

# **THE HYDROCHEMICAL CHARACTERISTICS OF GROUNDWATER IN THE INCOMATI ESTUARY**

Shaheeda Adonis

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## Abstract

### The Hydrochemical Characteristics of Groundwater in the Incomati Estuary

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The focus of this work was to monitor and evaluate the hydrochemical characteristics of the groundwater in the Incomati Estuary for a period of one year. The aims of this work were to:

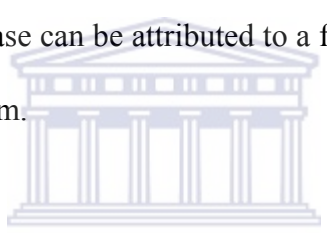
- ❖ To evaluate the groundwater chemistry data for any spatial and temporal variations and
- ❖ To evaluate the suitability of the groundwater for drinking and irrigation purposes.

The methodology was based on chemical analysis of water samples taken from boreholes located in a defined region of the Incomati Estuary sampled at different depths at different time periods. From the statistical analysis of the chemistry data (wide ranges and high standard deviations and medians), it is evident that there are substantial differences in the quality/composition of the groundwater within the study area.

Some degree of spatial variation was observed. Interpretation of Piper diagrams based on results obtained show that it is evident that the boreholes located in close proximity to the coast have a  $\text{Na}^+/\text{Cl}^-$  major ion composition. The high sodium and chloride concentrations obtained in the boreholes close to the coast serve as an

indication that the groundwater may be in contact with water of marine origin and that there is a possibility of saltwater intrusion into the aquifer at locations close to the coast.

Molar ratio plots of Cl and Na, however, were also used to investigate whether salinization of groundwater occur close to the coast. These diagrams illustrate that the boreholes close the coast have much higher Na/Cl molar ratios than the boreholes located further inland. This therefore substantiates the fact that there is intrusion of saltwater into the aquifer in the region close to the coast. A depth variation of TDS was also observed. In all sampling periods a sudden increase in TDS was observed at a depth of 43m. This increase can be attributed to a freshwater/saltwater interface at a depth between 35m and 43m.



The boreholes located more inland, however, have a major ion composition characteristic of freshly recharged groundwater ( $\text{Ca}^{2+}/\text{Mg}^{2+}/\text{HCO}_3^-$ ). It can be concluded that the boreholes located in the area of recharge (inland) are fresher than those located in the area of discharge (at the coast). From isotopic analysis a trend of TDS increase with isotopic enrichment was observed for certain samples, thus indicating mixing of fresh groundwater with seawater. No temporal / seasonal variations of the quality of the groundwater were observed over the study period.

From this study it is evident that the quality of the groundwater close to the coast is poor due to high solute concentrations. Better quality groundwater is located more inland. In addition, the deeper boreholes close to the coast have poorer quality water

than those that are more shallower. Although there is poor quality groundwater in certain areas of the Incomati Estuary, the groundwater does not pose an immediate and direct threat to human health. It could however, have serious implications if proper precautions and/or treatments are not employed soon.



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# TABLE OF CONTENTS

---

Page

Acknowledgements

Abstract

Table of Contents

List of figures

List of tables

## **Chapter 1: Introduction**

1.1 Introduction

1.2 Aims of the study



## **Chapter 2: Groundwater in coastal environments: a literature review**

2.1 Coastal aquifer groundwater

2.2 Groundwater and coastal ecosystems

2.3 The role of groundwater in a mangrove estuary

2.3.1 Groundwater fluxes in a mangrove estuary

2.3.2 Groundwater/surface water interface in a mangrove estuary

2.3.3 Salinity of groundwater in mangrove estuary

2.3.4 Groundwater as a nutrient source in a mangrove estuary

2.3.5 Effect of tidal hydrodynamics on groundwater in a mangrove estuary

2.4 The coastal ecosystem of Maputo Bay

2.5 Geology

2.6 Mangroves and Maputo Bay ecosystem

## **Chapter 3 : Methodology**

- 3.1 Field Sampling Methodology
- 3.2 Rationale for borehole sites
- 3.3 Water Analysis
  - 3.3.1 pH and electrical conductivity
  - 3.3.2 Alkalinity
  - 3.3.3 Major cations
  - 3.3.4 Major anions
  - 3.3.5 Dissolved organic carbon (DOC)
  - 3.3.6 Stable isotopes of hydrogen and oxygen
- 3.4 Accuracy check on chemical analyses
  - 3.4.1 Ionic Balance
  - 3.4.2 Piper Diagram

## **Chapter 4 : Analytical Results**

- 4.1 Results
  - 4.1.1 Major ions
    - a) Piper Diagrams
    - b) Bivariate Diagrams
    - c) Relationship between sodium and chloride
- 4.2 Isotope Analysis
- 4.3 Water quality assessment

## **Chapter 5 : Discussion and conclusion**

References

List of abbreviations

Appendix : Methods

- 1) pH Measurement
- 2) Electrical conductivity
- 3) Alkalinity
- 4) Major cations (K, Na, Ca and Mg)
- 5) Dissolved Organic Carbon(DOC)
- 6) Chloride and Sulphate
- 7) Orthophosphate
- 8) Ammonia
- 9) Nitrate





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## LIST OF FIGURES

---

- Fig.1 Features affecting coastal aquifers
- Fig.2 Map of Maputo Bay
- Fig.3 Geological Map of the Study Area
- Fig.4 Study area and model boundaries
- Fig.5 Transect conceptual model
- Fig.6 Map of sampling sites
- Fig.7 Classification diagram for anion and cation facies  
in terms of major-ion percentages
- Fig.8 Piper diagram for March 2004 sampling run
- Fig.9 Piper diagram for April 2004 sampling run.
- Fig.10 Piper diagram for August 2004 sampling run.
- Fig.11 Rainfall
- Fig.12 Cl/HCO<sub>3</sub> ratio vs. Cl for March 2004.
- Fig.13 Cl/HCO<sub>3</sub> vs. Cl for April 2004.
- Fig.14 Cl/HCO<sub>3</sub> vs. Cl for August 2004.
- Fig.15 Na/Cl molar ratios for March & April 2004
- Fig.16 Na/Cl molar ratios for August 2004
- Fig.17 TDS for drilled samples
- Fig.18 TDS vs sample location
- Fig.19 Cl(mg/L) vs. Oxygen-18 for August 2004

---

## LIST OF TABLES

---

Table 1	Results for March 2004
Table 2	Results for April 2004
Table 3	Results for August 2004
Table 4	Results – analytical statistics
Table 5	Sample Identification Table for March 2004
Table 6	Sample Identification Table for April 2004
Table 7	Sample Identification Table for August 2004
Table 8	Comparison of borehole water quality with the limits as set out by DWAF & WHO for domestic purposes as well limits as set out by DWAF for livestock watering and irrigation
Table 9	Calculated SAR values of samples compared to SAR limits of DWAF



# **Chapter 1**

## **1.1 Introduction**

Increasing urbanization is taking place along coastlines and estuaries and causing increased use of groundwater that will have a large impact on the quality and quantity of aquifer water (Campbell et al, 1992). To meet the ever-increasing water demand in the world, groundwater is being extensively used to supplement the available surface water. When one considers the water resources in areas bordering seas, coastal aquifers become a very important source of fresh water (Ranjan, 2005). Groundwater is increasingly being subjected to over-exploitation for agricultural, urban and industrial uses, leading to the deterioration of groundwater in coastal areas through saltwater intrusion. Additional problems such as the discharge of untreated or inadequately treated wastewater, agricultural runoff from farms and discharge of untreated sewage can all lead to the deterioration and contamination of groundwater in coastal aquifer (Younsi, 2004).

Salinisation, however, is the most widespread form of groundwater contamination, especially in coastal aquifers, and is represented by the increase of total dissolved solids (TDS) and some specific chemical constituents such as  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  (Nadler et al.,1981; Magaritz and Luzier,1985; Dixon and Chiwell, 1992; Morell et al.,1996; Sukhija et al.,1996 and Giménez and Morell, 1997). Potential salinisation sources are diverse, including natural saline groundwater, seawater intrusion, domestic, agricultural and industrial effluents. Among these sources, seawater intrusion is the most common and widespread in coastal areas, and forces the abandonment of water wells in many instances. Saltwater intrusion is natural process, but it becomes an environmental problem when excessive pumping of fresh water from an aquifer reduces the water pressure and intensifies the effect, drawing salt water into new areas. Many of the coastal aquifers in the world already experience saltwater intrusion caused by both natural as well as anthropogenic processes. It therefore becomes necessary to understand the patterns of movement and mixing between the freshwater and the saltwater as well as the possible factors

that can influence these processes (Ranjan, 2005). A case study was carried out at Jeju volcanic island, Korea to identify the origin of saline groundwater in the eastern part of the island. From the hydrogeochemical characteristics based on bivariate diagrams of both major and minor ions it was evident that the changes in the chemical composition of the groundwater in the study area are mainly controlled by the salinisation process, followed by cation-exchange reactions (Kim et al, 2003).

Even though surface water is the main source of water in the urban areas, groundwater is being heavily used for drinking water purposes (FAO Land and Water Development Division, 2005). Most of the country's population, however, (49%) obtain drinking water from wells, whereas 29% is obtained from surface waters, 20% from pipes and 1% from rain (Matimula, 2003). The effects and disruptions caused by the civil war, which ended in 1992, are still being felt in Mozambique, especially in the coastal areas. As more people returned to Mozambique after the civil war, the demand for resources such as food and water increased. Only about 36% of the population in Mozambique has access to safe drinking water whereas the other communities have to make use of inadequate or contaminated water sources.

The densely populated peri-urban areas of Maputo however rely on the exploitation of shallow groundwater. According to DAR (Department of Rural Water, Mozambique), groundwater is estimated in certain areas to serve as many as 500 people in a radius of 500 meters. 35% of the population in rural areas and 30% in small towns receive water pumped from boreholes. In the villages, where water systems exist, the local authorities manage the water systems (Ibraimo, 1999).

In the central districts of the city of Maputo, where a public water supply network is in place and water is piped in from outside the city, local groundwater still accounts for a significant portion of the total consumption (Corbo et al, 1992). Groundwater from the shallow aquifer below the city is mostly used as potable water and for domestic purposes and to a lesser extent for the irrigation of family plots. In some cases groundwater is also used for irrigation of agricultural plots or animal breeding.

A reported number of 600 wells was recorded for Maputo, although no reliable data is available on the number of active wells of the present time (Corbo et al, 1992). Most of these wells are private wells, serving a single family or a small group of families. Public wells are also scattered in the suburban districts of Maputo.

The pollution of surface and coastal waters is also an emerging problem in Mozambique (United States Central Intelligence Agency, 2004), which can lead to an increased demand for cleaner groundwater. Despite the fact that industrialization and production levels in Mozambique are relatively low, the urban population, industry and agro-industries are sources of pollution that can have a large impact on the surrounding population. Since most of the industrial activities are located in heavily populated areas, there are numerous examples of polluting activities, such as petroleum refining industries situated in the major cities discharging untreated effluent; industrial chemicals, fertilizers, pesticides, organic pollutants and paints from the chemical industry, all of which discharge untreated effluent (Mendes et al, 2004).

Domestic water contamination in rural, urban and peri-urban areas is also widespread. Adequate treatment of human wastes using drainage pipes and septic tanks occurs in only 2% of families in Mozambique, of which 11% are in urban and less than 1% in rural areas. About 65% of the families living in Mozambique do not have access to any type of sanitary facility. They either have to defecate in open spaces or create pit latrines. These are the types of practices that can significantly contribute to groundwater contamination and water-borne diseases in Mozambique (Matimula, 2003).

Although it has been long recognized that activities taking place within catchments can and do have an impact on the coastal ecosystem, the linkage between human activity in catchments such as farming, irrigation and water abstraction, ultimately the impact on coastal resources is still unknown. The Tri-Partite Technical Committee, which coordinates the regional water regulatory bodies in the Incomati Estuary,

recognised the need to integrate the inter-dependence of coastal function and livelihoods with catchment management. The Incomati catchment or estuary is extensively affected by the human activity, thus raising concerns that this may have a detrimental but unquantified effect on the economically coastal resources. Based on this, Incomati River-Maputo Bay system was then used as case study for this project (Monteiro& Matthews, 2003).

For this reason the CSIR Catchment-2-Coast project was initiated (CSIR C2C Brochure, 2003). The Catchment-2-Coast (C2C) project is a major research and modelling project that is looking at the impacts of river catchment developments on the sustainability of downstream coastal resources which provide important livelihoods to urban and rural communities. Focused on the Incomati estuary and Maputo Bay in Mozambique, southern Africa, the project aims to establish what impact human activity in the catchment is having on the shrimp industry in Maputo. Shrimp are an economically important resource in Maputo Bay and at one time were responsible for the highest export earnings for Mozambique. Thirty-five per cent of all export earnings in 1996 were derived from the shrimp industry and approximately 3000 artesanal and semi-industrial fishers derived a direct livelihood from this resource (Hoguane, 1999).

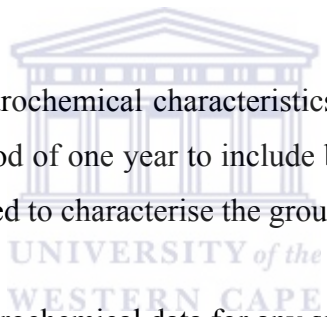
The project took an interdisciplinary, systems approach to develop an understanding of the linkages between the main domains of river catchments and their associated coastal environments. Using a variety of models it seeks to translate human development needs upstream into cost-based consequences at the coast.

This focus represents a departure from past practices. River management has traditionally been focused on water supply and extraction for human needs in the catchment. This means that economically important coastal resources, such as Maputo Bay, are often affected in an unknown way by catchment projects that do not explicitly internalise these costs. The Catchment-2-Coast project aims to remedy this by designing, implementing and validating an integrated catchment-to-coast planning

and management support system, not only for the region under study, but for other areas in southern Africa and beyond (Monteiro & Matthews, 2003).

The work described here forms part of the groundwater component of the Catchment-2-Coast project. The objective of the groundwater component of the Catchment-2-Coast project however is to define a relevant event scale of aquifer-based processes that links catchment activities to the coastal zone and to quantify groundwater physiochemical outputs. The focus of this work is, however, to monitor and evaluate the hydrochemical characteristics of the groundwater in the Incomati Estuary over a period of 1 year. The data will also be used to evaluate the suitability of the groundwater for drinking and irrigation purposes.

## **1.2 Aims of the project**

- 
- To monitor the hydrochemical characteristics of groundwater in the Incomati Estuary over a period of one year to include both the wet and the dry seasons. The data will be used to characterise the groundwater.
  - To evaluate the hydrochemical data for any spatial and temporal variation.
  - To evaluate the suitability of the groundwater for the purposes of drinking and irrigation, with reference to recommended limits set by both DWAF and WHO.

## **Chapter 2**

### **Groundwater in coastal environments: a literature review**

#### **2.1 Coastal aquifer groundwater**

A coastal aquifer is defined as a water bearing geological formation hydraulically connected to the sea (Johannes, 1980). The movement of water in coastal aquifers is generally towards the sea/ estuary. This is as a result of the positive hydraulic gradient set up by the balance between recharge inland and discharge towards the sea / estuary.

When dealing with the exploitation, restoration and management of fresh groundwater in coastal aquifers, the key issue that arises is that of saltwater intrusion. Coastal regions face many hydrological problems like flooding due to cyclones, wave surge and drinking fresh water scarcity due to problem of saltwater intrusion. The natural balance between freshwater and saltwater in coastal aquifers is disturbed by groundwater withdrawals and other human activities that lower groundwater levels, reduce fresh groundwater flow to coastal waters and ultimately causing saltwater to intrude coastal aquifers (Barlow, 2003). Features which can affect coastal aquifers are summarised in Fig 1

The extent of saltwater intrusion into a coastal aquifer depends on several factors, including the rate of groundwater that is withdrawn compared to the total freshwater recharge to the aquifer, the distance of the wells and drainage canals from the source or sources of saltwater, the geologic structure and distribution of hydraulic properties of the aquifer (Barlow, 2003). Saltwater can intrude into coastal freshwater aquifers through several pathways, including lateral flow from the ocean, an upward intrusion from deeper and more saline zones of the groundwater system as well as by downward intrusion from coastal waters (Reilly & Goodman, 1987). Saltwater intrusion reduces freshwater storage in coastal aquifers and can result in the



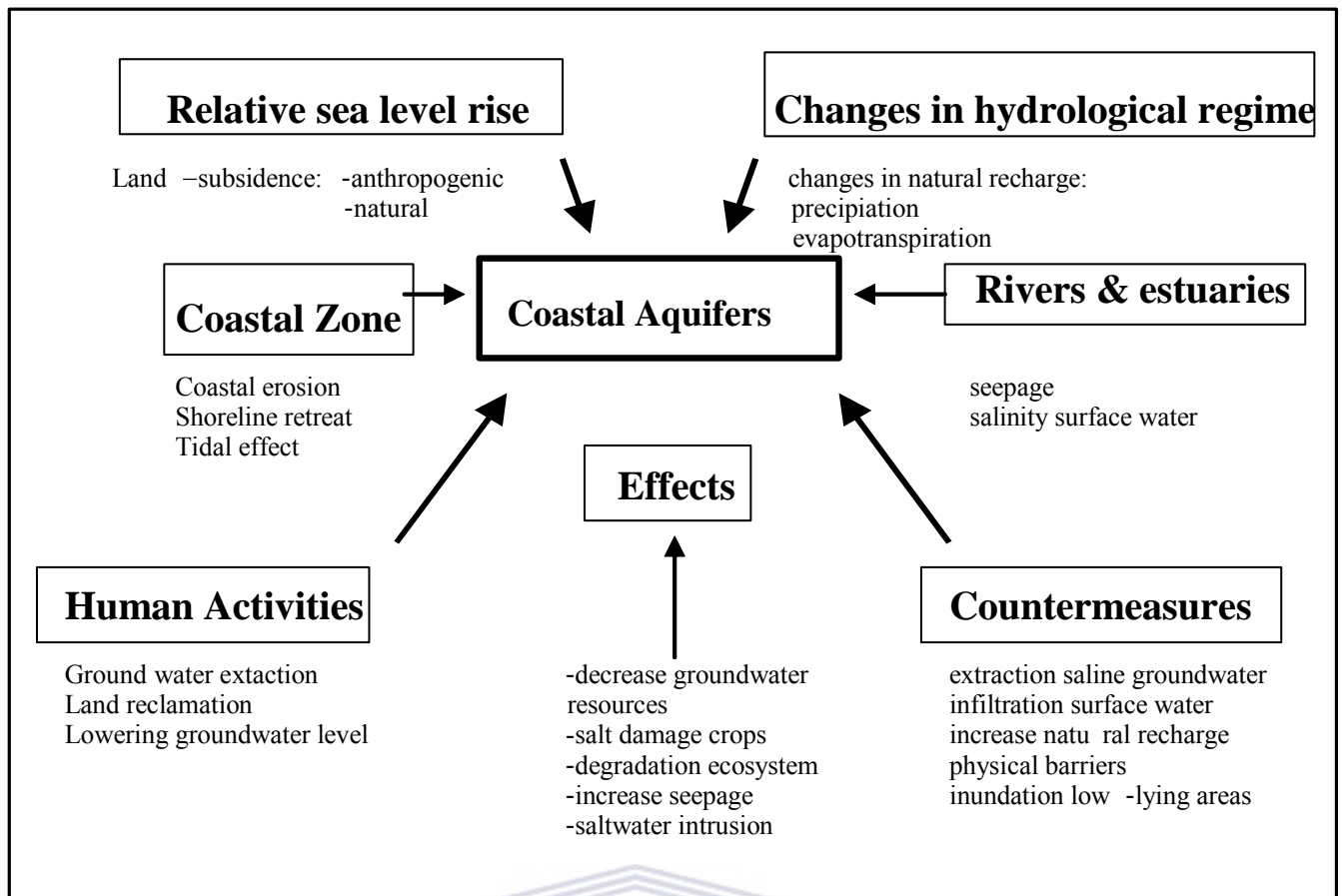


Fig.1 Features affecting coastal aquifers

abandonment of freshwater supply wells when concentrations of dissolved ions exceed drinking-water standards. The degree of saltwater intrusion varies widely among localities and hydrogeologic settings. In view of the fact that most of the sediments of coastal aquifers are of marine origin, salt leaching can be seen as another threat to the quality of groundwater in coastal aquifers. As a result of their marine nature, the sediments have a high calcareous content and high alkalinity, of which the calcareous content is mainly due to shells and calcareous algal fragments. The dissolution of these components into groundwater leads to high salt content (Rust, 1987).

Salinity is by far the most significant form of contamination in coastal aquifers. There is also other forms of contamination, namely due to human influences that also pose a serious threat to the quality of groundwater in coastal aquifers. Contamination due to human influences can be attributed to:

- Sources designed to discharge substances into the earth, eg. Wastewater treatment plants.
- Sources designed to store and dispose of substances, eg. Graveyards, dumps and pit latrines
- Sources designed to retain substances during transport, eg. pipelines.
- Sources discharging substances as a consequence of planned activities, eg. irrigation and fertilizer application (Wright, 1991).

