Investigation of Hydrogeochemical Processes and Groundwater Quality in the Chókwè District, Mozambique

Paulo Sérgio Lourenço Saveca

Master of Science in Geohydrology
June 2016

INVESTIGATION OF HYDROGEOCHEMICAL PROCESSES AND GROUNDWATER QUALITY IN THE CHÓKWÈ DISTRICT, MOZAMBIQUE

PAULO SÉRGIO LOURENÇO SAVECA

Submitted in fulfilment of the requirements in respect of the
Master's Degree qualification

Master of Science majoring in Geohydrology

at the Institute for Groundwater Studies

in the Faculty of Natural and Agricultural Sciences

at the University of the Free State

Supervisor Mr Eelco Lukas
Co-supervisor Prof Dinís Juízo

Bloemfontein

June 2016

DECLARATION

I, Paulo Sérgio Lourenço Saveca, declare that the master's degree research dissertation that I herewith submit for the master's degree qualification *Master of Science majoring in Geohydrology* at the University of the Free State is my independent work and that I have not previously submitted it for a qualification at another institution of higher education.

I, Paulo Sérgio Lourenço Saveca, hereby declare that I am aware that the copyright is vested in the University of the Free State.

I, Paulo Sérgio Lourenço Saveca, hereby declare that all royalties as regards intellectual property that was developed during the course of and/or in connection with the study at the University of the Free State will accrue to the University.

…………………………………… …………………………..

Paulo Sérgio Lourenço Saveca Date

DEDICATION

I proudly dedicate this dissertation to my parents, Lourenço Paulo Saveca and Maria Armando Mondlane, for support and encouragement, giving me the freedom to go forward.

To my late brother, Armando Lourenço Saveca, who serves as my inspiration, to strengthen and rejuvenate my fighting for life all the time**.**

To my youngest sister, Miquelina Lourenço Saveca, for support and advice.

Finally, my special dedication to my lovely wife, Salmina F. Chume Saveca, for her social support, and loving commitment all the time.

ACKNOWLEDGEMENTS

First of all, I would like to thank God for giving me health to move forward and strength, even with so many difficulties and challenges in my daily life.

I would like to express my appreciation and gratitude to my supervisors, Mr Eelco Lukas and Prof Dinís Juízo, for their guidance and endless support, always finding time and patience for advising me in this research. Thank you so much.

For all staff members from the Institute for Groundwater Studies, I am grateful for your scientific and technical assistance during the fieldwork, as well as with the laboratory analysis. A special thank you to Mr Fanie de Lange, for technical help to transport samples from Mozambique to the IGS laboratory; to Mrs Lore-Mari, including other laboratory staff, for understanding of the physicochemical analysis; to Dr Modreck Gomo, for helping me to understand and interpret the hydrogeochemistry of the Chókwè district; and to Mrs Dora du Plessis (former staff member), for excellent technical editing and proofreading of my dissertation.

My special thanks goes to the NUFFIC project, which gave me the opportunity to study.

I also extend my grateful expression to the Mozambique government through their water sectors for their permission and technical support in my fieldwork. My special thanks are due to:

DNA – through Dr Chairuca and Renato Solomone Engineer, for advances and scientific support.

ARA-Sul – through Dr Lizete Dias, head of Water Resources Services, for helping me to identify the study area in Mozambique.

SDPI – through João Chivambo, at the head office, for technical support and allowing me the access and use of district borehole reports.

FIPAG – through José Chiúre, at the head office, and technical engineer, Nelson Mabunda, for their encouraging, significant technical support and assistance. Their generous collaboration, as well as immediate response, influenced and accelerated the present study to be done on time.

I am also thankful for all colleges and friends who have assisted and supported me in my thesis. Thank you.

Finally, I would like to express my deepest gratitude, to my family who has always been loving me no matter what.

TABLE OF CONTENTS

CHAPTER 3
LITERATURE REVIEW 30

CHAPTER 4
RESULTS AND DISCUSSION 58

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS AND ABBREVIATIONS

ANOVA	Analysis of Variance
ARA-Sul	Regional Administration of Water in the South
ASSG	Alluvium, sand, silt gravel
BH	Borehole
BS	Base Saturation
Ca H	Calcium hardness
CAI	Chloro-Alkaline Indices
CENACARTA	Mozambique National Cartography and Remote Sensing Centre (Centro Nacional de Cartografia e Teledetecção)
CIS	Chókwè Irrigation Scheme
CWERC	Colorado Water and Energy Research Center
df	Degrees of Freedom
DNG	National Directorate of Geology (Direcção Nacional de Geologia)
EC	Electrical Conductivity
EFCS	Eluvial floodplain clayey sand
EPA	Environmental Protection Agency
ETo	Evapotranspiration reference (ETo)
FAEF	Faculty of Agronomy and Forestry Engineering (Faculdade de Agronomia e Engenharia Florestal)
FAO	Food and Agriculture Organization
FIPAG	Water Supply Investment and Assets Fund (Fundo de Investimento e Património de Abastecimento de Água)
GEOMOC	Geotechnical of Mozambique (Geotecnia de Moçambique)
GPS	Global Positioning System
Ha	Alternative Hypothesis
Ho	Null Hypothesis
HP	Hand Pump
IB	Ion Balance
IC	Iron Chromatography
ICP	Inductively Coupled Plasma
IDRAS	Internal dune, red aeolian sand
IGS	Institute for Groundwater Studies
IHP	International Hydrological Programme
INE	Statistic National Institute (Instituto Nacional de Estatística)

IS	Irrigation Scheme
Mg H	Magnesium hardness
MISAU	Ministry of Health (Ministério da Saúde)
MRC	Mineral Resources Centre
NEPAD	New Partnership for Africa’s Development
PANESA	Pastures Network for Eastern and Southern Africa
RBD	Randomised Block Design
SADC	Southern African Development Community
SAR	Sodium Adsorption Ratio
SDPI	District Service for Planning and Infrastructure (Serviço Distrital de Planeamento e Infra-estrutura)
TDS	Total Dissolved Solids
TH	Total Hardness
UNEP	United Nations Environment Programme
WHO	World Health Organization

LIST OF SYMBOLS

Al	Aluminium
As	Arsenic
B	Boron
Br	Bromine
Ca	Calcium
Ca^{2+}	Calcium Ion
Cl	Chlorine
Cl^{-}	Chloride Ion
CO_3^{2-}	Carbonate Ion
Cr	Chromium
Cu	Copper
F	Fluorine
Fe	Iron
H^{+}	Hydrogen Ion
HCO_3	Bicarbonate
HCO_3^{-}	Bicarbonate Ion
H_2CO_3	Carbonic Acid
K	Potassium
K^{+}	Potassium Ion
Mg	Magnesium
Mg^{2+}	Magnesium Ion
Mn	Manganese
Na	Sodium
Na^{+}	Sodium Ion
NO_3	Nitrate
NO_2	Nitrite
Pb	Lead
pH	Hydrogen potential
PO_4	Phosphate
Si	Silicon
SiO_2	Silica
SO_4	Sulphate
SO_4^{2-}	Sulphate Ion
Zn	Zinc
μ_1	Mean value of population 1
μ_2	Mean value of population 2
$\sigma_1^{\ 2}$	Variance of population 1
$\sigma_2^{\ 2}$	Variance of population 2

LIST OF UNITS

km	kilometer
m	meter
m/day	meter per day
m^3/h	cubic meter per hour
meq/L	milliequivalents per liter
mg/kg	milligram per kilogram
mg/L	milligram per liter
ml	milliliter
mm/year	millimeter per year
mm^3/year	cubic millimeter per year
µS/cm	micro Siemens per centimeter
µS/m	micro Siemens per meter

ABSTRACT

Groundwater has been recognised in Sub-Saharan countries as the main source of potable water in rural areas. In semi-arid regions, the climatic and anthropogenic factors both significantly affect groundwater quality. The present study was carried out in the Chókwè district, one of the semi-arid regions in Mozambique within the Limpopo River basin. About 33 water sources (27 groundwater, five surface water and one rainwater) were sampled from July to December 2015 for physicochemical parameters.

This study focused on investigating hydrogeochemical processes in groundwater chemistry and their influence on water quality, as well as spatial variability in the Chókwè district. The hydrogeological approaches (WISH) and geospatial tool (Quantum GIS), combined with statistical analyses, were used to assess the groundwater quality. Geochemical ratios, correlation, graphical methods were also applied to understand the local hydrogeology on groundwater hydrochemistry. In addition, the Mozambique standards for drinking water and those of the World Health Organization were used for the assessment of groundwater quality.

The analytical results of groundwater chemistry indicated that the order of abundance of cation concentration were $Na^+ > Mg^{2+} > Ca^{2+} > K^+$, while those of anions were $Cl^- > HCO_3^- > SO_4^{2-}$. There is a dominance of Na-Cl hydrochemical facies, and high mineralised groundwater occurs in aquifers underlined by two geological units, namely: alluvium, sand, silt, gravel geological units and eluvial floodplain clayey sand geological units. The alluvium, sand, silt, gravel showed that the content of electrical conductivity (EC) ranged from 603 to 12 000 µS/cm with an average value of 2 364 µS/cm, while for total dissolved solids (TDS) it ranged from 488 to 7 626 mg/L, with an average value of 1 621 mg/L. In the eluvial floodplain clayey sand geological unit the content of EC ranged from 522 to 5 530 µS/cm with an average value of 2 300 µS/cm, while for TDS it ranged from 406 to 3 537 mg/L with an average value of 1 562 mg/L. It was also observed that 15% and 30% of groundwater samples were classified as poor and unacceptable for drinking. For hardness, 7% and 30% of groundwater was hard and very hard, respectively. All parameters in the surface water are within the desirable limits, unlike that of groundwater.

Weathering, ion exchange, dissolution and precipitation are the main hydro-geochemical processes. In aquifer mineralogy there is a dominance of sodic plagioclase (Albite), calcic plagioclase (Anorthite), halite, dolomite and calcite.

Generally, the groundwater is saline and the land use, chemical evolution, as well as the local hydrogeology, are the factors affecting the spatial variability of water quality. Therefore, groundwater of the Chókwè district would not be safe to use for irrigation over the long term, due to a sodium and salinity hazard.

Keywords: Groundwater quality; hydrogeochemical processes; hydrochemical facies, aquifer mineralogy, Chókwè district.

Chapter 1

INTRODUCTION

1.1 GENERAL BACKGROUND AND PROBLEM STATEMENT

Groundwater is an important resource which is considered in many countries as the purest form of water in the natural environment. Nevertheless, this resource is widely used for different purposes, namely: In agriculture for irrigation, in rural or urban areas for potable water supply and in industrial areas for water supply in mining (Janardhana *et al*., 2013; Zektser and Everett, 2004). The United Nations Environment Programme (UNEP, 2008) and Meybeck *et al.* (1996), affirm that different natural factors such as geological, topographical, meteorological, hydrological and biological, as well as the human influence, affect the quality and composition of surface water and groundwater. In the meantime, the interaction of these factors represents an important key and significant influence in the hydrogeochemical processes to determine the groundwater type and quality (Ostovari *et al*., 2013).

The groundwater quality is a result of the interaction with water of rock material and aquifer minerals. The understanding of groundwater hydrogeochemical process in each geological area is an important key needed to manage groundwater quality. This also provides information of the predominant hydrogeochemical process which leads and affects the quality of water. Therefore, through which process the groundwater quality is originated, better options and ecological solutions can be designed either for urban and rural areas to supply drinking water.

In arid and semi-arid regions, the natural water resources are limited and the rainfall, as well as the runoff, show temporal and spatial variability. These regions are also characterised by their water balance deficit, particularly with regard to exchange with the atmosphere. As a consequence, in arid and semi-arid regions the water quality and scarcity is the dominant problem, as well as the challenges in water management (Araújo*, 2012;* Mathias and Wheater, 2010; Sadashivaiah *et al.,* 2008).

In Mozambique, despite of considerable occurrences of surface water, the groundwater plays an important role in arid and semi-arid regions (rural and urban areas). The groundwater is widely used for potable water supply by the following providers: District Service for Planning and Infrastructure (SDPI), Water Supply Investment and Assets Fund (FIPAG) and other private providers. The Chókwè district, one of the arid regions in the south of Mozambique (north of the Gaza Province), has been facing water quality issues. Performed physical and chemical analysis by FIPAG and SDPI from most used boreholes, hand pumps and wells, the results show high values of Electrical Conductivity (EC) and Chloride (Cl) concentration (3 670 µS/cm and 1 240.75 mg/L, respectively). These values are out of desirable limits for drinking water standards in Mozambique. So, the rural areas are more affected than urban areas because the drinking water is not treated and is obtained directly from hand pumps and wells. Therefore, it represents a challenge to supply fresh water in the Chókwè district, specifically in rural areas.

As a consequence of high values of EC and Cl, the groundwater in certain villages of the Chókwè district (Punguíne, Duvane, Conhane, Lionde, Massavasse, Mapapa and Nwachicoluane) is brackish and not suitable for drinking. Due to this reality, some drilled boreholes, as well as hand pumps in rural areas, are abandoned and not used to get fresh water. The population from these villages suffer to get drinking water and need walk about five kilometres to get fresh water. Unfortunately, few studies have been conducted in the Chókwè district to know what, how and why the salinity of the water is affecting those villages. Because of this lack of information the management of groundwater to supply fresh water is very difficult. From the total capacity of 1 065 m^3/h at the pump station in the district, the FIPAG only uses 590 m^3/h, corresponding to 55%, due to the undesirable quality of the groundwater. And the water treatment is limited because of unknown water facies occurring in the Chókwè district, including the affected rural areas.

