NOVEL APPROACH OF USING HYDROGEOCHEMISTRY, HYDROGEOLOGIC AND HYDROSTRATIGRAPHIC TECHNIQUES IN EVALUATING COASTAL AQUIFERS IN HEUNINGNES CATCHMENT, SOUTH AFRICA

Submitted by:

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A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

In

Environment and Water Sciences

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October 2019

Keywords

Coastal Aquifers

Electrical Resistivity Imaging

Groundwater Salinity

Groundwater Quality

Hydro-geochemical Processes

Heuningnes Catchment

Seawater intrusion

Geochemical methods

Abstract

The increasing population in search for better social and economic development in coastal areas puts groundwater resources under pressure because of the high fresh water demand for domestic and agriculture use. Seawater intrusion is widely recognised as major concern in coastal aquifers across the globe and is influenced by multiple factors, being climate variation which is projected to adjust recharge of groundwater because of decreased precipitation patterns and to increase sea level variations and over-abstraction due to high freshwater demand as a result of increased population and agricultural practices, thereby inducing salinization in groundwater. The coastal aquifer in Heuningnes Catchment is not exempted from these issues and salinization is a major concern in the area affecting groundwater quality. In Heuningnes Catchment and South Africa in general there is limited knowledge on the application of integrated approach for assessing groundwater quality especially salinization mechanism in coastal aquifers. The main goal of this research is to test and demonstrate the viability of using joint interpretation approach of geophysics, geochemical and geological information to investigate groundwater quality in coastal aquifers thus improving on the understanding of using such approach.

This work offers the initial thorough assessment of groundwater quality and understanding of the salinity sources and hydro-geochemical processes governing the chemical composition of groundwater in the region. Thus provide advice on the fitness of this water for consumption and irrigation purposes. Thirty-two groundwater samples were collected and analysed for (Mg^{2+}), (Ca^{2+}), (Na^{+}), (K^{+}), (Cl^{-}), (SO_4^{2}), (HCO_3^{-}), (pH, TDS and EC). To estimate fitness of groundwater quality for consumption purposes WHO (2011) and SANS241 guideline were used and for irrigation utilization the water quality indices (EC), (Na^{+}%), (SAR), (RSC), (KR) and (MR) were used. Statistics approaches were employed to ascertain the primary geochemical processes governing the chemical composition of groundwater in the research region. Lastly, the spatial distribution maps were created by means of ArcGIS. Electrical resistivity method was used to map the extent of saline distribution within the subsurface.

The findings of this study revealed that groundwater in the region is alkaline type and TDS, EC, Na^+, Cl^- exceeded WHO and SANS241 guidelines for consumption water. The geophysical investigation revealed that the sandy clay/clayey sand, fine sand and fractured sandstone units make up the coastal aquifer systems within the area. Further, revealed that these aquifers were saturated with fresh, saline or brackish water depending on the subsurface layer. The presence of saline and brackish was confirmed by the chemical results which indicated a Na^+-Cl^- type as a dominant water type. Also classifying groundwater based on EC and TDS supports these findings. The foremost hydro-geochemical processes that controls the salinity and quality of groundwater in the study region as indicated by Gibbs plot are water-rock interaction followed by evaporation process. Furthermore, analysis of hydrochemical data also proposes that weathering of silicate minerals, ion-exchange and dissolution of carbonate minerals amended ion concentration in groundwater thus influencing salinisation in certain parts of the study region. Also assessment of ionic-ratios displays influences of marine sprays as well as seawater, on the chemical structure of groundwater within the Heuningnes Catchment aquifer.

Valuation of groundwater quality and its fitness for ingestion and irrigation purposes, the results indicated that shallow groundwater in the area is not suitable for any use; however, groundwater from deeper boreholes was found fresh and appropriate for irrigation and household purposes. Findings of this study indicated that salinity is the major groundwater quality issue for this area and that monitoring of groundwater quality in Heuningnes Catchment is limited. The absence of consistent monitoring program on groundwater quality makes it difficult to ascertain long term trends on groundwater quality parameters. Therefore, this study emphasizes the need for regular groundwater quality monitoring to assess the trends of these parameters in order to make an informed decision as to what can be done for mitigation purposes.

CONTRIBUTION OF THE STUDY

1. PUBLICATIONS [JOURNAL ARTICLE]

Mokoena, P., Kanyerere, T. & van Bever Donker, J. Hydrogeochemical characteristics and evaluation of groundwater quality for domestic and irrigation purposes: a case study of the Heuningnes Catchment, Western Cape Province, South Africa. SN Appl. Sci. 2, 1548 (2020). https://doi.org/10.1007/s42452-020-03339-0

Mokoena, P., Manyama, K., van Bever Donker, J. et al. Investigation of groundwater salinity using geophysical and geochemical approaches: heuningnes catchment coastal aquifer. Western Cape Province, South Africa. Environ Earth Sci 80, 191 (2021). https://doi.org/10.1007/s12665-021-09507-8

Fuku X, Modibedi M, Matinise N, Mokoena P, Xaba N and Mathe M (2019) Single step synthesis of bio-inspired NiO/C as Pd support catalyst for dual application: Alkaline direct ethanol fuel cell and CO2 electro-reduction, Journal of Colloid and Interface Science 545 (2019) 138–152, https://doi.org/10.1016/j.jcis.2019.03.030

Kanyerere, T., Tramberend, S., Mokoena, P., Mensah, P., Chingombe, W., Goldin. J., Sumbul, F., Prakash, M., and Xu, Y., (2018) Water futures and solutions. In Mensah P., Katerere, D., Hachigonta, S. and Roodt A (Eds), Options to enhance water security in Africa systems analysis approach for complex global challenges. https://doi.org/10.1007/978-3-319-71486-8 ISBN 978-3-319-71485-1

2. CONFERENCE PROCEEDINGS AND PROJECT REPORT

Portia Mokoena, Jan Van Bever Donker and Thokozani Kanyerere (2015). The use Electrical Resistivity to map saline water intrusion in coastal aquifers: case study Heuningnes catchment, South Africa, 14th Biannual groundwater conference

Portia Mokoena, Jan Van Bever Donker and Thokozani Kanyerere (2016) Using joint interpretation of electrical resistivity imaging with geochemical data to assess groundwater quality (salinity) in Heuningnes catchment, South Africa during International Young Science Summer Programme [SA-YSSP2015/2016 Cohort], Bloemfontein, Free State, South Africa

Mokoena P, Bever Donker, JV and Kanyerere T (2016) Delineation of brackish/saline groundwater using electrical resistivity survey in coastal aquifers: Heuningnes Catchment, 17th Waternet Conference, Botswana, 26-28 October 2016

Lalumbe L, Mokoena P, Bever Donker, JV and Kanyerere T (2019) Groundwater quality analysis in the Eastern Kalahari Hydrogeological Region, South Africa, WaterNet/WARFSA/GWP-SA Symposium, Johannesburg, Four Ways, South Africa 30 October 2019

Lalumbe L, Mokoena P, Bever Donker, JV and Kanyerere T (2019) Baseline determination and status of compliance for SDG6.3.2 reporting 2nd SADC Conference, Johannesburg, South Africa,4-6 September 2019

Declaration

I, Portia Leah Mokoena declare that the thesis, which I hereby submit for the degree Doctor of philosophy (*Novel approach of using hydrogeochemistry, hydrogeologic and hydrostratigraphic techniques in evaluating coastal aquifers in Heuningnes Catchment, South Africa)* at the University of Western Cape is my own work, that it has not been submitted for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

Full names: Portia Leah Mokoena Date…29 October 2019.................

Signed………………………………

Acknowledgments

I am grateful for the grace of God that carried me through the entire process of starting and completing this thesis. Without his love and mercy I would not be here and have the strength to accomplish what I have. I also want to extend my gratitude to my supervisors Prof Jan Van Bever Donker and Dr Thokozani Kanyerere who never gave up on me and pushed me to complete this work, their efforts, constructive criticism and guidance have encouraged me and made this possible. I thank my mother Norah Ngwenya, my sister Goodness Mgijima and my family for showing love and support throughout. I am also grateful to my husband Dr Xolile Fuku who was and is the pillar of strength always. I want to show my appreciation to the Department of Water and Sanitation (DWS) for assisting me with data, my DWS colleagues who supported me Chetty Thiruvheni, Lindelani Lalumbe, Charles Pule for landing a helping hand, the Maleka family for their encouragement. I thank NRF for funding my study not forgetting WRC for allowing me to be part of their project. Also special thanks to the EWS team who assisted during field work, SANparks's Agulhas National Park, Heuningnes farming community for allowing this project to take place in their farming land.

This thesis is dedicated to my beautiful children; Luthando, Lwandle and my late son Lukhanyo Fuku rest in peace my baby.

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Acronyms and abbreviations

µS/cm	milisiemens per centimetre
Boreholes	BH
Ca^{2+}	Calcium
CA	Cluster Analysis
CAB	Cation- Anion Balance
CFB	Cape Fold Belt
Cl^{-}	Chloride
DRIF	Elandsdrift-Wiesdrif
DWA	Department of Water Affairs
DWAF	Department of water Affairs and Forestry
DWS	Department of Water and Sanitation
DWS	Department of Water and Sanitation
EC	Electrical Conductivity
ER	Electrical Resistivity
FA	Factor Analysis
FAO	Food and Agriculture Organization
GIS	Geographical Information System
GPS	Global Positioning System
HCA	Hierarchical Cluster Analysis
HCO_3^{-}	Bicarbonate
IAEI	International Atomic Energy Agency
IGRAG	International Groundwater Resources Assessment Centre
K^{+}	Potassium
KR	Kelly's Ratio
m	Meters

MAP	Mean Annual Precipitation
mg/L	milligrams per litre
Mg^{2+}	Magnesium
MR	Magnesium Ratio
Na^{+}	Sodium
PCA	Principal Component Analysis
PZ	Piezometer
QA/QC	Quality Assurance/Quality Control
RMS	Root Mean-Squared error
RSC	Residual Sodium Carbonate
SANS	South Africa National Standards
SAR	Sodium Adsorption Ratio
SO_4^{2-}	Sulphate
SPSS	Statistical Package for Social Sciences
T	Temperature
TDS	Total Dissolved Solids
TMG	Table Mountain Group
VOEL	Voelvlei
WHO	World Health Organization
WRC	Water Research Commission
ZOEN	Soetendalsvlei

Chapter 1: INTRODUCTION

1.1. Background

Groundwater is the most important source of freshwater on planet earth, which makes it an essential source for human consumption and the overall development of a region (Kumar et al. 2013). On a global scale two thirds of the freshwater resources in the world is from groundwater (McQuarrie, 2012). For decades the development of groundwater has provided a source of socio-economic benefits to humanity and currently groundwater is projected to supply over fifty percent of consumption water globally (Adewuyi et al. 2010). The resource serves as a critical buffer during periods of droughts especial in arid and semi-arid areas where water is limited and seasonal like South Africa.

South Africa is recognised as a semi-arid state, unlike most other countries, water is scarce and to date freshwater resources of the country are under great stress. Most of South Africa's water supply is sourced from groundwater (Mukheibir, 2010), over 60% of the South African population benefit from groundwater supply for consumption, agricultural and industrial uses (Lourens, 2013). Currently, 27% of the total volume of water resource in South Africa is from groundwater resources, about 60% of this is utilised for irrigation and only 8% accounts for mining and domestic water supply (DWS, 2016). According to Kinoti (2018) utilisable groundwater exploitation potential is about 10 343 million m^3 each year (or 7 500 million m3 per year in drought circumstances) while the quantity that is in usage currently is reported to vary from 2000 and 4000 million m^3 each year**.** Groundwater in the country is considered as the key element in the fight against poverty; however, its shortage in terms of quantity and quality serves as a stumbling block for the country's socio-economic growth.

Groundwater quality in South Africa is considered potable for major part of the country, however, groundwater with high levels of salinity is marked in the very arid regions and some coastal regions of the country (DWS, 2016). Human activities such as urban developments, mining and agricultural practices are some known issues affecting groundwater quality and quantity concerns in the country as reported by (DWAF, 2000). However, the geological aspect of it is often not well explored and it exerts quite a role in the chemical evolution of groundwater. The use of groundwater is often determined by its quality, and the quality of groundwater is often threatened by salinity. Normally salinity in groundwater can be explained using the chloride or TDS content (TDS) (Monjerezi, 2012). High concentration of salinity in groundwater restricts its utilisation for various purposes. This does not only cause restriction but also enhanced mobilization of possibly poisonous minor elements in groundwater, mainly owing to development of metal-chloride complexes (Monjerezi, 2012). Most of the population residing in coastal areas are dependent on groundwater as their key source of fresh water provision. However, high content of salinity in coastal groundwater has caused restrictions for domestic and agricultural usage of this resource.

Naturally coastal aquifers are more delicate and overexploitation of groundwater resources from these aquifers has increased the risk of being depleted in various areas around the world (Sonkamble, 2014). Although groundwater in coastal aquifers is abundant, quality remains the main concern. Therefore, quality of groundwater should be similarly considered as quantity due to the fitness of water for different applications. The observed variations in groundwater quality in a particular zone is a function of physical and chemical parameters subjected to different geological formations and anthropogenic activities (Prasath et al. 2012). However, for coastal aquifers the chemical configuration of groundwater reflects not only the geology of the area and or period the water is in interacts with the rock medium, but also reflects contributions from seawater intrusion.

Salinization of coastal aquifers is a major growing concern, groundwater in coastal aquifers become saline as an outcome of seawater intrusion. Seawater intrusion if often accelerated by the increase of population in coastal areas because they often rely on fresh groundwater resources for domestic, industrial and agricultural uses (Lewis et al. 2004; Gaaloul et al. 2012). This high demand of freshwater has introduced problems to coastal aquifers, such as depletion of shallow aquifers resulting in declining water levels (Trabelsi et al. 2006) because of overexploitation which in turn increase the chances of salt water encroachment. Despite, seawater intrusion known as the major basis of saline groundwater in coastal aquifers as identified by various studies (Sonkamble, 2014; Badana et al. 2018), it is however, not the only source, other sources include sea spray, past marine transgression, infiltration of saline surface water and so on. Depicting individual elements liable for groundwater contamination in coastal areas is very complex, since there are multiple factors causing salinization of groundwater in coastal aquifer therefore, it is necessary to use integration approach to acquire a clear image of the groundwater quality variations.

To understand groundwater quality variations in coastal aquifers the facts about spatial distribution of fresh/saline groundwater and the processes that control the advancement of salinity becomes an important component. There are various methods available for assessing groundwater quality in coastal aquifers. Geophysical and geochemical methods being the most used ones and have been used by a number of studies around the world, (Kelly, 2011; Tembo, 2014; Chongo et al. 2015) used geophysical methods to investigate groundwater salinity whereas Monjerezi (2012) used the hydro-geochemical method to better understand the sources of saline/brackish groundwater resources. It is clear from the literature that using these methods in isolation may hinder important information that can provide comprehensive understanding of the total groundwater quality status of a particular area especially in coastal aquifer which is mostly affected by various factors. A number of studies have combined geochemical and geophysical studies to study groundwater quality in coastal areas around the world (Craig, 2008; Sonkamble, 2014; Khaki et al. 2014), seawater mixing (Sathish et al. 2011; Oyeyemi et al. 2015 Badana et al. 2018). Therefore, integrated approach is slowly gaining interest in groundwater quality investigations across the globe more especially in topics involving identification of sources of salinity in coastal areas.

Geophysical method is one of the preferred methods when it comes to assessment of salinity in groundwater, mainly because of its high sensitivity to salinity or pore-water in the subsurface and its capability to differentiate the contrast in resistivity values between freshwater and saltwater (Kelly, 2011). Also, the fact that it is also a cheaper option compared to drilling exploration methods and in addition it can cover large areas in a short space of time. However, the geophysical method has its own limitations: it cannot reveal the geochemical facies present within an aquifer, mixing processes that often give details regarding the origin of salinity within the aquifer and the fitness of groundwater for a particular purpose, whereas on the contrary the geochemical method is able to do so and provide insight to the prevailing quality of groundwater. Therefore, in order to supplement the limitation of geophysical methods in hydrogeological investigations, hydro-chemical analysis of groundwater samples can be used in conjunction with the geophysical method to obtain a full comprehensive image of groundwater quality in coastal aquifer systems.

This study intends to demonstrate the feasibility of using the joint interpretation approach of geochemical, geological and geophysical techniques to assess groundwater salinity in coastal aquifer environment. The assessment is limited to the chemical configuration of groundwater, ascertaining the chemical types of groundwater, outlining the processes governing the groundwater chemistry and evaluating the groundwater quality for consumption/irrigation uses. With this approach an understanding of the hydro-geochemical evolution of different groundwater types, the mixing behaviour between different end- members, groundwater age and vertical and horizontal distribution of groundwater can be achieved.

1.2. Scope and nature of the Study

The main goal of this study is a contribution towards scientific knowledge on the application of an integrated approach for groundwater quality assessment in coastal aquifers. This study aims to provide information of the source(s), mechanism(s) of formation and hydro-geochemical progression of saline groundwater prevailing in both the shallow and deep aquifer systems in the Heuningnes Catchment (Western Cape). General emphasis is on the characterisation, analysis and interpretation of hydro-geochemical, hydrogeological, and geophysical data as a joint approach in improving understanding on the evolution of groundwater salinization processes in a coastal aquifer system within a catchment. The study will also map water quality in different hydro-geologic units and assess the fitness of this water quality for consumption and agricultural purposes.

This includes (1) collecting and analysing water samples for major- and minor-ion chemistry; (2) characterizing lateral and vertical differences in ground-water chemistry; (3) interpreting the source, movement, and relative age of ground water, with a focus on discriminating between natural ground water and seawater and (5) analyse geophysical subsurface data. (6) Map the major geological structure controlling groundwater flow, (7) asses the role of stratigraphy for groundwater salinity distribution in Heuningnes catchment.

1.3. Research justification

In general, coastal aquifers are known to be the significant source of freshwater supply in many states around the globe, particularly in arid and semi-arid regions. As population increases and agricultural activities rise, so does the demand for freshwater supply. There is no doubt that this increased demand has placed enormous stress on coastal aquifers which may have led to the introduction of saltwater intrusion.

Under normal, uninterrupted conditions, hydraulic gradient in the aquifer containing freshwater is expected to have a seawards flow direction. This is changed when seawater enters the aquifer system, because of the fact that it has higher density than freshwater as it carries more solutes. Thus, the denser saltwater flow in from the sea and a wedge-shaped form of saltwater is created underneath the less dense freshwater and gradually increases the salinity (Rahman and Bhattacharya, 2014). By far the intrusion of saltwater in coastal aquifers is the most recognised source of pollution and it has clear implications for groundwater utilisation. Groundwater in the region is the chief source of water supply and any threat to this resource will lead to problems in the socio-economic development of the area and affect crop production since the area practice commercial farming.

The highlights of groundwater quality in the area were reported almost two decades ago with the recent being seven years ago, thus this study wishes to provide a more recent detailed and comprehensive valuation of groundwater quality in the research area. The identification of sources contributing to salinity, groundwater types and geochemical processes controlling the chemistry of groundwater which were not covered in earlier studies were covered in this study. This study did not just assess groundwater quality but also demonstrated the feasibility of using a joint interpretation approach to evaluate the quality of ground-water in coastal aquifers. The findings of this study therefore, provide sound background information regarding groundwater quality and also highlights affected areas in terms of salinity which will then advice as to where to site boreholes/wells for potential groundwater exploration in the area. In addition, the challenge of data availability will be eliminated which will ease the stress in future research interests.

This study is significant also, because it forms part of a big assignment initiated by the Water Research Commission-WRC to study the entire Catchment with the aim of understanding the sustainability of surface water bodies and the role that groundwater plays in the catchment as well as the salinity problems prevailing in the catchment. This project was conducted concurrently with other WRC funded projects. The other projects focused on Aquifer characterization and groundwater flow systems; Groundwater Recharge System; Water use using remote sensing and hydro-census methods; Water Quality using hydrochemical analysis image and isotope; Water balance Study; Landcover-Landuse characterization; Stream contribution and imaging effect of alien vegetation; surface and groundwater interactions. The current study incorporated selected results from some of these projects. This project together with other projects fulfils the major goal of the WRC to generate knowledge about the catchment.

1.4. Statement of the Research Problem

Heuningnes Catchment has a great potential for irrigated agriculture therefore, development of groundwater resources of good quality is highly beneficial. However, the area is experiencing water quality problems such as groundwater salinity. Between 1998 and present the work that has been done on the catchment involved hydrogeological assessment of the study area for the purpose of drilling boreholes for water supply by Toens et.al. (1998). Later SRK consulting, HilLand

Associates (2008) also conducted preliminary geological and hydrogeological investigations. The results from these investigations all acknowledge the occurrence of saline groundwater and that the groundwater is not suitable for consumption and irrigation purposes in some parts of the catchment. Although, they did highlight the status of groundwater quality, there was however, no follow-up in-depth investigation to understand the variation in groundwater quality specially the actual source of salinity, the processes governing the chemistry of groundwater and the general groundwater type in the area were not reported. There is no published or unpublished work that is intensively assessing the quality of groundwater the area. Thus, a gap exists in this sense and without the knowledge of how groundwater (fresh or saline) is spatially dispersed and the processes determining the development of salinity and the general groundwater quality status in the catchment, it is difficult to advice on future groundwater resource planning. The lack of scientific explanation on the variation of groundwater quality and the limited knowledge on the use of joint approach in assessing groundwater quality in the area and coastal areas of South Africa in general has prompted this study. Therefore, this study attempt to close that gap by improving the knowledge on the use of a joint interpretation approach to assess groundwater quality in coastal aquifers, thus providing comprehensive assessment of groundwater quality in the area including its fitness for various uses.

1.5. Research Question

The main question this study seeks to answer is can a comprehensive assessment of groundwater quality be achieved through a joint approach of geophysics, geochemical and geological interpretation in coastal aquifers?

The sub-questions following the main question are as follows:

- What are the principal factors and mechanisms controlling the geochemistry of the groundwater?
- What are the variants of electrical resistivity underneath the surface and the main distribution pattern of saline groundwater in the region?

- What is the quality of groundwater and its fitness for consumption and irrigation purposes?
- Which part of the aquifer system is affected by salinization, and is there a clear distinction among fresh-water and salt water zone within the aquifer?

1.6. Research Hypothesis

Effective management of coastal ground-water resources doesn't hinge on planning and regulations only but on the exact estimate of the behaviour of saltwater-freshwater interface relating to natural and man's development activities as well. This study contends that using a combination of geophysical, geochemical and geological information in a multi-technique approach can advance the existing knowledge of groundwater salinization processes in coastal aquifers. The hydro-chemical conceptual model from this study can be used to predict/map the source and movement of groundwater salinity in coastal aquifers and areas with similar geological settings. This conceptual model can be tested and calibrated accordingly and be used for management purposes, such as planning for better intervention programs and for demarcation of protection zones. It will also improve the understanding on groundwater occurrence, flow patterns, the extent and spatial variation of groundwater quality from recharge to discharge in the area.

1.7. Research Aim

The core objective of the research is to test and demonstrate the feasibility of using joint interpretation approach of geophysics, geochemical and geological information to investigate groundwater quality in coastal aquifers thus improving on the understanding of using such approach.

1.8. Research Objectives

- To examine the link concerning groundwater chemistry and geology in order to recognize the dominant Hydro-geochemical processes controlling the spatial variation in the chemistry of the groundwater.
- To evaluate the feasibility of mapping groundwater quality through a joint approach of geophysics, geochemical and geological information.

- To appraise the spatial and temporal groundwater quality and its fitness for consumption and irrigation uses.
- To identify parts of the aquifer systems that are contaminated by salinity thereby delineating fresh/salt water interface.
- To map and infer, the distribution of electrical resistivity in the subsurface by means of electrical resistivity imaging.

1.8. Significance of the Research and Contribution to Science

In many coastal areas like the current study area, groundwater is the only supply of freshwater for domestic and agricultural needs. However, groundwater in coastal areas is constantly under threat of saline water intrusion which has now become a global problem. Therefore, understanding the factors contributing to salinity and the extent of saline water distribution in the coastal environment helps in devising appropriate strategies for managing and protecting groundwater resources thus demarcating groundwater protection zones.

This current study is important because it provides new and most recent information on the groundwater geochemistry, and occurrence of fresh and saline groundwater quality, which is likely to explain the processes that determine salinity in the catchment. Limited knowledge on the actual hydro-geochemical processes active in the aquifer system of the region makes it impossible for sustainable exploitation of available groundwater resources.

Thus this study intends to contribute to the baseline geochemical information of the study area. To provide references on the suitable areas for and depths to fresh groundwater resources, thus, improving success rates of drilling for fresh supply of good quality consumption water. This will result in increased access of groundwater which is the prime factor in improving poverty, stabilizing populations and minimising the need for farmers to migrate when drought threatens agricultural livelihoods.

The study will also improve the knowledge on the application of the joint approach of using geophysical, geochemical and geological data for assessing groundwater quality (salinity), especially in coastal aquifers. This study is also important because it will contribute to the science/research community through publications. Thereby, giving circumstantial evidence, to water resource experts, researchers and the public in general, regarding the magnitude, distribution and severity of groundwater salinity in the Heuningnes Catchment.

The study uses a case approach to understand the current status of groundwater quality in Heuningnes Catchment. Currently groundwater quality varies significantly in the study region, with the key problem being the increasing salinity in groundwater. The cause of this salinity is unknown; there could be many factors associated with it such as salinization by seawater intrusion, geological influence or anthropogenic effects etc. There are many negative outcomes associated with high saline groundwater such as health complications, decrease agricultural yields and returns, destroyed fertile agricultural lands, jeopardized livelihoods, increased expenses of infrastructure maintenance, charges of industrial processes and change or even destruction of ecosystems. Therefore, it is imperative to understand the causes of salinity to be able to prevent it from contaminating the remaining fresh water resource. Exploitation of groundwater resources is of great developmental interest in the study area because of the potential for irrigated agriculture.

1.9. Outline of thesis

This thesis explains the origin and occurrence of groundwater salinity in coastal aquifers from geologic, hydrostratigraphic, hydrogeologic and hydro-geochemical aspects, and evaluates the fitness of water for consumption and agricultural purposes. This thesis consists of 8 chapters in total the outline of the thesis is presented below:

Chapter 1 Introduction: Chapter one presents an overall background about groundwater salinity and briefly defines the objectives, research problem statement, research questions and thesis outline.

Chapter 2 Literature Review-: This chapter gives a theoretical background of the applied research approach. This involves the review on basic groundwater assessment methods and principles, quality in terms of salinity, a review on hydro-geochemistry, hydrogeology, geophysical controls on groundwater occurrence and salinity. This chapter is divided into subsections, each focusing on a specific objective and ending with a summary of the chapter

Chapter 3 Study Area Description: The chapter describes the study region with respect to its position, topography, climate and rainfall, land use, geology and hydrogeology setting.

Chapter 4 Methodology and Research Design: Full description of the sample sites and methods such as data collection, data analysis methods, QC/QA and ethical consideration will be discussed in detail in this chapter.

Chapter 5: In this chapter the distribution and the extent of saline groundwater within the coastal aquifer is mapped using geophysics. This chapter also seeks to show the reliability of using electrical resistivity for mapping saline groundwater in coastal environment.

Chapter 6: Hydro-geochemical Analysis: In this chapter the dynamics of salinity in the shallow coastal aquifer system and its origin, water types and geochemical processes will be explained. In this chapter also the conceptual model will be developed and defined.

Chapter 7: This chapter will evaluate groundwater quality and its fitness for domestic and irrigation purposes.

Chapter 8: This chapter provides general conclusion of the entire study and list significant recommendations for future works. General conclusion will be drawn from the combined outcome of the three sub-disciplines.

Chapter 2: Review of Literature

2.1. Introduction

This chapter wishes to deliberate groundwater quality issues in particular salinity issues in a coastal environment and the approaches that are used to evaluate groundwater quality in such an environment. The chapter starts with an overview of the origin and occurrence of groundwater salinity in coastal aquifers, followed by the theoretical framework of groundwater quality. It then proceeds to discuss factors that affect groundwater quality and possible sources and processes that add to saline groundwater in coastal aquifers. It concludes by discussing the various methods of assessing groundwater quality especially in coastal areas, starting with geophysical techniques followed by hydro-geochemical, modelling methods, and lastly multivariate techniques for groundwater quality assessment. These methods will be used to address the objectives of the study.

2.2. Groundwater occurrence

Groundwater is regarded as one of the most essential resource on the earth. It is mostly needed for household, irrigation and industrial uses as well as to maintain soil moisture, stream flow, wetlands the ecosystem. Water that exists below the subsurface generally in soils, fractures and permeable geological formations is defined as groundwater Freeze and Cherry (1979). Generally, it accounts for about 97% of the earth's usable freshwater resource. It starts of as meteoric water from precipitation in the form of rain or snow (IAEA, 2004). Not all water from precipitation can infiltrate the groundwater as some is lost through evaporation, some in transpiration and some to stream flow; only the excess of water then infiltrates the ground where it is stored as groundwater in saturated or unsaturated zone separated by the water table.

The hydrological cycle also known as the water cycle (Figure 2.1) is a conceptual model that describes the uninterrupted flow of water above, on, and beneath the subsurface (Lourens, 2013). The movement of water within the hydrologic cycle occurs through various forms such as rainfall, runoff, interception, infiltration, evaporation, storage, transportation and percolation.

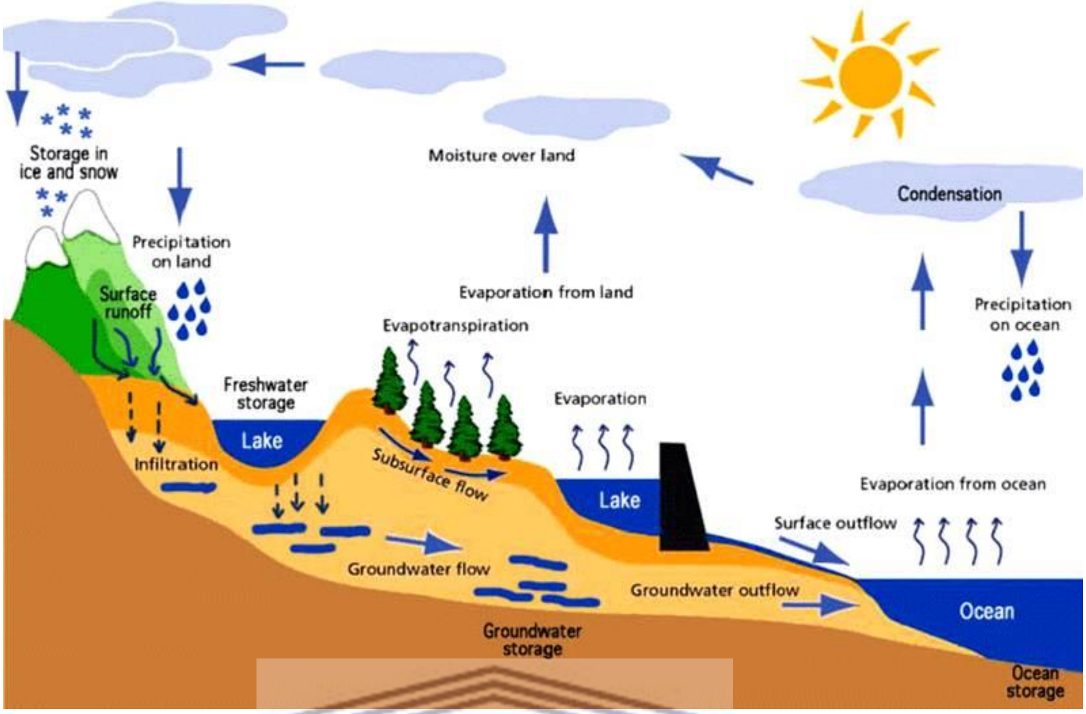


Figure 2. 1: Hydrological cycle showing the movement of groundwater (Lourens, 2013).

Basically water evaporates from the oceans in enormous quantities as rainfall either on land surface or ocean. The precipitation that lands on the ground evaporates, transpired by plants, runs off, or penetrates into the subsurface. Between these different phases of the Hydrologic Cycle, the water transfers between provisional storage zones (Figure 2.1) which are often called reservoirs (Lourens, 2013). The water that penetrates the soil will slowly move down-gradient (groundwater flow) and will eventually end up in the ocean reservoirs. Precipitation, vegetation, soil water content and surface gradient are the principal factors known to decide on the amount of water to be infiltrated in the groundwater system.

2.2.1. The occurrence of ground-water in coastal environment

The vulnerability of groundwater resources in coastal regions as an effect of social and economic advancement has been recognised by many around the world (Cary, 2015) and this has led to high water demand to supplement the growing needs of consumption water supply and agricultural practices. As climate changes, groundwater recharge patterns are modified because of the decrease precipitation, and sea level rise variations increases (Post et al. 2018). These factors put coastal aquifers in danger of seawater intrusion which causes salinization thus altering the quality of groundwater as a result of groundwater over-abstraction.

Coastal aquifer systems are considered as intricate environments (Kumar, 2016), whereby the distribution of fresh and saline waters is controlled by various factors such as groundwater well pumping rates, spatial and temporal variations in the flow field geological heterogeneity, and surface-ground water interactions, (Rahman and Bhattacharya, 2014). Fresh groundwater occurring in coastal aquifers meets up with the saline water from the sea. In coastal aquifers that are hydraulically linked to the sea, a boundary exists where fresh groundwater transition to saline groundwater.

At this point where both fluids are present in the aquifer, seawater will move at the foot of the aquifer and freshwater will float on top mainly because seawater is slightly denser than fresh groundwater (Nair et al.2015). thus will form a wedge like shape termed the diffusion zone where mixing occurs (Figure 2.2). This mixing zone is also known as the saline interface where the mixed water transforms from fresh water to that of seawater (Craig, 2008) this is a result of process of dispersion and molecular diffusion. According to the Ghyben-Herzberg relation the density difference between saltwater and freshwater is an important factor for the approximation of the depth to salt-water based on the thickness of the freshwater above sea level Rahman and Bhattacharya (2014). Under normal conditions, equilibrium exists within an aquifer, with excess freshwater flowing to the ocean (Ramli, 2009), however, a slight change in the hydrological conditions (Lee, 2015) as a results of. excessive groundwater extraction from the upper fresh water body will result in the interface shifting towards inland and upwards (Figure 2.2), thereby introducing saline groundwater which will be a threat to groundwater in the wells and the environment. In (Figure 2.2) (a) denotes undisturbed condition, (b) denoted saltwater intrusion owing to groundwater abstraction.

Theory states that for every 1 meter that the water table adjacent to a wetland is raised above the water level within the wetland, fresh-saltwater interface will stabilise at a depth of about 40 m (Anderson, 2017). Over-abstraction of groundwater will introduce problems because for every 1 m that the water table is pumped down for irrigation, domestic, mining or industrial use, the fresh-saltwater interface will rise by approximately 40 m. seawater will intrude freshwater aquifer and this process if often intensified by pumping freshwater at high rates or pumping a number of wells at the same time (Klassen et al. 2014) this process impact the natural balance between freshwater and saltwater thus shifting the hydraulic gradient. Therefore, pumping of groundwater from aquifers adjacent to saltwater bodies should be critically managed. Furthermore, the chloride content of groundwater from wells located close to the coast should be checked, because rising levels of chloride in groundwater from these wells may be a reasonable indication of saline intrusion (Igrac, 2008). In cases where depths of wells are not available for obtaining groundwater quality data for salinity purposes, field measured EC values can be used as an alternative indicator for salinity, as EC-values are also good indicators of salinity.

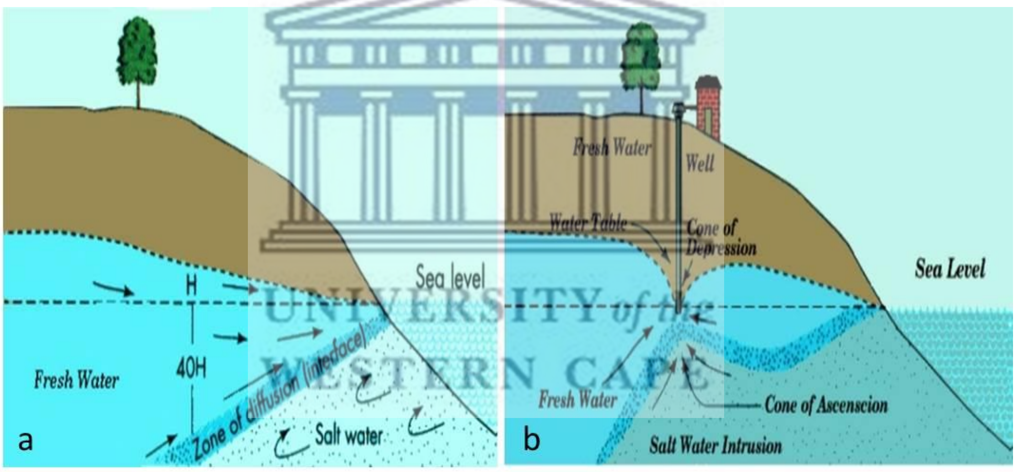


Figure 2. 2: Interaction between fresh groundwater and saline seawater).

2.2.2. Origin and occurrence of saline groundwater in coastal aquifers

Ground-water in general contains concentrations of dissolved salts such as sodium chloride, magnesium, calcium sulphate and carbonates and their concentration differs depending on the location on the earth (Tembo, 2014). The concentration level of these salts defines the quality of water as saline or not. Salinity in groundwater is often expressed as total dissolved solids in (mg/L) however, Cl^- content (mg/L) or EC, in (µS/cm) are used as classification for groundwater salinity (IGRAC, 2008). Because TDS and EC account for the activity of all the bodies dissolved in water, they are used as the main indicators of salinity, whereas the chloride concentration is a specific indicator of water more especially in seawater (Post et al. 2018), given the content of TDS as tabulated in Table 1. Different classifications are used to rank water resources based on levels of salinity. These classifications differ in numbers and names of classes, values of class limit and the parameters to which class limits are related (e.g. Cl^-, EC, and TDS content). In this study the classification presented by Freeze and Cherry (1979) was used, which is established from TDS levels (Table 1).

Table 1: Water salinity classification

Class name	Class limit (TDS range in mg/L)
Fresh water	0 to1000
Brackish water	from 1000 to10 000
Saline water	from 10 000 to 100 000
Brine	> 100 000

Modified after Freeze and Cherry (1979)

In coastal aquifers groundwater quality is strongly inclined to the contact between the sea and the adjoining aquifer system. During this process two things can happen either freshening of saline aquifers or salinization of fresh-water bodies. In some cases, both situations can occur in one aquifer medium. Although the freshening or salinization process is hydro-dynamically motivated (Kumar, 2016), the physical and chemical process within the aquifer also plays a major role in changing groundwater composition. Such as cation exchange process as it results in a hydrochemical spectrum of groundwater types reflecting both the hydrodynamic and hydrochemical characteristics of the aquifer. Other geochemical processes used to explain groundwater salinization include seawater intrusion as a result of over-exploitation (Post et al. 2018), deep saline palaeo-waters e.g. estuarine/marine water recharged during past transgressions, which progressed through interacting with fresh-water, rock-water interface or after evaporation in lagoons (Cary, 2015), evaporites dissolution with/without additional water-rock contacts.

Therefore, the understanding of groundwater quality in its natural form and active processes governing it within a coastal aquifer, Walraevens and van Camp (2004) suggest a good knowledge of hydrodynamics and hydrochemical behaviour and the linkage between them, because it is the interaction among the two that can only elucidate the apparent quality distributions. Groundwater flow and the hydro-geochemical processes along the flow-path have a strong hold in the resultant groundwater quality distribution, therefore, an integrated approach of both hydrochemical and hydro-dynamically analysis is crucial.

To assess groundwater quality and predict saline groundwater in coastal aquifers direct and indirect methods have been widely applied around the world. These include modelling, geophysical methods (electrical resistivity), hydrochemical and isotopic techniques. The direct methods which are groundwater sampling for isotopic indicators and hydrochemistry normally encompass boring of wells/boreholes or using current bore/well networks for sampling and chemical analysis of groundwater. The boreholes can assist in establishing groundwater movement patterns, established from measured piezometric levels, and to define the susceptibility of a coastal aquifer to seawater invasion.

2.3. Groundwater quality assessment using Geophysical methods

Geophysical methods have successfully proven to be the most accurate and dependable means of all surveying for subsurface investigations (Alisiobi and Ako, 2012). The spatial distribution of the physical properties of the subsurface such as geological formation, fluid content and its quality can be easily understood by using geophysical techniques (Craig, 2008). Geophysical methods are able to assist with the visualization of geological units and salinity underneath the ground particularly where borehole records are lacking, or resources are inadequate. However, geophysical methods cannot directly conclude on water quality or the geologic units beneath the subsurface. The distributions and magnitudes of the physical properties found from geophysical surveys should be interpreted in conjunction with the geology of the area and chemical analysis to obtain more accurate results.

In groundwater exploration a number of geophysical methods are used. These are electrical resistivity, electromagnetics, seismic, ground penetrating radar, gravity and magnetic methods. These methods are used to determine thickness and composition of the subsurface layers, as well as depth to rock for the purpose of identifying water bearing zones. Some are used to conclude the amount of water present in the aquifer (District et al. 2012). Among these methods the electromagnetic and electrical resistivity techniques are the most applied geophysical methods when it comes to groundwater exploration, especially when investigating groundwater quality in terms of salinity. This is because groundwater occurrence tends to lessen the resistivity of all rocks and sedimentary materials via electrolytic conduction (Cherop, 2016). Electrical resistivity is a basic function of groundwater chemistry; thus the degree of saline intrusion can be readily interpreted. It can easily discriminate a great resistivity divergence between the presence of seawater that strongly reduces the resistivity values and a saturated freshwater layer (Mogren, 2015) this makes it ideal for salinity investigation studies.

Electrical resistivity is a non-invasive method and it offers quick cost effective access to information about the subsurface properties, such as thickness of layers, fracture zones and faults, depth to bedrock, position and orientation of bedrock fractures (Khaki et al. 2014). The method investigates the subsurface by analysing the electric potential distribution that reflects geo-electrical structure. During the application of this method valuable subsurface information can be acquired without damaging the ground, or unearthing hazardous materials underground as this method required minimal contact with the ground. Jansen (2011) states that resistivity surveys are important for mapping aquifer and aquitard systems, demarcate areas of saline water or brackish water and to also identify nearly vertical structures such as faults that may exert certain force in the migration of groundwater.

2.3.1. Theoretical background of the Electrical Resistivity method

Electrical resistivity surveys are meant for defining the subsurface resistivity distribution by making measurements on the ground surface. The accurate resistivity of the subsurface can therefore, be estimated from these measurements. The resistivity of different earth materials is not the same because resistivity of the ground is often controlled by various factors such as available fluids, mineralogy, porousness of the rocks/ soil and amount of water saturated in the rock (Loke, 2001). For instance, igneous and metamorphic rocks often have high resistivity values (1000 Ω.m to 10 000 000 Ω.m) depending on the intensity of fracturing and proportion of the fractures filled with groundwater.

The resistivity varies depending on the rock's physical condition like whether it is wet or dry. This is normally beneficial in the uncovering fracture zones and other weathering elements for instance in engineering and in groundwater surveys. Sedimentary rocks on the other hand, have lower resistivity values compared to igneous and metamorphic rocks due to the fact that they are more porous and have relatively high water contents. Therefore, their resistivity values range from 10 to 10 000 Ω.m, with most values below 1000 Ω.m. In this case resistivity values are influenced by the available pore spaces of the rock and the salinity of the contained water.

Loose sediment will exhibit lower resistivity values compared to sedimentary rocks. Here resistivity values depend on the clay content present as well as porosity, provided that all pores are saturated. In most cases clayed soil will have lower resistivity values than sandy soil. When it comes to groundwater, resistivity ranges from 10 to 100 Ω.m subjected to the degree of dissolved salts. Seawater has high salt content therefore, it will have resistivity values of 0.2 Ω.m or less, this is the why the resistivity technique is more suited for mapping the saline and fresh water boundary in coastal areas (Loke, 2001) or mapping water quality in general. Table 2 shows resistivity range for different materials.

Table 2:Summary of resistivity of different earth materials (Kelly, 2011).

Material	**Resistivity Range (Ω-m)**	**Material**	**Resistivity Range (Ω-m)**
Seawater	0.1 – 0.3	Wet sand	20 – 150
Saline	0.3 – 0.9	Sandstone	30 – 300
Brackish	0.9 - 5	Limestone	100 – 300
Fresh water	5 – 80	Dry sand	250 - 4000
Clay	5 – 30	Granite	1000 – 20 000

2.3.2. Principles of the Electrical Resistivity Method

The ultimate physical law applied in resistivity surveys is Ωm's Law that governs the flow of current through a medium, in this case the ground. The equation for Ωm's Law is given by

$$I = V / R,$$

Where ***I*** is the current induced through the current electrodes A and B and ***V*** is the voltage measured between electrodes M and N (or in other words: ***V*** is the difference between the equipotential line at electrode M to the equipotential line at electrode N). Transformation of Ωm's law provides resistivity ***R*** as $R = V / I$.

To acquire the resistivity of the ground a current is injected into the ground via a pair if electrodes (A and B) and the equivalent potential variance is calculated among the potential electrodes (M and N) (Figure 2.3), and is to the apparent resistivity value.

There are two forms in which resistivity survey can be achieved either by vertical sounding or by horizontal profiling. Often vertical soundings are suited for gaining variations in resistivity with depth at a specific position in contrast to horizontal profiling which detects lateral variations in resistivity at specified depths of enquiry (Kelly, 2011). What differentiates the two is that during vertical sounding, the centre of the array is unchanged and the measurements are obtained in a sequence as the electrodes are shifted as the distance progresses away from each other to permit better depth of enquiry. In the profiling procedure, the space between the electrodes is left unchanged, and for each measurement, all 4 electrodes are moved horizontally over the same distance.

