	Variable	N, Cl
INTRODUCTION OF WATER SERVICES SYSTEM					
Water supply system	Increase	Extensive	Continuous	Positive	None
Unsewered sanitation	Increase	Extensive	Continuous	Negative	N, FP
Main sewered sanitation	Marginal increase	Extensive	Continuous	Marginal negative	N, FP, DOC

Cl	Chloride and other major ions	HC	Hydrocarbon fuels
N	Nitrogen compounds	FP	Faecal pathogens
DOC	Dissolved organic carbons	CHC	Chlorinated hydrocarbons

3.1.1.1 Precipitation

Figure 1 schematically illustrates some of the many routes by which precipitation recharges groundwater in urban areas. In addition to direct recharge in parks and gardens, localised recharge often occurs along the edges of paths and roads, where no formal stormwater drainage exists. This case is likely to occur in arid and semi-arid areas and in many rapidly urbanising cities, where little storm-drainage infrastructure exists. Thus, many more routes exist for urban than for rural recharge. In addition, Figure 1 does not represent the multiplicity of locations where each recharge route can occur, caused by the high variability of land use and the complexity of the water-carrying infrastructure. Thus, depending on the stormwater drainage arrangements, the net change in the overall groundwater recharge rate can be anything from a major reduction to a modest increase (Foster *et al.*, 1998).

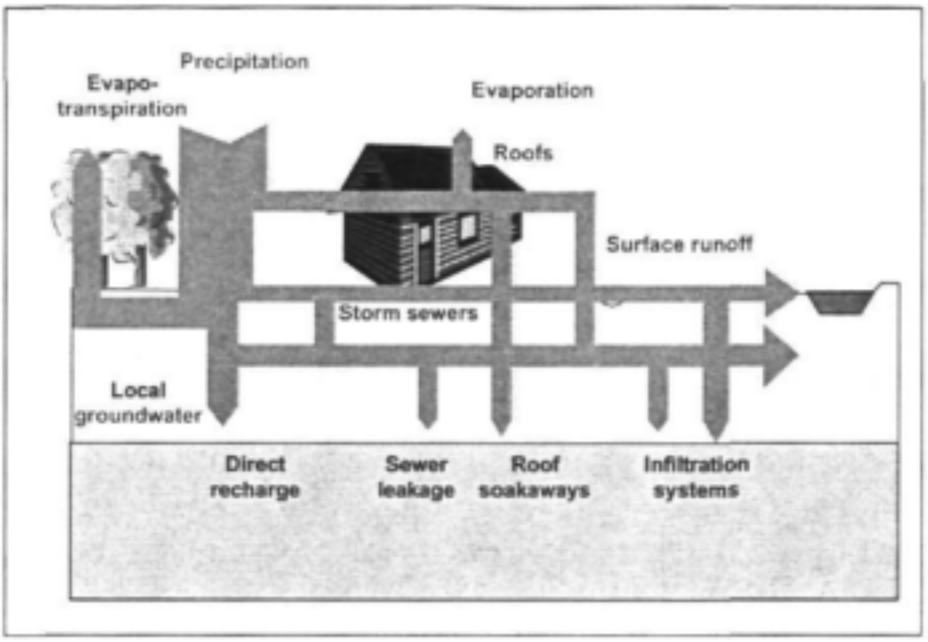


Figure 1. Pathways for precipitation to recharge groundwater in urban areas (Yang, 1999)

Surface impermeabilisation processes include the construction of roofs and of paved areas, such as roads, parking lots, industrial premises, and airport aprons. While the proportion of land area covered is a key factor, some types of urban pavement, such as tile, brick, and porous asphalt, are quite permeable, and conversely, some unpaved surfaces become highly compacted with reduced infiltration capacity. If no stormwater drainage is installed, runoff will infiltrate via soakaways or at the edge of impermeable surfaces; will enter drainage channels; will accumulate in land surface depressions; or will do a combination of these, depending on rainfall intensity and antecedent soil moisture.

The reduction in direct groundwater recharge caused by land surface impermeabilisation is often balanced by increases in indirect recharge of drainage that is routed to soil soakaways or infiltration basins, rather than to urban watercourses via storm drains.

However, this represents a significant increase in the risk of groundwater pollution. Soakaways and stormwater drainage systems are often used for the casual disposal of liquid waste from residential areas, such as used motor oils, or for the illegal connection of septic tank overflows.

3.1.1.2 Imported water

South African cities are characterized by the **import**, utilisation and export of large volumes of mostly surface water from widely differing sources. This imported water is available for recharge (see Figure 2) and sometimes is equal to or exceeds the recharge derived from direct precipitation sources.

The development of a reticulated water supply results in a large volume of water circulating (in pipes) below the ground surface, together with the subsequent disposal of most of this water in sewers or on-site facilities such as septic tanks. Water mains are, for the most part, highly prone to leakage because they are constantly pressurized. However, quantifying this recharge is difficult as no direct measurements are feasible. Rates of leakage of 20 to 25% are common, and rates of up to 50% have been observed (Lerner, 2002). Isotope studies on private boreholes in the northern suburbs of Pretoria found that the concentration of **mains water in the groundwater** ranged from **10 to 100%** (Butler and Verhagen, 1997). However, the most commonly cited sources of unaccounted water include losses on consumer premises, fire fighting, mains flushing and illicit connections. These often represent 30 to 60% of the overall supply. Moreover, a proportion of subsurface leakage may be intercepted by tree roots or enter sewers (or other subsurface ducts) and not reach aquifers, especially if the aquifer is confined.

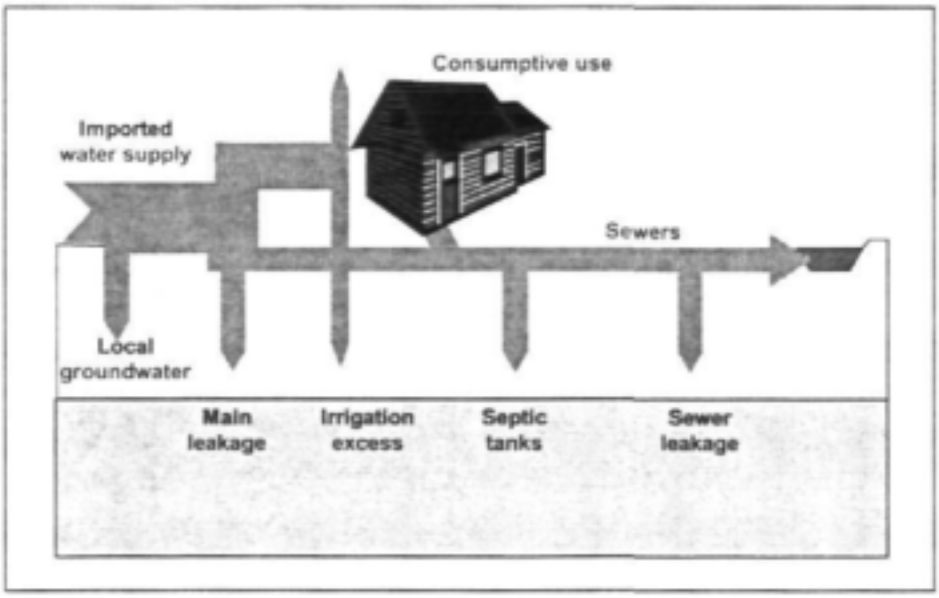


Figure 2. Pathways water supply and sewage to recharge groundwater in urban areas (Yang, 1999)

In cases where cities are sewered, most of the imported water is re-exported and does not become part of the recharge. There is, however, potential for leakage from the sewer systems.

Unsewered sanitation greatly increases the rate of urban groundwater recharge.

Given estimates of consumptive water use in the domestic situation of 5 to 10 % of the water supply, more than 90 % of the water provided will end up as recharge to groundwater, if all wastewater is disposed of to the ground via on-site sanitation units. This recharge will generally have a major influence on the urban groundwater balance, especially in areas of high population density with piped supply (Foster et al., 2002).

3.1.2 *Quantifying Urban Recharge*

The quantifying of urban groundwater recharge is a complex problem that requires a multi-tiered approach. One such an approach is outlined in Figure 3.

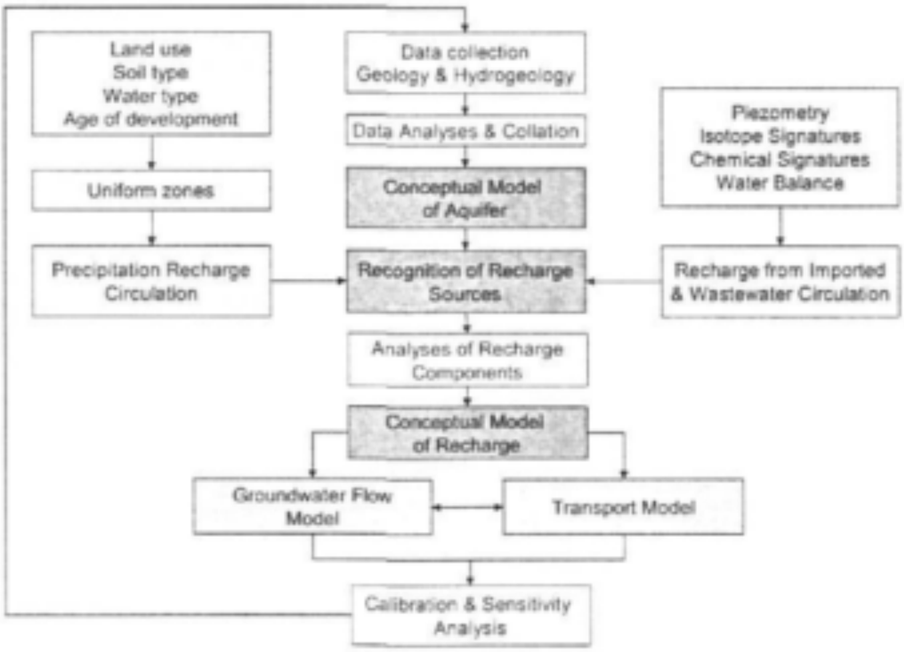


Figure 3. Flow chart of recharge quantification methodology.

In order to form the correct conceptual model of the aquifer under consideration, adequate data of all geological and geohydrological features need to be collected, analysed and collated. The detail and extent of this data collection will be determined by factors such as the required level of sophistication of recharge determination as well as the size of the study area.

The next important step is the recognition of recharge sources. Often recharge is calculated for zones of uniform land use, soil type and water infrastructure (Lerner, 2002). The simplest method to determine direct recharge from precipitation is from the equation (Lerner, 2002):

$$\text{Precipitation} = \text{Evapo(transpi)ration} + \text{Runoff} + \text{Recharge} \qquad \text{Equation (1)}$$

If one considers the errors in measuring the evapotranspiration and runoff on a citywide scale, Equation (1) is probably not an accurate method to estimate recharge, or even to distinguish between the results of rural and urban analyses. This suggests that an analysis of each of the recharge components is more likely to be satisfactory. Stephenson (1992) and Lambourne and Coleman (1992) established methodologies to estimate effects of urbanization on run-off in urban catchments in South Africa. Although these methodologies have their restrictions, they are valuable in terms of the applicability to the typical South African environment.

3.1.2.1 Recognition of recharge sources

Types of urban recharge can be described as (Lerner, 2002):

- direct recharge,
- localized recharge,
- leaking sewers, and
- stormwater infiltration systems (combining several different recharge routes).

One of the most frequently used methods to estimate *direct recharge* is a soil-moisture balance (SMB) (Bredenkamp, *et al*., 1995). Little is known on the significance of *localized recharge* in urban areas. Most cities have many paths, parking lots, compacted soils, driveways, and other low permeability surfaces that do not have any storm drainage associated with them. It is likely that localised recharge occurs from such "low" permeability surfaces. Lerner (2002) suggests that if such localised recharge occurs, it passes through the soil zone and so plays some part in the SMB. Hence, a proportion of the impermeable area (perhaps 50%) should be treated as permeable, particularly in residential areas. This percentage can even be greater when considering areas where rapid urbanization takes place (e.g. informal townships on the outskirts of South African cities and towns), because proper infrastructure such as tarred roads, drainage systems, etc. lags behind the development.

Stormwater recharge is also difficult to estimate. This source could consist of localised recharge, e.g. recharge through soakaways on individual properties; leaks from stormwater sewers, drains and ditches; infiltration from stormwater retention ponds and deliberate artificial recharge through infiltration basins or injection boreholes. Thus to make good estimates of stormwater recharge, information describing the stormwater drainage network and its condition are needed. Estimating leakage rates is difficult, given that leakage occurs mainly in transient conditions at high-flow periods. In most cases, a simple empirical approach is adopted, either by assuming that a proportion of storm flow (or rainfall) becomes recharge, or by ignoring the effects of impermeabilisation for part of the land surface (as suggested above for localised recharge) (Lerner, 2002).

As previously discussed (Section 3.1.1.2) the main source of recharge in the urban setting is *imported mains water*. This source has many possible routes of recharge and a combination of methodologies must be followed to make a realistic calculation of this recharge source. The principal routes of imported water to groundwater are leaking water mains and sewers; infiltration from septic tanks (and similar wastewater facilities) and over-irrigation. Thus, a complete urban water balance should take account of water infrastructure. The most practical method of estimating recharge from imported water is likely to be an overall water balance of the water supply and disposal system. This approach requires only a measurement of the total imported water supply and an estimate of consumptive use, which is feasible if the sewer outflow is measured. An overall water balance is, however, unlikely to be accurate in most cases.

The most effective way of dealing with the recharge contribution from *leaking mains water* is to calculate the water balance of the water supply network by means of measurement of the Minimum Night Flow (Lerner, 2002). This is done by isolating a zone of the city so that all water supply flows through one pipe in which the flow is measured during the night-time, between 2 and 4 a.m., when legitimate uses are few.

Leaking sewers are less significant in their contribution to recharge volumes and can be estimated by empirical water balance methods.

3.1.2.2 Use of chemical signatures

The approach of calculating a water balance does not work when the recharge is a small proportion of the water balance; when the data have high uncertainty; or when alternative destinations exist for the water. In such cases, other approaches, such as the use of chemical signatures need to be taken (Lerner, 2002).

The concentrations of various solutes in water, or the ratios between solute concentrations, define the chemical signature of the water. Such signatures are widely used in hydrogeology to identify waters and their origins and potential exists for using such markers for identifying various sources of urban recharge. Barrett *et al.* (1999) argue that an ideal recharge marker is an easily analysed solute that is unique to one source and to one pathway, at a constant concentration in the source, and non-reactive in all conditions. They point out that such solutes are rare.

Potential marker solutes are divided into four categories, as follows (Barrett *et al.*, 1999):

- *Inorganic*, which are further grouped into major cations (Ca, Mg, K, and Na) and anions (HCO_3, SO_4, and Cl), nitrogen species (NO_3 and NH_4), metals (Fe, Mn, and trace metals), and other minor ions (B, PO_4, Sr, F, Br, and CN).
- *Organic*, of which the most relevant are chlorofluorocarbons (CFCs); trihalomethanes (THMs); faecal compounds, such as coprostanol and 1-aminopropanone; detergent-related compounds, such as optical brighteners and EDTA; and industrial chemicals, including chlorinated solvents and many hydrocarbons.
- *Particulate*, including faecal microbiological species and various colloidal particles.
- *Isotopes*, particularly the stable isotopes (^{2}H, ^{15}N, ^{18}O, and ^{35}S).

The problem with this methodology is that multiple sources exist for most potential tracers. For example, boron (B) is a component of domestic detergent but is found in industrial processes and also has a geochemical origin. Therefore, its presence in groundwater is not in itself proof of leaking sewers or infiltration from septic tanks. The same difficulty applies to virtually all other tracers and no universally applicable tracers are known for identifying recharge sources. In other cases, combining the evidence from multiple tracers has greatly increased confidence in the outcome, despite the uncertainties involved in determining the origin of each individual tracer.

Occasionally, the use of single tracers, particularly isotope tracers, can identify a source of urban recharge. Verhagen and Butler (1995) tested the use of isotope signatures for estimating the proportion of mains water that enters aquifers in urban environments in South Africa. The mains water supply in the Midrand and Pretoria areas was found to have a distinctive δ^2H - $\delta^{18}O$ composition, which differs from the naturally recharged groundwater. This difference in mean $\delta^{18}O$ and δ^2H values amounted to thirty times the standard deviation of the measurements, which allowed for the detection of as low as 10% of mains water in the groundwater.

3.1.2.3 Modelling of recharge

Once all the recharge components are analysed, a conceptual model of the urban groundwater recharge can be formed. This is then fed into a flow model where there is the option of enhancing calculations with a transport or solute model (Yang *et al.*, 1999). Recharge is used as the calibration parameter in the flow model, provided there is available data on all other parameters and state variables (Lerner, 2002). Information on solute loadings to an aquifer and concentrations in groundwater are used to analyse the subdivision of recharge into some of its components, but only if the solute is conservative and, loadings and concentrations are in steady state.

3.1.3 Summary of urban recharge characteristics

It is now widely recognized that urban recharge is as high, or higher, than in equivalent rural areas. The losses of recharge due to hardening or surfaces are balanced or exceeded by the additional recharge from imported water supply networks, through leaking water mains and septic tanks. Unfortunately, the variance and complexity of the land surface and water-carrying infrastructure in urban areas makes it difficult to estimate urban recharge accurately. The usual methods of estimating recharge can be used, but keeping in mind that the complexities of the city and the lack of adequate data lead to high uncertainties. A holistic approach is recommended, where a combination of recharge estimations are used to identify and quantify recharge via various pathways.

3.2 Mechanisms of groundwater contamination in urban areas

There are an ever-increasing number of soluble chemicals derived from urban effluents, industrial activities, and solid waste disposal that are posing a threat to groundwater resources (Figure 4).

The slow movement of water from the land surface through the vadose zone to deep aquifers means that it may be many years after a chemical first enters the ground before it affects the quality of groundwater resource. This lag results in problematic concentrations of contaminants being detected long after the initial incidence of pollution has occurred.

The ability of natural subsoil profiles to attenuate many water pollutants has long been implicitly recognized by the widespread use of the subsurface as a potentially effective system for the safe disposal of human excreta and domestic wastewater (Foster *et al.*, 1998).

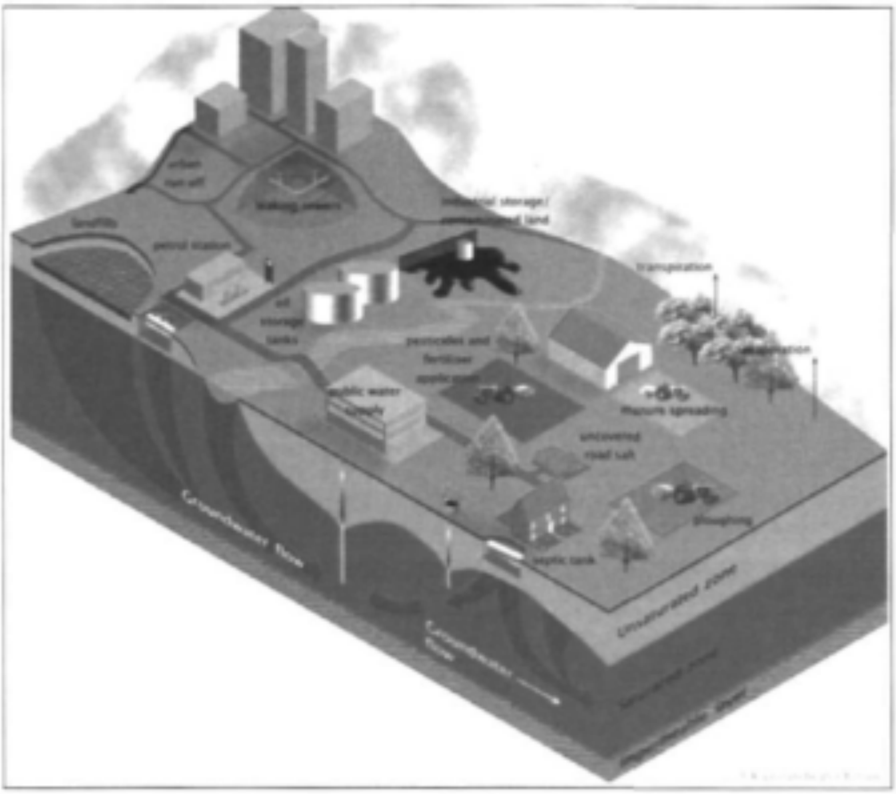


Figure 4. Sources and mechanisms of groundwater contamination (http://www.nwl.ac.uk/gwf)

To a lesser degree, the attenuation processes continue below the soil, deeper in the vadose zone, especially where unconsolidated sediments (as opposed to consolidated fissured rocks) are present. Thus the natural thickness of this zone is an important factor, one that in an urban setting may be modified by engineering disturbance or by-passed by some effluent or drainage soakaways. In addition, once urban recharge reaches the water table, hydrodynamic dispersion of contaminants in groundwater flow will dilute persistent and mobile pollutants. Further mixing and dilution will take place in production boreholes from which water supplies are pumped because such boreholes generally intercept or induce groundwater flows at various depths and from various directions, not all of which will normally be contaminated.

However, not all soil profiles and underlying hydrogeological environments are equally effective in pollutant attenuation. Moreover, the degree of attenuation will vary widely with types of pollutants and polluting processes in any given environment. The risk of groundwater pollution is therefore relative. Aquifer vulnerability is a helpful concept widely used to indicate the extent to which groundwater can be adversely affected by an imposed contaminant load. Improved methods for aquifer vulnerability assessment and vulnerability maps are being developed taking into account information on soils under a current (2003 – 2006) WRC-funded project (K5/1432).

A contaminant introduced into the soil-rock-groundwater system will spread within the system only if a transport mechanism is available, for example, a flowing liquid. As soon as the contaminant reaches the subsurface water in the unsaturated or saturated zone, various processes determine its fate (Zaporozec, 2002):

- *physical processes:* advection, dispersion, evaporation, filtration, and degassing;
- *geochemical processes:* acid-base reactions, adsorption-desorption, ion exchange, oxidation-reduction, precipitation-dissolution, retardation, and complexation; and
- *biochemical processes:* transpiration, bacterial respiration, decay, and cell synthesis

Many of these processes are related to each other or interact in some way. Some of them may attenuate the contaminants, while others have the reverse effect. The soil zone is the most reactive part of the system due to the soil-water-air environment, soil-plant behavior and microbiological activity. Short-circuiting of this zone, which is common due to construction activities in the urban environment, makes the soil-rock-groundwater system much more vulnerable to contaminant.

Contaminants are carried by moving groundwater (*advection*) and travel at the same rate as the average linear velocity of groundwater. The process of *dispersion* acts to dilute the contaminant and lower its concentration. For example, because of hydrodynamic dispersion, the concentration of a waste plume will decrease with distance from the source. Dispersion increases with increasing groundwater velocity and aquifer heterogeneity. However, for removal of bacteria and viruses by filtration, a fine-grained and homogeneous material is needed. Volatile products of microbiological processes, such as carbon dioxide, nitrogen, or methane, and volatile organic compounds may be removed by degassing.

Chemical reactions, such as adsorption-desorption and ion exchange, can retard the rate of movement of specific types of contaminants. Adsorption and desorption are characterized by a distribution coefficient, which expresses the ratio of the amount of contaminant adsorbed, per gram of soil material, to the amount of contaminant remaining in groundwater. The distribution coefficient can be used to compute the retardation of the movement of the contamination front (Fetter, 1999).

Even though organic contaminants are generally considered to be non-aqueous phases, most are partially soluble. Thus if these contaminants reach the water table, a portion of these contaminants will move in pollution plumes, analogous to those of inorganic contaminants. The major difference is that most of these dissolved phases are not conservative and several mechanisms lead to the differential characteristics of organic contaminants within plumes.

Bacteria use the reaction energy of oxidation-reduction (redox) reactions for their metabolism. After free oxygen is used up, anaerobic bacterial respiration may successfully reduce nitrate, sulphate and even carbon dioxide and decompose organic compounds. Many toxic organic chemicals can undergo microbial decay to more simple compounds.

The complexity of contaminant attenuation mechanisms are illustrated using an example of nitrogen (nitrate and ammonium) contamination by fertilizers. Crops will take up some of the nitrogen released from the fertilizers. However, about 30 to 70 % of the consumable nitrogen output of a farm is typically leached into the subsoil and further concentrated in the unsaturated zone by evaporation. A part of the dissolved nitrogen will be removed, while the remainder will be added to the soil water. Removal takes place by bacterial cell synthesis and further by nitrate respiration under anaerobic conditions, when bacteria break nitrate down to molecular nitrogen. Decay (mineralization) of litter by bacteria will add nitrate and ammonium to the system. Ammonium ions are readily adsorbed on clay particles, but under aerobic conditions, ammonium is subsequently oxidized to nitrate, which is soluble, poorly adsorbed and very mobile. The nitrate moves with the infiltrating water to the saturated zone (advective transport) and is diluted by dispersion. The dispersive capacity of the porous medium is directly proportional to the pore-water velocity and the heterogeneity of the aquifer materials. During residence in an anaerobic saturated zone, nitrate may be reduced to nitrogen gas by biological denitrification in the presence of denitrifying bacteria and organic carbon. Nitrate may also be reduced to nitrogen by reaction with ferrous iron, e.g. in pyrite. In turn, pyrite is oxidized and may release other contaminants, particularly heavy metals, e.g. bivalent Cd, Ni, or Zn, which become mobile under acidic conditions or by complexation with organic substances (Zaporozec, 2002).

4. Prioritisation of contaminants and sources in South African urban environments

4.1 General

A rating or ranking system (prioritisation system) gives an idea of the magnitude of the problem associated with a potential contaminant and allows energy and resources to be directed to better understanding, regulating or engineering control measures for the most serious threats (Johansson and Hirata, 2002). Detailed ranking/prioritisation systems are given in Appendix B.

Johansson and Hirata (2002) make a distinction between ranking and rating systems. Ranking is used for a relative, subjective arrangement of contaminants from most to least hazardous or by any other priority. This is the system often used by regulating authorities. Rating occurs when contaminant sources are given a quantitative or qualitative measure of the potential hazard they pose to groundwater. Prioritisation methods focus on aspects such as contaminant loading, mobility, persistence and hazardousness while risk assessment develops these further into potential human health impacts. A risk analysis estimates the probability and consequences of a contaminant event and usually considers both the properties of the contamination source and the hydrogeological environment. A similar approach will be followed in this section.

