

**Establishment of the Relationship between the
Sediments Mineral Composition and
Groundwater Quality of the Primary Aquifers in
the Maputaland Coastal Plain**

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Establishment of the Relationship between the Sediments Mineral Composition and Groundwater Quality of the Primary Aquifers in the Maputaland Coastal Plain

By

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DECLARATION

This is to declare that the work in this dissertation was preformed in the Departments of Chemistry and Hydrology at the University of Zululand, KwaDlangezwa. This is the original work performed by the author and has never been published by anyone else in any form of the award of a Diploma or Degree at this University or other institutions.

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ABSTRACT

The Maputaland coastal plain has the largest primary aquifers in South Africa. It has highly permeable sediments that promote rapid recharge to the aquifers and strong interactions with wetlands in the region. The hydrochemical study of the Richards Bay aquifers suggested that there is rising levels of dissolved minerals in the Science Center aquifer. This study was designed to determine the relationship between sediment mineral composition and the groundwater quality of the selected primary aquifers of the Maputaland coastal plain.

The aquifers of interest were classified into Cretaceous, Miocene, Pleistocene and Holocene Units, depending principally on a specific type of rock Formation penetrated during the drilling process. The sediments of the aquifers were classified into the Kwambonambi, Sibaya, Kosi Bay, Port Durnford, Uloa and St Lucia Formations, according to the established lithological Units, using the grain size, texture and colours of the sediments.

Water samples taken from the boreholes were assumed to represent all aquifers intersected during the drilling process.

Maputaland aquifers are low in potassium, sulphate and magnesium ions. Sodium and chloride ions remain unevenly distributed throughout the entire selected Maputaland coastal plain aquifers. The Miocene Unit is characterized by two chemical signatures, calcium and bicarbonate ions dominance and sodium, calcium and bicarbonate ions dominance. The Pleistocene Unit is characterized by three chemical signatures, sodium and bicarbonate ions dominance, calcium and bicarbonate ions dominance and sodium and chloride ions dominance. The Holocene Unit is characterized by two chemical signatures, sodium and chloride ions dominance and calcium and bicarbonate ions dominance.

The Richards Bay sediments of the shallow Units are predominantly acidic with high clay minerals, while the deep Units are mostly neutral or alkaline.

It was concluded that the sediments in the shallow aquifers are acidic due to high rainfalls that leaches calcium and carbonate ions from the sediments resulting in weathering of the sediments to high clay minerals. Sodium and chloride ions were assumed to be contributed by marine sediment deposits, coastal-influence precipitation or direct recharge from surface water resources. These ions are exchanging sites with calcium and bicarbonate ions resulting in sodium and chloride ions dominance.

Although the groundwater quality of the Maputaland region has elevated total dissolved solids with unevenly distributed sodium and chloride ions, low calcium and bicarbonate ions in the shallow aquifers, the chemical composition of the groundwater is still suitable for potable purposes, except in areas where the pH is low with elevated dissolved ferrous, fluoride, aluminium and manganese ions.

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LIST OF ABBREVIATIONS

APPA:	Air Pollution Prevention Act
CAPCO:	Chief Air Pollution Control Officer
DEA:	Department Environmental Affairs
DMR:	Department of Minerals and Resources
DWA:	Department of Water Affairs
EIA:	Environmental Impact Assessment
FM:	Formation
NEMA:	National Environmental Management Act
NWA:	National Water Act
OM:	Organic Matter
TDS:	Total Dissolved Solids
RBCAA:	Richards Bay Clean Air Association
RDP:	Reconstruction and Development
TSS:	Total Suspended Solids
WMA:	Water Management Areas
TLC:	Transitional Local Council
SANS:	South African National Standard
HRU:	Hydrological Research Unit
RBM:	Richards Bay Minerals
PVC	Poly-vinyl Chloride

CHAPTER ONE

1. Introduction

South Africa is a semi-arid country, where water is scarce compared to most other countries. The utilization of water resources in a sustainable and wise manner is essential for the future of the country. The freshwater resources of the country are already under stress⁵⁴. Water in South Africa is recognized as a fundamental element in the fight against poverty, the cornerstone of its prosperity, and its shortage can be a limiting factor to growth⁵⁵. The water supply is becoming a major restriction to the future socio-economic development of the country, in terms of quantity and quality. Many of the water resources are polluted by industrial effluents, domestic and commercial sewage, acid mine drainage, agricultural runoff and litter⁵⁶. Because of a water shortage in South Africa, large water projects were created to supplement water within the country. The Lesotho Highlands Project (including Katse Dam) which provides water to Gauteng Province was the biggest Water Project ever established in South Africa to connect the two countries⁵⁷. The Tugela Transfer Scheme which provides water from KwaZulu-Natal to supplement Gauteng region was also established¹. This project causes a severe strain on KwaZulu-Natal water resources.

South Africa is emerging from a period of unsustainable and inequitable developments⁶³. The outcome has been the environmental degradation with significant economic and social impacts. Therefore, the country has developed the central guiding principles that embrace protection, use, development, conservation, management and control of water resources⁴², to promote sustainable use of water resources and equitable access to water to all South Africans, as stipulated in the South African Constitution³⁹. Therefore, there is a need of greater understanding of hydrological and geological processes that promote sustainable development of water resources.

South African environmental legislations promote development that is economically, socially and environmental sustainable, in which all sectors of

society must have equitable sharing of development opportunities, benefits and equitable provision of services aiming at significantly improving the life of the previously disadvantaged majority. The National Environmental Management Act ³⁸ requires industrial developments which use cleaner technologies and production methodologies that promote the sustainable development.

Although extensive legislations and regulations have been promulgated over the past years to address the threat to the environment and human health, a number of limitations are still evident ⁶³.

1.1 The importance of water in Zululand coastal plain

The Maputaland coastal plain supports large urban and industrial developments, extensive farming, rural communities, commercial enterprises, mining and forestry industries. In addition, many developments along the coastal plain from Richards Bay to Maputo have been proposed for economic growth. Continual developments are recognized as crucial for KwaZulu-Natal and South Africa to support government initiatives for poverty relief and economic growth, but these developments can have huge environmental impacts². As part of development initiative within the framework of the Industrial Development Zone (IDZ) for the region, several large industries have been developed or proposed for the region of Richards Bay. Aluminium processing capacity has expanded and production of heavy minerals increased with commissioning of new smelter facilities in the region. Pulp and paper industries, fertilizer manufacturers and steel works have been established as core industries.

These developments put great demands on water resources for their sustainability. They are likely to adversely impact on the water quality of surrounding water resources, through industrial waste discharge. Water resources management strategies implementations are necessary for these developments in order to protect the life of people and to secure ecological sustainability and use of water resources.

The Department of Environmental Affairs (DEA) through the National Environmental Management Act³⁸ requires consideration, investigation, assessment (EIA), reporting and management of environmental impacts of listed activities for the new developments or activities. Environmental impacts assessed for an activity must be managed through an approved environmental management plan (EMP) to support the precautionary approach principles (section 2 NEMA). The Department of Water Affairs (DWA) through the National Water Act⁴² requires protection of water resources in an equitable and sustainable manner as stipulated in Chapter 1 of NWA. The Department of Environmental Affairs (DEA) through the NEM-Air Quality Act 39 (Act 39 of 2004) requires maintenance of air emissions within permitted limits as defined by the South African National Standard (SANS).

Some of the Richards Bay industries exceed SANS concentration limits³. The law requires reporting of such incidents that have had impacts on the environment or health of people to the Chief Atmospheric Pollution Control Officer (CAPCO) and preventing recurring of such incidents. High levels of atmospheric pollution are likely to lead to serious concerns for the water environment as rainfalls often transfers atmospheric pollutants to the groundwater, especially in the unconfined aquifers of the Zululand coastal plain.

Because of public concerns regarding levels of atmospheric pollution in Richards, major industries in the region developed the Richards Bay Clean Air Association (RBCAA) in 1997⁵⁸. The association launched an atmospheric monitoring programme to determine levels of pollution in the region and to implement remedial actions where necessary in compliance with the law (Atmospheric Pollution Prevention Act 45 of 1965).

Mining concessions are required by law (DMR) through the Minerals and Petroleum Resources Development Act⁴¹ to implement an environmental management plan performance assessment, to monitoring programmes during

operational and closure phases. The assessment is conducted to protect the environment for present and future generations by continually assessing environmental liabilities. However, some industries are not required to undertake an environmental assessment provided that they do not contravene the effluent discharge regulation/legislation or do not undergo mining activities. Legislations provide levels of protection but compliance and monitoring frameworks are not yet being enforced. Therefore, there has been continual environmental degradation/pollution because there is little control of impacts on the regional water resources.

Some industries monitor their sites and submit their data to DWA as the requirement of NWA. However, DWA has not made the monitoring data submitted by these organizations publicly available for scrutiny.

Effluent discharge and leakage of waste products are potential pollutants to the groundwater¹². These are major potential pollutants related to industrial areas and numerous fertilizer companies¹². The contamination associated with these industries is localized but further exploitation by water abstraction from the aquifer has a potential of causing the contamination to spread.

The use of inorganic fertilizer has lead to a marked increase in the nutrient load of many rivers and the solubility of nitrates in particular⁴³. The agricultural sectors are the major contributors to nitrate loadings in freshwater systems. The agricultural sectors have caused an increase of salinity in ground water from intensive irrigation⁴³.

1.2 Water Resources in Maputaland Coastal Plain

The Maputaland coastal plain (sometimes referred to as the Zululand coastal plain) has the largest primary aquifer in South Africa. The uppermost stratigraphic formation on this coastal plain forms the main unconfined aquifers that promote rapid recharge and strong interactions with water bodies (wetlands) in the region.

It has many estuaries and coastal lakes that are linked to primary aquifers through direct seepage and via local streams and rivers which also form part of the tidal system. Over the years, some of these estuaries have been blocked-off from the sea to form inland fresh water lakes (such as Lakes Sibaya, Bangazi, Mzingazi, and Cubhu). Kelbe¹ has shown that there is a strong link between shallow aquifers and the coastal lakes in Richards Bay.

The water resources of Richards Bay are divided into systems according to their interaction with underlying aquifers. The systems that have minimal groundwater interaction are dominated by river systems and are distinct from those that are often an extension of the groundwater. The main water resources of the Richards Bay area are associated with coastal freshwater Lakes of Mzingazi, Nhlabane, Nsezi, Cubhu, and Mangeza, Mhlathuze River and extensive Coastal Primary aquifers (Figure 1). The main lakes are all situated in the coastal plain where they form an extension of the aquifers. The shallow unconfined aquifers along the coastal plain have been used to supply water to local mining industries but these well-fields have been closed in preference to surface water supplies.

1.2.1 Maputaland Coastal Lakes

The Zululand Coastal Lakes have significant flow-through characteristics, where there is generally a continuous and simultaneous recharge and discharge through various parts of the lake bed to the aquifer⁵. The seepage rate is greater at the surface shoreline and decreases exponentially with the distance underneath the lake. The Lakes are assumed to be supplied through direct rainfall interception, surface run-off from riparian zones, stream flow and groundwater recharge. Richards Bay Lakes (Lake Nhlabane, Lake Mzingazi and Lake Cubhu) are controlled by subsurface water conditions.

1.3 Groundwater resources of the Maputaland coastal plain

Groundwater resources of KwaZulu-Natal have not been utilized to the same extent as the surface water resources¹. During drought groundwater provides the

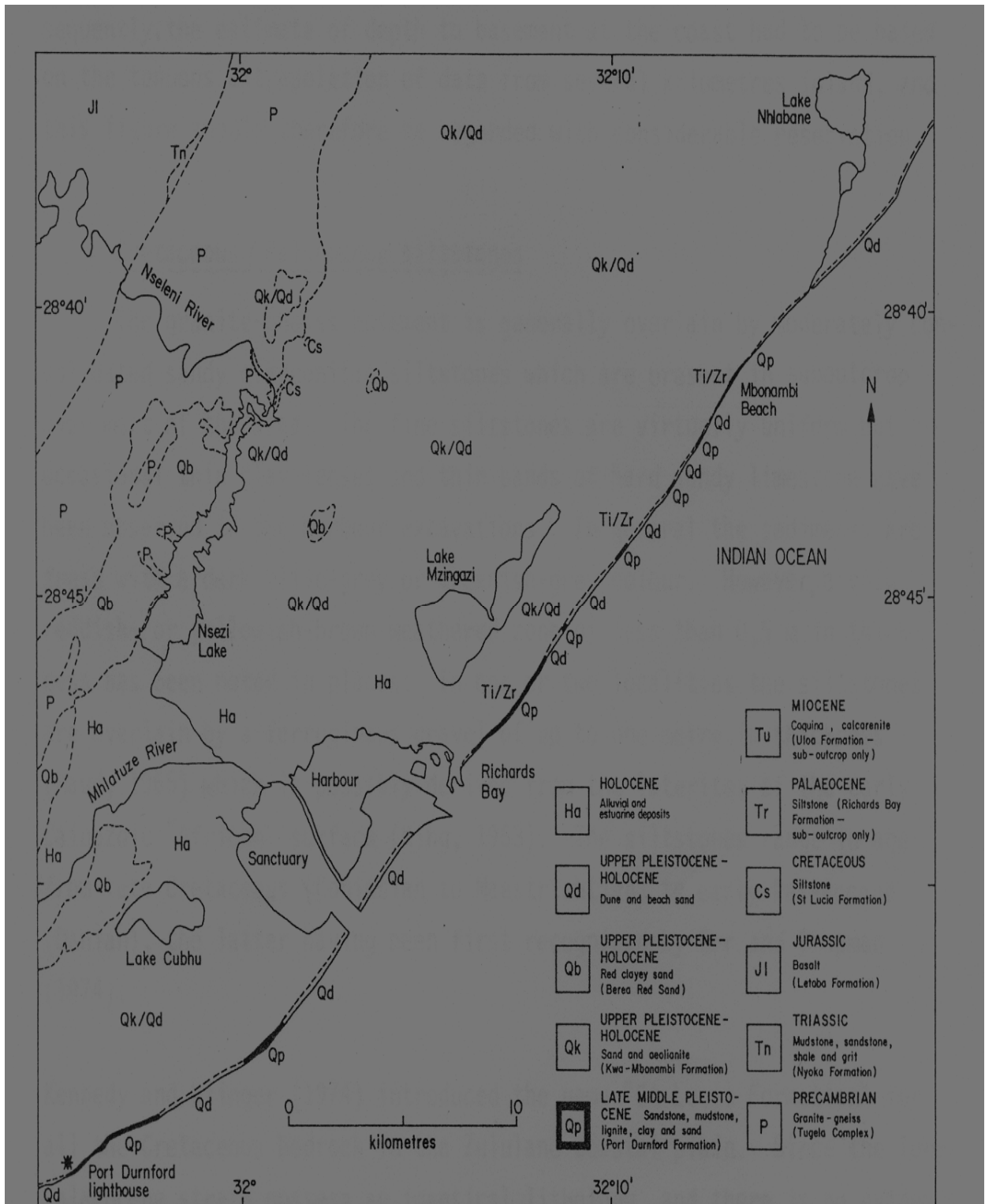


Figure 1: Simplified geographic map of Richards Bay regions which also shows the location of water resources ⁶.

sole exploitable and reliable resource available for survival of humans and the environment⁷.

Groundwater forms part of the integrated water resources. Water contained within the hydrological cycle resides in different storage compartments for a varying length of time as shown in Figure 2. The Terrestrial branch of the cycle involves water which arrives through precipitation and returns to the ocean in various pathways that always involve surface and groundwater components, except in extreme circumstances when it runs off in vast quantities through abnormal flood events. Consequently, it is difficult to distinguish an exact interface between surface water and groundwater. The National Water Act⁴² recognized that water resources are intrinsically linked between surface and subsurface components.

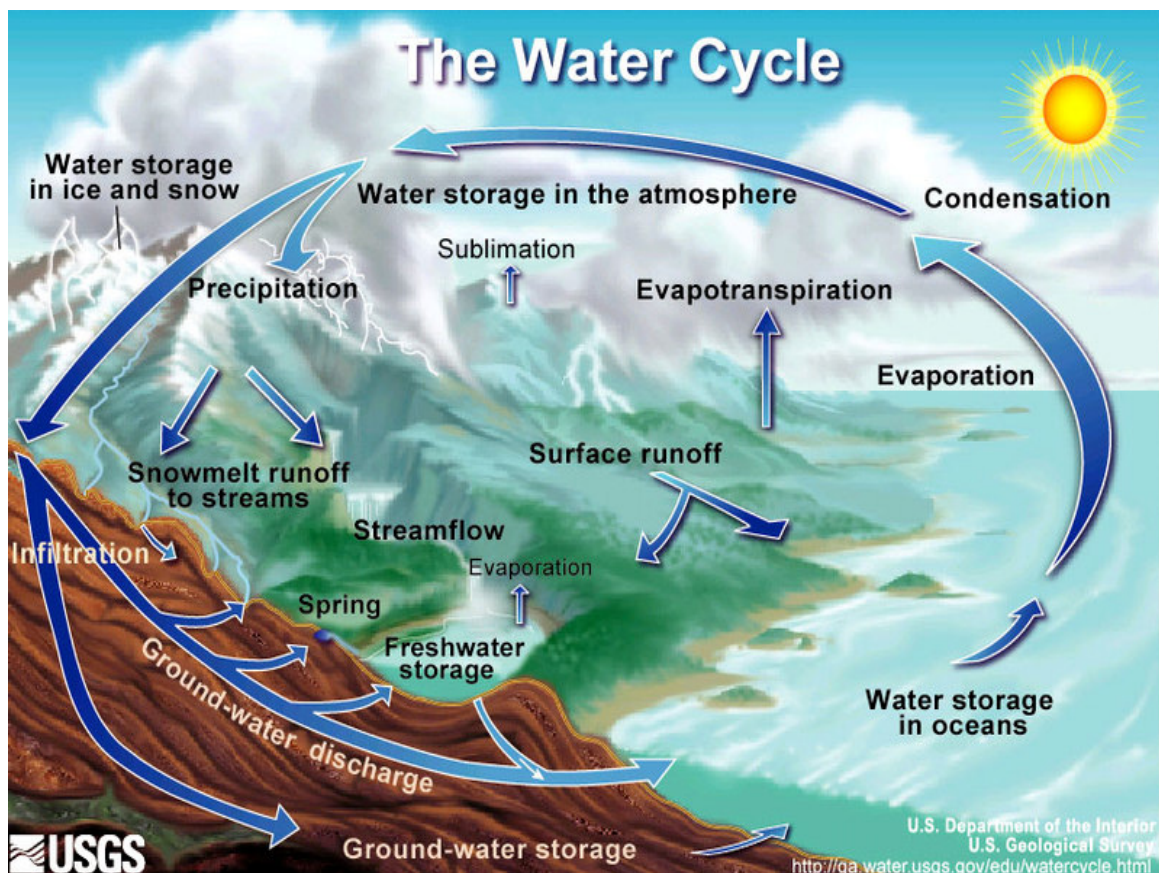


Figure 2: The hydrological cycle⁸.

The country's water resources have been conceptualized and categorically divided into surface and groundwater systems, which are treated as total separate entities⁶². However, there are instances where the water table is exposed at the topographic surface and the difference between the two water categories becomes difficult to qualify. The exposed groundwater components called wetlands have immense ecological and social importance and require careful examination for their potential exploration and sustainability as water resources.

Water management strategies are required to comply with the Constitution, which promotes access to sufficient water, protection of people's health and their well-being, and securing ecological sustainable development and use of natural resources while promoting justifiable economical and social development. Development and management of groundwater is, therefore, essential for the rights of people, particularly with respect to rural water supply, helping the previously disadvantaged communities as a means of poverty eradication.

1.4 Groundwater and the Ecosystems

Maputaland is located in one of the highest rainfall regions of South Africa. The region has important water resources and a large diversity of ecosystems, which are required to sustain the highest population density of South Africa.

Groundwater plays an important role in the sustainability of certain types of aquatic, terrestrial and coastal ecosystems associated with landscape, both in humid and arid regions. Groundwater is thus a key component in maintenance of the ecological integrity of the ecosystem. Lack of control over groundwater resource development and protection has already created negative impacts on certain aquatic flora and fauna⁹. In some intensively developed aquifers, the ecological function of groundwater has already been largely lost as a result of the lowering water table. Consequently, the ecosystem is threatened by the deterioration of groundwater quality due to diffuse of pollution especially from nutrients and pesticides⁹ and industrial waste discharge.

Groundwater ecosystems provide important services in an environment. Water is purified through microbial processes that remove pathogens and eliminate chemical contaminants. The ecosystems recycle organic matter transported by water and redistribute energy and matter. Groundwater also contributes to the sustainability of surface ecosystems⁹.

Organisms living underground within the aquifer are subject to extremely different conditions compared with the surface life. Species living in groundwater need special adaptations to survive. Groundwater organisms are more commonly found near the surface, where oxygen and food are more abundant. This is especially true in the hyporheic zone¹¹. In many areas groundwater is responsible for maintaining the hydrological balance of surface streams, springs, lakes, wetlands, and marshes.

While rainfall in these areas may be seasonal, groundwater can provide a year-round source of water and prevent damage that can result from droughts. Due to the seasonal nature of rainfall in some areas, surface ecosystems may draw groundwater during the dry season and then recharge the aquifer during the wet season.

1.5 Maputaland Climatic Conditions

The region is characterized by hot, humid summers and cool, drier winters with no frost occurring in the winter season ⁶⁴. The mean annual temperature varies from 21°C along the Lebombo Mountain to 23°C in the centre of the coastal plain, moderating slightly along the coast to 22°C. The average rainfall in winter for this region is about 25 to 30% of the average summer rainfall ¹.

The surface water and groundwater regime in Zululand coastal region are a direct response to the local geology and climatic conditions. Rainfall recharges the system while run-offs and evaporation cause depletion of surface and subsurface moisture. The type of rainfall and its frequency of occurrence have a strong influence on the hydrological processes that determine the surface run-off rate and groundwater recharge rate ¹ (Figure 2).

The climate is characterized by alternating wet and dry seasons, which may favour weathering reactions that produce a considerable amount of soluble inorganic matter in some seasons of the year. Cold climates (low temperature) inhibit weathering reactions on water composition by at least 2-fold. In warm seasons, temperature promotes solubility of minerals from their parent material to leach into the groundwater¹³. The climate of the Maputaland is described as moist tropical/subtropical along the coast becoming dry tropical/subtropical a short distance inland. The annual rainfall in Maputaland averages to about 1100mm per annum along the coast which declines progressively inland to as low as 500-600mm on the western plain ^{14, 15} but it increases to over 800mm per annum along the top of the Lebombo Mountain ^{16,15}. The rainfall increases southwards towards St Lucia and Richards Bay where it averages to 1400mm. The highest monthly precipitation occurs between October and April ¹⁵.

1.6 Development of Water Quality

The processes of rock weathering are strongly influenced by temperature and by an amount and distribution of precipitation. The bicarbonate ions tend to predominate in water in areas where vegetation grows profusely. Some metals are accumulated by vegetation and may reach maximum concentration (above the SANS limits). The plant-decay cycle can cause extra amounts of these metals to enter the groundwater¹³.

Soil property controls water quality in hydrological systems and plays a role in major geochemical cycles. Water is lost and also contaminated by soil. The quality of water in rivers, lakes and underground aquifers are being threatened by pollution. Soil can accumulate large amounts of carbon dioxide from soil organic matter, leading to global climatic changes (greenhouse effect). Surface runoff and subsurface leaching of soluble minerals in the soil such as phosphates and potassium can contribute to eutrophication in freshwater bodies. Eutrophication is linked to ecological and health problems. Carbonic acid and sulphurous acid

produced by the dissolution of carbon dioxide and sulphur dioxide can cause mobility of mineral ions into groundwater.

Groundwater quality can be improved by understanding its flow patterns, resident time and geohydrochemical composition. The long residence time of water in contact with a rock, can provide time for a chemical reaction to achieve its equilibrium through dissolution and precipitation of rock minerals (e.g. calcium carbonates). Groundwater hydrochemical composition mostly depends on its geochemical composition and land-use (human activities). Groundwater is also used by plants, which results in chemical exchange between the plants and aquifers¹⁰. This process changes the chemical composition of the groundwater.

Chemical ions in solution and microbial activity in the groundwater contaminate most shallow aquifers. The contaminant can penetrate deep within the aquifer particularly the sandy unconfined aquifer of Maputaland. This is especially true for the chlorinated organic liquids that are immiscible, and approximately 50% denser than water. The chlorinated organic solvents are common groundwater contaminants because they are used widely for cleaning many industrial products¹⁰. Heavy mineral ions contaminants tend to migrate both downward and laterally until they reach a stable configuration. They exist either as residual fractions left behind within the pore spaces, as the contaminant plume moves or as residual pools of free contaminants. The compounds may be soluble or slightly soluble in water, and may be taken up as groundwater flows past the contaminant. In contrast the light immiscible phase contaminants tend to rise in the groundwater system¹⁰.

Water quality and quantity are interdependent and need management in an integrated manner. The quality of water indicates water suitability for usage especially in South Africa where there is a shortage of water. Deterioration in water quality can cause problems of water supply as water will require pre-treatment which is a costly exercise. The typical pollutants of South African

water systems are mainly industrial effluents, domestic and commercial sewage, acid mine drainage, agricultural runoff and animal litter ⁴. Activities associated with water consumption or usage such as agriculture sectors, industries and domestic usage require water to have the certain water quality specifications for them to be viable. Meeting the water basic needs requirements of all South Africans depends on meeting both water quality and quantity objectives which also depends on consideration of the limitation of the carrying capacity of the water resources.

Deterioration of water quality can impact on human health and aquatic ecosystem which can lead to environmental liabilities especially for agricultural sectors and industries. However, the health and ecological problems are not all a result of the anthropogenic impacts. They can be associated with the geological composition of the area.

1.6.1 Salinisation

Salinisation is a persistent water quality problem in South Africa. It is determined by total dissolved solids (TDS) measurements. it is can be caused by natural or anthropogenic processes. Anthropogenically induced causes of salinisation include discharge of municipal and industrial effluents, irrigation return flows, urban storm-water runoffs, surface mobilisation of pollutants from mining and industrial operations and seepage from waste disposal sites, mining and industrial operations and salt water intrusion⁴. Diffusion of pollutants to groundwater is difficult to remediate but can be controlled at the source. Salinisation can cause reduction in crop yields, increased scale formation and corrosion in domestic and industrial water conveyance systems, increased requirement for pre-treatment of selected industrial water uses, and changes in biota.

1.6.2 Eutrophication

Eutrophication is also one of South African water quality challenges. It is the process whereby excessive algal and macrophyte grows as a result of water

enrichment with plant nutrients, such nitrates and phosphates (NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} , orthophosphates). It may impact on composition and functioning of the aquatic biota. Excessive algal and macrophyte growth leads to water purification problems⁴.

1.6.3 Microbiological Quality

Microbiological quality refers to micro-organisms and parasites in the water. Micro-organisms and parasites may enter the water system in partially-treated sewage effluents, seepage and run-off from inadequate sanitation and waste disposal. Water contamination by faecal matter is the medium for the spread of diseases such as dysentery, cholera and typhoid.

1.6.4 Acidification

The pH is an important characteristic of water for all beneficial uses²⁹. The pH of natural waters is determined largely by geological and atmospheric influences⁴. Freshwater resources in South Africa are relatively-well buffered due to the presence of calcium carbonate ions. Dissolution of CO_2 ⁵², nitrate and sulphate ions⁵³ either from plant decomposition or from atmospheric emissions may result in a low pH. Dissolved minerals in the form of cations or anions contribute to TDS in the groundwater. High temperature in the aquifer may increase the solubility and rate of dissolution of minerals. The major cation contributing to TDS in groundwater are usually sodium, calcium and magnesium. The major anions are carbonates, bicarbonates, chlorides, sulphates and sometimes nitrates. Most common groundwater has pH values ranging from 6 to 8.5.

However, the groundwater can be impacted by human-induced acidification, from industrial effluents, mine drainage and acid precipitation which can lower the pH, leading to mobilisation of elements²⁹.

The dissolved minerals may impact on the biota, as well as mining, domestic, industrial and agricultural users.

1.7 Statement of the Problem

Several studies in Richards Bay area have been conducted to examine the primary aquifers of Richards Bay. Worthington⁶ described the main features of the primary aquifers of Richards Bay region. Hydrochemical analyses conducted by Kelbe¹⁷ in Richards Bay region, suggested that there is a rising level of dissolved mineral ions in groundwater in Richards Bay. Of all studies conducted, few studies have been conducted to examine the natural geohydrochemical nature of the aquifers in the Maputaland Coastal plain.

1.8 Aim of the Study

The aim of the study is to develop an understanding of the relationship between sediments mineral composition and the groundwater quality of the primary aquifers of the Maputaland Coastal plain, in order to describe its natural background geochemistry.

1.9 Objective of the Study

1. Establish the origin and physical characteristic of the Maputaland aquifers (soil composition);
2. Establish the hydrological processes that influence the composition and the structure of the aquifer material and water quality;
3. Establish type and locations of aquifers;
4. Determine suitable location for investigation and identify the measurements of the geochemistry and hydrochemistry analysis;
5. Do a preliminary soil analysis in strategic sites to develop a geochemical profile;
6. Do detailed geochemical analysis of classified stratigraphic units.
7. Analyse hydrochemical data of the study area to identify an indicator for the comparative study;
8. Analyse water quality derived from the selected boreholes representing the different aquifers;

9. Establish comparable relationship between soil mineral composition and water quality;
10. Evaluate results in relation to sources and levels of pollution.

1.10. Limitation of the study

1. The study was limited to a relatively low funding. Therefore, some of the geochemical analysis that was required for accurate correlation to the hydrochemistry could not be conducted.
2. The geochemical samples lithological units were never accurately logged by professional geologists, but they were requested to have a quick look at the sediments sample to predict the lithology.
3. Hydrochemical samples taken from the boreholes were assumed to represent all aquifers intersected during the drilling process.

1.11. Suggestion for further work

1. A further study is required to correlate dissolved chloride, sodium, potassium and sulphate ions to the geochemistry of the Maputaland aquifers.
2. Professional logging of the geochemical sample is also required.

CHAPTER TWO

STUDY AREA

2 Introduction

The Maputaland coastal plain stretches from Maputo Bay southward to Richards Bay (Figure 3). The area is bordered in the north by the Inkomati and Limpopo River in southern Mozambique and in the south by Mlalazi Estuary in northern KwaZulu-Natal and in the west by the Lebombo Mountain Range⁵³.

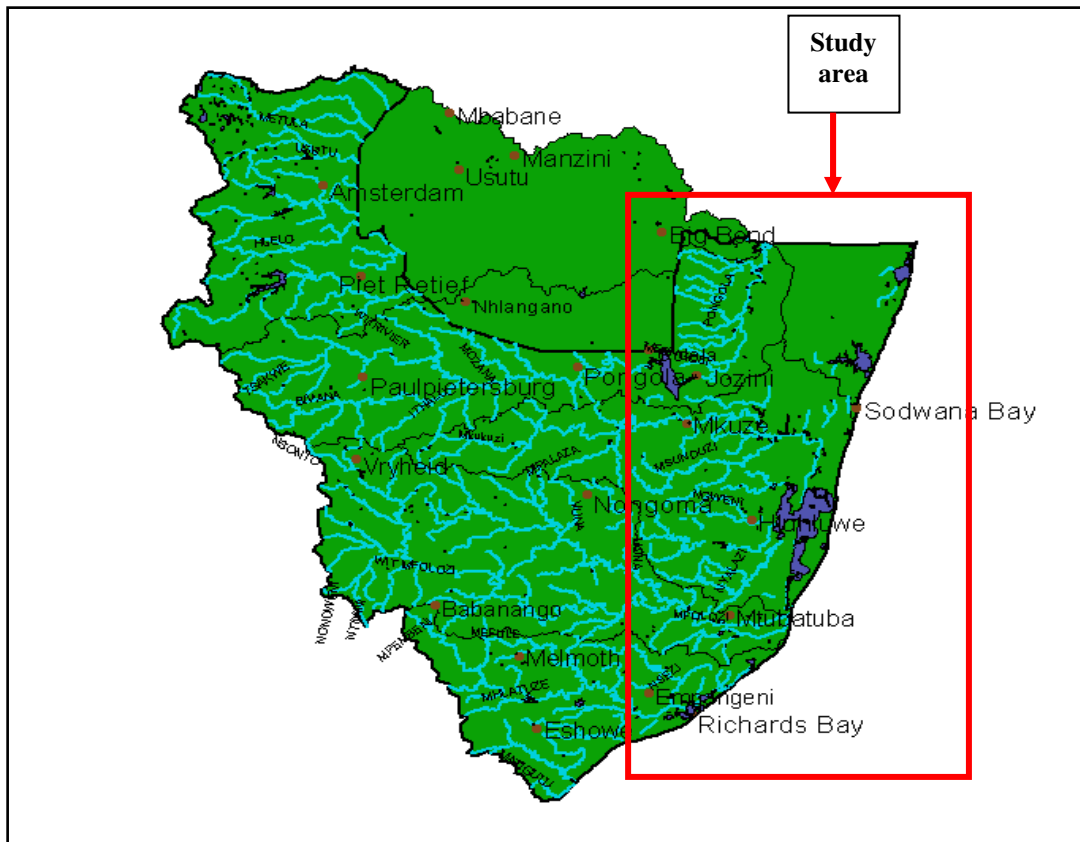


Figure 3: Map showing the study area. ⁴

The Maputaland region is not exceptionally renowned as a region of cultural diversity when compared with other parts of southern and central Africa. However, the region is populated with townships, rural areas and urban developments, especially along the coast plain.

Maputaland is also rich in cultivation practices such as industrial timber and sugarcane farming which has threatened and degraded the ecosystem⁶¹. The cultivation practices include large scale commercial agricultural farming and subsistence farming. Subsistence farming occurs mainly in communal areas and consists mainly of shifting cultivation.

The topography of the Maputaland coastal plain region is diverse, ranging from ancient to young sandy dunes and low-lying plains to the east and a series of rugged terraces deeply incised by river valleys in the central and western parts. Most of the region is covered by the recent, infertile, wind distributed (aeolian) sands. This resulted in the Formation of a series of north-south aligned dune ridges orientated parallel to the present coastline¹⁸.

The oldest of these, is adjacent to the Lebombo Mountain and appears to be of Plio-Pleistocene age¹⁹. Steep-sided frontal dunes along the shoreline are young, and are still forming in many places. Sometimes almost 200m in height, these dunes are amongst the tallest vegetated dunes in the world¹⁴. The incised coastal river valleys filled as sea levels rose during the late Holocene, resulting in the deposition of fertile alluvial material along the drainage lines and the Formation of pans, swamps, and veils where drainage lines become submerged¹⁸.

2. 1 Coastal Geology

2.1.1 Literature Review

Several geohydrological investigations of different scales have been conducted along the parts of the Zululand coastal plain. A number of geohydrological studies were done on the coastal lake systems frequently found on the coastal plain. The early studies were conducted by the Hydrological Research Unit (HRU) of the University of Witwatersrand which concentrated on the Lake St Lucia and Lake Sibaya systems.¹

The first serious and comprehensive attempt to document the geohydrology of the Maputaland area was conducted by van Wyk ²⁰ who looked at the

groundwater for the Northern KwaZulu-Natal region covering a very large area, including the coastal plain. Kelbe and Rawlins ²¹ and Meyer and Godfrey ²² studied the central region around Lake St Lucia, Worthington ⁶ and Simmonds ⁴⁵ focused mostly on the southern region around Richards Bay, Lake Mzingazi and Lake Nhlabane.

Worthington's ⁶ approach was that of integrated geological and geohydrological investigations, directed at detailed evaluations of hydrological conditions around the Richards Bay and Lake Mzingazi areas. The geophysical results, all based on the interpretation of 900 direct current Schlumberger resistivity sounding, were used to establish the geological succession above the extensive and impermeable siltstone of Cretaceous and Paleocene ages. He concluded that the compacted coquina and calcarenite of Miocene age overlying the siltstone in places constitutes the major aquifer and attains thicknesses in the excess of 20m in places. The younger overlying Pleistocene succession of fine-grained sand, clay and lignite is less of an aquifer and generally give rise to a leaky confined aquifer condition in Richards Bay.

The interpretation of the geo-electrical data supported by calibration soundings and lithostratigraphic records from boreholes logs provided an adequate definition of the Miocene (Uloa formation) aquifer that is present discontinuously, and irregularly within the southern part of the Zululand coastal plain.

Worthington ⁶ also studied the pollution vulnerability of aquifers and subdivided the area into six zones. He further warned that because of the effectively steady-state condition of the area, any serious change to the water balance by excessive surface and groundwater abstraction, will cause a significant interaction between the different fresh water regimes which might in turn have undesirable consequence from a pollution vulnerability point of view.

Lindley and Scott ²³, Rawlins ²⁴ conducted an investigation into the geohydrology of the area between the coastal dune cordon and the eastern shores of Lake St

Lucia. A comprehensive network of shallow borehole, meteorological stations with continuous rainfall monitoring and stream gauging was installed by Kelbe and Rawlins for a period of 3 years. The application of a regional groundwater flow model also reiterated the belief that the sea water intrusion into the coastal aquifer is unlikely, unless a substantial groundwater abstraction scheme close to the coastline were to be established. Groundwater quality, with the exception of its Cretaceous sediments, is generally of good quality.

Initial hydro-chemical analyses in Maputaland region by Kelbe¹⁷, suggested that there is a rising level of dissolved substances in the groundwater aquifers in the Miocene Formation in the Richards Bay area which may be due to natural geological processes. However, the chemical nature of the groundwater is determined largely by the geochemical composition of the porous material through which it moves within the aquifer and its residence time which establishes the level of reaction equilibrium. Thus, there is a need to determine the geochemical nature of the aquifer in order to understand the hydrochemical nature of these vulnerable aquifers.

2.2 Maputaland Geology

2.2.1 Introduction

The geological strata form the basic physical features of the primary aquifers. They are created by geological processes that generated its physical and chemical characteristic during formations. The sediments that overlay the entire Maputaland coastal plain are formed from aeolian and alluvial deposits.

2.2.2 The Coastal Geology

The entire Maputaland coastal plain was formed in recent geological times (the last few million years) through sedimentary erosion and deposition along the marine zone.¹ In Zululand, near Empangeni, the granite-gneiss basement was elevated between east-west crustal fractures to form the elongated fault block of the uNgoye Range. The basement rocks are overlain by the Natal Group. Upon this basement, there are sandstones that in turn are overlain by sedimentary

strata of the Karoo Super Group and topped off with volcanic lava flows, known as the Lebombo Group with attending faulting. These geological strata are found at the depth below Maputaland coastal plain. Overlying strata are thick sediments that were deposited in a marine environment during Mesozoic era.