## **2.2 Groundwater and coastal ecosystems**

There are several ways in which groundwater interacts with and affects coastal ecosystems. Groundwater discharge sustains the flow and aquatic habitats of coastal streams during periods when surface runoff is low. Groundwater discharge also helps to maintain water levels and water budgets of freshwater lakes, ponds and wetlands (Kumar, 2003)

The role of groundwater in delivering contaminants to coastal water has become an area of growing interest and concern. Although many types of chemical constituents have contaminated coastal groundwater systems, much of the concern to date has been focused on the discharge of excess pollutants into coastal ecosystems. Nutrient contamination of coastal groundwater occurs as a consequence of activities such as wastewater disposal from septic systems and agricultural and urban uses of fertilisers.

Excessive pollution can however lead to excessive production of algal biomass and loss of important habitats such as mangroves (US National Research Council , 2000).

Groundwater reaches coastal environments either by direct discharge or as baseflow in the streams and rivers that drain coastal areas. It is however becoming evident that in some coastal environments, direct groundwater discharge can be a substantial contributor of fresh water and dissolved constituents. It has been shown that groundwater input into coastal waters accounts for as much as 65% of the total freshwater inflows (Bokuniewicz, 1980).

## **2.3 The role of groundwater in a mangrove estuary**

### **2.3.1 Groundwater fluxes in a mangrove estuary**

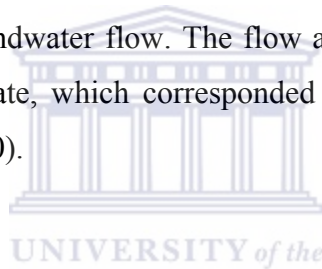
The recharge and discharge of groundwater in estuaries are controlled by a combination of periodic tidal and evapotranspiration fluctuations, irregular rainfall and regional groundwater flow. Groundwater fluxes have been found to be important factors affecting the wetland productivity through their influences on the accumulation and removal of chloride, nutrients, toxins, hypersalinitation, sediment oxidation, pH and soil moisture content (Hughes et al, 1998). Based on the fact that the fluxes of groundwater can also be seen to have an amplified influence on the benthic communities and porewater environments, large scale phenomena such as sediment erosion and deposition can be linked to offshore groundwater fluxes.

Burrows also play a significant role in the exchange between surface and groundwaters in a variety of marine and freshwater environments. The flushing of animal and crab burrows situated in the beds and banks of estuaries and ocean coasts, provide a mechanism which can enhance water exchange and thus the transport of materials such as salt, nutrients, oxygen and pollutants( Riedel et al, 1997)

The transport of salt is of vital importance in a mangrove system. Mangrove roots absorb porewater from the sediments. This results in an increase in salt concentration in the soil surrounding the mangrove roots. This soil then becomes highly impermeable and greatly retards the diffusive transport of the salt away from the roots. In mangrove swamps without burrows, the salt must diffuse from the roots to the surface waters. However, with burrows, the distance over which diffusion occurs is much shorter, resulting in a significant decrease in the diffusion time. The removal of the burrow water then completes the salt removal process. As a high tide floods a swamp, the water surface area is small due to vegetation, but has a significant slope. The pressure difference that exists across the burrow opening, due to this slope, causes a flow in the burrow that results in the flushing of the burrow water, thus removing the salt. The burrow flushing process can provide a much faster mechanism

for salt-removal from the root to surface compared to diffusion from root to surface (Ridd, 1996).

It has been observed that in the initial stages of the rising water at flood tide, a sheet of water advances into a swamp from creeks that are often blocked by vegetation. The first few millimeters of flooding water at a given point is not due to the water from that sheet but is believed to come from the ground through numerous holes burrowed by crabs. These crab burrows enhance the flow of groundwater. A swamp can also be draining out through groundwater flow, as was observed in the Bashita – Minato mangrove swamp in Japan (Mazda et al, 1990). After storms the tidal creek was occasionally ponded by a sill at the mouth. It was found that when the creek was ponded, the water level in the creek decreased by up to 10cm/day, which is about 15 times larger than the evaporation rate. It was then suggested that the creek was draining out through groundwater flow. The flow also appeared to be limited to the upper 90cm of the substrate, which corresponded to the maximum depths of crab burrows (Mazda et al, 1990).



### **2.3.2 Groundwater/surface water interface in a mangrove estuary**

It has long been known that groundwater and surface waters are intrinsically linked systems. The areas around coastal environments, like estuaries, represent zones of interaction and transition between groundwater and the estuary where dissolved constituents such as pollutants, nutrients, etc. can be diluted, exchanged, transformed and destroyed. To identify predominant processes affecting solute exchange across transition zones it is critical to assess contaminant fluxes to the sediment/water interface.

Groundwater / surface water interactions in estuarine environments are influenced by a number of processes forming complex spatially and temporally variable systems. Tidal activity often induces a fluctuating water table as well as an infiltration of surface water into the coastal sediments, forming a “mixing” zone with groundwater

discharging from the adjacent aquifer. Even though there is no theoretical definition for such a zone, the term groundwater / surface water interface is commonly used (White, 1993). The transition of groundwater into the sediments and surface waters of an estuary can represent a significant environmental change from the relatively stable groundwater environment. Changes in surrounding sediment chemistry, biological activity and groundwater flow paths can be expected to influence the movement and fate of contaminants in the groundwater environment.

### **2.3.3 Salinity of groundwater in mangrove estuary**

The salinity of groundwater can be defined as being the dissolved mineral concentration in the water. The intrusion of seawater into an aquifer at its place of discharge to the sea or the diffusion / leakage of saltwater through poorly permeable deposits into an aquifer are but just a few of the natural ways through which the salinisation of groundwater in coastal areas is brought about. The over-exploitation of groundwater in coastal areas is clearly a crucial problem due to large population growth and the fact that 70% of the world population occupies coastal regions . Owing to the expansion of both aqua-culture and agricultural activities in coastal areas like estuaries, the over-exploitation of the groundwater resources causes groundwater levels to fall which is coupled with land subsidence.

Consequently the hydrostatic balance between the groundwater and seawater interface can be broken, causing seawater intrusion into the aquifer and thereby causing deterioration of the quality of the groundwater. In nature the groundwater–saltwater interface seldom remains stationary. Large-scale recharging into the aquifer, as well as withdrawals from the aquifer, result in the movement of the interface from one position to another. The movement will be advancing or retreating depending on whether the freshwater flow through the aquifer is decreased or increased. Changes in groundwater recharge directly affect the changes in fresh groundwater resources. Consequently, the salinisation of coastal aquifers will accelerate due to the reduction of groundwater recharge. This can lead to a reduction of fresh groundwater resources.

The mangroves are well adapted to the high salinity of the surrounding water and soils in an estuary. The salinity limit of mangroves in an estuary is considered to be 90 parts per thousand (Smith, 1988). An increase in salinity will significantly decrease the leaf emergence, the growth rate as well as seedling mortality. Groundwater, however, can play a very vital role in this regard. The discharge of groundwater can be regarded as a very important flushing mechanism that can clean the mangrove soil from salt and other contaminants left over after evapotranspiration. The discharge of groundwater into an estuary has also been seen to dilute the salinity, as was observed in False Bay, South Africa. The potential discharge of groundwater seepage in False Bay was estimated to be between 0 and 120m<sup>3</sup>/day, diluting the salinity from an average of 35<sup>0</sup>/<sub>0</sub> to 34.5<sup>0</sup>/<sub>0</sub> at the place of discharge (Giljam, 2002).

#### **2.3.4 Groundwater as a nutrient source in a mangrove estuary**

Groundwater may be an important source of nutrients to the coastal ocean and other standing bodies of water (Valiela et al, 1990). Many dissolved nutrients and constituents, both natural and anthropogenic, can be carried to the surface waters through submarine groundwater discharge (SGD). Sewage, mining waste or other soluble refuse percolating into an aquifer might eventually enter coastal waters via groundwater discharge. Depending on the concentrations and flow paths of these contaminated constituents, the ecology of the coastal waters could be impacted where they can cause eutrophication and an increase in labile organic matter in the ecosystem.

The concentration of many contaminants in groundwater is typically several times higher than seawater even in pristine waters due to the fact that groundwater normally has a different composition than that of receiving coastal waters. The inter-relationship between estuaries and groundwater is complicated as tidal fluctuations may cause pressure waves to propagate inland, causing groundwater levels and hydraulic gradients to fluctuate (Serfes,1991). Furthermore, if a change in the water level of an adjacent estuary results in an increase in the hydraulic gradient, there will

be an associated increase in groundwater discharge to the estuary and the concomitant potential for increased nutrient loading (Staver & Brinsfield, 1996).

Due to the high organic content in mangrove sediments, high levels of organic phosphorus and nitrogen can be present in mangrove sediment. The mangrove sediments can remove phosphorus from sewage effluent but is limited by the availability of exchange sites in the phosphorus rich sediments as well as by the precipitation of ferrous hydroxide. Much of the nitrogen present occurs as organic nitrogen, whereas the inorganic nitrogen occurs in the form of ammonium. The lack of oxygen will further hinder the oxidation process. Nitrate is rapidly denitrified by anaerobic bacteria, under reducing conditions to gaseous nitrogen. The interstitial ammonium is highly mobile, making it very susceptible to leaching by heavy rains or lost through drainage following tidal inundation, which leads to contamination of groundwater. The uptake of nutrients by mangroves can also lead to the immobilization of significant amounts of nitrogen and phosphorus in a mangrove estuary. The nutrients absorbed by the mangroves would eventually be returned to the ecosystem in the form of leaf litter and then most probably flushed away by the tide.

### **2.3.5 Effect of tidal hydrodynamics on groundwater in a mangrove estuary**

Coastal aquifers are complex zones due to the combined influences of oceanic oscillations and inland groundwater forces. These influences lead to complex behaviour of subsurface contaminants discharging into the sea or estuary. Important, unique factors of a coastal aquifer system include the influence of the density contrast between the salt water and fresh groundwater and tidal fluctuations. Their net effects lead to complicated hydrodynamic conditions in coastal aquifers, which in turn could influence the local ecological environment (Ataie-Ashtian et al, 1999; Bear et al., 1999). In coastal aquifers the groundwater level/water table fluctuates with time in response to the water level fluctuations of the tidal water body (sea or estuary). This natural phenomenon has the potential to provide a convenient, economic and reliable

way of identifying coastal hydrogeological conditions in large scale. This could be one of the reasons why the study on the dynamic relation between seawater and coastal groundwaters became such an active research area since the 1950's. The influence of sea tide on the mean groundwater levels became one of the aspects that immediately relate to the estimation of submarine groundwater discharge (Moore, 1999).

As tidal water table fluctuations propagate inland their amplitude is attenuated and phase-shifts can take place. A typical damping distance for tidal watertable fluctuations in an unconfined aquifer is several hundred meters and in a confined aquifer it can extend landwards by several thousands meters (Lanyon, 1982). These tidal fluctuations were found to largely affect the groundwater flow and mass transport in both a confined and an unconfined aquifer (Lie et al., 2000). Tidal fluctuations can also be seen to affect the intrusion of seawater into an unconfined aquifer since the tidal fluctuations of the sea level can influence the groundwater/seawater interface. It was found that tidal activity can force seawater to intrude inland and creates a thicker groundwater/seawater interface. In cases where an aquifer extends to a river, lake or estuary the effect of tidal fluctuations on seawater intrusion into the aquifer might be stronger due to the reduction of groundwater flux attributed to the over-height in water table caused by tidal fluctuations (Ataie-Ashtiani et al., 1999).

The fate of constituents like nutrients and heavy metals discharged into the mangrove system are influenced by the frequency and duration of tidal inundation, as well as the pattern of water movement and drainage in the mangrove system. In many cases the frequency and duration of tidal inundation may have a greater influence on the removal and immobilisation of nutrients and heavy metals in sediments than the chemical and biological characteristics of sediments in a mangrove system. Mangrove swamps help control the tidal hydrodynamics of many tropical estuaries. It was determined that peak tidal velocities of more than 1m/s in the tidal creek of Coral Creek, Australia were slowed down to less than 0.7m/s in the mangrove swamp situated 50m from the creek. From statistical experiments it was suggested that the



destruction of vegetation or the recovery of mangrove land could reduce the peak tidal current as well as the asymmetry of the tidal current. This would consequently result in siltation of the channel (Wolanski, 1992). It is, however, important not to neglect the effects of tidal fluctuations and hydrodynamics when one wants to evaluate the quality of groundwater.

#### **2.4 The coastal ecosystem of Maputo Bay**

Maputo Bay receives inflow from the rivers Inkomati, Maputo and Umbelzi that flow into the Indian ocean. The Maputo Bay ecosystem is characterised by the mangrove forests. It is a highly eutrophic ecosystem that is very important to the coastline, as it protects the coastline from erosion and it provides important artisanal fisheries to local communities. The estuary also plays a crucial role in the economical and social life of Maputo. The health and productivity of the Maputo Bay ecosystem is also dependent on the quantity and quality of the freshwater inflow from the main inflowing source of freshwater – the Maputo River and also to some extent to the quantity and quality of groundwater discharge.

The climate of Maputo can be characterised as tropical with summer rains. The mean monthly temperature around Maputo is fairly stable with an annual average of about 23°C. The average maximum temperature varies from 25°C in July – August to 30°C in January. The minimum temperature varies from 14°C in July – August to 20°C in January. The average rainfall for Mozambique is 980mm and is about 800mm in Maputo Bay (Hoguane, 2002). There are high river flows for 3-4 months during the summer season and low flows during the remaining part of the year in many of the rivers. Droughts are also a common phenomena in Mozambique, especially in the south. These can be related to the erratic distribution of the rainfall during the wet season. The drought periods are often followed by heavy storms (Hoguane, 2002).

The capital of Mozambique, Maputo, lies on Maputo Bay. City residents rely considerably on fishery resources, both for consumption and economic reasons. Maputo Bay beaches also serve many residents and tourists as a leisure spot throughout the year. Yet despite its beauty, there is growing evidence that the waters inside the bay are polluted by untreated sewage coming from new developments in the city that are not connected to the existing sewage and drainage facility and water treatment plants.

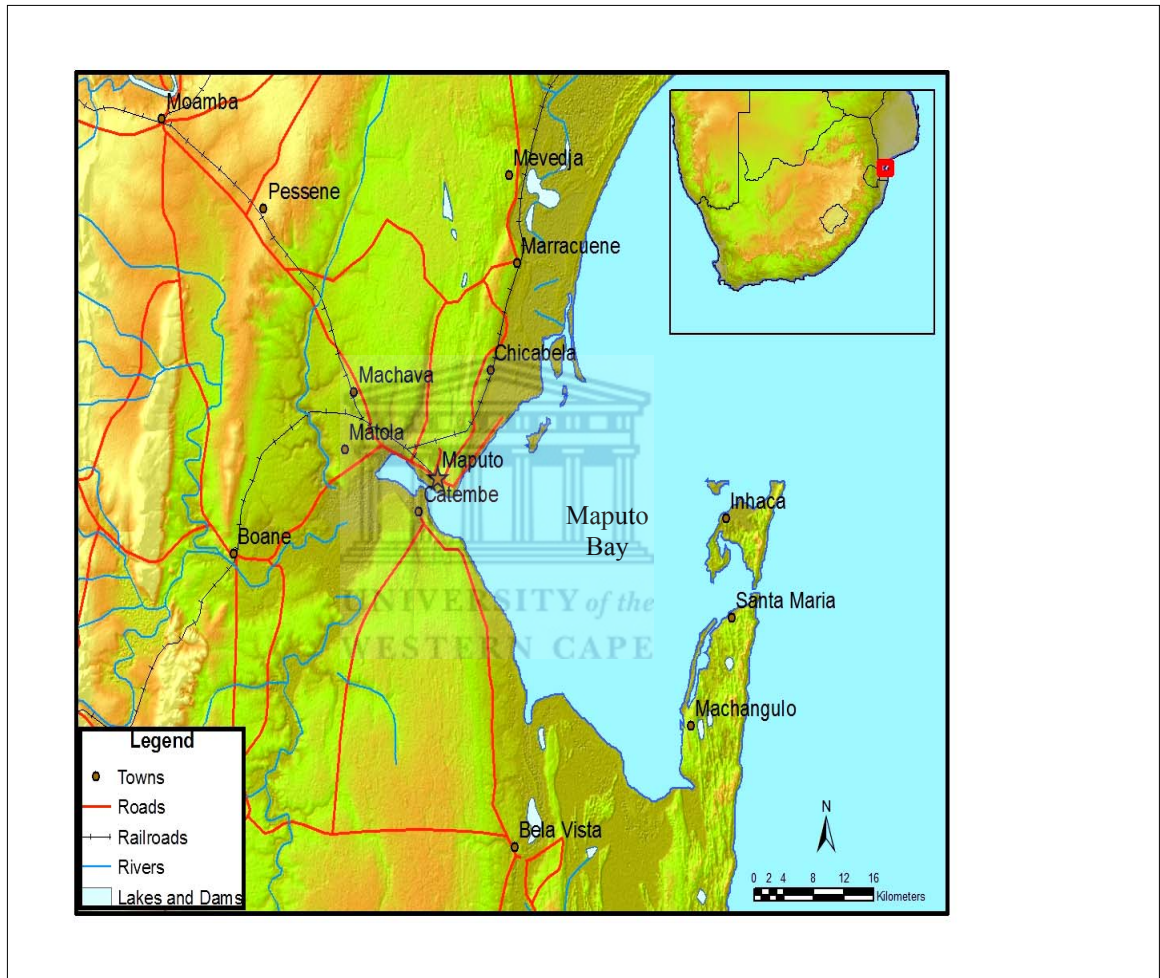


Fig.2: Map of Maputo Bay

The population of Mozambique in 2003 was estimated by the United Nations at 18,863,000, which placed it as number 54 in population among the 193 nations of the world. According to the UN, the annual population growth rate for 2000–2005 is 1.75%, with the projected population for the year 2015 at 22,537,000. It was

estimated by the Population Reference Bureau that 40% of the population of Mozambique lived in urban areas in 2001 and the capital city, Maputo, had a population of 2,867,000 in that same year.

Mozambique is one of the poorest and most aid-dependent countries in the world. Much of Mozambique's economy was devastated by almost three decades of internal warfare during which millions of Mozambicans were displaced and many killed. Characterized as a dual economy because of the large divide between the dynamic, capital-intensive sector and under-performing traditional sector, Mozambique's economy is today relatively diversified. The economy of Mozambique heavily depends on the exploitation of its fishery and agricultural resource base. All sectors make an important contribution, although agriculture is the most important contributor employing 80% of the population. Mozambique produces a surplus of agricultural products. The main cash crops are sugar, copra, cashew nuts, tea, and tobacco.

About 50 000 to 60 000 people in Mozambique are employed in the fisheries sector. This makes a substantial contribution to the economy of the country. The fisheries sector represents approximately 40% of the total export earnings. The most valuable fishery resources of Mozambique are shallow and deep water shrimp, scad and makerel (Hoguane,2002). The shrimp production in Mozambique has an average annual catch of about 185 ton/year (estimated value 3 million US\$ a<sup>-1</sup>). Fish catches in Maputo Bay amount to 550 ton/year (estimated value 0.8 million US\$ a<sup>-1</sup>) (Sengo, 2003).

## **2.5 Geology**

The area of Maputo forms part of the southern sedimentary basin with eastward dipping deposits. Almost all the deposits in the South Mozambique Sedimentary

basin are mainly of marine origin and have been formed during transgressions phases. Within the study area the oldest layer is the Grudja Formation of Upper Cretaceous age consisting mainly of clayey sandstones, marls and clays. On top of it the Lower Tertiary Salamanga Formation was deposited. Around Maputo the lithology of this Formation changes from calcareous sandstones in the West via argillaceous sandstones in the central part to calcareous sandstones and sandy carstified limestones in the East (IWACO/DNA, 1986). These formations were covered by dunes during the Upper Pleistocene forming the present landscape.

From a hydrogeological point of view, the fine grained Grudja deposits can be regarded as an impermeable base. The Salamanga deposits have moderate to high transmissivities and are indicated as the second aquifer. The first aquifer is the dune formation. In the coastal plain, the river valleys and its borders, the two aquifers are separated by semi-permeable clayey layers thus creating semi-confined conditions in the second aquifer.