Based on the amount of data available a tiered approach is followed when considering risk assessments. The first tier (LEVEL 0) is a rapid assessment of sources and associated contaminants in which minimal data are required and it produces low confidence results. This assessment should be completed within a few minutes and is based on a rating system. LEVEL 1 is the second tier which is an intermediate assessment of contaminants on a local scale. It is intended to give the assessor a guideline of the risks. The assessment should take a couple of hours to complete. The next tier (LEVEL 2) is a comprehensive assessment. The first step in the comprehensive assessment is to collect all relevant data. Data requirements include aquifer and contaminant parameters, as well as health information. General information will be obtained from databases, but it is sometimes necessary to have site-specific data. The confidence attached to this assessment should be medium to high. Both the first and second levels include risk assessments based on a fuzzy logic methodology. Each of the components of the prioritisation methodology (Figure 5) will be discussed in more detail in the following sections.

4.2 National ranking of contaminants and sources

4.2.1 National ranking of sources

Sources, refer to the origin of the substances that are causing, or may potentially cause, contamination. A simplified classification based on that of Nonner (2002) was used to prioritise South African sources (see Table 2). Weights were assigned to the different conditions listed in Table 2. These were then included in a rating system similar to that of Johansson and Hirata (2002).

Table 2. Systems for prioritisation of groundwater contamination sources

Classification based on	Conditions
Loading history	Spill or continuous
Location of source	Above ground surface, below surface
Degree of localization	Point (or line) and non-point sources
Likelihood of groundwater contamination	Contained or uncontained
Likelihood of occurrence	For example petrol service stations found more often than chemical manufacturing plants

4.2.2 National ranking of contaminants

There are various ways in which to group groundwater contaminants. The contaminants are then rated within each group:

- Fate in the environment
    - The method used to rate this aspect is documented in Section 5.
- Human health impacts
    - Non-harmful substances, which have no observed effects on human health

  - Toxic substances, which 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 are assigned to each contaminant according to health effects associated with that contaminant.

4.3 Tier 0: Regional prioritisation of sources and contaminants

Tier 0 is a basic screening level assessment using professional judgement and considers only 3 factors for source evaluation:

- Source: this allows the contaminant sources classified by danger rating of high, medium or low. These ratings come directly from the national ranking of sources discussed in Appendix A.
- Estimated number of similar sources within study area. The following rating is used:
  - 1 – 5 sources ⇒ low rating
  - 5 – 10 sources ⇒ medium rating
  - ≥ 10 sources ⇒ high rating
- Level of management at the source is also rated:
  - Exceptional level of management ⇒ low rating
  - Average level of management ⇒ medium rating
  - Unsatisfactory level of management ⇒ high rating

Contaminants related to the sources can also be evaluated taking the following into account:

- Fate of the contaminant in the environment and
- Health impacts related to the contaminant
- Prioritisation of the source.

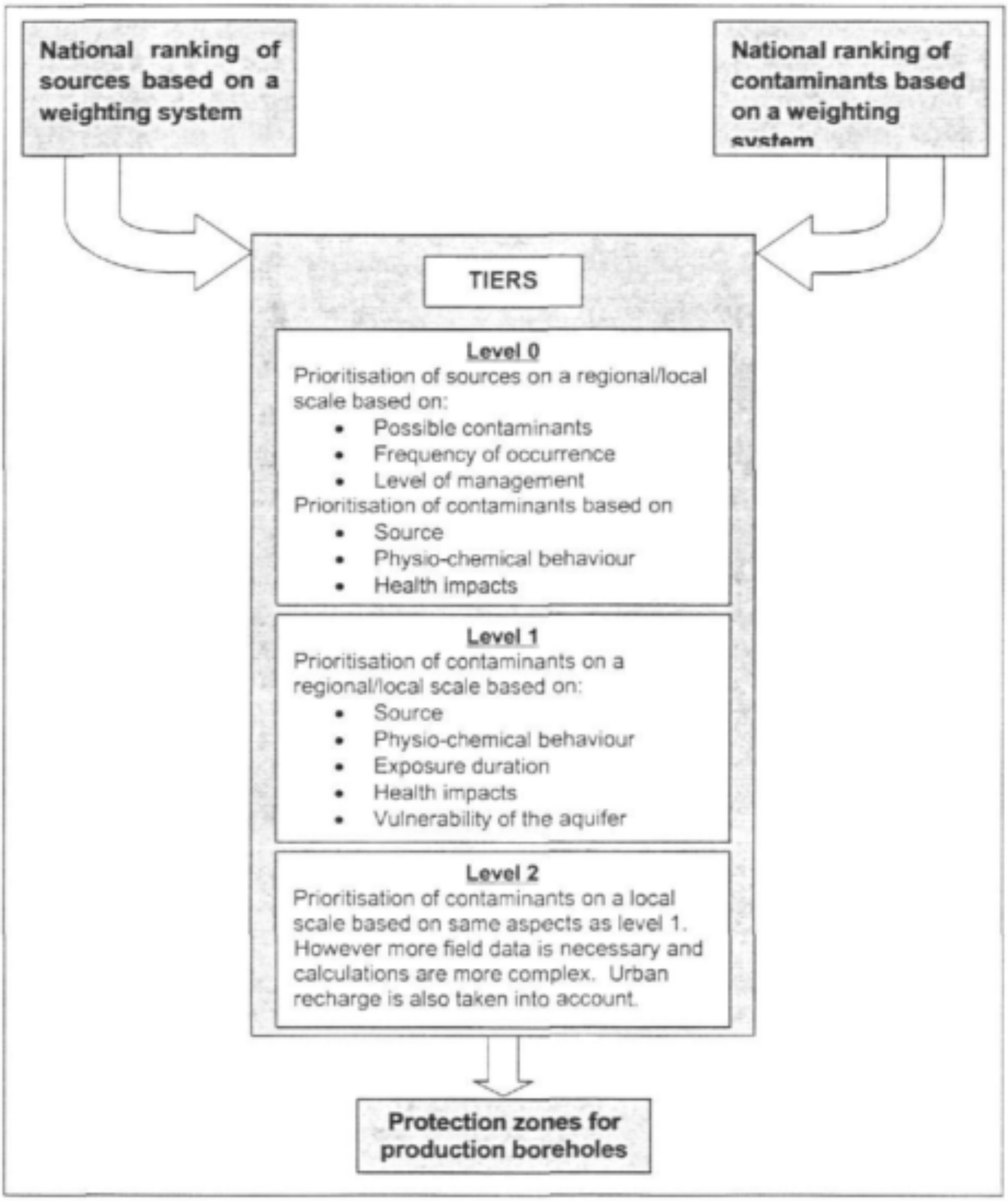


Figure 5. Tiered approach to South African prioritisation methodology

4.4 Tier 1 & 2: Prioritisation of contaminants on a local scale

4.4.1 *Factors taken into account in the risk assessments*

A fuzzy logic based approach was followed when conducting the risk assessments. For a detailed explanation of this methodology refer to Appendix C. The factors taken into account in the risk assessments are:

- Exposure is defined by the frequency, magnitude and duration of contact with the contaminant. Frequency refers to whether a person is exposed daily or just occasionally. The magnitude refers to the amount of exposure; occupational exposure will be greater than community exposure. The duration refers to whether any single exposure episode may last for minutes, hours, days or years.
- Aquifer vulnerability represents the intrinsic characteristics that determine the sensitivity of an aquifer to the adverse effects resulting from the imposed contaminant (Lynch *et al.*, 1994). The DRASTIC approach was followed to determine the vulnerability of an aquifer. The parameters needed for describing vulnerability are:
    - Depth to groundwater: this gives an indication of the distance and time required for the contaminant to move through the unsaturated zone to the aquifer.
    - Recharge: the primary source of groundwater is precipitation which aids the movement of a contaminant to the aquifer. In the TIER 2 assessment urban recharge is taken into account by taking into considerations the factors listed in Table 1. In addition the methods used to calculate recharge become more complex in TIER 2 (Refer to Appendix C).
    - Aquifer media: the consolidated or unconsolidated rock matrices that serve as water-bearing units. In this approach, the fractures that occur in the rock matrix will also be taken into account.
    - Soil media: this consists of the upper portion of the vadose zone (Aller *et al.*, 1987). The soil media can affect the rate at which contaminants migrate to groundwater.
    - Topography: will give an indication on whether a contaminant will run off or remain on the surface long enough to infiltrate into the groundwater.
    - Impact of the vadose zone: this is defined as that portion of the geological profile beneath the earth's surface and above the first principal water-bearing aquifer (Lynch *et al.*, 1994). The vadose zone can retard the progress of the contaminant.

- Health effects of contaminant. A groundwater health risk assessment can be defined as a qualitative or quantitative process to characterise the probability of adverse health effects associated with measured or predicted levels of hazardous agents in groundwater. Once a contaminant is released into the groundwater, its resultant concentrations found in the human body is dependent upon the physical and chemical properties of both the contaminant and the groundwater. In addition the concentrations found in a human are subject to the person's exposure to groundwater. Once the contaminant is inside the body it may be further transformed via metabolism or detoxification. The ability to transform chemicals varies. Children, the elderly and those with chronic conditions, for instance, react differently to the same dose than the average, healthy middle-aged adult (Schwab and Genthe, 1998).
- Source type is directly linked to the national ranking of contaminant sources discussed in Section 4.2.1.
- Physio-chemical aspects of contaminants. A wide literature and internet search was carried out to determine the physio-chemical properties of contaminants and include them in the excel database information system. Three physio-chemical processes were identified to be particularly relevant to groundwater pollution: volatilization, sorption and degradation (decay). Volatilization can be described with Henry's constant (H_c), sorption with the organic carbon partition coefficient (K_{oc}) and degradation with half-life ($t_{1/2}$). These properties are also generally used in index methods to rank contaminants according to their physio-chemical properties (Rao *et al.*, 1985). The Excel database together with the physio-chemical rankings are discussed in detail in Section 5.

4.4.2 Assumptions and limitations

4.4.2.1 Level 1 risk assessment

- No chemical analyses are needed and the concentrations of the contaminants are therefore not included in the assessment. If there are also no field observations for the data discussed in Table 3, then values from maps or the literature recorded in a database can be used.
- In addition exact exposure durations are not included in the calculations. The following exposure categories are used:
    - Contamination may be seconds, minutes or hours
    - Contamination occurs at intermittent periods < 2 years
    - Contamination > 90 days and < 2 years
    - Contamination occurs at intermittent periods > 2 year

  - Continuous contamination > 2 years
- The exposure pathway (oral, dermal and inhalation) is not taken into account.
- Only natural recharge is taken into account.

4.4.2.2 Level 2 risk assessment

- It is assumed that an adult weighs 70 kg.
- It is assumed that a child weighs 10 kg.
- It is assumed that a person drinks 2 liters of water a day.
- It is assumed that a person inhales 20 m^3 of air a day.
- It is assumed that the average lifetime of human is 70 years.
- Only direct exposure (oral, dermal or inhalation) to groundwater is considered. Indirect pathways are not taken into account, for example eating foods irrigated with contaminated groundwater.
- If the pollutant is not carcinogenic, or toxic then health risks are considered to be zero.
- If the exposure to a pollutant is zero, then the health risks are considered to be zero.
- Only the carcinogenic effects of radioactive elements are considered.

4.4.2.3 General

No ecological aspects are taken into account as many of the impacts of contaminants are not accurately documented.

4.4.3 Data requirements for risk assessments

Table 3 is a summary of the data required for the risk assessments.

Table 3. Data required for risk assessments

Data required	**Level 1**	**Level 2**
Vulnerability assessment		
Depth to groundwater	User	User
Recharge	Map[1]/User	Map[1] OR
Rainfall	-	User
Chloride in rainfall	-	Laboratory analyses
Chloride in groundwater	-	Laboratory analyses
Water levels in boreholes	-	User
Information concerning area		User
Aquifer media	Geological map/User	Borehole logs/augering
Soil media	Soil map[2]/User	Soil map[2]/Laboratory analyses
Topography	Topographical map/User	Topographical map/Field data
Vadose zone information	Database[3]	Database[3]/Field data
Health assessment		
Chemical	User to choose from list in software	User to choose from list in software
Concentration	-	Laboratory analyses
Cancer potency factor	-	Database[3]
Reference dose	-	Database[3]
Average intake rate	-	Average values documented software
Body weight	-	Average values documented in software
Life time age of person	-	Average values documented in software
Exposure assessment		
Exposure duration	User to choose from values in software	User
Source assessment		
Source	Risk rating directly from national assessment	Risk rating directly from national assessment
Physio-chemical assessment		
Henry's constant	Excel database	Excel database
Organic carbon partitioning coefficient	Excel database	Excel database
Half-life	Excel database/User	Excel database/User

[1-2]Maps included in software. [3] Information included in software

4.4.4 *Calculating risk factors*

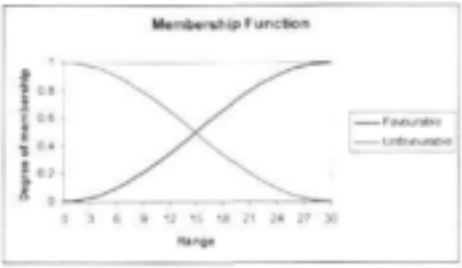
4.4.4.1 Vulnerability assessment

As already mentioned a fuzzy logic based assessment (see Appendix C) was used, the membership functions used are shown in Table 4.

Table 4. Membership functions for vulnerability assessment

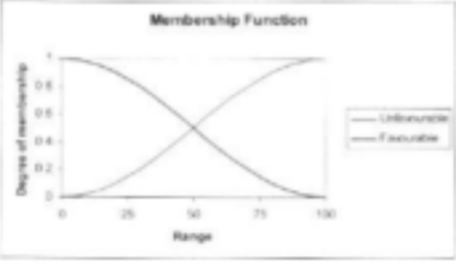
Vulnerability membership functions/values

Depth to groundwater[1] (m)



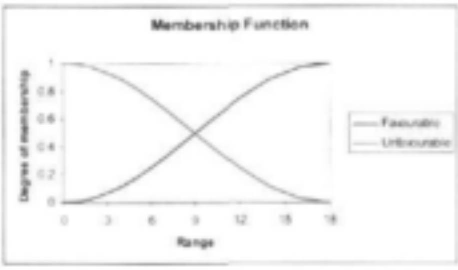
Unfavourable limit	**Favourable limit**
0	30

Recharge[1] (mm/year)



Unfavourable limit	**Favourable limit**
100	0

Topography[1] (%)



Unfavourable limit	**Favourable limit**
0	18

Soil media[1]

Type[2]	**Membership**
SaCl, SaCl-Cl	0.6
SaClLm-Cl, SaClLm-SaCl0.6	
SaClLm, SaLm-SaCl	0.5
SaLm-SaClLm	0.5
SaLm	0.4
Sa-LmSa, SaLmSa etc	0.35
Sa-SaLm, LmSa-SaLm, LmSa	0.3

Aquifer Media[1]

Type	**Membership**
Dolomite (massive)	1.0
Intergranular	0.2
Fractured	0.4
Fractured and weathered	0.7
Dolomite (karstic)	0.0

Impact of the vadose zone

Type	**Membership**
Beach sands and Kalahari	0.0
Dolomite	0.1
Table Mountain, Witteberg, Granite, Natal, Witwatersrand, Rooiberg, Greenstone, Dominion, Jozini	0.4
Karoo (southern)	0.5
Ventersdorp, Pretoria, Griqualand West, Malmesbury, Van Rhynsdorp, Uitenhage, Bokkeveld, Basalt, Waterberg, Soutpansberg, Karoo (northern), Bushveld, Olifantshoek	0.6
Gneiss, Namaqua metamorphic rocks	0.7

[1] Taken from Lynch *et al.* (1994). [2] Sa = sand, Lm = loam, Cl = clay.

4.4.4.2 Health assessment

Tier 1

A fuzzy logic approach is once again followed, therefore the membership functions are listed in Table 5.

Table 5. Membership functions for health at Tier 1 assessment

Tier 1 Health Risk Assessment Membership Functions			
Toxic			
Range		**Membership value**	
Death		0.0	
Effects common		0.25	
Long-term effects		0.4	
Few effects		0.8	
Carcinogen		**Exposure duration**	
Range[1]	**Membership value**	**Exposure**	**Membership value**
A: known human carcinogen	0.0	Contamination may be seconds, minutes or hours	0.9
B1: probable human carcinogen (limited data)	0.25	Contamination occurs at intermittent periods < 2 years	0.6
B2: probable human carcinogen (inadequate data)	0.25	Contamination > 90 days and < 2 years	0.6
C: possible human carcinogen	0.5	Contamination occurs at intermittent periods > 2 year	0.3
D: Not classified as a human carcinogen	0.75	Continuous contamination > 2 years	0.0
E: Evidence that not a human carcinogen	1.0		

[1] Taken from US EPA Classification of Carcinogens (EPA, 1988).

Tier 2

For this assessment the EPA (2000) methodologies where followed. Toxic and carcinogenic assessments take into account the routes of exposure as documented in Table 6.

Table 6. Exposure pathways considered in groundwater driven risk assessments (Maxwell *et al.*, 1998)

Routes of exposure	Groundwater exposure pathway
Ingestion	Drinking groundwater
Inhalation	Inhalation of contaminant transferred from water to vapor in air
Dermal sorption	Sorption through skin in baths and showers

Before calculating the risks associated with both these assessments, the total dose, average daily dose and lifetime average dose have to be defined. The equations used to define risks associated with human exposure to contaminated groundwater are generally based on those specified in the EPA "Risk Assessment Guidance for Superfund" (EPA, 1989). For each pathway, the total dose that will reach a human has to be calculated. The total dose is defined as:

$$\text{Dose} = C \times IR \times ED$$

where

Dose = Total dose
C = Maximum concentration
IR = Average intake rate
ED = Exposure duration

The average daily dose (ADD) is determined by dividing an estimate of the total dose accrued during the exposure duration from a pathway by an averaging time or an expected lifetime:

$$\text{ADD} = \frac{\text{Dose}}{\text{BW} \times \text{ED}}$$

where

BW = Average body weight over exposure period

Carcinogenic risk assessments are determined over a human's lifetime. Therefore the lifetime average daily dose (LADD) is calculated as:

$$\text{LADD} = \frac{\text{Total dose}}{\text{BW} \times \text{lifetime}}$$

The carcinogenic risk calculation is based on a Poisson model:

$$\text{Risk} = 1 - e^{-\text{LADD} \cdot \text{CPF}} \approx \text{LADD} \times \text{CPF}$$

where CPF is the cancer potency factor. The potency factor is the slope of the percentage of animals developing cancer versus the dosage level of a particular chemical. The slope of this curve is then extrapolated to the low doses expected to be encountered by humans who may be exposed to the same chemical. Because of the complex uncertainty involved with calculating the cancer potency, these values are obtained from the IRIS (EPA, 1988) database and included in the software.

The toxic risk is calculated as:

$$\text{Risk} = \frac{\text{ADD}}{\text{RfD}}$$

where

RfD = Reference dose

The reference dose is an estimate of daily exposure to the population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. These values are documented in the IRIS database (EPA, 1988) and will be included in the database (See Excel spreadsheets).

4.4.4.3 Physio-chemical assessment

The physio-chemical assessment is discussed in detail in Section 5.

4.5 Protection of groundwater resources

A capture area or zone is defined as the area contributing flow to that particular borehole. If the groundwater heads are flat, the capture zone is radially symmetrical, centered on the borehole and extending as far as the cone of depression. However, if there is a slope in the groundwater heads, there is regional groundwater flow and the capture zone is asymmetrical, with the greatest extent in the up-gradient direction. The shape of the capture zone is a function of the average linear groundwater velocity, the quantity of water being pumped from the aquifer, and the distribution of hydraulic conductivity. The up-gradient extent of the capture zone depends on the length of time over which the pumping occurs (Fetter, 1999). Traditionally numerical models have been used to determine capture zones. However there may not always be sufficient data to use this methodology. Therefore if there is insufficient data available, wellhead protection areas (WHPAs) need to be delineated. A WHPA can be defined as the surface and subsurface area surrounding a production borehole or wellfield, through which contaminants are reasonably likely to move and reach such a borehole or well field. In many cases it is difficult to protect the whole area, therefore various zones are established within the area. These zones are defined and discussed in Table 7.

Table 7. Zones within WHPA (Summarised from Braune, 2000; EPA, 2001 and Boulding, 1995)

Zone	**Definition**	**Calculation**
Zone 1: Accident prevention or sanitary protection.	Highly protected area around the borehole or spring. Its purpose is to protect the borehole or spring from the direct introduction of contaminants into the borehole and its immediate area from spills, surface runoff, or leakage from storage facilities or containers. Potential contaminant sources in Zone 1 should be strictly monitored.	Determine 50 day travel time: $r_{50} = \frac{50K\frac{dh}{dl}}{n_e}$ where K = hydraulic conductivity, dh/dl = groundwater gradient and n_e = effective porosity.
Zone 2: Attenuation	Is established to protect a borehole from contact with pathogenic micro-organisms (e.g. bacteria and viruses) which can emanate from a source (eg septic system) located close to the borehole, as well as to provide emergency response time to begin active cleanup and/or implementation of contingency plans should a chemical contaminant be introduced into the aquifer near the borehole.	2 year TOT[1] radius area. The radius is calculated as: $r_{TOT} = SF\sqrt{\frac{Qt}{n_e D\pi}}$ where Q = Annual average pumping rate, n_e = effective porosity, D = saturated thickness of aquifer, t = 2 years time of travel and SF = safety factor (=1.3 when all values are known, = 1.5 when there are some unknowns). In the case of a fractured rock system, the porosity must reflect the nature of the system.
Zone 3: Remedial action	Is designed to protect the borehole from chemical contaminants that may migrate to the borehole; it typically includes a major portion of the recharge area or the capture zone.	5 year TOT radius. The radius is calculated as: $r_{TOT} = SF\sqrt{\frac{Qt}{n_e D\pi}}$ where Q = Annual average pumping rate, n_e = effective porosity D = saturated thickness of the aquifer, t = 5 years time of travel and SF = safety factor (=1.3 when all values are known, = 1.5 when there are some unknowns). In the case of a spring determine radius of influence with t = memory time of the spring. In the case of a fractured rock system, the porosity must reflect the nature of the system.

[1] The TOT criterion bases WHPA delineations on the amount of time it takes groundwater to travel from a point source to a borehole.

4.6 Example using the risk assessment software: A wastewater treatment works

4.6.1 *Background*

The City of Cape Town (CCT) is located in the Western Cape Province on the south-eastern corner of South Africa (see Figure 6). CCT has a mean annual rainfall of 515 mm/annum and an average temperature of 16.7 °C. It is a winter rainfall area. The current population of the CCT is estimated at 3.2 million with the highest population density occurring on the Cape Flats and there are approximately 90 000 consumers on informal sites

Wastewater plants pose a risk to groundwater contamination and thus it is important to have proper management strategies in place. In general the waste management process in natural systems often involves chemical consumption, disposal, recycling, storage, concentration, dispersion and detoxification. There are 21 wastewater treatment plants within the CCT (see Figure 7) and 3 additional treatment plants in the area surrounding the CCT.

Figure 6. Location (*taken from www.capetown.gov.za*)

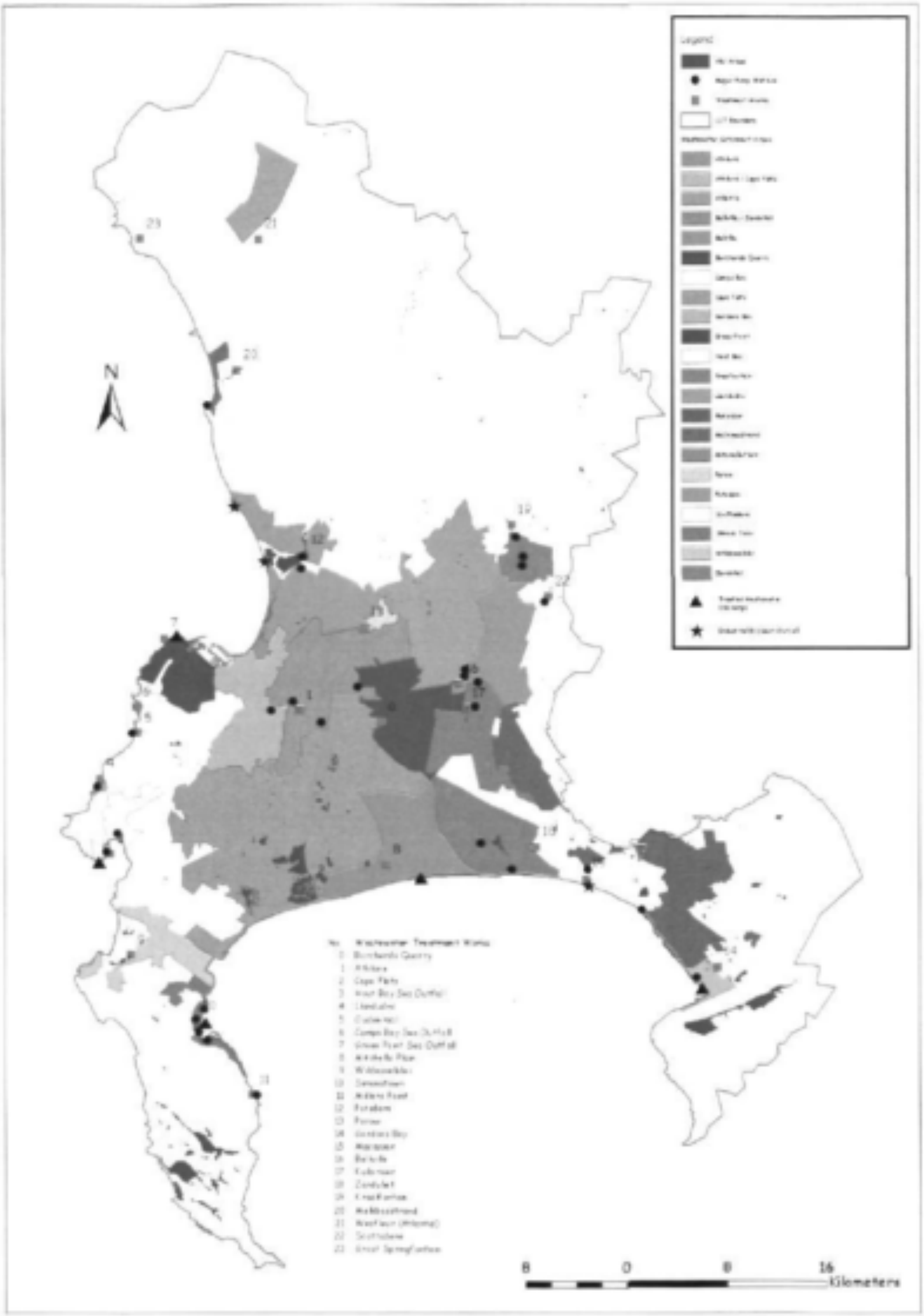


Figure 7. Wastewater treatment works (*taken from www.capetown.gov.za*)

4.6.2 Analysing risk using the Urban Risk Assessment Software (URA)

When opening the software a start-up screen as shown in Figure 8 appears. There are 7 menus namely:- Intro, Prioritisation, Tier 0:RA, Tier 1: RA, Tier 2: RA, Risk Log and Protection Zones. In the bottom left-hand corner of the screen there is a button that takes the user to the Excel-based database to be discussed in Section 5. Each of these screens will be discussed in more detail in the following sections.