The lower layer of the Cretaceous consists of river and beach deposits, where the main rocks are chalky sandstones, shale and limestone.²⁵ The upper Cretaceous consists of deep-water marine sediments that have been deposited on a seaward sloping continent. During the late Cretaceous period, when the coastal plain of Natal was below sea level, sediments were deposited along the continental shelf to form siltstones and mudstone marine strata that slope down toward the east at angle of about 2-3°⁶.

Following coastal upliftment and declining sea levels, these marine strata were elevated above sea level and eroded so that they are now exposed along the banks of the principal river valleys in Zululand (uMfolozi, uMzinene and Mkhuze) and around sections of the coastal lakes. With the exception of St Lucia erosion channels most of the Cretaceous sediments are covered by Neogene and Quaternary sediments⁶.

2.2.3 Cretaceous (St Lucia Formation)

The granite-gneiss basement is generally overlain by moderately consolidated sandy glauconitic siltstones which are present in sub-outcrops over most part of the area. These Cretaceous age fine siltstone are virtually uniform but occasionally thin clay lenses and thin bands of hard sandy limestone have been observed in the harbour excavations.⁶

The sediments are dark olive-grey or greenish-grey colour. However, a thin reddish-brown or yellowish-brown weathered zone less than 0.5 m in thickness has been noted in some places.⁶ In one or two localities the siltstone is overlain by ferruginous gravel of up to one meter in thickness.³⁰ The siltstones range in age from late Cretaceous to early Paleocene (Danian). The rock sub-outcrops of the St Lucia Formation become progressively younger in a seaward direction of

the Paleocene sub-outcrops.²⁶ The Danian strata extend across the full width of what is now the Maputaland Coastal plain prior to the erosion which exposed the underlying Cretaceous sediments. The strike of Formation is roughly parallel to the coast but the Cretaceous elevation apparently increases in the northern direction.⁶

2.2.4 Tertiary Sediments

The Cretaceous and Paleocene siltstones are overlain erratically by relatively thin Miocene sediments which strongly resemble the outcrops. The Miocene Unit in Richards Bay has been termed the “Uloa Formation” in recent geological classifications (Figure 4). Maud²⁶ described the Miocene strata as comprising a lower Coquina (Uloa) and an upper calcarenite (Umkhwelane formation). The coquina (Uloa formation) which rests unconformably on the siltstones is hard and coarse with abundant mollusk fossils. The top of the Cretaceous layer frequently contains pebble rich glauconite derived from the underlying siltstones. The upper surface of the Coquina has apparently been subjected to Karst solution weathering and deposition of overlying calcarenite.

The Coquina is generally coloured yellowish–brown and is frequently leached. The calcarenite is hard light–grey sandy limestone, the lowermost section of which is coarse and well–bedded, suggesting shallow marine. The upper part is typical aeolian sand with steep cross-bedding karst solution. Weathering of the upper surface of the calcarenite has been noted in boreholes samples from the Mhlathuze floods plain.⁶

2.2.5 Pleistocene Deposits

The Miocene and pre-Miocene sediments are extensively overlain by a complex succession of loosely consolidated sands, silts, clay and lignite of late middle

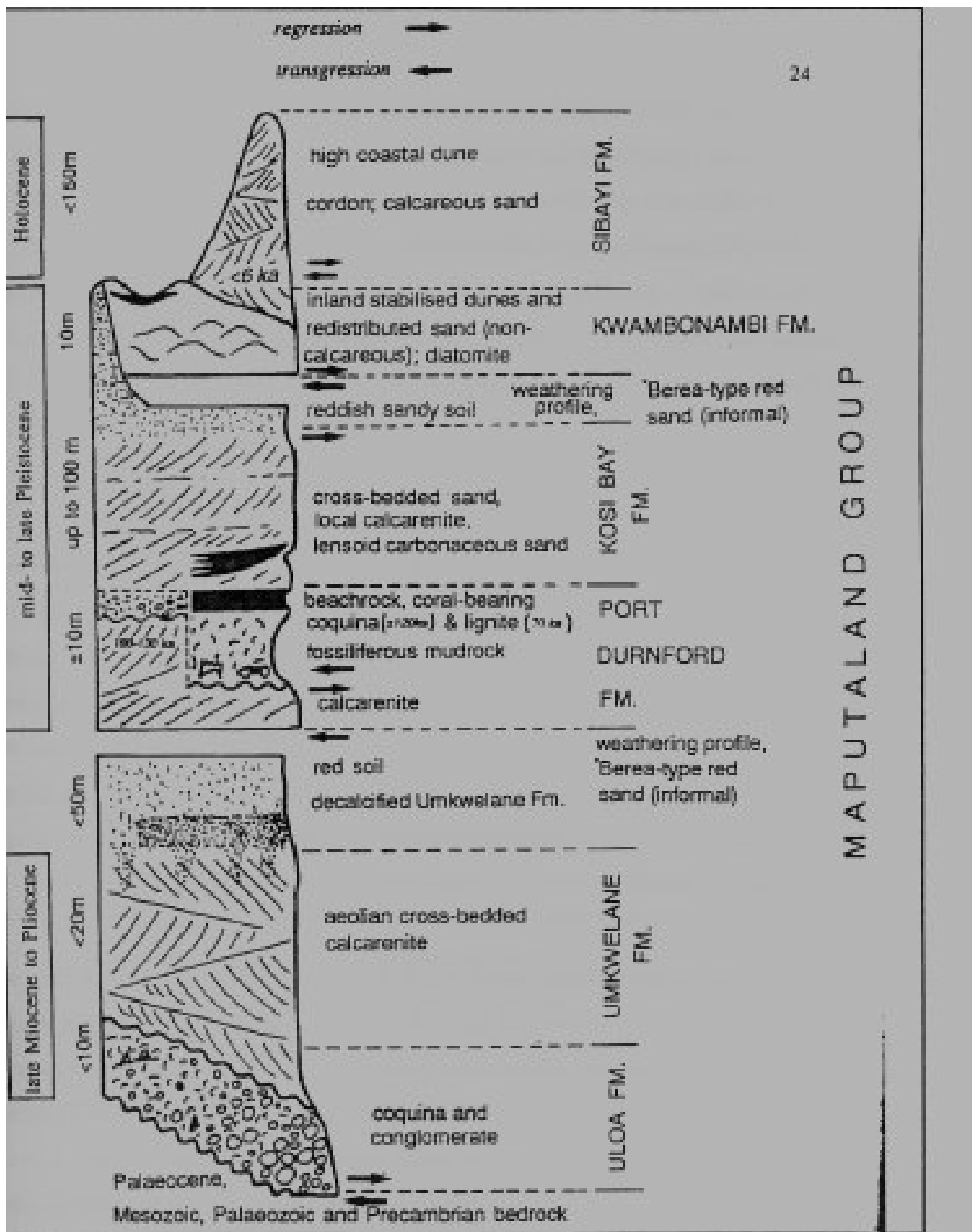


Figure 4: Stratigraphy of Zululand coastal region as proposed by Botha²⁷

Pleistocene age. These constitute the Port Durnford Formation named after the location type near Port Durnford lighthouse

The Port Durnford Formation is exposed in eroded cliffs along the coast extending north and south of Richards Bay and constitutes a major coastal barrier complex. The Formation is present beneath the Richards Bay and Mhlathuze flood plain due to the late Pleistocene drainage erosion⁶. A recent 3-partite subdivision of the Port Durnford Formation has been observed comprising of lowermost argillaceous member separated from a Kosi Bay (uppermost) arenaceous member by a persistent but discontinuous lignite band.

The lowermost argillaceous member contains marine and estuarine facies. This is exposed as blue-grey sandy mudstone, overlain by thin yellow-brown ferruginized sandstone.²⁸ The mudstone is overlain by reddish fossiliferous sandstone that is the basal member of Port Durnford succession. The reddish sandstone is no longer visible along the Port Durnford coast because sea erosion has caused the cliffs to retreat significantly over the past few decades. The total thickness of the lowermost argillaceous member at Port Durnford is estimated to be 10-12m with the base of the Formation lying several meters below mean sea level.⁶

A prominent lignite band of thickness about 1.3m can be traced northwards from south of the Port Durnford lighthouse to north of Mbonambi beach (Figure 4). In other places, its composition is in the form of carbonaceous sand and it is occasionally split into several thinner beds by clean quartz sand of up to one meter in thickness. The elevation of the lignite band varies from about two to four meter above mean sea level⁶.

The uppermost arenaceous member (Kosi) comprises predominantly of aeolian facies with large scale cross-bedding. It is generally white, yellow or yellowish-orange in colour, and is predominantly fine grained. Discontinuous thin beds of

carbonaceous sand and lignite occur at various levels. The thickness of the uppermost arenaceous member at the coast is about 15m with a surface elevation of up to 20m above mean sea level.

The total thickness of the Port Durnford and the Kosi Formation is believed to reach 25-30m height at the coast. However, as the Unit grades westwards into a variable succession of sands, clays and silts, it becomes extremely difficult, if not impossible, to distinguish between the uppermost part of the Port Durnford Formation and the overlying Holocene sands⁶. For this reason the western limit of the Formation could not properly be defined although it is almost certain that the inland plateau areas are essentially the result of the Port Durnford deposition (Figure 4).

At intervals along the Zululand coast and in the immediate vicinity of the shoreline, the Port Durnford Formation/Kosi is overlain by calcareous beach-rock and aeolianite deposits, termed “First aeolianite” ²⁸. This consists of thinly bedded hard fossiliferous sandstone which is apparently the result of calcareous cementation following glacio-eustatic changes in the sea level during late Pleistocene period. The calcareous fragments have been found in the Richards Bay harbour excavations overlying either the lowermost Port Durnford beds or the Paleocene sediments ²⁶. However, the most extensive development almost certainly occurs offshore as fragments of this material are frequently washed-up onto the beaches ⁶. This is grouped with other aeolian sands under the name “Kwambonambi Formation” in recent geological maps (Figure 4).

2.2.6 Recent Deposits (Holocene)

The Port Durnford/ Kosi Bay/ Kwambonambi Formation are overlain by fluvial and aeolian sands of late Pleistocene and Holocene age (Table 1). The deposition of red, brown and grey cover sands by wind action has given rise to the plateau features which characterize the Maputaland coastal plain. The plateau consists of a series of ridges approximately aligned in North-South direction. Certain inter-dune hollows contain accumulations of peat of meters in

thickness. The sands vary themselves from unconsolidated to loosely consolidated beds and are predominantly fine-grained. Along the coast, Holocene dunes have established themselves on the framework provided by the Pleistocene coastal barrier complex.

TABLE 1: Generalized Geological Succession in the Richards Bay Area ⁶

	Period	Epoch	Lithology	Formation	Present at Richards Bay
Cenozoic	Quaternary	Holocene	Sand, Silt Clay(alluvial)		Yes
		Upper Pleistocene	Dune and beach sand		Yes
			Sand and aeolianite	Kwambonambi	Yes
		Middle-Upper Pleistocene	Mudstone, shale, sandstone, lignite sand	Port Durnford	Yes
			Berea red clayed sand , sand	Bluff	Only South of Richards Bay
	Tertiary	Miocene	Calcareous sandstone	Uloa	Yes
			Siltstone, sand stone	Richards Bay	??
	Cretaceous	Senonian	Siltstone, sand stone	St Lucia	Yes
	Juristic		Dolerite intrusions	Karoo	??
			Basalt		

These modern dunes frequently attain heights in excess of 100m compared with the 25-30m elevation of the exposed Port Durnford Formation. Present coastal barrier complex is therefore a composite feature that owes its origin to discrete stages of construction. The recent dune sands range in colour from cream-white and yellow to light grey, brown and red. They are essentially quartzitic fine-grained and well sorted, and possess a heavy mineral content of about 7-10 % from which ilmenite and zircon are now being extracted commercially.

2.3 Water catchment areas

The main water resources of Richards Bay are associated with coastal freshwater lakes, such as Mzingazi, Cubhu, Nsezi and Mangezi, Mhlathuze River and, extensive coastal primary aquifers. Water abstracted from these resources supports local communities, agricultural and industrial sectors through various authorities. Water is also transferred regularly from the Mhlathuze River to Lake Nsezi and from the uMfolozi River to the holding dams at Sokhulu to supplement the mining industry in Richards Bay.

2.3.1 Mhlathuze Water

Mhlathuze water flows into the Richards Bay Estuary which has been divided into two compartments by a berm wall. The Northern part of the estuary has been developed as a deep water harbour while the southern section is retained as natural estuary with dredging of the new mouth directly opposite the river inlet. Mhlathuze River is fed by three main tributaries, Mhlatazana, the Mfule and the Nseleni River and regulated by Goedertrouw Dam.

2.3.2 Coastal Lakes

Zululand coastal lakes have significant flow-through characteristic with continuous and simultaneous recharge and discharge through various parts of the lake bed to the aquifer.⁵ The seepage rate is greater at the surface shoreline and decrease exponentially with a distance underneath the lake.

2.3.3 Lake Mzingazi

Water is abstracted from the lake to supply Richards Bay Municipality, Aluminium and RBM companies as well as the Richards Bay Country Club and small users situated directly next to the lake. The southern compartment is approximately 14m below sea level at the deepest point, therefore the lake is susceptible to saline intrusion. Water is officially abstracted when the lake is above a specified minimum storage level set to reduce the impact of saline intrusion.⁵⁹ A temporary salt water barrier was constructed in 1992 and has been recently

upgraded to a more permanent structure. The borehole monitoring between the lake and salt barrier was started in 1993. The barrier has a large effect on reducing the declining water table elevation between the lake and the sea.

2.3.5 Lake Nsezi

The Nsezi lake is fed by the Nseleni River which passes to the north of Empangeni and Nseleni. It is maintained by groundwater seepage from local primary aquifers and a direct recharge from rainfalls. There is also a permanent augmentation scheme which pumps water from the Mhlathuze River to the lake. The augmentation scheme that commenced in October 1992 continues even when the lake is overflowing in order to dilute the lake's salinity⁶⁰. Lake Nsezi is the major reservoir for water abstraction by the Mhlathuze Water¹ to supply Empangeni Transitional Local Council (TLC) and many industries.

2.4 Groundwater Chemistry

Water passing through the soil interacts with its surrounding media. Its chemical composition reflects the journey it has traveled. The start of the journey in nature is the precipitation with its characteristic signature. However, it may be polluted by anthropogenic sources creating solutions with many dissolved substances. These properties result in the wide range of water qualities found in nature.²⁹

Groundwater acquires its chemical composition during recharge either as infiltration of precipitation on the basin margin, as seepage from rivers, or as groundwater flows from adjacent aquifer systems that borders the basin.²⁹ Water chemistry differs depending on the source of water, the degree to which it has been evaporated, the type of rocks and mineral it has encountered, and the time it has been in contact with reactive minerals.

Therefore, water commonly differs in concentration of any particular reactive mineral and the concentration of that reactive mineral relative to other reactive

minerals. These distinct differences assist in delineation of areas of the aquifer that have similar geochemical “signatures.”

The geohydrology and geology of areas can provide information about the groundwater-flow systems. For instance, the geochemistry of an area with a particular signature can be compared with the geochemistry of an area in which water moves through a source of a known formation.

The landscape of the areas can also broadly define the directions of groundwater flow. Also, the vertical extent of groundwater in the aquifer having a particular chemical signature can indicate how well water is mixing vertically through the aquifer. If this vertical extent is known, the approximate volumes of groundwater with different signatures can be calculated and used to estimate the relative amount of recharge from different sources.

The interpretation of the hydrochemical data is most reliably made within a conceptual framework of the groundwater system that has been derived from several additional types of hydrological and geological data, such as water levels that indicates general directions of groundwater flow. In combination with the multitude of hydrological and geological data obtained, hydrochemistry data have improved the understanding of the aquifer through recognition of groundwater sources, delineation of flow paths, and determination of groundwater travel times calculated using isotopic data. The groundwater chemistry patterns assist in defining important concepts about its flow directions and its travel time.

The hydrochemistry of a groundwater sample can be thought of as a chemical signature that reflects the sum total of all physical processes and chemical reactions that affected the water from the time it began as rainfall, infiltrated the soil above the water table, passed into the aquifer (groundwater recharge), and traveled, sometimes for long period of time over great distances and depth, to the point of sample collection or discharge from the aquifer.

Groundwater contains cations and anions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), sulfate (SO_4^{2-}), and bicarbonate (HCO_3^-) ions. The main sources and reactions that influence the concentrations of these ions are;

- The dissolution of limestone (calcite, CaCO_3) and dolomite ($\text{Ca/Mg}(\text{CO}_3)_2$) that affects the Ca^{2+} , Mg^{2+} , and HCO_3^- concentrations.
- The dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) that influence the Ca^{2+} and SO_4^{2-} concentrations.
- The dissolution of halite (NaCl) that influences the Na^+ and Cl^- concentrations.
- Ion exchange reactions on the surfaces of some clay minerals whereby sodium ions are released to the water in exchange for calcium ion or magnesium ions.
- Sodium is also derived from the dissolution of silicate minerals, such as plagioclase feldspars, which make up some of the sand and gravel and,
- Potassium is derived from the dissolution of some silicate minerals in granite rocks and from reactions with some clay minerals.

Few reactions remove these seven solutes from groundwater. However, some minerals, such as calcite (CaCO_3), can precipitate from solution to into an insoluble form.²⁹

The mineralogy of aquifers is divided into relatively reactive minerals and unreactive minerals. Aquifers composed of reactive rocks, minerals such as limestone, dolomite, gypsum, halite, and organic matter can influence dissolved mineral ions concentrations (and isotopic compositions) significantly with distance along a groundwater flow path, reflecting extensive chemical reactions. In aquifers composed of mostly unreactive material, such as sand and gravel from the chemical and mechanical breakdown of silicate rocks and minerals, the mineral ion concentrations change only slightly with a distance down a flow path. In these relatively unreactive aquifers, water tends to acquire its predominant

chemical composition during the process of recharge and retains that composition as it flows through the aquifer. The variability of the chemical composition in the aquifer will reflect the reactivity of the system.

Waste disposal practices are the most notable human activities affecting the groundwater quality. Pollutants associated with domestic and industrial waste range from simple inorganic ions, such as nitrates (feedstock) and chlorides (municipal water waste), heavy metals such as chromium (plating operations), and to synthetic organic chemicals, such as carbon tetrachloride (dry cleaning and metal degreasing wastes). Other pollutants are associated with waste disposal activities, such as domestic and industrial waste disposal on or below land surfaces. This includes municipal and individual sewage disposal systems (septic tanks), surface disposal of sludge (including mineral sludge) or solid waste (landfills), industrial waste water impoundments (unlined), disposal of mine waste and brines, disposal of animal feedstock waste, deep-well injection of liquid waste, and the collection, treatment and disposal of municipal waste water. Because of the number of waste processes and disposal sites, the potential contamination of groundwater is great. Sources of contamination not only related to waste disposal practices, includes accidental spills and leaks, infiltration from polluted surface water, mining, and agriculture²⁹.

Monitoring of water boreholes helps in understanding of the existing and potential sources of contamination in addition to the local geology and hydrology. There is no universally defined “safe distance” between a well and a source because there are so many factors that affect the transport of water and contaminants. Mathematical models are used to predict the movement of groundwater ²⁹. Movement of the groundwater and contaminants is greatly affected by the nature of the soil and aquifers. Water and dissolved substances move slower in dense strata, such as clay and heavy loam, than in sands and gravels. In addition, contaminants may be dispersed by diffusion and mechanical mixing, retarded by ion exchange or sorption to soil, and degraded by natural chemicals and

biological processes. The behavior of a particular contaminant in the groundwater is dependent on its physical and chemical nature and the processes that influence its transport and environmental persistence ²⁹.

2.4.1. Groundwater Composition

Dissolved mineral ions (the cations or anions) contribute to TDS in the groundwater. The TDS can also be caused by the dissolution of atmospheric or organic carbon dioxide (CO₂). High temperature increases the solubility and rate of dissolution of minerals. The main cations contributing to TDS in groundwater are the sodium, calcium and magnesium ions. The major anions are carbonate, bicarbonate, chloride, and sulphate and sometimes nitrate ions. The most chemical reactions that affect the pH of natural waters involve the dissolution of carbon dioxide in water to form carbonic acid. The carbonic acid dissociates to bicarbonate ions (HCO₃⁻) and hydrogen ions are released.



Further, the bicarbonate ions dissociate to the carbonate ions (CO₃²⁻) releasing additional hydrogen ions.

The hydrogen ions then react with calcium and carbonate ions to form bicarbonate ions, resulting in decrease in hydrogen ions in groundwater.



The pH of the groundwater is affected by these chemical reactions and is ultimately determined by the combination of many interrelated chemical equilibria. The pH of the groundwater has a huge impact on the mobility of heavy elements, which thus affect water quality for different users.

2.4.2 Calcium (Ca) and Magnesium (Mg)

Calcium ions are major cations in most natural fresh waters. Magnesium ions are less abundant than calcium ions. Calcium and magnesium ions are primary

elements contributing to water hardness. Calcium carbonate is abundant in many minerals and may dissolve as water passes through or over them. The amount of calcium ions retained in the soil is dependent on a variety of chemical equilibrium.

In groundwater, cation-exchange processes may affect the occurrence of calcium ions. Calcium ions are held more strongly to the negatively charged exchange sites of the soil minerals than a monovalent ion such as sodium (Na^+). Natural water softening may occur when Ca^{2+} ions in groundwater displaces Na^+ ions on the mineral exchanges sites. This increases the ratio of sodium to calcium in the water. The reverse is also possible if water high in sodium ions passes through a mineral Formation with exchangeable calcium. However, the concentration of sodium ions has to be much higher than that of calcium ions to overcome the effects of calcium ions for cation exchange to occur. The threshold of calcium and magnesium in potable water is 150 mg/L and 70mg/L respectively ⁴⁴.

2.4.3 Sodium and Potassium

Once sodium salts are dissolved in water Na^+ ions tend to stay in solution. There is no major precipitation equilibrium that controls the amount of sodium ions dissolved in natural water. For this reason, levels can become very high in water exposed to soluble sodium bearing mineral, such as halite (NaCl). The level of sodium chloride (brine), such as connate waters, may exceed 100, 000 mg/L. Sodium ions can be present because of a natural ion-exchange phenomenon, or because of pollution. Sea water intrusion is the major source of sodium ions in fresh water aquifers of coastal areas. The average concentration of sodium ions in sea water is 25, 000mg/L.

Domestic waste water can also contribute to the presence of sodium ions. Municipal discharge of waste water adds up to 50 mg/L of sodium ions, primarily from urine and washing products. Certain industrial waste is another source of sodium ions enrichment related to human activities. Water containing a relatively high amount of sodium salts tends to displace exchangeable calcium and

magnesium held on the clay mineral surfaces; high levels of sodium cause certain soils and clay minerals to swell, which result in soil with poor permeability. Potassium ions in natural water are typically much lower in concentration compared to surface water. This is due to the greater resistance to chemical weathering of potassium minerals and the preferential incorporation of potassium ions into clay or mica minerals structure. The threshold of sodium and potassium in potable water is 200 mg/L and 50mg/L respectively⁴⁴.

2.4.4 Sulphates

Sulphate ions are the most common form of sulphur found in water. The natural water contains various levels of sulphate ions concentration. The main sources of sulphate ions in groundwater include evaporite sediments that contain calcium sulphate such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4) or the sulphate of magnesium and sodium. The oxidation of iron pyrites (FeS_2) produces sulphate ions, ferrous iron and hydronium ions. The presence of H^+ ions and SO_4^{2-} as sulphuric acid causes the decrease in the pH of the water. The threshold of sulphates in potable water is 400 mg/L⁴⁴.

2.4.5 Chlorides

The major sources of chloride ions in natural water are the sedimentary rocks, particularly the evaporites and sea water intrusion. Industrial and domestic waste water also contribute to chlorides ions. High chloride ions in the groundwater may be caused by industrial waste discharged. Chloride ions are extremely stable in water, as do not form insoluble salts or stable solute complexes with other ions. The threshold of chlorides in potable water is 200 mg/L⁴⁴.

2.4.6 Nitrogen Compounds

They include nitrites (NO_2^-) and ammonium ions (NH_4^+). Nitrogen is present in a wide variety of organic compounds, such as protein and biological waste products (e.g. urea, NH_2CONH_2).

Nitrogen is rapidly cycled through the biosphere and only a small amount is contained in minerals. Most of the earth's nitrogen is found in the atmosphere and in soils or biological materials. Nitrates enter groundwater primarily by leaching from soils. It may originate in soils from natural process (nitrogen fixation, decomposition of biological materials) or be deposited because of human activities. In agricultural areas nitrates in groundwater have resulted from the application and leaching of nitrogen-rich fertilizers. Similarly, nitrates could be released from urea and other organic nitrogen compounds found in domestic and industrial waste waters.

Other sources include animal waste, such as feedlots discharge, and leachates from waste disposal dumps, sanitary landfills, sewage lagoons and septic tanks. The high level of nitrates in groundwater may signal the presence of other contaminants, such as pathogenic organisms. The maximum level of nitrate ion in potable water is 10mg/L⁴⁴.

2.4.7 Iron {Fe (II)}

Iron-bearing minerals include sulphides such as pyrites or marcasite (FeS_2), carbonates such as siderites (FeCO_3), hydroxides such as limonite [$\text{Fe}(\text{OH})_3$], and oxides such as magnetite (Fe_3O_4). Some minerals contain iron in reduced Fe (II) state. Weathering of the minerals results in its oxidation to iron (III) state. Nearly all of the iron found in sedimentary or alluvial materials is in the iron (III) state. Sedimentary deposits in lakes or stream beds may become a source of iron (III) in local groundwater under reducing conditions. Iron can exist in variety of forms in water. The Fe (II) form of ions occurs only in waters devoid of oxygen. The ferric iron (oxidized form as Fe (III)) is found in oxygenated waters and usually exists as a colloidal precipitate. Iron may also react with natural organic substances to form soluble organic complexes. Infiltration of organic waste into an aquifer can indirectly affect the forms and concentrations of iron species by contributing to the creation of reducing conditions. Iron bacteria may acceleration the oxidation of Fe (II) to Fe (III) ions. In the absence of oxygen, dissolved Fe (II)

ions may occur in relatively high concentration. In the presence of oxygen, iron is oxidized to ferric form and very little Fe (II) ions remain in solution. The Fe (III) ions are significant when pH is less than pH 3.5.

The presence of carbonates limit concentration of dissolved iron in groundwater. One iron salt that is quite insoluble is iron (II) carbonate (FeCO_3). The solubility of iron (II) carbonate ($K_{sp} = 3.13 \times 10^{-11}$) is less than the solubility of calcium carbonate ($K_{sp} = 4.95 \times 10^{-9}$). In the presence of carbonate, Fe (II) may precipitate as iron (II) carbonate. In the absence of dissolved oxygen, the amount of Fe (II) ions in the groundwater may be limited by carbonates alkalinity. However, most of the alkalinity found in the groundwater is due to the bicarbonates rather than carbonates. The threshold of ferrous iron in potable water is 0.20 mg/L⁴⁴.

2.4.8 Manganese

The manganese ions (Mn^{3+}) are unstable in water and decompose into manganese (IV) oxide.



Soluble manganese exists in groundwater as reduced manganese (II) ion (Mn^{2+}). The oxidation of manganese ions result in the precipitation of manganese (IV) oxide (MnO_2) in the groundwater. Manganese (IV) oxide has an intense black colour in contrast to the reddish brown colour of iron (III) oxide. Both iron and manganese react with dissolved oxygen to form relatively insoluble precipitates, the oxidation reaction with Mn^{3+} ions proceed much slowly than with Fe^{2+} ions. Thus manganese in the reduced form (Mn^{2+}) exists for longer period of time in oxygenated water than does iron (II) ions.

In acid soils (pH < 6) manganese ions can be toxic to crops. The maximum level of manganese ions recommended by SANS Water Quality Criteria for protection for crops is 0.2 mg/L. The secondary drinking water level standard for

manganese ions is 0.05mg/L. The threshold of manganese in potable water is 0.10 mg/L⁴⁴.

2.4.9 Silica

Silica is the major component of most rocks and soils. The term silica (SiO_2) is commonly used to refer to silicon in the water. The actual form is hydrated and is called silicic acid ($\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The concentration of silica in natural water is usually in the range of 1-30mg/L. The hydrated form of silica (silicic acid) dissociates to silicate ions (H_3SiO_4^-).



However, below pH 8.0 the dissociation is insignificant. Silica is undesirable in many industrial process waters as it forms scale in boilers and on steam turbines.²⁹

CHAPTER THREE

METHODOLOGY

3. Introduction

The dissolved minerals ions in the groundwater are expected to reflect the geochemistry of the aquifer. It is vital importance to understand how the water quality of the aquifers is achieved. The water quality established under natural conditions is difficult to control, but the pollutant can be traced to a source which may be controlled, minimized and remedied. Consequently, it is important to determine the background of natural water through its water quality composition.

The groundwater quality is determined through groundwater drilling and sampling. Selected techniques for drilling, well construction, sampling, sample handling should be based on the complete evaluation of the site conditions, sampling needs and information needed for the program.

3.1 Selection of Sample Sites

The area of interest is the primary aquifers of the Zululand coastal plain. Specific sites have been identified and monitoring boreholes established by Professor Kelbe. The monitoring boreholes (Figure 5), which are located in Richards Bay, St Lucia, and northern (Mseleni) Maputaland, were chosen to represent different aquifer units in different regions covering the Zululand Coastal Plain.

3.2 Geological Sampling

The boreholes were drilled at different times, with different drilling techniques (Table 2.1). Soil samples from these sites were collected during the drilling process. The type of drilling techniques depended principally on the rock formation expected to be penetrated and the equipment available.

Samples were collected at approximately one meter intervals from the surface until the drill reached the pre-determined depth of the specific soil type that was

considered to be representing a hydrostratigraphic boundary (base of the aquifer green-grey clay of the St Lucia formation)

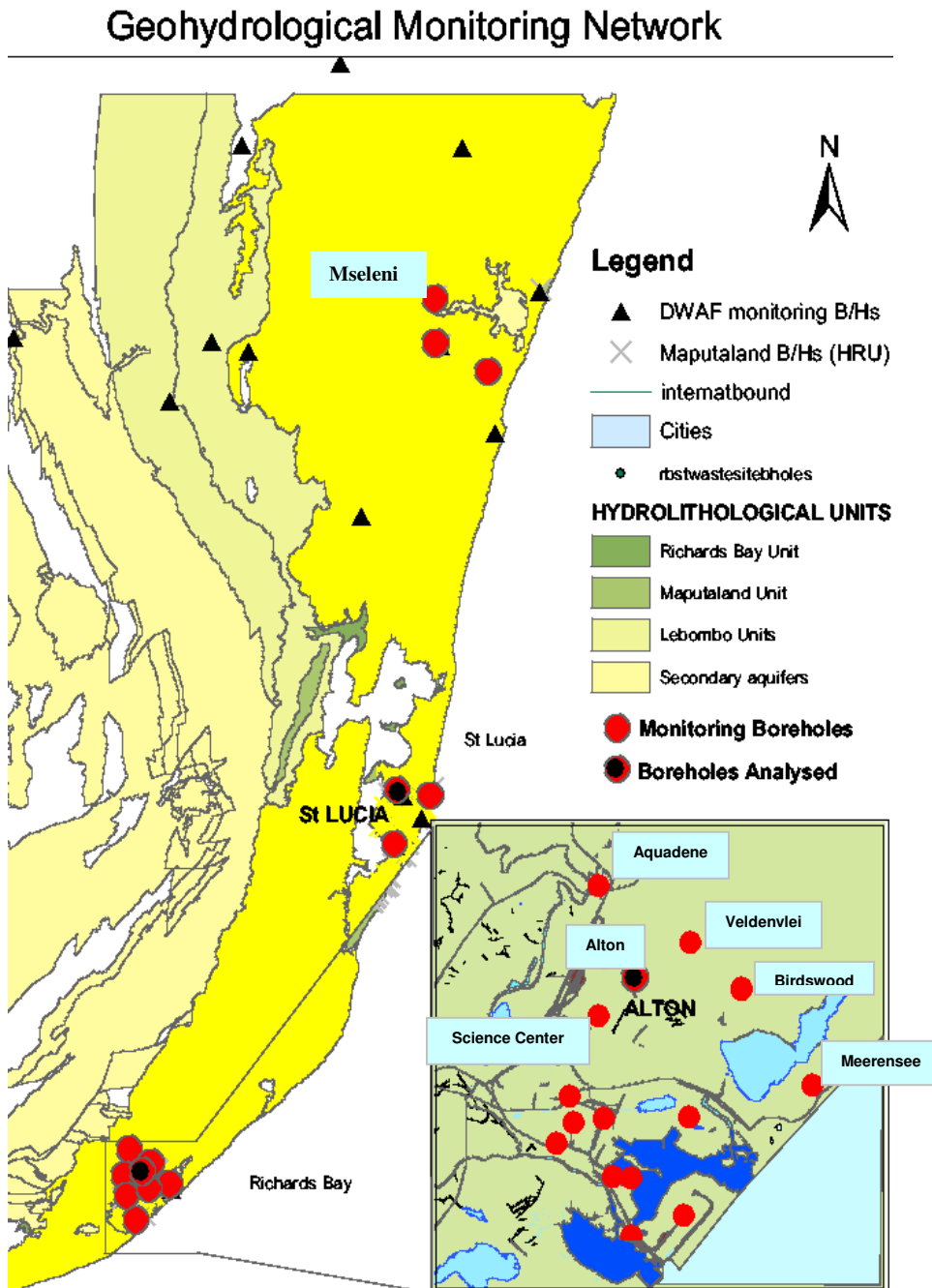


Figure 5: Geohydrological Monitoring network for Maputaland region showing location of monitoring sites.

Table 2.1: Available monitoring boreholes of Maputaland Coastal plain

Station	Region	Stratigraphic units	Elevation (m)	Depth (m)	Drilling method	casing
Elephant -Boma	St Lucia	Pleistocene		24	RC-Air	PVC
Mfabeni Plain	St Lucia	Pleistocene	12	18	RC-Air	PVC
Cape Vidal	St Lucia	Pleistocene		26	RC-Air	STEEL
Forest	St Lucia	Pleistocene		44	RC-Air	STEEL
Alton(NW-corner)	R/ Bay	Pleistocene	33	25	Mud rotary	PVC
Alton (S. Canal)	R/ Bay	Pleistocene	33	25	Mud rotary	PVC
Alton(Airport)	R/ Bay	Pleistocene	33	25	Air rotary	PVC
S/centre BH3	R/ Bay	Holocene		8	Mud rotary	PVC
S/centre BH2	R/ Bay	Pleistocene		24	Mud rotary	PVC
S/centre BH1	R/ Bay	Miocene	33	36	Mud rotary	PVC
Aquadene	R/ Bay	Pleistocene	53	30	RC-Air	PVC
Birdswood sub 1	R/ Bay	Pleistocene		18	RC-Air	Steel
Birdswood sub 2	R/ Bay	Miocene		18	RC-Air	PVC
Birdswood sub 3	R/ Bay	Cretaceous	22	60	RC-Air	PVC
Veldenvlei -1	R/ Bay	Pleistocene		18	RC-Air	PVC
Veldenvlei-2	R/ Bay	Miocene	22	25	RC-Air	PVC
Meerensee	R/ Bay	Holocene		20	RC-Air	PVC
Meerensee	R/ Bay	Pleistocene		30	RC-Air	PVC
Meerensee	R/ Bay	Miocene	24	40	RC-Air	PVC
Mabaso	Mbazwana	Pleistocene		52	RC-Air	Steel
Mseleni	Mbazwana	Pleistocene	66	48	RC-Air	Steel

Drilling in unconsolidated materials requires a technique to stabilize the soil and prevent it from collapsing before the casing can be installed. The RC-Air method used a large steel shaft which was withdrawn after the borehole casing was installed. This also prevented any cross contamination. The mud rotary used a natural gum to bond the soil particle and prevent it from collapsing. The samples were then taken from the stream of material being discharged as a stream of return mud. After collection (Figure 6), samples were labeled according to depth of the drilling bit. Each sample was logged on characteristics such as colour, texture and the conceptual lithological model, on-site. Samples were retained for laboratory analysis.



Figure 6: Soil sampling for analysis for the mud rotary technique (picture taken by Professor Kelbe in 2003)

3.3 Effect of Sampling on the Sample Materials

Collection of representative sediment samples from boreholes using regular drilling techniques can be problematic. The problem varies with drilling techniques. The sampling method can greatly affect the hydrochemical analysis. The aquifer is composed of different materials under different hydraulic conditions (pressure and temperature). Sampling of these materials can influence their chemical and physical properties. Rapid reduction in pressure and exposure to oxygen of the soil sample can cause rapid change in the sample composition. Consequently, it is important to understand sampling method and geochemical composition of the aquifer.

3.4 Sampling Techniques

There are two types of drilling techniques used in the geochemical sampling in this study, namely the mud rotary and the RC-air drilling methods.

3.4.1 Mud Rotary

Samples from the Mud Rotary drilling are collected at intervals and laid out in sequence before captured into plastic bags for laboratory analysis.

In the Direct Mud Rotary method, the rotary drill {Figure 7) (a)} operates by rotating a bit at the lower end of a string of the drill pipe, which transmits the rotary action from the rig to the bit ^{30, 31, 32, 33 and 34}. A water-based drilling fluid (mud) is pumped down the pipe to lubricate and cool the bit, to pick up material from the bottom of the hole and to clean the hole by transporting the cutting to the surface in an annular space between the uncased hole wall and the drill pipe.

