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GEOCHEMICAL ASSESSMENT OF GROUNDWATER QUALITY AND SUITABILITY FOR DRINKING AND IRRIGATION PURPOSES IN NEWCASTLE, KWAZULU-NATAL, SOUTHAFRICA

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Abstract

Groundwater is one of the most valuable natural resources on earth and it forms an important part of the total water resources of South Africa. For this reason, this resource should be monitored and controlled on a regular basis. The study was conducted in Newcastle, in the KwaZulu-Natal province of South Africa. The aim of this study was to assess groundwater quality geochemically and determine its suitability for domestic and irrigation purposes. For the purpose of this study 31 samples were collected from 31 boreholes in and around the town of Newcastle. The samples were analysed for Magnesium (Mg^{2+}), Calcium (Ca^{2+}), Sodium (Na^{+}), Potassium (K^{+}), Chloride (Cl^{-}), Sulfate (SO_4^{2-}), Bicarbonate (HCO_3^{-}), Nitrate (NO_3^{-}), Fluoride (F^{-}) (pH, TDS and Ec. The SAQWG (DWAF, 1996) and the WHO (2011) water standards were used as the basis of evaluating the suitability of groundwater for drinking purposes. For irrigation, Electrical Conductivity (EC), Sodium Percent (Na %), Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC), Kelly's Ratio (KR), Magnesium Ratio (MR) and Permeability Index (PI) were used to evaluate suitability. Classical hydro-chemical methods together with multivariate statistical methods were used to further understand the composition controlling processes. Lastly, the spatial distribution of the results was presented using ArcGIS.

The results showed that the groundwater is alkaline in nature and that most of the samples are within the permissible range of both SAWQG (DWAF, 1996) and WHO (2011). Few samples showed concentration of Na^{+}, Cl^{-}, SO_4^{2-} , F^{-} and TDS above the guideline value as per WHO (2011) standards. The order of abundance of major ions in the groundwater, based on their mean values is as follows: $Na^{+}>Ca^{2+}>Mg^{2+}>K^{+}$ and $HCO_3^{-}>SO_4^{2-}>Cl^{-}>NO_3^{-}$.

Classical hydro-chemical methods revealed four hydro-chemical facies in the study area, which are Ca-Mg-HCO3, Na-HCO3, Ca-Na-SO4-HCO3 and Na-Cl. The major ion chemistry analysis revealed that the main composition controlling processes in the study area is rock-water interaction. It further revealed that the ionic concentration is due to silicate weathering, carbonate weathering, cation exchange, gypsum dissolution and halite dissolution. Factor analysis indicated three factors, which explained 79.71 % of the total variance in the water quality data. The first factor which accounted for the highest variance in the data was the Alkalinity factor, followed by the Hardness factor and the Anthropogenic factor which accounted for the least variance. The cluster analysis revealed five clusters and discriminant analysis showed that Na^+, TH, HCO_3^- and SO_4^{2-} discriminate these clusters by 96.8%.

In conclusion, the study revealed that the groundwater in most of the boreholes in the study area is generally suitable for drinking and irrigation. This is with exception to boreholes 13 and 31 which showed concentrations higher than the permitted level by WHO (2011) standards of TDS, Na^+, Cl^-, SO_4^{2-} and F^-. Similarly, 45.16% the groundwater samples showed that the groundwater has high sodium hazard potential which makes water from these boreholes unsuitable for irrigation purposes without proper treatment.

Declaration

I declare that the thesis titled “Geochemical Assessment of Groundwater Quality and Suitability for Drinking and Irrigation Purposes in Newcastle, KwaZulu-Natal, South Africa” is my own work, and that all the sources I used or quoted have been indicated and acknowledged by means of complete references.

………………………………. ……………………………

Signed Date

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Abbreviations

Ca^{2+}	Calcium ion
CA	Cluster Analysis
$CaCO_3^-$	Calcium carbonate
$CaMg(CO_3)_2$	Calcium Magnesium Carbonate
Cl^-	Chloride ion
MAP	Mean Annual Precipitation
CO_2	Carbon dioxide
DA	Discriminant Analysis
DEM	Digital Elevation Model
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
DWS	Department of Water and Sanitation
EC	Electrical Conductivity
ESRI	Environmental Sciences Research Institute
F^-	Fluoride
FA	Factor Analysis
Fm	Formation
GEOSS	Geo-hydrological and Spatial Solutions
GPS	Global Positioning System
GIS	Geographic Information System
HCA	Hierarchical Cluster Analysis
HCO_3^-	Bicarbonate ion
IDW	Inverse Distance Weighted
ILWIS	Integrated Land and Water Information System software
K^+	Potassium ion

KR	Kelly’s Ratio
MAP	Mean Annual Precipitation
MR	Magnesium Ratio
meq/l	Milli equivalents per Litre
Mg^{2+}	Magnesium ion
mg/L	Milligrams per Litre
mS/m	MilliSiemens per meter
Na^{+}	Sodium ion
Na %	Sodium Percentage
NO_3^{-}	Nitrate ion
PI	Permeability Index
r	Correlation coefficient
RSC	Residual Sodium Carbonate
SAR	Sodium Adsorption Ratio
SAWQG	South African Water Quality Guidelines
G	Group
SO_4^{2-}	Sulphate ion
SRTM3	Shuttle Radar Topography Mission 30 m resolution
TDS	Total Dissolved Solids
TH	Total Hardness
TWQR	Target Water Quality Range
TZ^{+}	Total Cations
USGS	United States Geological Survey
UTM	Universal Transverse Mercator
WHO	World Health Organization
WMA	Water Management Area
WTW	Water Treatment Works

WRC	Water Research Commission

CHAPTER 1

INTRODUCTION

This chapter provides a general background introduction to the study and describes the aims and objectives of the study. It also includes a description and geographical location of the study area. The chapter also presents the layout of this thesis.

1.1. Background Information

Groundwater is defined as water that is found underneath the surface of the earth. It forms an important part of the water cycle. Sources of groundwater include rain, snow, hail and sometimes surface water (e.g. Rivers). The water infiltrates into the ground because of gravity, passes through the soil and rocks until it reaches a depth where the water can no longer infiltrate and is stored. Groundwater is stored in an underground porous and permeable rock called an aquifer that enables the water to infiltrate and allows movement within the rock.

Groundwater is one of the most valuable natural resources on earth and it is an important part of the total water resources of South Africa. Some towns and villages in South Africa are virtually entirely dependent on groundwater for all water requirements. Numerous other towns use both surface and groundwater conjunctively thus both quantity and quality are major concerns in the use of groundwater. This study will mainly focus on groundwater quality.

The principal dissolved components of groundwater are six major ions Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^- and SO_4^- and they constitute 90% of the total dissolved solids (TDS) content. The minor ions include K^+, Fe^-, NO_3^- and F^-. Due to human activities such as mining and irrigation, some of these minor ions are raised to higher levels reaching concentrations equivalent to that of major ions (Hiscock, 2005). Groundwater composition is mostly influenced by the rocks and other material it traverses through from recharge to discharge. When it flows through geological formation a number of processes occur which cause an exchange of soluble solids between the rocks and water. Thus mineral composition of the rocks consequently plays a major role in the chemical constituents of groundwater (Elango and Kannan, 2007).

The chemical composition of groundwater is directly linked to the quality of groundwater. Changes in the concentrations of ions in the water of an aquifer, whether from natural or anthropogenic activities, may alter the suitability of the aquifer system as a source of water (Herring et al., 2002). The accepted quality of water is subjective to what the water is going to be used for and this directly translate to the procedures that can be used to determine the availability and presence of ion species in the water (Cordoba et al., 2010).

According to Ravikumar at el. (2011) the composition of groundwater in a region can be altered by processes such as evaporation and transpiration, wet and dry deposition of atmospheric salts, oxidation and reduction, cation exchange, dissociation of minerals from soil and rock–water interactions, precipitation of secondary minerals, mixing of waters, leaching of fertilizers and manure and biological process.

Therefore to ensure that water is suitable for human consumption and use, standards and guidelines were developed by organisations such as Department of Water and Sanitation (DWS) and World Health Organisation (WHO) as criteria to determine suitability. Guidelines are set to describe reasonable minimum requirements of safe practice to protect the health of consumers. The guidelines are in the form of numerical values for constituents of water or indicators of water quality (WHO, 2008).

Frengstad et al. (2001) stated that several naturally occurring major, minor and trace elements in drinking water can have major effects on human health either through deficiency or excessive intake. For example, an increase in concentration of Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^- and SO_4^{2-} ions in water, increases Total Hardness (TH). Hard water, after long term consumption might lead to an increased incidence of urolithiasis, anecephaly, pre-natal mortality, some types of cancer and cardiovascular disorders (Sengupta, 2013). An excess Na^+ causes hypertension, congenial diseases, kidney disorders and nervous disorders in human body (Ramesh and Elango, 2012).

Likewise, chemical constituents in water can also have negative effects on plant life. Irrigation water can affect plant health directly through toxicity or deficiency, or indirectly by altering plants ability to take in nutrients (Rahman at el., 2012). Excess Na^+ in irrigation water has been reported to cause hardening of the soil, so much that the soil becomes impervious and limits the ability of the roots to uptake water (Naseem et al., 2010).

Consequently, it is very important to understand the processes that control groundwater quality in order to adequately manage this resource. One of the methods of assessing water quality is by conducting a geochemical study of the groundwater. Geochemical studies involve an in-depth evaluation of the chemical composition of groundwater in relation to the geology and therefore offer a better understanding of possible changes in quality. Hence such studies promote sustainable development and effective management of groundwater. These studies have become very popular in determining the suitability of groundwater, mainly because of the rising need of clean water resources.

This study aims to conduct a geochemical assessment of the groundwater in Newcastle which is located in the province KwaZulu-Natal in South Africa. The approach will involve the use of an appropriate assessment technique to determine the suitability for drinking and irrigation purposes of groundwater in the area. This requires the concentrations of important parameters such as pH, electrical conductivity (EC), (TDS), (TH), Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cl^{-}, HCO_3^{-}, SO_4^{2-}, NO_3^{-} and F^{-}, and comparing the concentrations of these ions with guidelines/standards set for water consumption and use.

1.2. Aim

The aim of the study is to assess the quality of groundwater in Newcastle, to determine the major composition controlling processes and to determine if it is suitable for domestic and irrigation purposes.

1.3. Objectives

The main objectives of this project are to:

- Compare the groundwater quality/chemistry to the approved water standards.

- Characterize and classify the groundwater chemically using classical hydrochemical methods and multivariate statistical methods.
- Assess the spatial distribution of ionic concentration results of the groundwater quality using ArcGIS 10.

1.4. Problem Statement

The main source of water in the Newcastle area is from the Ngagane Water Treatment Works. However there is an increase in water quality problems at the Ngagane WTW due to coal mining activity and pollution by saline and nutrient enrichment from large irrigation areas. With this large quality impact on surface water from mining/industrial and farming activities, groundwater should be considered as the first option for rural domestic use and the conjunctive use of groundwater and surface water should receive more attention. Furthermore, with the growing population comes an increase in the demand of water. The total population of Newcastle is recorded as 363,263 as of the 2011 census. Comparing population from the 2011 census with that of 2001, which was 332, 981, it shows a population growth of 0.87% per annum. This growing population together with growing economic activities (manufacturing and agriculture) and surface water quality problems are driving an increase in water requirements. Therefore alternative or additional sources of water are of importance in order to ensure the water supply meets the demand. Groundwater could be used as an additional source of water. Though a very important resource, groundwater is also under studied.

1.5. Motivation for Study

Understanding the quality of groundwater is a very important factor in determining whether the source could be used to supply suitable water for human consumption and use. As a scarce resource, groundwater requires continuous monitoring through quality assessments and management for sustainable use and contamination protection. Geochemical assessments aid in understanding how anthropogenic and geogenic activities affect groundwater quality. Application of quality assessments of groundwater in the Newcastle area has important implications in the groundwater's potential as a resource and can indicate where negative impacts may be mitigated and efficiency of water conservation programs can be evaluated.

1.6. Study Area

1.6.1. Location

The study area is located in the Karoo Basin of South Africa in Newcastle which is Northwest of KwaZulu-Natal (KZN) (fig 1.1). It forms part of the Amajuba district. Newcastle lies within the coordinates of 27° 44' 47" S latitude and 29°55'58'' E longitude.

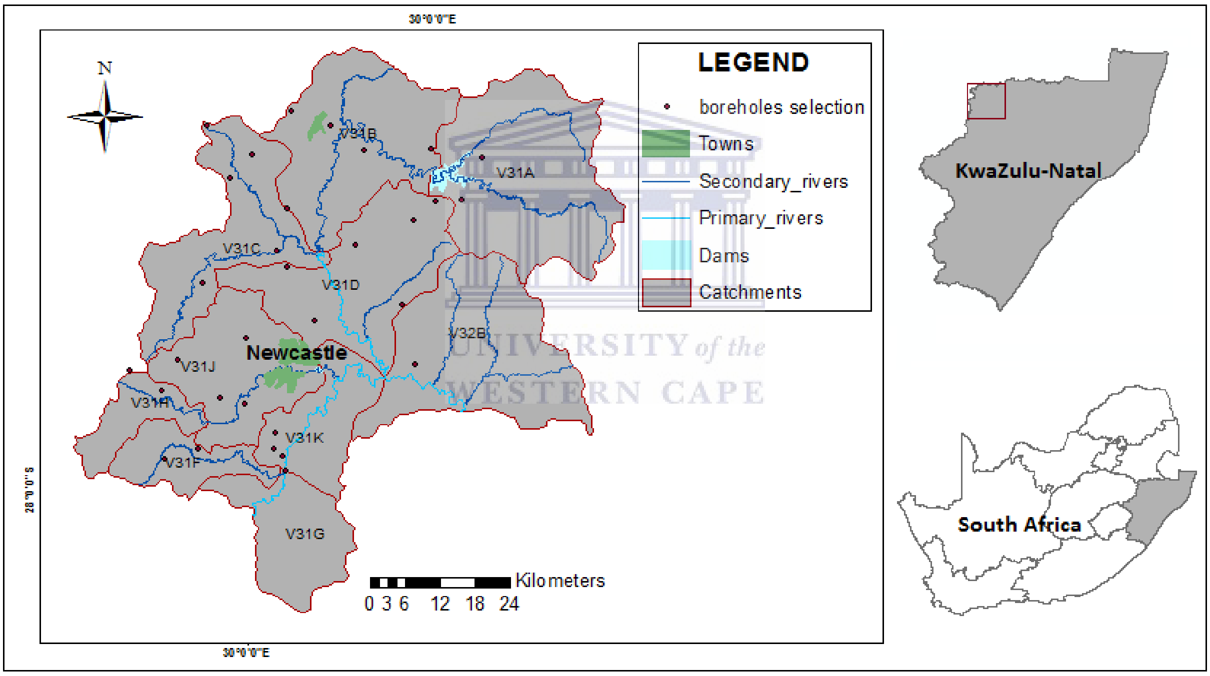

Fig 1.1: Study area and location of boreholes

1.6.2. Climate and Rainfall

The climate in Newcastle can generally be described as temperate with warm summers (maximum temperature close to 30°C) and cold winters (minimum temperature of 2°C). Newcastle normally receives about 687mm of rain per year, with most rainfall occurring mainly during mid-summer. The chart in figure 1.2 shows that the maximum rainfall occurs generally in summer (October-April), while the minimum rainfall occurs in winter from May-September.

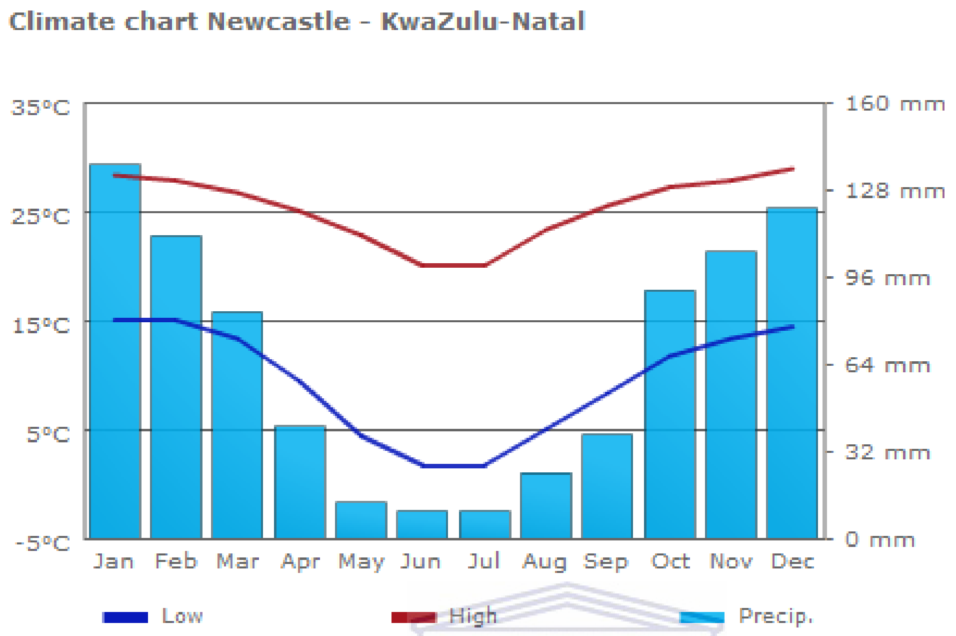

Fig 1.2: Newcastle Climate chart (www.climatedata.eu)

1.6.3. Economic Activities

The town of Newcastle is the third largest urban centre in KZN and is one of the main manufacturing towns in the Thukela Water Management Area (WMA). Major economic activities in the area include the manufacturing, agricultural activities and mining industry.

1.6.3.1. Manufacturing Industry

Manufacturing is the main economic sector in Newcastle and has the largest contribution to the districts economy. According to the Newcastle local municipality economic development strategy (2007) manufacturing in the Amajuba district contributes 5% to KZN's economy, of this Newcastle comprises 58.3% of the input. A large part of the sector is made up of metal (steel), machinery and equipment production, followed by chemicals, petroleum products, rubber and plastic as well as textiles manufacturers, clothing and leather production, including the largest producers of socks and school uniforms in Southern Africa (LED case study, 2010).

1.6.3.2. Agricultural Activities

Agricultural activities are moderately small sector in terms of jobs and GDP but are considered to have a potential (LED case study, 2010). These activities include irrigation, livestock farming, maize and dairy farming. This town also serves surrounding maize, livestock and dairy farmers.

1.6.3.3. Mining Industry

Mining in Newcastle is mainly in the form of coal mining. The coal mining in this area consists mainly of anthracite. A considerable amount of the anthracite is taken to the coal terminal at Richards Bay, from where it is exported.

1.6.4. Water Sources and Consumption

1.6.4.1 Surface water

The Newcastle water supply scheme is currently supplied by the Ngagane Water Treatment Works (WTW). The Ngagane WTW is supplied by three sources which are the Ntshingwayo Dam, abstraction works in the Ngagane River downstream of the dam and the Buffalo river abstraction works. Ntshingwayo Dam contributes 33.0 million m^3/a, 11.0 million m^3/a from the Ngagane River and 11.0 million m^3/a from the Buffalo River (DWA, 2011).

The major water users like irrigation agriculture and steel production for Arcelor Mittal South Africa receive an allocation of 26.47 million m^3/a and 7.05 million m^3/a respectively (DWA, 2011).

1.6.4.2. Groundwater

According to DWAF (2008) nothing is known about the extent of groundwater use by the 14 irrigation boards that occur in this region. Although, it is assumed that groundwater is definitely being used but the level of use needs to be determined. It also is possible that the coal mines in this region might use some groundwater. Groundwater in the form of springs is mostly used in rural areas for domestic and irrigation purposes.

1.7. Research Methodology

1.7.1. Research Steps

The objectives of the research were achieved by following the steps below:

1. Tabulation of the descriptive statistics of physiochemical parameters and comparison with SAWQG (DWAF, 1996) and WHO (2011) water standards to assess water for drinking purposes.
2. Computation of parameters used to assess groundwater for irrigation purposes such as; SAR, Na%, RSC, MR, KR and PI.
3. Application of correlation analysis to understand the relationships that exist between physiochemical parameters.
4. Application of classical hydro-chemical methods to reveal hydro-chemical patterns, water types/facies and to understand processes affecting ground water quality.
5. Characterisation and classification using factor analysis, cluster analysis and discriminant analysis multivariate statistical methods.
6. Creation of spatial distribution maps for water quality parameters.

1.8. Chapter Layout

This study consists of six chapters and is highlighted as follows:

Chapter 1: Introduction

This chapter entails a general introduction to the subject of the research. It includes the general background of study area, research aim, objectives, problem statement, motivation of research, research methodology and research content.

Chapter 2: Literature Review

This chapter includes the description of water quality and factors affecting water quality. It also presents the water quality standards or guidelines such as World Health Organisation (WHO) guidelines, South African Water Quality Guidelines (SAWQG). The different methods such as the classical hydro-chemical methods, multivariate methods and the use spatial distribution maps in water quality assessments are also reviewed.

Chapter 3: Geological setting and Hydrogeology

This chapter describes the geology of the area, major rock types and divisions. It also includes a description of the aquifer types found in the area of study.

Chapter 4: Methodology

This chapter elaborates on the methods that were used to process and analyse the data to achieve the aims and objectives of the project.

Chapter 5: Results and discussion

This chapter includes the results and discussion from data analysis.

Chapter 6: Conclusion

This chapter states the conclusions and recommendations from this study

CHAPTER 2

LITERATURE REVIEW

This chapter takes an account of the literature used in understanding the concept of water quality, factors affecting water quality and all other factors related to the subject. It also presents the water quality standards or guidelines such as World Health Organisation (WHO) guidelines, South African Water Quality Guidelines (SAWQG). It also presents different methods such as the classical hydro-chemical methods, multivariate statistical methods and the use spatial distribution maps in water quality assessments.

2.1. Water Quality

2.1.1 Water Quality Description

DWAF (1996) defines the term water quality as the physical, chemical, biological and aesthetic properties of water which determine its fitness for a variety of uses and for protecting the health and integrity of aquatic ecosystems. The concept of water quality is directly related or dependent on the intended use of water. Different uses of water such as drinking, irrigation or recreation require different criteria (Cordoba et al., 2010).

2.1.2 Factors Influencing Groundwater Quality

The quality of water is affected by a wide range of natural and anthropogenic influences that change the concentration of chemical constituents in the water. This change in the quality of water occurs with depth and over geographic distances; this is because of several processes that affect the water in the different environments it travels through (Al-Aboodi, 2008). These factors mainly include the dissolution of ions in soils, sediments and rocks (Nur et al., 2012). Anthropogenic influences mainly include effluents generated by human, urban, agricultural, and industrial activity (Beamonte et al. 2007).

Major sources of groundwater include rain and snow; these sources contain slight amounts of dissolved solids and gases such as carbon dioxide, sulfur dioxide, and oxygen. Consequently, when precipitation infiltrates through the soil, carbon dioxide reacts with the water to form a weak solution of carbonic acid. If the water continues to infiltrate deeper into the ground the oxygen may react with reduced iron minerals such as pyrite which adds to the acidity in groundwater. The slightly acidic water dissolves soluble rock material, thereby increasing the concentrations of chemical constituents such as calcium, magnesium, chloride, iron, and manganese (Herring et al. 2002). The overall effects on water quality mainly depends on the chemical nature of the initial water, composition of the rocks below and the flow path of the water as it determines the occurrence, sequence, rates and progress of reactions (Hiscock, 2005).

Contamination from agricultural activities includes nitrate and pesticides used in intensive farming practices that often affect wide areas of aquifer outcrop (Hiscock, 2005). Nitrate is the principal nutrient in most fertilizers and it also very soluble, when leached into groundwater it becomes very mobile (British Geological Survey, 2009). Other sources of contamination from agricultural activities arise from livestock and poultry farming through the intensive management of grazing pasture and operation of concentrated feeding operations (Hiscock, 2005).

In urban or industrialized regions, the expansion and industrial activity in these areas is often accompanied by continual disposal and spillage of potentially polluting wastes, which pose threat sources in the area. Also, in addition to the accompanying urbanization growth is the need to dispose of domestic municipal and septic waste. The disposal of these wastes lead to the risk of contamination from toxic material and sewage. Other sources of pollution in the urban environment include the application of fertilizers and pesticides in parks and gardens (Hiscock, 2005).

2.2. Water Quality Standards/Guidelines

Water quality is defined based on a set of physical and chemical variables that are closely related to the water’s intended use. Solsona (2002) defined a standard as a rule or principle considered by an authority and by general consent as model in comparative evaluation. He continued to say, a proper standard for drinking water quality should therefore be a reference that will ensure that the water will not be harmful to human health. For each variable, acceptable and unacceptable values must then be defined. If the water meets the pre-defined standards for a given use, it is considered suitable for that use. If the water fails to meet these standards, it must be treated before use (Cordoba et al., 2010).

2.2.1. Evaluation for Drinking water Purposes

2.2.1.1 World Health Organization (WHO) Guidelines

The primary purpose of the guidelines for drinking water quality is the protection of public health and to improve access to safe drinking water (WHO, 2004). The WHO water guidelines are divided into four aspects. These aspects are microbial aspect, chemical aspect, radiological aspects and the acceptability aspect (aesthetic aspect).

According to WHO (2008) the biological properties refer to the presence of organisms that cannot be seen by the naked eye and these include microorganisms such as protozoa, bacteria and viruses.. The physical properties define the water quality properties that may be determined by physical methods such as conductivity, pH and turbidity measurement. The physical quality mainly affects the aesthetic quality (taste, odour and appearance) of water. The chemical aspects describe the nature and concentration of dissolved substances such as salts, metals and organic chemicals. Generally, many chemical substances at the appropriate concentrations in water are essential nutrients that are required for daily intake but at high concentrations, they make water unpalatable and cause illnesses.

The guideline values selected represent the concentration of a constituent that does not result in a significant risk to the health of the consumer after long term consumption. Guideline values have been set based on the practical level of treatment achievability or analytical achievability (WHO, 2004).

2.2.1.2 South African Water Quality Guidelines (SAWQG)

The South African water quality guidelines were developed by the Department of Water Affairs and Forestry (DWAF) as its primary source of information and decision-support to judge the fitness of water for use and for other water quality management purposes (DWAF, 1996).They are used to inform water users about the physical, chemical, biological and aesthetic properties of water. The quality criteria, consists of a Target Water Quality Range (TWQR). The TWQR for a particular water constituent describes the range of the concentrations at which the constituent would have no known adverse effects on the suitability of the water when used continually.

2.2.2. Evaluation for Irrigation Water Purposes

The quality of water for irrigation is determined by both its effects on the soil and plant health (Ramesh and Elango, 2012). Fipps (1996) suggested that in irrigation, the main problem comes from salt level in the water. He further stated two types of salt problems, those that are associated with salinity (salinity hazard) and those associated with sodium (sodium hazard). These problems affect both soil and crop health.

To evaluate these problems, the total concentration of soluble salts, the relative proportion of sodium to the other cations and the bicarbonate concentration as related to the concentration of calcium and magnesium need to be evaluated. The individual levels and association of these constituents describe the suitability of water for irrigation (Fipps, 1996). The parameters below encompass all of the above mentioned conditions and therefore can be used to evaluate suitability of water for irrigation purposes:

1. Electrical Conductivity (EC) :
   Electrical conductivity is one of the most important parameters to be considered when evaluating quality of water for irrigation as it is directly related to salinity problems. It is a good measure of salinity hazard to crops as it reflects the TDS in groundwater (Sundariah et al. 2014).

2. Sodium Adsorption Ratio (SAR):
   Sodium adsorption ratio (SAR) is the measure of relative portions of Na^+ to Ca^{2+} and Mg^{2+}. It measures the ability of irrigation water to induce sodic conditions in the soil (DWAF, 1996). SAR also indicates the degree to which irrigation water tends to enter into cation-exchange reactions in soil. When sodium replaces adsorbed calcium and magnesium it creates a problem as it may cause the soil to become compact and impervious (Joshi et al. 2009).

3. Sodium Percentage (Na %):

   Sodium is an important parameter for irrigation water as it has direct effects on soil permeability. Sodium percentage (Na %) is also an estimation of the sodium hazard in the use of water for irrigation like SAR; it expresses the percentage of sodium out of the total cations (Nasher and El-Sagheer, 2012).

4. Residual Sodium Carbonate (RSC):

   Residual Sodium Carbonate is an important parameter in determining the suitability of water for irrigation; it indirectly indicates the sodium hazard potential of irrigation water. High concentration HCO_3^- and CO_3^- in water tend to precipitate Ca^{2+} and Mg^{2+} which results in an increase in the relative levels Na^+ ions in the water as sodium bicarbonate (Sadashivaiah, et al., 2008).

5. Magnesium Ratio (MR) :

   Generally, Ca^{2+} and Mg^{2+} maintain a state of equilibrium in groundwater. More Mg^{2+} present in waters affects the soil quality by converting it to alkaline and as a result crop yield is decreased. MR is a measure of Mg^{2+} ion to Ca^{2+} ion in water (Ramesh and Elango, 2012).

6. Permeability Index (PI):

   PI is a measure of the effects irrigation water might have on soil permeability. PI values also depicts suitability of groundwater for irrigation purposes by evaluating the Na^+, Ca^{2+}, Mg^{2+} and HCO_3^- contents in water, it measures long term use of the water on soil permeability (Sundariah et al. 2014).

7. Kelly's Ratio (KR):

   Kelly's ratio is a measure of Na^+ against Ca^{2+} and Mg^{2+}. KR is used to measure Na excess in irrigation water (Ramesh and Elango, 2012).

2.3. Geochemical Assessment of groundwater

Geochemical assessments provide a better understanding of possible causes in the changes in the quality of groundwater. The assessments involve an in-depth evaluation of the chemical components of groundwater in relation to the geology and other land uses in the area.

2.3.1 Major Ion chemistry

The concentration and presence of dissolved ions in groundwater system is a result of the different geochemical processes that operate in the subsurface. Therefore, the availability of these ions present in aquifers can be used to identify the occurrence of different geochemical processes (Nur et al., 2012).

2.3.1.1 Calcium and Magnesium

Calcium and Magnesium are very common and abundant elements in nature. These elements are present in all natural waters and they constitute 48% of cations in groundwater (Nur et al., 2012). The most common source of calcium and magnesium in groundwater is the weathering of rocks, such as limestone and dolomite.

The dominance of Ca^{2+} and Mg^{2+} among cations in groundwater is usually indicative of dissolution of carbonate minerals (Zabala et al., 2015). During infiltration or along the flow, groundwater may dissolve Calcium Carbonate ($CaCO_3$) or Calcium Magnesium Carbonate ($CaMg(CO_3)_2$) present in the rocks which increases the concentration of Ca^{2+} and Mg^{2+} ions present in the water. This is mainly caused by rainwater saturated with CO_2 and become rich in carbonic acid (equation 1)(Elango and Kannan, 2007).

$CO_2 + H_2O = H_2CO_3$…………. (Formation of carbonic acid) 1

The acidic water influences the dissolution of carbonate minerals (calcite and dolomite) in the aquifer system. The release of these ions is indicated by equations 2 and 3:

$CaMg(CO3)2 + 2H_2CO_3 = Ca^{2+} + Mg^{2+}$………….. (Dolomite dissolution) 2

$CaCO3+H_2CO_3 = Ca^{2+}+2HCO_3$………………………….. (Calcite Dissolution) 3

Ca^{2+} ions in groundwater could also be an indication of other sources such as weathering of plagioclase and other feldspars and the dissolution of gypsum/anhydrite.

2.3.1.2 Sodium and Potassium

All groundwater contains sodium because most rocks and soils contain sodium compounds from which sodium is easily dissolved. In concentration it is normally lower than calcium and magnesium in fresh water (Kannan and Joseph, 2009). The most common sources of elevated sodium levels in groundwater include weathering of sodium bearing rocks, irrigation returns, and pollution by sewage effluent and sea water intrusion (Dinka, et al., 2015).

The most common processes responsible for sodium ions in groundwater are silicate weathering, ion exchange processes or halite dissolution (Subramani et al., 2010). The weathering of soda feldspar (albite) (Eq 4) and potash feldspars (orthoclase and microcline) is greatly responsible for the contribution of Na^+ and K^+ ions to groundwater.

$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O = Al_3Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4 + 2HCO_3$ ……..(silicate weathering) 4

The ratio of sodium to chloride determines halite dissolution and this is often the case when sodium is found in a 1:1 ratio with chloride. However, at higher concentration of sodium, this is considered as the release of sodium from silicate weathering (Elango and Kannan, 2007).

In addition to origin from silicate weathering, potassium is also an indicator of pollution from human activities. Potassium is a major constituent from fertilizers which is widely used in agricultural activities (Dinka, et al., 2015).

2.3.1.3 Bicarbonate and Sulphate

The dominance of bicarbonate (HCO_3^-) among anions in groundwater suggests either silicate weathering or carbonate weathering and sometimes this may be a combination of both processes (Elango and Kannan, 2007). Generally, bicarbonate is released together with calcium when carbonic acid reacts with calcium carbonate (Eq 3). Also, bicarbonate can be release when carbonic acid reacts with plagioclase as indicated in equation 4. Sulphates (SO_4^{2-}) are dissolved from rocks containing gypsum, iron sulfides, and other sulfur compounds. It is also commonly present in mine water and in some industrial wastes.

2.3.1.4 Chloride and Nitrate

Chlorides (Cl^-) ions are dissolved from rocks and soils. They are also present in sewage, sea water, and industrial brine (Provin and Pitt, 2002). The sources of nitrate (NO_3^-) in groundwater include decaying organic matter, legume plants, sewage, nitrate fertilizers, and nitrates in soil. High levels of nitrate in groundwater are usually indicative of the contamination from anthropogenic activities (Abudaya et al., 2014).

2.3.2. Hydro-chemical Facies

The term hydro-chemical facies or water type refers to zones in groundwater that have a distinct level of cations and ions (Hiscock, 2005). The nature and distribution of hydro-chemical facies can provide insights into how groundwater quality changes within and between aquifers (fig 2.1) (Sivasubramanian et al., 2013). These different facies are mainly due to the different kinds of rock-water interaction during groundwater subsurface flow, as shown in figure 2.1. Another important factor that plays a role in the rise of different water facies is the order in which groundwater encounters rocks of different mineralogical composition (Freeze and Cherry, 1979).