4.6.2.1 Intro screen

The start-up screen (Figure 8) is an introduction to the software and includes the names of the development team and basic steps to guide the user.

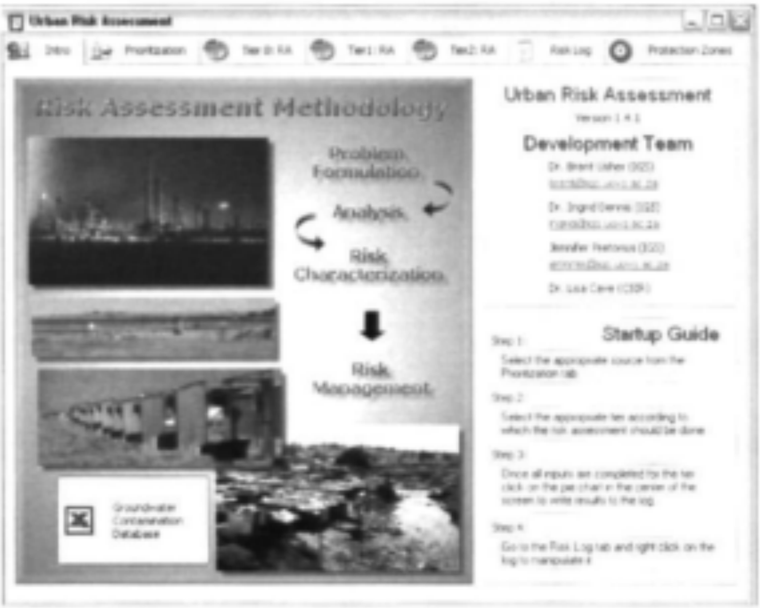


Figure 8. Start-up screen

4.6.2.2 Prioritisation Screen

The prioritisation screen lists a national prioritization of sources and contaminants. For each source highlighted it gives the user a list of expected contaminants, a classification and some useful information (Figure 9). Wastewater treatment works are rated 29th on the list of national sources.

Sources

Source Prioritization (Top to Bottom)

Stormwater/ sewer systems
Automotive refinishing and repair
Other metal product manufacturing
Railroad yards
Non-metallic Mineral products
Abbatoir
Agriculture (General and crop cultivation)
Paper/pulp industry
Research and educational institutions
Petroleum refining and reuse. Also [illegible] refinery
Solvents, chlorinated
Solvents(nonchlorinated)
Munitions manufacturing
Hazardous waste sites
Marine maintenance industry
Dry cleaning activities
General/ Domestic waste sites
Textile manufacture

Classification

Urban settlement (Domestic/ Commercial)

Typical Contaminants

ammonium, nitrate, potassium, phosphate, chloride, sulphate, COD, diverse industrial chemicals, faecal pathogens, metals

Comments

Depending on the type of water treatment process and management of the works, the likelihood of groundwater contamination may increase

Chemicals

Chemical Prioritization (Top to Bottom)

Vinyl Chloride
Uranium
Trichlorophenol 2,4
Dichloropropene 1,2
Cyanide
Chromium VI
Chlorine
Benzene
Dichlorophenol 2,4
Arsenic
Monosodium-Methyl Arsenate
Acrylonitrile
Strontium
Mercury
Cadmium
Nitrite
Nitrate
Trichloroethane 1,1,1,-
Pentachlorophenol
Lead
Ethylene Dibromide
Chlorine Dioxide
Carbon Tetrachloride
Beryllium
Dioxane 1,4
Ethylene oxide
Xylene
Toluene
Sulphur

NOTE
Items that are highlighted together share the same priority
This applies to the Chemical Prioritization list above

Figure 9. Prioritisation screen

4.6.2.3 Tier 0: RA

The 3rd menu from the left is Tier 0:RA. This allows the user to complete a low confidence risk assessment based on the number of sources of this kind within the area, the contaminants that can be found at such sources and the level of management. This is the first screen on which the user can supply information concerning the sources and contaminants for in the region. According to TIER 0 the wastewater treatment works are rated as the 13th highest contaminant source within the CCT. The rating (highest to lowest risk) of typical contaminants found at wastewater treatment works is:

- Nitrate
- Ammonium
- Chloride & sulphate
- Phosphate
- Potassium

4.6.2.4 Tier 1: RA

A site-specific risk assessment is calculated for a treatment works situated on the Cape Flats. The wastewater treatment works has unlined sewage sludge drying ponds. The wastewater treatment works are situated on an unconfined primary sand aquifer. The information used to determine a site-specific risk is listed in Table 8. For the sake of demonstration only the risks for nitrates will be determined.

Table 8. Information used in site-specific risk assessment

Parameter	Assigned value
Vulnerability	
- Recharge	65 mm/yr
- Soil media	Sa-LmSa
- Aquifer media	Intergranular
- Vadose zone	Beach sand
- Groundwater depth	8 m
- Topography	1 %
Duration	Continuous
Contaminant*	Nitrate
Level of management	Low

*Once the contaminant is entered the software automatically pulls in the health risk information and physio-chemical behaviour from a database.

The results of the assessment are summarized in Table 9.

Table 9. Table 5. Results of risk assessment

Assessment	Risk (%)*
Source	37
Vulnerability	52
Health	80
Physio-chemical	99
TOTAL	70

* higher the risk higher the negative impacts

The results of the risk assessment for nitrates indicate there is a 70% chance that there are going to be negative impacts on the environment (including human health) as a result of groundwater becoming contaminated with nitrates as a result of the wastewater treatment works (Figure 10).

Figure 10. Results of Tier 1:RA

Note: Tier 2 is similar to Tier 1 except it takes into account urban recharge and requires more site-specific data. The results thereof have a higher confidence rating.

4.6.2.5 The risk log

The second last menu is called the risk log menu and is used to rate the risks associated with various potential contaminants and the sources thereof.

4.6.2.6 Protection zones

The distance between a pollution source and a protected borehole can be calculated to ensure the borehole is not polluted. The zone of protection can then be delineated around the borehole. These wellhead protection zones can also be used to plan new boreholes. If all pollution sources are known then the 'safe' distance from a source can be calculated.

Wellhead protection zones were calculated for boreholes in the Cape Flats. Table 10 contains the information needed for the calculations and Table 11 defines the protection zones and gives the radius of protection zones.

Table 10. Data used to calculate protection zones

Parameter	Assigned value
Abstraction rate	10 l/s
Transmissivity	100 m^2/d
Effective porosity	0.1
Hydraulic gradient	0.01
Saturated thickness	20 m

Table 11. Calculated protection zones

Definition	Radius (m)
Zone 1: Highly protected area around the borehole. Its purpose is to protect the borehole from the direct introduction of pollutants into the borehole and its immediate area from spills, surface runoff, or leakage from storage facilities or containers. Potential pollutant sources in Zone 1 should be strictly monitored.	25
Zone 2: Is established to protect a borehole from contact with pathogenic micro-organisms which can emanate from a source located close to the borehole, as well as to provide emergency response time to begin active cleanup and/or implementation of contingency plans should a chemical contaminant be introduced into the aquifer near the borehole.	470
Zone 3: Is designed to protect the borehole from chemical contaminants that may migrate to the borehole; it typically includes a major portion of the recharge area or the capture zone.	750

5. The Excel-based database

5.1 Background

The objective of the Excel-based data information system is to provide a user-friendly, easy-to-update inventory on South Africa's groundwater contaminants in urban catchments. The idea originated from the need to capture, store and make information easily accessible, as well as for future linkage with national GIS-database systems. The Excel database includes the following components:

I. An inventory of inorganic and organic contaminants and associated sources in major urban areas of South Africa (Gauteng, Durban, Port Elizabeth, Cape Town)
II. An inventory of properties of inorganic and organic contaminants
III. A simple model for site-specific ranking of priority contaminants

The inventory of inorganic and organic contaminants includes the type of source (urban settlement, agriculture, mining, non-metallurgical industry, metallurgical and metal products manufacturing), expected contaminants, examples and references.

The inventory of properties of inorganic and organic contaminants includes values of properties for about 2500 contaminants. These properties are mainly relevant to groundwater pollution, for example Henry's Law constant for volatilization, half-life and the organic carbon partitioning coefficient. CAS numbers are available for each contaminant, as well as links to international web sites where properties can be found, in particular those that are variable depending on environmental conditions and are not filled in the Excel-database.

A simple model developed by Rao *et al.* (1985) was included in the Excel database as a tool for prioritization and site-specific ranking of contaminants. The model of Rao *et al.* (1985) calculates the attenuation and retardation factors of specific contaminants, based on properties of contaminants included in the database (Henry's constant, half-life and organic carbon partitioning coefficient) and user's input of hydrogeological characteristics (groundwater depth and net recharge rate, air-filled soil porosity, volumetric soil water content at field capacity, soil bulk density and organic carbon content in the soil).

5.2 Ranking of priority contaminants

Ranking of priority contaminants is done using the model of Rao *et al.* (1985), based on the attenuation factor (AF) and retardation factor (RF). The model calculates AF as:

$$AF = M_2/M_0 = \exp(-B)$$

Where

M_2 = Total amount of contaminant leaching (calculated)

M_0 = Total amount of contaminant added at the surface (user's input)

$$B = (0.693\ t_r/t_{1/2})$$

Where

t_r = Travel time

$t_{1/2}$ = Half-life (from database of properties of contaminants)

Travel time is calculated as:

$$t_r = L\ RF\ FC / q$$

Where

t_r = Travel time

$t_{1/2}$ = Half-life (from database of properties of contaminants)

L = Groundwater depth (user's input)

RF = Retardation factor

FC = Volumetric water content at field capacity in the unsaturated zone (user's input)

q = Net recharge rate (user's input)

The retardation factor is calculated as:

$$RF = 1 + BD\ OC\ Koc / FC + AC\ Kh / FC$$

Where

BD = Bulk density (user's input)

OC = Organic carbon content (user's input)

K_{OC} = Organic carbon partitioning coefficient or sorption coefficient (from database of properties of contaminants)

AC = Air-filled porosity (user's input)

K_h = Henry's Law constant (from database of properties of contaminants)

Therefore, the input used in the model includes the properties of contaminants retrieved from the database (half-life, sorption coefficient and Henry's Law constant) and the hydrogeological properties entered by the user (groundwater depth and net recharge rate, air-filled soil porosity, volumetric soil water content at field capacity, soil bulk density and organic carbon content in the soil). This makes the model applicable to any catchment and type of contaminant.

The user manual for the database is included in Appendix D.

5.3 Case study: City of Cape Town

The Excel database was used for ranking of priority contaminants occurring in Cape Town as an example.

In the absence of measured data of groundwater contamination, the first step of the procedure involved the identification of the pollution sources occurring in the city of Cape Town. For this purpose, the tables included in Product 1, Section 6.3, were used. In addition, a list of substances known to occur in groundwater with associated sources was used (Table 1.2, Fetter, 1999), based on the contaminant sources occurring in Cape Town. The complete list of contaminants considered in the ranking for Cape Town is included in Table 12.

The model of Rao *et al.* (1985), included in the Excel database, was used to calculate the retardation and attenuation factors for each contaminant. For this purpose, the properties of individual contaminants included in the Excel database were used. The full set of properties (organic carbon partitioning coefficient, Henry's Law constant and half-life) was available only for the contaminants reported in bold face in Table 12. Contaminants missing one or more properties were not included in the ranking.

The following hydrogeological properties were used as input:
Bulk density = 1600 kg m^{-3}
Organic carbon content = 0.01
Field capacity = 0.2 m3 m^{-3}
Air content = 0.2 m3 m^{-3}
Depth to groundwater = 4 m
Net recharge rate = 0.03 m a^{-1}

The results of the ranking calculation are shown in Table 13. The retardation factor represents the retardation of contaminant leaching through the unsaturated zone due to volatilisation and sorption. The attenuation factor includes the degradation of contaminants in the transport process through the unsaturated zone. Therefore, the ranking according to the attenuation factor does not necessarily match the ranking using the retardation factor.

The contaminants with the highest potential for groundwater contamination were 1,4-dioxane, diethyl ether, ethyl acetate and most inorganic compounds. 1,4-dioxane, diethyl ether and ethyl acetate are mostly associated with solvent, cleaning, painting and textile industries, whilst inorganic compounds are associated with a wide range of sources.

The top 25 organic contaminants ranked with the Excel database were compared to the 25 highest ranked organic contaminants from US and German waste disposal sites, based on frequency of detection (Kerndorff *et al*., 1992). The Excel database produced four contaminants in common with the German list (1,1,1-trichloroethane, 1,2-dichloroethane, vinyl chloride and 1,1,2-trichloroethane) and three contaminants in common with the US list (1,1-dichloroethane, 1,1,1-trichloroethane and 1,2-dichloroethane).

This ranking with the Excel database was specifically done for Cape Town. However, similar results could be expected for other South African urban areas, due to the general similarity in activities and contaminant sources (Product 1, Section 6).

The Excel database can be used for preliminary ranking of priority contaminants in terms of their relative potential to contaminate groundwater, as demonstrated in the example for Cape Town. However, it should be noted that this methodology has limitations:

I. The types of contaminants selected for the ranking were based on knowledge of potential sources, rather than on actual measurements of groundwater contamination.

II. The number of potential sources was known, but not the quantities of contaminants discharged.

III. Not all potential groundwater contaminants were included in the ranking, due to lack of data on their properties.

IV. Half-lives of many contaminants may vary by orders of magnitude depending on specific conditions.

V. Other contaminants that are not commonly associated with the sources considered may be occurring in Cape Town groundwaters.

VI. The retardation and attenuation factors are indexes that can be used to compare a large number of contaminants, but they were not designed for predictive purposes.

Table 12. List of contaminants used in the case study for Cape Town

1,1-Dichloroethane
1,1-Dichloroethylene
1,1,1-Trichloroethane*
1,1,2-Trichloroethane*
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
1,2-Dichloroethane
1,2-Dichloroethylene (cis- and trans-)
1,2-Dichloropropane
1,2,4-Trichlorobenzene
1,2,4-Trimethylbenzene
1,4-Dioxane*
2-Aminoanthraquinone*
2-Chloronaphthalene
2-Propanol
2-Propyl-1-heptanol
2,4-Dichlorophenol
2,4-Dimethyl-3-hexanol
2,4-Dimethyl phenol
4-Nitrophenol
6-Propylpiperonyl butyl diethylene glycol ether*
Acetanilide
Acetic acid
Acetone*
Acetyl chloride
Acrylonitrile*
Alkyl benzene sulfonate
Alkyl sulfonate
Aluminum*
Ammonia*
Aniline
Anthracene
Antimony*
Arsenic*
Asbestos*
Azinphos-methyl
Barium
Benzene*
Benzidine*
Benzophenone
Benzoyl chloride
Benzyl alcohol
Benzyl benzoate*
Beryllium*
Bis-2-chloroisopropylether
Bis-2-ethylhexylphthalate
Bismuth*
Boron*
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Fluoranthene
Fluorene
Fluorescein
Fluoride
Fluoridebenzene*
Fluorocarbon 113*
Fluoroform
Formaldehyde*
Formic acid
Furan*
Glyphosate
Heptane, N*
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
Hexane, N*
Hydrochloric acid*
Iprodione
Iron*
Isopropyl benzene
Lead*
Lignin
Lithium
Magnesium
Manganese
MEK*
Mercury*
Mercury sulphate*
Methane*
Methanol
Methyl bromide
Methylcyclohexanone
Methylene blue activated substances
Methylene chloride*
Methyl ethyl ketone
Methylphenyl acetamide
MOCA
Molybdenum
Naphtalene
n-Butyl-benzylphthalate
Nickel*
Nitrate*
Nitrobenzene
n-Nitrosodiphenylamine
n-Propylbenzene
o-Chlorotoluene
o-Dichlorobenzene
o-Nitroaniline
Oxalic acid*
Palladium
PBB

Butadien, 1,3*
Butyl acetate
Cadmium*
Carbon tetrachloride*
Chloride*
Chlorine*
Chlorine dioxide*
Chlorobenzene
Chloroform*
Chlorohexane
Chloromethane
Chloromethyl sulfide
Chlorpyrifos
Chromium*
Chrysene
Cobalt*
Copper*
Creosote*
Cyanide (CN-)*
Cyclohexane
Deltamethrin
Dibromochloromethane
Dibromoethane
Dibromomethane
Dichlorobenzene*
Dichlorobenzidine
Dichloroethyl ether
Dichloromethane
Dichloropentadiene
Dicyclopentadiene
Diethyl ether
Diethyl phthalate
Dihydrotrimethylquinoline
Diiodomethane
Diisopropyl ether
Dimethylformamide
Di-n-butyl phthalate
Di-n-octyl phthalate
Dioxin*
Dodecyl mercaptan
Endosulfan*
Ethyl acetate*
Ethyl acrylate
Ethylbenzene*
Ethyl chloride
Ethylene dibromide*
Ethylene oxide*
PCB*
p-Chlorotoluene
p-Dichlorobenzene
Penconazole
Pentachlorophenol*
Perchloroethylene*
Phenanthrene
Phenol*
Phenylmethyl benzoate*
Phosphate*
Phosphoric acid*
Phthalic acid
Potassium*
Potassium dichromate*
Propane
Prothiofos
Pyrene
Rubidium*
Selenium
Silver*
Silver bromide*
Simazine
Sodium*
Strontium*
Styrene*
Sulphate*
Tannin
TCE*
Tetrachloroethane*
Tetrachloroethylene
Tetrahydrofuran
Thallium
Tin*
Titanium*
Toluene*
Tributyltin oxide*
Trichloroethylene*
Trichlorofluoromethane
Trichlorotrifluoroethane
Trinitrotoluene
Uranium*
Vanadium*
Vanmidothion
Varsol
Vinyl chloride*
Xylene*
Zinc*

* Product 1, Section 6.3
The remaining contaminants were taken from Fetter (1999).
Contaminants included in the ranking are in bold face.

Table 13. Ranking of contaminants with the highest potential for groundwater contamination, based on retardation and attenuation factor

Contaminant	Retardation factor	Attenuation factor
1,4-Dioxane	2	1
Diethyl ether	6	2
Sulfate	7	3
Ethyl Acetate	8	4
Aluminum	10	5
Antimony (metallic)	10	5
Barium	10	5
Beryllium and compounds	10	5
Boron And Borates Only	10	5
Cadmium	10	5
Chloride	10	5
Chlorine	10	5
Cobalt	10	5
Copper	10	5
Fluorine (Soluble Fluoride)	10	5
Iron	10	5
Lead And Compounds	10	5
Lithium	10	5
Magnesium	10	5
Manganese	10	5
Mercuric Sulfide	10	5
Mercury (elemental)	10	5
Molybdenum	10	5
Nickel Soluble Salts	10	5
Nitrate	10	5
Silver	10	5
Sodium	10	5
Strontium, Stable	10	5
Thallium (Soluble Salts)	10	5
Tin	10	5
Titanium	10	5
Vanadium, Metallic	10	5
Zinc (Metallic)	10	5
Ammonia	11	6
Dichloroethyl ether	12	7
Selenium	15	8
Chlorine Dioxide	16	9
Dibromomethane	17	10
Dibromochloromethane	19	11
1,1-Dichloroethane	22	12
Vinyl Chloride	23	13

Contaminant	Retardation factor	Attenuation factor
Ethylene dibromide	25	14
1,2-Dichloroethane	26	15
1,1-Dichloroethylene	27	16
Propane, 2,2'-oxybis[1-chloro-	24	17
1,1,1-Trichloroethane	28	18
1,1,2-Trichloroethane	30	19
1,2-Dichloropropane	31	20
Propane, 1,2-dichloro-	31	20
Carbon tetrachloride	29	21
Methanol	1	22
1,1,1,2-Tetrachloroethane	32	23
Trichlorofluoromethane	33	24
Tetrachloroethylene	35	25
Simazine	37	26
Dibromoethane, 1,2-	25	27
Glyphosate	13	28
Nitrobenzene	39	29
Hexachloroethane	40	30
Cyclohexane	41	31
Ethylene oxide	3	32
1,1,2,2-Tetrachloroethane	34	33
Ethyl chloride	18	34
Arsenic, Inorganic	45	35
Methyl ethyl ketone	5	36
Dichlorobenzene, 1,4-	46	37
Dichlorobenzene, 1,3-	47	38
Dichlorobenzene, 1,2-	48	39
o-Dichlorobenzene	48	39
Chloroform	21	40
Toluene	43	41
Isopropylbenzene	55	42
Benzene	38	43
Hexachlorobutadiene	56	44
Acrylonitrile	9	45
Styrene	50	46
Chlorobenzene	42	47
Perchloroethylene	35	48
Bromodichloromethane	20	49
4-Nitrophenol	44	50
Pentachlorophenol	62	51
Diethyl phthalate	36	52
Di-n-butyl phthalate	57	53
Acetone	4	54
2,4-Dichlorophenol	53	55

Contaminant	Retardation factor	Attenuation factor
Dichlorobenzidine, 3,3'-	65	56
Naphthalene	59	57
Xylene, (total)	49	58
Xylene, Mixture	49	58
1,2,4-Trichlorobenzene	54	59
Hexachlorocyclopentadiene	58	60
PCB-1221	66	61
PCB-1232	66	61
Chloromethane	14	62
Chlorpyrifos	63	63
2-Chloronaphthalene	61	64
Ethylbenzene	51	65
Phenanthrene	71	66
PCB-1016	72	67
Endosulfan	68	68
PCB-1248	73	69
PCB-1242	74	70
Benzidine	60	71
Anthracene	70	72
Fluorene	67	73
2,4-Dimethylphenol	52	74
MOCA	69	75
Fluoranthene	75	76
PCB-1254	76	77
N-Nitrosodiphenylamine	64	78
Dioxin	77	79
bis(2-Ethylhexyl) phthalate	78	80
Chrysene	81	80
Di-n-octyl phthalate	79	80
PCB-1260	80	80

It is clear that the method of Rao *et al.* (1985) provides a rapid effective ranking on contaminants based on their physiochemical transport properties.

6. Conclusions and recommendations

Case studies from literature were intended to provide a baseline of the current level of groundwater contamination in South Africa's urban areas. Data that exists is often localised to a particular industry and in most cases no time series data is available. The availability of published data and information, however, proved to be a major limitation in quantifying groundwater contamination in South Africa's urban areas. One of the problems is that under South African law (National Water Act, Act 36 of

1998), monitoring of potential pollution sources is the responsibility of the polluter. This means that any data relating to the impact of polluting activities also resides with the polluter and they may be reluctant to release it to the public domain. Despite this, a large set of representative case studies has highlighted problems and lessons at different urban activities, with regards to groundwater quality.

The reviews of the transport of contaminants has revealed the importance of proper hydrogeological characterisation, as this largely determines the risk that a pollutant holds. The fuzzy logic approach combines the expert knowledge generated in this project with site-specific considerations so that sources and pollutants can be identified and prioritised in any area, at various scales of implementation. Using a multi-tiered approach facilitates management of sources, according to available information and expertise of the user. Through case studies, both real and generic, the methodologies and tools developed in this project have been tested and refined.

The results of this project therefore include:

- A national South African priority list of contaminants and contaminant sources in urban areas has been established.
- Priority lists of contaminants and contaminant sources have been derived for Gauteng, Cape Town, Port Elizabeth and Durban.

The priority lists have shown that several high priority contaminants have not yet received adequate attention in terms of water management in this country.

In conclusion, these documents and the associated software should serve as a good guide to expected contaminants associated with different activities. Methodologies have been created whereby a water manager in any urban area can identify and prioritise the potential groundwater contaminants in the area. The software packages should be useful tools for persons ranging from municipal water managers to researchers and geohydrologists with detailed knowledge of a site.

Groundwater monitoring in urban areas needs to be addressed as a matter of priority. Based on the research conducted in this project, several sources and contaminants have been highlighted as potential priorities. Of great concern is the fact that for many of these the currently available datasets show that very little attention has been paid to the constituents in most groundwater monitoring programs. The following contaminants of concern are highlighted:

- Petroleum products, industrial thinners and mineral oils and other non-aqueous phase liquids represent a category of potential pollutants that have been largely overlooked by regulatory agencies and legislature, despite their harmful effects at small concentrations. Research in this current project, has shown these contaminants to be of the most problematic in urban groundwater resources. There is an urgent need for published research into NAPL contamination in South Africa.
- Based on the paucity of groundwater-related microbial data encountered in this project, the inclusion of these aspects in urban groundwater management must be regarded as a priority. In order to evaluate the public health threat posed by waterborne micro organisms, rapid and accurate methods for the detection of these organisms within large populations of other bacteria are therefore essential and further research and inclusion in groundwater monitoring should be promoted.
- A general lack of data on groundwater pollution from pesticides is evident. This is due to: i) surface waters are the main source of water supply in the country (little data is available on groundwater pollution); ii) cost and difficulty to measure organic contaminants; iii) private companies are often sensitive to make public data related to pollution problems. There is therefore need to monitor groundwaters and to develop modeling tools for the prediction of the fate and behaviour of pesticides.
- High nitrate concentrations have been found to occur from sources ranging from agricultural fertilizing (especially the application of sludge to land) to pit latrines and explosives companies. There is, no directed programme to monitor nitrate in urban and peri-urban areas and hence the gap in information.