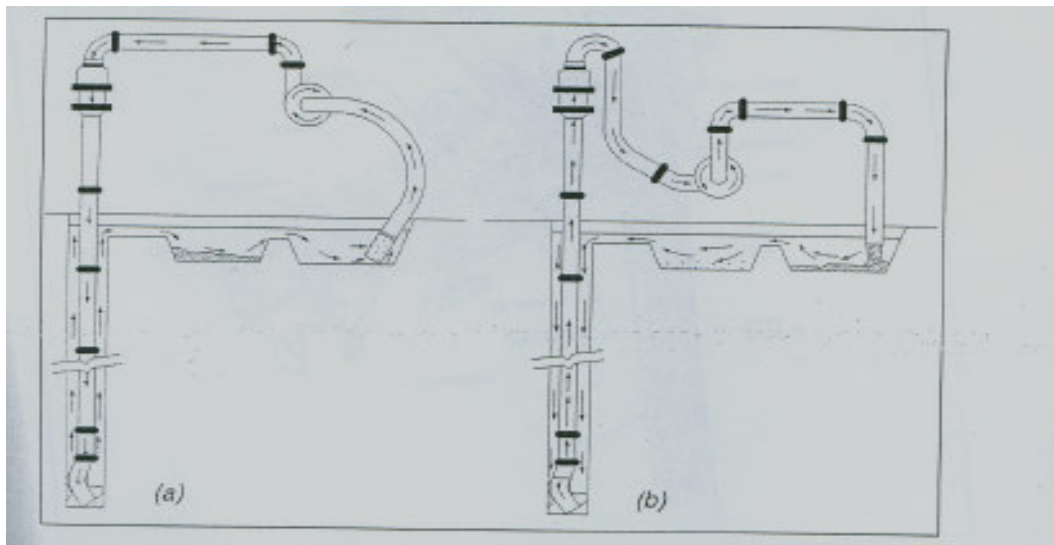


Figure 7: Diagram of (a) direct and (b) reverse rotary circulation system; arrows indicating the direction of the mud circulation. ^{31, 32, 33, 34, 35}

The water based drilling fluid also forms a thin layer of mud on the wall of the hole which reduces seepage losses and, together with the hydrostatic head exerted by the mud column, holds the hole open. At the surface the overflowing fluid is channeled into a setting drop out. Clean fluid is then picked up by the pump at the far end of the pit and circulated down the hole. The samples are then taken from the overflowing pipe (Figure 8).

Water based drilling fluid with clay or polymeric additive such as guar gum is commonly used in unconsolidated formations, while air base fluids is used in consolidated rock and sediment, and clean water is used by reverse rotary

drilling equipment for drilling large diameter wells in unconsolidated or semi-consolidated sediments (Table 2.2).



Figure 8: Mud Rotary drilling sampling point (photo taken by Kelbe in 2003)

3.4.2. Air Drilling Technique

The direct air Rotary equipment is essentially the same as for direct mud rotary drilling except that the fluid channels in the bit are of uniform diameter rather than jets, and the mud pump is replaced by an air compressor.

Table 2.2: Types of Drilling Fluids in the Water Well Industry³⁰.

Water Based	Air Base
1. Clean, freshwater	Dry air
2. Water with clay additives	Mist: droplets of water entrained in the air stream
3. Water with polymeric additives	Foam: air bubbles surrounded by film of water containing a foam stabilizing surfactant
4. Water with clay and polymeric additives	Stiff foam: foam containing film strengthening material such as polymeric and bentonite

Air is circulated down the drill string to cool the bit and to blow cuttings to the surface.^{32, 33, 34} The method is mostly used in hard rock terrain where water is

encountered in fractures or similar openings and wells are completed as open holes. Penetration rates are often faster and bit life longer when using air compared with water-based drilling fluids. If too much water from the formation come into the hole during drilling, however, the penetration rate is no better than when drilling with water-based drilling fluids.^{30, 34}

In air drilling techniques, samples are collected using a bucket suspended in the fall out zone from the blow-out at the top of the drilling rig (Figure 9). This leads to soil loss that may influence the analysis.

The reverse air circulation method used for the drilling in this study used a steel shaft which was replaced by a screening PVC casing once the required depth has been achieved. However, in many cases, it was too difficult to remove the steel casing in this study.



Figure 9: Sampling for the Air Rotary drilling technique (photo taken by Professor Kelbe in 2003)

The Air drilling technique could possibly impact on the sample particles size as samples are blown up to the surface and possibly most of the clay and fine minerals particle size could be lost before the sample is collected.

CHAPTER 4

EXPERIMENTAL

4.1 Laboratory geological sample preparation

Geological samples collected during the drilling process of the Maputaland boreholes were obtained from the laboratory of the Department of Hydrology in the University of Zululand. Samples were obtained stored in plastic sample bags classified into different boreholes. Some of the samples required drying prior to analysis.

Wet and semi-dry samples were dried at 40°C in a programmed Scientific Series 2000 oven. Dried samples were cooled to room temperature (25°C) in open air. Plant composition materials (such as leaves and roots), pebbles, stones and large over sized distribution materials were removed from samples prior to sieving. The samples were then broken down into loose particles using a wooden spatula and a mortar, and then passed through a 2mm sieve. 100.0g dried and sieved composite samples were weighed into a sample bottles and labeled according to the borehole's name and the sample depth. The remaining extra samples were retained into the original sample bag and returned to the laboratory of the Department of Hydrology.

4.1.1 Lithostratigraphic Units classification

Due to the large total numbers of samples for geochemical analysis (about 300 samples), professional geologists namely Dr Botha (the geologist with the Council of Geosciences), Mr. Lyn (Geotechnical Consultant with Davies Lynn and Partners) and Mr. Simonis (Senior Lecturer in Department of Hydrology, University of Zululand) were requested to have a quick look at the samples to predict the lithology of the boreholes using grain size, colour and texture according to the lithology formulated by Botha²⁷. The samples were classified into Kwambonambi, Sibaya, Kosi Bay, Port Durnford, Uloa and St Lucia Formations, depending on the borehole sediment types, location and depth (Appendix 1).

4.1.2 Composite samples for Lithological Units

Samples of different layers of the same lithology of the borehole were mixed together to form a 100.0g lithological composite sample. The composite sample was then stored in a glass sample bottle, labeled according to the borehole's name and the lithostratigraphic Unit and kept for analysis.

4.1.3 Grounding of samples

20.0±0.001g of the lithological composite sample was ground to powder (75.0µm) using a pestle and mortar. The ground sample was then stored in a glass sample vial, labeled according to the borehole's name and the lithostratigraphic Unit and kept for analysis.

4.2 Analytical methods

4.2.1 Determination of sediment pH

10.0±0.001g of unpulverized sample and 20.0mL of deionized water were mixed on a 250mL glass beaker. The mixture was stirred for 5 minutes at approximately 400r.p.m on a magnetic stirrer. It was allowed to stand for 30 minutes in open air at room temperature (25°C).³⁵ The pH was then read on the Hanna pH/temperature laboratory bench meter, calibrated using pH solution buffers 4.0, 7.0 and 10.0. The samples were analyzed in duplicate. Some of the samples became milky depending on the clay content in the sediments.

4.2.2 Determination of sediment organic matter

The method is based on Walkley–Back Method which measures organic matter (OM). Organic matter is oxidized by potassium dichromate ($K_2Cr_2O_7$) in a sulphuric acid (H_2SO_4) medium. The excess dichromate is determined by titration with a standard iron (II) sulphate solution. 0.5000±0.0001g of the ground sediment was placed in 500mL flask. 10.0mL of 0.2008M $K_2Cr_2O_7$ solution and 20.0mL of concentrated 98% H_2SO_4 were accurately added using a measuring cylinder. The flask was swirled while the acid was added. The flask with the solution was then allowed to cool to room temperature because of the exothermic

reaction. After 30 minutes of standing, 200.0mL of deionized water, 10.0mL of 85% phosphoric acid (H_3PO_4) and 1.0mL of diphenylamine indicator were added. The aliquot was then titrated from a blue to green end-point with 0.2503M ammonium sulphate solution (standardized using 0.2496M ceric sulphate solution).³⁶ Samples were analyzed in duplicate.

4.2.3 Determination of sediment calcium carbonate

1.0±0.001g air-dried sample (75µm particle size) was weighed into a 250mL Erlenmeyer flask. 10.0mL 0.9987M HCl solution was added to the flask with a pipette. The flask was then heated to 50-60°C and allowed to cool to room temperature. About 50-100mL of deionized water followed by 2-3 drops of phenolphthalein indicator were added. The solutions were titrated with 0.9992M sodium hydroxide (standardized using 0.9987M HCl) to the faint pink endpoint.³⁵ The samples were analyzed in duplicate.

4.2.4 Determination of sediment particle size by pipette method

20.0±0.001g of the unpulverized analytical sample was weighed on a analytical balance using the weighing boat. The sample was transferred to a 250mL glass beaker and 10.0mL of 30% H_2O_2 was added (H_2O_2 is a strong oxidizer and will readily react with hair, skin, eyeballs, clothes, etc). When the reaction diminished, 50.0mL of distilled water was added and the mixture was brought to boil for 15-20minutes. The mixture was cooled to room temperature and 20.0mL of sodium hexametaphosphate (Calgon) was added. The mixture was then left on the shaker overnight. The 63µm sieve was placed over the big plastic funnel set on top of the 1000.0mL cylinder. The sample was poured through the sieve and all silt and clay washed through the sieve using distilled water. The remaining sand on the sieve was washed into a 50mL pre-weighed glass beaker and water was evaporated in the Scientific Series oven at 110°C. The sand particles were then dried in the oven until all the water had evaporated. After cooling, the dried sand fraction percentage was determined by difference.

The cylinders with the silt and clay fractions were filled to the 1000mL mark with distilled water. Three beakers (fine/silt/clay, silt/clay and clay fractions) for each sample were weighed. The temperature of the water in the cylinder was recorded to determine the time and depth at which water must be pulled (Table 3). The samples were agitated for 20 seconds. Immediately after stirring of the samples ceased, the timer was started. At each required time, from a depth of 10cm, 20.0mL of the sample was extracted using a pipette. The 20.0mL sample was dispensed into the 50ml reweighed glass beaker designated for the size fraction. The pipette was washed with distilled water into the beaker.³⁷

Table 3: Particle size Sampling Parameters

Diameter of the particle size(mm)	Fine/Silt/Clay	Silt/Clay	Clay
	0.2-0.02	0.02-0.002	<0.002
Depth of withdrawal(cm)	10	10	5
Time of withdrawal	seconds	Min'/sec''	Hour:/min
Temperature (Celsius)			
20	29	7'40''	4:05'
21	28	7'29''	4:00'
22	27	7'18''	3:54'
23	27	7'08''	3:48'
24	26	6'58''	3:43'
25	25	6'48''	3:38'
26	25	6'39''	3:33'
27	24	6'31''	3:28'
28	24	6'22''	3:24'
29	23	6'13''	3:10'
30	23	6'06''	3:05'

The sample was dried in the oven, cooled in a desiccator and weighed. The blank for the Calgon was determined to eliminate error in the clay fraction.

The % fractions were determined back to the original the sample weights. The samples were all analyzed in duplicate.

4.2.5 Sediment total-iron, silicate and manganese ions extraction method

0.2500±0.001g of a pulverized sediment sample was weighed into 250mL metallic beaker. 10.0mL of 1.9995M ammonium oxalate solution was added into the beaker and the beaker was placed in a shaker at 400 r.p.m for 4 hours in a dark room. The extract was filtered and diluted (1ml extract: 4mL sodium hydroxide) to give a convenient concentration.

4.2. 5.1 Determination of manganese in an extract

Manganese was determined using the UV-vis Spectrophotometer, as the Atomic Absorption Spectrophotometer was not operational at that time. Organic matter and chlorides as interferences were removed by adding 5.0mL of concentrated (98%) sulphuric acid, and 5.0mL concentrated (65%) nitric acid to 10.0mL of manganese extract, 10.0ml standards and 10.0ml blank while mixing between the additions. The solutions were evaporated on the hot plate until sulphur trioxide (SO₃) fumes were evolved. They were cooled down to a lower temperature. 20mL of distilled water was added and solutions were further cooled to room temperature. 2.0mL of nitric acid, 5.0mL of 85% phosphoric acid and 0.3000±0.0001g of potassium metaperiodate (KIO₄), 0.5000±0.0001 sodium paraperiodate (Na₃H₂IO₆) were added to the solutions. 20.0±0.0001mg of silver nitrate was added to improve manganese sensitivity. The beakers were covered with watch glasses and solutions brought to a gentle boil on a hot plate for 5 minutes or until a purple colour developed. Samples were analyzed in duplicate. The absorbance was measured at 540nm on a Lambda 20 UV-vis Spectrophotometer using quartz cuvettes (1cm cell path). Standard samples for calibration were prepared from a 100mg/L manganese standard. Blank, 0.01mg/L, 0.10 mg/L, 0.25mg/L, 0.50mg/L, 1.0mg/L, 2.0mg/L, 5.0mg/L, 10mg/L, 25mg/L and 40mg/L standards were prepared for the calibration curve for the samples.

4.2.5.2 Determination of total iron in an extract

Iron (II) in this method reacts with 1, 10 –phenanthroline to form an orange-red complex $[(C_{12}H_8N_2)_3Fe]^{2+}$. The colour intensity depends on the acidity of the solution. Iron (III) was reduced to iron (II) with 10% hydroxylammonium chloride. The serious interferences are silver, bismuth, copper, nickel and cobalt ions. 5ml aliquot of the oxalate extract was transferred into the 100ml volumetric flask. The pH of the aliquot was adjusted to 3.5 ± 1.0 using acetate 10.0mL of 1.0004M sodium acetate solution. About 5.0mL of 10% hydroxylamine hydrochloride was added to all samples to reduce iron (III) ions. 4mL of 0.25% 1, 10-phenanthroline solution was added to the samples to form an orange-red colour complex with iron (II). The solutions were then diluted to 100ml.

Sample absorbance was measured at 515nm on a Lambda 20 UV-vis Spectrophotometer using quartz cuvettes (1cm cell path). Standard samples for calibration were prepared from a 100mg/L iron standard. The calibration curve was obtained from 0.025mg/L, 0.10mg/L, 0.25mg/L, and 0.50mg/L, 1.0mg/L, 2.0mg/L, 5.0mg/L, 10mg/L, 25mg/L, 40mg/L, 60mg/L, 80mg/L, 100mg/L and Blank standards.

4.2.6 Determination of ammonium ions

Ammonium ions in this method react with phenol and hypochlorite in alkaline solution to form an indophenol blue colour. Nitroprusside was used as a catalyst. The Ammonium ions were extracted by shaking 3.0 ± 0.0001 g of sediment with 30mL of 2.0013M KCl for 30minutes in the shaker at 400 r.p.m. The solution was filtered using No. 2 Whatman filter paper. 10.0mL aliquot of the extract was transferred into a 100.0mL volumetric flask. 0.5mL of the 10 % (m/v) phenol solution (in 95% ethanol) and 0.5mL of 0.5 % (m/v) sodium nitroprusside were added into the flask with proper mixing. 1mL of alkaline solution (1:4 mixture 20 % (m/v) tri-sodium citrate and sodium hypochlorite) was also added mixed thoroughly. The samples were stored in the dark for 2hours for colour to develop. Sample absorbance was measured at 640nm on a Lambda 20 UV-vis Spectrophotometer using quartz cuvettes (1cm cell path). Standard samples for

calibration were prepared from a 100mg/L prepared ammonium sulphate standard. The calibration curve was obtained from 0.025mg/L, 0.10mg/L, 0.25mg/L, and 0.50mg/L, 1.0mg/L 2.0mg/L, 5.0mg/L, 10mg/L, 25mg/L, 40mg/L, 50mg/L and Blank standards.

4.2.7 Determination soluble reactive phosphorus

Phosphorus was extracted by shaking 1.0 ± 0.001 g of air-dried sediment in 10.0 mL of 0.0249 HCl and 0.0299M NH_4F for 5 minutes. The extract was filtered. 5.0mL aliquot of the extract was transferred into a 100.0mL plastic volumetric flask. 5.0mL of 5:2:2:1 mixture of 15% H_2SO_4 , 3% ammonium molybdate, 5% ascorbic acid and 0.1% potassium antimony tartrate solution was added into the aliquot. The mixture was properly shaken and allowed to stand for an hour, until the colour developed.

Sample absorbance was measured at 885nm on a Lambda 20 UV-vis Spectrophotometer using quartz cuvettes (1cm cell path). Standard samples for calibration were prepared from a 100mg/L phosphate solution (KH_2PO_4). The calibration curve was obtained from 0.025mg/L, 0.10mg/L, 0.25mg/L, and 0.50mg/L, 1.0mg/L 2.0mg/L, 5.0mg/L, 10mg/L, and Blank standards.

CHAPTER FIVE

MAPUTALAND HYDROCHEMISTRY

5. Introduction

Many factors can affect the groundwater quality. The primary factors are the chemical composition of the recharging sources, the lithological and hydrological properties, various chemical processes occurring within the geological Units and the residence time of water in the geological Units. These factors result in dissolved constituents in groundwater. Most common abundant cations in the groundwater are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+)⁶⁵. The most abundant anions are bicarbonate ions (HCO_3^-), chloride ions (Cl^-), and sulphate ions (SO_4^{2-}). The ionic composition of the water can therefore be determined by measuring the cations and anions concentrations in the groundwater. This will assist in characterization of the groundwater chemical composition. The ionic composition of water in this study is classified into ionic types, based on dominant dissolved cations and anions which are expressed in milli-equivalent per liter (Meq/L).

The objective of this section is to determine the hydrochemical properties of different strata of the Maputaland boreholes in order to establish their physical characteristic. Each borehole classified in a particular lithological Unit is characterized based on the dominant cations and anions obtained from the hydrochemical data of the selected Maputaland boreholes.

5.1 Hydrochemical analysis of Maputaland aquifer

The hydrochemical analysis of the Maputaland aquifers was conducted at different time intervals as the borehole network expanded from its inception in 1999 with the development of boreholes at Science Centre in Alton area (Figure 5). Analysis of the monitoring boreholes was conducted for the assessment of variability in water quality in the Richards Bay area (Table 4). Some of the boreholes used in the study are utilized by industries in monitoring the groundwater quality changes between their upstream and downstream

monitoring points across the industrial sites. The hydrochemical data used for aquifers' characterization in this study was conducted by the CSIR (Durban) for the Department of Water Affairs (DWA) and the Mhlathuze Water Laboratory for the Hydrological Research Unit (HRU) at the University of Zululand.

Table 4: The selected borehole and aquifers used for the study (see Figure 5)

Station	Location	Stratigraphic Units	Elevation (m)	Depth (m)	Screen Length	Drilling method (rotary)	# Samples
Mfabeni Plain	St Lucia	Pleistocene	12	18	6m	Air	1
Alton 1	R/ Bay	Pleistocene	33	25	7m	Mud	1
					3m		
Alton 2	R/ Bay	Pleistocene	33	25	7m	Mud	1
					3m		
Alton 3	R/ Bay	Pleistocene	33	25	6m	Mud	1
S/centre BH1	R/ Bay	Miocene	33	36	9m	Mud	3
Aquadene	R/ Bay	Pleistocene	53	30	6-24m	Air	1
Birdswood	R/ Bay	Cretaceous	22	60	6m	Air	2
					48-54m		
Veldenvlei-2	R/ Bay	Miocene	22	25	3m	Air	2
					20-23		
Meerensee	R/ Bay	Miocene	24	40	3m	Air	3
					34-37		
Mseleni	Mbazwana	Pleistocene	66	48	6m	Air	1

All boreholes characterized in this study are located within the Maputaland region, as shown in Figure 5. Three of the boreholes (St Lucia, Mseleni and Birdswood) could not be properly characterized using piper diagrams due to the incomplete hydrochemical analyses (cations and anions analyses). Boreholes which were easily characterized are Alton (Alton 2, Alton 3), Science Centre, Veldenvlei, Aquadene and Meerensee (Table 4).

5.2 Short background of chosen boreholes

5.2.1 Alton aquifers

Alton boreholes are located in an area previously disturbed by eucalyptus globulus or timber forestation, within the heavy industrial area of Alton. They were drilled in 2005 by the mud rotary drilling technique (Table 4). They are 25m in depth, with the top of the casings at 33m above sea level (same elevation as Science Centre boreholes). The boreholes were drilled deep to reach the Pleistocene Unit. Both Alton 2 and 3 sediment samples were chosen for the geochemical study.

5.2.2 Science Centre aquifers

The Science Centre is located within the University of Zululand Science Training Centre in the heavy industrial area of Alton (Figure 5). It has three boreholes of 8m, 24m and 36m in depth that were drilled using the mud rotary drilling technique (Table 4). The 8m (shallow) borehole was assumed to represent the Holocene Unit, the 24m (middle) borehole represented the Pleistocene Unit and the 36m (deep) borehole represented the Miocene Unit. The deeper Unit sediment samples (from the 36m borehole) were chosen for the geochemical study as they covered all other Units in the other boreholes.

5.2.3 Aquadene aquifer

Aquadene aquifer is located close to the Aquadene suburb within the eucalyptus globulus or timber forestation (Figure 5). The aquifer has one borehole drilled in 2002 by the air rotary drilling technique. It was drilled deep to reach the

Pleistocene Unit. The borehole is 30m deep with the top of the casing at 53m above sea level (the highest elevation in Richards Bay). The sediment samples were chosen for geochemical study.

5.2.4 Veldenvlei aquifers

The aquifer is located in the Veldenvlei suburb (Figure 5). It has two boreholes, 18m (assume to represent the Pleistocene Unit) and 24m (assumed to represent the Miocene Unit) in depth. The boreholes were drilled in 2002 using the air drilling technique. They both have the top of the casings at 22m above sea level. The deeper borehole sediment samples were chosen for the geochemical study.

5.2.5 Birdwood aquifers

Birdwood aquifer is located within the Birdwood suburb, close to Richards Bay Airport and Mzingazi Lake (Figure 5). The aquifer has two boreholes of 18m (assumed to represent the Port Dunford) and 60m (assumed to represent the Cretaceous Unit) in depth. They were drilled in 2002 using air drilling technique. They both have the top of the casing at 22m above sea level. The Cretaceous sediment samples were chosen for the geochemical study.

5.2.6 Meerensee aquifers

The aquifer is located within the Meerensee suburb (Figure 5). It is located between the sea and the Mzingazi Lake. It has three boreholes at 20m (assumed to represent the Holocene Unit), 30m (assumed to represent the Pleistocene Unit), and 40m (assumed to represent the Miocene Unit) in depth, located close to each other. They were drilled in 2002 for groundwater quality monitoring. The boreholes have the top of the casings at 24m above sea level. The sediment samples representing Miocene Unit was chosen for the geochemical study.

5.2.7 St Lucia aquifers

Mfabeni aquifer is located within the St Lucia Wetland Park Reserve, Figure 5.

The aquifer has one borehole of 15m in depth (assumed to represent the Pleistocene Unit), which was drilled in 2002 by air rotary technique. The borehole is 12m above sea level. The sediment samples were chosen for the geochemical study.

5.2.8 Mseleni aquifers

The aquifer is located in the Mseleni area, Figure 5. It has one borehole of 48m in depth (assumed to represent the Pleistocene Unit), drilled by air rotary technique. It has the top of the casing (steel) at 66m above sea level. The borehole sediment samples were chosen for the geochemical study.

5.3 Groundwater Chemistry of Maputaland Aquifers

Maputaland boreholes analyzed in this chapter are classified into different Units, such as the Cretaceous, the Miocene; the Pleistocene and the Holocene Units (Table 4). Each borehole classified under a particular Unit is compared and characterized in terms of dominant cations and anions in order to determine the mineral composition of the aquifer.

It has to be considered that samples were obtained from the screened sections assumed to represent different lithological Unit.

5.3.1 Cretaceous Aquifer

The Birdwood borehole (60m) is the only borehole that was classified under the Cretaceous Unit. Its hydrochemical data is presented in Figure 10 and Tables 19 (Appendix II). The hydrochemical analysis conducted does not cover all anions and cations required for characterization, therefore only the available ions are considered. The results in Figure 10 show a hydrochemistry characterized by high sodium ions (197mg/L) dominance over calcium ions (88mg/L), with low magnesium ions (20mg/L) which concurs with Hattingh⁴⁶.

Due to the high concentration of sodium ions, chloride ions are presumed to be dominant for the anions, because no chloride ions were determined. Therefore,

Birdswood Cretaceous borehole is assumed to be characterized by a sodium and chloride ions type of water-chemistry. High sodium and chloride ions may indicate presence of briny component as stated by Hattingh⁴⁶.

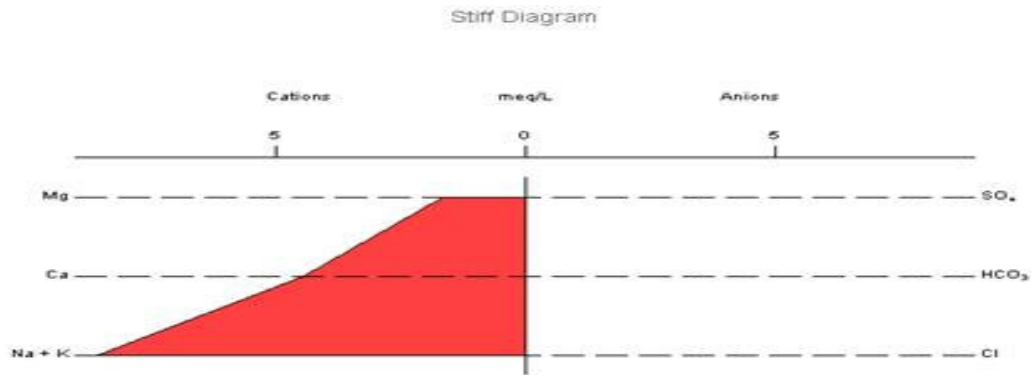


Figure 10: The hydrochemistry of Birdswood for the Cretaceous Unit indicated using the stiff-diagram, red shaded area indicating ions dominance (in meq/L). Data was obtained from DWA.

5.3.2. Miocene Aquifers

Miocene boreholes are distributed along the Richards Bay coastal plain from Science Centre to Meerensee. The hydrochemical data of the 3 boreholes (the Science Centre, the Veldenvlei and the Meerensee,) are presented in Figure 11 and Tables 16, 18 and 20 (Appendix II).

The results in Figure 11 show a hydrochemistry characterized by low magnesium (range 5-20mg/L), sulphate (19-58mg/L) and potassium ions (range 2-4mg/L), which concurs with Hattingh⁴⁶. Potassium ions in the water can be low due to the high degree of stability of potassium-bearing alumino-silicate minerals¹³. Magnesium ions can be lost through precipitations in solution or through ion-exchange reaction with sodium ions on surface of the clay mineral.

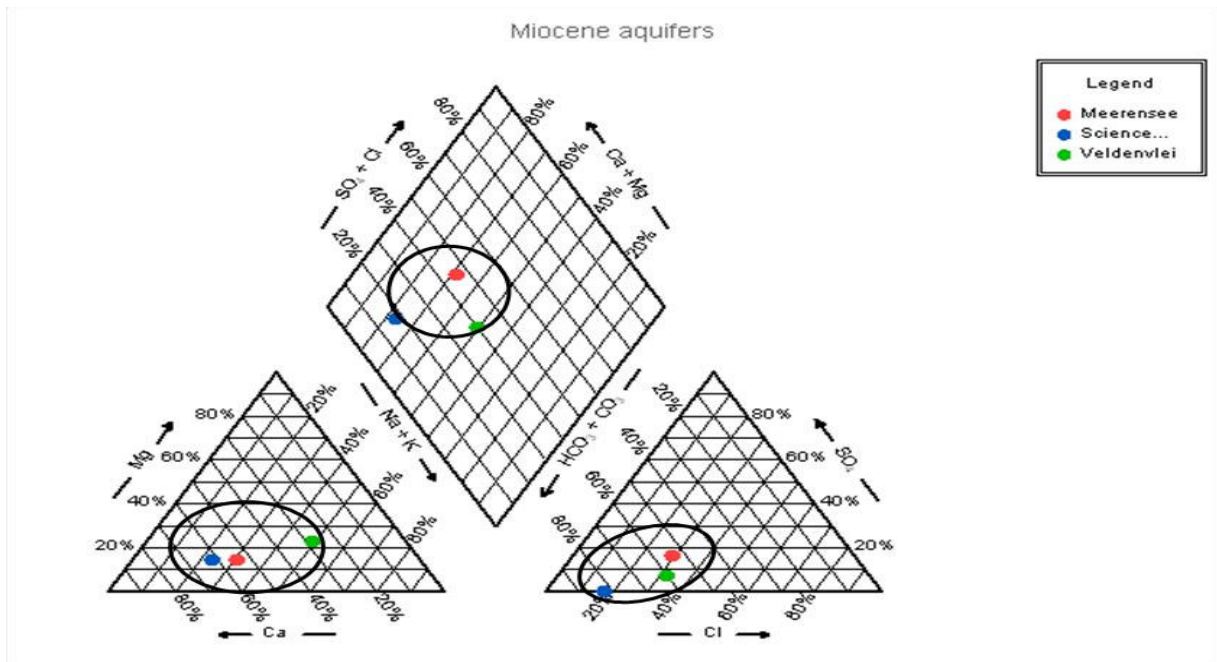


Figure 11: The hydrochemistry of the Miocene Unit indicated using piper diagrams, grouping show concurrence with Hattingh⁴⁶. Data obtained from HRU, Univ. Zululand.

The water is neutral to slightly alkaline (pH ranges from 6.53 to 7.8) due to bicarbonate ions (HCO_3^-) dominance. Chloride ions are slightly higher than sodium ions, and calcium ions exceed magnesium ions (Ca: Mg ratio 2:1).

In Figure 11, the Miocene Unit is dominated by bicarbonate ions in terms of the anions. There is a shift toward calcium ions dominance in Meerensee and Science boreholes in terms of the cations. There is also a shift towards sodium ions dominance in Veldenvlei with medium calcium ions.

The Miocene Unit is characterized by calcium and bicarbonate ions type of water-signature in Science Centre and Meerensee, and by a sodium, calcium and bicarbonate ions type of water-signature in Veldenvlei. The water in the Veldenvlei aquifer seems to be mixed.

5.3.3 Pleistocene Aquifers

The Pleistocene boreholes are distributed along the Maputaland coastal plain from Alton to Mseleni. The Hydrochemical data of the nine of boreholes (Alton,

Science Centre, Veldenvlei, Aquadene, Birdswood, Meerensee, St Lucia, and Mseleni) are presented in Table 15 to 22(Appendix II). Birdswood, St Lucia and Mseleni boreholes hydrochemical data could not be presented in Figure 12 due to the incomplete hydrochemical analysis in terms of cations and anions.

The results in Figure 12 and Table 15 to 22(Appendix II) show that the hydrochemistry of the Pleistocene Unit is characterized by a low magnesium (<31mg/L), sulphate (range from 2-119mg/L) and potassium ions (<17mg/L), which are slightly higher than that of the Miocene Unit. The water is acidic to slightly acidic (pH ranges from 5.43 to 6.10) due to low bicarbonate ions (HCO_3^-), except for Veldenvlei and Meerensee boreholes in which the pH was neutral (7.4) to alkaline (12.1) as result of HCO_3^- ions dominance. Chloride ions are slightly higher than sodium ions, and calcium ions exceed the magnesium ions (ratio Ca: Mg ratio exceeds 2:1).

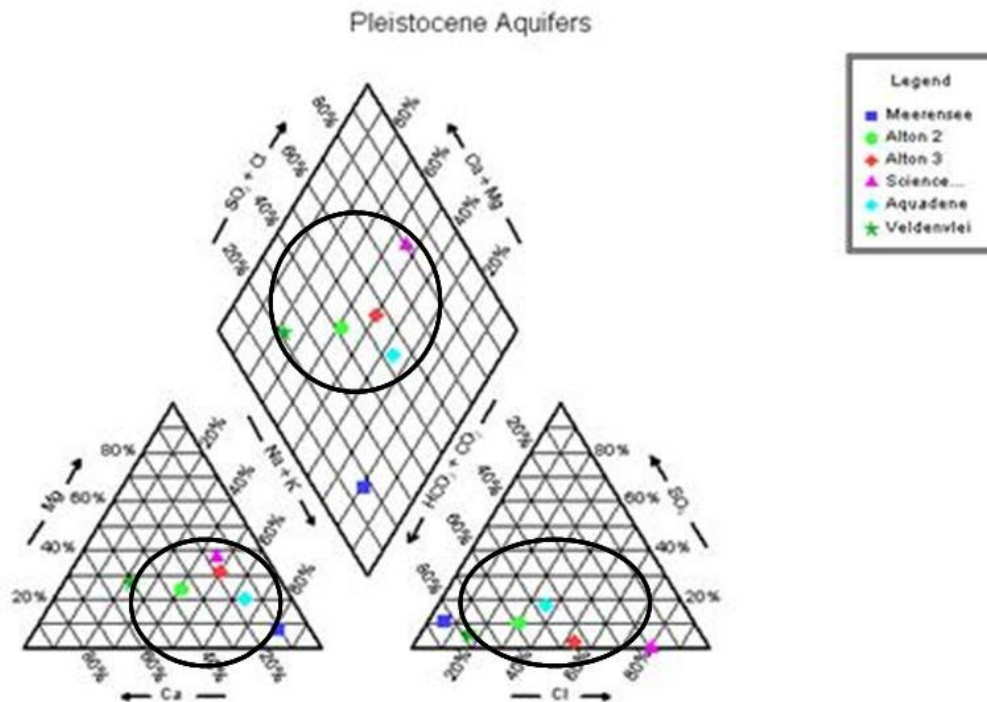


Figure 12: The hydrochemistry of the Pleistocene Unit indicated using piper diagrams, grouping show concurrence with Hattingh⁴⁶. Data obtained from HRU, Univ. Zululand.

In Figure 12, the Pleistocene Unit hydrochemistry is dominated by bicarbonate ions in Alton 2, Meerensee, Aquadene and Veldenvlei which does not concur with Hattingh⁴⁶, and by chloride ions in Alton 3 and Science Centre which concurred with Hattingh⁴⁶. Sodium ions are more dominant than calcium ions, which does not concur with Hattingh⁴⁶, except in the Veldenvlei which concurred with Hattingh⁴⁶.

Therefore, the Pleistocene Unit is characterized by three chemical signatures that are (1) a sodium and bicarbonate ions type of water-signature in most boreholes, (2) a calcium and bicarbonate ions type of water-signature in the Veldenvlei boreholes and (3) a sodium and chloride ions type of water-signature in Science Centre and Alton 3 boreholes.

5.3.4 Holocene Aquifers

Holocene boreholes are located along the Richards Bay coastal plain, in Science Centre and Meerensee aquifers. The Hydrochemical data of the two boreholes is presented in Figure 13 and Table 13 & 20 (Appendix II). The results from Figure 13 show that the hydrochemistry of the Holocene boreholes is completely different from each other, which could indicate different geological Formations.

The Science Centre borehole is characterized by slightly higher magnesium (24.3 mg/L) than calcium ions (17.5 mg/L), probably from the direct surface recharge or calcium ions are undergoing cation-exchange with sodium ions (Figure 12). Sodium (65.0 mg/L) and chloride ions (58.9 mg/L) are close to unity. The potassium ions (2.5 mg/L) are low. The water is acidic (pH 5.79) due to low bicarbonate ions (HCO_3^-).

The Meerensee borehole is characterized by higher calcium (170.3mg/L) and potassium ions (50.5mg/L), which are higher than that of the underlying Units. Chloride ions (64.5 mg/L) are higher than sodium ions (39.7 mg/L). The water is Alkaline (pH 12.5) due to the dominance of bicarbonate ions (HCO_3^-). Potassium

ions in natural water are generally lower than sodium ions. The higher potassium ions could indicate saline intrusion ⁴⁷.

The Science Centre borehole is characterized by a sodium and chloride ions type of water-signature while the Meerensee borehole is characterized by a calcium and bicarbonate ions type of water-signature.

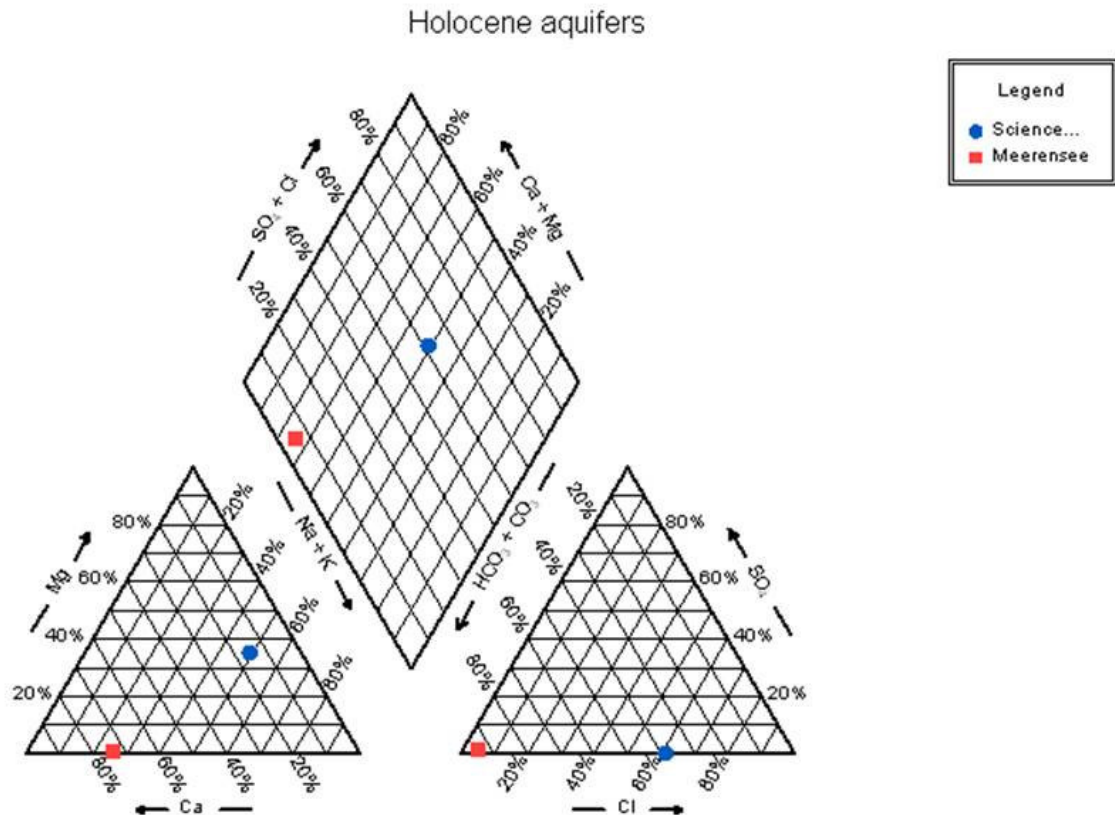


Figure 13: The hydrochemistry of the Holocene Unit indicated using piper diagrams, grouping show concurrence with Hattingh⁴⁶. Data obtained from HRU, Univ. Zululand.