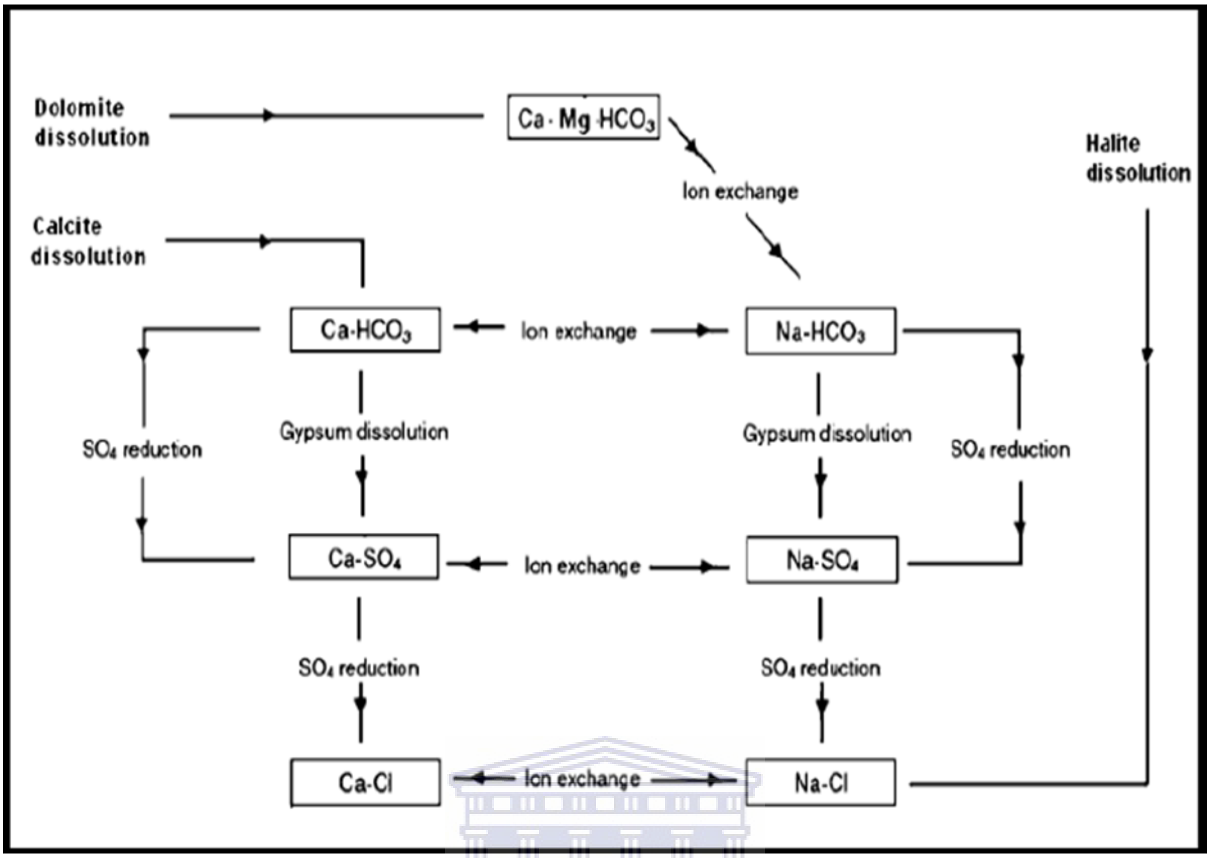

Fig 2.1: Rock-water interaction and resulting water types (Elango and Kannan, 2007).

The groundwater type is determined by the percentage of chemical constituents present in it. Hydro-chemical diagrams such as the Piper (1994) diagram (2.2) and Chadha's (1999) diagram (Fig 2.3) are used to delineate hydro-chemical facies, because they graphically demonstrate relationships between the most important dissolved constituents in a set of groundwater samples (Chandrasekar et al., 2014).

Generally, Ca-HCO3, Ca-Mg-HCO3, Ca-Cl, Na-HCO3, Na-Cl, Ca-SO4 and Na-SO4 are the most important groundwater types found throughout the world. Dissolution of calcite, dolomite, gypsum and halite will give rise to Ca-HCO3, Ca-Mg-HCO3, Ca-SO4 and Na-Cl type of groundwater respectively. Na-HCO3, Ca-Cl and Na-SO4 may result from cation exchange processes and reverse exchange processes (Elango and Kannan, 2007).

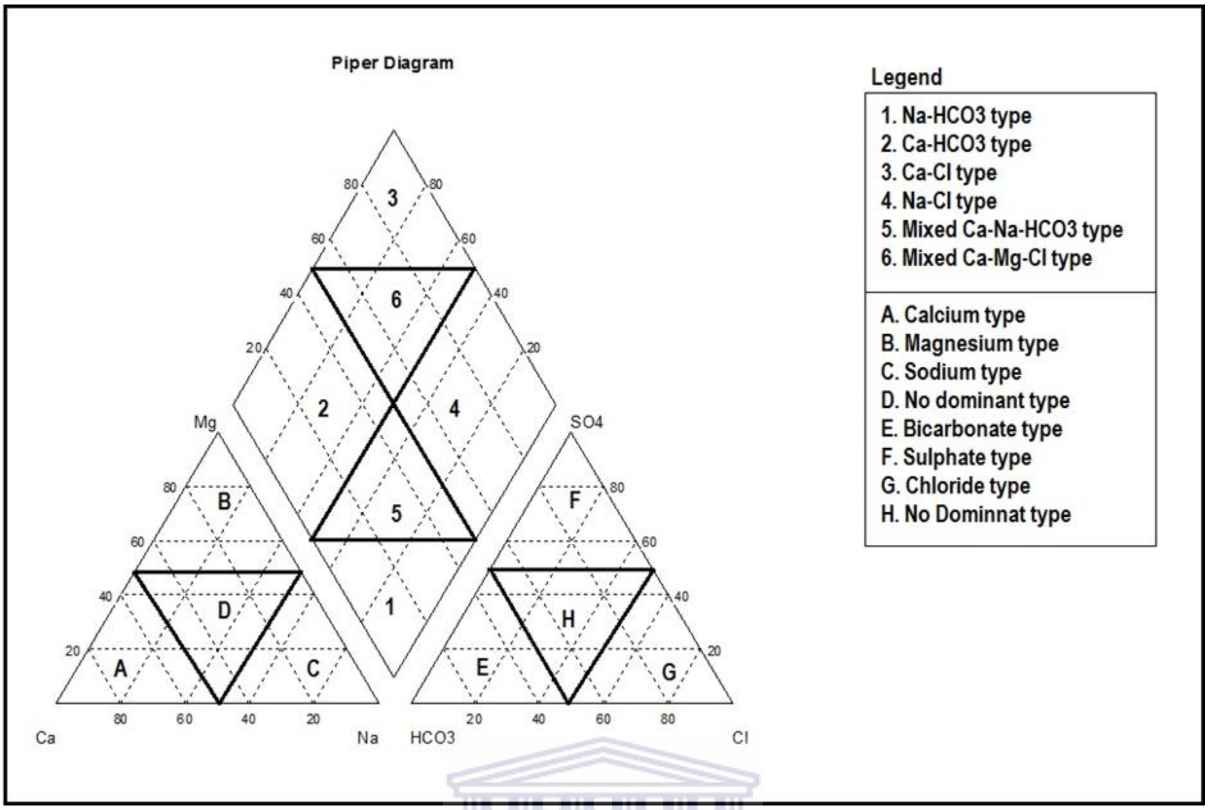

Fig 2.2: Piper plot diagram showing different water type/hydro-chemical facies (Ravikumar et al., 2011)

The Chadha’s (1999) diagram (see fig 5.5) has all the advantages of the diamond-shaped field of the Piper diagram but the main advantage of the Chadha’s diagram is that it can be plotted using any spread sheet. Like the Piper (1994) this diagram can be used to study various hydro-chemical processes, such as base cation exchange, mixing of natural waters, sulphate reduction, saline water intrusion and other related hydro-chemical problems. The square or rectangular field describes the overall character of the water. In order to define the primary character of water, the diagram (fig 2.3) is divided into eight sub-fields, each of which represents a water type, as follows (Chadha, 1999):

1. In this subfield alkaline earths exceed alkali metals.

2. Alkali metals exceed alkaline earths.

3. Weak acidic anions exceed strong acidic anions.

4. Strong acidic anions exceed weak acidic anions.

5. Alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions, respectively. The positions of data points represent Ca-Mg-HCO3 type, Ca-Mg dominant HCO3 type, or HCO3 dominant Ca-Mg type waters.

6. Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions. The positions of data points represent Ca-Mg-Cl type, Ca-Mg dominant Cl type, or Cl dominant Ca-Mg type waters.

7. Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions. The positions of data points represent Na-Cl type, Na-SO4-type, Na dominant Cl type, or Cl dominant Na type waters.

8. Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions. The positions of data diagram represent Na-HCO3 type, Na-dominant HCO3 type, or HCO3 dominant Na type waters

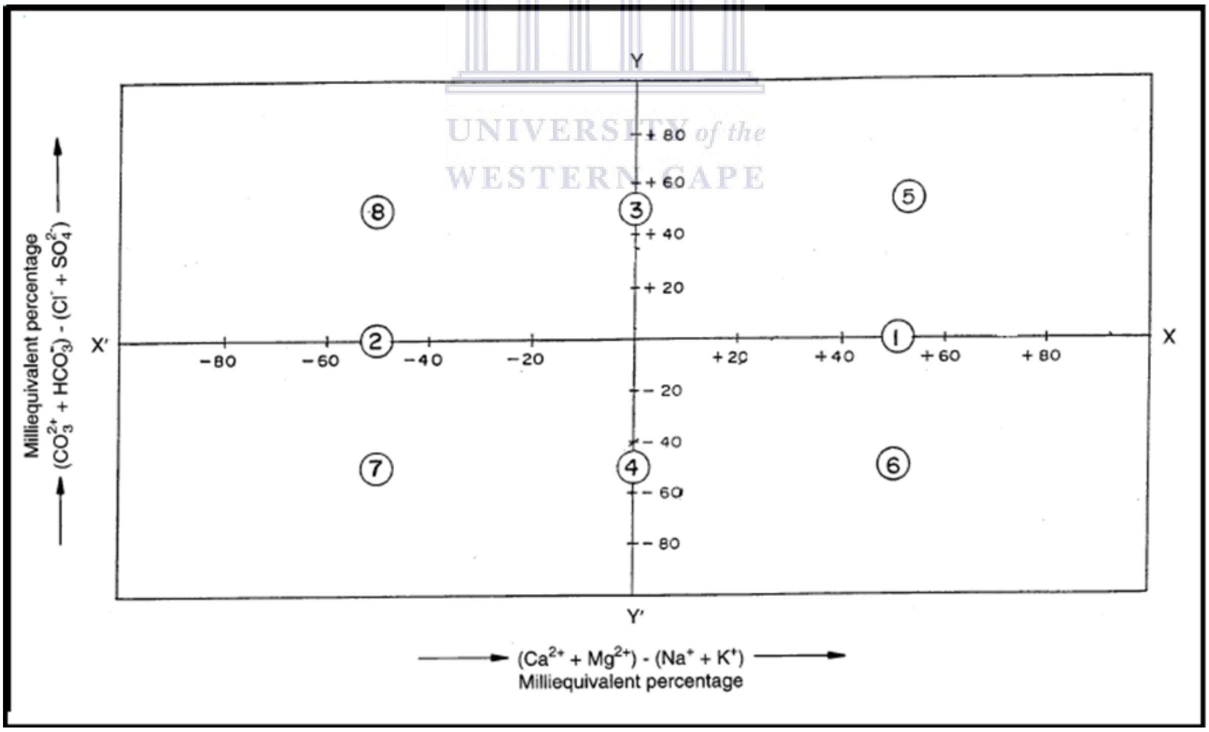

Fig 2.3: Chadha's diagram demonstrating geochemical classification and hydrochemical processes of groundwater (Chadha, 1999).

The use of hydrochemical facies in groundwater assessments aids in understanding groundwater evolution through its flow path and these facies can serve as geochemical signatures that can be used to identify groundwater interaction/processes at that point.

2.3.3 Multivariate Statistical Methods in Geochemical Assessments

Multivariate statistical methods have been extensively used in solving environmental related problems and in understanding natural processes (Yidana et al., 2010). These techniques are very useful in evaluating and interpretation of multi-constituent chemical data (Kumar et al., 2011). Multivariate statistical analysis is also useful in characterizing and evaluating groundwater quality and in verifying spatial variation caused by natural and anthropogenic processes (Belkhiri and Mouni, 2011).

Multivariate statistical techniques include cluster analysis (CA), factor analysis (FA) and discriminant analysis (DC). These techniques have been broadly used in the analysis of water quality data for drawing meaningful conclusions (Singh et al., 2004). For instance, factor analysis is a statistical method used to identify the relationship among a number of observable quantitative variables and represents them in terms of a few underlying quantities called factors (Suk and Lee, 1999). Cluster analysis is similar to factor analysis, in that it also observes the full complement of inter-relationships between variables. Cluster analysis reduces the number of observations or cases by grouping them into a smaller set of clusters. These smaller cluster sets usually represent the major processes affecting a system. Discriminant is useful in discriminating and characterising multiple predefined groups.

Shrestha and Kazama (2007) used CA, Principal Component Analysis (PCA), FA and DC in evaluating temporal special variation and interpreting large complex water quality data in Fuji river basin, Japan. In later studies, (Singh et al., 2011) integrated multivariate statistical analysis with GIS for geochemical assessment of groundwater quality in Shiwaliks of Punjab, India. With the use of multivariate analysis they were able to conclude that geochemical processes and anthropogenic activities were the main processes affecting groundwater and to also determine the main mechanism of enriching groundwater with metals.

These techniques do not only allow the identification of the possible factors influencing the system they also offer solutions to pollution problems and better ways to manage water resources (Simeonov et al, 2003).

2.3.4 Geographic Information system (GIS)

Geographic information System (GIS) is a very important tool in understanding and solving problems related to water management. It can help in organizing collected data about the problem and in understanding their spatial relationships. GIS analysis abilities enable the modelling and generation of information that contribute to making informed decisions for resource management across a wide range of scales (Johnson, 2008).

GIS can be used in developing solutions for water resources problems such as assessing water quality, determining water availability, understanding the natural environment, and managing water resources (Johnson, 2008). Nur et al. (2012) used geographical information system (GIS) to discuss the chemical evolution of groundwater.

GIS's organize data by layers; these map layers are geographically referenced and registered to a common projection as illustrated in figure 2.4. These layers each contain different information that can be logically related by its location. These layers are precisely overlaid onto each other so that every location is correlated to its corresponding locations on all the other maps as to make proper relation (Johnson, 2008).

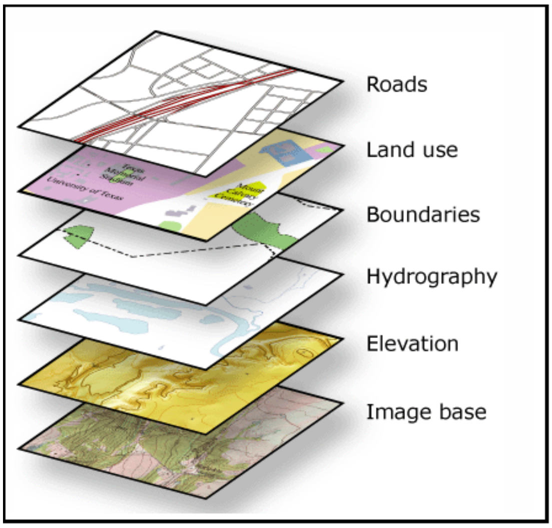

Fig 2.4: Multiple layers of data from various sources combined in the GIS (desktop.arcgis.com)

The ability of GIS to overlay information or layers from different sources enables proper correlation of these layers to determine how they influence each other. Several studies have used GIS to relate element distribution with land use and geology. Nur et al. (2012) also stated that through the spatial distribution of different hydro-chemical facies, areas of good and inferior quality can be identified, and groundwater chemical evolution can be mapped to uncover interaction between groundwater and rocks

CHARPTER 3

GEOLOGICAL SETTING

This chapter describes the geology of the area, major rock types and divisions. It also includes a description of the water resources and aquifer types in the area of study.

3.1 Regional geology

The Study area is located in the Karoo Basin (Fig 1); this basin is a retro-arc foreland basin bounded by a fold-thrust belt (Cape Fold Belt) lying along the southern margin of the basin, the cratonic basement to the west, north and northeast, and the Indian Ocean to the southeast (Woodford and Chevallier, 2002). The deposition of sediments in this basin began late Carboniferous and continued to accumulate until Early Jurassic when it was interrupted and eventually brought to a close by widespread flood basaltic volcanism (Catuneanu, 2005).

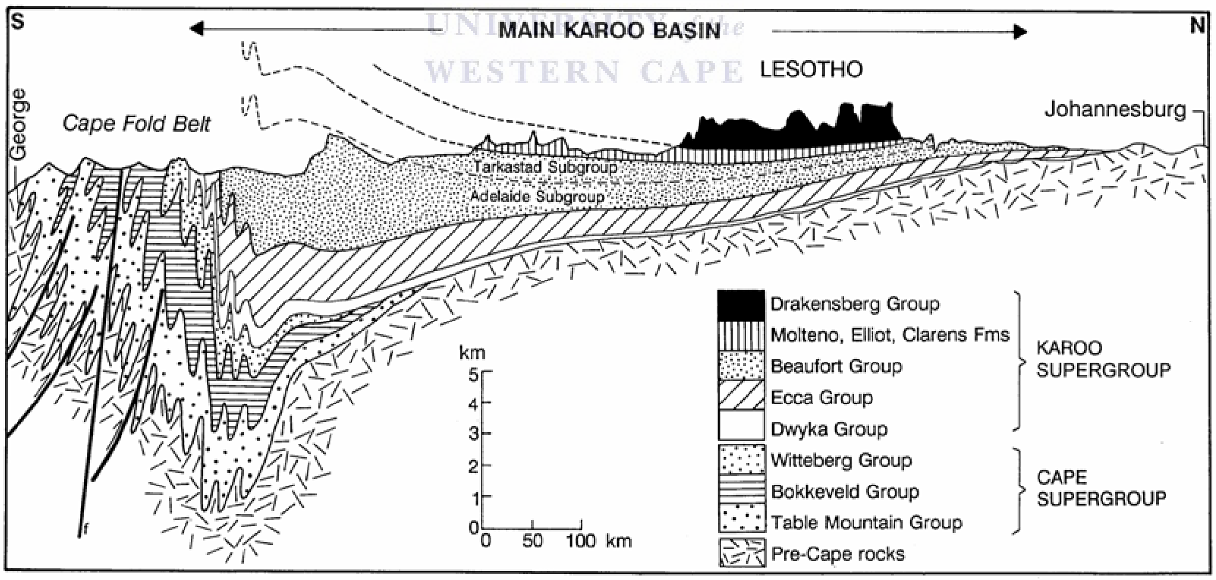

Fig 3.1: Cross-section of the Main Karoo Basin (Woodford and Chevallier, 2002).

The Karoo Super Group ranges from late carboniferous to middle Jurassic and attains a total cumulative thickness of approximately 12 km (Johnson et al., 2006). The Karoo Super Group is composed of five sequential groups namely (from oldest to youngest) the

Carboniferous to early Permian Dwyka Group (which is mainly composed of the rock tillite), the Permian Ecca Group (sandstone and shale), the Permo-Triassic Beaufort Group (mud and sandstone) and the entire sequence is capped by basaltic and rhyolitic magmas of the Drakensburg Group (Catuneanu, 2005).

3.2. Local Geology

The rocks that outcrop in the study area belong to Beaufort Group, Karoo Dolerite and the Volksrust and Vryheid Formation (Fm) of the Ecca Group (fig 3.2). Of these, however, the Vryheid formation is the most dominant in the study area.

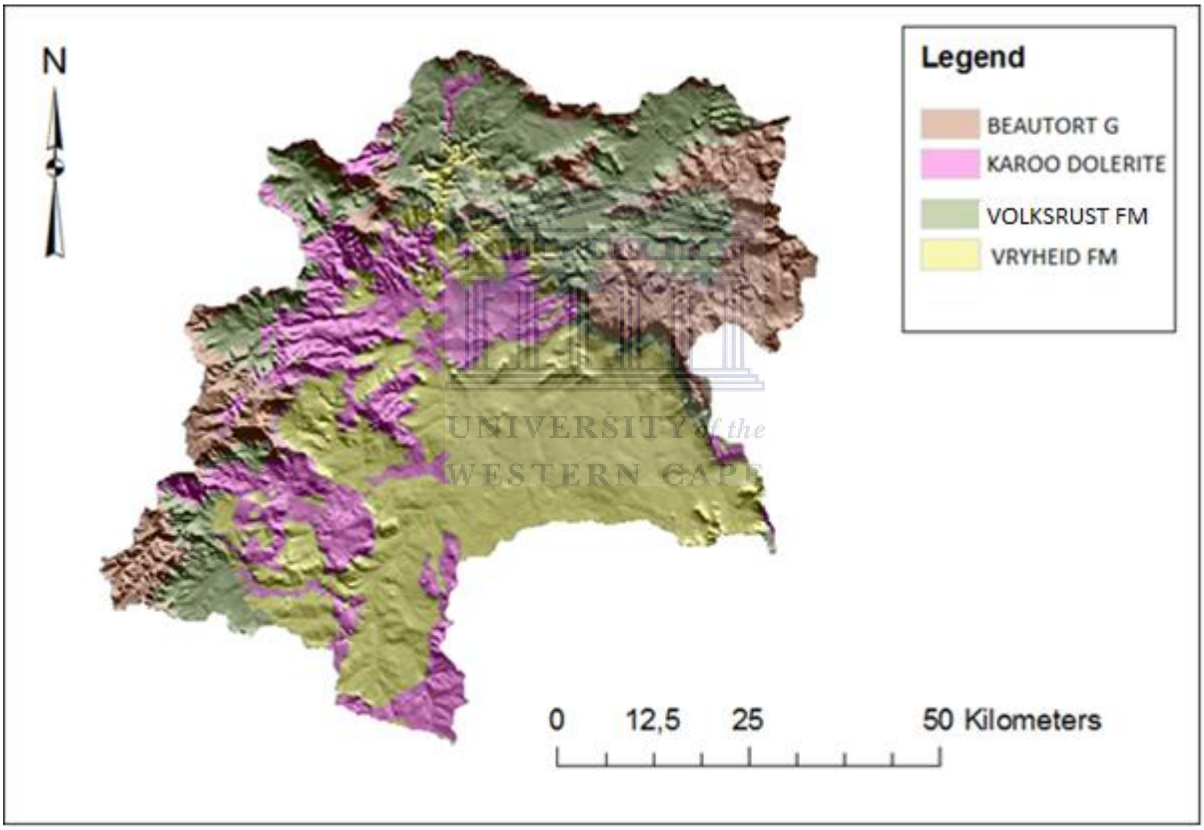

Fig 3.2: Local geology of the study area.

The deposition of the Vryheid Fm took place during a gradual transformation from marine to non-marine conditions whereby extensive coal deposits within a mudstone-sandstone succession were formed (Green and Smith, 2012). The strata consist primarily of sandstone, carbonaceous siltstone, shale, minor conglomerate and several coal seams (Cairncross et al., 2001).

The Vryheid Fm can be subdivided into a lower fluvial-dominated deltaic interval, a middle fluvial interval and an upper fluvial-dominated interval in the east. These subdivisions correspond approximately to lower sandstone, coal zone and the upper sandstone respectively (Johnson et al., 2006). According to Linstrom (1987) the Vryheid Fm can be genetically subdivided into a number of regressive cycles of sedimentation which are mainly of deltaic in origin. The ideal vertical arrangements of litho-facies from base upwards are:

> Dark-grey to black pro-delta shale and siltstone, grading through a transition zone of interlaminated shale, siltstone and cross-laminated to horizontally laminated fine grained sandstone, which represents a distal distributary mouth-bar succession. The above is overlain by a thick, fine to coarse-grained cross bedded distributary mouth-bar sandstone, which is sharply overlain by overbank delta-plain siltstone, fine-to-coarse grained and black shale containing seams in places, sometimes by thick medium to coarse grained cross bedded distributary channel sandstone with scattered thin gritstone and small-pebble conglomerate beds or lenses.

The Coal seams originated as peat swamps which developed on broad abandoned alluvial plains, less commonly, in interfluves (back swamps). The coals are seldom more than a few 100 m below surface in areas where they are actively mined. The only major disturbances are in the form of intrusive dolerite sills and dykes, particularly in the eastern regions in KwaZulu–Natal (Cairncross, 2001).

The Vryheid Fm is conformably overlain by the Volksrust Fm. The latter Formation consists of grey to black, silty shale with thin, usually bioturbated, siltstone or sandstone lenses and beds, particularly towards its upper and lower boundaries. Thin phosphate and carbonate beds and concretions are relatively common (Woodford and Chevallier, 2002).

3.3. Hydrogeology and Aquifer types

The largest river in KZN is the Thukela River, with a catchment area of about 28 000 km^2. The Thukela Water Management Area (WMA) corresponds fully to the catchment area of the Thukela River and is comprised of 86 quaternary catchments. The mean annual runoff (MAR) of the Thukela catchment is about 3865million m^3/a and mean annual precipitation

(MAP) 840 mm. The Major tributaries include the Little Thukela, Bushman's, Sunday, Mooi and Buffalo River (www.dwa.gov.za).

The Thukela WMA is divided into four main subareas/catchments according to the major rivers in the area, these are; Upper Thukela River, Mooi/Sundays subarea, catchment of the Buffalo River and the lower Thukela subarea. The Newcastle area is situated in the catchment of the Buffalo River and it is located in the sub-catchment of the Ngagane River with the Ncandu River being one of the major tributaries (DWA, 2011).

The Buffalo River is the main northern tributary of the Thukela River and it flows in a south easterly direction from the Eastern escarpment (Newcastle area) to its confluence with the Thukela River. It has a MAR of about 941 m^3/a. There are two main storage dams in the Buffalo catchment, the Ntshingwayo Dam and the Zaaihoek Dam. The Ntshingwayo Dam has a capacity of 199 million m^3. The dam was built to supply water to the town of Newcastle, Eskom's thermal power station and irrigation farmers downstream (DWAF, 2004). Zaaihoek Dam was built with an original capacity of 193 million m^3. Zaaihoek Dam is on the Slang River, a tributary of the Buffalo River, and is used to transfer water to the Vaal system and the Majuba Power Station (DWAF, 2004).

3.3.1 Aquifer Types

The Thukela WMA is generally comprised of 'hard rock' secondary porosity aquifers of the 'weathered and fractured' and 'fractured' aquifer classes. Increases zones of groundwater commonly occur in faults, joints and intrusive Karoo dolerite contacts in the regional hard rocks. The sandstones of the Vryheid Fm are the best aquifers in the interior of the Thukela WMA while the poorest aquifers in the region are the Dwyka tillite's (DWAF, 2004).

The indicated aquifer types in the Newcastle area are intergranular and fractured aquifers with an extremely low to medium development potential. The underlying geology is mostly arenaceous rock of the Ecca Formation (DWAF, 2008). The host geology of the area consists of consolidated sediments of the Karoo Super Group and consists mainly of sandstone, shale and coal beds of the Vryheid Formation. Most of the groundwater flow will be along the fracture zones that occur in relatively competent host rock.

CHAPTER 4

METHODOLOGY

This chapter elaborates on the methods that were used to process and analyse the data to achieve the aims and objectives of this study.

4.1 Data collection and Data Preparation

The data was supplied by the Department of Water Affairs (DWA). For the purposes of this study 31 samples were used, which were collected from 31 different wells. The wells are located in 10 Quaternary catchments areas in Newcastle. The samples were analyzed for the following: Magnesium (Mg^{2+}), Calcium (Ca^{2+}), Sodium (Na^{+}), Potassium (K^{+}), Chloride (Cl^{-}), Sulfate (SO_4^{2-}), Bicarbonate (HCO_3^{-}), Nitrate (NO_3^{-}), Fluoride (F^{-}), pH, Total Dissolve Solids (TDS) and Electrical Conductivity (EC).

4.2. Data Analysis

4.2.1. Univariate Analysis

Physicochemical variables of the groundwater samples were analysed using Microsoft Excel Spread sheet. This software was utilized for descriptive statistical analysis of the groundwater samples to produce a table which contain the maximum, minimum, mean and standard deviation. The descriptive statistics were then used for classification and standard comparison of the groundwater.

4.2.1.1. Standard Water Comparison

Standards are used as guidelines to regulate the concentration of chemical constituents in water to ensure that the level is not harmful to human health (WHO, 2008). The groundwater geochemistry data from the Newcastle area was compared to water standards to assess whether the quality of the groundwater in the area meets the criteria.

The guidelines used for classification and evaluations of the groundwater in the study area are:

- For drinking:
    - SAWQG (DWAF, 1996) Domestic water use
    - WHO (2011) Guidelines for drinking water quality
    - Davis and DeWiest (1996) Water classification based on TDS
    - Freeze and Cherry (1979) Water classification based on TDS
    - Sawyer and McCarty (1967) Water classification based on TH and
    - US Salinity Laboratory Staff (1954) Salinity hazard classification based on EC
- For irrigation
    - Electrical Conductivity (EC)
    - Sodium Adsorption Ratio (SAR), which is computed using the formula:

$$\text{SAR} = \frac{\text{N}^{+}}{\sqrt{(\text{Ca}^{2+}+\text{Ma}^{2+})2}}$$

With all concentrations expressed in meq/l

- Kelly’s ratio (KR), computed using the formula:

$$\text{KR} = \frac{\text{Na}^{+}}{\text{Ca}^{2+}+\text{Mg}^{2+}}$$

With all concentrations expressed in meq/l

- Sodium Percentage (Na%), which is expressed as:

$$\text{Na\%}=\frac{(\text{Na}^{+}+\text{k}^{+})\times 100}{(\text{Ca}^{2+}+\text{Mg}^{2+}+\text{Na}^{+}+\text{K}^{+})}$$

With all concentrations expressed in meq/l

- Residual Sodium Carbonate (RSC) which is expressed using the formula:

$$\text{RSC}= (\text{HCO}_3^{-} + \text{CO}_3^{-})\text{-}(\text{Ca}^{2+}+\text{Mg}^{2+})$$

With all concentrations expressed in meq/l

- Magnesium Hazard (MR), which is expressed using the formula:

$$\text{MR}=\frac{\text{Mg}^{2+}\times 100}{\text{Mg}^{2+}+\text{Ca}^{2+}}$$

With all concentrations expressed in meq/l

- Permeability Index (PI), which is described by the formula:

$$\text{PI} = \frac{(\text{Na}^{+}+\sqrt{\text{HCO}_3{}^{-}})\times 100}{\text{Ca}^{2+}+\text{Mg}^{2+}+\text{Na}^{+}}$$

With all concentrations expressed in meq/l

4.3 Bivariate Analysis

4.3.1. Correlation Analysis

Correlation analysis is a bivariate statistical method used to describe the degree of relation between two variables (Venkatramanan et. al., 2013). A correlation coefficient (r) is used to represent the association between the variables. A correlation coefficient near 1 or -1 indicates a strong relationship between two variables, while r closer to zero suggests no relationship between the variables (Ha and Ha, 2011). A positive value of r indicates a direct relationship between the variables while a negative value of r indicates an inverse relationship (Salvendy, 2012). Parameters showing $r > 0.7$ are considered to be strongly correlated, whereas if the r value is between 0.5 and 0.7, the two parameters have a moderate correlation (Venkatramanan, 2013).

The EC, TDS, TH, pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^- , NO_3^- and F^- from the groundwater samples were analysed for their interrelation using bivariate correlations method with Pearson correlation coefficient and a two-tailed test of significance in IBM® SPSS® Statistics 21 (IBM).

4.4. Classical hydro-chemical Analysis

4.4.1. Hydro-chemical Facies

The nature and distribution of hydro-chemical facies provides insights into the chemical processes that affect groundwater during its flow path (Sivasubramanian et al., 2013). To identify and interpret these hydro-chemical facies in a groundwater system, hydro-chemical diagrams can be used (Chadha, 1999). These diagrams can delineate hydro-chemical facies by graphically representing relationships between dissolved cation and anions in groundwater samples (Chandrasekar, 2014). For the purpose of this study two hydro-chemical diagrams were used, which are the Piper triplot developed by Piper (1944) and Chadha's (1999) diagram.

The Piper (1944) consists of two triangles and a diamond shaped field in-between them. Before values can be plotted on the trilinear diagram the concentrations of the six ions of interest are converted into milliequivalent per litre (meq/L), a unit of concentration equal to the concentration in milligrams per liter divided by the equivalent weight (atomic weight divided by valence) (Herring et al., 2002).

In the Piper (1944) diagram each cation value is plotted, as a percentage of the total concentration (meq/L) of all cations under consideration, in the lower left triangle of the diagram. Likewise, individual anion values are plotted, as percentages of the total concentration of all anions under consideration, in the lower right triangle (Herring et al., 2002). The sample concentrations are then projected into the central diamond-shaped field, which provides the overall character of the water. Interpretation of the chemical nature of water is based on the location of the sample values within the central field (Kumar, 2013).

In the Chadha's (1999) diagram the difference in milliequivalent percentage between alkaline earths (Ca^{2+} + Mg^{2+}) and alkali metals (Na^+ + K^+), is plotted on the X axis, and the difference in milliequivalent percentage between weak acidic anions (CO_3^- +HCO_3^-) and strong acidic anions (Cl^- + SO_4^{2-}) is plotted on the Y axis. The resulting field of study is a square or rectangle, depending upon the size of the scales chosen for X and Y co-ordinates. The milliequivalent percentage differences between alkaline earths and alkali metals, and between weak acidic anions and strong acidic anions, plots in one of the four possible sub-fields of the diagram. The hydrochemical facies is determined by the location of the points in the four sub-fields (Chadha, 1999).

The Piper Trilinear diagram was plotted using AquaChem 3.70 and the Chadha's diagram was plotted using Microsoft Excel Spread sheet. Major ions used in plotting both these diagrams were Mg^{2+}, Ca^{2+}, Na^+, HCO_3^- , Cl^- and SO_4^{2-}.

4.4.2. Major Ion Chemistry

Investigating the major ion chemistry of groundwater is a recommended method of determining the major processes that resulted in the ionic composition of groundwater (Elango and Kannan, 2007). Hence it can be used to determine the dominant process that influenced the water chemistry.

The presence of rock water interaction was identified using TDS vs. Na^+/ (Na^++ Ca^{2+}) and TDS vs. Cl^-/ (Cl^- +HCO^3) scatter diagrams as suggested by Gibbs (1970). The (Ca^{2+} + Mg^{2+}) vs. (HCO_3^- +SO_4^{2-}) scatter diagram was used to analyse the samples for silicate or carbonate weathering sources. To further understand the dominance of calcite and dolomite as possible sources, the Ca^{2+} vs. HCO_3^- scatter plot was used. The Ca^{2+} vs. SO_4^{2-} scatter plots were used to determine the possible contribution of gypsum and/or anhydrite in the SO_4^{2-} and Ca^{2+} concentrations (Subramani et. al., 2010).

The influence of silicate weathering on the groundwater chemistry was determined using scatter plots that depict the relationships between Na^++K^+, $Ca^{2+}+Mg^{2+}$ and Total Cations (TZ) and the meq/L ratios of these cations to the total cations (Subramani et. al., 2010).