Based on the recommendation of the Steering committee, aquifer vulnerability considerations have not received detailed attention in this project. A project is underway to address this on a national scale, and the results from this project should be taken cognisance of. It is recommended that the national vulnerability and prioritisation results be merged at some point in the future to improve site-specific and regional identification and prioritisation of areas of concern.

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8. APPENDIX A: Physicochemical properties affecting migration of groundwater contaminants

8.1 Physicochemical attributes of inorganic contaminants – Chloride as tracer of plume migration

8.1.1 Introduction

Metal chlorides are generally very soluble and highly mobile under various environmental conditions. Chloride is an effective tracer of groundwater flow direction and often serves as a reference ion to explain changes in the groundwater composition with increasing salinity or to simulate the 'maximum spreading' of dissolved solutes emanating from a pollution source. In addition, the chloride concentrations are not influenced by attenuation processes usually attributed to decreasing concentrations of organic pollutants. However, the **chloride** concentrations **may be affected** by the **processes** of evaporation and transpiration, dissolution of evaporates, dissolution of host-rock, hyperfiltration, radiolysis and mixing with a more or less saline groundwater.

The distribution of the chloride concentrations, as a conservative tracer, in the saturated zone may thus simulate the solute transport of more reactive chemicals such as soluble inorganic species and the dissolved phases of both light non-aqueous phase liquids (LNAPL's or 'floaters') and dense non-aqueous phase liquids (DNAPL's or 'sinkers').

Example: Solid waste with a high chloride concentration deposited in a landfill such as the Borden landfill site in Ontario, Canada is underlain by an unconfined sand aquifer. Figure 11 illustrates the vertical and longitudinal distribution of the chloride concentrations in cross-section. The center of mass of the chloride tracer sank vertically (i.e. due to density differences with surrounding 'unpolluted' groundwater) and later moved in the direction of groundwater flow (i.e. longitudinal dispersion). The vertical spreading of the chloride tracer is not as significant.

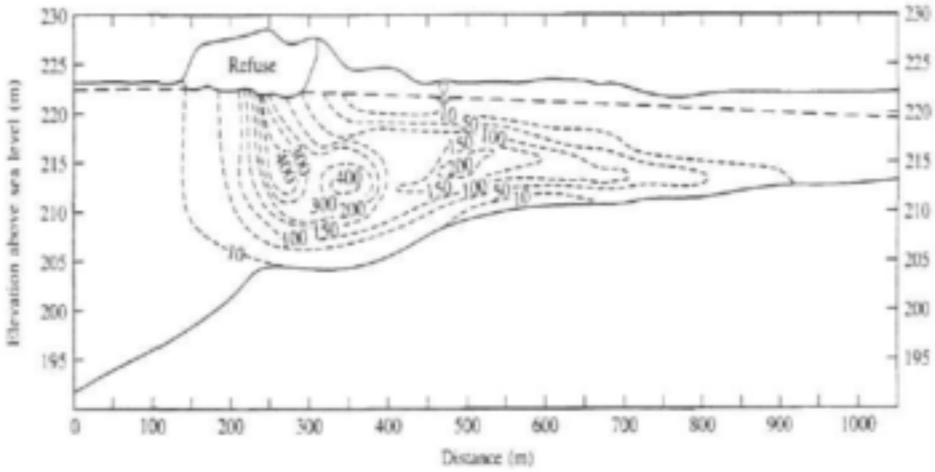


Figure 11. Vertical and longitudinal distribution of the chloride concentrations in cross-section.

In plan view the plume can therefore be seen as spreading in the direction of flow and also laterally. The Cl plume can thereby provide an indication of the heterogeneity of the aquifer resulting in the longitudinal and transversal dispersion.

8.1.2 Transport Mechanisms in Saturated Zone

The optimal behavior of the dissolved phase of a contaminant plume in the saturated zone can be simulated through the distribution of chloride concentrations affected by the following transport mechanisms:

- Advection
- Dispersion
- Molecular Diffusion

or in reality a

- Combination of different transport mechanisms superimposed in a complex heterogeneous subsurface system.

9.1.2.1 Advection

Advective transport, or convection is simply the **movement of mass** (i.e. dissolved substances) in flowing ground water. The amount of dissolved substance (or solute) that is being transported is a function of the solute concentration in the ground water and the quantity of the ground water flowing. In general terms, the average rate of solute migration equals the average linear velocity, while the quantity of water flowing is equal to the average linear velocity times the effective porosity. However, the apparent rate of solute migration differs from the average linear velocity in cases where the solute reacts with the aquifer matrix due to attenuation processes, while the colloidal transport of organic contaminants should also be considered.

The average linear velocity, or 'true' velocity, is the rate at which the flux of water across the unit cross-sectional area of interconnected pore space occurs. The average linear velocity concept takes account of the effective porosity of a medium but is not the average rate at which the water molecules are moving along individual flowpaths. The **effective porosity** of a medium is the **interconnected porosity** through which flow can occur. The term excludes non-interconnected and dead-end pores.

Advective transport in different strata can result in solute fronts spreading at different rates both longitudinally and transverse to the flow direction. Advective transport thus transfers solute mass in the general direction of flow but also tends to spread/disperse the solute concentration transversely because the groundwater velocity varies spatially and temporally. The latter may be attributed to the heterogeneity of geologic materials through which the flow occurs. Contaminant sampling from a borehole that penetrates several strata will produce a composite sample that is a mixture of water containing the transported solute coming from one stratum and uncontaminated ground water coming from a different stratum where the average linear velocity is lower. As a result, the concentration of the contaminant in the composite sample may thus be less than in the source.

9.1.2.2. Dispersion

As indicated, spatial and temporal variations lead to the longitudinal and transverse dispersion as well as the dilution of solute concentrations.

Mechanical dispersion

Mechanical dispersion occurs when ground water is moving at rates that are both greater and less than the average linear velocity due to (Figure 12) variations in flow velocity at various scales. The microscopic to macroscopic scales between pores and grains as water will move faster in the center of a pore than along the edges. In addition, some pores are larger than others, which allow the fluid flowing through these pores to move faster. Some fluid particles travel along longer flow paths in heterogeneous porous media with resultant changes in groundwater flow paths/directions. Temporal changes in the seasonal hydrologic regime also result in changes in the groundwater flow regime.

The mixing, both longitudinally and transverse to the flow path, that occurs due to velocity differences in the groundwater flow is called mechanical dispersion, and results in a dilution of the solute.

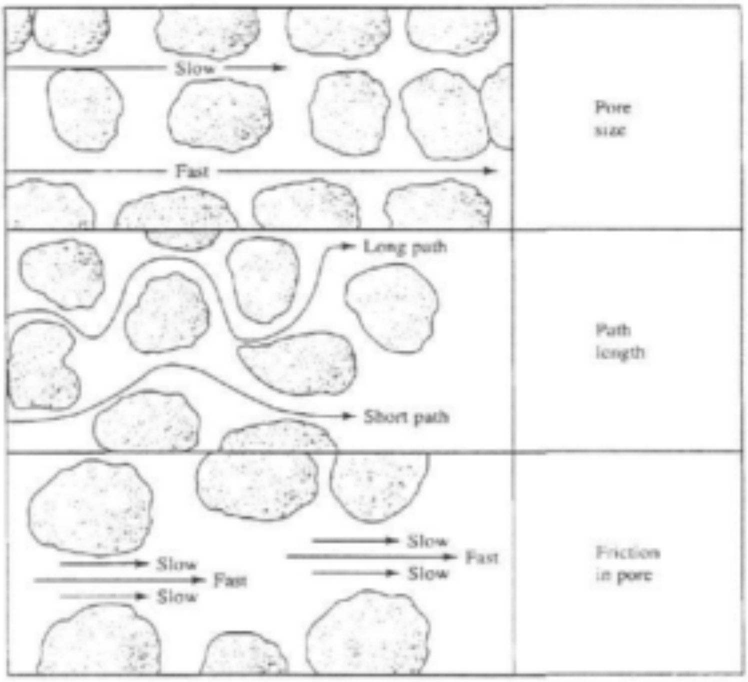


Figure 12. Factors causing mechanical dispersion, predominantly longitudinal dispersion, at the microscopic to macroscopic scale (from Fetter, 1993).

Longitudinal dispersion describes mixing along the direction of the flow path, while mixing in directions normal to the flow path is called transverse dispersion. Longitudinal dispersion is usually more significant than transverse dispersion.

Hydrodynamic dispersion

A term that incorporates both molecular diffusion and mechanical dispersion. Both processes occur simultaneously in flowing groundwater (Figure 13).

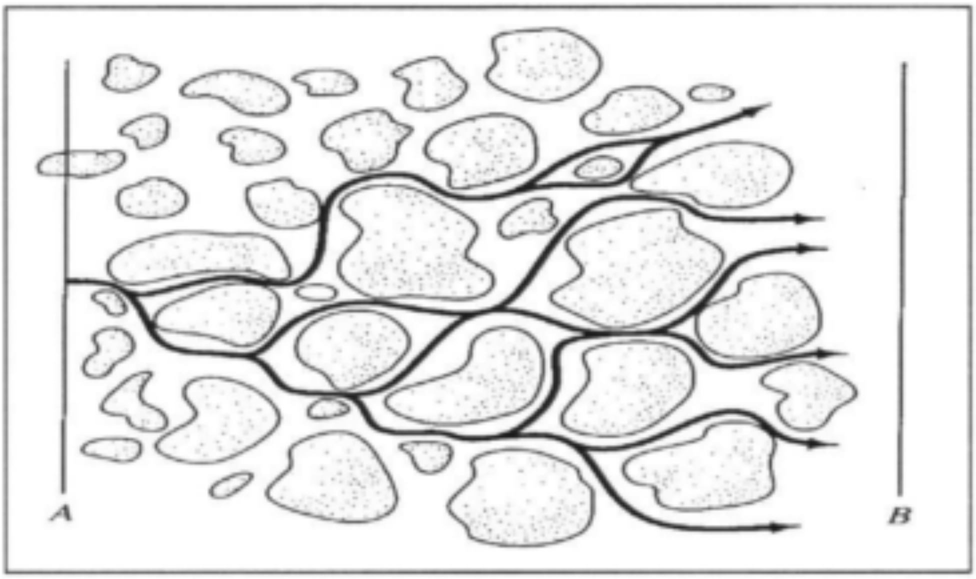


Figure 13. Flow paths in a porous medium that result in lateral hydrodynamic dispersion (from Fetter, 1993).

9.1.2.3 Molecular diffusion

A solute in water will move from an area of greater concentration toward an area of lesser concentration. This process is known as molecular diffusion, or diffusion. Diffusion results in the gradual spreading of the solute as long as concentration gradient exists, even in the absence of any groundwater flow. The diffusion process is generally slow compared to the other mass transport mechanisms and is the dominant mode of transport in low permeability material. This mode of mass transport is particularly important for nuclear waste disposal in low permeability material.

The mass of fluid diffusing is proportional to the concentration gradient (which can be expressed as Fick's first law), while Fick's second law applies where the solute concentrations are changing with time (Figure 14). In landfill sites, for example, the solute concentrations (i.e. chloride concentrations) may remain constant due to continuous replenishment.

In geological materials such as porous media, the diffusion process is generally slow since the dissolved ions must follow longer pathways around mineral grains. As a result, the diffusion process in well-sorted sediment will tend to be faster than in poorly sorted sediment due to shorter flow paths for the water molecules. On the other hand, the diffusion process is slower for substances that are more readily absorbed onto mineral phases compared to those substances with a higher affinity for the dissolved phase.

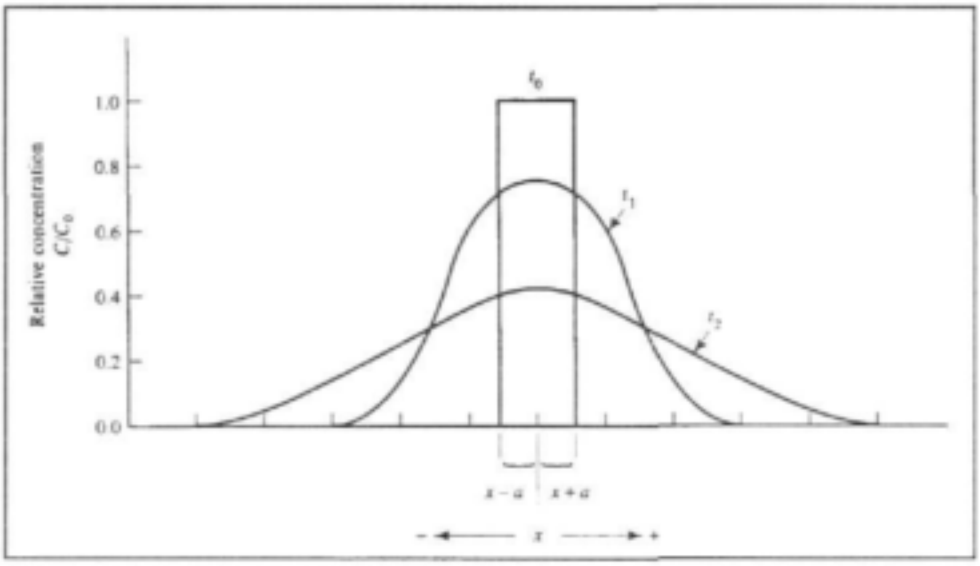


Figure 14. Changes in the relative concentration, or the spreading, of a solute with time due as a result of diffusion (from Fetter, 1993).

8.2 Physicochemical attributes of organic contaminants

8.2.1 General

Organic contaminant transport in the subsurface is subject to a host of influences, many of which are not important in inorganic contamination hydrogeology. Organic compounds can exist in the subsurface either as pure compounds, a mixture of compounds or dissolved species in water.

The physical and chemical properties of the organic compounds affect their behaviour in the subsurface (Fetter, 1999).

The physical properties are, for example, interfacial tension and wettability, density, viscosity, solubility, Henry's law constants, capillary pressure, and relative permeability. The chemical properties typically relate to the molecular weight and structural complexity of the compound. The characteristics of the subsurface also play a major role in the transport and flow of organic contaminants. Table 14 summarises some of the important physical properties of organic compounds and how these affect their behaviour as groundwater contaminants.

Table 14. Physical properties of organic compounds (After Fetter, 1999)

Parameter [and Units]	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 vapor as a function of temperature
Specific Gravity	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 vapor pressure.	More soluble substances have a greater potential mobility. The solubilities of organic compounds can range from being completely miscible with water to being totally immiscible (insoluble) with water.
Octanol-Water Partition Coefficient (K_{ow})	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)	K_d: A measures 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.

Parameter [and Units]	Derivation	Behaviour
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 vapor state (i.e. a measure of how readily a substance will evaporate).	The greater the vapor pressure, the more volatile the substance.
Vapor Density (of a gas)	The vapor density is related to the equilibrium vapor 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. Can 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 volatilization from soil or water.

When organic chemicals are released into the environment from a mixture like a petroleum hydrocarbon fuel, the water **solubilities** of the chemicals are typically far lower than their published solubilities. For example, the solubility of benzene is around 1750 mg/l, but typical maximum benzene concentrations resulting from equilibrium between petrol and water are only 20 to 40 mg/l. This occurs because the concentration (or **effective solubility**) depends on the **relative abundance** of the chemical in the fuel. The behaviour is based on an extension of Raoult's Law and is related to the relative mol fraction of the contaminant within the total spill or release of organics (Schwarzenbach *et al.*, 1993). This can be calculated as:

$$C_w = x_o\, S \qquad \text{Equation (2)}$$

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. The mole fraction is calculated from:

$$x_o = MF_x\, MW_o / MW_x \qquad \text{Equation (3)}$$

where MF_x is the mass fraction of the selected organic compound in the mixture, MW_o is the average molecular weight of the mixture and MW_X is the molecular weight of the selected compound.

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 an organic solvent. The substance is mixed with equal amounts of two immiscible fluids, water and octanol. The coefficient is given by the ratio:

$$K_{ow} = C_{octanol} / C_{water} \qquad \text{Equation (4)}$$

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).

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

$$K_h = C_a / C_w \qquad \text{Equation (5)}$$

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 can 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).

Density, defined as mass per unit volume (in g/cm^3 or g/ml), is closely related to **specific gravity**, which is the ratio of a substance's density to that of water. Density differences of as little as ~ 1%, may influence fluid movement in the subsurface. In many situations, organic contaminant densities differ from that of water by 10 to 50%. The relatively high density of dense non-aqueous phase liquids (DNAPLs), means that they may penetrate the water table and flow downward, directed by paths of least capillary resistance (possibly against the direction of groundwater flow). Typical density values of organic compounds are given in Table 15.

Table 15. Density of common organic contaminants

Chemical	Density (g/ml)
benzene	0.88
toluene	0.87
ethylbenzene	0.87
o-xylene	0.88
p-xylene	0.86
m-xylene	0.86
decane	0.73
undecane	0.74
tetradecane	0.76
1,3,5-trimethylbenzene	0.88
naphthalene	1.03
benzo(a)pyrene	1.35
dichloromethane	1.33
chloroform	1.49
bromodichloromethane	1.97
1,1-dichloroethane	1.17
tricloethylene	1.46
tetrachloroethylene	1.63

Bulk density is defined as the weight of a unit volume of **soil/rock** including its pore space. Since soil is a porous medium, with water and air contained in the pore space between the solid inorganic and organic particles, the concept of soil bulk density must include the voids. Bulk density appears because concentrations in the water phase are measured relative to volume of water and sorbed concentrations are measured relative to the solid mass.

The nature of the media though which the organic contaminants move plays a very important role in the way in which they are transported.

While the properties of the aquifer media are also important for the water movement itself, the interaction between the subsurface media, both soils and aquifers, with different organic chemicals is far more diverse. The factors in the subsurface that influence the transport processes include: naturally occurring organic content, porosity and relative permeability to gas and water.

The soil water distribution or **partition coefficient** (K_d) is often approximated by an assumed relationship between partitioning of hydrophobic chemicals to organic carbon. In this approach the chemical is assumed to partition to the organic carbon in the aquifer and not the mineral surfaces. Therefore, K_d is given by:

$$K_d = K_{oc} + f_{oc} \qquad \text{Equation (6)}$$

where f_{oc} is the fraction organic carbon in the aquifer, and K_{oc} is the organic carbon partition coefficient of the compound in question.

The **retardation coefficient** (R) expresses how much slower a contaminant moves than does the water itself:

$$R = 1 + \rho_b k_d / \theta \qquad \text{Equation (7)}$$

where, R is the retardation coefficient, ρ_b is the bulk density, k_d is the sorption coefficient, and θ is the porosity. Higher levels of organic carbon in the aquifer can increase sorption and elevate retardation effects. Table 16 below shows that retardation factors range over two orders of magnitude. The higher molecular weight aliphatic compounds are most strongly retarded (Lyman *et al.*, 1992).

Table 16. Estimated retardation factors for hydrocarbon gasoline constituents (Lyman *et al.*, 1992)

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

[*] Using Equation 7, a bulk density of 1.8L/kg and soil porosity of 0.20

8.2.2 Petroleum hydrocarbons

Liquid petroleum (crude oil) is a naturally occurring mixture of hydrocarbon compounds of varying molecular weight. There have been over 600 individual hydrocarbon compounds identified in petroleum (Hunt, 1979). Crude petroleum is refined into various products, mostly fuels (e.g. petrol, diesel, kerosene (jet fuel), which may find their way into the groundwater as contaminants. The liquids in petroleum are generally immiscible with water and are classified as nonaqueous phase liquids (NAPLs). The rate of movement is controlled by the permeability of the subsurface and the density of the NAPL relative to water. Most compounds in petroleum have a lower density than water and behave as light nonaqueous phase liquids (LNAPLs) in the subsurface.

Table 16 shows some physical properties of petroleum hydrocarbons. The retardation factors for these compounds range over two orders of magnitude. The higher molecular weight aliphatic compounds are most strongly retarded (Lyman *et al.*, 1992).

8.2.3 Pesticides

Pesticides include a wide range of organic compounds used as insecticides, herbicides, fungicides, microbiocides, rodenticides and other substances used to control pests. The physical properties that affect the behaviour of pesticides in groundwater are listed in Table 17.

Table 17. The influence of pesticide physical properties on their potential contamination of groundwater

Parameter and units	Contaminant levels
Water solubility [ppm, ppb]	Pesticides with water solubility >3 mg/l have potential to contaminate groundwater. However, pesticides with water solubilities < 3 mg/l have been found in groundwater.
Half life [days]	Soil half-life: Pesticides with an aerobic soil half-life >690 days or an anaerobic soil half-life >9 days have the potential to contaminate groundwater.
	Photolysis half-life: Pesticides with a photolysis half-life >14 days have the potential to contaminate groundwater.
	Hydrolysis half-life: Pesticides with a hydrolysis half-life >14 days have the potential to contaminate groundwater.
Absorption Coefficient (K_{oc}) or Distribution Coefficient (K_d)	Pesticides with a K_{oc} value < 1.900 have the potential to contaminate groundwater.
Vapor Pressure [mm Hg]	Pesticides with vapor pressures > 10^{-6} mm Hg can readily volatilise and drift from the site of application

More information on pesticides may be obtained from the Pesticide Action Network (PAN) of North America (PAN website: http://docs.pesticideinfo.org/documentation4/ref_waterair1.html, last visited December 2003).

8.2.4 *Chlorinated solvents*

Chlorinated solvents include a range of organic compounds of relatively low molecular weight, which have one or more chlorine atoms substituted for hydrogen on the molecule. The more common chlorinated solvents are tetrachloroethene (or perchloroethene, PCE), trichloroethene (TCE), dichloromethane (or methylene chloride) and 1,1,1-trichloroethane (TCA). The physicochemical properties of several chlorinated solvents are shown in Table 18.

Table 18. Physicochemical properties of chlorinated solvents and associated compounds. All values are at 20°C, unless indicated (From USACE, 2002).

	PCE	**TCE**	**1,1-DCE**	**t-1,2-DCE**	**c-1,2-DCE**	**VC**	**1,1,1-TCA**	**1,1-DCA**	**CA**
Formula	C_2Cl_4	C_2HCl_3	$C_2H_2Cl_2$	$C_2H_2Cl_2$	$C_2H_2Cl_2$	C_2H_3Cl	$C_2H_3Cl_3$	$C_2H_4Cl_2$	C_2H_5Cl
Molecular weight (g/mol)	165.85	131.40	96.95	96.95	96.95	62.5	133.42	98.97	64.52
Liquid density (g/cm^3)	1.625	1.46	1.214	1.257	1.284	0.9121^{1}	1.325	1.175	0.921$^{\#}$
Melting point (°C)	-22.6	-73.2	-122.8	-49.6	-81.7	-154.0	-33.2	-255.9	-141.0
Boiling point (°C)	120.9	86.9	31.5	47.7	60.1	-13.6	73.9	57.2	12.4
Vapour pressure (mm Hg)	14	69*	500	5.3	2.7	2300	100	182	1000
Water solubility (mg/l)	150	1100*	400	6300	3500	1100	950	5500	5700
Log (K_{ow})	3.14	2.42	2.13	2.09	1.86	1.23	2.49	1.79	1.43
K_{oc} (l/kg)	665	160	65	59	35	8.2	152	30	14.9
Henry's law constant (atm.m^3/mol)	0.023	0.0103*	0.154	0.0066*	0.0075*	0.695	0.0276*	0.0057*	0.011

[1] specific gravity measurement

[#] at 0°C

[*] at 25°C

Chlorinated hydrocarbons:		PCE	perchloroethene	TCE	trichloroethene
DCE	dichloroethene	VC	vinyl chloride	TCA	trichloroethane
DCA	dichloroethane	CA	chloroethane		

The extent of groundwater contamination by solvents has been gradually realised since the late 1970s, when standardized chemical analysis techniques became available that could detect µg/l concentrations of solvents dissolved in water and subsequent aquifer surveys were undertaken (Johnson and Pankow, 1992; Rivett *et al.*, 1990). Health concerns prompted drinking water standards to be set in the low µg/l range, in turn prompting much investigation and remediation of subsurface solvent contamination. Since the pioneering work of Schwille (1988), there has been considerable research into the subsurface transport and remediation of solvents. There has been extensive characterisation of dissolved solvent plumes at real sites with many plumes some extending to kilometres in length.

Most of the chlorinated solvents have a density greater than water and behave as dense non-aqueous phase liquids (DNAPLs) in the subsurface. The contaminant behaviour of DNAPLs is described in detail in Section 8.2.6.

8.2.5 Fate and transport of LNAPLs in the subsurface

This discussion on LNAPL behaviour is mostly taken from Fetter (1999). When spilled, petroleum hydrocarbons will move downward through the unsaturated zone under the influence of gravity and capillary forces, trapping small amounts in the pore spaces. Some of the components can dissolve in the groundwater and move as a plume of contaminated water by diffusion and advection with the groundwater. Benzene, toluene, ethylbenzene and xylene (BTEX) and methyl tertiary butyl ether (MTBE), an additive in petrol, have relatively high solubilities and are often used as diagnostic indicators of petrol contamination in groundwater. All of the BTEX components and MTBE have relatively high vapour pressures. MTBE, however, has a low partitioning coefficient (Henry's law constant) indicating a preference for the dissolved phase rather than the vapour phase, while the BTEX compounds have high Henry's law constants and are more easily lost by volatilisation.

In the aquifer, less dense NAPLs will tend to float on top of water with no significant penetration past the water table. These accumulate until a layer of floating "free product" is formed above the groundwater table. In the core of a thick zone of mobile LNAPL, the water table may be depressed by the weight of the "floating" petroleum product. The mobile LNAPL component can migrate through the unsaturated zone above the water table, following the slope of the groundwater table. The rate of flow is dependent on the density, viscosity and interfacial tension of the liquid involved, and may be faster or slower than the groundwater movement (Fetter, 1999).

Residual LNAPL material trapped in the pore spaces in the unsaturated zone can also partition into the vapour phase as well as a soluble phase in capillary water. The degree of partitioning will depend on the relative vapour pressure of the petroleum hydrocarbon compounds and their solubility in water. Those compounds with high volatility, such as alkanes, favour the vapour phase, while those with high solubility, such as benzene, favour the aqueous phase. The diffusive properties of the soil are important in controlling vapour phase transport.