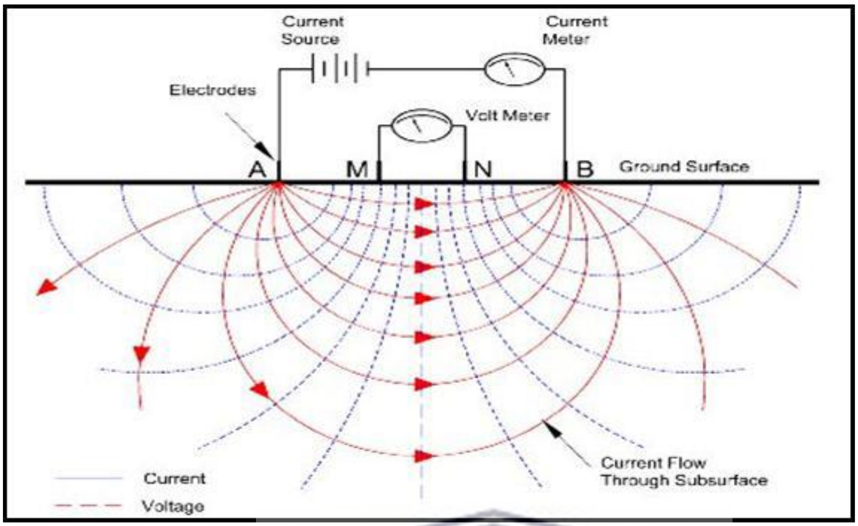


Figure 2. 3: Shows how resistivity is obtained from the subsurface

2.3.3. Electrical resistivity survey- field experiment

In a 2D resistivity survey, current is injected into the ground via a couple of stainless steel electrodes. As displayed in (Figure 2.3) Electrodes A and B are current electrode, and the electrode M and N are the potential electrodes. A current is introduced into the subsurface via current electrode A and travels in the subsurface (solid red line) normal to the equipotential lines (black dotted lines) to current electrode B. The possible difference is measured between electros M and N (Mtoni, 2013). A next couple of electrodes is thus used to quantitatively measure the voltage pattern on the surface resulting from the current flow pattern of the first duo of electrodes (Loke, 2001). The depth of the current penetration is usually relative to the spacing between the electrodes in homogenous ground (Kavidha et al. 2013) so that changing the electrode separation affords evidence about the stratification of the ground (Figure 2.3).

In the electrical resistivity technique various arrays exist (pole-dipole, Schlumberger; dipole-dipole; Wenner, pole-pole and Wenner-Schlumberger) which can be used depending on the field setting. However, only three of these are fit for all conditions namely Schlumberger, Polar-dipole and Wenner. In the Wenner array the electrodes are reserved in a straight line and the electrode spacing at equal distance for each measurement. Whereas in the Schlumberger array the same principles apply for the inner electrodes as they are kept at constant distance, however, the distance between the outer electrodes changes for each measurement (Kavidha et al. 2013). According to Loke (2001) selecting which type of array is to be used should be based on the following characteristics: the depth of investigation, both vertical and lateral alterations in the subsurface resistivity, horizontal data coverage and signal strength.

Wenner arrays have high signal strength and the ability to give good vertical resolution. This is an advantageous factor in areas with a lot of background noise. However, it is important not to neglect its shortfall: for 2D surveys this array has moderately to reduce horizontal coverage as the space between the electrodes is improved and this is even more problematic when using a system with limited number of electrodes. Electrode spacing along a survey line is important for the examination of lateral variation in earth resistivity. For instance, wider electrode spacing in an array gains more depth of penetration, and a narrow electrode spacing gains more resolution. In simple terms the depth to be penetrated depends on the electrode spacing.

To successfully execute 2D electrically resistivity survey a prerequisite of 25 or more electrodes connected to a multicore cable should be met. Then a microcomputer along with an electrical switching unit coupled to a laptop workstation (Kelly, 2011) is required for the selection of four applicable electrodes needed per measurement (Figure 2.4). The general set up for a 2D survey is displayed in (Figure 2.4). In this set up, a number of electrodes alongside a straight line are physically joined to a multi-core cable, at unceasing spacing between nearby electrodes. Then the microcomputer is used to input some information required for the survey into a text-file such as the type of array to use, the sequence in which measurements should be obtained, and other survey parameters required, later this information can be accessed through a computer programme in a laptop device.

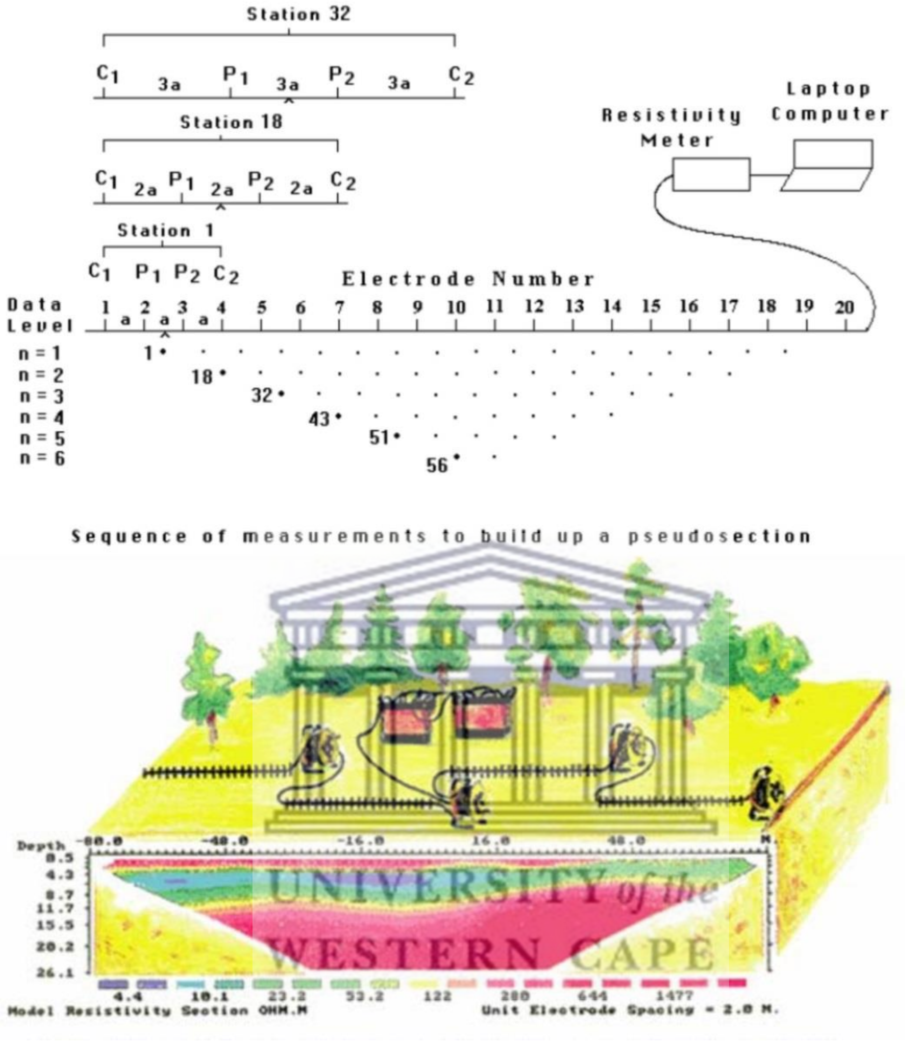


Figure 2. 4: Resistivity imaging showing the general set up and the resulting image processed by 2D inversion (after Kelly, 2011).

2.3.4. Data inversion of resistivity data

After the field survey is done, data inversion is initiated where the apparent resistivity measured from the field by the resistivity meter is processed in to a cross-section that will enable the 2D resistivity model creation that displays the true spatial distribution of resistivity beneath the electrical resistivity array. How this works is that the set of data initially acquired from a resistivity meter produces apparent resistivity data which can be plotted as an apparent resistivity pseudo-section, representing averages of the total material encountered on a given electrical field path before it reaches the potential electrodes whereby the potential difference (in volts) is measured. In an inversion process a model domain is broken down into a grid (e.g. rows and columns), each column in the grid is stripped of the weighted averaged of that column, and each square of the grid is assigned its own resistivity value (a “true” or “model” resistivity) (Kelly, 2011). Eventually the inversion process leads to a model cross-section of true resistivity that most approaches the sub-surface distribution required to generate the apparent resistivity values obtained with the resistivity meter at the surface. Resistivity data are easily processed by using the Res2Dinv, where a process of least squares inversion is one of the most common algorithms used in resistivity data processing. Least squared inversion according to (Loke, 2001) it works to replicate the measured value in the model by reducing the square of the change between measured and calculated apparent resistivity.

Although, electrical resistivity 2D imaging method is the best method for acquiring subsurface information, it is not 100% accurate it tends to be blinded by formations having similar resistivity clays, saline clays, sandy clays or material saturated with saline water, and discerning between these materials becomes challenge among (Khaki et al. 2014). In this case geochemical data should be integrated with the geophysical data to obtain more accurate results, as the geochemical analysis will validate the geophysical resistivity models thus eliminating uncertainties. Another problem can be poor electrode-ground contact and current penetration, which may produce unreliable results. However, this can be resolved in the field by wetting the ground with water for a better electrode-ground contact.

2.3.5. Previous studies on electrical resistivity

Electrical resistivity methods have been successfully used to solve geological, environmental and engineering problems in different environments such as hard rock terrain and in coastal areas. The method was also used to have an insight into the subsurface geology (Alisiobi and Ako, 2012), to identify subsurface anomalies that may be linked to karst or sinkhole activities, to investigate the nature of the subsurface lithology for groundwater exploration (Robert, 2012; Kavidha et al. 2013) and to map saline and brackish water zones in coastal aquifers (Jansen, 2011; Talabi et al. 2015) also used the method.

Electrical resistance depends on various factors such as mineral content, porosity, water content (Kavidha et al. 2013) in many cases groundwater explorers use the resistivity of the rocks as key information to identify water bearing zones and thus locating suitable sites for water well drilling. Since resistivity of rocks is controlled by the existence or absence of water content, location of water saturated zones (aquifers) in hard rock terrains is often challenging let alone locating suitable areas for water drilling. However, Oladunjoye et al. (2013) state that by using 2D resistivity technique in hard rock terrains, fractured and weathered zones can be easily identified which can improve drilling chances in these areas. Although, the 2D resistivity technique has been successfully used for groundwater prospecting in compact rock terrains, it is not well exercised in coastal aquifers. Thus, the knowledge on the use of this method in flat lying areas, where the geology and hydrogeology evidence are missing, especially in a coastal environment, is limited. Most of the reviewed studies used Vertical Electrical Sounding which is interpreted using a one- dimension (1D) resistivity model. The problem with the 1D resistivity model is that it is limited to depths below central point of the array only and this possibly will obstruct the competence of groundwater mining in many cases (Abdullahi and Iheakanwa, 2013). Therefore, the vertical electrical sounding survey at times is unable to detect aquifers between two points of study. In this case a 2D-reistivity model is more efficient because it is able to display resistivity variations in a vertical and lateral dimension more accurately.

Using a combined interpretation approach of the 2D geo-electrical models together with the geochemical analysis method Chandrasekhar et al. (2014) did a valuation of groundwater salinity in the Nellore district of Andhra Pradesh, India. The derived 2D geo-electrical models evidently show the horizontal extent and depth of salinity in the groundwater in their investigated area and the geochemical analysis findings were used to attest the observed salinity. The occurrence of salinity in their study region was assumed to be caused by rock water interactions especially at areas far from the coastline at shallow depths.

Therefore, this study aims to improve the knowledge on the use of joint interpretation of electrical resistivity data with geochemical data and geology to assess groundwater quality especially salinity in coastal environments. To also promote awareness of the 2D electrical resistivity method, and to generate information that facilitate WellPoint drilling for extraction and monitoring water wells and to map the distribution of salinity in a coastal environment as well as classifying the groundwater quality for various uses. Literature demonstrated the ability of the 2D electrical resistivity method to provide significant information on both the horizontal and vertical extension in the subsurface, which makes it easier to characterise shallow aquifers, demarcate depth to bedrock and identifying the boundary between fresh and saline groundwater, also Khaki et al. (2014) used 2D electrical resistivity method to assess groundwater quality and they investigated a maximum depth of 65 m, this shows that greater depths can be achieved using resistivity method. Based on this information this study has opted to use the electrical resistivity method to achieve the study's objectives.

2.4. Groundwater quality assessment using Hydrochemical analysis

The concentration of inorganic matter in groundwater can be measured by the elements available in the soil or rock through which the water encountered along the flow-path, solubility and adsorption of constituents and the sequences in which the water experienced numerous minerals arising from the geological strata along the travel-path (Freeze and Cherry, 1979). As water flows through these geological formations, the composition will start to change slowly from dilute rainwater to concentrated ionic composition at depth. This is as a result of progressive interaction between slowly moving water and the minerals that are in contact with water along the flow path.

The variation in water composition evolves along the groundwater flow direction even in homogeneous aquifers, due to chemical reactions and the length of time of the water being in contact with rocks (WRC, 2014). Different water facies along the stream lines from recharge to discharge zone and/or from shallow to deep groundwater circulation can tell us the distinct feature of water evolved from source to sink (WRC, 2014). Thus, the chemical nature of groundwater is determined by the dissolved mineral constituents, and the total ions, the concentration and type of ions will therefore, decide the suitability of groundwater for multiple uses.

Characterisation of the composition of the water therefore, is of great importance when investigating groundwater source, evolution and quality, making the geochemical examination of the groundwater an absolute essential tool with reference to the water usage. This investigation offers an enhanced understanding about the quality and development process arising in the region, which in turn advices about the restriction of absolute improvement or pave way for future groundwater development interventions necessary as a result of quality alteration in the near future.

Poor groundwater quality is a question of residence time, if the water stays longer or had long contact with the subsurface geological material. As groundwater flows through these geological materials, the chemistry will change as a result of the interaction between the water and soil, soil-gas interaction and rock-water interactions; during this time there will be an increase in dissolved solids and major ions (Hwang et al. 2017). The increased dissolved solids and major ions within the aquifer system may result in different hydro-geochemical processes such as dissolution, precipitation, absorption and desorption, and ion exchange reactions. When it comes to groundwater in coastal aquifers, the dynamic changes are a bit complex due to the threat of groundwater contamination by seawater.

As the ground water is transported from the recharge area to the discharge area, along the way groundwater chemistry is changed by a diversity of geochemical processes present (Nwankwoala and Udom, 2011). Additional factors that contribute to groundwater quality change or pollution include additional usage of manure in agricultural activities, extensive aquaculture in coastal surroundings and salt-pan industries. Therefore, evaluation of groundwater quality needs an understanding of the hydro-geochemical processes taking place within the aquifer system, to properly suggest ways to protect maintain and improve groundwater resources.

Hydrochemical data offers the best insight in terms of understanding groundwater quality in an aquifer. A critical review of hydrochemical data can define the condition of the aquifer such as the chemical processes, changes occurring within the aquifer and the cause of these changes (WRC, 2014). While chemical changes within an aquifer arise from different forms as such precipitation, seepage from surface water, inflows from other aquifers, (considerable) evaporation, saline intrusion or contamination (Igrac, 2008), the chemical interactions between groundwater, soil and aquifer material also play a role in the changes in groundwater quality. Therefore, understanding of groundwater quality data helps in determining the origin and age of the water, and therefore, supports groundwater flow analysis, by pointing out possible threats such as (up-coning or saline intrusion, contamination of groundwater and so forth). With this information it becomes easier to plan for groundwater development for a region. According to Hwang et al. (2017) Hydro-geochemical studies are often conducted to:

- Evaluate groundwater quality for multiple uses.
- Detect the root of anthropogenic pollution and the source of natural salinity.
- Estimate how long it will take to remove the impurities and clean the aquifer.
- Restrain the degree of the saltwater interference region.
- Isolate the form of the hydro-geochemical reactions that are active in an aquifer structure.
- Evaluate the fate of the pollutants in the subsurface environment.
- Map the extent and the 3D-picture of the contamination plume.
- Compute the natural capacity of the aquifer in attenuating the contaminants

- Detect the elements leading to the variations of the chemical composition of groundwater.

2.4.1. Graphical presentation of geochemical data

There are various graphical methods (Piper trilinear diagram, Durov diagram, Ion balance diagram, Pie chart, Radial plot, Collins Diagram, Schoeller diagram, and Stiff diagram) that can be used to present Hydro-geochemical data in order to understand geochemical processes along groundwater flow path, determine hydrochemical facies and hydrochemical processes existing within the aquifer system. However, the Piper trilinear diagram proposed by Piper (1953) usually gives a clearer picture of the cation distribution. This diagram is able to group numerous samples based on their chemical characteristics and display them on a single graph (Figure 2.5) and it becomes easy to visualize any trend on the data.

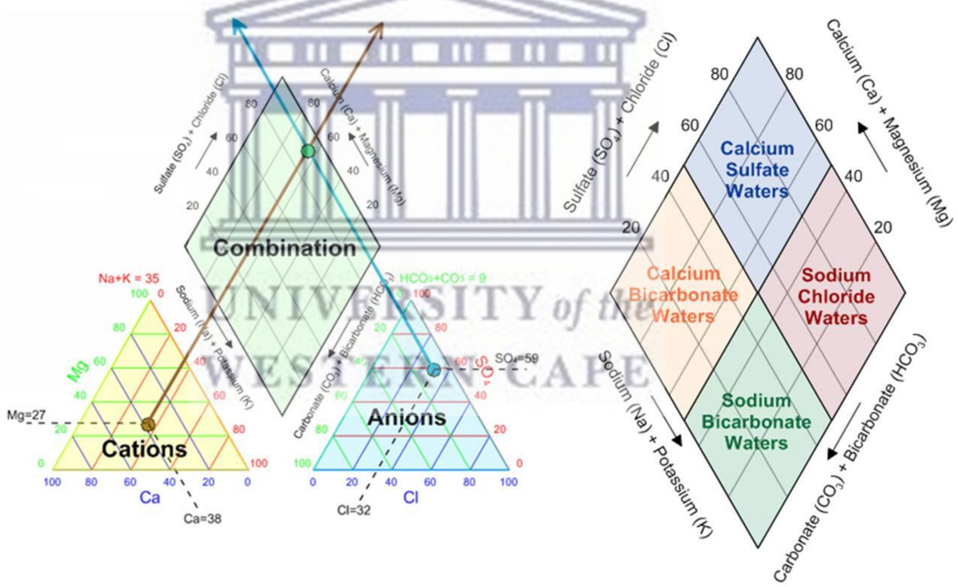


Figure 2. 5: Piper trilinear diagram proposed by Piper (1953).

The Piper trilinear diagram offers three distinct fields for plotting, two triangular fields at the bottom left and bottom right respectively, and a diamond-shaped diagram (Figure 2.5). All three fields have scales reading in 100 parts. The left triangular field represent the major cation (Ca^{2+} Mg^{2+}, Na^{+},) and are plotted as a single point as per conventional trilinear coordinates. The major anions (bicarbonate, sulphate and chloride $^{-}$) are plotted likewise in the triangular field on the bottom right. Thus, two points on the diagram, one in each of the two triangular fields, show the relative concentrations of the dissolved constituents of a groundwater (Figure 2.5). The diamond field can be used to infer groundwater types for instance samples in the top quadrant are calcium sulfate waters, the left quadrant indicate samples that are calcium bicarbonate waters, all samples falling in the right quadrant are sodium chloride waters, and the bottom quadrant represent samples that are sodium bicarbonate waters (Figure 2.5).The Hydro-geochemical approach has been widely used for groundwater investigation in coastal areas and it has been used in combination with the isotopic approach or geophysical techniques. Most applications of the Hydro-geochemical approach were used for the following:

- To determine the evolution of groundwater salinization in coastal aquifers (Senthikumar et al. 2014; Talabi et al. 2015),
- To map the origin, salinity and residence time of groundwater; Hydro-geochemical evolution and recharge process of groundwater (El-Fiky, 2010);
- To define source and flow of saline groundwater in coastal aquifer (Anders et al. 2013).

If salinity in groundwater is a result of seawater intrusion, then the groundwater displays extreme concentrations of TDS major ions as well as selective trace elements (Mondal et al. 2010) for this reason Oyeyemi et al. (2015) also used hydrochemical tools combined with geophysical technique to assess seawater intrusion in coastal aquifers.

2.4.2. Geochemical indicators of salinity in coastal aquifer

In coastal aquifers it is easy to detect early changes in the groundwater chemistry because of the sharp difference in solute concentration of seawater and fresh groundwater. Seawater's chemistry is general steady because of the lengthy residence of the principal constituent (Craig, 2008). Nair et al. (2015) indicated the major cations of seawater as Ca^{2+} Mg^{2+}, Na^{+}, and K^{+}; and major anions Cl^{-}, and SO_4^{2-}. Seawater is known to have high concentration of chloride and sodium and the TDS is roughly 35000 mg/L where Na and Cl^{-} accounts for 84% of the total concentration (Craig, 2008). On the contrary freshwater groundwater reflects a highly variable chemical composition, where HCO_3^-, SO_4^{2-} and Cl^- are the dominant ions and Ca^{2+} is often more than Mg^{2+} (Klassen et al. 2014). Unlike seawater, fresh groundwater is characterised by low TDS varying from 150 to 1500 mg/L, therefore, Cl^- above 1000 mg/L, TDS above 2000 mg/L and some minor ions is an initial indication of mixing between seawater and groundwater from, Nair et al. (2015) believe that high EC values above 5000 µS/cm is an indication of seawater intrusion while Craig (2008) considered EC above 3000 µS/cm. However, the use of EC alone to ascertain the presence of seawater as in groundwater is not adequate as suggested by Nair et al. (2015) but analysing the shift in molar ratio of ions can assist in confirming the ingress from the sea.

Many researchers who have dealt with the issue of seawater intrusion have use the ionic ratios (Craig, 2008; Babu et al. 2013; Ekhmaj et el. 2014; Khan et al. 2017) to estimate intrusion of seawater in coastal areas aiming at identifying the source and nature of the prevailing salinity. They suggested a criterion that can be used in identifying brackish or saline water and to confirm seawater incursion in coastal aquifers. The most ionic ratios applied include Ca^{2+}/ Mg^{2+}, Cl^-/SO_4^{2-}, Cl^-/CO_3^{2-} $+HCO_3^{2-}$, Mg^{2+}/Ca^{2+}, and Na^+/Cl^- ratios. The typical molar ratio of Na^+/Cl^- in seawater is 0.86 with a surplus of chloride exceeding the alkali ions whereas Mg^{2+}/ Ca^{2+} ratio in seawater is indicated by 4.5 to 5.2 with an excess of Mg^{2+}. These ratios more especially the Na^+/Cl^- ratio not only indicate seawater but can discern seawater intrusion and other causes of saltwater and further indicate the mechanism for saline intrusions (Craig, 2008). Therefore, these ratios were adopted for this study to measure the causes and origin of salinity in groundwater.

2.5. Assessing groundwater quality for consumption and irrigation uses

In coastal aquifers the demand of groundwater has increased over the years due to intense industrialization, urbanization, agriculture practices and population rise. Groundwater is considered pure and clean compared to surface water; it is becoming the most favourable reliable resource when it comes to water supply. Given its high demand background, it is vital to know the quality status of groundwater for multiple uses especially for domestic and irrigation uses. Although, groundwater is known as the most reliable resource when it comes to water quality, it does not mean it is pure and safe from contaminants or pollution specifically in coastal aquifers where most is threatened by seawater intrusion.

The quality of groundwater is a function of physiochemical parameters that are significantly swayed by geologic strata and anthropogenic activities (WRC, 2004). The quality of groundwater is judged based on its intended use and this is subjected to the chemical, physical, and biological characteristic of groundwater; more especially uses which are likely to cause health complications in humans and also affect the condition of the aquatic system itself (Ebenezer, 2014).

The classification of groundwater quality is crucial for determining whether a water resource meets the minimum standards required for domestic and agricultural use or any other intended uses. In the light of protecting groundwater dependent ecosystems there are local (South African National Standards (SANS241)) and international (World Health Organisation (WHO)) standards, set in place to be used as guidelines in the valuation of groundwater quality for various uses. The objective of the guidelines was mainly to describe the least prerequisite of safe practice to safeguard wellbeing of users and/or develop standard values for constituents of water, or markers of quality. National and international standards set by both SANS24 and WHO (2011) are tabulated in Table 2.3.

In the assessment of groundwater quality for various uses, physiochemical parameters are considered and these includes pH, EC, hardness, TDS, cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and anions (NO_3^-, Cl^-, SO_4^{2-}, and HCO_3^-). Each of these parameters there is a minimum which is considered to be the safe value and there is a maximum which indicates hazards and unsafe to use for the intended use as stipulated by SANS (2011) and WHO (2011) guidelines.

2.5.1. Assessment of groundwater fitness for consumption purposes

Consumption water limits are regulations set to regulate the degree of toxins in the public consumption water. In the world Health organization (WHO), these limits form part of the safe Consumption Water Act's "multiple barriers" approach to consumption water protection, which also take account of evaluating and protecting consumption water sources; guarding bores and collection structures; ensure water is treated by competent operators; guaranteeing the integrity of distribution systems; and avail the information to the public regarding the appropriateness of water for drinking water.

In South Africa, the quality of public drinking water is regulated by guidelines set by the Department of Water Affairs (DWA) presently recognised as the Department of Water and Sanitation (DWS). The guidelines are expressed as numerical constants indicating the maximum concentration of certain dissolved or suspended materials which can be harmful to human health if consumed past the recommended limit. In this study, selected physical properties and the concentration of certain dissolved and suspended materials were used to judge the quality of water with respect to the SANS241 guideline and compared with the international World Health Organisation (WHO) guidelines presented on (Table 3).

Proper classification of groundwater quality lies on the knowledge of certain parameters such as microbial, chemical and physical (Ebenezer, 2014). Most often the colour, temperature, odour, turbidity, and taste represent the physical qualities, and the pH, turbidity, major ions, and certain trace-metals form the chemical variables. Microbial analysis entails of checks to spot the existence of coliform organisms, which measures the hygienic fitness of water for public use, as selected coliform organisms lie in the bowels of both humans and animals (Mbewe, 2013; Nolankana, 2016; Khan and EghbalBakhtiari, 2017; Badana et al. 2018). Therefore, a sign of this organism in groundwater is a good indication of sewage source contact from both man and animals. Assessed of groundwater quality for consumption purposes can be done using physicochemical parameters presented in the (Table 3).

2.5.2. Physiochemical parameters (T, pH, TDS, EC and Alkalinity)

Temperature is one of the physiochemical parameter considered for groundwater quality as is has a direct effect on the prevailing chemical, physical, and biological characteristics of groundwater. Bacterial growth in groundwater tends to be influenced by temperature (Mbewe, 2013) where, high temperatures speed up the chemical reactions in water and lessens the solubility of gases that increases smell and taste. At high temperatures the pH of water is almost neutral at this point the development of micro-organisms is accelerated. The rise and fall of temperature in groundwater is subjected to the weather, type of season and time of the day. The suggested temperature scale for consumption water is 20-35 degrees Celsius established from SANS2011 and WHO (2011) criteria for household water.

According to WRC (2014) pH is described as the inverse logarithmic concentration of hydrogen atoms in water. The acidic or alkalinity of consumption water is usually measured by the pH level. The range is 0 - 14, where7 presents neutral, a $pH < 7$ specifies acidity, while a pH exceeding 7 denotes Alkalinity. The pH of water does not have a direct health threat except at extremes (e.g. $5<pH >11.0$) according to SANS241 and $6.5<pH< 8.5$ WHO (2011) where it can impair the portability of consumption water (Khan and EghbalBakhtiar, 2017). Conditions that accelerate production of hydrogen ions end up causing the pH to decline, i.e. an acidification process. Alternatively, pH will rise under conditions that promote neutralization of hydrogen ions such as an alkalinisation process.

Table 3: Guideline for groundwater quality as set out by the SANS and WHO

Parameter	WHO 2011 guideline (mg/L)	SANS241 guideline (mg/L)		Possible impact
		Guideline value (mg/L)	Maximum accepted (value mg/L)	
Chloride (Cl^-)	250	<300	600	Scales and scum
Nitrate as (NO_2^-)	0.1	<0.9		Blue baby syndrome (acute health)
TDS	1000	<1200		Taste corrosion/encrustation
pH	6.5 – 8.5	5<pH<9.7	10	High taste low corrosion
EC	1500	1700 µS/cm		Gastrointestinal disease
(Na^+)	<200	<200	<200	Aesthetic
(SO_4^{2-})	250	250	<500	
(Ca^{2+})	200			
(Mg^{2+})	100			
(K^+)	12			

The most important indicator of water quality is the TDS as it often accounts for the sum of dissolved salts present in the water (Deshpande and Aher, 2012). Most of the dissolved salt in natural water consists of the following inorganic salts potassium, bicarbonates, calcium, sulphates, chlorides, magnesium, and sodium and tiny quantities of organic matters that dissolve in water. Fundamentally, all natural-waters have variable concentrations of TDS as a consequence of dissolved minerals from rocks, soils and decomposed plant materials. When water slowly flows through various types of rocks, it chemically reacts and spatially and temporally varies in TDS (WRC, 2014). The TDS of natural water therefore, depends on the type of the geological formations through which groundwater circulates or comes in contact with.

High concentrations of dissolved ions as an effect of high levels of TDS causes water to be declared unfit because of its corrosive nature and brackish or salty taste that is beyond tolerable by humans. According to WHO (2011), TDS in consumption water should not exceed 1000 mg/L, whereas SANS241 limit is at 1200 mg/L.

The ability of water to conduct electricity is given by Electrical conductivity (EC) (Deshpande and Aher, 2012). This physical property of water is owing to the existence of ions in water such as nitrates, carbonates, sulphates, sodium, bicarbonates, potassium, magnesium and calcium, all of which transmit electrical charges (WRC, 2014). Most organic compounds which dissolve in water do not dissociate into ions, thus the electrical conductivity of water remains unaffected by them.

Alkalinity of water is dependent on the amount of hydroxides, CO_3^- and HCO_3^- present in soils or rocks the water is in contact with (Deshpande and Aher, 2012; Ebenezer, 2014). As a result, it is used to quantify dissolution of carbonate minerals such as calcitic limestone and dolomitic limestone. The known health risks associated with high alkalinity in groundwater are gas trouble; skin and mucus membrane; hardness of kidney stones; severe irritation of the eyes. For this aforementioned reasons WHO (2011) proposed that alkalinity should not be beyond 500 mg/L.

2.5.3. Major cations (Na^+, Mg^{2+}, K^+, Ca^{2+})

Both Mg^{2+} and Ca^{2+} are responsible to the total hardness in water. Magnesium is eroded from rocks and later is added in groundwater. Application of fertilizer and cattle feed are other sources of magnesium in groundwater (Deshpande and Aher, 2012). The problem with high amounts of magnesium in consumption water is the laxative effect. Since magnesium has a major role in the harness of water WHO (2011) has set the contamination limit for consumption water to be 100 and 150 mg/L and SANS241 (2011) limit is70mg/L. Whereas, the occurrence of Ca^{2+} in water is a manifestation that water has flown through calcium rock deposits such as gypsum, limestone, gypsiferous shale and dolomite. According to WHO (2011) 200 mg/L of calcium in groundwater is the upper limit for contaminant level in consumption waters while the SANS (2011) maximum limit is 150 mg/L.

Apparent sources of potassium in groundwater originate from agricultural runoff, dissolution of minerals, rainwater and also decaying plant material (Deshpande and Aher, 2012). Potassium is needed to boost human nutrition and maintain plant wellbeing therefore, to ensure no threat is inflicted, WHO (2011) proposed 200 mg/L as the international standard value for K^+ while the SANS (2011) set it to be 50 mg/L.

2.5.4. Major anions (Cl-, SO4-, HCO3-)

In many cases chloride is used as an indicator for pollution and is the most preferred parameter in water quality assessments (Ebenezer, 2014). Water that is not brackish nor saline should have natural concentration of chloride less than 100 mg/L (Balakrishnan et al. 2011). Apart from contamination from seawater other sources known to increase the level of chloride found in groundwater include sewage effluent discharges, domestic wastes, industrial waste, irrigation return flows brine and other anthropogenic sources. Chlorides are extensively dispersed in nature as salts of potassium-chloride, calcium chloride, and sodium chloride. Groundwater with high concentration of Cl^- is a major concern if is to be used for domestic purposes because it gives water bad salty taste and also causes corrosions of metal pipes (WRC, 2014).

Although, sulphates exist naturally in numerous minerals they can also be added in groundwater through atmospheric deposition and from industrial wastes. Sulphates are commercially important for chemical industries. Both SANS241 and WHO (2011), endorsed a limit of 250 mg/L for sulphate in groundwater. The studies that have assessed groundwater quality for consumption purposes indicate that high concentration of chemical constituents in groundwater may be harmful. Occurrence of these parameters in groundwater is natural however, anthropogenic tends to increase their concentration thus resulting in groundwater unsuitable for consumption.

2.6. Water Quality assessment for Agriculture usage

Numerous coastal regions around the world are encountering degradation of groundwater quality for irrigation of cropped land because of the increasing demand of water supply. Bhat et al. (2018), states that the crop yield is a function of the quality of soil and the quality of the water used for irrigation. The appropriateness of water for irrigation systems is dependent on the impacts of the mineral constituents present in water on plants and soils (Hwang et al. 2017). In this manner, common, assessment of the fitness of water for irrigation ought to pay attention on the Na^+ concentration, alkalinity, and salt content, occurrence of trace elements as well as nutrients, acidity, and hardness of the water. The development of plant may be affected because the high salt content in irrigation water restrict the uptake of water through alteration within the osmotic forms or chemically by metabolic reactions instigated by poisonous constituents (WRC, 2014; Hwang et al. 2017)

If water utilized for irrigation is characterised by elevated Na^+ also low Ca^{2+} and Mg^{2+} content, the cation exchange complex possibly will come to be saturated with sodium (WRC, 2014). This can terminate the soil structure owing to diffusion of the clay particles (Bhat et al. 2018) and this in turn decreases permeability, and aeration of the soil which will affect plant development by prohibiting the uptake of water and air. It is evident the overall development of plant and soil structure is entirely dependent on the composition of mineral of the water. Therefore, classification structure to measure the fitness of groundwater for irrigation purposes is based on certain hydrochemical parameters and the key ones are Residual Sodium Carbonate, EC, Na^+ (%), Salinity, Sodium Adsorption Ratio Permeability Index, Kelly's Ratio and Magnesium Ratio.

2.6.1. Sodium adsorption ratio (SAR)

Sodium adsorption ratio (SAR) is the effective parameter used for ascertaining the fitness of groundwater for irrigation purposes because it is a measure of alkali / sodium hazard for plants (Badana et al. 2018). High sodium in irrigation water affects the soil condition by reducing its permeability and raising its hardness (Bhat et al. 2018). The sodium adsorption ratio (SAR) is an index of the potential of a given irrigation water to induce sodic soil conditions. Sodicity in irrigation water is a consequence of high concentrations of Na^+ relative to Ca^{2+} and Mg^{2+}.

2.6.2. Electrical Conductivity (EC)

Electrical conductivity is one of the foremost imperative parameters to be considered when evaluating quality of water for irrigation system for it is straightforwardly related to saline issues. It is therefore, a perfect marker of salinity risk to crops as it reveals the TDS in groundwater.

2.6.3. Sodium Percentage (Na^+ %)

Sodium is considered as an essential parameter for irrigation water as it has direct effects on soil absorptivity. Sodium percentage is therefore, a good measure of sodium hazard especially in water used for irrigation. For instance, if sodium percentage in irrigation groundwater exceeds 60 then infiltration and aeration, damage of soil structure, accumulation of sodium will be encountered. This is because the high levels of sodium present in irrigation water compel the ions to be attached to clay particles and the position of Ca^{2+} and Mg^{2+} ions present in the soil is taken by sodium in the water Bhat e al. (2018). The after effect of this exchange process is reduced permeability in soil which eventually leads to soil characterised by poor drainage (Badana et al. 2018). Other aspects that contribute to the increase of Na^+ in groundwater include suspension of minerals from lithological composition, extended residence time of water, and expansion of chemical fertilizers with irrigation waters.

Water that is of poor-quality interferes with the development of plant as high salt content in irrigation water leads to osmotic pressure and ion-toxicity in crops (Bhat et al. 2018). High salt concentration is usually associated with Na^+ and Cl^- levels. Evaluation of groundwater quality for consumption and irrigation usage is essential especially in semi-arid and arid countries around the world in particular South Africa, where population growth and irrigation farming is gaining momentum. And this is also accompanied by salinization problems triggered by various processes, like seawater intrusion, salinization induced by irrigation, pollution by agrochemicals (Bhat et al. 2018). Therefore, to assess groundwater quality for irrigation uses, various authors (Bhat el at. 2018; Nolankana, 2016) have used the classification indices as discussed above applied these parameters in assessing groundwater quality for irrigation use. Following similar approach as these studies the current study attempt to assess groundwater quality for consumption and irrigation uses using the above mentioned parameters.

2.7. Hydro-geochemical modelling

In general modelling is a tool designed to facilitate our understanding of how an aquifer system functions. Geochemical models are defined as the tools that are useful in interpretation of the geochemical reactions in the groundwater (Ligavha-Mbelengwa, 2017). Previously, modelling of groundwater flow and geochemical processes within an aquifer system were done separately with different models, Modelling of groundwater flow (the hydro-dynamical aspect) has been done using flow-models such as MODFOLW or a mixture of flow and a solute transport model (MT3D) for mimicking salt transport; the SEAWAT model was used (Walraevens and van Camp (2004). Meanwhile, the hydrochemical aspects have a need for studies with hydro-geochemical models, centred on speciation and reaction schemes (Walraevens and van Camp, 2004). In hydro-geochemical models, groundwater flow did not play a major role for these models to be created, it was either not taken into account or, it was measured in a very basic manner (along a path-line). However, things evolve and models such as PHREEQ and Inverse Modelling were developed to make things easier in groundwater quality investigations, and these models have been successfully used to detect Hydro-geochemical processes interfering with chemistry of water in coastal aquifers.

A number of hydro-geochemical models exists that are used in the investigation of groundwater quality (Aquachem, PHREEQ, Inverse Modelling), and these models have been successfully used to identify Hydro-geochemical processes affecting water chemistry by employing the chemical and physical parameter of the water quality (Mtoni, 2013). Hydro-geochemical modelling is primarily utilized for classification of water information into diverse water types, it is additionally utilized for calculating the sum of mole exchange, and to distinguish the nature of Hydro-geochemical advancement along the flow path of water on its course; it is also used for speciation and to define the solid phase equilibrium saturation indices.

Major anions such as SO_4^{2-}, HCO_3^-, and Cl^- and major cations K^+, Ca^{2+}, $Mg2^+$ and Na^+ remain the main parameters used for understanding and modelling of hydro-geochemical process and advancement of groundwater.

2.7.1. Aquachem

Aquachem: is developed for the purpose of displaying graphical and numerical examination of geochemical data sets that enables the interpretation and the understanding of numerous complex interactions between the groundwater and aquifer formation (Mtoni, 2013). It consists of a fitted archive of inorganic parameters usually required for geochemical analyses, calculations and plotting. It is also capable of clustering chemical datasets and categorise different water types and source rock through piper or stiff diagram. Other plotting techniques available include scatter graphs, Durov, Langelier-Ludwig, pie charts, Schoeller and many more. In expansion, AquaChem highlights a built-in graphical interface to the prevalent geochemical modeling program PHREEQC for calculating balance concentrations of chemical species and saturation indices of phases in a solution.

2.7.2. PHREEQC:

PHREEQC version-2 is known to perform an extensive range of low temperature aqueous geochemical calculations and stimulates a multiple reactions and processes in natural water or laboratory tests. Any information relating to saturation, a reduction or oxidation of a solution and speciation can be deduced from this program (Mtoni, 2013) which is an important factor in the interpretation for the chemistry of water through the thermodynamic approach.

Speciation is the relative quantity of different species in a water solution whereas saturation is the evidence of specific minerals in a solution regardless of the outcome if is saturated or not saturated or in balance with an identified phase (Ligavha-Mbelengwa, 2017). Saturation index can be used to compute thermodynamic calculation which at the end reflects the condition of Hydro-geochemical balance of groundwater samples with solid mineral phases in an aquifer system. This is achieved by comparing the outcome of the activities of the ions (IAP) with the equilibrium constant K-const for the solubility of the mineral in a solution (equation 1).

$SI = logIAP/Kconst$……………………………………………(1)

2.8. The application of Multivariate Methods in Water Quality Analysis

Multivariate statistical approach is commonly used to aid in providing solutions to issues concerning the environment and propose evidence that can offer better understanding regarding naturally occurring developments (Yidana et al. 2010). This technique it enables easy interpretations of data consisting of multi component chemical and physical measurements; as such they have been highly favoured as fair methods for dealing with water quality data to make significant deductions (Khalid, 2012). Significant information from hydrochemical datasets in a compound system can be easily extracted using the multivariate statistical methods.

2.8.1. . Multivariate Techniques:

There are different components of multivariate statistical techniques, these contain, discriminate, cluster, principal component and factor analysis. Interpretation and understanding of intricate data matrices in particular data related to water quality is made easier through application of these different multivariate statistical components. This technique allows recognition of any potential threat that has an impact on the water bodies and presents a valued means for consistent management of water resources including quick resolutions for contamination problems (Khalid, 2012). Linkage between samples and/or variables can be detected fairly by using PCA and cluster analysis techniques. These relations, founded on similar magnitudes and deviations in physical and chemical elements, are likely to point out human or seasonal effects.

2.8.2. Principal component analysis (PCA)

Principal component analysis is great technique to ease the complexity of a dataset containing large number of inter-related variables. Basically the main function of PCA is to reducing the data by convert the original data set into smaller sets composed of uncorrelated factors identified as principal components. Most significant variables are extracted from the dataset and used to explain the original data without jeopardizing any loss of valuable information (Khelif and Boudoukha, 2018).

2.8.3. Cluster Analysis (CA)

Objects having similar attributes can be assembled together using cluster analysis for instance samples that poses identical physical and chemical characteristics will form one group (Singh et al. 2004). In cluster analysis technique objects are categorised in a manner that, similar objects are within the same group in accordance to a pre-set condition. Often these groups are not known but can later be established using the results. The final groupings of objects are expected to display homogeneity within the cluster and heterogeneity between clusters. Data can be easily interpreted and patterns recognised from CA results. In this view various types of cluster analysis have been used in this study to assess water quality data for both surface and groundwater's.

2.9. Application of Geographic Information system (GIS) in groundwater quality assessment.

Geographical information system has enabled evaluation of natural resources and environmental issues to be much easier. The application of GIS in groundwater investigations is mainly for estimating groundwater vulnerability to contamination, managing site inventory data, and groundwater flow modelling and other objectives (Krishnaraj et al. 2015). GIS is very effective especially for groundwater quality mapping it is also vital in detecting any apparent changes in the environment. In this manner it has been widely used for classification purposes particularly in groundwater quality maps by comparing TDS values with certain aquifer attributes or land use and cover (Khalid, 2012). In GIS also water quality maps based on concentration values of different chemical parameters can be prepared, such maps are useful in demarcating groundwater quality regions for various uses whether is for domestic use or for irrigation purposes (Balakrishnan et al. 2011). A Geographical Information System is equipped with various functions, such as storing, updating, capturing, analysing, displaying and handling of any sort of data that is georeferenced. All these abovementioned functions are subjected to availability of various factors such as a software, computer-hardware, non-spatial and spatial data, as well as operators (Figure 2.6).

Through GIS any problem relating to water management issues on a regional or local scale can be solved, this encompass issues relating to water availability, water quality or other environmental issues (Johnson et al. 2008) because GIS is able to assist in organising data, generate information that can be used for informed decision making and for managing resources (Nolankana, 2016).

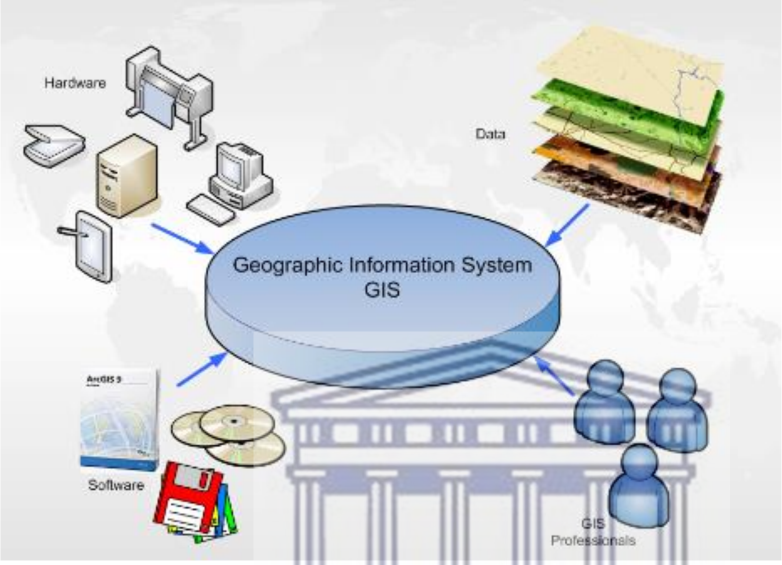


Figure 2. 6: Geographical Information System, showing a compilation of computer hardware, software, spatial and non-spatial data, and users (Khalid, 2012).

GIS, organises data inlayers that are georeferenced and registered to a mutual projection as demonstrated in (Figure 2.7). Different information is presented in each layer and can be easily connected by its location. These layers are accurately superimposed onto each other in order to ensure that each location is associated to its equivalent positions on all the other maps as to relate suitably (Nolankana, 2016). The bottom layer of this diagram holds a significant role as it denotes the position reference-system whereby all the maps have been correctly recorded.

2.9.1. GIS Data:

Data captured in the GIS originate either from paper plans, records or digital database and it gets converted to be compatible with the software by means of digitizing or scanning to pictures. GIS archives integrate two different branches, the spatial and the associated attribute archive. The spatial data have a "vector" structure made of features characterised as points, polygons, lines, and additional features. GIS spatial data are run as images, or "rasters," with simple row-and column formats (Khalid, 2012). Feature data can be manipulated in relational archive software which consists of records and fields, and the power of the relational model is applied to these data. These feature data are "tagged" to the spatial database to enable tabular data recoveries.