The influence of ion exchange in the rock-water reactions was determined using scatter plots showing the relationships between Na^+- Cl^- and $(Ca^{2+}+Mg^{2+})-(HCO_3^- + SO_4^{2-})$ (Fisher and Mullican, 1997) . To further understand the type of ion exchange the $Ca^{2+} +Mg^{2+}$ vs. SO_4^{2-} + HCO_3^- and $Ca^{2+}+Mg^{2+}$ vs. Na^+ scatter plots were used. The dissolution of halite (NaCl) as a possible additional contributing factor to Na^+ and Cl^- ions in the groundwater samples was checked using the Na^+ vs. Cl^- scatter plot. Furthermore probable influence from evaporation and land use on the groundwater chemistry was determined by studying the Na^+/Cl^- ratio versus EC and Cl^- vs. SO_4^{2-} scatter diagram, respectively.

4.5. Multivariate Statistical Analysis

4.5.1. Factor Analysis

Factor analysis (FA) is a statistical method used to identify the relationship among a number of observable quantitative variables and represent them in terms of a few underlying quantities called factors (Suk and Lee, 1999). It focuses on answering two main aspects, the number of factors and what they represent. The application of factor analysis to geochemistry can aid in identifying groups of elements which show similar behaviour in a particular geochemical environment and could serve as a pointer to elemental associations (Odokuma-Alonge and Adekoya, 2013). These associations can be used to identify the geochemical processes responsible for them.

Principal Components was selected as the extraction method. The total number of factors/components generated from a factor analysis indicates the total number of possible sources of variation in the data and the ranking of these factors is ordered according to their importance. The first factor or component represents the most important source of variation in the data while the last factor is the least important process contributing to the chemical variation (Yidana et al., 2008). Factor loadings on the factor loadings tables are interpreted as correlation coefficients between the variables and the factors, they represents how much each variable contributes to the factor (Yong and Pearce, 2013).

Eigenvalues were used to determine how many factors to consider. These values represent the amount standardised variance in the variable accounted for by a factor. The amount of standardised variance in a variable is 1 and sum of eigenvalues is the percentage of variance accounted for. Factor with eigenvalue >1 explain more total variation in the data than individual groundwater quality parameters, and factor with eigenvalue <1 explain less total variation than individual variable (Usman et. al., 2014).

Factor analysis was performed in IBM® SPSS® Statistics 21 (IBM) using EC, TDS, TH, and pH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-} , NO_3^{-} and F^{-}.

4.5.2. Cluster Analysis

Cluster analysis (CA) is as statistical method that works by combining variables into clusters. The clustering is based on similarities or dissimilarities in variables in such a way that each cluster represents a different process (Yidana et al., 2008). It starts with each variable as a separate cluster, and then combines the clusters successively, reducing the number of clusters at each step until only one cluster is left (Mooi and Sarstedt. 2011).

The hierarchical cluster analysis (HCA) was the clustering method for this study. Hierarchical cluster divides datasets into hierarchies based on similarity or dissimilarities in the field. The algorithm that was used was the agglomerate algorithm. This algorithm begins reducing the number of variables by combining the most similar variables to form different clusters at each step. Next, the most similar clusters are merged, this process continues until only one cluster is left containing all the clusters (Templ et al., 2006).

The method used for clustering was Wards method. This method is distinct from other methods because it uses an analysis of variance approach to evaluate the distances between clusters (Krishna et al., 2012). Cluster membership is assessed by calculating the total sum of squared deviations from the mean of a cluster.

Results from CA were represented by a diagram called the Dendogram. Samples that share similar characteristics and relationships are clustered together at low linkage distances, whilst dissimilar samples are linked at higher linkage distances (Yidana et al., 2008).

Cluster analysis was performed in IBM® SPSS® Statistics 21 (IBM) using EC, TDS, TH, and pH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-} , NO_3^{-} and F^{-}.

4.5.3. Discriminant Analysis

Discriminant analysis (DA) is used for devising rules for assigning new observation (x) characterised by a set of measured samples into a number of pre-defined groups (Siad et al., 1994). DA is used to determine which variables discriminate between two or more groups, that is, independent variables are used as predictors of group membership. Groups/clusters can be recognized by the use of several methods on raw data; in this case cluster analysis was used. The number of groups that exists is set before the DA analysis is performed (Chahouki, 2011).

Discriminant analysis works by creating a new variable called the discriminant function score, which is used to predict to which group a variable belongs. Discriminant function scores are computed using eigenvalues (Madaki, 2013). If the dependent variable defines two groups, one statistically significant discriminant function is required to distinguish the groups; if the dependent variable defines three groups; two statistically significant discriminant functions are required to distinguish among the three groups and so on (Marcoulides and Hershberger, 1997). If a discriminant function is able to distinguish among groups, it must have a strong relationship to at least one of the independent variables.

Since the direct discriminant method does not show the importance of the individual geochemical variables for the description of classified groups, or their importance in the classification itself, stepwise discriminant analysis method has to be considered (Siad et al., 1994). Stepwise discriminant analysis is a model of discrimination and is built step by step and at each step all variables are reviewed and evaluated to determine which one will contribute most to the discriminating between the groups. Discriminant analysis was done using IBM® SPSS® Statistics 21 (IBM).

4.6. Spatial Analysis

4.6.1. Data Preparation

The spatial analysis entails the use of geographical information system (GIS) to map the chemical evolution of groundwater. To show the distribution of major ions in the study area and to show the spatial distribution of the different facies identified. This analysis was used to delineate regions where groundwater is suitable or unsuitable for drinking and irrigation purpose. The methodology followed a spatial analysis method after Solomon (2013).

Data preparation was done using the ArcCatalog, ArcMap and the Spatial Analyst extension of ArcGIS 10.0 from ESRI®. The Water Management Areas, Catchments-SA (Quaternary catchment boundaries for South Africa) and other relevant vector data were acquired from the Water Resources of South Africa, 2005 study (WR2005). The water management areas and quaternary catchments of the study area were then extracted from these vector data.

The borehole points were imported into ArcMap using the latitude and longitude coordinates and projected using the WGS_1984_UTM_Zone_30S projection coordinate system. All the maps that were created for the purpose of this study were projected using the above-mentioned projection coordinate system with the WGS_1984 datum.

Shuttle Radar Topography Mission (SRTM3) elevation data of the study area were used to create orthorectified geological map. SRTM3 digital elevation model (DEM) for the study area was acquired from the U.S. Geological Survey's EROS Data Centre. The S27E29, S27E30, S27E31, S28E29, S28E30 and SS28E31 height files with an extension *.HGT from the SRTM3 were used for the study area. The height files were then imported to Integrated Land and Water Information System software (ILWIS) to generate a raster map using the DEM Visualization tool. The results of this visualization (closhadow raster maps) were used in ArcMap 10 to create orthorectified geological raster image of the study area.

The resulting raster maps of the height files created in ILWIS were then converted into a mosaic raster in order to obtain a single DEM raster map of the study area. The raster map of the study area was extracted using the boundaries of the Quaternary catchments that contain the borehole locations.

4.6.2. Spatial Data Presentation

Based on spatial distribution of the boreholes different maps displaying cation and anion variables, factor scores and hydro-chemical facies results were created against geology, quaternary catchments and land use for interpretation purposes.

The spatial distribution of the variables such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, NO_3^{-}, TDS, TH and the factor scores from factor analysis were displayed using Inverse Distance Weighted (IDW) interpolation method in ArcMap 10.0 to show the distribution of these variables and predict the values surrounding these measured variables. The WHO (2011) recommended levels of the variables as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, NO_3^{-} , F^{-} and TDS were displayed using reclassification method of the interpolated distributions of these variables.

4.7. Software's used

1. Microsoft Excel Spread sheet

2. IBM® SPSS® Statistics 21

3. AquaChem 3.70

4. ArcGIS 9.3 from ESRI.

CHAPTER 5

RESULTS AND DISCUSION

This chapter presents the results and discussion based on the groundwater chemistry and the methods that were used to further classify and characterise hydro-chemical processes responsible for the quality of the water.

5.1. Evaluation for Suitability

5.1.1. Evaluation for Drinking Purposes

Chemically, water used for drinking should be soft, low in dissolved salts and free from toxic constituents (Ramesh and Elango, 2011). The standards for drinking water by DWAF (1996) and WHO (2011) (table 5.1), were used as the basis of evaluating the suitability of groundwater for drinking purposes.

The pH of the water in the study area ranged between 6.65 and 10.09 with an average of 7.79, most of the samples fall within the target range and only 1 sample falls outside this range. Level of pH in water is controlled by dissolved carbonates and higher pH reflects high presence of acid neutralizing constituents (Abudaya et al., 2014). The pH of the water in the study area can be classified as being within the target range for domestic use and is indicative of the alkaline nature of the groundwater in the area. EC ranges from 4.9 to 186 mS/m with a mean value of 41.53 mS/m, 37 of the groundwater samples fall within the target range (0-70 mS/m) with only 4 of the samples falling outside this range as per SAQWG (DWAF, 1996). The high level of EC in these boreholes is mainly due to the high levels of Na^+ and Cl^-. High EC in water is known to cause gastrointestinal irritation in human beings after long term use (Ramesh and Elango, 2012). The concentration of TDS in the groundwater varies from 29 to 1091 mg/l with an average of 324.77 mg/l. Most of the samples fall within the desirable range with only 5 out of 31 samples falling outside this range as per SAWQG (DWAF, 1996) and 2 as per WHO (2011) standards. Figure 5.5 shows the two areas that show an increase in TDS concentration which are located in boreholes 13 and 31 situated on the Vryheid Fm. High TDS values in these two boreholes is mainly related to high levels of Na^+, Cl^- and SO_4^{2-} ions.

The order of abundance of major ions in the groundwater, based on their mean values is as follows: $Na^+>Ca^{2+}>Mg^{2+}>K^+$ and $HCO_3^->SO_4^{2-}>Cl^->NO_3^-$. The desirable range for Na^+ according to the SAWQG (DWAF, 1996) is ≤ 100 mg/l and ≤ 200 according to WHO (2011) standards. Na^+ in the study area varies from 2.7 to 350.5 mg/l with an average of 49.11 mg/l, most of the samples fall within the target range, 4 samples fall out of the desirable range as per SAWQG (DWAF, 1996) and 1 as per WHO (2011) standards. Figure 5.1 shows that the latter sample comes from borehole 13, situated in the Vryheid Fm, the source of high Na^+ ions in this borehole might be from silicate weathering. Borehole 13 also shows high levels of Cl^-, this might also be indicative of halite dissolution as another source of these ions in the area.

Ca^{2+} in the study area ranged between 0.5 and 123.6 mg/l with an average of 24.26mg/l and the SAWQG (DWAF, 1996) target range is <32 mg/l. 23 of the samples fall within the target range while 8 are outside this range. The concentration of Mg^{2+} found in the samples of the study area ranges between 0.5 to 47.5 mg/l with average value of 10.37 mg/l. The target range according to the SAWQG (DWAF, 1996) is <30 mg/l, 29 of the samples in the area fall within the target range. Calcium and Magnesium do not have WHO guideline value assigned to them because they are not of concern in values found in water (WHO, 2011). But all values do fall within the taste threshold values as per WHO (2011) (Fig A.1 and Fig A.2).

HCO_3^-, which is the most dominant anion in the study area, has concentrations that vary from 13.3 to 355.3 mg/l and an average of 146.66 mg/l. The HCO_3^- levels in water are directly related to the alkalinity of the water (Elamassi, 2011) and the high levels of HCO_3^- indicate that the groundwater is alkaline in nature. The target range for Cl^- according to the SAWQG (DWAF, 1996) is 0-100 mg/l and ≤ 250 mg/l according to WHO (2011) standards, the concentration in the study area ranges from 1.5 to 430.7 mg/l with an average of 23.10mg/l. Only 1 sample exceeds both the SAWQG (DWAF, 1996) and WHO (2011) target range for Cl^-, figure 5.3 shows that this sample is situated on the Vryheid Fm in borehole 13. The high levels of Cl^- in this borehole correlate with high levels of Na^+ and this could be an indicative of halite dissolution as source of Cl^- ions in this borehole. SO_4^- levels range from 2 to 525.7 mg/l with an average of 33.67 mg/l and 1 sample falls outside the target range as per SAWQG (DWAF, 1996) and WHO (2011) standards; this sample is situated in borehole 31(fig 5.2). The source of SO_4^{2-} in this borehole might be due to gypsum dissolution, because this borehole also shows high concentration of Ca^{2+}. The concentration of F^- in the study area ranges between 0.11-1.91 mg/l with an average of 0.42 and 2 of the groundwater samples fall outside the desirable range as per SAWQG (DWAF, 1996) and WHO (2011) standards. Fluoride in groundwater can be as a result of geogenic or anthropogenic sources. High levels of F^- in drinking water result in fluorosis, a condition characterised by malting and staining of teeth and in some case it affect skeletal bones (Shaji et al, 2007).

Table 5.1: Descriptive statistics of groundwater chemistry compared with SAWQG (DWAF, 1996) and WHO Drinking Water Standards (WHO, 2011)

Variable	Min	Max	Mean	Standard Dev.	SAWQG (DWAF,1996) Target Range	Number of samples exceeding the SAWQG Target Water range	WHO (2011) Water Standards (mg/l)	Number of samples exceeding WHO recommended limit
pH	6.65	10.09	7.79	0.52	6.0-9.0	1	-	
EC	4.9	186	41.53	37.49	0-70	4	-	
TDS	29	1091.00	324.78	253.51	0-450	5	1000	2
TH	3.31	504.23	103.29	104.07	-	-	-	
*Ca^{2+}	0.5	123.6	24.26	25.71	0-32	8	250	0
*Mg^{2+}	0.5	47.5	10.37	11.08	0-30	2	100	0
Na^+	2.7	350.5	49.11	68.55	0-100	4	200	1
*K^+	0.15	4.84	1.55	1.25	0-50	0	12	0
Cl^-	1.5	430.70	23.10	77.03	0-100	1	250	1
F^-	0.11	1.91	0.47	0.42	0-1.1	2	1.5	2
HCO_3^-	13.3	355.3	146.66	77.10	-	1	-	
SO_4^-	2	525.7	33.67	97.30	0-200	1	250	1
NO_3^-	0.02	4.78	0.64	1.16	0-6	0	50	0

N=31. All values are in mg/L except EC, in mS/m and pH (no units); - no standard available, *No WHO guideline value assigned, values in the table represent taste threshold value

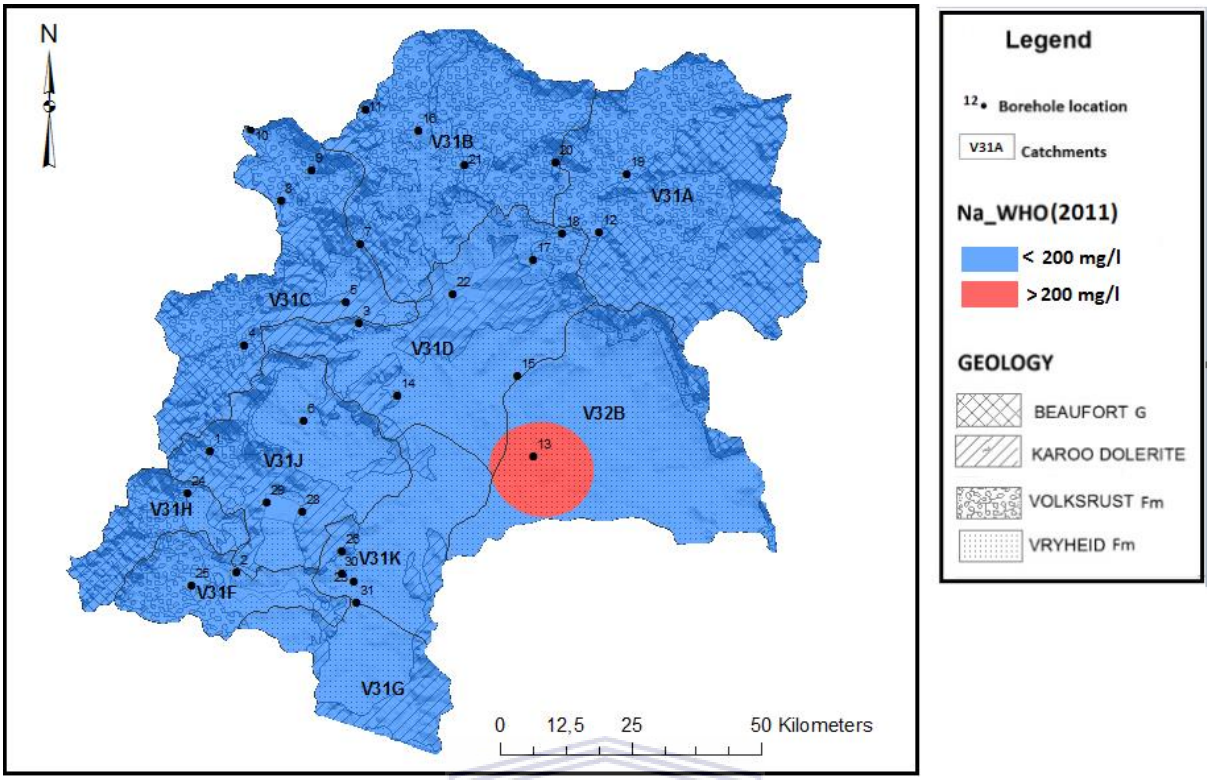

Fig 5.1: Na^+ concentration classification of the groundwater samples based on WHO (2011) drinking water guideline

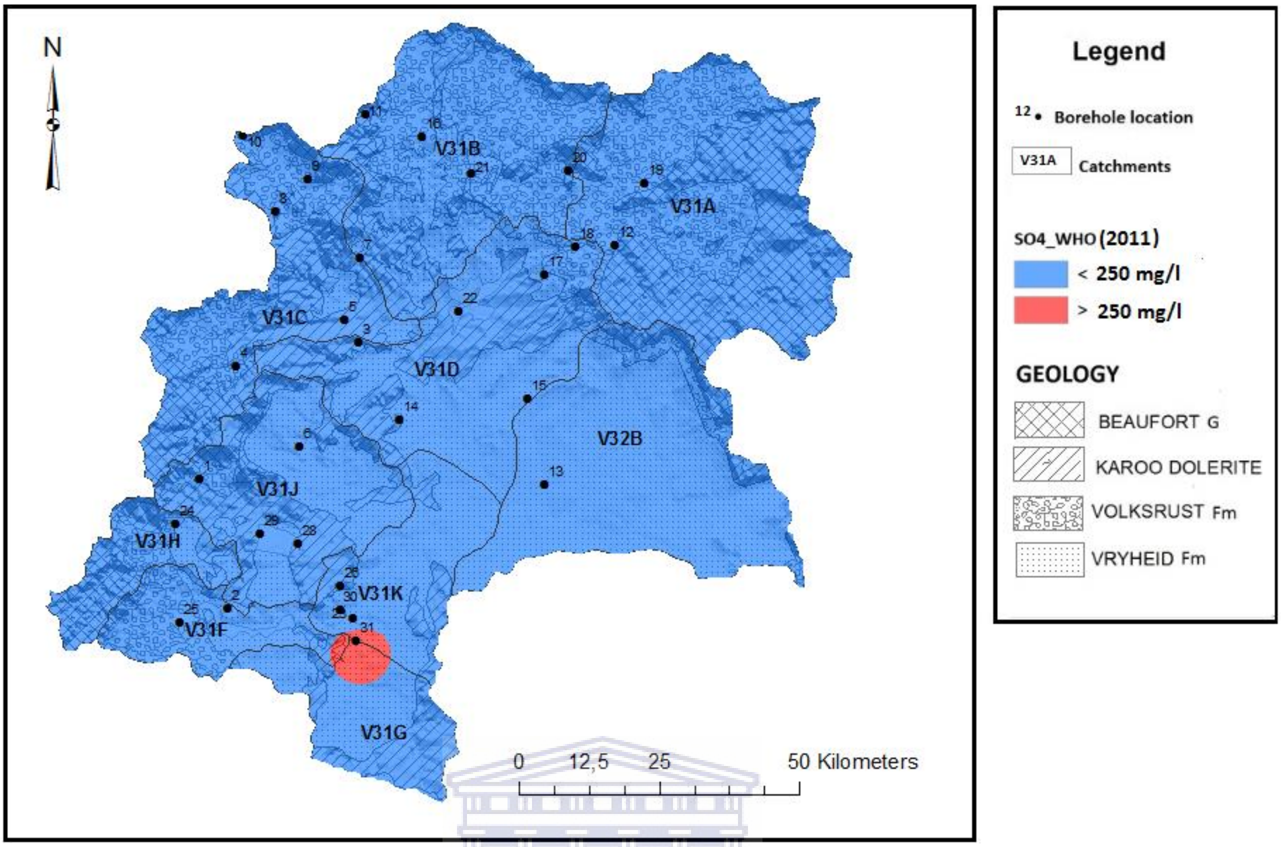

Fig 5.2: SO_4^{2-} concentration classification of the groundwater samples based on WHO (2011) drinking water guidelines

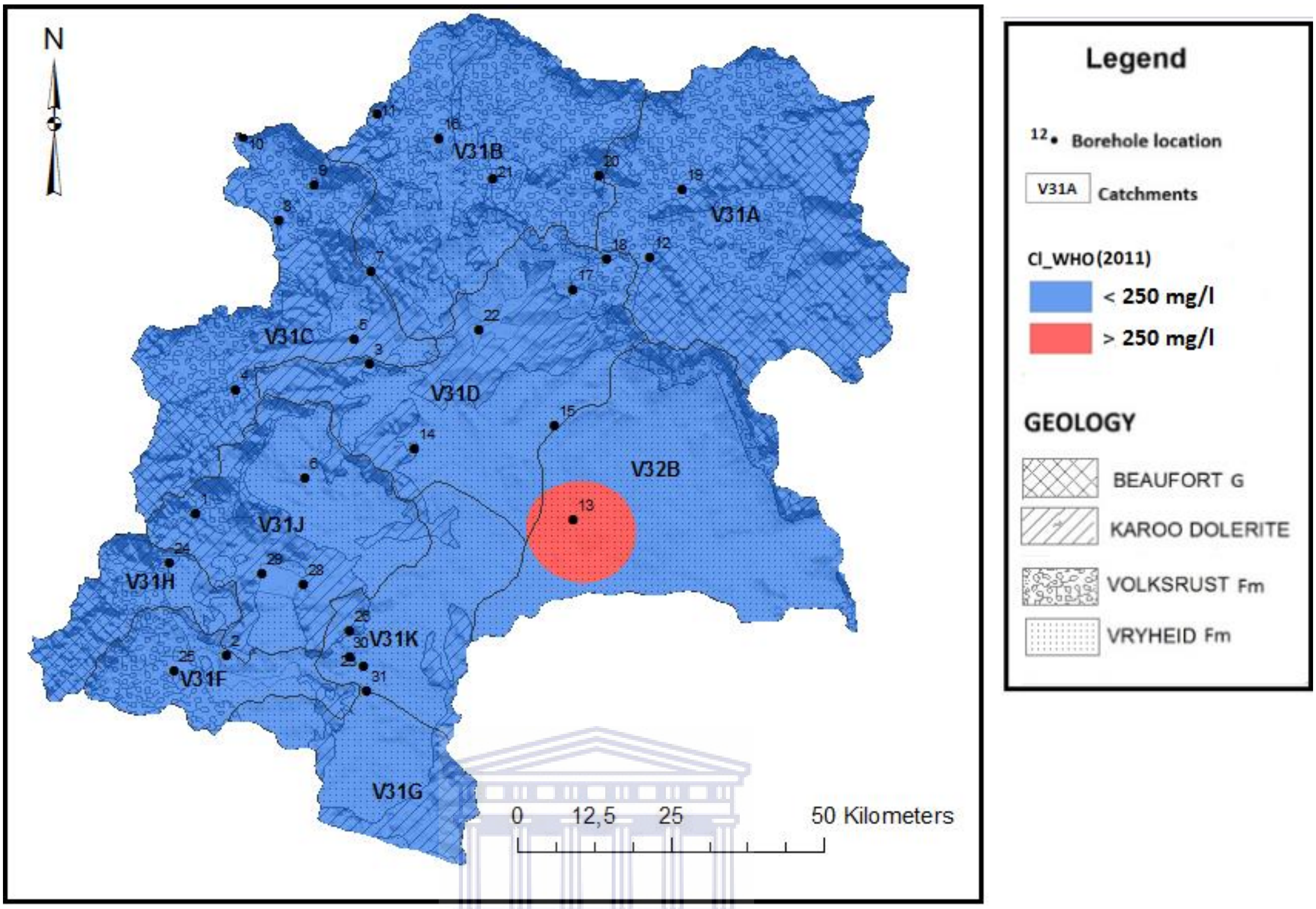

Fig 5.3: Cl$^-$ concentration classification of the groundwater samples based on WHO (2011) drinking water guidelines

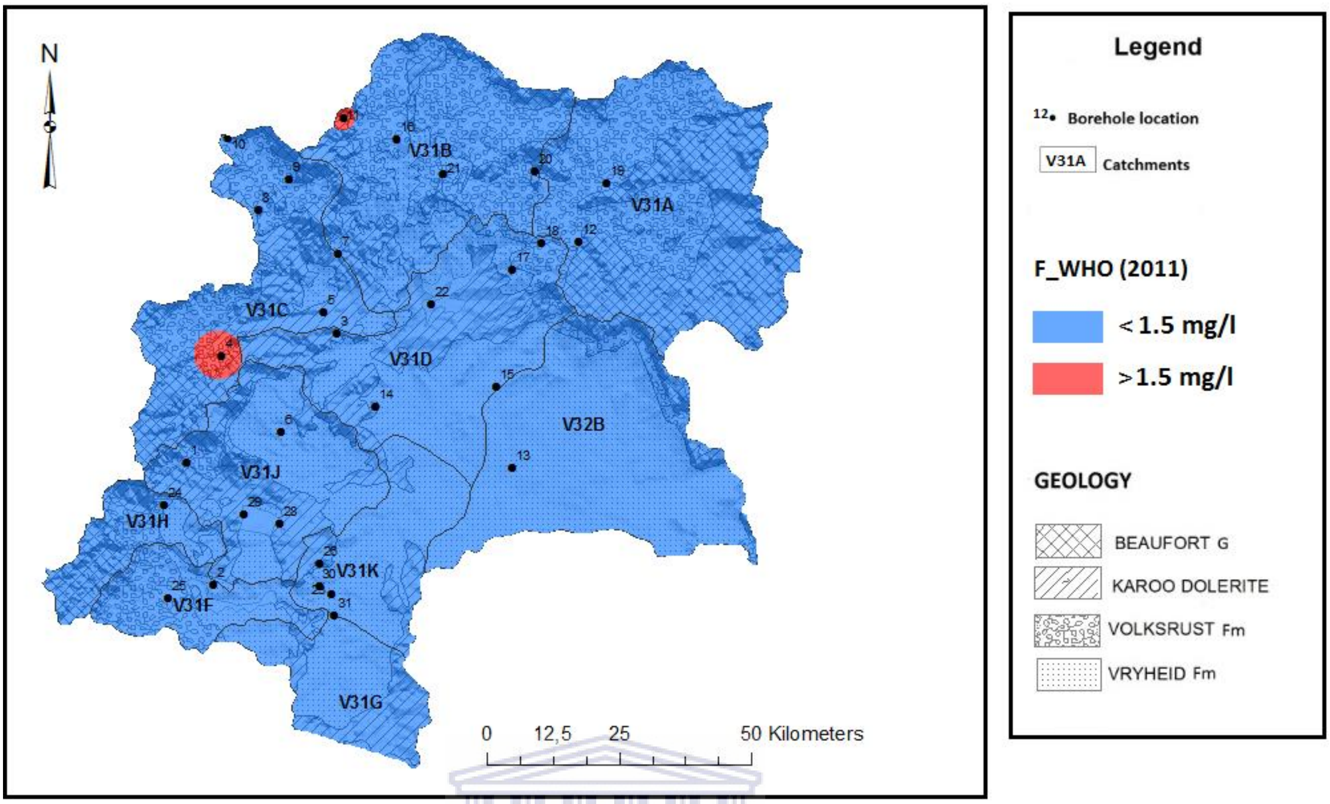

Fig 5.4: F$^-$ concentration classification of the groundwater samples based on WHO (2011) drinking water guidelines

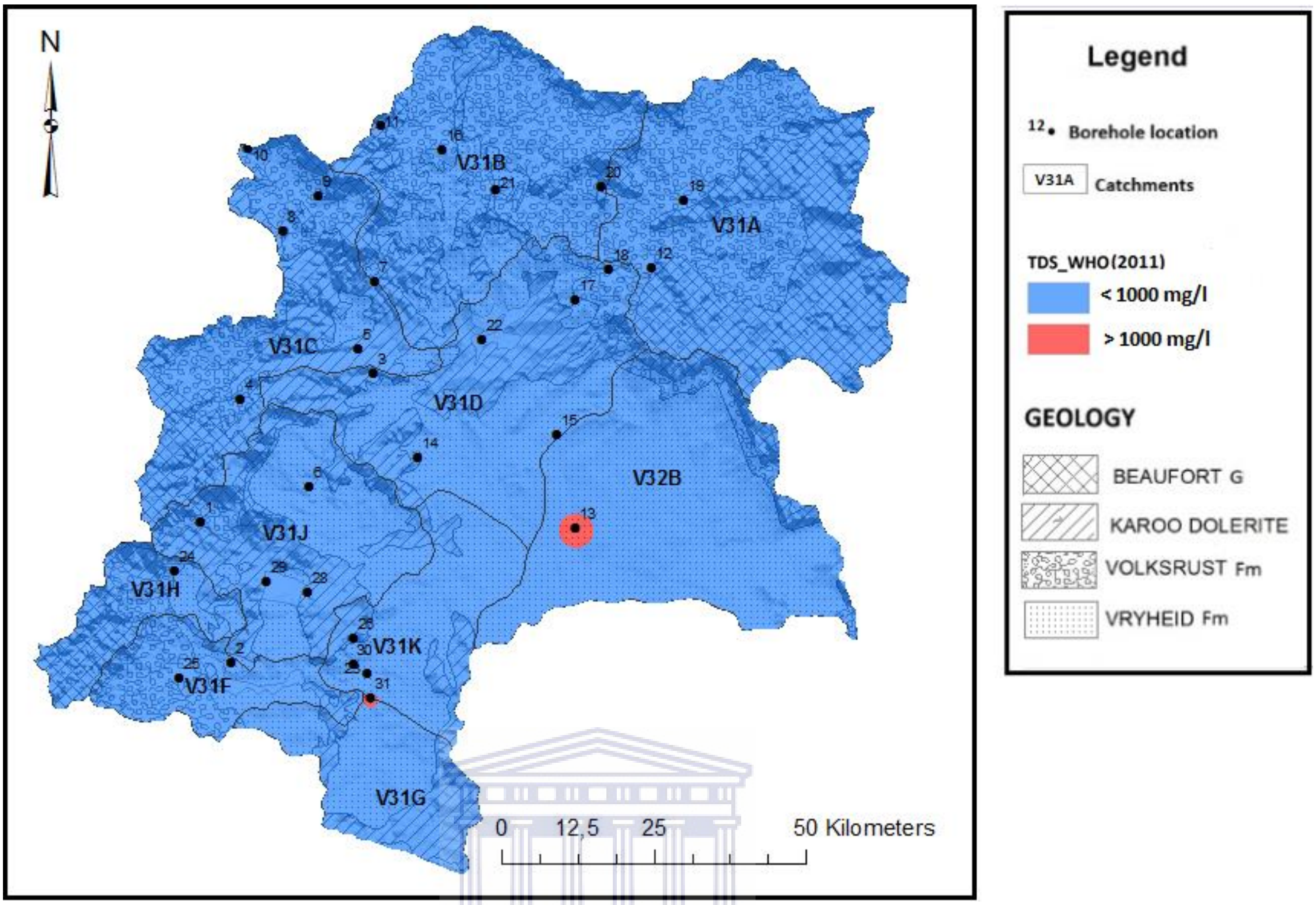

Fig 5.5: TDS concentration classification of the groundwater samples based on WHO (2011) drinking water Guidelines.

TDS is one of the most important parameters used to investigate water suitability for drinking. Davis & DeWiest (1996) and Freeze & Cherry (1979) devised classification methods to classify water suitability according to TDS levels. Results from these two classifications for the groundwater from the study are shown below.

According to Davis and Dewiest (1966) groundwater classification based on TDS (Table 5.2), 83.87% of the groundwater in the study area is desirable for drinking and 9.68% of the groundwater samples indicate permissible TDS values. Furthermore, 6.45% of the groundwater samples in the study area are useful for irrigation purposes. None of the samples fall into the unfit for drinking classification. The high levels of TDS in this water are mainly due to high levels of Na^+, Cl^- and SO_4^{2-} ions in these boreholes. Based on this classification the water is suitable for both drinking and irrigation.

Table 5.2: Davis and DeWiest (1966) Classification based on TDS.

TDS(mg/l)	Classification	Number of samples	Cumulative %
<500	Desirable for drinking water	26	83.87%
500-1000	Permissible for drinking water	3	93.55%
1000-3000	Useful for irrigation water	2	100%
>3000	Unfit for drinking and irrigation	0	0

Classification based on TDS according to Freeze and Cherry (1979) (table 5.3) shows that 93.54% of the groundwater samples are considered fresh water while 6.45% is classified as brackish water type. The two samples that fall into the brackish classification are the same samples that showed high levels of TDS above the WHO (2011) standards, these samples are situated in borehole 13 and 31. The Brackish water in these two boreholes is due to the high levels of Na^+, Cl^- and SO_4^{2-}, the brackish nature of this water might present a salty taste.

Table 5.3: Freeze and Cherry (1979) classification based on TDS

TDS (mg/l)	Classification	Number of samples	Percentage
<1000	Fresh water	29	93.54%
1000-10000	Brackish water type	2	6.45%
10000-100000	Saline water type	0	0
>100000	Brine water type	0	0
Total		31	100

Hardness in drinking water can cause health problems such as kidney failure (WHO, 2008). Classification of water based on TH by Sawyer and McCarthy (1967) (table 5.4) indicates that 54.84 % of the groundwater samples fall into the soft category, 19.35% moderately high classification, 22.58% hard and 3.23% fall within the very hard classification.

Table 5.4: Sawyer and McCarthy (1967) classification based on TH

TH (mg/l)	Classification	Number of samples	Percentage
<75	Soft	17	54.84%
75-150	Moderately high	6	19.35%
150-300	Hard	7	22.58%
>300	Very Hard	1	3.23%

Figure 5.6 below illustrates the spatial distribution of concentration of TH with consideration to the Sawyer and McCarty (1967) classification. Concentration between 150 and 300 (hard category are found in boreholes 30, 24, 14, 5, 3, 16, and 19 and concentration of > 300 which belong to the hard category are found in borehole 31. The reason for high TH in these boreholes especially 31 is due to the high concentration of Ca^{2+} and Mg^{2+}, which could be due to silicate weathering, carbonate weathering and gypsum dissolution in the Vryheid and Volksrust Fm.