The transport of contaminants from petroleum hydrocarbon spills needs to be described in terms of a multiphase flow system in the unsaturated zone, taking into account contaminant movement in each of the three phases, air, water and free LNAPL. Petroleum hydrocarbon behaviour in the subsurface is additionally complicated by the presence of multiple compounds, each with different properties. The net result is that some hydrocarbon fractions are transported faster than others and a contamination plume of varying intensity may spread over a large area. As an example, the selective partitioning of certain constituents into the aqueous phase means that compounds such as BTEX may reach the groundwater, via water infiltrating through a surface spill or zone of residual petroleum in the soil, long before any free product reaches the water table.

The flow of LNAPLs is also affected by the rise and fall of the water table with the seasons or with groundwater abstraction. As the water table falls, the layer of mobile LNAPL also falls, leaving residual hydrocarbons in the unsaturated zone above the oil table. When the water table rises, the LNAPL table also rises. If the water table rises faster than the LNAPL table can rise, pockets of free LNAPL might become trapped below the water table.

Although the free product rarely travels far from the surface source, dissolved-phase contamination can migrate thousands of meters through underground conduits, such as occurs in a fractured rock or karst system (Fels, 1999).

In these conduits, dissolved phase petroleum compounds such as BTEX compounds, may degas and partition out of the groundwater. Consequently, contaminated groundwater is not commonly found more than a kilometre or two from the source.

In addition to dispersion, diffusion and volatilization, organic compounds can also undergo adsorption and chemical or biological degradation which retard their movement in the subsurface. Many petroleum hydrocarbons can be degraded by naturally occurring subsurface bacteria, particularly under aerobic conditions. Long-chain alkanes are most susceptible to biodegradation, while aromatic components are generally more resistant to degradation. In environments where biodegradation rates are fast relative to hydrologic transport rates, intrinsic bioremediation (natural attenuation) by native micro-organisms can be effective in containing petroleum hydrocarbon contaminant plumes near the spill source.

The processes affecting the subsurface fate and transport of LNAPLs from a spill of petroleum hydrocarbons are summarised in Figure 15.

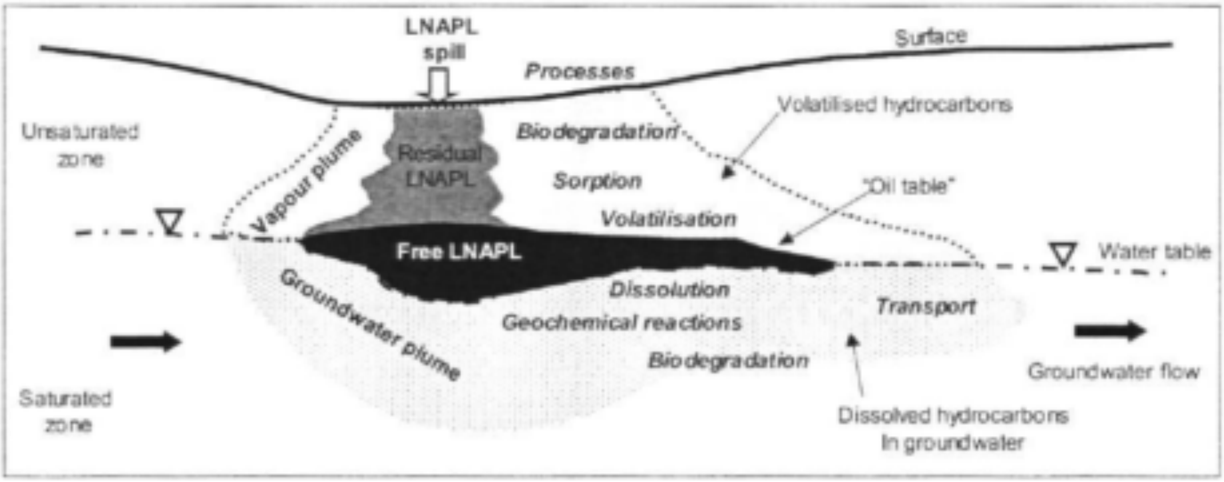


Figure 15. Processes affecting the fate and transport of a light nonaqueous phase liquid (LNAPL) contaminant in the subsurface (Fetter, 1999).

The physicochemical properties of the individual organic chemicals in the LNAPL plume determine the fate of each chemical in the subsurface. As the LNAPLs move from the source, the **contaminant mass will partition** into different media through which it moves. The **solubility** of each compound determines the **fraction distributed** to water, the volatility determines the relative fraction in the air and the amount sorbed in the subsurface is determined by the effective solubility and the retardation coefficient. The **remainder** will be transported as the pure **LNAPL phase**. Over time, these factors continue to redistribute the contaminant mass into the different phases.

The following equations provide a guide to evaluating the partitioning of LNAPLs into the various phases:

$$\text{Mass}_{\text{water}} = C_w\, S_w\, \rho \qquad \text{Equation (8)}$$

$$\text{Mass}_{\text{free NAPL}} = C_w\, K_o\, S_o\, \rho \qquad \text{Equation (9)}$$

$$\text{Mass}_{\text{air}} = C_w K_h S_a \rho \qquad \text{Equation (10)}$$

$$\text{Mass}_{\text{solid}} = C_w K_d \rho_b \qquad \text{Equation (11)}$$

where S_w = fraction of the pore space filled by water (water saturation)

S_o = fraction of the pore space filled by NAPL (NAPL saturation)

S_a = fraction of the pore space filled by air (air saturation)

K_o = NAPL/water partition coefficient

K_h = Henry's Law coefficient

K_d = soil/water distribution coefficient

C_w = effective solubility

ρ = porosity, and

ρ_b = bulk density.

8.2.6 Fate and transport of DNAPLs in the subsurface

Most chlorinated solvents, pesticides, polychlorinated biphenyl mixtures (PCBs), phthalate compounds, substituted aromatic compounds (e.g. nitrotoluenes, nitrobenzenes, chloroanilines, etc.) and other halogenated organics are more dense than water (see Table 15) and behave in the subsurface as DNAPLs.

When spilled, DNAPLs will move downward through the unsaturated zone, trapping small amounts of DNAPL in the pore space. If large volume of DNAPL is spilled and permeability exists in the subsurface, the DNAPL will penetrate past the water table and continue moving downward through the saturated zone due to gravity. The subsequent subsurface migration of DNAPLs is not a function of conventional groundwater transport mechanisms (i.e. advection, dispersion and diffusion), but rather a function of geological structures (i.e. fissures, bedding planes, etc.) and gravity (including the bedrock topography). However, **soluble constituents of DNAPLs will dissolve** into groundwater and their distribution is a function of the hydraulic gradient, resulting in a groundwater plume down gradient from the contaminant source.

The potential depth of DNAPL penetration through the vadose zone and into the groundwater will depend on:

- the properties of the DNAPL (e.g. density, viscosity, solubility, etc.)
- the nature of the DNAPL release (e.g. the rate of release, area of distribution, etc.), and
- the properties and geological structure within the vadose and groundwater zones.

The depth of penetration in the *unsaturated zone* may be coarsely estimated based on the volume released (V), the area of the release (A) and the retention capacity of the soil (Rs):

$$D = V/(A.Rs) \quad \text{Equation (12)}$$

assuming that the DNAPL penetrates directly downward from the release area with negligible lateral spreading. The retention capacities of the soil differ depending on the rate of DNAPL release. In one particular experiment on DNAPL infiltration, retention capacities were 1.3% for instantaneous release and 0.5% for drip release of the contaminants. Thus, for ongoing interrupted spills at a waste site, the retention capacity of the soil may be significantly lower than for an instantaneous one-off event, and the bulk retention capacities of soils may be significantly lower than those calculated from laboratory values.

Table 19 and Table 20 summarise some of the factors controlling DNAPL penetration through the subsurface.

Table 19. Factors which will facilitate DNAPL penetration through the unsaturated and groundwater zones

Factors facilitating DNAPL penetration	**Typical circumstances**
High DNAPL density	Chlorinated solvents PCB Aroclors Complex DNAPL mixtures. Chlorinated solvents
Low interfacial tension	Surfactants or miscible co-solvents such as methanol, methyl ethyl ketone or acetone in the DNAPL.
Low viscosity	Disposal of bulk liquid wastes in landfills, lagoons.
Large DNAPL volume release	On-going leakages
High permeability	Sand, gravel and fractured rock.
Vertical and sub-vertical geological structure	Angled beddings in sandy aquifers. Fractures, fissures, erosional windows in fine-grained aquitards. Fractured rock.

Table 20. Factors which inhibit DNAPL penetration through the unsaturated and groundwater zones

Factors inhibiting DNAPL penetration	**Typical circumstances**
Low DNAPL density	Coal tar/ creosote Chlorinated organics at low concentrations in petroleum hydrocarbons
High interfacial tension	Relatively pure chemical products
High viscosity	Coal tar/ creosote PCB Aroclors DNAPL mixtures with high concentrations of high molecular weight hydrocarbons.
Small DNAPL volume release	Small spills and leaks
Short duration of DNAPL release	Small one-time spills and leaks.
Low permeability	Unfractured clay and silt aquitards Unfractured rock
Horizontal geological structure	Horizontal bedding in sandy aquifers. Horizontal silt and clay aquitards. Horizontal bedding plane partings in sedimentary rock.

The behaviour of DNAPLs in the subsurface is similar to that of LNAPLs, with the distinction that free phase DNAPLs, instead of floating on top of the water table, sink through the groundwater to form pools of DNAPL at the base of the aquifer. The DNAPL pools can flow towards low points in the bedrock, collecting in bedrock hollows, or form perched layers over lenses of lower permeability in the aquifer.

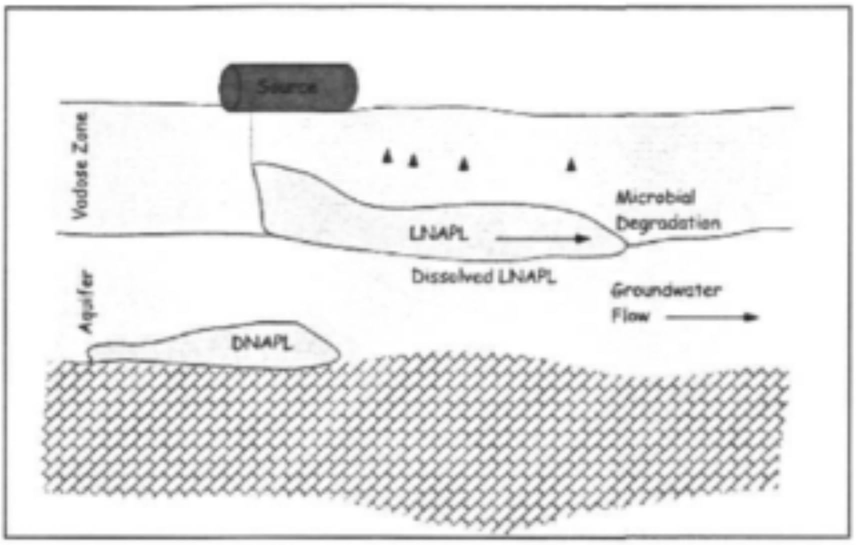


Figure 16. The behaviour of LNAPLs and DNAPLs in the subsurface

Some of the DNAPLs can dissolve in water and these **dissolved** contaminants form **plumes** of contamination that travel in the direction of groundwater flow. They can also be adsorbed onto the matrix or other particles, thus retarding the flow of the DNAPL relative to the velocity of the groundwater. The rate of dissolution of a DNAPL from the source zone at a contaminated site will influence the magnitude of the dissolved chemical concentrations in the groundwater as well as the length of time that the DNAPL zone will persist (Feenstra and Guiger, 1996). For a multi-component DNAPL, the driving forces of DNAPL migration are affected by changes in the DNAPL composition over time. Depending on the initial chemical composition, the DNAPL may become heavier or lighter as dissolution proceeds.

Above the water table, in addition to chemical partitioning into the aqueous phase (dissolution), DNAPL will also partition into the air phase (volatilisation) giving rise to vapor phase contaminant plumes. Below the water table, residual pooled DNAPL acts as a source for ongoing dissolved phase contamination of groundwater flowing through these regions. Since the drinking water guidelines for most DNAPL compounds are orders of magnitude below their aqueous solubility, it follows that the associated contamination plume will, in most cases, fail to comply with the guidelines for a very long time.

The movement of free phase DNAPL through a saturated porous aquifer will result in the formation of disconnected blobs of **residual DNAPL** at the trailing edge of the migrating body. Residual

DNAPL forms due to both snap-off and bypassing mechanisms. The blobs of residual DNAPL in the pores and pore throats can occupy from a few to several percent of pore space, with some studies reporting values as high as 43% (Figure 17). The magnitude of residual DNAPL remaining trapped in a particular aquifer depends on factors such as pore geometry, aspect ratio, interfacial tension and hydraulic gradient. If a large number of pores and pore throats are invaded by DNAPL, it follows that there are a great number of pores and pore throats in which residual organic liquid will be left behind once the migration process is complete.

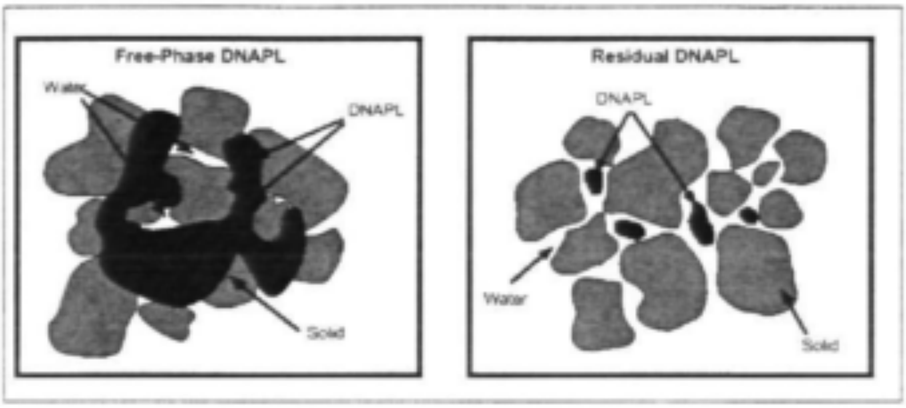


Figure 17. Free phase and residual DNAPL (Newell *et al.*, 1991)

Because many DNAPLs have a relatively low solubility and because most natural groundwater velocities are low, it may require up to **several decades (possibly centuries)** before residual and pool zones are **depleted** by natural dissolution alone. Consider a zone of residual contamination in 1 m^3 of an aquifer with 10 l/m^3 of dichloromethane, trichloroethene or tetrachloroethene; a flow velocity of 0.14 m/d; a hydraulic gradient of 0.005 and a porosity of 30%. Should the level of dissolved concentrations of the contaminants in the residual zone be maintained at saturation until the source is completely dissolved, then the estimated minimum source lives are: 46 days for dichloromethane, 2 years for tricholoethene and 13 years for tetrachloroethene.

The above estimates are an absolute minimum, and will be extremely longer for several reasons:

- The DNAPL within the residual zone may be heterogeneously distributed so that the dissolved concentration may not be produced throughout the 1m^3 residual zone.
- The presence of DNAPL residual will reduce the permeability of the residual zone to groundwater flow, and thus will reduce the mass flux out of the residual zone.

- Saturated concentrations will not be maintained as the residual mass is depleted.
- As residual DNAPL dissolves into groundwater, the volume of DNAPL per volume of porous medium decreases, and the DNAPL interfacial area per volume of porous media also decreases.

The migration of DNAPL in the subsurface is affected by gravity, pressure gradients in both the DNAPL and water phases and the distributions of capillary and hydraulic properties of the aquifer. Owing to the density of a DNAPL, the tendency is for the migration path to be generally downward. However, heterogeneity has a marked influence on the direction of DNAPL migration. A random distribution of permeability and displacement pressure will result in a highly erratic pattern of DNAPL flow, which complicates any characterisation and remediation of the contamination.

8.2.6.1 DNAPLs in fractured rock

In many cases, the volume of DNAPL released at ground surface will be sufficient to bring about migration through overburden deposits, so that the free phase DNAPL comes to rest above a fractured aquitard (or fractured bedrock) in the form of one or more pools. In order for DNAPL to enter a fracture underlying a pool, the capillary pressure at the base of the pool must overcome the entry pressure of the fracture (Figure 18). As the hydraulic head becomes greater (e.g. as one moves deeper into the earth surface), DNAPLs can intrude into smaller fractures. If the groundwater is being pumped near by, the entry pressure of the fracture will be reduced and the DNAPL will invade fractures not previously invaded.

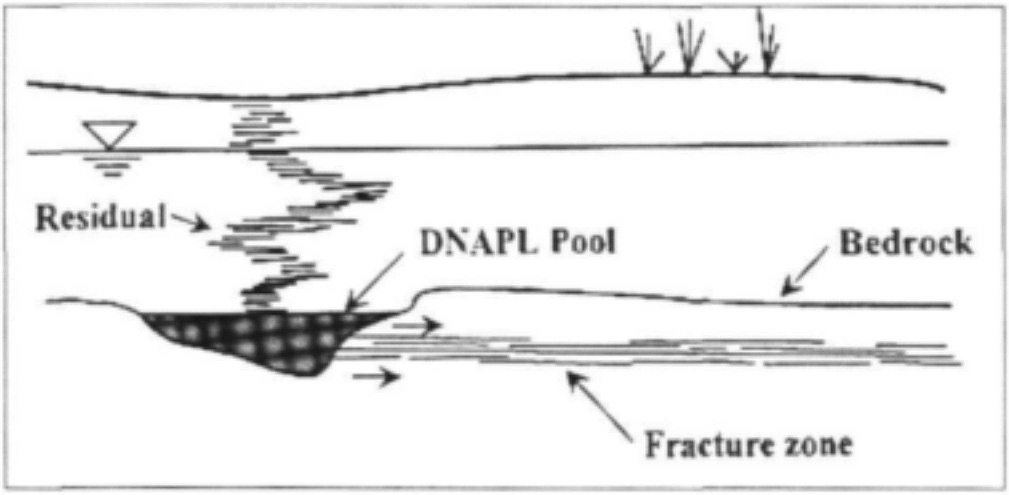


Figure 18. DNAPL pool feeding horizontal fractures in bedrock.

Once having entered a fracture, DNAPL will preferentially migrate through the larger aperture pathways of a fracture plane, since these offer the least capillary resistance to movement. Model simulations indicate that DNAPL may travel through single, rough walled fractures at rates ranging from minutes to several hours per one meter length of fracture. Various parameters influence DNAPL entry into and flow rates in fractures, including fracture aperture and aperture distribution, groundwater gradient, fracture dip from horizontal, diffusive loss to matrix materials, DNAPL pool height above the fracture and DNAPL fluid properties.

A free DNAPL solvent phase may persist in the fractures only for a short time relative to the typical age of the spill. For common chlorinated solvents, the concentration in groundwater obtained from monitoring or extraction boreholes located within, or close to, the DNAPL source zone, are seldom at the aqueous solubility limits. This is commonly attributed to dilution caused when the boreholes are purged and sampled. It is often assumed that some fractures contain groundwater that are at or near the solubility limit, and other fractures that are less connected to the DNAPL source have much lower concentrations. Thus upon sampling, a mixed or diluted value is obtained. Free DNAPL phases are seldom detected in monitoring boreholes in fractured porous aquifers.

In many instances, a possible explanation is that much of the DNAPL that once may have filled the fractures has been lost by diffusion into the rock matrix. As the porosity of the matrix increases, the rate of migration of the DNAPL front within fractures is retarded, due to dissolution and matrix diffusion. Some DNAPLs have limited but significant aqueous solubilities that allow the DNAPL phase to slowly dissolve across the contact area between a DNAPL and adjacent water. After dissolution a chemical concentration gradient will be established in the aqueous phase and the contaminant mass will move into the porous matrix by molecular diffusion. It has been shown, using 1-D and 3-D models, that in some fractured porous media, some DNAPLs (in particular chlorinated solvents) can disappear from fractures in a very short time, resulting in nearly all of the contaminant mass moving into the matrix as dissolved and sorbed contaminant (Parker *et al.*, 1995). The above process is illustrated in Figure 19, which shows the distribution of contaminant mass in fractured porous medium over time. All of the above factors could lead to the false impression that the overall system is in the process of being "cleaned up" due to flushing by groundwater flow, or that an aquifer is less polluted than it actually is.

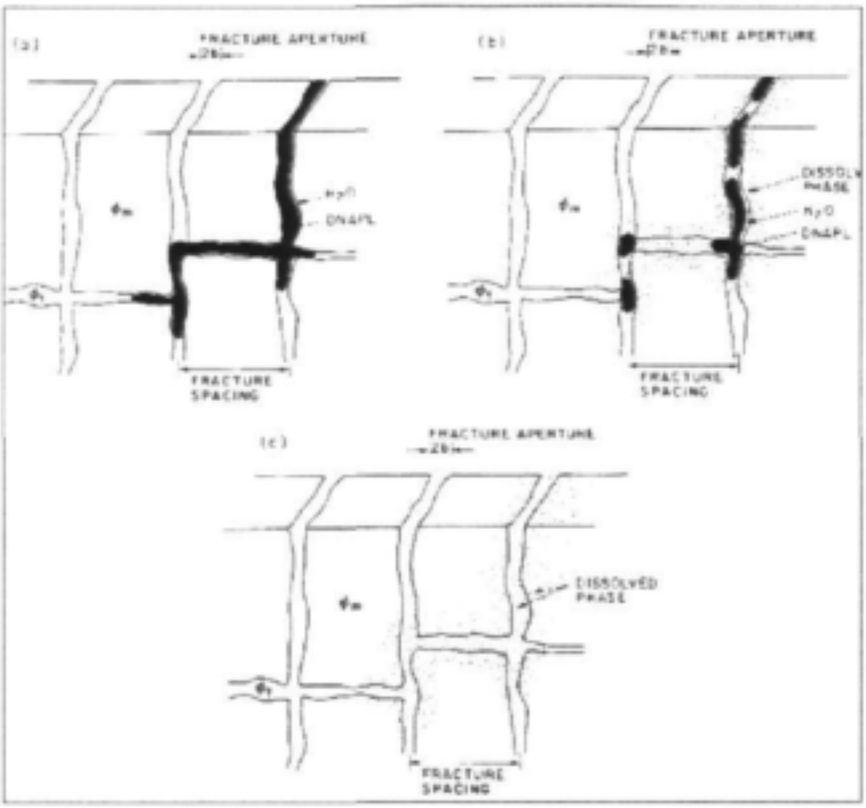


Figure 19. Conceptual model for the distribution of DNAPL in a saturated, fractured porous medium with DNAPL as the non-wetting fluid in the fractures (from Parker *et al.*, 1995) (a) early time: interconnected DNAPL phase. (b) intermediate time: disconnected DNAPL blobs. (c) late time: diffusion haloes in the matrix around fractures that once contained DNAPL.

The time period required for complete DNAPL phase disappearance is specific to the chemical and porous medium conditions. Flushing of the fractures with uncontaminated groundwater will cause diffusion of the DNAPL out of the matrix and into the moving groundwater as the concentration gradients are reversed.

8.2.6.2 Summary

Some of the salient points relating to DNAPL fate and transport in the subsurface are summarised here:

- DNAPL is often the non-wetting phase relative to water.
- DNAPLs can dissolve in water forming dissolved contaminant plumes that travel in the direction of groundwater flow.

- DNAPLs can also be adsorbed onto the matrix or other particles, retarding the flow of the DNAPLs relative to the velocity of groundwater flow.
- DNAPL prefers the fracture and does not spontaneously move into the matrix.
- DNAPL displaces water from an opening only after the entry pressure of the opening is exceeded.
- The entry pressure for fractures is very small relative to the entry pressure of matrix.
- Capillary pressure increases with depth so DNAPL may enter increasingly smaller openings with depth.
- Upward groundwater flow gradients may halt the migration of DNAPLs.

Dense Chlorinated Solvents and other DNAPLs in Groundwater by Pankow and Cherry (1996) is an excellent source of additional information on the transport and fate of DNAPLs in the subsurface.

8.3 Migration potential of microbial contaminants

The information in this section was obtained from a literature review on microbiological contamination of groundwater, conducted for the National Microbial Monitoring Programme for Groundwater (Du Preez *et al.*, 2003). Further details on the types of micro organisms found in groundwater and their health effects may be found in the original research report and the references it contains.

Micro-organisms, particularly viruses, are able to move through several types of soil to contaminate aquifers. Transport of microorganisms in the subsurface is affected by processes such as advection and dispersion, which control the fate of other suspended solid particles. In a homogeneous unconsolidated matrix, such as sand, viruses are usually transported at similar velocities to conservative salt tracers.

The occurrence of micro organisms in groundwater is governed by two main variables: the inactivation rate of the microbes and the speed at which they move through the soil. Both of these may be affected by the reversible or irreversible adsorption of the microbe to soil particles. Adsorption of viruses to soil particles is affected by several factors including:

- pH – adsorption generally increases with decreasing pH.

- Virus type – affects the surface charge and hydrophobicity of the viral surface coat.
- Soil type and composition – positively charged oxide surfaces are good adsorption sites for negatively charged viruses. Clays are better adsorbers than sands.
- Hydrophobic interactions – the interaction of hydrophobic groups is a major mechanism for virus attachment, especially at high pH.
- Ionic strength (or salinity) – viruses adsorb more strongly at high ionic strength.
- Presence of multivalent cations – favours attachment of viruses.
- Organic matter – inhibit viral adsorption by competing for surface sites.
- Soil water content – viruses are removed more efficiently under unsaturated conditions.

Viruses moving through the soil zone appear to undergo decreasing inactivation and adsorption with distance from the source. In the first few metres, viral removal occurs at a very high rate, but after this they move without much apparent hindrance. The non-linear inactivation rate allows viruses to travel great distances through soil and contaminate deep or distant aquifers. Viruses may be present in groundwater even when coliform tests show no evidence of faecal contamination, since coliform bacteria from the same source are more easily removed in the soil zone.

The microbial contamination risk of a groundwater source is dependent on the survival rate of the micro organisms. Viruses are inactivated by disruption of the surface proteins coat or degradation of nucleic acids. The factors influencing the inactivation of viruses in soil environments include:

- Temperature – virus survival decreases with increased temperature.
- Adsorption to solid particles – generally decreases viral inactivation.
- Unsaturated conditions – viruses are inactivated at a higher rate in the unsaturated zone.
- Microbial activity – bacterial inactivation of viruses can play a role in survival times.