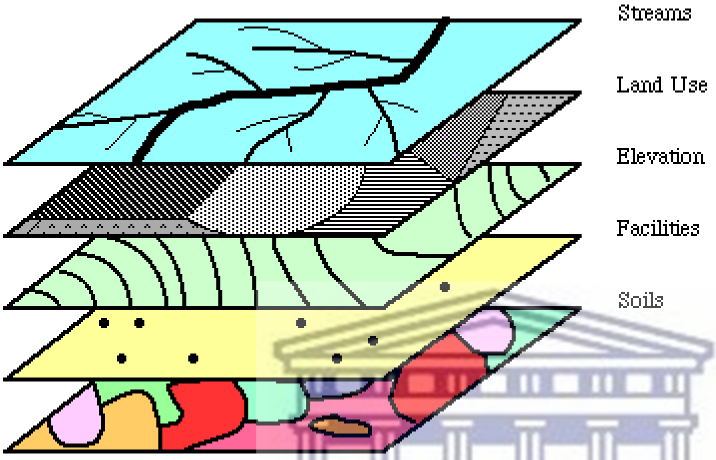


Figure 2. 7: Various layers of data from different sources joined in the GIS (Nolankana, 2016).

The competence of GIS to intersect information from diverse sources allows good connotation of these layers to define the impact they have on each other. Some scholars have applied GIS to relate element distribution with land-use and geology. Nur et al. (2012) used GIS to define the connection between groundwater flow-systems and the distribution of chemical facies. In this study water quality maps will be created using GIS. Such maps are crucial in the assessment of water appropriateness for consumption and for irrigation uses. According Nur et al. (2012) GIS can also be used to map spatial distribution of numerous hydro-chemical facies, evolution of groundwater can be mapped and relationship of between rock and groundwater can inferred.

Chapter 3: Physiographic description of the of the study region

3.1. Description of study Location

The Heuningnes Catchment is positioned on the southern-most part of South Africa and falls within the Eastern Overberg region in the Western Cape Province. The Heuningnes Catchment lies 160 kilometres south-east of Cape Town and 35 kilometres north of Cape l'Agulhas. It can be accessed using this coordinates (34º42'50"S; 20˚07'13"E). The catchment occupies overall area of 1400 km^2 and is among the 3rd order catchments of South Africa (Kinoti, 2018). It comprises of numerous surface-water bodies such as wetlands and rivers (riparian and non-riparian floodplains, pans, and freshwater springs). The main rivers feeding the catchment include Nuwejaars, Kars, and Heuningnes rivers (Figure 3.1). The major water bodies are Soetendalsvlei which is about 8 km long and 3 km wide followed by the Voelvlei having a length of 4 km and width of1.7 km and some small pans (Soutpan, Longpan and Roudenpan) (Figure 3.1). The pans and wetlands are directly connected to groundwater, indicating possible groundwater zones. Wetlands may also indicate a recharge zone for groundwater, depending on their topographic position.

The wetlands in the study region are saline to hypersaline. Elevated levels of salinity in this area gave the current study a great opportunity to use electrical characterization approaches such as electrical resistivity-imaging to map groundwater quality in conjunction with chemical methods. The contrast in resistivity values concerning saline groundwater's and fresh surface water will make it easier for this current study to display the deep subsurface image, and from the resistivity images distinct regions of saline ground water migrating from depth can be identified and processes controlling salinity can be inferred.

Figure 3. 1: Locality of the study region (Pauw, 2012).

3.1.1. Topography

In terms of topography, the area is characterised by a low slope starting at the base of the Bredasdorp mountain series to the NW, to the Indian Ocean in the SE causing major wetland development within the region (Figure 3.1). The elevations described in Kinoti, (2018) ranges from 14 to 833 m beyond sea-level. Higher elevation zones are marked by the Bredasdorpberge, Kouberge which forms sources of the streams adding to the Nuwejaars River and recharge localities for groundwater in the region.

3.1.2. Land-use and Land-cover

Bredasdorp, Elim including Napier are the major towns in the Heuningnes Catchment. About 56% of land coverage is natural vegetation consisting mainly of bushland, shrubland fynbos (limestone and sandplain), grassland, wetlands and water bodies (Herdien et al. 2005). The main activities in the area include wheat, vines, orchards and livestock farming (Russel and Impson, 2006). About 41% of the catchment is agricultural land (Figure 3.2), primarily used for provisional drying agriculture and improved grassland (Herdien et al. 2005). Small-scale irrigation accounts for 1.1% on orchards and vineyards cultivated area. Field observations reveal that the study area is dominated by calcareous sands, coarse sands, alluvial top soils and clays, acidic and highly leached soils. Peat layers are also visible in some areas and often occur between the top sandy layer and clay layer.

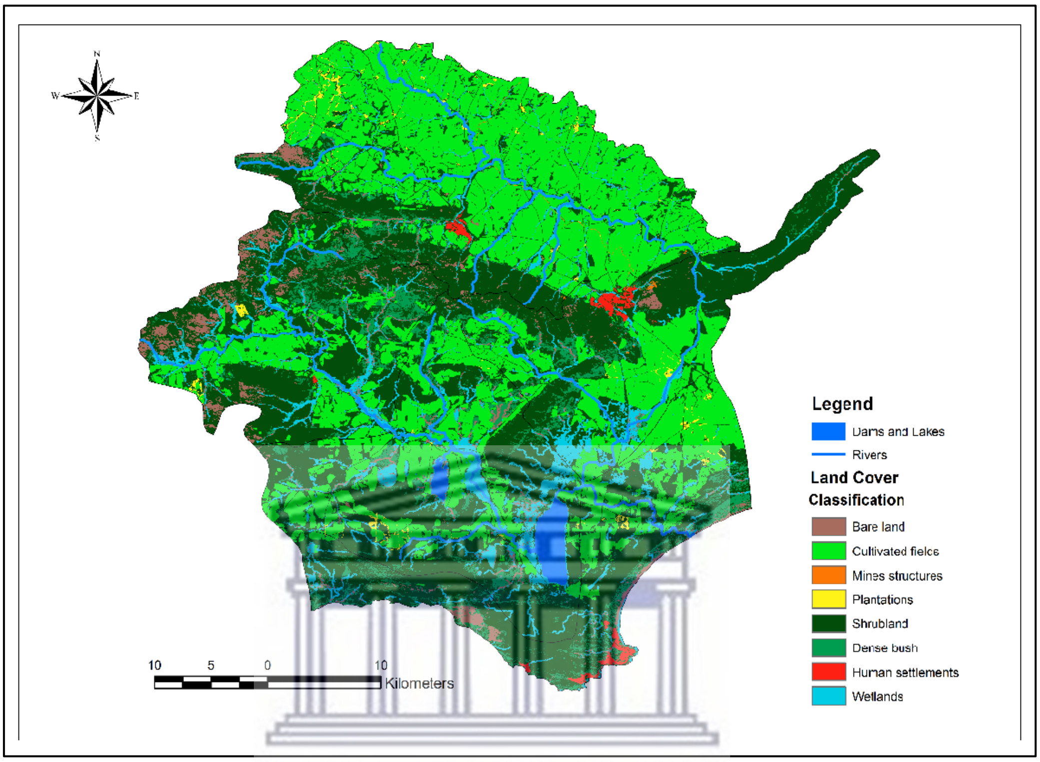


Figure 3. 2: Land use and land cover types in the Heuningnes Catchment (Mazvimavi, 2018).

Larger section of the land covering the Heuningnes catchment is occupied by private owners for crop farming and livestock production. The main crops are barley, canola, and wheat (Pauw, 2012). Also growing of grapes, especially for wine making, is an important land use in the catchment (Mazvimavi, 2018). Livestock production in the form of cattle and/or sheep is practised on most of the farms. Dairying is being practised at a small number of farms. Therefore, given the history of the area the knowledge about the status of groundwater is crucial for this area especially for domestic supply, livestock watering and for irrigation purposes.

Table 4: Percentage area under the various land use and land cover types the Heuningnes Catchment modified after (Mazvimavi, 2018).

	Heuningnes Catchment (%)
Dense bush	6.86
Cultivated land	38.75
plantations	0.61
Human settlements	0.71
Water bodies	8.67
Bare land	3.84
shrubland	40.56
	100.00

The land use activities in this area are important because they pose certain influence on the prevailing quality of the ground water, the type of fertilizers used may distort the quality of groundwater as it state in literature that agriculture practices affect groundwater quality. Monjerezi (2012), state that agriculture activities may cause soil and groundwater salinity through clearing of natural vegetation, in-flow of saline water in response to intense abstraction from irrigation and irrigation return-flow.

The major settlements are Bredasdorp, Napier and Elim. According to Mazvimavi (2018), Bredasdorp had a population of 15 524 persons, Napier 4 214 persons, and Elim 1 412 persons based on the results of the census conducted in 2011. Most of the farms are large-scale commercial farms with very low population numbers.

3.1.3. Climate and rainfall

South Africa is positioned nearly within the high pressure belt of the southern hemisphere, which at sea-level is set around 30º S latitude (Adelana, 2010). According to Midgley et al. (2005), the location of Africa along the equator results in its climate being mostly arid to semi-arid. The high pressure belt is exposed to a seasonal displacement of 4º latitude, its centre being positioned further south in February (Adelana, 2010). The unequal heating of the land between summer and winter, cause its high pressure belt to splits up into two cells, one at the Atlantic side and the other above the Indian Ocean (Midgley et al. 2005). Also the presence of the circumpolar Westerly Winds to the south of the high pressure belt is known to play a role in the prevailing the climate of South Africa. These Westerly Winds, at sea-level are at 35° S latitude, and occur at much lower latitudes in the upper atmosphere. Thus, the weather variation in South Africa is regulated by the perturbations in the westerly circulation of the Southern Hemisphere.

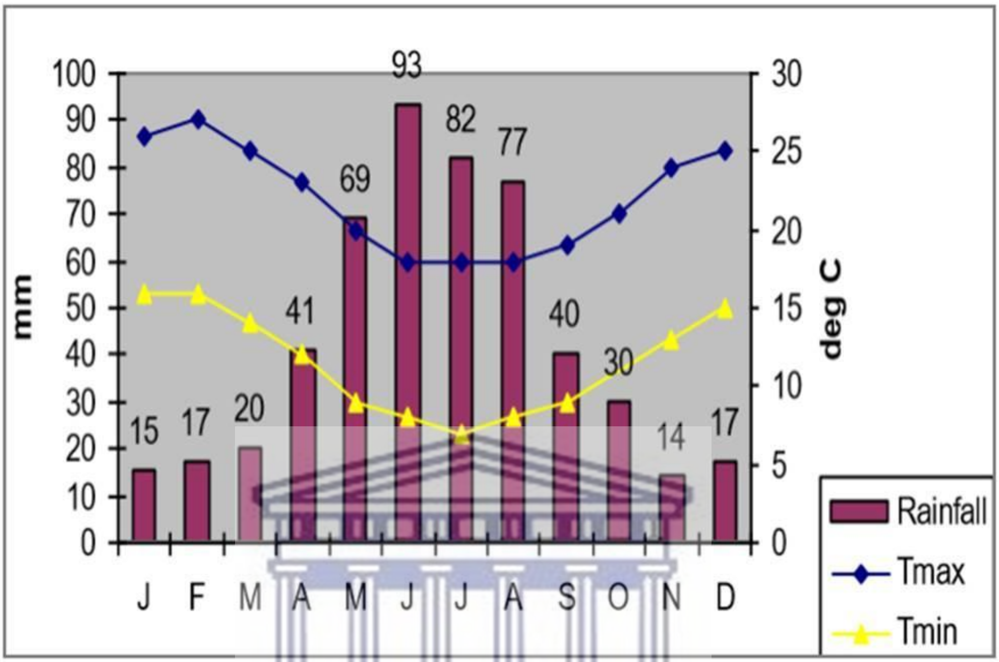


Figure 3. 3: Climate for the Western Cape Province, long-term rainfall, minimum and maximum temperature

The observed sharp climate alterations of the region are suspected to be greatly influenced by the mountainous nature of the Cape Fold Belt (Figure 3.4). The general temperature in the study region is of Mediterranean climate with warm, dry summers and cool, wet, windy, cold winters which is the general temperature across the Western Cape Province. Temperature variation in the area is controlled by its locality being near to the ocean. The average high temperature ranges from 18 to 25 C° and average low temperature from 8 to 18 C° in summer and winter respectively (Figure 3.3). Expected winds are mostly from the SE and SW in summer and westerly during winter period. The rainfall distributions are displayed in (Figure 3.4). Generally, about (65 to75%) of the rainfall is received during winter period from May to October and the Mean Annual Precipitation (MAP) is about 450mm (in the east), 540mm (in the west) to 650mm along the coast (Pauw, 2012) and this is where contribution of ground water recharge comes from.

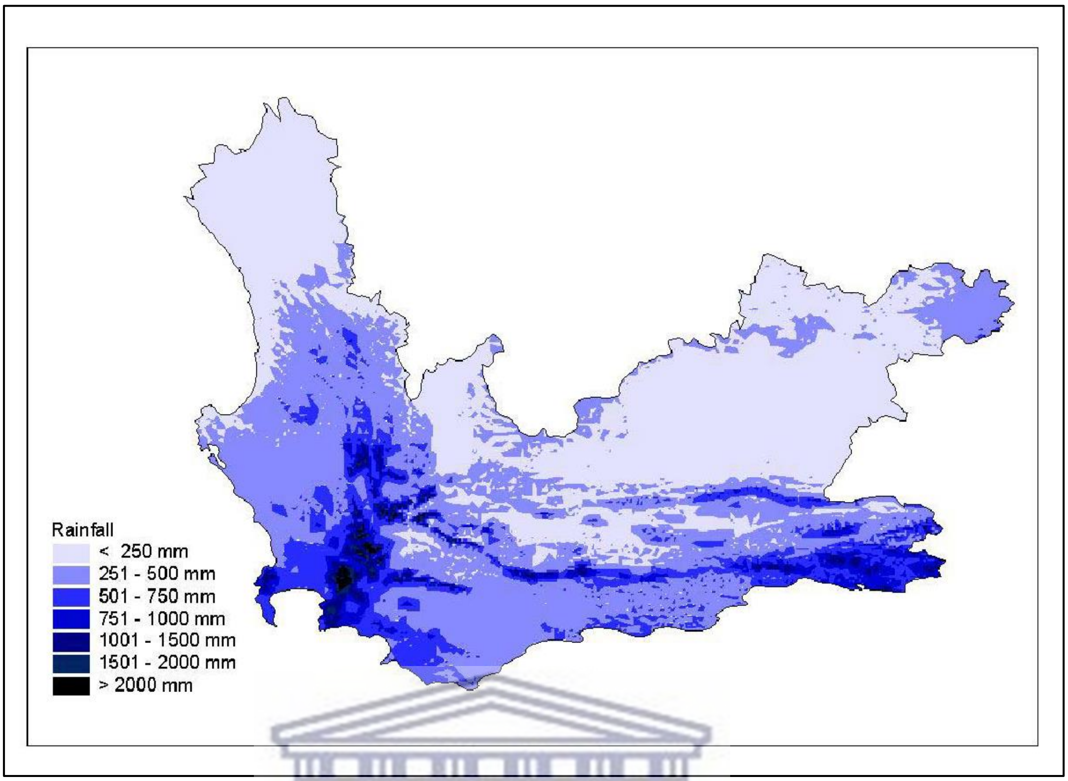


Figure 3. 4:Map showing rainfall distributions in the Western Cape (Midgley et al. 2005).

3.2 Geological setting

3.2.1 Introduction

Understanding the geology of the region is very imperative for the current study especially when dealing with groundwater and its quality. Often groundwater flow within an aquifer system is dependant by the present geological structures (e.g. faults, folds and fractures). The type of faulting will determine its permeability for instance reverse of thrust faults are caused by compression and they result in impermeable structures (Monjerezi, 2012). In contrast normal faults which occur in tensional environments they tend to form open voids which supports permeability to the surrounding bedrock. Therefore, geological structures provide flow-paths for groundwater migration especially deeper saline water that are under pressure. The current study has complex structures this may give an idea on the migration of the observed saline groundwater distribution.

It is reported that the sediments of the Cape Supergroup were deposited in different environments; some deposited under shallow marine conditions influenced by, tides, storms and waves, wave and storm influence, some in non-marine, braided-fluvial environment. Deposition of these sediments took place during the early Ordovician to early Carboniferous period. The 280-220-million-year old Orogenic belt known as the Cape Fold Belt (CFB) trending in the west and south coast of South Africa provides a clear picture of this siliciclastic sequence (Wu, 2005). This siliciclastic sequence consisting mainly of quartz-arenites, silt-stones and shales with conglomerates and thin diamictite units in some parts has been divided in to three groups known as the Witteberg, Bokkeveld and Table Mountain Groups. The recorded thickness of the Cape Supergroup for both eastern and western Cape, add up to 5,300m and 9,600m respectively. The characteristic nature of the quartz arenites, being medium to coarse grained in size and fractured as an effect of folding and faulting in the Cape Fold Belt, (Wu, 2009) provides a better chance for groundwater exploration that is of good quality.

3.2.2. Regional geology of the Western Cape

The meta-sediments of the pre-Cambrian Malmesbury Group (Ne) are defined as the oldest rocks in the Western Cape (Jia, 2007) and serve as the basement rocks to the Cape Supergroup. The Cape Supergroup, which occupies large portion of the Western and Eastern Cape, was deposited in a trough from early Ordovician to late Devonian age (Meyer, 2001). This Supergroup is differentiated into three components: the arenaceous Table Mountain Group (O-st) identified as the lowermost component and it overlies the Malmesbury, Klipheuwel and Cape Granites. Above it lies the argillaceous beds of the Bokkeveld Group (Db) which in turn is overlain by the youngest group called Witteberg Group (DW) (Theron et al. 1992) and consists of alternating shales and sandstones.

Late-Tertiary to Quaternary sediments, up to 50 meters thick (ranging in age between 12-0 Ma) overlay the older rocks in this area. Limited occurrences of Coastal Sands were deposited mainly along the coast between Agulhas and the Breede River Mouth (Meyer, 2001). Considerable deposits of alluvium consisting of clay, sand, pebbles and boulders occur in the valley of the Breed River and its tributaries.

3.2.3 Structural geology

The Cape Fold Belt (CFB) is the dominant structural feature in the greater Southern and Western Cape area (Figure 3.5). The CFB is a largely east-west striking feature and it consists predominantly of sedimentary and metamorphic rocks which were subjected to intense pressure, especially from the south (Meyer, 2001). The intense pressure on these aforementioned rocks resulted in a variety of geological features and structures which produced a wide range of aquifer characteristics peculiar to the region.

The apparent structures and thickness of the TMG formations are the effect of early deposition within an east west trending basin (Duah, 2010) along the southern and southwestern Cape areas, as altered the Permo- Triassic Cape Orogeny and the fragmentation of southwestern Gondwana during the Mesozoic era. The CFB is recognise as 2 branches the western and southern branches, and the centre of it lies the structural syntaxis (Figure 3.6), of which the structural pillar extending from the NW to the S near Cape Peninsula and curves to the E approaching Port Elizabeth. The study area Heuningnes Catchment is situated in the syntaxis domain and slightly on the southern branch of the CFB. According to Theron et al. (1992) this syntaxis comprise of diverse NE striking faults and is perceived as the part where the Cedaberg and Southern Cape branches unite. Depending on the diverse fold trends and shortening intensity, the syntaxis is classed into two individual domains positioned N and S of the Hex River anticline correspondingly. The northern field is characterised by N, NW, NE and slight E trending folds, while the southern field has only E and NE trending folds (Meyer, 2001). The syntaxis suffered more fracturing in comparison to the other branches of the CFB (Figure 3.5). Whereas, the southern branch displays northerly-verging, often overturned first-order folds, cut by a few thrusts and normal faults, with intense fracture cleavage in the quartz-arenites and slaty cleavage in the Cedarberg Formation (Booth and Shone, 1992).

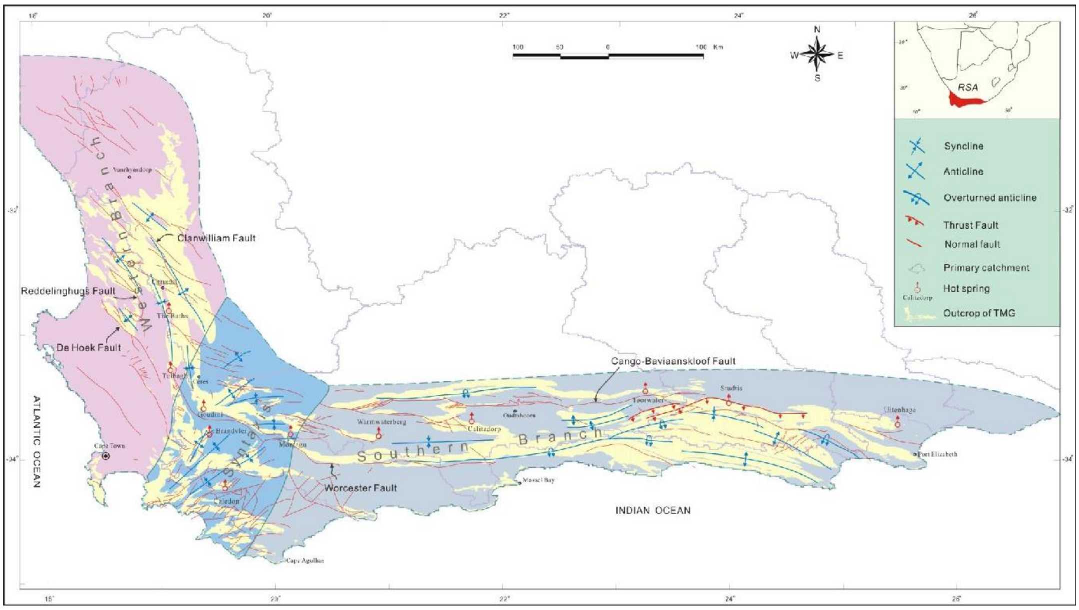


Figure 3. 5: Structural geology of the Cape super group (Wu, 2005).

3.2.4. Geology of Heuningnes Catchment

The catchment geology has been described by numerous authors and summarised in various reports by Toens and partners (1998). The basement geology of the area is made up of the meta-sediments of the Malmesbury Group, and then Table Mountain, Bokkeveld and the Enon Groups were deposited over the Malmesbury Group. There is no evidence of the Witteberg Group in the region; its absence may indicate either non-deposition or an erosion period. After the breakup of Gondwanaland the area along the coast was eroded to form a peneplain onto which the Bredasdorp Group was deposited about 70 million years ago. This could clarify the absenteeism of the Witteberg rock series in the region. The study region is locally confined within the TMG and the Bokkeveld Groups of the Cape Supergroup and the Bredasdorp Group. The succession of sandstone, shales and conglomerate of the Table Mountain and Bokkeveld Groups overlies the Malmesbury Group. The distributions of Bokkeveld Group and the TMG within the Cape Fold Belt are displayed in Figure 3.6.

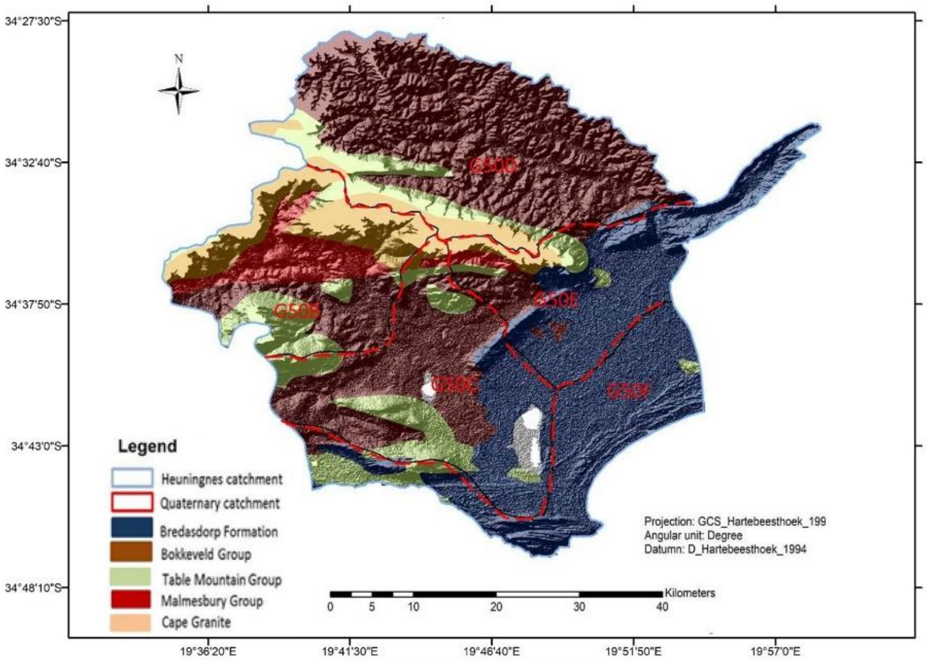


Figure 3. 6: The distribution of geology in the Heuningnes Catchment (Hartebeesthoek 1994).

3.2.4.1 Table Mountain Group

Table Mountain Group (TMG) typically is a Paleozoic cratonic sheet of sandstone dominating the upper catchment. Its high resistance nature to weathering processes led to TMG sandstone being the most noticeable feature in the landscape forming high ground and mountain ranges. This group is overlain by the Bokkeveld Group. The TMG is dominated by quartzitic sandstones, shales, siltstone and a few conglomerates. Xu et al. (2007) state that the quartzitic sandstones of the TMG were affected by deformation which resulted in the occurrence of faults, folds and joints in the area hence the presence of a fractured aquifer.

4.2.4.2 Bokkeveld Group

The Bokkeveld Group is Devonian of age and is divided into two subgroups namely the Ceres and Bidouw subgroups. Bokkeveld group is sandwiched between the Bredasdorp Group and the Table Mountain Group (TMG). In the Heuninges Catchment the shales and sandy shales of the Bokkeveld group occupies the eastern part of the catchment around Elim and Soetendalsvlei sites. Within the formation there are notable fractures and faulting. According to Gordon et al. (2011). Groundwater from this formation is saline.

3.2.4.3 Bredasdorp Group

Bredasdorp group is made up of Cenozoic shallow marine and aeolian deposits, which become progressively younger towards the sea (Malan, 1990). Bredasdorp rocks occur along the south coast from Standford to east of Witsand and overlies the Bokkeveld Group and the TMG rocks. Calcified dune sand and coastal limestone are the main lithological characteristics of the group. It is most dominant around the Heuningnes Estuary and Soetendalsvlei site also a portion of the estuary and some parts of Struisbaai are covered by unconsolidated sands (Bickerton and Pierce, 1984).

Table 5:Stratigraphic succession of the Cape Supergroup within the Heuningnes Catchment

Group	Subgroup	Lithology
Bredasdrorp beds		Coastal limestone, Calcified dune sands
Bokkeveld	Birdouw	Shale and sandy shale
Table Mountain	Nardouw	Quartzitic sandstones, shales, siltstone and a few conglomerates
Basement	The Malmesbury shales, and cape granite suite covers the TMG	

3.3 Hydrology

The flow of groundwater in the region is influenced primarily by the underlying geology and its structural characteristics. The flow direction of groundwater is the same as the surfacewater drainage and it mimics the topographic gradient. In the Heuningnes Catchment groundwater occurs in freshwater springs, primary-(intergranular) and secondary (fractured) porosity aquifer types (Figure 3.7). The primary aquifers are confined in the unconsolidated sediments deposited as alluvium in floodplans of major river system and ocean deposit during sea level changes. Meanwhile fracture-sets from hard, consolidated sediments of both Bokkeveld and Table Mountain Groups are strongly related to the secondary aquifers in the region (Mukheibir, 2007). Directly linked to the catchment geology, the upper part of the catchment is dominated by fractured aquifers meanwhile the intergranular primary shales with low yield occur at the lower part of the catchment (Figure 3.7). As stated by (Kinoti, 2018) the groundwater in the region is mainly used for household and livestock watering purposes.

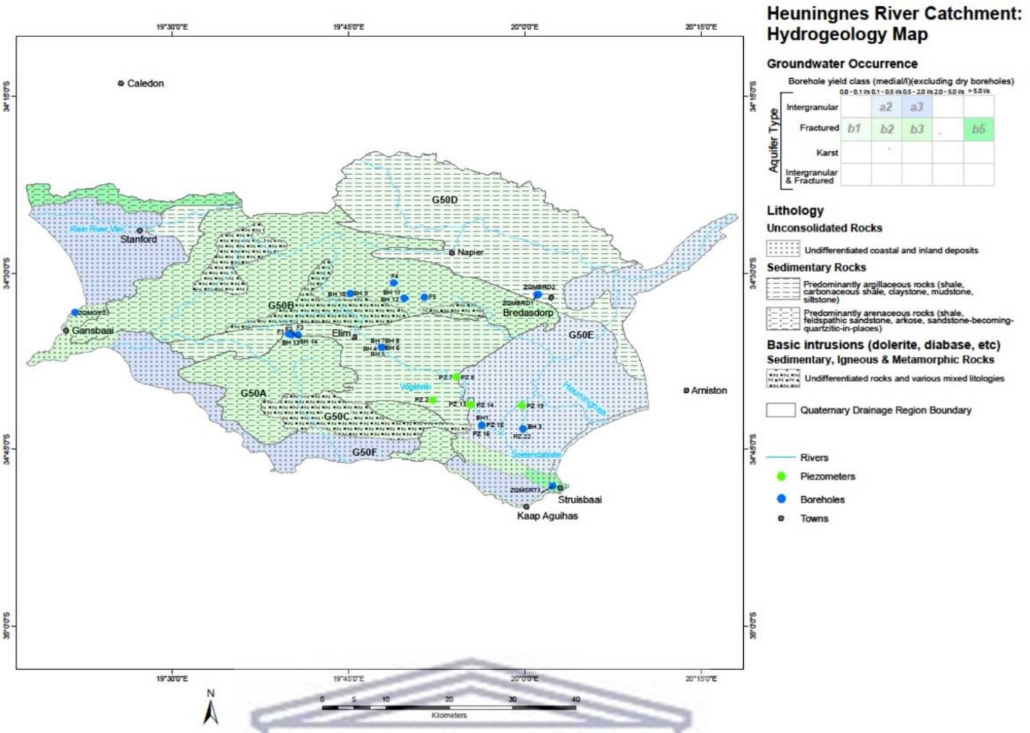


Figure 3. 7:Map showing the different aquifer types in the Heuningnes Catchment

3.3.1. Fractured aquifers

The TMG units form the most significant fractured aquifers in the area, because of the intricate network of fractures, joints, and fissures on the TMG making it the most productive aquifer in the area. While rocks of the Malmesbury (basement) can yield water where fractured, a number of perennial-springs feeding in to the wetland located south of Bredasdorp are hosted by the faulted and fractured quartzites of the TMG. These springs mostly occur on the Peninsula and Skuwerberg formations of the TMG. The Bokkeveld Group does not contribute much in terms of groundwater in the area because of lower borehole yield and poor quality (DWS, 2017). The formations within the Bokkeveld Group may act as an aquitard due to the argillaceous nature.

3.3.2. Intergranular

The intergranular aquifers are made of semi consolidated to unconsolidated alluvial and coastal deposits where groundwater is found within the pore spaces and in the granular interstices formed by Cenozoic deposits (Figure 3.7). This type of aquifer covers a small portion of the study area, mostly dominated at the lower part of the catchment and along the coastline forming coastal aquifers (Figure 3.8); at the eastern part of the catchment it stretches inland up to more than 10 km. The intergranular aquifers present inland are mainly composed of alluvium consisting of clay, sand, pebbles and boulders. The Bredasdorp Group aquifer can be described as an intergranular aquifer type, where water seeps relatively rapidly through the generally porous material to the underlying, impermeable pre-Bredasdorp beds. It moves in the lower conglomerate to lower lying outlet points, where it frequently emerges as springs. There are a couple of such springs in the De Hoopvlei conglomerate occurring between Gansbaai and Standford; these are used by local authorities as a source of water provision in the area. According to DWS (2017) higher yields are associated with the formation of the Bredasdorp Group to the west of Algulhas than to the east, thereof related to rainfall distribution, recharge and fractured rock aquifers and faulting.

3.3.3. Water quality

Groundwater associated with the Malmesbury Group is reported to be saline and of poor quality (Toens et al. 1998). Meanwhile in the TMG concentration of EC measured in groundwater ranges between 500 and 1500 µS/cm. The groundwater is typically corrosive, with pH of between 5 and 6. The iron concentrations are usually in excess of 1.0 mg/L thus the groundwater from the TMG aquifers will require treatment before considered fit for human consumption.

The Bokkeveld group is shale dominated and yields groundwater of poor quality, with EC's ranging between 5000 and 10000 µS/cm (Toens et al. 1998) this water is considered unsuitable for human consumption in its raw state. The poor quality stems from the geology.

In the Bredasdorp group, groundwater is characterised as being hard as a consequence of elevated concentration of Mg^{2+} and Ca^{2+}in the groundwater Water quality abstracted between Koppie Allen and Struisbaai have poor quality with EC in excess of 3000 µS/cm. However, groundwater from aquifers associated with basal conglomerate deposits of the De Hoovlei Formation is usually good quality with EC between 800 and 2000 µS/cm (Toens et al. 1998) from shallow boreholes.

The Heuningnes River has two tributaries, namely Kars and Nuwejaar Rivers, and these rivers later drain into the Soetendalsvlei. The water from these rivers have increased pH and TDS levels and are characterised as alkaline and brackish as a result of being in contact with the Bokkeveld shale and limestone-bearing sands formations. Soetendalsvlei and Voelvlei are characterised by saline waters with EC in the range of 3000 - 7000 µS/cm, meanwhile the small pans (Melkbospan, Soutpan, Vispan) in the area are considered super saline to hypersaline (Kinoti, 2018) having EC's between 24600 and 132300 µS/cm (Toen et al. 1998). These high salinity levels in the water result in water being incompatible for human consumption as well as irrigation of all except for crops that are salt-tolerant crops.

The stream waters occurring in the upper part of the mountain have low pH of 4.5 to5 and Electrical conductivity 430 µS/cm. The pH in the Heuningnes River system is 7 close to Elim town and rising to 8.5 in the Soetendalsvlei, while in the lowland wetland pH varies from 6 to 8.

Chapter 4: Methodology and Research design

4.1. Introduction

Chapter one has explained the main thesis, scope, problem, rationale and objectives of this study whereas, chapter two had outlined the theoretical background of groundwater quality and also reviewed the fundamental aspects governing groundwater quality assessment and application of Hydro-geochemistry, geophysics and hydrogeology approach in the context of the thesis. The current chapter refer to the approaches that were used to gather and examine the needed data to answer the research questions established in chapter one thereby accomplishing the goals for this research. It also highlights limitations of the study. The research basically comprised collection and analysis of groundwater samples.

This chapter contends that comprehensive description of i) research-design; ii) methods for data collection and analysis and iii) moral consideration are indispensable because they offer the basis for reliability and validity of the findings of the present investigation for present and future researchers. Below is the description of the main methods used in this study:

- Geophysical methods –Electrical Resistivity
- Hydrochemical analysis
- Multivariate statistical analysis and
- GIS

The principal aim the study was to define the modern status of groundwater quality within the Heuningnes Catchment especially since there are reported salinity issues. The sources of salinity were determined by identifying the species and total dissolved solids in the shallow groundwater through integrative approach. By combining methods of electrical resistivity and groundwater chemistry can define the quality of groundwater where the resistivity method can delineate the position of salinity within the catchment and the chemical analysis can be used to calibrate the resistivity results and indicate the origin of salinity.

4.2. Study sampling sites

This section presents the sites selected for groundwater chemistry, and resistivity surveys. Sampling sites for groundwater were chosen in a manner that allowed for coverage of various geological-formations, physiographic areas and the boreholes are homogeneously scattered in the study region (Figure 4.1). The attempt here was to ensure that the entire study region was covered for groundwater sampling in order to reach more meaningful and more realistic analysis with reference to characterisation of groundwater quality and its temporal variation. The information on the location of sites was gathered during reconnaissance field excursions during 2014. The groundwater sample locations of the study region are displayed in Figure 4.1. where the blue indicates all boreholes and green are the piezometers.

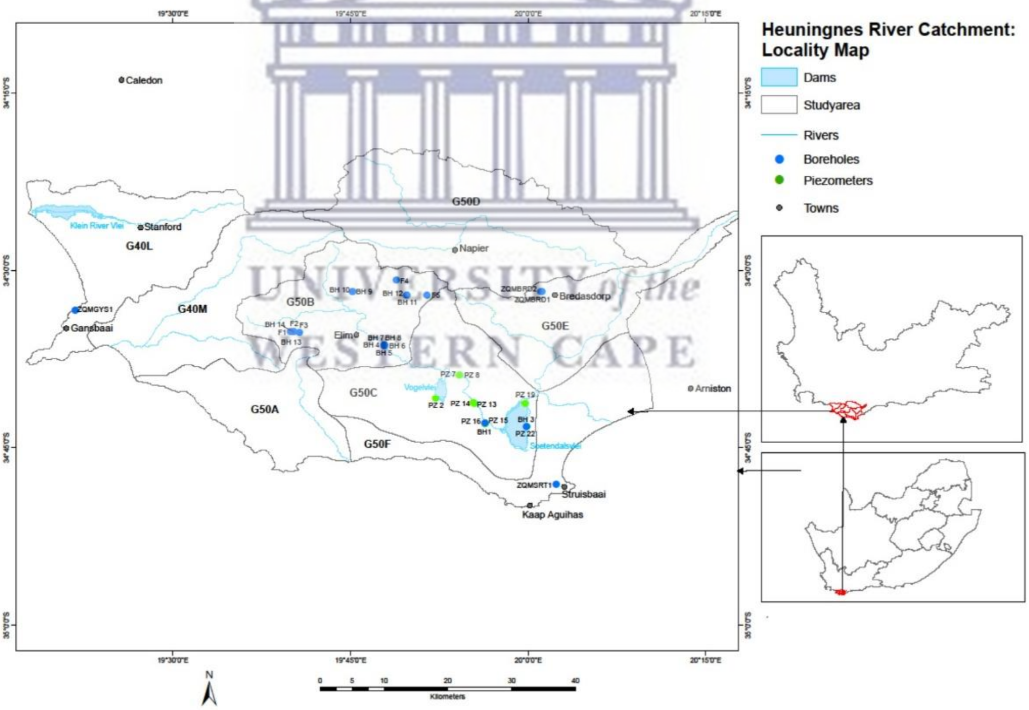


Figure 4. 1: Map shows all the sampling points for groundwater sampling

4.2.1. Study population and unit of analysis

Various parameters were measured within the Heuningnes Catchment for the investigation of groundwater quality. These included resistivity data, physiochemical measurements of groundwater from boreholes and piezometers. These data were obtained using passive and grab sampling techniques, which entailed resistivity surveying and collecting water samples upon fieldwork excursions. The present study examined the use of a multi-methodological approach to investigate the quality of groundwater.

4.2.2. Sampling design

A purposeful and random sampling design approaches were adopted in this study. Firstly, a site reconnaissance visit was undertaken in 2014. The main purpose of the field reconnaissance visit was to identify possible sampling sites for the present study. During this period, initial sites for groundwater quality characterization and resistivity survey sites within the Heuningnes Catchment were identified. These included identifying existing boreholes, identify sites for drilling new monitoring piezometers and new boreholes, and selecting sites to do the resistivity survey.

Groundwater sampling campaign began in 2015 July after the drilling of some monitoring boreholes and piezometers were completed. Sampling was done on both newly drilled and existing boreholes. Some of the existing boreholes were located in private properties, arrangements were made with the owners in time however, at times these boreholes were inaccessible therefore, sampling was done on different days.

The current study was both observational and experimental in a sense that the effectiveness of a multi-approach method to assess water quality was tested. The hydrochemical analysis of water sampled from aquifers and streams were used to describe the quality status of water within the catchment and assess its fitness for various uses especially domestic and agricultural practices.

There were two approaches followed for this part of the study. Firstly, it was the resistivity survey then followed by the collection of water samples for the quality of groundwater assessment. The data was collected at various sites within the Heuningnes Catchment and after rigorous mathematical (mass balance) and statistical (multivariate) expressions were applied. The aim was to test the applicability of the selected methods, while also assessing the status of groundwater quality for various uses.

4.3. Data collection methods

4.3.1. Water sampling for chemical analysis

The collection and generation of field data on groundwater for holistically evaluating the Heuningnes Catchment water resources and improving the understanding of the current water quality status using multi-method approach. Prior to sampling any groundwater in the field the well was purged until pH, specific conductance (SC) and temperature (T) readings were stable. The purpose of purging was to drain the stagnant water in the well casing before sampling to obtain a representative sample of in-situ groundwater with least disturbance of the flow system and the collected sample.

4.3.2. Data type and collection source

Land use and geological maps were used in this study to describe the catchment physiographical characteristics and land use activities, topographical, and geological setting. Additional available information regarding the catchment was sourced from previous reports. Thereafter, historical water quality data was retrieved from the Department of Water and Sanitation's database. To characterise groundwater quality for salinity investigation, water samples and physical parameters were obtained from ground and surface water during fieldwork excursions. To map the distribution of salinity within the catchment, and the subsurface lithology resistivity properties of the subsurface were measured using electrical resistivity technique.

4.3.3. Physiochemical parameters

A total of 29 ground water samples were collected at different water sampling points to assess the groundwater quality of Heuningnes Catchment, this includes 16 borehole samples and 13 piezometer samples. The samples were collected during July 2017 sampling period is representative of a wet season of the year Using a multi parameter probe pH, Total Dissolved Solids, Electrical Conductivity as well as Temperature, of groundwater were taken onsite. Thereafter, groundwater samples were collected for hydro-geochemical parameters cations (Mg^{2+}), (Na^{+}), (K^{+}), (Ca^{2+}), and anions as (Cl^{-}) (HCO_3^{-}) and (SO_4^{2-}), for laboratory analysis. Prior to sample collection, field variables were monitored until they stabilized, indicating equilibrium in the instruments measurements. When these parameters had stabilized, samples were collected and stored in polyethylene bottles (250 ml) that had been cleaned with dilute sulfuric acid (to pH 2.0) before used for chemical analysis. Ice was used to cool off samples during transportation to the laboratory. Failure to promptly transport sample to analysis laboratories, was avoided to prevent degradation of water samples prior to analysis.

1.3.4. Tool/equipment used

Secondary continuous groundwater quality data for three boreholes was electronically downloaded from the DWS database system. Tools that were used for the collection of water samples included an YSI Professional Plus 20™ Multi-parameter sonde, a submersible pump, 250 ml Polyethylene bottles, surgical gloves, ice bucket with ice and permeant marker for sample labelling. The requirement for a stopwatch was countered by the ability of the sonde to continuously measure physical water quality parameters at stipulated intervals.

1.3.5. Procedure followed

The collection of groundwater for chemical analysis as well the measurement of field parameters for water quality was done in accordance to standard sampling procedure (Weight, 2008). Prior to the collection of groundwater samples, a submersible pump was inserted into the borehole. The pump served as a means of removing at least three well volumes (purging) and retrieving a representative sample. Groundwater was pumped for a minimum of 15 minutes to achieve sufficient purging. To obtain samples that were representative of groundwater, physiochemical water quality parameters (T, EC, TDS, and pH) were measured until they stabilized. Thereafter, the samples were collected. Using 250 ml Polyethylene bottles (rinsed at least three times prior to collection using the water to be sampled) then collected samples were placed in a dark cooler box prior to refrigeration at 4°C. Furthermore, no specific sample preservation was required as the analysis was intended for the general chemistry of the water, however, storage at low temperatures and analysis was to be done as soon as possible (within one month) so as to retain the representative sample concentrations without disturbance. The collected samples were then sent to Bemlabs for chemical analysis.

4.5. Data analysis methods

Data analysis involved a wide variety of techniques in order to reach at more meaningful and realistic research finding and conclusions.

4.5.1. Hydrochemical analysis

4.5.1.1. Laboratory analysis

Water samples were analysed at Bemlabs in Strand, Western Cape. Analyses for all the samples were completed following the ISO/IEC 17025 standards and the testing laboratories are South African National Accreditation System (SANAS) indorsed. Samples using SANS accredited methodology (SANS 11885:2008). Cation analysis was done with Inductive Coupled Plasma Optic Emission Spectroscopy, while anions were analysed using Ion Chromatography. As indicated in the Bemlabs Methods description document, the uncertainty of measurement among all elements analysed ranged between 0.000% and 8.55 %, which is lower than the 10% recommended limit for uncertainty (Weight, 2008). The fitness of groundwater in the Heuningnes Catchment for irrigation purposes was measured by means of, the Sodium Absorption Ratio (SAR), Kelly's Ratio (KR) and Percentage Sodium (%Na) and were calculated (in meq/l) based on equation 2-4.

$$SAR = Na^{+} \div \sqrt{(Ca^{2+} + Mg^{2+}) \div 2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

$$Na\% = \frac{(Na^{+}+K^{+})}{(Ca^{2+}+Mg^{2+}+Na^{+}+K^{+})} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

$$KR = \frac{Na^{+}}{Ca^{2+}+Mg^{2+}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

In order to successfully describe the chemical and physical features of the ground water in the investigated area, statistical packages such as Microsoft Excel Spreadsheets, Microsoft Excel Add-on application, XLSTAT 2015 were employed to determine the statistical summaries; standard deviation, minimum, mean, and maximum values, and the range of each parameter considered for all the data sets. Additionally, classification of the groundwater found in Heuningnes Catchment was done on the basis of TDS and EC after the Freeze and Cherry, (1979); WHO (2011), SANS241 classification.

AquaChem 3.70 was also used for:

- Quality-Assurance and Quality-Control (QA and QC)
- Statistical examination
- Delineation of water-types
- Characterising the geology of the study region,
- Determination of the relationship between geology and quality of groundwater.

4.6. Graphical presentation of chemical data

Once quality assessment has been concluded on dataset, graphical data presentation methods are beneficial means for analysis. Data from this study was subjected to various methods for visual comparison of data this include, spatial representation of data by means of geographic information system (GIS) software Piper diagrams, and PCA results.