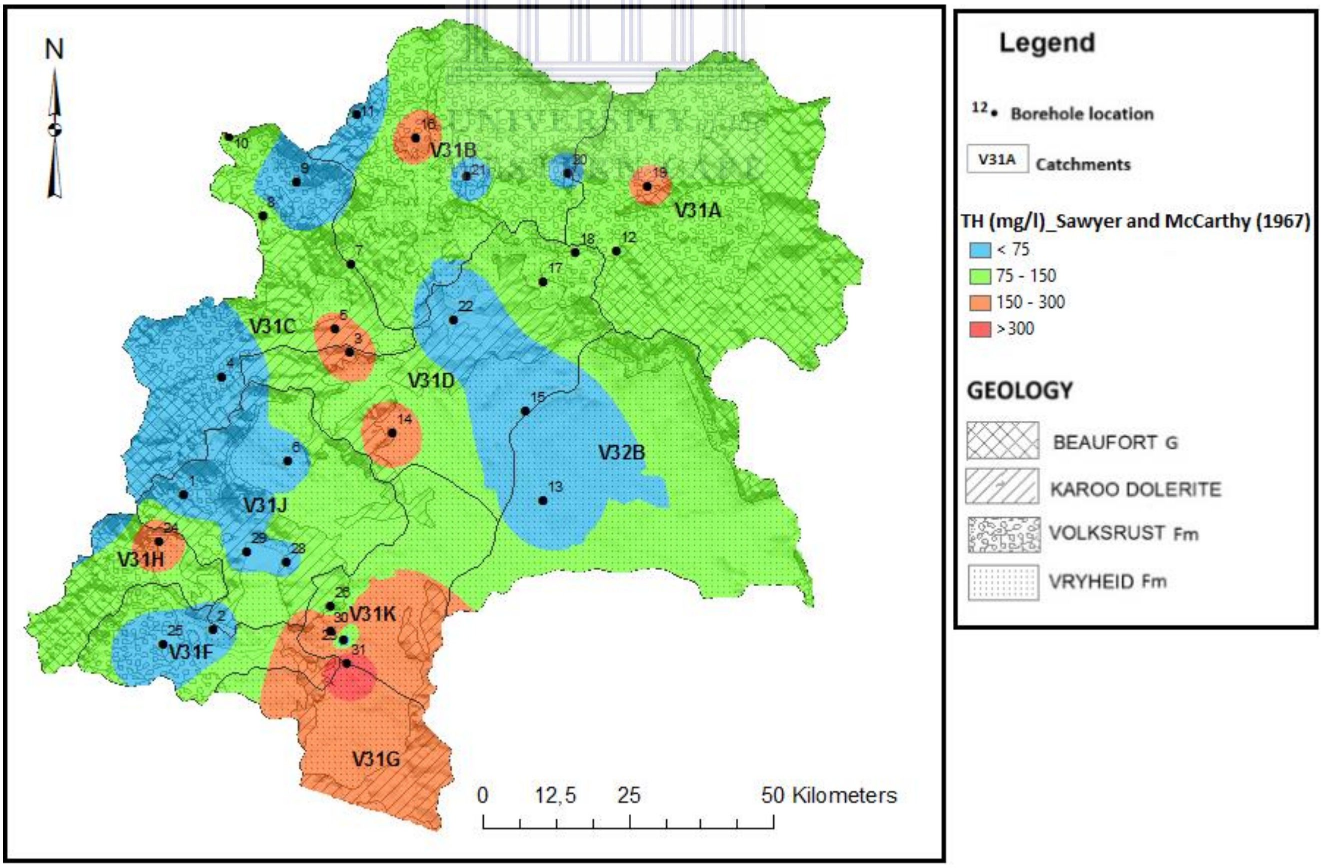

Fig 5.6: TH concentration classification of the groundwater samples based Sawyer and McCarty (1967) classification

5.1.2. Evaluation of water quality for irrigation

The quality of water for irrigation is determined by how the long term use of the water affects soil and plant health, the use of water with inferior quality for irrigation could lead to reduced crop yield (Ramesh and Elango, 2010). Parameters used to assess the quality of water for irrigation included total salt concentration measured by EC (salinity hazard), the relative proportion of sodium which indicate the sodium hazard, which are: the Sodium percent, Sodium absorption ratio, Residual sodium carbonate and Kelly's ratio, Permeability index and Magnesium ratio.

5.1.2.1. Salinity Hazard

The salinity hazard increases the osmotic pressure of the soil water and restricts the plant roots from absorbing water; this results in a physiological drought condition (Hiscok, 2005). Table 5.5 below shows the classification of water based on EC (US salinity Laboratory, 1954). According to this classification all the groundwater samples have low salinity hazard, this is due to the low TDS in the groundwater as shown in section 5.1.1. This shows that, with respect to salinity hazard the groundwater in the study area is suitable for irrigation.

Table 5.5: Classification of water based on EC (US salinity Laboratory, 1954)

Salinity Hazard	**EC (mS/m)**	**No. Of samples**	**%**
Low	<250	31	100
Medium	250-750	0	0
High	750-2250	0	0
Very high	>2250	0	0
Total		31	100

5.1.2.2. Sodium Hazard

The sodium hazard results from accumulation of sodium in an excessive amount which causes the physical structure of the soil to breakdown. When calcium and magnesium are replaced by sodium adsorbed on clays, the result is dispersal of soil particles. Consequently, the soil becomes hard and compact when dry and increasingly impervious to water resulting in plant roots not getting enough water (Hiscok, 2005). For this reason, the sodium in water is an important parameter when determining suitability of the water for irrigation.

5.1.2.2.1. Sodium Adsorption Ratio

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 due to high concentration of Na^+ relative to Ca^{2+} and Mg^{2+}. SAR is computed from the relative measures of these cations (DWAFF, 1996). Water with SAR ≤ 6 is more desirable for irrigation while water with SAR ≥ 9 may cause the soil structure to deteriorate resulting in slower water infiltration and residual soil reduced air movement (Peacock and Christensen, 2000).

The SAR is computed using the formula (Hem, 1991):

$$\mathrm{SAR} = \frac{\mathrm{Na^+}}{\sqrt{(\mathrm{Ca^{2+}}+\mathrm{Mg^{2+}})\times\frac{1}{2}}}$$

Where, the ion concentrations are expressed in meq/l

The minimum and maximum values of SAR for groundwater samples in the area were 0.22 and 21.88 respectively with an average value of 3.75 and standard dev. value is 5.91. 77.4% of the groundwater samples have SAR less than 6 while 12.90 % have SAR greater than 9 and 9.7% falls between 6 and 9. Majority of the samples have low SAR meaning they have more Ca^{2+} and Mg^{2+} relative to Na^+, which indicates that the capacity of the water to induce sodic conditions in the soil is low and are suitable for irrigation. Whereas, 12.90 % of the samples have SAR greater than 9 meaning they have more Na^+ than Ca^{2+} and Mg^{2+}, resulting in high capacity of the water to cause soil sodicity and therefore unsuitable for irrigation.

Figure 5.7 illustrates classification of groundwater in relation to salinity hazard (Ec) and sodium hazard (SAR) by the US salinity Laboratory (1954). According to the classification 87, 1% of the samples fall in the C1S1 (low salinity with low sodium) category which is good for irrigation, while 3.23% falls into the C1S2 (low salinity with medium sodium) category and 9.68% fall into the C1S3 (low salinity with high sodium). Low salinity also complicates the issue of sodicity in that irrigation water which is very low in salt concentration accentuates poor permeability resulting from high SAR (Bauder et al., 2008). Thus, water samples that fall into the C1S3 class, which are from borehole 13, 11 and 22 have a higher chance of lead in to alkali soils (Raju, 2007) which have very poor structure and low infiltration capacity.

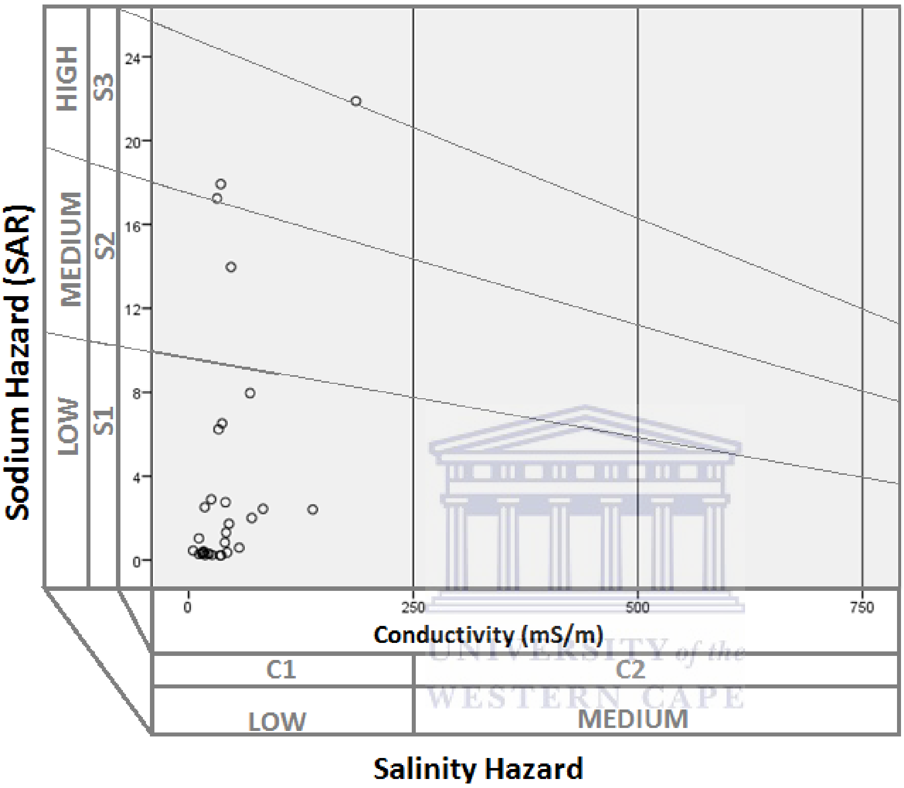

Fig 5.7: Classification of groundwater samples in relation to salinity hazard and sodium hazard (US salinity Laboratory, 1954).

5.1.2.2.2. Percentage of Sodium

Percentage of Na^+ is widely used for assessing the suitability of water for irrigation purposes. The sodium percentage (Na%) is computed with respect to relative proportion of cations present in water, where the content is expressed in terms of sodium percentage and is defined as:

$$\text{Na \%} = \frac{(Na^{+}+k^{+})\times 100}{(Ca^{2+}+Mg^{2+}+Na^{+}+K^{+})}$$

Where, all ionic concentrations are expressed in meq/l

Table 5.6: Classification of water based on percentage Na^+ (US salinity Laboratory, 1954)

Na%	Class	Number of samples	% of samples
<20	Excellent	10	32.26%
20-40	Good	6	19.35%
40-60	Permissible	4	12.90%
60-80	Doubtful	4	12.90%
>80	Unsuitable	7	22.58%
Total		31	100

According to the table above (table 5.6), 64.51% of the samples can be classified as permissible while 12.90% of the groundwater samples fall into the doubtful class. 22.58% of the samples fall into the unsuitable class for irrigation, meaning they have greater Na^+ levels relative to other cations in the groundwater samples.

5.1.2.2.3. Residual Sodium Carbonate (RCS)

High RSC in irrigation water indirectly results in an increase in Na^+ levels in the water which increases Sodium Hazard potential of irrigation water. RSC was calculated using the formula:

$RSC = (HCO_3^-)-(Ca^{2+}+Mg^{2+})$

(Concentrations are in meq/L)

Table 5.7: RSC Classification for the study area

RSC	Class	No. Of samples	% of samples
<1.25	Safe	24	77.42
1.25-2.5	Marginally Suitable	5	16.13
>2.5	Not suitable	2	6.45

Table 5.7 above shows that based on the RSC values for the samples in the study area 77.42% of the samples are safe for irrigation purposes, 16.13% fall under the marginally suitable class and only 6.45% are not suitable. This shows that the majority of the samples have higher Ca^{2+} and Mg^{2+} relative to HCO_3^-.

5.1.2.2.4. Kelly's Ratio

Kelly's ratio assesses irrigation water quality based on the level of Na^+ against Ca^{2+} and Mg^{2+}. Kelly's ratio more than 1 indicates an excess level of Na^+ in the water and therefore the water can be considered unsuitable for irrigation.

This was calculated employing the equation (Kelly, 1963) as:

$$KR = \frac{Na^+}{Ca^{2+} + Mg^{2+}}$$

(Concentrations are in meq/L)

Table 5.8: Kelly's Ratio (Concentrations are in meq/L)

KI	Classification	No. Of samples	% Of Samples
<1	Suitable	20	64.52
>1	Unsuitable	11	35.48

The results from the computed Kelly's ratio (table 5.8) show that 64.52% of the samples are within the recommended KR while 35.48% have excess Na^+.

5.1.2.3. Permeability Index

The quality of irrigation water can affect the permeability of the soil after long term use; this can be measured by computing the Permeability index (PI). PI is influenced by sodium, calcium, magnesium and bicarbonate contents of the soil. It can be classified into three classes; class I and II can be categorised as good for irrigation with ≥ 75% and 75 -25 % respectively permeability while class III water is classified as unsuitable with < 25% of permeability (Doneen, 1964). PI is calculated using the formula:

$$\mathrm{PI} = \frac{(\mathrm{Na}^{+} + \sqrt{\mathrm{HCO_3}^{-}}) \times 100}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+}}$$

Where, all ionic concentrations are expressed in meq/l.

PI values computed for the groundwater samples for the study area ranged from 41.0 to 229, 98% with mean value of 97.29%. According to the classification by Doneen the samples fall in the class I and class II which indicates that they are suitable for irrigation.

5.1.2.4. Magnesium Ratio

The use of water with high magnesium content for irrigation may pose a threat to crop yield as it may cause alkaline condition in the soil. Paliwal (1972) developed an index for calculating the magnesium hazard (magnesium ratio (MR). MR is calculated using the formula:

$$\mathrm{MR} = \frac{\mathrm{Mg}^{2+} \times 100}{\mathrm{Mg}^{2+} + \mathrm{Ca}^{2+}}$$

Where, all ionic concentrations are expressed in meq/l.

The computed MR values for the study area range between 15.48 to 72.14 % with mean value of 40.35%. A value of MR less than 50% is considered suitable for irrigation while more than 50% MR is considered unsuitable for irrigation practice. The results show that 74.19% of the samples from the study area are suitable for irrigation and 22.80% are unsuitable with respect to MR. This indicates that 22.80% of the groundwater samples have a potential to cause alkaline soil which is known to have low infiltration capacity.

5.2 Bivariate Analysis

5.2.1 Correlation Analysis

The relationships between hydro-chemical parameters were studied using correlation analysis and the results are shown in table 5.9. The results show that TDS and EC have a high correlation (r=0.99) with one another and a high to moderate relationship with Na^+, F^-, HCO_3^-, Cl^- and SO_4^{2-}. This suggests that TDS and EC are mostly controlled by these ions. The strong correlation (r=72) between Na^+ and HCO_3^- could be an indication of silicate weathering and ion exchange processes. The strong relationship between EC with Na^+ and EC with Cl^- is due to the relationship these two ions have with salinity (EC) in groundwater, which is directly proportional. The moderate correlation between Na^+ and Cl^- (r=0.65) could also be indicative of halite dissolution as another source of these ions in the groundwater. The correlation between Na^+ and SO_4^{2-} could be attributed to reverse ion exchange processes. Na^+ and HCO_3^- show a moderate positive relationship with pH. This could be an indication of pH on the solubility of these ions.

TH shows a strong positive correlation with Ca^{2+} and Mg^{2+} and weak but significant correlation with SO_4^{2-} . The strong correlation of Ca^{2+} and Mg^{2+} with TH shows and is mainly due to the fact that Ca^{2+} and Mg^{2+} are the main cations responsible for hardness in water. The strong correlation between Ca^{2+} and Mg^{2+} (0.87) could be an indication of carbonate dissolution as a source of these ions. The correlation between Ca^{2+} and SO_4^{2-} may indicate gypsum or anhydrite as another source of these ions in the water, but because the correlation is not strong it shows that gypsum or anhydrite dissolution is not the main source.

Table 5.9: Correlation analysis

Correlations														
		TDS	Ec	TH	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HO_3^{-}	Cl^{-}	F^{-}	SO_4^{2+}	NO_3^{-}
TDS	Pearson Correlation	1												
Ec	Pearson Correlation	**0.989****	1											
TH	Pearson Correlation	0.432*	0.428*	1										
pH	Pearson Correlation	0.494**	0.440*	-0.166	1									
Ca^{2+}	Pearson Correlation	0.444*	0.443*	**0.979****	-0.191	1								
Mg^{2+}	Pearson Correlation	0.346	0.341	**0.952****	-0.160	**0.873****	1							
Na^{+}	Pearson Correlation	**0.809****	**0.807****	-0.078	**0.518****	-0.007	-0.199	1						
K^{+}	Pearson Correlation	0.192	0.254	0.161	-0.041	0.217	0.110	0.315	1					
HO_3^{-}	Pearson Correlation	**0.925****	**0.873****	0.377*	**0.580****	0.366*	0.324	**0.721****	0.025	1				
Cl^{-}	Pearson Correlation	**0.690****	**0.760****	0.284	0.171	0.305	0.222	**0.648****	0.385*	0.499**	1			
F^{-}	Pearson Correlation	**0.562****	**0.524****	-0.250	**0.523****	-0.191	-0.351	**0.742****	-0.072	**0.579****	0.285	1		
SO_4^{2-}	Pearson Correlation	**0.645****	**0.630****	**0.492****	0.320	**0.519****	0.387*	**0.504****	0.244	**0.510****	0.360*	0.264	1	
NO_3^{-}	Pearson Correlation	-0.075	-0.024	0.271	-0.283	0.252	0.283	-0.227	0.065	-0.157	0.221	-0.331	-0.014	1
**. Correlation is significant at the 0.01 level (2-tailed).														
*. Correlation is significant at the 0.05 level (2-tailed).														

5.3 Classical Hydro-chemical Methods

5.3.1 Hydro-Chemical Facies

The Piper diagram and the Chadha's diagram were used to determine the nature of the hydro-chemical facies in the study area. Figure 5.8 shows the Piper diagram created using the groundwater samples from the study area. In the HCO3-Cl-SO4 triangle most samples are clustered in the HCO_3^- corner with only two closer to the SO_4^{2-} end member and only one in the Cl^- corner. This shows the dominance of HCO_3^- amongst other anions in the water types and indicates the alkaline nature of the water as observed in section 5.1. In the Mg-Ca-Na cation triangle are distributed in a curved path from in-between Ca^{2+} and Mg^{2+} to the Na^+ corner.

This classification with the samples from the study area produced four hydro-chemical facies, which are:

- Ca-Mg-HCO3
- Na-HCO3
- Ca-Na-SO4-HCO3 (Mixed water type)
- Na-Cl

The most occurring water type in the area is the Ca-Mg-HCO3 followed by Na-HCO3, only two samples showed the occurrence of the Ca-Na-SO4-HCO3 water type and only one samples reflected the Na-Cl water type.

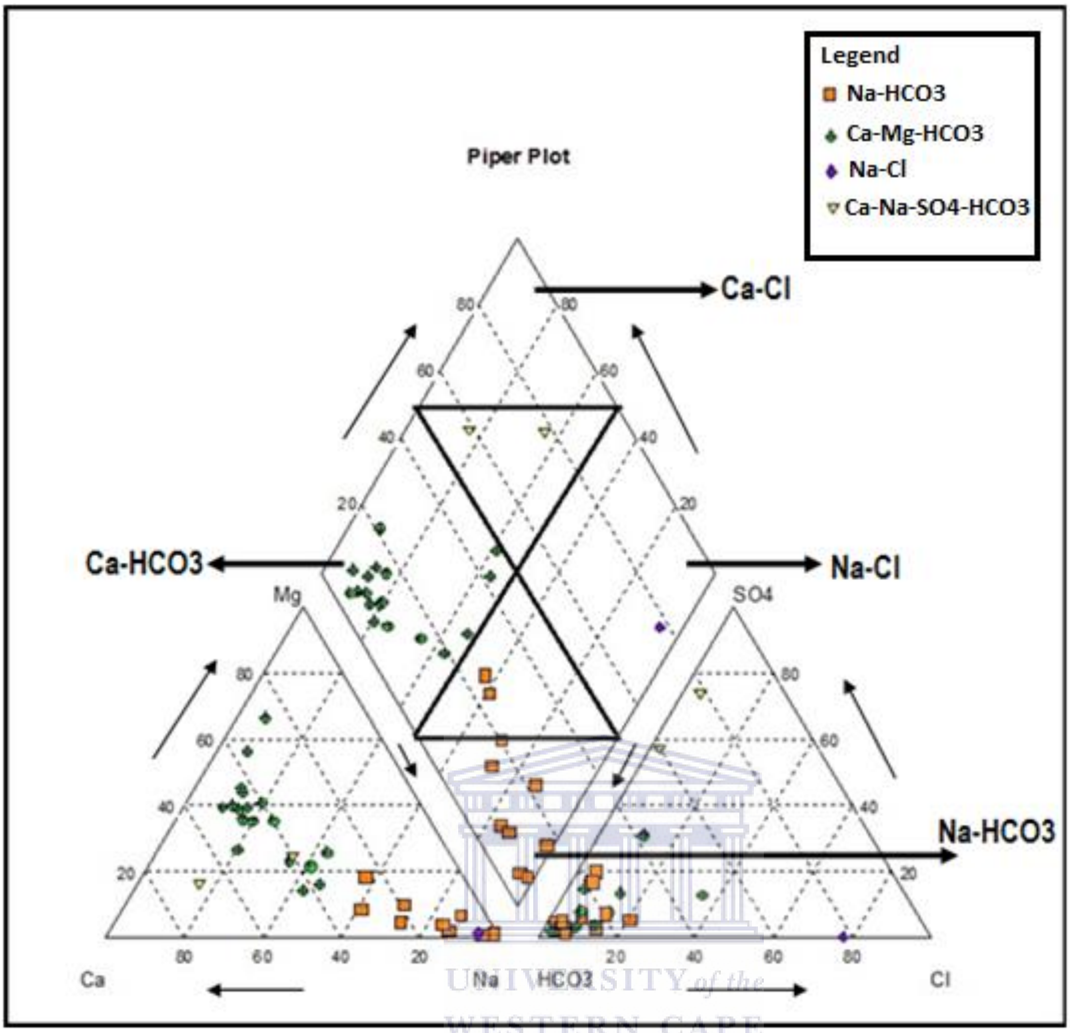

Fig 5.8: Piper plot showing hydro-chemical facies in the study area

Figure 5.9 shows Chadha’s diagram plotted using the groundwater data from the study area. Similar to the piper diagram four water types/facies were generated by the plot. The diagram shows that in most of the groundwater samples the weak acids exceed the strong acids and the alkali earth metals exceed the alkali metals. From this diagram it can be inferred that HCO_3^-, Ca^{2+}, Mg^{2+} and Na^+ are the most dominant ions in the aquifer. The water types deduced from the plot are Ca-Mg-HCO3, Na-HCO3, Ca-SO4 and Na-Cl which are similar to the ones produced by the piper diagram.

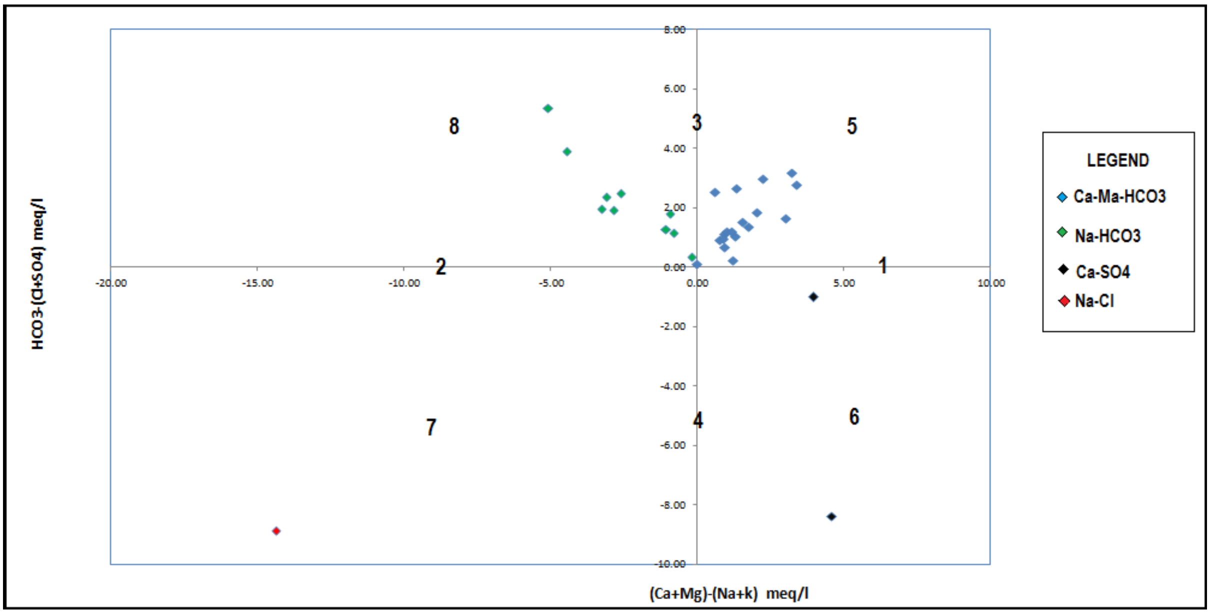

Fig 5.9: Chadha's diagram showing geochemical classification and hydro-chemical processes of groundwater in the study area.

Map in figure 5.10 shows the distribution of the hydro-chemical facies in the study area and their borehole location. The Ca-Mg-HCO3 facies mainly found in 18 of the boreholes in the study area, these boreholes are mainly distributed in the Vryheid Fm and in the contact zones between the Karoo dolerite with the Volksrust Fm and with the Vryheid Fm. This type of water is characterised by combined concentrations of Ca^{2+}, Mg^{2+} and HCO_3^- that exceeds 50% of the total dissolved constituent load in meq/L. Such waters are typical of fresh and shallow groundwaters. This water type is mainly attributed to the dissolution of carbonate minerals.

Na-HCO3 characterises 10 boreholes in the study area, which are situated in the Vryheid Fm and Karoo dolerite. This type of facies generally indicates the occurrence of ion exchange processes in the area. It could also be attributed to silicate weathering, because of the high levels of Na^+ and HCO_3^- which are end products of Albite weathering.

Ca-Na-SO4-HCO3 water type is a product of mixing of types characterises only two boreholes. This water type is mainly distributed in the contacts between the Vryheid Fm and Karoo dolerite. High Ca^{2+}, Na^+, SO_4^{2-} and HCO_3^- ions in this water type could be attributed to the combined influence of silicate weathering, calcite dissolution, ion exchange processes and gypsum dissolution.

Na-Cl facies is only found in one sample, which is situated in the Vryheid Fm. This facies is characterised by high levels of Na^+ and Cl^- ions, which could be attributed to halite dissolution and ion exchange processes.

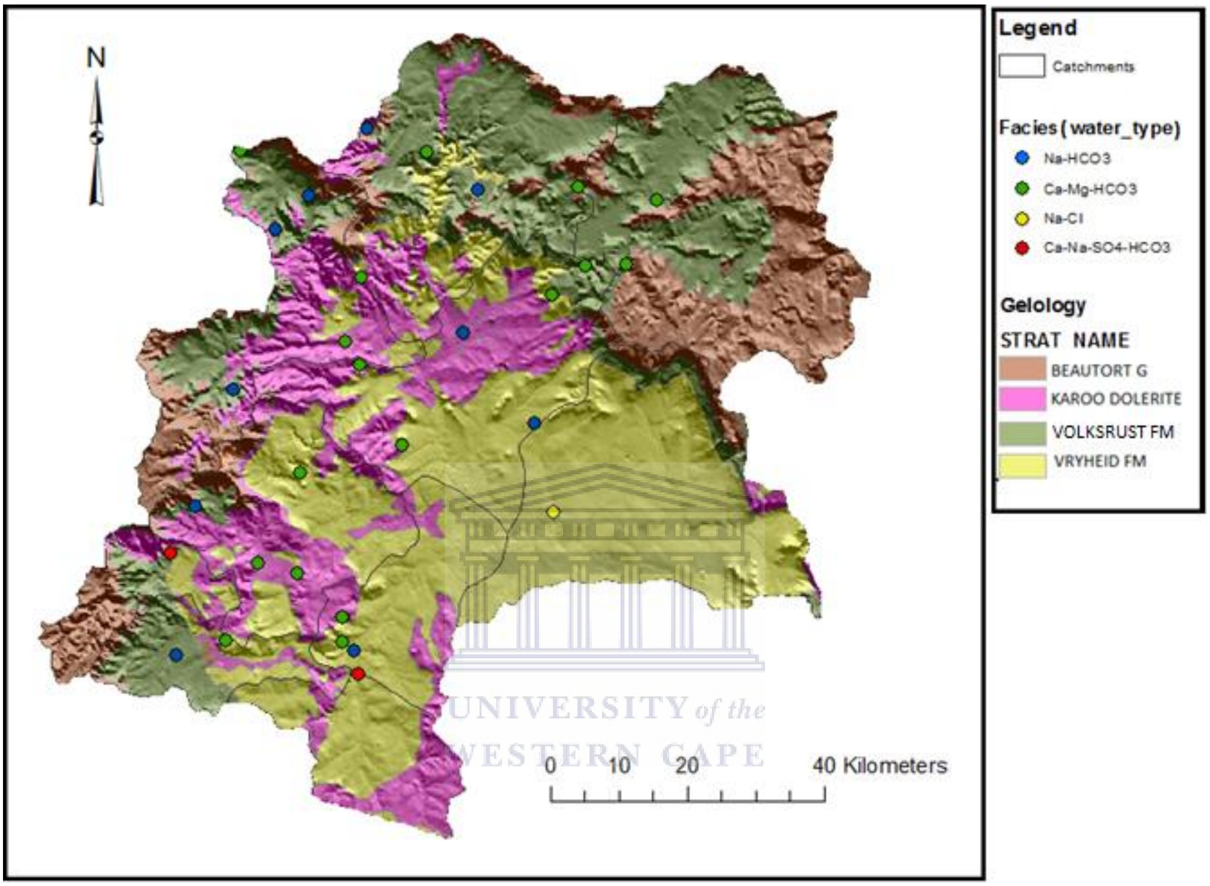

Fig 5.10: Map showing spatial distribution of Hydro-chemical facies/water type in the study area

Table 5.10 shows the descriptive statistics for the water types in the study area. The Ca-Mg-HCO3 water type characterises 58.06% of the groundwater samples and has the lowest concentrations of total dissolved solids. This water type also has the highest level of TH; hardness in this type of water is temporary and is mainly caused by calcium carbonates. The Na-HCO3 characterises 32.25% of the groundwater samples and has high pH, Na^{2+} and HCO_3^- levels, this shows that this water type is alkaline in nature. The Ca-Na-SO4-HCO3 which comprises 6.45% of the groundwater samples has high levels of Ca^{2+}, Mg^{2+}, Na^+, TDS and TH, this type of water can be characterised as hard water. The Na-Cl which only represents 3.2% of the groundwater samples has high Na^+, K^+, Cl^-, TDS and EC values and can be characterised as brackish water.

Table 5.10: Descriptive statistics for the hydro-chemical facies

Parameters	Ca-Mg-HCO3 (N=18)			Na-HCO3 (N=10)			Ca-Na-SO4-HCO3 (N=2)			Na-Cl (N=1)
	Range	Mean	STDEV	Range	Mean	STDEV	Range	Mean	STDEV	Value
pH	6.87-8.24	7.61	0.43	6.65-10.09	8.13	0.86	8.05-8.07	8.06	0.01	7.42
TDS	29.00-693.00	250.22	165.87	70-621	297.60	151.42	432.00-1091.00	761.50	465.98	1065.00
EC	4.9-82.60	31.12	20.44	11.2-68.20	34.70	15.86	56.00-138.00	97	57.98	186.00
Ca^{2+}	1.9-56.00	25.12	14.77	0.5-25	8.19	7.88	79.20-123.60	101.4	31.40	14.90
Mg^{2+}	0.5-31.70	13.35	8.92	0.5-4.4	1.93	1.50	11.80-25.24	29.65	25.24	2.700
Na^{+}	2.7-90.60	19.25	24.91	9.3-144.10	67.93	38.64	21.10-125.50	73.05	73.47	350.50
K^{+}	0.15-4.84	1.28	1.18	0.15-3.67	1.59	1.23	1.77-4.01	2.89	1.58	3.26
HCO_3^{-}	13.30-290.00	132.13	74.24	32.60-355.30	162.44	89.09	134.70-197.30	166	44.26	211.60
Cl^{-}	1.5-79.10	10.48	18.64	1.5-13.3	6.95	4.08	4.00-23.40	13.71	13.71	430.70
SO_4^{2-}	2.00-124.00	14.57	29.14	2.00-34.30	10.43	11.09	12.03-2.26	13.63	2.26	2.00
F^{-}	0.1-0.57	0.29	0.14	0.21-1.91	0.79	0.59	0.32-0.50	0.41	0.13	0.81
NO_3^{-}	0.02-4.79	0.91	1.45	0.02-1.20	0.28	0.44	0.05-0.06	0.06	0.01	0.40
TH	6.8-258.84	117.72	66.50	3.31-80.54	28.40	25.10	246.35-504.23	375.29	182.39	48.32

5.3.2 Major Ion chemistry

During movement of groundwater through its flow path, a number of processes occur which gives rise to the ionic composition of the groundwater. The major ion chemistry of the groundwater is a result of these processes and can therefore be used to determine the major processes that are responsible for the composition of the groundwater.

5.3.2.1 Rock Water Interaction

The TDS vs. Na^+/ (Na^++Ca^{2+}) and TDS vs. Cl^-/ (Cl^-+HCO_3^-) (Gibbs, 1970) scatter plot can be used to identify the occurrence of rock-water interaction processes. The diagram is divided into three fields, the rock-water interaction, precipitation and evaporation. In these diagrams the samples falling in the centre of the curve indicate an origin from rock-water interaction. Fig 5.11.a and b represent Gibbs TDS vs. Na^+/ (Na^++Ca^{2+}) and TDS vs. Cl^-/ (Cl^-+HCO_3^-) scatter plots plotted using groundwater samples from the study area . These results show that most of the groundwater samples fall in the centre of the curve, which is indicative of the dominance rock-water interaction as the main process in the study area.