There is some controversy over how long viruses can live in soils and groundwater. Studies have reported a 1-log reduction in concentration of poliovirus type 1 taking anything from 29 to 300 days.

The survival of metabolically active microorganisms such as bacteria and protozoa are limited by their dependence on the availability of nutrients. The inactivation rates (natural logarithm per day) of faecal indicator bacteria in groundwater at ambient temperatures have been found to be as low as 0.53 day^{-1} (faecal streptococci), 0.82 day^{-1} (faecal coliform) and 0.04 to 0.73 day^{-1} (*E. coli*). For pathogenic bacteria, inactivation rates of 1.42 day^{-1} (*Shigella spp.*) and 0.33 day^{-1} (*E. coli* 0157:H7) have been reported. Some pathogenic bacteria can, however, enter nonculturable, but still viable dormant states, which could further prolong their persistence in groundwater. Spores of pathogens such as *Clostridium spp.* may survive in the environment for several years while remaining viable.

Table 21 summarises the mobility and persistence characteristics of a range of commonly analysed microorganisms in groundwater.

Table 21. Factors associated with the likely presence and survival of various microorganisms in groundwater (After Du Preez *et al.*, 2003)

	Relative likelihood* of organisms reaching the saturated zone (based on organism size and unsaturated zone characteristics)						**Ability* of organisms to survive** (Persistence in the environment)
	Unconfined primary aquifer		Unconfined secondary aquifer		Semi-confined secondary aquifer		
	High K[1]	*Low K*	*High K*	*Low K*	*High K*	*Low K*	
Total coliforms	H	L	H	L	0	0	M
Faecal coliforms	H	L	H	L	0	0	M
E. coli	H	L	H	L	0	0	M
Faecal streptococci	H	L	H	L	0	0	H
Sulphite reducing clostridia & other anaerobes	H	L	H	L	0	0	VH
Bacteriophages	VH	M	VH	M	VL	VL	H
Viruses	VH	M	VH	M	VL	VL	H
Protozoan parasites	M	VL	M	VL	0	0	VH

* ranging from VH = very high, H = high, M= medium, L = low, VL = very low to 0 = almost zero.

[1] K = permeability

9. APPENDIX B: Methods for prioritising groundwater contaminants and pollutants

Classification and prioritisation are used as a means of making maximum use of the data collected from a contaminant inventory or monitoring programme.

The methods for classifying and prioritising (rating or ranking) contaminants are often applicable to specific conditions or situations, although there are some general methods that can be applied to most sites. Classification and prioritisation of contaminants has sometimes been used within a broader framework of pollution risk assessment methods and a risk-based framework for prioritisation of groundwater contaminants will be outlined in the next section. There is no standard accepted or regulated system for South Africa and methods of classifying and prioritising contaminants need to be established specifically for local conditions.

There is no shortage of literature on this topic. Table 22 contains a summary of some of the more recent classification and rating/prioritisation methods for groundwater contaminants. A couple of the more popular or promising methods will be described in more detail in this section. These methods have been used as the basis for the prioritisation framework developed for South Africa and discussed in Section 6.

Table 22. Examples of methods for prioritising existing and potential groundwater contamination sources (slightly modified from Johansson and Hirata, 2002).

Method	Type of source	Approach	Principle	Reference
Danish EPA*	general	general screening	qualitative, 3 classes	Danish EPA, 1995
Foster & Hirata*	general	general screening	qualitative, 4 classes	Foster & Hirata, 1988
Rao *et al**	pesticides	general screening	quantitative, equation	Rao *et al.*, 1985
Swedish EPA*	contaminated land	general screening	qualitative, 4 classes	Swedish EPA, 1995
Kerndorff *et al**	waste disposal	general screening	quantitative, statistical	Kerndorff *et al.*, 1992
MACRO-DB	pesticides	general screening or object-specific	quantitative, simulation model	Jarvis *et al.*, 1997

Method	Type of source	Approach	Principle	Reference
Danish EPA*	general	general screening	qualitative, 3 classes	Danish EPA, 1995
PRZM/ PRZM-2	pesticides	general screening or object-specific	quantitative simulation model	Carsel *et al.*, 1985 Mullins *et al.*, 1993
PROFILE	acidification	general screening or object-specific	quantitative simulation model	Warfvinge & Sverdrup, 1992
Foster & Hirata*	general	object-specific	qualitative numerical index	Foster & Hirata, 1988
Hirata*	general	object-specific	qualitative high to low	Hirata, 1994
Mazurek*	general	object-specific	qualitative, numerical index	Mazurek, 1979
ISAL	waste disposal	object-specific	qualitative, numerical index	ISAL, 1991
LeGrand*	waste disposal	object-specific	qualitative, numerical index	LeGrand,1964 and 1983
Phillips*	waste disposal	object-specific	semi-quantitative	Phillips *et al.*, 1977
Visual HELP	waste disposal	object-specific	quantitative, simulation model	Waterloo Hydrogeologic, 2000
WASP	waste disposal	object-specific	qualitative, numerical index	Parsons & Jolly, 1994
Hirata*	nitrate, pesticides	object-specific	semi-quantitative	Hirata *et al.*, 1993
MIFO	contaminated land	object-specific	qualitative, 4 classes	Swedish EPA, 1999
ARGOSS	on-site sanitation	object-specific	qualitative, risk assessment	Lawrence *et al.*, 2001
Knox & Canter*	general	general screening	quantitative, frequency of occurrence	Knox & Canter, 1994

*No formal name given.

Although classification of contaminants or contaminant sources is a useful starting point, **classification itself does not reveal anything about the potential hazard** of the type of source or activity. In general, some types of sources are known to pose a more or less serious threat than others. A rating or ranking system (**prioritisation system) gives an idea of the magnitude** of the problem associated with a potential contaminant and allows energy and resources to be directed to better understanding, regulating or engineering control measures for the most serious threats (Johansson and Hirata, 2002).

The prioritisation methods in Table 23 have been divided into general screening methods and object specific methods. General screening methods apply general knowledge of the threat to groundwater posed by the contaminant source, while object-specific methods use site-specific information for the rating. General screening methods are usually applied on a national or regional scale and object-specific methods to a much smaller area. Some of the methods have been developed for a specific type of contaminant activity e.g. waste disposal or pesticide application.

General screening methods are those that consider broader classification and prioritisation methods. They are generally used as ways of raising awareness where groundwater protection is concerned. Contaminant source identification as well as a rating based on expert judgement is included here. It requires a small amount of data and is quite easy to apply using a small technical team.

An outcome of this type of method is e.g. a map showing the sources of contamination. Here one does not explicitly express the degree of hazard of a particular contaminant, but rather prioritises them by assigning a qualitative rating based on the source and general knowledge of the activities and the nature of the contaminant (here referring to whether the contaminant is liquid or solid and the type and quantity of the substance used). General screening methods are also great tools for regional planning e.g. Vulnerability mapping.

The success of object specific methods is dependant on the amount of detailed data available for a specific site.

Field surveys or field investigations, together with all available data from authorities, e.g. DWAF, are required for such methods. The following aspects of contaminants or contamination are important when conducting object specific classification and prioritisation:

- type of contaminant (including the toxicity, mobility and persistence);
- amount of potential contaminants (in terms of concentrations and quantities);
- handling and storage of potential contaminants;
- treatment and disposal of solid and liquid wastes; and
- areas potentially affected by contaminants.

Objective specific methods yield results that can be used to assist in local planning, municipal planning as well as wellhead protection and aquifer contamination characterisation. Many of the object-specific methods have been developed as tools for groundwater protection at waste disposal sites

9.1 Assessment of subsurface contaminant load

A commonly cited example of a method for assessing groundwater pollution risk has been developed by Foster and Hirata (1988). Figure 20 shows an outline of the important processes and parameters in their groundwater pollution risk assessment framework. Classification and prioritisation of groundwater contaminants is the first step in the method, which the authors have labelled "subsurface contaminant load" (SCL). Johansson & Hirata (2002) also refer to this step as establishing the "contaminant potential" in their later modification of the method.

Classifying & prioritising contaminants

Groundwater Pollution Risk Assessment	
Subsurface Contaminant Load (SCL)	Class
	Intensity
	Disposition
	Duration
Aquifer Pollution Vulnerability (APV)	Groundwater occurrence
	Depth to water table
	Overall Lithology
Groundwater Pollution Risk	Interaction of SCL & APV
Impact on Groundwater Supplies	Lateral transport
	Well Construction

Figure 20. A scheme for groundwater pollution risk assessment (from Foster and Hirata, 1988).

Foster and Hirata's (1998) procedures for the assessment of groundwater pollution risk were developed in the Latin American-Caribbean region and should be applicable for the type of urbanization that characterizes developing countries such as South Africa.

The following parameters are used in assessing the subsurface contaminant load:

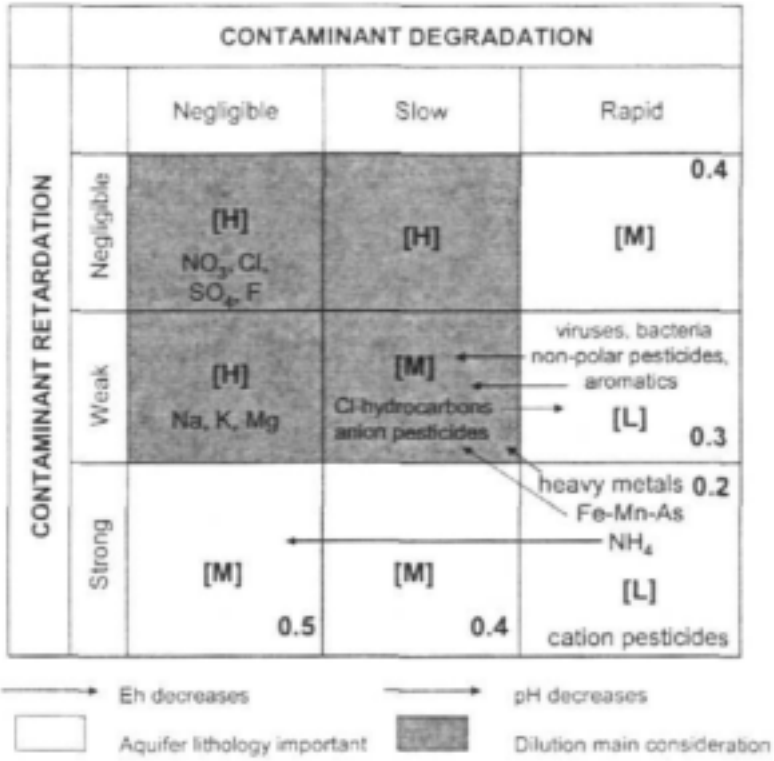
- contaminant class;
- intensity of contamination;
- mode of contaminant disposition; and
- duration of contaminant load.

Each aspect of the subsurface contaminant load, i.e. the class, intensity, mode of disposition and duration of contaminant load, is given a rating using graphs or matrices developed by Foster and Hirata (1988).

9.1.1 Contaminant class

The *class* of the contaminant considers the physicochemical behaviour, i.e. *degradation* and *retardation* of a contaminant in the subsurface. This is directly linked to the mobility of particular ions in the groundwater environment as well as the rate of breakdown of larger molecules (transformation). Foster and Hirata (1988) used the diagram in Figure 21 to assign a numerical value to the contaminant class. Although not explicitly included in the diagram, lithological characteristics cannot be ignored as they play an important role in processes such as sorption and ion exchange. In all likelihood, a particular contaminant will behave differently under different lithological conditions.

Figure 21 is a combination of the original method and a later modification. Foster and Hirata (1988) allocated the contaminants to their locations in the matrix and Johansson and Hirata (2002) assigned a rating to the classes, i.e. H = high, M= medium and L= low.

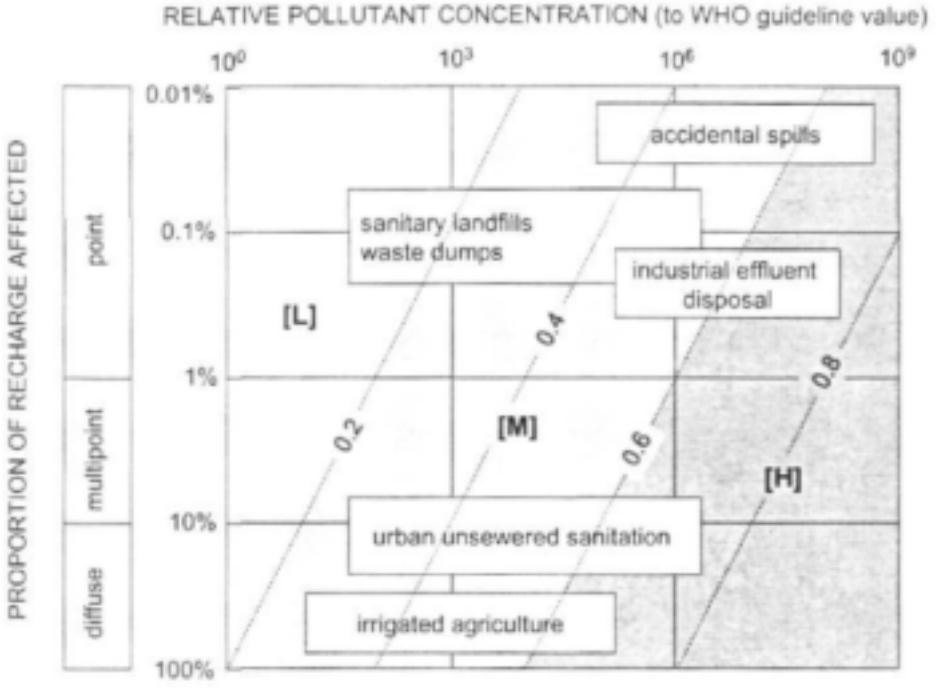


[ ] Johansson and Hirata's rating for potential contaminant load

Figure 21. Contaminant class diagram (Foster & Hirata, 1988 and Johansson & Hirata, 2002).

9.1.2 Intensity

Intensity considers the concentrations of contaminants relative to World Health Organisation guidelines, as well as the proportion of groundwater affected by the contamination (Foster and Hirata, 1988). In cases where persistent mobile contaminants such as NO_3 and Cl are present, the intensity of contamination becomes the key factor in prioritising the contaminant. Foster and Hirata (1988) rated various contaminant sources using the matrix in Figure 22.



[L] = low, **[M]** = medium and **[H]** = high intensity of contamination, as part of the characterisation of the contaminant load.

Figure 22. Contaminant intensity diagram (Foster & Hirata, 1988 and Johansson & Hirata, 2002).

The sources have been placed according to their potential pollutant concentrations relative to the guideline levels and the spatial magnitude of the source, in terms of what proportion of recharge over an area is likely to be affected by contamination. Johansson and Hirata (2002) have added the divisions showing high, medium and low contamination intensity to the matrix.

9.1.3 *Contaminant Disposition*

The mode of *contaminant disposition* considers the hydraulic load associated with the contaminant and the depth below surface at which leachate is discharged. The associated diagram is shown in Figure 23.

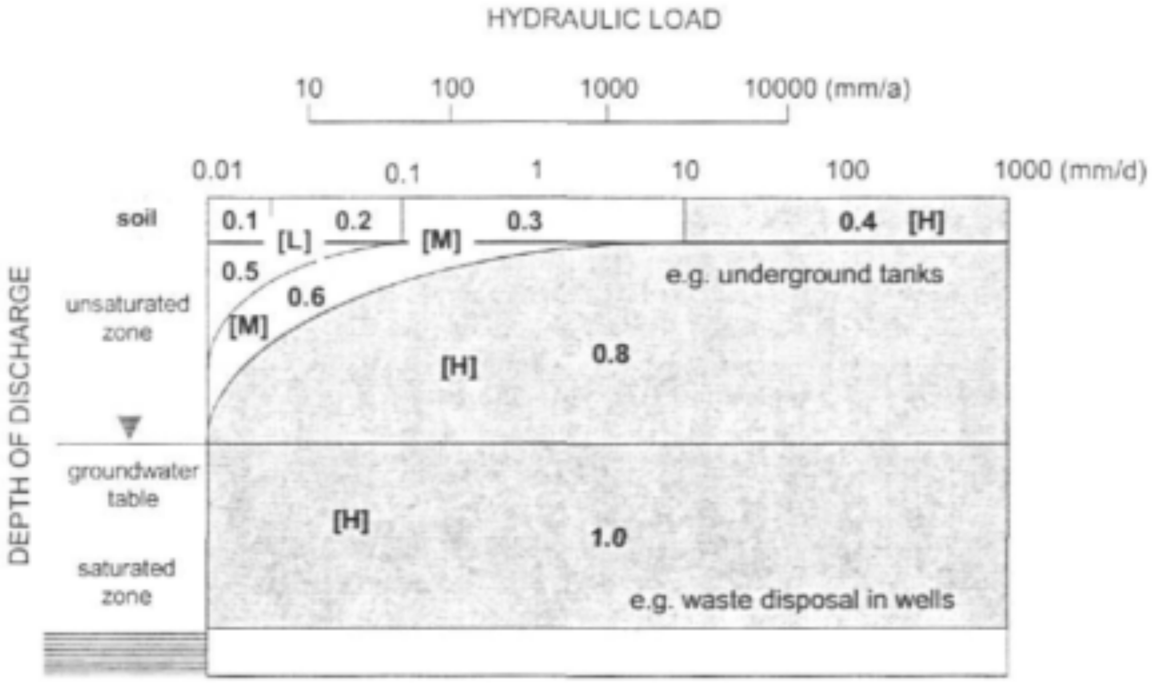


Figure 23. Mode of contaminant disposition (Foster & Hirata, 1988 and Johansson & Hirata, 2002)

This figure shows the numerical values assigned by Foster and Hirata (1988) and the relative ratings (high, medium and low) from the work of Johansson and Hirata (2002). Depth of discharge is indicated by the different zones of the subsurface, rather than an absolute depth measurement. It is important to take into account the groundwater recharge to an area as this determines the rate of infiltration in the hydraulic loading.

9.1.4 Duration of application of contaminant

Duration of application considers the probability that contaminants will be discharged to the subsoil as well as the period during which a specific load has been applied. The latter is expressed as the difference between a contaminant applied to an area for a one year period and continuous application over twenty years (Foster and Hirata, 1988). The figure used to derive the duration factor is shown in Figure 24.

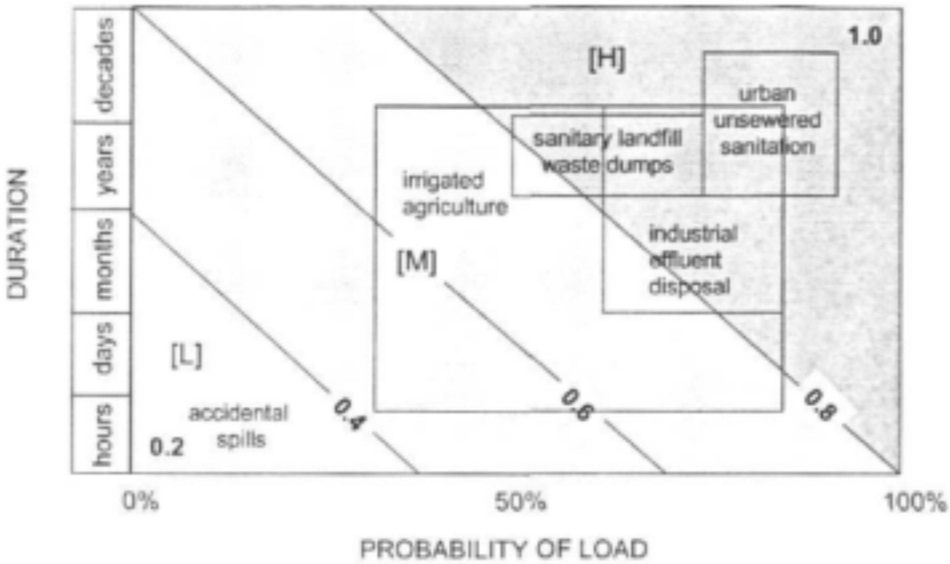


Figure 24. Duration of contaminant load (Foster & Hirata, 1988 and Johansson & Hirata, 2002)

9.1.5 Modified subsurface contaminant load method

Johansson and Hirata's (2002) combined all the matrices used for the subsurface contaminant load assessment into a comprehensive interconnected framework, rather computing a separate numerical score for each factor in the SCL. The diagram by Johansson and Hirata (2002) includes a contaminant transport matrix (a combination of the contaminant class and mode of disposition) and a contaminant source strength matrix (a combination of the relative contaminant load and duration of contaminant load) (Figure 25).

The main drawback of this method is the rigorous data requirements, since sufficient amounts of data of the required types are not always readily available. Hence, accurate quantification of contaminants is not always achievable, however a general idea of the extent or the severity of contamination at certain sites is known.

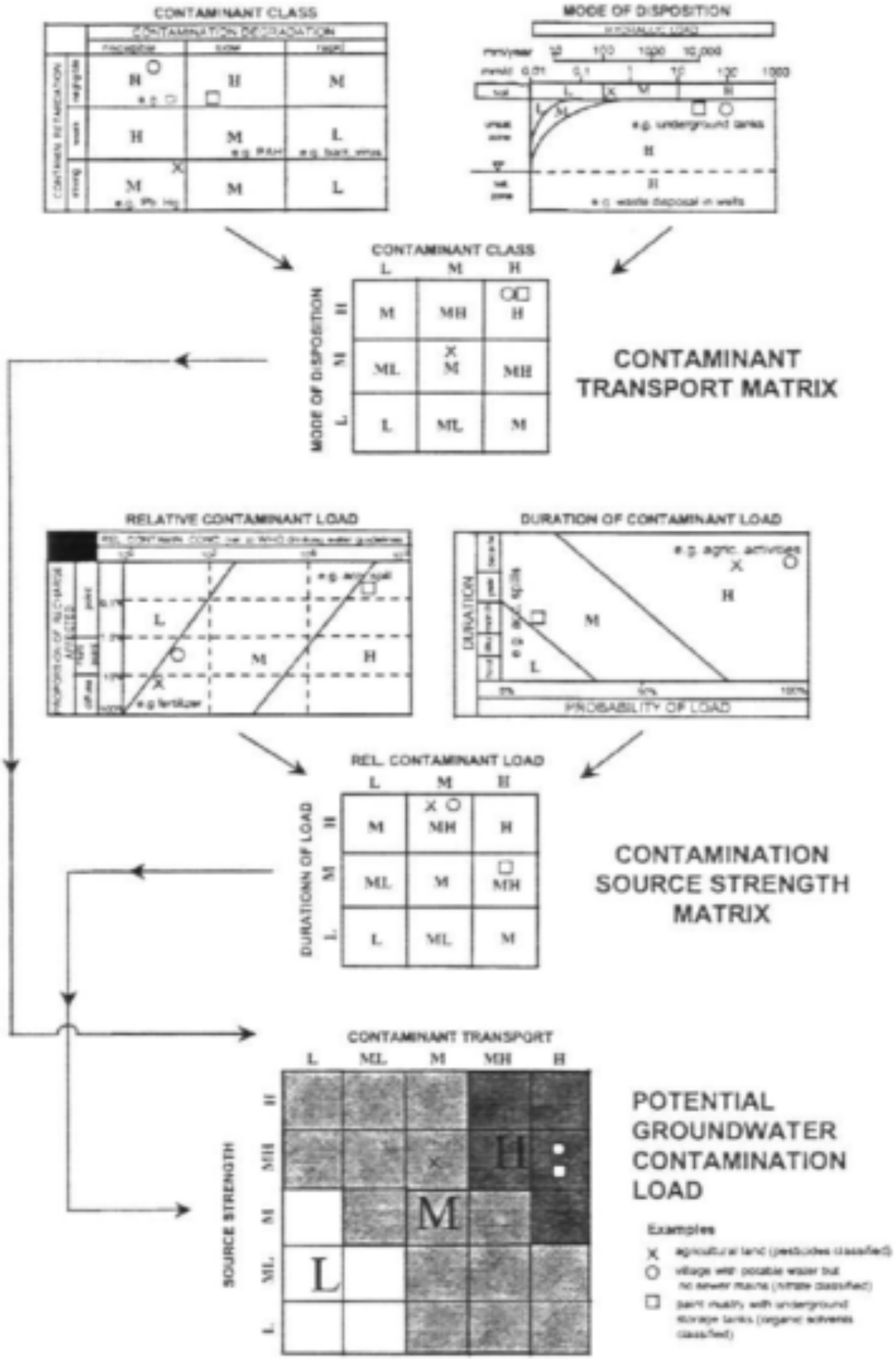
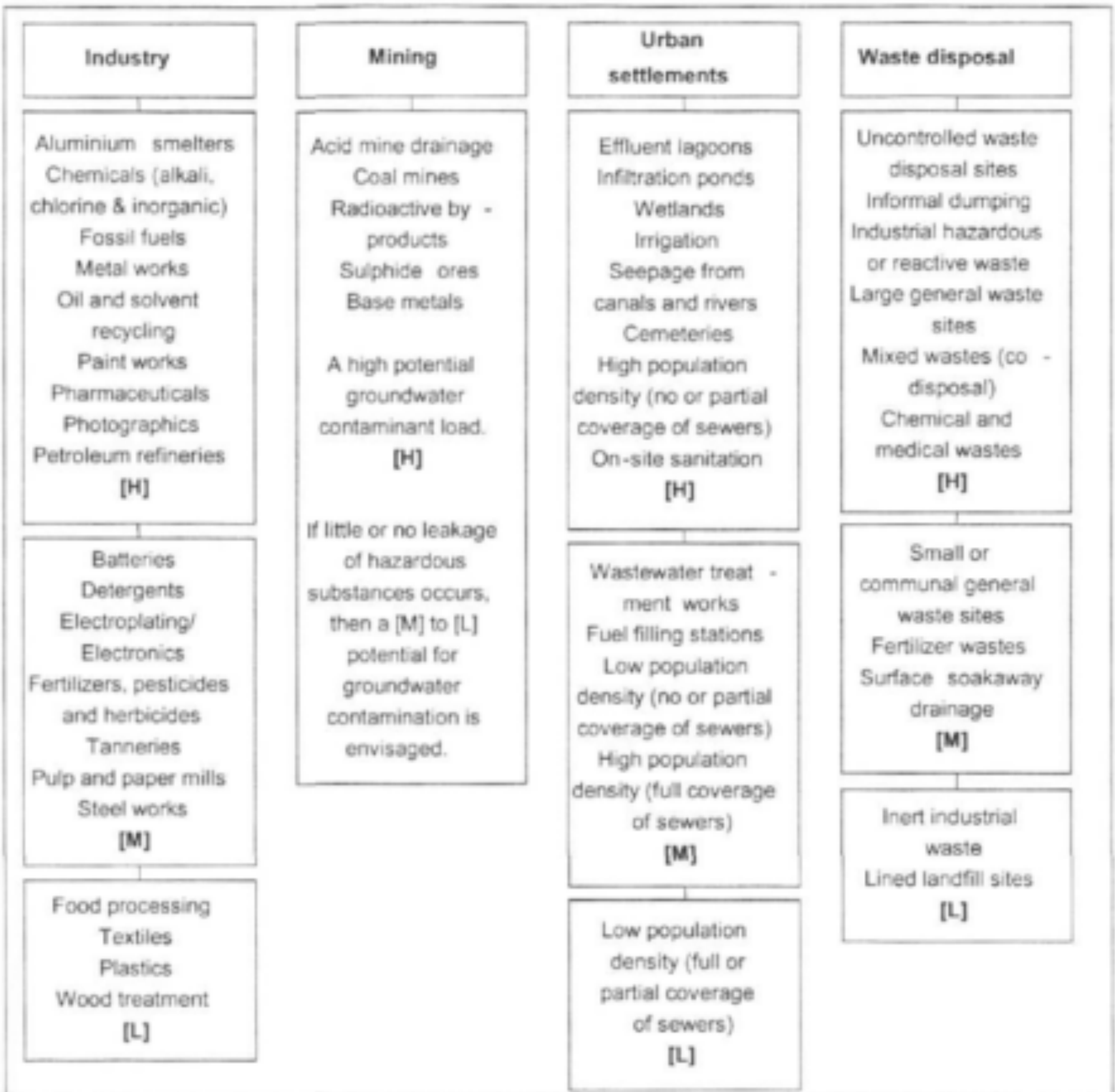


Figure 25. Johansson and Hirata's (2002) modification of the original contaminant load methodology developed by Foster and Hirata (1988).

