THE INFLUENCE OF URBAN DEVELOPMENT ON THE WATER CHEMISTRY OF THE CAPE FLATS AQUIFER

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ABSTRACT

Large quantities of water are available in the Cape Flats sandy aquifer in the Western Cape. Local industrial, agricultural, domestic and urban development activities are known to be potential polluters of this water through infiltration of wastewater, because of the unconfined nature of the aquifer. In order to determine the potential of the water in the aquifer, fifteen water samples from the Cape Flats were analysed and geochemically assessed prior to their quality being evaluated in terms of future use in domestic, irrigation and industrial activities.

Although all the samples displayed near neutral pH (6.3 to 7.6), there was much variation within the Cape Flats area. Most of the samples from the western part of the study area have an electrical conductivity (EC) in excess of 100 mS/m. Samples taken from the central and eastern parts generally showed conductivities below 100 mS/cm.

Most sampled waters had exceptionally high Ca^{2+} concentrations which is characteristic of the calcareous material in the Cape Flats aquifer. Except for Ca^{2+} and pH, the concentration of all the other major ions (Na^{+}, K^{+}, Mg^{2+}, SO_4^{2-}, Cl^{-}, NO_3^{-}, HCO_3^{2-}) are consistently higher in samples collected from the western part of the study area, compared to samples from the central and eastern parts. The east and central regions had K^{+} and Mg^{2+} values of up to 26 and 27 mg/L, while the west had values up to 60 and 40 mg/L, respectively. Also, the SO_4^{2-} and NO_3^{-} concentrations in the east and central regions were up to 89 and 83 mg/L, while the west had values as high as 192 and 99 mg/L, respectively. All of nitrate exists as NO_3^{-}, and no NH_4^{+} was detected.

The water quality is affected by land-use activities (particularly agriculture in Philippi), alkalinity and hardness from mineral dissolution. Samples from nearby informal settlements in Khayelitsha (east) did not show contamination.

For the most part, aquifer waters are supersaturated with respect to calcium carbonate and silica (SiO_2). The natural hardness of the groundwater and the sandy constitution of the aquifer, which is a consequence of overlying soil type, should be considered in order to develop a full understanding of the evolution of groundwaters in the Cape Flats aquifer. The absence of phosphate in these waters can be attributed to phosphate complexing with iron and calcium, making it unavailable in the solution. There is also a very low trace element concentration as well as total coliform and *Escherichia Coliform* (<10 counts per 100 ml).

In terms of domestic and irrigation suitability, most of the sampled waters were free from contamination in the Khayelitsha and Mitchell's Plain area. Sodium and chloride concentrations of aquifer waters were evaluated in terms of the DWAF (1999) guidelines for domestic water. Largely, both Na and Cl concentrations do not exceed 200 mg/L. Na and Cl average levels (60 and 140 mg/L) are mostly safe for general domestic purposes, but restrictions are placed on use of the water for irrigation purposes. However, calcium concentrations (up to 190 mg/L) in the Khayelitsha area are above the guideline value of 150 mg/L which is acceptable only for drinking, but can lead to water hardness when used for other domestic purposes such as bathing and laundry.

From this investigation it is clear that although the waters in the Cape Flats aquifer have been affected by land-use activities such as agriculture, some can be utilised for domestic use without extensive treatment. Since this study only considered a limited area in the Cape Flats,

it is recommended that further investigation be carried out north of the study area to determine if nearby industrial activities could affect the most productive part of the studied aquifer. This would assist in the development of a classification scheme, in terms both geochemical and quality criteria, which would facilitate the future management of the Cape Flats aquifer water resource.

ABBREVIATIONS

SYMBOL	DEFINITION
Alk	Alkalinity
AMD	Acid mine drainage
BOD	Biological oxygen demand
CCPP	Calcium carbonate precipitation potential
COMRO	Chamber of Mines Research Organization
COD	Chemical oxygen demand
Conc.	Concentration
CSIR	Council for Science and Industrial Research
DOC	Dissolved organic carbon
DWAF	Department of Water Affairs and Forestry
EC	Electrical conductivity
EDTA	Ethylene-diamine-tetraacetic acid
ESP	Exchangeable sodium percentage
L	Litres
L.S.I	Langelier saturation index
mamsl	Metres above mean sea level
mg/L	Milligrams per litre
mL	Millilitre
$mmol_c/L$	Millimoles charge per litre
mm/h	Millimetres per hour
mm/m	Millimetres per metre
mm/yr	Millimetres per year
mM	MilliMoles
mS/m	MilliSiemens per metre
M	Molar concentration

MIC	Microbially-induced corrosion
PWT	Physical water treatment
RO	Reverse osmosis
R.S.I.	Ryznar stability index
RSD	Relative standard deviation (in %)
S.I.	Saturation index
SAR	Sodium adsorption ratio
SD	Standard deviation
SLS	Sodium lauryl sulphate
SRB	Sulphate reduction bacteria
T.A.	Total alkalinity
TDS	Total dissolved solids
TH	Total hardness
TSS	Total suspended solids
μ	Ionic strength
μg/L	Micrograms per litre
μL	Microlitres
μm	Micrometres
μS/cm	MicroSiemens per centimetre

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1 Introduction

1.1 Aims of the study

The aim of this study is to investigate the influence of urban influence on the water chemistry of the Cape Flats aquifer. To achieve this aim the following certain key questions that have been posed about the Cape Flats aquifer are studied. The central key question is:

- How is the Cape Flats aquifer contaminated? This is in terms of pathways and chemical constituents.

Other key questions relating to the central one have also been posed:

- What is the best use for the water?

- Can the quality of the water be improved?

The approach of this study has been to focus on the interpretation of the analyses of collected data and to explain the results from a geochemical perspective. Use has been made of other data in order to examine historical trends of the aquifer. In this way the factors and processes controlling the water chemistry in the aquifer have been identified in order to answer the central key question. This has also made it possible to draw conclusions about the aquifer and to answer the other key questions.

The focus of this study is on the water chemistry, and the main purpose is to evaluate the water quality, because of the aquifer's importance as a potential water supply for the Greater Cape Town Metropolitan Area.

In answering the key questions, certain limitations had to be taken into account and accommodated in this study. These are mainly a result of the short period of duration of the study combined with the fact that the Cape Flats aquifer (CFA) has spatial variation. Land use activities and local geohydrology of the aquifer cause this variation, which result in dissimilarity in its physical, chemical and biological characteristics. Since data for this study could only be collected over a short period of time, more data was obtained from Department of Water Affairs and Forestry (DWAF). This data has assisted in making interpretations about the long-term behaviour of the system. Figure 1.1 shows the location of the area studied and extent of the aquifer in the Western Cape.

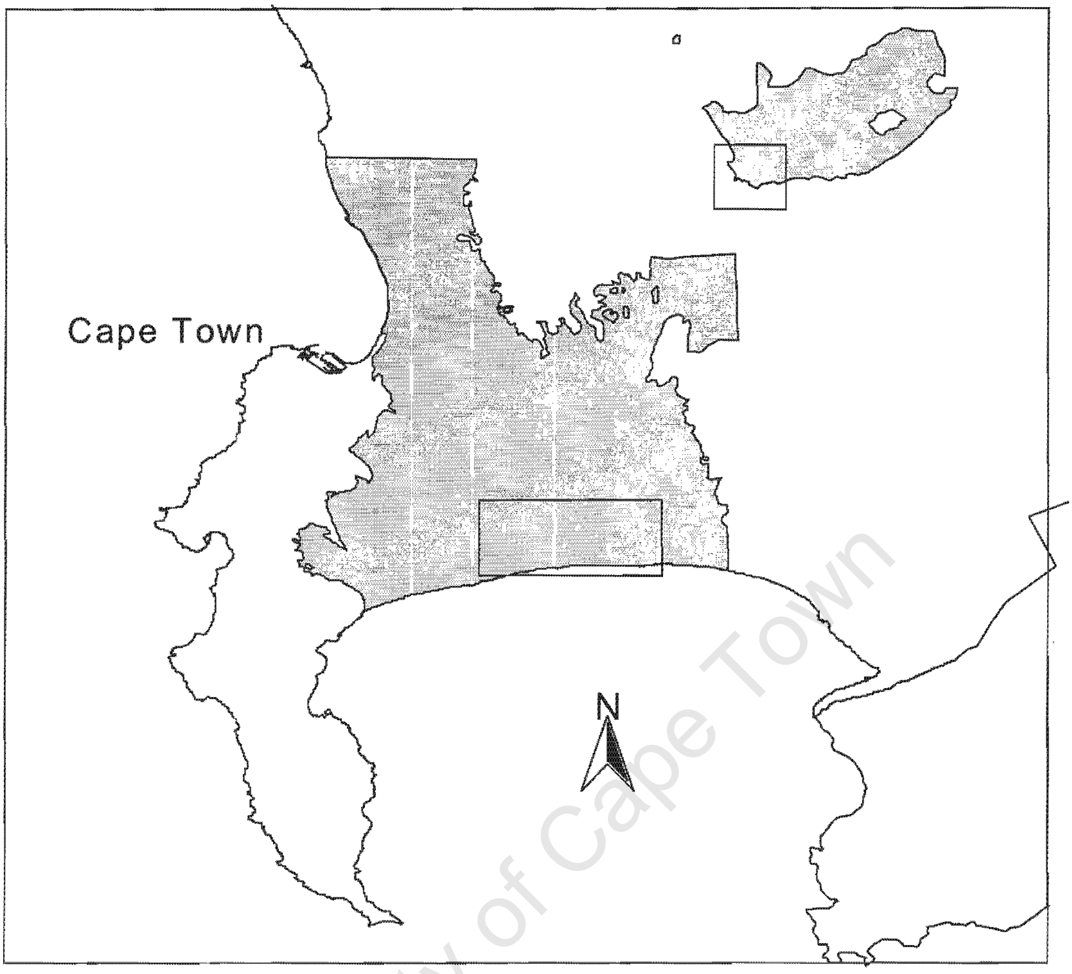


Figure 1.1: *The extent of the Cape Flats aquifer. The study area is marked with a rectangular box (Source: CSIR).*

1.2 The Cape Flats aquifer: history of water quality and the factors which affect it

1.2.1 Regional and local geology

According to Rogers *et al.* (1998), the Cape Flats aquifer consists of Cenozoic deposits underlain by essentially impervious Malmesbury Shales or Cape Granite. The sands, which cover an area of some 630 km^2, extend in a northerly direction along the West Coast. Sedimentation initially occurred in a shallow marine environment, subsequently progressing to intermediate beach and wind-blown deposits, and finally to aeolian and marsh (peat) conditions. A feature of the sediments is the presence of shelly material over most of the area. The sand body is generally stratified horizontally and several lithostratigraphic units can be recognised (Table 1.1). Calcareous sands and surface limestone deposits cover portions of the area. While silcrete, marine clays and bottom sediments of small inland water bodies also occur sporadically.

Table 1.1: *Cape Flats Lithostratigraphy.*

GROUP	FORMATION	PERIOD
Sandveld Group	Witzand Langebaan Veldrift Springfontyn Varswater Elandsfontyn	Tertiary and Quaternary
False Bay Dolerite		Cretaceous
Table Mountain Group	Pakhuis Peninsula Graafwater	Ordovician
Cape granite Suite	Cape Peninsula batholith	Cambrian
Malmesbury Group	Sea Point Bloubergstrand	Neoproterozoic

The Witzand formation consists of very fine to very coarse calcareous sands and has abundant small shells and shell fragments. These sands form an extensive system of parabolic, vegetation-bound coastal dunes.

The almost horizontal sandstones of the Peninsula Formation were originally linked to the same formation capping the Hottentots Holland Mountains on the eastern fringe of the Cape Flats. However, here the rocks are highly sheared, cleaved and folded, as part of the Cape fold belt proper (Figure 1.2). This deformation is of Permo-Triassic (~ 250 Ma) age. Post-Palaeozoic erosion has removed these sandstones between False Bay and Table Bay to create the Cape Flats, somewhat of a misnomer, as the topography is rarely flat. Rivers have carved valleys to both False Bay and Table Bay, the valleys usually being more incised closer to the mountains. Surf-zone erosion during transgressions has formed marine platforms between Gordon's Bay and Strand in the SE corner of the Cape Flats. This fluvial and marine erosion has shaped the topography of deeply weathered Malmesbury Group and Cape Granite bedrock on the Cape Flats.

Sediments of the Cenozoic Sandveld Group overlie bedrock over much of the Cape Flats. The Elandsfontyn is represented by a fluvial sequence of gravelly quartzose sands with intercalated peats that are found in boreholes in Noordhoek basin, south of Chapman's Peak.

The Springfontyn is a chiefly aeolian, coarser formation of fine to medium quartzose sand and it is exposed over most of the central part of the Cape Flats. It is exploited as glass sand in the Philippi area and it is the aquifer used for groundwater extraction near Atlantis in the area north of Cape Town. Grain size often increases with depth and thin calcareous clay and peat lenses may be present locally. The formation is relatively uniform and free of inclusions. The bedrock topography has a Palaeo-valley reaching more than 40 m below mean sea level just to the east of Zeekoevlei (Wright and Conrad, 1995). This runs northwards beneath the present-day Lotus River valley. This presumably represents a land surface related to a period of Late Tertiary low sea-level stand, perhaps even the major Oligocene regression, which reached down to about 400 m below present sea level. The bedrock is predominantly argillaceous weathered Malmesbury shale, with minor weathered granite in places. The weathered zone of the bedrock is up to 44 m thick.

The Velddrift Formation is a patchy deposit of poorly consolidated intertidal and estuarine sediments, best exposed immediately east of Swartklip (Figure 1.2). It is overlain by the cross-bedded, semi-consolidated aeolianites of the Langebaan Formation, their resistant calcretised upper surface helping to form cliffs up to 50 m high at Wolfgat, midway between Swartklip and Strandfontein along the northern coast of False Bay. The Langebaan Formation, locally called the Wolfgat Formation, consists of calcrete and very fine to fine calcareous sands, which along the coast contain cross bedding. The calcretized upper surface of this unit forms the cliffs seen along the shoreline. Massive sandy surface limestone, which forms a hard irregular layer, covers much of the eastern Cape Flats. The degree of the cementation, lime content and thickness of the unit vary considerably. The lime-rich bed over the greater part of the area is only a few metres thick and consists of an upper, hard, densely cemented zone of 250 to 350 mm, resting on soft, sandy yellow calcrete, which grades into calcareous sand, the lime content of which decreases with depth.

The original "hairpin" shapes of the parabolic coastal dunes that formed the Langebaan Formation are seen beside this coast and around the Cape Flats townships of Mitchell's Plain and Khayelitsha (cited further in the following chapters), as well as being clear from the air. Unconsolidated, often partially vegetated, calcareous dunes of the Witzand Formation are seen east of Swartklip, between the Wolfgat cliffs and Muizenberg.

1.2.2 Geohydrology of the Cape Flats Aquifer

In Table 1.1 and Figure 1.2, the Sandveld Group deposits constitute what is known as the Cape Flats aquifer. The aquifer is regionally unconfined, and is essentially free of lateral hydraulic or geological boundaries, which may influence regional behaviour internally. The aquifer is not hydrogeologically linked to any other aquifer. It pinches out against "impermeable" boundaries in the east, west and north, while the coastline extending along False Bay, between Muizenberg and Macassar defines the southern boundary. The weathered bedrock has generally been considered as the impervious basement of the primary aquifer (Wessels and Greef, 1980).

The generally shallow water table (average 3.75 m below surface), and medium- to coarse-grained nature of the saturated sands result in a primary aquifer of significant exploitation potential.

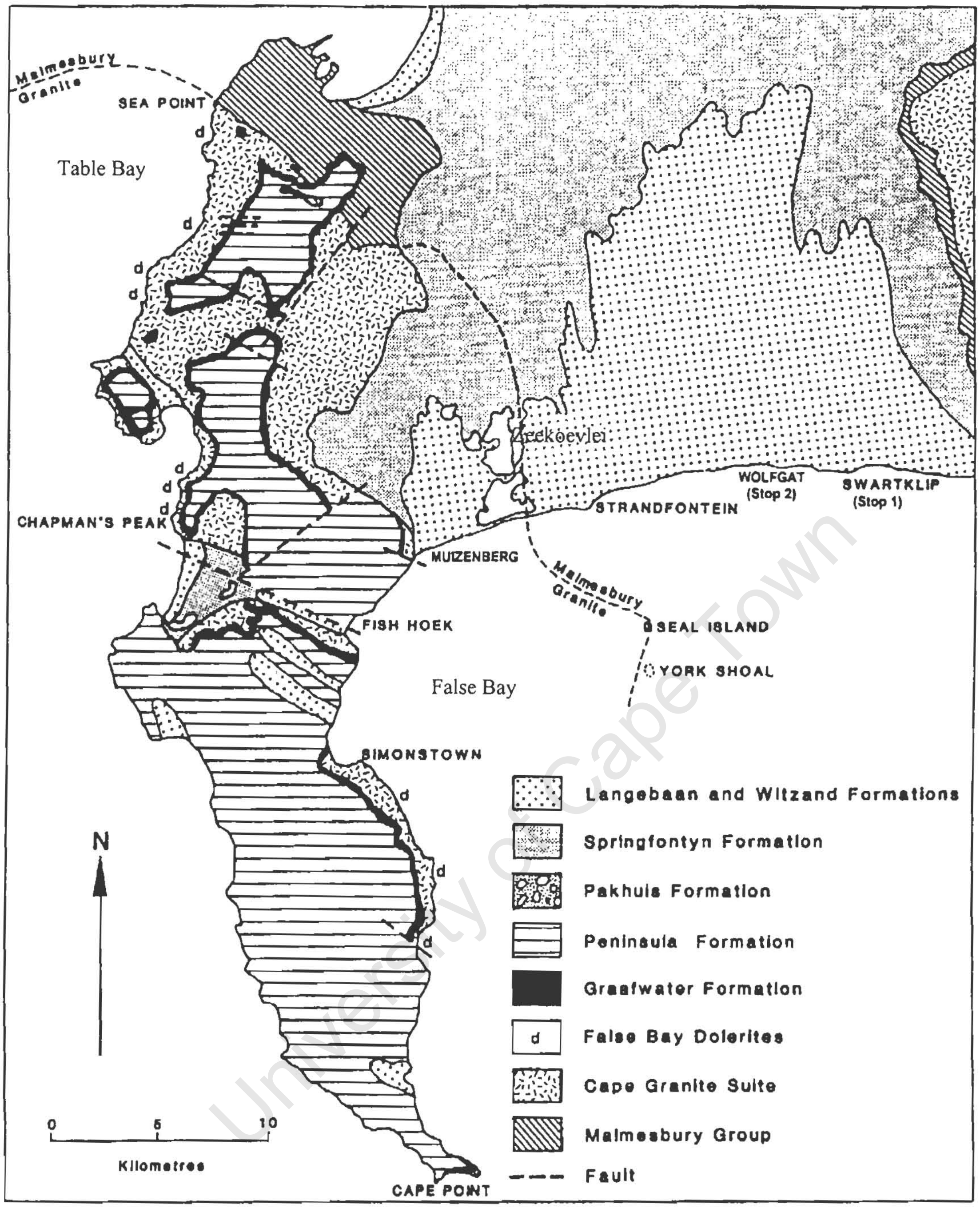


Figure 1.2: *Geological map of the Cape Peninsula and the Cape Flats from Oom (1997).*

Sands of the Witzand and Springfontyn Formations constitute the major groundwater target. These sands range in size from fine to coarse and are generally well sorted and rounded. These characteristics ensure above-average hydraulic conductivity (30-40 m/d in the central area and 15-50 m/d in the eastern portion) for this component of the aquifer (Vandoolaeghe, 1989). These formations do, however, possess a degree of heterogeneity and anisotropy due to vertical and lateral grain size graduation and the occurrence of sandy clay and clayey sandy lenses. As a result, anisotropic groundwater flow conditions and/or a vertical flow component (leakage, delayed yield) occur to a more or lesser extent in most places where this formation is pumped.

The calcareous clay and calcrete layers of the Langebaan Formation, where present, and act as a barrier and hinder the free flow of groundwater. This unit thus acts as an aquitard results in a semi-confined aquifer. The Varswater Formation can also be classified as an aquitard when the Witzand and Springfontyn Formations are present. The calcareous sands have relatively low hydraulic conductivities (1-10 m/d) and even the shelly gravel component has hydraulic conductivities between 6 and 23 m/d (Vandoolaeghe, 1989).

By virtue of this pelitic and extensively weathered nature of the Malmesbury metasediments, the bedrock is generally regarded as an impervious basement. The Malmesbury does, however, contain brittle sandstones and high yields have been obtained in these arenaceous units along the West Coast.

The aquifer is principally recharged from precipitation within the catchment. Average annual rainfall, which occurs mainly in winter and early spring (between May and September), ranges from 500 to 800 mm across the Cape Flats. Recharge from surface water bodies in the west is considered significant. Groundwater flow in the Cape Flats is either west to Table Bay or south to False Bay (Figure 1.2). In the main part of the aquifer (in the box in Figure 1.1), flow directions are either in a westerly direction towards Zeekoevlei or south towards Wolfgat (shown in Figure 1.2). Water level contours also suggest a lower hydraulic conductivity along the coast than inland. Water loss is along the whole coastline and not along well-defined "channels". Seasonal water level fluctuations range up to 2 m in the north-east.

Transmissivity values, determined from investigations by Gerber (1976), ranged from 50 to 650 m/d, with typical values ranging between 200 and 350 m/d. Vertical permeability was found to be smaller by a factor of 10 to 20 when compared with the horizontal permeability. Replenishment of the aquifer due to precipitation was calculated at 36×10^6 m^3 per annum and the losses by evapotranspiration are extremely high and exceed 80% (Wright and Conrad, 1995). Average evapotranspiration rates at ground level have been estimated to be 2×10^{-8} m/s. This is especially true in the eastern portion where the shallow calcrete units cause a perched water table.

Subsequent work by Vandoolaeghe (1989) confirmed that net groundwater recharge through sandy soils of the primary aquifers in the south-western Cape varies between 15% and 37% of the annual precipitation.

1.2.3 Climate

The south-western Cape, incorporating the Cape Peninsula and adjoining districts, experiences a typical Mediterranean climate, with wet winters and dry summers. The geographical and topographical features influence the climate of the region, resulting in highly localised microclimates. The annual precipitation in the area averages at 600 mm per year, but is highly variable and controlled by topography. The mountains of the Peninsula and the south-eastern ranges receive heavy orographic rains, with some areas, on the slopes of Table Mountain, receiving over 2000 mm per year (South African Weather Bureau, 1996). The Cape Town southern suburbs receive on average 1300 mm rain per year, and this decreases to about 500 mm a year as one moves towards the Cape Flats area, north and east of Cape Town's central business district. The Cape Town International Airport, which is on the Cape Flats, receives 515 mm of rain annually. This is slightly higher than the mean annual precipitation for South Africa of 500 mm.

The rainy season is normally from May to September, often extending into October, with the majority of winter rain associated with frontal depressions. The summers are predominantly dry, with the variability of rainfall amounts in summer generally quite small. Heavy precipitation episodes may occur during summer in the mountain regions, but these are generally short duration. The average monthly rainfall figures for the period from 1956 to 1996 are presented in Figure 1.3. The rainfall amounts vary over the South Western Cape, but the relative monthly distributions are quite similar over the region.

Monthly temperatures do not deviate greatly from the annual mean, and are relatively low due to the moderating effect of the sea. As one moves into the interior, diurnal and annual temperature ranges become more considerable. For example, Cape Town (33°50' S; 18°36' E; altitude 30 mm), has a mean January temperature of 21°C and a mean July temperature of 13°C. Whereas Ceres (33° 22' S; 19° 18' E; altitude 456m), has a mean January temperature of 22°C, and a mean July temperature of 9.1°C (Oom, 1997).