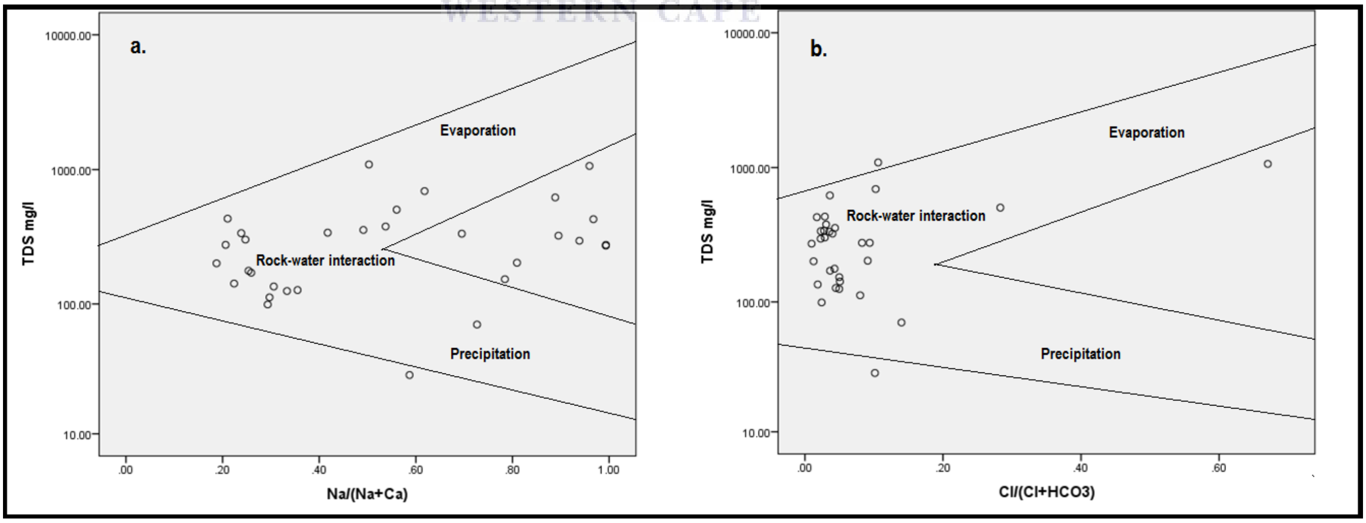

Fig 5.11: Rock-water interaction diagram

During the process of rock-water interaction a variety of chemical processes occur such as weathering and dissolution, ion exchange processes oxidation and reduction. The results in figures 5.11.a and b can be further classified into the above mentioned chemical processes by using their concentrations and associations.

5.3.2.1.1. Weathering and Dissolution

Carbonate weathering, silicate weathering, halite, gypsum dissolution and precipitation are common in an aquifer system (Elango and Kannan, 2007). Datta and Tyagi (1996) explained this using the Ca^{2+}+Mg^{2+} vs HCO_3^-+ SO_4^{2-} scatter plot (Fig 5.12). They explained that the points falling along the equiline suggest that these ions have resulted from weathering of carbonates, sulphate minerals (gypsum and anhydrite) and silicate minerals. They further explained that those that lie above the equiline are due to silicate weathering while those below the line are due to carbonate weathering.

Fig 5.12 represents the Ca^{2+}+Mg^{2+} vs HCO_3^-+ SO_4^{2-} scatter plot plotted using the groundwater samples from the study area, almost 50% of the sample points plot above the equiline, which indicates the dominance of silicate weathering in the study area. While the remaining points plot along the equiline which suggest the combined influence of weathering of carbonates, sulphate minerals (gypsum and anhydrite) and silicate minerals

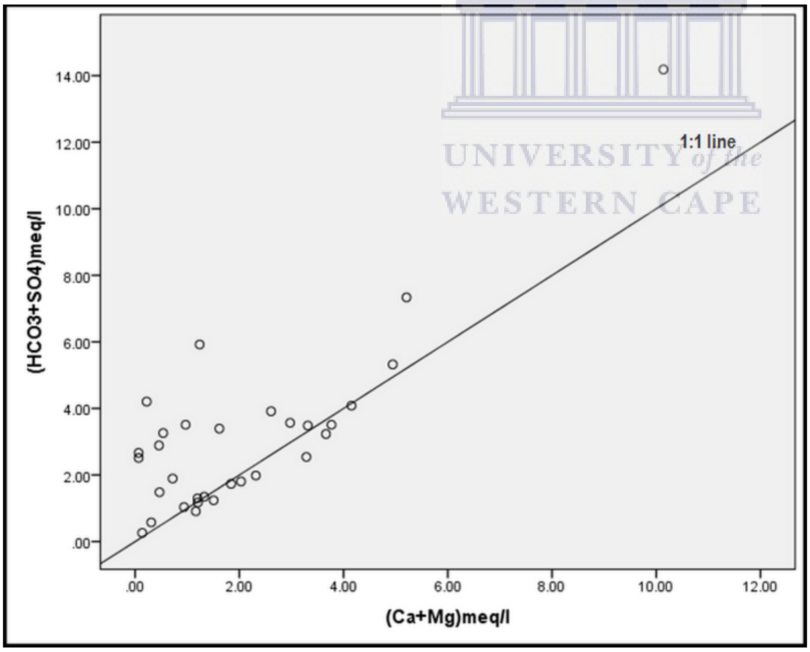

Fig 5.12: Ca^{2+}+Mg^{2+} vs HCO_3^- +SO_4^{2-}

In a silicate terrain, if the calcium and bicarbonate in groundwater originated from calcite, the equivalent ratio of dissolved Ca^{2+} and HCO_3^- in the groundwater should be 1:2, whereas if from dolomite weathering, it should be 1:4 (Subramani et al., 2010). In the Ca^{2+} vs HCO_3^- (fig 5.13) scatter plot, sample points that plot along the 1:2 line indicate contribution from calcite while those that plot along the 1:4 line indicate contribution from dolomite. Most of sample points from the study area plot along the 1:2 which indicates the dominance of calcite over dolomite as the source.

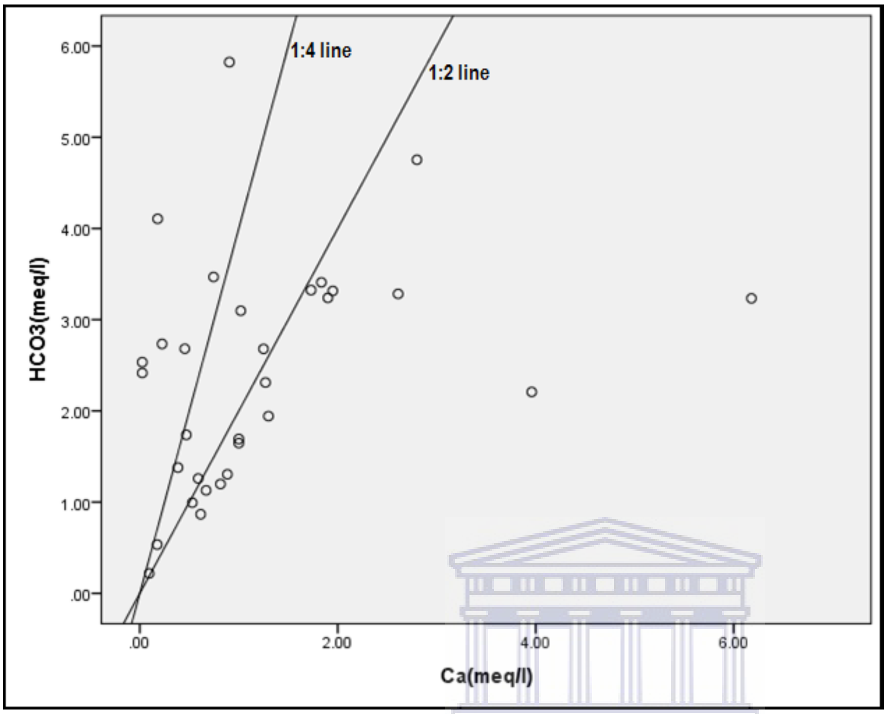

Fig 5.13: Ca^{2+} vs. HCO_3^- scatter diagram

Another source of Ca^{2+} and SO_4^{2-} in groundwater systems could be gypsum/anhydrite dissolution. If gypsum/anhydrite dissolution is the major source of the calcium and sulphate in the groundwater then the Ca^{2+}/SO_4^{2-} ratio should be almost 1:1 (Das and Kaur 2001). Ca^{2+} vs SO_4^{2-} (Fig 5.14) shows that most of the sample points plot below the 1:1 line, which indicates the excess of calcium over sulphate and highlights additional geochemical processes as the source of these ions.

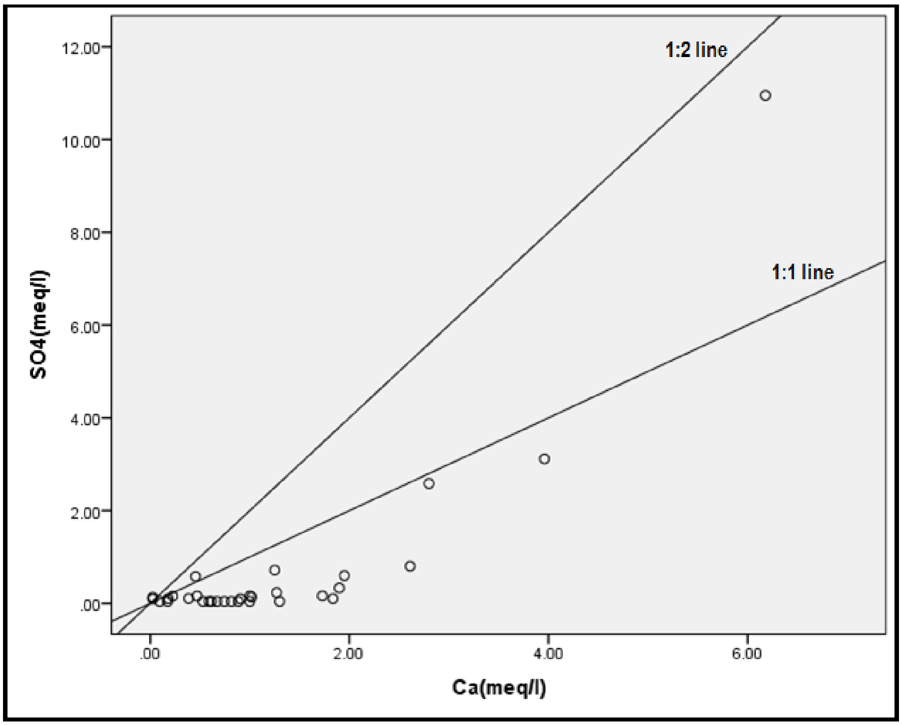

Fig 5.14: Ca^{2+} vs. SO_4^{2-} scatter diagram

Rock source deduction done using AquaChem software suggests that if the ratio of (Na^++K^+-Cl^-)/ (Na^++K^+-Cl^-+Ca^{2+}) is > 0.2 and < 0.8 then plagioclase weathering is possible but if the ratio is < 0.2 and > 0.8 then plagioclase weathering is unlikely. 51.61 % of the samples have values > 0.2 and < 0.8 shows the likelihood occurrence of plagioclase weathering and 48.39% have values that fall into < 0.2 and > 0.8 range, this suggests that another source of Ca^{2+} ions could be plagioclase.

The contribution of silicate weathering to cation concentration of the groundwater can also be explained (Na^+ + K^+)/Total cation index (Stallard and Edmond, 1983; Elango and Kannan, 2007). The Na^+ + K^+ vs. TZ^+ (Fig 5.15a) scatter plot shows that majority of the points plot above the 1: 1 and near the Na^+ + K^+=0.5*TZ^+, which suggest that cation in the groundwater might have been derived from silicate weathering. However, there are those few that deviate from this line, this suggest the likelihood of Ca^{2+}/Na^+ exchange processes which might have reduced the amount of Na^+ in the groundwater.

The Ca^{2+}+Mg^{2+} vs. TZ (fig 5.15b) scatter plot can also be used to verify the role of silicate weathering in cation concentration of groundwater (Maharana et al., 2015). Majority of the sample points lie above the 1:1 line and along the $Ca^{2+}+Mg^{2+} = 0.6*TZ$ line, this suggest an increasing contribution of Na^+ and K^+ from silicate weathering.

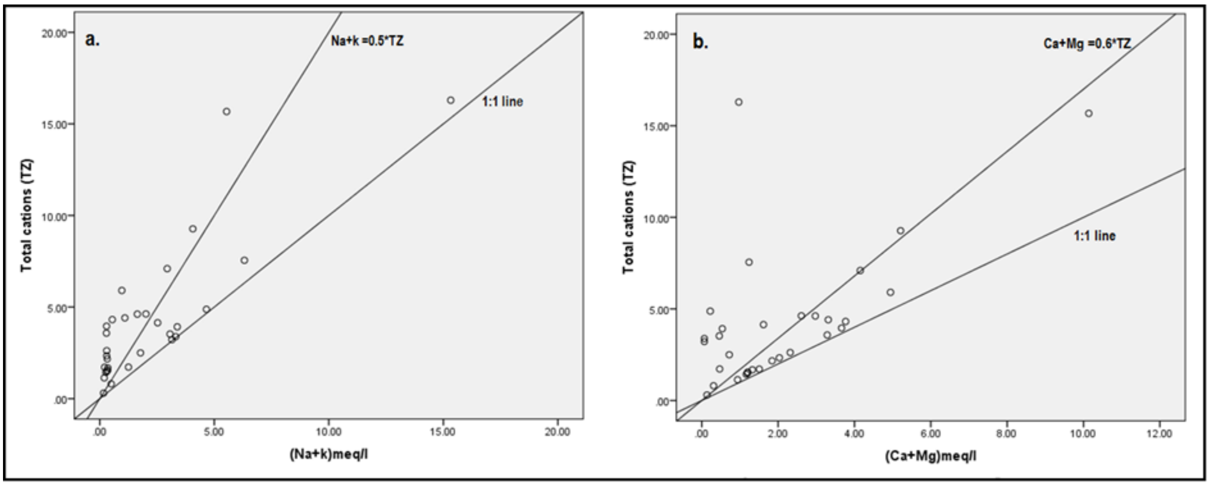

Fig 5.15 a: Na^++K^+ vs Total cations (TZ); 3b Ca^{2+} +Mg^{2+} vs Total cations (TZ)

The occurrence of silicate weathering in the study area can also be indicated by rock source deduction done using AquaChem. It suggests that if the value of TDS in the groundwater samples is greater than 500 mg/l then carbonate weathering or brine or seawater are the source and if TDS is less than 500 mg/l then it is due to silicate weathering. 83.87% of the groundwater samples have TDS values less than 500 mg/l which indicates the dominance of silicate weathering over carbonate weathering in the study area.

The dissolution of halite (NaCl) is understood as one of the major sources of both sodium and chloride in groundwater. In general, when halite dissolution is the source of these ions, Na^+ vs. Cl^- relationship gives 1:1 ratio (Nur et al., 2012). The Na^+ vs. Cl^- diagram (fig 5.16) of the study area shows that most groundwater samples fall below the equiline which indicates that halite dissolution is not the major process responsible for the Na^+ and Cl^- ion concentration in the groundwater. The enrichment of Na^+ more than Cl^- points to silicate weathering as a more likely source of Na^+ in the water.

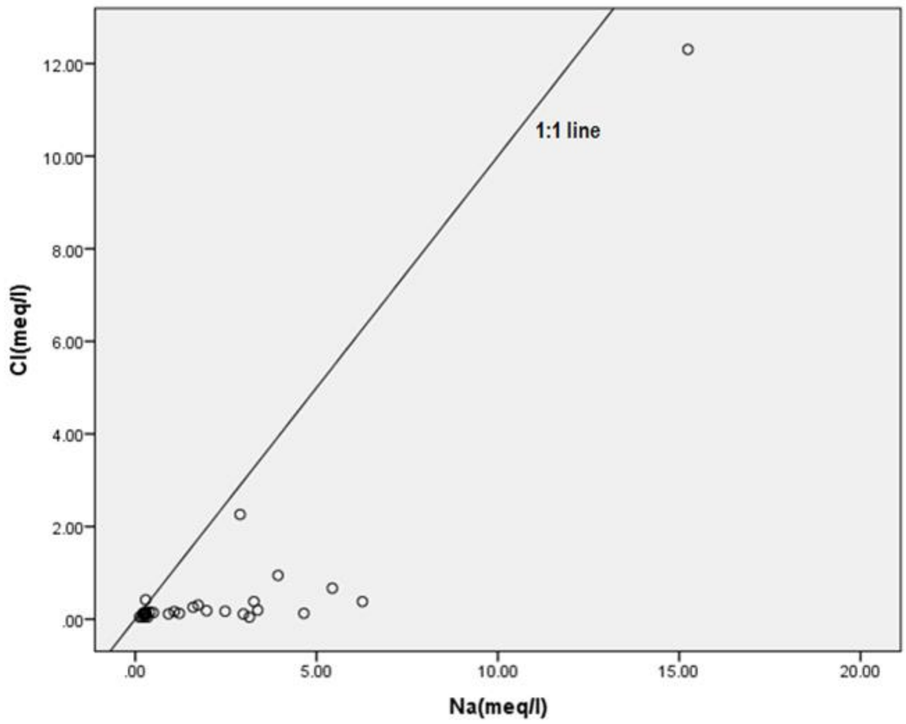

Fig 5.16: Relationships between Na^+ and Cl^-.

AquaChem rock source deduction also confirms another source of sodium in the groundwater samples other than halite. The software uses the ratio of ($Na^+/(Na^++Cl^+$) to deduce the source of sodium in the samples, if the ratio equals to 0.5 the sodium comes from a halite solution, if the ratio is greater than 0.5 it indicates sodium source other than halite. For all the groundwater samples in the study area the ratio is greater than 0.5 which indicates another source of sodium other than halite.

5.3.2.1.2 Ion Exchange processes

Fisher and Mullican (1997) reported that if ion exchange is a significant composition controlling processes in groundwater, the relationship between (Na^+- Cl^-) vs (Ca^{2+}+ Mg^{2+}) – (HCO_3^- + SO_4^{2-}) should be linear with a slope of −1.0. Figure 5.17 shows the ion exchange scatter plot for the groundwater samples from the study area. The groundwater samples of the study area define a straight line (R^2= 0.98) with a slope of −0.9, which indicates the occurrence of ion exchange in the study area.

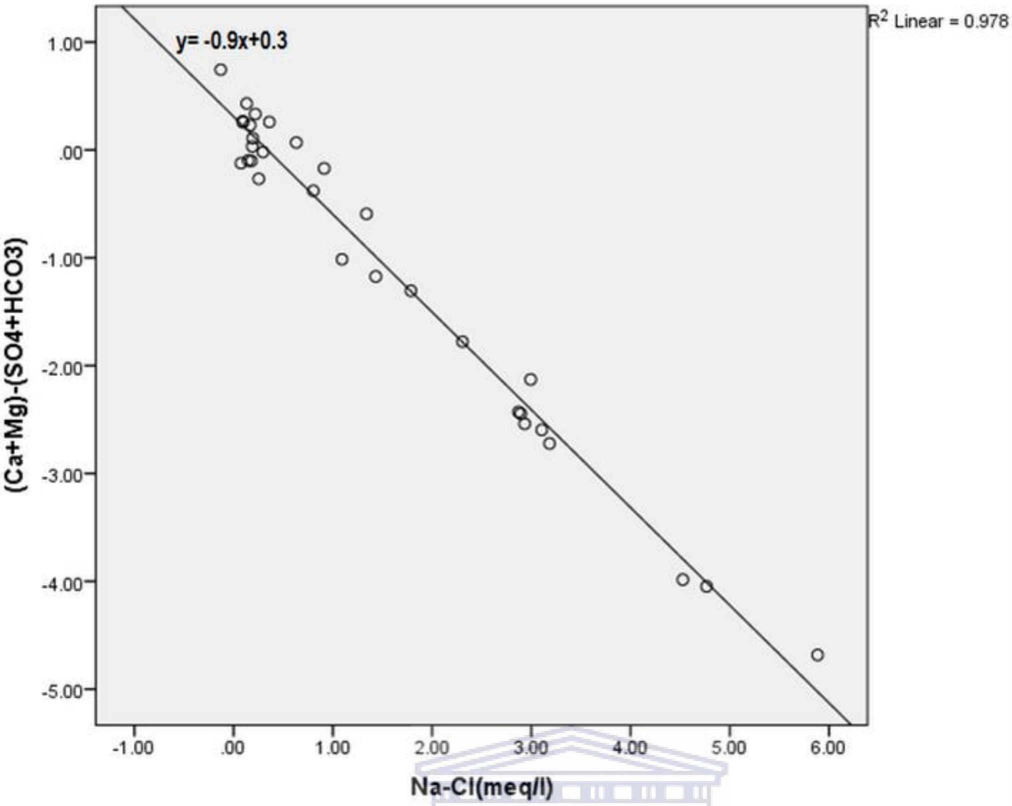

Fig 5.17: Ion exchange scatter diagram.

Further, it is reported that the plot for Ca^{2+} $+Mg^{2+}$ vs SO_4^{2-} + HCO_3^- can be used as an identifier of ion exchange process (Srinivasamoorthy et. al., 2012). If normal ion exchange is the process, the points shift to left side of the plot due to excess SO_4^{2-} + HCO_3^-. If reverse ions exchange is the process, points shift right due to excess Ca^{2+} $+Mg^{2+}$. In the Ca^{2+} $+Mg^{2+}$ vs SO_4^{2-} + HCO_3^- (fig 5.12) the most points shift to left side of the plot due to excess SO_4^{2-} + HCO_3^-, which is indicative of normal ion exchange in the study area.

Ca^{2+}+Mg^{2+} versus Na^+ plot can also be used to indicate the type 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 in this plot. Figure 5.18 shows the most of the samples fall toward the Ca^{2+}+Mg^{2+} concentration, indicating the occurrence of reverse ion exchange in the area.

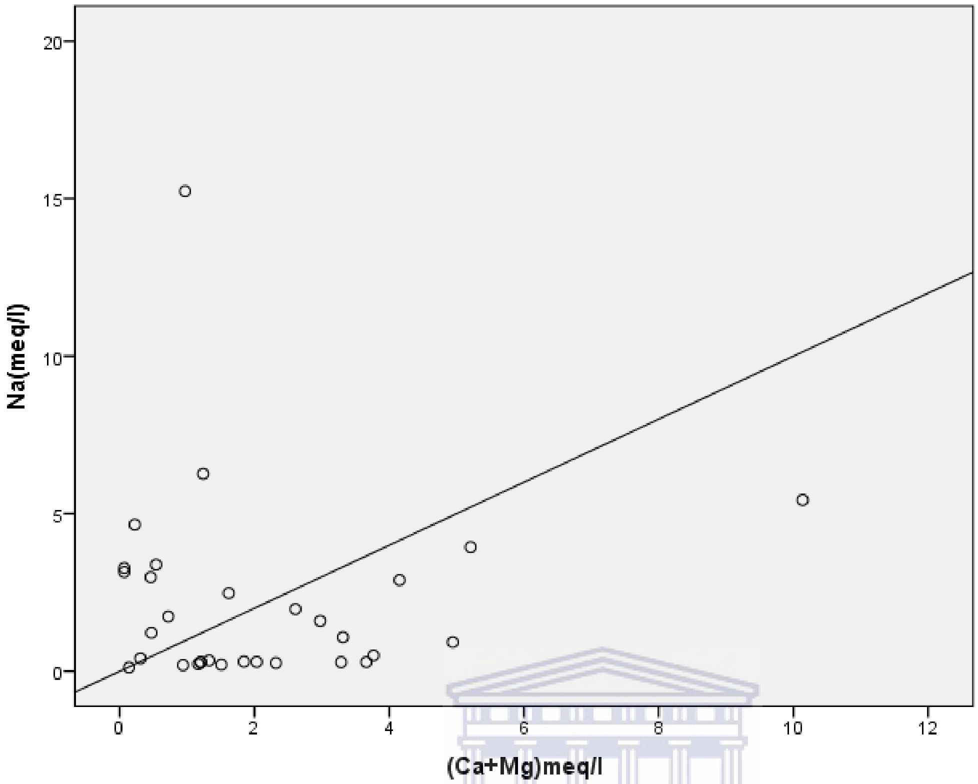

Fig 5.18: Na$^+$ vs. Ca^{2+}+Mg^{2+} plot showing increased concentration of Ca^{2+} compared to Na$^+$ indicating reverse ion exchange.

5.3.2.2. Evaporation

Evaporation is also one of the important processes that affect groundwater chemistry and the Gibbs plot in figure 5.11 shows some influence of evaporation in some samples in the study area. Na$^+$/Cl$^-$ ratio could be used to identify the evaporation process in groundwater (Subramani et. al, 2010). Evaporation will increase the concentration of total dissolved solids in groundwater, and the Na$^+$/Cl$^-$ ratio remains the same, and it is one of the good indicating factors of evaporation. If evaporation is the dominant process, Na$^+$/Cl$^-$ ratio should be constant when EC rises (Jankowski and Acworth 1997).

Figure 5.19 shows an inclined trend; Na$^+$/Cl$^-$ ratio slightly decreases with an increase in EC and only a few samples show an increase the concentration of total dissolved solids in groundwater as Na$^+$/Cl$^-$ ratio remains constant . This confirms that evaporation though might have played a part in the concentration of ions in the groundwater in the study area; it is not the main processes and this is also confirmed by figure 5.11.

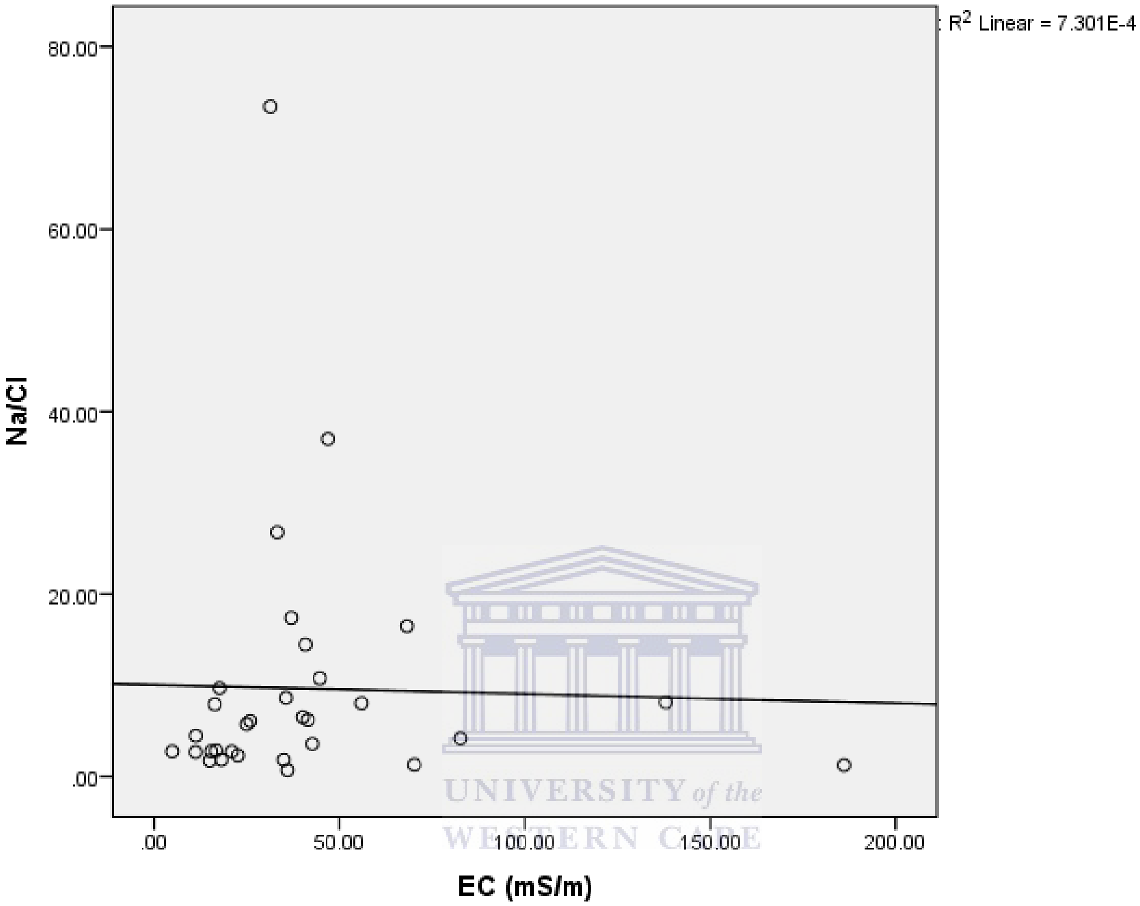

Fig 5.19: Relationships between Na^+/Cl^- and EC

5.3.2.3 Land use

Apart from the natural/geological controls on groundwater chemistry, land use plays a major role in altering the chemistry of groundwater. The correlation between sulphate and chloride can provide evidence or indicate the effects of surface contamination, especially irrigation return flows. If the correlation is strong it is indicative of a possible strong in influence of land use on groundwater chemistry (Subramani et al., 2010). Figure 5.20 represents the Cl^- vs SO_4^{2+} scatter plot for the study area. It shows that the relationship between Cl^- and SO_4^{2-} is not strong, which indicates that land use is not a major composition controlling processes in the study area.

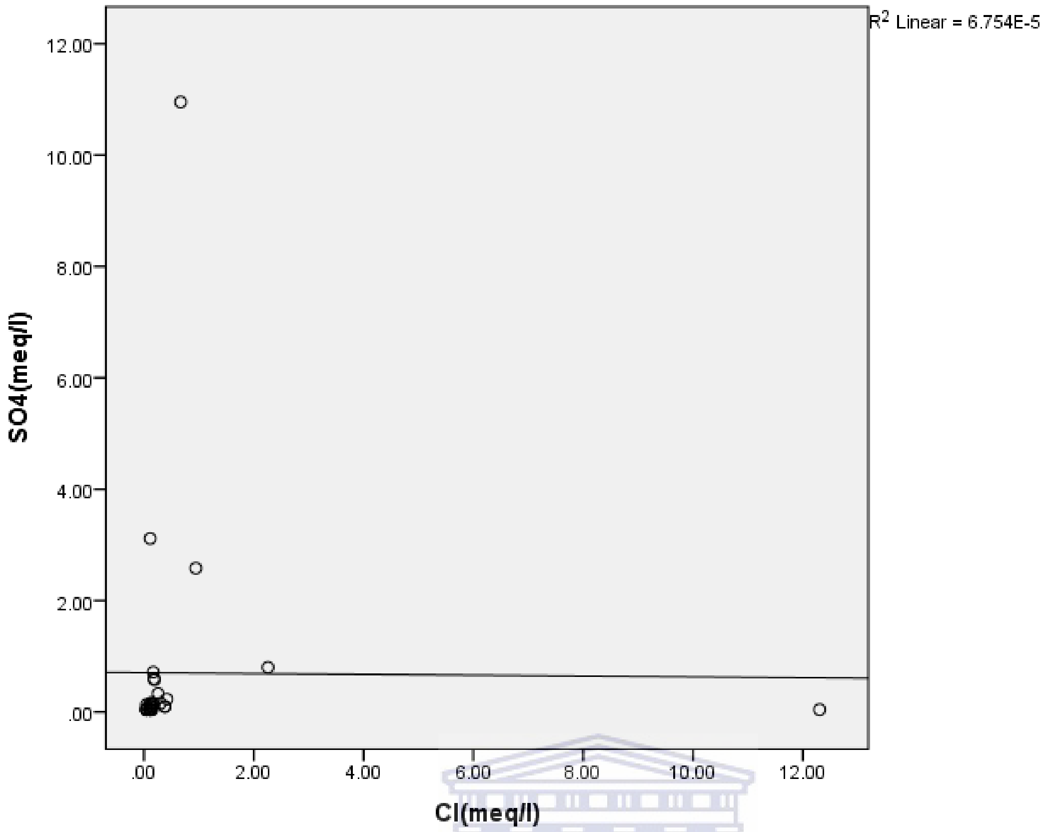

Fig 5.20: Cl^- Vs SO_4^{2-} (effect of land use on groundwater chemistry)

5.3.3. Spatial Distribution of Major Ions

The spatial distribution of major ions Ca^{2+}, Mg^{2+}, Na^+, k^+, HCO_3^-, Cl^-, SO_4^{2-} and NO_3^- in the study area is illustrated in the figures below. The distribution trends are analysed and correlated to the geology and land use. Most of these ions showed higher concentration in the southern part of the area in the Vryheid Fm.

Figure 5.21 and figure 5.22 show the spatial distribution of Ca^{2+} and Mg^{2+} respectively. Ca^{2+} and Mg^{2+} show similar distribution, they are higher towards southern part of the study area. They show high values in the dolerite, Volksrust Fm and Vryheid Fm. As mention in the section 5.3.2, the occurrence of these major ions is predominantly due to silicate weathering and carbonate weathering. Mg^{2+} is mostly higher in the dolerite than in the other formation, this is mostly attributed to its natural levels in the dolerite. Ca^{2+} is mostly higher in the Vryheid Fm which is most likely due to weathering of plagioclase in the silicate rocks and calcite dissolution.