5.4 General Conclusion to Maputaland Hydrochemistry

5.4.1 Cretaceous Aquifer

The Cretaceous Unit shows a chemical signature characterized by low magnesium and high sodium and chloride ions. Chloride and sodium ions can be a result of briny component presence in the Unit, as discovered by Martinelli and Associates⁴⁸ or from entrapped clays of recent marine sediments. It is

recommended that more cations and anions analysis (such as chloride ions) be determined in this Unit for better characterization. Therefore, the Cretaceous Unit is characterized by a sodium and chloride ions type of groundwater signature.

5.4.2 Miocene Aquifers

In the Miocene Unit, two different populations were distinguished on the basis of the groundwater chemistry. The first group (Science Centre and Meerensee boreholes) shows a high calcium and bicarbonate ions dominance over sodium and chloride ions which concurs with Hattingh ⁴⁶ for boreholes distributed along the coastal plains from Lake Mzingazi to Dukuduku in the north. The second group (Veldenvlei borehole) shows a sodium, calcium and bicarbonate ions dominance, indicating mixed water. Calcium and bicarbonate ions dominance can be attributed from dissolution of the calcite minerals from the Miocene sediments. Sodium ions dominance in Veldenvlei may indicate slightly depletion of calcium ions through cation-exchange with sodium ions or recharge of the Unit by sodium ions from the neighbouring stream of Veldenvlei borehole. The Miocene Unit is low in magnesium, sulphate and potassium ions which concur with Hattingh ⁴⁶. It is neutral to alkaline in pH, due to the dominance of bicarbonate ions (HCO_3^-). Chloride ions are slightly higher than sodium ions and calcium ions exceed the magnesium ions which concur with Hattingh ⁴⁶.

5.4.3 Pleistocene Aquifer

In the Pleistocene Unit, three different populations were distinguished on basis of the groundwater chemistry. The first group (Alton 2, Aquadene and Meerensee boreholes) shows the dominance of sodium and bicarbonate ions due to the depleted calcium ions. The second group (Veldenvlei boreholes) shows the dominance of calcium and bicarbonate ions. The third group (Science Centre and Alton 3 boreholes) shows the dominance of sodium and chloride ions due to low calcium and bicarbonate ions. The Pleistocene Unit is low in magnesium, sulphate and potassium ions, but slightly higher than that of the Miocene Unit, which concurs with Hattingh ⁴⁶. Calcium ions are lower than that of the Miocene

Unit, either from leaching of sediments or through cations exchange with sodium ions, resulting in low pH (acidic), except for Veldenvlei and Meerensee aquifers where the pH is neutral to alkaline due to the dominance of bicarbonate ions.

5.4.4 Holocene Aquifers

The Holocene Unit has two different populations in terms of groundwater chemistry. The first group (Science Centre borehole) shows a sodium and chloride ions dominance over calcium and bicarbonate ions. The second group (Meerensee borehole) shows a calcium and bicarbonate ions dominance over sodium and chloride ions. Magnesium and potassium ions are higher in the first group and second group respectively. Higher potassium ions may arise from the geological composition of the areas or from impacts by other sources.

CHAPTER SIX

MAPUTALAND LITHOLOGICAL UNITS CLASSIFICATION

6. Introduction

The geochemical analysis of the Maputaland was initially conducted in the St Lucia and Alton 3 boreholes. A large number of sediment samples per borehole were needed to be analyzed, as the samples were taken at one meter interval for the full depth of the borehole drilled. It was also necessary to conduct duplicate analysis to evaluate reliability of the analytical results and methods. Consequently, it was necessary to identify ways of reducing the number of geochemical samples for analysis. Therefore, the samples were combined to form a composite sample representing the same geological Unit. The samples were subjected to acid and water extraction depending on analytes of interest. When all analyses were completed, the results were then subjected to serious interpretation in order to determine the geochemistry of each borehole.

Figure 14 is an illustration of a borehole log that shows that adjacent layers of sediments have similar colours.

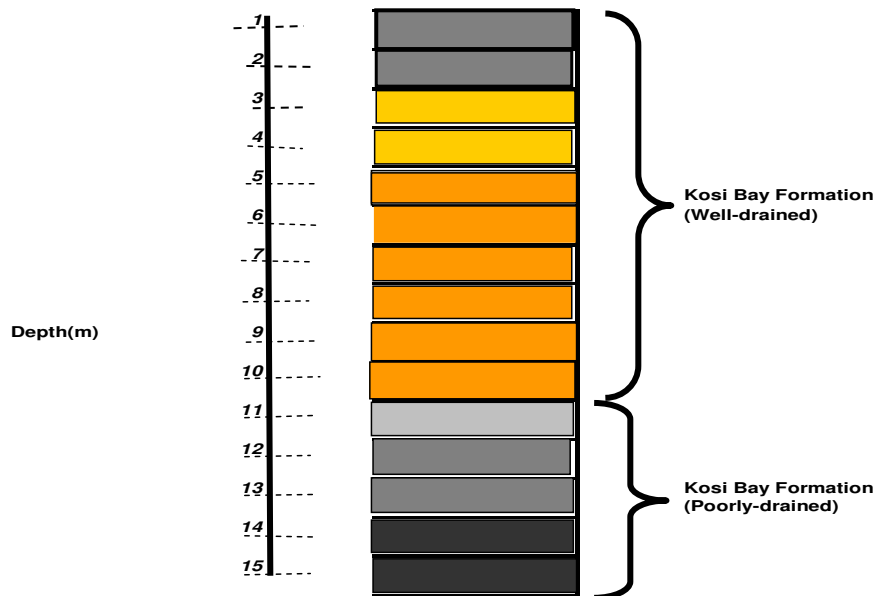


Figure 14: Sediment layers in the St Lucia aquifer, indicating different colours and lithological units

The geochemical analysis of these layers also indicated a distinct relationship in their chemical composition between samples. The analysis of all samples for the St Lucia boreholes illustrated that there is a higher level of correlation between adjacent samples, and that the significant changes can be attributed to change in lithology. A unique similar characteristic and chemical composition was displayed by these sediment layers (Figure 15).

Due to similar characteristics and chemical composition of the borehole sediments, classification of borehole samples into lithostratigraphic Units was then considered to be the most pragmatic way of compositing the soil samples. The classification was also considered to reduce a large number of samples needed to be analyzed and to check uniformity of analytical techniques.

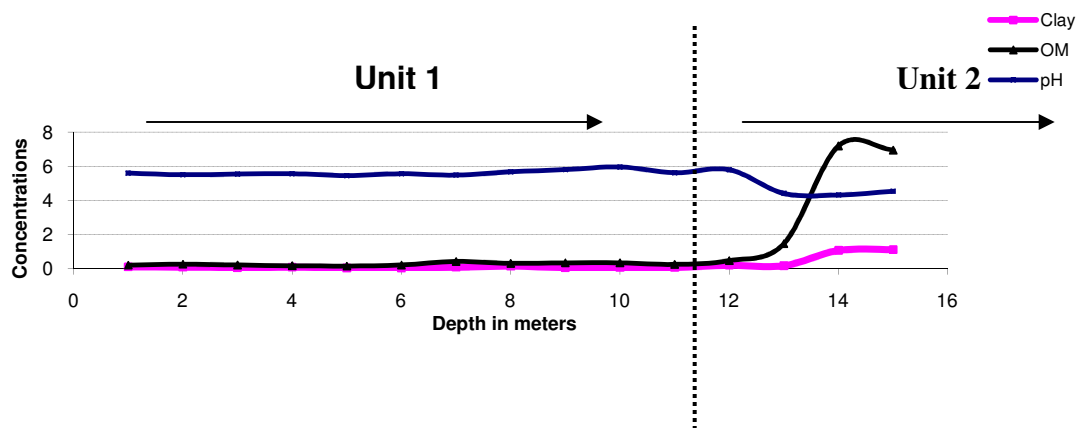


Figure 15: St Lucia geochemistry used for classification

Professional assistance to classify the boreholes samples into lithological Units was sought from KZN geologists namely Dr Botha (Council for Geosciences), Mr. B. Lynn (Geotechnical Consultant with Davies Lynn and Partners) and Mr. J.J Simonis (University of Zululand). The professionals were requested to have a quick look at the sediment samples to predict their lithology.

The prediction was based on samples grain size, soil texture and soil colour. The classification was based on the lithology formulated by Botha²⁷. Subsequently, all Sediment samples of the same borehole (previously classified in meters) which were classified into one Unit were combined together to form one

composite sample Unit (Figure 16). Sediments of all selected boreholes of Maputaland coastal plain were then classified into Kwambonambi, Sibaya, Kosi Bay, Port Durnford, Uloa and St Lucia Formations. The classification of all available samples is shown in Figure 16 and Figure 17.

6.1 Maputaland coastal plain lithostratigraphic Units description

Maputaland lithological Units are dominated by varying thickness of sediment layers. Most of the shallow Units (Kwambonambi, Kosi Bay Formation and Port Durnford) are dominated by organic matter content (ranging from 0.591 to 4.21%), which gave rise to the brownish colour of the sediments especially in the Kwambonambi Formation. The thickness of the shallow Units varies from 3m to 22m, in which the Kosi Bay is the thickest unit in most aquifers (Figure 16 and Figure 17). Maputaland sediments range from consolidated to unconsolidated, to loosely consolidated beds that are predominantly fine grained. Calcium carbonate content increases down the units, in which Uloa and St Lucia are the highest in calcite.

6.1.1 St Lucia Formation

The Science Center, Veldenvlei and Birdswood boreholes were drilled deep enough to intersect the St Lucia formation (Figure 17). Sediments in Science Center and Veldenvlei aquifers are dark greenish grey or olive green with fine siltstone materials rich in glauconitic mineral as identified by Worthington.⁶ In Birdswood aquifers the sediments are yellow/orange-brown in colour. The sediments are rich in clay materials and calcium carbonate content (Figure 17). The sediment thickness layer varies from 3m to 4m (Figure 16).

6.1.2 Uloa Formation (Miocene Period)

The Science Center, Veldenvlei and Meerensee boreholes intersected the Uloa Formation.

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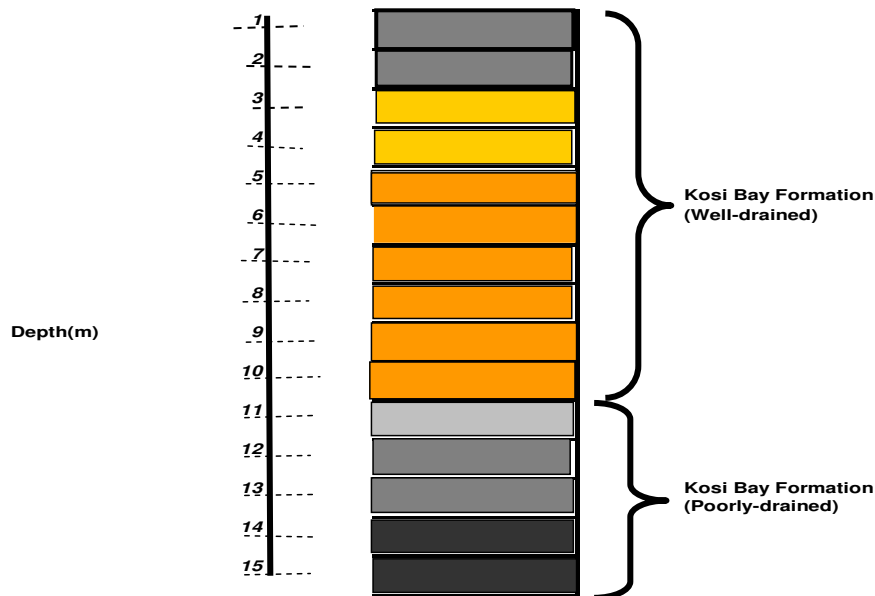


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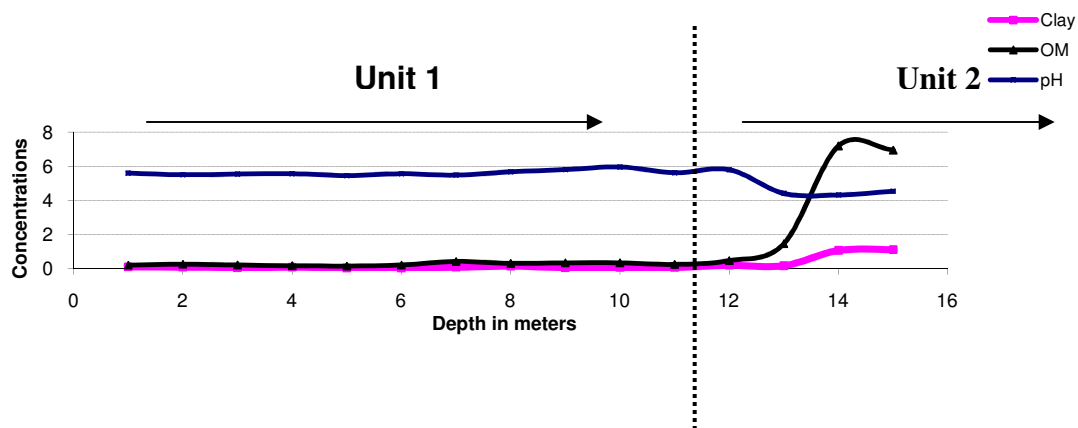


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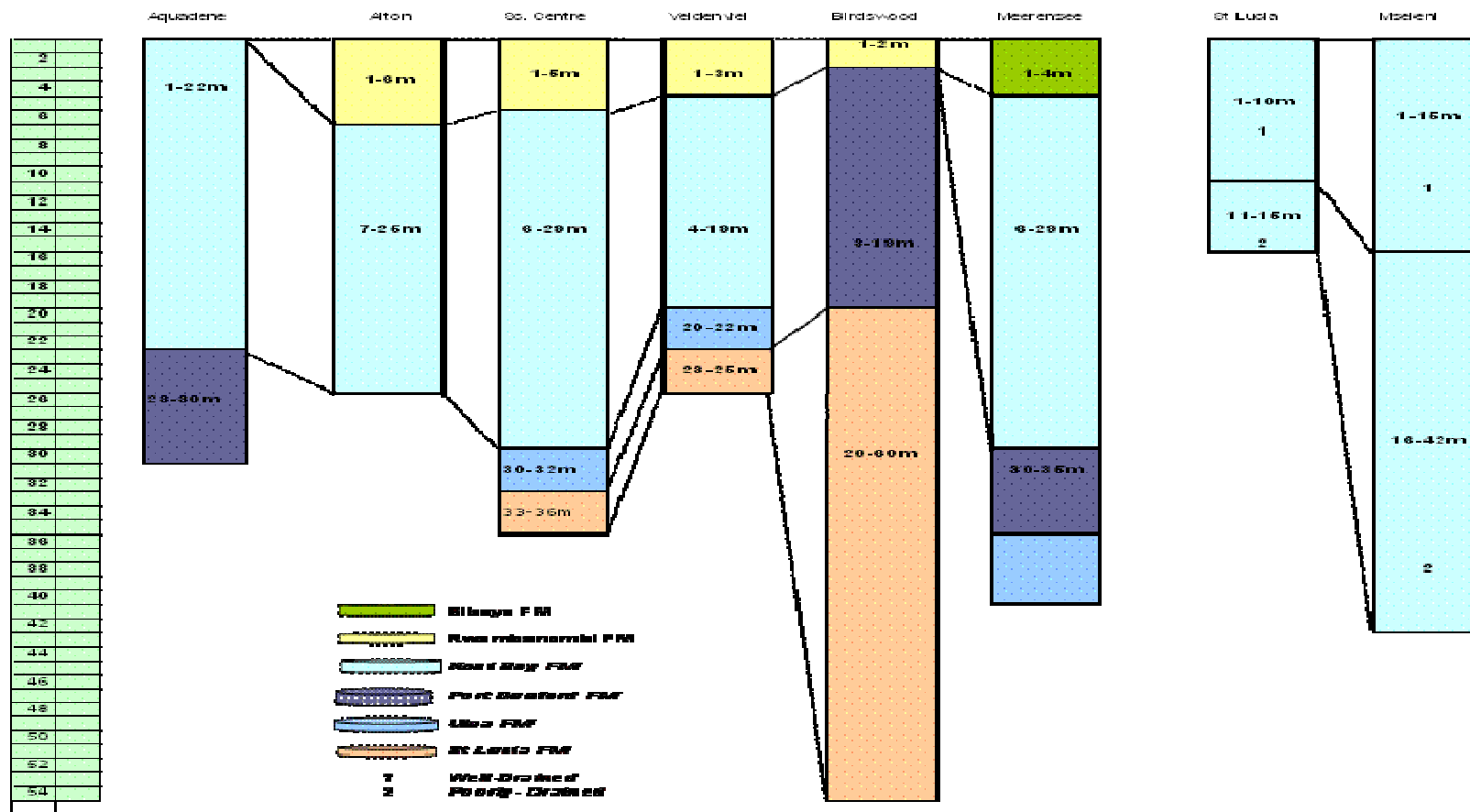


Figure 16: Drawing showing the lithostratigraphic units of Maputland Coastal Plain

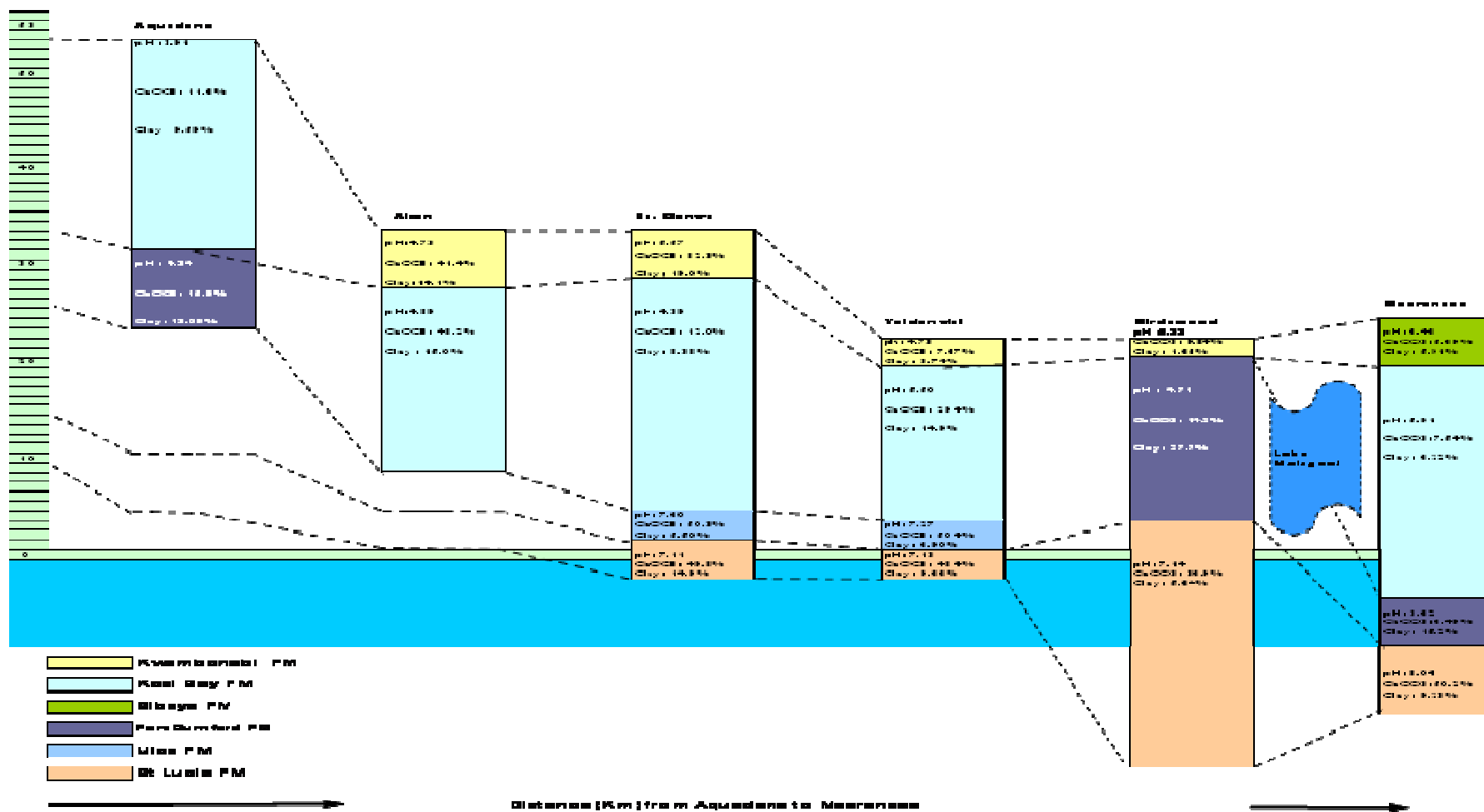


Figure 17 Lithological Units of the boreholes representing a cross-section of the Richards Bay Coastal Plain (See Figure 5 onset for location).

The sediments in the three aquifers are rich in yellow and orange sediments of hard and soft calcite rocks as describe by Maud.³⁰ Meerensee contained lignite conglomerates, while Veldenvlei and Science Center consists mainly of conglomerates. The sediments are rich thin lenses of clay, silt minerals and calcium carbonate content (Figure 17). The thickness of the Uloa Formation varies from 2m about 5m.

6.1.3 Port Durnford Formation

The Aquadene, Meerensee and Birdswood boreholes intersected the Port Durnford Formation (Figure 17). The Port Durnford Formation is composed of cream-white sediments in both Aquadene and Meerensee boreholes, while the Birdswood borehole sediments are yellow-brown. The Formation is mainly composed of thick clay layers with medium silt minerals. The sediments are predominantly acidic (Figure 17). The acidity of the sediments is due to a low calcium carbonate concentration. The Port Durnford Formation thickness varies from 2m to 17m (Figure 16).

6.1.4 Kosi Bay Formation (Pleistocene Period)

All the boreholes intersected the Kosi Bay Formation except for the Birdswood (Figure 17). The sediments are reddish-yellow to white in colour. They contain various levels of clay minerals. The sediments are predominantly acidic due low calcium carbonate concentration. The Kosi Bay Formation varies from 15m to about 23m in thickness (Figure 16).

6.1.5 Kwambonambi Formation (Holocene Period)

The Tata, Science Center, Veldenvlei and Birdswood boreholes intersected the Kwambonambi Formation (Figure 17). The sediments are light brownish-gray to black in colour due to the presence of organic matter. They contain fine grained particles with various levels of organic material. They also contain various levels of clay minerals. They are predominantly acidic due to low calcium carbonate

concentration (Figure 17). The Kwambonambi Formation varies from 2m to about 6m in thickness (Figure 16).

6.1.6 Sibaya Formation (Holocene Period)

The Meerensee borehole intersected Sibaya Formation. The sediments are light brownish gray in colour with low organic matter content. They contain clay minerals (Figure 17). They are slightly acidic with low calcium carbonate concentration. The Sibaya Formation has a thickness of 4m (Figure 16).

CHAPTER SEVEN

MAPUTALAND GEOCHEMICAL ANALYSES

The objective of the section is to determine the natural background geochemistry of the Maputaland aquifers by determining the geochemical composition of each classified lithological Unit of the selected borehole samples.

7. Geochemical analysis

The analysis was based on classified individual lithological Units rather than sample sequence (Table 5.1). Sediment mineral ions such as calcium (Ca^{2+}), carbonate (CO_3^{2-}), total iron (FeT), manganese (Mn^{2+}) and phosphate (PO_4^{3-}) ions were extracted using deionized water, acidic or alkaline solutions depending on the ions solubility required for comparison to hydrochemistry.

Other parameters such as pH, particle size (sand silt, and clay) and organic matter were also determined. Cations and anions analysis such as potassium, sulphate, magnesium, sodium and chloride ions could not be determined due to a shortage of financial support.

7.1 Maputaland aquifers geochemical composition

7.1.1 St Lucia Formation (Cretaceous sediments)

The St Lucia Formation is associated with the Cretaceous sediments²⁷. The type of sediments is found in the Veldenvlei, Birdswood and Science Centre boreholes, with a thickness of approximately 4 to 41 meters. The colours of the sediments ranged from olive green, black green to bluish green, agreeing with Worthington⁶. Fine grained glauconitic siltstones (Silt $\leq 10.7\%$), high clay mineral content (ranging from $5.64 \pm 0.02\%$ to $14.9 \pm 0.2\%$) and shell fragments dominate the sediments (Table 5.2). Organic matter and phosphate ions are quite evident (ranges from 0.330 ± 0.011 to $1.57 \pm 0.02\%$ and 0.030 ± 0.040 to $1.42 \pm 0.01\text{mg/L}$) which is assumed to be attributed by the shell fragments and the animal matter

buried in the Formation. Phosphate ions and organic matter concentrations are likely to have been reduced by decomposition process during long-term storage.

Table 5.1: The selected borehole and aquifers used for the study (see Figure 5)

Station	Location	Hydrochemical Stratigraphic Units	Depth (m)	Drilling method (rotary)	Geological lithology	Number of Samples
Mfabeni Plain	St Lucia	Pleistocene	18	RC-Air	Well drained Kosi Bay Formation	2
					Poorly drained Kosi Bay Formation	
Alton 2	R/ Bay	Pleistocene	25	Mud	Kwambonambi FM Kosi Bay FM	2
Alton 3	R/ Bay	Pleistocene	25	Mud	Kwambonambi FM	2
					Kosi Bay FM	
S/centre BH1	R/ Bay	Miocene	36	Mud	Kwambonambi FM	4
					Kosi Bay FM	
					Uloa FM	
					St Lucia FM	
Aquadene	R/ Bay	Pleistocene	30	RC-Air	Kosi Bay FM	3
					Port Durnford (Berea Red) FM	
					Port Durnford	
Birdswood	R/ Bay	Cretaceous	60	RC-Air	Kwambonambi FM	3
					Port Durnford (Berea Red) FM	
					Port Durnford	
Veldenvlei-2	R/ Bay	Miocene	25	RC-Air	Kwambonambi FM	4
					Kosi Bay FM	
					Uloa FM	
					St Lucia FM	
Meerensee	R/ Bay	Miocene	40	RC-Air	Kwambonambi FM	4
					Kosi Bay FM	
					Port Durnford	
					Uloa	
Mseleni	Mbazwana	Pleistocene	48	RC-Air	Well drained Kosi Bay FM	2
					Poorly drained Kosi Bay	

In Table 5.2 and Tables 24 & 26 (Appendix III), the sediments are dominated by calcium and carbonate ions ($\leq 19.9 \pm 4\%$ and $\leq 49.8\%$ respectively) resulting in neutral sediments ($\text{pH} > 7$). Calcium and carbonate ions are contributed by the mineral calcite and shell fragments which dominated the Cretaceous sediments. Carbonate ions buffered sediments against acidity through reaction with H^+ ions in solution thereby producing bicarbonate ions.

Table 5.2: St Lucia Formation geochemistry

Site	pH	% CaCO_3	% Ca	%OM	%Clay	% Silt	Fe (mg/L)	Phos. (mg/L)	Mn (mg/L)	Si (mg/L)
Sc. Centre	7.11 $\pm$ 0.03	49.8 $\pm$ 3.4	19.9 $\pm$ 0.5	1.57 $\pm$ 0.02	14.9 $\pm$ 0.2	10.4 $\pm$ 0.1	86.0 $\pm$ 0.2	0.444 $\pm$ 0.003	27.0 $\pm$ 0.2	0.443 $\pm$ 0.040
Veldenvlei	7.13 $\pm$ 0.10	48.4 $\pm$ 1.3	18.4 $\pm$ 0.4	0.920 $\pm$ 0.01	9.66 $\pm$ 0.30	10.9 $\pm$ 0.5	84.0 $\pm$ 0.8	0.030 $\pm$ 0.004	0.0 $\pm$ 0.0	0.470 $\pm$ 0.090
Birdswood	7.14 $\pm$ 0.20	36.9 $\pm$ 0.2	14.8 $\pm$ 0.2	0.330 $\pm$ 0.011	5.64 $\pm$ 0.02	3.15 $\pm$ 0.1	45.0 $\pm$ 0.2	1.42 $\pm$ 0.01	0.0 $\pm$ 0.0	1.22 $\pm$ 0.20
Average	7.13 $\pm$ 0.11	45.0 $\pm$ 1.6	17.7 $\pm$ 0.4	0.940 $\pm$ 0.010	10.1 $\pm$ 0.2	8.15 $\pm$ 0.2	71.7 $\pm$ 0.4	0.631 $\pm$ 0.006	9.00 $\pm$ 0.07	0.711 $\pm$ 0.110

The Formation shows a low total iron concentration ($\leq 86.0 \pm 0.2 \text{ mg/L}$) and manganese ions ($\leq 27.0 \pm 0.2 \text{ mg/L}$). Ions are assumed to exist either as low soluble or insoluble forms (such as iron carbonate), as the sediments do not show any degree of leaching. The sediments are also low in silicate ions ($\leq 1.22 \pm 0.20 \text{ mg/L}$).

7.1.2 Uloa Formation (Miocene Sediments)

The Uloa Formation is associated with the Miocene sediments ²⁷. The sediments are considered to be semi-confined with a storage provided by overlaying, less permeable sediments, Bachmat ⁵⁰ and Botha ⁵¹. The type of these sediments is found in Veldenvlei, Science Center and Meerensee boreholes, with a thickness of approximately 4 meters. The sediments are yellow and orange in colour, rich in coquina and calcite as described by Maud ³⁶.

In Table 5.3 and Tables 24 & 26 and 28 (Appendix III), the sediments are dominated by medium grained siltstones of the coquina (Silt $\leq 8.84\%$) and clay minerals (ranging from 5.5- 9.23%), which are lower than that of the St Lucia

Formation. Organic matter ranges from 0.444 to 0.792%, which is less than that of the St Lucia Formation.

The sediments are dominated by calcium and carbonate ions due to the presence of mineral calcite and shell fragments in the sediments, which resulted in neutral to alkaline (pH >7) sediments. High calcium carbonate content (>50.0%) and calcium ions (>20.0%) are also a result of the presence of the mineral calcite, shell fragments from coquina minerals found in the sediments.

The Formation shows a total iron concentration ($\leq 202\text{mg/L}$) and manganese ions ($\leq 32.4\text{mg/L}$) that are higher than that of the St Lucia Formation. Phosphate ions ($\leq 0.450\text{mg/L}$) are lower than that of the St Lucia Formation. Silicate ions ($\leq 4.56\text{mg/L}$) are 10-fold higher than that of the St Lucia Formation.

Table 5.3: Uloa Formation geochemistry

Site	pH	% CaCO ₃	% Ca	%OM	%Clay	% Silt	Fe (mg/L)	Phos (mg/L)s	Mn (mg/L)	Si (mg/L)
Sc. Centre	7.60 $\pm$ 0.10	50.3 $\pm$ 4.1	20.1 $\pm$ 0.1	0.519 $\pm$ 0.004	5.50 $\pm$ 0.01	7.72 $\pm$ 0.10	86.0 ($\pm$ 0.2)	0.361 ($\pm$ 0.005)	0.0 ($\pm$ 0.0)	0.194 ($\pm$ 0.010)
Veldenvlei	7.27 $\pm$ 0.10	50.4 $\pm$ 1.8	20.2 $\pm$ 0.3	0.792 $\pm$ 0.024	6.90 $\pm$ 0.12	5.08 $\pm$ 0.20	48.0($\pm$ 0.30)	0.100($\pm$ 0.060)	00($\pm$ 0.0)	0.420($\pm$ 0.040)
Meerensee	8.09 $\pm$ 0.30	50.2 $\pm$ 0.5	46.7 $\pm$ 0.2	0.440 $\pm$ 0.022	9.23 $\pm$ 0.44	8.84 $\pm$ 0.23	202($\pm$ 9)	0.450($\pm$ 0.030)	32.4($\pm$ 0.2)	4.56($\pm$ 0.60)
Average	7.65 $\pm$ 0.17	50.3 $\pm$ 2.1	29.0 $\pm$ 0.2	0.585 $\pm$ 0.017	7.21 $\pm$ 0.19	7.21 $\pm$ 0.18	95.3($\pm$ 3.2)	0.303($\pm$ 0.012)	10.8($\pm$ 0.6)	1.72($\pm$ 0.2)

7.1.3 Port Durnford Formation (Pleistocene sediments)

The Port Durnford Formation is associated with the Pleistocene sediments²⁷. The loosely consolidated sediments of the Port Durnford Formation overlay the Miocene sediments in other parts of the Richard Bay areas. The Port Durnford Formation sediment types are found in Aquadene, Birdswood and Meerensee boreholes, with a thickness ranging from 6 to 16m. The sediments colour range from yellow, red and brown to cream-white with high argillaceous minerals, especially in the Birdswood borehole.

In Table 5.4, and Tables 25, 27, 28(Appendix III), the sediments of the Port Durnford Formation are predominantly acidic (pH ranged from 3.62 $\pm$ 0.40 –

4.71±0.2) due to a calcium and carbonate ions (ranging from 4.6±0.17–6.18±0.22% and 6.49±0.08% - 18.2±1.7%, respectively) than that of the Uloa and St Lucia Formations. Calcium and carbonate ions seem to be leached from the sediments, probably by the prevailing rainfalls of the coastal plain. The sediments contain organic matter (ranges from 0.346 - 1.75%) that are higher than that of the St Lucia Formation, probably from overlaying units supply. They are dominated by high clay minerals (ranging from 14 -28%) with low silt minerals (≤5.07%) due to argillaceous minerals of the Port Durnford Formation.

The Formation shows a total iron concentration (ranges from 35 to 206mg/L) that is similar to the Uloa Formation, with low manganese ions (≤2.53±0.10mg/L). Phosphate (<0.910±0.002mg/L) and silicate ions (<6.43±0.05mg/L) are higher than that of the Uloa Formation. Phosphate ions are likely to be contributed by shell fragments of the argillaceous minerals.

Table 5.4: Port Durnford Formation geochemistry

Site	pH	% CaCO ₃	% Ca	% OM	% Clay	% Silt	Fe (mg/L)	Phos. (mg/L)s	Mn (mg/L)	Si (mg/L)
Aquadene	4.34±0.45	18.2 ±1.7	4.6.0±0.17	0.346±0.004	14.4±0.7	2.44±0.50	35.0± 0.4	0.365± 0.002	0.0±0.0	6.43± 0.05
Birdswood	4.71±0.20	14.2±0.5	5.69±0.05	1.10±0.015	27.7±0.2	0.530±0.50	20.0±0.8	0.033±0.001	0.0±0.0	1.64±0.20
Meerensee	3.62±0.40	6.49±0.08	6.18±0.22	1.75±0.50	15.2±0.6	5.07±0.18	206±6	0.910±0.020	2.53±0.11	2.48±0.50
Average	4.22±0.35	12.9±0.8	5.49±0.29	1.07±0.02	19.1±0.5	2.68±0.24	87.0 ±2	0.436±0.007	0.843±0.037	3.52±0.25

7.1.4 Kosi Bay Formation

The Miocene sediments are overlain by loosely consolidated sediments of the Kosi Bay Formation of middle the Pleistocene age. The type of sediments are identified in all aquifers (except in the Birdswood borehole), with a thickness of 15 to 42m. The sediments colour range from cream-white, yellow, yellow-orange to red.

In Table 5.5 and Tables 23-26 and 28-30(Appendix III), the sediments of the Kosi Bay Formation are predominantly acidic to slightly acidic (pH ranging from 3.91 to

6.25) due to low calcium and carbonate ions. Calcium carbonate concentration (ranges from 5.9.1% - 29.4%) and calcium ions (2.63 – 12.0%) are lower than that of the Uloa and St Lucia Formations. The sediments are dominated by silt ($\leq 9.28\%$) and clay minerals (ranging 1.77 to 15.0%) as result of weathering of the fluvial and aeolian sediment deposits. Organic matter ($\leq 4.21\%$) is higher than that of the Port Durnford Formation, which is assumed to be supplied by overlaying unit (Kwambonambi Formation).

The Formation shows a total iron concentration (range from 16 to 60.7mg/L), manganese (15.1 ± 0.9 mg/L) and phosphate ions ($< 0.604 \pm 0.008$ mg/L) that are lower than that of the Port Durnford Formation. Silicate ions ($< 22.0 \pm 0.3$ mg/L) are higher than that of the Port Durnford Formation.

Table 5.5: Kosi Bay Formation geochemistry

	pH	% CaCO ₃	% Ca	%OM	%Clay	% Silt	Fe (mg/L)	Phos (mg/L)s	Mn (mg/L)	Si (mg/L)
Alton 2	4.88 $\pm$ 0.40	6.13 $\pm$ 0.22	3.56 $\pm$ 1.0	0.444 $\pm$ 0.009	13.8 $\pm$ 0.4	4.80 $\pm$ 0.10	49.5($\pm$ 0.3)	0.383($\pm$ 0.016)	15.1 ($\pm$ 0.9)	22.0 ($\pm$ 0.3)
Alton 3	4.89 $\pm$ 0.50	4.82 $\pm$ 0.90	3.12 $\pm$ 0.6	0.970 $\pm$ 0.015	15.0 $\pm$ 0.3	1.66 $\pm$ 0.10	55.3($\pm$ 0.8)	0.512($\pm$ 0.010)	6.36 ($\pm$ 0.80)	1.94 ($\pm$ 0.10)
Sc. Centre	4.39 $\pm$ 0.50	12.0 $\pm$ 0.4	4.29 $\pm$ 0.26	0.372 $\pm$ 0.010	8.36 $\pm$ 0.08	9.28 $\pm$ 0.20	48.0($\pm$ 0.9)	0.604($\pm$ 0.080)	0.0 ($\pm$ 0.0)	0.401($\pm$ 0.010)
Aquadene	3.91 $\pm$ 0.21	11.6 $\pm$ 0.9	3.97 $\pm$ 0.19	1.09 $\pm$ 0.08	9.59 $\pm$ 0.07	2.83 $\pm$ 0.04	38.0($\pm$ 0.1)	0.530($\pm$ 0.020)	4.75($\pm$ 0.20)	1.21 ($\pm$ 0.06)
Veldenvlei	5.50 $\pm$ 0.30	29.4 $\pm$ 0.3	11.8 $\pm$ 0.7	0.393 $\pm$ 0.019	14.9 $\pm$ 0.7	1.48 $\pm$ 0.20	16.0($\pm$ 0.5)	0.054($\pm$ 0.011)	0.000($\pm$ 0.00)	1.64($\pm$ 0.10)
Meerensee	5.91 $\pm$ 0.10	7.54 $\pm$ 0.05	2.99 $\pm$ 0.33	0.580 $\pm$ 0.033	6.22 $\pm$ 0.43	6.43 $\pm$ 0.55	52.0($\pm$ 0.3)	0.210($\pm$ 0.012)	3.25($\pm$ 0.10)	2.29($\pm$ 0.60)
St Lucia *	5.07 $\pm$ 0.10	5.91 $\pm$ 0.82	2.63 $\pm$ 0.41	4.21 $\pm$ 0.90	1.77 $\pm$ 0.38	4.13 $\pm$ 0.22	51.8($\pm$ 0.9)	0.540($\pm$ 0.010)	4.40($\pm$ 3)	3.62($\pm$ 0.24)
Mseleni *	6.25 $\pm$ 0.10	6.74 $\pm$ 0.9	2.70 $\pm$ 0.15	0.140 $\pm$ 0.017	2.39 $\pm$ 0.20	1.78 $\pm$ 0.23	19.5($\pm$ 3)	0.350($\pm$ 0.024)	1.15($\pm$ 0.60)	3.00($\pm$ 0.82)
Average	5.10 $\pm$ 0.21	10.5 $\pm$ 0.6	4.38 $\pm$ 0.46	1.02 $\pm$ 0.13	9.00 $\pm$ 0.32	4.04 $\pm$ 0.21	42.3($\pm$ 0.9)	0.398($\pm$ 0.02)	4.38($\pm$ 0.70)	4.51($\pm$ 0.22)

* Poorly drains Kosi Bay results reported for St Lucia and Mseleni boreholes.