According to the Environmental Protection Agency (EPA, 2001), the high content of EC and Cl may increase the salinity of the water, as a result of inorganic salt and organic matter. Despite of non-direct effect on health or sanitary, the presence of a high salt content has significant influence in the Total Dissolved Solids (TDS) content of the water. In general, it also affects the water palatability and make the water unsuitable for human use.

In the aquifers, different processes or reactions may occur resulting in primary or secondary salinity. The processes or reactions such as dissolution, rock weathering, mixing, ion exchange and nitrification of organic matter have a direct influence to yield salt in water. Thus, the identification of aquifer mineralogy and the respective chemical reactions are important to understand the hydrogeochemistry behaviour of the aquifer (Chebbah and Allia, 2015; Shaw and Gordon, 2011).

To understand the reason for groundwater salinity of the Chókwè district it is necessary to carry out hydrogeochemical investigations to identify processes through which the water quality is affected. As a scientific contribution for groundwater quality management the present study were carried out in the Chókwè district from March to November of 2015 in Lionde, Macarretane and Chókwè administrative zones. It is expected to know the aquifer mineralogy, processes and chemical reactions, as well as the sources or factors affecting the salinity in groundwater. Also it is expected to give a better understanding of district hydrogeochemistry to help the water provider to solve the salinity issue through improving and adopting local strategies to manage the groundwater quality.

1.2 OBJECTIVES

1.2.1 Main objective

The main aim of this study is to analyse the groundwater chemistry of the Chókwè district and its influence on water quality. The study will also identify the hydrogeochemical processes and facies in order to show the spatial variability.

1.2.2 Specific objectives

The specific objectives of the study are to:

- complete a hydrocensus and measurement of groundwater levels;
- to carry out sampling and do an analysis of physical and chemical parameters of surface water and groundwater;
- classify and compare the physical and chemical parameters between surface water and groundwater; and
- provide a diagrammatic representation of physical and chemistry parameters of groundwater in a map.

1.3 LIMITATIONS OF THE RESEARCH

The district does not have a data base archiving groundwater quality and quantity, through which water quality variability may be understood.

Few groundwater studies and infrastructures are available (monitoring of boreholes, hand pumps or wells) to assess the water quality. Therefore, the study design, as well as the fieldwork, was only limited to existing groundwater infrastructures.

The present study was carried out only in a dry season due to the limited budget for field work. Therefore, the groundwater quality results may not be extrapolated to a wet season.

The study parameter was only the physical and chemical aspects of the aquifer. Thus, this may represent a limitation to understand the behaviour of microbiological parameters and organoleptic characteristics of groundwater (colour, smell, flavour and texture) in the Chókwè district.

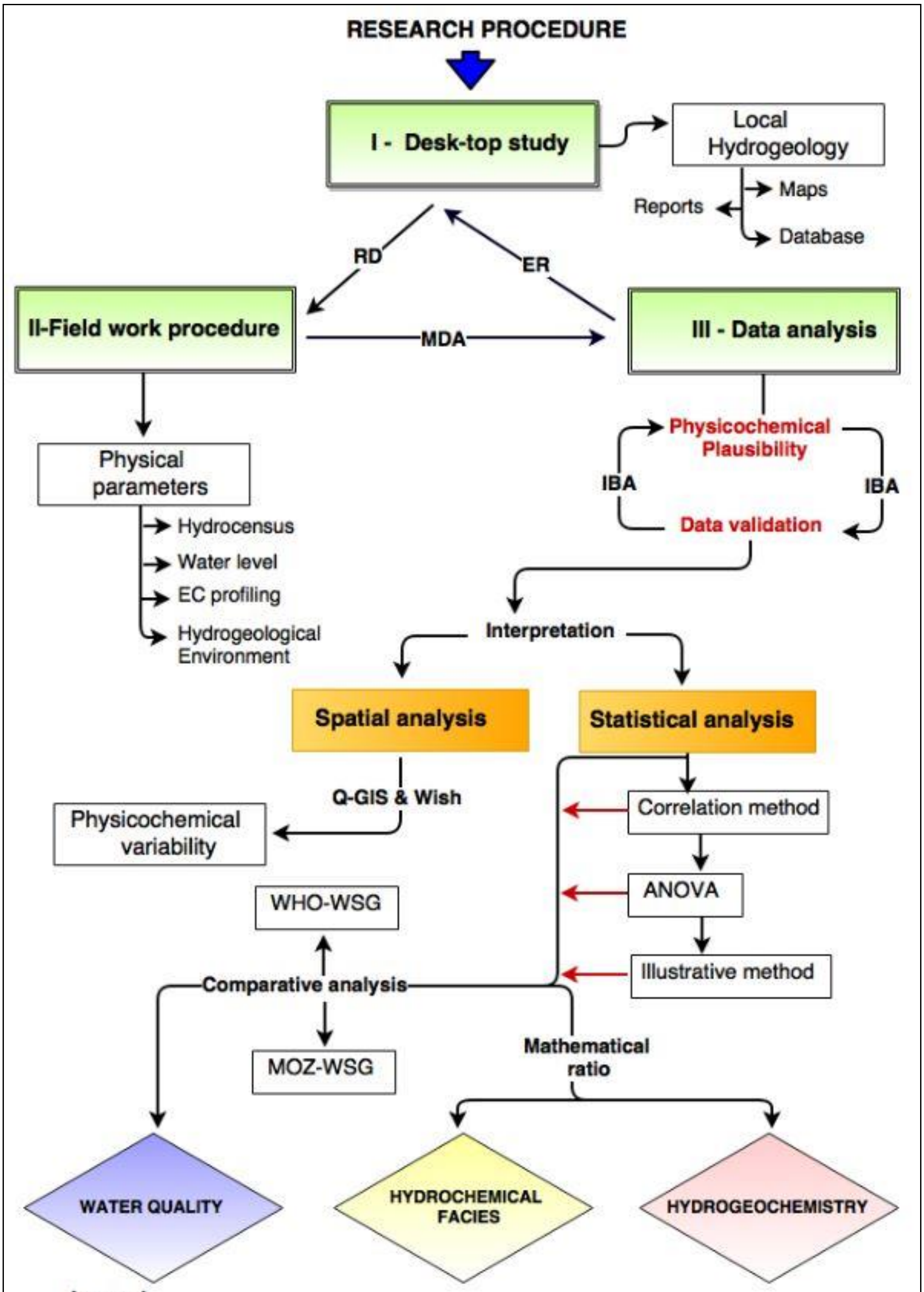
Another type of limitation to be considered is the impact limitation. As the Chókwè district hold the largest irrigation scheme of the country, the farmers are using surface water to irrigate their crops. In this context, it may represent less interest for the local (or provincial) government if the farming is the source of salinity in groundwater.

Despite the correlation method used in a wide range of variables, the interrelation do not indicate the causation. Also the correction method does not describe how the chemical variables interact.

The illustrative method is very superficial and do not describe the reason of chemical composition variability in groundwater. To enable an integrated data analysis, different approaches were used to minimise the advantages and disadvantages of each method.

1.4 METHODOLOGY AND STUDY DESIGN

In the present hydrogeochemical study, the methodological approach involved three general components, which are described below and summarised in Figure 1.1.



Legend

MOZ-WSG = Mozambique Water Standard Guideline
ANOVA = Analysis of Variance
WHO-WSG = World Health Organization Water Standard Guidelines
IBA = Ion Balance Analysis
MDA = Methods for Data Analysis
RD = Research Design
ER = Expected Results

Figure 1.1: Methodology components and study design structure used for the hydrogeochemical study

- **Desktop study**: Collection, compilation and interpretation of all existing information (maps, data base and reports) related to groundwater in the Chókwè district in order to design the study plan. The different maps used and analysed, were supplied by the Mozambique National Cartography and Remote Sensing Centre (CENACARTA) in shape file format.

- **Fieldwork procedure**: Sampling and measurement of physical and chemical parameters.

- **Data analysis and interpretation**: Description and characterisation of the physical and chemical parameters, using appropriate statistical methods and tools.

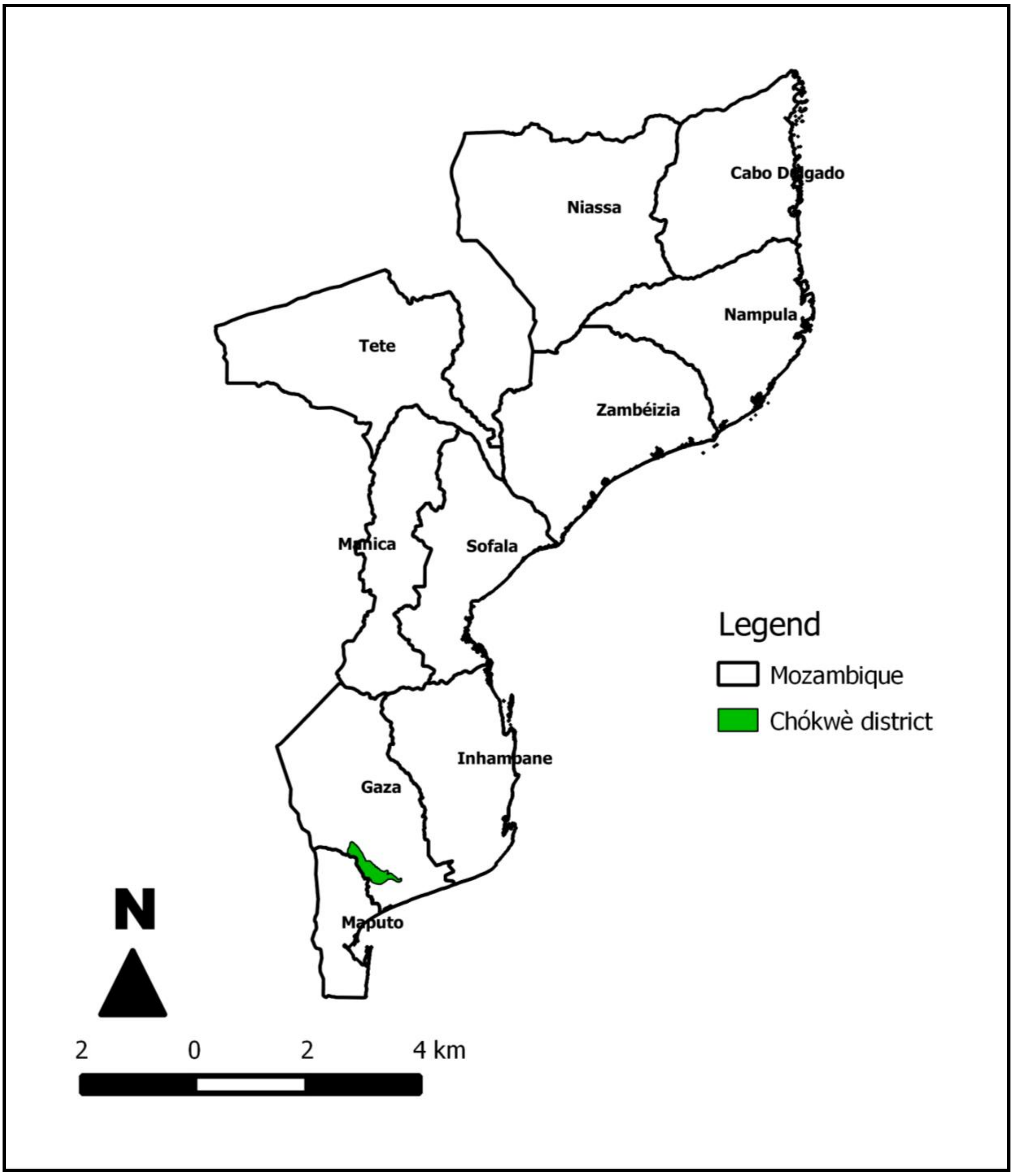
1.4.1 Fieldwork procedure

The fieldwork in the study area was based on the following activities:

- Water sampling and hydrocensus.
- Water level measurement (groundwater).
- Physical observation/description of the environmental aspects of the study area.
- Testing of field parameters.