Johansson and Hirata (2002) applied their prioritisation method to various generalised sources of groundwater contamination. This allows the contaminant sources classified by origin to be subdivided further based on activities that are assigned a priority rating of high, medium or low. This prioritised classification is shown in Figure 26 for activities classified as the industrial, urban settlement, mining and waste disposal categories used in the South African groundwater contaminant inventory.



Industry	Mining	Urban settlements	Waste disposal
Aluminium smelters Chemicals (alkali, chlorine & inorganic) Fossil fuels Metal works Oil and solvent recycling Paint works Pharmaceuticals Photographics Petroleum refineries [H]	Acid mine drainage Coal mines Radioactive by-products Sulphide ores Base metals A high potential groundwater contaminant load. [H]	Effluent lagoons Infiltration ponds Wetlands Irrigation Seepage from canals and rivers Cemeteries High population density (no or partial coverage of sewers) On-site sanitation [H]	Uncontrolled waste disposal sites Informal dumping Industrial hazardous or reactive waste Large general waste sites Mixed wastes (co-disposal) Chemical and medical wastes [H]
Batteries Detergents Electroplating/ Electronics Fertilizers, pesticides and herbicides Tanneries Pulp and paper mills Steel works [M]	If little or no leakage of hazardous substances occurs, then a [M] to [L] potential for groundwater contamination is envisaged.	Wastewater treatment works Fuel filling stations Low population density (no or partial coverage of sewers) High population density (full coverage of sewers) [M]	Small or communal general waste sites Fertilizer wastes Surface soakaway drainage [M]
Food processing Textiles Plastics Wood treatment [L]		Low population density (full or partial coverage of sewers) [L]	Inert industrial waste Lined landfill sites [L]

Figure 26. Prioritised classification of activities that pose a potential threat of groundwater contamination in the industrial, mining, urban settlement and waste disposal sectors. Generalised ratings have been assigned using the method of Johansson and Hirata (2002).

9.2 Tiered prioritisation method

Knox and Canter (1994) worked on a tiered prioritisation method for groundwater contaminants based on frequency of occurrence and health impacts. Their approach is summarised in Figure 27 below.

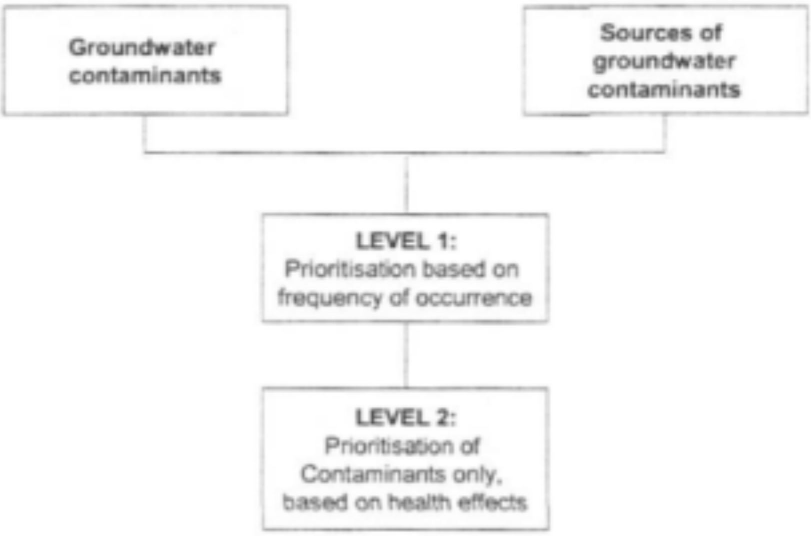


Figure 27. Prioritisation methodology proposed by Knox and Canter (1994).

Data collected for the prioritisation is weighted using a numbering system from 1 to 8 to describe the scope, geographical extent and comprehensiveness of the data sets used. For example, a weighting of 1 is given to an information source of limited scope, whereas data based on a wide scope of information is assigned a weighting of 8 (Knox and Canter, 1994). The same rating method used for groundwater contaminants was also used to rate sources of contamination.

9.2.1 *Contaminant frequency ratings*

LEVEL 1:

Knox and Canter (1994) consulted 13 sources from government departments for site-specific case studies in the USA. A group of individuals were given the opportunity to rank 200 contaminants individually and some time thereafter the group assembled to decide on the final rating for contaminants, based on their individual opinions of where each contaminant should rank. Only individual contaminants were classified, rather than groups of contaminants, e.g. heavy metals or volatile organic compounds (VOC's).

The type of information under consideration for the ranking system included:

- the number of wells contaminated or abandoned at the sites;
- percentage of contaminated wells;
- exceedence of legal maximum contaminant levels (MCL's);
- elevated concentrations of the contaminant detected;
- groundwater quality data; and
- lists of commonly found contaminants.

A product matrix was developed for about 200 contaminants using the equation:

(Importance weights x frequency ratings) = composite frequency score Equation (13)

Frequency scores obtained from the equation above ranged considerably, with a minimum value of 1 and a maximum of about 105 (Knox and Canter, 1994).

LEVEL 2:

The 200 contaminants were classified into high, medium and low occurrence levels. High priority was assigned to contaminants having scores ranging from 33 – 66, while medium priority was given to a range of values 17 – 31. Scores below 17 were assigned a low priority value.

According to Canter (1992), bacterial contamination is the most ubiquitous of all groundwater contaminants, but is often not routinely reported. Knox and Canter (1994) found that of the most frequently recorded contaminants, 9 were inorganic, 10 were organic and one is a radionuclide.

9.2.2 *Health risks of contaminants*

Knox and Canter (1994) also took into account the health effects contaminants could have on humans consuming the water from municipal water supplies. Contaminants were prioritised using one of the following factors related to health risk:

- carcinogenic potency and noncarcinogenic toxicity;
- hazardous chemical priorities;
- groundwater quality standards; and

- unknown health effects.

Knox and Canter (1994) chose carcinogenic potency and noncarcinogenic toxicity as the most suitable indicator and worked with a dose-response data set developed for human health risk assessments.

9.2.3 *Priority lists of contaminants and sources*

Knox and Canter (1994) developed the table below using their method for prioritising groundwater contaminants. Although they included both organic and inorganic contaminants, the table concentrates mainly on the inorganic species.

Table 23. Prioritisation of inorganic groundwater contaminants from site-specific case studies in the USA (Knox and Canter, 1994).

Group	Contaminants
Highest priority	Arsenic Chromium
Second highest priority	Nitrates Barium Selenium Lead Mercury
Third highest priority	Fluorides Silver Radium (combined) Cyanide
Fourth highest priority	Sulphates Chlorides Iron

According to Knox and Canter (1994), the highest priority organic contaminants in groundwater in the USA were:

- Carbon tetrachloride
- 1,1-dichloroethene,

- chloroform
- ethylene dibromine

The eight highest priority sources of groundwater contaminants in the USA were found to be:

- Agricultural activity
- Hazardous waste sites
- Landfills
- Industrial operations
- Septic tank systems
- Oil and gas field activities
- Urban land use; and
- Underground storage tanks

Of these sources, oil and gas fields are not common in urban areas of South Africa. Agricultural activity and septic tank systems are also activities that are expected to occur in peri-urban areas, although the effects of pollution from these sources should not be overlooked in the urban centres.

9.2.4 *Limitations*

Knox and Canter (1994) and other authors have noted certain limitations in applying prioritisation methods. The most notable limitation relates to data availability. Knox and Canter (1994) used a database where records were often found in duplicate or triplicate, which may have led to errors in the calculated frequency of occurrence. The inconsistent use of terminology in reports was also a limitation in their study. Another issue of concern is unreported contamination. This occurs especially in non-public water supplies in the USA and may be a major issue in informal settlements in South Africa, where little or no monitoring occurs. Industrial contamination cases are also either not reported or companies often do not allow to release the results of their site assessments to the public.

9.3 Summary of methods

Key features of the prioritisation methods discussed in this report are summarised below.

9.3.1 *Subsurface contaminant load method (Foster and Hirata, 1988)*

This method is recommended as a general screening method that can be tested for prioritisation of contaminant sources on a national scale. It can be applied to potential or existing sources of contamination.

Advantages:

- The method is comprehensive, considering a wide range of factors, including loading, contaminant behaviour and hazardousness.
- It is simple to apply and uses diagrammatic tools for rapid assessment.
- It is flexible and can be adapted for various levels of sophistication, depending on the availability of quantitative or qualitative data

Disadvantages:

- Estimates can be used where data is lacking, but these can be very subjective.
- Many contaminant sources are rated as high priority, but the method does not distinguish which will require the most urgent action.

Results of the method:

- A list or matrix of contaminants (or contaminant sources) rated as low, medium or high priority.

9.3.2 *Tiered prioritisation method (Knox and Canter, 1994)*

This method is used to assess contaminant loading from a variety of sources in urban areas. A numerical loading factor is calculated based on detection frequencies, concentrations, comparison with guidelines and percentage of affected boreholes. Water quality guidelines are combined with a detailed health risk assessment approach to give a more comprehensive assessment of the hazardousness of the contaminant than is done in any of the other methods. This method is more likely to be successful once monitoring systems are in place and data collection has been streamlined in the Catchment Management Areas of South Africa.

Advantages:

- Data reliability is specifically considered by weighting the information sources.
- A quantitative approach is taken to assessing hazardousness using toxicity and carcinogenicity data in addition to quality guideline values.

Disadvantages:

- Applications in South Africa may be limited by the requirements for concentration data for a range of parameters.
- Missing epidemiological data often hampers health risk assessment approaches.
- The prioritisation involves an importance rating in the loading factor, which is very subjective.

Results of the method:

- Assignment of contaminants to priority classes.
- Lists of highest priority contaminant sources.

9.4 Basic principles of prioritisation

The methods for classifying and prioritising individual groundwater contaminants, or groups of contaminants, focus on three main factors. These are:

- contaminant **loading**,
    - which considers aspects such as quantity, spatial extent and frequency of occurrence or probability of release to the environment;
- contaminant **behaviour**,
    - which takes into account aspects such as chemical mobility and persistence in the environment; and
- **hazardousness** of the contaminant,
    - in terms of its potential impacts on humans and ecosystems.

Some of the methods we have described prioritise contaminants only on the loading factors e.g. Kerndorff *et al.* (1992) use only concentration data to rank contaminants. Other methods, such as that developed by Foster and Hirata (1988), consider all three factors, but devote varying degrees of attention to each.

Prioritisation can also be taken to another level by focussing not only on contaminant properties, but also incorporating *aquifer vulnerability* assessment. The prioritisation methods can also be included in a *risk assessment* approach, which considers not only the contamination threats to groundwater, but also the potentially affected environment i.e. the impact on human and ecosystem receptors.

9.4.1 *Data requirements*

Data requirements for the prioritisation methods are variable and can range from large datasets of quantitative groundwater chemical analyses, as required for statistical methods such as Kerndorff *et al.* (1992) or Mull *et al.* (1992), to broad qualitative or descriptive information. Some of the methods are flexible enough to allow varying degrees of complexity, depending on the availability of information.

On a national scale, it would be impractical to analyse all quantitative data for contaminated sites in urban areas of South Africa. Any attempts at such an approach are also likely to be biased by the uneven distribution of monitoring networks, irregularity of data collection in some areas and inconsistent regulatory requirements for different potential polluters (e.g. waste sites are regulated, but wastewater treatment works and cemeteries are not).

In such a case it is probably more useful to consider generalised qualitative information on characteristic types of contaminant sources. Where quantitative data is not available, expert knowledge may be employed to estimate weightings or rankings in some of the methods. These are based on subjective decisions of the importance of a particular source or contaminant. For example, if there are no quantitative data for the concentration of contaminants in industrial effluent, it is not possible to determine whether or not WHO guidelines are exceeded for plotting on Foster and Hirata's (1988) contaminant intensity diagram (Figure 22). But it is still possible to estimate the approximate position of this type of source on the diagram, based on the judgement that concentrations are likely to be high.

9.4.2 *Outputs*

The level of detail of the assessment varies depending on the objectives. General screening methods apply generalised knowledge, while object specific approaches are usually applied to a particular source or site. General screening methods are probably more applicable for a national contaminant inventory than object specific approaches, as they can be applied on a large scale.

The outputs from the prioritisation methods can be used to produce products such as ranked lists of priority contaminants or maps of priority areas. Some methods assign numerical scores to the factors and others rank contaminants in a specific order of priority. The methods with less stringent data requirements often use broad classes, such as assigning ratings of high, medium or low. In this case, there is often no distinction between the contaminants or sources within a particular class.

9.5 Statistical methods for ranking contaminants

9.5.1 *Comparison of data up- and downgradient of the source*

This methodology, used by Kerndorff *et al.* (1992), is based on a statistical analysis of contaminant concentration data from a large number boreholes up- and downgradient of contaminated sites. The authors' study focused on abandoned waste disposal sites in Germany, but the approach could equally well be applied to any other point sources of contamination provided that the affected groundwater has concentrations of contaminants that are significantly higher than natural background levels in the aquifer.

Chemical data sets are initially sorted into upgradient (uncontaminated) and downgradient (contaminated) samples. The two data subsets are then analysed separately. Statistical analysis is undertaken for each analytical parameter (e.g. potassium, dissolved organic carbon, etc.) to develop a matrix including the following information:

- Number of analyses
- Detection limit
- Number of determinations above detection limit
- Frequency of detection (%)
- Mean concentration

- Maximum concentration
- 50%, 75% and 90% percentile concentrations (i.e. concentrations for which 50, 75 or 90 per cent of the samples are equal to or below the given concentration).

The statistical summary is then developed further to characterise the impact on groundwater.

9.5.2 *Contamination factors*

Kerndorff *et al.* (1992) developed a contamination factor (CF) using the ratio of the values in contaminated samples to those in uncontaminated samples. Contamination factors are calculated for the mean, maximum and percentile concentrations for each analytical parameter. For example, the mean concentration factor for potassium is calculated from the equation:

$$CF_{mean,K} = \frac{(Conc_{mean,K})_{downgradient}}{(Conc_{mean,K})_{upgradient}} \qquad \text{Equation (14)}$$

The contamination factors represent the extent of contaminant leakage from the source. Non-leaking sites have CF's near 1.0, whereas sites that have released contaminants will have CF values significantly above 1.0.

The highest CF values are used to identify those specific substances that are likely to be associated with leachate from contaminated sites. In the case of inorganic contaminants from waste disposal sites in Germany, Kerndorff *et al.* (1992) found high contamination factors for arsenic ($CF_{mean,As} = 122$); ammonium ($CF_{mean,NH4} = 65.5$); cadmium ($CF_{mean,Cd} = 26.9$); nitrite ($CF_{mean,NO2} = 25.7$); boron ($CF_{mean,B} = 21.6$); chromium ($CF_{mean,Cr} = 15.8$) and nickel ($CF_{mean,Ni} = 14.8$).

9.5.3 *Frequency exceedance of background concentrations*

An alternative approach to the contamination factors, also suggested by Kerndorff *et al.* (1992), is to rank the individual substances according to the frequency by which background concentrations are exceeded. Using this approach, the authors found that boron was a very good tracer of leachate from waste disposal, with boron concentrations downgradient exceeding those upgradient of the site in 88%

of the samples. Other inorganic substances, which exceed background concentrations are (in decreasing order of frequency): bicarbonate, sodium, chloride, magnesium, calcium, potassium, strontium, lead, nitrite, aluminium, selenium, cadmium and mercury (Kerndorff *et al.*, 1992).

9.5.4 *Characteristic contaminants*

A subset of inorganic parameters that are characteristic of groundwater contamination from a particular type of source can be derived from a combination of the above two approaches. Kerndorff *et al.* (1992) used the criteria of contamination factor greater than 10 and frequency of exceeding background concentrations greater than 50% to develop a subset of "characteristic contaminants".

The set of characteristic inorganic contaminants for abandoned waste disposal sites in Germany is: arsenic (CF 122; 61.3%); ammonium (CF 65.5; 53.6%); boron (CF 21.6; 85.7%); nickel (CF 14.8; 64.3%) and chromium (CF 15.8; 56.3%).

These would be the priority contaminants for monitoring to detect leakage from waste disposal activities. The prioritisation in this method is based only on likelihood of occurrence in groundwater, rather than the impact of the pollution, since it does not take into account the toxicity of the substances.

9.5.5 *Analysis of monitoring data variance*

Kerndorff *et al.* (1992) also include a different data analysis technique, based on changes in monitoring data variance over time, which was used in a study of waste disposal sites in the United States (Plumb, 1991). This method does not use the separation of samples into up- and downgradient data sets and so avoids the implicit assumptions of how chemicals behave at the contaminated sites. The analysis of variance method relies on the premise that the observed concentrations of an inorganic constituent, which is not involved in a leakage event, should be similar for all monitoring boreholes at the site i.e. the variance in the data for that substance should be low. If an inorganic contaminant is released from a point source into the groundwater, the concentration will increase at one or more monitoring points and the variance in the monitoring data will also increase.

The analysis of variance is used to characterise and prioritise the individual contaminants associated with leakage events. As for the previous method, the prioritisation reflects only the likelihood of occurrence in groundwater, but not the potential impact on water users. Kerndorff *et al.* (1992) point out the following three attributes of the variance technique:

- the distribution of the inorganic contaminants with high variance is not random. There are usually several constituents at a site that exceed the variance action limits when leakage has occurred.
- the combination of leaking chemicals can be used to fingerprint the leakage from a particular site or a particular industry.
- the contaminants can be ranked in order of relative importance by ranking them according to the number of times each contaminant is associated with a leakage event.

The variance in monitoring data was calculated for 16 inorganic parameters at 253 waste disposal sites in the United States (Plumb, 1991). The variance for each parameter was then categorised as low or high and the chemical parameters ranked according to the number of sites at which the variance was found to be high. For the US waste sites, the top ten contaminants are shown in Table 24.

9.5.6 *Comparison of methods for inorganic contaminants*

The results from the analysis of variance for US waste disposal sites are compared with those for the German waste sites using contamination factors and frequency of exceeding background concentrations in Table 24.

Table 24. Ten highest ranked inorganic contaminants from US and German waste disposal sites using statistical methods (Kerndorff *et al.*, 1992).

	Analysis of variance United States (253 sites)		**Statistical comparison of up- and down-gradient data** Western Germany (236 sites)					
Rank		Number of sites with high data variance		(a) CF_{mean}		(b) Frequency % > background		(a) x (b)
1	As	28	As	122	Na	83.4	As	7479
2	Cd	21	Cd	27	Cl	79.2	Ni	965
3	Na	18	Ni	15	Mg	76	Na	517
4	Hg	16	Al	11	Ca	74.5	Mn	476
5	Zn	14	Zn	9.7	SO_4	64.5	Cl	451
6	Pb	13	Mn	7.6	Ni	64.3	Cd	402
7	Ni	13	Cu	6.6	Mn	62.6	Zn	400
8	Se	12	Pb	6.3	As	61.3	Al	373
9	Mg	11	Na	6.2	Cu	52.4	Cu	346
10	Mn	11	Cl	5.7	Zn	41.2	Mg	258

The contamination factors and analysis of variance methods give similar results in that arsenic and heavy metals are often ranked highly. The frequency of exceeding background concentrations is slightly different, ranking the major ions as the most significant contaminants. This technique is likely to be affected by the high background concentrations of major ions in natural, uncontaminated groundwater, which may result in a low signal to noise ratio for the release of major ions from contaminated sites. Boron was not included in this comparison, as it is not analysed routinely at the US sites.

The results of the comparison suggest that for waste disposal sites *arsenic, cadmium* and *sodium* (and to a lesser degree *magnesium*, *zinc*, *nickel* and *chloride*) are the specific inorganic contaminants that are most frequently involved in leakage events.

9.5.7 *Frequency of detection of organic contaminants*

Organic substances differ from inorganic contaminants in two important attributes:

- the number of organic contaminants that could cause groundwater contamination is large in comparison to inorganic contaminants. Approximately 1200 organic contaminants have been found in groundwater at waste disposal sites in Germany and the United States (Kerndorff *et al.*, 1992)
- many of the synthetic organic chemicals do not occur naturally and so their presence in groundwater is an indication of anthropogenic pollution.

The simplest method of ranking organic chemicals for a large number of contaminated sites is to analyse their frequency of detection. Although the number of potential contaminants is large, in practice, only a small number of compounds are present on a frequent basis at concentrations clearly above established detection limits. There is a chance that bias will be introduced due to analytical methods and detection limits i.e. those compounds that are most frequently analysed will be those that are most frequently detected. Adequate sample preparation and GC/MS analytical data can generally minimise this problem since they are geared to determining the largest possible number of organic contaminants.

In Germany, 19 organic contaminants are reported to have a detection frequency of greater than 10% in groundwater samples from waste disposal sites (Kerndorff *et al.*, 1992). The most frequently detected group of compounds are the volatile halogenated compounds (VOX's), which also record the highest mean concentrations: 38 mg/L for dichloromethane; 22 mg/L for *cis*-1,2-dichloroethene; 1.7 mg/L for chloroethene and 1 mg/L for trichloroethene (Kerndorff *et al.*, 1992). This makes the VOX group the most significant class of compounds in terms of leakage from waste disposal sites.

Kerndorff *et al.* (1992) also report on the frequency of detection of organic contaminants for waste disposal sites in the United States. Twenty of the twenty-five most frequently detected organic chemicals are the same for Germany and the USA. The ranking of the organic contaminants is shown in Table 25.

Table 25. Twenty-five highest ranked organic contaminants from US and German waste disposal sites based on frequency of detection (Kerndorff *et al.*, 1992).

Rank	Germany	Frequency of detection (%)	United States	Approx. frequency of detection (%)
1	tetrachloroethene (PCE)	70.4	dichloromethane	31
2	trichloroethene (TCE)	55.6	trichloroethene (TCE)	29
3	*cis*-1,2-dichloroethene	30.1	tetrachloroethene (PCE)	21
4	benzene	29.1	*trans*-1,2-dichloroethene	20
5	1,1,1-trichloroethane	22.8	phenol	18
6	*m/p*-xylene	22.8	acetone	17
7	trichloromethane (chloroform)	22.0	trichloromethane	16
8	1,2-dichloroethane	18.8	1,1-dichloroethene	15
9	chloroethene (vinyl chloride)	17.7	1,1-dichloroethane	13
10	toluene	16.5	1,1,1-trichloroethane	12
11	dichloromethane	14.9	naphthalene	10
12	tetrachloromethane	14.4	toluene	10
13	4-methylphenol (*p*-cresol)	13.7	benzene	9
14	chlorobenzene	12.9	1,2-dichloroethane	9
15	2-methylphenol (*o*-cresol)	12.9	*o*-xylene	8
16	1,2-dichlorobenzene	12.2	2-butanone	7
17	1,4-dichlorobenzene	12.2	isophorone	6
18	naphthalene	12.1	ethylbenzene	5
19	ethylbenzene	11.3	chloroethene	5
20	*o*-xylene	9.5	4-methylphenol	5
21	2,4,6-trichlorophenol	8.9	chlorobenzene	5
22	3,5-dimethylphenol	8.0	2,4-dimethylphenol	4
23	phenol	8.0	2-methylphenol	4
24	1,1,2-trichloroethane	7.8	1,4-dichlorobenzene	4
25	1,3-dichlorobenzene	7.5	tetrachloromethane	4

The ranking of organic contaminant sources may be influenced by adequate access to and the availability of monitoring boreholes at a contaminant source. Preference may be given to certain types of contaminant sources (i.e. waste disposal sites) while access may be limited to industrial sites used for commercial purposes. In South Africa, an important consideration is the very low availability of data for individual organic compounds in groundwater. Analysis of organic contaminants has generally been viewed as a difficult and expensive procedure and regular monitoring is seldom undertaken unless serious contamination is expected to have occurred. The lack of routine analyses of organic parameters in groundwater is likely to hamper the application of statistical techniques for data analysis.