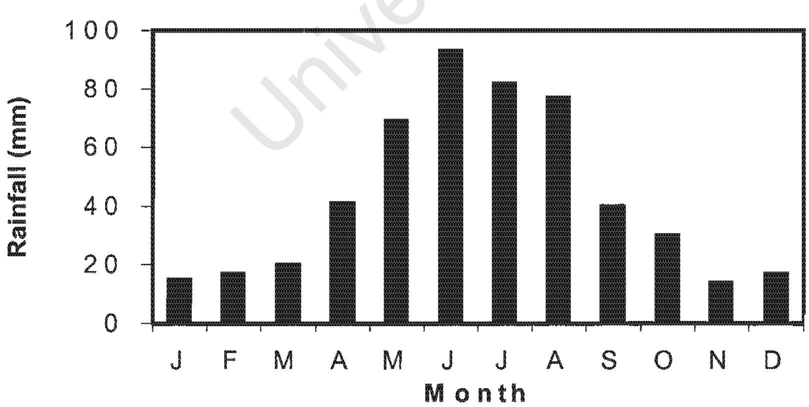


Figure 1.3: *50-year average for monthly precipitation at Cape Town airport on the Cape Flats (Source: South Africa Weather Bureau).*

1.2.4 Past and present use of the aquifer

The Cape Town Metropolitan region is supplied with mains water from several reservoir sources. Each reservoir has its own associated catchment area. Mains water is imported into the Cape Town Metropolitan region according to the available supply and demand.

Maclear (1995) highlighted the supply potential of the sand aquifer (in *Cape Town needs groundwater*) on which most of the Greater Cape Town Metropolitan Area (GCTMA) lies. He also highlights the merits of abstracting what he deemed as the presently under-utilised groundwater contained in this aquifer, by means of well-points, for small- to medium-scale use. Groundwater from the Cape Flats Aquifer Unit (CFAU) is presently utilised on a limited scale for irrigation of market-gardens and small-holdings mainly on the eastern part.

A pilot study of the Cape Flats aquifer carried out by DWAF in the 1980's, determined the supply potential for the central part of the CFAU to be 18 Mm^3/yr. Maclear (1995) considers this to be sufficient for localised use of the CFAU in providing groundwater for small-scale use such as garden irrigation, resulting in large water savings.

1.2.5 Informal settlement developments

South Africa has not escaped the demographic phenomenon of rapid urbanisation experienced by developing countries. More than 55% of the 41 million South Africans now live in urban areas. Much of this influx over the past two decades has been in the Black community and has placed considerable stress on an already vulnerable urban infrastructure. The result has been the development of vast informal settlements in and around existing centres. The demand for basic services in these settlements cannot be met and those located on the periphery of existing townships make use of existing services with the result that these are totally overloaded.

Much of the urbanisation in developing countries has been rapid and generally unplanned. The provision of mains water and more significantly, water borne sewerage has lagged markedly behind the population growth. A large part of the urban population growth is concentrated in marginal settlements, which normally have only limited access to public water and sanitation. This scenario poses an enormous threat to the environment (Wright, 1999). The effect that these settlements have on the environment, and in particular on groundwater, is relatively unknown.

The issue of urbanisation in Cape Town is further convoluted by the movement of people from the Eastern Cape who then choose to stay for good. The one-way migration leads to rural depopulation and it means informal settlements are set to continue to grow. The Cape Metropolitan Council has found that the traditionally circular migration of people from the Eastern Cape has virtually ceased, because migrants were choosing to stay. The phenomenon has far-reaching implications for the future planning of metropolitan Cape Town including water supply and quality issues. The stream of migrants to Cape Town between 1994 and 1998 was 49 000, highlighting the long-term effects of the increase in informal settlements. Against this trend, formal townships provide migrants with contacts and information so that they can establish themselves independently. After this they move on to the informal settlements, where they take up residence. Figure 1.4 shows an example of an informal settlement.

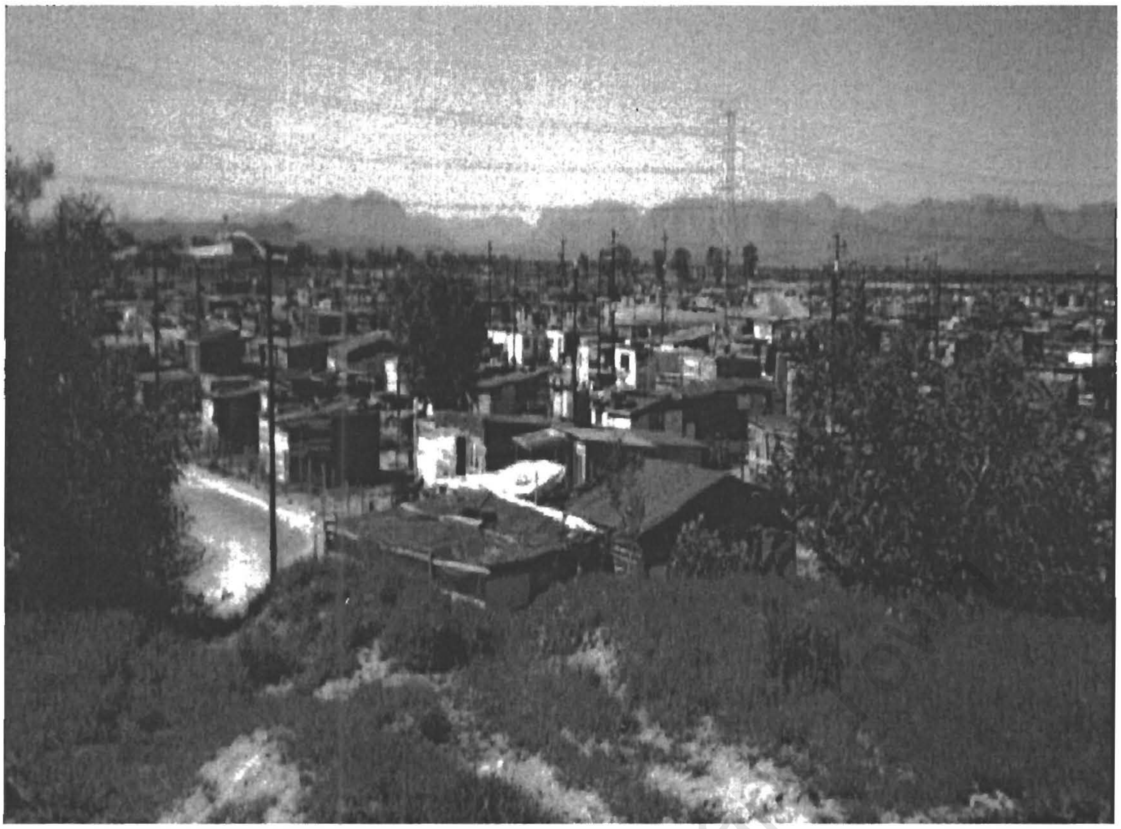


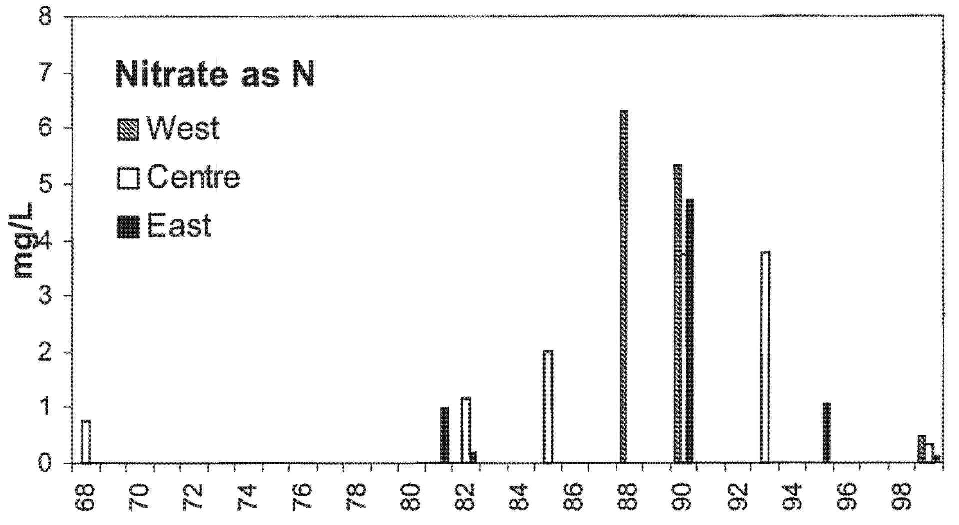
Figure 1.4: *An informal settlement development in Khayelitsha.*

1.3 Historical data

Apart from the field data collected in the duration of this study, use has been made of other data (e.g. DWAF), in order examine historical trends of the aquifer. Since data for this study could only be collected over a short period of time, more data was obtained from DWAF's database. This data has assisted in making interpretations about the long-term behaviour of the system. It also provides background information before delving into the current status of the aquifer.

1.3.1 Discussion

The figures below showing historical trends indicate historically high concentrations of the major ions in the western part of the study area. The data also shows that for the east and central regions there is no significant difference in ion concentration. The east has high Na and EC values compared to the other regions. Nitrate and potassium values are high in the western part, and this car be attributed to the predominant agriculture land-use in the region and use of fertilisers. There was no data recorded for the years between 1971 and 1980.



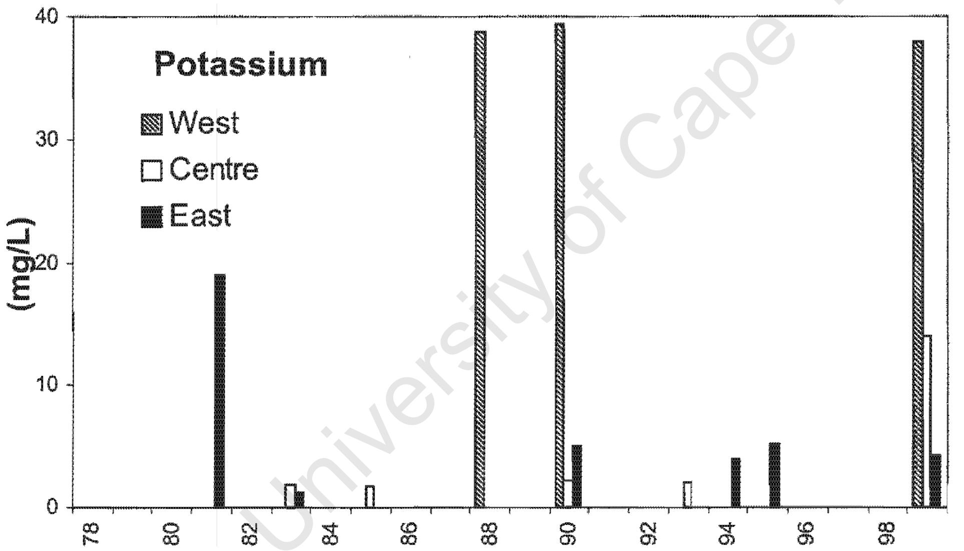


Figure 1.5: *Historical trends of selected chemical constituents for the Cape Flats aquifer (Source: Department of Water Affairs and Forestry).*

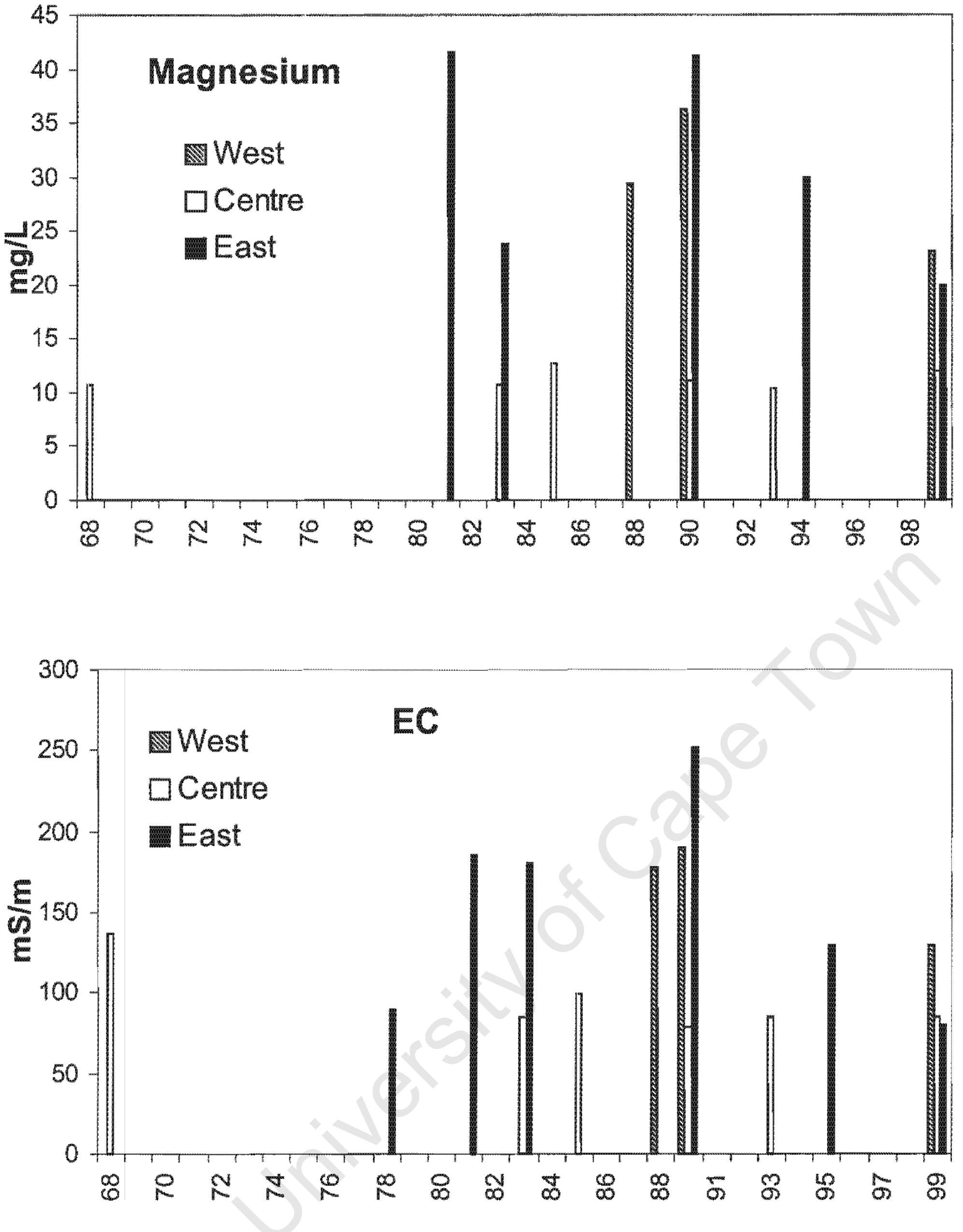
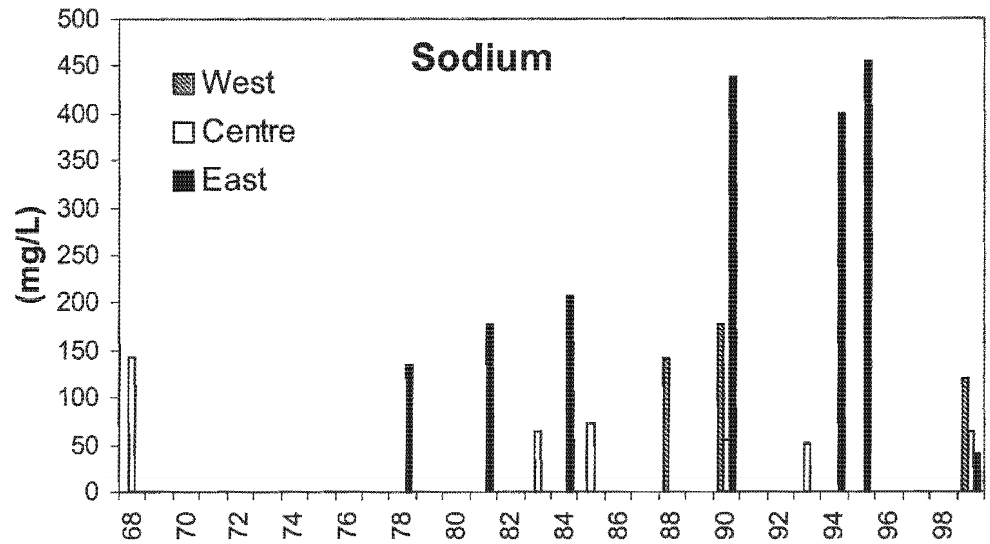


Figure 1.5 (Continued)



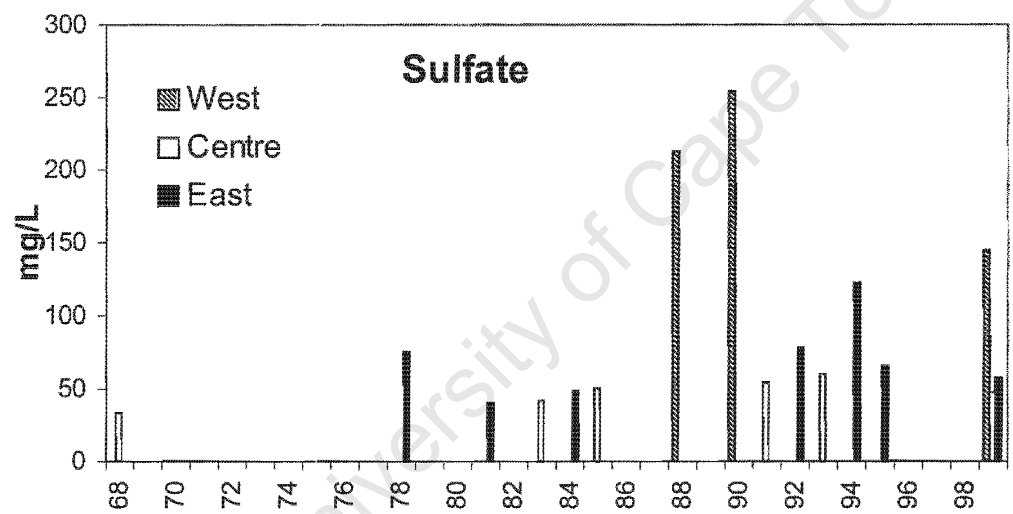


Figure 1.5 (Continued)

1.3.2 Conclusion

The available data shows that there are generally higher concentrations of ions in the western part of the Cape Flats aquifer due to land-use.

2 Geochemical Characteristics of Groundwater Contamination with Special Reference to Sandy Aquifers – A Review

2.1 Introduction

Groundwater provides half of the drinking water needs in the United States and one-third of the water used in agriculture in South Africa is from groundwater (DWAF, 1993b). Associated with extensive groundwater use are several deleterious consequences whose severity increases over time, including depression of water levels, soil salinization, ground subsidence, and water quality degradation. All of the degradation interferes with the prudent use of this essential resource on a sustainable basis (Criss and Davisson, 1995). Unconfined sandy aquifers are prone to contamination because of their accessible nature. To combat these problems new and accurate information on the origin, age, source, and migration paths of groundwater is needed for resource evaluation. Geochemical analysis methods, including isotope analysis methods, provide a well-tested means for practical water resources management.

2.2 Geohydrology of sandy aquifers

One of the origins of sandy aquifers is meltwater lakes that existed during Pleistocene time, during which deposits of glacial silt and clay were laid down offshore. These deposits form some of the most extensive shallow aquitards in North America (Freeze and Cherry, 1979). In some areas sand and gravel deposits laid down near shore and on beaches are aquifers. Glacial till is the most abundant material that was deposited on the land surface during Pleistocene time. In the Precambrian shield region, till is generally sandy, with variable amounts of silt and little clay. Sandy till forms local aquifers in some areas. In the region of sedimentary bedrock in North America, glacial erosion produced till that generally has considerable silt and clay and therefore has low permeability. Till layers of this type are aquitards. Most aquifers in the Midwest and Great Plains regions of North America are composed of glaciofluvial sand and gravel confined by deposits of till or glacial silt or clay. The aquifers occur as extensive blanket bodies or as channel deposits or buried valleys. The deposits of sand and gravel in buried valleys form aquifers that are generally many tens of kilometres wide. In many cases there are no surface indications of the presence of buried valley aquifers. The overlying till is usually some tens of meters thick or less, but occasionally may be on the order of a hundred meters thick.

In a study by Bjerg *et al.* (1991) of sandy aquifer geology in Denmark it was that Denmark was typical for the glacial outwash plains in the western part of the country, which are a result of glaciofluvial aquifers. As an example, one of the aquifers is a sandy aquifer with a thickness of 9-10 m. The groundwater table is situated 5 m below land surface. The glaciofluvial sediments are composed of medium- and coarse-grained sand with gravel, which was deposited in a braided river running into a small lake in the late Quarternary period. Water table depths of about 5 m below land surface are also typical of the Cape Flats aquifer.

In general, the sandy aquifers are inhomogeneous, anisotropic and phreatic, and at many locations they display semi-unconfined characteristics. This is often associated with delayed yield characteristics due to the presence of upper sand layers of markedly finer grain size or extensive calcrete lenses. Facies changes result in changes in hydraulic conductivity both with depth and laterally. A predominant factor controlling the hydraulic parameters is the grain size distribution of the quartz sand (Freeze and Cherry, 1979).

The heterogeneity of aquifers has led to a wide range of transmissivity values in studied sandy aquifers. A mean specific yield of 15% was suggested by Fleisher and Eskes (1992) following laboratory tests on aquifer material. The saturated thickness of aquifers varies considerably and the thickest regions are where abstraction takes place. This was of concern in the Cape Flats Groundwater Development Pilot Scheme which was established in Mitchell's Plain in the period 1983-85 by the Department of Water Affairs and Forestry in co-operation with the Municipality of Cape Town. The objectives of the scheme were to test the aquifer under concentrated stress conditions in an urban environment with respect to yield and aquifer response, and to monitor the quality of the water and the effect of water extraction on the environment. These effects are important because pumping large water volumes from a concentrated area in a sandy aquifer tends to place stress on an aquifer. Water removed from a pumping well results in a lowering of the water table at that point to create a cone of depression around the borehole. The effect is enhanced when boreholes are located in close proximity and these drawdown cones interfere with one another. This can cause serious problems when the water levels drop below the level of the pump inlets in a wellfield. Therefore, successful pumping can be demonstrated by an absence of significant cone depression around the wellfields even at the time of greatest pumping. In a report by Vandoolaeghe (1989) it was found that a rather limited regional watertable decline was generated by the Cape Flats Groundwater Development Pilot Scheme.

Under natural conditions groundwater flows and discharges along the coast in areas where the aquifer dips below sea level. Groundwater levels are relatively shallow and may be shallower after the rains.

Bjerg *et al.* (1991) in their study of sandy aquifers assert that the physical parameter of most concern is usually the hydraulic conductivity of the aquifer. This is partly because it may vary several orders of magnitude according to the geology of the area, and partly because the methods available for determination of hydraulic conductivity are costly or questionable with respect to accuracy. This data acquisition problem is particularly severe in contamination modelling, where recent investigations (e.g. Sudicky, 1986) have shown that the spatial variability of the local conductivity controls the advection and macrodispersion in solute transport.

McCarthy *et al.* (1993) found an unconfined, sandy coastal-plain aquifer with a thickness of ~3 m, with a clay layer at the bottom that is assumed to be an impervious boundary of the aquifer (the Cape Flats aquifer shows a similar resemblance, with an impervious bedrock). The aquifer exhibits distinct layers. Below the unsaturated soil, the saturated zone contains the lower portions of the B-horizon with iron oxide and some clay. At the bottom of the aquifer is a zone 15-30 m thick of slightly coarser sand that varies in colour. Most boreholes in earlier drilling schemes in the Cape Flats penetrated onto the bedrock, drilling generally being halted as soon as penetration speed fell off drastically and grey clay inclusions appeared in the samples (Vandoolaeghe, 1989).