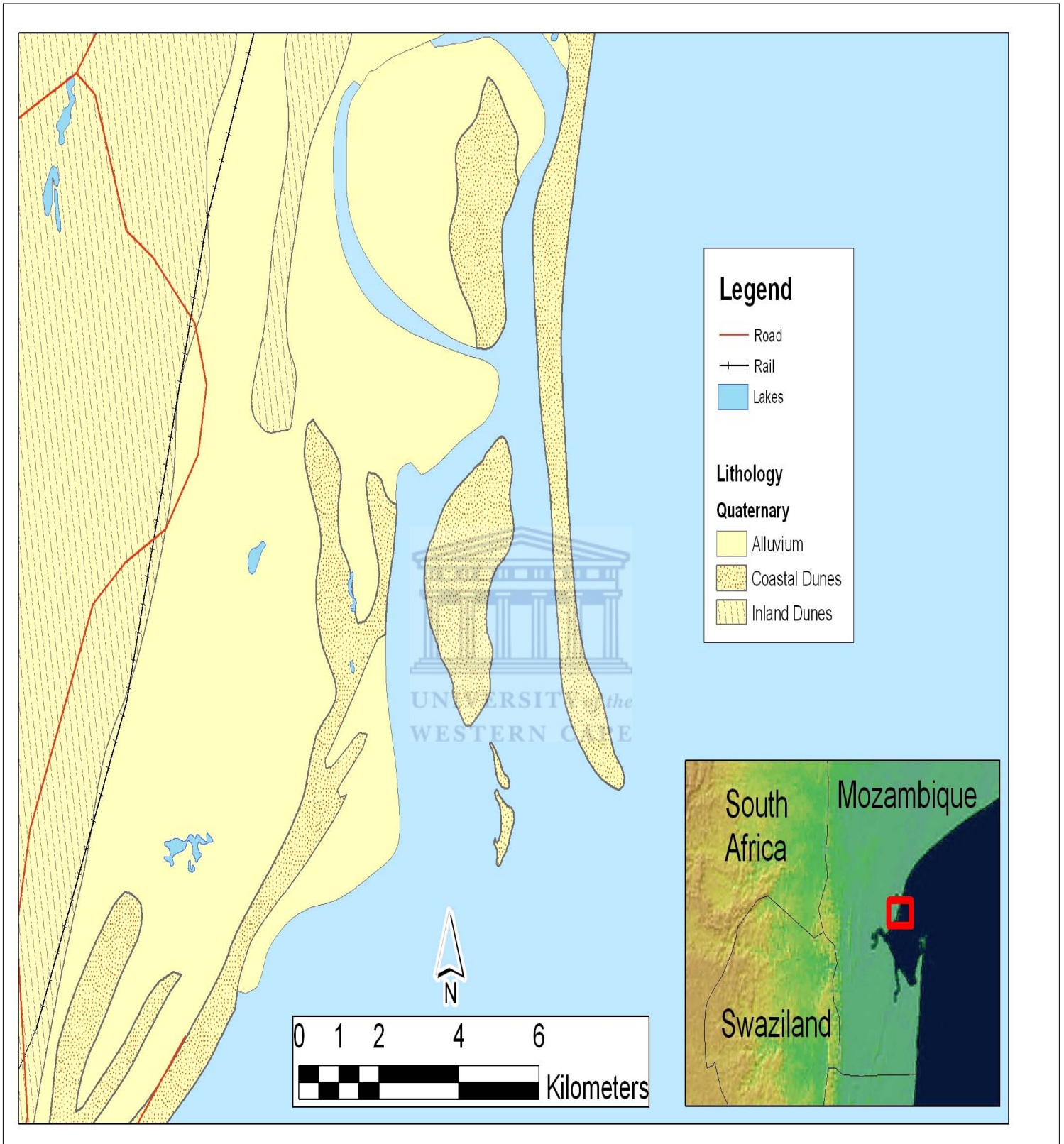


Fig 3. Geological Map of the Study Area



## **2.6 Mangroves and Maputo Bay ecosystem**

Mangroves are an important component of the intertidal ecosystem of Maputo Bay, in the form of nutrient source, nursery area, shore protection and habitat for other species (Semesi, 1998). Due to the dense population around Maputo Bay, the mangrove forests in these areas are under severe strain (Kalk, 1995). Mangroves are being used by the local population for several different reasons. The trees are used for fuelwood, either for domestic use or to sell. Mangrove wood is also used for the construction of fishing boat and fishing poles (Hatton, 1995).



## **Chapter 3**

### **Methodology**

This chapter discusses the methods used to collect and analyse groundwater samples from the study site. The rationale for the selection of the borehole sites is also described within this chapter.

#### **3.1 Field sampling methodology**

Groundwater samples were collected by technical staff of the CSIR from March 2003 to August 2004. Groundwater samples were collected following the sample protocol for groundwater sampling set out by Weaver (1992). Most of the boreholes were constructed for this study. Each borehole was pumped for a maximum of 30 minutes before samples were taken. This was done to ensure that fresh water was sampled from the aquifer rather than stagnant water from the borehole. The electrical conductivity of the groundwater was also measured during pumping and samples only collected after 30 minutes and once a stable conductivity reading was obtained. However, the same could not be done for the large diameter wells. Instead a 1L Teflon bailer was used to do the sampling.

Water samples for the laboratory analysis were collected in 300ml screw cap plastic bottles. For each sampling point, two plastic bottles were rinsed three times each with the water to be sampled and filled to the brim, before sealing tightly to include as little air as possible in the top of the bottle. The samples were then placed in cooler boxes at a temperature of  $< 4^{\circ}\text{C}$ . The samples were then placed in fridges and transported back to the laboratories of the CSIR in Stellenbosch for analysis. Samples for  $\delta^{18}\text{O}$  (oxygen-18) isotopes analyses were collected in glass bottles to minimize potential evaporation of the sample which could alter isotope ratios. Samples were then stored and transported to the CSIR laboratories in Pretoria for analysis. The pH and electrical conductivity were measured using a portable meter (Radiometer) adjusted for water temperature.

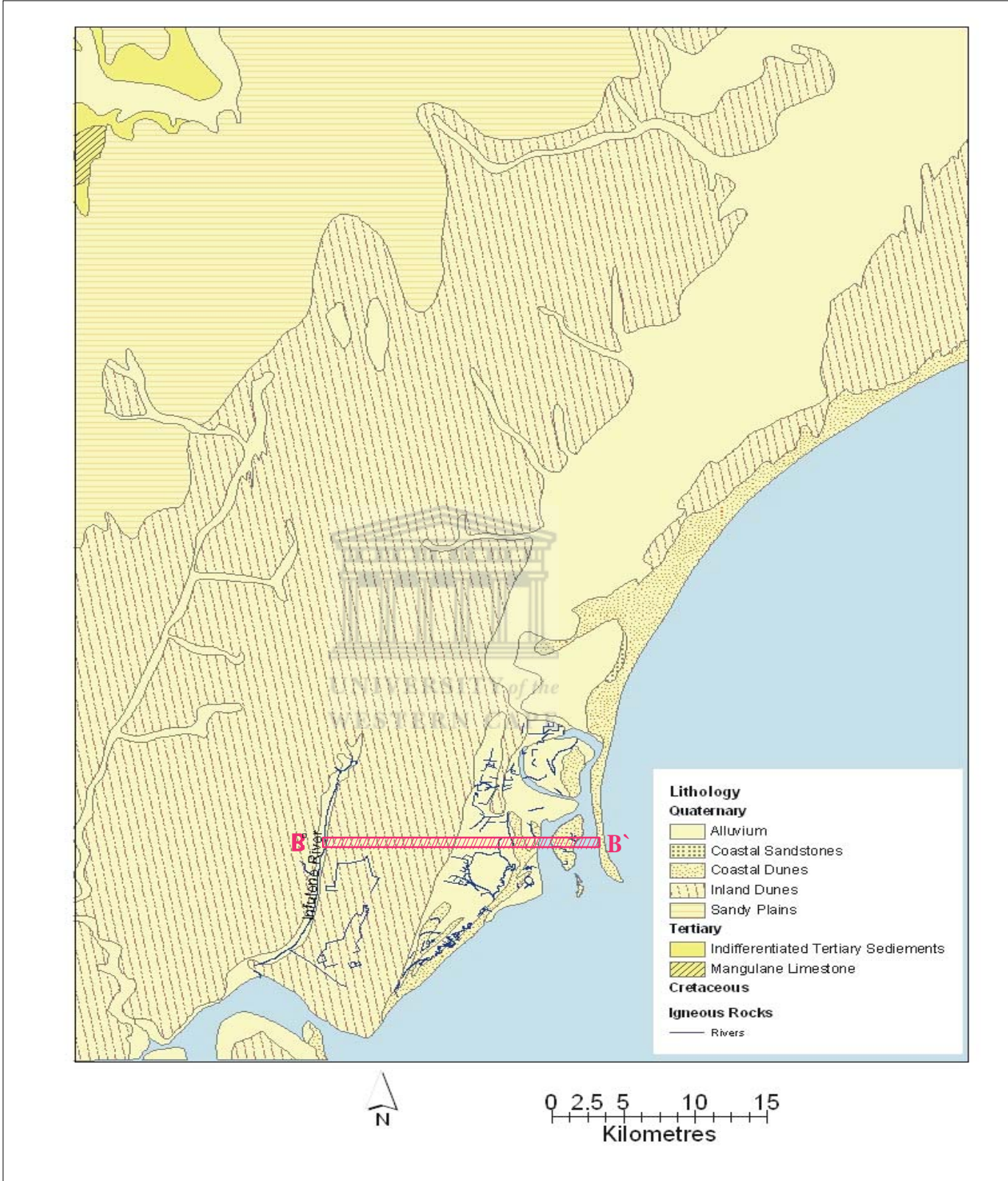


Figure 4: Study area and model boundaries



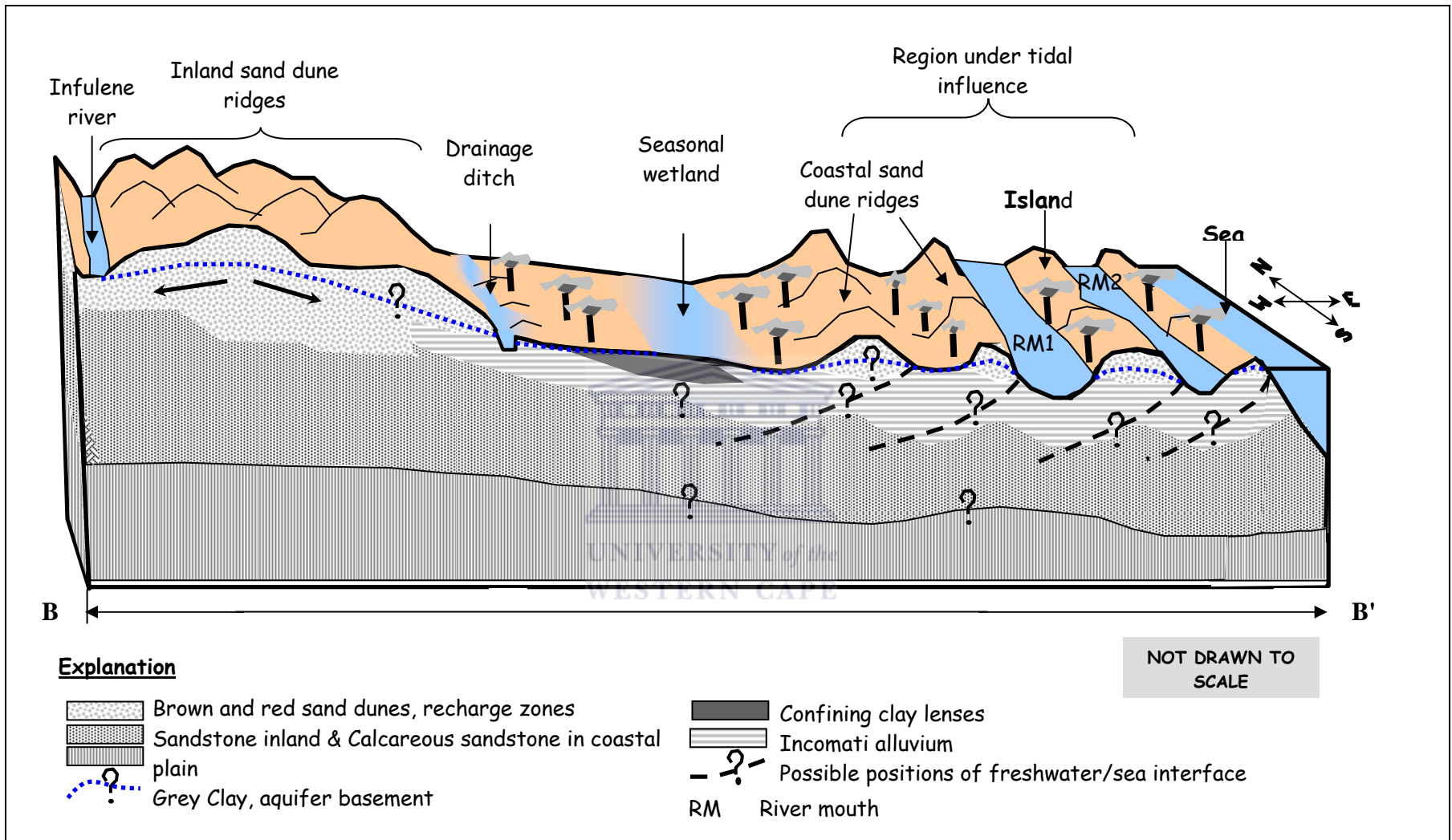


Fig.5: Transect conceptual model (approximately 18 500m length by 1000m width)

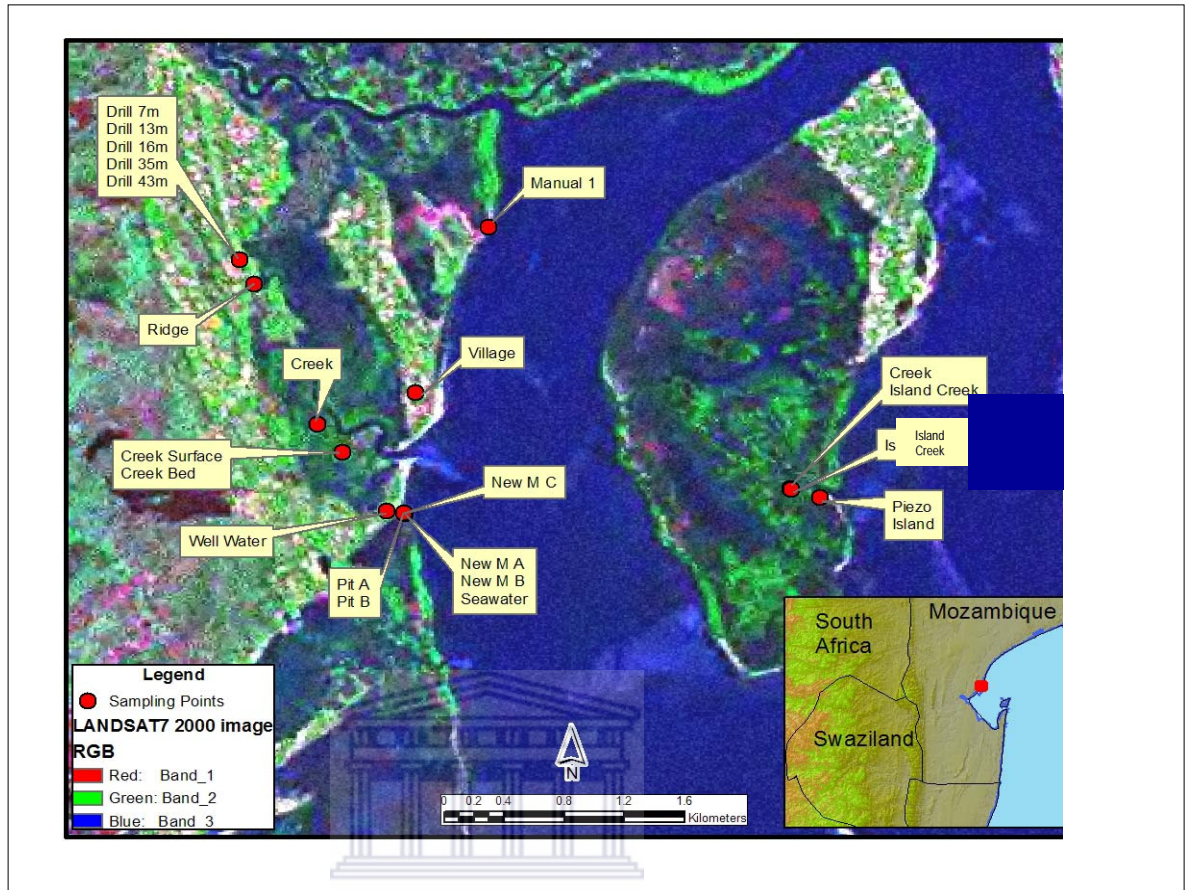


Fig.6: Map of sampling sites

### 3.2 Rationale for borehole sites

Fig 4 above illustrates the main lithologies and the boundaries of the transect (B-B') modelled for this project using Modflow. The modelling for this project was done by Freaternity Rusinga, a geologist that formed part of the Catchment-2-Coast (C2C) project. The approach to this study was firstly to characterise the dynamic hydrogeological flow regime, with particular reference to discharge to the estuarine mangrove areas. The conceptual understanding of the flow regime, based on field visits and existing data is outlined in the diagram on page 22 (Fig.5). The monitoring boreholes used for this study were then installed and located along this transect. Two multi-piezometer boreholes and four additional hand-augered piezometer boreholes were installed in the tidal zone. The multi-piezometer boreholes were at different

depths, namely 7m, 13m, 16m, 35m and 43m. The hydrochemical sampling for this study was done at the newly installed boreholes and existing community wells within the area of interest (Fig.6).

### **3.3 Water analysis**

For this study 38 water samples were collected, of which 35 were groundwater samples and 3 surface water samples (Seawater, Creek Surface and Creek Bed). All the water analyses, except the isotope analyses, were conducted by the author using the facilities of the Cape Water Program Analytical Services Laboratories of the CSIR in Stellenbosch. The isotope analysis was done by CSIR laboratories in Pretoria. The analytical methods are described briefly in this section, but details of the analytical procedures and data reliability have been confined to Appendix B.

#### **3.3.1 pH and electrical conductivity**

Water sample pH measurements in the laboratory were carried out using a Radiometer PHM82 standard pH meter and GK 2401C combined electrode, together with a stirrer. The pH reading was recorded while stirring. A Radiometer conductivity meter with platinum electrode cell and a thermometer was used for the electrical conductivity measurements. The measurements were taken after adjustment for temperature.

#### **3.3.2 Alkalinity**

The method of potentiometric titration to a preselected pH, as set out in Standard Methods (1995), was used for the alkalinity measurements. A Radiometer PHM 82 pH meter with a combined pH electrode, a stirrer and a Radiometer Autoburette ABU 80 in conjunction with Radiometer Autotitrator unit TTT 80 was used for the titration of the water samples. A 20mL sample was transferred with a volumetric pipette to a beaker and placed on the stirrer. The electrode and tip of the burette was

placed in the sample. The solution was titrated with the standard 0,010N HCl to the endpoint pH of 4,5.

### **3.3.3 Major cations ( $K^+$ , $Na^+$ , $Ca^{2+}$ , $Mg^{2+}$ )**

Major cations in natural waters are usually in proportion to the total dissolved salts of that water. In other words, by determining the electrical conductivity of a sample, an appropriate dilution can be made so that the sample falls within the range of the working standards, which is 1mg/L to 100mg/L for  $Na^+$  and  $Ca^{2+}$  and 0.3 mg/L to 30mg/L for  $K^+$  and  $Mg^{2+}$ . The water samples were analysed by atomic absorption spectrophotometry. A flame atomic absorption spectrometer consisting essentially of the following components was used :

- (i) A stable light source, emitting the sharp resonance line of the element to be determined.
- (ii) A flame system into which the sample solution may be aspirated at a steady rate
- (iii) A monochromator to isolate the resonance line and focus it upon a photomultiplier.
- (iv) A photomultiplier to detect the intensity of light energy falling upon it, which is followed by facilities for simplification and readout.
- (v) A chart recorder for recording the output.

The operating procedure for the analysis are confined in Appendix B: B1.4.

### **3.3.4 Major anions ( $Cl^-$ , $SO_4^{2-}$ , $NO_3^-$ , $PO_4^{3-}$ , $NH_4^+$ )**

Sulphates and chlorides in natural waters are usually in proportion to the total dissolved salts of the water. So by determining the conductivity of a sample, an appropriate dilution can be used so that the sample falls within the range of the working standards. For working range for sulphates and chlorides are 5mg/L to 250mg/L and 5mg/L to 500mg/L, respectively. The autoanalyser system used for

analysis consists of the following: recorder, colorimeter, mixing manifold with appropriate coils, proportioning pump and an automatic sampler.

The analyses for nitrate, ammonia and phosphate were also performed using an autoanalyser. Some of the samples that were below the detection limits for nitrate and ammonia (0.5mg/L) of the freshwater laboratory of the CSIR was analysed by the author in the marine laboratory of the CSIR in Stellenbosch , where the detection limit for nitrate and ammonia was 0.01mg/L.

### **3.3.5 Dissolved organic carbon (DOC)**

The water samples for the analyses of dissolved organic carbon (DOC) were first filtered through a 0.45µm microporous membrane filter prior to analysis. The analysis was performed by an autoanalyser using the persulphate – ultraviolet oxidation method for total organic carbon, set out in Standard Methods (1995) as Method 5310C.

### **3.3.6 Stable isotopes of hydrogen and oxygen**

The analyses for the samples collected for oxygen-18 and deuterium analyses were done by the CSIR Laboratories in Pretoria using a dual-inlet mass spectrometer. Water samples had to be converted to appropriate gases for measurement by the mass spectrometer.