9.5.8 *Multivariate statistical evaluation*

Multivariate statistical methods such as **principal component analysis** or **factor analysis** are often applied to geochemical data. These methods may provide useful tools for identifying characteristic contaminants from particular types of pollution sources when applied to groundwater data sets from contaminated sites (Kerndorff *et al.*, 1992). In general, several contaminants migrate simultaneously in a plume from a contamination source and there is a strong correlation between certain chemical parameters and the type of waste/pollution source.

Principal component analysis is a way of examining compositional variability between groups of samples. The technique transforms the original variables (e.g. concentrations) into a new set of variables called principal components, which display a decreasing amount of variance and are uncorrelated with each other. The principle components illustrate the maximum compositional variability i.e. they effectively highlight the differences between samples and help to identify outliers in the data sets.

Factor analysis involves more complex data rotations to identify a set of factors that correspond to scientific entities. The data is manipulated to derive factors that can be regarded as explanatory of the observed covariation of the variables. Factor analysis provides a statistical method of separating the effects of several interacting sources or processes. Factor analysis is widely used in the analysis of geological and geochemical data, but its use is still a controversial topic. One of the problems is that it provides a convenient "black box" approach. Data is fed in to a computer program, which conveniently calculates factors that are often misinterpreted as being the real cause of observed phenomena. It is usually possible to derive several sets of factors from the same original data set, depending on the rotation applied and a measure of skill is required in interpreting the validity of the results.

An example of the use of factor analysis using kaiser normalisation to rotate the factors is given by Kerndorff *et al.* (1992), who used the method to associate groundwater contaminants with different types of waste at waste disposal sites in Germany. The authors found that the original data set of groundwater samples from waste disposal sites in western Germany had to be restricted to a homogeneous set of samples downgradient of sites in the same geological formation to be able to make sense of the interpretation.

Five factors were found that account for 82% of the total variance in this smaller data set. The significance ascribed by the authors to each of the factors and the factor scores > 0.5 were as follows:

Factor 1: Municipal solid waste factor (37% of variance explained)

Temperature (0.651); Conductivity (0.803); Cl (0.812); Na (0.913); B (0.672); AOX[1] (0.558)
Leaching of Na and Cl from waste increases salinity and hence, conductivity. Some of the boron may have arisen from sewage sludge disposed with the waste. AOX, although not typical for municipal waste, was still found in significant amounts.

Factor 2: Industrial waste factor (15% of variance explained)

Trichloroethene (0.951); Tetrachloroethene (0.609)
These variables were considered explanatory of the influence of refuse from industry and have similar chemical characteristics.

Factor 3: Iron and manganese factor (12% of variance explained)

Fe (0.793); Mn (0.763)
This factor reflects the high natural concentrations of iron and manganese in the aquifer, which are intensified by the effects of contamination.

Factor 4: Construction waste factor (11% of variance explained)

SO_4 (0.846); Ca (0.618); Sr (0.680)
These variables were found to increase significantly in downgradient of sites whose content consists mainly of construction wastes (70-90%) due to the high amount of these ions in the leachate from such waste and their similar, relatively high mobility in the subsurface.

Factor 5: Business waste factor (8% of variance explained)

Pb (0.649); Cd (0.842)
These variables were considered explanatory of the influence of refuse from businesses and have similar geochemical characteristics.

The two principal explanatory factors (factors 1 and 2) are characterised by chemical parameters that are highly persistent and highly mobile in groundwater. These parameters, Na, Cl, Conductivity,

---

[1] AOX = Halogenated organic compounds that can be adsorbed with activated charcoal

Temperature, Boron, AOX, TCE and PCE, provide good screening parameters for detecting the initial release of leachate from waste sites (Kerndorff *et al.*, 1992).

9.5.9 Weighting system for nitrate, sulphate and CHCs

Mull *et al.* (1992) developed a system of prioritising groundwater contaminants from urban areas in Europe. Their ranking system was applied to the urban groundwater contaminants chlorinated hydrocarbons (CHC's), nitrate and sulphate at a site in Germany. The system is designed around the following questions, which are important when prioritising contaminants or contamination sites:

- What is the maximum exceedence of the tolerable concentration in drinking water (or in terms of the fitness of the water for any other use)?
- How extensive is the contamination in a specific area?
- What is the degree of degradation within the aquifer?

The tables that follow demonstrate how the parameters were applied. The maximum concentration by which the concentration within the aquifer exceeds the limit for drinking water standards is called the "factor of exceedence" (Shown for the selected parameters in Table 26). The weighting criteria (0) used for ranking show that the lower the maximum tolerable concentrations, the greater the risk related to the contaminant (Mull *et al.*, 1992).

This method appears to be useful, but is dependant on data availability. It also requires a good understanding of the extent of the aquifer and contamination within it.

Table 26. Maximum exceedence of Drinking Water Quality Standards (Mull *et al.*, 1992).

Chemical	**Highest detected concentration C_{gr} (mg/l)**	**Tolerable concentration C_{max}/C_{gr}**	**Factor of exceedence**
CHC	5	0.025	200
Nitrate	200	50	4
Sulphate	1000	250	4

Table 27. Distribution factor (Mull *et al.*, 1992).

Chemical	Distribution factor[1] %	Half distance[2] of chemical in system (m)
CHC	40	2000
Nitrate	15	300
Sulphate	42	8000

Table 28. Weighting factors for Mull *et al.* (1992) ranking system.

Weights	Factor of exceedence	Distribution factor[1] %	Half distance[2]
1	≤5	≤1	≤15
2	6-20	1-5	16-50
3	21-50	6-10	51-300
4	51-100	11-20	301-1000
5	101-150	21-40	1001-2500
6	151-200	41-60	2501-5000
7	>200	>60	>5000

[1] **Distribution factor**: Refers to the quotient of the area in which concentration is higher than the tolerable standards and the total area under investigation.

[2] **Half distance**: The distance in which half the chemical or biological substance transported within the groundwater is degraded to harmless material. Here the calculation is based on a groundwater velocity of 100 m/annum.

9.6 Summary of the statistical methods

9.6.1 *Statistical methods (e.g. Kerndorff* et al., *1992 and Mull* et al., *1992)*

These methods are applied to existing sources of contamination. If large datasets are available for a particular contaminant source or area, it may be useful to analyse these using statistical methods. In this case, the prioritisation of contaminants is used to rationalise monitoring requirements (e.g. by identifying suitable indicator parameters) and to provide input for the assessment of health and environmental risks related to the contaminant source type.

Advantages:

- Statistical methods provide a systematic approach to assessing contaminant loading.
- Contaminants can be ranked in terms of their effectiveness for detecting pollution leakage.
- The methods are useful for design of monitoring programmes and saving costs by avoiding unnecessary analyses.

Disadvantages:

- Data requirements are high. The methods rely on quantitative chemical datasets with records of the concentrations of a wide range of parameters. Background levels are also required.
- Data processing requirements are likely to be time consuming.
- Methods consider contaminant loading factors, but not hazardousness. Contaminant behaviour may be implicitly included by the relative concentrations and frequency of detection.
- The techniques could be applied to a specific area e.g. a mining or industrial district in a catchment, where the up and downgradient directions are known, but they are not really suited to large regional or national scale applications.

Results of the methods:

- Both methods can be used to produce a ranked list of characteristic contaminants.
- Kerndorff *et al.* (1992) based the ranking only on contaminant concentrations.
- Mull *et al.* (1992) have considered a spatial distribution factor as well as concentrations.

10. APPENDIX C: A fuzzy logic approach to risk assessments

10.1 What is fuzzy logic?

Conventional set theory (Boolean) states that an element is either a member of a set or not. Consider the following real life problem: *A person is said to be young when they are under the age of 25 and a person is said to be old when they are over 40. In which group would we place a person of the age of 30?*

Fuzzy logic is an extension of conventional set theory enabling an element to belong to a set to a degree. The degree of membership is a function that defines the membership of an element to a set according to the value of the element (see Figure 28).

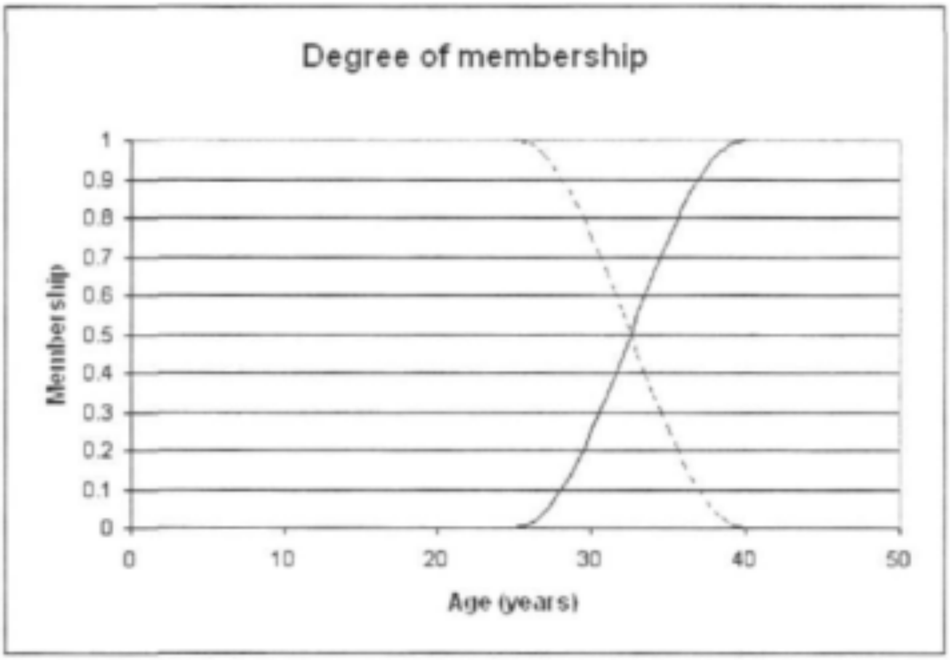


Figure 28. Membership function for young and old people

Membership is expressed as a value between 0 and 1. Zero implies 0% membership and 1 implies 100% membership. The solid line describes the membership function for the set of people older than 40 and the dotted line describes the membership function for the set of people younger than 25. Note that in most cases the membership functions of the two sets will be inverses.

To answer the question of where will a person of the age of 30 fit in can be answered as follows:

That person belongs 75% to the set of young people and 25% to the set of old people.

Selection of the membership function is done by an expert in the field of study. Linear membership functions are seldom used in practice in contradiction to sinusoidal functions which are very popular.

In most cases risk analysis will involve more than one input to be considered in the analysis. Fuzzy logic makes it possible to generate a set of decision rules according to the number of inputs and these rules must then be evaluated by an expert in the field of study.

The number of rules generated is given by the following equation is:

$n = 2^{inputs}$ where n represents the number of rules generated.

The rules consist of all possible binary combinations of the respective inputs with a weight assigned to each rule representing the risk. Table 29 shows the decision rules generated for 3 inputs. Instead of using true and false the terms favourable and unfavourable is used in the rules to make them easier to read.

Table 29. Decision rules for three inputs

Rule No	Weight	Input 1	Input 2	Input 3
1	0.0	Favourable	Favourable	Favourable
2	?	Favourable	Favourable	Unfavourable
3	?	Favourable	Unfavourable	Favourable
4	?	Favourable	Unfavourable	Unfavourable
5	?	Unfavourable	Favourable	Favourable
6	?	Unfavourable	Favourable	Unfavourable
7	?	Unfavourable	Unfavourable	Favourable
8	1.0	Unfavourable	Unfavourable	Unfavourable

Rule number 1 is read as: If input 1 is favourable and input 2 is favourable and input 3 is favourable then the risk is 0%. All of the other rules are read in the same fashion and an expert must evaluate each rule individually to assign the appropriate risk. For each input a membership function must be defined with a favourable and unfavourable limit defining the two sets. One function will represent the favourable set and the other the unfavourable set. Thus for each input a favourable and an unfavourable value can be read from the membership functions. For each input the table of decision rules is then populated with the respective favourable and unfavourable degree of membership.
The risk is then calculated using the following formula

$$\%Risk = \frac{\sum_{1}^{n} Wn * min(DOM)}{\sum_{1}^{n} min(DOM)} * 100\%$$

where

n = number of rules

DOM = degree of membership

Wn = Weight of rule n

Note: The minimum function must return the minimum value of all inputs for each rule.

11. APPENDIX D: The Excel-based database

11.1 Structure of the database

Eleven workbooks are included in the program. These are "General.xls", "Reference.xls" and the other nine workbooks are named after each Province's name ("Eastern Cape.xls", "Free State.xls", "Gauteng.xls", "Kwazulu Natal.xls", "Mpumalanga.xls", "Northern Cape.xls", "Northern Province.xls", "North West.xls" and "Western Cape.xls"). The help file of the database gives a detailed explanation on the background, structure, methodology and operations instructions of the database.

The file "General.xls" may be regarded as the main workbook and it consists of two worksheets, the one is a general list of chemicals and the other is a map index which can lead the user to the database of each Province in South Africa. About 2,500 contaminants have been included into the general list together with their chemical name, CAS# (Chemical Abstract Number) and main correlative properties in number format. More detailed information on each chemical may be accessed through the hyperlink that is accessible in the third column of the general sheet. The sheet of map index provides a map of South Africa, where the user can enter each Province's database by clicking the Province's name on the map.

The nine workbooks of each Province's database are designed with the same structure. Each workbook has a fixed sheet named as the capital city of that Province, but the user can add other cities or urban areas to this workbook. In the provincial databases, the data include detected chemical name, CAS# and site_ID. Soil properties of the site are bound to be user-specified inputs for calculation and contaminant ranking, while optional data on hydrogeology environment, borehole information etc. may be helpful to the user for different purposes.

12. User manual

12.1 The main workbook

12.1.1 Introduction sheet

The sheet "Welcome" shown in Figure 29 appears when the file "General.xls" is opened. It guides the user to two worksheets of the main workbook, the one for the contaminant properties list by clicking the button "View General", and the other for the map index by clicking the button "Go to Map Index". The button "Exit" is for closing the form.

Welcome to Groundwater Contamination Excel Database

University of the Western Cape
Groundwater Group
H Jia, Nebo Jovanovic, Y Xu, etc

Figure 29. Sheet "welcome"

12.1.2 General

12.1.2.1 The general worksheet

The sheet "General" provides a general list of about 2500 contaminants with their properties in number format (Figure 30). Organic carbon partition coefficient (K_{oc}), unitless Henry's Law constant (K_h) and half-life ($t_{1/2}$) are used in the calculation and contaminant ranking with the model of Rao *et al*. (1985). Leaving any one of them blank will yield no results.

The button "Main" at the top of this sheet leads the user to the form "Welcome" and then to the sheet "Map Index" (Figure 31). The user can also go to Map Index by simply choosing the sheet. The button "Add New Record" is used to insert blank rows for appending new records. The button "OK" will be explained in Section 12.2.2.

Figure 30. General contaminant properties list

12.1.2.2 The map worksheet

A South Africa's map with marked province is included in this sheet (Figure 31). Clicking on each Province's name leads to the Province's contaminants database. The button "Main" at the top of the sheet has the same function as in sheet "general".

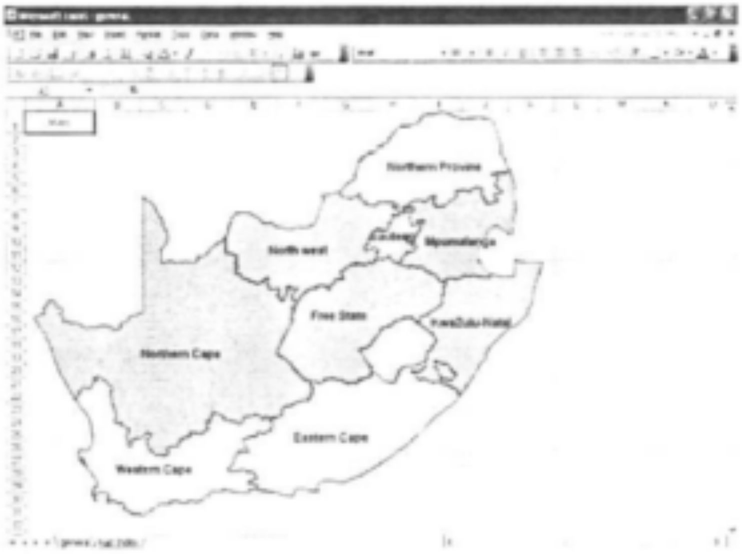


Figure 31. Map index

12.2 Provincial database

The structure of the provincial database has been indicated in Section 11.1. Most functions are integrated in the provincial database, such as enquiry, update, calculation and evaluation etc. Usually the workbook of provincial databases is not opened solely, but together with the general workbook. Here, we take only the workbook "Western Cape.xls" (Figure 32) as example to show the functions and steps performed by the buttons at the top of the sheet. For the sake of convenience, the following sub-titles of this section are captions of each button.

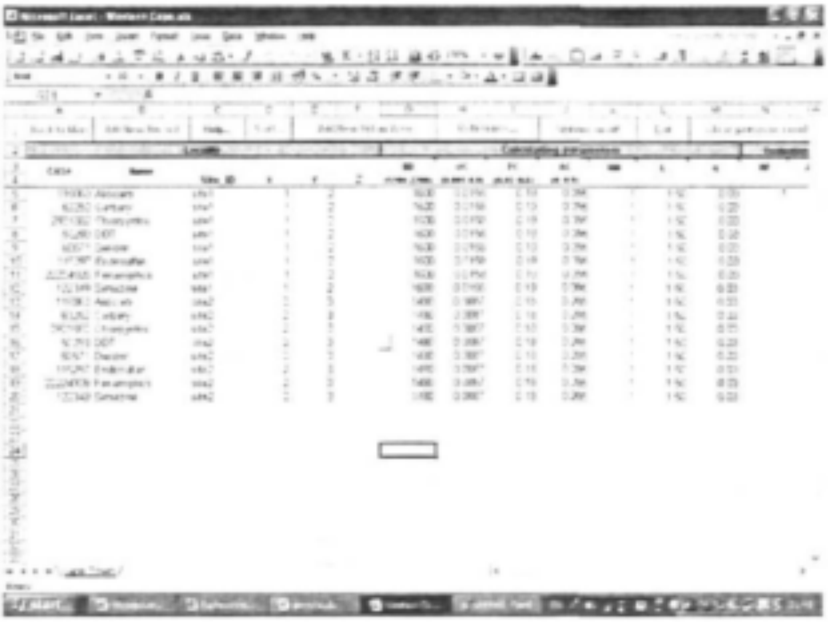


Figure 32. Contaminant database of Western Cape

12.2.1 Back to map

Clicking this button, the sheet "map index" in workbook "General.xls" will be activated for the user to enter another Province's database.

12.2.2 Add record

This button will prompt the input window in Figure 33. The user may type the name of a contaminant directly in the textbox or click on the button "Go..." to choose one or more contaminants at a time from the general list. If the user types a new contaminant name that is not included in the general list, he or she will be prompted on whether the new contaminant name should be added to the general list and to the provincial database. The first time window "Add new record" appears, the command button "Add record" of the window is disabled. If the user clicks on "Go...", the sheet of general list will be activated along with the message box: "Please select the name or the CAS# of the contaminants. Click 'OK' on the top after your selection" . Any no-name or no-CAS# cell that the user mis-selects is removed from the selection automatically. After the user's selection or input into the textbox, the window "Add new record" appears again and this time the command button "Add record" is enabled, so that new records can be appended to the provincial database. It should be noted that the site_ID and the value of 7 site-specific properties (BD, OC, FC, AC, M_o, L and q) in the provincial database as well as the value of 3 contaminant properties (K_{oc}, K_h and $t_{1/2}$) in the general database must be filled by the user.

Tip: Type the name of the new contaminant here or go to the general list to find the record.

Figure 33. Add new record

12.2.3 Delete record

This button is used to delete records. By clicking on this button, a message box pops up. The user needs to select cells included in the row that will be deleted. More than one row can be selected at once. Selected records are deleted by clicking on the "Delete record" button. This button should be used with caution because the "undo" function is disabled in the protected worksheet.

12.2.4 Help

By clicking on "Help…", the user accesses the on-line help file to get information on the background of the project, the structure of the database, the methodology of the ranking model and instructions on the operation of the program.

12.2.5 Sort

Clicking this button will prompt the form "Sort" (Figure 34). This looks like the form "Sort" in Excel and has almost the same functions. The only difference is that in the sheets of provincial databases, the sort function selects all the records on the sheet automatically before the form "Sort" shows in order to facilitate the user.

Sort...

Sort by: CAS# ● Ascending ○ Descending

Sort by: Name ● Ascending ○ Descending

Sort by: X ● Ascending ○ Descending

Figure 34. Form "Sort"

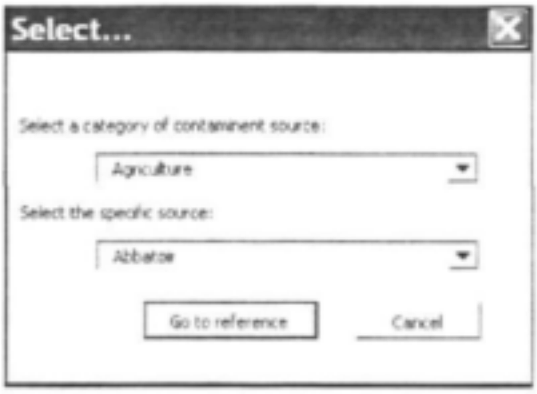
12.2.6 *Add new urban area*

With this function, another sheet can be added to the workbook to include the database of a new urban area, which has the default name "new city". The user can change the city name in the prompt message box. The sheet "new city" has the same structure as the fixed sheet, so the same functions can be carried out in every sheet of new urban areas.

12.2.7 *Reference*

The database also provides a reference workbook listing the source category, source type and possible contaminants. By clicking on this button, a form will appear including two list boxes, the one for source category and the other for source type (Figure 35). After selection from the drop down list and by clicking on "Go to reference", the workbook "Reference.xls" is opened and the first record of the selected group is highlighted (Figure 36). At this time, the user can also go back to the previous sheet by clicking the command button "Back", corresponding to the button "Cancel" in the form in Figure 36.

If specific contaminants are known but associated sources are sought, the Excel function "Find" can be used in the "Reference.xls" workbook to find possible sources.



Select a category of contaminent source:

Agriculture

Select the specific source:

Abbatoir

Figure 35. Form "reference"

Figure 36. Reference workbook

12.2.8 *Spinner on-off*

This button is very useful when the user enters or edits the values of the 7 site-specific properties. A spinner was added in every sheet of the workbook of provincial database to control the values. The button serves as a switch to turn on (make visible) or turn off (make invisible) the spinner. When the user types values into blank cells or copies values from one source to another, the spinner must be turned off. If the user wants to make small modification to some values, it is more convenient to turn the spinner on. Different properties have different maximum value, minimum value and increment when using the spinner.

12.2.9 Exit

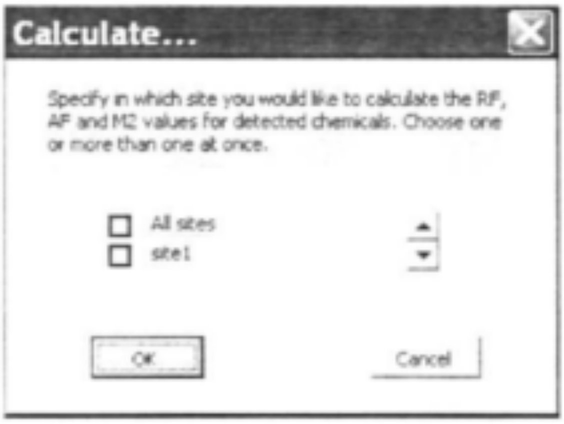
By clicking on "Exit", the workbook of provincial database is closed. The workbook needs to be saved in order to keep the data.

12.2.10 Clear previous results

Previously calculated values of RF, AF and M2, as well as ranking of RF and AF can be cleared by clicking on this button.

12.2.11 Calculate

The form "Calculate" is prompted by clicking on this button (Figure 37). It is recommended to check the values of all properties that will be used in the calculation, before using this function. Calculation is based on site_ID. The number of different Site_ID is automatically loaded in a list box in the form "Calculation…". The user can select one or more than one site for the calculation. The formulas and steps of the calculation have been explained in Section 5. In the process of calculation, the user is prompted if errors in the values of properties of some records occur, whilst the calculation for other records will continue.

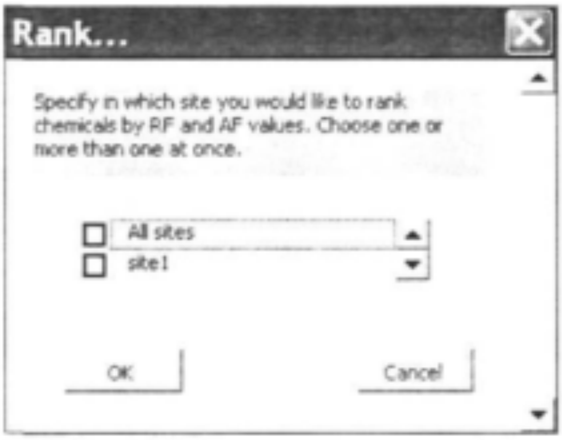


Specify in which site you would like to calculate the RF, AF and M2 values for detected chemicals. Choose one or more than one at once.

Figure 37. Form "calculate"

12.2.12 Ranking

After the RF and AF values have been calculated, these are sorted into a specific sequence by clicking on the button "Ranking" (Figure 38). Ranking is also based on site_ID. The user can rank the contaminants for one or more than one site at once. Each contaminant for a selected site will have an index value showing its significance to groundwater pollution. If the calculation for one site is executed incorrectly, the ranking for this site will stop, but it will not influence ranking for other sites.



Specify in which site you would like to rank chemicals by RF and AF values. Choose one or more than one at once.

☐ All sites
☐ site1

Figure 38. Form "ranking"

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Treatment of rural groundwater for potable use

Modise SJ; Krieg HM

High nitrate concentrations are prevalent in groundwater from various parts of the country. High nitrate-containing groundwater which is consumed by babies can lead to a blood illness methemoglobinaemia, or so-called "blue baby" syndrome. This project aims to evaluate various nanofiltration membranes for the removal of nitrates (and other unwanted salts, such as sulphates and bromides) from groundwater used for community water supplies in the North West Province.

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Water Research Commission
Private Bag X03, Gezina, 0031, South Africa
Tel: +27 12 330 0340, Fax: +27 12 331 2565
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