2.3 Major sources of groundwater contamination

Groundwater pollution is a cause for serious concern because of increasing demand for water supply and the extreme difficulty and expense of remediating contaminated groundwater. Where pollutants are persistent and groundwater travels slowly, clean up may be an impossible task. Groundwater pollution may also go unnoticed for a long time if the resource is not currently utilised or monitored.

Anthropogenic sources of groundwater contamination can be distinguished as point sources or non-point sources, depending on their degree of localisation. They can also be characterised in terms of their loading history and the type of contaminants emanating from the source.

2.3.1 Industry and mining

The nature of industries such as the Saldanha Steel plant quoted in an EIA case study (Cavé, 1998), is such that pollution of groundwater is likely to occur, regardless of the preventive measures taken. For this case study, the greatest danger would be the long-term pollution of Saldanha Bay by way of seepage of contaminated groundwater. Some of the sources of groundwater contamination identified are coal stockpiles, iron ore stockpiles and sludge disposal ponds. Spills and leaks from these sources could contaminate the groundwater. This is a problem because the same groundwater is earmarked for purposes such as irrigation and potential residential mains water supply. Other previous studies of the Cape Flats such as Vandoolaeghe's (1989), where it was found that polluted water was induced from a nearby Sewage Works maturation ponds in Mitchell's Plain, also demonstrate the impact of industry.

The composition of organic contaminants and the mechanism by which they are deposited, accumulate and degrade in the subsurface determines their effect on the geochemistry of an aquifer. Some major organic compound sources are spills, disposals and agriculture. The Cape Flats aquifer is prone to this pollution because of its unconfined nature.

1. Spills and leaks of nonaqeous phase liquids (NAPL), such as gasoline that provide a source of contaminants within days of the leakage are capable of continuous contamination for hundreds of years. In this type of contamination, the source material, in addition to the groundwater, may be mobile as a separate product. There is a effect on the geochemistry of the aquifer where these organics are soluble and biodegradable (Alley, 1993).
2. Disposal of municipal and industrial wastes in landfills and lagoons may be continuous sources of contaminants. These wastes and their products also have a significant effect on the geochemistry of the aquifer if the compounds are soluble in water and biodegradable.

2.3.2 Agriculture

Agriculture is the major user of groundwater in South Africa, particularly in the more arid regions of the country, yet several agricultural activities pose a threat to the quality of groundwater if improperly managed. Agricultural activities identified as posing the most serious threat to groundwater are: intensive animal feedlots, use of sewage sludge for preparing land for crop production, use of fertilisers, irrigation and use of pesticides (Tredoux, 1983). Feedlots and sludge applications are associated with nitrate pollution and significant organic carbon to groundwater. Irrigation is a source of groundwater salinisation, leaching soluble salts to the water table. Where inorganic fertiliser is applied at rates greater that that required for plant uptake, irrigation water can also leach these salts to the groundwater, and therefore contaminates the groundwater.

Contamination as a result of agriculture has been identified in the Cape Flats (Western Cape) in the past as irrigation return-flow. Tredoux (1983) determined that in the western part of the Cape Flats vegetable farming has been practised for more than a century. In most of these areas the sand is clayey and some parts are inundated during winter. The Philippi area in the Cape Flats has very high salt concentrations and Bertram (1989) showed that this was due to irrigation practices. High evapotranspiration rates in these vleis result in increased salinities. Also, due to the low transmissivities in these areas they were excluded from a groundwater abstraction scheme mentioned in section 2.2.

Agricultural application of organic chemicals on the land surface, such as herbicides, insecticides, and fungicides provides intermittent sources of contamination over large areas. These are incorporated into the crop biomass and can degrade or be transported in surface water and sediment. However, their effect on the chemical reactions in aquifers is generally considered to be minimal (Alley, 1993).

2.3.3 Urban and peri-urban development (with informal settlements)

One of the major sources of groundwater pollution arises from the disposal of solid wastes and wastewater from urban developments. Engineered sanitary landfills are sited and designed in such a way as to pose minimum risk to groundwater. Such attention has not always been given, and in some places is still not given, to protecting groundwater resources from landfill leachate, and many old waste sites were constructed as unlined, open dumps (Cavé, 1998). Water percolating through a waste site produces leachate containing large amounts of inorganic and organic contaminants.

Tredoux (1983) identified three major sources of groundwater pollution in the Cape Flats, viz. two waste disposal sites and a sewage works. Apart from these three sources impairment of the water quality could also result from the extensive housing schemes being developed in areas where the aquifer is best suited for groundwater abstraction.

Urban development can be a significant source of contamination in growing cities on sandy aquifers. Wright and Conrad (1995) cite an example of this in a report on the Cape Flats aquifer. Urban planners totally ignored the aquifer when developing the Cape Flats. They managed to locate a solid waste disposal site and wastewater treatment works directly above the most productive part of the aquifer. Besides these, the main portion of the aquifer contains a multitude of other potential pollution sources such as runoff and waste dumps.

There are many potential pollution sources of concern, as the sandy, unconfined nature of the aquifer makes it particularly vulnerable to pollution. In many places the groundwater level is close to the surface, which adds to the aquifer's susceptibility to pollution. The aquifer is already locally contaminated or even polluted (Vandoolaeghe, 1990).

Land-use is usually not homogeneous throughout large areas, and more than one land-use type can exist near a well. Different land-use types can affect groundwater differently. However, groundwater quality may be difficult to relate to land-use because the resolution of the land-use data is coarser than the contributing area of the sampled well or borehole. One approach to improve the information available on local land-use in the vicinity of shallow sampled wells is to document the land-use in the field at each well. For example, Hardy *et al.* (1989) present a special land-use-land-cover form that is filled out for each well and updated each time the well is resampled. The premise of this is that the key to success in understanding regional groundwater quality lies in linking observable spatial patterns in these attributes with water quality characteristics and processes observed in the field. Since sources of groundwater contamination are spatially diffuse and can be characterised only indirectly, the apparent causes of a particular problem may not turn out to be the primary ones (Alley, 1993).

A case study of the effect of informal settlement urbanisation on stormwater runoff by Wright (1993) concluded that the major form of pollution in runoff is of microbiological nature and is linked to population density, rather than land-use type or degree of infrastructure provided. The study investigated the magnitude of stormwater contamination in the Khayelitsha (Cape Flats) urban catchment, identified the pollution sources and assessed the resultant impact on the receiving water body. Groundwater is an example of a receiving water body through infiltration. The study looked at a classic Third World Type urban catchment which contains formal housing, site and service, and squatter camp areas.

2.4 Groundwater contaminants and their impacts

The majority of contaminants can have a significant impact on the use of groundwater as a resource.

2.4.1 Organic pollutants

Organic contaminants in groundwater occur as dissolved compounds or immiscible liquid phases. The non-aqueous phases are divided into light non-aqueous phase liquids (LNAPL) or dense non-aqueous phase liquids (DNAPL) depending on their density and behaviour. LNAPLs such as gasoline 'float' on top of an unconfined water table, while DNAPLs tend to sink through the groundwater and collect on top of impermeable rock layers. Common DNAPLs include chlorinated hydrocarbon compounds such as carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$).

Some of the more frequently occurring organic contaminants in groundwater are soluble aromatic hydrocarbons – from spills of petrochemicals or lubricants. There are also degradation products and waste solvents from waste disposal sites. Other contaminants include pesticides and herbicides in agricultural areas.

2.4.2 Major ions

The Atlantis study mentioned above concluded that Na^+, Mg^{2+} and Cl^- undergo little attenuation and are good indicators of the extent of groundwater pollution plumes (Cavé, 1997). Ca occurs in naturally elevated concentrations in the groundwater, but is removed from solution by cation exchange reactions involving Na sourced from waste. At higher concentrations, calcium is also likely to be immobilised by precipitation as carbonate minerals. The precipitation of carbonate minerals would have the additional effect of reducing alkalinity and "blocking" the aquifer by reducing hydraulic conductivity.

In the Atlantis study (Cavé, 1998) some changes in the ion composition cannot be accounted for by pure mixing of the groundwater with leachate from a domestic landfill site. There is evidence for geochemical processes that show an increase in sodium at the expense of calcium, but with little change in the relative amount of chloride. This cannot be explained by simple dissolution of sodium chloride from the waste pile. Processes such as sodium-calcium cation exchange reactions, precipitation of calcium minerals and/or acid-base reactions involving the carbonate and bicarbonate species also must occur.

Dissolution of calcium minerals is important for setting the Ca/alkalinity trends for the natural groundwater. The Ca/alkalinity signature of the leachate from a landfill is distinct from the natural ratio in that the proportion of alkalinity is much higher with respect to Ca concentrations. This is partly due to dissolution of CO_2 gas generated during the degradation of organic compounds in the waste. Other compounds with acid neutralising capacity such as phosphate and certain organic substances may also be added by the waste pile and so increase the alkalinity.

For transportation potential it is important to note that the neutral to alkaline pH and geological environment of calcium-rich limestones is a hostile environment for the transport of heavy metals in solution, and the various elements in solution travel at different rates.

For large sedimentary basins Freeze and Cherry (1979) describe a sequence in three main zones: the upper zone which has HCO_3^- as the dominant anion, the intermediate zone where sulphate is normally the dominant anion and the lower zone, where high Cl^- concentration is characteristic.

From a geochemical viewpoint the anion-evolution can be explained in terms of two main variables, mineral availability and mineral solubility. The HCO^-_3 content in groundwater is normally derived from soil zone CO_2 and from dissolution of calcite and dolomite. Since these minerals dissolve rapidly when in contact with CO_2-charged groundwater, HCO_3^- is almost invariably the dominant anion in recharge areas. The most common sulphate-bearing mineral is gypsum, which dissolves readily when in contact with water as

$$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

Large variations in the major cations commonly occur in groundwater flow systems. Since cation exchange commonly causes alterations or reversals in the cation sequences, generalisation of cation evolution sequences is not appropriate because of the many exceptions to the rule.

Many reactions and processes can be considered in terms of sources and sinks for major cations and anions. For example, sources of calcium are primarily from the weathering of plagioclase and other feldspars and the solution of calcite, dolomite, and gypsum. Ca is lost from water by precipitation of calcite and by exchange with Na and other ions on clays. The bicabornate ion has sources similar to that of Ca with a few modifications. Bicarbonate is removed from the water in an aquifer primarily by precipitation of calcite and discharge of groundwater, either directly into the ocean or into streams. Concentration of bicabornate in coastal aquifers commonly is several times, and as much as 10 times, greater than the bicabornate concentration in seawater (140 mg/L) because of combined effects of solution of calcareous material and removal of Ca by ion exchange.

The major sources of Mg, according to Alley (1993), are weathering of ferromagnesium minerals, alteration of clays, dissolution of dolomite and magnesium calcites. Within most groundwater regimes, the ratio of Ca to Mg exceeds 1. The primary sources of sulphate in coastal-plain aquifers are rainfall, oxidation of pyrite, dissolution of gypsum, leakage from fine-grained material, and effects of mixing groundwater with seawater in the aquifer. The loss of sulphate from the groundwater is primarily by reduction of sulphate ion to hydrogen sulphide.

Typical flow velocities within a coastal-plain aquifer are about 5 m per year, and the total dissolved solids increase downgradient along the paths of groundwater flow.

In a study of a local scale such as this, the inherent heterogeneity of mineralogy and hydrologic properties of the aquifer become controlling factors that preclude the assumption of homogeneity. Additionally, Alley (1993) asserts that the relatively rapid chemical reactions tend to dominate the chemistry of the water in this part of the geohydrologic regime.

The most extensive source of nitrate delivered to groundwater is agriculture. Numerous studies on various scales have shown that nitrate concentrations in groundwater (in shallow, freshwater aquifers) can be related directly to agricultural land-use. Many of these studies have shown dramatic increases in nitrate concentrations in groundwater moving from forested, and grassland areas to agricultural areas. As summarised by Keeney (1986), the greatest problem with nitrate in the United States arise with heavy fertilisation in the intensive row-cropping practices in rain-fed grain production (such as corn), in intensive irrigated grain agriculture, in the irrigation and fertilisation of shallow rooted vegetable crops on sandy soils.

In previous studies such as Vandoolaeghe (1989), high values for total dissolved salts (TDS), Ca, Mg and sulphate have been found in Philippi (see Figure 3.1) and are in line with the status of groundwater quality in that part of the Cape Flats. The deleterious effect of large scale irrigation with groundwater over the last few decades in this historic farming area has been reported.

2.4.3 Trace elements

Although these elements rarely occur in groundwater at concentrations large enough to comprise a significant percentage of the total dissolved solids, their concentration can, depending on the source and hydrochemical environment, be above the specified in drinking water standards.

Trace metals in natural or contaminated groundwaters, with the exception of iron, almost invariably occur at concentrations well below 1 mg/L. Concentrations are low because of constraints imposed by solubility of minerals or amorphous substances and adsorption on clay minerals. A characteristic feature of most trace metals in water is their tendency to form hydrolysed species and to form complexed species by combining with inorganic anions such as HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-, F^-, and NO_3^- (Freeze and Cherry, 1979).

2.4.4 Bacteria

Microbiologically polluted water has long been associated with the transmission of infectious diseases such as gastro-enteritis, cholera, typhoid fever and hepatitis A. A feature of bacterial pathogens is a generally high infective dose (10-1000 organisms required to cause infection) while viral pathogens and parasites have low infective doses (1-10 organisms). The protection of public health through control of microbial water quality is an important goal of water quality management (DWAF, 1993).

Faecal coliforms are the most common bacterial indicators of faecal pollution, and hence of the possible presence of faecally associated pathogens in domestic water supplies. Faecal coliform bacteria are almost definitely of faecal origin from warm-blooded animals and this correlation is strengthened if confirmation of Escherichia coliform (*E. coli)* is conducted. Total coliform gives an indication of the general sanitary quality of water since this group includes bacteria of faecal origin. However, according to the DWAF guidelines, many of the bacteria in this group may originate from growth in the aquatic environment. Total coliform is used to evaluate the general sanitary quality of drinking water and related waters. Faecal coliform and *E. coli* are rarely found in soil or water which has not been subject to faecal pollution.

2.5 Identification of groundwater contamination

2.5.1 Sampling

Groundwater sampling requires specialised precautions to ensure that the water sampled is representative of the in situ quality of groundwater in the aquifer. Unlike surface water, where sampling can often be effectively accomplished by filling up a bottle, groundwater sampling requires some attention. The following section is a modified extract from Weaver (1992) on groundwater sampling guidelines.

Access to the boreholes or wellpoints must be available. These need to be intelligently sited and have information on screen positions, etc. Stagnant water must be pumped out of the borehole before true conditions in the aquifer can be sampled. Purging is usually conducted until the pH, EC and Eh are stable. Groundwater samples should be collected before purging only if LNAPLs or DNAPLs are being investigated, in which case a bailer should be used. The redox potential, pH buffering, gas composition and temperature conditions in the subsurface may be vastly different from those at the surface. For this reason it is generally recommended that field measurements be taken of pH, Eh, dissolved oxygen, temperature and alkalinity. Preservation methods may be used to retard biological activity, retard chemical reactions and reduce volatility, thereby keeping the collected sample as close to its original state as possible. Using the same pumping and sampling equipment for different monitoring points poses a risk of introducing cross contamination. If possible, work must be done from the least contaminated to the most contaminated point, and clean equipment thoroughly between sampling runs.

Groundwater sampling and analysis requires special procedures mainly because of the fact that the pressure in the aquifer is higher than that at ground level (Tredoux, 1983). Usually gas is released from the water during sampling which leads to a change in equilibrium conditions especially with respect to the carbonic acid system. In some cases the water has some turbidity which has to be removed before analysis. Some techniques that are cited by Tredoux (1983) include aeration during sampling being kept at a minimum. The pH is measured immediately and sample bottles are filled completely and sealed as tightly as possible. In the laboratory electrical conductivity and total alkalinity are determined directly after the sample bottles are bottled. A portion of each sample is acidified to prevent precipitation of calcium carbonate and is used for cation analysis. Other analyses are carried out as soon as possible, especially those for nitrogen species, phosphate and the COD. Whenever microbiological analyses are required, separate samples are taken for this purpose.

2.5.2 Chemical data analysis

In identifying groundwater contamination Vengosh (1998) suggests the use of the Cl/Br ratio as a tracer for sewage contamination. The ratios of chloride to bromide have been extensively used to detect the origin of dissolved salts in groundwater and brines since both form stable anions of Cl and Br in water and are usually not affected by water-rock interactions (Davis *et al.,* 1998). Although many argue that decomposing organic matter and sorption of Br on clays and iron oxide in the soil affect Cl/Br ratios in water, numerous studies (e.g. Butters, 1989) demonstrate the conservative characteristics of Cl/Br ratios for tracing the origin of salinity in groundwater. Others have found that sewage effluents and street runoff have a large range of Cl/Br ratios. These examples show some quirky methods for analysing chemical data.

2.5.2.1 Anions

Bicarbonate can be calculated from pH, dissolved inorganic carbon (DIC) measurements and sulphate concentration. Increases in sulphate concentration suggest the dissolution of carbonate minerals and gypsum and/or oxidation of pyrite as groundwater moves through the system. Nitrate and dissolved oxygen concentrations and Eh values can be elevated in samples taken upgradient compared to downgradient wells because of denitrification and other interactions (Michelle *et al.*, 1999). High chloride concentrations are most likely anthropogenic and sea-water in origin. For example, the construction in the late 1970s and early 1980s of L-Bar uranium mine tailings ponds (in New Mexico) lined with sodium chloride-treated clay acted as a point source for NaCl (Michelle *et al.*, 1999).

2.5.2.2 Cations

In chemical data analysis of cations there are normal patterns of concentrations of K^+, Ca^{2+}, and Mg^{2+} that can be observed. In a groundwater geochemistry study by Michelle *et al.* (1999) it was observed that there were patterns of generally decreasing concentrations of cations with distance eastwards, suggesting that their sinks are the same. An additional tool to track such trends is the Piper trilinear diagram used to illustrate trends of increasing and decreasing cations in the direction of groundwater flow.

Na^+, Ca^{2+} and Mg^{2+} are the major cations in natural groundwaters, while potassium is usually strongly adsorbed to minerals with negative surface charge and occurs at much lower concentrations. There is often a tendency for groundwaters to evolve from Ca^{2+} or Mg^{2+} dominance to Na^+ dominance, a process referred to as natural water softening. Cation exchange processes, greater availability and solubility of sodium minerals, and the effects of calcium carbonate precipitation caused by increasing pH favour such a trend in cation composition (Freeze and Cherry, 1979).

The chemical quality of natural groundwater of a sandy aquifer is summarised in Table 2.1. The water generally has a fairly low salinity and its outstanding characteristic is a relatively high temporary hardness. The quoted guidelines are for drinking water from the Department of Water Affairs and Forestry (DWAF, 1993a).

Table 2.1 *A chemical quality of an indigenous groundwater of a sandy aquifer compared to drinking water guidelines (Tredoux et al., 1980, p80).*

CONSTITUENT mg/L	CONCENTRATION	
	1980 (MEDIAN)	**DWAF GUIDELINES**
Na^+	57	100
K^+	1.5	50
Ca^{2+}	102	32
Mg^{2+}	11	30
NH_3 (as N)	<0.05	1
SO_4^{2-}	30	200
Cl^-	99	100
NO_3^-(as N)	<0.1	10
NO_2	<0.05	<0.5
P	<0.1	<0.1
pH	7.7	5.5-9.5
EC (μS/cm)	78	300
Total alkalinity (as HCO_3^-)	248	No data

2.5.3 Stable isotopes of oxygen and hydrogen

Stable isotopes can be valuable tools for investigating hydrologic systems (Mazor, 1997). Their use is divided into studies using water isotopes and studies focusing on isotopes of solutes in the water. Whereas discrete physical measurements represent the system at a point in time when the measurement was taken, stable isotope compositions reflect the initial water entering the system, subsequent additions and withdrawals, and processes acting within the system. Water isotopes are ideal conservative tracers of water sources because they are part of the molecule itself. Stable isotopes of water are conservative in aquifers at low temperature because the vapour pressure of $^{16}H_2O$ is greater than $^{18}H_2O$ content after evaporation. Hydrogen and deuterium fractionate due to a large percent mass difference. Thus, characteristic $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios can fingerprint water sources. Hunt *et al.* (1998) used stable isotopes of water and strontium to: (1) identify sources of water; (2) investigate wetland evapotranspiration; and (3) examine the processes that control the source and transport of a solute in both systems.

The isotope ratios of a water may change as a consequence of the history and processes to which it has been subjected in the environment. The mass difference between the different isotopes of oxygen and hydrogen produce small differences in their chemical and physical behaviour, which, in turn, establish slightly different isotope composition (isotope fractionations), among co-existing compounds or phases. Fractionation can be caused by equilibrium effects, physical effects (e.g. phase changes) and kinetic effects.

The most important physical process causing variation of oxygen and hydrogen isotope composition in natural waters is vapour-liquid fractionation during evaporation and condensation. The vapour pressure of water containing the light isotopes (^{1}H and ^{16}O) is greater than that of water containing the heavier isotopes (D and ^{18}O). When liquid water and water vapour are in equilibrium, the isotope ratio of the vapour is lower with respect to both D/H and $^{18}O/^{16}O$ than the liquid, hence water vapour in the atmosphere has lower isotope ratios than water in the ocean (Drever, 1997).

When water vapour condenses to form rain, fractionation takes place in the reverse direction, with the liquid having a higher isotope ratio than the vapour. The fractionation during evaporation is thus largely reversed during condensation. If the condensed droplets again form a vapour, ^{18}O will be selectively removed from the vapour phase and the $\delta^{18}O$ of the vapour will become progressively more negative as the rain continues to fall. By this process of Rayleigh fractionation, rainfall produces progressively lower δD and $\delta^{18}O$ ratios as it occurs further from the ocean source. The δD and $\delta^{18}O$ values in the precipitation generally plot close to a straight line (the meteoric water line) with equation (Craig, 1961):

$$\delta D = 8\delta^{18}O + 10$$

Water with an isotope composition which plots on the meteoric line is assumed to have originated from the atmosphere and to be unaffected by other isotope processes. Evaporation from open water and exchange with rocks are two of the more commonly observed processes causing deviations from the meteoric water line (Domenico and Schwartz, 1990). In most cases, these isotope processes affect the relationship between $\delta^{18}O$ and δD in a unique way, so the positions of the data points on a graph of δD vs. $\delta^{18}O$ can be used to identify the process (Figure 2.1). Isotope data for the Cape Flats aquifer can be plotted, along with the global or local meteoric water line, to determine the controls on isotope fractionation. Figure 2.1 shows how the fractionation processes cause a deviation from the meteoric water line.