## **3.4 Accuracy check on chemical analyses**

### **3.4.1 Ionic Balance**

The ionic balance was determined for the results of the major cations and anions and the results are presented in the table of analysis in Chapter 4. The ionic balance was calculated by:

$$\text{Balance} = \frac{C(\text{meq/L}) - A(\text{meq/L})}{C(\text{meq/L}) + A(\text{meq/L})} \times 200$$

Where C (meq/L) is the total cation milli-equivalents per litre

A (meq/L) is the total anions milli-equivalents per litre

The ionic balance or charge balance error gives an indication of the accuracy of water analysis data. A fundamental condition of electrolyte solutions, such as groundwater, is that on a macro scale the sum of negative charges is equal to the sum of positive charges, i.e. that a condition of electro-neutrality exists (Freeze & Cherry, 1979). When significant deviation from equality occurs there must be either analytical errors in the concentration determinations or ionic species present at significant concentrations that were not included in the analysis. Normally a charge balance error of < 10% is considered to be acceptable. However, it should be remembered that large errors in individual ion analyses may balance each other out.

For all the water samples analysed during March 2004 to August 2004, the ionic balance was < 5%. This is an indication that the data sets obtained from March to August 2004 were of good quality and all 36 samples will be used to determine the hydrochemical character of groundwater in the Incomati Estuary.

### **3.4.2 Piper Diagram**

A need developed to find a more convenient way to refer to water compositions by identifiable categories and this is where the concept of hydrochemical facies was developed. Hydrochemical facies are distinct zones that have cation and anion concentrations describable within defined composition categories.

Piper Diagrams are one of the most useful ways of representing and comparing water quality. In the Piper Diagram cations, expressed as percentages of total cations in milliequivalents per liter, plots as a single point on the left triangle and anions,



similarly expressed as percentages of total anions, appear as a single point in the right triangle. These two points are then projected into the central diamond-shaped area parallel to the upper edges of the central area. This single point is thus uniquely related to the total ionic distribution. The Piper Diagram also conveniently reveals similarities and differences among groundwater samples. Those samples with similar qualities will tend to plot together as groups (Todd & Mays, 2005).

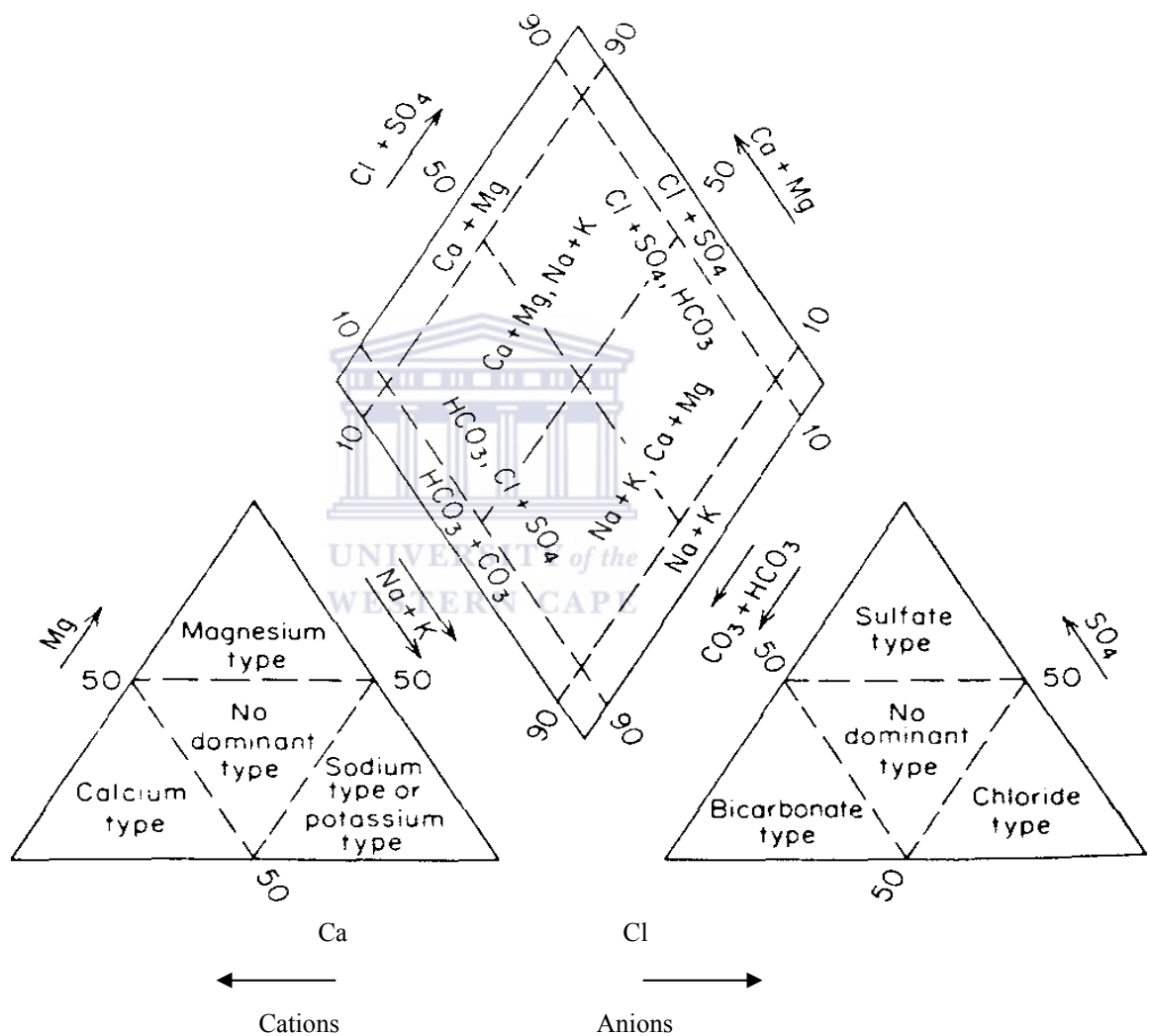


Figure 7: Classification diagram for anion and cation facies in terms of major-ion percentages. Water types are selected according to the area in which they occur on the diagram segments (Frreze & Cherry, 1979).

# Chapter 4

## Analytical Results

Table 1: Results for March 2004

Site ID:	Drill 7m	Drill 13m	Drill 16m	Drill 35m	Drill 43m	Manual 1	Piezo	Creek	Village	Ridge	Island
Sample Date:	19-Mar	19-Mar	19-Mar	17-Mar	19-Mar	17-Mar	17-Mar	19-Mar	19-Mar	19-Mar	18-Mar
Sample ID:	A	B	C	D	E	F	G	H	I	J	K
Potassium as K mg/L	23	22	20	21	329	300	365	105	6.5	7.3	308
Sodium as Na mg/L	173	351	198	144	6958	8327	10409	2540	79	19	8038
Calcium as Ca mg/L	567	119	420	95	650	357	446	120	45	18	339
Magnesium as Mg mg/L	0.1	0.1	0.5	0.1	670	1056	1350	300	6.8	5.5	936
Ammonia as N mg/L	1.3	5.0	0.8	0.8	5.8	2.9	1.0	0.1	0.5	0.1	0.1
Sulphate as SO4 mg/L	6.3	74	18	14	2137	1613	2097	617	30	12	1895
Chloride as Cl mg/L	118	630	123	250	12750	15385	18750	4542	135	30	14250
Alkalinity as CaCO3 mg/L	1599	190	1252	206	112	679	807	88	87	45	459
Nitrate plus nitrite as N mg/L	104	681	116	220	113	1333	1050	65	87	681	50
Ortho phosphate as P mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.79	<0.1	<0.1	0.95	<0.1
Dissolved Organic Carbon mg/L	26	368	24	11	24	5.7	3.3	3.9	23	1.3	<1
Conductivity mS/m (25°C)	7500	300	580	172	3500	4050	5000	1400	76	27	3950
pH (Lab) (25°C)	12.3	11.2	12.3	11.5	9.8	7.3	7.7	7.4	6.9	6.9	7.1
Hardness as CaCO3 mg/L	1417	298	1052	237	4381	5240	6674	1535	140	68	4702
SAR as mmol/L	2.0	8.8	2.7	4.1	45.8	50.1	55.4	28.2	2.9	1.0	51.0
Total Dissolved Solids (mg/L)	48000	1920	3712	1100.8	22400	25920	32000	8960	486.4	172.8	25280
% Difference	3.07	4.45	4.57	1.02	1.84	1.33	1.11	0.81	4.34	0.44	0.20
CATIONS meq/L	36.51	22.12	30.19	11.59	399.04	474.79	595.51	143.85	6.44	2.37	451.50
ANIONS meq/L	35.42	23.11	28.87	11.47	406.37	481.10	588.94	142.70	6.17	2.38	450.58



Table 2: Results for April 2004

Site ID:	Drill 7m	Drill 13 m	Drill 16m	Drill 35m	Drill 43m	Manual 1	Island Creek	Island. Creek at P	Piezo	Well water	New M A	New M B	New M C	Creek	Seawater
Sample Date:	April 04	April 04	April 04	April 04	April 04	April 04	April 04	April 04	April 04	April 04	April 04	April 04	April 04	April 04	April 04
Sample ID:	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Potassium as K mg/L	20	19	14	22	333	274	159	160	286	6.7	305	308	114	114	109
Sodium as Na mg/L	194	541	174	216	9314	8188	4552	4533	8000	86	9000	9141	3250	3125	3063
Calcium as Ca mg/L	527	115	375	25	663	340	182	169	318	43	341	330	125	123	115
Magnesium as Mg mg/L	0.40	35	0.40	10	1089	1042	542	545	947	8.0	1084	1073	406	399	393
Ammonia as N mg/L	1.6	<0.1	0.6	<0.1	2.7	3.1	<0.1	<0.1	<0.1	0.59	0.12	0.12	<0.1	<0.1	<0.1
Sulphate as SO4 mg/L	4.5	27	8.9	28	2552	1445	1125	1105	1797	35	2246	2227	828	781	785
Chloride as Cl mg/L	136	905	81	346	16429	14405	7714	7771	13625	145	16000	16429	5800	5650	5600
Alkalinity as CaCO3 mg/L	1512	254	1160	55	92	754	129	129	449	83	101	71	103	96	96
Nitrate plus nitrite as N mg/L	<0.1	<0.1	<0.1	0.34	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.44	<0.1	<0.1
Ortho phosphate as P mg/L	<0.1	0.10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dissolved Organic Carbon mg/L	23.0	110	17	8.0	10	7.8	1.8	2.1	0.8	23	2.9	2.3	2.2	2.9	2.9
Conductivity mS/m (25°C)	680	350	530	152	4550	3950	2300	2300	3900	150	4300	4300	1800	1750	1750
pH (Lab) (25°C)	12.4	7.6	12.3	9.0	8.5	7.1	7.6	7.6	7.3	7.1	7.1	6.7	7.6	7.7	7.7
Saturation pH (pHs) (20°C)	5.8	7.2	6.0	8.5	7.0	6.3	7.3	7.4	6.6	8.1	7.2	7.4	7.6	7.6	7.7
Total Dissolved Solids (Calc) mg/L	4352	2240	3392	973	29120	25280	14720	14720	24960	960	27520	27520	11520	11200	11200
Hardness as CaCO3 mg/L	1318	432	938	104	6139	5140	2686	2666	4694	140	5314	5239	1984	1950	1906
SAR as mmol/L	2.3	11.3	2.5	9.2	51.7	49.7	38.2	38.2	50.8	3.2	53.7	55.0	31.7	30.6	30.5
% Difference	3.57	4.73	4.06	4.64	3.50	3.23	4.98	3.99	4.27	4.30	1.08	0.20	0.55	0.15	1.23
CATIONS meq/L	35.39	32.65	26.71	12.00	536.50	466.09	255.73	254.54	449.11	6.76	505.47	510.16	183.94	177.82	174.08
ANIONS meq/L	34.17	31.18	25.67	11.47	518.37	451.49	243.60	244.77	430.71	6.48	500.09	511.18	182.93	177.56	176.23

Table 3: Results for August 2004

Site ID:	Drill 7 m	Drill 16 m	Drill 35 m	Drill 43 m	Manual 1	Creek Surf	Creek Bed	New Well	Pit A	Pit B
Sample Date:	11-Aug	11-Aug	11-Aug	11-Aug	14-Aug	15-Aug	15-Aug	11-Aug	12-Aug	12-Aug
Sample ID	A	B	C	D	E	F	G	H	I	J
Potassium as K mg/L	15	17	22	138	271	269	256	68	306	312
Sodium as Na mg/L	215	244	218	3846	7808	7077	6885	1377	8320	8360
Calcium as Ca mg/L	483	357	21	432	375	292	288	69	333	347
Magnesium as Mg mg/L	0.54	0.05	8.9	433	1002	866	840	119	1018	1023
Ammonia as N mg/L	1.2	1.0	0.50	4.4	2.2	<0.1	0.32	<0.1	0.21	<0.1
Sulphate as SO4 mg/L	21	28	2	1068	1528	1736	1852	269	2176	2141
Chloride as Cl mg/L	250	250	383	7333	14265	12794	12353	2294	15000	14853
Alkalinity as CaCO3 mg/L	1333	1050	65	87	681	116	50	220	113	104
Nitrate plus nitrite as N mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.19	0.13	0.90
Ortho phosphate as P mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.26	<0.1	<0.1
Dissolved Organic Carbon mg/L	25	21	4.4	3.0	5.5	1.8	1.0	17	1.1	1.3
Conductivity mS/m (25°C)	630	520	142	2110	3900	3510	3430	770	4100	4050
pH (Lab) (25°C)	12.3	12.2	9.3	8.5	7.3	7.5	7.3	8.3	7.6	7.7
Saturation pH (pHs) (20°C)	5.9	6.1	8.5	7.1	6.3	7.2	7.6	7.5	7.2	7.2
Total Dissolved Solids (Calc) mg/L	4032	3328	909	13504	24960	22464	21952	4928	26240	25920
Hardness as CaCO3 mg/L	1208	892	88	2862	5062	4293	4179	662	5024	5081
SAR as mmol/L	2.7	3.6	10.1	31.3	47.8	47.0	46.3	23.3	51.1	51.0
Kjeldahl Nitrogen as N mg/L	-	-	-	-	4.6	0.42	1.8	8.3	5.8	1.9
% Difference	0.56	1.16	2.72	1.10	0.01	0.29	0.40	0.17	0.12	1.60
CATIONS meq/L	33.95	28.97	11.83	228.33	447.84	400.49	389.55	74.87	470.13	473.14
ANIONS meq/L	34.14	28.64	12.16	230.84	447.78	399.34	388.00	74.74	470.68	465.68

Table 4: Results – analytical statistics

	Range	Mean	Median	Standard Deviation	Concentration limits for groundwater for domestic purposes (DWAf)	Seawater
<b>Major Cations (ppm)</b>						
<b>K<sup>+</sup></b>	6.5 - 365ppm	147ppm	114	129	50	390
<b>Na<sup>+</sup></b>	19.0 - 10409ppm	3921ppm	3188	3662	200	10 500
<b>Ca<sup>2+</sup></b>	18.0 - 663ppm	261ppm	290	181	150	410
<b>Mg<sup>2+</sup></b>	0.05 - 1350ppm	465ppm	403	453	100	1350
<b>NH<sub>4</sub><sup>+</sup></b>	<0.1 - 5.8ppm	1.4ppm	1	1.6	Ns	Ns
<b>Major Anions (ppm)</b>						
<b>HCO<sub>3</sub><sup>-</sup></b>	45.0 - 1599ppm	377ppm	115	454	Ns	142
<b>NO<sub>3</sub><sup>-</sup></b>	<0.1 - 1331 ppm	245ppm	87	393	10	Ns
<b>Cl<sup>-</sup></b>	30.0 - 18750ppm	6969ppm	5725	6583	200	19 000
<b>SO<sub>4</sub><sup>2-</sup></b>	2.0 - 2552ppm	929ppm	799	887	400	2700
<b>PO<sub>4</sub><sup>3-</sup></b>	<0.1 - 2.79ppm	1.0ppm	1	1.2	Ns	Ns
<b>Physical Parameters</b>						
<b>Conductivity mS/m</b>	27 - 7500	2213	1800	1874	150	5000
<b>pH (Lab)</b>	6.7 - 12.4	9.0	8	1.9	5.0 – 9.5	Ns
<b>Total Dissolved Solids (Calc) mg/L</b>	173 - 48000	14167	11 520	11994	1000	32 000

Ns= Not specific

Table 5: Sample Identification Table for March 2004

Site ID	Location	Project ID	Colour Code
Drill 7m	Drilled Multipiezo	A	Black
Drill 13m	Drilled Multipiezo	B	Dark Red
Drill 16m	Drilled Multipiezo	C	Green
Drill 35m	Drilled Multipiezo	D	Blue
Drill 43m	Drilled Multipiezo	E	Yellow
Manual 1	Coastal	F	Light Green
Piezo	Coastal	G	Red
Creek	Coastal	H	Dark Blue
Village	Inland	I	Magenta
Ridge	Inland	J	Yellow
Island	Coastal	K	Cyan

Table 6: Sample Identification Table for April 2004

Site ID	Location	Project ID	Colour Code
Drill 7m	Drilled Multipiezo	A	Magenta
Drill 13m	Drilled Multipiezo	B	Yellow
Drill 16m	Drilled Multipiezo	C	Green
Drill 35m	Drilled Multipiezo	D	Blue
Drill43m	Drilled Multipiezo	E	Cyan
Manual 1	Coastal	F	Dark Red
Island Creek	Coastal	G	Purple
Island Creek at P	Coastal	H	Teal
Piezo	Coastal	I	Olive Green
Well Water	Inland	J	Dark Green
New MA	Coastal	K	Orange
New MB	Coastal	L	Yellow
New MC	Coastal	M	Light Purple
Creek	Coastal	N	Red
Seawater	Coastal	O	Dark Blue

Table 7: Sample Identification Table for August 2004

Site ID	Location	Project ID	Colour Code
Drill 7m	Drilled Multipiezo	A	Black
Drill 16m	Drilled Multipiezo	B	Dark Red
Drill 35m	Drilled Multipiezo	C	Green
Drill 43m	Drilled Multipiezo	D	Blue
Manual 1	Drilled Multipiezo	E	Yellow
Creek Surface	Coastal	F	Light Green
Creek Bed	Coastal	G	Red
New Well	Coastal	H	Dark Blue
Pit A	Inland	I	Magenta
Pit B	Inland	J	Yellow

Table 4 gives a brief statistical summary of the data collected over the study period. In this table, the data collected over the study period are being compared to the guidelines for groundwater set by DWAF for domestic purposes and that of seawater. From this table very wide ranges and high standard deviations are easily recognised for most of the parameters. Such wide ranges for solutes concentrations suggest that multiple sources and/or complex hydrochemical process take place to generate the chemical composition. The high nitrate concentration (mean=245 mg/L) in the study area reflects a possible degradation of groundwaters due to anthropogenic contamination. The samples collected from the newly drilled multi-piezometer boreholes in the tidal area meet most of the requirements set by DWAF for drinking and irrigation purposes, except for conductivity and pH. All the other boreholes fail to meet the requirements. The standard deviations and medians are also very high for all the parameters analysed. This further illustrates

the vast difference in quality/composition of the groundwater within the study area differs. By comparing the values of the mean, median and standard deviation for the different parameters to the requirements set by DWAF and that of seawater, it is evident that seawater plays a very significant role in the quality / composition of the groundwater in the study area.