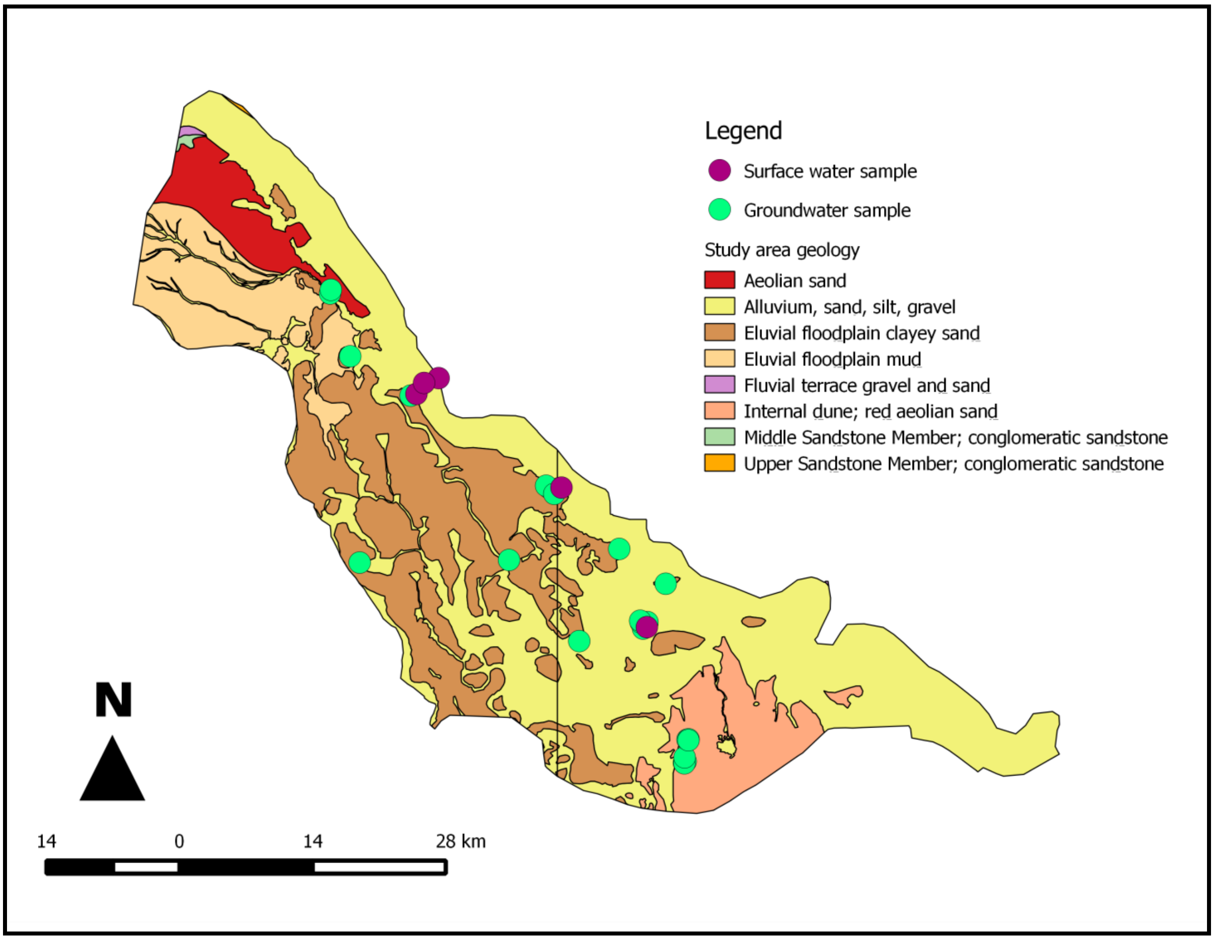
1.4.1.1 Water sampling and hydrocensus

A total of 33 water samples (27 from groundwater, six from surface water and one from rainfall) were collected in Lionde, Macarretane and Chókwè administrative zones for physical and chemical analysis. The samples were collected in the dry season between July and November 2015. To ensure better representative, the groundwater samples were taken from the main basic geological units of the Chókwè district. Figure 1.2 visualises the study area in Mozambique and Figure 1.3 the main geological units of the district, namely: aeolian sand; alluvium, sand, silt, gravel; eluvial floodplain clayed sand; eluvial floodplain mud; fluvial terrace gravel and sand; and internal dune, red aeolian sand.



Source: CENACRTA (2015).

Figure 1.2: *Mozambique map and location of the Chókwè district*



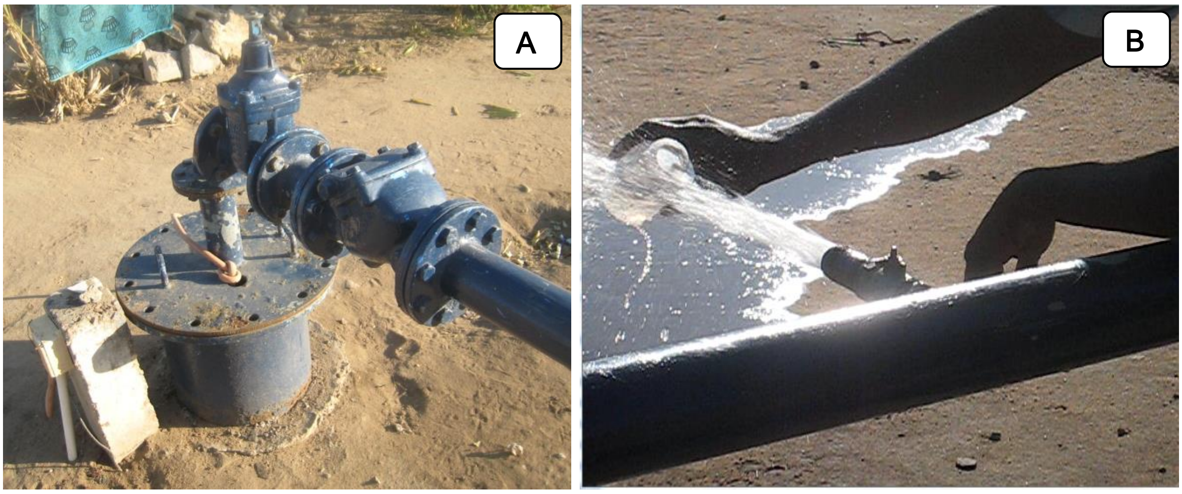
Source: Adapted from the National Directorate of Geology (DNG, 2006).

Figure 1.3: Overview of the study area hydrocensus in Chókwè district

The samples were collected from boreholes, hand pumps and wells, while the surface water samples in the Limpopo River, main canal of the Chókwè Irrigation Scheme (CIS) and swamp (shown below in Figure 1.4). The collection of groundwater samples in boreholes was done directly after the submersible pump was started. The water samples were taken five minutes after the submersible pump started working (including the hand pump) to ensure that representative water sample of the aquifer is collected from the valve. In some cases, due to the borehole design, it was possible to use a bailer (even for wells), as shown below in Figure 1.5. The bailer was tied with a rope and introduced into the boreholes or well until the desired depth to sample the groundwater. After water collecting, the sample was quickly transferred to the container (plastic bottle) minimising exposure to the atmosphere.

A = Sampling in Limpopo River B = Sampling in a well

Figure 1.4: Water sampling procedure during the field work

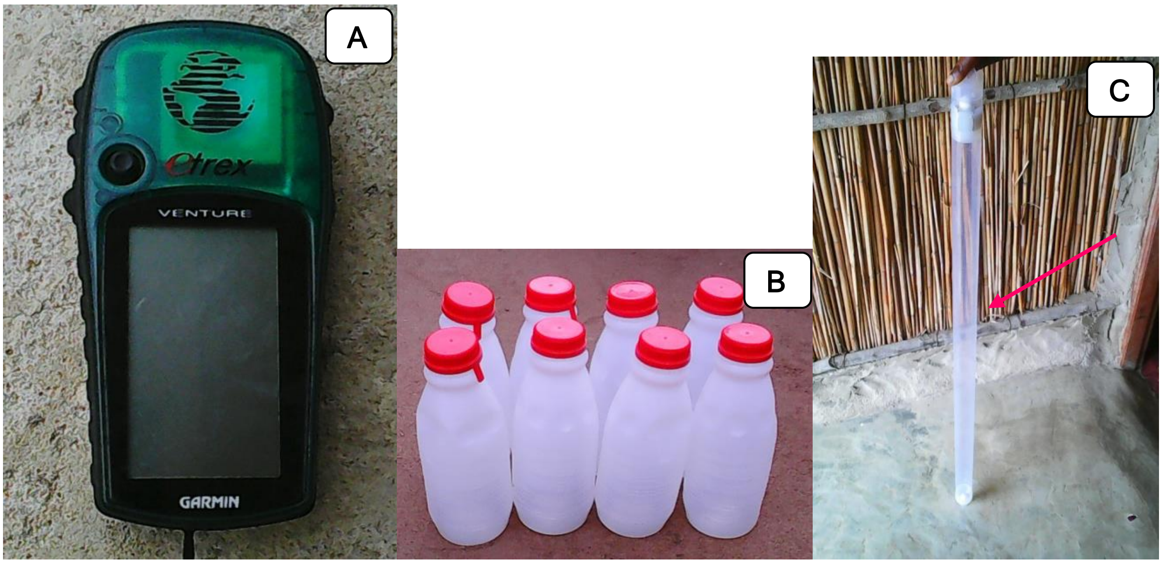


A = Borehole with submersible pump B = Valve of water sampling

Figure 1.5: Water sampling in submersible working pump

To conserve and avoid contamination, each sample was stored in a new clean plastic bottle (500 ml) as shown in Figure 1.6 below. The bottles were filled without overflowing and immediately closed after sampling to not allow the entry of air into the water. Finally, the plastic bottles containing the water samples were labelled with the date and location where the samples were taken. From the field to the laboratory analysis, the samples were kept conserved in a cooler box while being transported.

During the water sampling the hydrocensus was also done. The hydrocensus were carried out using a Global Positioning System (a Garmin Venture Etrex GPS) to record the coordinates (latitude, longitude and altitude) of sampled points in the study area (Figure 1.6 below).



A = GPS B = Plastic bottles C = Plastic bailer

Figure 1.6: Measurement equipment of water sampling and hydrocensus

1.4.1.2 Physical observation and description in the study area

The observation and descriptions for environmental aspects in the study area were done using a field notes form (Appendix 1). Aspects related to land use and local physical hydrology in each groundwater source were taken into account. This information provided a general overview of the surrounding environment in each of the water sources from the study area in order to understand their effect on groundwater quality.

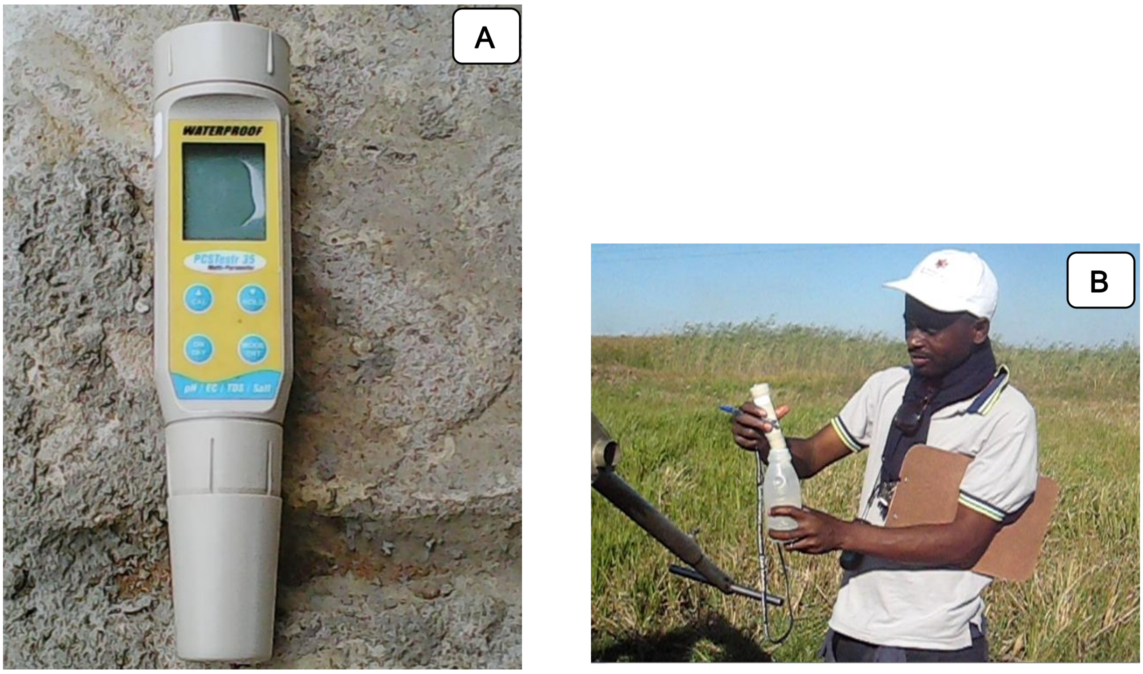
1.4.1.3 Water level measurement in groundwater

The water level depth was taken using a Water Level Metre (WLM) of all sited wells, and boreholes where possible, as shown in Figure 1.7 below. In some cases, to get the water level, the automatic diary measurement database given by FIPAG (for boreholes), the technical report from SDPI (for hand pumps), as well as the groundwater database from the Mozambique Regional Administration of Water in the South (ARA-Sul), were used. ARA-Sul also supplied most of the maps used for this study. The water level helped to provide information on the hydraulic gradient in order to determine the groundwater flow direction.

***Figure 1.7:	Illustration of water level metre used in the field***

1.4.1.4 Testing of field parameters

The field test (in situ measurements) was carried out for pH, Electrical Conductivity (EC), temperature (T), Total Dissolved Solids (TDS) and salt. The multiparameter PCS Testr 35 was used to test the mentioned chemical parameters, as shown in Figure 1.8 below. This tester is a waterproof, pocket-sized metre used for testing pH, conductivity, TDS, salinity and temperature.



A = Equipment used

B = Field test procedure

***Figure 1.8:	Multiparameter Testr 35 equipment used for field test parameters***

1.4.2 Laboratory analysis

The laboratory analysis of chemical parameters was carried out at the Institute for Groundwater Studies (IGS), University of the Free State. The major and minor physicochemical parameters analysed included pH, TDS, hardness and EC. (The results are shown in Appendix 2.) For cations analysis the Inductively Coupled Plasma (ICP) method, was used, and for anion analysis the Ion Chromatography (IC) method was used (Eaton *et al.,* 2005).

1.4.3 Data analysis and interpretation

Before any data analysis and interpretation could be done, the plausibility of all chemical analysis were first evaluated in order to ensure that results from the analysed samples are reliable. Therefore, Equation 1.1 was used for accuracy of the chemical analysis.

$$\text{IB (\%)} = \frac{\sum Cations[meq/L] + \sum Anions[meq/L]}{\sum Cations[meq/L] - \sum Anions[meq/L]} \times 100 \qquad \text{(Equation 1.1)}$$

Where IB is Ion Balance.