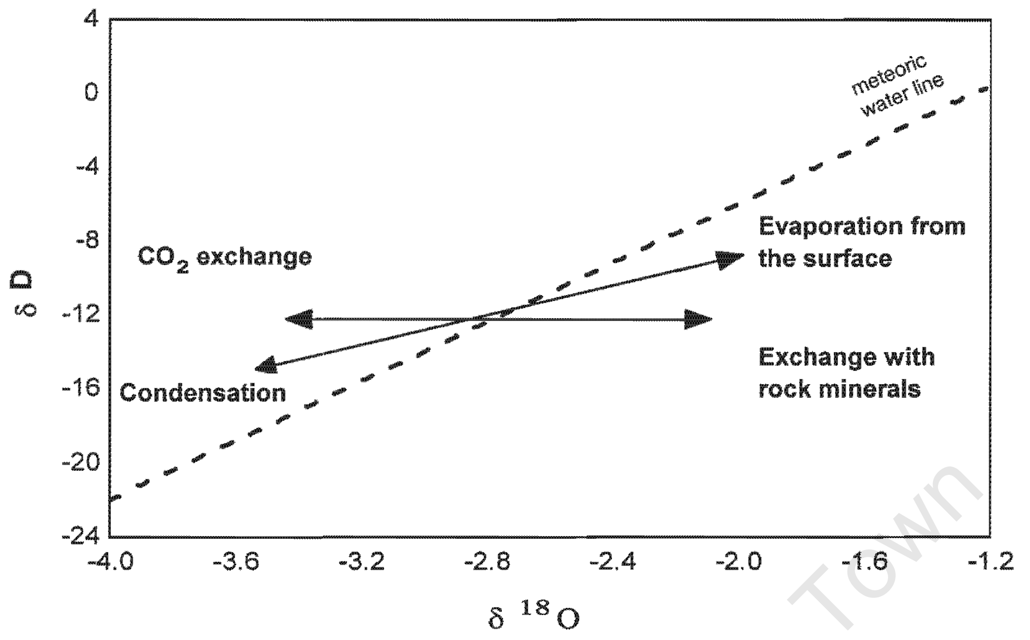


Figure 2.1: *Environmental isotopes of oxygen and hydrogen. The deviations in isotope compositions away from the meteoric water line as a consequence of various fractionation processes (After IAEA, 1983).*

2.5.4 Stable isotopes of groundwater

A local meteoric line, which is representative of modern precipitation in a local area, can be used as a reference. All modern samples analysed in a study of groundwater sampling by Michelle *et al.*, (1999) plot below and to the right of the local and global meteoric water lines indicating that precipitation has experienced evaporation prior to infiltration into the groundwater system (Figure 2.1). It is important to note that altitude effects may also affect the relative differences in isotopic composition between the collected groundwater samples if there was significant variation in recharge elevations.

2.5.5 Geochemical model

The geochemical model NETPATH (Plummer *et al.*, 1992) is used to elucidate the groundwater geochemical evolution and to compute groundwater ages. NETPATH calculates the net geochemical mass balance reactions between an initial (upgradient) water and a final (downgradient) water. The mass transfers simulated by NETPATH model are constrained by the elements used, such as C, Na^+, Ca^{2+}, K^+, Al, Si. The thermodynamic validity of each precipitation/dissolution reaction can be evaluated using saturation indices calculated by MINTEQA2, a thermodynamic equilibrium model. Speciation models calculate the thermodynamic properties of aqueous solutions, including the molalities and activities of aqueous species and saturation indices of minerals. Their primary purpose is to calculate mineral saturation indices which are indicators of the saturation state of a mineral with respect to a given water composition.

The main indicators that have been used for hydrochemical analyses in monitoring boreholes are pH, EC, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4, Cl^-, SO_4^{2-}, alkalinity, NO_x and DOC.

2.5.6 Subsurface microbiology

An understanding of subsurface microbiology is essential for determining the distribution and rates of microbially mediated processes occurring in groundwater systems. This information, when combined with appropriate hydrologic and geochemical data, allows a rational evaluation of how microbial processes influence water chemistry under pristine conditions, and how contamination events have altered water chemistry. In general, micro-organisms may be introduced into the subsurface environment by any practice that involves the application of domestic wastewater to the soil, which can potentially cause microbiological contamination of groundwater (Alley, 1993).

2.6 Conclusions

During recent years much of the emphasis in groundwater investigations in industrialised countries has shifted from problems of groundwater supply to considerations of groundwater quality. As a result of our consumptive way of life, the groundwater environment is being assaulted with an ever-increasing number of soluble chemicals. Urban and peri-urban development has exacerbated the problem by the infiltration of runoff from these new developments and industrial wastes into the underlying aquifers. Whereas the problem of achieving acceptable quality of surface waters focuses mainly on decreasing the known emissions of pollutants to these systems, the problem with the protection of groundwater resources is to identify the areas and mechanisms by which pollutants can enter aquifers. This is necessary as a basis for minimising the impact of existing or proposed industrial, agricultural, or municipal activities on groundwater quality. Fortunately the development of geochemical analytical methods have resulted in useful tools for Earth scientists. Stable isotopes have great applications as tracers, as they convey conservative properties of the groundwaters of interest. Applications of these methods include pollution monitoring, groundwater monitoring, as well as evaluating the suitability of groundwater resources for various anthropogenic activities.

3 The current status of groundwater on the Cape Flats

3.1 Introduction

Fifteen water samples were taken from boreholes in the Cape Flats aquifer. They were grouped into 3 regions of the study area: west (Philippi), east (Khayelitsha) and central region (Mitchell's Plain and Gugulethu). Large volumes of water reside in the Cape Flats aquifer and this resource is currently utilised to a small extent by a few farmers and community garden schemes. With urban sprawl on the aquifer area, it is essential to ascertain whether the informal settlements affect the water and to determine if it is suitable for use specifically in domestic and agricultural environments. This involves assessing the domestic suitability and health effects as well as considerations of various factors that may affect the crop yield, such as salinity, infiltration and other effects. Considerations relating to better understanding the geochemical nature and origin of the water are dealt with in Chapter 4.

3.2 Sampling

3.2.1 Sampling rationale

Water sampling consisted of obtaining selected samples from the different sectors of groundwater found in the Cape Flats area, in order to examine the water quality and geochemistry between the different areas. Water samples were collected from boreholes and irrigation schemes (using groundwater), in order to establish how the aquifer is contaminated in terms of pathways and chemical constituents. It is also hoped that, using stable isotope geochemistry, microbiological testing and other techniques, it can be determined how groundwater is different from surface water – to establish contamination a link.

Groundwaters in the Cape Flats area were sampled near the end of the wet season, in late August and early September. It was expected that dominant recharge of the groundwaters of the region would occur during the wet winter season, over the five month period extending from May through to September. Limited recharge is expected to occur during the dry summer months, as discussed in Chapter 2. The groundwater will not be subject to evaporation effects after infiltration has occurred, and therefore, it was assumed that the chemical composition of the groundwaters, for the purposes of the study, do not vary much throughout the year but only in the long term.

3.2.2 Sampling location

Samples were collected from the Cape Flats in and around the new formal townships and informal settlements, acquiring samples from locations that were as evenly distributed as possible. The positions of the sampled points, relative to Cape Town, are shown in Figure 3.1. The boreholes were identified from geohydrological maps of the Cape Flats, the Tygerberg Municipality irrigation schemes, community gardens and the Philippi farms. Most boreholes identified on the geohydrological maps were sampled, along with water from other operating irrigation schemes.

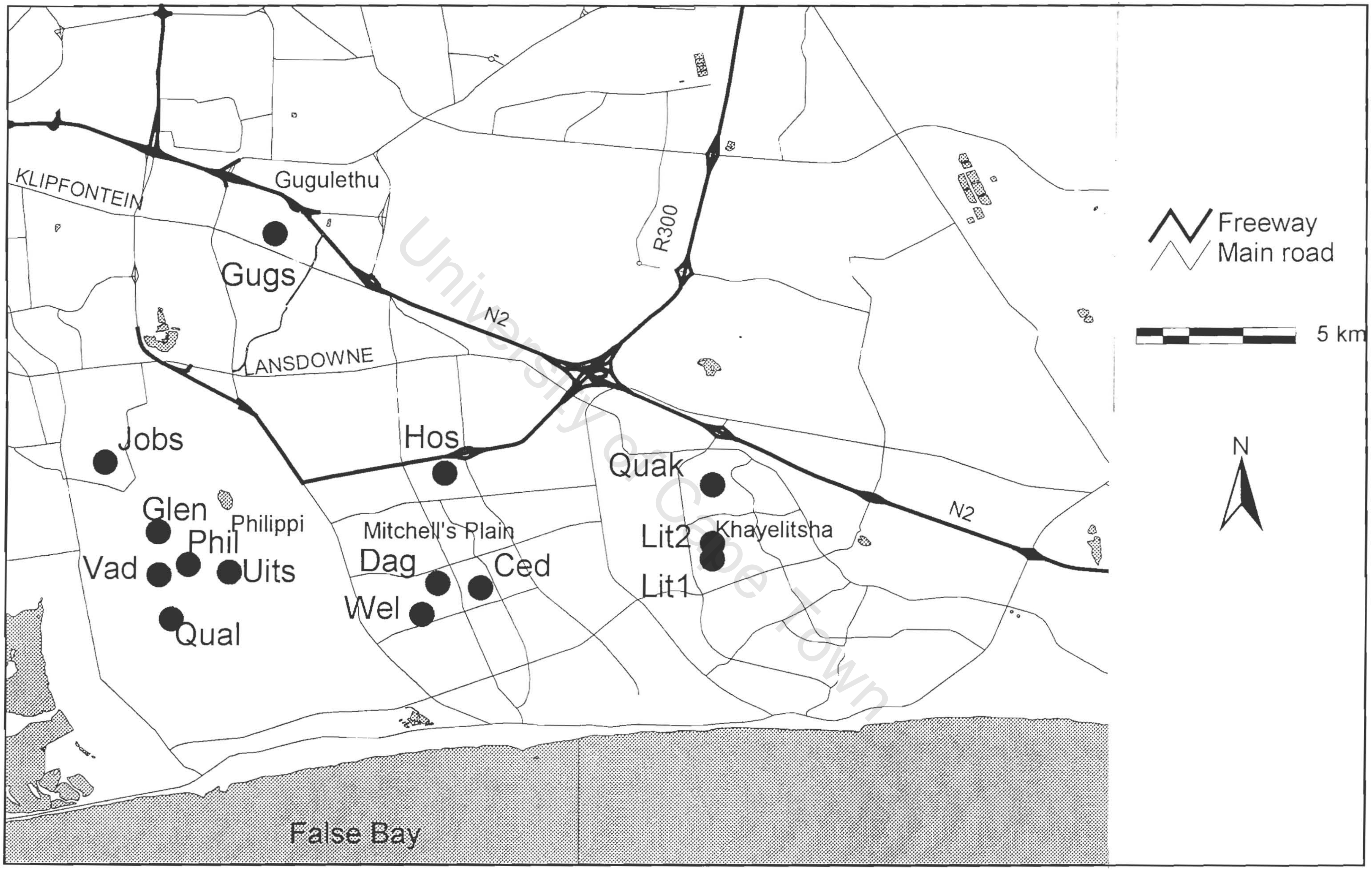


Figure 3.1: The sampling sites and the locations of the boreholes.

Groundwaters near the residential areas were sampled from boreholes (in Khayelitsha and Mitchell's Plain) which have been refurbished by a local engineering company as part of contract work with the Tygerberg municipality. Many of the boreholes sampled in Khayelitsha (east) are used daily for irrigation of parks and stadiums, while the Philippi abstractions are for the Philippi (west) market gardens. Boreholes in Mitchell's Plain (centre) are not currently in use and were constructed in the early 1980's as part of a pilot abstraction scheme that has since been abandoned. The positions of the boreholes sampled are shown in Figure 3.1.

3.2.3 Sample collection

Samples from all the boreholes were collected in pre-washed plastic bottles, which were totally filled, sealed and stored in a refrigerator. The samples taken for coliform count were kept in pre-treated plastic bottles in a cooler bag with ice packs and were delivered on the day of the sampling to the laboratory for the tests.

Groundwaters from the unequipped boreholes were sampled on 27th August 1999 using a petrol pump (Figure 3.2). The depth to the water table varied from 1.9m to 5m. Before sampling the boreholes were purged manually to remove any meteoric water which had accumulated in the boreholes as a result of runoff or direct entry. Electrical conductivity (EC) was used as a measure of the source of the water in the borehole, as the recent meteoric waters generally had a different EC to the background aquifer waters. Electrical conductivity in the aquifer was continually monitored using a Corning digital multimeter. Once the EC stabilised, it was assumed that the borehole was effectively purged, and any water seeping into the well was background aquifer water. The set-up of the sampling equipment is illustrated in figures Figure 3.2 and Figure 3.3.

Other samples were taken from water pipes abstracting water from boreholes. These were taken after watering had continued for an ample amount of time at the site, again, in order to obtain a representative groundwater sample.

3.3 Analytical Methods

The samples to be analysed for pH, conductivity and alkalinity required no pre-treatment. The samples used for major ion analyses, dissolved organic carbon (DOC), phosphorus and for elemental analysis by inductively coupled plasma - atomic emission spectroscopy (ICP-AES), were filtered through a 0.45μm filter before analysis.

3.3.1 pH

The pH was determined using a Crison micro pH 2001 pH meter, which contains a standard hydrogen electrode coupled to a reference calomel electrode. The meter was calibrated relative to pH 4.00 and pH 7.03 before any determinations were made. The pH was determined as soon as the samples were returned to the laboratory, which varied from one to five hours after sampling.

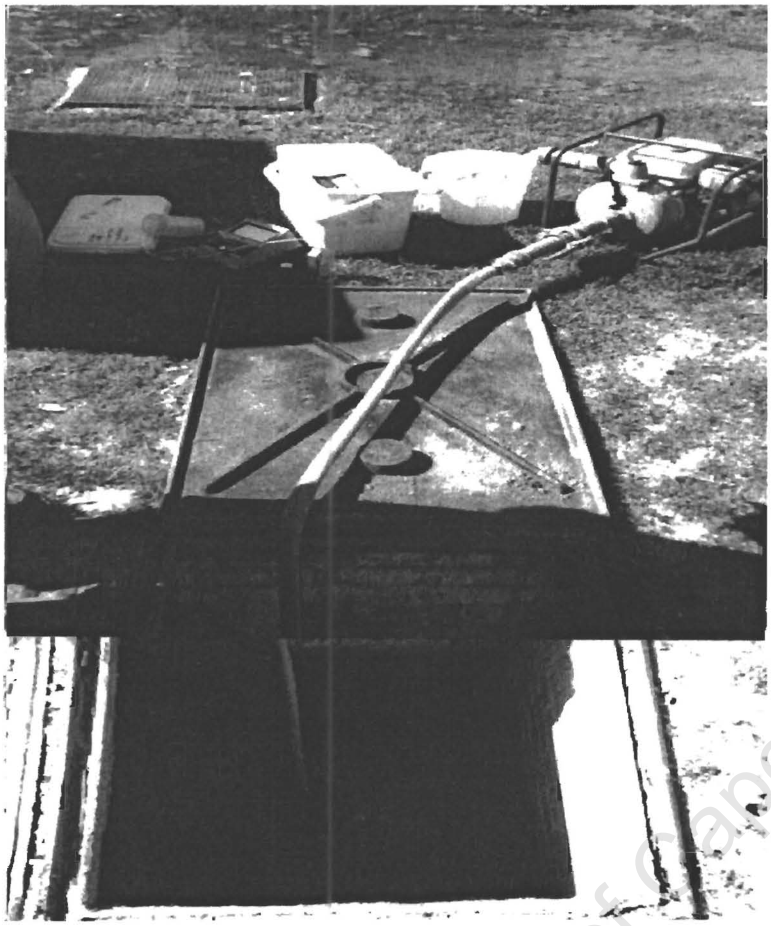


Figure 3.2: A complete set-up of the borehole sampling equipment.

Figure 3.3: Purging the borehole while continually monitoring the electrical conductivity.

3.3.2 Electrical conductivity

EC was measured using a Crison micro CM 2201 conductivity meter, and is expressed in siemens per unit distance, at a specific temperature.

3.3.3 Alkalinity

Alkalinity was determined using a Radiometer Copenhagen TTT85 Titrator, coupled to a Radiometer Copenhagen ABU80 Autoburrete. The samples were titrated to an endpoint of pH 4.5 using 0.01M HCl (American Public Health Association, 1985, pg. 63).

3.3.4 Major Ions

Major anions for the water samples were determined using high pressure ion chromatography (HPIC), which involves the separation of the ions in eluent on an exchange separator column and the comparison of the peak heights to calibration curves set up with solutions of known ion concentrations. Separate runs were done for cations and anions. Ions measured were the cations Na^+, Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ and anions Cl^-, SO_4^{2-}, NO_3, and Br^-.

The samples were diluted if necessary to reduce their EC to below $100\mu S.cm^{-1}$. The diluted sub-samples were analysed for anions using a Dionex DX300 series suppressed ion chromatography system, coupled with A1450 chromatography software. An HPIC-AS4A separator column, fitted with an HPIC-AG4A guard column, was flushed with a sodium carbonate/bicarbonate eluent (1.80 mM Na_2CO_3; 1.79 mM $NaHCO_3$) at a flow rate of 2.0 $ml.min^{-1}$. A MicroMembrane (AMMS) anion and cation autosuppressors were used. Cations were determined using a DIONEX HPIC-CS5 exchange column with 20mM methyl-sulphonic acid eluent. Flow rate was 1.0 $ml.min^{-1}$.

In addition, (ICP-AES) was used for further analysis of major ions and for comparison. Only Mg and Ca were analysed using the ICP-AES method.

3.3.5 Elemental analyses

The total elemental concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS). Andreas Spath of the ICP-MS laboratory at the Department of Geological Sciences (UCT) performed the analysis using a Perkin-Elmer ELAN 6000 ICP-MS.

3.3.6 Dissolved phosphorus determination

Phosphorus concentration was measured using the ascorbic acid method and the exact procedure given in Standard Methods (1995) was followed. This involves the formation of a blue coloured phospho-molybdate complex by reaction with a combined potassium antimonyl tartrate, ammonium molybdate and ascorbic acid reagent, and its subsequent concentration determination by colorimetry. For this, absorbance was measured at 880 nm using a TURNER Model 340 spectrophotometer, and P concentration was calculated for the samples from a calibration curve set up using the absorbance of solutions of known P concentration. All glassware was acid washed prior to analysis in order to minimise P contamination. Standards were analysed with every analytical run.

3.3.7 Dissolved organic carbon (DOC)

Filtered water samples (0.45 μm membrane filter) were supplied to Mike Louw at the analytical laboratories of the Cape Water Program, CSIR for analysis of DOC. The samples had been stored at 4°C since collection to limit biological degradation of organic matter. Analysis was performed by autoanalyser using the persulphate-ultraviolet oxidation method for total organic carbon (Method 5310C, Standard Methods, 1995).

3.3.8 Total iron

Total Fe concentration in the water samples was determined at the Chemical Engineering Department, UCT. The samples submitted for analysis had been filtered and refrigerated. The samples were analysed by the flame atomic absorption spectrometry (FAAS) method (Method 3500 – Fe B, Standard Methods, 1995).

3.3.9 Stable isotope analyses

Water samples in filled plastic bottles were submitted to Fayrooza Rawoot of the Stable Isotopes Laboratory at the Department of Geological Sciences, UCT for analysis of δD and $\delta^{18}O$. Stable isotope ratios were measured on gaseous samples, and a reference gas of a known isotope composition, using a Finnegan MAT 252 dual-inlet mass spectrometer.

3.3.10 Microbiological water testing

Water samples in filled sterilised plastic bottles were submitted to Ingrid Thompson of the Scientific Services Laboratory at the Cape Metropolitan Council, for analysis of faecal coliform and *escherichia coli (E. Coli)*. Samples were refrigerated immediately after collection and were analysed within six hours of collection. The faecal coliforms and *E. Coli* indicator bacteria were enumerated as counts per 100 ml. Due to logistical reasons only representative samples were collected for microbiological water testing.

3.4 Results and discussion

3.4.1 Quality control

A number of procedures for checking the accuracy of analyses are applicable to water samples for which relatively complete analyses have been made. Most of the checks performed here are based on calculations using the data already collected.

The anion and cation sums, when expressed as millimoles charge per litre ($mmol_c/L$), must balance, because all potable waters are electrically neutral. As a measure of the quality of the aquifer water analytical data, the anion-cation charge balance of each water sample was calculated using the method of Murray and Wade (1996). This data are presented in Table 3.1. Alkalinity measurements were also included in the charge balance calculations, as HCO_3^-. Measured ionic concentrations (mg/L) were converted to $mmol_c/L$ prior to calculating the percentage difference:

$$\text{mmol}_c/\text{L} = (\text{mg/L} / \text{atomic or molecular weight}) \times \text{ionic charge}$$

The percentage difference was calculated as follows:

$$\% \text{ difference} = 100 \times [(\Sigma \text{ cations} - \Sigma \text{ anions}) / (\Sigma \text{ cations} + \Sigma \text{ anions})]$$

Murray and Wade (1996) state that anion-cation differences of about 2 to 5% are acceptable for an anion range of 10 to 800 mmol_c/L. Differences of $\leq$ 10% are considered acceptable for the purposes of this study because of relatively low concentrations. Only two samples had charge balances outside this limit (LIT1A and GLEN) and, therefore, the ion chromatography (IC) data for all the water samples are considered to be of acceptable quality.

Another procedure commonly used to check the correctness of analyses is the correlation of measured EC against ion sums, as in Figure 3.4 and Figure 3.5. This procedure is based on the fact that the higher the EC the higher the concentration of ions in water. Both the anion and cation sums should correlate positively with the electrical conductivity such that they fall on a straight line. The data fit is good (R^2 = 0.92 and 0.82) which suggests that the data are of acceptable quality.

Since three analytical methods (IC, ICP-MS and ICP-AES) were used to measure the concentration of the major elements/ions, it was possible to check if the results from the three different methods were comparable. Only Mg and Ca were analysed using the ICP-AES method, and only the common elements/ions from all three methods were plotted for comparison. The correlation coefficients (R^2) in Figure 3.6 for most of the ions in the samples are above 0.90, and therefore the IC, ICP-MS and ICP-AES data for these water samples are considered to be of acceptable quality. Data is only considered acceptable if points lie close to the 1:1 line (solid line) shown in all the graphs in Figure 3.6. Most samples except for Cl show a good fit. This is because ICP-MS is undershooting Cl compared to IC.