## **4.1 Results**

### **4.1.1 Major ions**

#### **a) Piper Diagrams**

Fig.8, 9 &10 show the plots of the hydrochemistry of the water samples sampled during March 2004, April 2004 and August 2004 respectively on piper diagrams

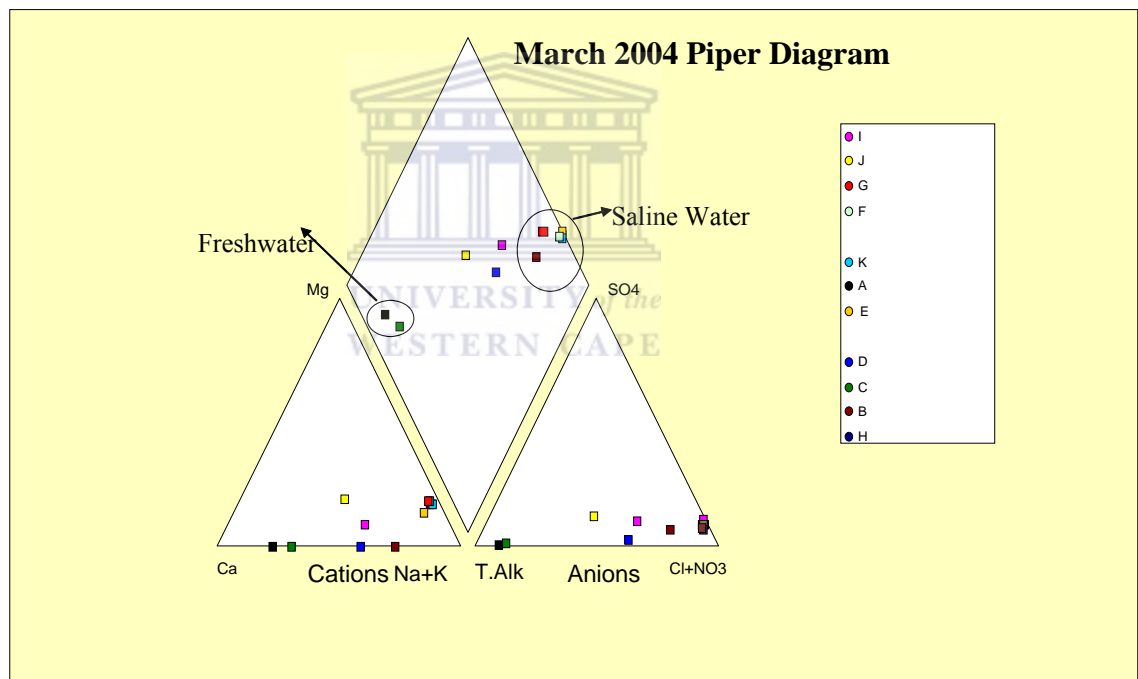


Fig. 8 Piper diagram for March 2004 sampling run

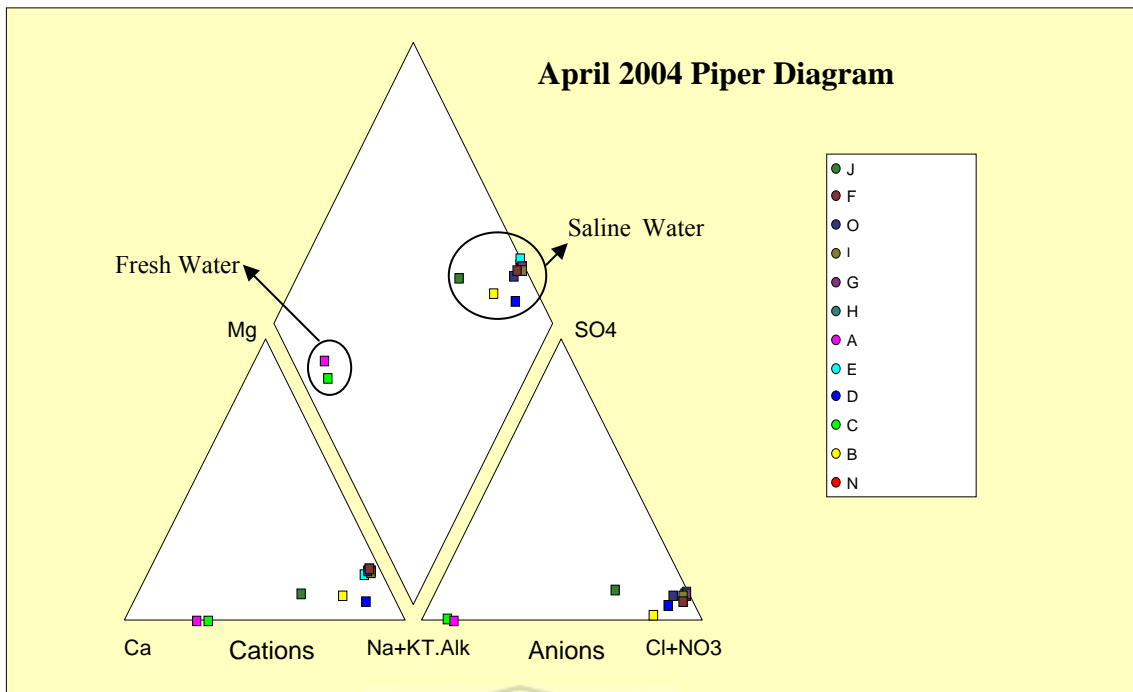


Fig. 9 Piper diagram for April 2004 sampling run

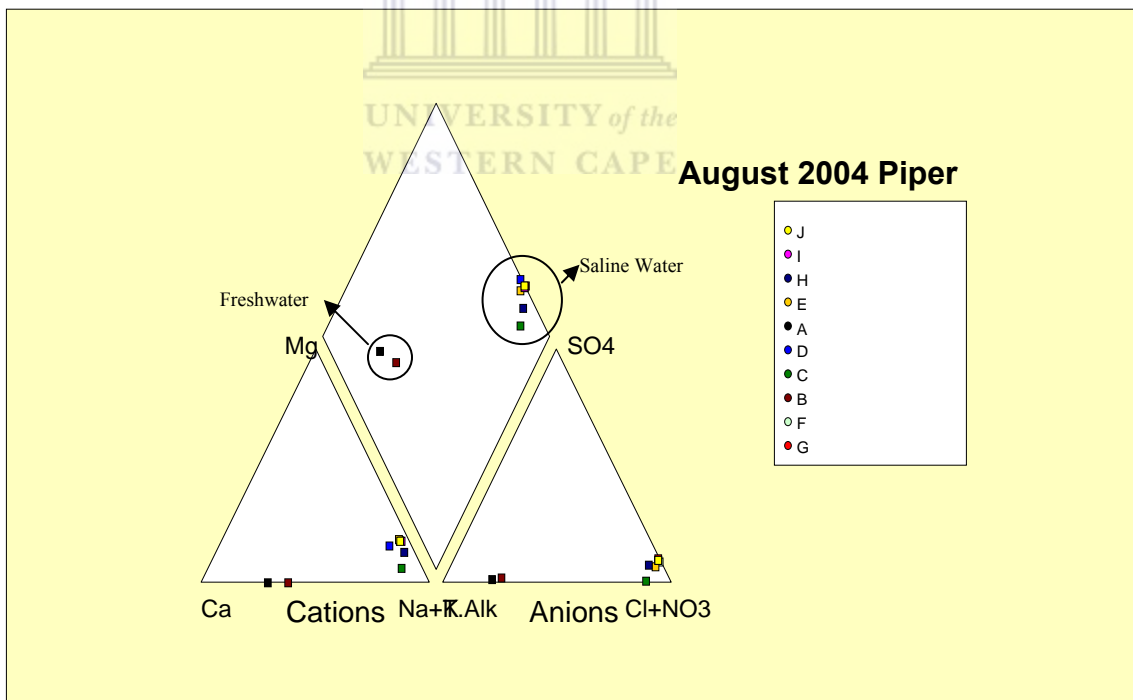


Fig.10 Piper diagram for August 2004 sampling run



All the boreholes sampled over the sampling period are illustrated in the above Piper Diagrams. Of all the boreholes, only three were sampled in March, April and August, namely Manual 1, Drill 7m, Drill 16, Drill 35m, Drill 43m and Creek. The Drill samples are all located at the same borehole, but sampled at the different depths. The following trends and characterization of the groundwaters in the study area were done by considering only these three boreholes / six different samples in the Piper Diagrams:

- Most of the samples are illustrated as being Na-Cl type waters, except the drill 7m and drill 16m being Ca-HCO<sub>3</sub> type groundwaters.
- From the above Piper Diagrams it is observed that all or most of the samples plotting in the saline region of the Piper Diagram, are the ones that are located in close proximity to the coastline and at greater depths (drill 35m and 43m), whereas the Ca-HCO<sub>3</sub> are at a shallower depth (drill 7m and 16m).
- When comparing the 3 Piper Diagrams one notices the difference in chemical composition of the drill 35m sample. In Fig.8 the drill 35m plots in the middle of the diamond shape within the Piper Diagram, whereas in Fig.9 and Fig.10, it plots in the saline / Na-Cl region. The difference in chemical composition of Drill 35m in the March Piper Plot compared to the April and August Piper Plots can be as a result of the rain experienced during the Wet Season (November to April), causing the groundwater at a depth of 35m to be influenced by the infiltration of the rain or due to a possible drop in the water levels towards the end of the Wet Summer Season in April and during the mid Dry Winter Season (See Fig.11).
- The fact that drill 35m plots in the saline region for both the April and August can possibly also be attributed to the high abstraction that would normally be encountered during the Dry Seasons (May to October).

- Besides for the difference in composition observed for drill 35m sample, no real seasonal variation is observed. Some spatial variation is however observed where the boreholes located a little further from the coast and at shallower depths have a composition resembling “fresh” groundwater compared to the boreholes situated near the coastline and at a greater depth.

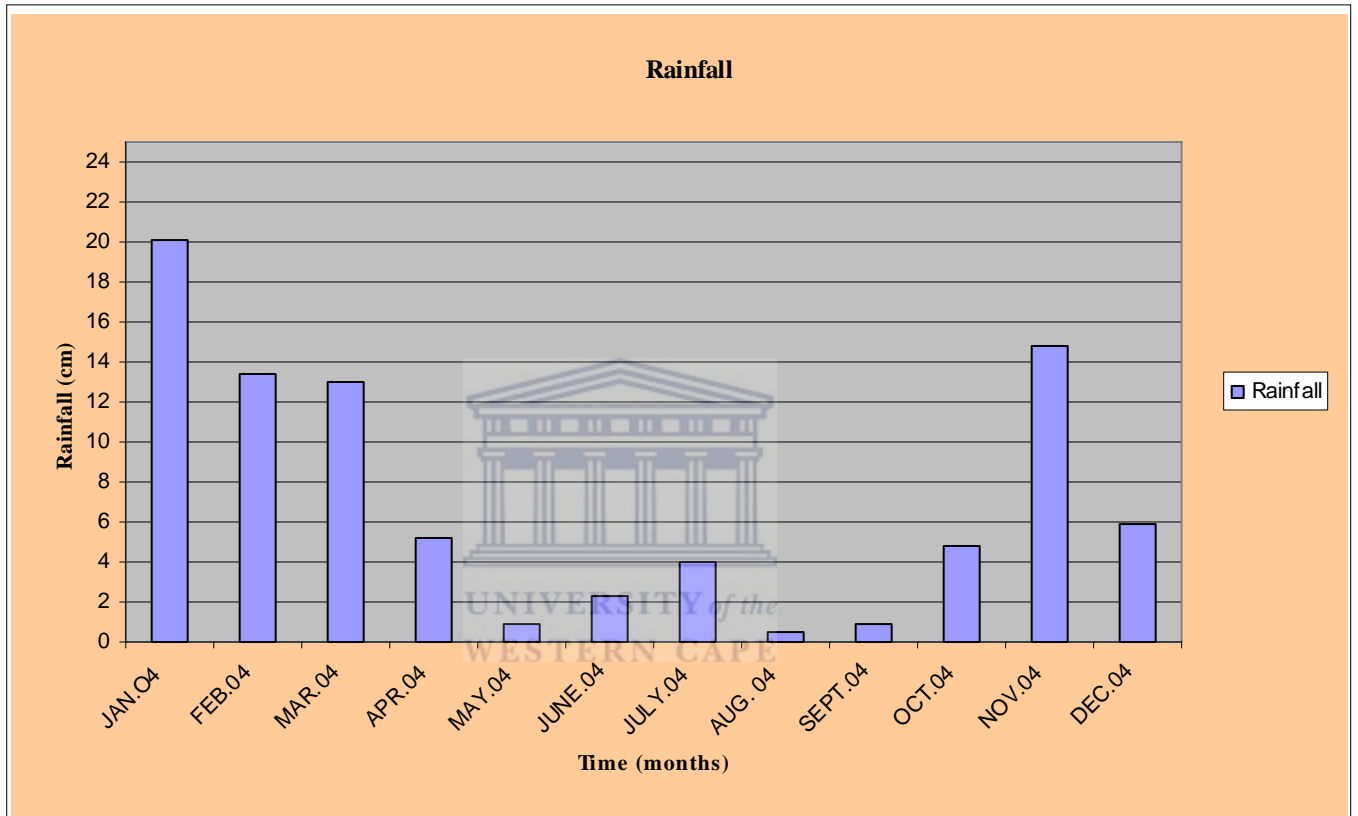


Fig.11 Rainfall

### **b) Bivariate Diagrams**

The changes in the chemical composition of the groundwater can be caused by mixing with saltwater as well as by chemical reactions, such as ion-exchange processes taking place within the groundwater system. A hydrogeochemical study done in Korea by (Kim,2003) was used to identify the origin of the saline groundwater in Korea. He made use of hydrogeochemical characteristics based on bivariate diagrams of major and minor ions to show that changes in chemical composition of groundwater are controlled by the salinization process followed by cation exchange processes. The following bivariate diagrams, namely Fig.12 to Fig 14, illustrate

the Cl/HCO<sub>3</sub> ratio vs. Cl relationship for the 3 sampling periods. These graphs allow one to identify the boreholes with “fresher” groundwater and those influenced by the intrusion of saline water.

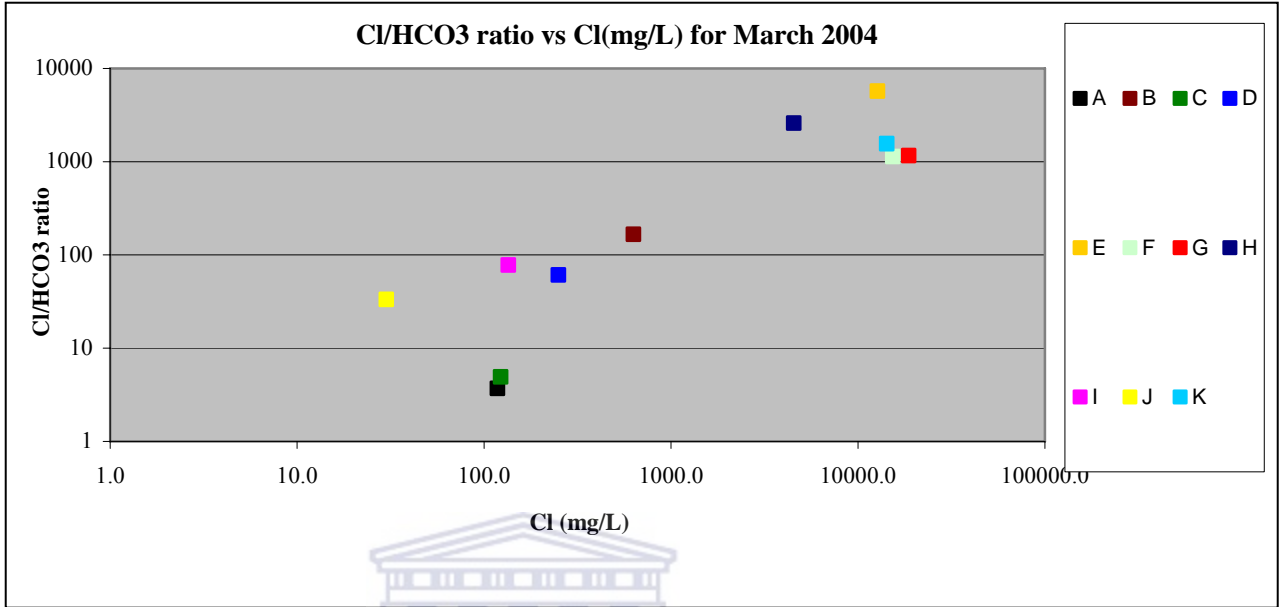


Fig 12: Cl/HCO<sub>3</sub> ratio vs Cl(mg/L) for March 2004

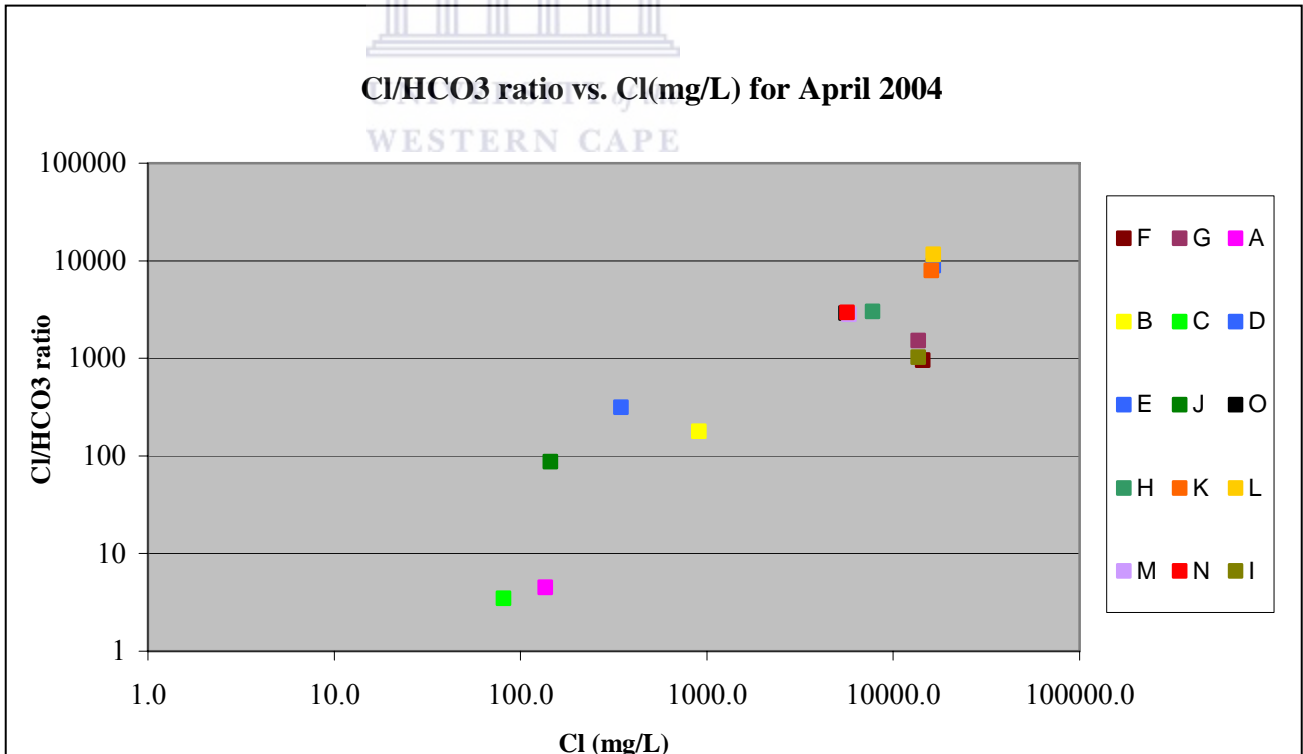


Fig 13: Cl/HCO<sub>3</sub> ratio vs Cl(mg/L) for April 2004

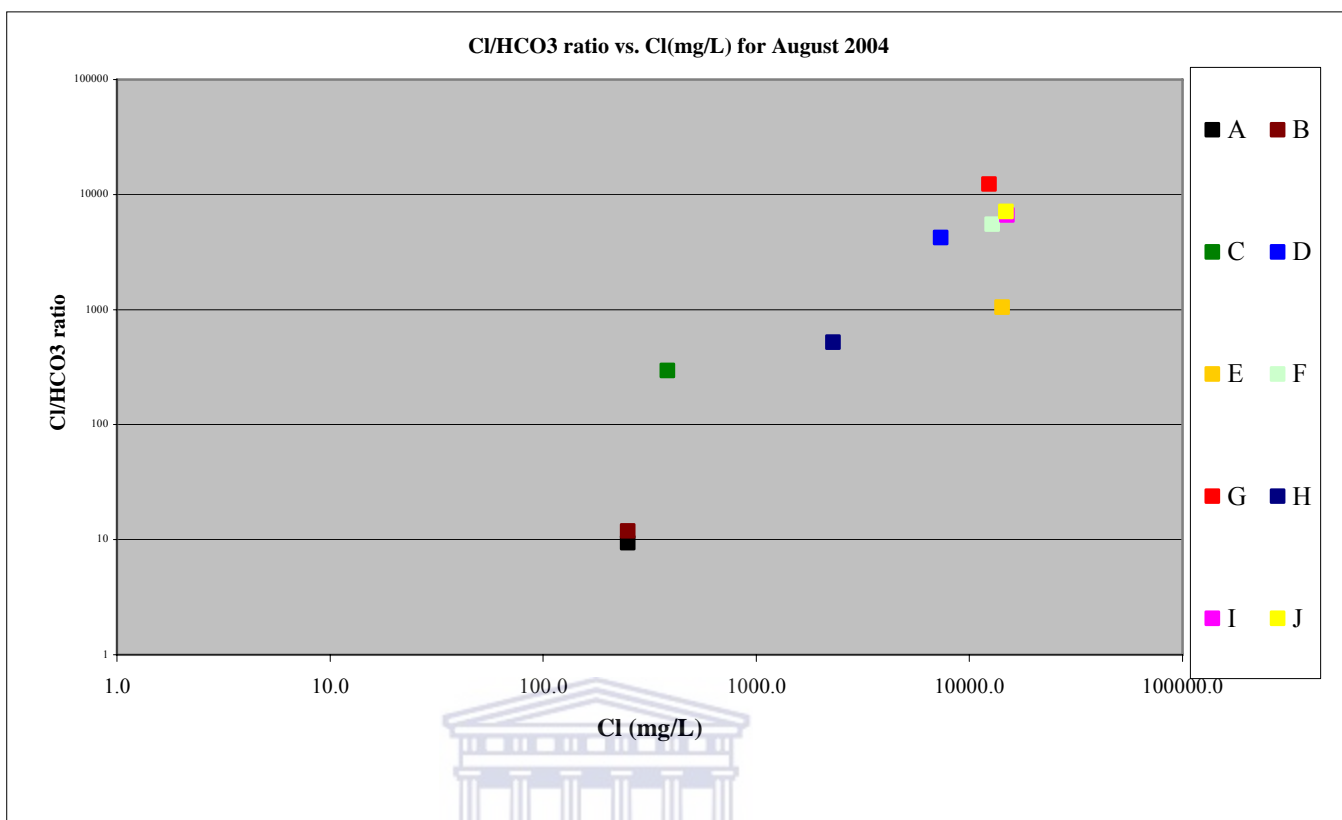


Fig 14: Cl/HCO<sub>3</sub> ratio vs Cl(mg/L) for August 2004

From the graphs one sees that some boreholes have much higher ratios compared to the others. The boreholes plotting in the lower ratios can be characterised as having “fresher” or more dilute groundwater, whereas the boreholes plotting in the higher ratios as saline groundwater, that has been influenced by the intrusion of seawater (Kim, 2003). These graphs further illustrates that the boreholes in close proximity of the coastline and at greater depths are influenced by the intrusion of saline water.