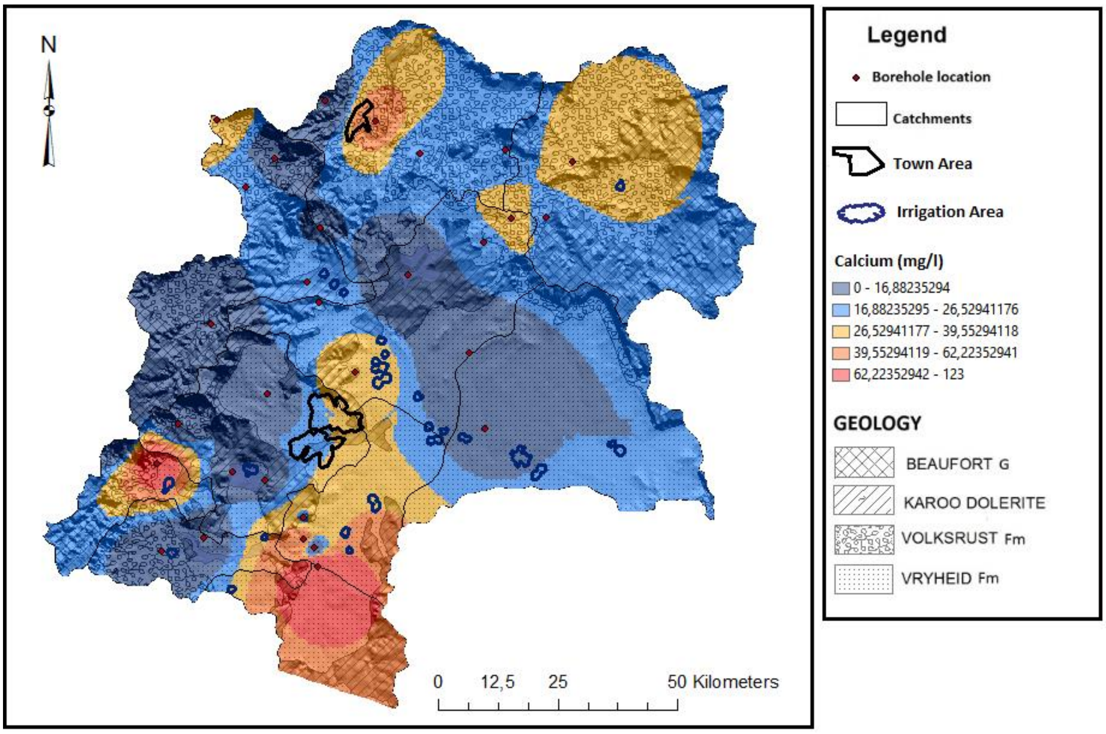

Fig 5.21: Spatial distribution of Ca^{2+}

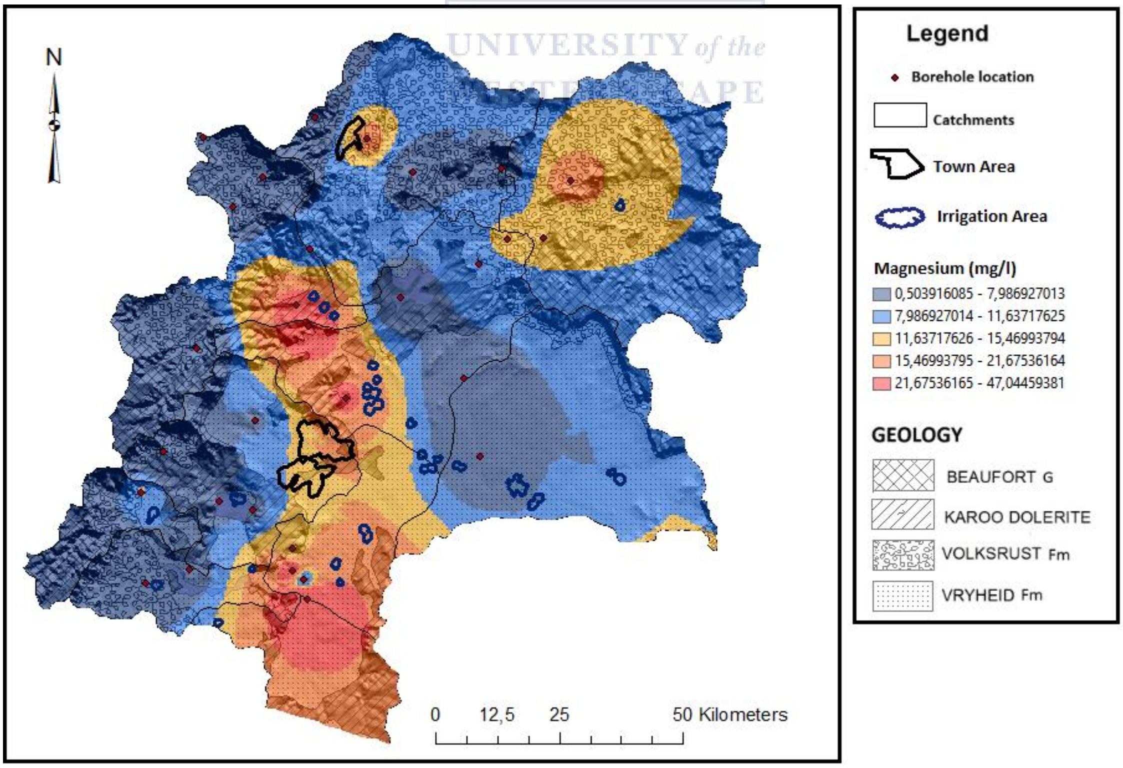

Fig 5.22: Spatial distribution of Mg^{2+}

Na^+ is mostly higher in the south eastern parts of the study area in the Vryheid Fm (5.23). High Na^+ in the study area is mainly attribute to silicate weathering, ion exchange processes and in some parts halite dissolution.

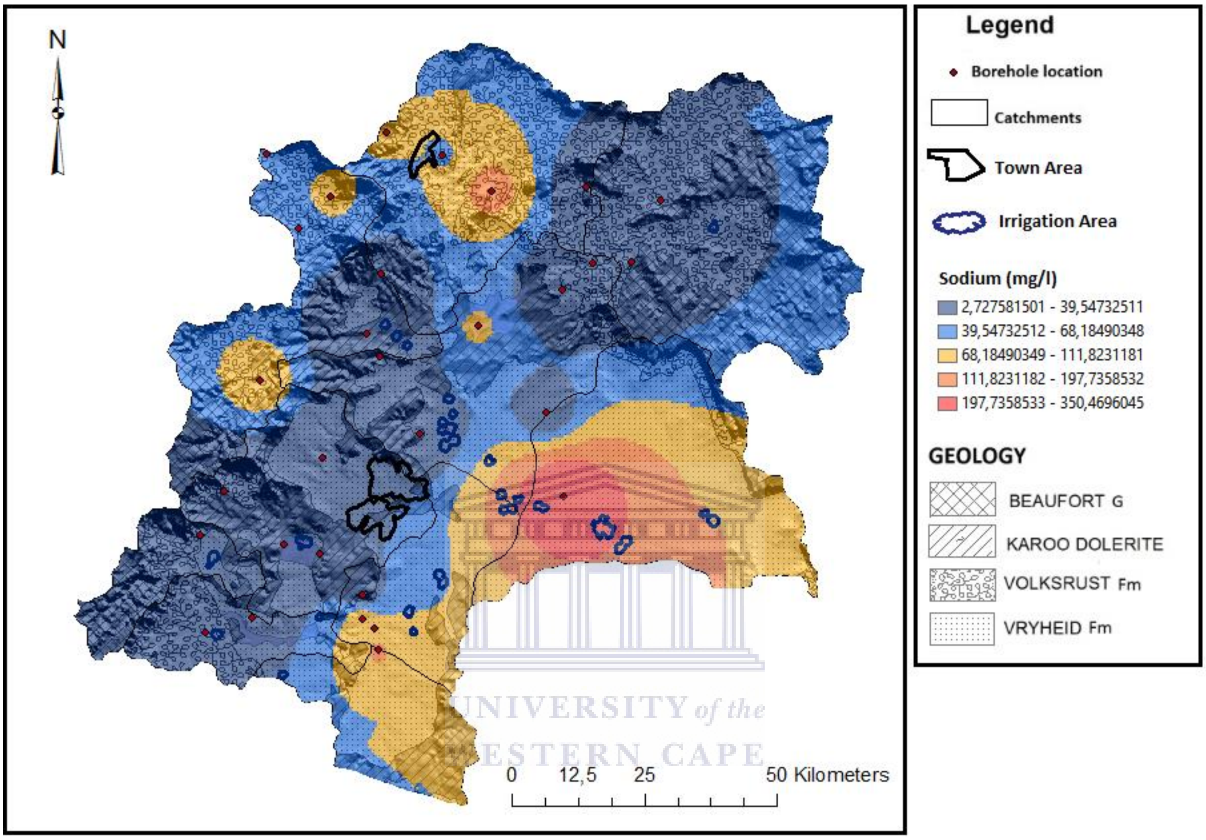

Fig 5.23: Spatial distribution of Na^+

HCO_3^- concentrations are generally higher throughout the area except in the south west corner of the map (fig 5.24). High concentrations of HCO_3^- in the Vryheid and Volksrust Fm can be attributed to the weathering of plagioclase and the dissolution of calcite.

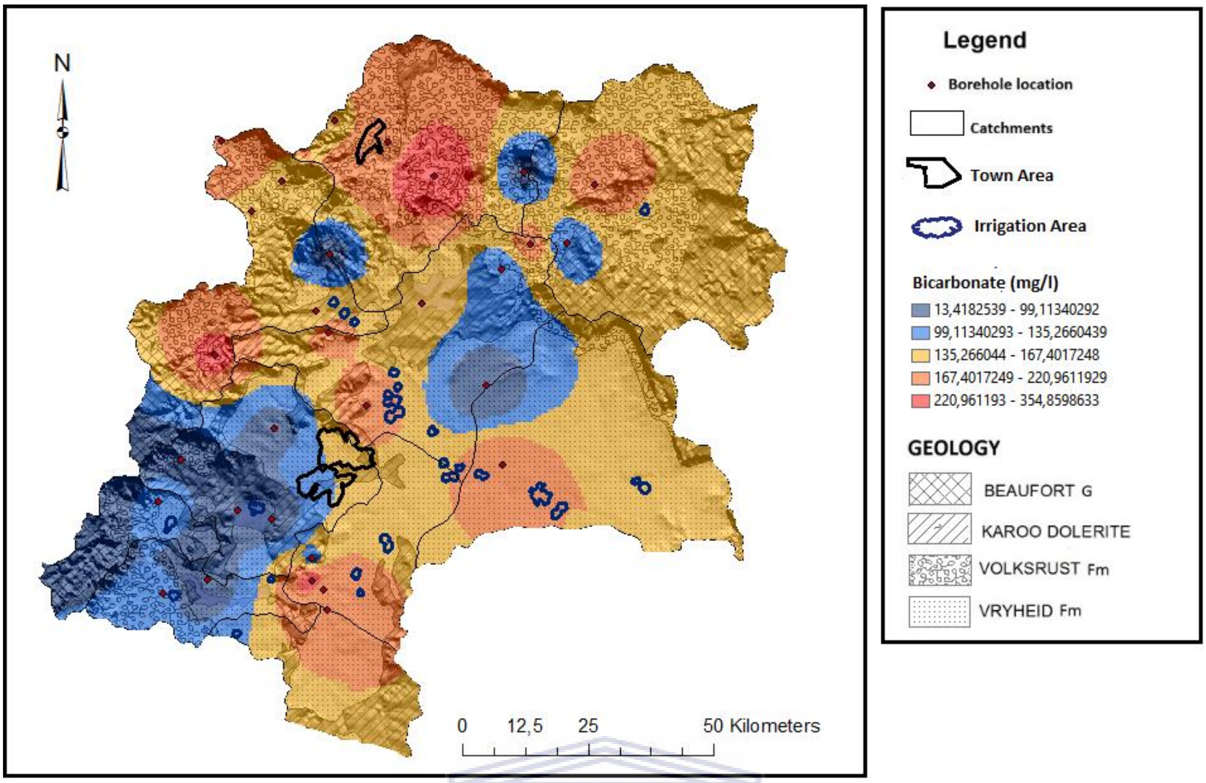

Fig 5.24: Spatial distribution of HCO_3^-

Fig 5.25 and Fig 5.26 illustrate the distribution of Cl^- and SO_4^{2-} respectively. Cl^- is mostly high in the south eastern part of the study area in borehole 13, same borehole where Na^+ is high. This could be indicative of some halite dissolution in this area. SO_4^{2-} is mostly higher in the southern area in borehole 31 in the Vryheid Fm, similar to that of Ca^{2+} and Mg^{2+}. SO_4^{2-} and Ca^{2+} both show high concentration in boreholes 24 and 31, this could be indicative of gypsum/anhydrite dissolution as a source of SO_4^{2-} in that area.

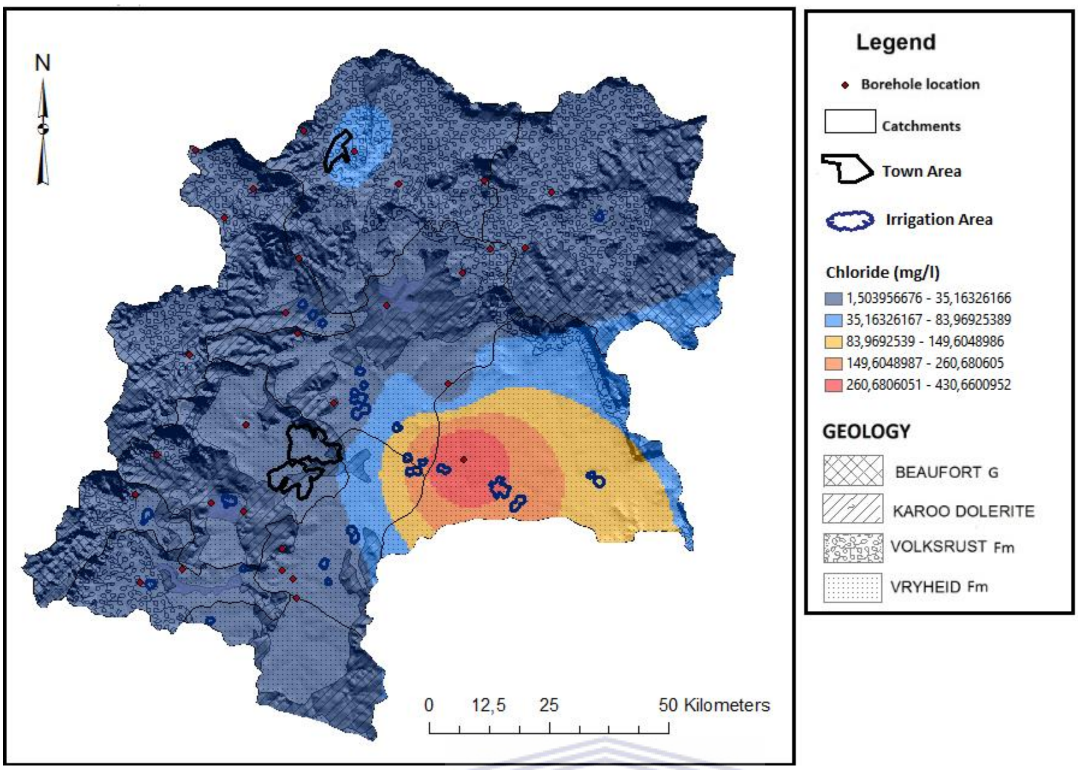

Fig 5.25: Spatial distribution of Cl^-

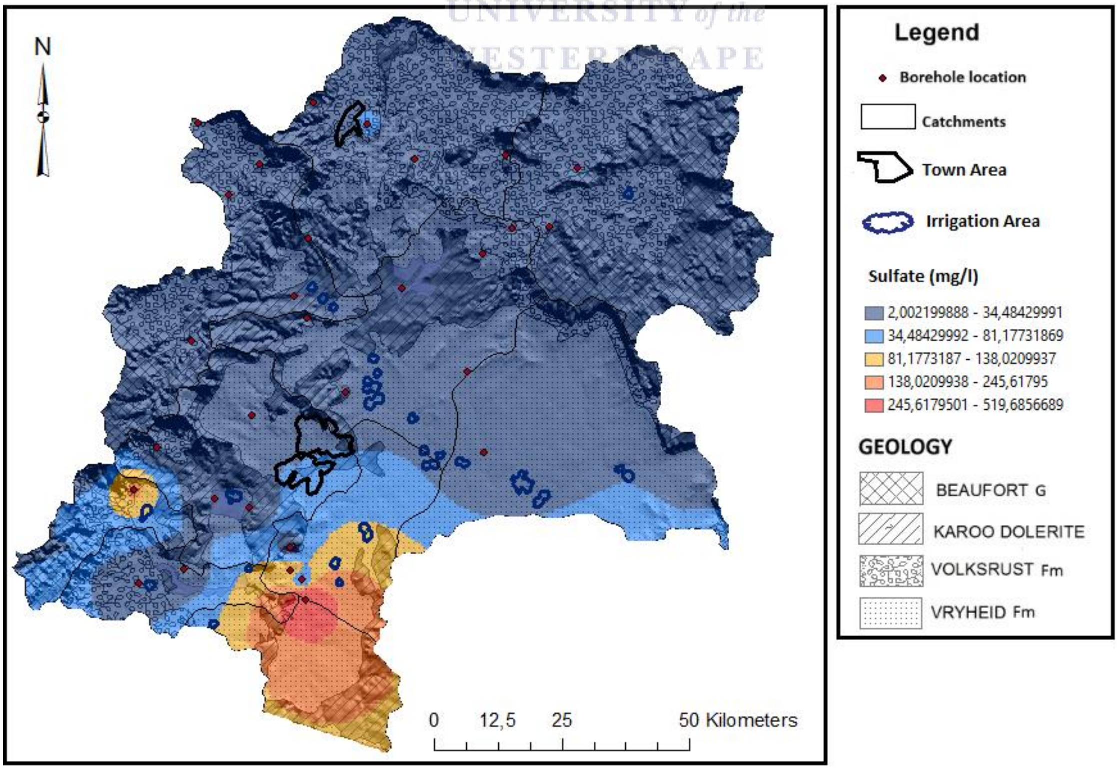

Fig 5.26: Spatial distribution of SO_4^{2-}

Potassium is mostly high in the southern parts of the study area (fig 5.27). The high concentration of K^+ in catchments V31J and V31B is likely due to effluent from domestic and agricultural contamination as these catchments are near the town areas and irrigation areas. In catchments V31K, V32G, V31D and V32B the observed high concentration of K^+ is most likely due to silicate weathering and cation exchange processes.

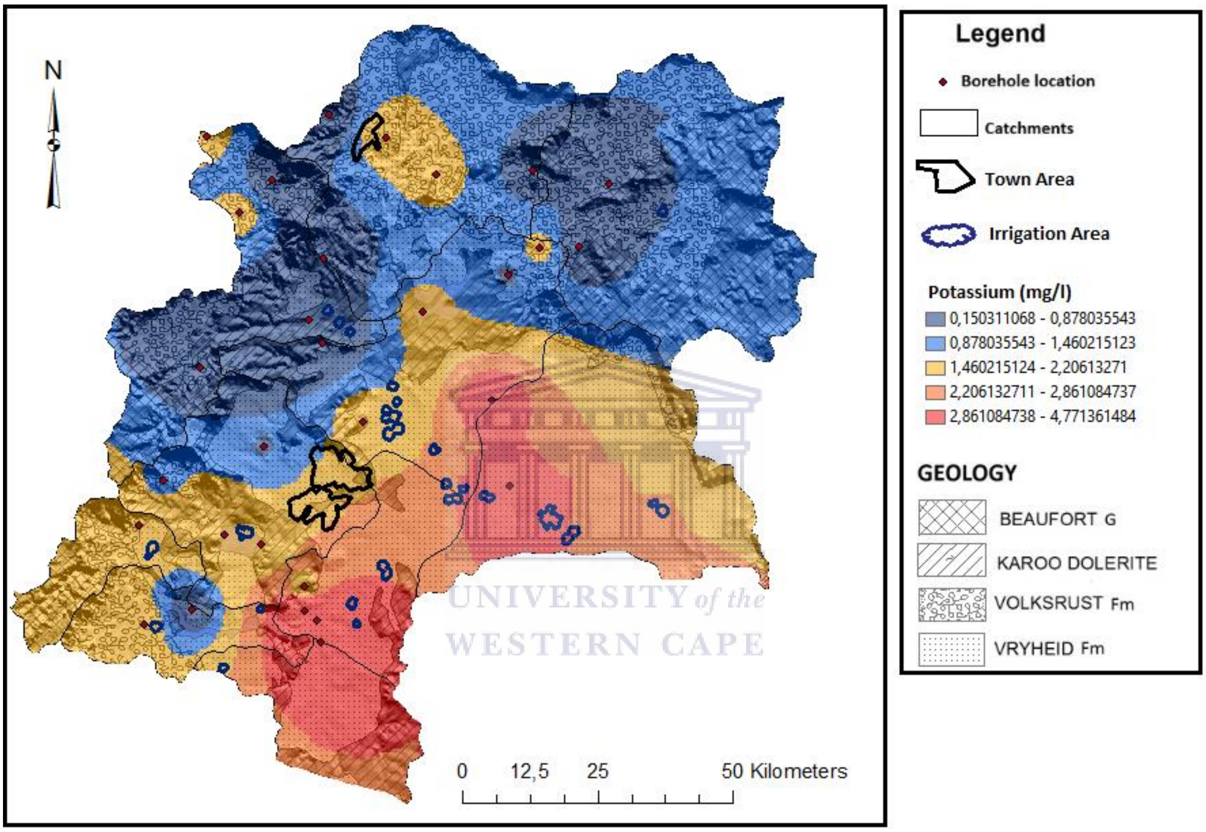

Fig 5.27: Spatial distribution of K^+

NO_3^- is highest concentrations are mostly higher in the north eastern part in catchment V31C area and in catchment V31J nearer to the town area (fig 5.28). The higher concentration of NO_3^- in catchments V31J might be due to application of fertilizers in gardens and parks in the town area and possible contamination from sewage water. Catchment V31C the high concentration of NO_3^- could be attributed to agricultural activity in the area.

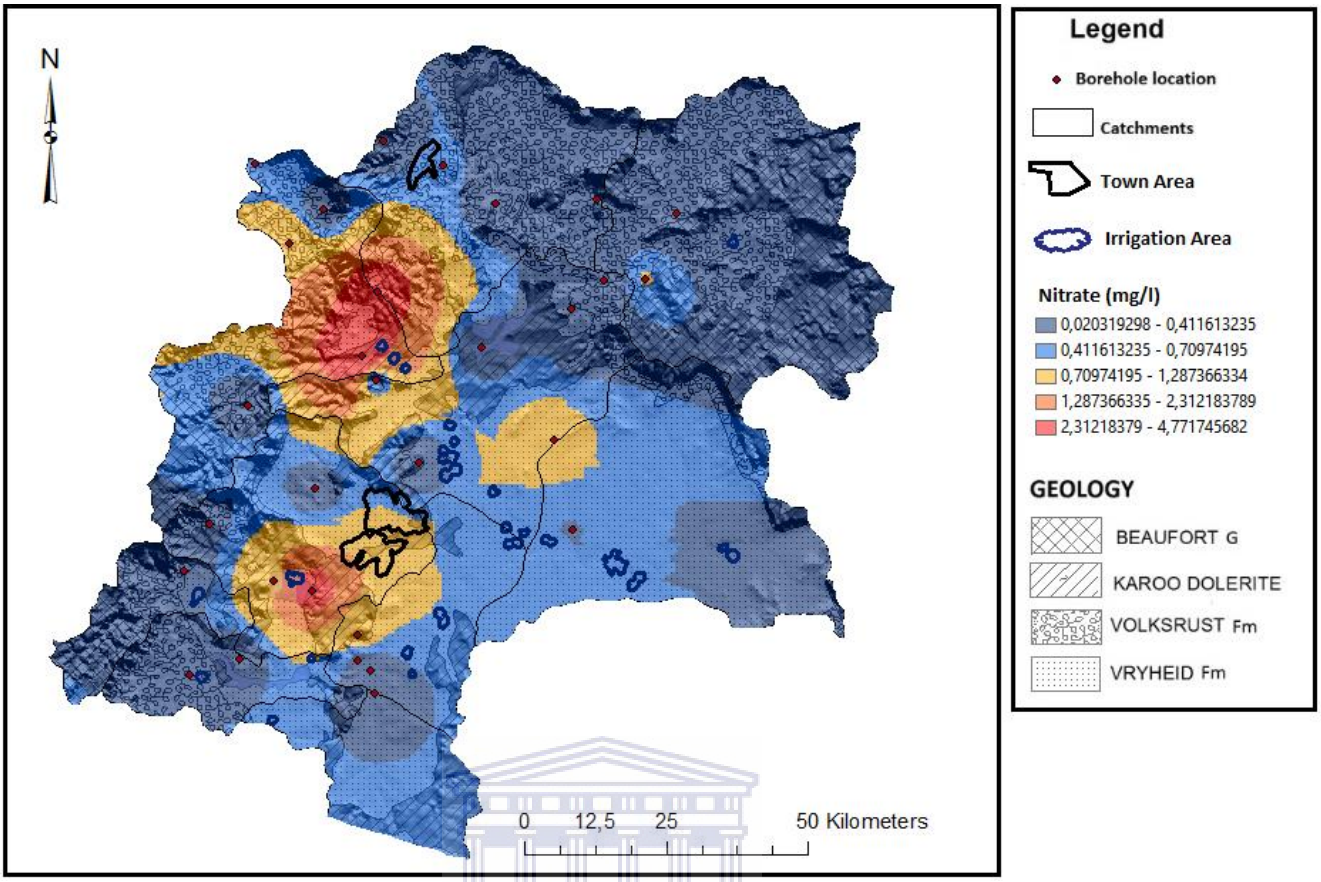

Fig 5.28: Spatial distribution NO_3^-

5.4 Multivariate Statistical Analysis

Multivariate analysis is a useful tool in characterising and classifying groundwater chemistry and has been used in several groundwater studies. Unlike trilinear plots such as piper diagrams used in classical hydro-chemical analysis methods which can only classify based on six major ions, multivariate analysis allows the use of multiple variables in the analysis, thus giving more clarity into the major composition controlling processes. Multivariate analysis was used in this study for further classification and characterisation groundwater samples form the study area. It revealed the important role of pH and NO_3^- in groundwater composition and also revealed the source of F^- buy its association; all these variables are not considered in the classical hydro-chemical methods. Multivariate statistics also reclassified some of the samples into different water types than that of Piper diagram. Multivariate analysis also revealed element association attributed to anthropogenic activities, showing the influence of land-use in addition to rock-water interaction.

Normalising Data

When using multivariate statistics, it is important to make sure that the data is normalised. Parameters are transformed to increase their normal distribution which is preferred for optimal results and reliable interpretation. The natural log function was used to transform data. After data transformation, to check for normality, histograms were used to show the difference between normalised data and the un-normalised data. A histogram is a graphical representation of the distribution of data. They allow visualisation of characteristics of the data such as skewness, outliers and normal distribution. To demonstrate normalised and un-normalised data Ca^{2+} and Cl^- histograms were used, which are shown in figure 5.29.

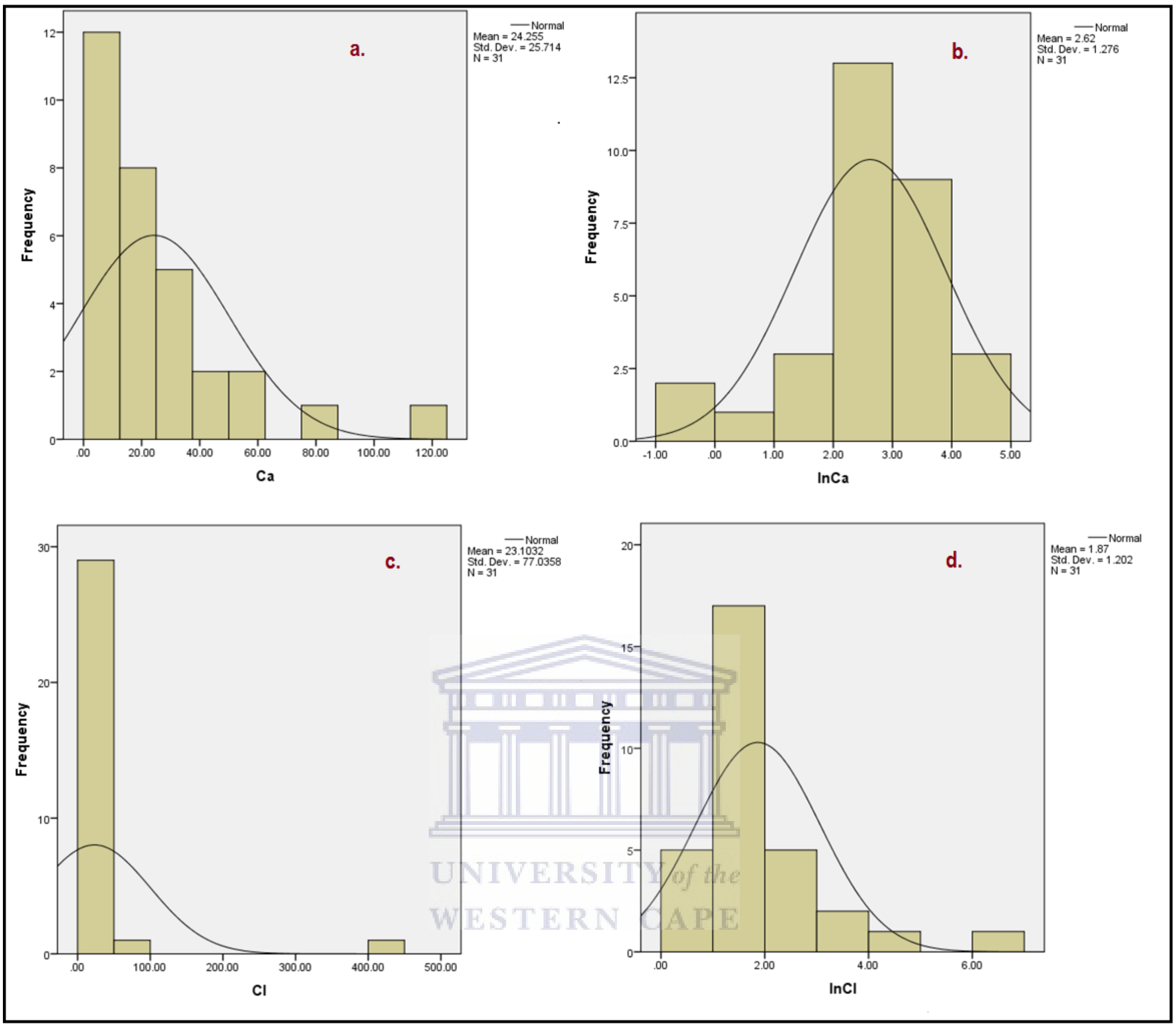

Fig 5.29: Histograms showing the distribution of un-normalise Ca^{2+} (a), Cl^- (c) and normalised Ca^{2+} (b) and Cl^- (d).

5.4.1. Factor Analysis

The tables below show results from the factor analysis completed using the groundwater samples from the study area. Thirteen variables were used for the analysis; pH, EC, TDS, TH, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^- , NO_3^- and F^-. Three factors were taken into consideration in showing the variance in the data; these factors were chosen because they have Eigenvalues ≥ 1 (table 5.11). These factors altogether account for 79.709% of the total variance in the original data, shown in table 5.13 (total variance explained). Factor 1 explains

38.58 % while factor 2 accounts for 29.23 % and factor 3 explains 12.27% of the information from the original data.

Table 5.11: Total variance explained

Total Variance Explained									
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		Rotation Sums of Squared Loadings			
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.674	43.647	43.647	5.674	43.647	43.647	5.015	38.576	38.576
2	3.398	26.140	69.787	3.398	26.140	69.787	3.671	28.236	66.813
3	1.290	9.922	79.709	1.290	9.922	79.709	1.677	12.896	79.709
4	.888	6.828	86.537						
5	.597	4.596	91.133						
6	.494	3.799	94.932						
7	.309	2.375	97.307						
8	.186	1.431	98.738						
9	.093	.713	99.451						
10	.053	.409	99.859						
11	.017	.129	99.988						
12	.001	.008	99.996						
13	.001	.004	100.000						
Extraction Method: Principal Component Analysis.									

Table (5.12) presents the loading of the variables under each factor. The first factor represents the most important process or processes controlling the composition of the groundwater, it has the highest eigenvalue and accounts for the highest variance among the factors. Factor 1 has strong positive loading Na^+, TDS, EC, F^-, HCO_3^-, pH and moderate positive loading of Cl^- and SO_4^{2-}. Factor 2 has high positive loading of TH, Ca^{2+} and Mg^{2+} and weak loading of SO_4^{2-} while factor 3 has high positive loading of K^+ and Cl^- and weak loading of NO_3^-.

Table 5.12: Factor analysis result: Rotated Component Matrix

Rotated Component Matrix^{a}			
	Component		
	1	2	3
Na^+	0.900		
TDS	0.892		
HCO_3^-	0.880		
EC	0.857		
F^-	0.802		
pH	0.720		
SO_4^{2-}	0.564	0.472	
TH		0.984	
Mg^{2+}		0.965	
Ca^{2+}		0.941	
K^+			0.790
Cl^-	0.537		0.674
NO_3^-			0.471
Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. a. Rotation converged in 5 iterations.			

The highest contributor in factor 1 is Na^+ followed by TDS, EC, HCO_3^-, F^-, pH, Cl^- and SO_4^{2+}, this shows or highlights the strong influence of Na^+ in this factor. HCO_3^- is also a major contributor in this factor; it’s the anion with the highest loading. The association of pH with these anions and the high concentration of HCO_3^- reflect the alkaline nature of this factor. Factor 1 can therefore be referred to as the Alkalinity Factor. Figure 5.30 shows that the alkalinity factor is mainly distribute in the Vryheid and Volksrust Fm. High association of Na^+ and HCO_3^+ in this factor is indicative of role of silicate weathering as a major contributing process in the composition of this factor. The loading of F^- on this factor also indicates natural sources of contamination. The association of Na^+ with Cl^- and SO_4^{2-} might also be indicative of the influence of dissolution of halite dissolution and ion exchange processes.