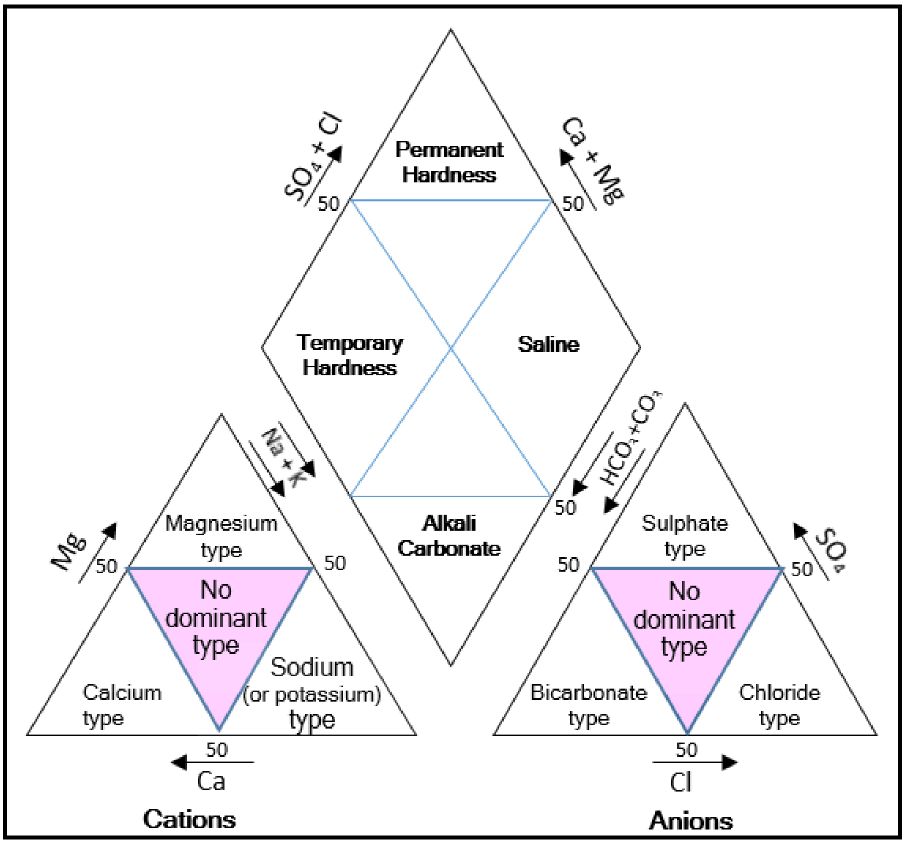
If IB is smaller than -5 or +5, the results are accepted.

If IB is greater than -5 or +5,, the results are not accepted.

To interpret and analyse the water quality, qualitative and quantitative assessments were used. The qualitative assessment was based on observation and description of the physical environmental of the study area. The quantitative assessment was based on statistical analysis using different tools and methods described below.

1.4.3.1 Quantum GIS 2.0.1 and WISH 3.01.188 software

These software were used to show the diagrammatical representation of groundwater quality, as well as their spatial distribution in the district. Using WISH 3.01.188 the hydrochemical facies were determined, plotting and displaying the cations and anions in a piper diagram, including stiff diagram. From the obtained hydrochemical facies in the piper diagram (Figure 1.9 below), it will be known whether the groundwater is within desirable limits according to the Mozambique Water Standard Guidelines, or whether the groundwater has been polluted.



Source: Drever (1997).

Figure 1.9: ***Hydrochemical facies, in percentage of total equivalents per litre***

1.4.3.2 Analysis of variance

The analysis of variance (ANOVA) was carried out at a significance level of 5%. The analysis was based in a randomised block design (RBD) with three categories of geological units as the group or block effects in water quality:

- Geological unit 1 – Alluvium, sand, silt gravel (**ASSG**)
- Geological unit 2 – Eluvial floodplain clayey sand (**EFCS**)
- Geological unit 3 – Internal dune, red aeolian sand (**IDRAS**)

The EC and TDS are the two parameters tested to evaluate the water quality and mineralisation among the geological unit groups. Groundwater sources observed in the same geological unit (boreholes, hand pumps, and wells) were considered as repetitions. Comparisons of water quality and mineralisation between geological units were performed using the t-test at a significance level of 5%.

The difference of variances between the geological unit groups was performed using the F-test, to test the validation of the null hypothesis. If the F-test $_{\text{calculated}}$ > F-test $_{\text{critical}}$, the null hypothesis is rejected. If the F-test $_{\text{calculated}}$ < F-test $_{\text{critical}}$ the null hypothesis is not rejected.

Ho: $\sigma_1^2 = \sigma_2^2$ (the variances of the two geological units are equal)

Ha: $\sigma_1^2 \neq \sigma_2^2$ (the variances of the two geological units are not equal)

Where Ho is the null hypothesis; Ha is the alternative hypothesis; σ_1^2 and σ_2^2 is the variance value of EC or TDS in geological unit 1 and 2, respectively.

As **ASSG**, **EFCS** and **IDRAS** geological units are heterogenic, two assumptions were taken into account to perform the ANOVA:

- Each geological unit has a specific characteristic and the main physicochemical parameters of water have slight variation within the groups.
- Among the geological units, the composition of the main physicochemical parameters of water is different and has significant variation.
- Mixed model, as the occurrence of the geological unit is aleatory and the groundwater physicochemical parameters are the constant in the geological unit.

The t-test at a significance level of 5% was used to compare means of TDS and EC between the geological units, when the null hypothesis is rejected in the F-test. In this context, three paired t-test comparisons were done, namely:

- ASSG *versus* EFCS.
- ASSG *versus* IDRAS.
- EFCS *versus* IDRAS.

If the t-test $_{\text{calculated}}$ > t-test $_{\text{critical}}$, the null hypothesis is rejected. If the t-test $_{\text{calculated}}$ < t-test $_{\text{critical}}$ the null hypothesis is not rejected. The mean values were compared based on the following formulated hypothesis:

Ho: $\mu_1 = \mu_2$ (the means of the two geological units are equal)

Ha: $\mu_1 \neq \mu_2$ (the means of the two geological units are not equal)

Where Ho is the null hypothesis; Ha is the alternative hypothesis; μ_1 and μ_2 is the mean value of EC or TDS in geological unit 1 and 2, respectively.

The assumptions taken into account to use the t-test are:

- Non-equal variances, when the null hypothesis is rejected in the F-test.
- Equal variances, when the null hypothesis is not rejected in F-test.

1.4.3.3 Correlation method

The correlation method was used to compare the chemical analysis in order to identify and find differences or similarities in water composition of the study area. From this method the correlation among types of water were determined, expressing the relationship among ions through mathematical ratios (as shown in Table 1.1 below). The mathematical ratio was used to identify the hydrogeochemical processes, aquifer mineralogy and their respective related groundwater quality. The Microsoft Excel 2007 spreadsheet was used as tool to determine the regression line and correlation coefficient (r), from Equation 1.2 and 1.3, respectively. Additional descriptive statistical analysis of physical and chemical data was carried out, namely minimum, maximum, average and standard deviation.

TABLE 1.1: SOURCE ROCK DEDUCTION, REACTION AND AQUIFER MINERALOGY

Parameter/ratio (meq/L)	Critical value	Conclusion	Sources
$\frac{Na^{+}+K^{+}-Cl^{-}}{Na^{+}+K^{+}-Cl^{-}+Ca^{2+}}$	>0.2 and <0.8 <0.2 or >0.8	Plagioclase weathering possible Plagioclase weathering unlikely	[1]
$\frac{Na^{+}-Cl^{-}}{Ca^{2+}+Mg^{2+}-SO_4^{2-}-HCO_3^{-}}$	= –1	Ion exchange	[2]
$\frac{Mg^{2+}}{Ca^{2+}+Mg^{2+}}$	***HCO_3^-/SiO_2 >10*** =0.5 <0.5 >0.5 ***HCO_3^-/SiO_2 <5*** <0.5 >0.5	**Carbonate weathering:** Dolomite weathering Limestone-dolomite weathering Dolomite dissolution, calcite precipitation or seawater **Silicate weathering:** Ferromagnesian minerals Granitic weathering	[1]
$\frac{Ca^{2+}}{Ca^{2+}+SO_4^{2-}}$	=5 <0.5; pH <5.5 <0.5 neutral >0.5	Gypsum dissolution Pyrite oxidation Calcium removal – ion exchange or calcite precipitation Calcium source other than gypsum—carbonates or silicates	[1]
$\frac{Ca^{2+}+Mg^{2+}}{HCO_3^{-}+SO_4^{2-}}$	<1 >1	Silicate weathering Carbonate weathering	[3]
$\frac{Na^{+}}{Cl^{-}}$	=1 >1	Halite dissolution Source of Na is silicate weathering	[4]
$\frac{Ca^{2+}}{Mg^{2+}}$	= 1 >1 >2	Dolomite dissolution; Ca and Mg from carbonate minerals Calcite Dissolution of silicates	[1] & [5]
TDS	>500 <500	Carbonate weathering or brine or seawater Silicate weathering	[1]
$CAI_1=\frac{[Cl-(Na+K)]}{Cl}$ $CAI_2=\frac{[Cl-(Na+K)]}{(SO_4+HCO_3+CO_3+NO_3)}$	>1 <1	Reverse ion exchange Ion exchange	[6]

[1] Hounslow (1995); **[2]** Fisher and Mullican (1997); **[3]** Nur *et al.* (2012)*;* **[4]** Richter and Kreitler (1993); Edmunds *et al*. (2003) referred in Monjerezi *et al*. (2012); **[5]** Mayo and Loucks (1995); **[6]** Laxman *et al*. (2014); Nagaraju *et al*. (2006); Chebbah and Allia (2015).

$$Y = \alpha + \beta x_i + \varepsilon_i \qquad \text{(Equation 1.2)}$$

Where:

Y = Predictable value of chemical concentration

x_i = Time or concentration of water sample

ε_i = error; E (ε_i) = 0, Var (ε_i) = σ^2

α = Intercept of the regression line

β = Slope of the regression line

$$r_{xy} = \frac{S_{xy}}{S_x S_y} \qquad \text{(Equation 1.3)}$$

Where S_x and S_y is the sample standard deviation and S_{xy} is the sample covariance.

When the correlation coefficient is close to 1, it can be concluded that the variables are positively linearly related.

If r_{xy} <1, there is negative correlation
If r_{xy} >1, there is positive correlation
If r_{xy} = or $\approx$1, there is correlation
If r_{xy} = or $\approx$0, there is no correlation

1.4.3.4 Illustrative method

As illustrative method, maps and graphs were used to show and display the groundwater quality of the study area. The Stiff diagram, frequency diagram and pie diagram were used to illustrate the data chemistry.

1.5 OUTLINE OF THE STUDY

Chapter 1 provides the general structure of the hydrogeological investigation, outlining the objective of the present study in the Chókwè district. Figure 1.10 shows the overview of the relationship among all chapters.

Chapter 2 gives the physical description of the study area. General and local hydrogeology is provided on aspects related to topography, climate, hydrogeology and soil characterisation.

In Chapter 3 aspects related to the hydrogeochemical investigation parameters will be discussed. This chapter describes in general the water quality parameters and the common methods or techniques used in hydrogeochemical studies. Also, the chapter indicates the preview studies and works (in general) and the importance of the current study in the Chókwè district.

Chapter 4 presents the results of groundwater physicochemical parameters in the Chókwè district. The groundwater quality parameters and their spatial variability are discussed and interpreted. Dominant hydrochemical facies and hydrogeochemical processes, including the aquifer mineralogy in the study area, is discussed. In addition, the factors affecting groundwater quality in the district is identified.

Finally, Chapter 5 gives the overall conclusion from the analysis of groundwater quality in the study area, including the recommendations arising from the present research.

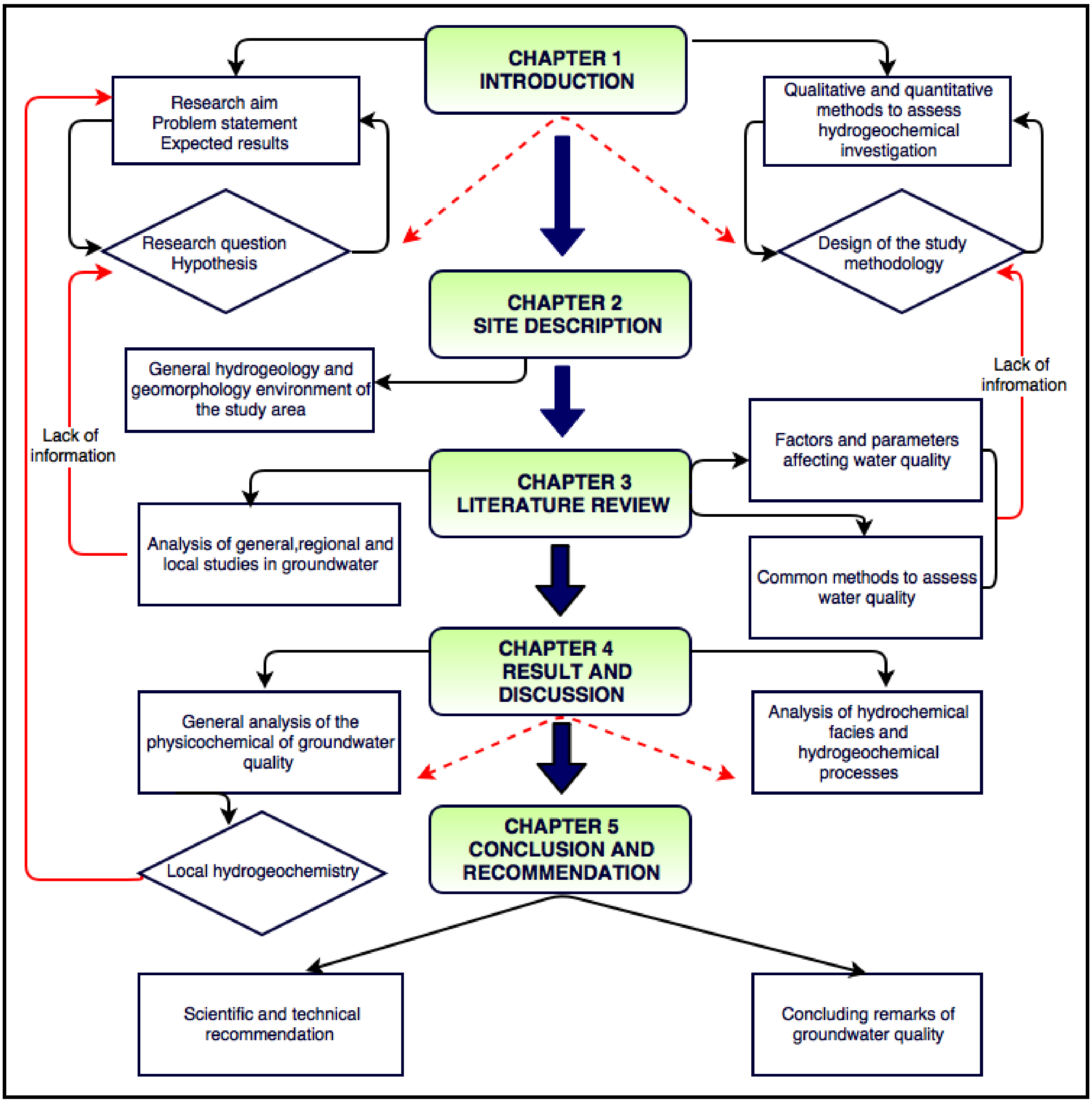


Figure 1.10: Outline of the thesis structure and respective link

Chapter 2
SITE DESCRIPTION

2.1 INTRODUCTION

In this chapter the general characteristics of the study area will be described. The description will be related to the following topics or items:

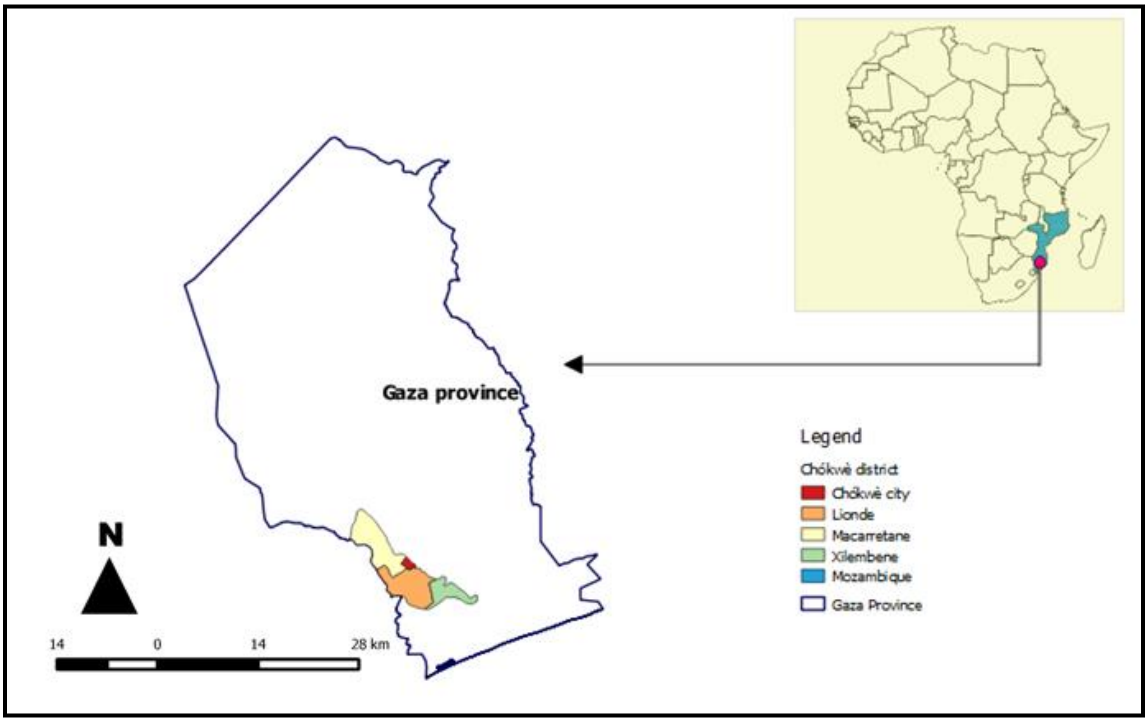
- General description of the study area.
- Climate characterisation.
- Hydrogeology.
- Geology setting.
- Land use and vegetation
- Soil characterisation.

2.2 GENERAL DESCRIPTION OF THE STUDY AREA

The present study was carried out in the Republic of Mozambique. The country is situated on the east coast of Southern Africa between 10˚27'S and 26˚52'S latitude and 30˚12'E and 40˚51'E longitude (Figure 2.1). The territory is divided into 10 provinces and 128 districts. The population is about 24.4 million with 31% living in urban areas and 69% in urban areas (Bouman and Ferro, 1987; INE, 2013).

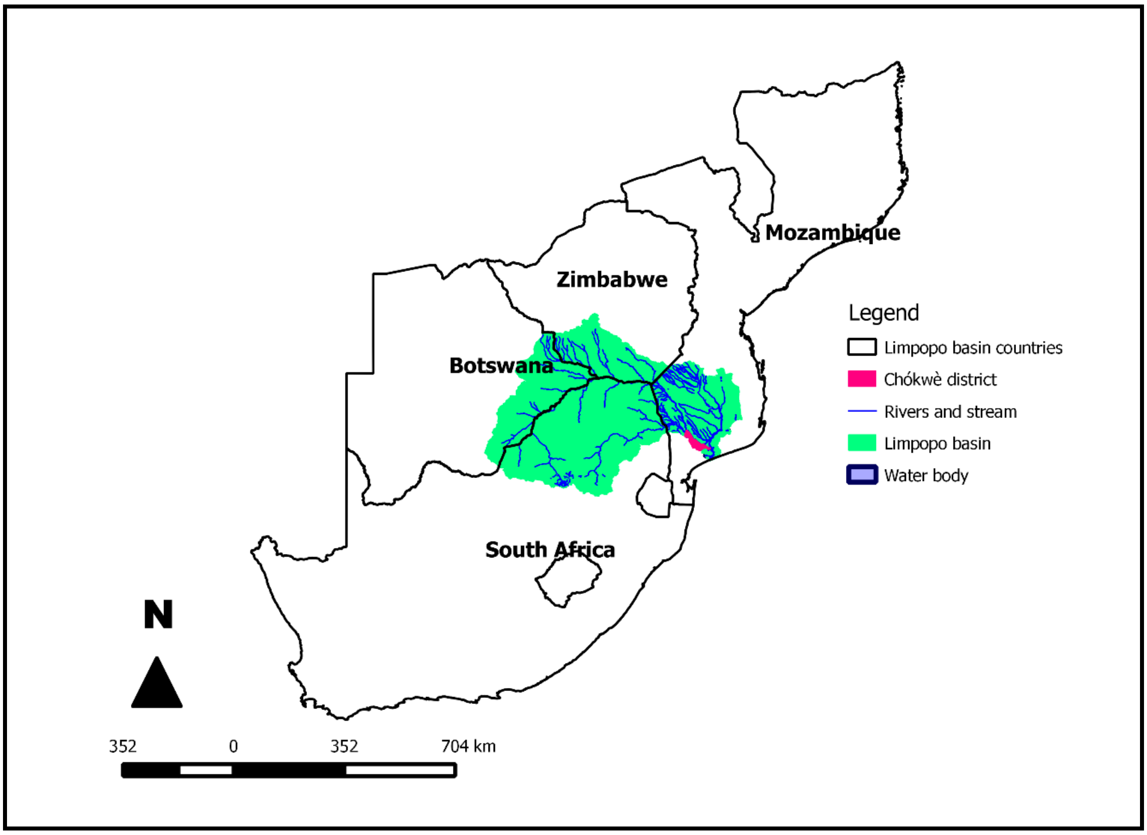
The study area is the Chókwè district, located in the Gaza Province, in the southern part of the country. The district has four administrative zones (Macarretane, Chilembene, Lionde and Chókwè City) and it is part of the Limpopo River basin in Mozambique. This river basin is shared by four Southern African Development Community (SADC) countries, namely: Botswana, Mozambique, South Africa and Zimbabwe, with an area of 73 000 km^2, 79 600 km^2, 193 500 km^2 and 68 000 km^2, respectively (Figure 2.1 and Figure 2.2).

The district is limited in the north by the Guijá and Mabalane districts, south by the Xai-Xai, Bilene and Magude districts, west by the Magude and Massingir districts and in the east by the Chibuto district. The population of the district is about 196 671 habitants, with a density of 80,5 people per km^2, as shown below in Table 2.1.



Source: ARA-Sul (2015).

Figure 2.1: ***General location of the study area in Mozambique***



Source: ARA-Sul (2015) and CENACARTA (2015).

Figure 2.2: ***Limpopo River basin and respective shared countries***

TABLE 2.1: DEMOGRAPHIC CHARACTERISATION OF CHÓKWÈ DISTRICT

Demography characterisation	Unit	Value
Total area of the district	km^2	2 443
Total population of the district	People	196 671
Population in rural area	People	114 069 (58%)
Population in urban area	People	82 602 (42%)
Population density	$People/km^2$	80,5
Growth rate	Percentage	2.1%

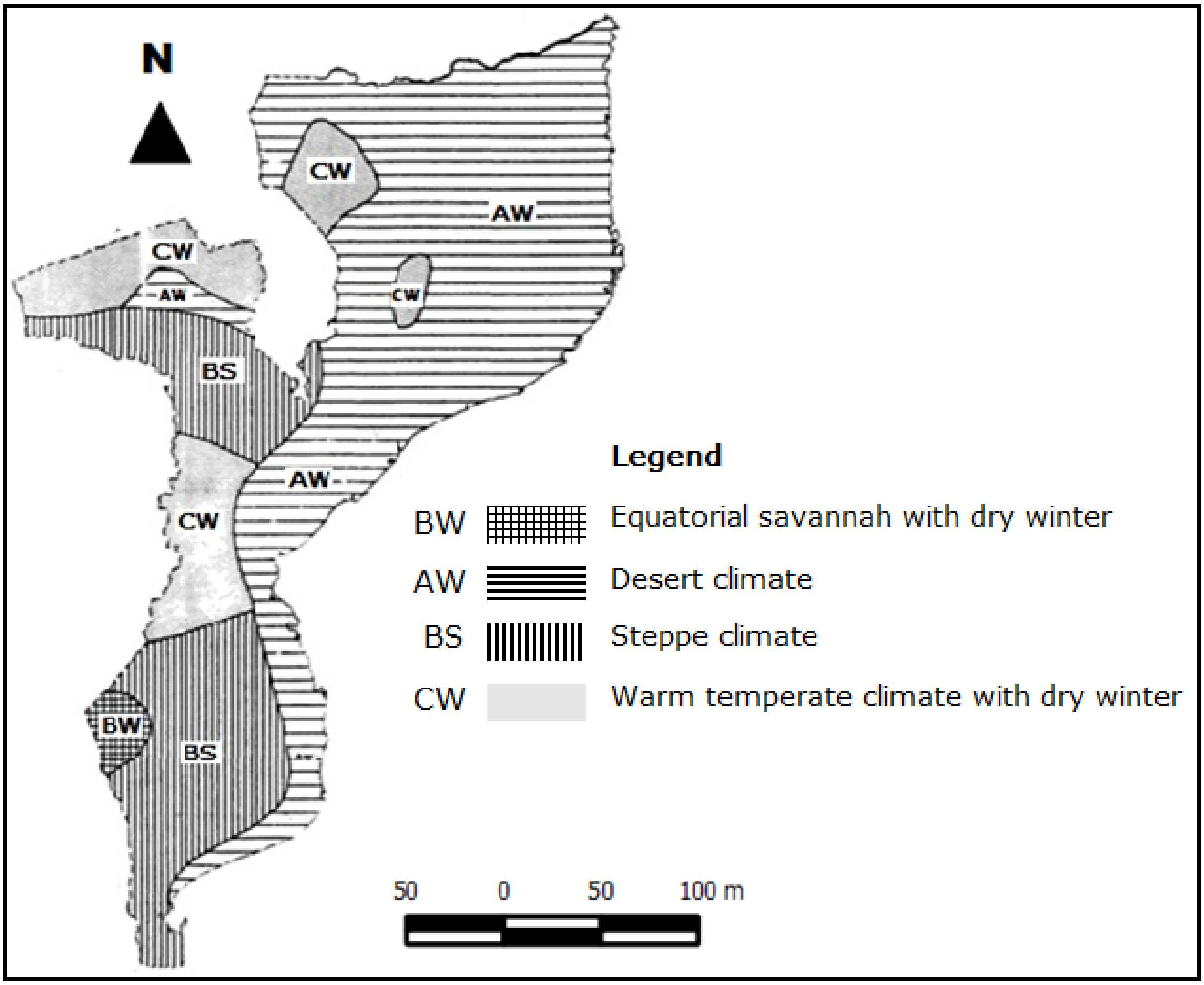
Source: INE (2012); INE (2013).

2.3 CLIMATE CHARACTERISATION

In a general way, according to the Köppen Climate Classification System (Reddy, 1984; Gomes and Famba, 1999, cited in Munguambe, 2007) it is possible to clearly identify four basic climate types dominant in Mozambique (Figure 2.3 below):

- **Equatorial savannah** (BW) with dry winters (or tropical savannah climate) in the north and west.
- **Steppe climate** (BS) (or dry Steppe climate) in the central south and central east.
- **Warm temperate climate** (CW) with dry winters (or temperate humid climate with a dry season in winter in high regions) in the Niassa Province, north of the Tete and Manica Provinces.
- **Desert climate** (AW) (or desert dry climate) in a small area in the eastern province of Gaza (Kottek *et al.,* 2006; Mihajlovich and Gomes, 1986).