7.1.5 Kwambonambi Formation

The Pleistocene sediments of the Kosi Bay and Port Durnford Formation are overlain by the loosely consolidated sediments of the Kwambonambi Formation. These sediments are recent (Holocene deposit) aeolian or alluvial deposits. The type of sediments is identified in most aquifers except in Aquadene, Meerensee,

St Lucia and Mseleni boreholes, with a thickness of approximately 3 to 6 meters. The sediments colour range from brownish gray to black, indicating richness in organic matter.

In Table 5.6 and Tables 23-24 and 26-28(Appendix III), Kwambonambi Formation is predominantly acidic (pH range from 4.73 ± 0.50 to 5.57 ± 0.20) which is lower than that of the Kosi Bay Formation). Calcium carbonate content (ranges from 1.92% to 9.84%) and calcium ions (range from 1.36 to 3.94%) which are lower than that of the Kosi Bay Formation. Sediments are dominated by various levels of clay minerals (ranging from 1.65 to 14.1%) and medium to low silt minerals (ranging from 1.08 and 4.32%).

Table 5.6: Kwambonambi Formation geochemistry

Site	pH	% CaCO ₃	% Ca	%OM	%Clay	% Silt	Fe (mg/L)	Phos (mg/L)s	Mn (mg/L)	Si (mg/L)
Alton 3	4.73 ± 0.50	4.14 ± 2.0	2.28 ± 0.2	2.28 ± 0.14	14.1 ± 1.0	4.32 ± 0.44	$54.0 (\pm 0.5)$	$1.50 (\pm 0.08)$	$6.07 (\pm 0.20)$	$3.12 (\pm 0.30)$
Alton 2	5.28 ± 0.40	1.92 ± 0.29	1.36 ± 0.05	0.933 ± 0.060	8.18 ± 0.60	2.95 ± 0.20	$48.0 (\pm 0.1)$	$0.740 (\pm 0.010)$	$7.60 (\pm 0.10)$	$1.46 (\pm 0.30)$
Sc. Centre	5.57 ± 0.20	8.23 ± 0.30	3.29 ± 0.19	0.653 ± 0.070	19.0 ± 1.0	1.76 ± 0.20	$60.0 (\pm 0.4)$	$0.652 (\pm 0.040)$	$0.0 (\pm 0.0)$	$0.912 (\pm 0.050)$
Veldenvlei	4.73 ± 0.30	7.67 ± 0.24	3.07 ± 0.06	0.591 ± 0.019	3.74 ± 0.30	4.48 ± 0.40	$82.0 (\pm 0.7)$	$0.351 (\pm 0.021)$	$0.0 (\pm 0.0)$	$3.04 (\pm 0.50)$
Birdswood	5.32 ± 0.30	9.84 ± 0.20	3.94 ± 0.40	0.520 ± 0.018	1.65 ± 0.11	1.08 ± 0.20	$40.0 (\pm 0.4)$	$0.594 (\pm 0.026)$	$0.0 (\pm 0.0)$	$0.440 (\pm 0.010)$
Average	5.13 ± 0.38	6.36 ± 0.56	2.79 ± 0.18	0.995 ± 0.0614	9.33 ± 0.60	2.91 ± 0.29	$56.8 (\pm 0.4)$	$0.767 (\pm 0.035)$	$2.73 (\pm 0.06)$	$1.79 (\pm 0.23)$

The Formation shows a total iron concentration (ranges from 40.0 to 67mg/L) and phosphate ions ($\leq 1.50 \pm 0.08$ mg/L) that are higher than that of the Kosi Bay Formation. Manganese ($\leq 7.60 \pm 0.10$ mg/L), silicate ions ($\leq 3.12 \pm 0.30$ mg/L) and organic matter ($\leq 2.28 \pm 0.20$ %) are lower than that of the Kosi Bay Formation.

7.1.6 Sibaya Formation

The Pleistocene sediments of the Kosi Bay and the Port Durnford Formation are overlain by the loosely consolidated Sibaya Formation in the Meerensee area. These sediments are recent (Holocene deposit) aeolian or alluvial deposits. The type of sediments was identified only in the Meerensee borehole with a thickness

of 4 meters. They range in colour from brownish gray to black, indicating richness in organic matter ($0.660 \pm 0.030\%$, (Table 5.7).

The organic matter is likely to be supplied from surface plantations. Calcium carbonate concentration ($2.29 \pm 0.07\%$) is low which is similar to that of the Kwambonambi Formation. Low carbonate ions caused the sediments to be slightly acidic (6.46 ± 0.10). Leaching of the sediments resulted in weathered sediments to medium clay and low silt minerals ($5.91 \pm 0.50\%$ and $1.93 \pm 0.13\%$ respectively). Manganese ($2.67 \pm 0.10 \text{ mg/L}$), phosphate ($0.080 \pm 0.010 \text{ mg/L}$) and silicate ions ($3.30 \pm 0.20 \text{ mg/L}$) are lower than that of the St Lucia Formation.

The Formation shows a total iron concentration ($\leq 136 \pm 3 \text{ mg/L}$) that is higher than that of the shallow units due to the richness of heavy minerals which are currently being mined in Meerensee.

Table 5.7: Sibaya Formation geochemistry

Site	pH	% CaCO ₃	% Ca	% OM	% Clay	% Silt	Fe (mg/L)	Phos (mg/L)s	Mn (mg/L)	Si (mg/L)
Meerensee	6.46 ± 0.10	5.60 ± 0.24	2.29 ± 0.07	0.660 ± 0.030	5.91 ± 0.50	1.92 ± 0.13	$136 (\pm 3)$	$0.080 (\pm 0.010)$	$2.67 (\pm 0.10)$	$3.30 (\pm 0.20)$

7.2 Conclusion on the Maputaland Geochemistry

7.2.1 St Lucia Formation

Sediments of the St Lucia Formation are rich in calcium carbonate content due to the calcareous nature of the Cretaceous deposits which are rich in calcite and shell fragments. This caused sediments to be dominated by calcium carbonate concentration ($45.0 \pm 1.6\%$, on average) which buffered sediments to a neutral pH (7.13 ± 0.11 on average). The reaction of hydrogen ions (H^+) in solution with carbonate ions (CO_3^{2-}) produces bicarbonate ions which buffers sediments against acidity.

The decomposition of marine animal and plant matter, and shell fragments in a reducing environment (lack of oxygen) formed the glauconitic minerals⁴⁰ which were identified by Worthington⁶ in the Cretaceous sediments. Glauconitic

minerals constitute to weathered olive green, black green to bluish green sediments, with high clay and silt minerals ($10.1 \pm 0.2\%$ and $8.15 \pm 0.2\%$ respectively, on average).

The fact that the sediments are dominated by animal and plant matter, and shell fragment of the marine deposits, this contributed to organic matter content ($0.940 \pm 0.010\%$, on average) that is higher than that of the Uloa Formation. Manganese ions could not be detected in the Veldenvlei and Science Centre boreholes which might indicate geochemical composition. Manganese ions are detected in Science Center with a concentration of $27.0 \pm 0.2 \text{ mg/L}$. The average total iron concentration ($85.0 \pm 5.0 \text{ mg/L}$) is lower than that of the Uloa Formation.

7.2.2 Uloa Formation

The sediments of the Uloa Formation are rich in calcium carbonate content due to the calcareous nature of the Miocene deposits. They are rich in coquina which is composed of marine shell fragments, plant and animal matter and calcite. This resulted in the sediments dominated by calcium carbonate concentration ($50.3 \pm 2.1\%$, on average) which controlled pH to neutral or slightly alkaline (7.65 ± 0.17 , on average), through production of bicarbonate ions. The sediments are weathered to high clay and silt minerals ($7.21 \pm 0.19\%$, and $7.21 \pm 0.18\%$ respectively, on average).

The presence of marine plant and animal matter deposits contributed to organic matter (on $0.585 \pm 0.016\%$, on average) that is lower than of St Lucia Formation. Manganese ions could not be detected in the Veldenvlei and Science Centre. Manganese ions are detected in Meerensee with a concentration of $32.4.0 \pm 0.2 \text{ mg/L}$. The total iron concentration is lower than that of the St Lucia Formation ($42.0 \pm 3.0 \text{ mg/L}$, on average) and is higher in the Meerensee ($202 \pm 9 \text{ mg/L}$). The average total iron concentration, phosphate and silicate ions are higher in the Meerensee borehole which might indicate different Units.

7.2.3 Port Durnford Formation

The Port Durnford Formation has leached sediments which have resulted in low calcium carbonate content ($12.9 \pm 0.8\%$, on average) and acidic sediments (pH of 4.22 ± 0.35 , on average). Leaching has also caused weathering of the sediments to high clay and low silt minerals ($19.1 \pm 0.5\%$ and $2.68 \pm 0.24\%$ respectively, on average).

Since the Port Durnford Formation has loosely consolidated sands of the fluvial or aeolian deposits, organic matter ($1.07 \pm 0.02\%$, on average) that is higher than that of the St Lucia and the Uloa Formations is assumed to be supplied by the overlaying units. Manganese ions could not be detected in Aquadene and Birdswood. Manganese ions are detected in the Meerensee aquifer with a concentration of $2.53 \pm 0.11 \text{ mg/L}$. The average total iron concentration ($87.0 \pm 2 \text{ mg/L}$) is higher than that of the St Lucia and Uloa Formations due to elevated total iron concentration in the Meerensee ($206. \pm 6 \text{ mg/L}$). Total iron concentration, phosphate and silicate ions are higher in the Meerensee aquifers which might indicate different Units.

7.2.4 Kosi Bay Formation

Sediments of the Kosi Bay Formation are also leached. They are low in calcium carbonate content ($10.5 \pm 0.6\%$, on average) and acidic (5.10 ± 0.21 , on average). They are weathered to medium clay and low silt minerals ($9.00 \pm 0.32\%$ and $4.04 \pm 0.21\%$ respectively, on average). Organic matter ($1.02 \pm 0.13\%$, on average) is higher than that of the Port Durnford Formation.

Since the Kosi Bay Formation has loosely consolidated sands of the fluvial or aeolian deposits, the organic matter is assumed to be supplied by the unsaturated sediments from the surface. The organic matter is likely to have also accelerated acidity and weathering of the sediments. The sediments are low in manganese ($\leq 4.75 \text{ mg/L}$), phosphate ions ($\leq 0.604 \text{ mg/L}$) and total iron concentration ($\leq 55.3 \text{ mg/L}$), but higher in silicate ions ($\leq 22.0 \text{ mg/L}$) than the underlying Formations.

7.2.5 Kwambonambi Formation

Sediments of the Kwambonambi Formation are leached. They are low in calcium carbonate concentration ($6.36 \pm 0.56\%$, on average) and acidic (pH range from 5.13 ± 0.38 , on average). They are weathered to medium clay and low silt minerals ($8.33 \pm 0.60\%$ and $2.91 \pm 0.29\%$ respectively, on average).

Since the Kwambonambi Formation has loosely consolidated sands of the aeolian deposits, organic matter ($0.995 \pm 0.614\%$, on average) that is lower than that of the Kosi Bay Formation but similar to that of the Port Durnford Formation, is assumed to be supplied through surface water percolation from vegetation on the surface. The sediments are low in manganese ($\leq 2.73 \text{ mg/L}$), phosphate ($\leq 0.767 \text{ mg/L}$), silicate ions ($\leq 1.79 \text{ mg/L}$) and total iron concentration ($\leq 57 \text{ mg/L}$), than that of the underlying units

7.2.6 Sibaya Formation

Sediments of the Sibaya Formation are only found in Meerensee. They are also leached. They are low in calcium carbonate concentration ($5.60 \pm 0.24\%$) and slightly acidic (6.46 ± 0.2). They are weathered to medium clay and low silt minerals ($5.91 \pm 0.50\%$ and $1.92 \pm 0.13\%$ respectively).

Since the Sibaya Formation has loosely consolidated sands of the aeolian deposits, organic matter ($0.660 \pm 0.030\%$, on average) that is lower than that of the Kosi Bay Formation but similar to that of the Port Durnford Formation is assumed to be supplied by plantation on the surface. The sediments are low in manganese ($2.67 \pm 0.10 \text{ mg/L}$), total iron concentration ($\leq 136 \pm 3 \text{ mg/L}$), phosphate ($0.080 \pm 0.010 \text{ mg/L}$) and silicate ions ($3.30 \pm 0.20 \text{ mg/L}$) than the underlying unit

CHAPTER EIGHT

GEOHYDROLOGICAL COMPARISON

The groundwater chemistry of the natural environment can assist in interpretation of the extent of the detrimental impacts associated with anthropogenic sources especially in a developing industrial region with the shallow aquifers such as Richards Bay. This requires understanding of the geochemistry and hydrochemistry of the aquifers as well as the land-use around the location of those aquifers.

Comparison of dissolved minerals in the groundwater against the sediment minerals of each aquifer can provide an approximate indication of the source of water quality constituents in the aquifers.

In this study, comparison between the hydrochemistry and lithology for the entire Maputaland coastal plain region was impossible to achieve as the lithology was uncertain. The samples were never logged by professional geologists. Due to the uncertainty of the lithology as well as the incomplete geochemical analyses, a decision was taken to compare only the boreholes located in the same geographical area.

8. Comparison between the boreholes in the same aquifer

8.1 Alton aquifers

8.1.1 Hydrochemistry of Alton aquifers

In Figures 18, 19 and 20, the hydrochemical composition of the Alton boreholes seems different. Alton 2 is characterized by a sodium and bicarbonate ions type of a water-signature while Alton 3 is characterized by a sodium and chloride ions type of a water-signature.

The presence of bicarbonate ions in Alton 2 seems to have slightly buffered the groundwater (pH is 6.10) against acidity compared to Alton 3. Low calcium and bicarbonate ions in Alton 3 resulted in acidic groundwater (pH is 5.43) and

caused the dominance of sodium and chloride ions, probably through cation exchange reactions.

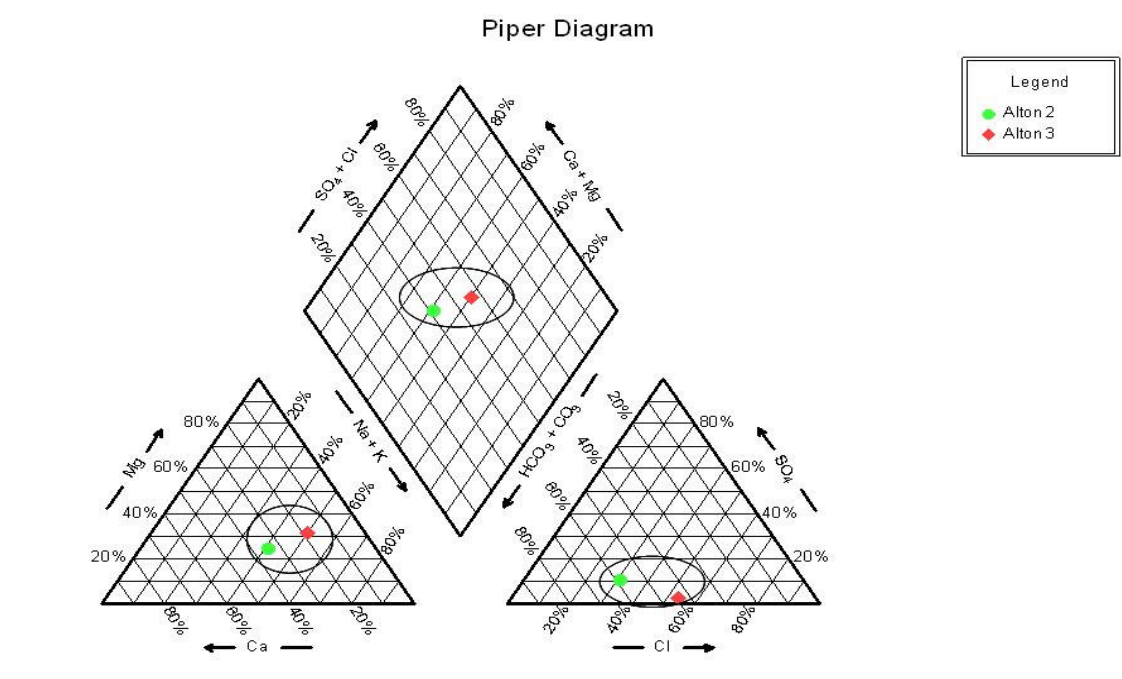


Figure 18: The hydrochemistry of the Pleistocene Unit of Alton boreholes displayed using piper diagrams. Grouping shows hydrochemistry that concurs with Hattingh⁴⁶.

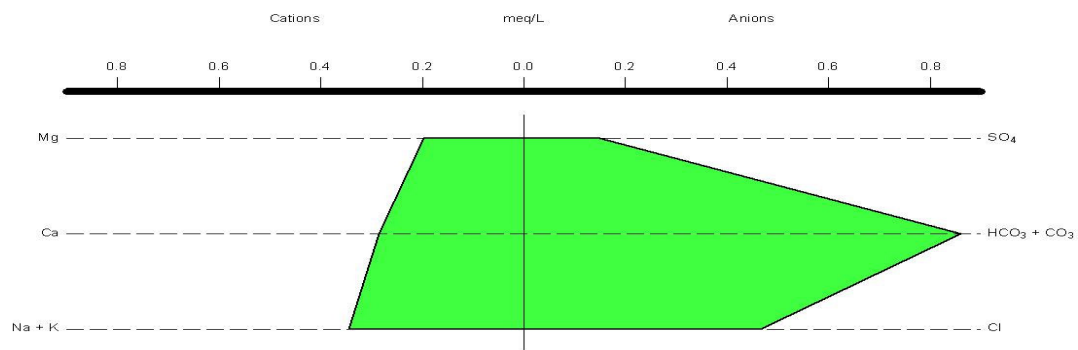


Figure 19: The hydrochemistry of Alton 2 displayed using Stiff diagram; shaded area indicating cations and anions dominance (in meq/L).

A low pH in Alton 3 caused the mobility of heavy minerals ions into solution resulting in a high TDS compared to the Alton 2 borehole.

The Alton boreholes are low in dissolved ions such as calcium (≤ 7.5 mg/L), magnesium (≤ 7.9 mg/L) and sulphates (≤ 7.2 mg/L), zinc (≤ 2.8 mg/L), manganese (2,6mg/L), aluminum (≤ 0.31 mg/L), potassium (≤ 2.4 mg/L), phosphate (≤ 0.30 mg/L), and nitrates ions (0.05mg/L, Figures 21 and 22).

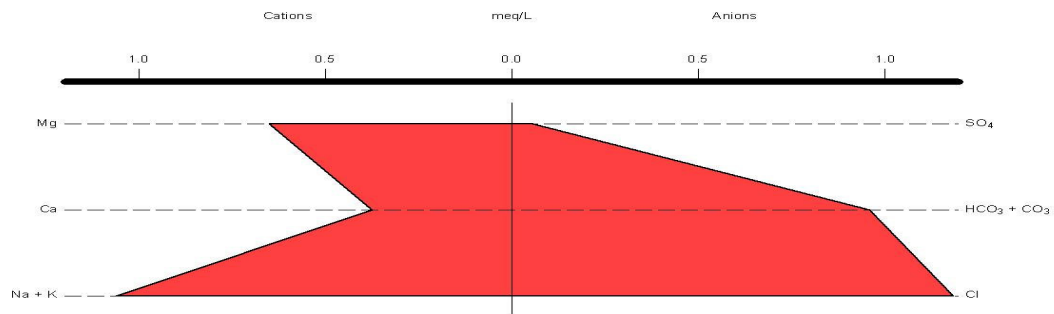


Figure 20: The hydrochemistry of Alton 3 displayed using Stiff diagram shaded area indicating cations and anions dominance (in meq/L).

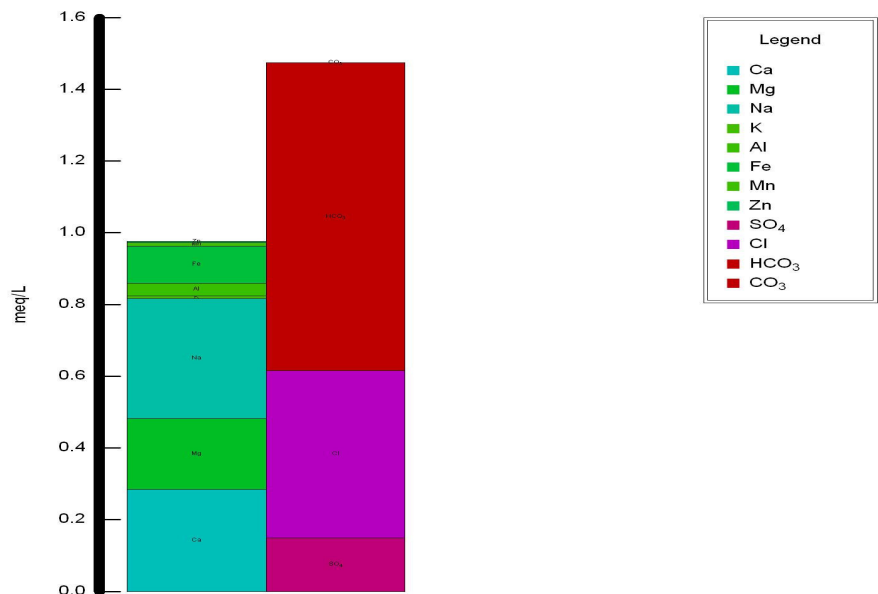


Figure 21: Ion Balance diagram for Alton 2 borehole

The dissolved minerals ions such as fluoride, ferrous iron, chloride, silicate, zinc, potassium, sodium, magnesium and manganese ions are dominant in the Alton 3. A low pH caused the mobility of these cations and anions from sediments (Figure 22) into the groundwater. Sulphate ions are slightly dominant in Alton 2 (Figure 21).

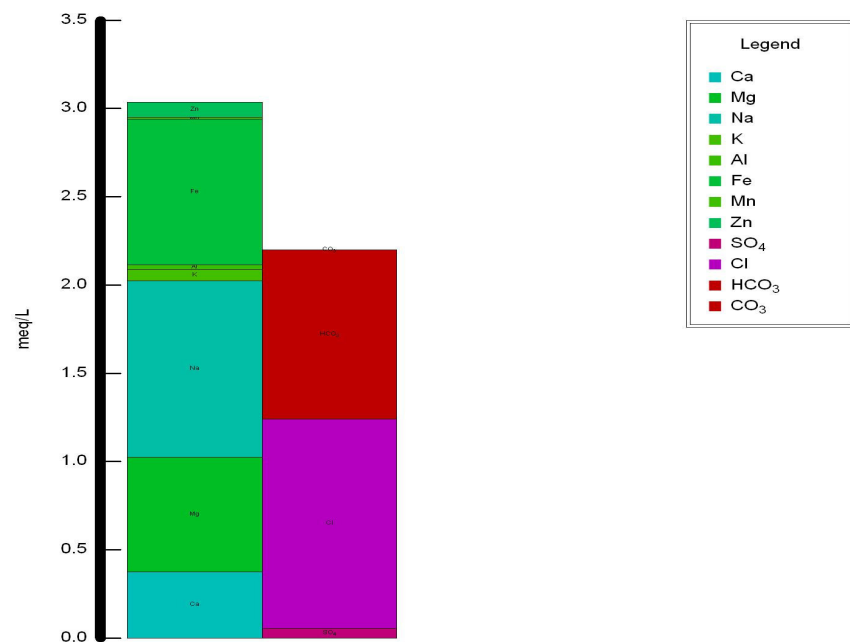


Figure 22: Ion Balance diagram for Alton 3 borehole

The mobilized cations and anions occurred as a result a low groundwater pH arising from low bicarbonate ions (Table 15 (Appendix II)). Chloride ions are higher than sodium ions which is similar to the Pleistocene aquifers. Calcium ions in Alton 2 exceed magnesium ions (Ca: Mg ratio 2:1), while in the Alton 3 magnesium ions are a Unit to calcium ions (Ca: Mg ratio is 1:1). The water is acidic (pH ranges from 4.73 to 6.10) in Alton boreholes which is similar to that of the Pleistocene aquifers.

8.1.2 Geochemistry of Alton aquifers

The Alton geochemical samples are classified into the Kwambonambi and the Kosi Bay Formations. The Formations are low in calcium (≤ 4.82 %) and

carbonate ions ($\leq 6.13 \text{ mg/L}$) which resulted in sediments being acidic (pH ranged from 4.73 to 5.28, Table 6.1).

The Kwambonambi Formation is shallow (approximately 4 to 6m in thickness). The carbonate ions range from 1.92 ± 0.29 and $4.14 \pm 0.2\%$ which was lower in Alton 2. It is mainly dominated by organic matter ($\leq 2.28 \pm 0.2\%$), phosphate ($\leq 1.50 \pm 0.08 \text{ mg/L}$), and ammonium ions ($\leq 42.0 \pm 0.3 \text{ mg/L}$), probably from the unsaturated layers which are supplied by decomposed surface plantation materials (Table 6.1). The unit is also exposed to domestic, industrial and agricultural activities.

Table 6.1: Geochemical results of Aton 2 & 3 boreholes

ALTON 3	pH	% CaCO ₃	% Ca	%OM	%Clay	% Silt	NH ₄ ⁺ mg/L	Fe(II) mg/L	Phosphates mg/L
Kwambo. FM	4.73 $\pm$ 0.50	4.14 $\pm$ 0.2	2.28 $\pm$ 0.2	2.28 $\pm$ 0.14	14.1 $\pm$ 0.1	.32 $\pm$ 0.44	37.6 $\pm$ 0.3	54.0 $\pm$ 0.5	1.50 $\pm$ 0.08
Kosi Bay FM	4.89 $\pm$ 0.50	4.82 $\pm$ 0.19	3.12 $\pm$ 0.06	0.970 $\pm$ 0.015	15.0 $\pm$ 0.3	1.66 $\pm$ 0.10	36.4 $\pm$ 0.5	55.3 $\pm$ 0.8	0.512 $\pm$ 0.010
ALTON 2	pH	% CaCO ₃	% Ca	%OM	%Clay	% Silt	NH ₄ ⁺ mg/L	Fe(II) mg/L	Phosphates mg/L
Kwambo. FM	5.28 $\pm$ 0.40	1.92 $\pm$ 0.29	1.36 $\pm$ 0.05	0.933 $\pm$ 0.060	8.18 $\pm$ 0.60	2.95 $\pm$ 0.20	42.0 $\pm$ 0.3	48.0 $\pm$ 0.1	0.740 $\pm$ 0.010
Kosi Bay FM	4.88 $\pm$ 0.40	6.13 $\pm$ 0.2	3.56 $\pm$ 0.10	0.444 $\pm$ 0.009	13.8 $\pm$ 0.4	4.80 $\pm$ 0.10	41.8 $\pm$ 0.6	49.5 $\pm$ 0.3	0.383 $\pm$ 0.016

Organic matter and phosphate ions are dominant in Alton 3 while ammonium ions are higher in Alton 2. The decomposition of organic matter can accelerate weathering of sediments through production of carbonic acid. Calcium and carbonate ions are lower than that of the Kosi Bay Formation.

The Kosi Bay Formation is approximately 19m to 21m in thickness. The carbonate ions range from 4.82 ± 0.29 and $6.13 \pm 0.2\%$ which was lower in Alton 3. It is mainly dominated by the high weathered sediments than the overlaying Formation. The clay and silt minerals are $\leq 15.0 \pm 0.3\%$ and $\leq 4.80 \pm 0.10\%$

respectively (Table 6.1). Clay minerals are likely to have been washed off from the overlaying Units due to their low particle densities. Calcium ions ($\leq 3.56 \pm 0.1\%$) are low but higher than that of the Kwambonambi Formation. The sediments of the Alton boreholes are low in total iron concentration, manganese and silicate ions.

8.1.3 Conclusion on the Alton aquifers geohydrochemistry

The Alton aquifer is low in dissolved magnesium (Mg^{2+}), sulphate (SO_4^{2-}) and potassium ions (K^+) which concurs with the Pleistocene Units findings by Hatting⁴⁶. The dissolved K^+ , Mg^{2+} , SO_4^{2-} , Na^+ , Cl^- ions, could not be verified by the geological analysis due to a lack of funds. The low calcium and carbonate ions of the sediments resulted in a low water pH in Alton boreholes, which caused the mobility of cations and anions especially in Alton 3. The depletion of calcium ions caused sodium ions dominance through cation-exchange. The carbonate ions are slightly higher in the Kosi Bay Formation of Alton 2 which resulted in the bicarbonate ions dominance. The presence of the bicarbonate ions in solution slightly buffered the groundwater against acidic compared to the Alton 3. This resulted in a sodium and bicarbonate ions type of a water-signature in Alton 2.

Alton 3 is low in calcium carbonate content in all Units, which resulted in the acidic sediments and groundwater quality. The depletion of calcium and bicarbonate ions attributed to a sodium and chloride ions dominance, causing a sodium and chloride ions type of water-signature in Alton 3. A low pH of the sediments and groundwater caused the mobility of cations and anions, resulting in high dissolved solids in Alton 3. The acidity of the groundwater accelerated weathering of the sediments in both Units, resulting in high clay minerals. Sodium and chloride ions are assumed to be introduced to the boreholes through the coastal-influence precipitation or from the recent marine sediments deposits. The sediments are rich in ammonium ions (NH_4^+) probably from geological composition of the sediments or from other sources of influence. The

Kwambonambi Formation of Alton boreholes are likely to vertically recharge the Kosi Bay Formation, as mineral ions seem to accumulate in the Kosi Bay Formation.

The Alton 3 dissolved mineral ions are likely to be influenced by the water quality of the small stream that runs downstream parallel to it. The groundwater quality in Alton boreholes is still suitable for drinking purpose, as it still falls under the Class 1 of South African Drinking Water Guideline Limit, except for the fluoride, manganese and ferrous ions.

8.2 Science aquifers

8. 2.1 Hydrochemistry of Science Centre aquifer

The hydrochemistry of the three boreholes seems different. Figure 23 and Table 16 (Appendix II), show that the Miocene borehole is dominated by calcium and bicarbonate ions, while the Holocene and Pleistocene boreholes are dominated by chloride and sodium ions.

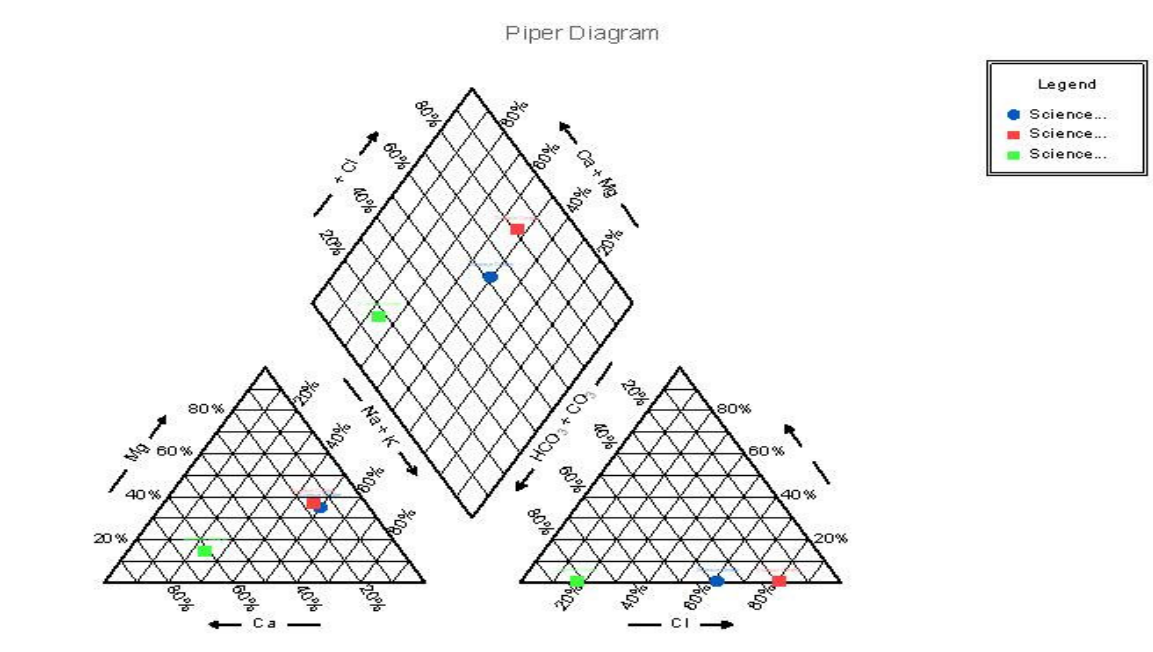


Figure 23: The hydrochemistry of the Holocene, Pleistocene and Miocene Units of Science Centre boreholes displayed using piper diagrams. The blue, red and green colours indicate the Holocene, Pleistocene and Miocene Units respectively.

The Miocene borehole is high in calcium and bicarbonate ions due to the calcareous glauconitic siltstones, calcite and the shell fragments of the marine deposits, which controlled the pH to neutral (6.53, Figure 24).

The low bicarbonate ions in the shallow boreholes resulted in a low pH (5.79 and 5.42 respectively, Figures 25 and 26) which still falls under the Class 1 of South African drinking water guideline.

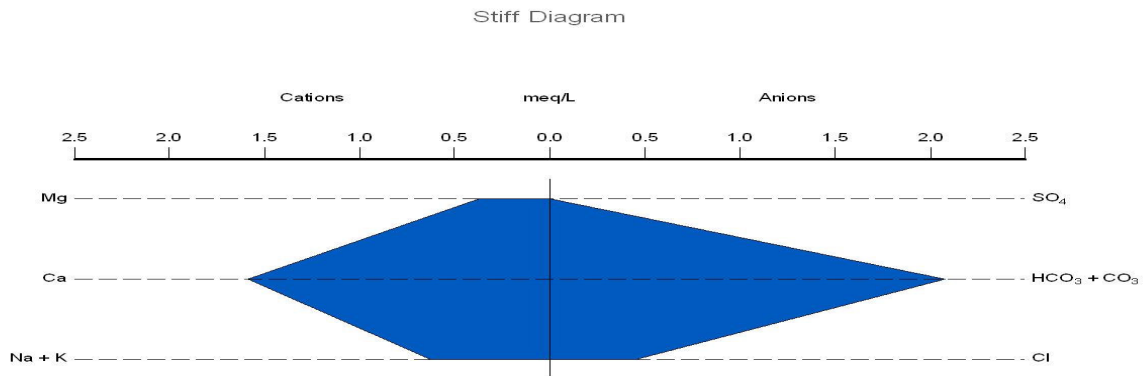


Figure 24: The hydrochemistry of Science Centre for the Miocene Unit displayed using Stiff diagram, shaded area indicating cations and anions dominance (in meq/L).

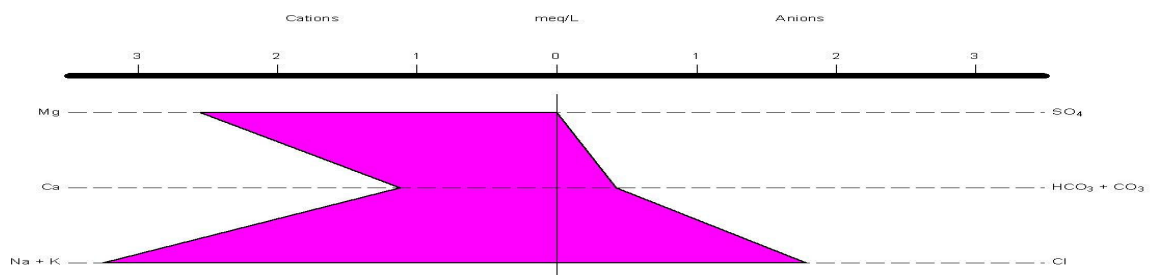


Figure 25: The hydrochemistry of Science Centre for the Pleistocene Unit displayed using Stiff diagram, shaded area indicating cations and anions dominance (in meq/L).

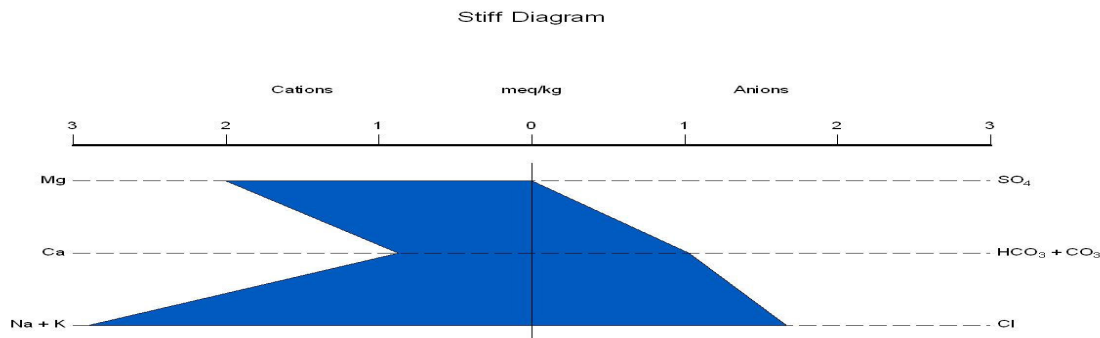


Figure 26: The hydrochemistry of Science Centre for the Holocene Unit displayed using Stiff diagram, shaded area indicating cations and anions dominance (in meq/L)

In Table 16 (Appendix II), calcium ions increase down the Units (from 43mg/L to 79 mg/L) while magnesium ions increase from the Holocene to the Pleistocene and dropped significantly in the Miocene (4.5 mg/L). Sulphate ions were not determined in the Science Centre.