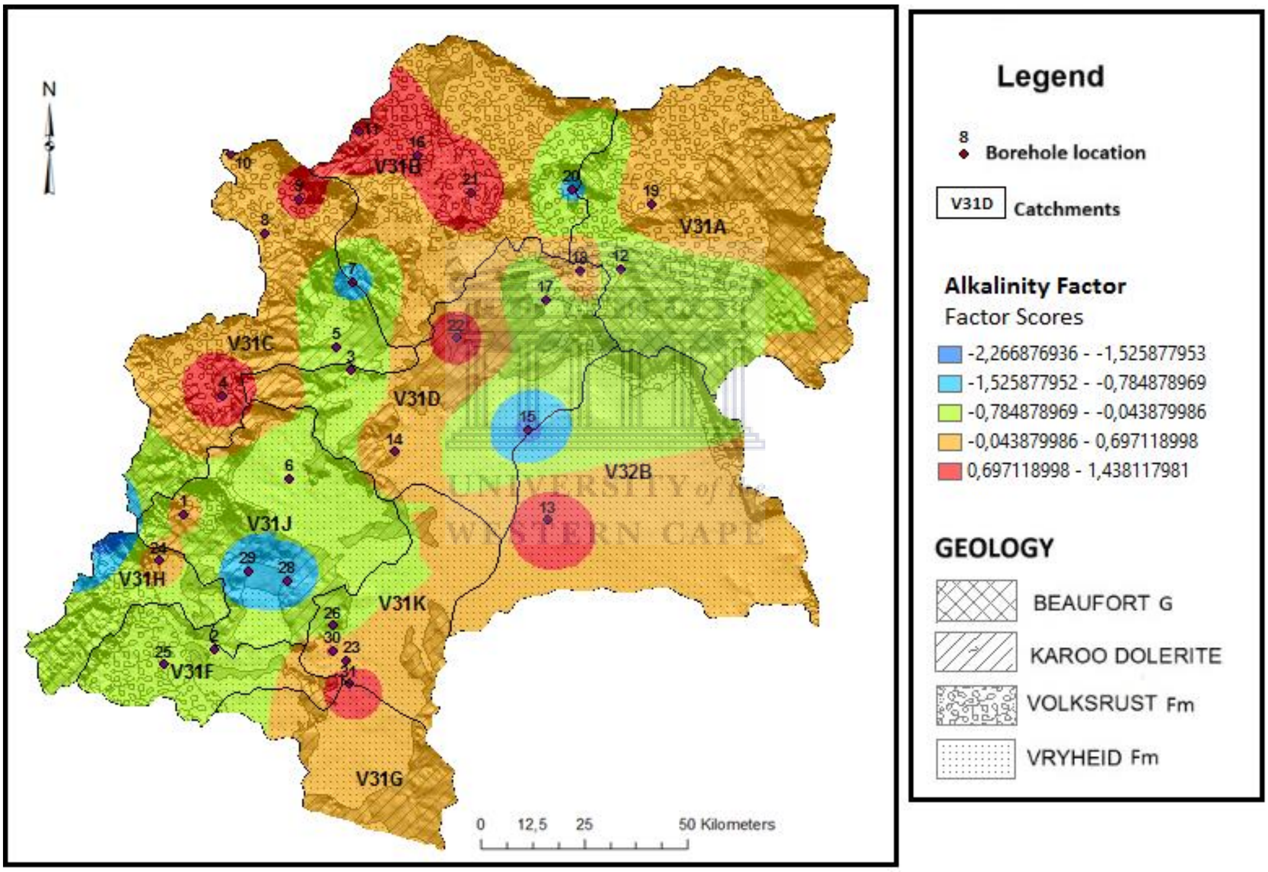

Fig 5.30: Spatial distribution of the Alkalinity Factor scores

Factor 2 is highly positively loaded with TH and Ca^{2+} and Mg^{2+}; this factor can therefore be referred to as the hardness factor. The hardness factor is mainly distributed in boreholes 31, 30, 24, 5 and 4 which are situated in the Vryheid Fm and the Karoo Dolerite (fig 5.31). The high association of Mg^{2+} and Ca^{2+} could be attributed to carbonate weathering. The association of Ca^{2+} and SO_4^{2-} in this factor might also be indicative of gypsum dissolution.

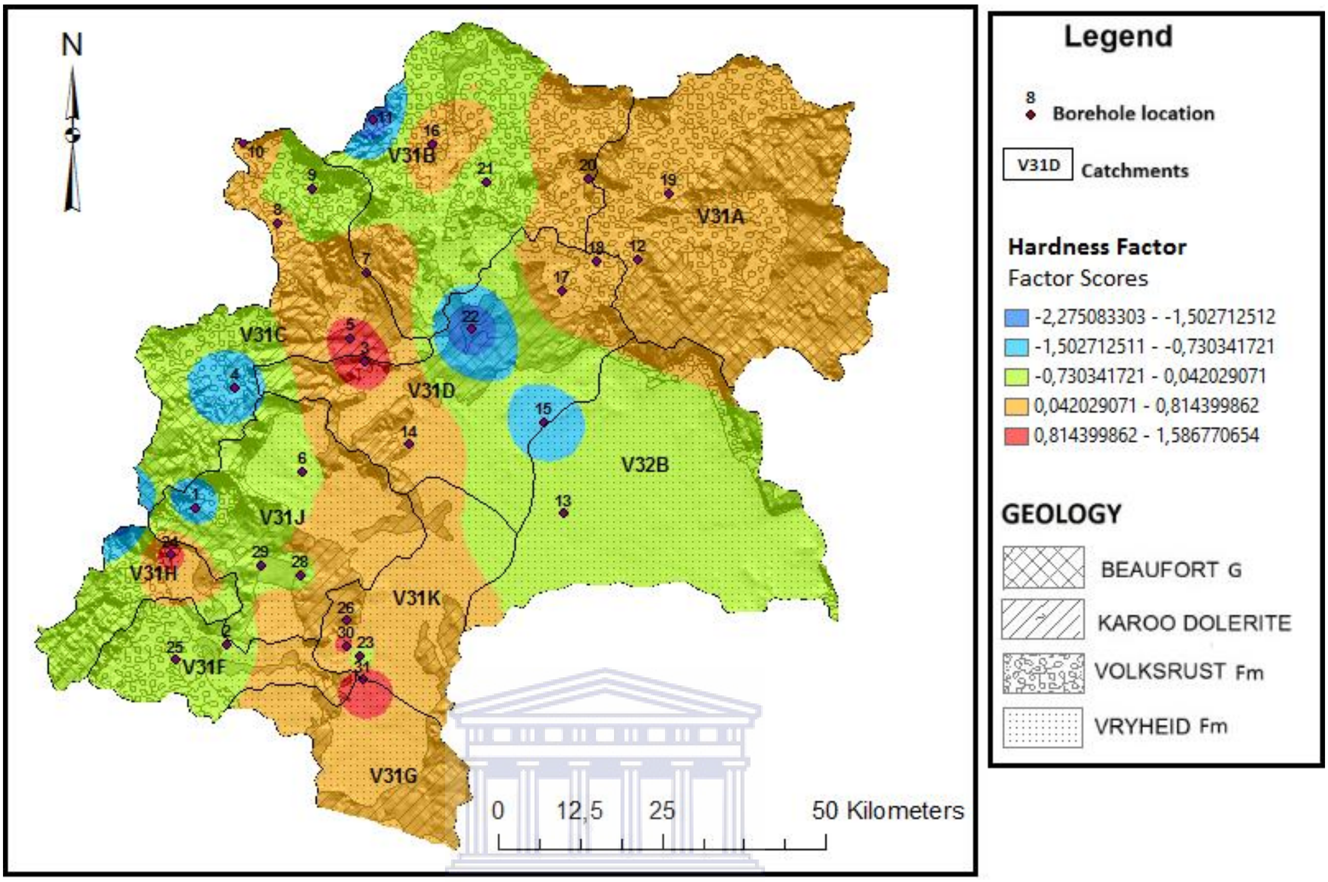

Fig 5.31: Spatial distribution of the Hardness Factor scores

Factor 3, which accounts for the lowest variance explained, can be referred to as the anthropogenic factor because of the association of K^+, Cl^- and NO_3^- . This factor is mainly distributed in the low lying south east side of the study area in catchments V32B, V31K and V31J near irrigation areas and in V32B near town area, as shown in figure 5.32. The association of these ions in groundwater is mainly linked to anthropogenic activities such as return flows from agricultural activities, sewage waste and industrial waste.

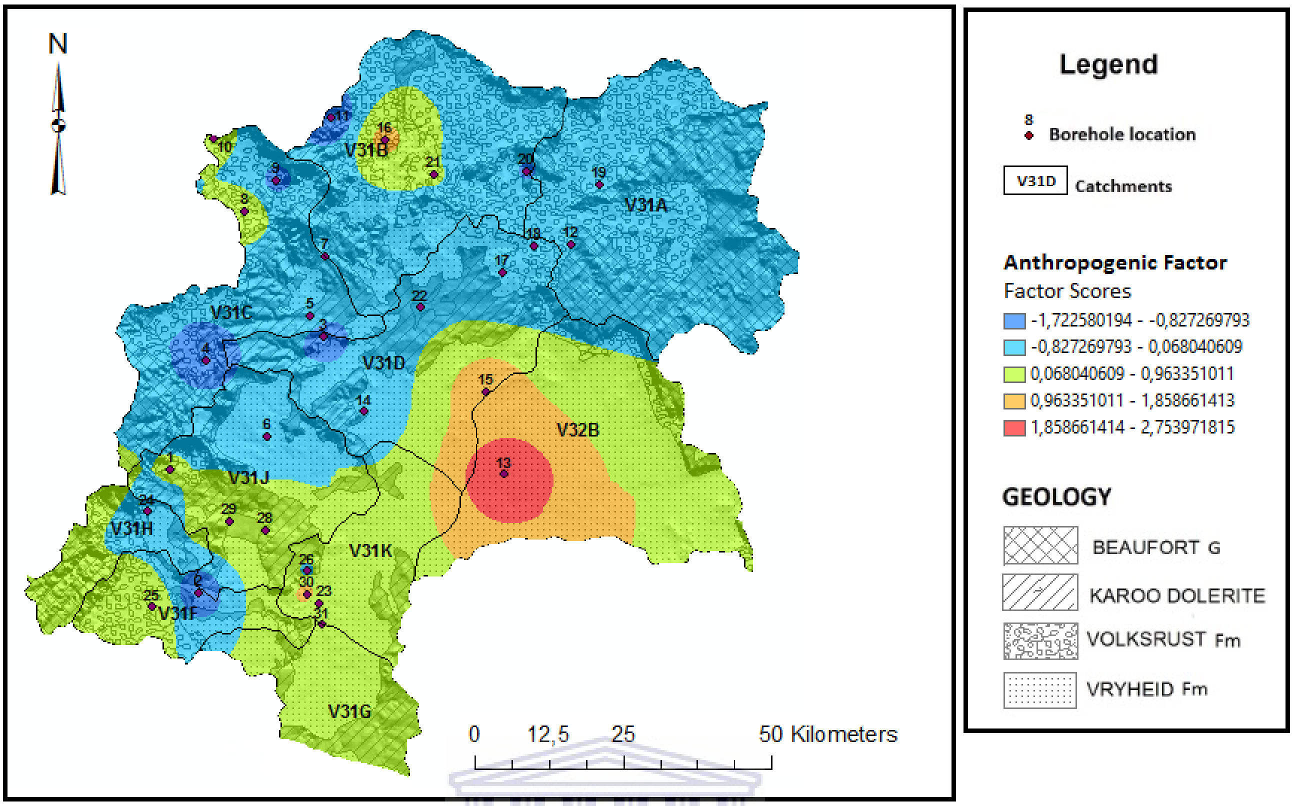

Fig 5.32: Spatial distribution of the Anthropogenic Factor scores

5.4.2. Cluster Analysis

Cluster analysis groups variables into clusters on the basis of their similarities or dissimilarities, such that each cluster represents a different process (Yidana et al., 2008). Cluster Analysis was performed on the Newcastle data and the results are shown below. The analysis grouped the 31 samples into 5 groups. These groups or clusters are illustrated by the dendogram in figure 5.33; the maroon line represents the level of similarity at which the groups were chosen. These clusters were characterised using discriminate analysis.

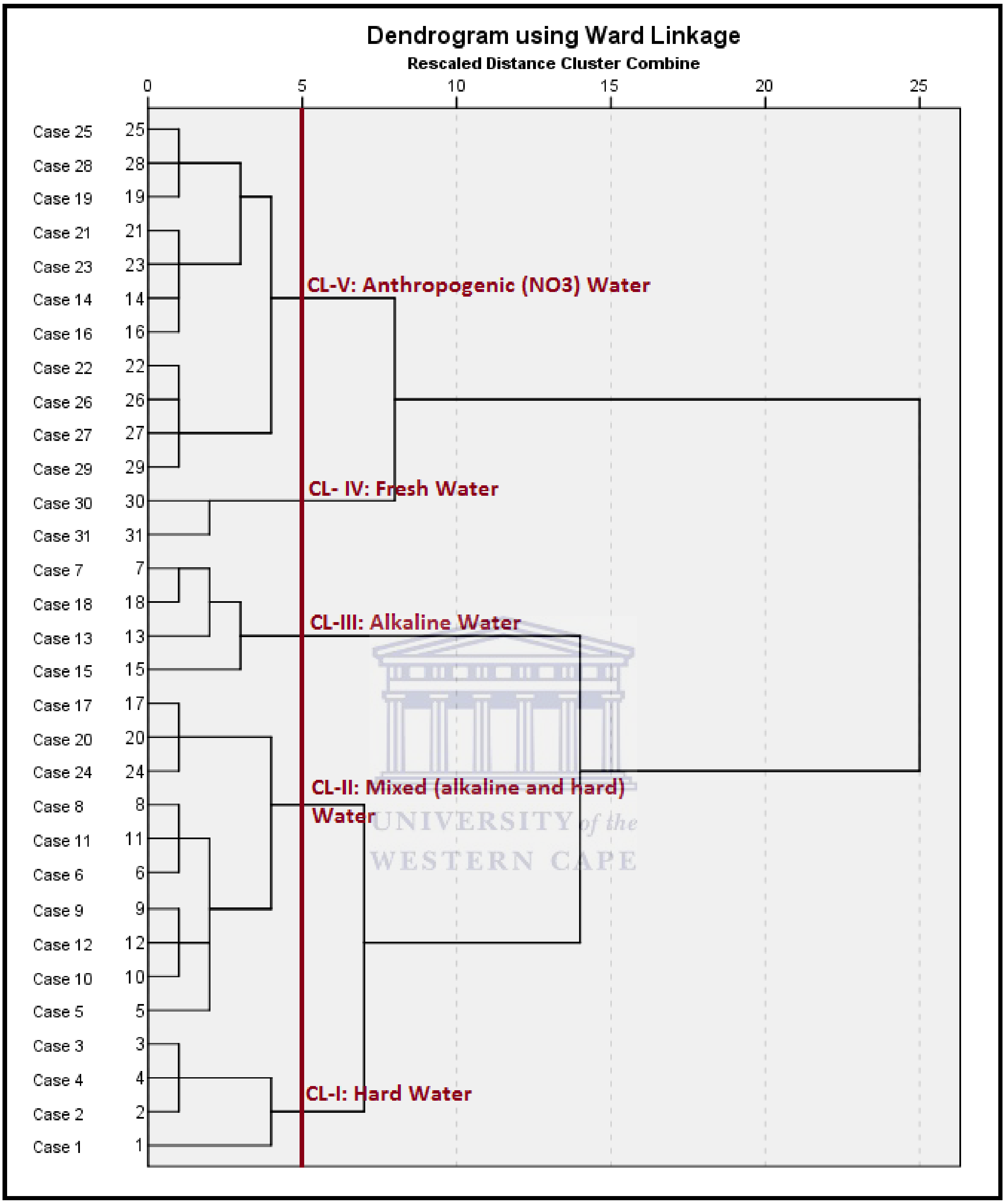

Fig 5.33: Dendogram showing results from the cluster analysis for the study area

5.4.3. Discriminant Analysis

Discriminant analysis was used to characterise the groups derived from cluster analysis. The results from the discriminate analysis show that pH, TDS, EC, TH, Na^+, Ca^{2+}, Mg^{2+}, K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- and F^- discriminate between the clusters dumps by 100%, with all the samples grouped (table 5.13).

Table 5.13: Classification results

Classification Results[a]

		Water Types	Predicted Group Membership					Total
			CL-I	CL-II	CL-III	CL-V	CL-IV	
Original	Count	CL-I : Hard Water	4	0	0	0	0	4
		CL-II : Mixed (Hard and Alkaline water)	0	10	0	0	0	10
		CL-III : Alkaline Water	0	0	4	0	0	4
		CL-V : Anthropogenic (NO3) Water	0	0	0	11	0	11
		CL-IV : Fresh Water	0	0	0	0	2	2
	%	CL-I : Hard Water	100.0	.0	.0	.0	.0	100.0
		CL-II : Mixed (Hard and Alkaline water)	.0	100.0	.0	.0	.0	100.0
		CL-III : Alkaline Water	.0	.0	100.0	.0	.0	100.0
		CL-V : Anthropogenic (NO3) Water	.0	.0	.0	100.0	.0	100.0
		CL-IV : Fresh Water	.0	.0	.0	.0	100.0	100.0

[a].100.0% of original grouped cases correctly classified.

Structure matrix (table 5.14) and functions at group centroids (table 5.15) show the correlation of the variables and clusters with functions 1, 2, 3 and 4 (fig 5.41). Function 1 characterises the Hard water, Mixed (Hard and Alkaline) water and Alkaline water and is positively correlated with Na^+, F^- and SO_4^{2-}. Function 2 characterises Hard water and Mixed (Hard and Alkaline) water and is positively correlated with TH, Ca^{2+}, Mg^{2+} and NO_3^-. Function 3 characterises Mixed (Hard and Alkaline) water, Alkaline water and Anthropogenic (NO_3^-) water and is positively correlated with HCO_3^-, TDS, EC and pH.

Function 4 characterises Mixed (Hard and Alkaline) water and Fresh water, this function is positively correlated with K^+ and negatively correlated with Cl^-.

Table 5.14: Correlation of the Discriminant function with the variables

Structure Matrix				
	Function			
	1	2	3	4
Na^+	**.602***	.152	.204	-.178
F^-	**.301***	-.103	.175	-.017
SO_4^{2-}	**.187***	.181	.093	-.002
TH	-.083	**.431***	.340	.147
Ca^{2+}	-.050	**.431***	.300	.215
Mg^{2+}	-.130	**.395***	.332	.035
NO_3^-	-.100	**.124***	.014	-.115
HCO_3^-	.289	.116	**.597***	.008
TDS	.368	.297	**.526***	-.244
EC	.350	.330	**.413***	-.309
pH	.242	-.167	**.325***	.056
Cl^-	.205	.366	.055	**-.443***
K^+	.105	.319	-.222	**.333***
Pooled within-groups correlations between discriminating variables and standardized canonical discriminant functions Variables ordered by absolute size of correlation within function.				
*. Largest absolute correlation between each variable and any discriminant function				

Table 5.15: Correlation of the cluster with the discriminate functions

Functions at Group Centroids				
Ward Method	Function			
	1	2	3	4
CL-I : Hard Water	3.891	4.878	-.146	-1.445
CL-II : Mixed (Hard and Alkaline water)	1.783	0.485	0.473	1.373
CL-III : Alkaline Water	5.031	-5.038	0.137	-1.013
CL-V : Anthropogenic (NO3) Water	-4.451	-0.303	0.818	-0.397
CL-IV : Fresh Water	-2.274	-0.441	-6.844	0.234
Unstandardized canonical discriminant functions evaluated at group means				

Based on the correlation of the variables and clusters with the discriminant functions, the clusters were characterised as:

Cluster I-Hard water: This type of water is characterised by Na^+, F^-, SO_4^{-2-}, TH, Ca^{2+}, Mg^{2+}, NO_3^- and Cl^-, it also shows high levels of TDS and EC (figures 5.34 to 5.40) . NO_3^- in this group accounts for the anthropogenic influence on the hardness of the water.The association of these ions indicates that the composition of this water can be attributed to silicate weathering and carbonate dissolution, halite and gypsum dissolution, ion exchange processes and anthropogenic activities.

Cluster II-Mixed Hard and Alkaline water: Characterised by Na^+, F^-, SO_4^{2+}, TH, Ca^{2+}, Mg^{2+}, NO_3^-, HCO_3^-, TDS, EC, pH and K^+ (figures 5.34 to 5.40). The composition also reveals the influence of silicate weathering, carbonate weathering, halite dissolution, gypsum dissolution and ion exchange processes.

Cluster III- Alkaline Water: This water is characterised by Na^+, F^-, SO_4^{2-}, HCO_3^-, TDS, EC and pH. Figures 5.35(a), 5.38(a) and 5.38 (b) show that this water types is mainly characterised by Na^+, F^- and pH. The high mean values of pH in this water also show the influence of pH on rock-water interaction processes. The composition of this water can be attributed to silicate weathering, gypsum dissolution and reverse ion exchange processes.

Cluster V- Anthropogenic (NO_3^-) Water: Characterised by HCO_3^-, TDS, EC, and pH. What differentiates this group form the others is the high levels of NO_3^- (Fig 5.36 (b)), which represent anthropogenic influence on the composition of this water in addition to rock-water interaction.

Cluster IV- Fresh Water: This water type negatively correlates with all the functions except for function 4 which is positively loaded with K^+. This water contains low concentration of all the ions than all the other water types (figures 5.33 to 5.39); this could be an indication of fresh and shallow groundwater.

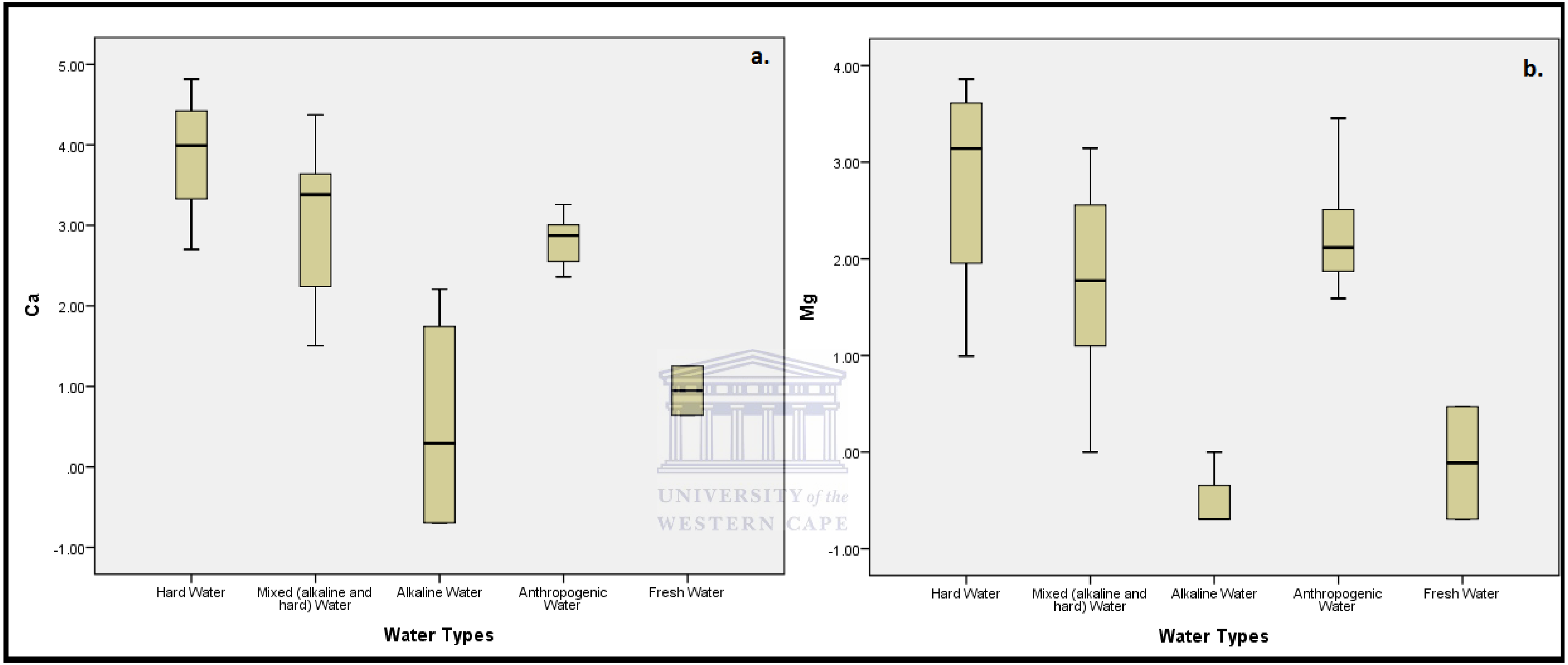

Fig 5.34: Distribution of Ca^{2+} (a) and Mg^{2+} (b) in the different water types

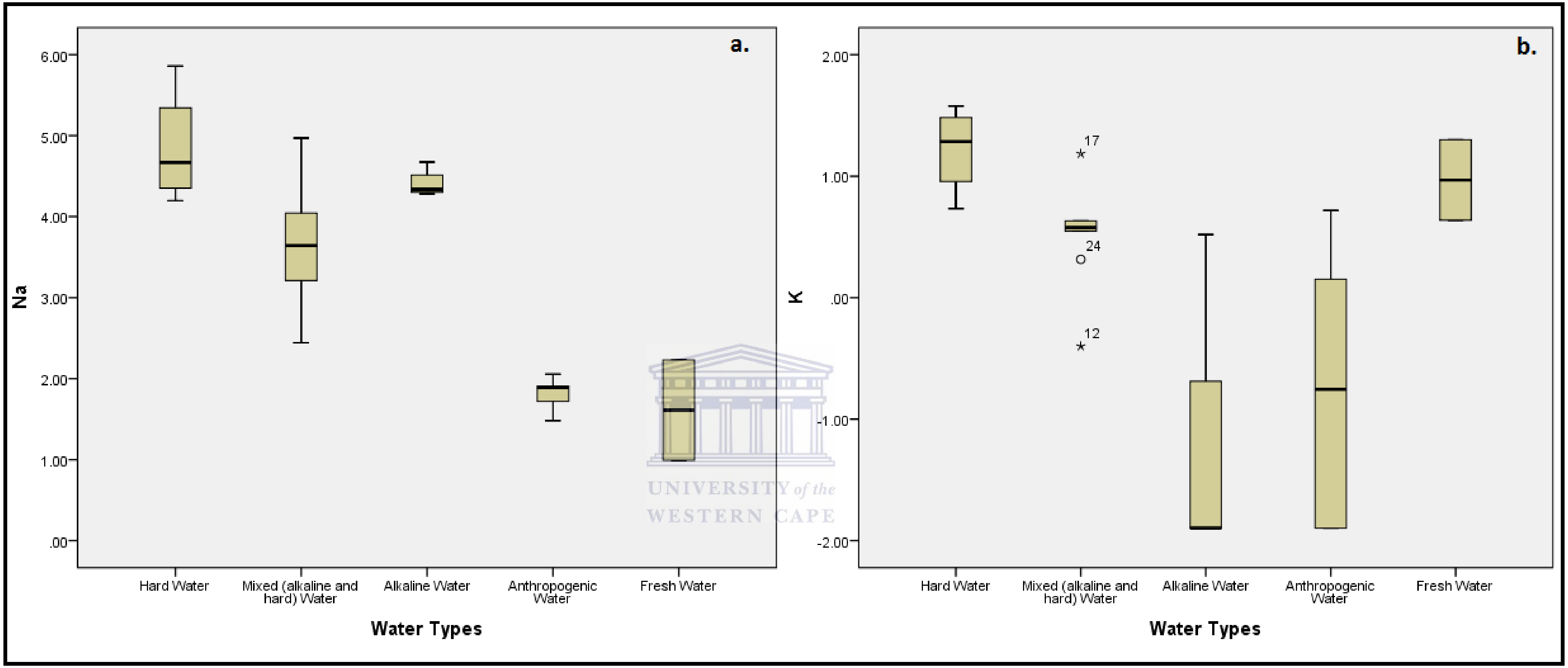

Fig 5.35: Distribution of Na^+ (a) and K^+ (b) in the different water types

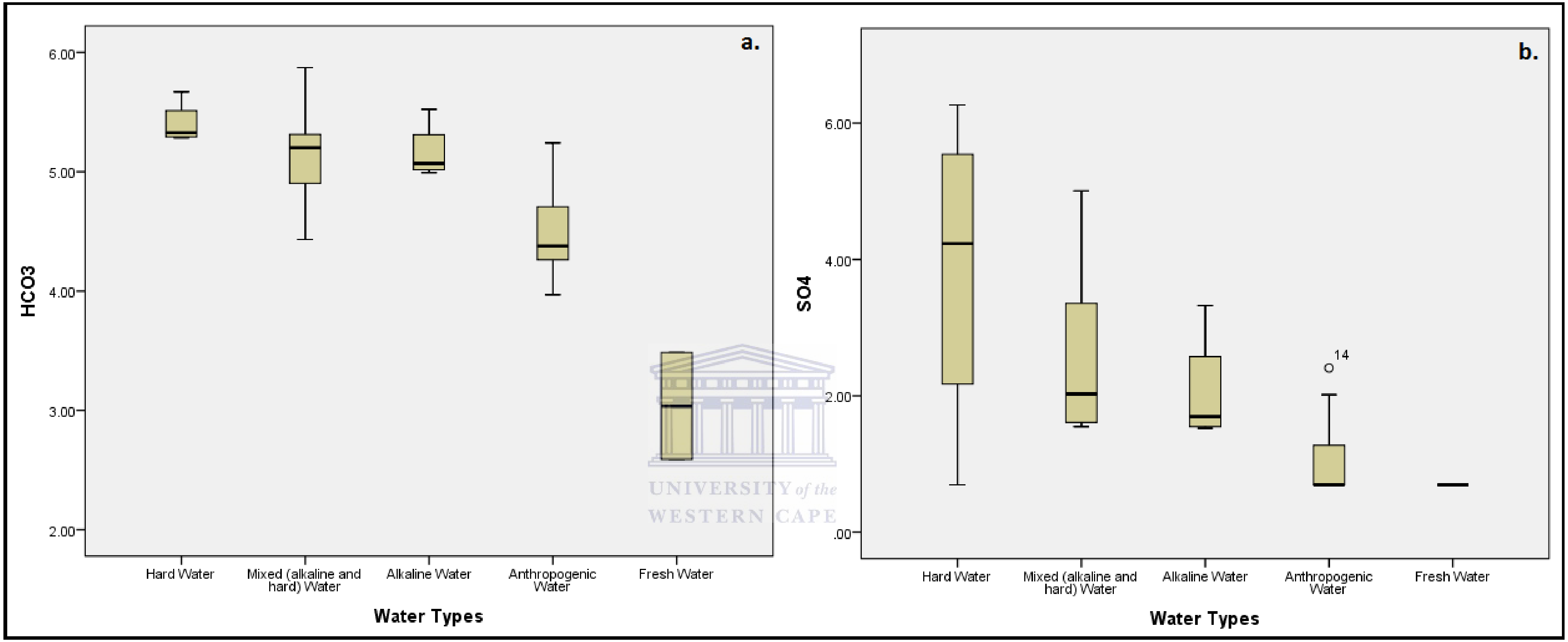

Fig 5.36: Distribution of HCO_3^- (a) and SO_4^{2-} (b) in the different water types