In the Chókwè district the climate is semi-arid and dry savannah (BS). Based on an agro-ecological classification, the district is dominated by an agro-ecological zone (R3), one of the most arid parts of Mozambique. The mean annual precipitation is approximately 630 mm/year with reference evapotranspiration (ETo) of 1 580 mm/year and an altitude of less than 200 m. Two seasons are predominating in the district: a dry season from May to September and a rainy season from October to April. The variability of precipitation is high over the year (25–50%) and the monthly relative humidity is around 68,3%, with the minimum and maximum monthly absolute temperature of 8 °C and 41,6 °C, respectively. The area is vulnerable to climate impact events such as droughts and floods. Since 1917 until 1995 the district has been affected by flood events, with differentiated impacts (FAEF, 2001; FEWS NET, 2014; INE, 2013; Munguambe, 2007; NEPAD, 2004).

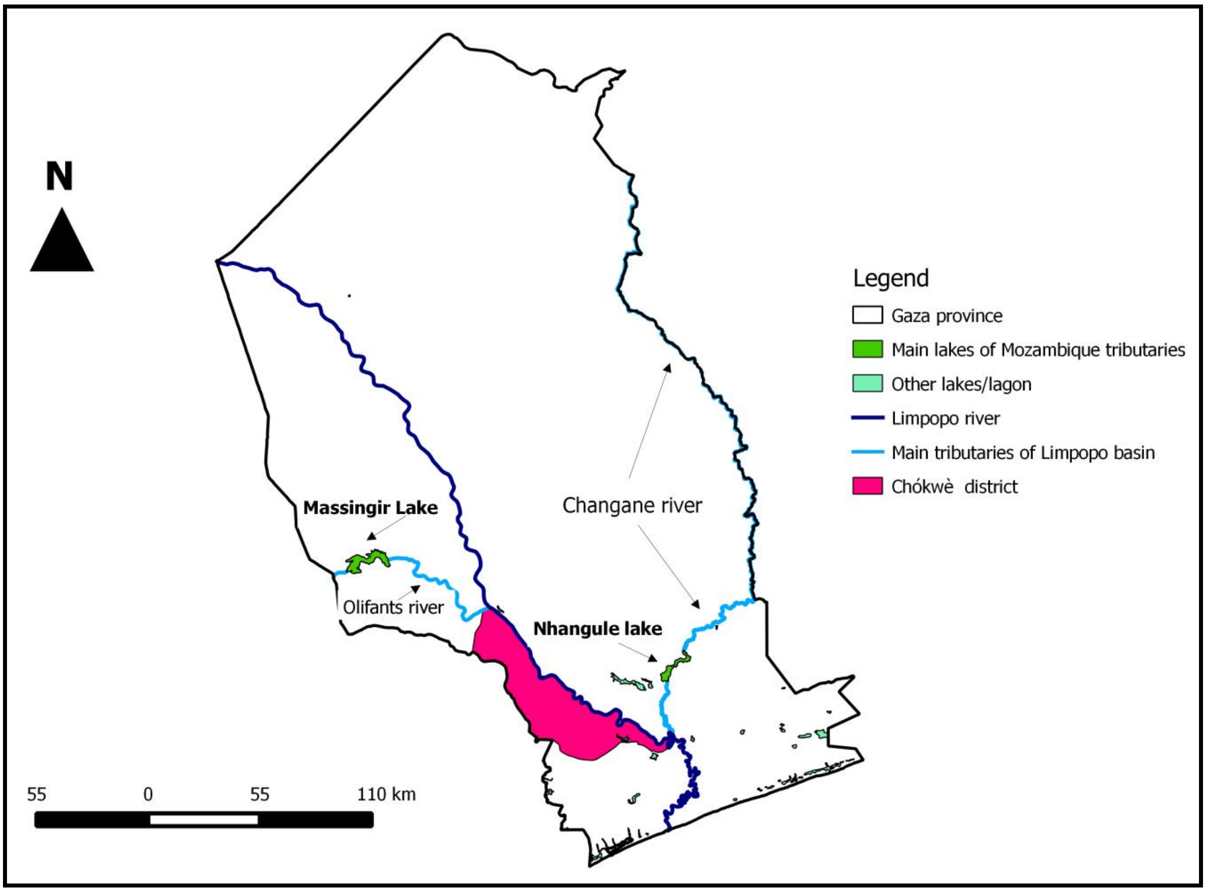


Source: Kottek *et al.* (2006); Mihajlovich and Gomes (1986).

Figure 2.3: Climate type of the study area

2.4 HYDROGEOLOGY

Mozambique is considered a quite privileged country in terms of surface water resources. Large parts of rivers in the country are international and characterised by flooding in the rainy season. The rainy season contributes 70% of annual runoff and the average runoff coefficient is about 12.8% (1.5% for the Limpopo River and 26% for the Licungo River in Zambézia). The Chókwè district is crossed by the Limpopo River, part of Limpopo basin. The Changane and Olifants (Elephant) Rivers is the main tributary for the Limpopo basin in Mozambique, Gaza Province (as shown in Figure 2.4). The water demand from the Limpopo River is mainly for irrigation (95.41%), while 3.18% and 1.41% is for rural and urban purposes, respectively. The total amount demanded from the river is about 283 mm^3/year (Bouman and Ferro, 1987; Munguambe, 2007; Mihajlovich and Gomes, 1986).



Source: ARA-Sul (2015) and CENACARTA (2015).

Figure 2.4: Main tributaries of the Limpopo basin in Mozambique

In general, the Mozambique hydrogeology is directly related to the common characteristics such as geology and climate in separated geographic locations. Therefore, six hydrogeological provinces were identified (see Appendix 3):

1. Basement complex (Precambrian).
2. Volcanic terrains (Post-Cambrian).
3. Middle Zambeze sedimentary basin (Karoo).
4. Maniamba sedimentary basin (Karoo).
5. Rovuma sedimentary basin (Meso-Cenozoic).
6. Mozambique sedimentary basin in north and south of the Save (Meso-Cenozoic).

The Chókwè district is located in the Mozambique sedimentary basin, south of the Save. This hydrogeological province is characterised by unconsolidated material and the climate is semi-arid. The groundwater is more recharged in dune areas than inland areas. The tertiary formation of sandstones is dominated in inland areas and the quaternary deposits cover approximately 70% of the basin. The aquifer type is alluvial and the salinity is the common problem in the water quality. The geological material is originated from marine inundations and saline formation water. Many streams and rivers are not permanent (dry in the dry season). The groundwater can be found up to 300 m below surface. Between 80 to 180 m the groundwater has low mineralisation and is fresh to slightly brackish. The hydraulic conductivity has values of 0.8, 5.4 and 19 m/day. A deep aquifer from 180 to 300 m is separated by clay layer with thick of 60 m. This aquifer is productive in 20 km (from north-west to south-east) and out of this area the water quality deteriorates. The hydraulic conductivity has values of 1.1, 2.4 and 15 m/day (Bouman and Ferro, 1987).

The quantitative information related to natural and artificial recharge is scare. The qualitative information available is based on annual rainfall (isohyets and colours) and recharge capacity of the soil (colour tonality). The average of 8% of the total rainfall contributes to the artificial recharge of groundwater (Bouman and Ferro, 1987; Mihajlovich and Gomes, 1986).

2.5 GEOLOGY SETTING

The geology setting of Mozambique has significant variations from north to south of the country. According to the Smedley (2002), the ancient crystalline rocks are dominant in the northern area, while the tertiary and quaternary sediments, including volcanic rocks, are dominant in the southern area. Based on lithostratigraphy characteristics, four groups of geological settings are dominant (Bouman and Ferro, 1987), namely:

Group 1: 57% of Precambrian crystalline rocks of the basement complex.
Group 2: 5% of Karoo sedimentary rocks.
Group 3: 3% of Post-Cambrian volcanic and igneous rocks.
Group 4: 35% of Meso-Cenozoic sedimentary rocks.

In the Chókwè district, differentiated units of sedimentary basins are represented by quaternary and tertiary rocks (Figure 2.5). The quaternary rocks are dominant and it consists of aeolian, eluvial, alluvial and fluvial deposits. This rock is significantly controlled by the sea-level fluctuation due to the glacial and interglacial processes (Grantham *et al*., 2011).

The dominant quaternary deposits are characterised by the occurrence of five basic units, namely:

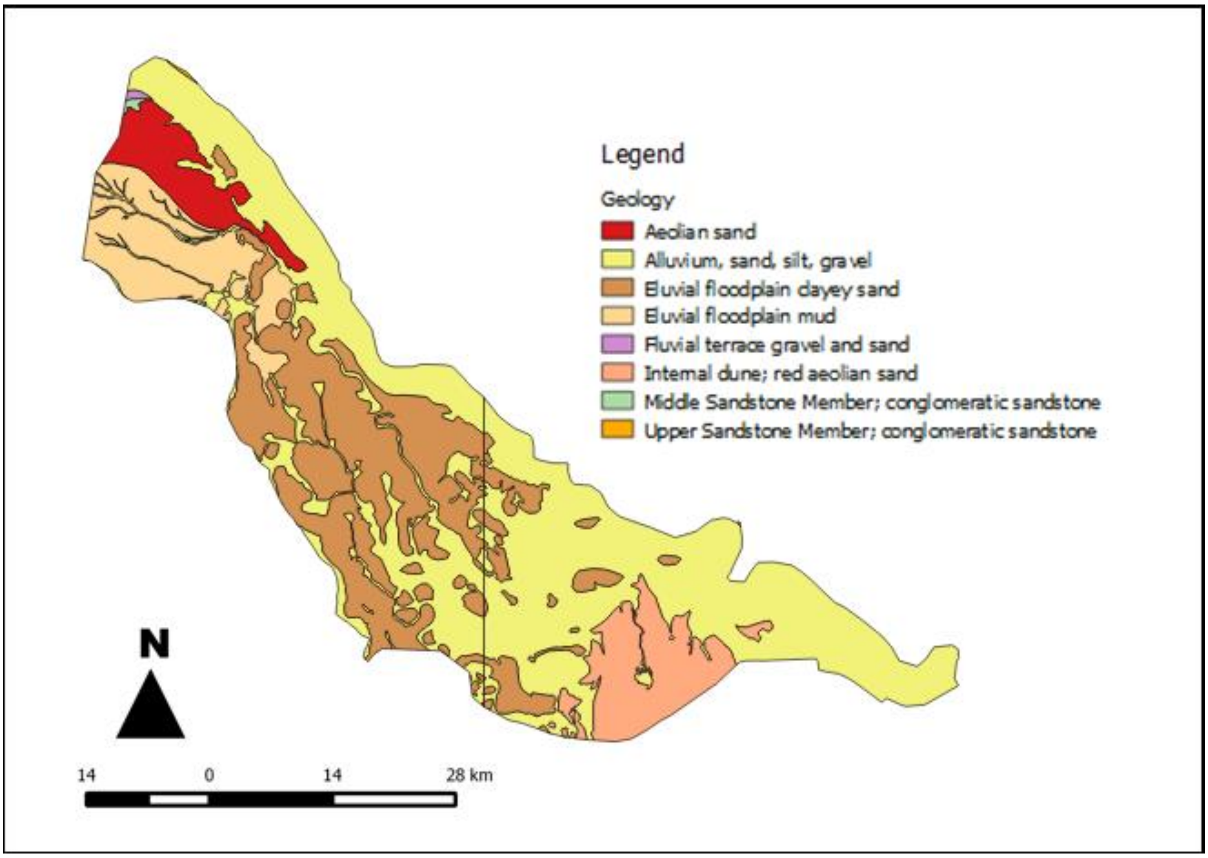
1. **Alluvium, sand, silt and gravel (Qa)**: The formation is resulting from fluvial processes such as deposition. Depending on the way how the material has been deposited, it is possible to visualise the grain size. If the geological material is deposited by running water it shows a differentiated granulometric arrangement (with conglomerates at the base and sand, as well as argillaceous upwards). For mass-flow deposits it is incipient and difficult to identify the grain size.
2. **Eluvial floodplain clayed sand (Qps)**: The formation is siliceous and it is resulting from widespread deposits of loose clays and sands without dune features or any remarkable relief. In this unit, the presence of argillaceous material causes retention of water over long periods and as a consequence small and shallow lakes can be formed. In general, due to hydraulic properties of the rock material (very permeable), the crop grows easily and dense vegetation can occur.
3. **Eluvial floodplain mud (Qpi):** Based on hydraulic properties, the permeability of eluvial floodplain mud is very low. This terrains occur in areas with flat morphology and low elevation.The colour of eluvial floodplain mud deposits are fine yellowish, with presence of lagoons and swamps occuring over a long period. This is a consequence of frequent floods and development of small, as well as shallow sea channels between the formations.
4. **Internal dune; red Aeolian sand (Qdi)**: The formation is a result of aeolian deposits, and the colours are red, brown to yellow sands, consolidated by vegetation.
5. **Aeolian sand (Qe)**: This formation is a result of aeolian deposits (ablation of internal dunes).

In a very small area of the Chókwè district two deposits units occur: (1) quaternary rocks represented by fluvial terrace gravel and sand, and (2) tertiary rocks represented by mapai formation (upper and middle sandstone).

1. **Fluvial terrace gravel and sand (Qt)**: This type of deposits are formed by three varieties of argillaceous units:
   - (a) Ferruginous sandstones.
   - (b) Calcareous sandstones and comglomeratic in places.
   - (c) Calcareous medium-grained sandstones.