The Holocene and Pleistocene Units are low in Mn^{2+} , Al^{3+} , Zn^{2+} , Fe^{2+} ions than the Miocene Unit (Figures 27, 28 and 29).

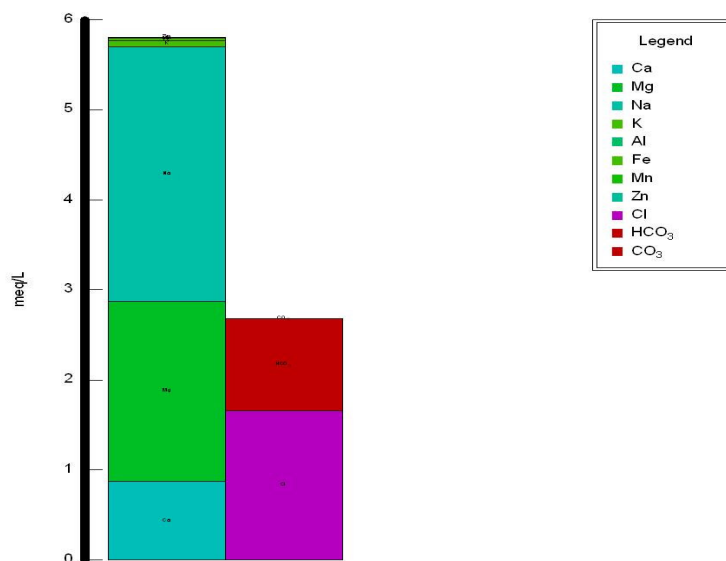


Figure 27: Science Centre Holocene Unit ion-balance diagram

Sodium (Na^+), chloride (Cl^-) and magnesium (Mg^{2+}) ions dominate the Pleistocene and Holocene Units (Figures 27, 28 and 29).

The bicarbonate ions are the highest in the Miocene Unit and the lowest in the Pleistocene Unit.

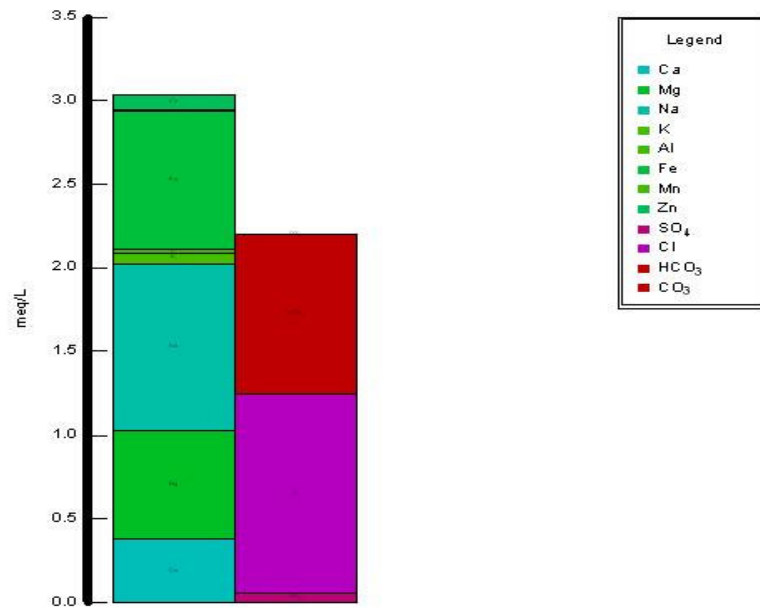


Figure 28 Science Centre Pleistocene Unit ion-balance diagram

The Miocene Unit is low in sodium (Na^+), chloride (Cl^-) and magnesium ions (Mg^{2+}) due to the dominance of calcium and carbonate ions (Figure 29).

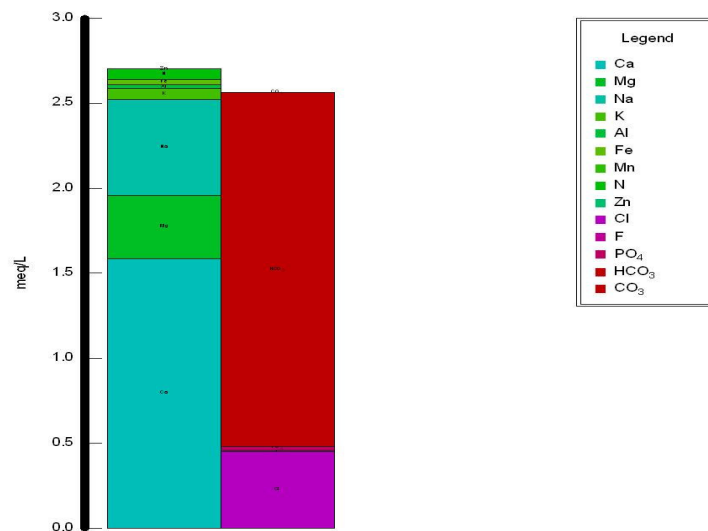


Figure 29: Science Centre Miocene Unit ion-balance diagram

Chloride ions in the Miocene are slightly higher than sodium ions. Calcium ions exceed magnesium ions (Ca: Mg ratio 2:1) in the Holocene and Pleistocene. Calcium ions are extremely higher than magnesium ions (Ca: Mg ratio was 18:1) in the Miocene due to the presence of calcite and the shell fragments. The TDS is higher in the Holocene and the Pleistocene Units, as the results of the mobility of ions from a low pH (Appendix II Table 16).

8.2.2 Geochemistry of Science Centre aquifer

The Miocene sample was chosen for the geochemical study. The lithology of Science Centre was classified into the Kwambonambi (representing the Holocene Unit), the Kosi Bay (representing the Pleistocene Unit), the Uloa (representing the Miocene Unit) and the St Lucia (representing the Cretaceous Unit) Formations. The sediments are acidic in the Kwambonambi and the Kosi Bay Formations (pH ranged from 4.39 to 5.57, Table 6.2), which concurred with Pleistocene aquifers geochemistry. The acidity of the sediments is due to low calcium carbonate content (ranging from 8.23 to 12.0%) which is required to buffer sediments against acidity. The sediments of the Uloa and the St Lucia Formation are neutral (pH ranging from 7.11 to 7.60) due to a high calcium carbonate content (ranging from 49.8 to 50.5%) provided by the calcite minerals in the sediments.

Table 6.2: Geochemical results of Science Centre boreholes

Units	pH	% CaCO ₃	% Ca	%OM	%Clay	% Silt	NH ₄ ⁺ mg/L	Fe(II) mg/L	Phos. mg/L
Kwambo. FM	5.57±0.20	8.23±0.3	3.29±0.19	0.653±0.070	19.0±0.1	1.76±0.20	18.7±0.4	60.0±0.4	0.652±0.004
Kosi Bay FM	4.39±0.50	12.0±0.4	4.29±0.26	0.372±0.100	8.36±0.08	9.28±0.20	25.2±0.2	48.0±0.9	0.604±0.008
Uloa. FM	7.60±0.10	50.3±4.1	20.1±1	0.519±0.004	5.50±0.01	7.72±0.10	41.5±0.9	36.0±0.2	0.361±0.005
St Lucia FM	7.11±0.03	49.8±3.4	19.9±0.5	1.57±0.02	14.9±0.20	10.4±0.1	31.4±0.7	86.0±0.2	0.444±0.003

The Kwambonambi Formation is shallow with a thickness of 5 meters. It is dominated by clay minerals (19.0±0.1%) and phosphate ions (0.652±0.004 mg/L)

due to weathered sediments and the decomposition of plant materials from the surface.

The Kosi Bay Formation is approximately 24 meters in thickness. It is dominated by (8.36±0.08%) and silt minerals (9.28±0.20, Table 6.2). Organic matter is the highest in the St Lucia Formation probably from plant and animal material of the marine deposits. Calcium ions (4.29±0.26%) in the Kosi Bay Formation are slightly higher than that of the overlaying Unit (Table 6.2). The ammonium ions (NH_4^+) increase down the Units to the Uloa Formation, and dropped slightly in the St Lucia Formation. Ammonium ions are likely to be recharged to the shallow Units through infiltration from agricultural activities, but in deep Units they are likely be arising from the geochemical composition or marine deposits.

8.2.3 Conclusion of Science Centre aquifers geohydrochemistry

The Science Centre boreholes are low in potassium (K^+) and ferrous iron (Fe^{2+}) ions. Magnesium ions (Mg^{2+}) are more dominant in the Holocene and the Pleistocene Units. Magnesium ions can be reduced by precipitation reactions in deeper Units as a result of oversaturation. In shallow Units magnesium ions are likely to be reduced through cation exchange with sodium ions.

The dissolved K^+ , Mg^{2+} , SO_4^{2-} , Na^+ , Cl^- , could not be verified by geological analysis due to lack of funds. A low calcium carbonate concentration of the Kwambonambi and the Kosi Bay Formations resulted in acidic sediments and a low pH of groundwater in the Holocene and the Pleistocene Units. This caused the mobility of cations and anions resulting in high dissolved solids. The depletion of calcium and bicarbonate ions caused the dominance of sodium and chloride ions through cation-exchange in the shallow boreholes. This resulted in a sodium and chloride ions type of a water-signature which is similar to Alton 3.

As the sediments of the Pleistocene Unit are more acidic than that of the Holocene Unit, more minerals were mobilized from the Kosi Bay Formation resulting in highest dissolved minerals in the Pleistocene Unit. The Pleistocene

Unit seems to be vertically recharged by the Holocene Unit. This could also contribute to the increased in the Pleistocene Unit dissolved minerals.

The Miocene is high in calcium carbonate ions due to the presence of the calcite minerals and the shell fragments of the marine deposits in the sediments. This resulted in well buffered groundwater and sediments. This resulted in low dissolved sodium and chloride ions in the Miocene Unit. The dominance of calcium and carbonate ions in the sediments resulted in a calcium and bicarbonate ions type of a water-signature. As the sediments are well buffered against acidity, the mobility of cations and anions is limited, which caused low dissolved minerals in the Unit.

Sodium ions and chloride ions in the aquifer are assumed to be introduced to the shallow boreholes through coastal-influence precipitation or recent marine sediment deposits. Organic matter decomposition during storage is assumed to have accelerated the weathering of sediments through production of carbonic acids. The sediments are rich in ammonium ions (NH_4^+), either from geological composition, agricultural, industrial or domestic activities.

Calcium ions exceed magnesium ions (Ca: Mg ratio 2:1) in the Holocene/Pleistocene Units). In the Miocene Unit, Ca: Mg ratio is 18:1. Sodium ions are higher than chloride ions in the Pleistocene and the Holocene Units. The Pleistocene Units seems to be vertically recharged by Holocene unit. The Miocene Unit does not seem to be receiving any vertical recharge from the Pleistocene Unit, since dissolved ions do not appear to increase to the Miocene Unit.

The water quality of the Science Center boreholes still falls under the Class 1 of the Drinking Water Guideline Limits of South Africa, except for ferrous iron and manganese ions in shallow Units which falls under Class 2 of the Guideline. Aluminium ions in Miocene Unit are higher than that of the Class 2 Level.

8.3 Veldenvlei aquifers

8.3.1 Hydrochemistry of Veldenvlei aquifers

The hydrochemistry of the Veldenvlei boreholes differs slightly from each other. In Figure 30 and Table 18 (Appendix II), the Pleistocene Unit is dominated by calcium and bicarbonate ions while the Miocene Unit is dominated by sodium, calcium and bicarbonate ions.

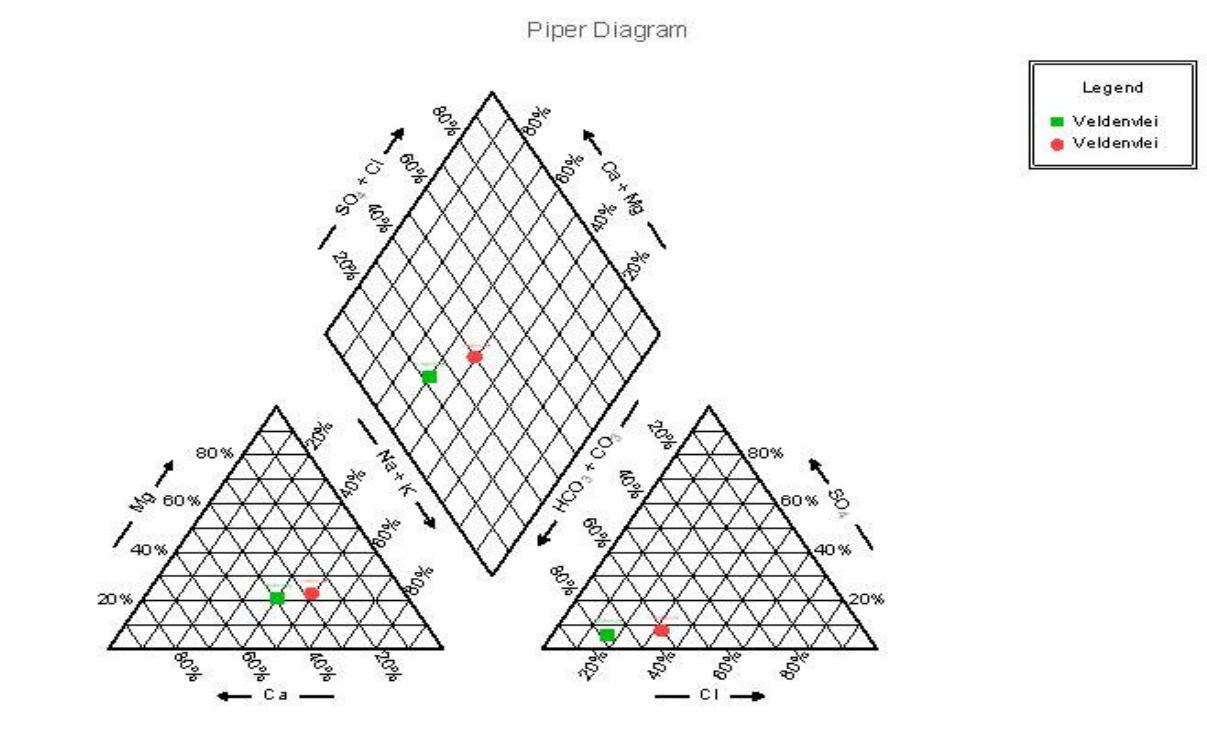


Figure 30: The hydrochemistry of the Pleistocene and Miocene Units of Veldenvlei boreholes displayed using piper diagram. The red and green colour indicating Pleistocene and Miocene Units respectively.

The Units are dominated by calcium and bicarbonate ions. The Miocene Unit seems to contain sodium ions which are slightly dominating resulting in mixed water. The bicarbonate ions dominance resulted in a neutral pH in both boreholes (7.4 and 7.8 respectively, Appendix II Table 18). Magnesium ($\leq 13.8\text{mg/L}$), potassium ($\leq 2.3\text{mg/L}$) and sulphate ($\leq 30.0\text{ mg/L}$) ions are low. Chloride ions are higher than sodium ions, and calcium ions exceed magnesium

ions. Ca: Mg ratio was approximately 2:1. Chloride ions are similar in both Units and sodium ions increase down the Units (higher in Miocene).

The Pleistocene Units are higher in calcium and bicarbonate ions than the Miocene (Figures 31 and 32).

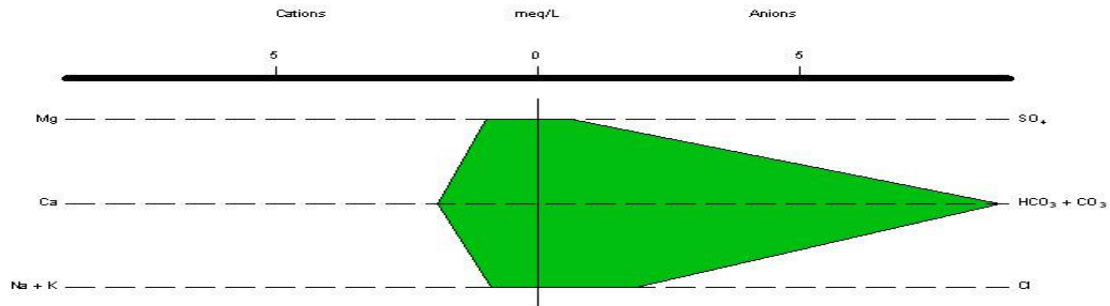


Figure 31: The hydrochemistry of Veldenvlei Pleistocene Unit displayed using stiff diagrams, shaded area indicating cations and anions dominance (in meq/L)

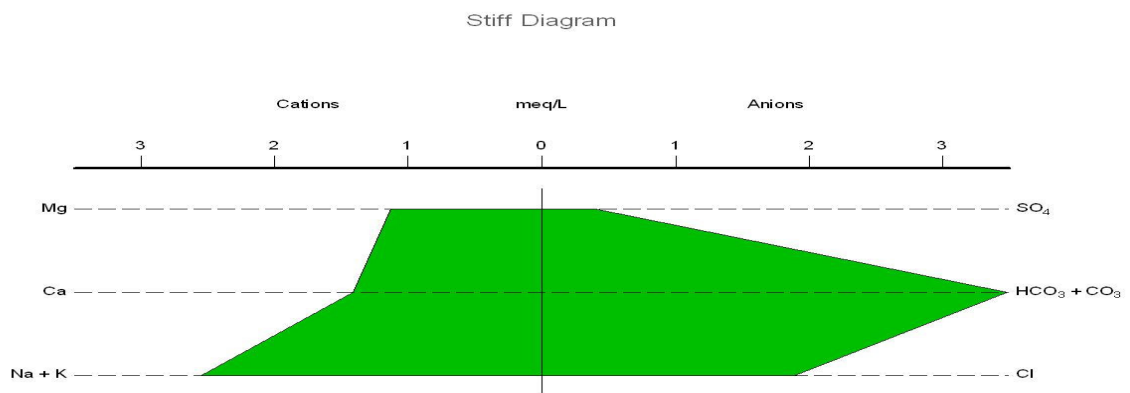


Figure 32: Water quality of the Veldenvlei Miocene Unit displayed using stiff diagram in which the shaded area indicates cations and anions dominance in meq/L.

The Miocene Unit is higher in potassium and sodium ions than the Pleistocene Unit (Figures 31 and 32). All the Units are low in potassium (K^+), zinc (Zn^{2+}), manganese (Mn^{2+}) and ferrous iron (Fe^{2+}) ions (Figures 32 and 33).

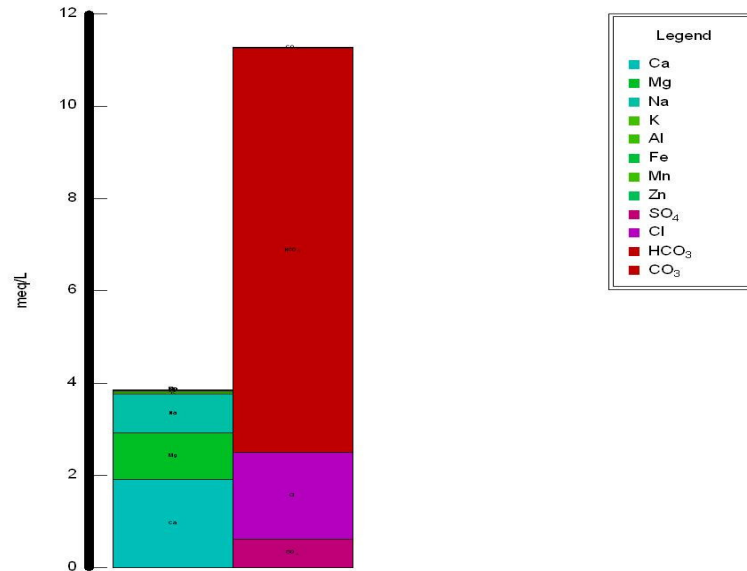


Figure 33: Veldenvlei Pleistocene Unit ion-balance diagram

Aluminium ions are slightly higher in the Miocene Unit (Figures 33 and 34) which is similar to that of the Science Center aquifers.

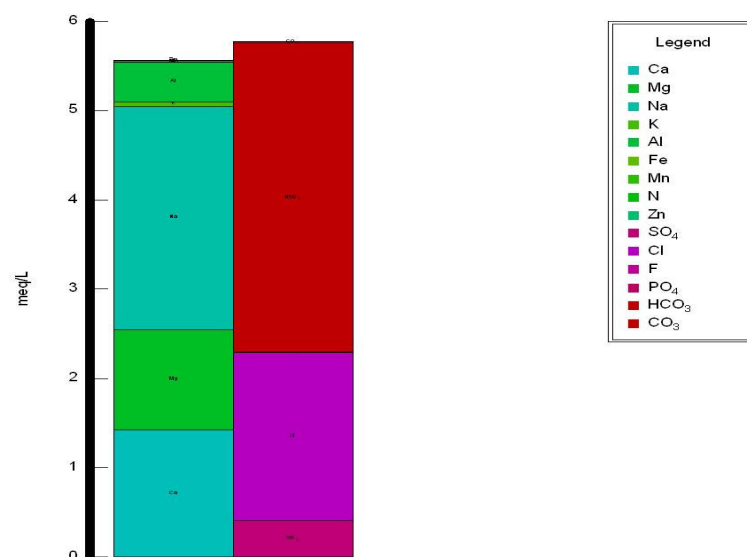


Figure 34: Veldenvlei Miocene Unit ion-balance diagram.

8.3.2 Geochemistry of Veldenvlei aquifer

The Miocene sample was chosen for the geochemical study. The lithology of Veldenvlei aquifer was classified into the Kwambonambi (representing the Holocene Unit), the Kosi Bay (representing the Pleistocene Unit), the Uloa (representing the Miocene Unit) and the St Lucia (representing the Cretaceous Unit) Formations. The lithology of Veldenvlei is similar to that of Science Centre. The sediments are acidic in the Kwambonambi and the Kosi Bay Formations (pH ranged from 4.73 to 5.50) similar to the Pleistocene aquifers (Table 6.3), despite the fact that the groundwater is very alkaline in the Pleistocene Unit.

Table 6.3: Geochemical results of the **Veldenvlei** boreholes

	pH	% CaCO ₃	Ca(mg/L)	%OM	%Clay	% Silt	NH ₄ ⁺ mg/L	Fe(II) mg/L	Phos. mg/L
Kwambo. FM	4.73±0.30	7.67±0.24	3.07±0.06	0.571±0.019	3.74±0.30	4.48±0.40	24.2±0.4	82.0±0.7	0.351±0.021
Kosi Bay FM	5.50±0.30	29.4±0.3	11.8±0.7	0.393±0.019	14.9±0.7	1.48±0.20	25.9±0.5	16.0±0.5	0.054±0.011
Uloa. FM	7.13±0.01	48.4±1.3	18.4±0.4	0.920±0.010	9.66±0.30	10.9±0.5	25.1±0.2	48.0±0.3	0.100±0.0006
St Lucia FM	7.27±0.10	50.4±1.8	20.2±0.3	0.792±0.024	6.90±0.12	5.08±0.20	36.7±0.6	84.0±0.8	0.030±0.004

Acidity can indicate the depletion of calcium and bicarbonate ions in the shallow Units through leaching of minerals or cation exchange reactions that replace exchangeable ions, resulting in slowly rising levels of sodium and chloride ions in groundwater.

Phosphate ions (0.351±0.021mg/L) are higher in the Kwambonambi Formation either from surface plantations, agricultural, industrial, or domestic activities, as the Formation is very shallow and receives direct recharge from the surface. The Kosi Bay Formation is most weathered to a clay mineral concentration of 14.9±0.7%. It is likely to be directly recharged by the Kwambonambi Formation, which may have caused increase in clay minerals. The clay minerals are probably washed from Kwambonambi Formation due to its low particle density. Ammonium ions are higher in St Lucia Formation (36.7mg/L) probably from plant and animal deposits of the marine deposits.

8.3.3 Conclusion of the Veldenvlei aquifers geochemistry

The Veldenvlei aquifer is low in potassium ions (K^+), ferrous iron (Fe^{2+}), sulphate (SO_4^{2-}) and magnesium ions (Mg^{2+}). The Pleistocene Unit is dominated by calcium and bicarbonate ions probably recharged from the nearby stream, as the sediments of the Unit are acidic. The dominance of calcium and bicarbonate ions controlled the pH of the Unit to neutral, similar to the Miocene Unit. The Miocene is dominated by sodium, calcium and bicarbonate ions, which controlled both water and sediments to a neutral pH. Calcium and bicarbonate ions are a result of calcareous sediments of the Miocene Unit, while sodium ions are probably from either marine sediment deposits, direct recharge from the Pleistocene Unit or recharge from the nearby stream. The elevated concentration of sulphate ions are also likely to have been recharged by the neighbouring stream.

The dominance of calcium and bicarbonate ions resulted in neutral the groundwater in both boreholes. The pH is within the South African Drinking Water Guideline Limit (Class 1) except for manganese ions which were within Class 2 of the Guideline. Chloride ions are higher than sodium ions and calcium ions exceed magnesium ions (Ca: Mg ratio was approximately 2:1). Ammonium ions dominate most of the Units of the aquifers, especially in the St Lucia Formation. The ions may be derived from geological composition or from the marine animal and plants deposits.

8.4 Meerensee aquifers

8.4.1. Hydrochemistry of Meerensee aquifers

The hydrochemistry of Meerensee boreholes seems difference. It is low in magnesium ions (≤ 31.0 mg/L) and elevated potassium, sulphate ions and alkalinity compared to other boreholes. The Holocene and the Miocene Units are dominated by calcium and bicarbonate ions while the Pleistocene is dominated by sodium and bicarbonate ions (Figure 35). Sulphate ions are higher in the Pleistocene Unit (119mg/L). Chloride ions are higher than sodium ions (Na^+) and calcium ions exceed magnesium ions (Ca: Mg ratio is 485:1 and 6:1 in the

Holocene and the Miocene respectively, Table 20 of Appendix II and Figures 36 and 37)

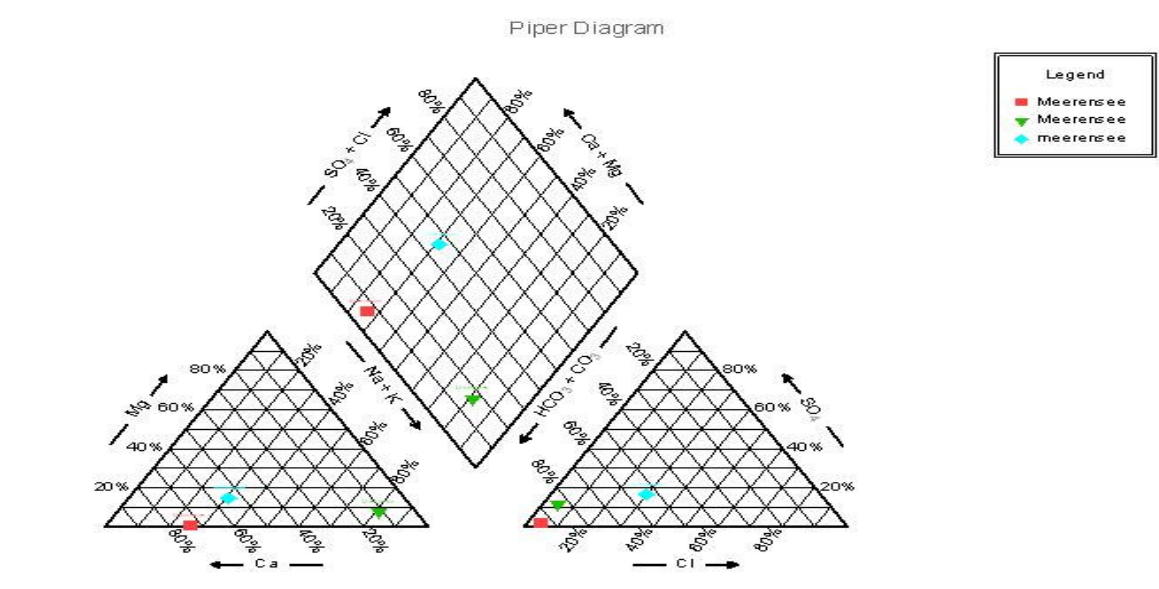


Figure 35: The hydrochemistry of the Holocene, Pleistocene and Miocene of the Meerensee aquifers displayed using Piper diagrams, in which red represents Holocene, green (Pleistocene) and blue (Miocene)

The bicarbonate ions dominance resulted in a neutral to alkaline pH (ranging from 7.5 to 12.5) in all Units.

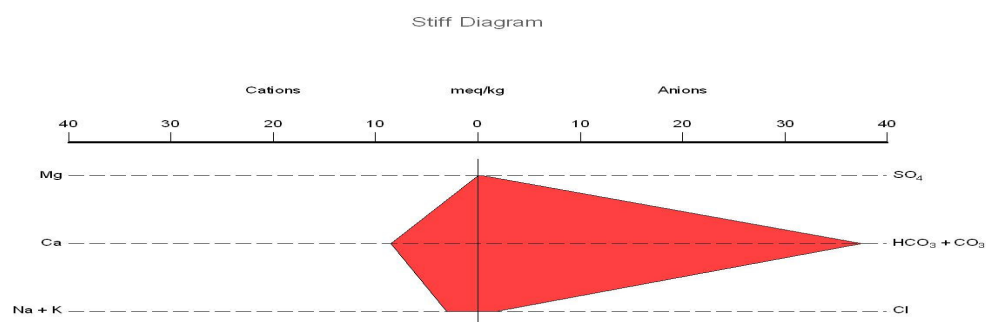


Figure 36: The hydrochemistry of the Meerensee Holocene Unit displayed using Stiff diagram, shaded area indicating cations and anions dominance (in meq/L)

The Holocene Unit is dominated by the bicarbonate ions which are approximately 4-fold higher than calcium ions and about 9-fold higher than in the Miocene Unit, with low concentration of magnesium and chloride ions than that of other Units (Figures 36 and 37).

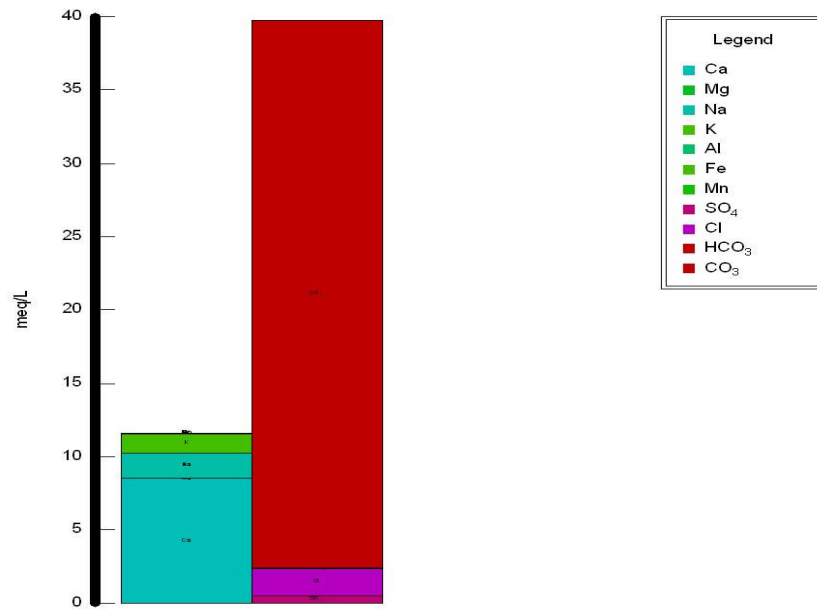


Figure 37: Meerensee Holocene Unit ion-Balance

Potassium ions are the highest in Holocene and are higher than sodium ions. Higher potassium ions could indicate sea water intrusion or surface water recharge to the boreholes, causing a high proportion of calcium and potassium ions in the Meerensee ⁴⁸.

The Pleistocene Unit is dominated by bicarbonate ions with lower calcium ions than that of the Holocene Unit (Figures 38 and 39). The bicarbonate ions in Holocene are about 2-fold higher than that of the Pleistocene Unit. The Pleistocene seems to receive vertical recharge from the Holocene Unit. The Units seems to be recharged by a source that is rich in bicarbonate ions, which has caused elevated concentrations of the bicarbonate ions that are 4 to 9-fold higher than that of the Miocene unit.

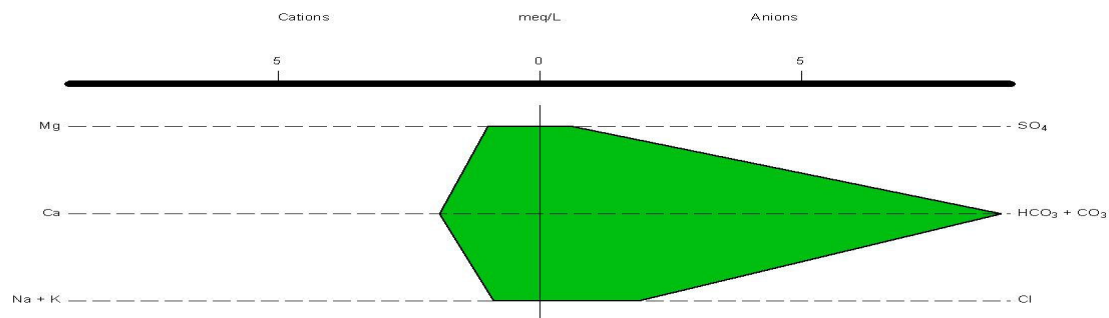


Figure 38: The hydrochemistry of the Meerensee Pleistocene Unit displayed using Stiff diagram, shaded area indicating cations and anions dominance (in meq/L).

The Pleistocene Unit is higher in sulphate ions and lower in chloride ions (Figure 39). The sulphate ions seem to increase from Holocene Unit to Pleistocene Unit, which might indicate ions are being recharge from the Holocene Unit.

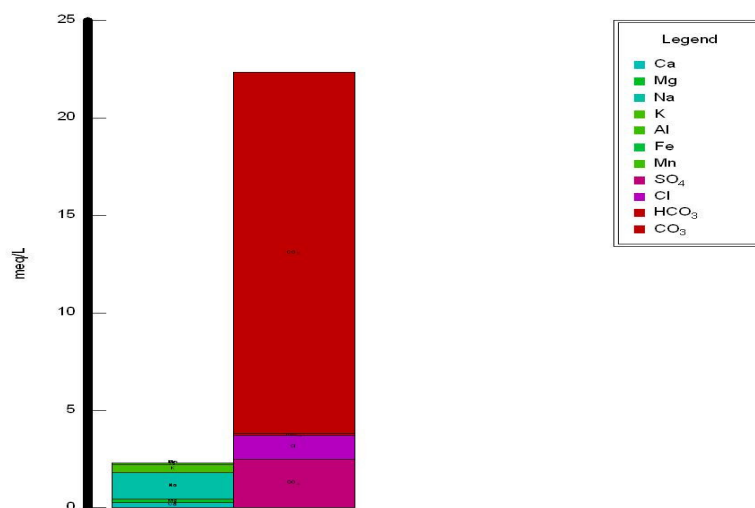


Figure 39: Meerensee Pleistocene Unit ion-balance diagram

The Miocene Unit is lower in calcium and bicarbonate ions than that of the Holocene unit. It is dominated by magnesium, sodium, and chloride ions which

are different from other Miocene Units (Figures 40 and 41). These ions are assumed be contributed by the sea intrusion to the aquifers.

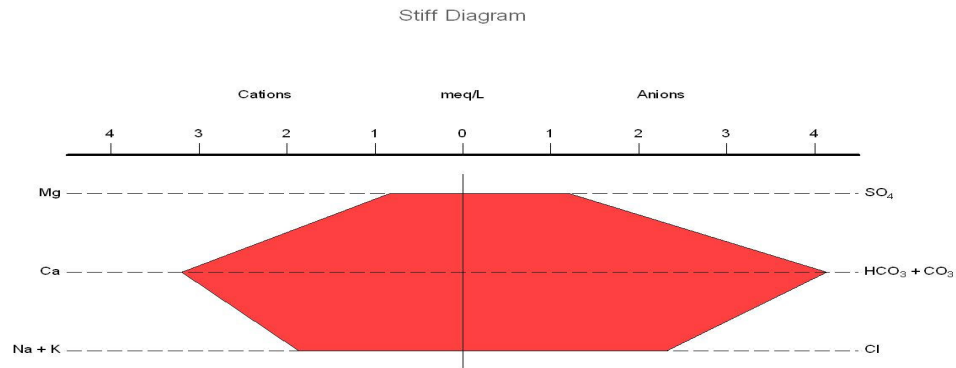


Figure 40: The hydrochemistry of the Meerensee Miocene Unit displayed using Stiff diagram, shaded area indicating cations and anions dominance (in meq/L).

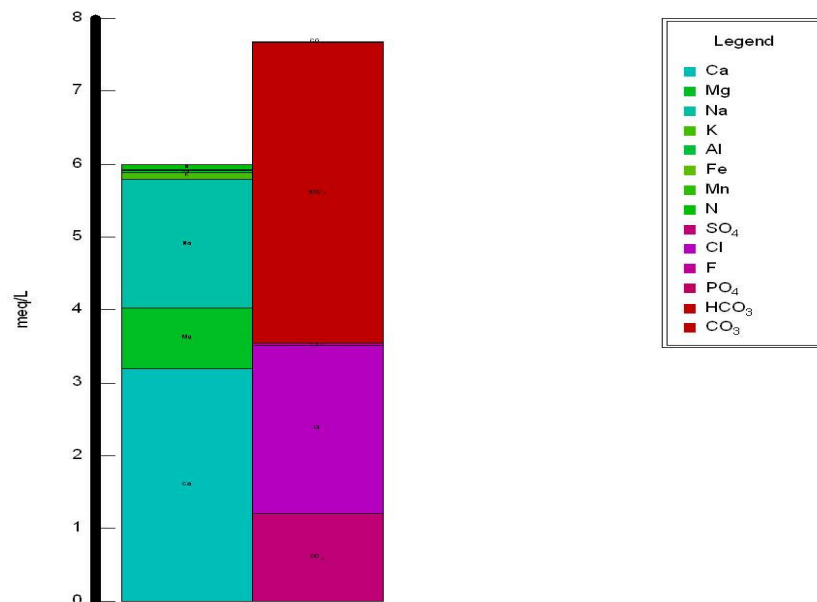


Figure 41: Meerensee Miocene Unit ion-balance diagram

8.4.2 Geochemistry of Meerensee aquifers

The Miocene sample was selected for the geochemical study. It was classified into Sibaya, Kosi Bay, Port Durnford and Uloa Formations. Sediments are neutral

in the Sibaya Formation with a pH of 6.46 ± 0.10 . The sediments are acidic in the Kosi Bay Formation and the Port Durnford Formation (pH from range 3.62 to 5.91, Table 6.4). The Uloa Formation is neutral because of the calcareous sediments. Clay minerals were higher in the Port Durnford and the Uloa Formations (15.20 ± 0.6 and 9.23 ± 0.44 respectively). The sediments are weathered in all Units especially in the Port Durnford Formation ($15.20 \pm 0.6\%$). Ammonium ions (NH_4^+) are low in the boreholes compared to the Richards Bay aquifers.