Table 3.1: *Analytical results obtained for all water samples, divided into three regions.*

	EAST				CENTRE				
Constituent (mg/L)	**Lit1a**	**Lit1**	**Lit2**	**Quak**	**Hos**	**Dag**	**Ced**	**Wel**	**Gugs**
Cations									
Na^+	20.4	54.8	24.9	33.3	89.2	22.1	82.5	57.5	33.9
K^+	4.1	3.3	3.5	9.4	2.4	19.3	26.5	9.7	8.8
Mg^{2+}	22.2	27.4	12.5	17.9	16.2	9.3	13.9	12.7	6.8
Ca^{2+}	131	108	61.9	163	143	91.3	116	134	145
Li^+	<0.1	0.7	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Anions									
SO_4^{2-}	44	68	29	89	40	46	25	66	57
F^-	0.61	0.66	0.91	0.14	<0.1	<0.1	<0.1	0.91	0.7
Cl^-	26	71	32	47	150	48	167	99	45
NO_3	14.4	0.0	5.5	6.8	14.2	9.8	0.0	0.0	83.0
PO_4^{3-}	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
HCO_3^-	230	336	202	435	262	218	233	260	215
pH	7.5	7.4	7.7	7.1	7.3	7.3	7.3	7.3	7.2
Alkalinity (as $CaCO_3$)	377	551	331	713	430	357	382	426	352
EC (mS/m)	51.1	77.7	88.4	99.0	105.2	54.0	102.0	97.8	75.0
DOC	1.5	2.5	1.3	3.3	1.3	1.7	<1.0	3.0	2.3
SAR (mmol/L)	0.61	1.79	1.10	0.98	3.11	0.85	2.80	1.85	1.17
$\sum$ cation ($mmol_c/L$)	9.3	9.7	5.1	10.4	10.1	6.5	10.8	10.5	7.9
$\sum$ anion ($mmol_c/L$)	5.6	8.9	4.9	10.4	9.6	6.0	9.0	8.5	7.3
Charge balance (% cation excess)	24	4.1	2.4	0	2.7	3.7	8.8	0.4	4.4

Table 3.1: (continued)

	WEST					
Constituent (mg/L)	**Qual**	**Jobs**	**Uitse**	**Vad**	**Phil**	**Glen**
Cations						
Na^+	202	83.7	74.1	39.4	124	99.7
K^+	59.8	78.9	40.4	4.4	40.9	13.1
Mg^{2+}	40.0	19.9	19.6	10.4	23.6	21.9
Ca^{2+}	105	59.2	193	90.3	177	149
Li^+	<0.1	1.1	<0.1	<0.1	<0.1	<0.1
Anions						
SO_4^{2-}	192	93	164	65	184	172
F^-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cl^-	406	158	148	71	232	188
NO_3	99	71	87	5.3	16.0	7.7
PO_4^{3-}	<0.1	<0.1	<0.1	2.3	<0.1	<0.1
HCO_3^-	328	85	297	138	212	85
pH	7.5	6.3	7.6	6.5	7.5	6.8
Alkalinity (as $CaCO_3^{2}$)	538	139	487	226	348	139
EC (mS/m)	169.0	99.4	164.0	52.0	147.9	102.5
DOC	18	43	22	6.1	22	13
SAR (mmol/L)	5.55	3.69	1.98	1.48	3.28	2.85
$\sum$ cation ($mmol_c$/L)	20.3	9.7	14.8	7.1	17.2	13.9
$\sum$ anion ($mmol_c$/L)	22.7	8.9	13.9	5.6	14.1	10.4
Charge balance (% cation excess)	-4.6	4.2	3.2	11	9.9	14

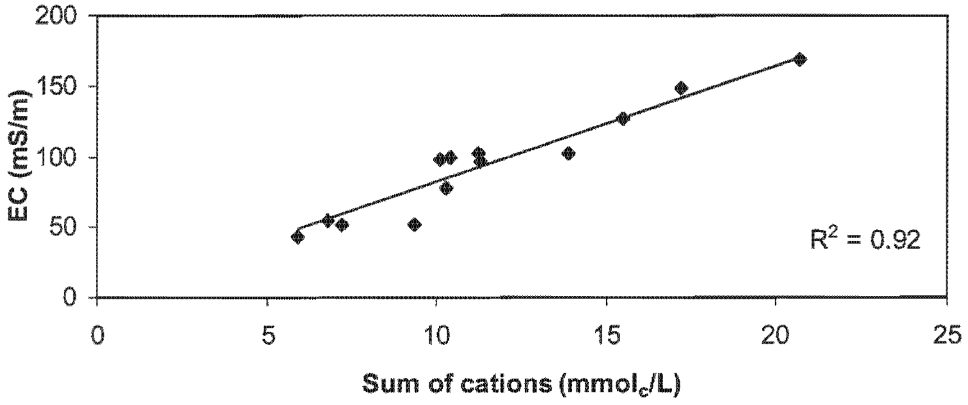


Figure 3.4: *Correlation between EC (mS/m) and total cation concentration (mmol$_c$/L) in all groundwater samples.*

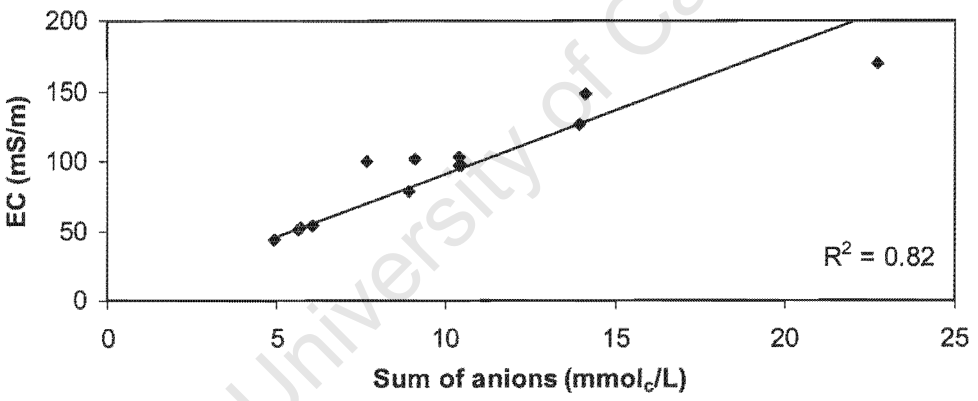


Figure 3.5: *Correlation between EC (mS/m) and total anions concentration (mmol$_c$/L) in all groundwater samples.*

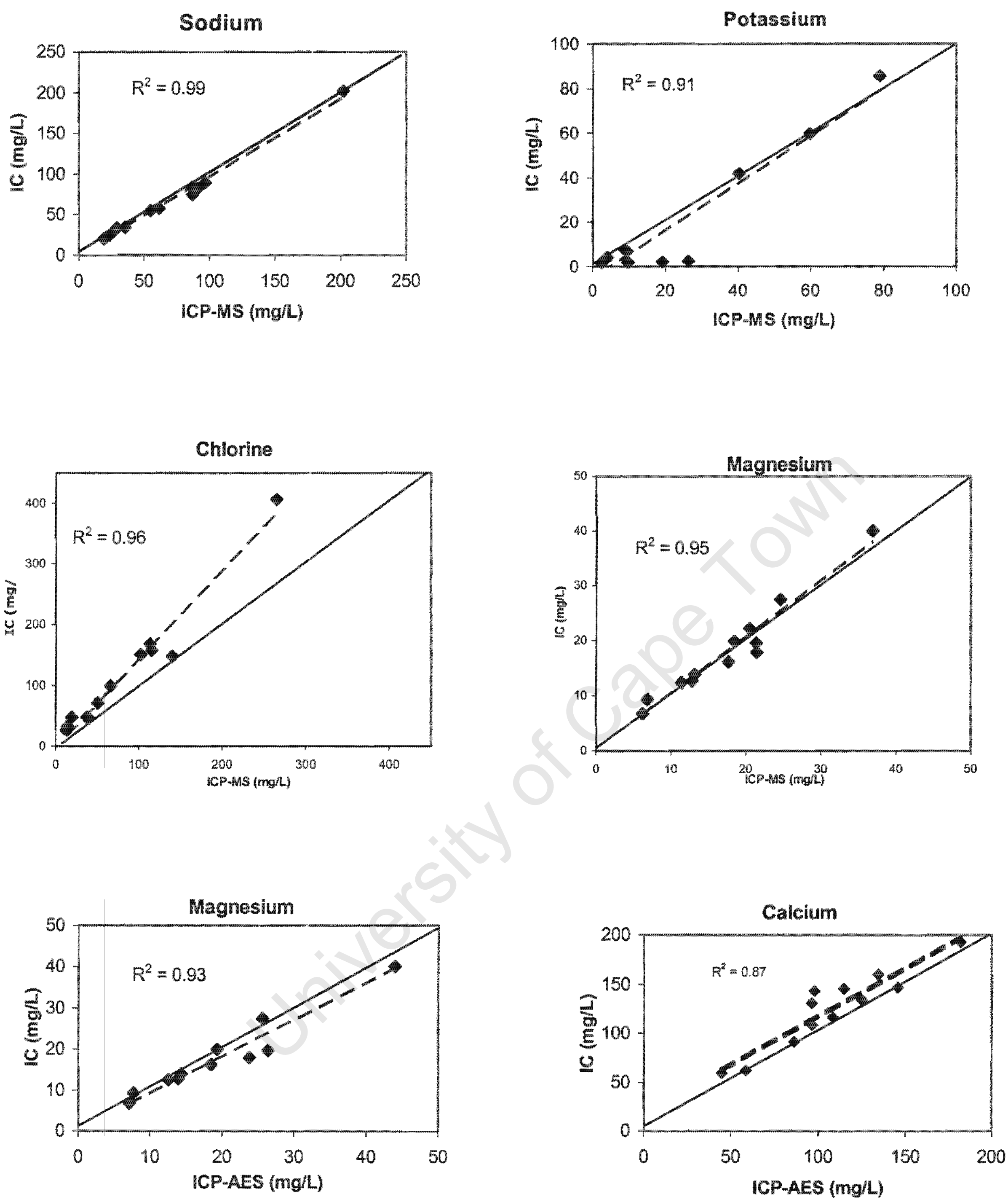


Figure 3.6: *Correlation between IC, ICP-MS and ICP-AES data in all groundwater samples. The correlations are acceptable only if they lies close to the 1:1 solid line.*

3.4.2 Domestic suitability

Large volumes of groundwater reside in the Cape Flats aquifer and are currently under-utilised. It has been postulated in several previous studies (Maclear, 1995; Tredoux, 1983 and Vandoolaeghe, 1989), with much contention, that this underground reserve can be used for various purposes, depending on its quality. It is essential to ascertain whether the current status of this water is suitable for several existing land-use activities in the Cape Metropolitan area, taking into consideration that the water quality requirements of the different user groups are not necessarily the same. In some instances they may even conflict. The Department of Water Affairs and Forestry (DWAF, 1993a) defines four main water uses for inland surface water: domestic, recreational, industrial and agricultural. They are explained in Table 3.2 below in further detail and are used to assess the results. The differences in the constituent guidelines imply that the water that would be ideally fit for use for one specific user group may not be ideally suited for another.

In addition, water seldom becomes totally unfit for use when the quality deteriorates. Quality is thus not an intrinsic property of water, but is linked to the use made of the water. A definition of what constitutes fitness for use is thus a key issue in the evaluation and management of the quality of water resources (DWAF, 1993a).

The term "domestic water", as used in the DWAF guidelines and this discussion, refers to water which is used in the domestic environment. This includes water for drinking, food and beverage preparation, hot water systems, bathing and personal hygiene, washing, laundry and recreational purposes, e.g. in swimming pools. Domestic water users may experience a range of impacts as a result of changes in water quality: health, aesthetic and economic impacts. Although the details of water quality constituent guidelines can be found in Table 3.2, they can be briefly categorised here as:

- Physical and organoleptic
- Physico-chemical
- Biological and microbiological
- Process-related constituents.

To discuss the results in terms of domestic suitability of the ions in the samples, it is necessary to separate the ions and present them in a graphic format as presented in the following sections. The detailed results of analyses were presented in Table 3.1.

3.4.2.1 Sodium and chloride

Most of the waters sampled from the east and central parts of the study area meet the guideline value for Na and Cl in Figure 3.7. Two chloride values from the western region exceed the guideline value of 200 mg/L for domestic water. In terms of Cl and Na the Cape Flats aquifer water may not require special treatment prior to use because most samples fall below the Na and Cl recommendation guideline value, which means it will not cause health concerns even with slight irritation to sensitive groups of people. As far as the east and central regions are concerned the water is fit for drinking and domestic purposes.

Table 3.2: Water quality constituents included in the South Africa water quality guidelines.

Guidelines	
Physical and organoleptic constituents	
• Electrical conductivity	• pH
• Odour	• Turbidity
Physico-chemical constituents	
• Heavy metals	• Iron
• Aluminium	• Manganese
• Fluoride	• Nitrite and nitrate
• Dissolved organic carbon	
Biological and microbiological constituents	
• Algae	• Faecal coliforms/*E. coli*
• Coliphages	• Enteric viruses
Process-related constituents	
• Corrosion and scaling	• Sediments
• Hardness	

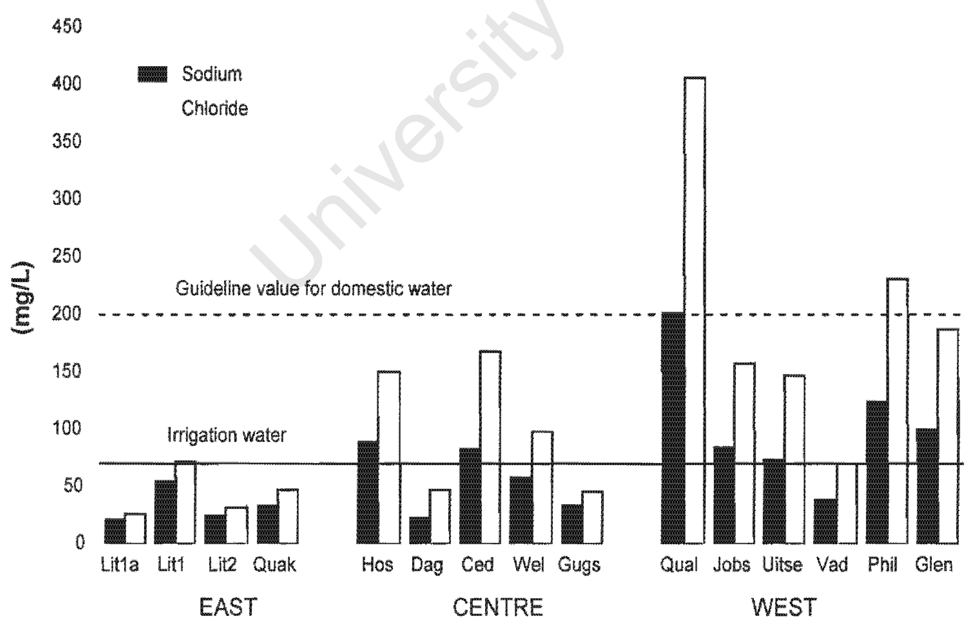


Figure 3.7: *Sodium and Chloride concentrations of aquifer waters in terms of the DWAF (1999) guidelines for domestic water. Both sodium and chloride concentrations should not exceed 200 mg/L.*

3.4.2.2 Potassium

As with Na and Cl the waters sampled from the east and central part of the study area meet the guideline value for K for domestic use. Two samples from the western part exceed the guideline value for K, and would require treatment prior to use (Figure 3.8). The Philippi area (west) in the Cape Flats has high salt concentrations and Bertram (1989) showed that this was due to irrigation practices. In previous studies such as Vandoolaeghe (1989), high values for total dissolved salts (TDS), Ca, Mg and sulphate have been found in Philippi groundwater and are in line with the status of groundwater quality in that part of the Cape Flats. The deleterious effect of large scale irrigation with groundwater mostly over the last few decades in this historic farming area has been reported. Nevertheless, with regard to K the water is suitable for domestic purposes, except for QUAL and JOBS.

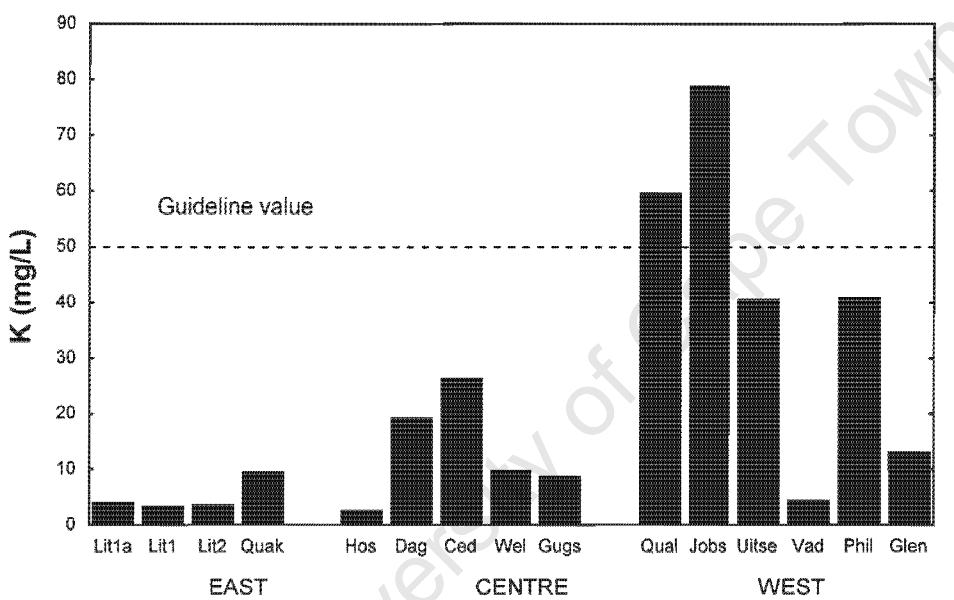


Figure 3.8: Potassium concentration of aquifer waters in terms of the DWAF (1999) guidelines for domestic water. The concentration should not exceed 50 mg/L.

3.4.2.3 Calcium

Ca in many of the waters tested is very close to 150 mg/L and some of the waters sampled exceed the Ca guideline value for domestic water use, particularly in Philippi. The elevated Ca concentrations in the samples QUAK, HOS, QUAL, UITSE and PHIL can be attributed to the nature of the sandy aquifer with the presence of upper sandy layers of markedly finer grain size or extensive calcrete lenses, as noted by Wright and Conrad (1995). It must be noted that the acceptable value of 150 mg/L in Figure 3.9 is for drinking water. This is because high Ca levels are not dangerous for drinking but can lead to hardness when used for other domestic purposes such as bathing and laundry. For this reason this water may require treatment to remove Ca in the form of $CaCO_3$ prior to use.

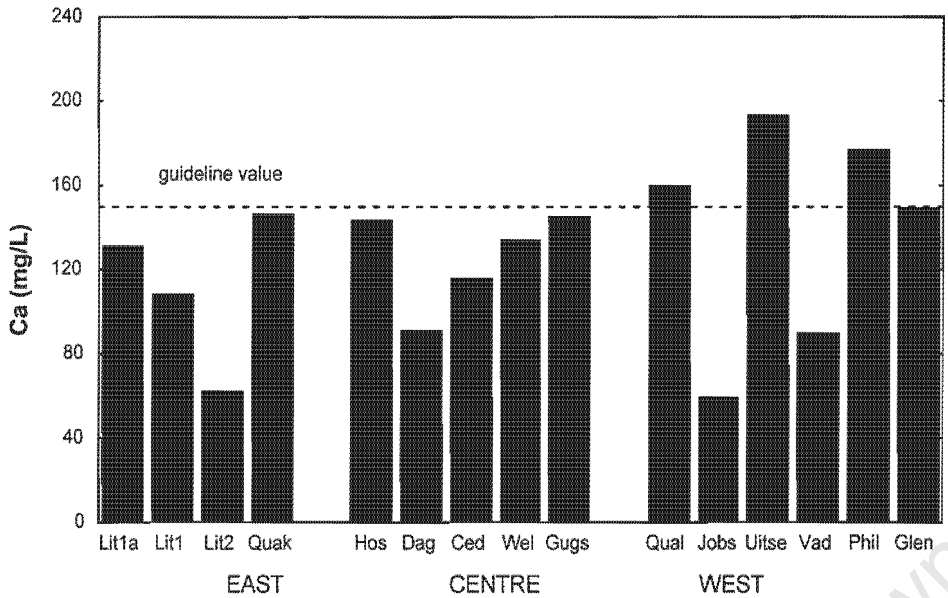


Figure 3.9: *Calcium concentration of aquifer waters in terms of the DWAF (1999) guidelines for drinking water. The concentration should not exceed 150 mg/L.*

3.4.2.4 Magnesium

Magnesium levels in all samples meet the 70 mg/L threshold for appearance of significant staining and taste problems. Concentrations in this detected range are tolerable, although slight aesthetic effects may occur. Unlike most of the major ion concentrations, Mg (Figure 3.10) does not show high concentration in Philippi, compared to Khayelitsha (east) and Mitchell's Plain (centre).

3.4.2.5 Nitrate and sulphate

The low sulphate concentration in all regions, render waters from these samples suitable for domestic use (Figure 3.11). However, highly elevated nitrate concentrations, particularly in samples from the west, is of concern (Figure 3.12). All samples from all three regions meet the guideline value for NO_3^- as N. The DWAF guidelines state that, nitrate in drinking water is primarily of health concern in that it can be readily converted to nitrite in the gastrointestinal tract as a result of bacterial reduction. Upon absorption, nitrite combines with the red blood pigment, haemoglobin, to form methaemoglobin, which is incapable of acting as an oxygen carrier. This condition can be particularly hazardous in infants. The recommended maximum of 10 mg/L for N is not exceeded by any of the samples. Nitrate from fertilisers is known to be the main source of the high N concentration in these groundwaters. Three samples from the west (QUAL, JOBS, UITSE) have relatively high concentrations of N compared to the east and central parts. In Khayelitsha (in contrast) the land had been pristine sand dunes until development started about 15 years ago. The development does not seem to have had an effect on the levels of N in these waters. Sample GUGS has a high N concentration and is not from Philippi. It is from a community garden located in Gugulethu north of Mitchell's Plain. This further substantiates the assertion that fertilisers are the main source of high N concentrations in water.

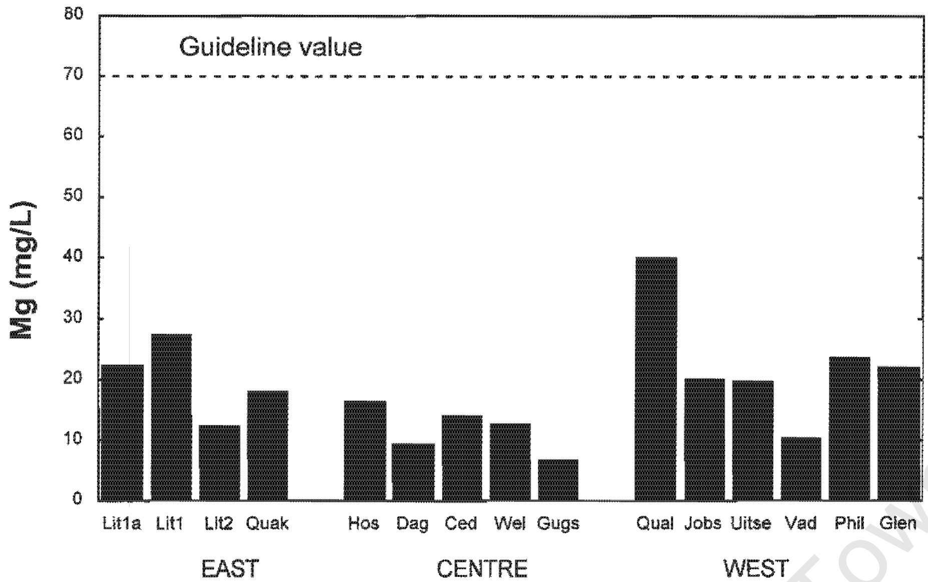


Figure 3.10: *Magnesium concentration of aquifer waters in terms of the DWAF (1999) guidelines for domestic water. The concentration should not exceed 70 mg/L.*

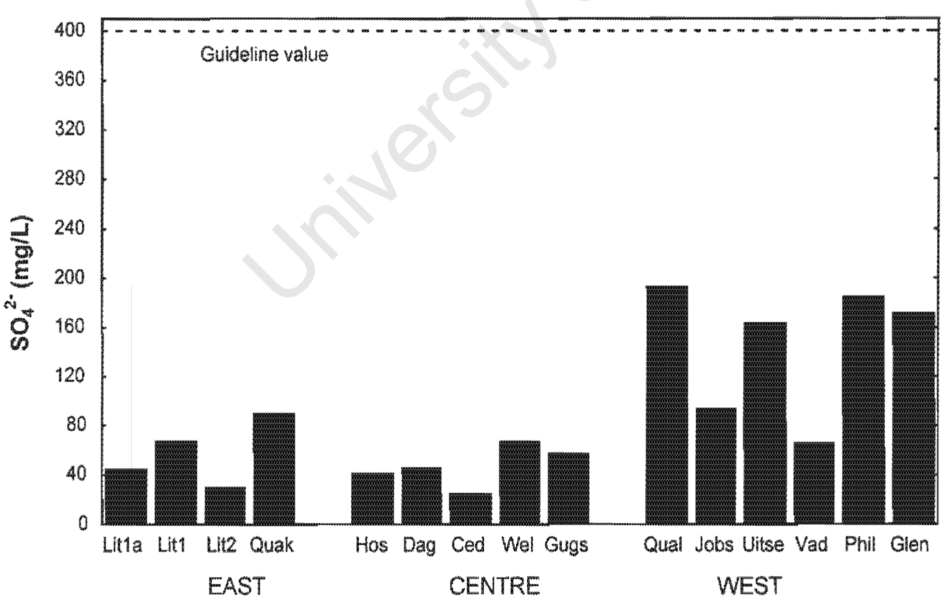


Figure 3.11: *SO_4^{2-} concentration of aquifer waters in terms of the DWAF (1999) guidelines for domestic water. The concentration should not exceed 400 mg/L.*

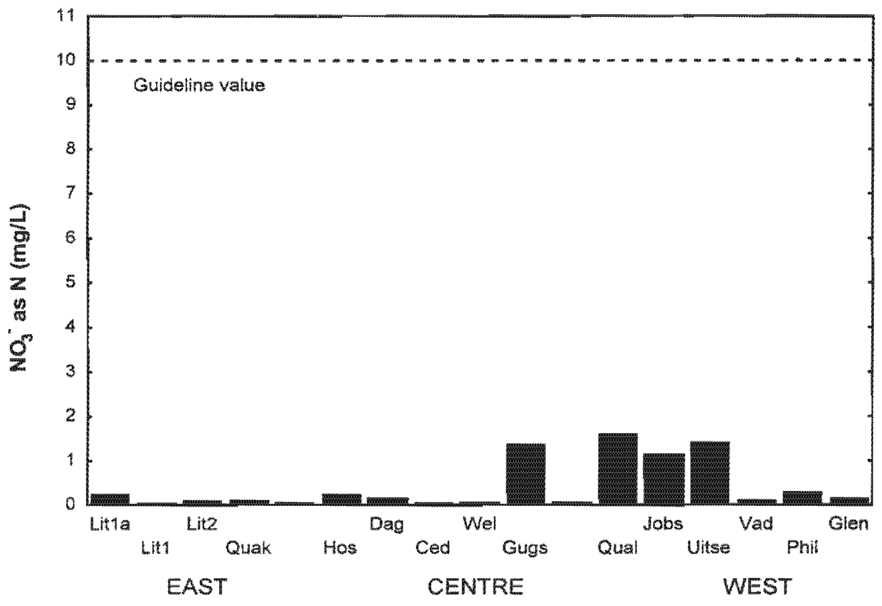


Figure 3.12: *NO_3^- as N concentration of aquifer waters in terms of the DWAF (1999) guidelines for domestic water. The concentration should not exceed 10 mg/L.*

3.4.2.6 Electrical conductivity

Figure 3.13 shows that most of the waters have EC values below the recommended level for domestic use. At the current levels the water has no marked salty taste and would probably be used if no alternative supplies were available. Short-term consumption may be tolerated, with no probable disturbance of the body salt balance. Ion exchange and electrodialysis are technically feasible processes to purify high EC water for other purposes, for example industrial processes. The high EC values in the west are commensurate with the higher ion concentrations in the area. In particular, sample QUAL and UITSE have EC values above the recommended drinking water level. Irrigation water guidelines are discussed in Section 3.4.3.