   Based on the arrangement of the geological material it is characterised by high clay content and varies from dark-brown to blackish and fine- to medium-grained sand.

2. **Mapai formation (TeA)**: This formation is located in the western part of the Limpopo River. Two sub-units of Mapai formation occur in a small area of the northern site in the Chókwè district. According to the National Directorate of Geology (DNG, 2006), from the general lithology (top to bottom) the formation is composed by upper sandstone with very coarse alluvium and middle sandstone with finer sands and siltstone.

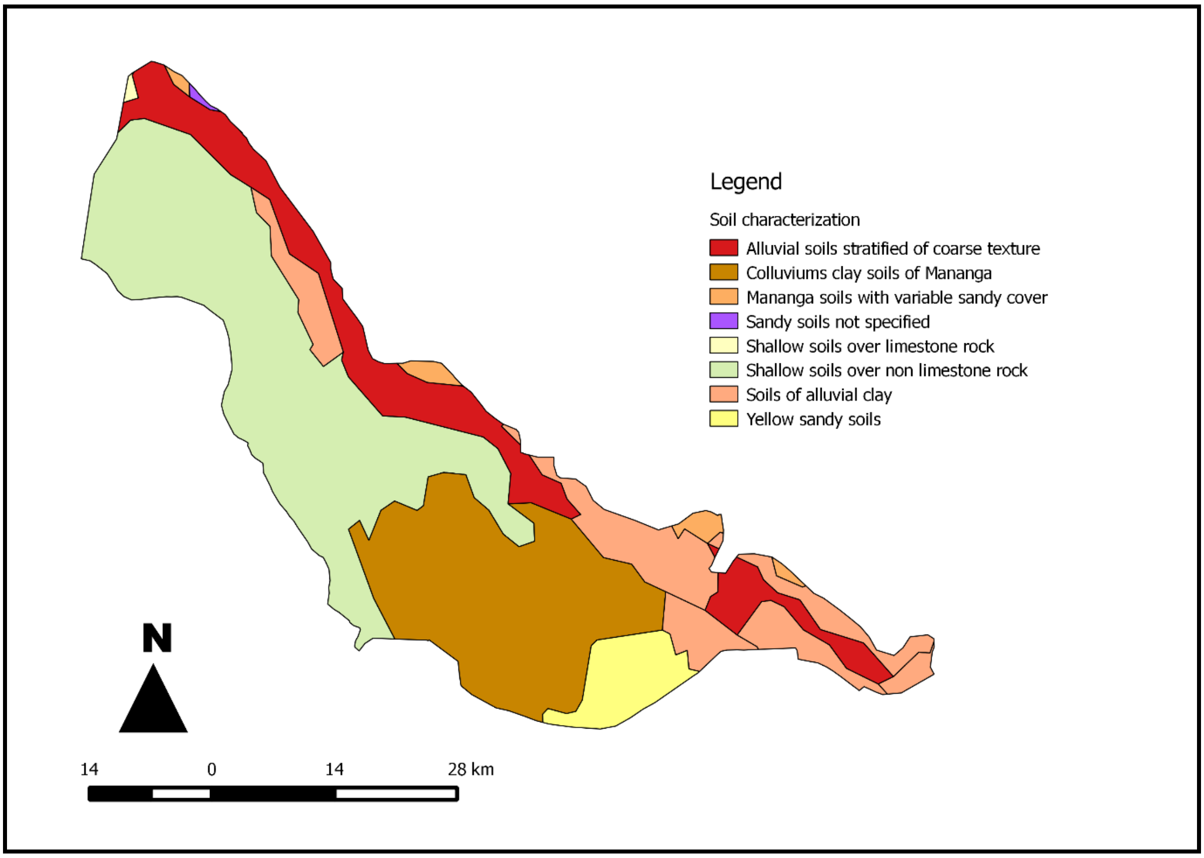


Source: Adapted from DNG (2006).

Figure 2.5:* *Geological description of the Chókwè district

2.6 SOIL CHARACTERISATION

According to the Faculty of Agronomy and Forestry Engineering (FAEF, 2001) the distribution of soil in the Chókwè district is mainly related and influenced by geomorphology. The study area is dominated by the following soil units: Alluvial soils stratified of coarse texture; colluvium clay soils of Mananga; soils of alluvial clay and yellow sandy soils. In small areas Mananga soils occur with variable sandy covers; sandy soils not specified; shallow soils over limestone rock and shallow soils over non-limestone rock (Figure 2.6).



Source: CENACARTA (2015); Mihajlovich and Gomes (1986).

Figure 2.6: Soil units of the Chókwè district

In summary, the occurring soil units are categorised in the following soils groups:

1. Clayey marine Pleistocene sediments with permeability of 0.07 m/day in upper layers.
2. Fluvial marine deposits with hydraulic conductivity of 0.07 m/day.

3. Fluvial sediments in highlands or depression with hydraulic conductivity varying from 0.07 to 0.65 m/day.
4. Soils of the internal sand-hill.

In general, due to insufficient internal and external drainage of Chókwè soils of irrigated areas, the risk of salinisation and/or sodification is evident, which is associated with the climate characteristics (high ETo and low rainfall) (Mihajlovich and Gomes, 1986).

2.7 LAND USE AND VEGETATION

The Chókwè district is primarily an agricultural area on the southern side of the Limpopo River. The irrigation scheme in Chókwè is the largest irrigated area within Mozambique, with approximately 30 000 ha mostly for rice, maize and vegetables. Other potential activities are pastures and animal fodder. The dry grazing areas surrounding the CIS are also used by small family plots to cultivate cassava, groundnut and sweet potato (Hakala and Pekonen, 2008; PANESA, 1988).

The predominant vegetation occurring over large inter-fluvial areas of southern Mozambique is savannah. Herbaceous species and grasslands are dominant, with less than 20% of tree and shrub covers. The local physiographics consist of Mopane woodlands, associated with nutrient-rich clay soils of the wide Limpopo flat valley. Different species such as *Panicum maximum*, *Cynodon dactylon*, *Strychnos spionsa, Sclerocara caffra* and *Cyperus spp* determine the type of vegetation in grassland areas (Timberlake and Chidumayo, 2011; PANESA, 1988; Ravichandran, 1999).

2.8 CONCLUSION

In this chapter, the description of the Chókwè district essentially focused on using geomorphological characteristics. The study area is semi-arid and lies in the mixed farming zone on the southern side of the Limpopo River. The local surface hydrology is mainly dominated by surface water from the Limpopo River; irrigation canals and their flow are entirely dependent on riparian countries. These water bodies, including swamps and lagoons, are the main sources of the groundwater recharge. During dry times of the year (scarce rainfall and occurrence of droughts), the groundwater hydrology is characterised by gaining streams. The losing streams are observed in a wet season where the flooding events are frequent (Figure 2.7). High demand of surface water is used for agricultural activities, the significant socio-economic input for the local economy and the entire country.

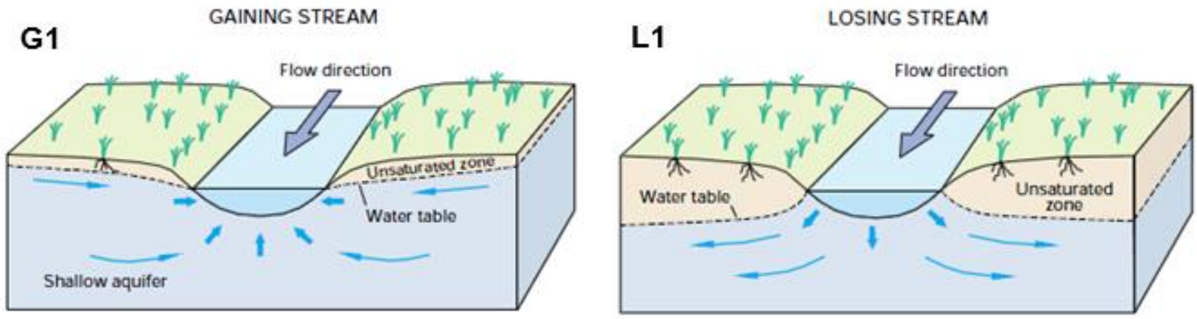
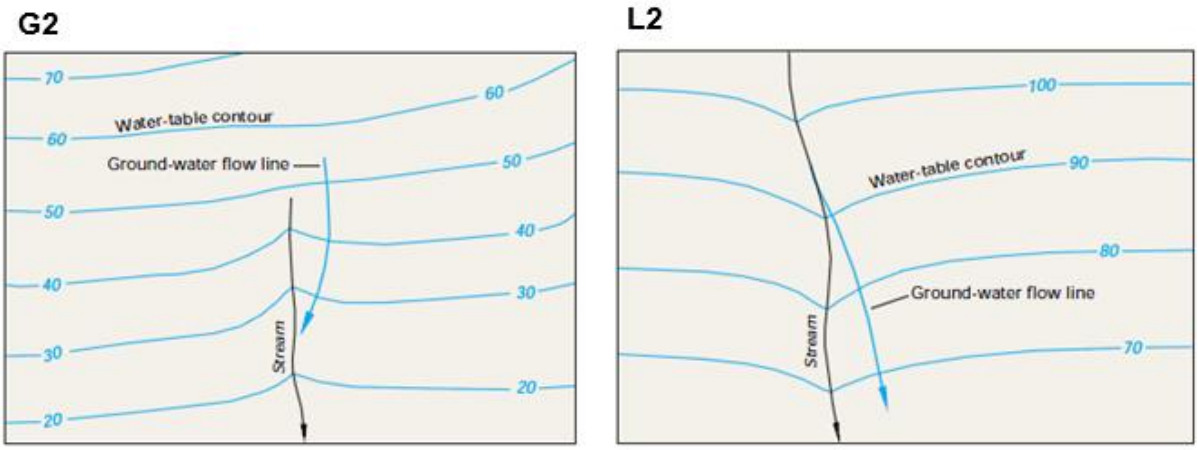


Illustration of landscape with gaining stream

Illustration of landscape with losing stream



Water table and groundwater flow direction in gaining stream

Water table and groundwater flow direction in losing stream

Source: Winter *et al*. (1998).

Figure 2.7: General diagram of the interaction between groundwater and surface water

Despite of its recognised potential in crop production, the Chókwè district has been faced with soil salinity due to agriculture land use which affects other ecosystems as a result of poor external drainage of soils. The local geology is dominated by quaternary and tertiary rocks. Unconsolidated sediments such as sand, gravel, alluvium and silt conglomerates are common in the Chókwè district. Presence of argillaceous and areas with flat morphology causes retention of water over long periods, due to low permeability of hydraulic conductivity that range from 0.07 to 0.65 m/day.

Chapter 3
LITERATURE REVIEW

3.1 INTRODUCTION

The objective of this chapter is to give an overview of the present research in hydrogeochemical processes and groundwater quality. The general and specific basics of water quality parameters will be identified and described, as well as a summary and analysis of previous studies already done. For better understanding the literature review will be based in the following topics: General concept of the hydrological cycle; Groundwater occurrence; Water quality, including factors and processes affecting water quality; Source and occurrence of ions in water; Groundwater sampling; Water quality analysis and interpretation; Methods to assess water quality; Reviews of studies and work.

3.2 GENERAL CONCEPT OF THE HYDROLOGICAL CYCLE

The hydrological cycle is a complex interdependent system, which describes the continuous movement or ever-changing migration of water (atmospheric, surface and subsurface). This movement or circulation of water is dependent of main pathways shown in the Figure 3.1 and Figure 3.2, namely precipitation, infiltration, recharge, runoff, evaporation, transpiration, base flow and capillary rise. Mathematically, the hydrological cycle can be expressed from Equation 3.1 in the global and basin scale to describe how water moves into and out of the following domains: atmospheric, land (surface and subsurface) and oceans (Clifton *et al.,* 2010, Davis and Wiest, 1966; Schwartz and Zang, 2003).

$$\text{Input} - \text{Output} = \text{Change of storage} \qquad \text{(Equation 3.1)}$$

On a global scale, the water balance can be expressed for one of the three mentioned domains of the hydrological cycle, as shown below in Equation 3.2, for land.