4.6.1. Spatial Data Presentation

Using spatial distribution of the boreholes different maps displaying major ions were created superimposed on the quaternary catchments, land-use and geology, for interpretation purposes. Spatial distribution maps were created for the following variables Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, Na^+, K^+, SO_4^{2-}, and TDS by means of Inverse Distance Weighted (IDW) method available in ArcMap 10.0. To further display the recommended levels as stipulated by both WHO (2011) and SANS241 reclassification method of the interpolated distributions of these variables was applied.

4.7. ArcGIS

Geographical information system known as GIS software its main functions are to characterise datasets spatially and to create maps and enable comparisons of the spatial data. All GIS visualizations can be achieved by using ArcMap®, version 9.3 which is a commercial product from ESRI (ESRI Inc., 2008). For this particular research all maps were created in the ArcMap that aided analysis for this research.

The coordinates obtained per sampling location in the Heuningnes Catchment area, were used to produce maps with marking of the sampling sites, geology maps, hydrological maps and results of geochemical sampling were prepared for this study. Also from the same program, maps showing the spatial distribution of the quality of groundwater were created.

4.8. Mapping the distribution of salinity using electrical resistivity Electrical Resistivity survey

4.8.1. Data collection

Geophysical data for this study was generated from 2D Electrical Resistivity Imagery (ERI) field survey which was carried out for a period of two months (September and October 2014) at three sites (Soetendalsvlei, Voelvlei and Wiesdrift-Elandsdrift) in the Heuningnes Catchment. To map the distribution of the salinity in the subsurface of Heuningnes Catchment eleven resistivity soundings were conducted around the vleis/lakes. The localities of these soundings were selected to provide the broadest spatial distribution, and were also selected based on the easy access in the area. The distribution of the resistivity lines around the Voelvlei, Soetendalsvlei and Elandsdrift-Wisdrift sites are presented by the yellow dots (Figure 4.2). The resistivity points were plotted on Google Earth using the co-ordinates taken on site during the survey.

Figure 4. 2:Map shows the areas where the resistivity survey was done.

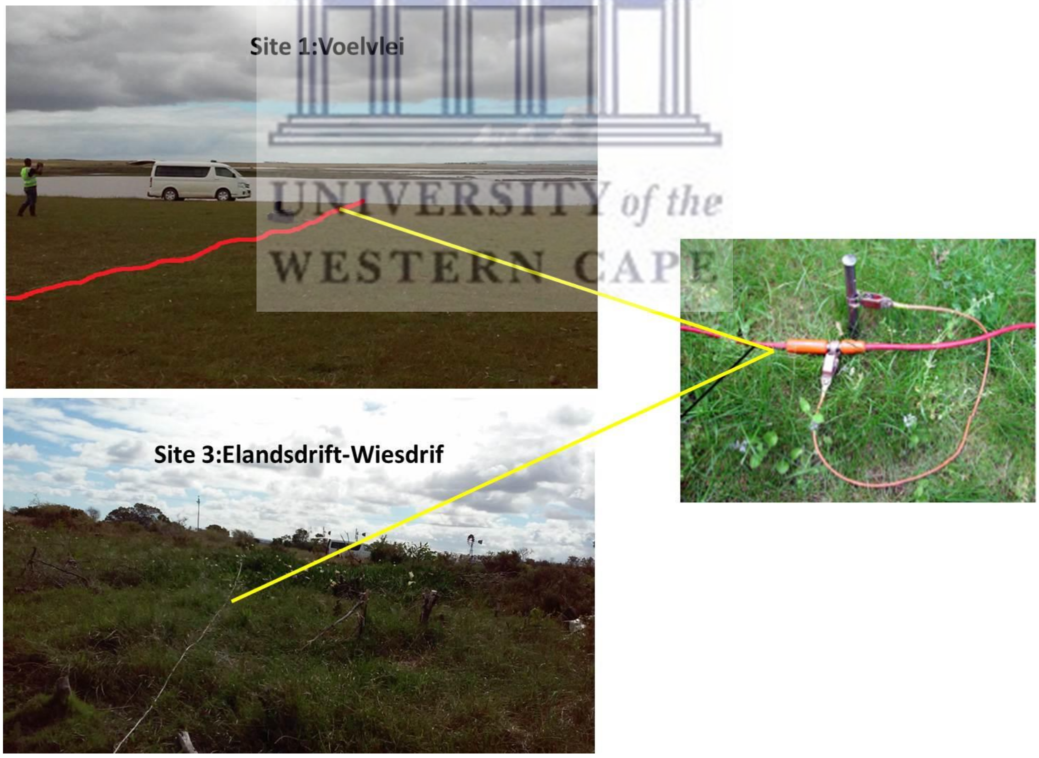


Figure 4.3: Resistivity profile lines carried in various sites in the study area.

4.8.2. Field measurements

The instrument that was used to complete the survey at these sites was the ABEM-SAS 1000 Terrameter instrument coupled with a multi-electrode switch system using a roll-along Wenner array configuration with 64 channels. A roll-along method is useful in extending horizontal area during a survey especially for a system with inadequate number of electrodes. In this study electrodes were joined by multicore cables to a switch board positioned at the center of the profiling (Figure 4.5). Then the potential and current terminals from switching-panel are joined to the matching terminals of the Terrameter. After an order of measurements, the cable is then shifted past one end of the line by few unit electrode spacing.

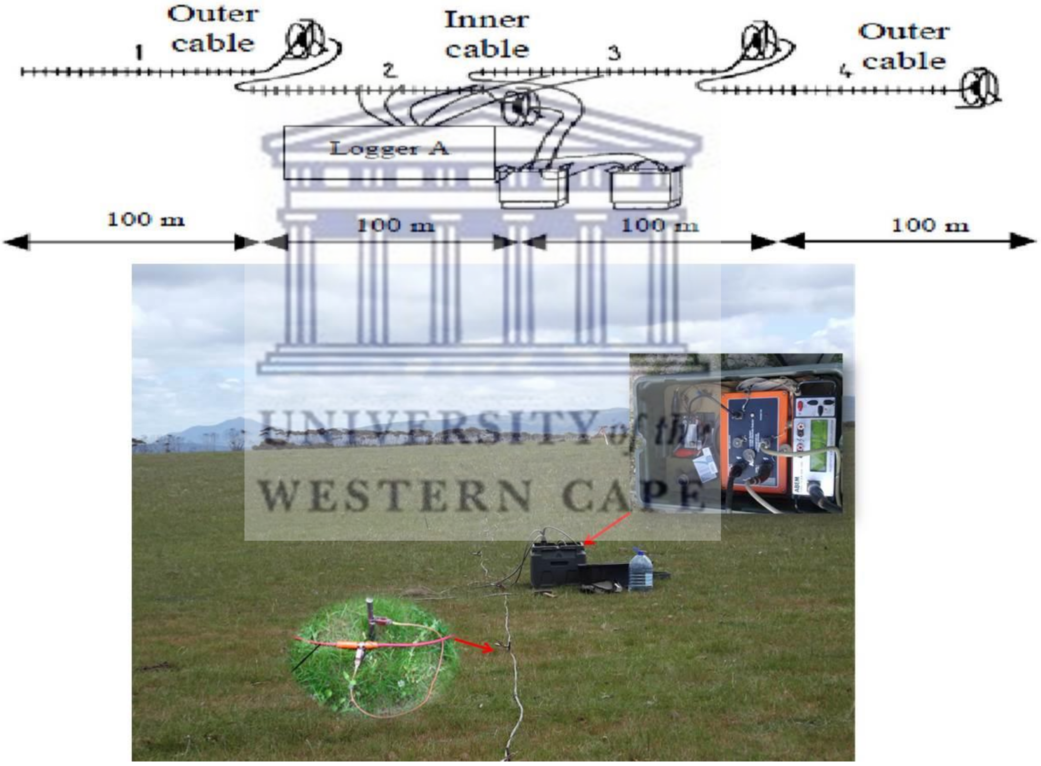


Figure 4.4: An illustration of the roll-along resistivity profiling in Voelvlei site

Electrode spacing along a survey line is important for the examination of lateral variation in earth resistivity. For instance, using larger electrode spacing in an array will gain more depth of penetration, whilst smaller electrode spacing gains supplementary resolution. In this study the electrodes were planted in the ground at about 30 centimetres deep with electrode spacing of 4 meters which acquired investigation depth of 25 meters (Figure 4.3 & 4.4). The traverses varied in length from 240 meters to 160 meters. This array was chosen because of its high signal strength and the ability to give good vertical resolution. This is advantageous factor in areas with lot of background noise. The input current varied from 20 to 200 milli amperes. Elevation for each traverse was recorded using a dumpy levelling tool (Figure 4.6) and GPS co-ordinates were recorded using a handheld Global Positioning System unit (GPS). The coordinates were taken at 40m interval along each traverse line.

Figure 4. 5: Dumpy levelling to map the elevation in the Voelvlei site.

4.9. Electrical Resistivity data analysis

4.9.1. Data processing of Electrical Resistivity data

In this study a software inversion algorithm called (RES2DINV) was used in processing the measured resistivity data by converting it from measured apparent resistivity to exact resistivity for the purpose of producing 2D-resistivity models for each site (Figure 4.7). The inversion routine applied in the RES2DINV programme is founded on a smoothness-constrained least square inversion algorithm (Oyeyemi et al. 2015). This programme executes this by breaking the subsurface into tiny grids (Loke, 2001). The apparent resistivity for his study was estimated according to the finite-difference procedure. The apparent resistivity values were then displayed by means of pseudo-section contouring technique.

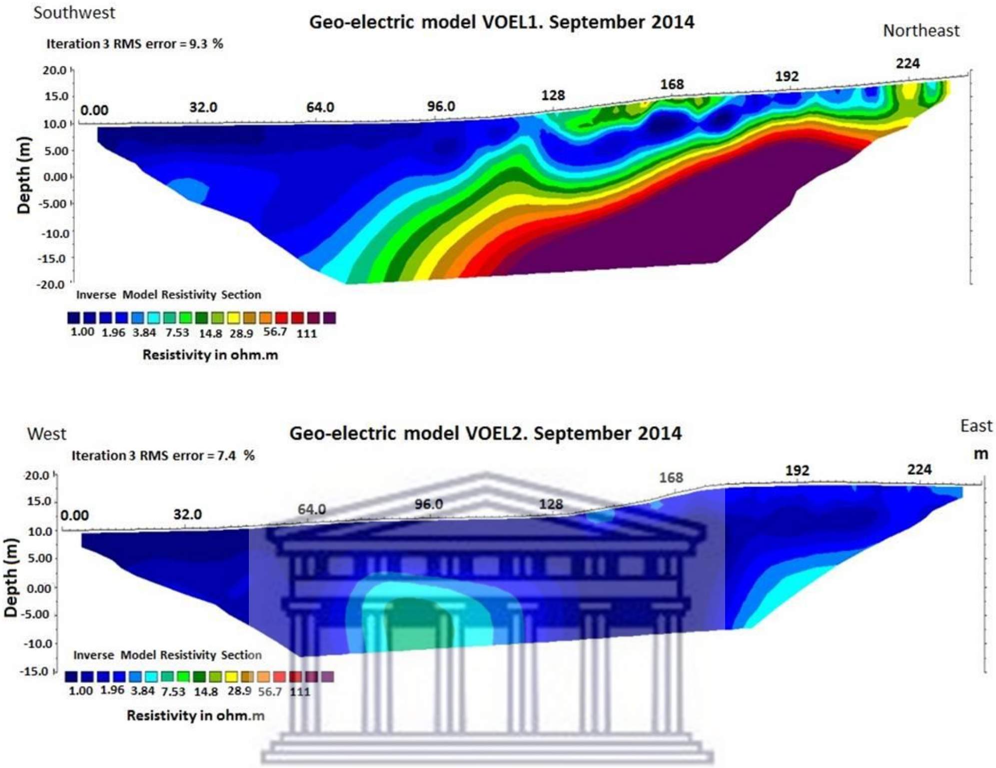


Figure 4. 6: The 2D-resistvity model produced from the software inversion algorithm (RES2DINV).

The RES2DINV uses the least-squares optimization technique which attempts to minimise any variations detected between the calculated and measured apparent resistivity values by modifying resistivity of the model blocks (Ravidran et al. 2012). Then root-means squared (RMS) error is used to specify any change between the measured and the modelled values. According to Loke (2001) a model projecting the minimum RMS error does not always indicate a good model as it can reveal impractical disparities in the final model (Irungu, 2011). In the investigated region the modelled data indicates variations of lowest RMS of 5.4 % to 31.5% high RMS error.

The final resistivity model is affected by any random high or low values of the apparent resistivity (Irungu, 2011). Therefore, to prevent any unnecessary alterations in the final resistivity model data from this study was amended accordingly to eliminate any extreme and invalid datum points. If topography is omitted, then the finite difference method is applicable and it was the case in this study. Since Heuningnes Catchment is characterised by moderately flat surface area, topography will not be an effect in the final resistivity model. Four nodes between neighbouring electrodes with a mesh enhancement of intermediate mesh size were used to obtain more accurate values of the calculated apparent resistivity. Any misfit from the individual data points was removed by applying the distribution of the % change between the logarithms of the observed and calculated apparent resistivity (Craig, 2008).

4.10. Hydraulic injection and drilling of new boreholes

Hydraulic injection was completed in some parts of the study area before the drilling commenced after completion of the geophysical survey. The nature of the site was the determining factor as to where hydraulic injection will be done. Because this technique uses water under pressure to extract subsurface material it only works on softer subsurface materials. Hydraulic injection was only conducted at Voelvlei and Soetendalsvlei sites (Figure 4.7). The purpose was to describe subsurface materials and their depths before the installation of monitoring piezometers. Hydraulic Injection method has its own shortfalls it’s not able to penetrate hard surfaces. Therefore, in areas where Hydraulic injection could not work Mud-Rotary method was proposed for drilling boreholes and piezometers

Figure 4.7: The figure shows the hydraulic injection at the Voelvlei site.

4.10.1. Drilling of boreholes

Drilling was completed in the study region to site monitoring boreholes, as well as to verify the geophysics results, to obtain the subsurface geological formation and validate the reliability of the resistivity technique. The drill depth for the piezometers was set to be 5 m and 10 m and borehole depths were 20 m and 40 m. The drill depth of each well was based on the interpretations of the resistivity models. The desired drill depth was not reached in some of the sites due to failure of equipment. In most cases the driller did not drill through the hard rock in this study described as shale of the Bokkeveld Group or sandstone of the Table Mountain Group.

4.11. Software's that were applied to assess data for this study

1. AquaChem 3.70
2. Res2DInv
3. Microsoft Excel Spread sheet
4. ArcGIS 9.3 from ESRI
5. IBM® SPSS® Statistics 21

4.12. Data Quality Control /Quality Assurance

In all groundwater assessment Quality Assurance (QA) and Quality Control (QC) are absolutely critical. Standardized approaches were applied and recorded all necessary parameters such as linearity, repeatability, storage and detection limits, environments of samples. Samples were taken in replicas and the average of each result was measured for the analysis. During the laboratory investigation quality assurance procedures applied in the involved rigorous contamination control actions (that is strict cleaning and washing procedures), analysis of routine blanks, constantly observing of blank levels of solvents, apparatus and other tools, monitoring of instrument response, linearity and quality of analysis.

After the generation of required data for the respective objectives, it was cleaned. During analysis, duplicates and blanks were added and re-calibration standards ran regularly to check the reliability of the calibration. Analysis of all blank samples did not detect any inherent bias in the method of analysis for analytes of interest. All variances measured in concentrations between duplicate sets fell within the accuracy of the technique for all analytes of interest. The process of cleaning the data involved checking for any blanks, removal of duplicates and backing up of data. To check the reliability of the data on physical water quality parameters, it was checked by calibrating the multi-parameter sonde every sampling day. Calibrations were confirmed with previous calibration information, because the device stores previous calibration information and produces a flag should the calibration be unsuccessful.

Water chemistry data was checked by evaluating the Charge-Balance Error of the samples. According to the Principle of Electroneutriality, Weight (2008) state that water is unable to carry a net electrical charge (positive or negative), but must always be electrically neutral. Therefore, a final test of data quality assurance must be done to check the validity of the data. This test is called the Cation- Anion Balance (CAB). Both Weight (2008) and Younger (2007) emphasize that the CAB is a useful test of completeness and accuracy of field and laboratory data and that only samples having CAB <=15% can be used in hydrochemical data interpretation. The CAB (Equation 5) is commonly calculated by the following equation:

$$CAB\% = \frac{(\Sigma \text{ meq cations} - \Sigma \text{ meq anions})}{(0.5(\Sigma \text{ meq cations} + \Sigma \text{ meq anions}))} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Data collected from ground water sampling spots was subjected to this quality check procedure and revealed that all of the sites had charge balance errors within the recommended range for use of chemical data for reporting.

4.13. Statement on ethical consideration

It is very crucial to seek permission to the land owners and the SAN Parks and the Department of Water and Sanitation prior to doing any fieldwork on the collection of required data within the Heuningnes Catchment since most boreholes were located on private land. This process enabled entry onto private land for groundwater sampling as well as entry into the restricted sites in the study area. Furthermore, permission on reporting on data retrieved from the DWS archive was sought. The resistivity lines injected to the ground for the 2D resistivity survey were not harmful to the ground; therefore, there was no damage or environmental alterations as a result of the resistivity survey during this research.

4.14. Limitations of the study

The main concern is from the retrieval of secondary data from DWS and the fact that methods of data generation are not included in the retrieved data. Therefore, there may be some discrepancy regarding the accuracy and reliability of these data. However, DWS regularly maintains the data loggers and collects the data with validation of the affectivity of the machinery with a manual method of cross checking the daily flow rates with a rating curve table that relates the stage of the stream to flow through that section. The collection of field and chemical water quality data followed the standard procedure. However, data discrepancies may arise from measuring errors introduced by the person doing the measurement. Therefore, to minimise that error one person was responsible for the collection of water samples, meanwhile another measures the field water quality parameters. Regarding the effectiveness of the machinery utilized, manual calibration was required to reduce instrumentation malfunctions and erroneous readings. Chemical analysis of the water samples had to be sent to a certified laboratory outside the university because there were challenges with the university laboratory instruments no analysis could be done at that time.

Furthermore, some challenges the study encountered during data collection, the spatial location of boreholes in the study area was not evenly distributed. As such, some parts of the area, especially the upper catchment is very mountainous and did not have boreholes where groundwater sampling could be done. However, there were springs identified in the upper catchment but no sampling was done on them due to road access issues. On the new piezometers that were drilled 2 of the piezometers were dry during sampling campaign, therefore, no sampling was done on them. Thus most of the sampling in Heuningnes Catchment took place in the central parts of the catchment.

Regarding the application of Electrical Resistivity Imaging, although, electrical resistivity 2D imaging method is the greatest method for acquiring subsurface information, it not 100% accurate it might be challenging to discriminate any changes from material of similar resistivity, such as saline-sand or saline-clay, and in situation where resistivity is low as a consequence of the quality of water. Also poor electrode ground contact and current penetration plays a role interfering with obtaining true subsurface information, however, this is a minor disturbance and can be resolved in the field by wetting the ground with water. Therefore, for a better understanding of the subsurface conditions, resistivity data should be interpreted taking into account surface and subsurface geology normally available from boreholes data.

Chapter 5: Geophysical investigation of groundwater quality in the Heuningnes Catchment

5.1 Geophysical survey in the Heuningnes Catchment

This chapter outlines outcomes of the main geophysical investigation of groundwater quality in the Heuningnes catchment. The 2D geo-electric models for this study are presented in Figures 5.2, 5.3 and 5.4 and the corresponding lithologs are accessible in Figure 5.5. The maximum depth of investigation reached during the resistivity survey ranged between 15 to 25 m and the measured lateral extent of the profile ranged from 128 to 240 m.

In this study the measured resistivity profile lines were named according to the sites where they were obtainedand also the final geo-electric models are given the same name. In Voelvlei the geo-electric models for this site are named (VOEL1, VOEL2, and VOEL3); in Soetendalsvlei site there were five resistivity profile lines and the geo-electric models were named as (ZOEN1, ZOEN2, ZOEN 3, ZOEN4, and ZOEN5), lastly in Elandsdrift-Wisdrift three geo-electric models were measured and were named (DRIF1, DRIF2 and DRIF3). The 2D electrical resistivity geo-electric models from here onwards in this chapter will be referred to as geo-electric models. In the geo-electric models, the blue shaded colour represents a low resistive zone, purple/red colour a high resistive zone and the greenish is interpreted as the intermediate resistive zone which represents either a transition zone from fresh water and brackish water or a poor clayey formation.

5.1.1. Site 1:Voelvlei

The Voelvlei is located north-west of the Soetendalsvlei along the Elim/Struisbaai road. This lake is roughly stretched by 3 km length with a width of 1.5 km and is connected by a 1.5 km long channel to the Nuwejaars River. It has a mean depth of 2 to 2.5 m and it is marked by large reed beds of the northern and southern shores (Gordon, 2011). Voelvlei drains into the Nuwejaars River, but when the river has high water levels, water flows back into the Voelvlei thereby acting as an overflow system for the river. Apart from the Nuwejaars River, other sources of freshwater for the lake come from streams in the south and during high rainfall (Gordon, 2011).

The geology in the Voelvlei area is mostly shale and sandy shale of the Bokkeveld Group. However, the south-western and southern parts of Voelvlei have sandstone and quartzite of the Table Mountain Group. The three resistivity profile lines carried in the Voelvlei are discussed below.

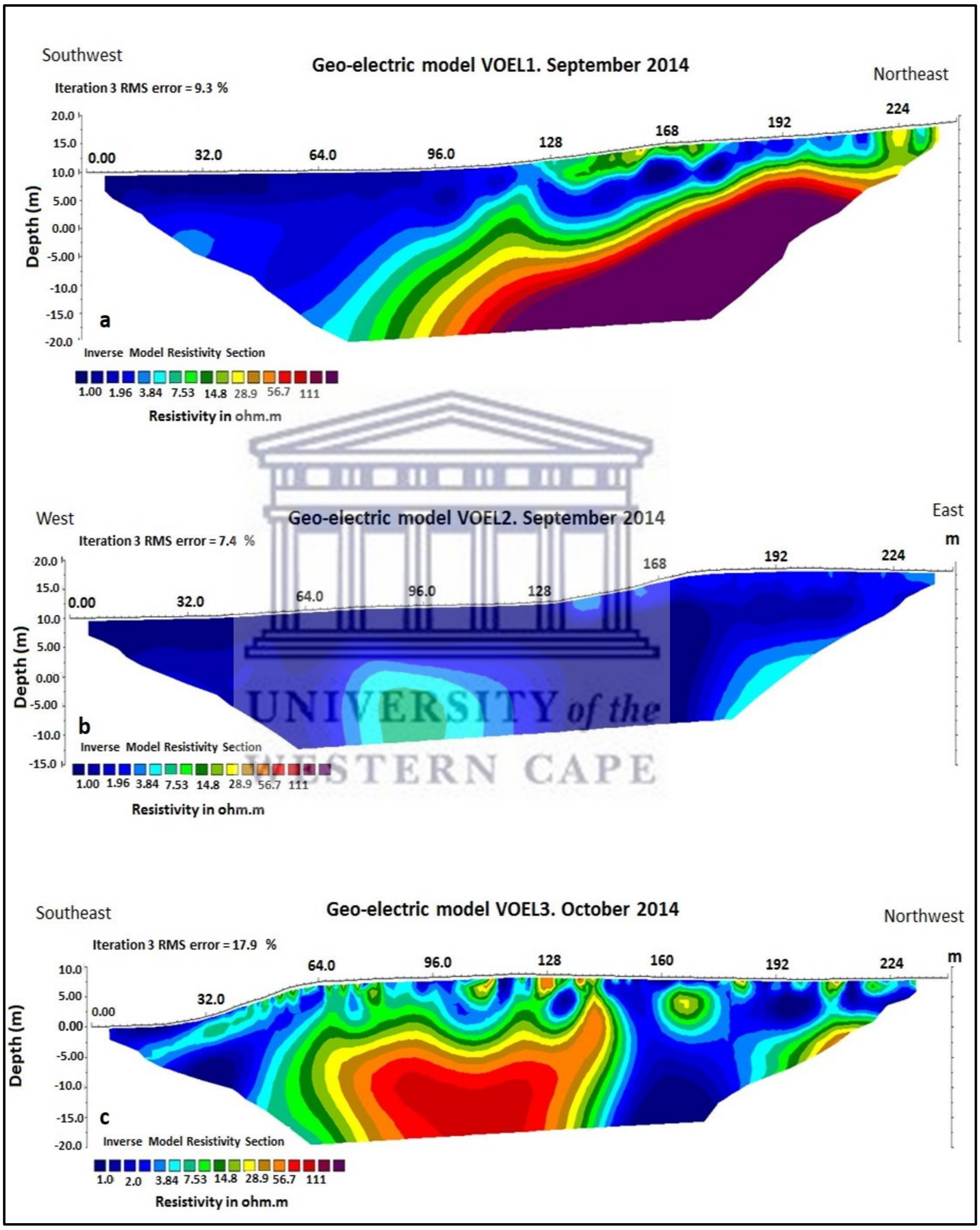


Figure 5. 1: Geo-electric models showing resistivity variation of the Voelvlei site.

All the geo-electric models in the Voelvlei site had a horizontal length of 240 m and the depth of investigation below the subsurface that was reached is 20 m. Geo-electric model VOEL1 is orientated in southwest to northeast trend and it was laid perpendicular to the Voelvlei Lake. The resistivity model VOEL1 shows three resistive layers, there is a clear distinction between the low resistive layer of (1 to 1.96 Ω.m) located at the top left corner of the model and the high resistive layer (56.7 to 111 Ω.m) located at the bottom right corner of the model (Figure 5.1). These two layers are separated by the intermediate resistive layer of resistivity ranging from 3 to 30 Ω.m (Figure 5.1 a). Given the geological history of these sites, the high resistive layer indicates possible freshwater saturated sandstone and the intermediate layer can be described as the weathered material of the sandstone. The low resistive layer may indicate a layer saturated with brackish water. The intermediate layer also appears near the surface at a distance between 128m and180 m; this layer can be described as sandy, more permeable material.

Geo-electric model VOEL2 is trending west -towards east direction (Figure 5.1.b), and it was carried out over 224 m of length, perpendicular to the Voelvlei lake. The depth of investigation below the subsurface that was reached is 15 m. Generally, the area is characterised by very low resistivity values of < 3 Ω.m, these low values are due to the presence of saline groundwater in the area. A pocket of fresh water was observed between the distance of 70 m and 100 m (Figure 5.1 b) having a slight increase in resistivity above 3 Ω.m.

Geo-electric model VOEL3 shows a variation of resistivity in the subsurface ranging from 1 Ω.m - 111 Ω.m. A high resistivity material (over 30 Ω.m) is detected and this layer indicates aquifer filled with freshwater this is observed at a distance of 64m to 140m (Figure 5.1 c). This layer is surrounded by the intermediate resistivity material of 3– 30 Ω.m. The low resistive layer (< 3 Ω.m) in VOEL3 is observed on the left and on the right side of the resistivity model. Several pockets of intermediate resistivity material (3 – 30 Ω.m) are present in the upper surface in VOEL3. The high resistivity layer is described as shale formation corresponding to the geology of the site.

5.1.2. Site 2: Soetendalsvlei

Soetendalsvlei is the largest shallow coastal lake located on the southern Cape coast in the Agulhas Plain district in the Western Cape province of South Africa. The lake has a water surface area of approximately 20 km^2 (Figure 4.2) and extends 8 km with a width of 2.5 km, it has 2 m average water depth, which tends to rise significantly through high precipitation and freshwater inflow seasons. In terms of water quality, Soetendalsvlei is moderately saline with EC of between 3000 and 7000 µS/cm, while the water from the river only get up to 2300 – 2800 µS/cm approximately during the dry seasons (January). According to Toens et al. (1998) groundwater entering Soetendalsvlei has an electrical conductivity of between 4000 and 10000 µS/cm approximately, depending on seasonal rainfall and groundwater recharge. Incoming water to the wetland is reported as brackish and alkaline as a result of passing through the limestone-bearing Strandveld sands and Bokkeveld shales (Gordon, 2011). Like in the Voelvlei, Soetendalsvlei has a large reed bed, extending over the total width of the wetland, which separates Soetendalsvlei into a northern and southern part. Agricultural practices on the eastern shore and abstraction of freshwater from the Nuwejaars River are the main anthropogenic influences on Soetendalsvlei.

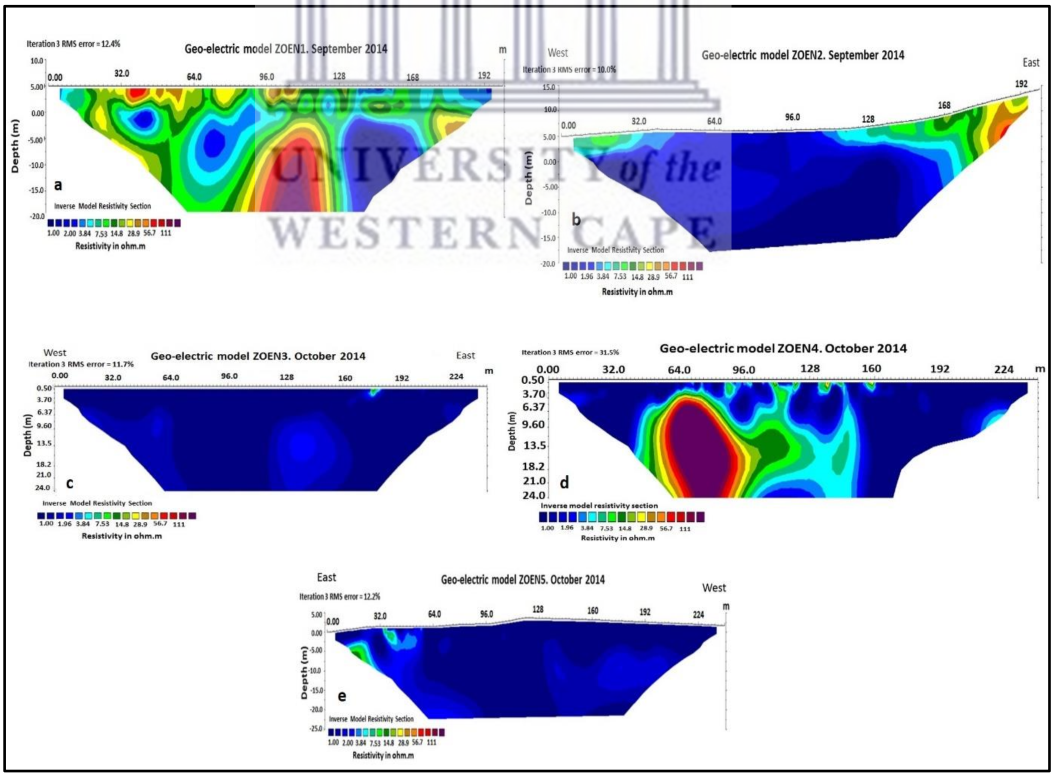


Figure 5. 2: Geo-electric models showing resistivity variation of the Soetendalsvlei site.

Geo-electric model ZOEN1 is oriented in northwest to northeast direction (Figure 5.2 a), and it was covered a length of 192 m, perpendicular to the lake. The maximum depth of investigation obtained in this area is 20 m. Resistivity model ZOEN1 shows variations in resistivity of the subsurface indicating different lithology and fluid content. A high resistive layer with resistivity values over 30 Ω.m appears between the distance of 80m and 110m. The low resistivity material of less than 3 Ω.m occurs in segregated pockets across the profile (Figure 5.2 a) and it is separated from the high resistivity layer by the intermediate (3 Ω.m to 30 Ω.m) resistivity layer indicated by the greenish colour on the model.

Geo-electric model ZOEN2 is oriented in west to east direction, and it was carried over a length of 192 m, perpendicular to the lake. The maximum depth of investigation obtained in this area is 20 m. The area indicated the presence of a conductive zone but mostly high resistivity numbers were encountered, indicating a less conductive zone. Between 110 meter to 165 meter the resistivity changes between 3.84 Ωm and 56.7 Ωm and this indicates a less brackish groundwater saturated layer compared to the first 109 m of the profile (Figure 5.2b), however, resistivity numbers below 10 Ωm indicates an introduction of brackish water and slightly fresh water at high resistivity number over 10 Ωm.

Geo-electric models ZOEN3 and ZOEN5 are both orientated from east to west direction (Figure 5.2 c and e), and they covered a length of 224 m, perpendicular to the Soetendalsvlei lake. The depth of investigation below the subsurface that was reached is 24 m. Both geo-electric models indicate a layer of low resistivity (1-3.84 Ωm) for the distance between 0 m to about 224 m (directed away from the lake). The low resistivity numbers encountered in these profiles could be associated with the salt mash in the Soutpan occurring adjacent to the lake and the presence of saline groundwater.

Geo-electric model ZOEN4 is orientated from east to west direction and was carried over a length of 224 m, perpendicular to the lake. The maximum depth of investigation reached is 24 m from the surface. Generally, ZOEN4 show variations in resistivity of the subsurface, indicating different lithological and fluid content. A high resistive layer with resistivity values of over 30 Ω.m appears between the distance of 50m and 80m (Figure 5.2 d). The low resistivity layer (<3 Ω.m) and the high resistivity layer (> 30 Ω.m) are separated by the intermediate resistivity layer (from 3 Ω.m to 30 Ω.m), indicated by the greenish coloured layer on the resistivity profile. The beginning of the resistivity survey is located close to the mouth of the lake which makes it to have relatively low resistivity numbers displaying the influence of saline groundwater. As expected, resistivity profiles conducted in the Soetendalsvlei show very low resistivity values due to the nature of the lake being hypersaline.

5.1.3. Site 3: Elandsdrift-Wiesdrif wetland

The Elandsdrift-Wiesdrif site is situated between Voelvlei and Soetendalsvlei with the Nuwejaars River passing through this site. This palustrine floodplain covers an area of approximately 6.7 km^2 (Mandlazi, 2017), which is the area between Elandsdrift bridge and Wiesdrift bridge. This floodplain lies in the shale debris, with low potential groundwater storage but allows for groundwater movement and has an elevation that ranges from 5 to 20 meters above sea level.

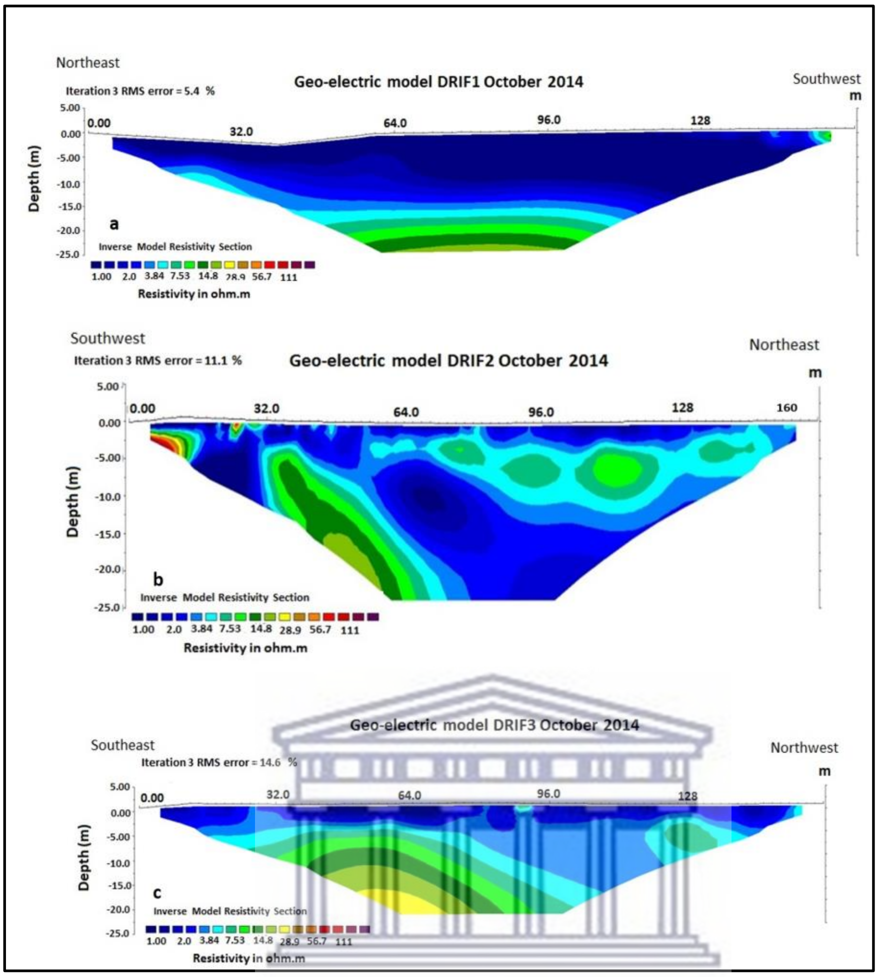


Figure 5. 3: Geo-electric model showing resistivity variation of the Elandsdrift-Wiesdrift site.

Geo-electric model DRIFT1 is positioned in northeast to southwest direction and was carried-out over a length of 160 m, on the right bank of the Nuwejaars River opposite the Wiesdrift homestead. The depth of investigation below the subsurface that was reached is 25 m. There are two distinct resistivity layers depicted from this geo-electric model. The top layer with 15 m thickness, reflects very low resistivity values between 1 to 3.84 Ω.m (Figure 5.3 a) and the bottom layer with a thickness of 10 m has intermediate resistivity values between 7.53 Ω.m and 14.8 Ω.m. The low resistivity values encountered in this site may be influenced by saline groundwater whereas the intermediate resistivity values indicate a brackish groundwater saturated zone. The geo-electric model DRIFT1 shows an increase of resistivity with depth indicating freshening of groundwater with depth.

Geo-electric model DRIFT2 is leaning in southwest to northeast direction and it was carried out over a length of 160 m, on the left bank of the Nuwejaars River across the valley close to Elandsdrift. The depth of investigation below the subsurface that was reached is 25 m. The resistivity value on this site ranges from 1 Ω.m to 15 Ω.m (Figure 5.3 b). However, a high resistivity layer exceeding 30 Ω.m appears at the top left corner of the model. The low resistivity value of < 3 Ω.m as reflected by this geo-electric model indicates a brackish saturated zone and resistivity from 3 Ω.m to 7 Ω.m can be interpreted as a clay poor layer or a layer saturated with fresher groundwater. The resistivity values that exceeds 7 Ω.m (the sub-vertical greenish layer) indicates materials that are part of the shale formation.

Geo-electric model DRIFT3 is orientated in southeast to northwest direction (Figure 5.3 c) and it was carried out over a length of 128m along the left bank of the Nuwejaars River close to the Elandsdrift homestead. The depth of investigation below the subsurface that was reached is 25 m. The resistivity model DRIFT3 shows an increase of resistivity with depth indicating freshening of groundwater. The model depicts two resistivity layers, a low resistivity layer ranging between 1 Ω.m and 3 Ω.m and intermediate resistivity layer ranging from 3.84 Ω.m to 28.9 Ω.m. The low resistivity is due to the presence of a clay formation saturated with saline water.

5.2. Correlation of geo-electric models with borewell lithologs

The resistivity data are interpreted in conjunction with the well lithology of the region. In all three areas surveyed the resistivity, along different profiles seem to project similar resistivity characteristics. Based on observation of all the resistivity profiles, four distinct geo-electric layers were distinguished within the depth of investigation as seen on the geo-electric models discussed above.

The stratigraphy logging recorded during the hydraulic jetting confirms the resistivity results of the two sites. Stratigraphy description in the Voelvlei site (VOEL3) showed that from the top surface to 2.8 m, it was mainly sandy clay which tested very salty, from 2.8 m to 5.6 m it was very fine clay mixed with marine deposits (Figure 5.1 a and c), then followed by very fine sand up to 6m where the bedrock was hit and further injection was not possible. The bedrock is suspected to be the sandstone of Table Mountain Group having resistivity values between 60 and 111 Ω.m (Figure 5.1 c).

At the Soetendalsvlei site the jetting equipment used was not strong enough to penetrate deeper to enable adequate subsurface description. It only penetrated up to approximately 2.5m and the only material that came out was very fine clay which was light grey in colour. This confirms the intermediate resistivity layer (3.84 Ω.m to 7.53 Ω.m) interpreted as clay material that appears on the western side of the geo-electric models ZOEN2 (Figure 5.2 b) between the distance of 0 m and 32 m.

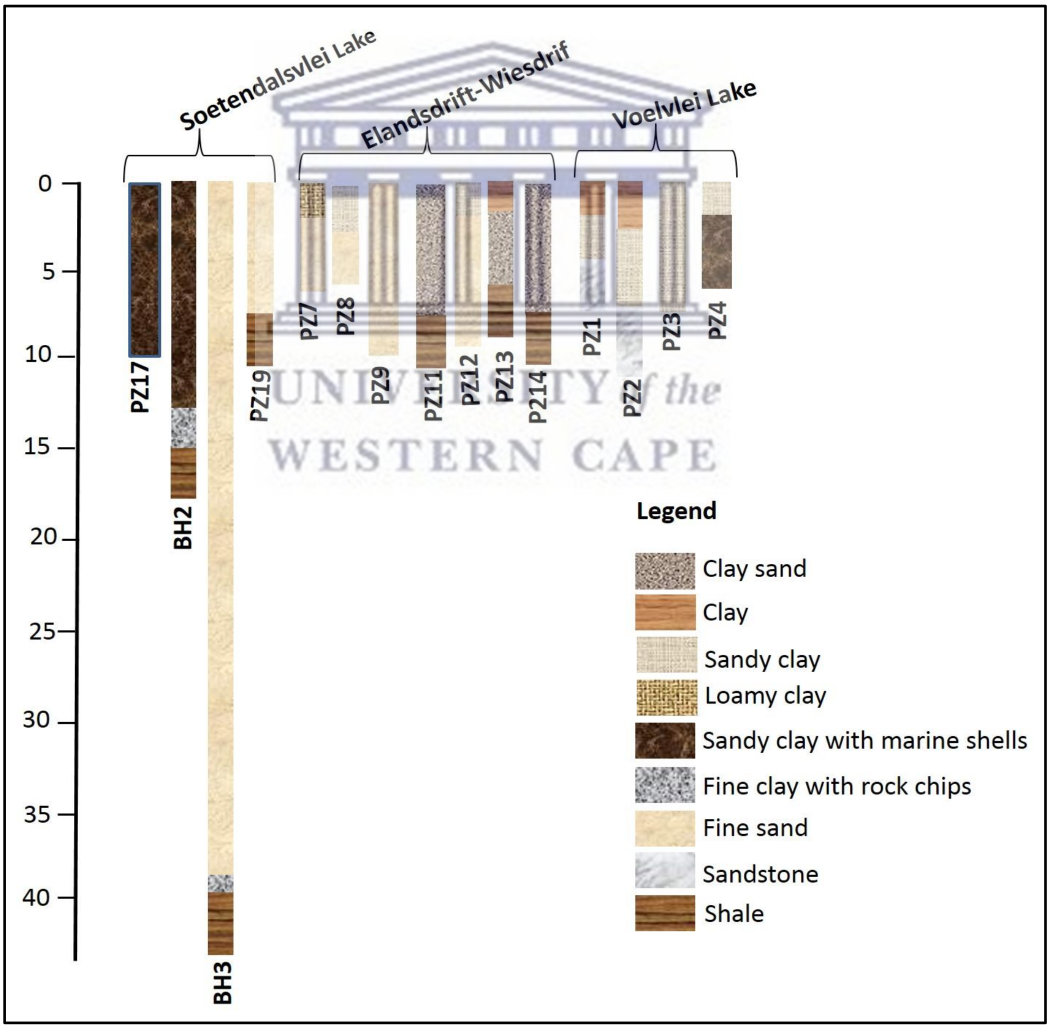


Figure 5. 4: Lithologic logs of the study area, derived from boreholes and piezometers.

The geological information of this area was used as a guide for the geophysical interpretation attained from the geophysical survey of the study region. The lithological sections from the drilled boreholes and piezometers are displayed in Figure 5.4 this indicates that the subsurface geology of the investigated region is made up of the following formations: from the upper surface the sequence comprises of clay, loamy clay, fine sand, sandy clay, fine clay with rock chips, sandy clay with marine shells, clay sand, shale and sandstone. This is in agreement with the results revealed by the resistivity results. Potential groundwater may be sourced from the sandstone and fine sand formations, from the resistivity models an 8 and 30 m primary aquifer was identified in Soetendalsvlei site and upon drilling freshwater was associated with these formations whereas saline water was associated with the clay layers.

5.2.1. Voelvlei site Piezometers

Piezometer 1 was drilled at 92 m along resistivity profile VOEL 1, (Figure 5.1) and the lithology description indicates that there is good agreement at 192 m horizontal distance. The geo-electric model indicates a low resistivity layer (<3 Ω.m) up to 4m depth from the surface and this layer represents the clay layer as presented by the lithology PZ1 (Figure 5.4). The sandstone formation begins to appear from 4 m onwards. The geo-electric model at 168 m horizontal distance is in agreement with the lithology from PZ2, which is characterised by clay with fine sand at the top layer, followed by sandy clay formation and thereafter the beginning of the sandstone at 6m. Along VOEL 2 at 64 m, PZ3 was drilled and the lithological description is in agreement with the geo-electric model at 32 m (Figure 5.1 b) where sandy clay occurs which has low resistivity values of <3 Ω.m.

The piezometer PZ4 (Figure 5.4) is in agreement with geo-electric model VOEL 2 (Figure 5.1 b), as the subsurface description for PZ4 lithology revealed a sandy clay top layer of 2 m followed by 8 m fine clay layer with shells (Figure 5.4) having low resistivity number of (<3 Ω.m) demonstrating the existence of brackish water.

Lithology description of PZ0 from the hydraulic jetting, corresponds with geo-electric model VOEL3, as at 96 m it shows an upper surface layer of 2 m followed by a 3.4 m fine clay layer with shells and beneath this layer is a thin layer of fine sand up to 6 m, there after shale formation starts to appear (Figure 5.4).