Table 6.4: Geochemical results of Meerensee boreholes

	pH	% CaCO_3	% Ca	%OM	%Clay	% Silt	NH_4^+ mg/L	Fe(T) mg/L	Phosphate mg/L
Sibaya FM	6.46 ± 0.10	5.69 ± 0.24	2.29 ± 0.70	0.660 ± 0.030	5.91 ± 0.50	1.92 ± 0.13	6.30 ± 0.10	136 ± 3	0.080 ± 0.010
Kosi Bay FM	5.91 ± 0.10	7.54 ± 0.05	2.99 ± 0.33	0.580 ± 0.033	6.22 ± 0.43	6.43 ± 0.55	14.8 ± 0.3	52.0 ± 0.3	0.210 ± 0.012
Pt Durn FM	3.62 ± 0.40	6.49 ± 0.08	6.18 ± 2.0	1.75 ± 0.50	15.2 ± 0.6	5.07 ± 0.18	20.2 ± 0.2	206 ± 6	0.910 ± 0.020
St Lucia FM	8.09 ± 0.30	50.2 ± 0.5	46.7 ± 0.2	0.440 ± 0.022	9.23 ± 0.44	8.84 ± 0.23	16.0 ± 0.2	202 ± 9	0.450 ± 0.030

8.4.3 Conclusion of Meerensee aquifer geochemistry

The Meerensee boreholes are low in magnesium (Mg^{2+}), ferrous iron (Fe^{2+}), and manganese (Mn^{2+}) ions. Sulphate ions are higher in Pleistocene Unit. Potassium and the bicarbonate ions dominate the Holocene Unit, resulting in alkaline water without any calcareous sediment. This might indicate the recently recharged groundwater. The Holocene is dominated by calcium and bicarbonate ions probably from the lake recharge or the sea intrusion, resulting in a calcium and bicarbonate ions type of a water-signature.

The Pleistocene Unit is low in calcium ions but high in bicarbonate and sodium ions. The bicarbonate ions are likely to be directly recharged by the Holocene Unit. This resulted in a sodium and bicarbonate ions type of a water-signature. The Miocene Unit is neutral due to the calcareous sediments of Miocene Unit. It is dominated by bicarbonate and calcium ions causing a calcium and bicarbonate

type of a water-signature. Chloride ions are higher than sodium ions (Na^+), and calcium ions exceed magnesium ions. The sediments consist predominantly of the sandstones and clay minerals. The sediments are neutral in the Sibaya Formation due to bicarbonate ions dominance. The Low calcium ions in the Kosi Bay and Port Durnford Formations resulted in acidic sediments. The water in the aquifer is generally of good quality (low TDS) being suitable for drinking although the pH is alkaline, with elevated potassium ions, which are above Class 1 of the South African Drinking Water Guideline Limit.

8.5 Comparisons among neighbouring aquifers

The Richards Bay boreholes located on the horizontal and vertical geographical positions are compared in this Chapter. The boreholes located in the vertical geographical position are the Science Centre, Alton and Veldenvlei while the Aquadene, Veldenvlei, Birdswood and Meerensee are located in the horizontal geographical positions, as indicated in Figures 5 and 42. The boreholes are compared according to their lithostratigraphic Units.

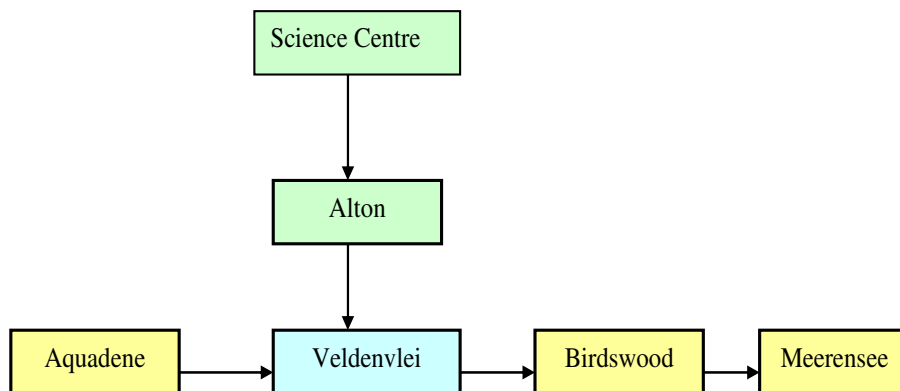


Figure 42: Boreholes located in the vertical & horizontal geographical positions

8.5.1 Comparison among horizontal boreholes

8.5.1.1 Miocene Unit

The Meerensee and Veldenvlei boreholes are the two boreholes drilled deep enough to reach the Miocene Units. They are low in sulphate, magnesium and

potassium ions as indicated by Hattingh⁴⁶. They are dominated by bicarbonate ions with to low chloride ions (Figure 43). Veldenvlei is dominated by sodium ions while Meerensee is dominated by calcium ions. Therefore, the Miocene Unit of the Veldenvlei borehole is dominated by a sodium, calcium and bicarbonate ions type of a water-signature while the Meerensee is dominated by calcium and bicarbonate ions type of a water-signature (Figure 43).

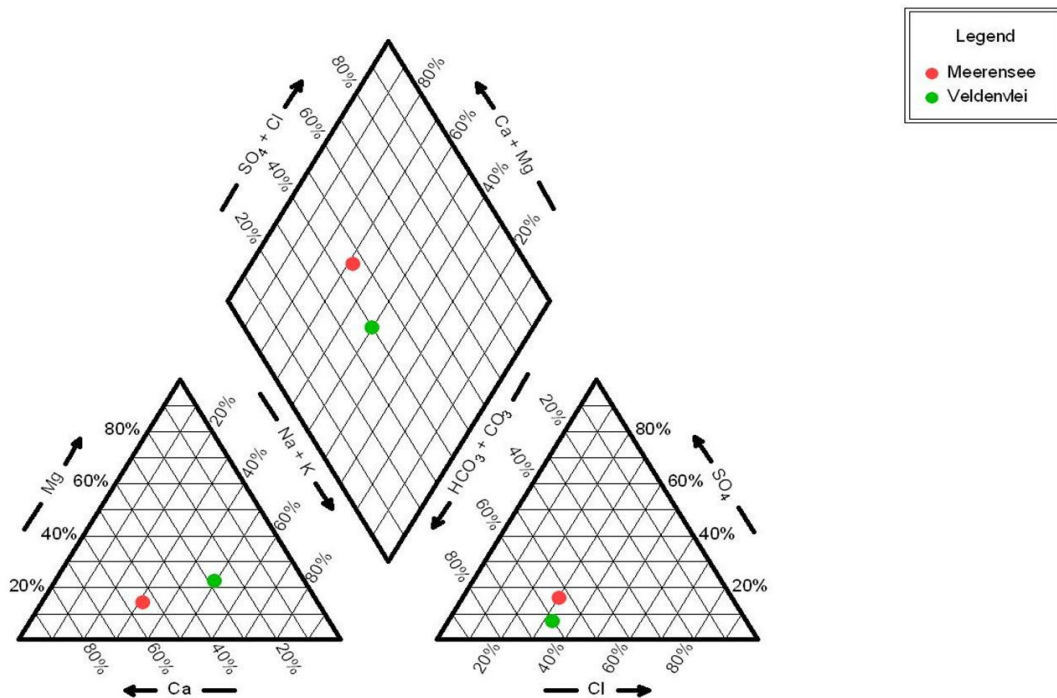


Figure 43: The hydrochemistry of Meerensee and Veldenvlei for the Miocene Units is presented using piper diagrams.

The results are within the ranged identified by Hattingh⁴⁶ under the Miocene Unit. The sediments comparison is based on the Uloa Formation. The sediments in both boreholes are neutral to slightly basic due to a high concentration of calcium carbonate. This resulted in well-buffered water against acidity in both boreholes. The sediments are slightly weathered in Meerensee. Organic matter and ammonium ions dominated Veldenvlei sediments, while phosphate, manganese and total iron concentration dominated Meerensee sediments.

8.5.1.2 Pleistocene Unit

The Meerensee, Aquadene, Birdswood and Veldenvlei boreholes were drilled deep to reach Pleistocene Unit. The results of Birdswood could not be included in the diagram due to incomplete analysis. The two boreholes are low in sulphate and magnesium ions as indicated by Hattingh⁴⁶ (Figure 44)

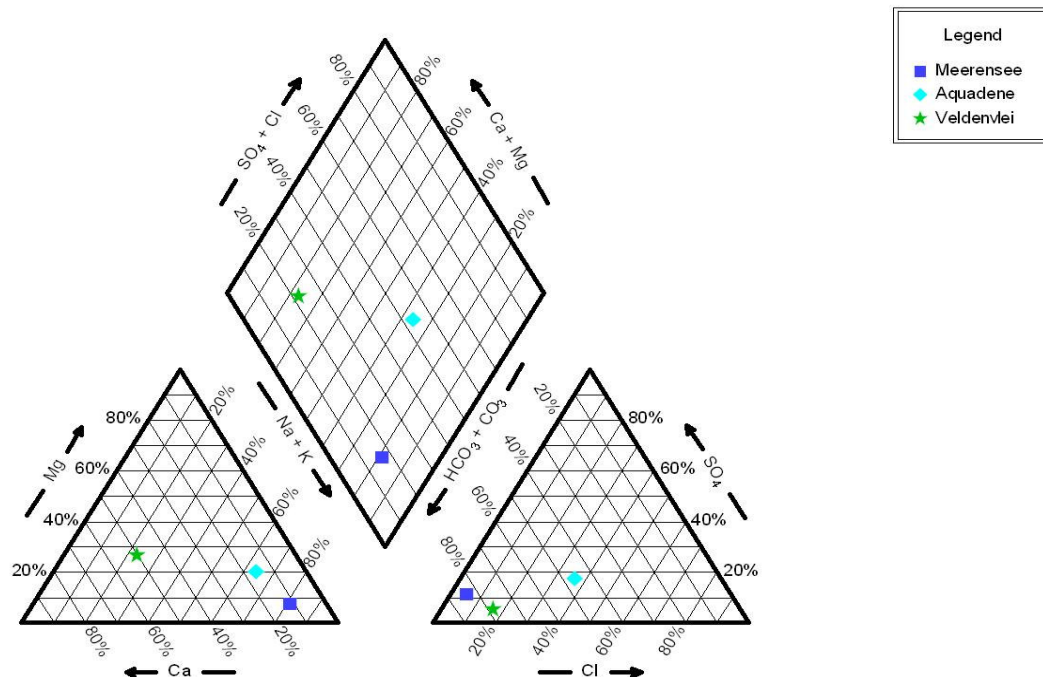


Figure 44: The hydrochemistry of Meerensee and Veldenvlei for the Pleistocene Units is presented using piper diagrams

Potassium ions are the highest in Meerensee. The bicarbonate ions dominate all boreholes especially in Meerensee and Veldenvlei due to low chloride ions (Figure 44). Meerensee and Aquadene are also dominated by sodium ions while Veldenvlei is dominated by calcium ions. Veldenvlei is higher in calcium than that identified by Hattingh⁴⁶. Therefore, the Pleistocene Units of Meerensee and Aquadene boreholes are dominated by a sodium and bicarbonate ions type of water-signature, while Veldenvlei is dominated by calcium and bicarbonate ions type of water-signature (Figure 44). The bicarbonate (in Meerensee and

Veldenvlei), calcium (in Veldenvlei) and potassium ions (in Meerensee) are higher than indicated by Hattingh⁴⁶ in the Pleistocene unit (Figure 44).

The sediments comparison is based on the Kosi Bay Formation. The sediments in Aquadene and Meerensee boreholes are acidic due to low calcium carbonate content. In Meerensee although the sediments are acidic the water is alkaline. This might indicate that there is an alkaline source that recharges the borehole. The sediments in Veldenvlei are neutral due to calcium and carbonate ions dominance. This resulted in well-buffered water against acidity in both boreholes. Veldenvlei is the lowest in phosphate ions and total iron concentrations. The sediments are low in organic matter in Veldenvlei and Meerensee while Meerensee is low in ammonium ions. Sediments in all boreholes have undergone weathering.

8.5.1.3 Conclusion in horizontal boreholes

The Miocene Unit of Meerensee and Veldenvlei show different chemical compositions. It is low in potassium and magnesium ions as indicated by Hattingh⁴⁶. The two boreholes are dominated by bicarbonate ions due to the calcareous nature of the Miocene sediments. Calcium ions dominance in Meerensee resulted in a calcium and bicarbonate ions type of water-signature. The cations exchange taking place between calcium and sodium ions in Veldenvlei has resulted in sodium and bicarbonate ions type of water-signature. Bicarbonate ions dominance caused the water to be neutral.

The Pleistocene Unit is low in sulphate and magnesium ions as indicated by Hattingh⁴⁶. Potassium ions are high in Meerensee probably from marine sediment deposits. The bicarbonate ions dominate all boreholes due to low chloride ions. Sodium ions dominated in Meerensee and Aquadene due to depleted dissolved calcium ions. Calcium ions are dominant in Veldenvlei. Meerensee and Aquadene boreholes are dominated by a sodium and

bicarbonate ions type of water-signature while Veldenvlei is dominated by calcium and bicarbonate ions type of water-signature.

8.5.2 Comparison among Vertical boreholes

8.5.2.1 Miocene Unit

The Centre and Veldenvlei boreholes were drilled deep enough to reach the Miocene Unit. The two boreholes are low in sulphate and magnesium ions, as indicated by Hattingh⁴⁶. The bicarbonate ions dominate both Science Centre Veldenvlei boreholes (Figure 45). Veldenvlei is dominated by sodium ions while Science Centre is dominated by calcium ions, similar to Meerensee borehole.

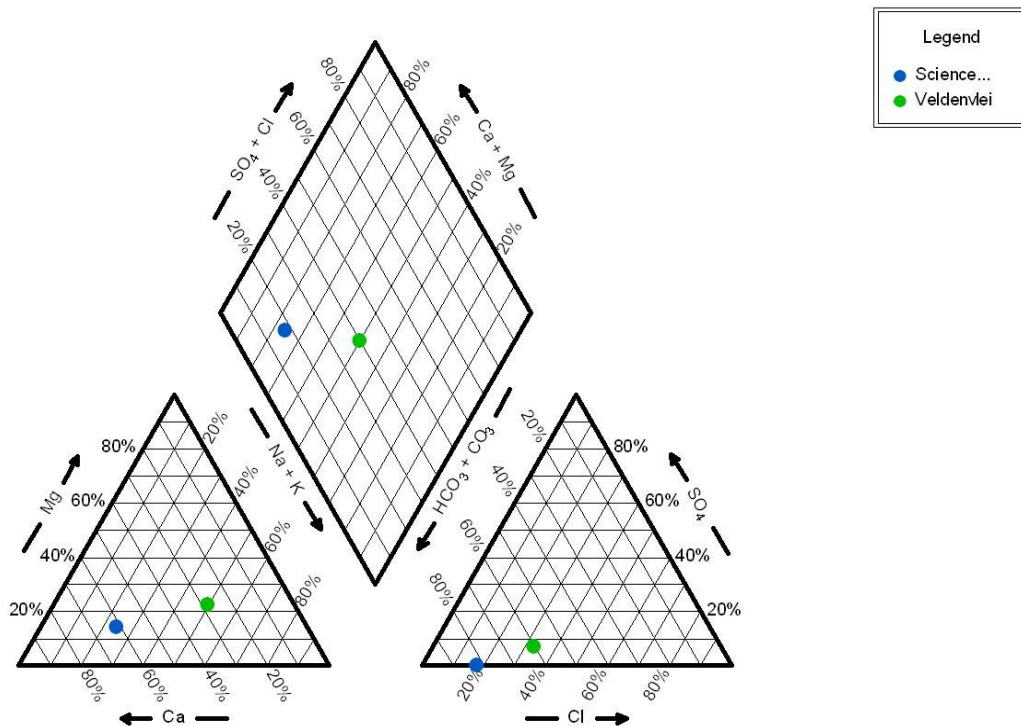


Figure 45: The hydrochemistry of Science Centre and Veldenvlei for the Miocene unit presented using piper diagrams

Therefore, the Miocene Unit of the Veldenvlei borehole is dominated by sodium and bicarbonate ions type of water while Science Centre is dominated by calcium and bicarbonate ions type of water-signature (Figure 45). The results are within

the ranged identified by Hattingh⁴⁶ for the Miocene Unit except for Science Centre bicarbonate ions which are slightly higher than those identified in the Miocene unit.

Sediments comparison is based on the St Lucia Formation. The sediments in both boreholes are neutral due to high concentrations of calcium carbonate content. This resulted in well-buffered water against acidity in both boreholes. The sediments are both weathered to fine particles, with high organic matter and ammonium ions. Phosphate, manganese ions dominated Science Centre. The total-iron concentration is similar in both Units.

8.5.2.2 Pleistocene Unit

The Science Centre, Alton and Veldenvlei boreholes were drilled deep enough to reach the Pleistocene Unit. The boreholes are low in sulphate, magnesium and potassium ions, as indicated by Hattingh⁴⁶. The bicarbonate ions dominate Alton 2 and the Veldenvlei boreholes, while chloride ions dominated the Alton 3 and the Science Centre boreholes (Figure 46). Veldenvlei is dominated by calcium ions while Science Centre and Alton are dominated by sodium ions. Therefore, the Pleistocene Unit in Veldenvlei is dominated by a calcium and bicarbonate ions type of water-signature, while in Science Centre and Alton 3 is dominated by a sodium and chloride ions type of water-signature, and Alton 2 is dominated by a sodium and bicarbonate ions type of water-signature (Figure 46). The results are within the ranged identified by Hattingh⁴⁶.

Sediments comparison is based on the Kosi Bay Formation. The sediments in Veldenvlei are neutral due to high concentration of calcium carbonate. This resulted in well-buffered water against acidity. The sediments in Science Centre and Alton are acidic due to low concentrations of calcium carbonate. This resulted in acidic water quality of the boreholes. The sediments are weathered in all boreholes. Organic matter is the highest in Alton 3 borehole. Ammonium ions dominate Alton sediments. Ammonium ions were equivalent in both Science Centre and Veldenvlei boreholes. No manganese ions were detected in Science

Centre and Veldenvlei boreholes. Phosphate ions and the total-iron concentration are the lowest in Veldenvlei borehole.

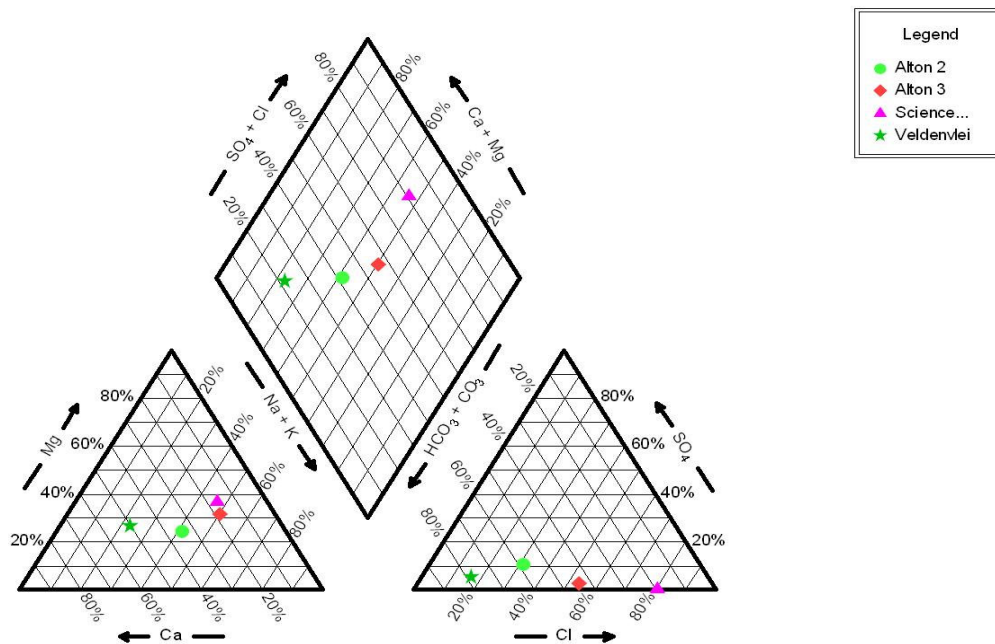


Figure 46: The hydrochemistry of Science Centre and Veldenvlei for the Pleistocene unit presented using piper diagrams

8.5.2.3 Conclusion in vertical boreholes

The Miocene Unit is low in sulphate and magnesium ions as indicated by Hattingh⁴⁶. The bicarbonate ions dominate both boreholes due to the calcareous nature of the Miocene sediments. Sodium ions dominated Veldenvlei while calcium ions dominated Science Centre. The Veldenvlei borehole is dominated by a sodium and bicarbonate ions type of water-signature while the Science Centre is dominated by calcium and bicarbonate ions type of water-signature.

The Pleistocene Unit is low in sulphate, magnesium and potassium ions as indicated by Hattingh⁴⁶. The bicarbonate ions dominate Alton 2 and the Veldenvlei boreholes while chloride ions dominated Alton 3 and the Science Centre borehole. Calcium ions dominated Veldenvlei while sodium ions dominated Science Centre and Alton boreholes. Veldenvlei borehole is

dominated by a calcium and bicarbonate ions type of water-signature while Science Centre and Alton 3 are dominated by a sodium and chloride ions type of water-signature, and Alton 2 by sodium and bicarbonate ions type of water-signature.

CHAPTER NINE

DISCUSSION AND RECOMMENDATIONS

9.1 Summary

The boreholes used in this study are Richards Bay monitoring boreholes managed by the Department of Water Affairs. The hydrochemical data analyzed was obtained from DWA and University of Zululand.

The main lakes situated in the coastal plain form an extension of the groundwater aquifers, Keble¹. Zululand Coastal lakes recharge and discharge through various parts of the lake beds to the aquifer (Townley ⁵), which might result in change or deterioration of the ground water quality. The seepage rate is greater at the surface shoreline and decreases exponentially with the distance underneath the Lake. Aquifers vary in chemical compositions depending on the location (due to land use) and the depth, and permeability of the aquifer. The dissolved minerals in the Richards Bay aquifers are higher in the shallow aquifers.

The Maputaland coastal plain selected boreholes for the study are classified into Cretaceous, Miocene, Pleistocene and Holocene Units depending principally on the type of lithology reached during the drilling process. The lithological Units of the sediments were predicted by professional geologists, in which the sediments were then classified into Kwambonambi, Sibaya, Kosi Bay, Port Durnford Uloa and St Lucia Formations.

The shallow aquifers (Holocene and Pleistocene Units) show high permeability, as the Pleistocene Units seem to be receiving direct recharge from the Holocene Units. The Miocene Unit seems to be less permeable as no direct recharge from Pleistocene Units was noticed. In the Veldenvlei aquifer vertical recharge from Miocene Unit to Pleistocene Unit was suspected due to high bicarbonate ions in the Pleistocene Unit. Meerensee hydrochemistry contains elevated sodium and chloride ions (still within the Drinking Water Guideline Limit of South Africa) that

are distributed to all Units. These ions are concentrated in the Miocene Unit, which might indicate ions were introduced during sea intrusion to the aquifers.

9.1.1 Maputaland Hydrochemistry

The Maputaland aquifers are low in dissolved sulphate, potassium, ferrous iron and magnesium ions. High sulphate (in Pleistocene Unit) and potassium (in Holocene Unit) ions are noticed in the Meerensee aquifers.

The hydrochemistry of the Cretaceous Unit (in Birdwood) is characterized by sodium and chloride ions type of chemical signature. The dominance of these ions is due to briny components discovered by Martinelli and Associates⁴⁸. The Miocene Unit hydrochemistry shows two different chemical signatures, one characterized by calcium and bicarbonate ions type (in Science Center and Meerensee aquifers) and the other by sodium, calcium and bicarbonate ions type of water signature (in Veldenvlei aquifer). The dominance of calcium and bicarbonate ions arises from the composition of the Uloa Formation sediments which are enriched in calcite and shell fragments of the marine sediment deposit. Sodium ions in Veldenvlei are likely to have been introduced by the recent marine sediment deposits, or recharged from the near stream running parallel to the borehole. Calcium ions may have been lost by precipitation in solution. Miocene aquifers are neutral to basic in pH, due to high bicarbonate ions dominance. Chloride ions are slightly higher than sodium ions and calcium ions exceed magnesium ions which concur with Hattingh⁴⁶.

The Pleistocene Unit hydrochemistry shows three different chemical signatures, one characterized by sodium and bicarbonate ions dominance (in Alton 2, Aquadene and Meerensee aquifers), one by calcium and bicarbonate ions dominance (in Veldenvlei aquifers) and the other by sodium and chloride ions dominance (in Science Centre and Alton 3 aquifers). The bicarbonate ions are lower than that of the Miocene Units as a result of leaching of sediments, except in Veldenvlei and Meerensee aquifers where the pH is neutral to basic due to

bicarbonate ions dominance. The Holocene Unit shows two different chemical signatures, one characterized by sodium and chloride ions dominance (in Science Center aquifer) and the other by calcium and bicarbonate ions dominance (in the Meerensee aquifer). Calcium and bicarbonate ions are depleted in Science Center which has caused dominance of the sodium and chloride ions as the sediments are leached and acidic.

9.1.2 Maputaland Geochemistry

Samples from the St Lucia Formation range from olive green, black green to bluish green in colour, as identified by Worthington⁶. The type of sediments is normally found in the lower part of the Cretaceous deposits. The colour is provided by glauconitic minerals due to alteration of the sediment deposits influenced by the decaying process of the organic matter in animal shells⁴⁰. This resulted in high organic matter for both aquifers (Science Center, Birdswood and Veldenvlei aquifers). The average thickness of St Lucia Formation is approximately 4 to 41 meters. St Lucia Formation is characterized by high calcium carbonate content due to calcite and shell fragments of the marine sediment deposits, which resulted in neutral sediments. Sediments are dominated by high clay and silt minerals due fine grain size sediments indicating weathering.

Samples from the Uloa Formation range from yellow to orange in colour. The Formation is rich in white calcite rock (solidified calcium carbonate rock) and coquina as described by Maud²⁶. The average thickness of Uloa Formation is approximately 4 meters. The type of sediments is found in Science Center, Meerensee and Veldenvlei boreholes. The Uloa Formation is characterized by high calcium and carbonate ions due to calcite and coquina deposits which resulted in neutral sediments. Calcium and carbonate ions are slightly higher than that of the St Lucia Formation. The sediments are dominated by medium clay and silt minerals indicating sediment weathering.

Samples from the Port Durnford Formation range from yellow, red brown to cream-white in colour. The type of sediments is found in Birdswood, Aquadene and Meerensee boreholes. They are rich in argillaceous minerals with low silt minerals especially in Birdswood. Meerensee contains carbonaceous materials at lower layers of the aquifer, which might indicate a lignite band identified by Worthington⁶. The Port Durnford Formation is characterized by low calcium and carbonate ions which resulted in acidic sediments. Sediments are high in organic matter and ammonium ions.

Samples in the Kosi Bay Formation range from yellow, orange, and brown to cream-white in colour. The type of sediments is found in all boreholes except for Birdswood. Most of the sediments in the Kosi Bay Formation are leached probably from high rainfalls. They are rich in clay minerals with low silt minerals. They are characterized by low calcium and carbonate ions which have resulted in a low pH. Organic matter is higher than that of the Port Durnford Formation.

Samples in the Kwambonambi Formation range from brownish gray to brown in colour, indicating the presence of organic matter, which could be supplied by surface plantations. The type of sediments is found in most aquifers except for Meerensee, Mseleni, St Lucia and Aquadene. They are characterized by low calcium and carbonate ions which have resulted in acidic sediments. The sediments are weathered to medium clay and low silt minerals. Organic matter is lower than in the Kosi Bay Formation but similar to Port Durnford Formation.

Samples in the Sibaya Formation were only found in the Meerensee boreholes. Low calcium and carbonate ions resulted in acidic sediments, which are slightly weathered to medium clay and low silt minerals. Organic matter is lower than that of the Kosi Bay Formation but similar to that of the Port Durnford Formation. The organic matter could be supplied by plantation on the surface. The sediments are low in manganese, phosphate and silicate ions and total iron concentration than that the underlying Unit.

9.1.3 Geohydrochemical comparison

Due to uncertainty of the lithology as well as incomplete geohydrological analyses a decision was taken to compare only the boreholes located in the same aquifer of the same area such as Alton, Science Center, Veldenvlei and Meerensee.

Alton aquifer shows low dissolved magnesium (Mg^{2+}), sulphate (SO_4^{2-}) and potassium ions (K^+) which concurs with the Pleistocene Unit findings by Hattingh⁴⁶. The ions could not be verified by geological analysis because of cost impacts. Two chemical signatures are observed in the Alton aquifer, one by sodium and bicarbonate ions dominance (in Alton 2) and the other by sodium and chloride ions dominance (in Alton 3). The bicarbonate ions dominance in Alton 2 slightly buffered the groundwater to a slightly acidic pH, although the sediments are acidic. The low calcium and carbonate ions in sediments of Alton 3 resulted in acidic water due to sodium ions and chloride ions dominance. The acidity of sediments has led to high dissolution of minerals such as fluoride and ferrous ions through reduction processes. The sediments are leached by prevailing rainfalls. Sodium and chloride ions in the aquifer are assumed to be due to coastal-influence precipitation. Ammonium ions (NH_4^+) can be generated by geological or other sources.

Science aquifer is low in potassium (K^+) and magnesium (Mg^{2+}) ions. Two chemical signatures are observed, one by sodium and chloride ions dominance (in Pleistocene and Holocene Units) and the other by calcium and bicarbonate ions dominance (in Miocene Unit). The sodium and chloride ions dominance is caused by the depleted calcium and bicarbonate ions resulting in sodium and chloride ions dominance. Miocene sediments are rich in calcium carbonate ions resulting in calcium and bicarbonate ions dominance. As shallow aquifers are vulnerable to surface influence, the sediments are leached with high dissolved minerals due to depleted calcium and carbonate ions. Sodium and chloride ions are assumed to be due to the coastal-influence precipitation or the recent marine sediment deposits. Ammonium ions (NH_4^+) are assumed to be generated by

surface influence or geological composition. The Pleistocene Unit seems to be receiving direct recharge from the Holocene Unit.

The Veldenvlei aquifer is low in potassium (K^+), magnesium (Mg^{2+}) and sulphate ions (SO_4^{2-}). Two chemical signatures are observed, one by calcium and bicarbonate ions dominance (in Pleistocene) and the other by sodium, calcium and bicarbonate ions dominance (in Miocene Unit). Both boreholes are rich in calcium and carbonate ions. The two Units are similar except that the Miocene seems to contain mixed water (sodium, calcium and bicarbonate ions). Mixed water in the Miocene may be due to either slight depletion of calcium ions by precipitation in solution giving rise to sodium ions dominance or from vertical recharge of the shallow borehole. Sediments of the shallow borehole are acidic due to exposure to surface influence such as rainfalls. This caused leaching of minerals resulting in depletion of calcium and carbonate ions in the sediments. Ammonium ions (NH_4^+) are assumed to be generated by surface influence or geological compositions.

The Meerensee aquifer is low in magnesium (Mg^{2+}) ions. Sulphate ions are high in the Pleistocene Unit. Two chemical signatures are observed, one by calcium and bicarbonate ions dominance (in Holocene and Miocene) and the other by sodium and bicarbonate ions dominance (in Pleistocene Unit). Potassium and bicarbonate ions dominate the Holocene Unit, resulting in alkaline water without any calcareous sediment. Ions are assumed to be caused by surface influence. The Pleistocene Unit is low in calcium ions but high in bicarbonate ions, which are assumed to be a direct recharge from the Holocene Unit, resulting in sodium and bicarbonate ions dominance. The water and sediment of the Miocene Unit are neutral due to calcareous sediments of the Miocene Unit. Sediments of Meerensee are only acidic in the Port Durnford Formation due to high organic matter.

The Miocene Unit is low in sulphate and magnesium ions as indicated by Hattingh⁴⁶. Bicarbonate ions dominate due to the calcareous nature of the Miocene sediments.

9.1.4 Comparison among vertical and horizontal boreholes

The hydrochemistry of Meerensee and Veldenvlei identified as horizontal boreholes drilled to reach the Miocene Unit is slightly different. The boreholes are low in potassium and magnesium ions. The water is dominated by bicarbonate ions due to the calcareous nature of the Miocene Unit. Calcium ions dominance in Meerensee resulted in a calcium and bicarbonate ions type of water, while Veldenvlei is dominated by a sodium, calcium and bicarbonate ions type of water. Calcium ions are depleted in Veldenvlei resulting in sodium ions dominance. Calcium might be lost through precipitation in solution.

Uloa Formations are similar in calcium and carbonate ions, clay content and organic matter (Table 26 and 28, Appendix III). Sediments in Meerensee are higher in calcium, silicate, total iron, phosphate ions and pH than in Veldenvlei. Veldenvlei is only higher in ammonium ions. This may indicate different geochemical compositions of the Miocene Unit in the two areas

The hydrochemistry of Aquadene, Meerensee and Veldenvlei boreholes drilled deep enough to reach the Pleistocene Unit is different. The water is low in sulphate and magnesium ions as indicated by Hattingh⁴⁶. Potassium ions are the highest in Meerensee. Bicarbonate ions dominate all boreholes due to low chloride ions. Sodium ions dominated Meerensee and Aquadene while calcium ions dominated Veldenvlei. Meerensee and Aquadene boreholes are characterized by a sodium and bicarbonate ions type of water-signature while the Veldenvlei is characterized by calcium and bicarbonate ions type of water-signature.

The sediments of the Kosi Bay Formation of Aquadene are higher in organic matter, phosphate, and manganese ions. They are the most acidic sediments

(Table 25, Appendix III) of all Pleistocene Units, due to leaching. Meerensee sediments are higher in total iron concentration and silicate ions (Table 28, Appendix III) while Veldenvlei sediments are only higher in clay mineral content (Table 26, Appendix III). This may indicate different geochemical compositions of the Pleistocene Units in the two areas, which may be affected by different sources.

The hydrochemistry of Science and Veldenvlei boreholes drilled deep enough to reach Miocene Unit is slightly different. The water is low in sulphate and magnesium ions as indicated by Hattingh⁴⁶. Bicarbonate ions dominate both boreholes due to the calcareous nature of the Miocene sediments. Sodium ions dominate Veldenvlei while calcium ions dominate Science Centre. The Veldenvlei borehole is characterized by sodium and bicarbonate ions type of water-signature while Science Centre is characterized by calcium and bicarbonate ions type of water-signature.

St Lucia Formation sediments of the two boreholes are similar in silicate, calcium, and carbonate ions, total iron concentration and pH (Table 24 and 26, Appendix III). Manganese, phosphate ions, clay and organic matter are higher in Science Center (Table 24 and 26, Appendix III). This may indicate the similar geochemical compositions of the Miocene Unit in the two areas, in which calcium ions in Veldenvlei are precipitating in solution causing a decrease in dissolved calcium ions or the nearby stream is recharging the aquifer with high sodium ions water quality.

The hydrochemistry of Alton, Science Centre and Veldenvlei boreholes drilled deep enough to reach Pleistocene Unit is different. The water is low in sulphate and magnesium, potassium ions as indicated by Hattingh⁴⁶. Bicarbonate ions dominate Alton 2 and Veldenvlei aquifers while chloride ions dominate Alton 3 and Science Center boreholes. Calcium ions dominate Veldenvlei while sodium ions dominate Science Center and Alton boreholes. The Veldenvlei borehole is

characterized by a calcium and bicarbonate ions type of water-signature while Science Centre and Alton 3 are characterized by sodium and chloride type of water-signature, and Alton 2 by sodium and bicarbonate type of water-signature.

The Kosi Bay Formation of Veldenvlei is the highest in calcium and calcium carbonate which resulted in a neutral pH of the sediments than other boreholes (Table 26, Appendix III). Total iron concentration is similar in the Alton and Science Centre boreholes (Table 23 and 24, Appendix III). The clay content is similar in Alton and Veldenvlei boreholes (Table 23 and 26, Appendix III). Organic matter and phosphate ions are higher in Alton 3 while manganese and silicate ions are higher in Alton 2 (Table 23, Appendix III).

9.1.5 Identification of impacting ions.

To define groundwater pollution, one has to understand the meaning of pollution. Pollution can mean contamination of groundwater by chemical and synthetic pollutants that render the water unfit for normal use by plants and animals. The contamination in this text is defined as the use of anthropogenic sources that change the water quality to such an extent that the sustainability of the water resources is compromised making it unfit for use by humans.

Most of the major dissolved cations and anions analyzed in the study are within Class 1 of the Drinking Water Guideline of South Africa⁴⁴ (Figure 7). Dissolved fluoride ions are exceeded in Alton 3 probably from geochemical composition of the area or from other sources that increased the fluoride ions in the water such as industrial water run-offs or atmospheric emissions. The fluoride ions are higher than the Class 2 of the guideline Limit. The ferrous iron concentration is exceeded in Science Center (within Class 2), Alton 3 (about 12 fold higher than the Class 2), Birdswood in Pleistocene Unit (within Class 2), and Mseleni (above Class 2) boreholes. The increase in ferrous iron concentration is probably from high acidity of the sediments, causing iron mobility into solution or high concentration of low oxygen.