### c) Relationship between sodium and chloride

As we investigate the quality and/or composition of groundwater in the study area that is determined by saline water and/or water–rock interactions, the chemistry of the water can be explained with respect to plots of dissolved species vs. chloride, due to the fact that chloride behaves conservative as far as the salinization process is concerned. For this study the molar

ratios of sodium vs. chloride was plotted to determine or investigate the chemistry of the groundwater in the study area.

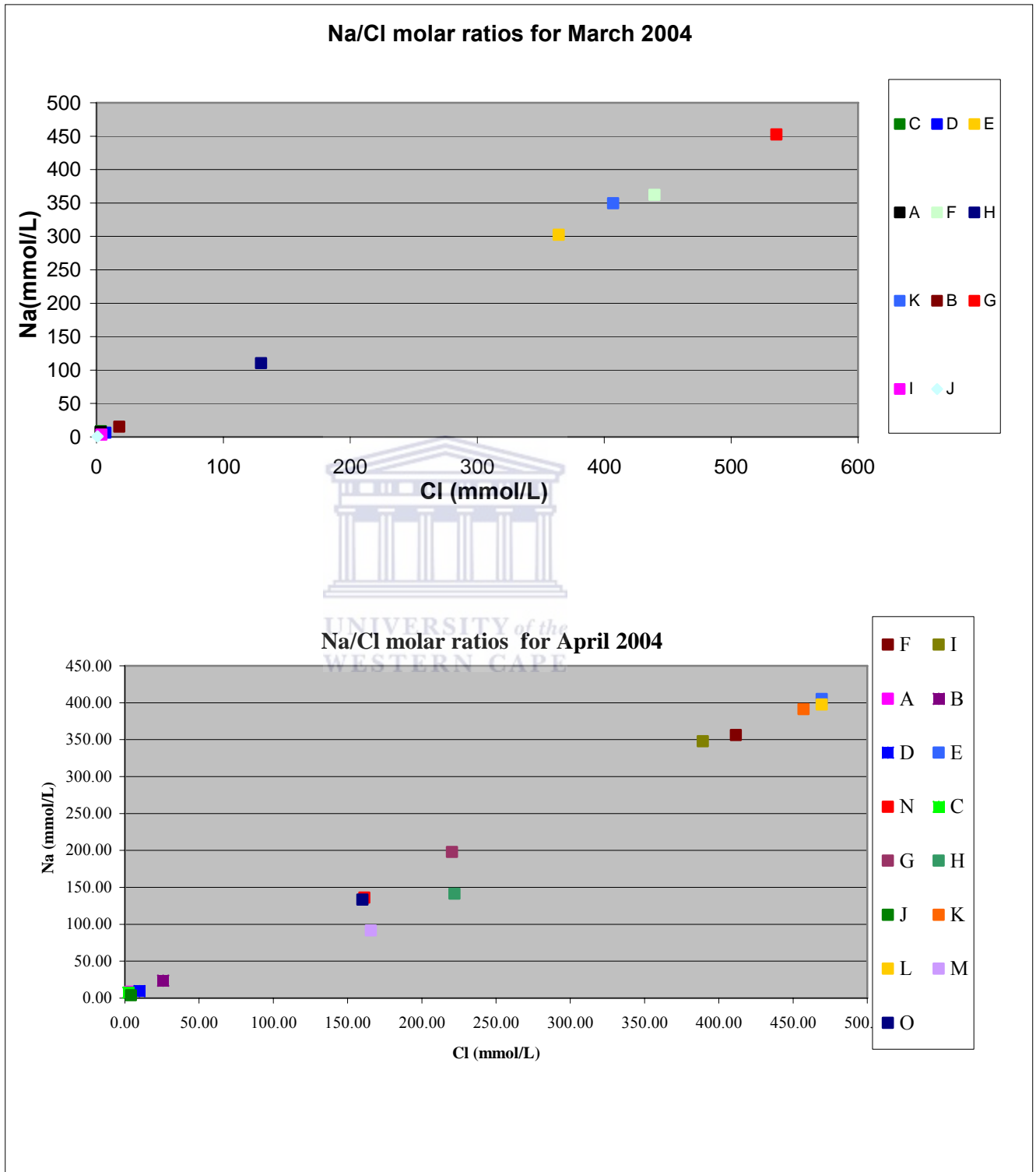


Fig 15. Na/Cl molar ratios for March & April 2004

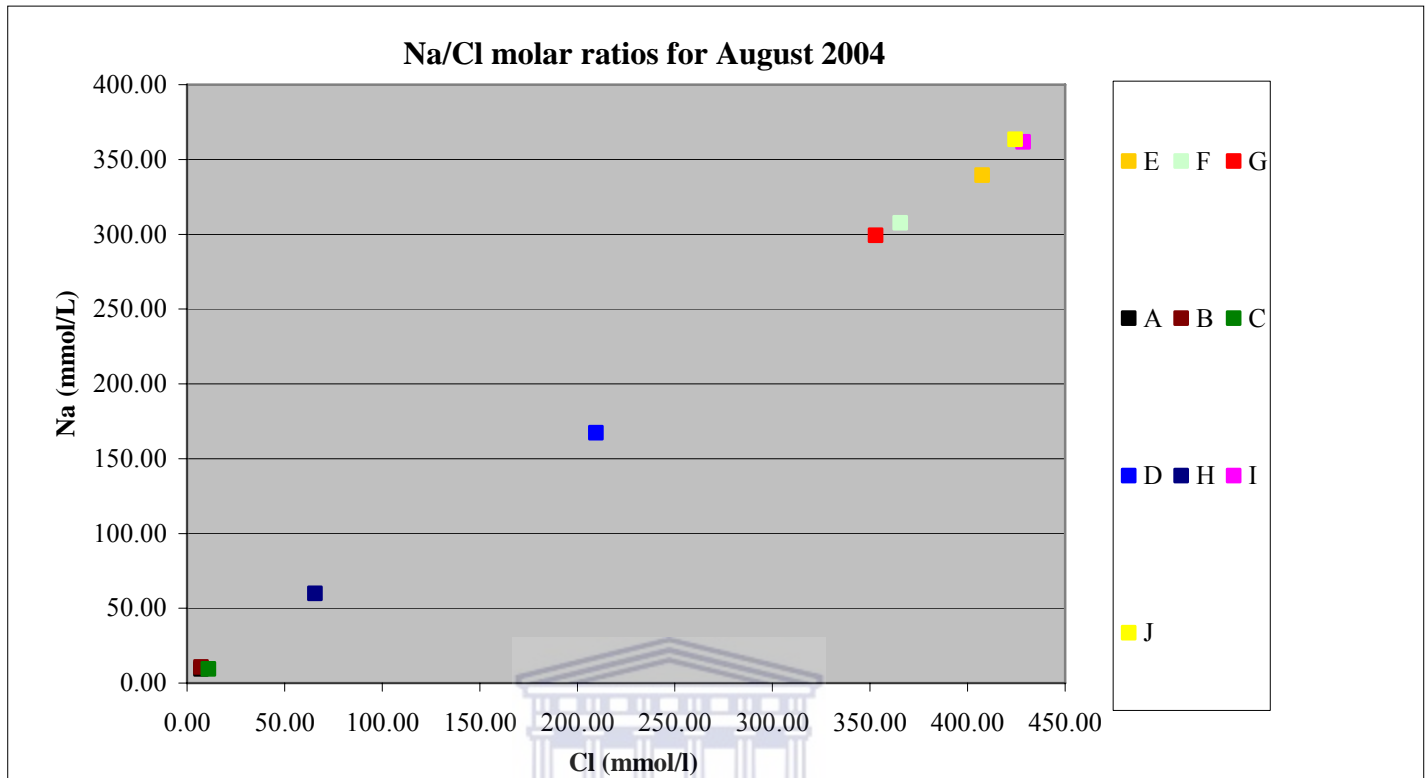


Fig.16 : Na/Cl molar ratios for August 2004

As shown in figures 15 and 16, the coastal boreholes and the drill 43m sample are the ones with high Na/Cl molar ratios compare to the other boreholes at a distance further from the shore and at lesser depths. The boreholes having the high Na/Cl molar ratios are also the ones with the higher TDS values (Figs. 17 & 18). The high TDS value encountered in Sample H during the March 2004 sampling run can possibly be attributed to anthropogenic or point source contamination. The combination of the high Na/Cl molar ratios, combined with the high TDS values again serves as evidence that seawater intrusion could be main cause of salinization of these boreholes. This trend is observed in all three plots.

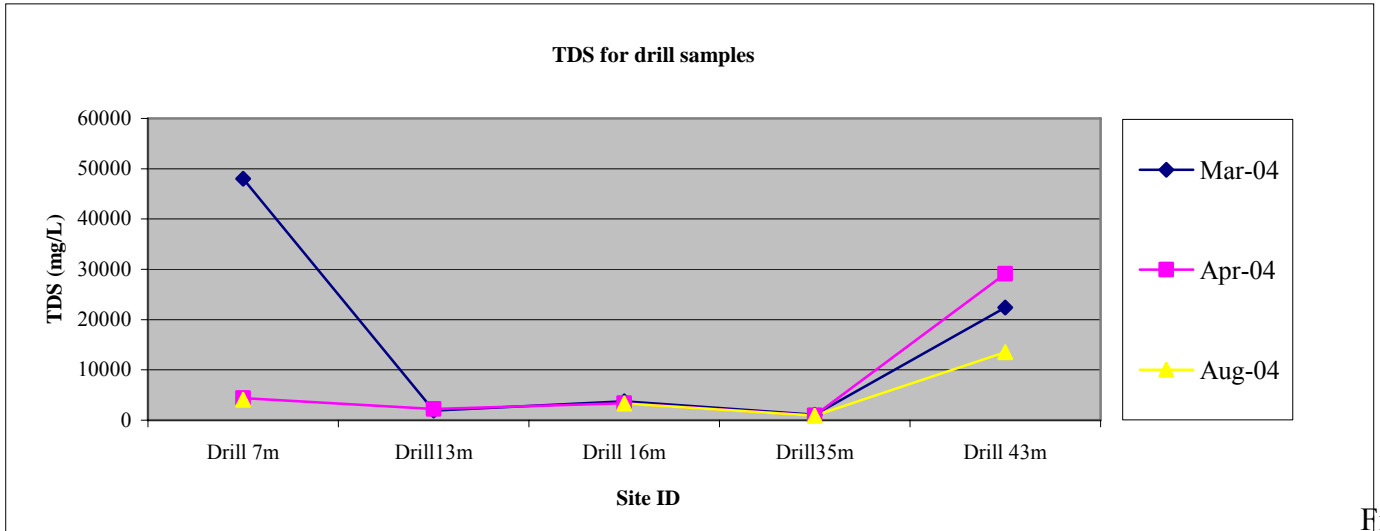


Fig.

17: TDS for drilled samples

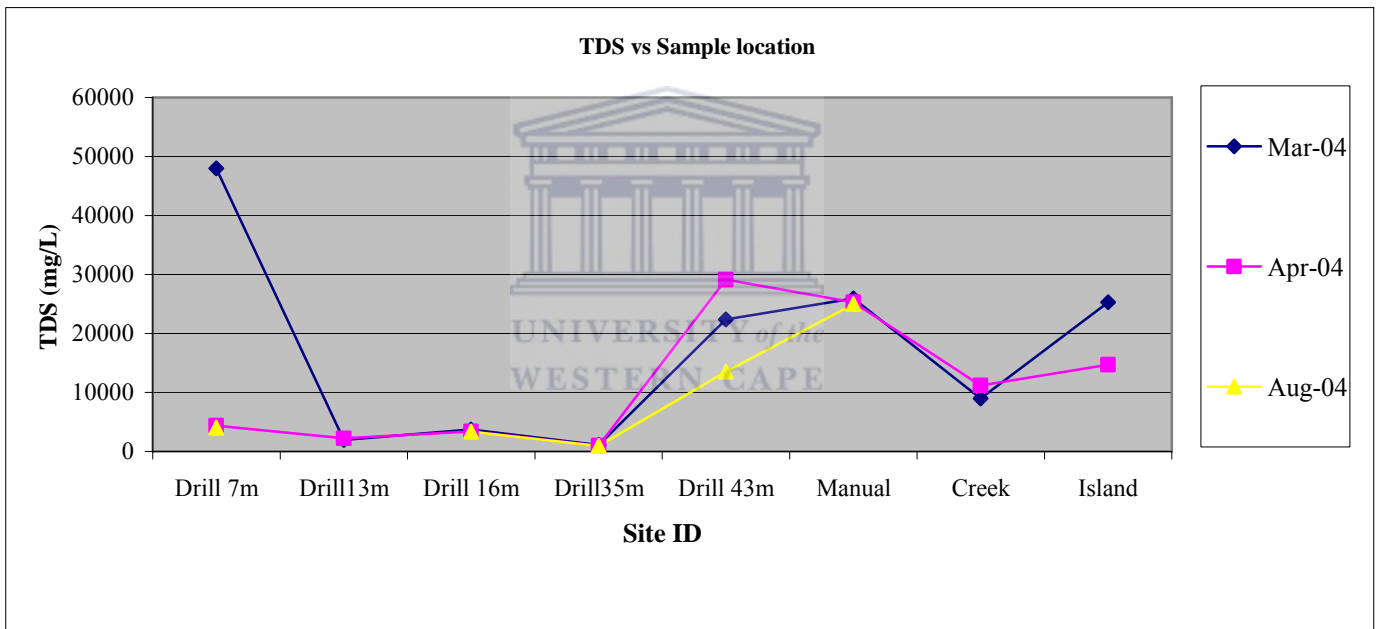


Fig.18: TDS vs sample location

#### 4.2 Isotope Analysis

The naturally-occurring stable isotopes,  $\delta D$  and  $\delta^{18}O$  have become useful tools in groundwater studies. The main hydrogeological use for environmental isotopes can be summarized as follows:

- To identify the occurrence of mixing two or more water types
- To provide signature to a particular water type



- To provide residence time information about groundwater

Isotopes of oxygen and hydrogen are in some instances, ideal geochemical tracers of underground water because their concentrations are not subject to changes by interaction with the aquifer material (UNESCO, 1973). Once the water is underground and removed from zones of evaporation, the isotope ratios do not change, except by mixing. When precipitation infiltrates to recharge the groundwater, mixing in the unsaturated zone controls the isotopic variations. The water in the saturated zone then has a composition corresponding to the mean isotopic composition of infiltration in the area. Analyses of  $\delta D$  and  $\delta^{18}O$  can be used to identify the probable source of an underground water.

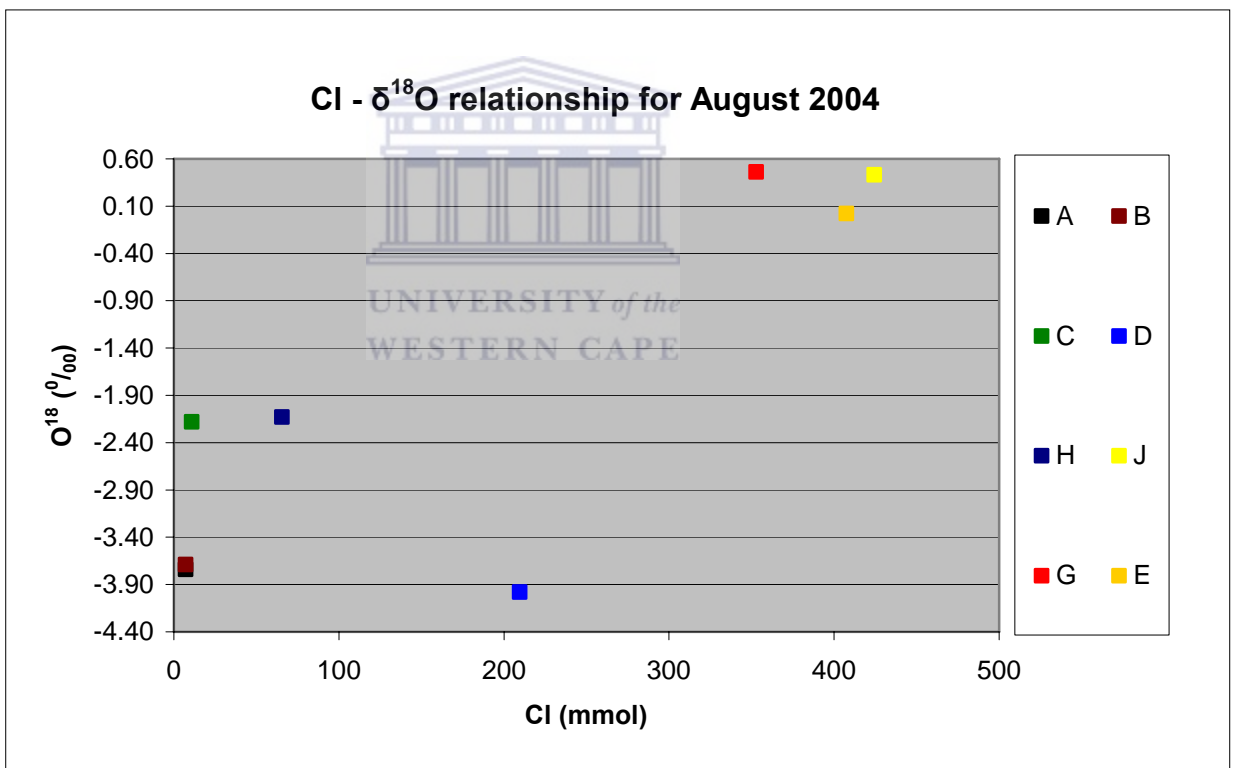


Fig.

19 Cl(mg/L) vs. Oxygen-18 for August 2004

The Cl -  $\delta^{18}O$  relationship reveals that three of the samples from the August 2004 sampling period follows a trend of TDS increase with isotopic enrichment, indicating mixing of fresh groundwater

with seawater (Faye et al, 2004). One the samples, namely L (Drill43m), has a trend of high TDS without isotopic enrichment. Other processes whose effects can be combined can be used to explain this trend. Among them are the following:

- (1) mixing process of different waters along flow paths, combined with evaporation,
- (2) the isotopic contents of the local rainfall
- (3) transpiration from vegetation cover is also known to abstract water without causing isotopic fraction
- (4) dissolution of the salt minerals could change the interstitial water chemistry, thereby increasing the TDS in the transition zone (Gat, 1981).

### **4.3 Water quality assessment**

The quality of most of the boreholes sampled in this study can be described as poor, based on guidelines set out for drinking water purposes by the World Health Organisation (WHO) and the Department of Water Affairs and Forestry (DWAF), even though a large number of the population living in Maputo rely on groundwater as water supply. High solute concentrations were obtained in most of the boreholes sampled over the sampling period. These high concentrations limit the potential use of these water sources.

From the data in the table below, it is evident that the boreholes located further from the coast and at shallower depths are of a better quality than those located near the coast, according to the specification of DWAF and WHO as illustrated in Table 1 above. The boreholes near to the coast and at greater depths have TDS and chloride concentration much higher than the boreholes located further inland and at shallower depths. Due to the high TDS(>10 000mg/L) and chloride(> 5000mg/L) values of these boreholes, the groundwater has a very salty taste, making it almost impossible to use for drinking purposes.

**Table 6 :**Comparison of borehole water quality with the limits as set out by DWAF & WHO for domestic purposes as well limits as set out by DWAF for livestock watering and irrigation (All values are expressed as mg/L)

	<b>TDS</b>	<b>SO<sub>4</sub><sup>2-</sup></b>	<b>Cl<sup>-</sup></b>	<b>Na<sup>+</sup></b>	<b>Ca<sup>2+</sup></b>	<b>Mg<sup>2+</sup></b>	<b>Hardness</b>
<b>DWAF (drinking)</b>	<b>450</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>32</b>	<b>30</b>	<b>50</b>
<b>WHO (drinking)</b>	<b>1000</b>	<b>500</b>	<b>250</b>	<b>200</b>			<b>500</b>
<b>DWAF(Livestock)</b>	<b>100</b>	<b>1000</b>	<b>1500</b>	<b>200</b>	<b>1000</b>	<b>500</b>	
<b>DWAF(Irrigation)</b>			<b>&lt;100</b>	<b>&lt;70</b>		<b>0.2</b>	
<b>Sample Location</b>							
Drill 7m (P7)	4192	10.6	168	194	526	0.35	1314
Drill 13m (P13)	2080	50.5	767	446	117	17.6	365
Drill 16m (P16)	3477	18.3	151	205	384	0.32	961
Drill 35m (P35)	994	15	326	193	47	6.3	143
Drill43m (P43)	21675	1919	12171	6706	582	731	4461
Manual (Coastal)	25387	1529	14685	8108	357	1033	5147
Piezo (Coastal)	28480	1947	16187	9204	382	1148	5684
Creek (Coastal)	10080	699	5096	2832	121	350	1742
Village (Inland)	486	30	135	79	45	6.8	140
Ridge (Inland)	172	12	30	19	18	5.5	68
Island (Coastal)	25280	1895	14250	8038	339	936	4702
Well water (Inland)	960	35	145	86	43	8.0	140
New Well (Coastal)	4928	269	2294	377	69	119	662

According to the requirements by the World Health Organisation (WHO) and the Department of Water Affairs and Forestry(DWAF) for groundwater for the purpose of domestic use, most of the objections to the groundwater quality are based on taste and aesthetic considerations, rather than the risk of adverse health effects (WHO, 1994). Groundwater having high chloride, sodium and TDS concentrations may indicate contact with water of marine origin (Bouwer 1978). Due to the poor quality of the groundwater close to the coast, the people living in these areas are therefore forced to travel long distance to obtain fresher groundwater from the boreholes that are located more inland.