5.2.2. Soetendalsvlei site Piezometers

The lithology description from the lithologs obtained at Soetendalsvlei agrees with the geo-electric models of Soetendalsvlei. The general geology on this site is dominated by clay sand, fine sand and sandstone. The borehole BH3 was drilled up to 40 m in the eastern part of the Soetendalsvlei along the resistivity profile line ZOEN2 at 96 m (Figure 5.2 b). The lithology description from this borehole lists fine sand from surface to 38 m and below this layer is a 2 m layer of fine clay with rock chips (Figure 5.4), lastly a shale formation appears from 40 m. Piezometer 19 was drilled along ZOEN4 at 64 m and PZ17 was drilled along resistivity profile ZOEN2 at 111 m (Figure 5.2 b) these lithologs correspond with the resistivity results.

5.2.3. Elandsdrift-Wiesdrif Piezometers

Comparison of the geo-electric model (DRIFT1) in (Figure 5.3 a) and the piezometer lithology of PZ14 (Figure 5.4) drilled at 64 m along the profile indicate that there is good agreement between geo-electric model and piezometer derived lithology. In PZ7 we first encountered a 2 m loamy clay layer (Figure 5.4) with low resistivity values of less than 3 Ω.m. Beneath this layer from 2 m up to 6 m, is a fine sand layer with moderate resistivity values ranging from 3 Ω.m to 7 Ω.m; this corresponds with the geo-electric model DRIFT3 at 128 m along the profile line (Figure 5.3 c). Along the same geo-electric model at the distance of 64 m lithology description of PZ9 (Figure 5.4) indicates fine sand saturated with brackish water in agreement with this low resistivity layer of DRIFT3 (Figure 5.3 c). Piezometer PZ11 was drilled at 10 m distance along the resistivity profile line DRIFT2 (Figure 5.3 b). The subsurface lithology description matched with the geo-electric model where the upper layer has low resistivity values < 2 Ω.m (Figure 5.4), followed below by the shale formation of the Bokkeveld Group having high resistivity values about 56 Ω.m. In PZ12 the first 2 m thick layer is described as sandy clay (Figure 5.4), this corresponds with the low resistivity layer depicted by the geo-electric model DRIFT2 at 96 m distance (Figure 5.3 b).

5.3. Overview and summary

The Electrical resistivity method was used in this study for the purpose of mapping the spatial distribution of saline groundwater in the Heuningnes Catchment. This particular technique was chosen for this investigation because of the sharp electrical resistivity contrast between fresh groundwater and salty groundwater, as well as between aquifers and the background geology (Chongo et al. 2015). Salt water intrusion zones or saline groundwater zones are normally expected to have relatively low resistivity values (high conductivity). However, shale layers also exhibit a similar trend, as shale layers are known to be electrically conductive as a consequence of the high surface conductivity associated with clay particles. In areas where both saline/saltwater saturated layer and shale layer exist it becomes extremely difficult to differentiate between the two. In such a situation the geological condition of the area in conjunction with the areas drill logs becomes important for the interpretation of the electrical resistivity models.

Electrical resistivity of the subsurface is govern by a number of aspects such as the texture of the rock, mineral content, porosity, water content and salinity (Kavidha et al. 2013). Resistivity also tends to increase with grain size especially in an aquifer saturated with freshwater, however, increasing clay content will reduce resistivity drastically. The resistivity models' values ranged from 1 to 111 Ω.m across the study area. The 2D imaging of the subsurface variation in resistivity depicts different lithologies and fluid content.

Different materials have different resistivities as such that the silt content of the sand or degree of salinity controls the final resistivity, where sandy zones occupied with freshwater or air will have resistivity numbers between the ranges 30 to 50 Ω.m or higher, whereas, sandy zones saturated with brackish or saline water reflects low resistivity usually 1 - 10 Ω.m or lower (Johnson et al. 2008; Jansen, 2011). Similar resistivity values were encountered in the study area which suggests four geologically distinct subsurface features identified as clay, sandy clay, shale, and sandstone.

The resistivity profiles in all the sites depict four layers of resistivities: a brackish water saturated layer (1 Ω.m -3 Ω.m); a transition layer or rather poor clayey layer

(3 Ω.m – 8 Ω.m), a clay layer (8 – 30 Ω.m), and finally a layer of sandstone or shale (56 Ω.m – 111 Ω.m). The low resistivity (1-3 Ω.m) layer reflects an aquifer containing material saturated with brackish water. In VOEL1 the low resistivity layer intrudes the low permeable layer as presented by the green shade in the resistivity model. This is the suggested preferential flow path for the distribution of saline/brackish water into aquifers. In VOEL 3 and DRIF 2 (Figure 5.1 c and Figure 5.3 b) the clayey poor layer saturated with fresher water is more dominant near the surface at depths of less than 10m and the presence of fresher water compared to the brackish water in parts of the aquifer may indicate fresh rain water that was recently recharged or recharged water from the lake to the shallow aquifer. Whereas, the fresher water at depth may be related to fresh water from a deeper aquifer. The high resistivity layer (over 30 Ω.m) usually appearing from 5 m below surface from most of the geo-electric models, represents shale or fractured sandstone filled with either fresh water or air. In some models such as ZOEN1 the aquifers are separated by the clay poor layer having resistivity values of 3-30 Ω.m.

Some of the resistivity models such as (DRIF 2, DRIF 3 and VOEL 2) reveal a dominant trend of increasing resistivity with depth which designates decreasing salinity with depths. This trend corresponds with the information given by the farmers that groundwater at greater depths is less brackish compare to groundwater at shallow depths. In geo-electric models VOEL1, ZOEN2 and ZOEN4, salinity increases horizontally with increasing distance whereas, in the Soetendalsvlei the models show variations of resistivity in the subsurface. The resistivity layer reflected by these models corresponds with the local geology of the area suggesting that the near surface material comprise of fine sandy to clayish material, while the deeper material varies from sandstone of the Table Mountain Group to shale of the Bokkeveld Group. This is also supported by the borehole lithologs obtained during drilling. Weathering of these materials explains the change in high resistivity to lower resistivity which in this study is described as the transition zone. Also, the transition zone serves as the boundary separating the aquifer containing saline water from the aquifer saturated with fresh water (VOEL 1, ZOEN 1). The degree of weathering increases towards the east (ZOEN4) and southwest (VOEL1), causing a decrease in resistivity and consolidation of the subsurface in these directions.

Given the assessment of the resistivity results, it seems that there is no indication of seawater intrusion in the area or at least at the depths investigated. Therefore, seawater intrusion can be ruled out as the source of saline groundwater occurrence in these sites. This then means there are additional sources accountable for the high salinity found in groundwater in this area. Therefore, the underlying geology of the area is suspected to exert some sort of control in the prevailing salinity in the area more specifically the sandy shales or limestone of the Bokkeveld Group. Also, other sources that can be considered to be adding to the high salinity level in the investigated area especially in the Soetendalsvlei are the salt pan called Soutpan which is situated on the western site of the Soetendalsvlei, activities taking place in the region such as farming and agricultural practices. The fertilizers used in these practices also contribute to salinization especially on the upper layers of the subsurface of the study region or rather on the shallow aquifers of the Heuningnes Catchment. The resistivity models for ZOEN2, ZOEN3 and ZOEN5, display a subsurface saturated with brackish water having resistivity below 3 Ω.m serve as proof.

The typical geology of the study region is comprised of shales and sandy shales of the Bokkeveld Group and quarzitic sandstone of the TMG, and the surface geology is mostly covered by calcified dune sands of the Bredasdorp group. The lithological description of the drilled logs corresponds with the geology of the area and the different subsurface geology and fluid content thus explain the variation of the resistivity displayed by the geo-electric models.

One of the study objectives was to use geophysical methods such as the electrical resistivity technique to map the spatial distribution of saline groundwater and to demonstrate the effectiveness of using the resistivity technique in mapping salinity and subsurface conditions in the Heuningnes Catchment. It was anticipated that by using this technique, current groundwater quality status within the study area can be understood. The 2D geo-electrical resistivity models provided significant insight on the area's subsurface geology and the distribution of saline, brackish and fresh water within the aquifers. The interpretation of the resistivity data specifies presence of three layers established from the resistivity values in the study region.

These are a) a low resistive layer, b) an intermediate resistive layer and c) a high resistive layer. The assessment of lithological logs obtained during drilling of boreholes and piezometers reveals that the investigated zone is regarded as alternating layers of sandy clays, clays, sandstone and shales of various grade of weathering.

The interpretation of the drill lithologs was in agreement with the resistivity subsurface results. Saline and brackish water were associated with layers of low resistivity (less than 30 Ω.m) saline water having lower resistivity below 3 Ω.m, whereas, freshwater was associated with high resistivity layers (above 30 Ω.m). In all three sites the dominant layer is the low resistive layer which corresponds to a layer saturated with saline groundwater. This is not surprising the wetland itself is characterised by high salinity levels especially the Soetendalsvlei site. Although, seawater intrusion was not the main focus of the study, it is only fair that its contribution to salinity is not ignored if there is. Therefore, it is significant to note that despite the area's location in a coastal area no seawater intrusion was detected in the surveyed area based on the resistivity as seawater has resistivity of 0.3 Ω.m on average and the lowest resistivity encountered in this study was from 1 to 3Ω.m which is an indication of saline groundwater but not of seawater intrusion. It is suspected that the geology of the region and the saline water from the vleis are the major sources of contribution to the occurrence of salinity prevailing in Heuningnes Catchment. Although, the findings from the geophysical survey correspond with the geology of the area, hydrochemical investigation is required to validate the resistivity results and to also obtain an overview of the general groundwater quality of the area in terms of water type, dominant geochemical processes controlling the quality and well as the origin of groundwater in the area. The hydrochemical interpretation to substantiate the geophysics results will be discussed in chapter 6.

From a methodological point of view, the electrical resistivity method was able to characterise subsurface layers, reveal their approximate thickness and their resistivity properties. Most of all the technique was able to map zones saturated with brackish/saline water and fresh water and the boundary between the different water qualities was clear from the geo-electric models.

Chapter 6: Hydro-geochemical evolution of groundwater in the Heuningnes Catchment

6.1 Introduction

The knowledge of groundwater quality is crucial for socio-economic expansion of any district around the world. The fitness of groundwater for agricultural, industrial or domestic, uses greatly relies on the chemical composition of the groundwater. The main dissolved chemical parameters found in groundwater include HCO_3^-, Ca^{2+}, K^+, Na^+, SO_4^{2-}, Mg^{2+}, and$^-$. The abovementioned parameters are significant in the classification and assessment of groundwater quality. In this chapter outcomes obtained from hydrochemical analysis of groundwater and surface water and the prime Hydro-geochemical processes governing groundwater quality in the Heuningnes Catchment will be discussed. The study is focusing on groundwater strictly, the purpose of sampling surface water was to show its recharge influence on the shallow groundwater and if it had any effect on the quality. Therefore, surface water will not be discussed as much but rather referred to when necessary.

This chapter discuss the principal hydrochemical facies and geochemical processes in groundwater. Furthermore, using the hydrochemical analysis findings the hydrochemical characteristics of groundwater of the Heuningnes Catchment a well as its fitness for domestic and irrigation use will be evaluated. The chemical data of this study area was interpreted using a number of techniques such as US Salinity Laboratory, (1954) for classification of irrigation water, spatial distribution maps, scatter, piper diagrams and ionic ratios.

6.1.1. Composition of physiochemical variables

The outcomes of the chemical constituents of the water samples are shown in Table 6 and Table 7 gives the statistical variation of the various investigated parameters. These were compared with World Health Organisation standards (WHO, 2011) and the South African National Standards (SANS 241 (2011). Most of the water wells investigated in the area are tapping from both shallow aquifers (<10 m and represented by the piezometers PZ1- PZ13) and deep aquifers (>10 m and represented by boreholes F1-BH13).

In this study pH, Electrical Conductivity (EC, µS/cm) and temperature were measured on site. Total Dissolved Solids (TDS, mg/L) for all samples except for ZQMBRD1, ZQMBRD2, ZQMGYS1 and ZQMSRT1 were calculated using the EC values in µS/cm according to the following equation from Weaver (2007):

TDS mg/L =EC (µS/cm) *0.64 ……………………………… (6)

pH, acidity and alkalinity

Various chemical parameters were determined for 32 groundwater samples the raw chemical results are presented in appendices; shallow groundwater Appendix A; deep groundwater Appendix B). The groundwater samples in the study area shows a general temperature of 12 to 23 °C. There is no standard temperature value recommended for groundwater by both WHO (2011) and SANS 241. In general pH is considered as the prime variable to measure the quality of water if it's acidic or alkaline in nature (Kokkat et al. 2016). The pH is scaled from 0 to 14. Water is considered acidic if its pH is less than 7, whereas, pH exceeding 7 is alkaline and pH of 7 indicates neutrality. (Bhat et al. 2018). For consumption water, an accepted pH ranges from 6.5 and 8.5, while 9.2 are set as the maximum allowable limit by the WHO (2011). Seawater has a pH value of 8.2 (Mtoni, 2013). The results show that pH values of the shallow groundwater samples ranged from 6.6 to 7.5 with a mean of 7.1 (Table 6), indicating that shallow groundwater in the region is slightly acidic to alkaline. Deep groundwater in the area has pH values that vary from 4.9 to 8.5 with a mean of 6.5, indicating groundwater that is acidic to alkaline. Majority of the samples in the area are neutral to alkaline and only 15 % are acidic in nature. The high alkalinity may be attributed to presence of considerable amounts of sodium, calcium, magnesium, and bicarbonate ions which gradually increase the pH and alkalinity also the high pH is attributed to the flowing of rivers though the limestone-bearing sands and Bokkeveld shale in the area. Groundwater in the region is within the permissible limit for consumption water.

Table 6: Statistical summary of physiochemical parameters of water samples in Heuningnes Catchment

ID	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	TDS	T	pH	EC
Shallow Groundwater (Piezometers) (n= 9)											
Min	66	29	118	26	98	193	26	907	17	6.6	1354
Max	381	707	11383	88	254	40988	1609	48977	21	7.5	73100
Mean	225	355	4771	62	189	9580	399	27799	18	7.1	41490
S.D	104	219	3702	21	49	13683	535	16452	1	0.3	24555
Deep Groundwater (Boreholes)(n= 22)											
Min	2	5	34	1	5	56	1	112	14	4.9	320
Max	211	260	6450	86	268	11290	645	9367	22	8.5	13980
Mean	49	59	973	15	98	1546	112	1990	18	6.7	3018
S.D	65	79	1603	28	94	2734	178	2989	2	1.1	4443

**Note all ionic concentrations are in mg/L, EC is in µS/cm, TDS is in mg/L, pH general units, Temp (°C), S.D is standard deviation, n is sample size.*

Full chemical data for the baseline monitoring is presented in appendices (ZQMBRD1 Appendix C; ZQMBRD2 Appendix D; ZQMSTR1 Appendix E, and ZQMGSY1 Appendix F). Groundwater temperature of the baseline monitoring wells in the study site ranges from 10 – 23 °C (Table 7). Historical monitoring data of the ZQMRST1 borehole show an EC that differs from 778 to 1096 µS/cm with mean of 909 µS/cm. As for ZQMBRD1 EC range from 221 to 772 µS/cm with average of 530 µS/cm and ZQMBDR2 the EC fluctuates from 465 to 603 µS/cm with average of 542 µS/cm. Lastly in borehole ZQMGSY1 EC ranged from 665 to 2560 µS/cm with an average of 1774 µS/cm. total dissolved solids (TDS) concentration of borehole ZQMRST1 ranges from 467 to 650 mg/L with mean of 618,while for ZQMBRD1 the TDS fluctuates from 113 to 481 mg/L with an average of 272 mg/L, while for ZQMBRD2 the TDS ranges from 225 to 304 mg/L with mean of 260 mg/L. The pH values for ZQMRST1 range between 7.7 to 8.7 with an average of 8.2 and for borehole ZQMBRD1 pH values vary from 4.8 to 6.9 with an average of 6.2; for ZQMBRD2 indicated pH values range from 5.3 to 6.8 with an average of 6 and lastly in ZQMGSY1 we have a pH range from 6.2 to 8.5 with an average of 7.9 (Table 7). Two of the boreholes have water that is acidic to near alkaline (ZQMBRD1 and ZQMBRD2) meanwhile the ZQMSTR1 have alkaline water and ZQMGSY1 have acidic to alkaline water based on the pH values.

Electrical Conductivity (EC)

Electrical conductivity is favoured in groundwater quality studies since it is a measure of the capability of water to pass an electrical current. Most dissolved salts in groundwater occurs in ionic forms and are able to conduct current (Deshpande and Aher 2012), therefore, conductivity will be high if there are more dissolved ions present. The overall amount of dissolved solids and major ions in water is given by EC, according to Mtoni (2013) seawater have EC value of 35000 µS/cm, thus seawater intrusion or salinisation can be easily detected using EC as an indicator. The spatial distribution of EC from evaluated groundwater samples in the study area is presented in Figure 6.1 raw chemical data for shallow groundwater is Appendix A and deep groundwater is in appendix B.

The electrical conductivity (EC) of the water samples ranges from 619 to 73100 µS/cm. The shallow groundwater of the study region has an EC range from 1354 to 73100 µS/cm with an average of 41490 µS/cm. The deep groundwater samples reveal an EC range from 320 to 13980 µS/cm, with average of 1318 µS/cm. The EC of the groundwater in the area indicates that there are quite high amounts of salts that are over the accepted limit for regular consumption groundwater.

Low EC values are confined to the upper catchment where recharge to aquifers is taking place. Moving from upper catchment towards the lower catchment (which is towards the coast), the EC seem to be increasing. Therefore, an increasing trend of EC is observed from inland recharge parts towards lowlands and discharge zone in the sea. The high EC values above 3000 µS/cm in the area are associated with shallow groundwater especially around the Soetendalsvlei and Voelvlei sites. This is in agreement with was described previously by Toens et al. (1998) that water around these sites is characterised by saline waters with EC values between 1300 to 1700 µS/cm. Piezometers (PZ2, 7, 8, 13 and 14) EC values exceed that of the seawater intrusion of 35000 µS/cm. There might be a possibility that the shallow groundwater has been affected by seawater intrusion because fresh groundwater that is has not been in contact with intrusion according to (Kumar, 2016) is characterised by low values of EC and Ca^{2+}-Mg^{2+}-HCO_3^- or Ca^{2+}-HCO_3^- water type. In the study region 41.9% samples are not affected by seawater intrusion more especially groundwater from deep aquifer. Whereas, mixing between freshwater and saltwater is characterised by groundwater samples with EC between1000 and 5000 µS/cm, and samples with EC exceeding 10,000 µS/cm denote strong seawater influence (Alfarrah and Walraevens, 2018). About 19.3% of the samples in the study region indicate mixing and 38.7% indicate strong seawater influence majority being the groundwater from shallow aquifer.

Table 7:Statistical summary of physiochemical variables of secondary groundwater quality data

ID	**Ca^{2+}**	**Cl^-**	**TDS**	**K^+**	**Mg^{2+}**	**Na^+**	**SO_4^{2-}**	**Talk**	**EC**	**Temp**	**PH**
Year (1994 -2017) (n = 23) ZQMRSTR1											
Min	55	114	467	2	11	80	21	142	778	21	7.7
Max	89	168	650	4	15	95	37	239	1096	22	8.7
Mean	83	152	618	3	13	85	26	210	909	16	8.2
S.D	7	13	46	1	1	3	4	18	65	9	0.3
year (1994 – 2016) (n = 15) ZQMBRD1											
Min	3	56	113	3	3	34	7	2	221	-	4.8
Max	47	159	481	7	15	97	36	108	772	23	6.9
Mean	7	129	272	3	9	79	20	14	530	16	6.2
S.D	11	201	80	2	3	17	8	26	161	16	0.5
year (2001 – 2017) (n = 13) ZQMBRD2											
Min	3	117	225	2	5	64	16	4	465	-	5.3
Max	6	160	304	7	12	86	30	12	603	-	6.8
Mean	4	141	260	3	8	76	21	6	542	22	6
S.D	1	13	20	1	2	5	4	3	324	-	0.5
year (1994 – 2016) (n= 19) ZQMGSY1											
Min	74	195	648	3	7	65	28	128	665	10	6.2
Max	127	488	1430	11	36	286	105	297	2560	21	8.5

Mean	99	343	1092	8	28	213	65	241	1774	18	7.9
S.D	19	120	338	3	10	76	28	53	592	4	0.6

**Note all ionic concentrations are in mg/L, EC is in µS/cm, TDS is in mg/L, pH general units, Temp (°C), S.D is standard deviation, n is sample size.*

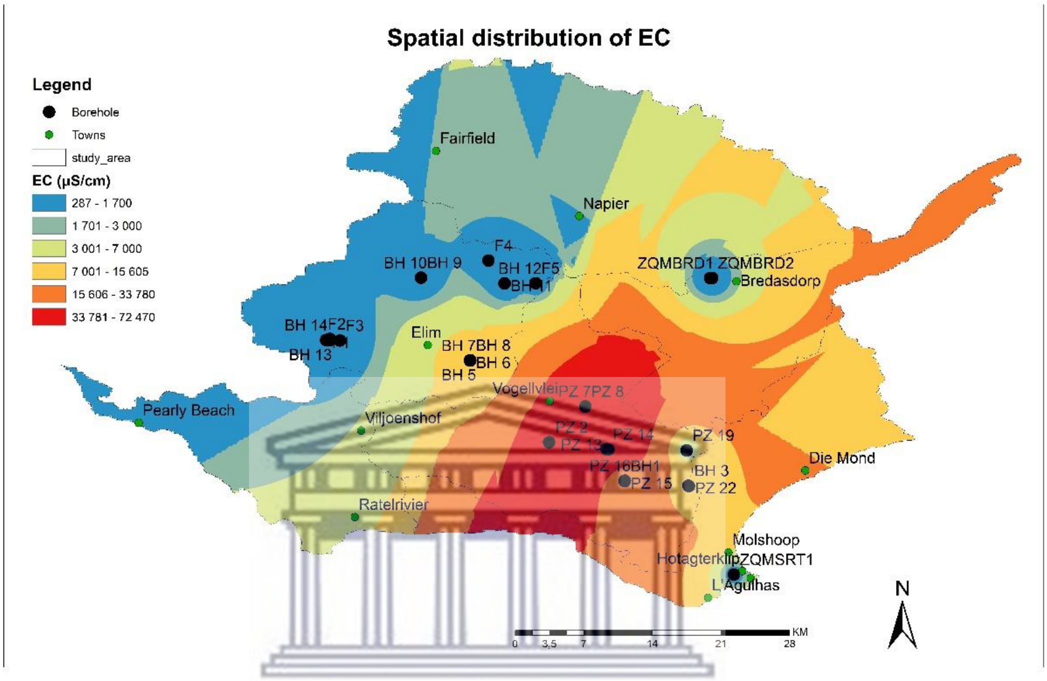


Figure 6. 1: Spatial distribution of (EC) (µS/cm) in the study area.

Total Dissolved Solids (TDS)

Total dissolved solids (TDS), is the total concentration of dissolved minerals in water and it is considered as a gauge of water salinity. Groundwater in its natural form is composed of the major ions (Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, HCO_3^{-} and SO_4^{2-}) and minor ions (i.e. K^{+}) and NO_3^{-} (Kumar, 2016). A relationship exists between TDS and EC, a clear positive correlation of TDS and EC of groundwater samples in the studied site can be seen (Figure 6.2).

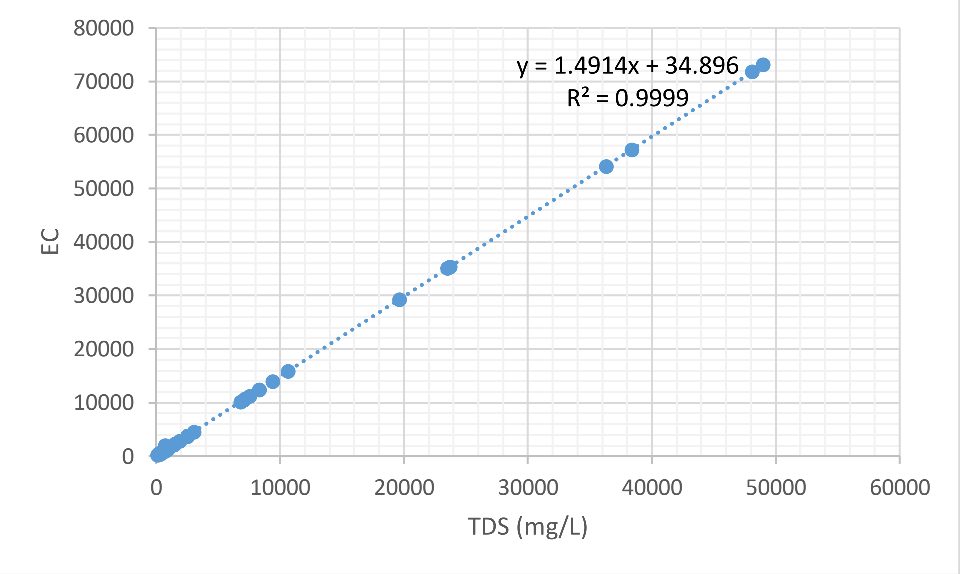


Figure 6. 2: Correlation of (TDS) and (EC) of groundwater samples in the study area.

Dissolved ions in water can be attributed to natural (seawater intrusion) or/and from human activities (waste water discharges, agricultural and urban runoff. Mineral particles dissolved in water commonly do not exceed 5000 mg /L, nonetheless brine contains as much as 300,000 mg /L (Mtoni, 2013). Similar to EC also TDS of 35,000 mg/L is a typical measure of seawater. However, the definite TDS content might be different within comprehensive limits from one sea to another. The spatial distribution of TDS from studied water samples in the study region is presented in Figure 6.3. The total TDS which is a measure of groundwater quality is in the range of 907 to 48977 mg/L having an average of 27799 mg/L for shallow groundwater and 214 to 9367 mg/L for deep groundwater with an average of 1990 mg/L. High TDS could be attributed to lengthier residence time. Spatial distribution map of TDS shows high concentrations at the southern part of the catchment. The TDS follows the same trend as the EC whereby high TDS are also recorded from the shallow groundwater and the trend is increasing towards the sea. The TDS limits as per WHO (2011) criteria, the appropriate limit of TDS is 500 mg/L and the maximum admissible limit is 1,500 mg/L; most water samples in the region from both shallow and deep groundwater exceeded these maximum limits.

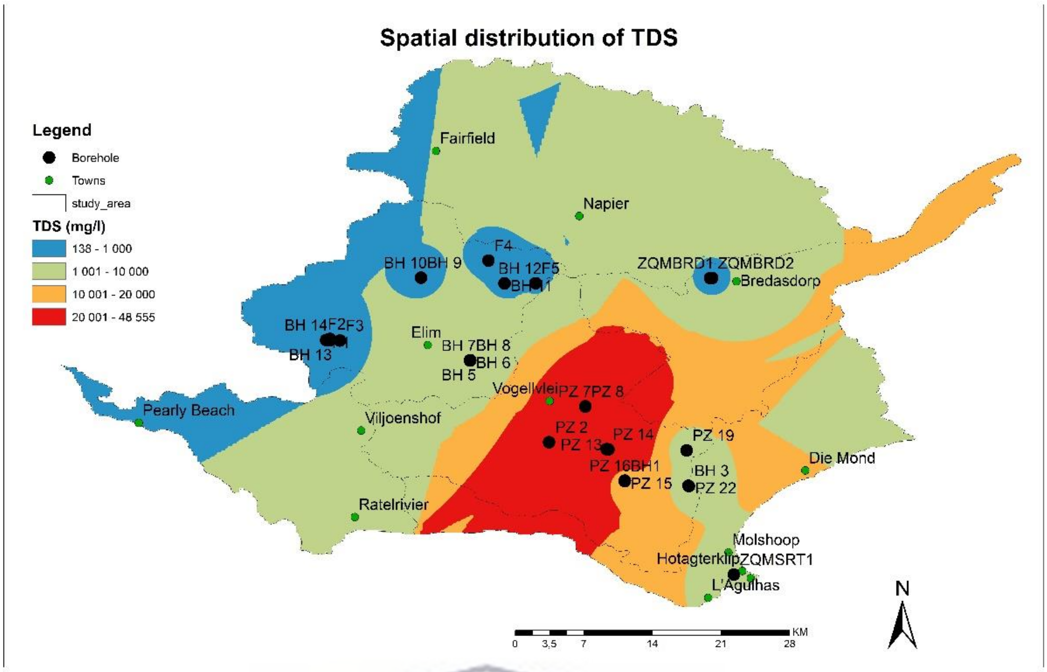


Figure 6. 3: Spatial distribution of total dissolved solids (TDS) (mg/L).

6.1.2. Spatial distribution of major ions

The spatial distribution of major ions K$^+$, SO$_4^{2-}$ Na$^+$, Mg^{2+}, Cl$^-$, HCO$_3^-$ and Ca^{2+}, in the study region is exemplified in the figures below. All the major cations and anions show a similar trend of increasing concentrations from the upper catchment to the lower catchment approaching the seaside. The high concentration of these ions observed at the lower and central parts of the catchment may be due to either the influence of the seawater or the geological material of the area, as high concentrations are mostly associated with samples sited near the coast and around the hypersaline Lake called Soetendalsvlei.

6.1.2.1spatial distribution of major cations Ca2+, Mg2+, Na+ and K+.

Natural source of sodium is from clay minerals such as feldspars (albite), and evaporates (halite). Concentration of sodium is normally < 200 mg/L in natural water, nearly 10,000 mg/L in seawater, and roughly 25,000 mg/L in brines (Mtoni 2013). During weathering of silicate minerals such as albite sodium gets released into groundwater. In coastal aquifers intrusion of seawater is one of the main source responsible for elevated sodium concentration in groundwater, other forms include are sewage, and industrial effluents. Sodium concentration in the study region is very high it is dominant compared to all major cations in the study area. The range of Na^+ in deep groundwater is 34 to 6450 mg/L (Table 6), meanwhile shallow groundwater ranges from 118 to 11383 mg/L. Majority of the water samples in the study exceed the recommended limits of 200 mg /L set by both WHO (2011) and SANS 241. This high increase is a sign of the intense effect of seawater incursion along the coast. Also high levels of Na^+ may be owing to cation exchange where Ca^{2+} from groundwater is adsorbed on clayed materials in exchange of Na^+ (Kumar et al. 2013).

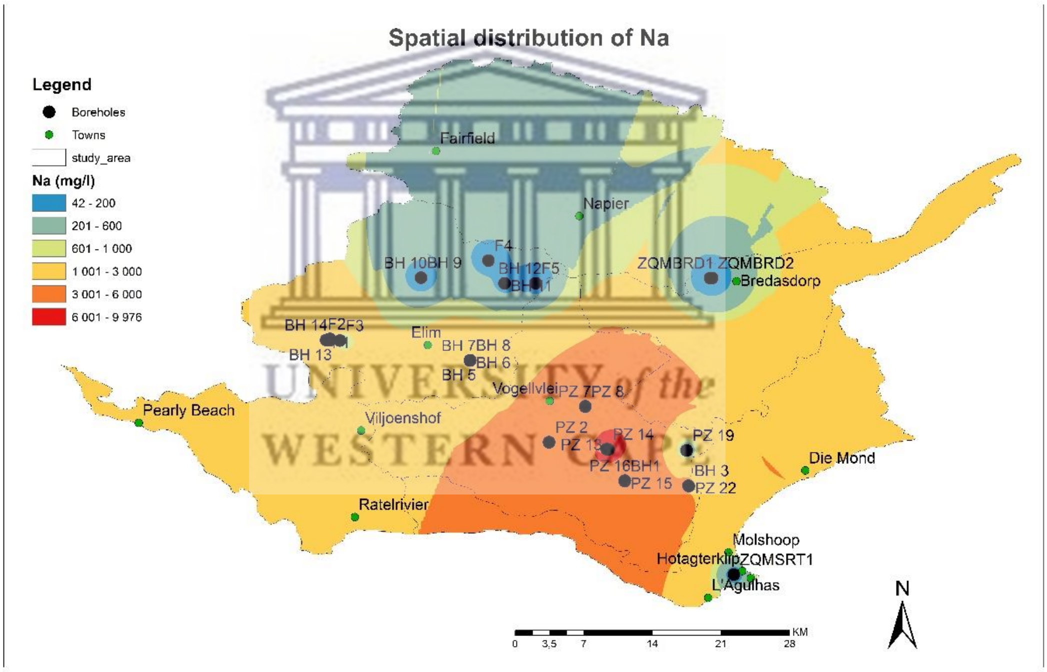


Figure 6. 4: Spatial distribution of Na+ concentrations (mg/L) in the study area.

Groundwater has higher concentrations of salts and minerals as opposed to surface water sources. The salty taste of water is a result of high concentrations of sodium and chloride. Spatial distribution of sodium seems to be high in the lower catchment and low in the upper catchment (Figure 6.4). Recharge occurs in the upper catchment, the high levels of Na^+ in the area can be ascribed to ion exchange process.

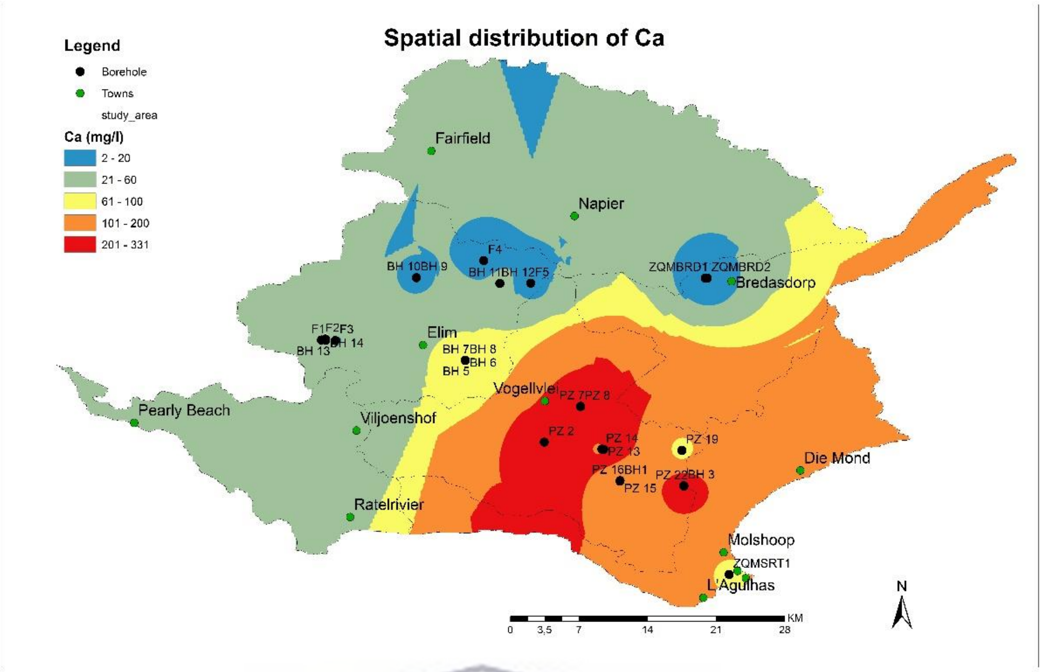


Figure 6. 5: Spatial variation of Calcium concentration mg/L in the study area.

Calcium occurs naturally in water and it is derived from sulphates and carbonates, principally gypsum limestone, and dolomite which are rich in (Ca^{2+}). The concentration level of calcium for shallow groundwater range from 66 to 381 mg/L, whereas, deep ground water has Ca^{2+} concentration levels range of 2 to 211 mg/ L (Table 6). The presence of calcium in groundwater in the region of interest is most probably derived from silicate group minerals found in sandstone, shale, and carbonate rocks in the area. In general, calcium concentration is expected to be greater than magnesium however, in the study area the opposite was encountered, in most of the samples in the region $Ca^{2+}$is lower than magnesium. The desired minimum value of Ca^{2+} in groundwater is 75 mg/L and 200 mg/L is the maximum and should not be exceeded in consumption water as stated by WHO (2011). In the shallow groundwater, a low concentration was detected at PZ 19 (66 mg/L) and a high amount at PZ 13 (381 mg/L) whereas, in the deep groundwater, a low concentration was observed at F4 (2 mg/L) and a high concentration was observed at B3 (211mg/L). Figure 6.5 demonstrate the spatial distribution of calcium with higher levels towards the seaside of the catchment. In the study area calcium is general within the recommended limits except for few locations (PZ2, PZ7, PZ8, PZ13, PZ16, PZ22 and BH3) The high concentrations must be derived from the seawater intrusion, whereby cation exchange transpires when saltwater interrupts the freshwater aquifer, leading to extra amount of Ca^{2+}.

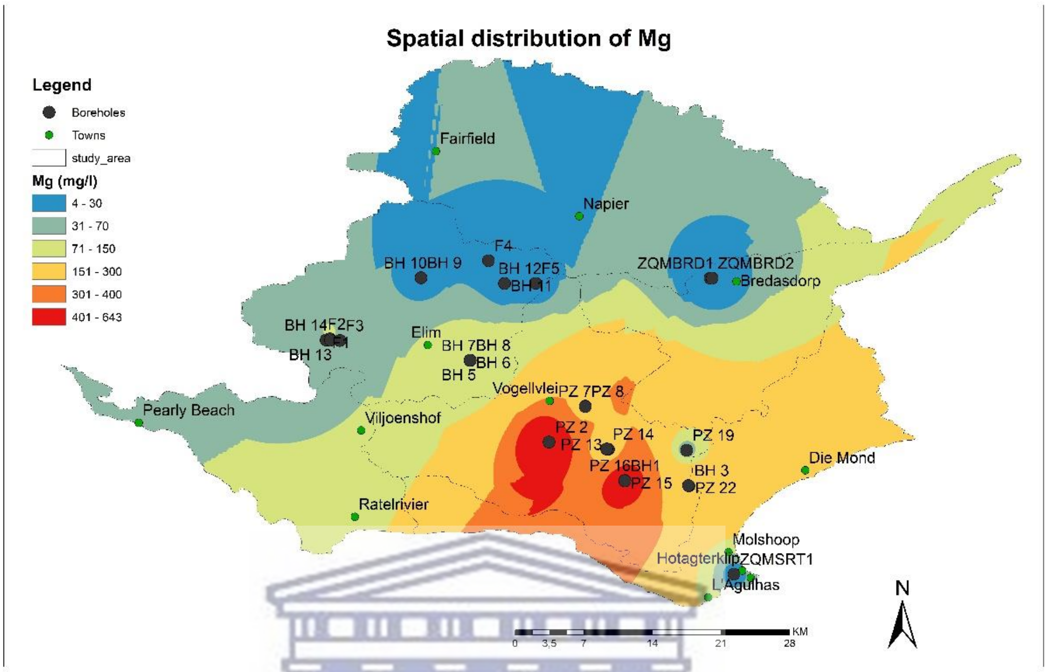


Figure 6. 6: Spatial distribution of Mg2+ concentration mg/Lin the area.

Magnesium present in water is likely to be a product of weathering of rocks containing ferromagnesium minerals, clay minerals or dolomite (Bhat et. al 2014). Natural water contains Mg^{2+} not more than 50 mg/L and about 1000 mg/L in seawater. Concentration of Mg^{2+} in the measured samples ranged between 5 and 707 mg/L, magnesium concentration range for shallow groundwater is 29 to 707 mg/L while deep groundwater has Mg concentration of 5 to 260 mg/L (Table 6).

Spatial distribution map of magnesium is displayed in (Figure 6.6). The map illustrates higher concentrations on the southern part of the catchment similar trend as observed on the spatial distribution of Ca^{2+}. The increasing trend of Mg^{2+} towards the sea as observed in some samples (Figure 6.6) suggest possible admixture of freshwater with seawater. A range of 1 to 86 mg/L was recorded in the deep groundwater of the study region.

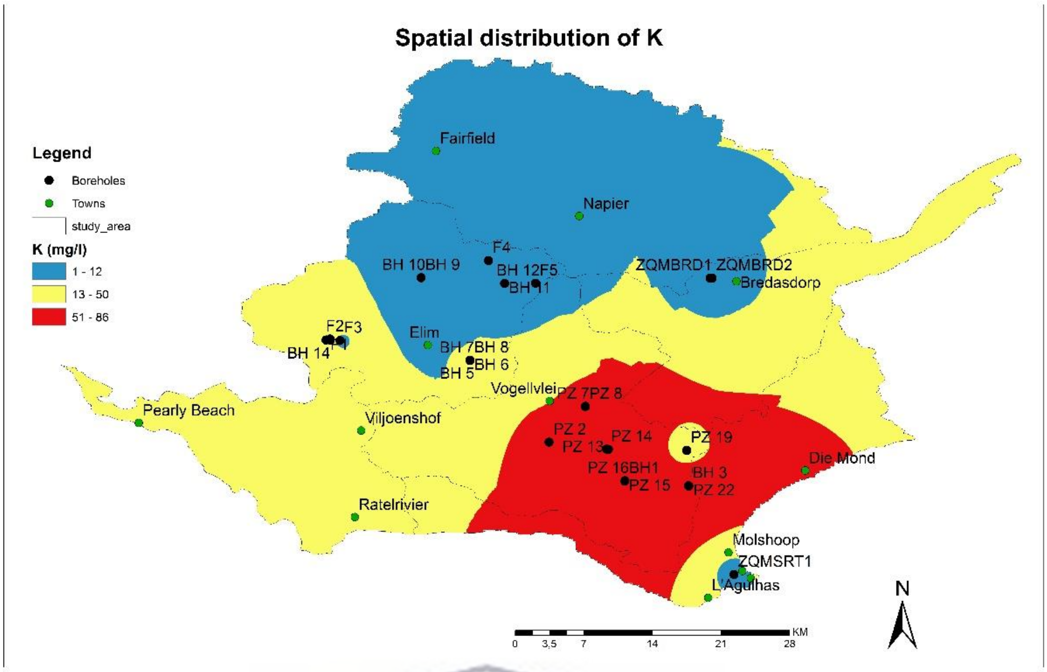


Figure 6. 7: Spatial variation of K+ mg/L in the area.

Spatial distribution of potassium in the region illustrate that potassium is mostly high in the southern parts of the region (Figure 6.7). The potassium concentration in the investigated region is generally low and within the limits as per WHO (2011) and SANS 241. Only a few locations had higher concentrations of potassium than the general range, which is from 1 to 88 mg/L (Figure 6.7). The high concentration of K^+ in the area as indicated by samples from PZ 2, PZ8, PZ 13 PZ 15, PZ 16, PZ 22, F2, BH1 and BH3, is possible owing to contamination by effluent from household and agricultural waste as these locations are located closer to irrigation zones. The high concentration of K^+ detected in the study region is probably product of cation exchange processes and silicate weathering.

6.1.2.2. Spatial distribution of major anions Cl-, HCO3- and SO42-

Chloride ions exist in natural water in fairly low concentration, usually <100 mg/L except for when the water is brackish/saline. High concentration of chloride gives groundwater an unpleasant salty taste. In humid areas concentrations of chloride in natural water is usually lower than 10 mg/L in and can go up to 1000 mg/L or more in arid regions Mtoni (2013). Other factors known to contribute to the chloride occurrence in the subsurface include sewage, industrial discharges, road salting and animal wastes (Shankar et al. 2014). In addition, saline water intrusion is also a known common source of chloride in groundwater and is approximately 19,300 mg/L. The distribution of chloride ion concentrations independently reveals the water interaction with the rocks, the permeability differences of the aquifer and it infers transmissivity of rocks.

In the area of interest, the lowermost chloride concentration is depicted at F4 with 83 mg/L and the highest concentration at PZ13 with 40988 mg/L. About 58% of the groundwater samples exceed the maximum suggested limit of Cl^- of 250 mg/L as stipulated in WHO (2011) and SANS 241 standards. Shallow groundwater the Cl^- varies from 143 to 40988 mg/L while for deep groundwater the range is 83 to 11290 mg/L. The highest levels of Cl^- were recorded in the piezometers which are at close proximity to the coast (Figure 6.8), the Cl^- seem to be increasing towards the sea following similar trend of EC.

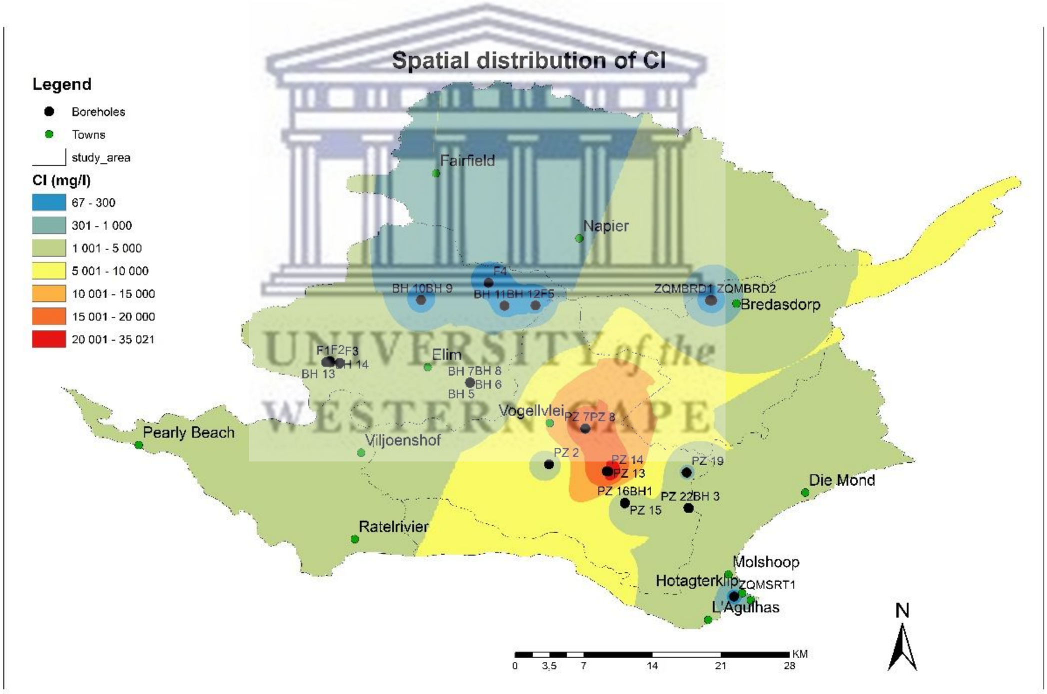


Figure 6. 8: Spatial variation of Cl- mg/L in the area.