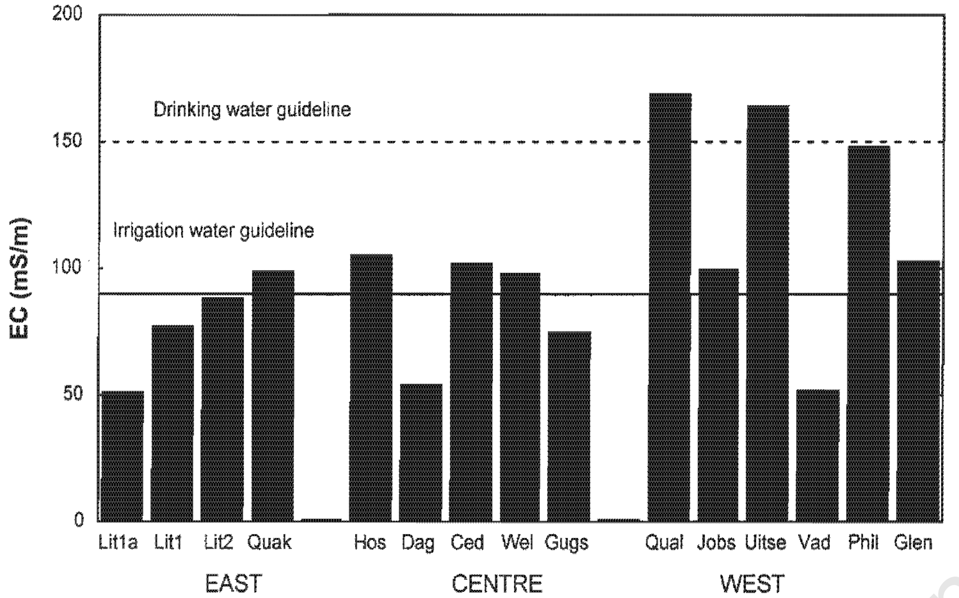


Figure 3.13: *Electrical conductivity levels of aquifer waters in terms of the DWAF (1999) guidelines for drinking water. The concentration should not exceed 150 mS/m for drinking water and 90 mS/m for irrigation water.*

3.4.2.7 Hardness as $CaCO_3$

To the general public hardness refers to the way water behaves when it is boiled or when soap is added to it. Calcium, magnesium, and other less abundant ions in hard water react with soap to form insoluble compounds. In practical terms, soap is wasted since it will not cleanse or lather until the offending ions are precipitated. Heating hard water (in a boiler, for instance) results in precipitation of a coating of calcium and magnesium carbonates, calcium sulphate, and other dissolved compounds. Thus hardness is a rather vague term referring to the overall effect of several dissolved constituents (Brownlow, 1994).

Contrary to the regular trend perceived so far, the hardness levels of the sampled waters are higher in the eastern region compared to the centre and west. Figure 3.14 shows high values for hardness, which indicate that the water is probably not suitable for domestic use without prior treatment because it is too hard, especially in the east. Again, the primary ion responsible for this hardness is calcium, which was discussed in Section 3.4.2.3. Generally, in Khayelitsha (east) this water cannot be utilised directly for domestic purposes, although it can be used for human consumption. However, in places such as Philippi this water is suitable for domestic use without prior treatment, although on average this water barely qualifies for domestic suitability. The waters requiring no treatment before use are JOBS, VAD and GLEN. Hardness is commensurate with high Ca concentrations and is an indication of possibly more calcareous material in the Khayelitsha area than in Philippi.

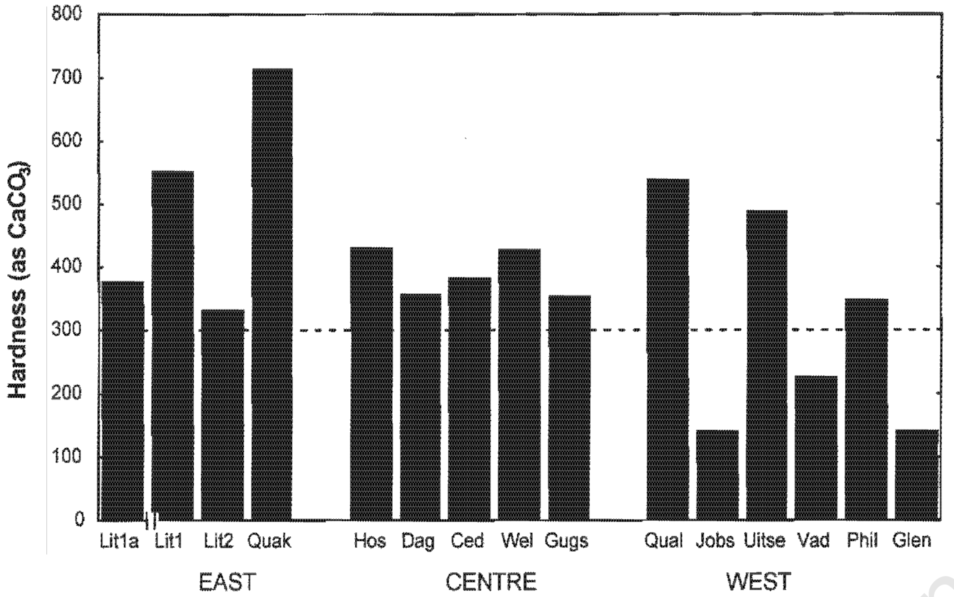


Figure 3.14: *Hardness (as $CaCO_3$) levels of aquifer waters in terms of the DWAF (1999) guidelines for domestic water. The concentration should not exceed 300 mg/L.*

3.4.2.8 Other problems

The pH of the aquifer waters (Table 3.1) is within the guideline levels (6.5 to 8.5) for domestic water. This is because for this aquifer water samples there are no extreme ion concentrations indicating direct contamination or geochemical processes such as pyrite oxidation.

Microbiological indicators for the aquifer waters, however, give a different portrayal (Table 3.3). The DWAF target guideline range for faecal coliform is zero, where there is negligible risk of microbial infection. In the range between 0 and 10 counts/100 ml there is a slight risk of microbial infection from continuous exposure, but occasional or short term exposure is expected to have negligible effects. In Table 3.3 four samples are within the target guideline for drinking water (WEL, GUG, VAD and HOS). The rest are above the 20/100 ml barrier that is an alert signal for a significant and increasing risk of infectious disease transmission from continuous exposure. Consequently, on the basis of the target guideline for faecal coliform, only water from WEL, GUG, VAD and HOS can be used as safe drinking water. However, the rest of the sample waters can be used for irrigation as discussed in section 3.4.3.

Table 3.3: *Microbiological water quality testing of Cape Flats aquifer water samples.*

Sample	Faecal Coliform / 100 ml	*E. coli* / 100 ml
QUAL	28	22
PHIL	50	20
CED	80	80
GLEN	380	340
WEL	<10	<10
HOS	<10	<10
GUG	<10	<10
VAD	<10	<10

3.4.3 Irrigation suitability

Of the three agricultural water uses (including livestock watering and freshwater aquaculture), irrigation is the most visible in the public eye since it accounts for almost 50% of the water used in South Africa, and is expected to remain the major water user for the foreseeable future. The climatic conditions in South Africa are such that irrigation is a viable option for many farmers. With a high evaporative demand in many areas, a highly variable rainfall pattern and low annual rainfall, it is understandable that full scale and supplementary irrigation has always been in the spotlight as a means to increase and stabilise food and fibre production (DWAF, 1993b).

Ayers and Westcot (1985) have defined guidelines for the evaluation of water samples in terms of their use in irrigation. The guidelines are given Table 3.4.

Table 3.5 shows the suggested maximum concentrations of some trace elements in irrigation water. The maximum concentration is based on a water application rate which is consistent with good irrigation practice of 1000 mm/yr. (Azzie, 1998). Trace elements occur in almost all water supplies but at very low concentrations, usually less than a few mg/L, with most less than 0.1 mg/L. Many are essential, in small quantities, for plant growth (Fe, Mn, Mo, Zn), and not all trace elements are toxic.

3.4.3.1 Salinity

Irrigation water salinity (EC) can severely influence crop tolerance and yield potential. Not all crops respond to salinity in a similar manner. Some crops can produce acceptable yields at much greater soil salinity than others. This is because some are better able to make the needed osmotic adjustment enabling them to extract more water from saline soil (Ayers and Westcot, 1985).

Table 3.4: *Guidelines for evaluating water quality for irrigation purposes (from Ayers and Westcot 1985).*

Potential irrigation problem		Degree of Restriction on Use		
		None	**Slight to moderate**	**Severe**
Salinity				
EC	mS/m	< 70	70 - 300	> 300
Infiltration				
SAR=0-3 and EC =	mmol$_c$/L	> 70	70 - 20	< 20
SAR=3-6 and EC =		> 120	120 - 30	< 30
SAR=6-12and EC =		> 190	190 - 50	< 50
SAR=12-20 and EC =		> 290	290 - 130	< 130
SAR=20-40 and EC =		> 500	500 - 290	< 290
Specific Ion Toxicity				
Sodium (Na)				
Surface irrigation	SAR	< 3	3 - 9	> 9
Sprinkler irrigation	mmol$_c$/L	< 3	> 3	
Chloride (Cl)				
Surface irrigation	mmol$_c$/L	< 4	4 - 10	10
Surface irrigation	mmol$_c$/L	< 3	> 3	
Boron (B)	mg/L	< 0.7	0.7 - 3.0	> 3.0
Trace Elements (see ***Table 3.5***)				
Miscellaneous Effects				
Nitrogen(NO_3 - N)	mg/L	< 5	5 - 30	> 30
Bicarbonate (HCO_3)	mmol$_c$/L	< 1.5	1.5 - 8.5	> 8.5
pH		Normal range 6.5 - 8.4		

The primary crops grown in the vicinity of the Cape Flats aquifer include tomato, spinach, potato, onion and carrot. In terms of the susceptibility of crops as defined by Ayers and Westcot (1985) a full yield potential should be obtainable for most of the primary crops, particularly with the water from the east and central regions, since most waters here are <100mS/m (Figure 3.13). Carrot and onion are the most sensitive crops and a 100% potential yield would only be obtainable with waters from LIT1A, VAD and DAG (Figure 3.13) because they fall below the 50 mS/m barrier for 100% yield. However, according to Ayers and Westcott (1985) a 90% yield potential would be achievable with all the waters from the east and central regions. Potato, spinach and tomato are less sensitive and can be achievable at 100% yield potential with most sample waters.

Table 3.5: Recommended maximum concentrations of selected trace elements in irrigation water (from Ayers and Westcot 1985).

Element	Recommended max conc. (mg/L)	Remarks
Al	5.0	Can cause non-productivity in acid soils (pH<5.5), but alkaline soils at pH>7.0 will precipitate the ion and eliminate any toxicity.
Cr	0.10	Not generally recognised as an essential growth element. Conservative limits recommended due to a lack of knowledge on its toxicity to plants.
Cu	0.20	Toxic to a number of plants at 0.1 to 1.0 mg/L in nutrient solutions.
F	1.0	Inactivated by neutral and alkaline soils.
Fe	5.0	Not toxic to plants in aerated soils, but can contribute to soil acidification and loss of availability of essential phosphorus and molybdenum. Overhead sprinkling may result in unsightly deposits on plants, equipment and buildings.
Li	2.5	Tolerated by most crops up to 5 mg/L, mobile in soil. Toxic to citrus at low concentrations (<0.075 mg/L).
Mn	0.20	Toxic to a number of crops at a few tenths to a few mg/L, but usually only in acid soils.
Ni	0.20	Toxic to a number of plants at 0.5 mg/L to 1.0 mg/L, reduced toxicity at neutral or alkaline pH.
Zn	2.0	Toxic to many plants at varying concentrations, reduced toxicity at pH>6.0 and in fine textured or organic soils.

Samples QUAL and UITSE from the west region have the highest salinity values (169 and 164 mS/m, respectively) and only tomato can be obtainable at 100% yield potential with such salinity. At 75% yield potential even the most sensitive crop currently grown on the Cape Flats aquifer would be able to use the water from all the sampled sites. All the waters from east and central region and some from the west can be used without loss of potential yield for tomato and spinach, since their limits are 170 and 130 mS/cm, respectively. According to the classification in Table 3.6 (Classification of water in terms of its fitness for use for irrigation) the EC values in Table 3.1 and Figure 3.13 could be classified for most of the water samples as Class II. This means that the water can be used for all but the most sensitive crops and soils, with no reduction in yield or the need for special management practices. Table 3.6 classifies water in terms of its fitness for irrigation use, and suggests that if water may not be suitable for one crop it can be fit for another.

Table 3.6: *Classification of water in terms of its fitness for use for irrigation (after DWAF 1993b). The class number is linked to percentage yield.*

Class	Fitness for use
Class I	The water can be used for even the most sensitive crops and soils without any reduction in yield or the need for special management practices.
Class II	The water can be used for all but the most sensitive crops and soils, with no reduction in yield or the need for special management practices.
Class III	Some yield loss is experienced even though special management practices are implemented, but a reasonable profit is realised.
Class IV	Yield losses and/or the need for special management practices are such that the economic viability of irrigation is questionable. Certain crops can, however, still be produced in special circumstances or by using special management practices.

3.4.3.2 Sodium

Irrigating with sodic (i.e. sodium-rich) water induces soil sodicity. Sodium affected soils exhibit impaired soil physical conditions. The most prominent impairment to soil physical conditions under irrigation is reduced soil permeability, which could, in turn, result in the soil not being able to absorb sufficient water to supply crop water requirements. The sodium adsorption ratio (SAR) is an index of the potential of a given irrigation water to induce sodic soil conditions. It is calculated from the concentrations of sodium and magnesium in water and gives an indication of the level at which soil exchangeable sodium percentage will stabilise after prolonged irrigation with water (DWAF, 1993b). A target guideline for sodium in irrigation water as suggested by Ayers and Westcot (1985) is 0 – 3.0 mmol/L. A SAR <3 mmol/L should prevent sodium toxicity from developing in plants sensitive to sodium, provided that irrigation water is applied so that it limits sodium uptake to that through the roots. SAR was calculated using the following equation:

$$SAR = Na / [(Ca+Mg)/2]^{0.5}$$

Four water samples are found to be above the SAR target guideline of 3.0 mmol/L (QUAL, JOB, HOS and PHIL). Figure 3.15 shows that sample waters from the east and central regions of the Cape Flats aquifer meet the SAR target guideline, and three from the west. The three samples that are above the 3.0 mmol/L guideline in Figure 3.15 represent the lower third of the SAR range to which moderate restrictions on use of the water are attached by internationally accepted guidelines. Sample QUAL has the highest SAR value of 5.55 mmol/L, which falls in the middle third of the SAR range (Table 3.4) to which moderate restrictions on use are attached by internationally accepted guidelines (DWAF, 1993b). This is provided that irrigation water is applied to the soil surface (i.e. wetting of crop foliage is excluded) limiting sodium uptake to that through the roots. In fact, according to the guidelines none of the sample waters have a severe restriction imposed on its use because of exceeding the range.

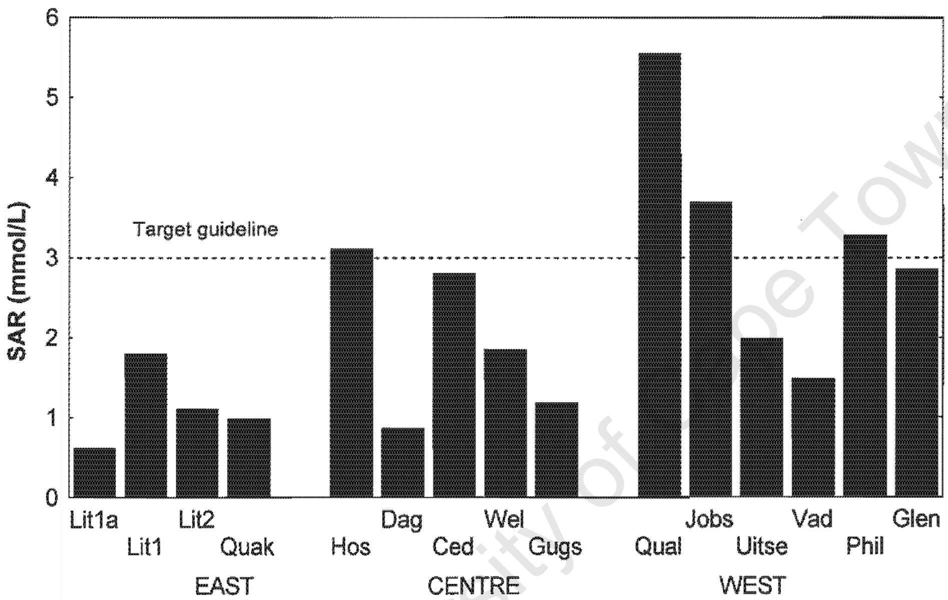


Figure 3.15: *Sodium adsorption ratio concentration of aquifer waters in terms of the DWAF (1993b) guidelines for irrigation water. A SAR < 3 should prevent sodium toxicity in plants sensitive to sodium.*

3.4.3.3 pH

Since soil is more strongly buffered against changes in pH than water, irrigation water will cause soil pH to change only slowly, and is seldom a problem itself. Provided the pH of water is within range of 6.5 to 8.4, it presents no cause for concern (Ayers and Westcot, 1985). A pH outside this range may be an indication of other problems and the need for further evaluation. The pH values in Table 3.7 are all within the recommended range except sample JOBS which has a pH (6.3) outside the range of 6.5-8.5.

3.4.3.4 Other indicators

In Table 3.7 LIT1A, DAG and VAD have low EC values, which indicate no restriction on use of the waters for irrigation. The rest fall within the slight to moderate restriction on use. For SAR values, LIT1A, DAG and JOBS require slight to moderate restriction on use of the water, while the rest indicate no restriction on use. There is no shading for all of the boron and nitrate samples, indicating no restriction in terms of boron and nitrate.

3.4.3.5 Trace elements and their potential toxicity

Fertile soils supply plants with all of the trace elements essential for growth (Fe, Mn, Zn, B, Cu, Mo and Cl). Deficiencies can occur either because plants or soils contain extremely low concentrations of these elements or the elements are in insoluble forms. Also, many trace elements can reach concentrations that are toxic to plants and micro-organisms (for example, Hg, Pb, Cd, Cu, Ni and Co).

Modern analytical methods (as used in this study) can detect most of the natural elements in soils at some level of concentration. If elemental concentrations are greatly in excess of those expected for a particular soil type, this may be a sign of pollution from human activity or accumulation from natural biogeochemical processes (Mcbride, 1994).

Most trace elements accumulate in the soil in a process that tends to be irreversible. Therefore, repeated applications of amounts in excess of plant needs eventually contaminate a soil and render it non-productive or the plant product unusable. Although plants do take up trace elements, the uptake is normally too small to reduce appreciably the trace element concentration in the soil in any reasonable time period (Ayers and Westcot, 1985). The trace element concentrations in the Cape Flats aquifer waters were evaluated in terms of whether they exceed a recommended maximum concentration defined by Ayers and Westcot (1985). The results of trace elements analysed in Table 3.8 show that some elements at certain sites of the aquifer waters have concentrations above the recommended maximum concentrations that are in Table 3.5 (Cr: UITSE, VAD, GLEN; Mn: DAG; Ni: HOS, DAG, GLEN).

3.4.3.6 Dissolved organic carbon

The measure of the total concentration of organic solutes is the concentration of dissolved organic carbon (DOC), which is measured by converting all the organic material in solution to CO_2 and then measuring the CO_2 produced. Rainwater has DOC concentrations of about 0.5 to 1.5 mg/L. DOC concentrations in groundwaters are typically about 5 mg/L, in rivers and lakes they are typically about 2 to 10 mg/L with values up to 60 mg/L in rivers draining swamps and wetlands. Values in soil water can be as high as 260 mg/L (Drever, 1997).

DOC results in Table 3.1 show a range of DOC values for the aquifer waters between <1 and 43 mg/L. Like most constituents, the DOC concentrations are low in the eastern and central parts of the study area (<1 to 3.3 mg/L) compared to the western part (6 to 43 mg/L). The most likely reason for the high values in the western part can be attributed to the different land-use activities in the region. As mentioned earlier, the primary land-use activity in Philippi is agriculture. The relatively high DOC concentrations can be directly attributed to the intensive use of fertilisers in the area.