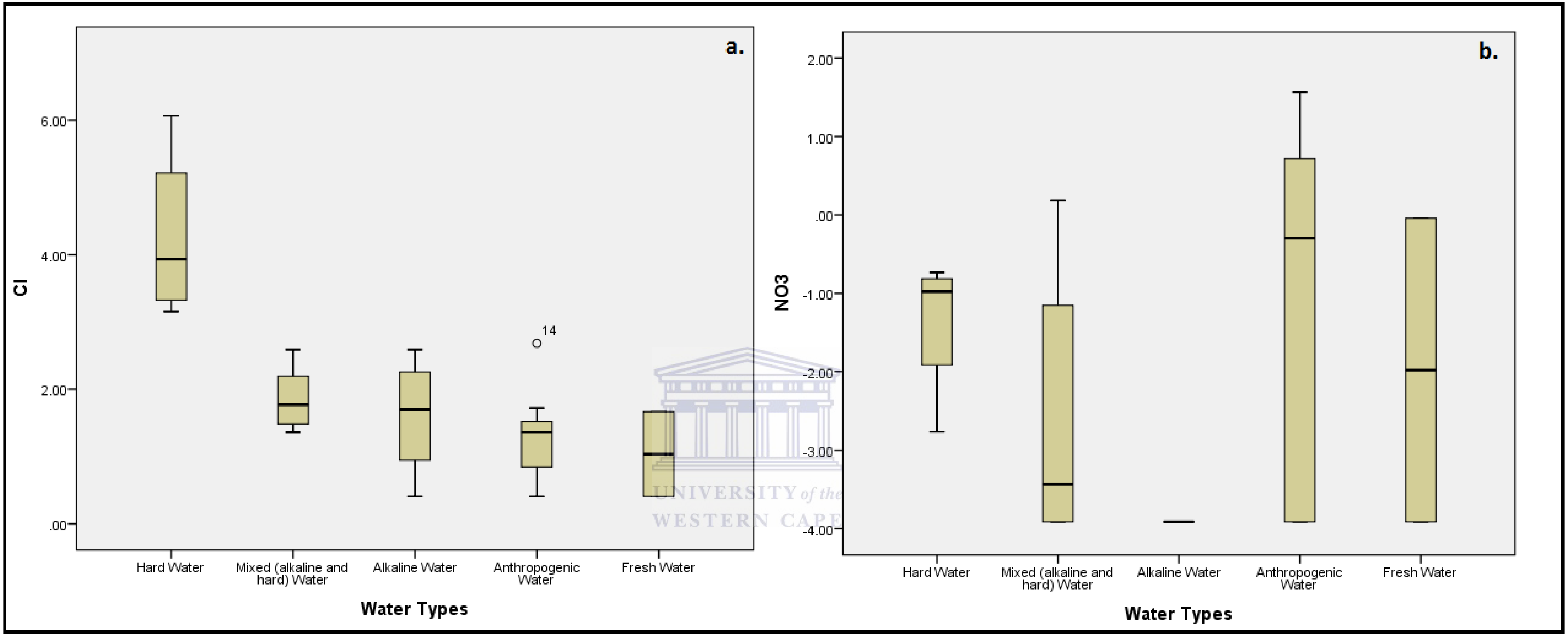

Fig 5.37: Distribution of Cl^- (a) and NO_3^- (b) in the different water types

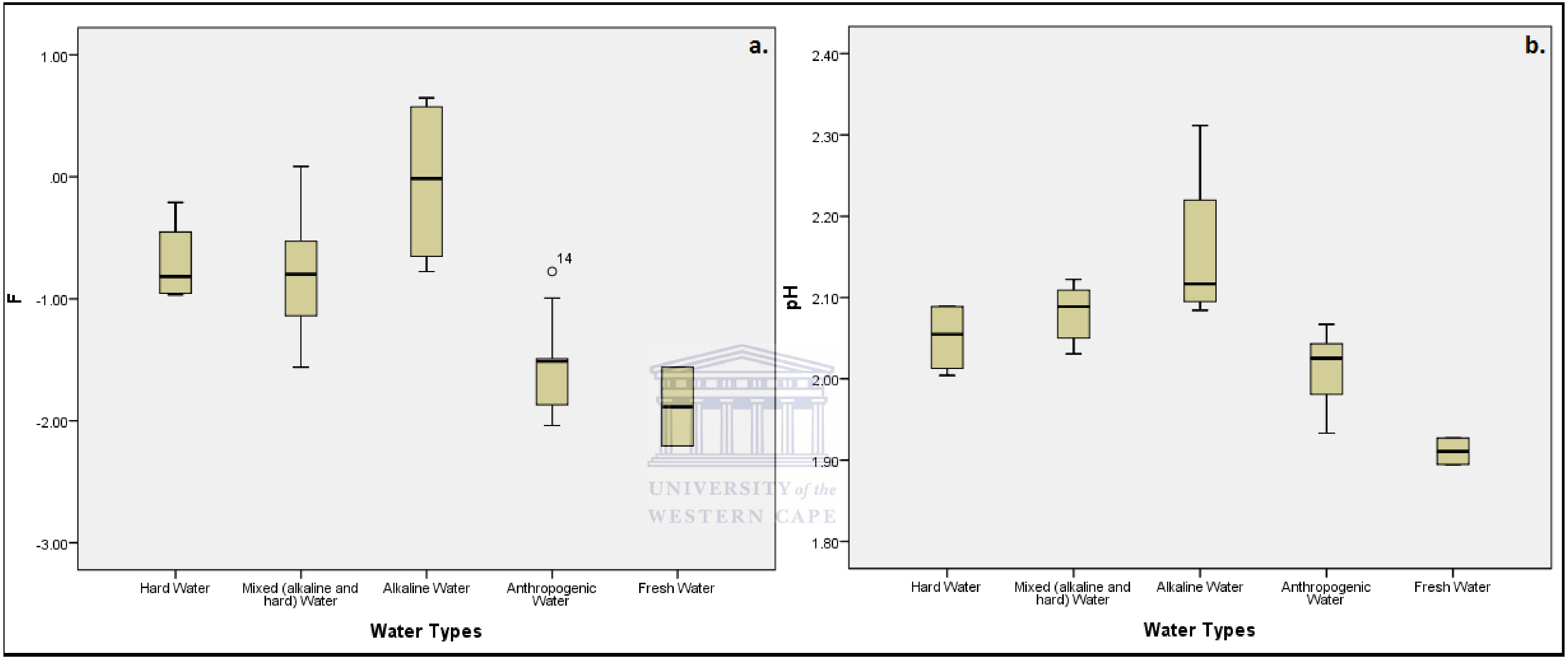

Fig 5.38: Distribution of F^- (a) and pH (b) in the different water types

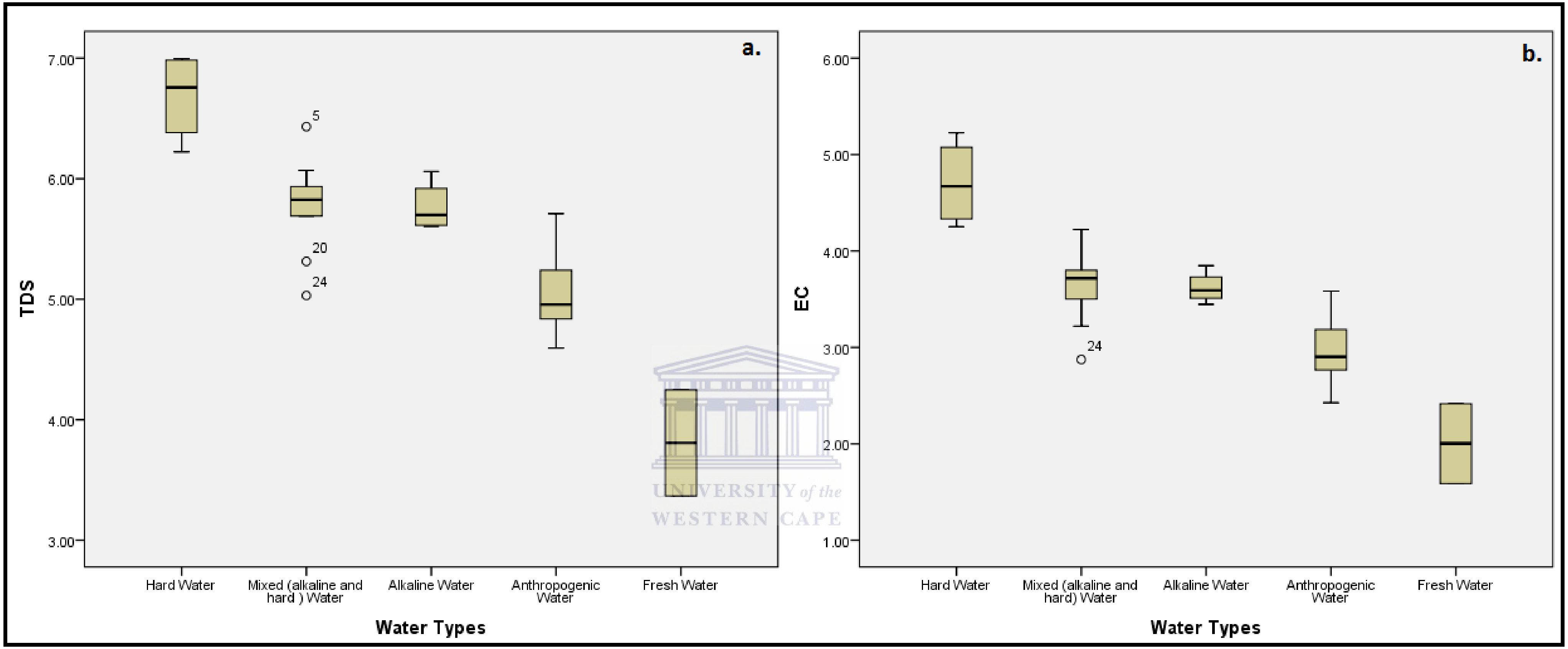

Fig 5.39: Distribution of TDS (a) and EC (b) in the different water types

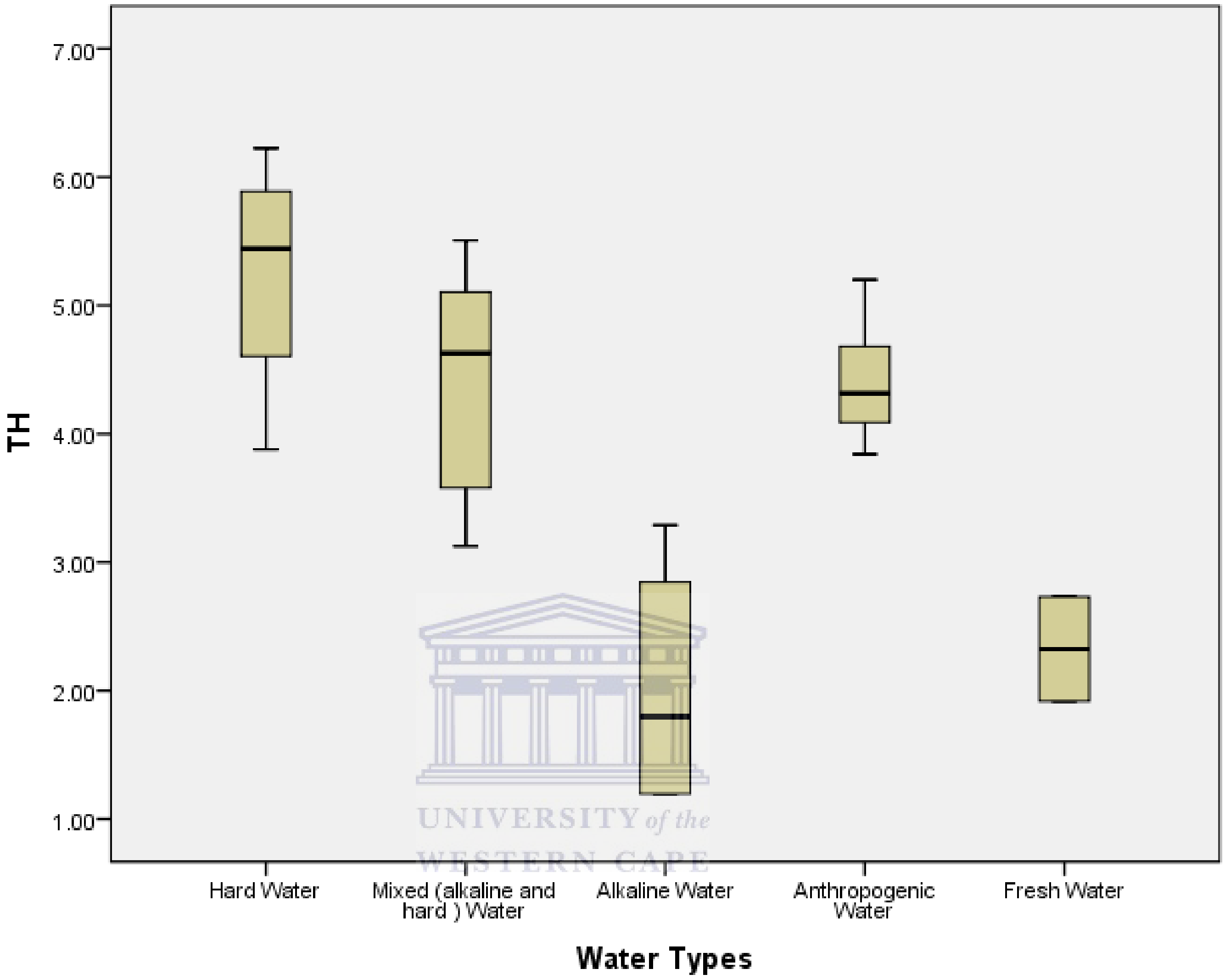

Fig 5.40: Distribution of TH in the different water types

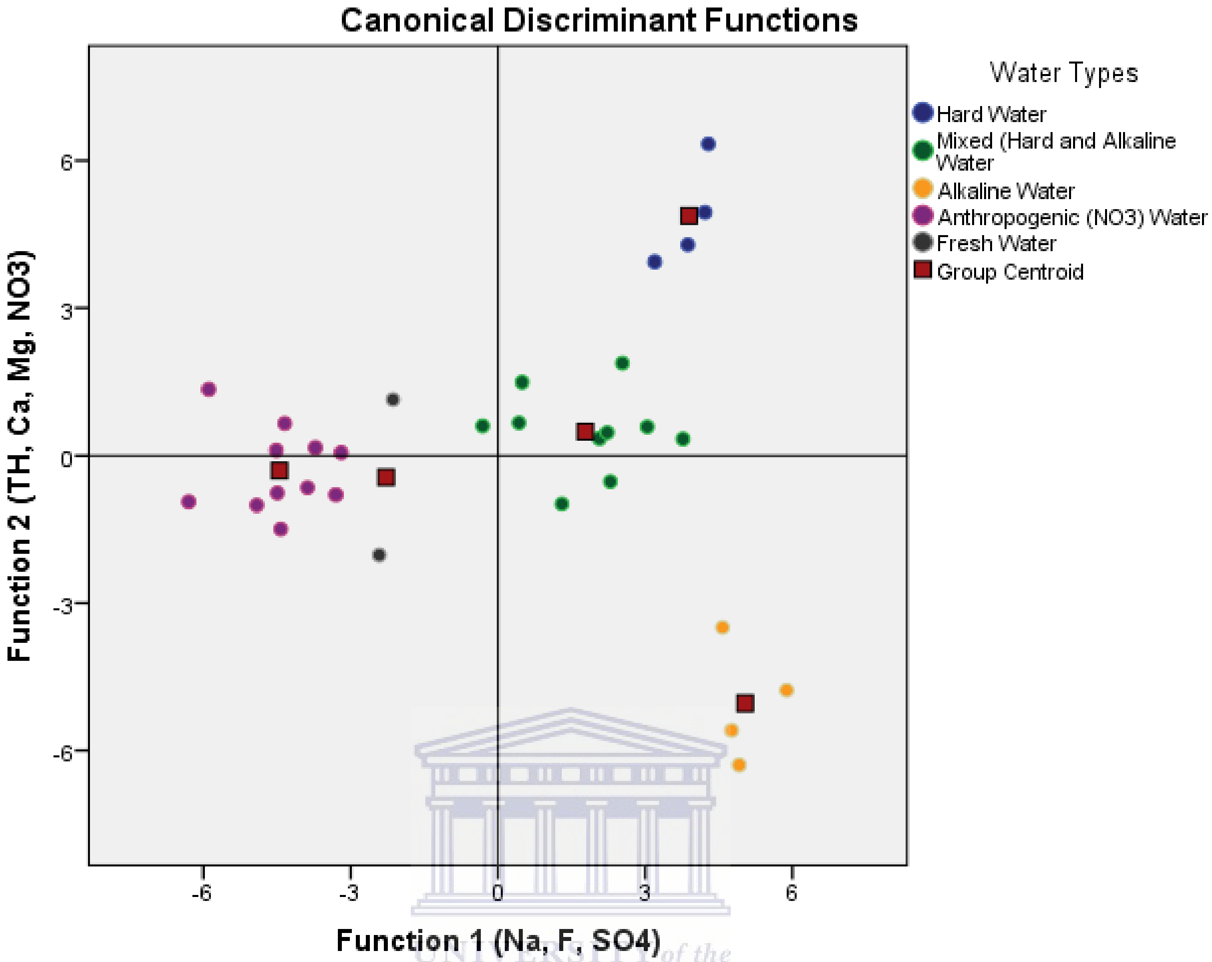

Fig 5.41: Discriminant plot showing graphical representation of the different water types

5.4.3.1. Stepwise Discriminant Analysis

Stepwise discriminant analysis is a model of discrimination and is built step by step and at each step all variables are reviewed and evaluated to determine which one will contribute most to the discriminating between the groups.

The table 3 shows the results from the stepwise discriminant analysis performed using the groundwater samples from the study area. The classification results show that the Na^+, TH and HCO_3^- and SO_4^{2-} discriminate the clusters by 96.8%. Table 3 shows the contribution of each variable in the discrimination.

Table 5.17: Results from stepwise discriminant analysis

Element	% of Discrimination
Na^+	64.5
TH	25.8
HCO_3^-	3.2
SO_4^{2-}	3.3
Total	96.8

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1. Conclusions

The aim of this study was to evaluate the quality of groundwater in Newcastle and to determine the suitability of the water for drinking and irrigation purposes. To achieve this, the SAWQG (DWAF, 1996) and WHO (2011) water guidelines were used as the basis of evaluating the groundwater for drinking purposes. For irrigation, EC (salinity hazard), Sodium percent (Na%), Sodium adsorption ratio (SAR), Residual sodium carbonate (RSC), Kelly’s ratio (KR), Magnesium ratio (MR) and Permeability index (PI) were used. The hydro-chemical data was further analysed using Classical Hydro-chemical methods and multivariate statistical methods. The spatial distribution of these results was presented using ArcGIS.

The results revealed that most of the samples are within the permissible range for both the SAWQG (DWAF, 1996) and WHO (2011) water guidelines. The groundwater was found to be generally alkaline, soft to hard and fresh to brackish in nature. The dominance of major ions in the area is as $Na^{+}>Ca^{2+}>Mg^{2+}>K^{+}$ and $HCO_3^{-}>SO_4^{2+}>Cl^{-}>NO_3^{-}$.

Based on the EC and PI all the samples were found suitable for irrigation while the SAR, Na%, RSC, KR and MR showed that the water from boreholes and catchments 1;V31J, 3;V31D, 4;V31C, 5;V31J, 6,V31J, 9;V31C, 11;V31B, 12;V31A, 13;V32B, 14;V31D, 21;V31B, 22;V31D, 23;V31K, 25;V31F respectively, were found to be unsuitable for irrigation because of their potential to cause sodium hazard.

Classical hydro-chemical methods showed the existence of four hydro-chemical facies/water types in the area, the Ca-(Mg)-HCO3, Na-HCO3, Mixed water Ca-Na-SO4-HCO3 and the Na-Cl water type. The facies show the evolution of ground from Ca-Mg-HCO3 to Na-HCO3 through silicate weathering and reverse ion exchange processes and to Na-Cl through halite dissolution and ion exchange processes. The Ca-Na-SO4-HCO3 water type is a result of mixing of different water type.

The analysis of the major ion chemistry and their spatial distribution indicated the dominance of rock-water interaction as the main process controlling groundwater chemistry in the area. It also indicated the influence of anthropogenic activities in the area. It further showed that the ionic concentration in is due to silicate weathering, carbonate weathering, cation exchange (both reverse and normal), gypsum dissolution and halite dissolution, with silicate weathering being the most dominant.

Factor analysis reduced the hydro-chemical data to three factors which account for 79.71% of variance in the data. The first factor which accounted for the highest variance in the data was the Alkalinity factor, followed by the Hardness factor, and the Anthropogenic factor which accounted for the least variance. Cluster and discriminant analysis characterised the hydro-chemical data into 5 water type, namely Hard water, Mixed hard and alkaline water, Alkaline water, Anthropogenic water and Fresh water.

In conclusion, the study revealed that the groundwater in most of the boreholes in the study area is generally suitable for drinking. This is with exception to boreholes 13 and 31 which show concentrations higher than the permitted level by WHO (2011) standards of TDS, Na^+, Cl^-, SO_4^{2-} and F^-. The analysis revealed that about 45.16% the groundwater samples show that the groundwater has high sodium hazard potential which makes water from these boreholes unsuitable for irrigation purposes without proper treatment.

It can be inferred from the hydro-chemical facies, major ion scatter plots, factor, and cluster and discriminant analysis that the major process affecting the groundwater chemistry in the area is rock-water interaction. Further, the ionic concentration is due to silicate weathering, carbonate weathering and ion exchange processes. The role of anthropogenic activities is also evident by the association of ions such as NO_3^-, K^+ and Cl^-.

6.2. Recommendations

In view of the findings of the study, it is recommended that the water in boreholes that exceeded the WHO (2011) guidelines and in the boreholes that showed high sodium hazard potential should be treated before use. In future studies, more parameters should be analysed and observed, such as heavy/trace metals and organics (pesticides and pharmaceuticals) and effects of seasonal changes or influences on the groundwater should also be monitored. Programs should also implemented on how to better protected groundwater anthropogenic impact.

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APPENDICES

Appendix A: Ion concentration classification of the groundwater samples based on WHO (2011) drinking water guideline

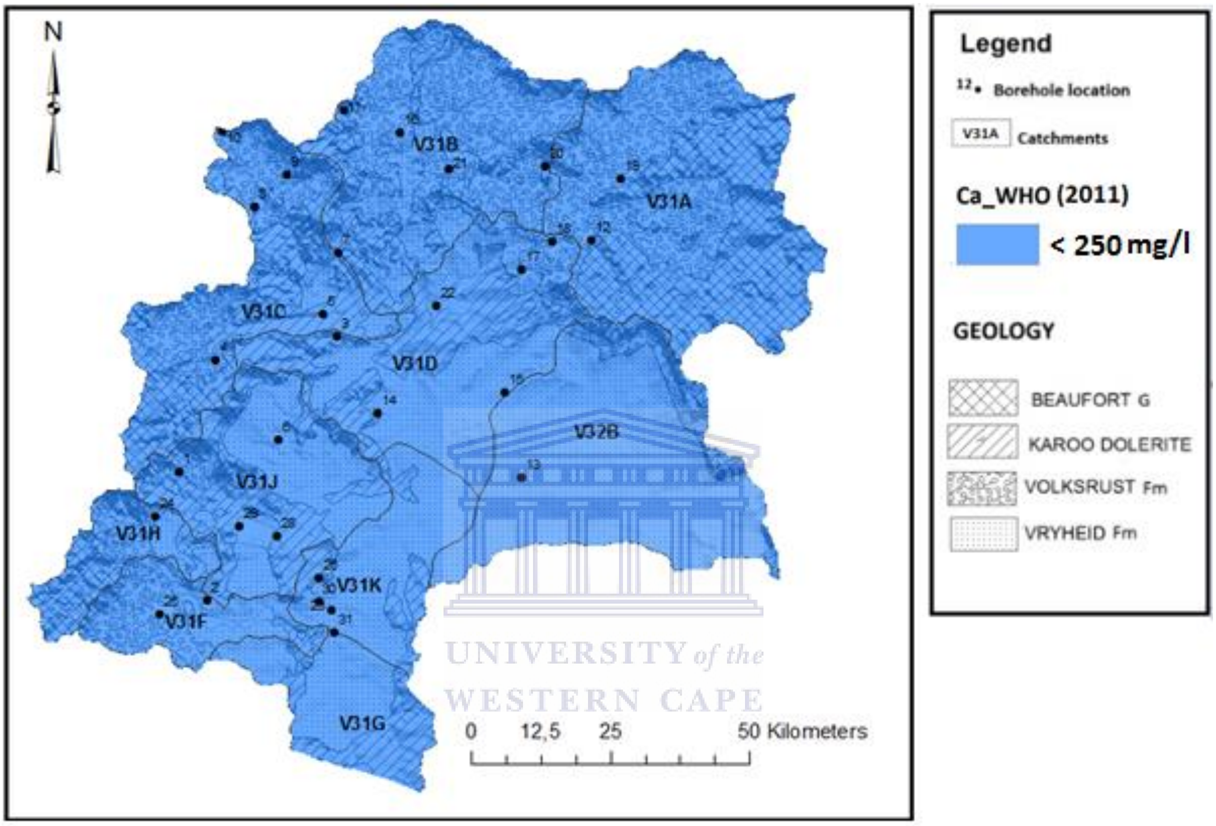

Fig A.1: Ca^{2+} concentration classification of the groundwater samples based on WHO (2011) drinking water guideline

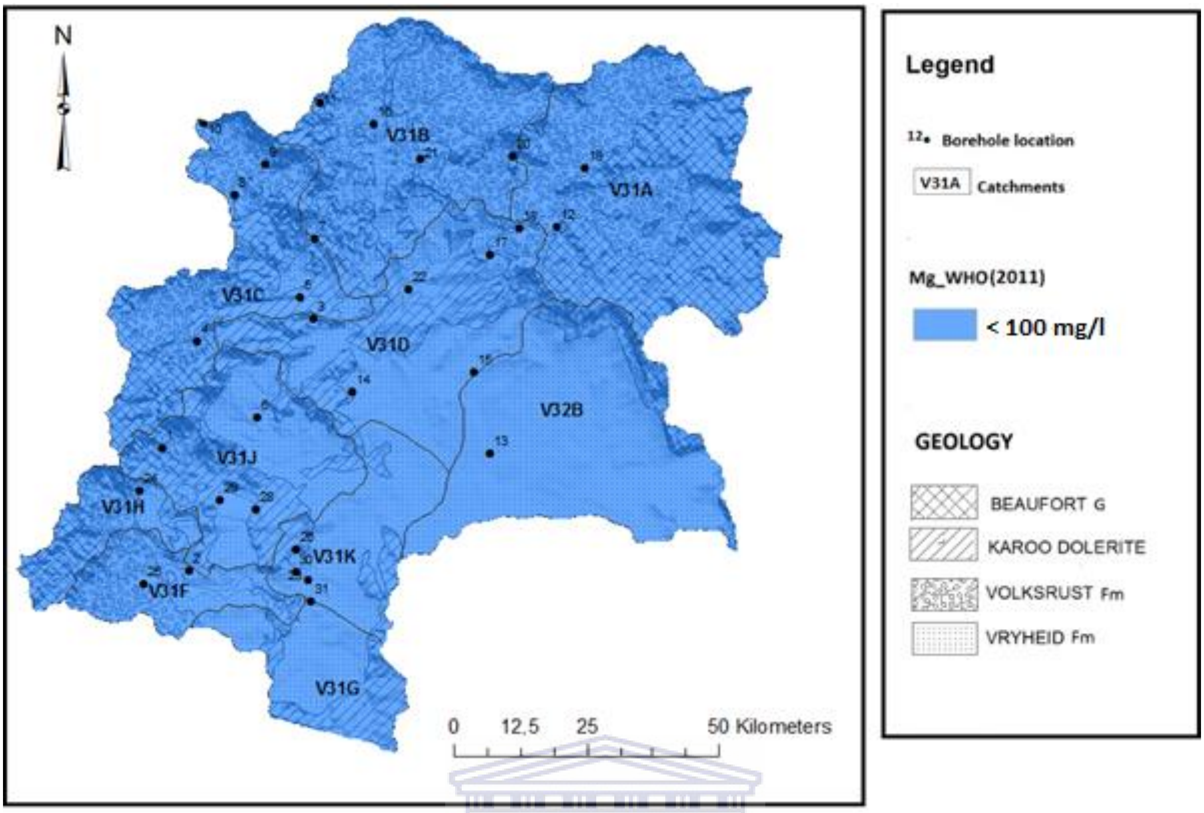

Fig A.2: Mg^{2+} concentration classification of the groundwater samples based on WHO (2011) drinking water guideline

Appendix B: Study Area Hydrochemical Data

Monitoring Point ID	Latitude	Longitude	Located on Type	Drainage Region Name	Ca	Cl	TDS	Ec	K	Mg	NO3	Na	PO4	SO4	HCO3	pH
173716	-27,7825	29,77194	Borehole	V31J	7,7	4,4	153	17,7	1,37	1	0,315	28	0,033	5	84,1	8,35
173717	-27,8892	29,84	Borehole	V31F	10,6	1,5	99	11,3	0,15	4,9	0,02	4,4	0,012	2	60,6	7,61
173733	-27,6183	29,88972	Borehole	V31D	20,4	5,6	302	35	0,15	31,7	0,17	6,7	0,014	6,4	189	7,9
173734	-27,6722	29,775	Borehole	V31C	3,6	4,4	428	46,9	0,15	0,5	0,02	107	0,066	4,8	250,5	8,21
173735	-27,6022	29,86889	Borehole	V31C	25,4	14,6	276	36	0,15	24,2	4,788	6,6	0,011	11,1	141	7,73
173736	-27,7258	29,8625	Borehole	V31J	11,8	3,6	127	15,4	0,83	7,3	0,02	6,5	0,012	2	76,8	7,7
173737	-27,5439	29,86583	Borehole	V31C	16,3	3,9	142	18,2	0,15	8,3	3,481	4,7	0,006	2	73,1	7,58
173738	-27,5247	29,76889	Borehole	V31C	25	6	334	40,8	1,88	4,4	1,202	57	0,009	34,3	163,5	7,69
173739	-27,4875	29,79167	Borehole	V31C	9,1	6,8	323	37	0,15	1	0,02	77,7	0,007	27,8	163,6	8,04
173740	-27,4658	29,71333	Borehole	V31C	39	6,4	378	44,7	1,79	7,9	0,453	45,3	0,003	28,7	202,3	8,1
173752	-27,4144	29,82889	Borehole	V31B	0,5	1,5	272	31,4	0,15	0,5	0,02	72,4	0,014	6,2	154,6	8,4
173756	-27,4644	30,11556	Borehole	V31A	20	4,5	177	22,6	0,15	12,4	0,743	6,8	0,014	7,5	100,5	7,44
173757	-27,695	30,11806	Borehole	V32B	14,9	430,7	1065	186	3,26	2,7	0,409	350,5	0,036	2	211,6	7,42
173758	-27,6767	29,95361	Borehole	V31D	36,7	4,9	337	42,7	1,84	23,2	0,02	11,5	0,029	4,8	208	8,1
173759	-27,6233	30,07444	Borehole	V31D	3,5	5,3	70	11,2	3,67	1,6	0,958	9,3	0,025	2	32,6	6,65
173761	-27,4197	29,89222	Borehole	V31B	52,2	79,1	504	70,2	2,08	18,5	0,479	66,5	0,014	38,4	200,3	8,08
173762	-27,5092	30,05417	Borehole	V31D	20	3,9	171	21	0,8	10,1	0,02	7	0,014	2	103,2	6,91
173766	-27,4761	30,07722	Borehole	V31D	38	9	356	41,5	1,73	12,9	0,02	36,7	0,02	15,8	197,6	8,24
173768	-27,4019	30,12667	Borehole	V31A	34,6	5,8	340	40,1	0,67	19	0,02	24,8	0,016	7,7	202,8	7,77
173769	-27,41	30,0475	Borehole	V31B	17,7	1,5	135	16,4	0,47	5,3	0,02	7,8	0,011	2	79,6	6,94
173770	-27,4386	29,95222	Borehole	V31B	18,1	13,3	621	68,2	1,88	4	0,02	144,1	0,017	4,7	355,3	8,29
173772	-27,5647	29,98	Borehole	V31D	0,5	13,3	276	35,6	1,68	0,5	0,02	75,3	0,014	4,6	147,4	10,09
173779	-27,865	29,96722	Borehole	V31K	4,5	3,9	296	33,2	3,27	2,8	0,02	68,6	0,446	7,4	166,8	7,96
173781	-27,8283	29,76194	Borehole	V31H	79,2	4	432	56	1,77	11,8	0,052	21,1	0,01	149,5	134,7	8,05

Appendix B: Continued

173782	**-27,915**	**29,79611**	**Borehole**	**V31F**	**9,4**	**10,6**	**203**	**25**	**1,74**	**3**	**0,281**	**39,9**	**0,016**	**7,5**	**106**	**7,62**
173783	**-27,8386**	**29,94528**	**Borehole**	**V31K**	**26**	**1,5**	**201**	**25,9**	**1,66**	**12,2**	**1,237**	**6**	**0,006**	**2**	**118,5**	**7,89**
173784	**-27,8144**	**29,70556**	**Borehole**	**C13C**	**1,9**	**1,5**	**29**	**4,9**	**1,89**	**0,5**	**0,02**	**2,7**	**0,152**	**2**	**13,3**	**6,87**
173786	**-27,8125**	**29,88944**	**Borehole**	**V31J**	**12,3**	**4,6**	**112**	**15**	**1,63**	**6,6**	**3,374**	**5,2**	**0,174**	**2**	**52,9**	**7,17**
173787	**-27,8142**	**29,84917**	**Borehole**	**V31J**	**13,4**	**3,6**	**125**	**16,8**	**2,05**	**6,4**	**1,159**	**6,7**	**0,009**	**2**	**68,9**	**7,33**
174066	**-27,8597**	**29,95222**	**Borehole**	**V31K**	**56**	**33,1**	**693**	**82,6**	**4,84**	**28,9**	**0,347**	**90,6**	**0,023**	**124**	**290**	**7,55**
174071	**-27,8839**	**29,97778**	**Borehole**	**V31G**	**123,6**	**23,4**	**1091**	**138**	**4,01**	**47,5**	**0,063**	**125**	**0,008**	**525,7**	**197,3**	**8,07**

Appendix C: Calculated Hydrochemical Parameters

Monitoring Point ID	Latitude	Longitude	Located on Type	Drainage Region Name	TH	SAR	%Na	Mg hazard/MAR	Kelly's ratio	PI %	RSC
173716	**-27,7825**	**29,77194**	**Borehole**	**V31J**	**23,34**	**2,52**	**72,78**	**17,79**	**2,60**	**141,86**	**0,91**
173717	**-27,8892**	**29,84**	**Borehole**	**V31F**	**46,65**	**0,28**	**17,22**	**43,52**	**0,20**	**105,16**	**0,05**
173733	**-27,6183**	**29,88972**	**Borehole**	**V31D**	**181,48**	**0,22**	**7,46**	**72,14**	**0,08**	**51,89**	**-0,56**
173734	**-27,6722**	**29,775**	**Borehole**	**V31C**	**11,05**	**13,97**	**95,46**	**18,80**	**20,99**	**137,03**	**3,88**
173735	**-27,6022**	**29,86889**	**Borehole**	**V31C**	**163,08**	**0,22**	**8,13**	**61,36**	**0,09**	**50,57**	**-0,98**
173736	**-27,7258**	**29,8625**	**Borehole**	**V31J**	**59,53**	**0,37**	**20,23**	**50,76**	**0,24**	**94,84**	**0,06**
173737	**-27,5439**	**29,86583**	**Borehole**	**V31C**	**74,88**	**0,24**	**12,14**	**45,91**	**0,14**	**75,92**	**-0,31**
173738	**-27,5247**	**29,76889**	**Borehole**	**V31C**	**80,54**	**2,76**	**60,98**	**22,68**	**1,53**	**100,50**	**1,06**
173739	**-27,4875**	**29,79167**	**Borehole**	**V31C**	**26,84**	**6,51**	**86,27**	**15,48**	**6,28**	**128,06**	**2,14**
173740	**-27,4658**	**29,71333**	**Borehole**	**V31C**	**129,92**	**1,72**	**43,59**	**25,24**	**0,76**	**82,80**	**0,71**
173752	**-27,4144**	**29,82889**	**Borehole**	**V31B**	**3,31**	**17,24**	**97,93**	**62,50**	**47,22**	**147,45**	**2,47**
173756	**-27,4644**	**30,11556**	**Borehole**	**V31A**	**101,00**	**0,29**	**12,84**	**50,82**	**0,15**	**67,80**	**-0,39**
173757	**-27,695**	**30,11806**	**Borehole**	**V32B**	**48,32**	**21,88**	**94,05**	**23,20**	**15,71**	**105,50**	**2,50**
173758	**-27,6767**	**29,95361**	**Borehole**	**V31D**	**187,18**	**0,36**	**12,68**	**51,30**	**0,13**	**54,97**	**-0,36**
173759	**-27,6233**	**30,07444**	**Borehole**	**V31D**	**15,33**	**1,03**	**61,78**	**43,24**	**1,31**	**159,30**	**0,23**
173761	**-27,4197**	**29,89222**	**Borehole**	**V31B**	**206,53**	**2,01**	**41,50**	**37,13**	**0,70**	**66,78**	**-0,87**
173762	**-27,5092**	**30,05417**	**Borehole**	**V31D**	**91,53**	**0,32**	**14,99**	**45,70**	**0,17**	**74,79**	**-0,15**
173766	**-27,4761**	**30,07722**	**Borehole**	**V31D**	**148,01**	**1,31**	**35,54**	**36,13**	**0,54**	**74,28**	**0,26**
173768	**-27,4019**	**30,12667**	**Borehole**	**V31A**	**164,64**	**0,84**	**24,85**	**47,79**	**0,33**	**66,07**	**0,01**
173769	**-27,41**	**30,0475**	**Borehole**	**V31B**	**66,02**	**0,42**	**20,93**	**33,29**	**0,26**	**88,93**	**-0,02**
173770	**-27,4386**	**29,95222**	**Borehole**	**V31B**	**61,67**	**7,96**	**83,60**	**26,92**	**5,06**	**115,66**	**4,59**
173772	**-27,5647**	**29,98**	**Borehole**	**V31D**	**3,31**	**17,93**	**98,03**	**62,50**	**49,11**	**144,53**	**2,35**
173779	**-27,865**	**29,96722**	**Borehole**	**V31K**	**22,77**	**6,23**	**87,00**	**50,91**	**6,51**	**134,73**	**2,28**
173781	**-27,8283**	**29,76194**	**Borehole**	**V31H**	**246,35**	**0,58**	**16,30**	**19,89**	**0,19**	**41,01**	**-2,74**
173782	**-27,915**	**29,79611**	**Borehole**	**V31F**	**35,83**	**2,89**	**71,19**	**34,72**	**2,41**	**124,36**	**1,02**

173783	**-27,8386**	**29,94528**	**Borehole**	**V31K**	**115,16**	**0,24**	**11,58**	**43,88**	**0,11**	**64,19**	**-0,37**
173784	**-27,8144**	**29,70556**	**Borehole**	**C13C**	**6,80**	**0,45**	**54,82**	**30,49**	**0,86**	**229,98**	**0,08**
173786	**-27,8125**	**29,88944**	**Borehole**	**V31J**	**57,89**	**0,30**	**18,70**	**47,21**	**0,19**	**83,19**	**-0,30**
173787	**-27,8142**	**29,84917**	**Borehole**	**V31J**	**59,82**	**0,38**	**22,23**	**44,32**	**0,24**	**90,59**	**-0,07**
174066	**-27,8597**	**29,95222**	**Borehole**	**V31K**	**258,84**	**2,44**	**43,82**	**46,24**	**0,76**	**66,90**	**-0,46**
174071	**-27,8839**	**29,97778**	**Borehole**	**V31G**	**504,23**	**2,41**	**35,33**	**39,04**	**0,54**	**46,45**	**-6,90**