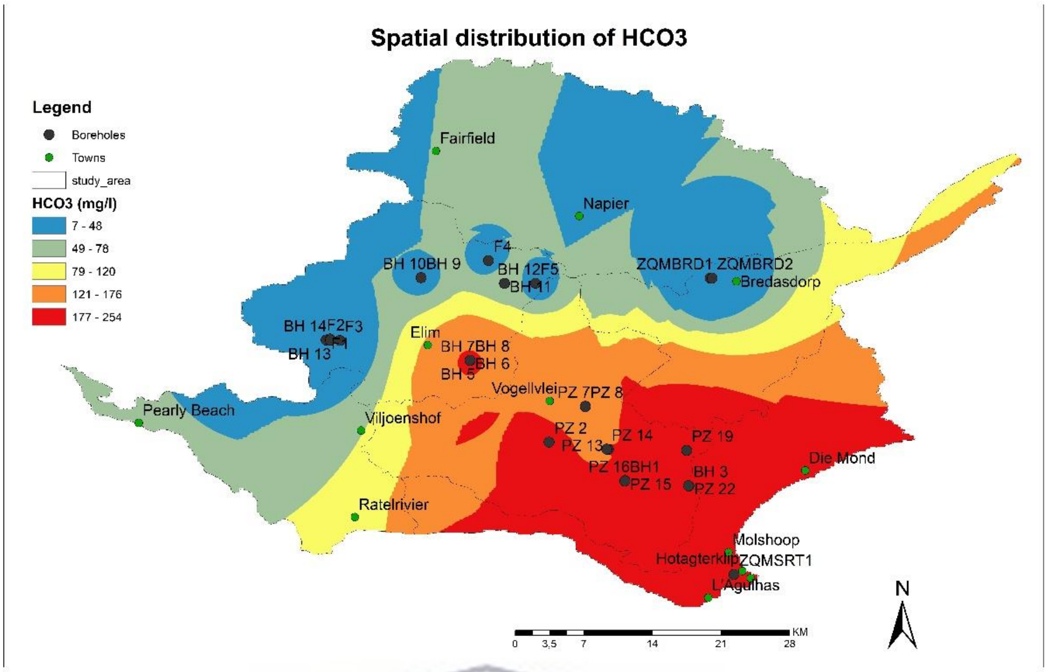


Figure 6. 9: Spatial distribution of HCO3- concentrations (mg/L) in the area.

Natural water has bicarbonate less than 500 mg/L (Mtoni, 2013) and this is usually elevated by the dissolution of carbonate minerals (calcite and dolomite) in the groundwater. In the study region bicarbonate levels in the shallow groundwater varies from 98 to 254 mg/L; for deep groundwater the range is from 5 to 268 mg/L. The low values of bicarbonate in the area suggest that dissolution of carbonate minerals is low in the area. Spatial distribution of bicarbonate in the study area is increasing towards the southern part of the catchment towards the ocean (Figure 6.9). Although, the southern part of the catchment has high bicarbonate it is within the limits for consumption water based on WHO (2011) standards which was set to be 500 mg/L (Figure 6.9).

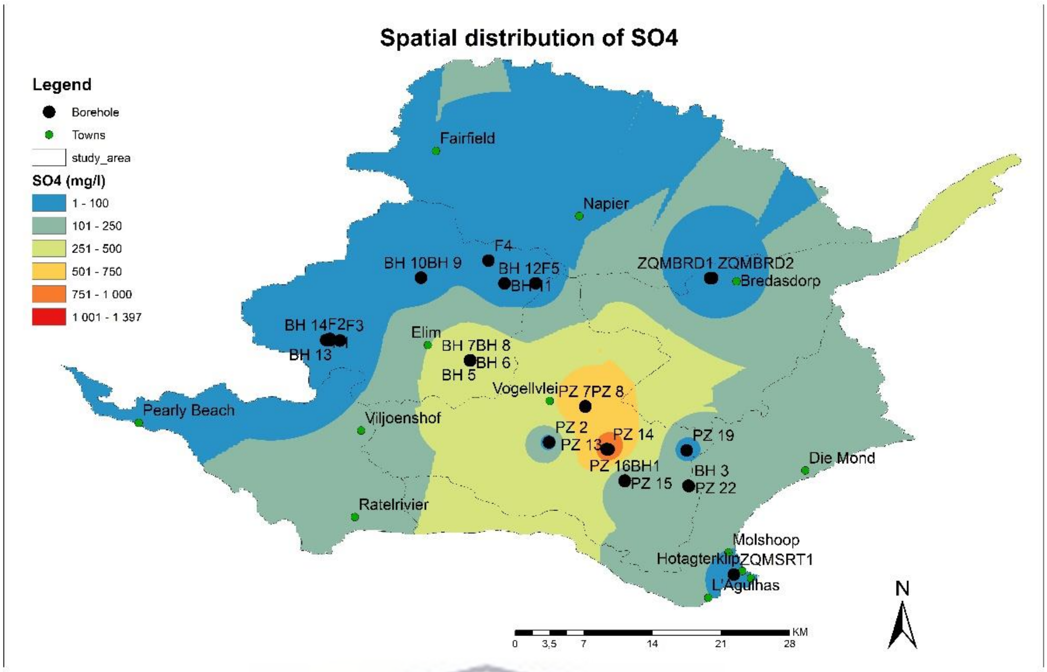


Figure 6. 10: Spatial distribution of SO42- concentration mg/L.

Concentration of sulphate is often influenced by various geochemical processes, residence time and sources. In groundwater an imperative source of sulphate is the dissolution or weathering of sulphur from evaporate minerals such as anhydrite and gypsum. In this study a hydro-geochemical study displays that concentration of sulphate ranges from 1 mg/L to 1609 mg/L. The shallow groundwater range is 26 to 1609 mg/L and for deep groundwater is 1 to 645mg/L. Figure (6.10) presents the spatial distribution of sulphate of groundwater samples in the study region. The spatial dissemination of sulphate shows low concentrations in the upper catchment, however, in the middle of the catchment boreholes (BH3-6, BH8, PZ13, PZ7-8 and PZ13-14) have a sulphate concentration above the limit for consumption water as per WHO (2011) and SANS 241 standards (Figure 6.10).

6.2. Correlation coefficient of hydrochemical data

Table 8 :Relationships between hydrochemical data were studied using correlation coefficient.

Parameter	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**Cl^{-}**	**SO_4^{2-}**	**TDS**	**EC**	**HCO_3**	**pH**
Ca	1.00									
Mg	**0.84**	1.00								
Na^{+}	**0.83**	0.69	1.00							
K	**0.79**	0.65	**0.78**	1.00						
Cl^{-}	0.57	0.22	**0.75**	0.54	1.00					
SO_4^{2-}	0.52	0.19	0.70	0.39	**0.88**	1.00				
TDS	0.60	0.42	0.67	0.58	0.71	0.67	1.00			
EC	0.60	0.42	0.67	0.58	0.71	0.67	**1.00**	1.00		
HCO3	0.60	0.49	0.46	0.55	0.28	0.38	0.36	0.36	1.00	
PH	0.30	0.24	0.09	0.06	0.00	0.14	0.14	0.15	0.54	1.00

A strong correlation among TDS and EC with a coefficient of (r=1), implies an absolute direct relationship between electrical conductivity and the TDS in the groundwater across the study region (Table 8). The strong correlation relationship of these parameters may suggest that they play a substantial part in the geochemistry of the groundwater in the research site. According to Idowu (2017), high correlation of parameters in groundwater suggests that those parameters/ions regulate the chemistry of the groundwater. Correlation of TDS and EC with the rest of the parameters varies from moderate to weak where the weak correlation of these ions with EC and TDS may suggest that they made a lesser contribution to the salinity of the groundwater. Meanwhile Na^{+}, Cl^{-} and SO_4^{2-} show moderate correlation with both EC and TDS; this may suggest that these contributed to the salinity in the area and thus control the chemistry of the groundwater. Calcium shows very high correlation with Mg^{2+} (r=0.84), Na^{+} (r=0.83) and K^{+}(r=0.79,) whereas Mg^{2+} shows a moderate correlation with Na^{+} (0.69) and K^{+} (0.65) and weak correlation with the rest of the ions. The strong correlation of Mg^{2+} and Ca^{2+} indicate common origin from calcite and dolomite dissolution in the study site.

Sodium have a high correlation relationship with K^{+} (r=0.78), Cl^{-} (r=0.75) and SO_4^{2-} (r=0.70). The correlation between Na^{+} and SO_4^{2-} in the area is attributed to reverse ion exchange processes. Potassium is weakly correlated with Cl^-, SO_4^{2-}, TDS, EC, and HCO_3^- and very weakly correlated with pH. Whereas, Cl^- seems to have a very high correlation with SO_4^{2-} (r=0.88) and a high correlation with TDS (r=0.71 and EC (r=0.71) and shows a very weak correlation with HCO_3^- (r=0.28), it illustrates no correlation at all with the pH. Weak correlation (0.57) was noted between Ca^{2+} and Cl^- (Table 8), this suggest that during seawater intrusion into the coastal aquifer, Ca^{2+} was replaced by Na^+ in the seawater on exchange sites, enabling the water to stay oversaturated with respect to calcite (Mtoni, 2013). The seawater intrusion into the aquifer resulted into calcite precipitation during the cation exchange process.

The strong correlation between Cl^- and SO_4^{2-} indicates a clear effect of land use on the groundwater chemistry in the area. Sulphate is reasonably correlated with TDS and EC and weakly correlated with HCO_3^- and pH. The weak correlation between HCO_3^- and TDS can be attributed to calcite precipitation in the water. Overall the major parameters that governs the groundwater chemistry in the research site are EC, TDS, Na^+, Cl^- , SO_4^{2-} and Ca^{2+}, meanwhile HCO_3^-, Mg^{2+} and K^+ had lesser control and pH has very low impact on the geochemistry of the groundwater.

Based on the hydro-geochemical results it is evident that multiple processes are liable for the major ionic composition of groundwater in the region of interest. There was a noticeable chemical variation of major ions in the groundwater samples. The observed, abundance of total cations declines in the order $Na^+>Mg^{2+}>Ca^{2+} >K^+$ and of anions in the order $Cl^- > HCO_3^- > SO_4^{2+}$ nevertheless, the sequence change for the major anions in the shallow groundwater where SO_4^{2-} dominates over HCO_3^- also the major cations sequence changed in few of the deep groundwater samples (6) where Ca^{2+} was observed to dominates over Mg^{2+}. The correlation coefficient results for the chief cations and anions suggest that groundwater salinization process as specified by positive correlation of Na^+, K^+, Mg^{2+}, Cl^- and SO_4^{2-} and dissolution of calcite/dolomite minerals in the aquifer shown by a positive correlation of Ca^{2+}, Mg^{2+} and HCO_3^- are the main processes that play a major part in forming the observed chemistry of the groundwater in the region.

6.3. Hydro-geochemical evaluation of groundwater

6.3.1. Hydrochemical facies

In the appraisal of the hydrog-eochemistry of groundwater in the Heuningnes Catchment the piper diagram was used. The concept of Hydro-geochemical facies has been used (Khan and EghbalBakhtiari 2017; Nolankana, 2017) to symbolise the diagnostic chemical character of water solutions in hydrologic systems.

In general sample points can be classified into 6 fields or water types in the piper diagram. These are 1. Ca^{2+}-HCO_3^- type; 2. Na^+- Cl^- type; 3. Ca^{2+} -Mg^{2+} - Cl^- type; 4. Ca^{2+} - Na^+-HCO_3^- type 5. Ca^{2+}- Cl^- type 6. Na^+-HCO_3^- type. However, in the current investigation large number of the samples are confined in the field of Na^+-Cl^- type, Na^+-K type, and Cl^--type this was influenced by the dominance of Na^+ and Cl^- ions in the groundwater (Figure 6.11). Water plotting in this field of Na^+-Cl^- type suggests water derived from marine or deep ancient groundwater (Khan and EghbalBakhtiari, 2017), whereas, Mandlazi (2015) suggests that it is water derived from saltwater intrusion to groundwater, weathering of geological material and anthropogenic inputs. There are three samples (ZQMSTR1, ZQMGYS1 and PZ 19) that fall in the mixed Ca^{2+}-Mg^{2+} - Cl^- type whereas, three other samples plotted in the field where there is no-dominant type, indicative of mixed water in the absence of cation beyond 50%.

Estimation of the water types using the piper plot suggests a good indication of seawater intrusion/saline water in the research site. This is supported by the fact that in the area the alkali cations (Na^+ and K^+) dominate over the alkaline earth cations (Mg^{2+} and Ca^{2+}) and anions of strong acids (SO_4^{2-} and Cl^-) dominated over weak acids (HCO_3^- and CO_3^-) see Figure 6.11 which according to (Khan and EghbalBakhtiari, 2017) indicates seawater mixing with these aquifers. The dominance of Na^+, Cl^- and SO_4^{2-} ions over other ions causes the increase in the EC and TDS observed in the area. Therefore, based on the piper classification of the water samples, groundwater in the study area originates from marine and deep ancient groundwater (Babu et al. 2013); this is also supported by the high concentration of these ions. This is not surprising given the location of the study site being less than 10 kilometres from the sea. There was enough time for the interaction of the aquifer and the saltwater bodies over a period of thousand years which explains why the majority of the samples all indicate marine origin. Please note boreholes are indicated by colour black and blue and the piezometers are red (Figure 6.11).

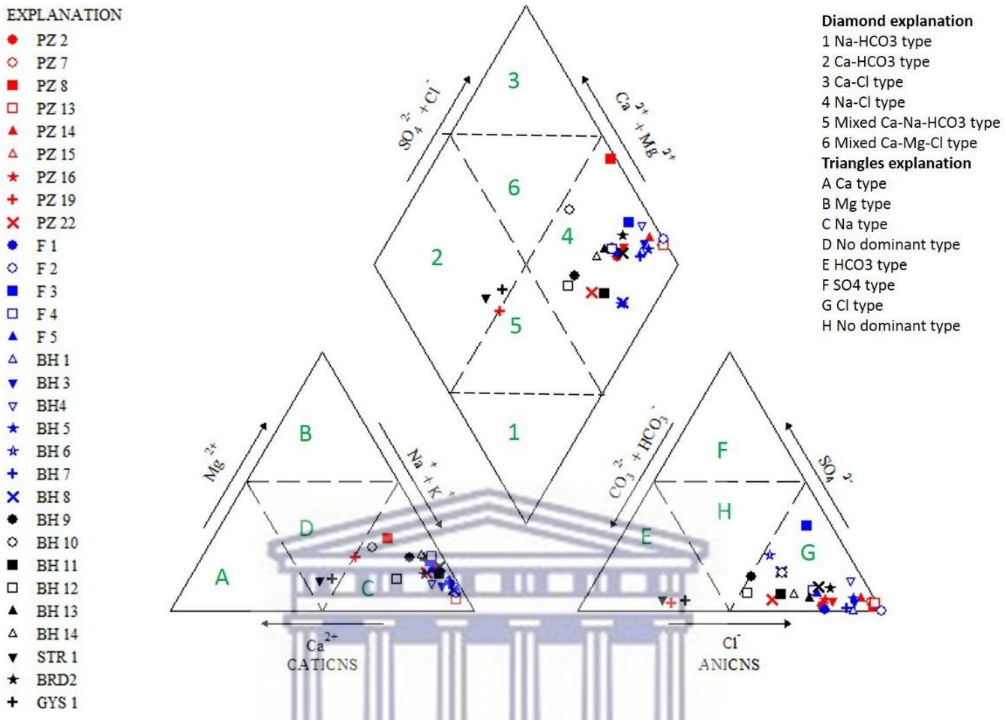


Figure 6. 11: Piper diagram of groundwater samples of Heuningnes Catchment

6.3.2. Classification of groundwater

There are many factors that contributes to salinity in groundwater. These includes, but are not limited to saltwater bodies in proximity to the aquifer and anthropogenic activities such as irrigation. In general TDS and EC are used as indicators of salinity in groundwater and are often subdivided into classes. Saxena et al. (2003) classified groundwater salinity based on EC values into three classes- Fresh with EC range of < 1500 µS/cm; Brackish where the range is between (1,500–3,000 µS/cm) and lastly Saline water with EC values > 3000 µS/cm (Table 9). On the other side Freeze and Cherry (1979) classified groundwater salinity based on TDS values into four classes: fresh (<1000 mg/L), brackish (1000 - 10 000 mg/L), saline (10 000 – 100 000 mg/L) and brine (> 100 000 mg/L). Following Freeze and Cherry class 22.5% of the groundwater is saline and 32.5% is brackish only 45% indicated fresh water.

Table 9 Water salinity classification based on EC Sexana et a, (2003

Class	EC range in µS/cm	Sample size	(%)
Fresh	<1500	15	37.5
Brackish	1 500 – 3 000	7	17.5
Saline	>3 000	18	45

The shallow groundwater in the study area can be classified as saline water based on Freeze and Cherry (1979) salinity classification. The only sample that falls in the fresh water zone is represented by PZ 19 with TDS concentration of 907 mg/L. Deep groundwater in the study area can be classified as freshwater except for BH 1-8 which are brackish in nature based on their TDS concentration.
The classification of shallow groundwater based on EC follows the same trend of TDS, only PZ is classified as fresh and the rest of the shallow groundwater samples are saline with EC concentration over 3000 µS/cm (Table 9). Whereas, only 3 samples are classified as brackish (BH3, BH 8 and ZQMGSY1) and boreholes (BH1, BH4, H5, BH6 and BH 7) are classified as saline having high EC values ranging from 3770 to 13980 µS/cm. The rest of the deep groundwater samples are classified as fresh water with EC range from 230 – 1054 µS/cm. The general quality of water in the study region established from the EC is as follows: only 37.5% of the water samples are considered fresh, 17.5% is brackish water and 45% of the water samples indicate saline water. In terms of TDS classification 45% of the water samples are fresh and 32.5% indicate brackish water while 22.5% show presence of saline water in the area.

Sources of soluble salts encountered in groundwater of the study region may be ascribed to dissolution of minerals from bedrock. The high concentration of TDS in groundwater of the study area suggests seawater influence as mixing of seawater with groundwater disturbs the hydro-geochemistry of groundwater thereby increasing the TDS (Khan and EghbalBakhtiari, 2017). Another factor that may influence seawater intrusion is when there is low recharge of aquifers as a result of scarce rainfall and retreating of rivers, both phenomena are applicable in the study area which receives much of its rainfall during winter time and if during the year there was not enough rainfall, the rivers and lake decline or dry up in some worst case scenario, a situation that gives a great opportunity for the seawater intrusion to contaminate groundwater in the aquifer system both shallow and deep.

6.3.3. Hydro-geochemical processes

Various factors contribute to the chemical composition of groundwater these includes minerals found in evaporation in geological materials, precipitation and anthropogenic activity. Chemical characteristics of groundwater is also influenced by the hydrochemistry of surface water in the recharge locality and at discharge points, because of the extended residence, prolonged contact with the aquifer medium, groundwater tends to show higher mineral concentrations at the discharge zone as opposed to recharge zones (Freeze and Cherry, 1979). Overall the amount of ions present in groundwater is often controlled by the type of geochemical processes active within an aquifer system (Hwang et al. 2017). It is for this reason that hydro-geochemical processes occurring in aquifer system can be readily determent by using the concentrations of major-ions found in groundwater. According to Hwang et al. (2017) combination of two or more major ions groups for instance potassium and sodium, chloride and sulphate, magnesium and calcium, can be used to deduce main type of ions in solution, weathering sort of solutes, and influence type for joint interaction between one ion particle and another. Therefore, the study of ionic relations by means of scatter plots or bivariate plots can assist in explaining numerous hydro-geochemical mechanisms present in the progression of the water chemistry.

6.3.3.1. Weathering Processes affecting groundwater quality

Silicate weathering

Apart from other geochemical processes silicate weathering is one of the chief processes accountable for the chemical alterations of ground water (Li et al. 2017). The molar Na^+/Cl^- ratio is one of the factors used to discriminate saline sources, dissolution of minerals and ion-exchange reactions (Badana et al. 2018). Halite and silicate rocks are sources of sodium in groundwater, if dissolution of halite is the reason for concentration of sodium, then Na^+/ Cl^- ratio is expected reach unity (1) since dissolution of halite relieves equivalent amounts of sodium and chloride in the solution Liu et al. (2015), whereas, ratio above one is assumed as Na^+ came from reaction of silicate weathering. However, if the ratio of Na^+/ Cl^- < 1, then ion exchange and carbonate weathering can be assumed as the main process taking place (Ligavha-Mbelengwa, 2017). This is true for 61.3% of the tested samples which had ratio less than 1 (Figure 6.12d) indicating that carbonate dissolution or ion exchange process was prominent especially in the upper catchment which receives greater quantity of recharge through rainfall in this area (Abu-alnaeem et al. 2018). Whereas, 38.7% have ratio above 1 and shows enrichment of Na^+ (Figure 6.12a) suggesting effect from silicate weathering.

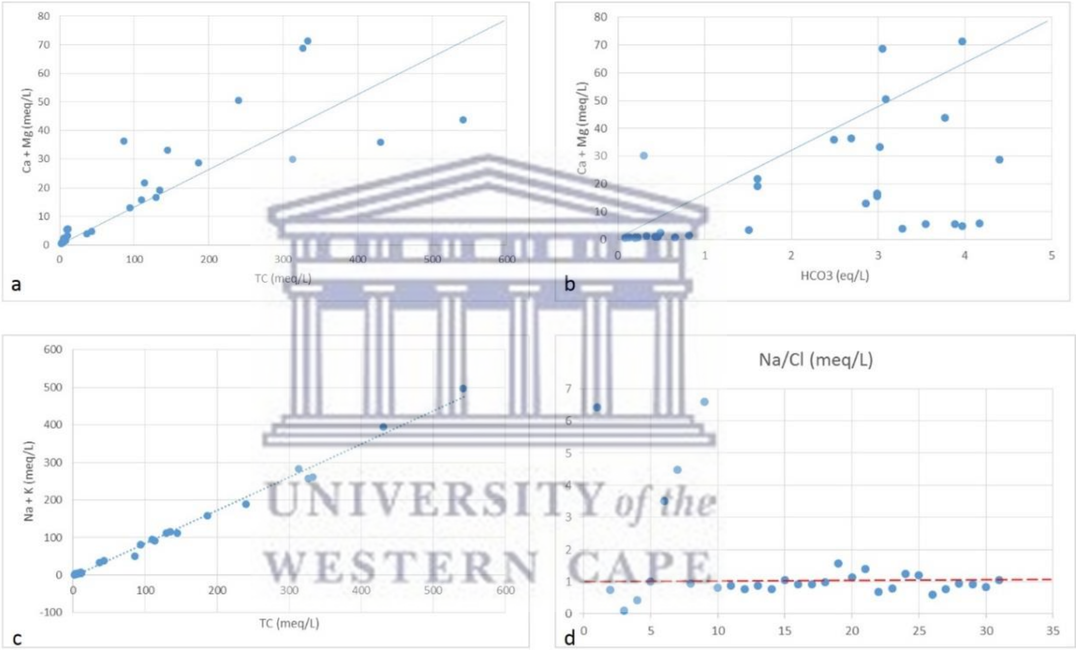


Figure 6. 12: Relations between (a) (Ca^{2+} + Mg^{2+}) versus total cations (TC) and; (b) (Ca^{2+} + Mg^{2+}) versus HCO_3^-, (c) (Na^+ + K^+) versus total cations indicating silicate weathering and(d) Na+/Cl-ratio and the samples.

Also according to Kumar et al. (2013) effect of silicate weathering on groundwater can be assumed by computing the ratio between Na^+ plus$^+$ and total cations (TC). The connection of Na^+ plus K^+ and total cations (TC) of the research site indicates most of the tested samples plots near and along the 1:1 line (Figure. 6.12c). This reflects contributions from silicate weathering, in which potassium plus sodium ions are supplemented in the groundwater of the study region (Hwang et al. 2017). The Mg^{2+} plus Ca^{2+}vs total cations (TC^+) plot of the sampled groundwater (Figure 6.12a) indicates an almost linear spread of the samples plots close to the 1:1 line and some deviate away from the line at higher concentrations. This also supports the interpretation that weathering of silicate minerals occurs in the system. Also Figure 6.12b show excess of HCO_3^{-} due to silicate weathering, and also the enrichment of Na^{+} over Cl^{-} attest to silicate weathering.

Also relationships of Ca^{2+}+Mg^{2+} versus HCO_3^{-} can act as evidence of silicate weathering. If dissolution of dolomite and calcite is the main source for the origin of calcium and magnesium, then the samples would plot along the aquiline. This is not the case in the study region as many samples fall below the aquiline with the exception of three samples. In this case the alkali metals were responsible for balancing any additional alkalinity in the water (Figure 6.12b). Most of the samples plot far from the aquiline, showing enrichment in HCO_3^{-} suggesting an additional source of calcium (Figure 6.12b). Most of the samples have $(Ca^{2+}+Mg^{2+})/(HCO_3^{-.})$ ratio above 0.5 which indicate reverse ion-exchange process (Kanagaraj et al. 2017).

6.3.3.2. Carbonate weathering and dissolution

If the geological setting of an area is dominated by carbonate formations such as limestone and dolomitic-limestone, carbonate weathering is likely to take place. It is possible that the current carbonates in these rocks are dissolved and added to the groundwater system during groundwater movement or rainfall infiltration or irrigation. The origin of $^{+}$, HCO_3^{-} , Ca^{2+}, $Mg^{2}$and SO_4^{2-} are ought to show a close relation if they are derived from dissolution of carbonate minerals (Kumar, 2016). Therefore, scatter diagram of $(Ca^{2+}+Mg^{2+})$ vs. $(HCO_3^{-}+SO_4^{2-})$ can be used to explain weathering processes existent within the aquifer such as silicate weathering which is indicated by enrichment of $(HCO_3^{-}+SO_4^{2-})$ and samples will plot below the equiline, whereas, carbonate weathering is indicated by cumulative of $(Ca^{2+}+Mg^{2+})$ (Kanagaraj et al. 2017) and samples will tend to plot above the dissolution line (Figure 6.13). Samples falling along the 1:1 line, indicates the dissolution of gypsum, calcite, and dolomite. Observation made from the current study is that most of the samples plots above the 1:1 equal line suggesting reverse ion exchange as a product of weathering of carbonate minerals (El-Sayed et al. 2012).

The samples that plot below the 1:1 equal line which suggests ion exchange due to silicate weathering. The deviation of these samples away from the 1:1 dissolution line implies that dissolution reactions of gypsum, calcite, and dolomite are not leading in the system (Figure 6.13). However, those plotting near or along the line show origin from dissolution of carbonate mineral.

According to Abu-alnaeem et al. (2018) an Mg^{2+}/Ca^{2+}molar ratio of < 1 indicate dissolution of calcite as major contributor to the water chemistry whereas, ratio equal to or >1 suggest dominance of dolomite dissolution, silicate weathering can be represented by a lower of < 0.5. Based on the Mg^{2+}/Ca^{2+}molar ratio only 2 samples have ratio < 0.5 and 2 had ratio <1 which suggest that silicate weathering and dissolution of calcite is insignificant in this area, whereas, 87% of the sample have ratio above 1 indicating that groundwater chemistry is predominantly controlled by dissolution of Bokkeveld limestone in this area. This supports the weathering of carbonate mineral process.

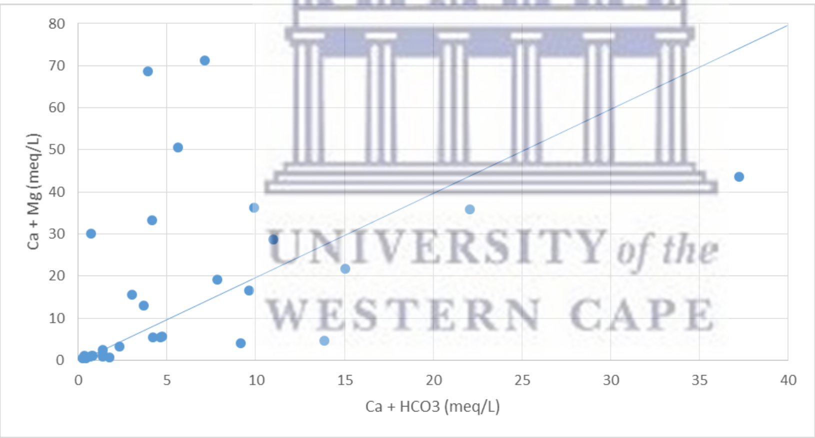


Figure 6. 13:Bivariate plot displaying the relation between Ca^{2+} + Mg^{2+}+ and HCO_3^{-} + SO_4^{2-}

6.3.3.3. Ion exchange

Ion exchange is the process whereby ions adsorbed on the surface of the fine-grained materials of the aquifers are substituted by ions that already exist in the solutions. The most common ion exchangers in aquifer systems and soils are clay minerals. The cations found in the clay and groundwater are exchangeable easily as compared to anions. The pH of a solution also influences the exchange processes. To check if the process of ion exchange or reverse ion exchange was the cause for modifying the groundwater chemistry in the research site the following ratios were used: Ca^{2+}/Na^{+}, Na^{+}/Cl^{-} vs EC, Na^{+}/Cl^{-} vs Cl^{-}, $Ca^{2+} + Mg^{2+}$ vs Cl^{-}.

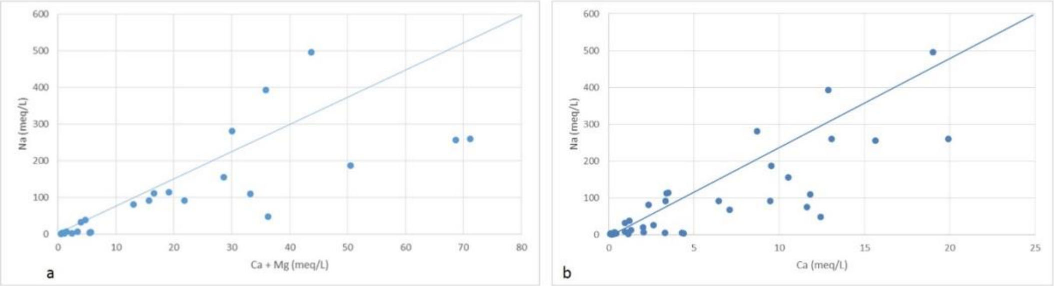


Figure 6. 14: (a) Na+ vs. Ca2+ + Mg2+plot showing amplified concentration of Ca2+ compared to Na+ indicating reverse ion exchange (b) Ca2+ vs Na+ indicating ion exchange.

Ca^{2+}+Mg^{2+} versus Na^{+} plot can also be used to indicate the sort of ion exchange occurring in an area. A high concentration of Ca^{2+}+Mg^{2+} over Na^{+} generally indicates reverse ion-exchange, while high Na^{+} over Ca^{2+}+Mg^{2+} indicates normal ion-exchange. Figure 6.14a shows that most of the samples lean towards the Ca^{2+}+Mg^{2+} concentration, indicating the occurrence of reverse ion exchange in the area. Whereas, the Ca^{2+} /Na^{+} suggest ion exchange increasing concentration of calcium in groundwater (Figure 6.14b).

6.3.3.4. Cation exchange process

The dispersal and existence of ions in groundwater are influenced by geochemical reactions such as cation-exchange reactions (Senthilkumar and Elango, 2013). During seawater intrusion, a number of chemical reactions take place, which alters the hydrochemistry of the coastal aquifer. As noted by Alfarrah and Walraevens (2018) reverse cation exchange is the significant one whereby modifications of the theoretical mixture of seawater and freshwater occur between the clays and the aquifer water. An extreme concentration of Na^{+} with respect to Cl^{-} or reduction of Na^{+} with respect to Cl^{-} is proof of cation-exchange reactions. In the normal ion-exchange reaction, Ca^{2+} is absorbed by the aquifer material and sodium ion is freed to water.

The surplus Na^{+} as a product of ion-exchange reaction is stabilised by alkalinity or SO_4^{2-} instead of Cl^{-}. Likewise, during the reverse ion-exchange, the aquifer material will consume Na^{+} let go of the Ca^{2+} in the water. In this case, Ca^{2+} and Mg^{2+} will balance any additional Cl^{-} that is more than the Na^{+} in the solution. Hence, ion exchange reactions are best indicated by surplus Na^+ over Cl^- or vice versa. Of all the tested samples 61.3% confirms reverse ion-exchange reactions and 38.7% of the samples indicate effect of cation exchange.it is concluded that The conclusion is therefore, that the chemical make-up of groundwater in the region is driven by reverse ion-exchange processes followed by cation exchange process.

6.3.3.5. Evaporation

The ratio of Na^+/ Cl^- is a good indicator of evaporation processes in groundwater. Ligavha-Mbelengwa (2017), states that the process of evaporation escalates the concentration of TDS in groundwater, although, this only happens when the Na^+ versus Cl^- ratio remains unchanged with increasing EC. According to Hago (2014), no change in the Na^+/Cl^- ratio indicates dominance of evaporation process this is true if there is no precipitation of mineral species active. A horizontal line in the plot of EC versus Na^+/Cl^- is evidence enough of concentration by evaporation/ evapotranspiration (Hwang et al. 2017). Similar pattern was observed in the study region as the Na^+/Cl^- versus EC plot gave a horizontal line signifying ion concentration in the water samples as a consequence of evaporation (Figure 6.15). However, some samples plotted above the horizontal line indicating ion exchange whereas the ones plotted below the horizontal line indicated reverse ion exchange. Also at higher EC the Na^+/Cl^- ratio decreases indicating either of two things, reverse ion-exchange is far more prevalent in comparison to ion-exchange or the ratio is close to seawater ratio of 0.86 The Na^+/Cl^- versus Cl^- plot also suggest reverse ion-exchange in the study region (Figure 6.15b).

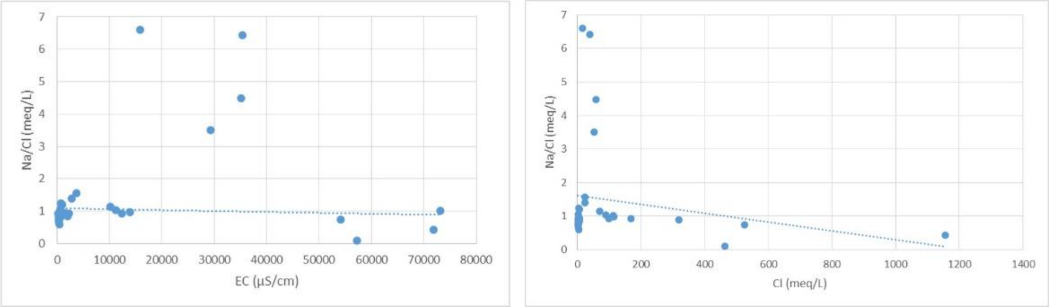


Figure 6. 15: (a) Na+/Cl- versus EC indicating evaporation process, (b) Na+/Cl- versus Cl- indicating reverse ion exchange.

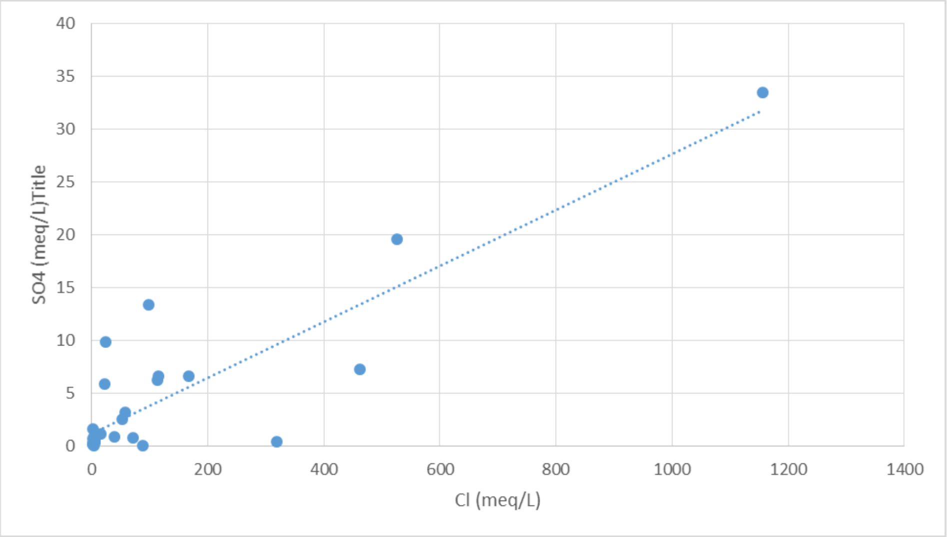


Figure 6. 16: Correlation of Sulphate vs Chloride.

In most cases groundwater chemistry is often affected by natural and geological processes, however, the land use patterns are also an influence in modifying the final chemical composition. The bond that chloride and sulphate has can be utilized to show the influence on the groundwater chemistry of surface pollution by domestic sewage water and irrigation return flows (Badana et al. 2018). In the investigated area the observed average concentrations of chloride and sulphate in shallow groundwater are 9580 +/- 13683 and 399+/-535 (mean+/- SD) and for deep groundwater they are 1546+/- 2734 and 112+/-178 (mean+/- SD). The standard deviation of Cl^- and SO_4^{2-} suggest that these are likely to have derived from multiple sources. Also Cl^- and SO_4^{2-} display good correlation and possibly originate from multiple sources such as surface contamination, dissolution of halite and gypsum/anhydrite, saline causes, and (Figure 6.16). However, the plot of Cl^-/SO_4^{2-} (Figure 6.16) does not support gypsum dissolution, therefore, this is ruled out.

6.4. Mechanisms Controlling Groundwater Chemistry

Groundwater quality is controlled by the reactions among groundwater and the aquifer constituent minerals (Nagaraju et al. 2014). To understand the origin or the controls of groundwater chemistry Gibb’s plots are suggested which uses the ratios of the most prominent anions and cations plotted against TDS (Figure 6.17). These graphs are broadly used to indicate the principal mechanism governing the hydrochemistry of groundwater in the aquifer such as such as rock, precipitation, and evaporation dominance (Chung et al. 2014; Nagaraju et al. 2014; Kumar, 2016). In this study the Gibbs plot reveal that 80% of the samples plot in the rock dominant zone and the remaining 20% plots in the evaporation dominant zone (Figure 6.17). This illustrates that the weathering of rock-forming minerals is the major control of the groundwater quality in the area. Evaporation escalates salinity by causing Na^+ and Cl^- to rise with relation to TDS, the positive correlation amongst these parameters support this process (Figure 6.15a). As indicated above the Na^+/Cl^- vs EC plot is considered an effective indicator for evaporation

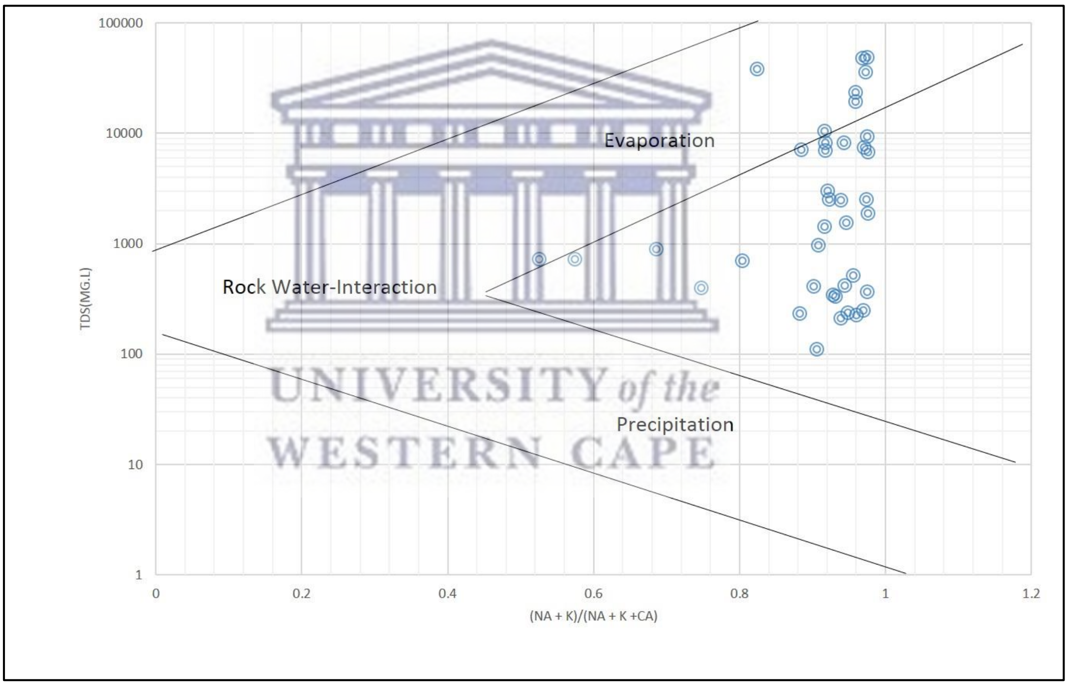


Figure 6.17: Gibbs plot showing the mechanisms controlling the hydrochemistry in the groundwater of the study area

The hydrochemical processes and hydro-geochemistry of the groundwater will differ from space and time, this is mainly dependent on the type of geology and geochemical processes present within the aquifer. Thus, the chemical structure of groundwater as stated by (Nwankwoala and Udom, 2011) is influenced by ion-exchange processes, dissolution, the residence time along the flow path and precipitation. In the study area the major processes controlling the water quality are the, rock water contact, reverse ion-exchange, evaporation and to a less extent silicate weathering.

6.5 Assessment of the magnitude of seawater invasion in the study region

Seawater incursion is expressed as the movement of salt water into freshwater aquifers because of groundwater over abstraction. In many cases the existence of any saline or brackish water along the coastal formations is misinterpreted as the result of seawater intrusion, based on the high concentration of EC or TDS. The EC or TDS of groundwater alone does not provide concrete evidence on the occurrence of seawater because seawater incursion involves interaction of freshwater and saline water therefore, a good indication of seawater intrusion would rather be the increase of Cl^- as suggested by Korfali and Jurdi (2010). The salinity can be due to several reasons and mostly it can be due to the leaching out of the salts from the aquifer material. To avoid misinterpretation of temporary increases of total dissolved salts or EC as seawater intrusion (Baskaran et al. 2016) recommended the use of ionic ratios as reliable criterion to estimate the presence of seawater incursion.

Groundwater having high concentrations of TDS and Na^+ and Cl^- of nearly 35,000 mg/L (Klassen et al. 2014) gives a good indication of presence of seawater. However, the best way to ascertain the salinity ingress from the sea is simply by studying the changes in molar ratios of the ions (Nair et al. 2015). Assessing the magnitude of seawater interruption in coastal aquifers has been achieved by applying various approaches such as studying the ratios of major constituents in water samples; the most applied ionic ratios are the Na^+/Cl^- and the Simpson's ratio which use the chloride content to the concentration of bicarbonate in a water sample (Cl^-/HCO_3^-) as well as the Mg^{2+}/Ca^{2+} ratio. Sodium and magnesium are used as indicated because they are generally higher in seawater than in freshwater, unlike bicarbonate which is found in smaller amounts in seawater. In seawater the known molar ratio of Na^+/Cl^- is 0.86 with a surplus of Cl^- exceeding alkali ions (Na^+) while the molar ratio of Mg^{2+}/Ca^{2+} in seawater is 4.5 to 5.2 with an excess of Mg^{2+} (Bankaran et al. 2016). Many researchers (Nair et al. 2015; Mtoni, 2013; Craig, 2008; Kanagaraj et al. 2017; Babu et al. 2013) have applied the ionic ratios to estimate seawater incursion in coastal regions and to ascertain the source and nature of the salinity existing in groundwater. For this study, Na^+/Cl^-, Mg^{2+}/Ca^{2+}, Cl^-/HCO_3^- were considered to demarcate the zones indicating signs of seawater effects.

6.5.1. Na+/ Cl- ratio

The relationship of Na^+ and Cl^- molar ratio with theoretical mixing line was used to distinguish between groundwater samples interrupted by either seawater mixing or other processes (Figure 6.18). The samples that plots close to the mixing line signifies the impact of seawater mixing within the aquifer medium, whereas samples plotting far from the line can be ascribed to other sources of Na^+ or cation exchange process altering the groundwater chemistry by substituting it with Ca^{2+} and Mg^{2+} (Kumar, 2016). Of all the samples tested in the research area most of them show depletion of Na^+ in water and plots below but very close to the mixing line (Figure 6.18), indicating salinization and it relates to samples with high Cl^- proposing impact of seawater interaction in the aquifer. Only five samples digress away the mixing line and this implies a surplus or reduction of Na^+ as compared to Cl^- (Mtoni, 2013) these samples suggest cation process changing the chemical composition of groundwater by replacing it with Ca^{2+} or and Mg^{2+}.

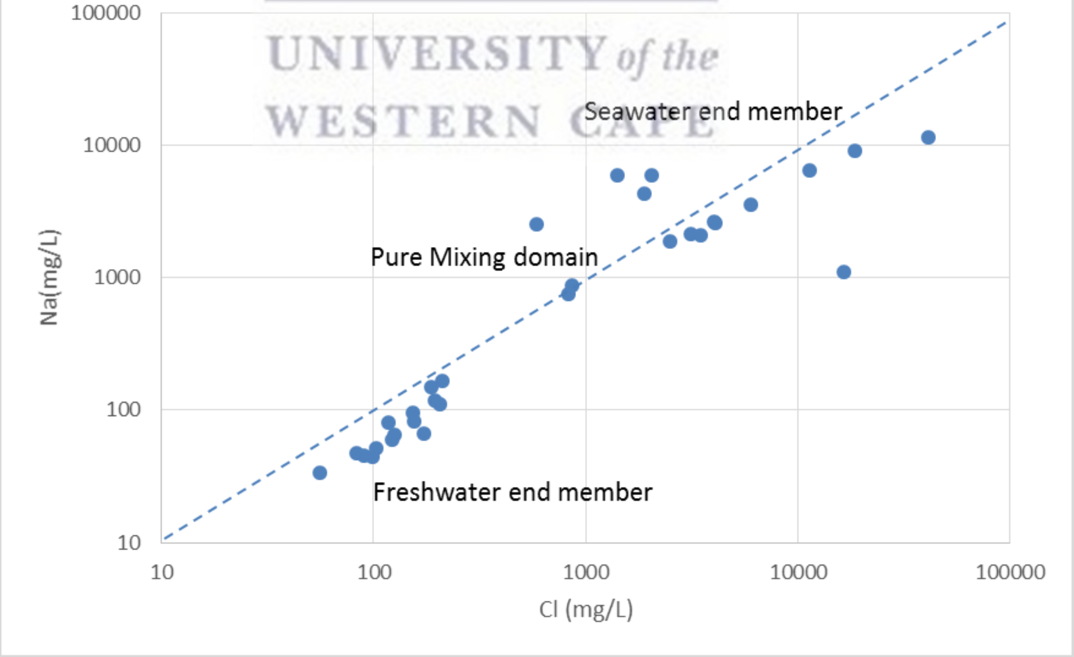


Figure 6. 18: The figure shows log Na+/Cl- indicating possible seawater intrusion.