Table 3.7: *Assessment of the Cape Flats aquifer water for irrigation purposes. The darkly shaded areas indicate severe restrictions on use, lightly shaded areas indicate slight to moderate restrictions on use, and the non-shaded areas indicate no restrictions on use.*

		EAST				CENTRE				
		Lit1a	**Lit1**	**Lit2**	**Quak**	**Hos**	**Dag**	**Ced**	**Wel**	**Gugs**
Salinity										
EC	mS/m	51.1	77.7	88.4	99.0	105	54.0	102	97.8	75
Infiltration										
SAR	mmol/L	0.61	1.79	1.10	0.98	3.11	0.85	2.80	1.85	1.17
Specific Ion Toxicity										
Sodium: Surface	SAR	0.61	1.79	1.10	0.98	3.11	0.85	2.80	1.85	1.17
Sprinkler	$mmol_c/L$	0.89	2.38	1.09	1.45	3.88	0.96	3.59	2.5	1.47
Chloride: Surface	$mmol_c/L$	0.75	2.02	0.9	1.34	4.26	1.35	4.72	2.79	2.79
Sprinkler	$mmol_c/L$	0.75	2.02	0.9	1.34	4.26	1.35	4.72	2.79	2.79
Boron	mg/L	0.1	0.11	0.06	0.1	0.09	0.04	0.07	0.06	0.09
Miscellaneous Effects										
Nitrogen (NO_3 - N)	mg/L	0.61	1.79	1.10	0.98	3.11	0.85	2.80	1.85	1.17
Bicarbonate (HCO_3)	$mmol_c/L$	3.77	5.5	3.31	7.1	4.3	3.6	3.83	4.26	3.5
pH		7.5	7.4	7.7	7.1	7.3	7.3	7.3	7.3	7.2

Table 3.7: (continued)

		WEST					
		Qual	**Jobs**	**Uitse**	**Vad**	**Phil**	**Glen**
Salinity							
EC	mS/m	169	99.4	164	52	147	102
Infiltration							
SAR	mmol/L	5.55	3.69	1.98	1.48	3.28	2.85
Specific Ion Toxicity							
Sodium: Surface	SAR	5.55	3.69	1.98	1.48	3.28	2.85
Sprinkler	$mmol_c/L$	8.79	3.64	3.22	1.71	5.39	4.34
Chloride: Surface	$mmol_c/L$	11.4	4.45	4.16	1.99	6.45	5.3
Sprinkler	$mmol_c/L$	11.4	4.45	4.16	1.99	6.45	5.3
Boron	mg/L	0.2	0.09	0.01	0.01	0.08	0.03
Miscellaneous Effects							
Nitrogen (NO_3 - N)	mg/L	5.55	3.69	1.98	1.48	3.28	2.85
Bicarbonate (HCO_3)	$mmol_c/L$	5.4	1.4	4.87	2.26	3.47	1.39
pH		7.5	6.3	7.6	6.5	7.5	6.8

Table 3.8: *Selected trace elements in Cape Flats aquifer waters (µg/L).*

	EAST				CENTRE							WEST			
µg/L	Lit1a	Lit1	Lit2	Quak	Hos	Dag	Ced	Wel	Gugs	Qual	Jobs	Uitse	Vad	Phil	Glen
Al	14.9	96.3	371.0	78.2	417.0	11.3	11.4	132.9	77.7	78.2	1409.5	131.5	150.1	183.5	289.3
Cr	<0.1	<0.1	<0.1	9.1	<0.1	<0.1	58.2	<0.1	<0.1	9.1	<0.1	122.5	108.0	82.6	120.2
Mn	3.6	152.2	2.6	22.5	90.9	247.5	56.6	73.1	16.0	22.5	21.7	15.8	80.5	25.3	95.3
Fe	101.1	129.1	60.7	50.0	63.0	97.0	44.1	1063.9	50.0	74.0	78.9	159.3	197.3	358.2	200.0
Ni	11.4	10.5	7.0	50.2	1686.3	434.3	4.7	19.4	21.2	50.2	10.0	41.9	60.0	33.3	301.3
Cu	72.2	14.2	36.2	126.7	15.4	9.8	17.2	49.7	41.8	126.7	57.0	105.5	100.0	70.9	120.5
Li	22.1	9.0	41.4	47.1	12.9	4.9	10.2	6.8	35	47.1	2.6	40.9	45.5	45.8	52.3
Zn	412.4	70.7	106.5	353.8	47.3	106.2	297.8	975.4	1502	353.8	136.2	99.0	145.0	302.2	258.0

3.4.3.7 Microbiology

Faecal coliforms, and more specifically *Escherichia coli*, are the most common bacterial indicators of faecal pollution, and hence of the possible presence of faecally-associated pathogens in domestic water supplies (DWAF, 1993a). All the samples collected were within the 1000 counts/100 ml guideline level for domestic purposes. The guideline for irrigation water recommends levels that are typical of river and stream levels. The stringent levels recommended are < 1000 counts/100 ml (Adele Fortune, *pers. comm.* from the Scientific Services laboratory of the Cape Metropolitan Council).

Numerous physical, physicochemical and biochemical-biological factors influence the rate of die-off or disappearance of bacteria after discharge into water. Among the most significant are the organism and its physiological state, sunlight, temperature, pH, salinity, competition, predation, algae, nutrient deficiencies, toxic substances and organism density in the discharge. Extremes in pH, elevated temperatures and solar radiation promote microbial decay, while elevated nutrient concentrations and lower temperatures promote microbial survival (DWAF, 1993a).

There is a pattern that could lead to identifying the source of higher bacteria levels observed in CED, QUAL, GLEN and PHIL (Table 3.3), because three of these 4 samples with detectable amounts of bacteria are from the same region (Philippi). QUAL, GLEN and PHIL are from the western part of the study area but CED is from the central part. On the other hand, of WEL, GUG, HOS and VAD (with no detectable amounts) all are from the central part, while VAD is from the western part. A possible reason for the emergence of sample VAD in the adulterated group is that this sample was collected from a borehole in Philippi that had not been purged to obtain representative groundwater. Nevertheless, the higher bacteria levels in the west are not of concern since the results show that it is fit for irrigation, and because the groundwater in this area is currently used only for irrigation. A high nutrient concentration in Philippi, as a result of fertiliser application, could be leading to the higher bacteria levels.

3.4.4 Stable isotopes of oxygen and hydrogen

Isotope ratios for oxygen and hydrogen have been determined for Cape Flats waters. The naturally occurring stable isotopes, hydrogen (H), and Deuterium (D), oxygen-16 (^{16}O) and oxygen-18 (^{18}O) are useful tools in hydrogeological studies. These may provide a signature to a particular water type, identify the occurrence of mixing water types and provide information about the age, source and conditions of groundwater recharge (Lloyd and Heathcote, 1985). More review on isotope ratios, physical processes and fractionation has been discussed in Section 2.5.3.

Water with an isotope composition which plots on the meteoric line is assumed to have originated from the atmosphere and to be unaffected by other isotope fractionating processes. Evaporation from open water and exchange with rocks are two of the more commonly observed processes causing deviations from the meteoric water line (Domenico and Schwartz, 1990). In most cases, these isotope processes affect the relationship between $\delta^{18}O$ and δD in a unique way, so the positions of the data points on a graph of δD vs. $\delta^{18}O$ can be used to identify the process. Isotope data for the Cape Flats aquifer was plotted, along with the local meteoric water line, to determine the controls on isotope fractionation (Figure 3.16).

Most of the points in Figure 3.16 plot close to the meteoric water line. Figure 2.1 illustrates the general trends for deviations from the meteoric water line for a range of fractionation processes. Evaporation from an open water body causes enrichment in the heavier isotopes such that the isotope composition of the water follows an "evaporation line". All water samples seem to follow this trend. The isotope ratios of the surface water appear to have shifted upwards along the meteoric water line. The isotope ratios are normal and expected for the rainfall in the semi-arid climate and the upward shift is probably due to evaporation of the water. It is also possible that local meteoric conditions do not fit ideally to the global isotope pattern, and the sample compositions may deviate slightly from a meteoric water line.

Analyses of δD and $\delta^{18}O$ can also be used to identify the probable source of underground water. If the isotope composition of groundwater plots close to the meteoric water line, in a position similar to that of present-day precipitation in the same region, the water is almost certainly meteoric (Drever, 1997). When precipitation infiltrates to feed groundwater, mixing in the unsaturated zone smoothes the isotope variations, so water in the saturated zone has a composition corresponding to the mean isotope composition of infiltration in the area. This may differ slightly from the mean isotope composition of precipitation due to the fact that not all precipitation during the year infiltrates in the same proportion (Brown, 1973).

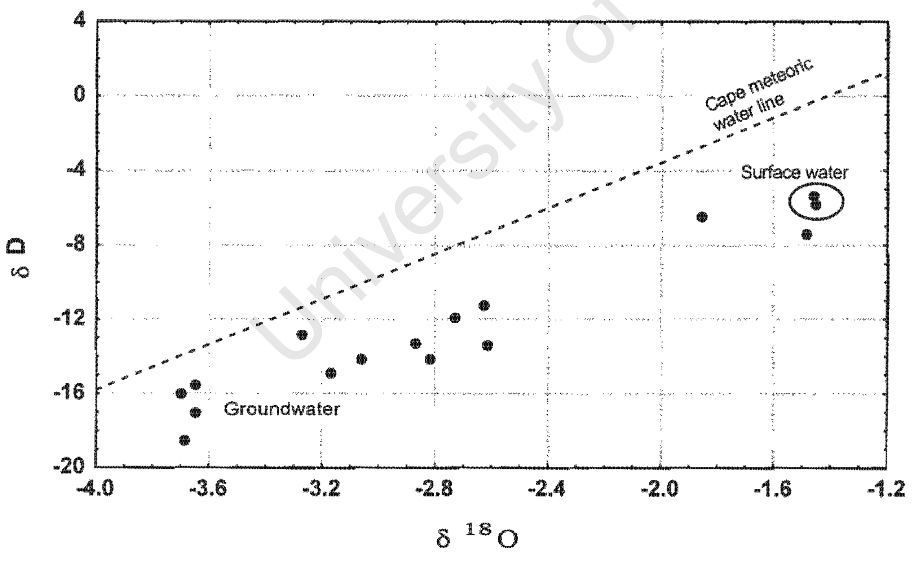


Figure 3.16: *Environmental isotopes of oxygen and hydrogen in the Cape Flats aquifer waters.*

Groundwater recharged by seepage from surface waters, such as rivers or lakes, should reflect the isotope signature of the surface water body. For example, a river may collect water that originates at higher altitudes and is depleted in heavy isotopes, while seepage from surface waters that have been evaporated will be enriched in heavy isotopes.

The groundwater samples from the Cape Flats are depleted, rather than enriched in heavy isotopes. They lie near the meteoric water line, and so are expected to be recharged by rainfall that has not undergone evaporation in an open water body. Vandoolaeghe (1989) confirms that the Cape Flats aquifer has favourable storage conditions and that evidence suggests that the effective porosity of the aquifer, more in particular the Springfonteyn sands geological unit, is higher than generally accepted. Still, it is easy to derive accurate conclusions about the origin of groundwater recharge, because the information on the isotope signature of the local rainfall is available. The different groundwater samples plot near different sections of the meteoric water line and may have been recharged by different rainfall events, or some of the samples may contain a greater component of deeper groundwater from a different recharge source.

The δD values for the groundwater samples are relatively steady, but there is some variation in the ^{18}O data. According to Cavé (1997) this is typical of waters that have undergone isotope exchange with minerals containing oxygen. The size of the "oxygen shift" away from meteoric water line is proportional to the difference in original $\delta^{18}O$ between the water and the rock, the temperature, and the time of contact, and inversely proportional to the water-rock ratio (Domenico and Schwartz, 1990). Also the greater oxygen shift for the groundwater samples on the extremes could mean that these are older waters, which could support the theory that older groundwater, which has had a longer equilibration period with the aquifer minerals, has a contribution to the composition of these samples. The analytical uncertainty associated with measurement of $\delta^{18}O$, however, is greater than that of δD and should also be taken into account when interpreting shifts in $\delta^{18}O$ data.

3.5 Conclusions

This study indicates that the widespread urbanisation in the Greater Cape Town Metropolitan area has not contaminated the aquifer as severely as was expected. The concentration levels of analysed constituents indicate that some areas are more or less pristine and others are affected by agricultural land-use.

Although all the samples displayed near neutral pH (6.3 to 7.6), there was much variation within the Cape Flats area. Generally, samples from the western part of the study area have EC levels in excess of 100 mS/m. Samples taken from the central and eastern parts generally showed conductivities below 100 mS/cm. Calcium concentrations were considerably higher in the east compared to the west, which means that the water from this area would require water softening treatment such as ion exchange prior to domestic use.

Groundwater from the different areas was suitable for different purposes. High sodium and chloride values (particularly in the west) denote that the groundwater can only be utilised with slight to moderate degree of restriction for irrigation, while groundwater from the east requires none to slight restriction on irrigation use. However, Na and Cl levels meet the DWAF standards for drinking water in most areas. High Ca concentrations in the waters from the east and central parts of the study area do not meet the DWAF guidelines for domestic purposes because of the water hardness. Despite the high Ca levels the groundwater would be suitable for drinking purposes.

Water from Philippi (west) has high concentration for most ions because of Philippi's predominant agricultural land-use. High potassium and nitrate concentrations are a conceivably direct consequence of fertiliser application in this area due to infiltration into the aquifer. Consequently, from this assessment it has been found that groundwater from the Cape Flats aquifer is not suitable for all purposes, in all areas. Rather, different regions contain groundwater than can be used for one purpose and not the other (for example, irrigation and not domestic use).

Other pollutants commonly found in urban areas such as heavy metals were found in very low concentrations. Part of the reason for absence of contaminants in most sampled areas is that the more hazardous runoff enters the paved and developed sewerage systems. This partly ensures that hazardous runoff does not infiltrate into the aquifer, as infiltration is the dominant runoff process in sand environments.

The aquifer remains highly susceptible to groundwater contamination. Currently groundwater abstraction does not occur within any of the informal settlements and the greater pollution risk is where increasing use is being made of shallow wellpoints for garden irrigation.

4 Geochemical characterisation of groundwater from the Cape Flats aquifer

4.1 Introduction

Extensive analyses covering a wide range of analytical techniques were conducted on the Cape Flats groundwater, followed by modelling using both MINTEQA2 and PHREECQ software to determine ion speciation and saturation indices. This chapter presents and describes how the software has been used to better understand the geochemical nature and origin of the water. Considerations relating to water quality and use were dealt with in Chapter 3.

4.2 Ion speciation

Ure and Davidson (1995) define speciation as either "the process of identifying and quantifying the different and defined species, forms or phases present in a material"; or "the description of the amounts and kinds of these species, forms or phases present". Ionic speciation was modelled in this study in order to characterise the most important forms of the elements present in the water bodies. This information was then used to understand the transformations between forms that could occur, and to infer from this the likely environmental consequences.

The analytical data for all water samples was modelled using the computer program MINTEQA2. This is a geochemical speciation model for dilute aqueous systems. It is complemented by PRODEFA2, which is an interactive program used to create the input which MINTEQA2 models. MINTEQA2 is based on equilibrium thermodynamics and calculates the equilibrium composition of dilute aqueous systems between soluble, adsorbed and gas phases in dilute aqueous systems. It can also be used to calculate the mass distribution between dissolved, adsorbed, and multiple solid phases under a variety of environmental conditions, such as pH, ionic strength, temperature and redox conditions. The program also includes an extensive database, which includes thermodynamic data for soluble complexes, mineral solubilities, gas solubilities and redox couples (Allison *et al.*, 1991).

Input to the model required the total measured concentrations of constituents in the aquifer water samples in mg/L. The pH and temperature of the samples, at which analyses were conducted, were also entered into the model. The Davies equation was used to compute the activity coefficients. This equation is an extension of the Debye-Huckel equation and was preferred because only the ionic strength of the medium and the charge on the species are required to calculate the activity coefficients (Lumsdon and Evans, 1995). Iron was assumed to be present as Fe^{3+}. Similarly, manganese was entered into the program as Mn^{2+}. The relative distributions of dissolved and adsorbed ionic species, within each of the water samples, are presented in the appendix.

4.3 Mineral saturation indices

The saturation indices (S.I.) give an indication of the extent to which mineral dissolution and/or precipitation reactions are likely to influence the composition of the water. A positive saturation index implies that the water is supersaturated with respect to a particular mineral phase, and therefore, that mineral could be expected to precipitate out of solution given a set of suitable conditions. A saturation index of zero implies that the water has a composition consistent with equilibrium with a particular mineral phase and that the mineral in question should therefore neither precipitate from nor dissolve in the water. A negative saturation index implies that the water is undersaturated with respect to a particular mineral phase, and therefore, that mineral will dissolve if brought into contact with water of this composition. The concept therefore represents a powerful tool for the geochemical interpretation of water quality.

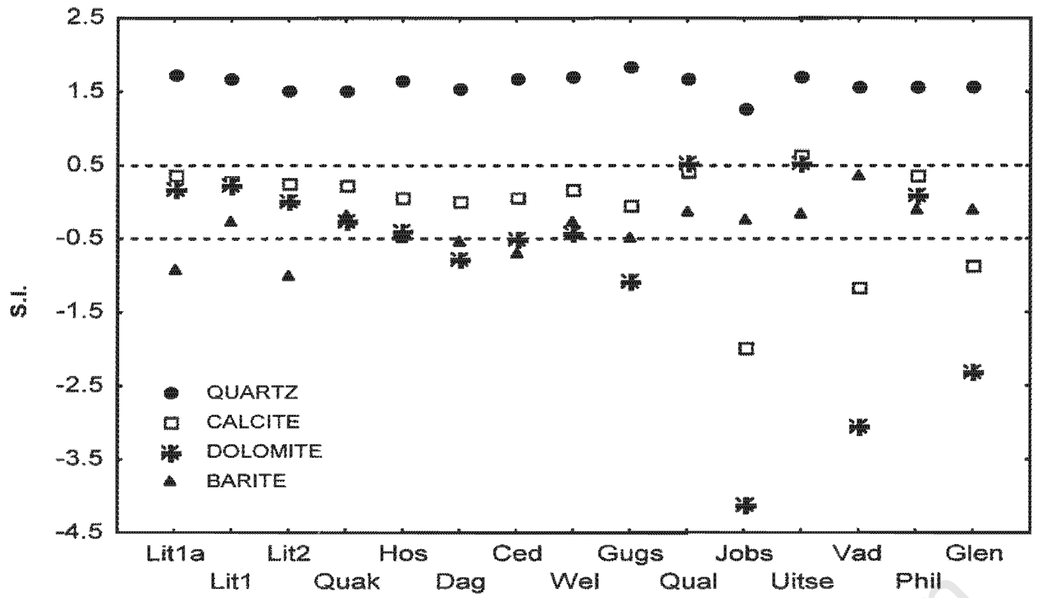
The saturation indices of all the potential minerals were calculated by MINTEQA2 using the formula:

$$SI = \log (IAP/K_{eq})$$

Where, IAP = ion activity product and K_{eq} = equilibrium constant.

Carbonate alkalinity was specified as inorganic carbon. The saturation indices of only those minerals likely to affect the potential of the water for domestic use are presented in Figure 4.1.

There is some uncertainty in the saturation indices for the carbonate minerals. For the most part, except in waters with relatively high sulphate concentrations, dolomite appears to be near saturation, if an uncertainty of ± 0.5 units is accepted. A large proportion of the aquifer waters sampled were found to be undersaturated with respect to the carbonate minerals, specifically calcite, dolomite and magnesite. Only a few samples are undersaturated with respect to barite (LIT1A, LIT2 and CED) and all are undersaturated with respect to other sulphate minerals, such as gypsum and celestite. Quartz is supersaturated consistently for all the samples, while strontianite and celestite are also undersaturated for all the samples. Very small Sr concentrations are the reason for such undersaturation in strontionite and celestite minerals. Except for samples LIT1 and QUAL, sepiolite is undersaturated. Many mineral saturation indices exhibit interesting relationships when considered for the collection of waters as a whole. These will be discussed in section 4.4. It can be noted that the saturation indices recorded for calcite are, for the most part, close to zero and in three cases undersaturated. Therefore, calcite is more likely to dissolve than precipitate. Complete S.I. values are given in Table 4.1.



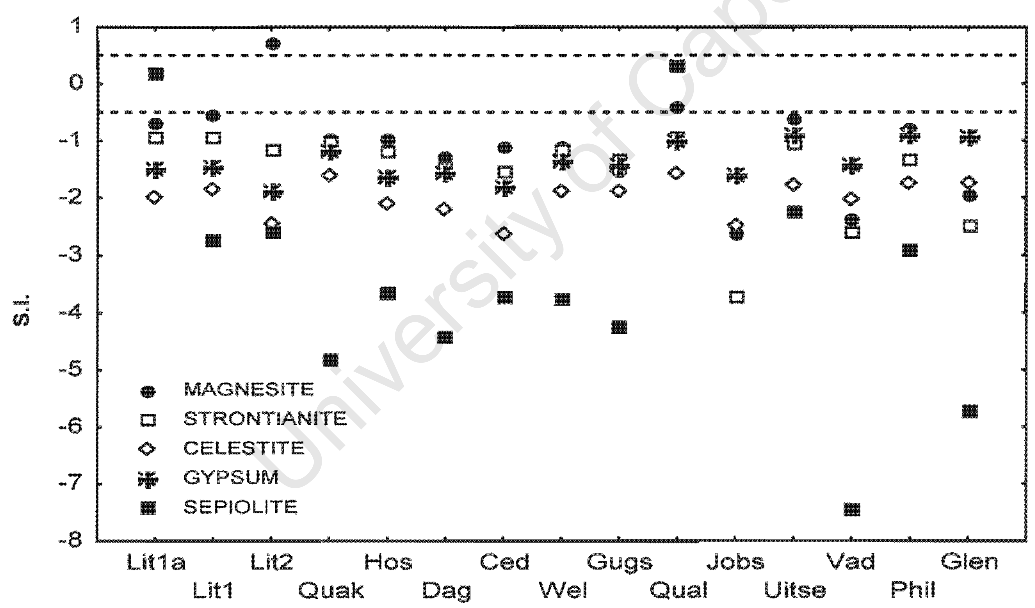


Figure 4.1: *Saturation indices for quartz, calcite, dolomite, barite, magnesite, strontianite, celestite, gypsum and sepiolite. The dotted lines between 0.5 and -0.5 show a neutral region (no saturation or undersaturation) to compensate for errors and assumptions made in the calculations.*

Table 4.1: *Saturation indices calculated, using MINTEQA2, for water samples from the Cape Flats aquifer.*

		EAST				CENTRE				
Mineral	**Chemical Formula**	**Lit1 a**	**Lit1**	**Lit2**	**Quak**	**Hos**	**Dag**	**Ced**	**Wel**	**Gugs**
Quartz	SiO_2	1.74	1.69	1.53	1.53	1.66	1.55	1.68	1.70	1.84
Calcite	$CaCO_3$	0.37	0.28	0.25	0.22	0.08	0.00	0.07	0.17	-0.03
Dolomite	$CaMg(CO_3)_2$	0.19	0.23	0.02	-0.25	-0.40	-0.77	-0.52	-0.43	-1.07
Magnesite	$MgCO_3$	-0.68	-0.55	0.73	-0.97	-0.98	-1.27	-1.10	-1.10	-1.54
Strontianite	$SrCO_3$	-0.95	-0.93	-1.16	-1.01	-1.19	-1.45	-1.54	-1.16	-1.33
Barite	$BaSO_4$	-0.93	-0.25	-1.00	-0.17	-0.48	-0.53	-0.69	-0.27	-0.47
Celestite	$SrSO_4$	-2.00	-1.85	-2.44	-1.61	-2.10	-2.21	-2.62	-1.87	-1.89
Gypsum	$CaSO_4.2H_2O$	-1.50	-1.45	-1.89	-1.19	-1.65	-1.56	-1.81	-1.35	-1.41
Sepiolite	$Mg_4Si_6O_{15}(OH)_2{\bullet}6H_2O$	0.20	-2.73	-2.58	-4.79	-3.65	-4.42	-3.71	-3.76	-4.23

Table 4.1: (continued)

		WEST					
Mineral	**Chemical Formula**	**Qual**	**Jobs**	**Uitse**	**Vad**	**Phil**	**Glen**
Quartz	SiO_2	1.68	1.28	1.71	1.58	1.58	1.58
Calcite	$CaCO_3$	0.41	-1.99	0.64	-1.17	0.37	-0.85
Dolomite	$CaMg(CO_3)_2$	0.52	-4.11	0.54	-3.05	0.09	-2.31
Magnesite	$MgCO_3$	-0.39	-2.62	-0.60	-2.38	-0.78	-1.96
Strontianite	$SrCO_3$	-0.94	-3.71	-1.05	-2.58	-1.31	-2.47
Barite	$BaSO_4$	-0.12	-0.24	-0.15	0.38	-0.11	-0.10
Celestite	$SrSO_4$	-1.55	-2.49	-1.79	-2.02	-1.75	-1.73
Gypsum	$CaSO_4{\bullet}2H_2O$	-1.01	-1.59	-0.91	-1.42	-0.88	-0.93
Sepiolite	$Mg_4Si_6O_{15}(OH)_2{\bullet}6H_2O$	0.32	-8.59	-2.25	-7.42	-2.90	-5.71

4.4 Geochemical interpretation

4.4.1 Solubility of minerals

None of the samples in Table 4.1 have calcite S.I. values that show supersaturation. All are <0.5 except UITSE (0.64). There were no calcite granules in the solutions, as calcite did not precipitate. Calcite is a common mineral that should be considered in almost all types of water-rock interactions. Studies of carbonate ground waters in Nordstrom and Munoz (1994) found that most of the waters were at or near saturation equilibrium for calcite, as the Cape Flats aquifer samples are also at or near saturation equilibrium (Figure 4.1 and Figure 4.2). The saturation indices for calcite from the Cape Flats aquifer are plotted as a function of pH in Figure 4.2. Within the error of the data, a clear indication of the solubility control is reflected by the saturation indices reaching the equilibrium value of 0 but not surpassing it by much (~0.5), compared to surpassing -1. Part of this could be explained by the fact that there is increased dissolution of calcite at higher partial pressures of CO_2 which, in turn, causes the pH, alkalinity, and calcium concentration to increase until solubility equilibrium with respect to calcite is reached (or just surpassed). So, as pH increases the S.I. values approach solubility equilibrium and (just) surpass it. Otherwise, if the pH of the solution is less than 7 (acidic) then $CaCO_3$ dissolution of CO_2 increases.