Most of the samples, with the exception of a few, also exceed the required or recommended limits for livestock watering and irrigation purposes. Due to the high solute contents of most of the groundwater in the study area, the greatest risk or threat in terms of irrigation is the risk of soil degradation because of the high salinity of these waters. Sodicity hazard, for soil degradation, was also evaluated by calculating the sodium absorption ratio (SAR) in mmol/L, using the formula (Sposito, 1989) :

$$\text{SAR} = \frac{[\text{Na}^+]}{\sqrt{\frac{[\text{Ca}^{2+}] + [\text{Mg}^{2+}]}{2}}}$$

where  $[\text{Na}^+]$ ,  $[\text{Ca}^{2+}]$  and  $[\text{Mg}^{2+}]$  are the concentrations of these cations in mmol/L.

The SAR values for the boreholes sampled over the study period are as follows:

The following is a sample calculation for two of the sampled boreholes:

**SAR calculation for Drill 13m in March 2004**

$$\begin{aligned} \text{SAR} &= \frac{[15.3]}{\sqrt{\frac{[6.0 + 8.3 \times 10^{-3}]}{2}}} \\ &= 8.8 \text{ mmol / L} \end{aligned}$$

**SAR calculation for Creek in April 2004**

$$\begin{aligned} \text{SAR} &= \frac{[135.8]}{\sqrt{\frac{[6.1 + 33.2]}{2}}} \\ &= \mathbf{30.6 \text{ mmol / L}} \end{aligned}$$

The recommended or allowable SAR limit according to guidelines set by DWAF for groundwater is 3-4 mmol/L. See table below for the calculated values of the SAR ratios for the sampled boreholes.

**Table 7: Calculated SAR values of samples compared to SAR limits of DWAF**

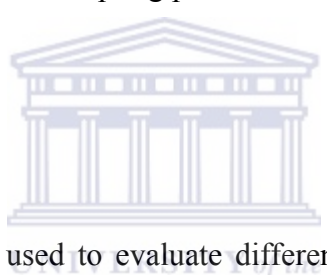
<b>Sample ID</b>	<b>March 2004</b>	<b>April 2004</b>	<b>August 2004</b>
<b>DWAF SAR Allowable Limit</b>	<b>3-4mmol/L</b>	<b>3-4mmol/L</b>	<b>3-4mmol/L</b>
Drill 7m	2.0	2.3	2.7
Drill 13m	8.8	11.3	
Drill 16m	2.7	2.5	3.6
Drill 35m	4.1	9.2	10.1
Drill43m	45.8	51.7	31.3
Manual	50.1	49.7	47.8
Piezo	55.4	50.8	
Creek	28.2	30.6	
Village	2.9		
Ridge	1.0		
Island	51.0		
Island Creek Piezo		38.2	
Well Water		3.2	
New MA		53.7	
New MB		55.0	
New MC		31.7	
Creek Surface			47.0
Creek Bed			46.3
New Well			23.2
Pit A			51.1
Pit B			51.0

## **Chapter 5 : Discussion and Conclusions**

Although some of the findings in this study have already been discussed in chapter 4, the main findings and conclusion will be summarised in this chapter and placed in the context of the original study objectives. The original study objectives, stated in chapter 1, were to evaluate the hydrochemical characteristics of the groundwater in the Incomati Estuary over a period of one year to include both the wet and the dry seasons. The data obtained over this period will be used to characterise the groundwater. This second objective was to establish whether any spatial or temporal variations in groundwater quality occurred. The third objective was to evaluate the suitability of the groundwater in the area for drinking water and irrigation purposes and to also establish if the groundwater could have an effect on the estuary. A total of 36 samples were taken and analysed by the author over the study period. High solute concentrations were obtained in most of the boreholes over the sampling period.

### **Major ions**

#### **Piper Diagrams**



The Piper Diagrams were used to evaluate differences in major ion chemistry in groundwater flow systems. From the Piper Diagram (fig 9, 10 & 11) it is clear that different water types are present in the groundwater system. As shown in all three Piper Diagrams, most of the samples plot in the chloride and sodium regions of the two triangle plots respectively. A difference in chemical composition was however observed for one of the samples namely Drill 35m. In the March 2004 Piper Diagram, Drill 35m plots midway of the saline region and the freshwater region in the diamond shape of the Piper Diagram. As discussed earlier, this could be attributed to the rain experienced during the Wet Season, causing the groundwater to be diluted due to infiltration.

Besides for the drill 35m sample, no real seasonal variation was observed over the study period. Some degree of spatial variation was however observed. As shown by the diagrams, the boreholes located a little further from the coast appear to plot in the freshwater region and those closer to the coast in the saline region. This further indicates that groundwater in close proximity of the

coast are influenced by the intrusion of saltwater. When considering the Piper Diagrams (Figs 9, 10 & 11) the following conclusions can be drawn:

- In view of the fact that sodium and chloride are the dominant ions in the boreholes located close to the coast and at greater depth, it therefore serves as evidence that there is an intrusion of saltwater into the aquifer at locations close to the coast and at a certain depth. Bouwer (1978) also found that boreholes containing high chloride and sodium concentrations can serve as an indication that the groundwater is in contact with water of marine origin.
- The boreholes appearing in the “mixed” region have a  $\text{Na}^+/\text{Ca}^{2+}/\text{Mg}^{2+}-\text{Cl}^-$  major ion composition. A major ion composition of this nature is characteristic of stagnant groundwater zones or of groundwater at some distance along a flow path.
- The boreholes plotting in the freshwater region have a  $\text{Ca}^{2+}/\text{Mg}^{2+}-\text{HCO}_3^-$  major ion composition. This is characteristic of freshly recharged groundwater that has equilibrated with  $\text{CO}_2$  and soluble carbonate minerals under open system conditions in the soil zone.
- From all three Piper Diagrams it is evident that the boreholes located in the area of recharge (boreholes located inland) are fresher than the ones located in the area of discharge (boreholes near the coast).

#### **$\text{Cl}^-/\text{HCO}_3^-$ ratio vs $\text{Cl}^-$ and molar ratios of $\text{Cl}^-$ vs $\text{Na}^+$**

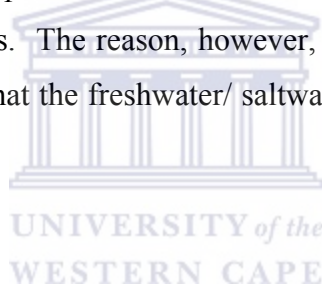
Graphs representing the relationship between  $\text{Cl}^-/\text{HCO}_3^-$  ratio vs  $\text{Cl}^-$  and bivariate diagrams of  $\text{Cl}^-$  vs  $\text{Na}^+$  and  $\text{Cl}^-$  vs  $\text{SO}_4^{2-}$  (Figs. 13 to 17) were plotted to distinguish mixing mechanisms with saline water from chemical reactions in the groundwater system.

From the  $\text{Cl}^-/\text{HCO}_3^-$  ratio vs  $\text{Cl}^-$  graphs ( Figs. 13 to 15) it is evident that the boreholes at shallower depth and inland have a much lower ratio compared to the boreholes at the coast and at greater depths. This further supports the evidence of saltwater intrusion into the aquifer at boreholes close to the coast and at a depth greater than 35m (Kim, 2003).



The molar ratio plots of  $\text{Cl}^-$  vs  $\text{Na}^+$  illustrates a strong correlation between chloride and sodium. This strong correlation indicates that such ions are derived from the same source of saline waters. However, the boreholes with the higher molar ratios are representative of the more saline groundwater and the boreholes plotting in the lower molar ratios of the more “fresher” groundwater. These diagrams therefore further substantiate the fact that there is salinisation of groundwater in the region close to the coast (Faye, 2004).

Even though no seasonal trends were observed in total dissolved solids (TDS) from the boreholes sampled over the sampling period, a spatial variation (Fig.19) as well as a vertical variation was observed in the TDS (Fig.18) values of the samples collected over the sampling period. The graphs further supports the fact that the boreholes located near the coast and those at a greater depth ( $> 35\text{m}$ ) have much higher TDS values than the other samples. This trend in TDS values can be attributed to the possible intrusion of saltwater or as a result of evaporation and condensation in these areas. The reason, however, for the sudden increase in TDS at a depth of 43m serves as indication that the freshwater/ saltwater interface exists at a certain depth between 35m and 43m.



### **Groundwater quality**

From the data that was collected over the monitoring period it is evident that the main processes controlling the hydrochemistry of the groundwater in the Incomati Estuary are mixing and dissolution reactions, respectively.

### **Effect on the Estuary**

What effects do groundwater quality have on the Incomati estuary? The Incomati estuary ecosystem depends upon its mangrove forests. The mangroves trees are believed to be very well adapted to the high and variable salinities of its surrounding water.

Although it is believed that estuaries receive their primary freshwater input from fluvial discharge, there is good evidence that direct groundwater discharge maybe responsible for up to 10% of the total freshwater input to estuaries and the ocean (Garrels & Mackenzie, 1979). From the results obtained in this study it is clearly shown that the nutrient loading through groundwater

discharge will not be greatly impact the ecosystem of the Incomati Estuary, since the highest obtained values were 4.1mg/L for  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$  and 5.8mg/L for  $\text{NH}_3$ .

The intertidal and subtidal sediments in estuaries consist of a biogeochemical dynamic. A range of chemical transformation and exchanges between the sedimentary material and interstitial groundwater are thus expected as water passes the sediments and the adjacent beachface (Ullman, 2003). It can thus be concluded that the groundwater that is discharged will therefore have a different composition to the groundwater confined in the aquifer. To what extent the mangroves depend on the discharge of the groundwater is unknown and serves as grounds for further research.

### **Groundwater use for drinking and irrigation purposes**

What does the quality of the groundwater mean for the people living in and around the Incomati estuary? From the results it is evident that the boreholes located close to the coast and at greater depths, due to their high solute concentrations, are not suitable for domestic purposes, as they do not comply to the limits set by the WHO and DWAF. The inland boreholes and the groundwater sampled from shallower depth are of a much better quality. No microbiological analyses were performed on the samples, but a  $\text{H}_2\text{S}$  test was used in the field and it gave us an indication that some form of bacteria are present. The source for this could be the use of on-site sanitation systems, mostly the pit latrines that are extensively used in the rural areas (Samaja, 1993).

As urban and industrial development continues to expand around the coastal areas of Mozambique, especially Maputo, so will the demand for fresh water. A proper desalination treatment system should be implemented as treatment for the more saline groundwaters around the coastal areas. Above and beyond the high salinity obtained in certain boreholes, the groundwater in the area does not appear to pose an immediate and direct threat to human health. A monitoring program should be employed to monitor for future groundwater pollution.

Due to the high solute concentrations, the boreholes close to the coast are also not suitable for irrigation and livestock watering purposes, as they do not comply with the limits set out by DWAF. The inland boreholes, however all fall within the limits set by DWAF for irrigation and

livestock watering purposes. The SAR values obtained for the all samples also fall outside the limit of 10 set by DWAF. If these waters are not properly treated by making use of proper desalination treatment plant, it can lead to the degradation of the soil in the area and this can have detrimental effects on the people living in these areas as they depend on the selling of their crops for survival.



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## List of Abbreviations

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- ❖ C2C : Catchment -2- Coast
- ❖ DNA : National Water Directorate, Mozambique
- ❖ CSIR : Council for Scientific and Industrial Research
- ❖ DWAF : Department of Water Affairs and Forestry
- ❖ WHO : World Health Organisation
- ❖ IWACO : Consultants for Water and Environment



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## APPENDIX: Methods

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### Water analysis

#### 1. pH measurement

##### Principle

The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode is commonly used. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by extrapolation. This method is applicable to the determination of pH in all water samples.

##### Reagents

a) Saturated potassium chloride solution.

##### b) Reference buffer solutions.

###### (i) pH 4, 00 @ 25° C - potassium hydrogen phthalate

Dry 15g  $\text{KHC}_8\text{H}_4\text{O}_4$  at 105° C for two hours and cool in a dessicator. Dissolve 10,12g in water and dilute to 1000mL.

###### (ii) pH 6, 86 @ 25° C - phosphate reference buffer solutions

Dry  $\text{KH}_2\text{P}_0_4$  and  $\text{Na}_2\text{HP}_0_4$  at 105°C for two hours and cool in a dessicator. Dissolve 3,39g  $\text{KH}_2\text{P}_0_4$  and 3,53g  $\text{Na}_2\text{HP}_0_4$  in water and dilute to 1000mL.

pH 10, 01 @ 25° C - sodium bicarbonate - sodium carbonate reference buffer solution. Dry  $\text{Na}_2\text{C}_0_3$  at 105° C for two hours and cool in a dessicator. Dry  $\text{Na}_2\text{C}_0_3$  and 2,092g  $\text{NaHC}_0_3$  in water and dilute to 1000mL.

### **Equipment**

A Radiometer PHM82 STANDARD pH METER and GK 2401C combined electrode is used together with a stirrer.

### **Interference**

The glass electrode is relatively free from interference from colour, turbidity, colloidal matter, oxidants, reductants or high salinity, except for a sodium error at a pH > 10. Samples with low buffering capacity are susceptible to pH changes.

### **Calibration**

Use two buffers to calibrate the meter, usually pH 7,00 or 6,86 and pH 4.01.

Select the pH mode (released push button). Select a pH buffer 7 or 6.86 and dip electrode in the buffer and switch on stirrer. Leave stirrer on until pH measurements are completed. After stable reading is obtained, turn the BUFFER knob to make the PHM82 indicate the pH of the buffer and then rinse the electrode with deionised water.

Select pH buffer 4.01 and dip electrode in the buffer and allow to stabilise, while stirring. Adjust by turning the SENS.adjuster on the meter until the display indicates 4,00. Rinse electrode.

### **Analytical procedure**

Rinse electrode and immerse in the sample to be tested.

Read the pH of the sample while stirring. Record the results and after use, store the electrode in a pH 4 buffer solution.

### **Calculation of results**

The measured pH is read directly from the instrument display. Report the results to the nearest 0, 1 pH unit.

## **2. Electrical Conductivity**

### **Principle**

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. The physical measurement made in a laboratory determination is usually of resistance. The resistance of a conductor is inversely proportional to its cross-sectional area and directly proportional to its length. The magnitude of the resistance measured in an aqueous solution therefore depends on the characteristics of the conductivity cell used, and is not meaningful without knowledge of these characteristics.

The term "conductivity" is preferred and is usually reported in microhms per centimeter. The SI units use the Siemens (the reciprocal of the ohm) and conductivity is reported as milli-siemens per meter (mS/m).  $1 \text{ mS/m} = 10 \text{ micro ohms/cm}$ . To report results in SI units, divide phos/cm by 10.

### **Reagents**

Dried potassium chloride(KCl) at  $105^\circ \text{C}$  for two hours and cooled in a dessicator. To prepared a solution of a particular conductivity, select the corresponding mass of KCl from the table below. Weigh out the exact mass and transfer quantitatively to 1 litre volumetric flask. Dissolve the appropriate mass of KCl in approximately 500ml reagent grade water and dilute to 1000mL.

M KCl	mass KCl	Conductivity mS/m @ $25^\circ \text{C}$
0,005	0,3728	71,8
0,01	0,7456	141,2
0,02	1,4912	276,5
0,05	3,7280	666,7
0.1	7,4560	1289,0

Table 2A: Potassium chloride solutions KCl

## **Equipment**

Conductivity meter with platinum electrode cell and a thermometer

## **Interference**

Electrolytic conductivity (as opposed to metallic conductivity) increased with temperature at a rate of approximately 1,9% °C. Significant errors can result from inaccurate temperature measurement.

## **Analytical Procedure**

Rinse cell with one or more portions of sample. Adjust temperature. Measure sample conductivity.

## **Calculation of results**

Direct reading @ 25° C from conductivity meter.



## **3. Alkalinity**

### **Principle**

The alkalinity of water is defined as the capacity that some substances have to take up protons. In other words, to react with an equivalent quantity of a strong acid. Examples of such substances are hydroxide ions and anions of weak acids, eg. bicarbonate, carbonate, phosphate and silicate. The equivalent quantity of strong acid required to neutralise these ions is equal to the total alkalinity. The alkalinity is calculated by titrating a known volume of sample to a predetermined endpoint, using an auto-titrator.

### **Reagents**

#### **Standard Hydrochloric acid 0,01 N.**

Disodium carbonate  $\text{Na}_2\text{CO}_3$  was dried at 105°C for two hours and cooled in a desiccator. 2,65g  $\text{Na}_2\text{CO}_3$  was weighed out and dissolved in 1000mL  $\text{CO}_2$  free water. This stock solution has an

alkalinity of 2500mg/L as CaCO<sub>3</sub>. The stock solution was diluted further to make working solutions.

### **Equipment**

A pH meter that can be read to 0,05p1-I units equipped with a combined pH electrode. (Radiometer PHM 82), a stirrer and a Radiometer Auto burette ABU 80 was used in conjunction with Radiometer Autotitrator unit TTT 80)-.

### **Interferences**

Soaps, oily matter, suspended solids or precipitates may coat the glass electrode and cause sluggish response. Allow additional time between additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate or alter sample.

### **Analytical Procedure**

- Rinse Autoburette with acid used for titration. Calibrate pH meter using 6.86 and 4.0 pH buffers.
- Potentiometric titration to pre-selected pH
- An endpoint pH of 4,5 was used.

Transferred 20mL sample with a volumetric pipette to a beaker and placed it on the stirrer. Placed the electrode and tip of the burette in the sample. Titrated the solution with the standard 0,010N HCl to the endpoint pH of 4,5. Note the titration reading down.

### **Calculation of results**

Total Alkalinity as CaCO<sub>3</sub> mg/L =  $\frac{\text{mL } 0,01\text{N HCl} \times 0,01 \times 1000 \times 50}{\text{mL sample volume}}$



#### **4. Major cations : Calcium, Magnesium, Potassium and Sodium**

##### **Principle**

Atomic absorption spectrometry resembles emission flame photometry in that a sample is aspirated into a flame and atomised. The major difference is that in flame photometry the amount of light emitted is measured. Whereas in atomic absorption spectrometry a light beam is directed through the flame, into a monochromator and onto a detector that measures the amount of light absorbed by the atomised element in the flame. For some metals, atomic absorption exhibits superior sensitivity over flame emission. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used, this makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range.

##### **Reagents**

###### **a) Cesium -lanthanum interference suppressant solution**

Added 2L deionised water and 1L hydrochloric acid to a 5L volumetric flask. Added 60g La<sub>2</sub>O and CsCl (both AR grade), and shook to dissolve. Allowed solution to cool down to room temperature and made it up to the mark. This solution contains 5,5g/L Cs and 10,2g/L La.

###### **b) Standard stock solutions**

Use analytical grade standard solutions (1000mg/L) for the preparation of working standard solutions.

###### **i) Preparation of stock mixed standard solution (100mg/L Ca, 100mg/L Na, 30mg/L K and 30mg/L Mg)**

Add 200mL each of 1000mg/L Ca and Na standard, and 60mL each of 1000mg/L K and Mg standard into a 2000mL volumetric flask. Add 200mL of the La/Cs solution and made it up to the mark.

###### **ii) Preparation of working standards**

Add to 100mL volumetric flasks the following volumes of stock mixed standard:

Table 4A: Preparation of major cation working standards

Volume Added	mL La/Cs added	Working standard concentration			
		Na	Ca	K	Mg
2,5	10	2,5	2,5	0,75	0,75
5	10	5	5	1,5	1,5
10	10	10	10	3	3
20	10	20	20	6	6
30	10	30	30	9	9
40	10	40	40	12	12
50	10	50	50	15	15
60	10	60	60	18	18
70	10	70	70	21	21
80	10	80	80	24	24
100	-	100	100	30	30

### **Equipment**

A flame atomic absorption spectrometer consisting essentially of the following components was used :

- (i) A stable light source, emitting the sharp resonance line of the element to be determined.
- (ii) A flame system, into which the sample solution may be aspirated at a steady rate, and which is of sufficient temperature to produce an atomic vapour of the required species from the compounds present in the solution.
- (iii) A monochromator to isolate the resonance line and focus it upon a photomultiplier.
- (iv) A photomultiplier to detect the intensity of light energy falling upon it, which is followed by facilities for simplification and readout.
- (v) A chart recorder for recording the output.