In coastal areas the ionic connection of sodium ion with chloride is used to define the degree on the complete groundwater salinity. According to Idowu (2017) groundwater impacted by seawater intrusion possesses low values of Na^+/Cl^- ratios because marine values of Na^+/Cl^- ratio are < 0.86. Thus, low values of Na^+/Cl^- ratios in conjunction with other geological factors can be indicative of the impact of seawater intrusion. The calculated Na^+/Cl^- ratio in the study site displayed samples that were below and just above the seawater standard ratio of 0.86. The overall Na^+/Cl^-ratio for tested groundwater samples in the investigated site lie within 0.10 to 6.60 range, where 0.10 to 6.60 are shallow groundwater samples while those taken from deep groundwater vary from 0.59 to 1.57. The lower Na^+/Cl^- ratios than the 0.86 are product of reverse ion exchange reactions with clay minerals replacing sodium ion with calcium and magnesium ion which is a common phenomenon in saline groundwater (Mtoni, 2013; Nwaonkwala, 2013; Alfarrah and Walraevens, 2018).

About 35.5% of the tested groundwater samples from both aquifers (shallow and deep) are impacted by seawater intrusion as they have low Na^+/Cl^-ratio than the standard seawater ratio and majority being from the deep groundwater samples. Mixing of seawater and freshwater was also detected (Figure 6.18) which according to Nair et al. (2015) lies between the seawater ratio 0.86 and 1 freshwater ratio and only 6.5% of the samples indicate mixing. The remaining 58% of the samples (PZ2, PZ 14, PZ 15, PZ 16, PZ 22, BH1, BH6, BH7, BH 8, BH 11, BH 12 and ZQMBRD2) having higher Na^+/Cl^- ratio above 0.86 and half of these had ratio above 1 suggesting effects of cation exchange or silicate weathering process or anthropogenic effect such as saltwater pans (Babu et al. 2013) saltwater pans in this study region is attributed to the Soetendalsvlei and the Voelvlei. The leaching of saltwater from the salt pans affected the samples within the shallow aquifer.

Similar study by Khan and EghbalBakhtiari (2017), also found similar results where Na^+/Cl^- ratio < 1, and suggested probable pollution of the aquifer by seawater intrusion. They further stated that the Na^+/Cl^- ratio is reduced because Cl^- tends to show conservative behaviour, so its occurrence in the system is representative; however, Na^+ may be scavenged by any process like adsorption or co-precipitation.

6.5.2. Mg2+/Ca2+ ratio

Calcium is generally found in freshwater in high amounts as opposed to magnesium which is more concentrated in seawater. This means that using the Mg^{2+}/Ca^{2+} or Ca^{2+}/Mg^{2+} ratio may indicate some degree of seawater contamination because magnesium is present in seawater in a much greater concentration than calcium (Babu et al. 2013). High concentration of Mg^{2+}/Ca^{2+} is attributed to seawater intrusion and the range for Mg^{2+}/Ca^{2+} ratio in seawater is 4.5 -5.2 with an excess of Mg^{2+} as given by Nair et al. (2015). An Mg^{2+}/Ca^{2+} ratio >1 can indicate other factors contributing to groundwater chemistry (reverse cation exchange, saltwater up-coning, sewage invasion or dolomite dissolution processes).

The groundwater samples in the region have Mg^{2+}/Ca^{2+} ratio range of 0.26 to 5.77. Almost all groundwater samples (87%) that were tested have Mg^{2+}/Ca^{2+} ratios exceeding 1, however, they do not fall within the seawater intrusion range of 4.5 – 5.2 except for BH7, F4 and ZQMBRD2 indicating effect of seawater intrusion in these samples. These samples with the ratio falling out of the seawater intrusion range suggest that other processes such as cation exchange was responsible for altering water chemistry in these locations as noted by Rout et al, (2012) and this could indicate inland in origin of the groundwater salinization. On the other hand there were 4 samples (PZ19, BH 12, ZQMSTR1 and ZQMGSY1) which had ratios less than 1 which suggest that calcite-dissolution is insignificant (appendix H).

6.5.3. Cl-/ HCO3-

Groundwater from coastal aquifer which having high amounts of chloride and sodium insinuate the impact of seawater mixing while high values of $HCO_3^-$and Ca^{2+} are indicators of the impact of water-rock interaction in the aquifer (Khan and EghbalBakhtiari, 2017). Hence, low values of HCO_3^-/Cl^- and Ca^{2+}/Na^+ ratios are indicative of a high impact of seawater incursion. The ratio of Cl^- /HCO_3^-range for contaminated groundwater owing to seawater incursion is divided into five classes, ratio < 0.5 decent quality; 0.5 – 1.3 marginally polluted; 1.3 – 2.8 reasonably polluted; 2.8- 6.6 injuriously contaminated and 6.6- 15.5 extremely contaminated (Idomu, 2017; Ekhmaj et al. 2014) whereas, a ratio of over 200 indicates definite contamination by seawater intrusion (Babu et al. 2013). 25.8% of the tested samples fall between 0.5 and 6.6 range indicating samples that are slightly affected to injuriously pollute and 74.2% are above 6.6 and indicate that these samples area highly contaminated. Total cation (Ca^{2+} + Mg^{2+} + K^{+} and Na^{+} in meq/L) over Cl^{-} ratio is also a convenient means to measure the effect of salinity origins and dissolution of mineral present in groundwater since this ratio disregards the effects of ion-exchange reactions Badana et al. (2018). The plot of TC/Cl^{-} shows a good linear relationship suggesting seawater intrusion is active in the study area (Appendix I).

6.6. Chapter summary

Examination of hydrochemistry data indicate that groundwater in the region is extremely impacted by salinity and show high Na^{+}, Cl^{-} , TDS, and EC levels. As a result, groundwater in the investigated range is characterised by Na^{+}/Cl^{-} water-type although there are three samples which indicated mixed Mg^{2+}-Ca^{2+}-Cl^{-} water type. Elevated levels of sodium ions in groundwater are ascribed to cation exchange where Ca^{2+} from groundwater is adsorbed on clayed materials in sodium interchange. The abundance of total cations declines in the sequence of $Na^{+}>Mg^{2+}>Ca^{2+}>K^{+}$ and anions follow the order of $Cl^{-}>HCO_3^{-}>SO_4^{2+}$. Strong positive correlation of Na^{+}, K^{+}, Mg^{2+}, Cl^{-} and SO_4^{2-} suggest that these ions influenced groundwater salinisation in the area. Also the strong correlation of Ca^{2+}, Mg^{2+} and HCO_3^{-} indicate dissolution of calcite or dolomite minerals in the aquifer. Effect of seawater is also indicated by strong correlation of Cl^{-} with some ions. Also the spatial distribution of Na^{+}, Cl^{-}, TDS, and EC seem to be increasing towards the coast suggesting influence of seawater. Spatial distribution of chemical parameters displays same trend they area are increasing towards the sea side this indicate that the lower catchment is highly mineralised as all the chemical consequents in groundwater were very high.

Salinisation in both deep and the shallow aquifer systems appears to be compelled by various geochemical processes such as evaporation process, rock-water interaction, silicate weathering as well as to a certain extent seawater intrusion, ion exchange, and dissolution processes as depicted from the ion ratios and bivariate plots. Also other factors contributing to salinity in the study area taking in to account salts that are naturally occurring in the host aquifer material, surface water ingress, lateral movements from some adjacent saline aquifers, and perhaps slow rate of groundwater movement and a lack of sufficient drainage.

Chapter 7: Assessment of Groundwater quality for irrigation usage.

7.1. Introduction

Fitness of groundwater for irrigation looks at many aspects like the effects of the waters’ mineral concentration on the plants and soils. The chemical composition of the water for irrigation is mainly controlled by high dissolved solids and salt concentrations. The sum of dissolved solids may influence the intake of water and nutrients by the plants resulting in plant growth being disturbed. If water intended for irrigation contains too much salt, growth of the plant will be affected, physically by impeding water uptake through chemical means as the metabolic reaction or by alteration in osmotic pressure (Sughosh et al. 2018). Therefore, irrigation water may have an influence on the growth of plants. Furthermore, high salt concentrations more especially high Na^+ and Cl^- ions in the water for irrigation may affect the soil structure together with the permeability rate resulting in growth of the plant being affected.

These ions may be generated from dissolution or weathering of soil and rocks (Madhav et al. 2018), what happens is after evaporation of water takes place, salt accumulate at the roots and cause a blockage and plan are unable to such water from soil thus causes limited moisture. Certain ions may also be toxic to the growth of plants if they are abundant in the water (Singhal and Gupta, 2010). To evaluate the aptness of groundwater for irrigation the resulting water quality guides were considered for this study: SAR, Sodium Percentage Kelly Ratio, HCO_3^-, Total Dissolved Solids, Electrical Conductivity (EC), Chloride (Cl^-), and Sulphate (SO_4^{2-}) the results are presented in Table 10 the calculated values for all the irrigation indices can be found in the appendix section.

Table 10: Table Classification of groundwater samples for irrigation suitability

Parameter	Range	Water Class	No. of samples	(%)
SAR (meq/l)	<2	Excellent	0	0
	2-8	Good	16(15DGW,1SGW)	50
	8-15	Doubtful	1(SGW)	3.2
P	>15	Unsuitable	15(8DGW,7SGW)	46.8
KR(meq/l)	<1	Suitable	3(2DGW,1SGW)	9.7
	>1	Unsuitable	28(20DGW,8SGW)	90.3
Salinity Hazard EC (µS/cm)	<750	No problem of salinity	11(DGW)	35.4
	750 - 3000	Increasing problem of salinity	7(6DGW,1SGW)	22.6
	>3000	Severe problem of salinity	13(5DGW,8SGW)	42
Na%(meq/l)	<20	Excellent	0	0
	20 – 40	Good	0	0
	40 – 60	Permissible	5(3DGW,2SGW)	16.1
	60 -80	Doubtful	14(10DGW,4SGW)	45.2
	>80	Unsuitable	12(9DGW,3SGW)	38.7
TDS(mg/L)	<450	safe	12DGW	37.5
	450 - 2000	Medium risk	7(6DGW, 1 SGW)	21.9
	>2000	Sever risk	13(5DGW, 8 SGW)	40.6

7.1.1. Sodium adsorption ratio (SAR)

In the assessment of water fitness for irrigation purposes SAR is considered as the utmost effective parameter (Bhashir et al. 2013). In South African Water Quality Guidelines (SAWQG) the sodium hazard is divided into four categories (Table 10.). Using the SAR values, four classes can be considered for irrigation water where SAR <2, indicates low sodium water that presents nearly no threat of interchangeable Na^+ ion, moderate Na^+ water with SAR >2 but <8 illustrate substantial danger, while high and extremely high Na^+ waters with SAR between 8 - 15 and over 15, correspondingly are observed as unacceptable and are likely to introduce harmful amounts of transferable Na^+ in soils (Shyni and Unnikrishnan, 2015). The effects it has on soils and plants, sodium thus is the foremost factor controlling irrigation water (Nwankwoala and Udom, 2011). Therefore, sodium adsorption ratio serves as a guide for potential of a given irrigation water to prompt sodic soil conditions. Sodicity in irrigation water is an outcome of high concentration of Na^+-ion relative to magnesium and calcium.

The results of calculated SAR from water samples in the study region indicate that 50% portrays low sodium concentration implying that these waters are good for irrigation (Table 10). In contrast to 46.8% % of the samples indicate very high sodium hazard and are thus unsuitable for irrigation. Using this water for irrigation will negatively affect the crop yield and quality as a result of sodium uptake through the roots of sodium sensitive plants only 3.2 % show to have high sodium hazard which is considered doubtful for irrigation.

7.1.2. Salinity Hazard (EC)

The total concentration of dissolved salts in irrigation water can be expressed in electrical conductivity (EC) for classification purposes. In this study we follow the classification by FAO (2007) for irrigation use. In their guidelines EC is grouped into three classes based on the relationship between the EC of water and the EC of saturated soil extracts, to specify the salinity hazard. There is no problem with salinity if the water has an EC < 750 µS/cm. An EC between 750 to 3000 µS/cm indicates an increasing problem of the salinity and lastly when EC > 3000 µS/cm there is a severe problem of salinity. The conductivity across the investigated zone fluctuates from 320 to 73100 µS/cm. Groundwater classification established from EC ranges is displayed in (Table 9). In the study area the shallow groundwater samples fall within the 3rd class where EC is above 3000 µS/cm suggesting a severe problem of salinity, except for one sample that falls in the second class of increasing problem. This therefore, suggests that shallow groundwater in the area is not suitable for irrigation. As for deep groundwater 11of the samples fall in the first class indicating no problem of salinity having an EC < 750 µS/cm, whereas, 6 samples falls in the second class and only 5 samples are not suitable for irrigation as they fall in the 3rd class with EC > 3000 µS/cm. Overall, 35.2% of the groundwater in the area is suitable for irrigation in terms of the salinity hazard, whereas 42% of the groundwater poses high salinity hazard and is not to be used for irrigation purposes (Table 10) except for very salt-tolerant plants whereby exceptional drainage, frequent leaching, and intensive management is available.

7.1.3. Percentage sodium (Na^+ %)

Percentage sodium is capable in distinguishing water because a high value suggests soft water whereas, hard water will be characterised by a low value. Sodium hazard in irrigation water can be quantified by %Na^+, Table 10 displays the results of Na^+% for the study. As stated by Bhat et al. (2018) high Na^+ in the groundwater reflects various contributions such as dissolution of minerals from rock compositions, extended residence time of water, and accumulation of chemical manures within irrigation waters. The prominence of sodium levels in the classification of irrigation water is paramount for sodium exerts deep influence on soil absorbency and soil structure to such an extent that high concentration can result in little or no plant growth. In the investigated region only 16.1% of the water samples meet the desired limits for irrigation and 45.2% are rendered as doubtful based on the Na^+%. About 38.7% of the samples fall outside the desired limit for irrigation as shown by the high concentration of sodium being over 80%. Therefore, using this water for irrigation in the study region may cause toxic effect on crops, and it is highly possible that soil colloidal particles will be dispersed causing the soil to be impervious, thus resulting on elevated osmotic pressure and the plants roots experiencing difficulties in retaining water.

7.1.4. Kelly's ratio (KR).

Kelly's Ratio is among key parameters used to weigh fitness of water for irrigation and it can be understood by quantifying the level of sodium against magnesium and calcium. Water considered fit for irrigation based on Kelly's ratio should be < 1, anything above this value indicates excess of sodium and rendered unsuitable for irrigation usage (Mirza et al. 2017). The calculated results based on KR are tabulated in (Appendix I) and shows 9.7 % of the water samples in the investigated region can be applied in irrigation and the remaining 90.3% (Table 10) is not appropriate for irrigation purposes.

7.1.5. TDS classification for irrigation

Salinity in irrigation water meant for irrigation usage can be quantified by means of Total dissolved solids, and it is often expresses as ppm or mg/L. In this study TDS is expressed in mg/L. According to salinity management (www.salinitymanagement.org/), TDS can be classified in to three groups for irrigation purposes: groundwater with TDS amounts < 450 mg/L is considered safe for irrigation, concentrations between 450 and 2000 mg/L is classified as low -tojudicious risk and TDS values above 2000 mg/L, poses extreme threat of alkalinity. The groundwater samples collected in the study region shows extremely elevated levels of dissolve solids in most sites. The TDS values falls under all three categories (Table 10) 37.5% of the samples falls under the safe category (TDS<450) and 21.9 % falls under the slight - to - moderate risk (450 to 2000 mg/L) whereas, 40.6% of the samples indicate a severe risk of alkalinity (TDS >2000 mg/L). High TDS values are mostly observed from piezometers i.e. the shallow groundwater of the area, while the deep groundwater TDS concentrations are low as only a few boreholes have high TDS above the permissible limits for irrigation (BH1 – BH7).

Table 11:Chloride concentration guide for irrigation water (Mass, 1990).

Cl mg/L	**Effects on crops**	**number of samples**	**no of samples in %**
<70	mostly safe for all plants	1DGW	3.1
70 - 140	delicate plants displays injury	7DGW	21.9
141 - 350	moderately tolerant crops demonstrate damage	8(7DGW,1SGW)	25
>350	Can lead to extreme threats	16(8DGW,8SGW)	50

As for irrigation water, concentration of Cl^- above certain limits may pose toxicity in plants and this may cause tissue impairment of the crop or burns on the leaves. The concentration of chloride in water was classified by Mass (1990) into four groups for irrigation purposes. Based on Mass (1990), classification, water in the study area falls in all four classes. About 50% of the samples indicate that Cl^- concentrations are such that they can cause severe problems as they contain above 350 mg/L (Table 11). Only 25 % fall in the third class which indicates the moderately tolerant plants show injury and 21.9 falls in the second class indicating injury to plants (Table 11).

7.1.6. Bicarbonate (HCO_3^-)

Assessing water for irrigation use based on HCO_3^-, the FAO (2007) guideline divided the concentration of HCO_3^- into three classes: water is safe for irrigation is values are <1.5 meq/L this is equivalent to (91.5 mg/L). If the range is between 1.5 and 8.5 meq/L (91.5 and 457.5 mg/L), indicate a rising threat whereas values past 8.5 meq/L (457.5 mg/L) introduces extreme threats. Based on this classification the water in the study of interest is confined to two classes, the “no problem” class and the “increasing problem” class. Shallow groundwater in the area in terms of HCO_3^-

classification falls under the second class i.e. the "increase problem", as the HCO_3^- vary from 1.61 to 4.17 and have a mean of 3.09 meq/L, while deep groundwater has (0.08 – 4.40 with an average of 1.61 meq/L) and falls in the first two classes. The slightly high alkalinity is a consequence of the application of fertilizers which are known to increase carbonate amount. The general range of HCO_3^- in the area is from 0.082 to 4.39 with an average 1.89 meq/L. The highest concentration is 4.40 meq/L which is less than the upper limit of the second class limit as per FAO (2007) guideline (8.5 meq/L), in this case bicarbonate is at fairly safe levels and is not too much of a concern in the region.

7.2. Chapter summary

It is concluded that shallow groundwater in general and a few deep groundwater samples in the investigated region do not meet the required standards for drinking purposes. In terms of fitness for irrigation based on SAR, %Na^+, TDS, EC the waters were classified as bad quality and unfit for irrigation usage. However, there were few samples which met the standards especially from the deep groundwater samples. The groundwater in the region was categorized as brackish to saline based on TDS and EC classification. Analysis of groundwater samples from the region of investigation showed signs of deterioration, and this calls for the need of a viable utilization of precious resources. Groundwater that exists in the shallow aquifers and few samples from deep aquifers were found to be deprived in quality and past the drinkable limit as per World Health Organization and SANS standards. The concentrations of Na^+, TDS, chloride, and EC exceeded the SANS241 as well as WHO (2011) standards for water consumption particularly the shallow and fewer deep groundwater samples. In this manner the quality of groundwater in the research site is significantly degraded and experience high degree of salinity due to influence of the geological setting, anthropogenic effluence also seawater mixing. However, there were some areas where the water quality was adequate (geochemically) but requires attention.

Farmers in the area rely on groundwater for their agricultural practices therefore; to maintain the sustainability of crop production under the circumstance of bad groundwater quality meant to be used in irrigation as established from various classifications, it is best or recommended to plant crops that are highly tolerant to the salinity and sodicity in this catchment. Although, water in some parts of the investigated region was determined to be suitable for consumption and irrigation, a high percentage of water in the region was not appropriate for either domestic usage or consumption and could cause harm to human health. Therefore, proper mitigation plans are required to manage and monitor the groundwater resource for irrigation and consumption in this area. The results of this study can serve as baseline information to initiate a monitoring program more specifically special monitoring program for water quality in the area.

Chapter 8: Overall Discussion

8.1. Introduction

The present study was carried out in Heuningnes Catchment, where large portion of the land covering the Heuningnes catchment is privately owned for crop farming and livestock production. The main crops are barley, canola, and wheat (Pauw, 2012). Also growing of grapes, especially for wine making, is an important land use in the catchment (Mazvimavi, 2018). Livestock production in the form of cattle and/or sheep is practised on most of the farms. Dairying is being practised at a small number of farms. Within the catchment there are several salt pans which are characterised as saline to hypersaline.

Recently groundwater has become the principal source for agriculture, human ingestion, and livestock watering in the study region. In the search for groundwater resources, water quality is as important as groundwater quantity. Therefore, knowledge of the physio-chemical attributes of the groundwater is vital for evaluating the fitness of the water for a number of purposes such as domestic, usage, and agriculture. The observed quality of groundwater might also differ as a result of seasonal variations and is predominantly administered by the degree and type of dissolved solids. The common anthropogenic and natural factors that affect the quality of water are mostly irrigation practices, local climate as well as the geology. Hence, the longer the water resides in the aquafer, the greater the possibility that the mineral composition of groundwater at the discharge zone is high compared to recharge point.

Deterioration of the quality groundwater as a result of high salinization is described from certain parts of the study region, predominantly from the lower part of catchment. Knowledge of the Hydro-geochemical processes that govern its chemical composition provides a better perspective on the understanding of hydrochemical systems and as a result enhances how the groundwater resources can be used and managed by illustrating relations among many hydrogeological parameters. In the present investigation, hydro-geochemical characteristics of groundwater in parts of the Heuningnes Catchment have been examined to note the distributions of groundwater geochemistry and the hydro-geochemical progression patterns in the region. The hydrochemical findings were subsequently used to evaluate the quality of groundwater with reference to its fitness for domestic and agricultural purposes.

8.1.1. Joint interpretation of chemical, geological and geophysical results for groundwater quality assessment

Geophysics was used to map groundwater quality and characterise the subsurface geology. Chemical data and lithological data from piezometers and boreholes were used to substantiate the geophysical measurements and make a conclusive interpretation regarding groundwater quality status in the Heuningnes Catchment. Based on the geophysical investigation, combined with hydrochemical and geological investigation, the resulting interpretations were deduced.

The geo-electric resistivity models showed a high contrast of resistivity in the subsurface material across the area in the range of 1 to 111 Ω.m. The measured resistivity variations in the subsurface reflect different lithologies and fluid content. The subsurface geology from the surface is made up of sandy clay with other different material of low to medium resistivity values, clay, clay-sand fine-sand, shale and sandstones as depicted by the resistivity geo-electric models. The sand layers and sandy-clay make up the shallow aquifer in the study region and these correspond with the description made from the lithologs.

The resistivity result also reveals layers with different water quality, as saline saturated layers corresponded with the very low resistivity values, and the fresh groundwater saturated layer is represented by high resistivity values and lastly, an intermediate resistivity layer is representing the transition zone or sandy layer filled with brackish water. Resistivity of groundwater is expected to range from, 10 Ω.m - 100 Ω.m subjected to the amount of dissolved salts (Loke, 2001). In literature, freshwater is assumed to have resistivity from 5-80 Ωm, whereas for other materials such as wet sand the resistivity is given as 20-150 Ωm, while sandstone is 20-300 Ωm and limestone is 100-800 Ωm Kelly (2011). In the study area fresh water is confined to the fine sands and the fractured sandstone as described from the lithologs; the fine sands and the sandstone make up the deep aquifers ranging from a depth of 10 to 0ver 40 m.

The issue with groundwater quality in the area was high salinity content which was not defined as either a result of seawater intrusion or other sources of salinity. According to Satriani et al. (2011) aquifers saturated with saline groundwater tend to have resistivity less than 10 Ωm whereas, aquifers affected by seawater will have even lower resistivity below 1 Ωm and approximately mean of 0.3 Ωm. In support with this statement Johnson et al. (2008) and Jansen (2011) state that sandy areas saturated with saline/brackish water are characterised with low resistivity of 1 to 10 Ω.m or lesser, depending on the salinity content present in water.

In the study area the shallow aquifer units as revealed by the resistivity models have very low resistivities (>4 Ω.m) and this implied that these layers have been impacted by saline or brackish water, which is suspected to be coming from the hypersaline lakes (Soetendalsvlei and Voelvlei) or as a result of the increase of dissolved salt content due to evaporation, or an increase in clay content which is known to reduce resistivity drastically. The latter option needs to be considered as clay layers were encountered in the study region specifically in the Soetendalsvlei and Voelvlei sites. The dominance of low resistivity across the study region implies that the groundwater in this particular region had high levels of TDS, especially sodium and chloride ions, as the presence of such ions in greater amounts will result in the water being saline, thus reducing the resistivity.

Analysis of the chemical results supported the resistivity results, groundwater in the area especially in the shallow aquifers represented by the piezometers was found to be containing high levels or TDS, EC, Cl^- and Na^+. In particular Cl^- had ranges of 59 to 40988 mg/L and Na^+ had ranges of 34 to 11383 mg/L whereas, TDS ranged from 112 to 48977 mg/L and EC the 230 to 73100 µS/cm showed large variations. These values are way above the sanctioned limits for water consumption as per WHO(2011) and SANS241, also exceeds the seawater benchmark of 35000 mg/L TDS, 19000 Cl^- mg/L and 3000 µS/cm EC (Klassen et al. 2014).The high EC levels found for the shallow aquifers was expected, as similar results were reported by previous studies done by Toens et al. (1998), where they indicated that the groundwater associated with the shales of the Bokkeveld Group had EC values of 5000 and 10000 µS/cm which is high above the recommended limits. Also saline water bodies in the area, namely Voelvlei and Soetendalsvlei are reported to have (EC) that ranges between 3000 to 7000 µS/cm as reported by HilLand associates (2008), this clearly shows that these lakes had a great influence on the EC levels in the shallow aquifer as all samples taken around this area had very high EC recordings. This means that water from this lake to some extent recharged the shallow aquifer in this area and influenced its quality.

The elevated amounts of Na^+ and Cl^- in this area indicate influence of saline water due to proximity to the sea, as groundwater in coastal aquifers is expected to have a high concentration of these parameters (Kanagaraj et al. 2017). Various studies (Ekmaj et al. 2014; Babu et al. 2013; Mtoni, 2013) conducted in coastal environment have found this to be true as their results also reveals groundwater with high sodium and chloride ion content which many ascribed to the impact of seawater. Large variations of Na^+, Cl^-, TDS and EC in the study region indicate that the chemistry of groundwater in the researched site is affected by multiple processes including mixing of saltwater to some extent. However, the effect of seawater invasion on the chemical DNA of groundwater in the region is questionable as the resistivity models did not indicate any sign of seawater intrusion. To understand whether the source of salinity is from seawater or other sources ionic ratios were studied.

8.1.2. Influence of Seawater intrusion on groundwater quality in the Heuningnes Catchment.

Globally, numerous aquifers along the coast are at risk of being invaded by seawater (Post et al. 2018) this often happens when the coastal aquifers are over-abstracted (Badana et al. 2018) which paves a way for seawater to enter freshwater aquifer and contaminate it. Salinity in groundwater is often indicated by high levels of EC, TDS and Cl^- and high levels of these parameters in groundwater from coastal aquifers is mostly associated with seawater influence. However, seawater is not the only process that may cause these parameters to rise in coastal groundwater. Apart from seawater intrusion, salinity in coastal aquifers is also associated with fossil seawater or ancient saline groundwater (Post et al. 2018), sea-spray dissolution of evaporitic deposits and pollution from anthropogenic activity such as return flow from irrigation Milnes et al. (2006), leaching out of the salts from the aquifer material (Baskaran et al. 2016) and water-rock contact or after evaporation in lagoons (Cary, 2015).

In many cases there is a misinterpretation of attributing the manifestation of any saline/brackish water to seawater intrusion in particular along coastal formation because of high levels of the aforementioned parameters. In this study high EC, TDS, and Cl^- levels were observed especially in boreholes from shallow aquifers. Like many other authors the ionic ratios and bivariate plots were applied to assess origin of salinity. Seawater has a distinct signature of chemical composition it is mostly characterised by chloride in excess of alkali ions (Na^+ plus K^+) and Mg^{2+} dominates Ca^{2+} (Korfali and Jurdi, 2010). In contrary continental fresh groundwater are characterised by variable chemical composition, where HCO_3^-, SO_4^{2-} and Cl^- are the dominant ions respectively and the cations are Ca^{2+} and Mg^{2+} and to a lesser degree the Na^+ and K^+, often times Ca^{2+} dominates over Mg^{2+}. In coastal aquifer groundwater that is affected by seawater encroachment is likely to deviate from the conservation saltwater freshwater interaction (Korfali and Jurdi, 2010). As stated previously that the value of EC and TDS alone is not enough to assess seawater intrusion, various authors (Idowu, 2017; Khan and EghbalBakhtiari, 2017, Kumar, 2016, Klassen et al. 2014) proposed the application of ionic-ratios to measure seawater invasion in coastal aquifers. The most common indicators used are the ratios of Na^+/Cl^-, Cl^-/HCO_3^- and Mg^{2+}/Ca^{2+} same ratios were applied in this current study.

The Na^+/Cl^- ratio for seawater is 0.86, where above 1 is freshwater or groundwater affected by anthropogenic sources as reported by (Idowu, 2017). And Mg^{2+}/Ca^{2+} ratio for seawater range from 4.5 - 5.2 (Babu et al. 2013). Magnesium in seawater is higher than calcium Srinivas and Nageswararao (2013) chloride is the dominant ion in seawater this is the reason why these are used as indicators of seawater intrusion. Srinivas and Nageswararao (2013) state that these ionic ratios should be interpreted taking into consideration of the resident geology which many cases contribute to the anomalies in ratios. The ratio of Cl^-/HCO_3^- range for contaminated groundwater due to seawater intrusion is divided into five classes, ratio <0.5 noble quality; 0.5–1.3 marginally impacted; 1.3–2.8 reasonably impacted; 2.8- 6.6 injuriously polluted and 6.6- 15.5 highly contaminated (Idomu, 2017; Ekhmaj et al. 2014).

In the research region, 25.8% of groundwater samples are in the 0.5 to 6.6 ranges of the Cl^-/HCO_3^- ratio indicating samples that are slightly affected to injuriously contaminated, and 74.2% are above 6.6 and indicate that these samples area highly contaminated. Whereas, the overall Na^+ / Cl^-ratio for tested groundwater samples in researched site ranges from 0.10 to 6.60 and 35.5% (PZ7, PZ8, PZ13, F1, F3, F5, BH9, BH10, BH13, BH14, ZQMGYS1) of these groundwater samples from both shallow and deep aquifers are impacted by seawater intrusion as they have lower Na^+/Cl^-ratio than the standard seawater ratio and most impacted samples are from the deep groundwater aquifer. Mixing of freshwater and salt water lies between the 0.86 (seawater) and 1 (freshwater) according to Nair et al. (2015), only 2 samples indicated mixing in this area and they account for 6.5% the remaining 58% (PZ2, PZ 14, PZ 15, PZ 16, PZ 22, BH1, BH6, BH7, BH 8, BH 11, BH 12 and ZQMBRD2) had ratio above 1suggesting effects of cation-exchange process altering groundwater's chemistry. These samples also indicate anthropogenic effect such as saltwater pans (Babu et al. 2013), salt pans in this study are attributed to the Soetendalsvlei and the Voelvlei. If seawater intrusion was a factor governing groundwater quality in the region, then Na^+/Cl^-plot was expected to have a linear relationship along the seawater dissolution line. Most of the samples plots below but very close to the mixing line (Figure 6.19), depicting influence of seawater mixing in the aquifer. However, there were few that deviates from the mixing line and these are attributed to cation exchange.

Using the Mg^{2+}/Ca^{2+} ratio the sampled groundwater in the region exhibited ratio in the range of 0.26 to 5.77. About (87%) of groundwater samples that were tested have Mg^{2+}/Ca^{2+} ratios exceeding 1, however, they do not fall within the seawater intrusion range of 4.5 – 5.2 except for BH7, F4 and ZQMBRD2 indicating effect of seawater intrusion in these samples. The samples with the ratio falling out of the seawater intrusion range suggest that other processes such as cation exchange was responsible for altering water chemistry of these samples as noted by Rout et al. (2012), because water that is influenced by seawater intrusion will have values close to five excluding where cationic-exchange processes are active as other additional processes, in that case the values could be 4 or less. It is therefore, concluded that certain portions of the catchment experienced seawater incursion where other are affected mainly by other processes such as cation exchange process based on the compelling evidence from the chemical analysis, piper plot and ionic relationship.

8.1.3. Influence of geochemical processes in groundwater quality

Classification of groundwater in the considered study location based on TDS and EC indicated that the samples falls in either fresh, brackish or saline class depending on the type of subsurface layer, this corresponds with the resistivity results which indicated different subsurface layers saturated with fresh, saline and brackish water. Meanwhile piper classification indicates Na^+-Cl^- water type as the principal water-type in the region and only three samples (PZ19, ZQMSTR1and ZQMGYS1) indicated mixed water type. The dominance of Na^+-Cl^- type suggests that groundwater in the area is influenced by marine deposits. Rivera-Hernandez et al. (2017) indicated that many coastal aquifers will portray Cl^-, and Na^+-Cl^- type water because of saline invasion processes triggered by strong interaction between freshwater and seawater as it is within the current study location. Just like the study's findings, also Badana et al. (2018) encountered similar result when they evaluated sources of pollution, groundwater quality and geochemical processes in the coastal aquifer of Tugela Catchment, by means of geochemical and statistical methodology. Their results showed that boreholes near the coast were invaded by saline water and ruled by Na^+-Cl^- water type.

The hydrochemical processes and groundwater's chemical composition changes in space and time, subjected to the type of geological condition and geochemical processes within an aquifer medium (Kazemi and Mohamad, 2012). In coastal aquifers groundwater chemistry is often administered by close contact between water and aquifer material, precipitation, and other processes such as evaporation, and to illustrate evidence of this geochemical processes, various authors have used the Gibbs diagram (Kazemi and Mohamad, 2012; Kumar, 2016; Badana et al.

2018). Findings from Gibbs diagram (1970) for this research area indicates that in 80% of the sampled groundwater rock water-contact process was the foremost factor influencing the chemical chemistry of groundwater and only 20% suggest influence from evaporation process. In support of this the Na^+/Cl^- versus EC graph gave a horizontal line demonstrating ion concentration in the water samples as a result of evaporation. According to Ligavha-Mbelengwa (2017) evaporation process increases the concentration of TDS therefore, high levels of TDS above 1000 mg/L is also an indicative of active evaporation process, this is true for groundwater in the shallow aquifer of the region in particular where TDS levels were extremely high as opposed to the deep groundwater samples. Also, climate conditions increase evaporation rates, thus raising TDS, Na^+, Cl^- and salinity. According to Rivera-Hernandez et al. (2017) the dominance of weathering processes as an effect of water infiltrating the subsoil and poor drainage condition which result in long resident time of groundwater, enhances rock-water interaction process.

Other geochemical processes that can be active and influences the chemistry of groundwater are dissolution, groundwater resident time along the travel path and ion exchange processes (Nwankwoala and Udom, 2011). The lower Na^+/Cl^- ratios of the saline groundwater in the area may be attributed to reverse ion-exchange of sodium in place of Ca^{2+} and Mg^{2+} in clays, this process is expected especially where coastal aquifers are impacted by intrusion of seawater (Kumar, 2016). In addition, the concurrent enrichment in both chloride and sodium ions within groundwater point to concentration by process of evaporation or dissolution of chloride salts (Nwankwoala, 2013) and this is expected in groundwater that is impacted by seawater intrusion this was observed in some parts of the study region more especially in shallow aquifer.

In the investigated region, dissolution of halite is not evident at all, as the Na^+/Cl^- molar ratio is between 0.10 and 6.60. About 61.2% of the tested samples indicate Na^+/Cl^- molar ratio of below one, which point toward ion exchange being the major process controlling groundwater in those locations. Meanwhile, the remaining 38.8% proposes that silicate weathering process was responsible for altering chemical composition of groundwater. Based on the Mg^{2+}/Ca^{2+}molar ratio only 2 samples have ratio < 0.5 and 2 had ratio < 1, whereas, 87% of the sample have ratio above 1 indicating that groundwater chemistry is primarily controlled by dissolution of dolomite in this area.

The overall joint interpretation of hydro-geochemical, geophysical and geological analysis insinuates that various factors including geology, the nature and source of aquifer recharge, and the overall rate of groundwater movement within the aquifer system influenced the quality of groundwater in the Heuningnes Catchment. The results indicate that quality and hydrochemistry of deep groundwater in the region emanates from weathering of mineral during rock-water interaction whereas, shallow aquifer geochemistry is controlled mainly by evaporation processes. However, carbonate weathering and silicate weathering processes in the study region, are also liable for the supply of some ionic species to the groundwater as indicated by Na^+/Cl^- ratio. The link amongst the sum of cations, (K^++Na^+), (Mg^{+2} + Ca^{+2}) and Cl^- also attest the impact of silicate weathering and inputs from seawater incursion on the prevailing chemical composition of groundwater. The extents of their influence differ in each sample.

Considering the ionic relations in the study area it may be assumed that saline intrusion is not the sole factor for the observed high EC and TDS of some locations in the study area. However, evaporation process played a major role and this was supported by the Gibbs plot, Na^+/Cl^- vs EC plot. In addition, the limestone and shales of the Bokkeveld Group and the lakes in the lower catchment area exerts a significant influence on major ion chemistry especially in the shallow aquifer where groundwater recorded high concentration of Cl^-, Na^+, and TDS, EC and seawater infiltration.

8.1.4. Evaluation of groundwater quality for irrigation and consumption uses

In terms of quality, overall groundwater in the research region can be defined as fresh to brackish and fluctuates from acidic to alkalinity in nature. There are clear standards for water consumption as stipulated in SANS241 and WHO guidelines, for instance 250 mg/L is a benchmark for Cl^- concentration. Many of the tested samples in the research area are impacted by salinization this is shown by the high content of sodium, electrical conductivity, chloride and total dissolved solids, as observed is the area. About 99% of the tested shallow groundwater and less than 37% of the deep groundwater samples exceeded the acceptable standards for consumption water as endorsed by World Health Organization and SANS241 guidelines. This is a concern, South Africa is facing drought problems especial in the Western Cape which is home of the current study, suffered severe drought episode between the years 2017 to 2019. There is high demand of freshwater since the water levels from the dams has decreased drastically groundwater is the only hope for the province.

However, groundwater in most of the sampled area is unsuitable for domestic or irrigation uses this has unfortunately heightened the scarcity of freshwater resources in the Western Cape region in general. This does not offer any solution to the current drought problems, but puts pressure, leading to a chain of seawater intrusion, declining groundwater table, decrease of available freshwater, and ultimately increase abstraction of the residual freshwater. The future end result of this cycle is not good as it will end by deterioration of groundwater quality of the region according to Han and Currel, (2018) this situation is to be expect in coastal regions like the current study. This means the fresh groundwater from deep boreholes in the study area which is currently unaffected by salinization is under threat. As it stands from the findings of this study the coastal aquifer of Heuningnes Catchment is greatly affected by salinization especially the shallow groundwater, this will exert pressure on freshwater supply and may cause obstruction of future social and economic improvement of the region.

Excessive concentration of dissolved ions in water used for irrigation affects soil configuration, air circulation and absorbency which affect the development of plant. In this study assessing appropriateness of water to be used for irrigation was based on four main parameters which are salinity, sodium absorption ratio, soluble sodium percentage and EC values, linked to the sum of soluble salts in water applied in irrigation. Excessive salt in the irrigation water, result in the uptake of water by plats to be restricted through osmotic pressure (Madhav et al. 2018) thus interfering with the plant development. Based on SAR 50% of the samples are good for irrigation and 46.8 were unsuitable, whereas, using salinity 35.4% indicated no problem and 42% indicate severe salinity hazard. Using the Na % classification for groundwater only 21.1% of the samples are acceptable for irrigation and 48.2% are rendered as doubtful based on the Na^+%, whereas, 30.7% of the samples are unsuitable for irrigation as indicated by the high concentration of sodium being over 80%. Therefore, using this water for irrigation in the considered study region may have a toxic effect on crops, and it is highly possible that soil colloidal particles will be dispersed causing the soil to be impervious, thus resulting in raised osmotic weight and trouble in water retention by plant roots.

The high levels of chloride in the irrigation water may pose toxicity which will cause the leaf to burn or tissue damage of the crop whereas the TDS and EC poses high alkalinity to the water, 50% of the regions water is not appropriate for irrigation because of elevated TDS, EC and Cl^- values. Shallow groundwater in the region was found unsuitable for consumption and irrigation uses based on the assessment by SAR, Na^+% and groundwater classification. Groundwater occurring in the shallow aquifer exceeded all the recommended limits in terms of consumption water standards set by both WHO and SANS. However, groundwater from deeper aquifers was within accepted standards hence safe for both consumption and irrigation purposes.

9. Conclusion.

In this research how a joint approach of geophysics, geochemical and geohydrology can be used to evaluate the chemical characteristic of groundwater and further delineate the extent of saline water in coastal aquifers was exposed. Using geophysical survey has demonstrated to be a valuable technique in matters pertaining groundwater resources, whether is for locating suitable site for drilling boreholes or for groundwater quality purposes and for mapping the subsurface material. Provided that the data is interpreted accurately it is most likely that the groundwater quality can be assessed using geophysics, especially when coupled with chemical data and geological knowledge as it was done in this study.

The inferred lithologies from the 2D geo-electric resistivity imaging depict the top soil which comprises of sandy-clay, clay, sandy-clay or clayey-sand, fine-sand, shale as well as sandstone. In the investigated area the fine-sand, fractured sandstone units, sandy-clay and clayey-sand, make up the coastal aquifer systems within the area. Further the resistivity results revealed different subsurface layers that were saturated with fresh or saline or brackish water. This varied in thickness from the surface in some locations a depth of 25 meter saturated by saline groundwater was encountered and this was mostly at the Soetendalsvlei site. A clear lateral and depth extent of salinity in the groundwater was revealed by the 2D geo-electric models across the Heuningnes catchment. the lateral and The presence of saline and brackish water was established from chemical results which displayed chloride water type as principal water type in the region and this was further supported by the high TDS, EC and Chloride levels. Also classification of water based on TDS and EC supports these findings. These results are expected not only because the area is located in a coastal environment but also because of the nature of the geology of this area exerts a major part in the resulting chemistry of its groundwater.

The hydrochemical analysis revealed the dominant sequence of the major ions as $Na^{+} > Mg^{2+} > Ca^{2+} > K^{+}$ for cations and $Cl^{-} > HCO_3^{-} > SO_4^{2+}$ for ions. The chief Hydro-geochemical processes that are accountable for the salinity and chemical composition of groundwater in the investigated region as indicated by Gibbs plot are rock-water interaction followed by evaporation process. Furthermore, analysis of hydrochemical datasets also suggests that silicate weathering of minerals, carbonate dissolution and ion exchange were responsible for the modification of ion concentration in groundwater thus influencing salinization in some parts where seawater was not dominant source of salinity. Various ionic ratios revealed the effect of marine sprays as well as seawater on the geochemistry of groundwater of the Heuningnes Catchment aquifer. This was also supported by piper diagram which indicated Na^{+}/Cl^{-} water type as the main dominant water type through the area.

Assessing the chemical composition of groundwater as well as fitness for different uses in the selected region shown that shallow groundwater is not fit for any use, however, groundwater from deeper boreholes was found to be fresh and that it can be utilized for consumption and irrigation means. Findings of this study reveal that salinity is the major groundwater quality issue for this area and that monitoring of groundwater quality in the Heuningnes Catchment is limited. The absence of a consistent monitoring program of groundwater quality makes it difficult to ascertain long term trends on groundwater quality parameters. Therefore, this study emphasizes the need for regular groundwater quality monitoring to assess the trends of these parameters in order to make an informed decision as to what can be done for mitigation purposes in protecting the resource.

10. Recommendations

In this study a once off sampling run was done to attain the current status of groundwater quality in the area and map the extent of salinity using a combined approach of different techniques; the purpose was to provide baseline information/data on the chemical composition character of groundwater in the region of interest. High levels of Cl^- , TDS, and EC concentration were recorded in the area, however, it is difficult to observe a trend, i.e. whether these parameters are decreasing or increasing. Long term hydrochemical data is required to understand the behaviour of these parameters, therefore, it is recommended that a study is done to monitor these parameters over a long term and in both wet and dry seasons to see if there are any changes. This would also give more clarity on the issue of seawater intrusion and whether it is responsible for the salinity in this area or not. Therefore, a consistent long term groundwater quality monitoring will be beneficial for this area.

Based on the outcomes of this study it is apparent that there might be different salinization processes taking place in the area. Therefore, it is recommended that a study is carried out by means of environmental isotopes and traces to ascertain the different sources of salinity and define the origin of groundwater in the area. The use of Cl^- as a tracer could be beneficial as it is known to be best in monitoring salinity evolution. The use of geochemical modelling cold prove to be useful for this area. The result of the current study can serve as a start-up data set for long term monitoring.

Also in the assessment of groundwater quality, the role of microbial processes in biogeochemical cycle is important to understand such as any potential contamination due to pathogens, nutrients or anthropogenic contaminants should be known therefore, such studies in this aspect are recommended for future work in the Heuningnes Catchment. Due to high salinity in groundwater it would be beneficial for the farmers in the area to look into planting salt tolerant crops to sustain their farming business.

11. References

Abdullahi N.K and Iheakanwa A (2013) Groundwater Detection in Basement Complex of Northwestern Nigeria using 2D Electrical Resistivity and Offset Wenner Techniques. International Journal of Science and Technology 2 (7).