Table 7: South African Water Drinking Standard (SANS 241 of 2005)⁴⁴

Analytes Analysis Results mg/l	SANS Standards -241 (2005)	
	<i>Class I</i> <i>(Recommended operational limit)</i>	<i>Class II</i> <i>(Maximum allowable to limited duration)</i>
<i>Total Dissolved Solids</i>	<i>< 1 000</i>	<i>> 1 000 - 2 400</i>
<i>Nitrate & Nitrite as N</i>	<i>< 10</i>	<i>> 10 - 20</i>
<i>Chlorides as Cl</i>	<i>< 200</i>	<i>> 200 - 600</i>
<i>Total Alkalinity as CaCO₃</i>		
<i>Fluoride as F</i>	<i>< 1.0</i>	<i>> 1.0 - 1.5</i>
<i>Sulphate as SO₄</i>	<i>< 400</i>	<i>> 400 - 600</i>
<i>Total Hardness as CaCO₃</i>		
<i>Calcium Hardness as CaCO₃</i>		
<i>Magnesium Hardness as CaCO₃</i>		
<i>Calcium as Ca</i>	<i>< 150</i>	<i>> 150 - 300</i>
<i>Magnesium as Mg</i>	<i>< 70</i>	<i>> 70 - 100</i>
<i>Sodium as Na</i>	<i>< 200</i>	<i>> 200 - 400</i>
<i>Potassium as K</i>	<i>< 50</i>	<i>> 50 - 100</i>
<i>Iron as Fe</i>	<i>< 0.20</i>	<i>> 0.20 - 2.0</i>
<i>Manganese as Mn</i>	<i>< 0.10</i>	<i>> 0.10 - 1.0</i>
<i>Conductivity at 25° C in mS/m</i>	<i>< 150</i>	<i>> 150 - 370</i>
<i>pH-Value at 25 °C</i>	<i>5.0 - 9.5</i>	<i>> 4.0 - 10.0</i>
<i>Aluminium as Al</i>	<i><0.30</i>	<i>>0.30 - 0.5</i>

Manganese ions are exceeded in Science Center shallow Unit (within Class 2), Aquadene (within Class 2), Veldenvlei (within Class 2), Birdswood (within Class 2), Meerensee deep Unit (within Class 2), and Mseleni (within Class 2) boreholes, which could be the same effect as ferrous iron. Aluminium ions are

exceeded in Aquadene (2 fold higher than Class 2), Science Center Miocene Unit (about 8-fold higher than Class 2) and Meerensee in Pleistocene (slightly higher than Class 2) boreholes due to acidity of the sediments.

The TDS is only slightly exceeded in the Birdswood borehole (within Class 2) while potassium ions are exceeded in the Meerensee borehole in the Holocene Unit (within Class 2)

The groundwater quality of Alton, Science Center (shallow Units), Aquadene, St Lucia and Mseleni are acidic due to low calcium and bicarbonate ions. The boreholes water quality is affected by the geochemical composition of the sediments. The sediments are leached and acid, which has affected hydrochemistry of the boreholes, especially in the shallow Units.

9.2 RECOMMENDATIONS

An attempt should be taken to professionally log all the Maputaland aquifers geochemical samples according to Botha²⁷. This can provides a better correlation to the hydrochemistry. Further studies should be undertaken to determine chloride, sodium, potassium, sulphate and silicate ions in the Maputaland sediments to compare to the dissolved ions of the aquifers.

CONCLUSION

The water quality of the Maputaland selected boreholes falls mostly within the South African Drinking Water Guideline Limit. The TDS limit is slightly exceeded in the Birdswood Miocene Unit borehole (1047mg/L), probably from the elevated concentrations of sodium and chloride ions. The fluoride ions limit is slightly exceeded in Alton 3, likely from surface run-off or from atmospheric emission. The ferrous iron limit is exceeded in the Science Centre, Alton 3, Birdswood and Mseleni boreholes, probably from weathering on the sediments. The manganese ions limit is exceeded in the Science Centre, Aquadene, Veldenvlei, Birdswood, Meerensee and Mseleni boreholes while the aluminium ions limit is exceeded in the Aquadene, Science Centre and Meerensee boreholes.

The Maputaland boreholes are predominantly low in dissolved sulphate, potassium, magnesium ions and ferrous iron concentration. The most common dissolved minerals are the silicate, chloride, and sodium ions. The dissolved minerals are elevated in the shallow Units with depleted calcium and bicarbonate ions, contributing to sodium and chloride ions dominance. The depletion of the bicarbonate ions in the shallow aquifers caused the water quality of the boreholes to be acidic.

The hydrochemistry of the Cretaceous Unit is characterized by a sodium and chloride ions type of a chemical-signature due to the presence of glauconitic minerals. The Miocene Unit shows two different chemical signatures, one characterized by calcium and bicarbonate ions type and the other by a sodium, calcium and bicarbonate ions type of a chemical-signature.

The Pleistocene Unit shows three different chemical signatures, one characterized by a sodium and bicarbonate ions type, one by a calcium and bicarbonate ions type and the other by sodium and chloride ions type of a chemical-signature. The Holocene Unit shows two different chemical signatures, one characterized by a sodium and chloride ions type and the other by a calcium and bicarbonate ions type of a chemical-signature. Both

the Holocene and Pleistocene units have depleted calcium and bicarbonate ions causing dominance of sodium and chloride ions through cation exchange.

The sediments of the shallow Units are predominantly acidic due to a low calcium carbonate concentration. They are dominated by clay and silt minerals indicating weathering. The Port Durnford Formation is the most weathered Formation of all shallow units (clay $\leq 27.7\%$). The sediments of the deeper Units are predominantly neutral due to high calcium carbonate concentration.

Nitrates ions (as NH_4^+) are distributed all over the Maputaland region in which Aquadene has the highest concentration of 47.5 ± 2 mg/L in the Port Durnford Formation. Nitrates seem to be the lowest in Meerensee.

It is concluded that even though the dissolved mineral ions are rising in the shallow Units, the groundwater quality of the Maputaland boreholes is still suitable for potable purposes where the water quality still falls within Class 1 of the Water Quality Guideline Limit of South Africa, except in boreholes where there is elevation minerals ions. Pollution in groundwater is assumed to be caused mostly by natural processes. For instance, sodium and chloride ions are assumed to be contributed by marine sediment deposits, coastal influence precipitation or recharge from the surrounding surface water resources. The sediments are assumed to be leached by rainfalls which has accelerated weathering of the sediments and caused acidity of the groundwater and the sediments in the shallow aquifers. The acid rain due to dissolved gases (such as SO_2) is likely to have accelerated weathering of the sediments and deterioration of the groundwater quality.

Further study is required to correlate dissolved chloride, sodium, potassium and sulphate ions to the geochemistry of the Maputaland aquifers. An attempt should be taken to log all the geochemical samples according existing lithology.

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APPENDIX I

MAPUTALAND PRIMARY AQUIFERS

BOREHOLE LOGS INFORMATION

Table 8: St Lucia borehole Log Information

Depth (m)	Lithology	Colour	Texture	Screens location	UNITS
1	O/burden	Dull brown	Fine		Kosi Bay formation Well drained
2	Sand	Dull brown	Medium		
3	Sand	Yellow orange	Medium		
4	Sand	Yellow orange	Medium		
5	Sand	Orange	Medium		
6	Sand	Orange	Medium	SCREEN	
7	Sand	Orange	Fine		
8	Sand	Orange	Medium		
9	Sand	Orange	Medium		
10	Sand	Dull orange	Medium		
11	Sand	Brownish gray	Medium		Kosi Bay formation Poorly drained
12	Sand	Brownish gray	Medium		
13	Sand	Black	Medium		
14	Sand	Black	Medium		
15	O/burden	Dull brown	Fine		

Table 9: ALTON 3 borehole Log information:

Depth (m)	Lithology	Colour	Texture	Screens location	UNITS
1	Sand	Brownish gray	Fine		Kwambonambi Formation
2	Sand	L/brownish gray	Fine		
3	Sand	L/brownish gray	Fine	SCREEN	
4	Clay sand	L/brownish gray	Very fine		
5	Clay sand	L/brownish gray	Very fine		
6	Clay sand	L/brownish gray	Very fine		
7	Clay sand	Dull orange	Very fine	SCREEN	Kosi Bay formation
8	Clay sand	Orange	Very fine		
9	Clay sand	Orange	Very fine		
10	Clay sand	Orange	Very fine		
11	Clay sand	Orange	Very fine		
12	Clay sand	Orange	Very fine		
13	Clay sand	Orange	Very fine		
14	Clay sand	Orange	Very fine		
15	Clay sand	Orange	Very fine		
16	Boulders	Orange	Medium coarse		
17	Boulders	Orange	Medium coarse		
18	Sand	Dull orange	Medium fine		
19	Sand	Dull orange	Medium fine		
20	Sand	Dull orange	Medium fine		
21	Sand	Dull orange	Medium fine		
22	Sand	Dull orange	Medium fine		
23	Sand	Dull orange	Medium fine		
24	Sand	Dull orange	Medium fine		
25	Sand	Dull orange	Medium fine		

Table 10: Mseleni borehole Log information:

Depth (m)	Lithology	Colour	Texture	Screens location	UNITS
1	Sand	Dark red	Medium fine		Kosi Bay formation Well drained
2	Sand	Dark red	Medium fine		
3	Sand	Dark red	Medium fine		
4	Sand	Dark red	Medium fine		
5	Sand	Red	Medium fine		
6	Sand	Dark orange	Medium	SCREEN	
7	Sand	Dark orange	Medium		
8	Sand	Dark red	Medium		
9	Sand	Dark orange	Medium		
10	Sand	Dark orange	Medium		
11	Sand	Red	Medium		
12	Sand	Red	Medium		
13	Sand	Red	Medium		
14	Sand	Red	Medium		
15	Sand	Red	Medium		
16	Sand	Bluish yellow	Medium		Kosi Bay formation Poorly drained
17	Sand	Bluish yellow	Medium		
18	Sand	Bluish yellow	Medium		
19	Sand	Bluish yellow	Medium		
20	Sand	Bluish yellow	Medium		
21	Sand	Bluish yellow	Medium fine		
22	Sand	Bluish yellow	Medium fine		
23	Sand	Bluish yellow	Medium fine		
24	Sand	Bluish yellow	Fine		
25	Sand	Bluish yellow	Fine		
26	Sand	Bluish yellow	Fine		
27	Sand	Bluish yellow	Fine		
28	Sand	Bluish yellow	Fine		
29	Sand	Bluish yellow	Fine		
30	Sand	Bluish yellow	Fine		
31	Sand	Bluish yellow	Fine		
32	Sand	Bluish yellow	Fine		
33	Sand	Bluish yellow	Medium fine		
34	Sand	Bluish yellow	Medium fine		
35	Sand	Bluish yellow	Medium fine		
36	Sand	Bluish yellow	Medium fine		
37	Sand	Bluish yellow	Medium fine		
38	Sand	Bluish yellow	Medium fine		
39	Sand	Bluish yellow	Medium fine		
40	Sand	Bluish yellow	Medium fine		
41	Sand	Bluish yellow	Medium fine		
42	sand	Bluish yellow	Medium fine		

Table 11: Birdwood borehole Log Information:

Depth (m)	Lithology	Colour	Texture	Screens location	UNITS
1	sand	Brown	Fine		Kwambonambi Formation
2	Sand	Brown	Medium		
3	Sand	Dark orange	Medium		Port Durnford Formation
4	Sand	Dark orange	Medium		
5	Sand	Dark orange	Medium		
6	Sand	Dark orange	Medium	SCREEN	
7	Sand	Red	Medium		
8	Sand	Red	Fine		
9	Sand	Red	Medium		
10	Sand	Orange	Medium		
11	Sand	Orange	Medium		
12	Sand	Orange	Medium		
13	Sand	Dark Orange	Medium		
14	Sand	Orange	Medium		
15	Sand	Orange	Medium		
16	Sand	Orange	Medium		
17	Sand	Orange	Medium		
18	Sand	Orange	Medium		
19	Sand	Orange	Medium		
20	Sand	Orange	Medium		St Lucia Formation
21	Sand	Orange	Medium		
22	Sand	Orange	Medium		
23	Sand	Orange	Medium		

TABLE 12: Meerensee borehole Log information:

Depth (m)	Lithology	Colour	Texture	Screens location	UNITS
1	Overburden	Light brown	Fine		Kwambonambi Formation
2	Overburden	Light brown	Fine		
3	Sand	Light orange	Medium	SCREEN	
4	Sand	Light orange	Medium		
5	Sand	Light orange	Medium		
6	Sand	Light orange	Medium		Kosi Bay formation
7	Sand	Light orange	Medium		
8	Sand	Light orange	Fine		
9	Sand	Light orange	Medium		
10	Sand	Light orange	Medium		
11	Sand	Light orange	Medium		
12	Sand	Light orange	Medium		
13	Sand	Light orange	Medium		
14	Sand	Light orange	Medium fine		
15	Sand	Light orange	Medium fine		
16	Sand	Light orange	Medium fine		
17	Sand	White	Medium		
18	Sand	White	Medium		
19	Sand	White	Medium		
20	Sand	White	Medium		
21	Sand	White	Medium		
22	Sand	White	Medium		
23	Sand	White	Medium		
24	Sand	White	Medium		
25	Sand	White	Medium		
26	Sand	White	Medium		
27	Sand	White	Medium		
28	Sand	White	Medium		
29	Sand	White	Medium		
30	Sand	Red	Medium fine		Port Durnford Formation
31	Sand	Red	Medium fine		
32	Sand	Red	Fine		
33	Sand	Red	Fine		
34	Sand	Red	Fine	SCREEN	
35	Sand	Brown	Fine		Uloa formation
36	Sand	Brown	Medium		
37	Sand	Brown	Very coarse		
38	Sand	Brown	Fine		
39	Sand	Brown	Very fine		
40	Sand	Brown	Very fine		

TABLE 13: Science Centre borehole aquifer Log information:

Depth (m)	Lithology	Colour	Texture	Screens location	UNITS
1	Sand	Dark brown	Very coarse		Kwambonambi Formation
2	Sand	Reddish brown	Very coarse		
3	Sand	Reddish brown	Very coarse		
4	Sand	Light brown	Very coarse		
5	Sand	Light brown	Very coarse		
6	Sand	Light brown	Very coarse		Kosi Bay formation
7	Sand	Light orange	Very coarse		
8	Sand	Light orange	Very coarse		
9	Sand	Light orange	Very coarse		
10	Sand	Light orange	Very coarse		
11	Sand	Light orange	Very coarse		
12	Sand	Light orange	Very coarse		
13	Sand	Light orange	Very coarse		
14	Sand	Light brown	Very coarse		
15	Sand	Light brown	Very coarse		
16	Sand	Light brown	Very coarse		
17	Sand	Light orange	Very coarse		
18	Sand	Light orange	Very coarse		
19	Sand	Light orange	Very coarse		
20	Sand	Light brown	Very coarse		
21	Sand	Light brown	Very coarse		
22	Sand	Light brown	Very coarse		
23	Sand	Light brown	Very coarse		
24	Sand	Light brown	Very coarse		
25	Sand	Light brown	Very coarse		
26	Sand	Light red	Very coarse		
27	Sand	Light red	Very coarse		
28	Sand	Red	Very coarse		
29	Sand	Red	Very coarse		
30	Sand	Red	Very coarse		Uloa formation Formation
31	Sand	Light red	Very coarse		
32	Sand	Light orange	gravel		St Lucia Formation
33	Sand	Light orange	gravel		
34	Sand	Light orange	gravel		
35	Sand	Dark brown	gravel		
36	Sand	Dark brown	gravel	SCREEN	

TABLE 14: Veldenvlei borehole Log information:

Depth (m)	Lithology	Colour	Texture	Screens location	UNITS
1	Overburden	Brown	Fine		Kwambonambi Formation
2	Sand	Orange	Fine		
3	Sand	Orange	Fine	SCREEN	
4	Sand	Orange	Fine		Kosi Bay formation
5	Sand	Orange	Fine		
6	Sand	Orange	Fine		
7	Sand	Orange	Fine		
8	Sand	Orange	Fine		
9	Sand	Orange	Fine		
10	Sand	Orange	Fine		
11	Sand	Orange	Fine		
12	Sand	Orange	Fine		
13	Sand	Orange	Fine		
14	Sandstone	Orange	Fine		
15	Sandstone	Orange	Fine		
16	Sandstone	Orange	Fine		
17	Sandstone	Orange	Fine		
18	Sandstone	Orange	Fine		
19	gravel	Orange	Very coarse		Uloa formation Formation
20	gravel	Brownish	Very coarse	SCREEN	
21	gravel	Brownish	Very coarse		
22	gravel	Brownish	Very coarse		St Lucia Formation
23	gravel	Brownish	Very fine		
24	gravel	Brownish	Very fine		
25	gravel	Brownish	Very fine		

APPENDIX II

MAPUTALAND PRIMARY AQUIFERS

HYDROCHEMICAL ANALYSES

Table 15 : Alton Aquifers Hydrochemistry

Analytes	Analytical units	Tata2	Tata3
Total alkalinity as CaCO ₃	mg/L	43	48
Nitrogen ammonia as N	mg/L	0.05	0.05
Calcium hardness as CaCO ₃	mg/L	14	19
Calcium as Ca	mg/L	5.7	7.5
Electrical conductivity at 25°C	mS/m	12.6	32.4
Chloride as Cl	mg/L	16.5	42
Nitrate as N	mg/L	0.10	0.10
Sulphates as SO ₄ ²⁻	mg/L	7.2	2.7
Fluorides as F	mg/L	0.30	4.15
Iron as Fe	mg/L	2.91	23.1
Magnesium as Mg	mg/L	2.4	7.9
Manganese Mn	mg/L	0.26	0.26
Magnesium hardness as CaCO ₃	mg/L	10.0	33
Soluble ortho phosphate as PO ₄ ³⁻	mg/L	0.30	0.03
pH at 25°C		6.10	5.43
Potassium as K	mg/L	0.30	2.4
Silica as SiO ₂	mg/L	13	32.9
Sodium as Na	mg/L	7.7	23
TDS	mg/L	49	222
Zn	mg/L	0.13	2.81
Dissolved oxygen(DO)	mg/L	3.8	3.3
Aluminium	mg/L	0.31	0.24

Table 16 : Science Center Aquifer Hydrochemistry

Analytes	Analytical	Science Center aquifer(2003)		
	units	Shallow (8m)	Middle (24m)	Deep (36m)
Total alkalinity as CaCO ₃	mg/L	51	21	104
Nitrogen ammonia as N	mg/L	0.05	0.05	0.22
Calcium hardness as CaCO ₃	mg/L	43	56	79
Calcium as Ca	mg/L	17.5	22.6	31.8
Electrical conductivity at 25°C	mS/m	70.4	77.6	28.4
Chloride as Cl	mg/L	58.9	63.2	16.1
Fluorides as F	mg/L	0.13	0.13	0.11
Iron as Fe	mg/L	0.86	0.57	0.80
Magnesium as Mg	mg/L	24.3	31.0	4.5
Manganese Mn	mg/L	0.14	0.11	0.02
Magnesium hardness as CaCO ₃	mg/L	100	128	19
Soluble ortho phosphate as PO ₄ ³⁻	mg/L	0.13	0.14	0.77
pH at 25°C		5.79	5.42	6.53
Potassium as K	mg/L	2.5	1.3	2.4
Silica as SiO ₂	mg/L	17.2	18.5	16.0
Sodium as Na	mg/L	65.0	74.0	13
TDS	mg/L	407	492	170
Zn	mg/L	0.01	0.01	0.01
Dissolved oxygen(DO)	mg/L	6.7	6.6	6.4
Aluminium	mg/L	0.01	0.01	3.97

Table 17 : Aquadene Aquifer Hydrochemistry

Analyses	Analytical units	Hydrochemistry of Aquadene
Total alkalinity as CaCO ₃	mg/L	23.9
Nitrogen ammonia as N	mg/L	0.14
Calcium hardness as CaCO ₃	mg/L	15
Calcium as Ca	mg/L	6
Electrical conductivity at 25°C	mS/m	28.4
Chloride as Cl	mg/L	13.4
Sulphates as SO ₄ ²⁻	mg/L	8.5
Fluorides as F	mg/L	0.29
Iron as Fe	mg/L	0.11
Magnesium as Mg	mg/L	4.65
Manganese Mn	mg/L	0.51
Magnesium hardness as CaCO ₃	mg/L	19.5
Soluble ortho phosphate as PO ₄ ³⁻	mg/L	0.05
pH at 25°C		6.10
Potassium as K	mg/L	2.4
Silica as SiO ₂	mg/L	22.5
Sodium as Na	mg/L	27
TDS	mg/L	91.5
Dissolved oxygen(DO)	mg/L	4.0
Aluminium	mg/L	1.01
COD		14

Table 18 : Veldenvlei Aquifer Hydrochemistry

Analytes	Analytical units	Veldenvlei 18m	Veldenvlei 26m
Total alkalinity as CaCO ₃	mg/L	440	174
Nitrogen ammonia as N	mg/L	0.01	0.01
Calcium hardness as CaCO ₃	mg/L	96	70
Calcium as Ca	mg/L	38.4	28.4
Electrical conductivity at 25°C	mS/m	55.2	50.2
Chloride as Cl	mg/L	66.3	66.9
Nitrate as N	mg/L	0.11	0.01
Sulphates as SO ₄ ²⁻	mg/L	30.0	19.4
Fluorides as F	mg/L	0.17	0.23
Iron as Fe	mg/L	0.07	0.07
Magnesium as Mg	mg/L	12.2	13.8
Manganese Mn	mg/L	0.27	0.25
Magnesium hardness as CaCO ₃	mg/L	57.0	50.0
Soluble ortho phosphate as PO ₄ ³⁻	mg/L	0.01	0.01
pH at 25°C		7.4	7.8
Potassium as K	mg/L	2.20	2.30
Silica as SiO ₂	mg/L	19.2	13.5
Sodium as Na	mg/L	43.9	57.3
TDS	mg/L	274	308
Zn	mg/L	0.01	0.01
Dissolved oxygen(DO)	mg/L	5.6	2.2
Aluminium	mg/L	0.23	0.23
COD		17	19

Table 19: Birdswood Aquifer Hydrochemistry

Analytes	Analytical units	Birdwood 60m	Birdswood 18m
Calcium hardness as CaCO ₃	mg/L	222	48
Calcium as Ca	mg/L	88.8	19.3
Nitrate as N	mg/L	0.09	0.23
Iron as Fe	mg/L	0.07	1.07
Magnesium as Mg	mg/L	20	5.1
Manganese Mn	mg/L	0.47	0.63
Magnesium hardness as CaCO ₃	mg/L	82.0	21
Sodium as Na	mg/L	197	47
TDS	mg/L	1047	245
Dissolved oxygen(DO)	mg/L	2.3	3
Aluminium	mg/L	0.08	0.23
COD		22	36
Soluble ortho phosphate as PO ₄ ³⁻	mg/L	0.84	0.49
Total Hardness as CaCO ₃	mg/L	304	69

Table 20: Meerensee Aquifer Hydrochemistry

	Analytical units	Meerensee 20m	Meerensee 30m	Meerensee 40m
Total alkalinity as CaCO ₃	mg/L	1872	932	207
Nitrogen ammonia as N	mg/L	0.28	0.11	0.23
Calcium hardness as CaCO ₃	mg/L	425	12	160
Calcium as Ca	mg/L	170.3	5	64
Electrical conductivity at 25°C	mS/m	626	303	579
DO	mg/L	5.8	2.1	2.4
Chloride as Cl	mg/L	64.5	43.1	82.1
Nitrate as N	mg/L	0.09	0.01	0.01
Sulphates as SO ₄ ²⁻	mg/L	25.9	119	57.9
Fluorides as F	mg/L	0.47	0.50	0.46
Iron as Fe	mg/L	0.07	0.07	0.07
Magnesium as Mg	mg/L	0.35	2	10.1
Manganese Mn	mg/L	0.002	0.002	0.36
Magnesium hardness as CaCO ₃	mg/L	1.0	8.0	42
Soluble ortho phosphate as PO ₄ ⁻³	mg/L	0.01	0.01	0.01
pH at 25°C		12.5	12.1	7.5
Potassium as K	mg/L	50.5	17.3	3.9
Silica as SiO ₂	mg/L	1.6	2.6	19.5
Sodium as Na	mg/L	39.7	31.5	40.6
TDS	mg/L	228	266	298
Aluminium	mg/L	0.30	0.54	0.18
COD		626	303	579

Table 21 : St Lucia Aquifer Hydrochemistry

Analytes	Analytical units	Meerensee 20m
Calcium hardness as CaCO ₃	mg/L	3
Total hardness as CaCO ₃	mg/L	10
Calcium as Ca	mg/L	1.10
DO	mg/L	4
Nitrate as N	mg/L	0.48
Iron as Fe	mg/L	0.19
Magnesium as Mg	mg/L	1.70
Manganese Mn	mg/L	0.03
Magnesium hardness as CaCO ₃	mg/L	7
Sodium as Na	mg/L	14
TDS	mg/L	62
Aluminium	mg/L	0.03
COD		122

Table 22 : Mseleni Aquifer Hydrochemistry

Analytes	Analytical units	Mseleni 42m
Calcium hardness as CaCO ₃	mg/L	15
Total hardness as CaCO ₃	mg/L	28
Calcium as Ca	mg/L	6
DO	mg/L	4.3
Nitrate as N	mg/L	0.09
Iron as Fe	mg/L	2.63
Magnesium as Mg	mg/L	3.2
Manganese Mn	mg/L	0.23
Magnesium hardness as CaCO ₃	mg/L	13
Sodium as Na	mg/L	61
TDS	mg/L	302
Aluminium	mg/L	2.42
COD		469
PO ₄ ⁻³	mg/L	1.15

APPENDIX III

MAPUTALAND PRIMARY AQUIFERS

GEOCHEMICAL ANALYSIS

Table 23: Alton Borehole Geochemistry

ANALYTES	Units	ALTON 3		ALTON 2	
		Kwambonambi Formation	Kosi Bay Formation	Kwambonambi Formation	Kosi Bay Formation
Bulk density	(g/ml)	1.20 ($\pm$ 0.07)	1.16($\pm$ 0.03)	1.28 ($\pm$ 0.11)	1.22($\pm$ 0.01)
pH		4.73 ($\pm$ 0.50)	4.89 ($\pm$ 0.50)	5.28 ($\pm$ 0.40)	4.88 ($\pm$ 0.40)
OM	%	2.28 ($\pm$ 0.14)	0.970 ($\pm$ 0.015)	0.933 ($\pm$ 0.060)	0.444 ($\pm$ 0.009)
Ca	%	2.28 ($\pm$ 0.2)	3.12 ($\pm$ 0.6)	1.36 ($\pm$ 0.5)	3.56 ($\pm$ 0.1)
Sand	%	81.6($\pm$ 0.10)	83.4 ($\pm$ 0.3)	88.9 ($\pm$ 0.4)	81.4 ($\pm$ 0.3)
Silt	%	4.32 ($\pm$ 0.44)	1.66 ($\pm$ 0.10)	2.95 ($\pm$ 0.20)	4.80 ($\pm$ 0.10)
Clay	%	14.1 ($\pm$ 0.10)	15.0 ($\pm$ 0.3)	8.18 ($\pm$ 0.60)	13.8 ($\pm$ 0.4)
PO ₄ ³⁻	(g/mL)	1.50 ($\pm$ 0.08)	0.512 ($\pm$ 0.010)	0.740 ($\pm$ 0.010)	0.383 ($\pm$ 0.016)
NH ₄ ⁺	(g/mL)	37.6 ($\pm$ 0.3)	36.4 ($\pm$ 0.5)	42.0 ($\pm$ 0.3)	41.8 ($\pm$ 0.6)
SiO ₂	(g/mL)	3.12 ($\pm$ 0.30)	1.94 ($\pm$ 0.10)	1.46 ($\pm$ 0.30)	22.0 ($\pm$ 0.3)
Mn	(g/mL)	6.07 ($\pm$ 0.20)	6.36 ($\pm$ 0.80)	7.60 ($\pm$ 0.10)	15.1 ($\pm$ 0.9)
Fe	(g/mL)	54.0 ($\pm$ 0.5)	55.3 ($\pm$ 0.8)	48.0 ($\pm$ 0.1)	49.5 ($\pm$ 0.3)
CaCO ₃	%	4.14 ($\pm$ 0.2)	4.82 ($\pm$ 0.9)	1.92 ($\pm$ 0.9)	6.13 ($\pm$ 0.2)

* Analysis for each analytes were done in duplicate

Table 24: Science Center Borehole Geochemistry

ANALYTES	Units	SCIENCE CENTRE			
		Kwambonambi Formation	Kosi Bay/Port Durnford Formation	ULOA Formation	ST LUCIA Formation
Bulk density	(g/ml)	1.44 (±0.20)	1.40 (±0.10)	1.30 (±0.02)	1.26 (±0.01)
pH		5.57 (±0.20)	4.39 (±0.50)	7.60 (±0.10)	7.11 (±0.03)
OM	%	0.653 (±0.070)	0.372 (±0.100)	0.519 (±0.004)	1.57 (±0.002)
Ca	%	3.29 (±0.09)	4.29 (±0.16)	20.1 (±1.0)	19.9 (±1.0)
Sand	%	79.3 (±0.6)	82.4 (±0.2)	86.8 (±0.11)	74.7(±0.1)
Silt	%	1.76 (±0.20)	9.28 (±0.2)	7.72 (±0.10)	10.4 (±0.10)
Clay	%	19.0 (±0.1)	8.36 (±0.08)	5.50 (±0.01)	14.9 (±0.02)
PO ₄ ³⁻	(g/mL)	0.652 (±0.040)	0.604 (±0.080)	0.361 (±0.005)	0.444 (±0.003)
NH ₄ ⁺	(g/mL)	18.7 (±0.4)	25.2 (±0.2)	41.5 (±0.9)	31.4 (±0.7)
SiO ₂	(g/mL)	0.912 (±0.050)	0.401 (±0.010)	0.194 (±0.010)	0.443 (±0.040)
Mn	(g/mL)	0.00(±0.00)	0.00 (±0.00)	0.00 (±0.00)	27.0 (±0.2)
Fe	(g/mL)	60.0 (±0.4)	48.0 (±0.9)	36.0 (±0.2)	86.0 (±0.2)
CaCO ₃	%	8.23 (±0.03)	12.0 (± 0.4)	50.3 (±0.4)	49.8 (±1.4)

* Analysis for each analytes were done in duplicate
Only Kosi Bay formation was considered in the study rather than Port Durnford formation.

Table 25: Aquadene Borehole Geochemistry

ANALYTES	Units	AQUADENE	
		Kosi Bay Formation	Port Durnford Formation
Bulk density	(g/ml)	1.56(± 0.01)	1.36(± 0.02)
pH		3.91(± 0.21)	4.34(± 0.45)
OM	%	1.09(± 0.08)	0.346(±0.004)
Ca	%	3.97(± 0.09)	4.99(±0.07)
Sand	%	87.6(±0.7)	83.2(±0.1)
Silt	%	2.83(± 0.04)	2.44(±0.50)
Clay	%	9.59(±0.70)	14.4(± 0.7)
PO ₄ ³⁻	(g/mL)	0.530(± 0.020)	0.365(± 0.002)
NH ₄ ⁺	(g/mL)	30.4(±0.16)	35.4(±0.1)
SiO ₂	(g/mL)	1.21(± 0.06)	6.43(± 0.05)
Mn	(g/mL)	4.75(±0.20)	0.00(±0.00)
Fe	(g/mL)	38.0(±0.1)	35.0(± 0.4)
CaCO ₃	%	11.6(±0.9)	18.2 (±0.7)

* Analysis for each analytes were done in duplicate

Table 26: Veldenvlei Borehole Geochemistry

ANALYTES	Units	VELDENVLEI BOREHOLE			
		Kwambonambi Formation	Kosi Bay Formation	Uloa Formation	St Lucia Formation
Bulk density	(g/ml)	1.58(±0.20)	1.41(±0.10)	1.42(±0.10)	1.22(±0.10)
pH		4.73(±0.30)	5.50(±0.30)	7.27(±0.10)	7.13(±0.10)
OM	%	0.591(±0.019)	0.393(±0.019)	0.792(±0.024)	0.920(±0.010)
Ca	%	3.07(±0.6)	11.8(±0.7)	20.2(±1.3)	18.4(±0.4)
Sand	%	91.8(±0.5)	83.6(±0.5)	88.0(±0.2)	79.5(±0.5)
Silt	%	4.48(±0.40)	1.48(±0.20)	5.08(±0.20)	10.9(±0.50)
Clay	%	3.74(±0.30)	14.9(±0.70)	6.90(±0.12)	9.66(±0.30)
PO ₄ ³⁻	(g/mL)	0.351(±0.021)	0.054(±0.011)	0.100(±0.060)	0.030(±0.004)
NH ₄ ⁺	(g/mL)	24.2(±0.4)	25.9(±0.5)	25.1(±0.2)	36.7(±0.6)
SiO ₂	(g/mL)	3.04(±0.50)	1.64(±0.10)	0.420(±0.040)	0.470(±0.090)
Mn	(g/mL)	0.000(±0.00)	0.000(±0.00)	0.000(±0.00)	0.000(±0.00)
Fe	(g/mL)	82.0(±0.7)	16.0(±0.5)	48.0(±0.30)	84.0(±0.8)
CaCO ₃	%	7.67(±0.14)	29.4(±0.3)	50.4(±0.8)	48.4(±1.3)

* Analysis for each analytes were done in duplicate

Table 27 : Birdswood Borehole Geochemistry

ANALYTES	Units	BIRDSWOOD		
		Kwambonambi Formation	Port Durnford Formation	St Lucia Formation
Bulk density	(g/ml)	1.69(±0.10)	1.46(±0.10)	1.36(±0.14)
pH		5.32(±0.30)	4.71(±0.20)	7.14(±0.20)
OM	%	0.520(±0.018)	1.10(±0.015)	0.330(±0.011)
Ca	%	3.94(±0.04)	5.69(±0.05)	14.8(±0.2)
Sand	%	97.3(±0.8)	71.4(±0.5)	86.2(±0.2)
Silt	%	1.08(±0.20)	0.530(±0.50)	3.15(±0.10)
Clay	%	1.65(±0.11)	27.7(±0.20)	5.64(±0.02)
PO ₄ ³⁻	(g/mL)	0.594(±0.026)	0.033(±0.001)	1.42(±0.01)
NH ₄ ⁺	(g/mL)	27.8(±0.5)	30.7(±0.3)	23.8(±0.1)
SiO ₂	(g/mL)	0.440(±0.010)	1.64(±0.20)	1.22(±0.20)
Mn	(g/mL)	0.000(±0.00)	0.000(±0.00)	0.0(±0.0)
Fe	(g/mL)	40.0(±0.4)	20.0(±0.8)	45.0(±0.2)
CaCO ₃	%	9.84(±0.02)	14.2(±0.5)	36.9(±0.2)

* Analysis for each analytes were done in duplicate

Table 28 : Meerensee Borehole Geochemistry

ANALYTES	Units	MEERENSEE AQUIFER			
		Sibaya Formation	Kosi Bay Formation	Port Durnford Formation	ULOA Formation
Bulk density	(g/ml)	1.54(±0.10)	1.41(±0.10)	1.34(±0.10)	1.24(±0.03)
pH		6.46(±0.10)	5.91(±0.10)	3.62(±0.40)	8.09(±0.30)
OM	%	0.660(±0.030)	0.580(±0.033)	1.75(±0.50)	0.440(±0.022)
Ca	%	2.29(±0.17)	2.99(±0.03)	6.18(±0.22)	46.7(±1.2)
Sand	%	92.3(±0.3)	87.3 (±0.2)	79.7(±0.6)	81.9(±0.2)
Silt	%	1.92(±0.13)	6.43(±0.55)	5.07(±0.18)	8.84(±0.23)
Clay	%	5.91(±0.50)	6.22(±0.43)	15.20(±0.59)	9.23(±0.44)
PO ₄ ³⁻	(g/mL)	0.080(±0.010)	0.210(±0.012))	0.910(±0.020)	0.450(±0.030)
NH ₄ ⁺	(g/mL)	6.300(±0.010)	14.8(±0.3)	20.2(±0.2)	16.0(±0.2)
SiO ₂	(g/mL)	3.30(±0.20)	2.29(±0.60)	2.48(±0.50)	4.56(±0.60)
Mn	(g/mL)	2.67(±0.10)	3.25(±0.10)	2.53(±0.11)	32.4(±0.2)
Fe	(g/mL)	136(±3)	52.0(±0.3)	206(±6)	202(±9)
CaCO ₃	%	56.9(±0.4)	7.54(±0.25)	6.49(±0.08)	50.2(±0.5)

* Analysis for each analytes were done in duplicate

Table 29 : St Lucia Borehole Geochemistry

ANALYTES	Units	ST LUCIA	
		Kosi Formation Well drained	Kosi Bay Formation Poorly drained
Bulk density	(g/ml)	1.56(±0.20)	1.43(±0.50)
pH		5.58(±0.12)	5.07(±0.10)
OM	%	0.420(±0.020)	4.21(±0.90)
Ca	%	1.77(±0.11)	2.63(±0.21)
Sand	%	96.8(±0.8)	94.1(±0.1)
Silt	%	3.12(±0.27)	4.13(±0.22)
Clay	%	0.060(±0.002)	1.77(±0.38)
PO ₄ ³⁻	(g/mL)	0.340(±0.090)	0.540(±0.010)
NH ₄ ⁺	(g/mL)	32.7(±0.4)	37.6(±0.8)
SiO ₂	(g/mL)	2.37(±0.15)	3.62(±0.24)
Mn	(g/mL)	6.46(±0.25)	4.40(±3)
Fe	(g/mL)	60.7(±0.6)	51.8(±0.9)
CaCO ₃	%	3.62(±0.13)	5.91(±0.18)

* Analysis for each analytes were done in duplicate

Table 30 : Mseleni Borehole Geochemistry

ANALYTES	Units	MSELENI BOREHOLE	
		Kosi Bay Formation (Well drained)	Kosi Bay Formation Leached
Bulk density	(g/ml)	1.62(±0.10)	1.49(±0.11)
pH		5.24(±0.14)	6.25(±0.17)
OM	%	0.610(±0.033)	0.140(±0.017)
Ca	%	1.99(±0.03)	2.70(±0.05)
Sand	%	98.0 (±1.0)	95.9(±0.9)
Silt	%	1.27(±0.24)	1.78(±0.23)
Clay	%	0.750(±0.028)	2.39(±0.2)
PO ₄ ³⁻	(g/mL)	0.390(±0.016)	0.350(±0.024)
NH ₄ ⁺	(g/mL)	14.7(±0.4)	6.77(±0.32)
SiO ₂	(g/mL)	1.73(±0.06)	3.00(±0.82)
Mn	(g/mL)	4.27(±0.15)	1.15(±0.60)
Fe	(g/mL)	41.9(±0.6)	19.5(±3)
CaCO ₃	%	5.06(±0.04)	6.74(±0.19)

** Analysis for each analytes were done in duplicate*