### **Interference**

In the field of water analysis, the most commonly encountered interferences are chemical and ionization interferences. Other types, less commonly encountered; include non-atomic

absorption and matrix interferences. Chemical interferences occur when the element being determined combines chemically with another reactive component in the sample. The resulting compound influences the atomization process in the flame, thus altering the number of free atoms available to absorb light. Chemical interferences can be controlled by either:

- Addition of a releasing agent: A releasing agent is a chemical which reacts preferentially with either the element being determined or with the interfering component. A common example is the addition of a solution of a lanthanum salt to calcium solutions to overcome the depressing effect of phosphate on the calcium signal.
- Use a higher temperature flame: this can overcome many interferences because more energy is available to break down compounds which would be stable in cooler flames. For example, the interference of phosphate on calcium observed in the air-acetylene flame is eliminated in the nitrous oxide-acetylene flame.

Ionization interferences occur when the flame temperature is high enough to ionize a significant fraction of the element being determined. This lowers the number of atoms which can absorb radiation and reduces the analytical signal. Analytical errors can occur when the sample and standards exhibit different degrees of ionization. The simplest way to control ionization interferences is to add a large excess of an easily ionisable cation, such as cesium, to both samples and standards. The electrons provided by the more easily ionized element combine with the ions of the element being determined, and increase the number of atoms which can absorb radiation. A common example is the addition of a solution of a cesium salt to barium solutions to overcome the ionization of this metal in the nitrous oxide-acetylene flame. The use of lower temperature flame can also control ionization effects. For example, sodium is partially ionized in the air-acetylene flame, but ionization is negligible in the air-propane flame.

- (c) Non-atomic absorption results from the absorption of radiation from the hollow cathode lamp by materials in the flame other than the element of interest. It may be due to either:
  - (i) Molecular absorption, which is caused by the presence of molecular species which absorb light at the same wavelength as that of the element being determined.
  - (ii) Light scattering by particles in the flame, which occurs when solutions containing high amounts of dissolved solids are aspirated into the burner?

Non-atomic absorption maybe controlled by the use of a 'continuum source corrector', which may be either a hydrogen-filled hollow cathode lamp or a deuterium arc lamp. Matrix interferences occur when the sample matrix is so complex that viscosity, surface tension and components cannot be accurately matched with standard, resulting in the uptake rate, nebulization efficiency and atomization processes in the flame being affected. causing erroneous results. Matrix interferences may be controlled by use of standard addition techniques or by means of MIBK extractions with APDC, which are particularly useful with seawater samples, for example.

### **Analytical Procedure**

#### **i) Pretreatment**

Major cations in natural waters are usually in proportion to the total dissolved salts of that water. In other words, by determining the electrical conductivity of a sample, an appropriate dilution can be made so that the sample falls within the range of the working standards; the following table is used:

Conductivity mS/m	Volumetric Flask size (mL)	Pipette size (mL)	Volume La/Cs (mL)	Dilution factor
0 - 70	25	20	2,5	1,25
70 - 90	25	15	2,5	1,666
90 - 110	50	25	5	2
110 - 135	25	10	2,5	2,5
135 - 180	50	15	5	3,333
180 - 270	50	10	5	5
270 - 360	100	15	10	6,666
360 - 450	100	10	10	10
450 - 900	100:50	10:25	5	20
900 - 1125	100:25	10:10	2,5	25
1125 - 1500	100:50	10:15	5	33,333
1500 - 2250	100:50	10:10	5	50
2250 - 3000	100:100	10:15	10	66,66
3000 - 4500	100:100	10:10	10	100
4500 +	100:100	15:5	10	133,33

Table 4B: Dilution table for cation analysis

A list of recommended wavelengths and flame gases for each metal determined is shown below.

Element	Wavelength (nm)	Flame gases
Calcium	422,7	Air-acetylene or nitrous oxide-
Magnesium	285,2	Air-acetylene or nitrous oxide-
Potassium	766,5	Air-acetylene
Sodium	589,5	Air-acetylene

Table 4C: Recommended wavelength and flame gases

Because of the difference between makes and models of atomic absorption spectrometers, it is not possible to formulate instructions applicable to every instrument. The manufacturer's instructions for each particular instrument should be followed. In general; however, the following procedure is employed (air-acetylene flame):

- (a) Install the hollow cathode lamp for the metal being measured and roughly set the desired wavelength (see Table 1).
- (b) Set the slit width and lamp current at the values suggested in the manufacturer's instructions and allow the instrument to warm up until the energy source becomes stable (10 - 20 minutes).
- (c) Readjust the current as necessary after warm up.
- (d) Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained.
- (e) Align lamp in accordance with manufacturer's instructions.
- (f) Install air-acetylene burner and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the metal being measured.
- (g) Turn on acetylene, adjust flow rate to value specified, and ignite flame.
- (h) Aspirate a standard solution of the desired metal and adjust aspiration rate of the nebulizer (if variable) to obtain maximum sensitivity. Aspirate a standard solution near the middle of the linear working range and adjust the burner vertically and horizontally to obtain maximum response.
- (I) The instrument is now ready for operation.

On completion of the analysis, extinguish flame by turning off first acetylene and then air.

However, for determination involving the use of a nitrous oxide-acetylene flame, proceed as in (a) to (c) above and then continue as follows:

- (a) Install nitrous oxide-acetylene burner and adjust burner head position.
- (b) Turn on acetylene (without igniting flame) and adjust flow rate to specified value, then turn off acetylene.
- (c) With both, air and nitrous oxide supplies turned on, set the T-Junction valve to nitrous oxide and adjust flow rate to specified value.
- (d) Turn the switching value to the air position and check that flow rate is the same. Turn on acetylene and ignite to a bright yellow flame. With a rapid motion, turn switching value to nitrous oxide.
- (e) The flame should now have a red cone above the burner. If not, adjust the fuel flow to obtain a red cone. After ignition, allow the burner to come to thermal equilibrium before commencing analysis.
- (f) Aspirate a standard solution of the desired metal and adjust aspiration rate of the nebulizer (if variable) to obtain maximum sensitivity. Aspirate a standard solution near the middle of the linear working range and adjust the burner vertically and horizontally to obtain maximum response.
- (g) The instrument is now ready for operation.

On completion of the analysis, extinguish flame by first turning the switching valve from nitrous oxide to air and then turning off the acetylene. This procedure eliminates the danger of flashback occurring on direct ignition or shut down of nitrous oxide and acetylene.

## **5. Dissolved Organic Carbon (DOC)**

### **Principle**

The method utilises an automated persulphate -ultraviolet oxidation method using calorimetric detection of CO<sub>2</sub> generated. Organic carbon is oxidised to CO<sub>2</sub> by

persulphate in the presence of ultra violet light. The CO<sub>2</sub> produced diffuses through a gas permeable membrane and is measured by the decrease in absorbency of a phenolphthalein solution. Inorganic carbon is removed by acidifying the sample to pH 2 or less to convert the inorganic species to CO<sub>2</sub> and then purging the sample with a purified gas (N<sub>2</sub>) to strip off the CO<sub>2</sub>.

### **Reagents**

#### **(a) Stock Organic Carbon solution**

Dissolve 2.1254g potassium biphthalate (dried at 105°C for 24 hours) in 500mL and make up to 1000mL with water. Dilute 40mL of stock solution to 200mL = 200mg/L as C. Prepare working standards in 200mL volumetric flasks as follows:

Table 5A: Preparation of DOC working standards

mL 200 mg/L in 200mL Flask	5,0	10,0	15,0	20,0
Standard conc. mg/L as C	5,0	10,0	15,0	20,0

#### **(b) Potassium persulphate solution**

Dissolve 24g potassium persulphate in 800mL water and dilute to 2000mL.

#### **(c) Phenolphthalein 1 %**

Dissolve 1,0g of phenolphthalein in 80mL methanol and dilute to 100mL with methanol.

#### **(d) Sodium Carbonate 0,1 M**

Dissolve 10,6g sodium carbonate in 800mL deionised water and make up to 1000mL.

**(e) Sodium bicarbonate 0,1 M**

Dissolve 8,4g sodium bicarbonate in 800mL deionised water and make up to 1000mL.

**(f) Carbonate-Bicarbonate Buffer**

Mix 150mL of the 0.1M sodium solution with 300mL of the 0.1 M sodium bicarbonate solution. Use this solution for the preparation of the colour reagent.

**(g) Phenolphthalein colour reagent**

Pipette 1,0mL of the 1 % Phenolphthalein solution into a 1000mL volumetric flask. Add 800mL deionised water and 15,0mL of the carbonate-bicarbonate buffer mixture and 0,5mL of Brij 35. Dilute to 1000mL with deionised water.

**(h) Hydroxylamine ammonium chloride**

Dissolve 70g of hydroxylamine ammonium chloride in 800mL deionised water, add 28mL of conc. sulphuric acid, mix well and make up to 1000mL with deionised water.

**Equipment**

Automated system consisting of the following:

Recorder, Calorimeter, Mixing manifold with appropriate coils, proportioning pump and an automatic sampler.

**Interferences**

Persulphate oxidation of organic molecules is slowed in the presence of chloride by the preferential oxidation of chloride; at a concentration of 0,1% chloride, oxidation of organic matter may be inhibited completely. To remove this interference hydroxylamine ammonium chloride is added

**Analytical Procedure**

Set up manifold and complete system as shown in figure 7.

**Calculation of results**



Prepare standard curves by plotting peak heights of standards processed through the manifold against DOC concentrations in standards. Compute sample DOC concentration by comparing sample peak height with standard curve.

## **6. Chloride and Sulphate**

### **Principle of the chloride method**

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms a highly coloured ferric thiocyanate, of which the intensity is proportional to the chloride concentration. There are no significant interference, however turbid samples needs to be filtered.

### **Principle of the sulphate method**

The method is based on the formation of low solubility barium sulphate( $\text{BaSO}_4$ ) suspension in a gelatine medium. ( $K_{sp}$  of  $\text{BaSO}_4 = 9.2 \times 10^{-11}$ ). The degree of suspension of the  $\text{BaSO}_4$  is dependent on the reaction condition and it is necessary to ensure that the conditions that are required with regard to the reagents must be strictly followed. The addition of hydrochloric acid prevents the formation of precipitates of sulphite, carbonate and phosphate with barium.

### **Reagents**

A mixed stock standard containing 2000mg/L chloride and 1000mg/L sulphate was prepared. The stock standard was prepared by dissolving 6.5928g sodium chloride ( $\text{NaCl}$ ) and 2.9574g sodium sulphate ( $\text{NaSO}_4$ ) in deionised water and made it up to 2000ml. From this stock solution, the working standards were prepared in 200ml volumetric flasks as follows:

Table 6A: Preparation of Cl and  $\text{SO}_4$  working standards

mL of	2.5	5	10	15	20	30	40	50
2000mg/L Cl and 1000mg/L								

SO <sub>4</sub> in a 200ml flaks								
Standard conc. of Cl(mg/L)	25	50	100	150	200	300	400	500
Standard conc. of SO <sub>4</sub> (mg/L)	12.5	25	50	75	100	150	200	250

**a) Stock mercuric thiocyanate solution for chloride analysis**

Dissolved 4.17g mercuric thiocyanate Hg(SCN)<sub>2</sub> in about 500mL methanol, dilute to 1000ml with methanol. Mix and filter.

**b) Stock ferric nitrate solution for chloride analysis**

Dissolved 202g ferric nitrate ( Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) in 500ml deionised water. Carefully added 21ml conc. nitric acid. Dilute to 1000ml with deionised water and stored solution in an amber bottle.

**c) Colour reagent for chloride analysis**

Add 150ml stock ferric thiocyanate to 150ml stock ferric nitrate solution, mix and dilute to 1000ml with deionised water. Stored solution in an amber bottle.

**d) Buffer solution for sulphate analysis**

Dissolve 40g EDTA, 7g ammonium chloride and 57mL ammonium hydroxide in 800mL water and make up to 1000mL.

**e) Barium chloride - Gelatin solution for sulphate analysis**

Boil 200mL water in a 1000mL beaker, add 2g gelatin and stir until dissolved. Add 20g BaCl<sub>2</sub> and stir to dissolve. Add 10mL concentrated hydrochloric acid and make up to 1000mL

## **Equipment**

The autoanalyser system used consists of the following:

A recorder, colorimeter, mixing manifold with appropriate coils, proportioning pump and an automatic sampler.

## **Analytical procedure**

Major anions (sulphates and chlorides) in natural waters are usually in proportion to the total dissolved salts of the water. So by determining the conductivity of a sample, an appropriate dilution can be used so that the sample falls within the range of the working standards. The following table was used:

Table 6B: Dilution table for Cl and SO<sub>4</sub> analysis

Conductivity (mS/m)	Volumetric size(mL)	flask Pipette size(mL)	Dilution factor
0-170	No dilution necessary	0	0
170-280	50	25	2
280-500	50	15	3.33
500-700	50	10	5
700-1200	100	10	10
1200-2000	200	10	20
2000-4000	500	15	33.33
4000-	500	10	50

Switched on the chart recorder and colorimeter. Allowed the system to warm up until a stable baseline is obtained.

## **Calculation of results**

Prepared a standard curve by plotting peak heights of standards processed through the manifold against the chloride and sulphate concentrations by comparing sample peak height with standard curve.

## **7. Orthophosphate**

### **Principle of the method**

Ammonium molybdate and potassium antimonyl tartrate react with orthophosphate in an acid medium to form an antimony-phosphomolybdate complex, which on reduction with ascorbic acid, yields an intense blue colour suitable for photometric determination.

### **Reagents:**

A mixed stock solution for ammonia, nitrate and phosphate was prepared with a concentration of 1000mg/L. This solution was prepared by dissolving 4.393g anhydrous potassium dihydrogenphosphate ( $\text{KH}_2\text{PO}_4$ ), 3.819g anhydrous ammoniumchloride ( $\text{NH}_4\text{Cl}$ ) and 7.218g potassium nitrate( $\text{KNO}_3$ ) in deionised water and made up to 1000ml, after it has been dried at  $105^\circ\text{C}$ . This solution has a concentration of 1000mg/L each for  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$  and  $\text{PO}_4\text{-P}$ .

Diluted 20ml of this 1000mg/L solution to 1000ml to obtain a solution of 20g/L each of  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$  and  $\text{PO}_4\text{-N}$ . The working standards were prepared from this solution in 200ml volumetric flasks as follows:

Table 7A: Preparation of Orthophosphate working standards

ml of 20mg/L in 200ml flask	5	10	15	25	50	75	100
Standard conc. In mg/L	0.5	1	1.5	2.5	5	7.5	10

### **a) Potassium antimonyl tartrate solution**

Dissolved 0.3g  $\text{K}(\text{SbO})\text{C}_2\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$  in 50ml deionised water and diluted it to 100ml. The solution needs to be stored at  $4^\circ\text{C}$  in an amber bottle with a glass stopper.

**b) Ammonium molybdate solution**

Dissolved 4g  $(\text{NH}_4)_6\text{MoO}_{24} \cdot 4\text{H}_2\text{O}$  in 100ml water and stored it at 4°C in a plastic bottle.

**c) Ascorbic acid solution**

Dissolved 2g ascorbic acid in 100ml deionised water and stored the solution at 4°C. This solution is only stable for a month.

**d) Dilute sulphuric acid**

Slowly added 10ml of conc.  $\text{H}_2\text{SO}_4$  to 600ml deionised water and diluted it to 1000ml when cooled.

**e) Combined reagent**

Mixed the above reagents in the following proportions for 100ml of combined reagents:

50ml dilute 5N sulphuric acid ( $\text{H}_2\text{SO}_4$ ), 5ml potassium antimonyl tartrate, 15ml ammonium molybdate and 30ml ascorbic acid solution. Mix after the addition of each reagents. This solution is only stable for one day.

**Equipment**

An autoanalyser system consisting of the following was used:

Recorder, colorimeter, mixing manifold with appropriate coils, proportioning pump and an automatic sampler.

**Analytical procedure**

Set up manifold and complete system as shown in figure c

Switched on chart recorder and colorimeter and allowed system to warm up or until a stable baseline is obtained.

**Calculation of results**

Prepared standard curves by plotting peak heights of standard processed through the manifold against  $\text{PO}_4\text{-P}$  concentrations in standards. Compute sample  $\text{PO}_4\text{-P}$  concentration by comparing sample peak height with standard curve.

## **8. Ammonia**

### **Principle of the method**

Alkaline salicylate and hypochlorite react with ammonia to form a green-blue colour, the absorption of which is proportional to the ammonia concentration. The colour is intensified by the addition of sodium nitro prusside.

### **Interference**

In alkaline solution calcium and magnesium will interfere by forming a precipitate. Sodium citrate buffer prevents this interference.

### **Standards**

#### **Stock solution**

Dry  $\text{NH}_4\text{Cl}$  at  $105^\circ \text{C}$  for two hours and a cool in dessicator. Dissolved 3,819g  $\text{NH}_4\text{Cl}$  in water and dilute to 1000mL. Dilute 20mL of stock solution to 1000mL to give 20mg/L.

#### **Working standards**

Prepare working standards in 20mL volumetric flasks as follows.

mL 20mg/L in 200mL flask	5	10	15	25	50
Standard concentration mg/L	0,5	1,0	1,5	2,5	5,0

Table 8A: Preparation of ammonia working standards

### **Reagents**

#### **a) Sodium salicylate solution**

Dissolve 90g of sodium salicylate in 800mL water and make up to 1000mL.

#### **b) Sodium nitroprusside solution**

Dissolve 0,5g of sodium nitroprusside in 800mL water and make up to 1000mL.

c) **Sodium hypochlorite solution**

Dilute 75mL of commercial bleach (Javell) to 250mL with water.

d) **Buffer solution**

Sodium Citrate 300g, EDTA 10g, Sodium hydroxide 5g

Dissolve these chemicals in deionised water and make up to 1000mL with water.

**Equipment**

Auto Analyser system consisting of the following:

Recorder, Colorimeter, Mixing manifold with appropriate coils, Proportioning pump and an automatic sampler.

**Analytical Procedure**

Switch on pump, colorimeter, chart recorder and allow to stabilize so as to obtain a stable baseline with all reagents, feeding water through the sample line.

**Calculation of results**

Prepare standard curves by plotting peak heights of standards processed through the manifold against  $\text{NH}_4$  - N concentrations in standards. Compute sample  $\text{NH}_4$  - N concentration by comparing sample peak height with standard curve.

**9. Nitrate**

**Principle of the method**

$\text{NO}_3$  - is reduced almost quantitatively to  $\text{NO}_2$  - in the presence of cadmium. This method uses commercially available Cd granules treated with  $\text{CuSO}_4$  and packed in a column. The  $\text{NO}_2$  - thus produced is determined by diazotising with sulphanilamide and coupling with N - (1 - naphthyl) - ethylenediaminehydrochloride to form a highly coloured azo dye that is measured colorimetrically.

A correction may be made for any  $\text{NO}_2^-$  in the sample by analysing without the reduction column step.

### **Reagents**

#### **a) Stock solution**

Dissolve 7,218g  $\text{KNO}_3$  (dried at  $105^\circ \text{C}$  for two hours) in distilled water and make up to 1000mL. This solution contains 1000mg/L  $\text{NO}_3^-$ -N.

#### **Working standards**

Prepare working standards in 200 mL volumetric flasks as follows:

mL 20 mg/l in 200mL Flask	5	10	15	25	50	75	100
Standard Concentration mg/L	0.5	1.0	1.5	2.5	5.0	7.5	10.0

Table 9A: Preparation of nitrate working standards

#### **b) Copper sulphate solution**

Dissolve 20g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 500mL and dilute to 1000mL with water.

#### **c) Ammonium chloride solution**

Dissolve 85g  $\text{NH}_4\text{Cl}$  in water and dilute to 1000mL. Add to 0,5mL Brij 35.

#### **d) Colour Reagent**

Add to 800mL water while stirring, 1000mL conc. phosphoric acid, 40g sulphanilamide, and 2g N-(1naphthyl) - ethylenediamine hydrochloride. Stir until dissolved and dilute to 1000mL. Store in brown bottle.



e) **Copper-Cadmium granules**

Wash 25g new or used 40-60 mesh Cd granules with 6N HCl and rinse with water. Swirl Cd with 100mL 2% CuSO<sub>4</sub> solution for 5 min or until blue colour partially fades. Decant and repeat with fresh CuSO<sub>4</sub> until a brown colloidal precipitate begins to develop. Gently flush with water to remove all precipitate Cu.

**Equipment**

Auto Analyser system consisting of the following:

Recorder, Colorimeter, Mixing manifold with appropriate coils and Cadmium reduction column, proportioning pump and an automatic sampler.

**Analytical Procedure**

**Preparation of cadmium reduction column**

Insert a glass wool plug into the bottom of the reduction column and fill with distilled water. Add sufficient Cu-Cd granules to produce a column 18,5cm in length. Switch on pump, colorimeter, chart recorder and allow to stabilize so as to obtain a stable baseline with all reagents, feeding water through the sample line.

**Calculation of results**

Prepare standard curves by plotting peak heights of standard processed through the manifold against NO<sub>3</sub>-N concentrations in standards. Compute sample NO<sub>3</sub>-N concentration by comparing sample peak height with standard curve.