Abu-alnaeema M.F, Yusoff I, Tham F. N, Yatimah A, May R (2018) Assessment of groundwater salinity and quality in Gaza coastal aquifer, Gaza Strip, Palestine: An integrated statistical, geostatistical and Hydro-geochemical approaches study. Science of the Total Environment 615, 972–989.

Adelana S.M.A (2010) Groundwater resource evaluation and protection in the Cape Flats, South Africa. PhD thesis, department of Earth Sciences, University of the Western Cape, pp 306.

Adewuyi G.O, Oputu O.U, Opasina M.A (2010) Assessment of Groundwater Quality and Saline Intrusions in Coastal Aquifers of Lagos Metropolis, Nigeria. Journal of Water Resource and Protection, 2, 849-853.

Alfarrah N and Walraevens K (2018) Groundwater Overexploitation and Seawater Intrusion in Coastal Areas of Arid and Semi-Arid Regions. Water Journal. http://dx.doi.org/10.3390/w10020143

Alisiobi A.R and Ako B.D (2012) Groundwater Investigation Using Combined Geophysical Methods, 40914.

Anderson D.J (2017) Coastal Groundwater and Climate Change, WRL Technical Report 2017/04. A technical monograph prepared for the National Climate Change Adaptation Research Facility. Water Research Laboratory of the School of Civil and Environmental Engineering, UNSW, Sydney.

Anders R, Mendez G.O, Futa K, Danskin W.R (2013) A Geochemical Approach to Determine Sources and Movement of Saline Groundwater in a Coastal Aquifer by Robert. National Groundwater Association. http://doi.org/10.1111/gwat.1208

Babu M.M, Viswanadh G.K, Rao SV (2013) Assessment of saltwater intrusion along coastal areas of Nellore District, A.P. International Journal of Scientific and Engineering Research, 4(7).

Badana N, Vetrimurugan E, Natarajan R (2018) Coastal Aquifer Contamination and Geochemical Processes Evaluation in Tugela Catchment, South Africa—Geochemical and Statistical Approaches. Water 2018 10(687). https://doi.org/10.3390/w10060687

Balakrishnan P, Saleem A, Mallikarjun N.D (2011) Groundwater quality mapping using geographic information system (GIS): A case study of Gulbarga City, Karnataka, India. African Journal of Environmental Science and Technology 5(12), pp. 1069-1084.

Bashir E, Naseem S, Pirzada T (2013) Geochemical study of groundwater of Uthal and Bela areas, Balochistan and its appraisal for drinking and irrigation water quality. Int. J. Agric. Environ (2)

Bhat MA, Wani AS, Vijay K, Jyotirmaya S, Dinesh T (2018) An Overview of the Assessment of Groundwater Quality for Irrigation. J Agri Sci Food Res 9: 209

Baskaran V, Mangalam M, Murugaiyan V (2016) Study of seawater intrusion in a coastal aquifer by hydrochemical method – a review. International Journal of Advanced Research, 4 (2), 120

Bickerton I and Pierce S. (1984) Estuaries of the cape. Part II: Synopses of Available Information on Individual,

Booth P.W.K. and Shone R.W. (1992) Folding and thrusting of the Table Mountain Group at Port Elizabeth, Eastern Cape, Rep. of South Africa. In: De Wit, M.J. and Ransome, I.G.D. (eds.) Inversion tectonics of the Cape Fold Belt, Karoo and Cretaceous basins of South Africa. Balkema, Rotterdam. 207-210.

Cary L, Petelet-Giraud E, Bertrand G, Kloppmann W, Aquilina L (2015) Origins and processes of groundwater salinization in the urban coastal aquifers of Recife

(Pernambuco, Brazil): a multi-isotope approach. Science of the Total Environment, Elsevier, 530-531, pp.411-429.

Chandrasekhar E, Ramesh D, Gurav T, and Biswal T K (2014) Assessment of groundwater salinity in Nellore district using multi-electrode resistivity imaging technique. Journal of Earth Systems Science 123(8) pp. 1809–1817.

Cherop K.H (2016) Groundwater investigation and characterisation in Marigat area, Baringo County, using vertical electrical sounding resistivity surveys. Master of Science thesis in the school of pure and applied sciences of Kenyatta University.

Chongo M, Bauer-Gottwein P, Vest A, Christiansen A, Nyambe I, Larsen F (2015) Investigating groundwater salinity in the Machile-Zambezi Basin (Zambia) with hydrogeophysical methods. Kgs. Lyngby: Technical University of Denmark, DTU Environment.

Chung S.Y, Venkatramanan S, Kim T.H, Kim D.S, Ramkumar T (2014) Influence of Hydro-geochemical processes and assessment of suitability for groundwater uses in Busan City, Korea. Environ Dev Sustain, https://doi.org/10.1007/s10668-014-9552-7

Craig D.S.A (2008) The Saline Interface of a Shallow Unconfined Aquifer, Rangitikei Delta. Unpublished MSc thesis, School of Geography, Environmental and Earth Sciences, Victoria University of Wellington. pp173.

Deshpande SM, Aher KR (2012) Evaluation of Groundwater Quality and its Suitability for Drinking and Agriculture use in Parts of Vaijapur, District Aurangabad, MS, India. Res. J. Chem. Sci. 2(1), 25-31

District K.N, Province N, Namwamba S (2012) Hydrogeological and Geophysical Investigations Osembe African Devine Church Water Project Kisumu North Division Water, Sanitation and Environmental Engineering. (31).

Duah A.A (2010) Sustainable Utilisation of Table Mountain Group Aquifers, PhD Thesis. University of the Western Cape pp 182.Gresse PG, Theron JM (1992)

Geology of Worcester area. Explanation Sheet 3318, Geological Survey of South Africa.

DWAF (Department of Water Affairs and Forestry) (2000) South African water quality guidelines, 2nd edn, 4. Agricultural use: irrigation

Ebenezer A (2014) Assessment and mapping of groundwater quality in the Thiririka sub catchment Kiambu country, Kenya. A Thesis Submitted in Partial Fulfilment of the Requirements for the Award of the Degree of Master of Science in Integrated Watershed Management in the School of Pure and Applied Sciences of Kenyatta University pp192.

El-Fiky A.A (2010) Hydro-geochemical Characteristics and Evolution of Groundwater at the Ras Sudr-Abu Zenima Area, Southwest Sinai, Egyp. KAU: Earth Sci.,21(1), pp: 79-109, https://doi.org/10.4197 / Ear. 21-1.4 .

El-Sayed M.H, El-Fadl M.M.A, Shawky H.A (2012) Impact of hydrochemical Processes on Groundwater Quality, Wadi Feiran, South Sinai, Egypt. Australian Journal of Basic and Applied Sciences, 6(3): 638-654.

Ekhmaj A, Ezlit Y, Mukhtar E (2014) The Situation of Seawater Intrusion in Tripoli, Libya. International Conference on Biological, Chemical and Environmental Sciences 14-15.

Freeze RA, Cherry JA (1979) Groundwater. Prentice-Hall Inc., Englewood Cliffs, p 604

FAO (Food and Agriculture Organization) (2007) Prospects for food, nutrition, agriculture, and major commodity groups. World agriculture: toward 2030–2050, Interim report. Global PerspectiveStudies Unit. FAO, Rome

Gaaloul N, Pliakas F, Kallioras A, Schuth C, Marinos P (2012) Simulation of Seawater Intrusion in Coastal Aquifers: Forty-Five-Years Exploitation in an Eastern Coast Aquifer in NE Tunisia Hydrology Journal. 6, 31-44.

Gordon N, Adams J. B, Garcia-Rodrigue F (2011) 'Water quality status and phytoplankton composition in Soetendalvlei, Voëlvlei and Waskraalsvlei, three shallow wetlands on the Agulhas Plain, South Africa', African Journal of Aquatic Science, 36: 1, 19 — 33.

Hiland Associates (2008) Situation assessment for Heuningnes Estuary. Report AGU07/596/02 pp1-36.

Herdien E.L, Petersen C, Reed C, Impson D, Belcher A, Ndiitwani T, Buthelezi S, Matoti A (2005) Technical Report: Ecological Status for Rivers of the Overberg Region 2004/2005

Hwang J.Y, Park S, Kim H.K, Kim M.S, Jo H.J, Kim J.I, Lee G.M, Shin I.K, Kim T.S (2017) Hydrochemistry for the assessment of groundwater quality in Korea. J Agric Chem Environ 6:1–29. https://doi.org/10.4236/jacen .2017.61001

IAEA (International Atomic Energy Agency) 2004: Origin of salinity and impacts on fresh groundwater resources: Optimisation of isotopic techniques. Technical report 2000-2004.

IGRAC (International Groundwater Resources Assessment Centre) (2008) Guideline on: Groundwater monitoring for general reference purposes. Report nr. GP 2008-1.

Irungu M.W G (2011) Application of 2D electrical resistivity tomography to assess the influence of geology and geological structures on groundwater occurrence and potential in Konza area, Kenya. MSc thesis, the department of geology, University of Nairobi, pp 109.

Jansen J.R (2011) Geophysical Methods to Map Brackish and Saline Water in Aquifers.

Jia H (2007) Groundwater resource evaluation in Table Mountain Group Aquifer Systems, PhD Thesis. Cape Town, South Africa: University of the Western Cape.

Johnson T.A, Matsumoto N, Jansen J.R (2008) Time Domain Electromagnetic Induction and High Resolution Electric Resistivity Soundings to Map Salt Water Intrusion in Coastal Sandy Aquifers, Los Angeles County, California.

Kavidha R, Elangovan K, Nadu T (2013) Delineation of Groundwater Prospective Zones by Electrical Resistivity Method in Erode District, Tamilnadu, India.,2(1), pp.14–18.

Kazemi G.A and Mohammadi A (2012) Significance of Hydro-geochemical Analysis in the Management of Groundwater Resources: A Case Study in Northeastern Iran, Hydrogeology - A Global Perspective, A Global Perspective, Dr. Gholam A. Kazemi (Ed.), 602(Ed.), ISBN: 978-953-51-0048-5, InTech.

Kelly B. B (2011) "Using Electrical Resistivity Imaging to Map Saline Groundwater and Subaqueous Spring Discharge: An example from The Saline Wetlands of Eastern Nebraska". Dissertations and Theses in Earth and Atmospheric Sciences. Paper 21.

Khaki M, Yusoff I, Islami N (2014) Groundwater quality assessment of a freshwater wetland in the Selangor (Malaysia) using electrical resistivity and chemical analysis. water science and technology, 14(2) 255-264.

Khan A and EghbalBakhtiari A (2017) Groundwater Assessment of Coastal Aquifers in Karachi: Impact of Seawater Intrusion. International Journal of Ground Sediment and Water, 6.

Khalid S.E (2012) Assessment of groundwater quality using multivariate and spatial analyses in Gaza governorate-Palestine. MSc thesis, Faculty of Science, The Islamic University-Gaza pp106.

Khelif S and Boudoukha A (2018) Multivariate statistical characterization of groundwater quality in Fesdis, East of Algeria. Journal of Water and Land Development. No. 37 p. 65–74. https://doi.org/10.2478/jwld-2018-0026

Kitoni I (2018) Integrated hydrological modeling of surface and groundwater interactions in Heuningnes catchment (South Africa). MSc thesis, Geo-Information Science and Earth Observation, University of Twente, p73.

Kokkat A, Jegathambal P, James E.J (2016) Spatial and Temporal Variation in Groundwater Quality and Impact of Seawater in the Cauvery Delta, South India.

International Journal of Earth Sciences and Engineering. ISSN 0974-5904, 9 (3) pp. 383-392.

Kumar A, Bhawsar N.G, Khandelwal S, Sherebano S, Sakir S, Ahuja M, Pathak RK, Hanote SR, Gayakwad S.R, Khasdeo K (2013) Physico-chemical parameters apply to analysis of drinking water from some selected area of Betul District, Madhya Pradesh. International Journal of Pharmaceutical, Chemical and Biological Sciences 3 (4), 1109-1114.

Kumar P.J.S (2016) Deciphering the groundwater–saline water interaction in a complex coastal aquifer in South India using statistical and hydrochemical mixing models. Model. Earth Syst. Environ 2:194. https://doi.org/10.1007/s40808-016-0251-2

Lee S (2015) Investigating the origin and dynamics of salinity in a confined aquifer system in Southeast Australia (Western Port Basin). MSc thesis, School of Civil Environmental and Chemical Engineering College of Science Engineering and Health RMIT University, pp 314.

Lewis A.L, Lautier J.C, Wilson N.C, Chianese G, Webb S (2004) Geophysical monitoring and evaluation of coastal plain aquifers. National groundwater association 42 (1), pp59-67.

Ligavha-Mbelengwa L (2017) Investigation of the Groundwater Hydrogeochemistry Characteristics in Beaufort West, South Africa. MSc thesis, Faculty of Natural and Agricultural Sciences, University of the Free State, pp 180.

Liu F, Song X, Yang L, Zhang Y, Han D, Ma Y, Bu H (2015) Identifying the origin and geochemical evolution of groundwater using hydrochemistry and stable isotopes in the Subei Lake basin, Ordos energy base, Northwestern China Hydrol. Earth Syst. Sci., 19, 551–565.

Loke M.H (2001) Electrical imaging surveys for environmental and engineering studies, user manual for Res2dinv Electronic version available from http://www.geometrics.com.

Lourens P.J.H (2013) The relation between South African Geology and Geohydrology. MSc thesis, Faculty of Natural Sciences and Agriculture, Institute for Groundwater Studies, University of the Free State, Bloemfontein, pp 355.

Madhav S, Ahamad A, Kumar A, Kushawaha J, Singh P, Mishra PK (2018) Geochemical assessment of groundwater quality for its suitability for drinking and irrigation purpose in rural areas of Sant Ravidas Nagar (Bhadohi), Uttar Pradesh, Geology, Ecology, and Landscapes 2:2, 127-136. https://doi.org/10.1080/24749508.2018.1452485

MacQuarrie K, Butler K, Mott E, Green N (2012) A case study of coastal aquifers near Richibucto, New Brunswick: Saline groundwater occurrence and potential impacts of climate change on seawater intrusion. pp 1-18

Malan J.A (1990) The stratigraphy and sedimentology of the Bredasdorp group, Southern Cape Province. MSc thesis, Geology department, Science faculty, University of Cape Town, pp220.

Mandlazi N.P (2017) Hydrological characterisation of Wetlands: understanding wetlands-Catchment Linkages. MSc Thesis University of the Western Cape, Earth Science department, p 137.

Mazvimavi D (2018) Finding "new" water to address conflicting and competing water demands in the Nuwejaars Catchment, Cape Agulhas. WRC Report No 2324/1/18

Meyer P.S (2001) An explanation of the 1:500 000 General Hydrological Map of Cape Town 3317. Department of Water Affairs and Forestry, 59pp.

Milnes E, Meilhac C, Yeo D, Renard P, Hunkeler D, Schnegg P, Bourret F (2006) Hydro-geochemical and hydrogeological investigation in the Akrotiri aquifer: identification of multiple salinisation processes and implementation criteria for monitoring networks. Proceedings 1st SWIM-SWICA Joint Saltwater Intrusion Conference, Cagliari-Chia Laguna, Italy - September 24-29.

Midgley G.F, Chapman R.A, Hewitson B, Johnston P, de Wit M, Ziervogel G, Mukheibir P, van Niekerk L, Tadross M, van Wilgen B.W, Kgope B, Morant P.D, Theron A, Scholes R.J, Forsyth, G.G (2005) A Status Quo, Vulnerability and Adaptation Assessment of the Physical and Socio-economic Effects of Climate Change in the Western Cape. Report to the Western Cape Government, Cape Town, South Africa. CSIR Report No. ENV-S-C 2005-073, Stellenbosch.

Mogren S (2015) Saltwater Intrusion in Jizan Coastal Zone, Southwest Saudi Arabia, Inferred from Geoelectric Resistivity Survey. International Journal of Geosciences, 6, 286-297.

Mondal N.C. Signh V.P, Signh V.S, Saxena V.K (2010) Determining the interaction between groundwater and saline water through groundwater major ions chemistry. Journal of Hydrology 388, 100-111.

Monjerezi M (2012) Groundwater Salinity in lower Shire River valley (Malawi) Hydro-geochemical and isotope constraints on sources and evolution. PhD thesis, Department of Chemistry Faculty of Mathematics and Natural Sciences University of Oslo pp188.

Mtoni Y (2013) Saltwater intrusion in the coastal strip of Dar es Salaam Quaternary aquifer, Tanzania. PhD thesis, Ghent University, Faculty of Sciences, Belgium, 395 pp.

Mukheibir P (2007) The impact of climate change on small municipal water resource management. The case of Bredasdorp, South Africa. Pp1-20.

Mukheibier P (2010) The potential economic impact of climate change on equitable water access in small towns: a South African case study. Int. J. Water, 5(3)

Nagaraju A, Kumar K.S, Thejaswi A, Sharifi Z, (2014) Statistical Analysis of the Hydro-geochemical Evolution of Groundwater in the Rangampeta area, Chittoor District, Andhra Pradesh, South India. American Journal of Water Resources, 2 (3), 63-70.

Nair I.S, Rajaveni S.P, Schneider M, Elango L (2015) Geochemical and isotopic signatures for the identification of seawater intrusion in an alluvial aquifer. J. Earth Syst. Sci. 124(6)

Nolankana P (2016) Geochemical assessment of groundwater quality and suitability for drinking and irrigation purposes in Newcastle, Kwazulu-Natal, South Africa. MSc thesis, University of the Western Cape pp13.1.

Nwankwoala H.O and Udom GJ (2011) Hydrogeochemical evaluation of groundwater in parts of Eastern Niger Delta, Nigeria Department of Geology, University of Port Harcourt, p.m.b 5323, Choba, Port Harcourt, Nigeria. Journal of academic and applied Studies 1(2), pp. 33-58

Nwankwoala H.O (2013) Ionic Abundance and Distributions in Groundwater Systems: A Case Study. Greener Journal of Physical Sciences, 3 (4), pp. 115-130.

Nur A, Ishaku J, Taiyib A (2012) Spatial distribution of chemical facies using geographical information system (GIS) in Michika, northeastern Nigeria, Res J Eng Appl Sci, 1(2), pp. 102-109.

Oladunjoye M.A, Akanji A.O, Akingbesote O.T (2013) Groundwater exploration in alakuta-awotan area of Ibadan, Southwestern Nigeria. J. Geol. Geosci., 2. 10.4172/2329-6755.1000124.

Oyeyemi K.D, Aizebeokhai A.P, Oladunjoye M. A (2015) Integrated Geophysical and Geochemical Investigations of Saline Water Intrusion in a Coastal Alluvial Terrain, South-western Nigeria. Int. J. of App Enviro Sci ISSN 0973-6077 10(4), pp. 1275-1288.

Pauw T (2012) Assessment of spot 5 and ers-2 Obia for mapping wetlands. Dissertation, University of Stellenbosch

Piper A. M (1953) A graphic procedure in the geo-chemical interpretation of water analysis, USGS groundwater note no, p 12.

Post V.E.A, Eichholz M, Brentführer R (2018) Groundwater management in coastal zones. Bundesanstalt für Geowissenschaften und Rohstoffe (BGR). Hannover, Germany, 107 pp.

Rahman M.M. and Bhattacharya A.K. (2014) Saline Water Intrusion in Coastal Aquifers: A Case Study from Bangladesh. IOSR Journal of Engineering (IOSRJEN) 2250-3021, 4(1) PP 07-13.

Ramli M (2009) Numerical modeling of groundwater flow in multi-layer aquifers at coastal environment. Kyoto university pp198.

Ravindran A.A, Ramanujam N, Sudarsan R (2013) Delineation of Saltwater and Freshwater Interphase in Beach Groundwater Study Using 2D ERI Technique in the Northern Sector of the Gulf of Mannar Coast, Tamilnadu. Water journal, p 1-11.

Rivera-Hernández J R, Green-Ruiz C, Pelling-Salazar L, Trejo-Alduenda A (2017) Hydrochemistry of the Mocorito river coastal aquifer, Sinaloa, Mexico: water quality assessment for human consumption and agriculture suitability. Hidrobiológica 27 (1): 103-113

Robert T. R (2012) Geophysical identification, and monitoring of preferential flow paths in fractured media. PhD thesis, ArGenCo department, university of Liege, Belgium, pp183.

Russel I.A and Impson N.D (2006) Aquatic systems in and adjacent to Agulhas National Park with particular reference to the fish fauna. Koedoe [online], 49(2): 45-57.http://koedoe.co.za/index.php/koedoe/article/viewArticle/120

SANS (2011) South African National Standards (SANS 241). Drinking water: Quality requirements

Sathish S, Elango L, Rajesh R, Sarma S (2011) Assessment of seawater mixing in a coastal aquifer by high resolution electrical resistivity tomography. Int. J. Environ. Sci. Tech., 8 (3), 483-492.

Satriani A, Loperte A, Proto M (2011) Electrical resistivity tomography for coastal saltwater intrusion characterization along the Ionian coast of Basilicata region (southern Italy).

Senthilkumar G, Ramanathan A.L, Nainwal H.C, Chidambaram S (2012) Hydrogeochemical aspects in coastal aquifers - a case study from Cuddalore District, South India. International journal of Life Science and Pharma Research, 2(4).

Senthikumar G, Ramanathan A.L, Nainwal H.C, Chidambaram S (2013) Hydro-geochemical Characteristics and Evolution of Coastal Groundwater at Cuddalore Area, Tamilnadu, India International Journal of Engineering Research and General Science .2(2) ISSN 2091-2730.

Singh K.P, Malik A, Mohan D. and Sinha, S (2004) Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India) a case study, Water research, vol. 38(18), pp. 3980-3992.

Sonkamble S (2014) Electrical Resistivity and Hydrochemical Indicators Distinguishing Chemical Characteristics of Subsurface Pollution at Cuddalore Coast, Tamil Nadu Journal Geological society of India 83, may 2014, pp.535-548.

Sughosh M.S, Ahamad A, Kumar A, Kushawaha J, Singh P, Mishra P.K (2018) Geochemical assessment of groundwater quality for its suitability for drinking and irrigation purpose in rural areas of Sant Ravidas Nagar (Bhadohi), Uttar Pradesh, Geology, Ecology, and Landscapes, 2:2, 127-136, https://doi.org/:10.1080/24749508.2018.1452485

Talabi A.O, Ajayi C.A, Afolagboye L.O, Oyedele A.A, Ojo O.F, Olofinlade S.W (2015) Evaluation of salt-water Intrusion in the Coastal Area of Igbokoda, Southwestern Nigeria. International Journal of Scientific Research and Management (IJSRM), 6(1).

Tembo A (2014) Characterisation of saline groundwater based on ground-based Time-Domain Electromagnetic soundings in the Machile River Basin, South-

Western Zambi. MSc thesis in integrated water resources management the University of Zambia Lusaka.

Theron J.N, Gresse P.G, Siegfried H.P, Rogers J (1992) Geology of the Cape Town Area. Explanation sheet 3318, Geological survey of South Africa. Department of Minerals and Energy.

Toens P.D, Visser D, Van Der Westhuizen C.R, Stadler W, Rasmussen J.M (1998) Overberg Coastal Water Resources (Volume II): A Report to DWAF on the Groundwater Resources, Current and Future Water Requirements of the Coastal Strip and Adjoining Hinterland between the Potberg and Quoin Point, TandP 980148, Toens andPartners, Cape Town, February.

Trabelsi F, Mammou A.B, Tarhouni J, Piga C. Deidda G.P, Ranieri G (2006) Salt Water intrusion characterisation in the Coastal Aquifer of Nabeul Hammamet Using Geophysical Methods. Proceedings 1st SWIM-SWICA Joint Saltwater Intrusion Conference, Cagliari-Chia Laguna, Italy - September 24-29.

Weight WD (2008) Hydrogeology Field Manual. 2nd ed. New York, USA: McGraw-Hill Companies Inc.

WHO (2011) Hardness in Drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality, 11p

Walraevens K and Van Camp M (2004) Advances in understanding natural groundwater quality controls in coastal aquifers.

WRC (Water Research Commission) (2014) Assessment of Groundwater potential in fractured hard rocks around Vryburg, North West Province, South Africa. WRC Report No. 2055/1/13 ISBN 978-1-4312-0510-3, pp 172.

Wu Y (2005) Groundwater recharge estimation in Table Mountain Group aquifer systems with a case study of Kammanassie area. PhD Thesis, Dept. of Earth Sciences, University of the Western Cape.

Wu, C, 2009. Groundwater occurrence in the Table Mountain Area of Cape Town, South Africa. MPHIL, Dept. of Earth Sciences University of the Western Cape pp 124.

Xu Y, Wu Y, Duah A (2007) Groundwater recharge estimation of Table Mountain Group aquifer systems with case studies. WRC Report No. 1329/1/07.

Xu Y, Lin L, Jia H (2009) Groundwater Flow Conceptualization and Storage Determination of the Table Mountain Group (TMG) Aquifers. MPHIL, Dept. of Earth Sciences University of the Western Cape pp 124.

Yidana S.M, Banoeng-Yakubo B, Akabzaa T.M (2010) Analysis of groundwater quality using multivariate and spatial analyses in the Keta basin, Ghana, Journal of African Earth Sciences, 58(2), pp. 220-234.

Appendices

Appendix A: Hydrochemical data of shallow groundwater

ID	Ca	Mg	Na	K	HCO_3	Cl	SO_4	TDS	T	pH	EC
PZ 2	313	645	5888	74	186	1413	41	23718	18	7.4	35400
PZ 7	258	280	9040	50	152	18659	941	36314	18	7.1	54200
PZ 8	249	290	1107	56	164	16408	348	38391	18	7.4	57300
PZ 13	381	300	11383	88	230	40988	1609	48106	18	6.9	71800
PZ 14	70	190	2625	40	98	4019	300	48977	17	6.8	73100
PZ 15	191	498	4310	65	188	1896	122	19631	19	6.9	29300
PZ 16	262	707	5966	72	242	2054	152	23517	19	6.6	35100
PZ 19	66	29	118	26	254	193	26	907	21	7.1	1354
PZ 22	237	260	2507	85	184	586	54	10626	18	7.5	15860

*Note all ionic concentrations are in mg/L, EC is in µS/cm, TDS is in mg/L, pH general units, S.D, Temperature **(°C)** is standard deviation Max is maximum and Min is minimum Total number of samples is 9.

Appendix B: Hydrochemical data of deep groundwater

ID	Ca	Mg	Na	K	HCO_3	Cl	SO_4	Cal TDS	T	pH	EC
F1	5	11	82	1	20	156	1	418	19.7	5.3	624
F2	174	260	6450	81	18	11290	19	371	18.8	5.7	553
F3	3	7	52	2	8	103	77	239	18.2	6.1	357
F4	2	7	47	1	12	83	12	229	19.3	4.9	342
F5	3	5	45	1	12	90	11	214	17.6	6.5	320
BH1	67	150	2120	78	182	3141	1	7544	18.6	7.3	11260
BH 3	211	220	3575	86	268	5960	318	1544	18.2	5.5	2320
BH 4	190	150	2100	11	98	3476	645	8281	15.6	7.7	12360
BH 5	68	160	2575	24	182	4071	319	9367	15.7	8.0	13980
BH 6	24	43	880	7	242	865	476	2526	15.2	8.0	3770
BH 7	47	130	1855	12	174	2507	39	6814	14.3	7.8	10170
BH 8	19	37	745	8	200	825	283	1883	16.2	8.2	2810
BH 9	6	7	44	1	40	99	35	235	18.6	5.9	350
BH 10	23	16	65	3	30	126	42	404	17.8	5.8	603
BH 11	7	14	150	1	50	187	26	519	18.7	6.2	774
BH 12	41	16	165	3	92	211	38	706	18.7	6.7	1054
BH 13	5	10	66	1	28	173	16	334	18.1	6.0	498
BH 14	5	10	60	4	26	122	15	346	15.8	6.0	517
SRT1	88	14	95	3	237	154	36	729	21.0	8.4	939
BRD1	4	3	34	2	5	56	8	112	22.0	6.2	230
GYS1	86	15	112	4	216	204	31	724	17.3	8.5	2021
BRD2	3	9	80	2	14	117	20	249	21.5	6.6	546

.

Appendix C: Hydrochemical data of ZQMDRD1

Year	**Ca**	**Cl**	**TDS**	**K**	**Mg**	**Na**	**SO$_4$**	**Talk**	**EC**	**T**	**PH**
1994	47	152	481	4	15	95	36	108	772	-	4.8
1995	5	159	316	7	10	91	30	10	687	11	5.4
1996	6	150	302	7	9	88	24	16	759	22	6.8
1997	3	141	268	2	9	82	14	14	512	20	6.3
1998	4	143	268	2	10	84	23	2	570	23	5.7
1999	5	155	283	2	10	84	19	4	573	22	6.1
2000	5	139	256	2	8	78	16	5	550	-	6.2
2001	5	155	297	2	9	91	23	9	588	-	6.2
2003	5	124	240	2	8	70	19	9	485	-	6.9
2004	4	151	283	2	10	83	24	7	596	-	6.2
2006	4	120	234	2	9	68	20	8	480	-	6.3
2013	4	92	184	3	5	56	12	9	370	-	6.8
2014	3	57	-	-	3	-	7	5	221	-	6.2
2015	4	148	290	3	10	97	20	5	557	-	6.1
2016	4	56	113	2	3	34	8	5	230	-	6.2

Appendix D: Hydrochemical data for ZQMBRD2

Year	**Ca**	**Cl**	**TDS**	**K**	**Mg**	**Na**	**SO$_4$**	**Talk**	**EC**	**T**	**PH**
2001	5	160	304	7	9	86	30	6	603	-	5.8
2002	4	135	259	3	7	79	19	9	546	-	5.4
2003	4	144	275	3	8	81	20	12	540	-	5.5
2004	4	145	258	2	9	74	18	4	558	-	5.6
2005	5	136	254	3	9	75	21	4	561	-	6.8
2006	5	142	259	3	9	76	19	4	541	-	6.2
2007	4	136	257	3	8	76	24	4	514	22	5.9
2008	5	140	-	3	9	74	24	-	533	-	6.2
2009	5	156	-	3	9	73	20	4	542	-	6.2
2010	4	151	263	3	5	74	21	4	533	-	5.3
2012	6	119	225	3	7	64	16	7	462	-	6.1
2014	4	149	-	-	12	-	25	5	570	-	5.8
2017	3	117	249	2	9	80	20	14	546	-	6.6

*Note all ionic concentrations are in mg/L, EC is in µS/cm, TDS is in mg/L, Talk is total alkalinity in mg/L, pH general units, S.D is standard deviation Max is maximum and Min is minimum Total number of samples is 13. The dash areas indicate that there is no reading.

Appendix E: Hydrochemical data for ZQMSTR1

Year	Ca	Cl	TDS	K	Mg	Na	SO$_4$	Talk	EC	T	PH
1994	83	149	612	3	12	85	23	208	810	-	8.7
1995	81	152	611	4	12	89	23	204	1044	11	7.9
1996	79	140	596	2	11	83	26	207	1096	22	7.9
1997	85	149	619	3	12	85	25	212	910	21	8.3
1998	85	153	623	3	12	86	27	209	845	21	7.8
1999	84	140	606	3	12	85	26	209	895	22	8.1
2000	86	146	632	3	13	86	37	212	929	-	7.7
2001	85	153	619	3	12	83	30	206	932	-	8.3
2002	83	156	609	3	13	80	24	204	876	-	8.2
2003	87	163	632	3	12	81	26	212	930	-	8.0
2004	86	151	626	3	13	85	26	215	930	-	7.9
2005	88	152	622	3	12	84	23	212	904	-	8.2
2006	83	157	620	3	13	85	24	209	912	-	8.2
2007	87	158	632	3	12	85	28	212	924	-	8.2
2008	84	168	-	3	14	83	21	239	891	-	8.2
2010	86	193	-	4	13	85	-	215	912	-	8.5
2011	55	114	467	4	12	85	24	142	857	-	8.5
2012	75	150	582	4	12	84	22	193	872	-	8.2
2013	83	148	630	4	12	86	26	222	778	-	8.3
2014	82	148	-	-	15	-	23	212	909	-	8.2
2015	89	153	643	4	12	90	25	219	904	-	8.5
2016	86	157	650	3	14	88	26	225	915	-	8.4
2017	88	154	729	3	14	95	36	237	939	-	8.4

*Note all ionic concentrations are in mg/L, EC is in µS/cm, TDS is in mg/L, Talk is total alkalinity in mg/L, pH general units, S.D is standard deviation Max is maximum and Min is minimum Total number of samples is 23.

Appendix F: Table Hydrochemical data for ZQMGYS1

Year	Ca	Cl	TDS	K	Mg	Na	SO$_4$	Talk	EC	T	PH
1994	117	457	1367	9	36	271	86	297	2310	-	8.5
1995	113	450	1348	9	34	286	87	278	2240	10	6.7
1996	108	412	1293	9	35	259	76	297	2560	20	7.0
1997	114	441	1347	9	35	275	86	292	2025	20	7.7
1998	116	426	1319	9	35	265	79	293	2070	21	7.8
1999	88	195	684	3	13	108	26	200	1059	21	6.2
2001	114	424	1305	10	35	253	87	280	2130	-	8.1
2002	87	312	963	7	27	181	56	221	1647	-	8.2
2003	112	438	1326	10	35	265	82	291	2105	-	8.1
2004	99	378	1214	10	35	239	105	253	2080	-	7.8
2005	121	463	1375	11	38	270	89	291	2425	-	8.2
2006	127	488	1430	11	36	284	91	288	2305	-	8.2
2008	95	383	-	16	40	282	87	160	2200	-	8.4
2009	91	359	-	7	25	180	54	206	1650	-	8.2

2012	51	117	423	7	7	65	18	128	665	-	8.0
2013	74	191	682	4	19	113	29	201	1012	-	8.4
2014	86	215		-	17	-	32	198	1103	-	8.3
2015	83	181	683	5	14	120	28	200	1085	-	8.5
2016	89	196	717	4	15	112	32	214	1046		8.4

*Note all ionic concentrations are in mg/L, EC is in µS/cm, TDS is in mg/L, Talk is total alkalinity in mg/L, pH general units, S.D is standard deviation Max is maximum and Min is minimum Total number of samples is 19. The dash areas indicate that there is no reading.

Appendix G: Calculated ionic ratios of the study area

ID	TC	Ca/HCO3	TA	Cl/TA	CL/SO4	SO4/CL	CL/HCO3	HCO3/CL	CA/MG	MG/CA	CA/CL	CA/SO4	Na/Cl
PZ2	326.701	5.125	43.762	0.911	46.197	0.022	13.063	0.077	0.295	3.393	0.392	18.125	6.427
PZ7	430.438	5.165	548.244	0.960	26.883	0.037	211.079	0.005	0.559	1.790	0.024	0.658	0.747
PZ8	85.880	4.620	472.636	0.979	63.924	0.016	172.036	0.006	0.521	1.921	0.027	1.717	0.104
PZ13	541.115	5.040	1193.109	0.969	34.537	0.029	306.434	0.003	0.770	1.299	0.016	0.568	0.428
PZ14	134.342	2.173	121.172	0.935	18.161	0.055	70.511	0.014	0.223	4.477	0.031	0.560	1.008
PZ15	239.689	3.091	59.091	0.905	20.990	0.048	17.339	0.058	0.232	4.305	0.178	3.741	3.507
PZ16	332.554	3.289	65.061	0.890	18.345	0.055	14.597	0.069	0.224	4.455	0.225	4.134	4.479
PZ19	11.479	0.791	10.152	0.536	10.070	0.099	1.307	0.765	1.380	0.725	0.605	6.090	0.943
PZ22	144.470	3.914	20.660	0.800	14.687	0.068	5.474	0.183	0.551	1.814	0.715	10.502	6.602
F1	4.747	0.761	4.746	0.927	211.392	0.005	13.405	0.075	0.276	3.628	0.057	11.995	0.811
F2	312.729	29.413	319.080	0.998	805.641	0.001	1078.554	0.001	0.406	2.464	0.027	21.970	0.881
F3	3.039	1.141	4.628	0.626	1.808	0.553	22.068	0.045	0.260	3.848	0.052	0.093	0.781
F4	2.746	0.507	2.781	0.839	9.354	0.107	11.863	0.084	0.173	5.773	0.043	0.400	0.876
F5	2.544	0.761	2.952	0.856	11.043	0.091	12.839	0.078	0.364	2.749	0.059	0.654	0.775
BH1	109.905	1.120	91.582	0.967	4258.471	0.000	29.676	0.034	0.271	3.692	0.038	160.736	1.041
BH3	186.349	2.396	179.094	0.939	25.412	0.039	38.243	0.026	0.582	1.720	0.063	1.592	0.925
BH4	113.458	5.899	113.051	0.867	7.307	0.137	60.993	0.016	0.768	1.302	0.097	0.707	0.932

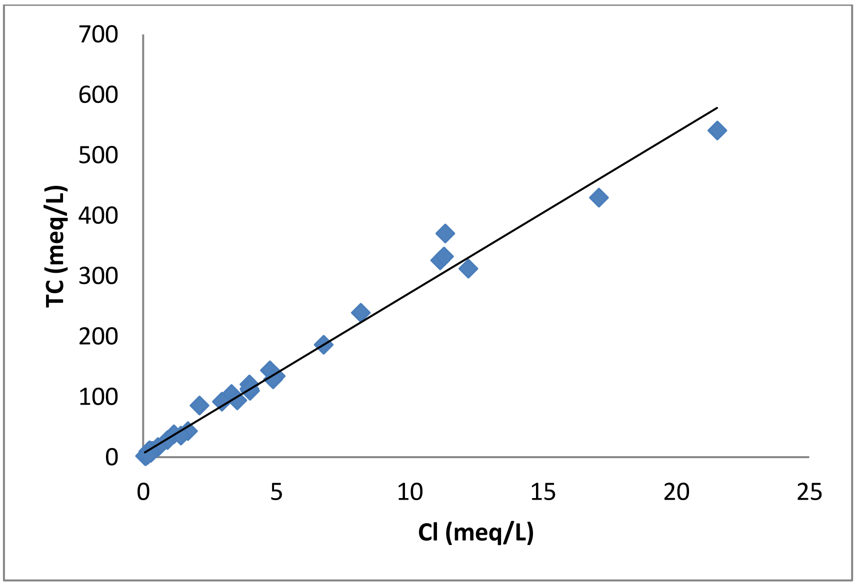
BH5	129.188	1.137	124.426	0.923	17.303	0.058	38.464	0.026	0.258	3.881	0.030	0.511	0.976
BH6	43.196	0.302	38.276	0.638	2.465	0.406	6.150	0.163	0.338	2.955	0.049	0.121	1.568
BH7	94.044	0.822	74.362	0.951	87.152	0.011	24.775	0.040	0.219	4.562	0.033	2.891	1.141
BH8	36.606	0.289	32.432	0.717	3.952	0.253	7.093	0.141	0.311	3.212	0.041	0.161	1.393
BH9	2.815	0.456	4.167	0.668	3.823	0.262	4.242	0.236	0.520	1.924	0.108	0.411	0.688
BH10	5.369	2.333	4.913	0.722	4.061	0.246	7.211	0.139	0.872	1.147	0.323	1.314	0.797
BH11	8.052	0.426	6.627	0.795	9.737	0.103	6.422	0.156	0.303	3.299	0.066	0.646	1.239
BH12	10.617	1.356	8.248	0.721	7.527	0.133	3.943	0.254	1.554	0.644	0.344	2.588	1.206
BH13	3.969	0.543	5.669	0.860	14.656	0.068	10.622	0.094	0.303	3.299	0.051	0.750	0.589
BH14	3.785	0.585	4.174	0.823	11.012	0.091	8.058	0.124	0.303	3.299	0.073	0.800	0.760
SRT1	9.694	1.129	8.966	0.484	5.861	0.171	1.117	0.895	3.890	0.257	1.011	5.923	0.947
BRD1	1.975	2.252	1.820	0.861	9.193	0.109	19.121	0.052	0.660	1.516	0.118	1.082	0.929
GYS1	10.523	1.209	9.949	0.578	8.926	0.112	1.622	0.617	3.386	0.295	0.746	6.655	0.844
BRD2	4.400	0.561	3.937	0.837	7.998	0.125	14.244	0.070	0.173	5.773	0.039	0.315	1.055

The TC stands for Total Cations, and TA Total Anions. The pre-fix ZQM was removed from the BRD1, GYS1, BRD2 and SRT1 boreholes during the table formatting; however, in text these boreholes are referred to as ZQMBRD1, ZQMBRD2, ZQMSRT1 and ZQMGYS1 respectively.

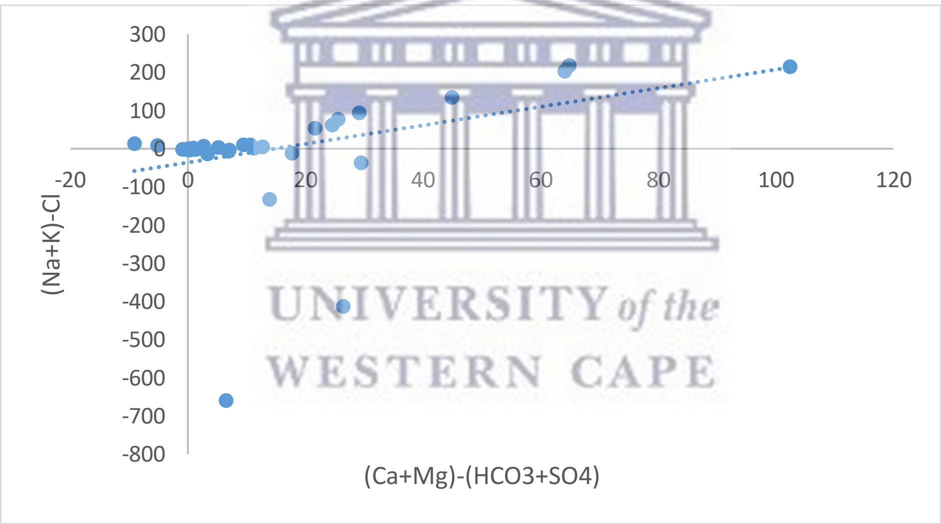
Appendix H: Water quality indices for irrigation

ID	SO4	CL	HCO3	K	NA	MG	CA	SAR	KR	Na%	MH
PZ 2	0.86	39.85	3.05	1.90	256.12	53.05	15.63	43.71	3.73	78.98	77.24
PZ 7	19.57	526.18	2.49	1.28	393.24	23.04	12.87	92.79	10.95	91.66	64.16
PZ 8	7.24	462.71	2.69	1.43	48.15	23.87	12.43	11.30	1.33	57.74	65.76
PZ 13	33.47	1155.87	3.77	2.25	495.16	24.69	19.01	105.93	11.33	91.92	56.50
PZ 14	6.24	113.32	1.61	1.02	114.19	15.64	3.49	36.92	5.97	85.76	81.74
PZ 15	2.55	53.46	3.08	1.65	187.49	41.02	9.53	37.29	3.71	78.91	81.15
PZ 16	3.16	57.93	3.97	1.84	259.50	58.16	13.06	43.49	3.64	78.59	81.67
PZ 19	0.54	5.45	4.17	0.67	5.13	2.39	3.29	3.05	0.90	50.52	42.02
PZ 22	1.12	16.52	3.02	2.19	109.05	21.43	11.81	26.75	3.28	76.99	64.46
F1	0.02	4.40	0.33	0.03	3.57	0.91	0.25	4.69	3.09	75.68	78.39
F2	0.40	318.39	0.30	2.07	280.58	21.40	8.68	72.35	9.33	90.38	71.14
F3	1.60	2.90	0.13	0.05	2.26	0.58	0.15	3.75	3.12	76.12	79.37
F4	0.25	2.33	0.20	0.03	2.04	0.58	0.10	3.52	3.02	75.39	85.23
F5	0.23	2.53	0.20	0.03	1.96	0.41	0.15	3.70	3.49	77.94	73.33
BH1	0.02	88.58	2.98	2.00	92.22	12.35	3.34	32.93	5.88	85.73	78.69
BH 3	6.61	168.08	4.40	2.20	155.51	18.11	10.53	41.10	5.43	84.63	63.23
BH 4	13.42	98.03	1.61	0.28	91.35	12.35	9.48	27.65	4.19	80.76	56.56
BH 5	6.64	114.81	2.98	0.61	112.01	13.17	3.39	38.93	6.76	87.18	79.51
BH 6	9.90	24.41	3.97	0.18	38.28	3.54	1.20	24.87	8.08	89.03	74.72
BH 7	0.81	70.70	2.85	0.31	80.69	10.70	2.35	31.60	6.19	86.13	82.02
BH 8	5.89	23.27	3.28	0.20	32.41	3.05	0.95	22.94	8.12	89.09	76.26
BH 9	0.73	2.78	0.66	0.03	1.91	0.58	0.30	2.89	2.19	68.90	65.80
BH 10	0.87	3.55	0.49	0.08	2.83	1.32	1.15	2.55	1.15	54.10	53.43
BH 11	0.54	5.27	0.82	0.03	6.53	1.15	0.35	7.53	4.35	81.35	76.74
BH 12	0.79	5.95	1.51	0.08	7.18	1.32	2.05	5.54	2.13	68.33	39.16
BH 13	0.33	4.88	0.46	0.03	2.87	0.82	0.25	3.92	2.68	72.98	76.74
BH 14	0.31	3.44	0.43	0.10	2.61	0.82	0.25	3.56	2.43	71.66	76.74
SRT1	0.74	4.34	3.89	0.07	4.11	1.13	4.39	2.48	0.75	43.12	20.45
BRD1	0.17	1.57	0.08	0.05	1.46	0.28	0.18	3.02	3.14	76.49	60.25
GYS1	0.64	5.76	3.55	0.10	4.86	1.27	4.29	2.91	0.87	47.17	22.80
BRD2	0.41	3.29	0.23	0.05	3.48	0.75	0.13	5.24	3.96	80.03	85.23

The pre-fix ZQM was removed from the BRD1, GYS1, BRD2 and SRT1 boreholes during the table formatting; however, in text these boreholes are referred to as ZQMBRD1, ZQMBRD2, ZQMSRT1 and ZQMGYS1 respectively.



Appendix I: The total cations vs. chloride



Appendix J: Figure showing the indication of ion exchange process.