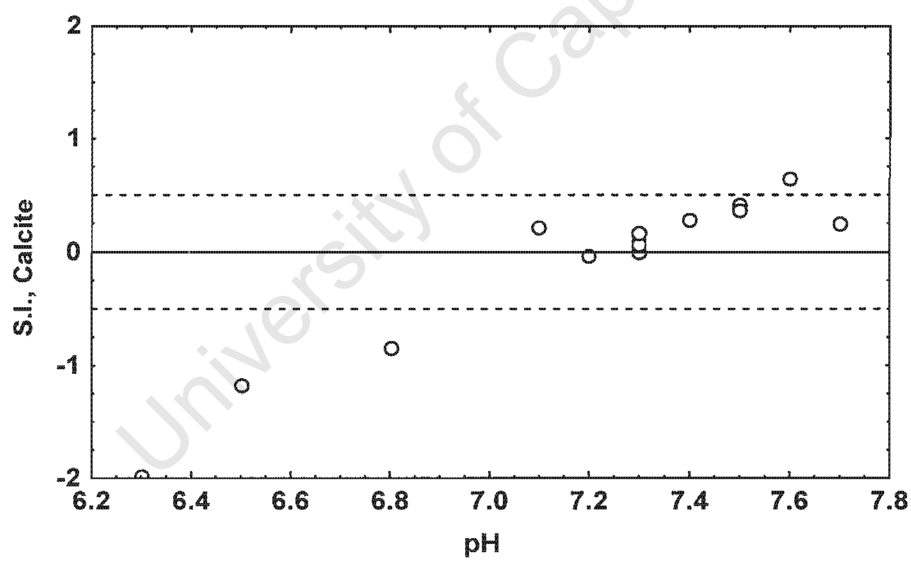


Figure 4.2: *Saturation indices for calcite plotted against pH.*

Additionally, CO_2 from the soil greatly increases the amount of $CaCO_3$ the water can dissolve. The amount of $CaCO_3$ dissolved per litre of percolating water (and hence the Ca^{2+} concentration in the water) depends on the initial CO_2 concentration and on the extent to which the CO_2 in the water can be replenished by exchanging with a gas phase. If CO_2 is not replenished (the system is *closed* to exchange of CO_2 gas), the amount of calcite that a water can dissolve is essentially limited by the amount of CO_2 present initially, since dissolution follows the equation:

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^-$$

If the system is open to CO_2, the CO_2 will be transferred from the gas phase to replace the CO_2 consumed by dissolution of calcite (Drever, 1997). In the case of the Cape Flats aquifer, the dissolution of calcite may not be limited by the availability of CO_2; more of calcite will dissolve because of the unconfined nature (open-system) of the aquifer.

The S.I. values for dolomite in Table 4.1 resemble that of calcite. Dolomite has a chemical formula $CaMg(CO_3)_2$ and a crystallographic structure similar to that of calcite. Also, Drever (1997) advises that the weathering of dolomite is closely analogous to that of calcite, except for that the rates are slower.

The S.I. values for quartz are all positive – showing supersaturation. Quartz is an important mineral in the Cape Flats aquifer because of the sandy nature of the aquifer. This means the water in the aquifer is in close contact with quartz, and the dissolution of quartz is a simple example of mineral-solution equilibrium. Drever (1997) presents this equilibrium (at pH values below 9) by the equation:

$$SiO_{2(quartz)} + 2H_2O \leftrightarrow H_4SiO_{4(aq)}$$

with an equilibrium constant $K_{eq} = 1 \times 10^{-4}$. Since the Cape Flats aquifer water is supersaturated then it must have a higher equilibrium constant. Generally, at higher pH values, the total dissolved silica concentrations are higher and the solubility equilibrium equation becomes more complicated.

4.4.2 Evolution of the aquifer water

In a study of the Madison limestone, a regional-scale aquifer system, Plummer *et al.* (1990) found that, during the evolution of the groundwater, calcite and dolomite reached saturation to supersaturation quickly, compared to anhydrite and celestite. Anhydrite and celestite tended to reach equilibrium in only the highest sulphate concentrations.

From Figure 4.1 it is apparent that during the evolution of the groundwater in the Cape Flats aquifer waters, calcite and dolomite mostly reached saturation to supersaturation and maintained that state, whereas celestite, strontianite and gypsum never reach equilibrium. S.I. values for celestite start at below -2 and rise never reach equilibrium. The reason for not reaching equilibrium is that the celestite elemental concentrations are very low. As discussed above, the samples from the west seem to have a high variation in S.I. values, and that is in line with the relatively high concentrations of constituents in the west.

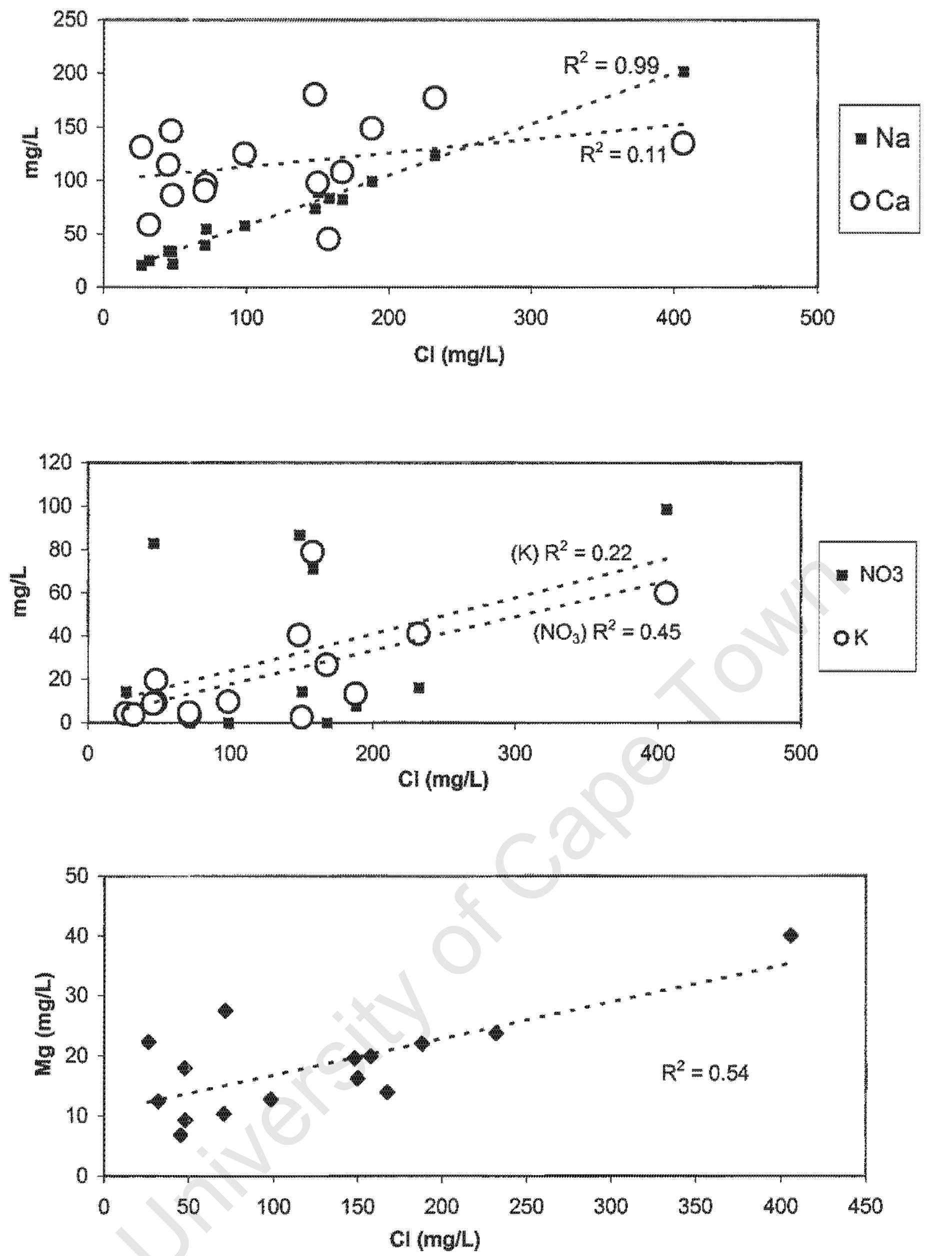


Figure 4.3: *Comparison of chloride concentration as a function of Na^+, Ca^{2+}, NO_3, K^+ and Mg^{2+}.*

A comparison of chloride and other major ions can indicate pollution if the ions do not plot on a straight line. In Figure 4.3 only Na plots on a straight line vs. Cl. Ca, K, Mg and nitrate do not show a good fit, especially Ca (r^2=0.11) and NO_3 (r^2=0.22). Mg and K have a weak correlation which may not be an indication of contamination because the trend does not level off at high Cl concentrations, but is rather spread out. Comparisons of this kind are commonly more useful with numerous data points. It is difficult to ascertain the trends with few sample points. Also, this technique works better if the samples were taken over a time period. That way it is easier to observe the changes with time. However, for the Cape Flats aquifer sample points we can assert that there is no contamination because of the good fit in

Figure 4.3. The data from the DWAF database in Chapter 1 also shows that there is no contamination in the sampled areas, although the data trends are similar.

4.4.3 Comparison with other ground waters

Table 4.2 shows how the Cape Flats aquifer water compares with water from another coastal aquifer on the west coast of South Africa, the Atlantis aquifer. The aquifer is similar to the Cape Flats aquifer because they are both primary sandy and unconfined coastal aquifers. The Atlantis aquifer, whose town is dependent on groundwater for water supply, is recharged during winter months and serves as a reliable source during long dry summers. Groundwater is extracted from the aquifer in well fields, treated in an ion-exchange water softening plant, distributed, utilised, collected, treated and artificially recharged together with urban stormwater runoff back into the aquifer. Maximum use is thus made of the water from the aquifer. With an idea of possibly utilising the Cape Flats aquifer water in a similar way to that of the Atlantis aquifer, it is appropriate to compare data from the two aquifers.

In Table 4.2 the Cape Flats aquifer water has higher values for Ca, K and hardness and lower values for the other constituents. Although the two aquifers are alike overall, the Cape Flats aquifer might have less sea influence because the Cl and Na concentrations (from sea salt) are lower. However, the higher K concentration in the Cape Flats aquifer is a possible consequence of fertilisers (from KNO_3) in the western region (Philippi). The DOC and N concentrations are about the same.

Also, groundwaters generally have higher dissolved mineral concentrations than surface waters because of the intimate contact between the CO_2-bearing water and rocks and soils in the ground and the length of time for dissolution.

Table 4.2: *Comparison of the Cape Flats aquifer waters with the mean ground water of another coastal aquifer (Source for Atlantis: CSIR).*

Constituent (mg/L)	Atlantis aquifer	Cape Flats aquifer
DOC	9.7	10.0
Ca^{2+}	101	116
Mg^{2+}	35	18
Na^{+}	153	69
K^{+}	6.7	22
SO_4^{2-}	109	89
Cl^{-}	257	126
NO_3^{-} as N	1.8	0.4
EC (mS/m)	127	99
Total hardness as $CaCO_3$	175	386

4.4.4 Geochemical processes affecting water quality

Water with a pH below 4.0 can dissolve and hold large amounts of aluminium. In contrast, at pH values between 4 and 9, the solubility of aluminium is usually less than 1 mg/L. The acid condition of the water below pH 4.0 allows it to react with silicate and other minerals and take into solution a large amount of various ions, indicated by the high specific conductance value for dissolved solids (Brownlow, 1994). The pH values of the Cape Flats aquifer samples are between 6.3 and 7.7, and are the reason for the absence of aluminium in the samples (Figure 3.8).

Subsurface waters tend to contain more dissolved material than river water because of their more intimate and longer contact with organic material and with soil and rock particles. Subsurface waters tend to be less well mixed and thus less homogenous than surface waters. Often there is a fairly direct relationship between the composition of a given subsurface water and its host rock or soil (Brownlow, 1994).

An even more detailed explanation for the composition of the Cape Flats aquifer water could be given by using knowledge of the mineralogy and chemistry of the Witzand and Langebaan formations, which constitute the aquifer. The Witzand formation consists of very fine to very coarse calcareous sands and has abundant small shells and shell fragments. These sands form an extensive system of parabolic, vegetation-bound coastal dunes all along the Cape Flats. The dominant anion in the Cape Flats aquifer waters, as is characteristic of subsurface waters of low mineral content associated with common rock types, is HCO_3^- for all types of host rock. The dominant cations are Na^+, Ca^{2+} and Mg^{2+}.

Often, strong anion-metal ion attraction is manifested as a tendency to form insoluble precipitates. Anions such as phosphate complex with Fe^{3+}. Phosphate bonds strongly with Fe^{3+}, resulting in the precipitation of the very insoluble solid, $FePO_4$ (McBride, 1994). None of the samples from the aquifer contained any measurable phosphate. The fact that phosphate anions complex with Fe^{3+} to form an insoluble solid could explain the absence of phosphate in the samples, because the samples were filtered through a 0.45 μm membrane prior to phosphate analyses by colourimetry. Since the analyses were for dissolved phosphate, the phosphate from the $FePO_4$ solid would not have been detected. Not coincidentally, there was no Fe detected in any of the samples: all the samples contained less than 0.01 mg/L of iron, measured by atomic absorption. Also, this could have been more likely due to pH being high enough for Fe to precipitate. For the same complexation reason, the $FePO_4$ complex may have rendered Fe unavailable in solution. So the solution was effectively deprived of dissolved iron and phosphate.

The precipitation of calcium phosphate could also be another explanation for the low phosphate concentrations (below detection limit). Since Ca concentrations in the samples are high, any phosphate in the solution could have complexed with Ca to form an insoluble solid which would have been filtered out, and therefore not detected.

4.5 Conclusions

The results of this study confirm that moderate quantities of chemical constituents are dissolved in most of the waters in the Cape Flats aquifer and therefore the water is to be utilised with caution. Comparisons were made with published guidelines in order to determine the potential use. Many of the sampled waters appear to be sufficiently suitable for irrigation use as their composition may have little effect on either crop yield or the physical properties of the soil in which the crops grow.

Moreover, the water is suitable for either irrigation or domestic use, but high calcium concentrations would probably require some form of amelioration in the eastern parts. Chemical comparisons with natural groundwater in the area clearly indicate that informal settlements have not impacted groundwater in the sampled areas. In addition, the concentration of calcium and magnesium (i.e. hardness) are mainly indicative of the geohydrological features (the presence of calcrete lenses) of the Cape Flats aquifer.

For the most part the aquifer waters are undersaturated with respect to most minerals except for quartz. The natural hardness of the groundwater, which may be a consequence of the local geology, should, however, be considered in order to develop full understanding of the evolution of aquifer waters.

The significance of this study lies in the fact that it provides a geochemical assessment of the current status of waters in the Cape Flats aquifer. This will assist in the understanding of how the processes acting in these waters will affect their final composition.

4.6 Recommendations

- A brief hydrocensus should be undertaken to determine what groundwater abstraction takes place in and around each informal settlement. This could incorporate an awareness programme to warn residents of the relevant hazards.
- A study compiling the impact of all industries in the Cape Flats should be conducted to determine how much of the impact could be attributed to industries compared to residential areas.
- Future urban land-use planning must include a hydrogeological component, as part of impact assessment in order to classify the urban area with regard to groundwater resources potential.

Many people question the suitability of the Cape Flats aquifer water as a source of water supply for the Cape Town metropolitan area. This study has shown that the water is definitely usable for different purposes at different abstraction locations. It is by no means an all-purpose water resource. Still, regular monitoring should be implemented in order to determine how much water is available and with what chemical quality. It is anticipated that this would prove to be particularly costly. Considering the fact that this water resource is earmarked for future use, it is worth investing now to facilitate informed decision-making in the future.

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Appendix

Table A1: *Ion speciation calculated for water samples from the Cape Flats aquifer.*

		Lit1 a	Lit1	Lit2	Quak	Hos	Dag	Ced	Wel	Gugs	Qual	Jobs	Uitse	Vad	Phil	Glen
Na^+	Na^+	99.7	99.6	99.7	99.5	99.7	99.7	99.8	99.7	99.7	99.4	99.7	99.5	99.8	99.7	99.6
K^+	K^+	99.9			99.7	99.9	99.8	99.9	99.8	99.8	99.5	99.7	99.5	99.8	99.5	99.5
Mg^{2+}	Mg^{2+}	94.7	92.6	93.0	91.6	95.0	94.6	96.1	93.5	94.3	90.1	93.9	90.3	94.6	90.7	91.7
	$MgSO_4AQ$	2.3	3.6	2.2	4.9	2.2	2.9	1.4	3.5	3.3	6.9	5.6	6.6	4.1	7.2	7.7
	$MgHCO_3^+$	2.4	3.4	2.6	3.9	2.6	2.3	2.4	2.6	2.2	2.7		2.7	1.0	1.9	
Ca^{2+}	Ca^{2+}	95.1	92.6	93.7	91.8	95.2	94.7	96.4	93.7	94.4	89.6	93.3	89.9	94.5	90.1	90.8
	$CaSO_4AQ$	2.7	4.1	4.0	4.9	2.5	3.3	1.6	4.0	3.8	7.9	6.3	7.6	4.6	8.2	8.7
	$CaHCO_3^+$	1.9	2.7	2.0	3.1	2.1	1.8	1.9	2.0	1.5	2.1		2.1		1.5	
F^-	F^-	95.4	74.8													
	MgF^+	3.1														
	$Ca F^+$	1.5														

		Lit1 a	Lit1	Lit2	Quak	Hos	Dag	Ced	Wel	Gugs	Qual	Jobs	Uitse	Vad	Phil	Glen
Cl^-	Cl^-	100		100	100	100	100	100	100	100	100	100	100	100	100	100
NO_3^-	NO_3^-		100	100	100	100	100			100	100	100	92.5	100	100	100
SO_4^{2-}	SO_4^{2-}	76.1	79.8	78.8	77.1	80.9	81.7	79.9	78.8	80.0	78.8	86.2	76.0	81.5	76.0	77.1
	$CaSO_4AQ$	19.0	13.9	17.9	19.1	14.6	15.6	16.0	17.9	18.0	5.7	7.3	19.9	15.4	18.9	18.0
	$MgSO_4AQ$	4.7	5.7	2.6	3.4	3.5	2.3	3.0	2.6	1.5	13.2	4.7	3.1	2.6	3.7	3.9
	$NaSO_4^{-1}$										1.8				1.1	
CO_3^{2-}	HCO_3^-		90.8	89.3	85.0	89.5	89.6	89.4	89.3	87.5	91.8	50.6		81.5	91.5	75.5
	H_2CO_3AQ		6.9	8.7	12.8		8.7	1.3	8.6	19.3	5.3	48.7		15.4	5.4	22.5
	$CaHCO_3^+$				1.6	1.2	1.2	8.6	1.5	1.2	1.3			2.6	1.8	1.4
H_4SiO_4	H_4SiO_4	99.7	99.7		99.9	99.8	99.8	99.8	99.8	99.8	99.7	100	99.6	100	99.7	99.9

		Lit1 a	Lit1	Lit2	Quak	Hos	Dag	Ced	Wel	Gugs	Qual	Jobs	Uitse	Vad	Phil	Glen
Li^+	Li^+		99.8													
Fe^{3+}	Fe^{3+}	69.0														
Sr^{2+}	Sr^{2+}	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Ba^{2+}	Ba^{2+1}	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Table A2: *Trace element concentration from all the samples analysed.*

Element ($mmol_c/L$)	Lit1a	Lit1	Lit2	Quak	Hos	Dag	Ced	Wel	Gugs	Qual	Jobs	Uitse	Vad	Phil	Glen
Li^+	0.00	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00
Na^+	0.89	2.38	1.09	1.45	3.88	0.96	3.59	2.50	1.47	8.79	3.64	3.22	1.71	5.39	4.34
NH_4^+	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K^+	0.10	0.08	0.09	0.24	0.06	0.49	0.68	0.68	0.23	1.53	2.02	1.03	0.11	1.05	0.34
Mg^{2+}	1.83	2.25	1.02	1.47	1.33	0.77	1.14	1.04	0.56	3.29	1.64	1.61	0.86	1.94	1.80
Ca^{2+}	6.49	4.83	2.89	7.24	4.88	4.30	5.39	6.23	5.72	6.71	2.24	8.98	4.51	8.83	7.43
Cr^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr^{2+}	0.05	0.04	0.00	0.00	0.00	0.02	0.02	0.04	0.00	0.03	0.01	0.00	0.00	0.00	0.00
Ba^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
Total cations	**9.36**	**9.70**	**5.19**	**10.40**	**10.15**	**6.55**	**10.82**	**10.54**	**7.98**	**20.34**	**9.72**	**14.85**	**7.19**	**17.21**	**13.90**
F^-	0.08	0.09	0.05	0.01	0.00	0.00	0.00	0.10	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Cl^-	0.75	2.02	0.90	1.34	4.26	1.35	4.72	2.79	1.28	11.45	4.45	4.16	1.99	6.54	5.30
NO_2^-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Br^-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
NO_3^-	0.23	0.00	0.09	0.11	0.23	0.16	0.00	0.00	1.34	1.59	1.15	1.40	0.09	0.26	0.12
PO_4^{3-}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00	0.08	0.00	0.00	0.00
SO_4^{2-}	0.91	1.41	0.60	1.86	0.84	0.96	0.52	1.38	1.19	4.00	1.93	3.42	1.35	3.83	3.58
HCO_3^-	3.77	5.50	3.31	7.10	4.30	3.60	3.83	4.26	3.50	5.40	1.40	4.87	2.26	3.47	1.39
Total anions	**5.65**	**8.93**	**4.95**	**10.41**	**9.62**	**6.07**	**9.07**	**8.53**	**7.31**	**22.72**	**8.93**	**13.94**	**5.69**	**14.11**	**10.40**
Cation excess (expressed as %)	**24.7**	**4.14**	**2.42**	**0.04**	**2.69**	**3.74**	**8.77**	**0.38**	**4.36**	**-5.53**	**4.24**	**13.9**	**5.69**	**14.1**	**10.4**