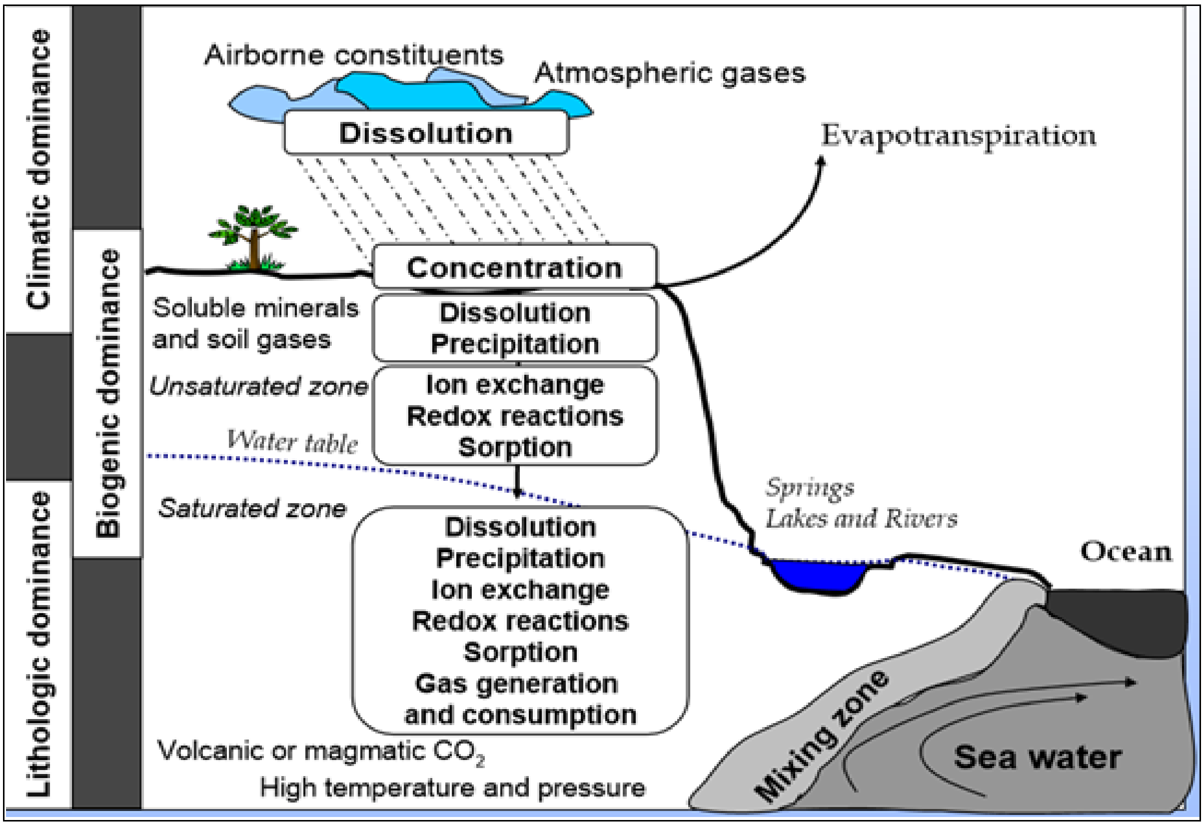
$$P - E - T - R_o = \Delta S \qquad \text{(Equation 3.2)}$$

Where P is precipitation on land (mm);
E is evaporation from land (mm);
T is transpiration from plants (mm);
R_o is the total outflow from land to ocean (mm); and
ΔS is the change of water storage on and under land.

However, for the basin scale, the water balance for groundwater is expressed from Equation 3.3, shown below.

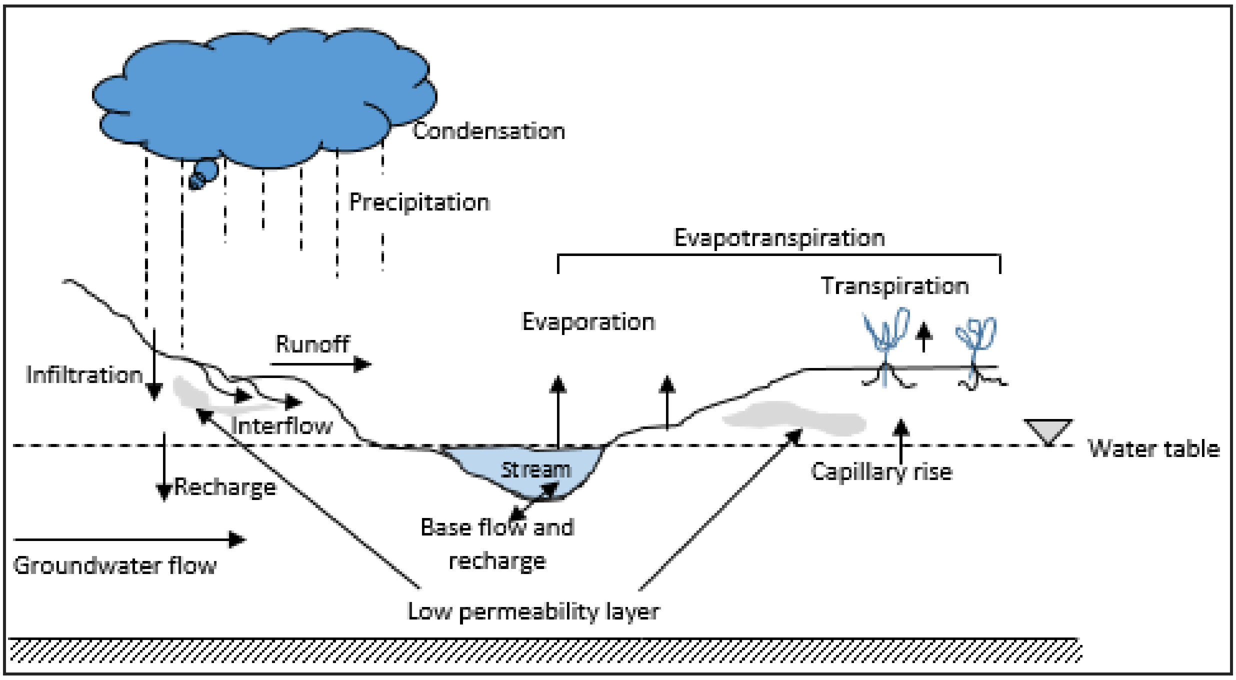
$$R_N + Q_i - T - Q_o = \Delta S \qquad \text{(Equation 3.3)}$$

Where R_N is the recharge to groundwater (mm), Q_i is surface water inflow to groundwater (mm), T is transpiration (mm), and Q_o is outflow (mm) from groundwater storage to surface water (mm).



Source: Sundaram *et al.* (2009).

Figure 3.1: Hydrological cycle incorporating the hydrogeochemical process



Source: Adapted from Charbeneau (2000); Davis and Wiest (1966);
Drever (1997); Schwartz and Zang (2003).

Figure 3.2: ***Schematic view of the conceptual hydrological cycle***

3.3 GROUNDWATER OCCURRENCE

Groundwater (also subsurface water) is water that exists in the pore spaces and fractures in sediments and in different types of rocks (igneous, sedimentary and metamorphic), beneath the land surface. This water is derived from rainfall and it infiltrates through diffusive or preferential flow within the normal hydrological cycle and is called meteoric water. If the subsurface water results from water having been trapped in marine sediments at the time of their deposition, is connate water. If the water is originated from the fact of climate change phenomena (change of wet weather to dry in the aquifer area), it is called fossil water (Rail, 2000).

The subsurface occurrence of three types of groundwater in the aquifer may be divided into two zones: aeration (or unsaturated) and saturation. The unsaturated zone is occupied partially by water and air, while in the saturation zone all interstices are filled with water under hydrostatic pressure, illustrated in Figure 3.3. Therefore, the water that occurs in the saturated zone is only groundwater.

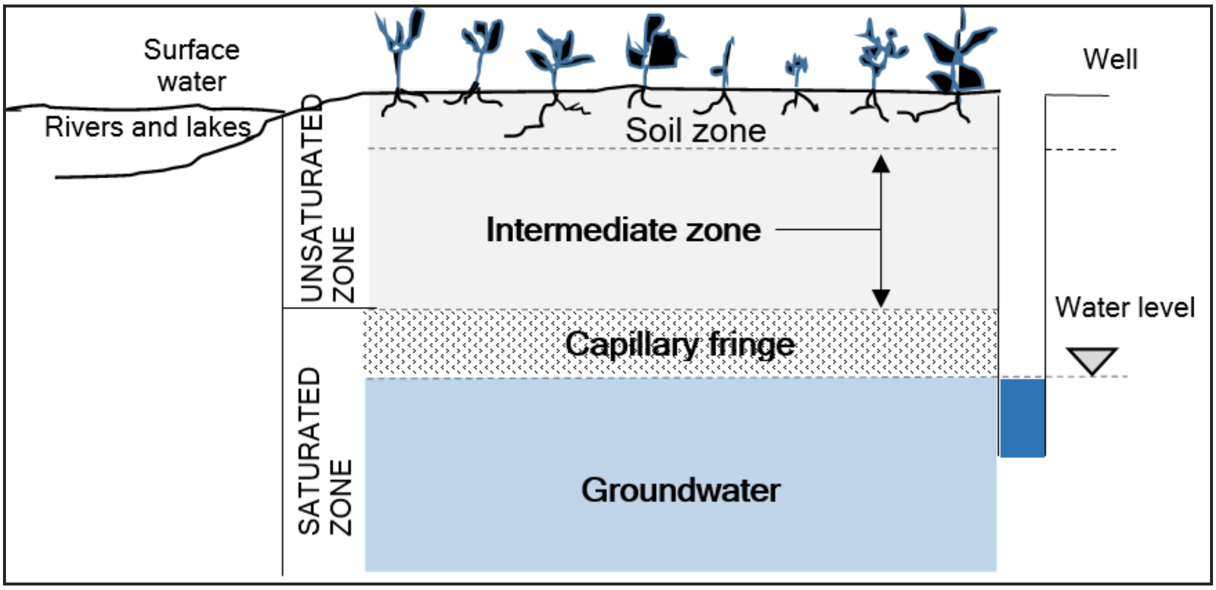
In general, the groundwater that occurs in a saturated permeable geological unit is called an aquifer. In the aquifer the groundwater moves through interconnected space (effective porosity) and it may be found in unconsolidated and consolidated material. Therefore, as a consequence of variability in rock material, lithology as well as the stratigraphy of the region, the groundwater may occur in three main types of aquifer, namely: confined, unconfined and leaky aquifers, as shown in Figure 3.4 below (Block *et al.,* 1995; Kruseman and De Ridder, 1994):

- **Confined aquifer**: When the groundwater in the aquifer is bound below and above by impermeable geological formations (Aquiclude).
- **Unconfined aquifer**: Aquifer that does not have an overlying confining layer and the water table is free to fluctuate.
- **Leaky aquifer**: Also known as semi-confined aquifer is the aquifer where the bounded layers (upper or lower) are semi-permeable.

Mathematically, the groundwater quantity and availability can be expressed using Equation 3.4, shown below:

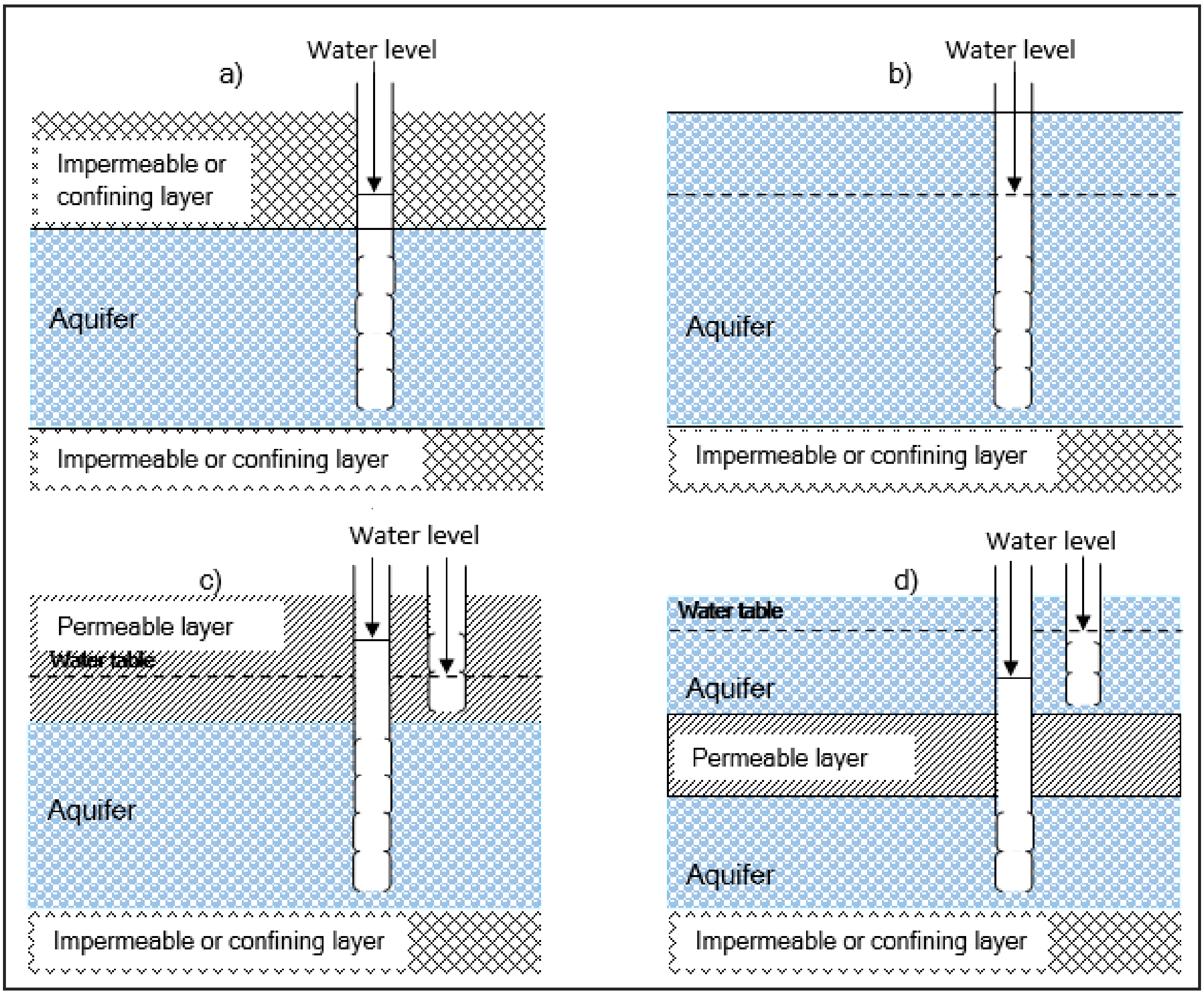
$$\Delta S_{gw} = \mathrm{R} - \mathrm{D} \qquad \text{(Equation 3.4)}$$

Where ΔS_{gw} represents the change in groundwater storage;
R is the natural or artificial recharge of groundwater (mm); and
D is the natural or artificial discharge of groundwater (mm).



Source: Heath (1987).

Figure 3.3: Schematic cross-section of groundwater occurrence in the subsurface



a = Confined aquifer; b = Unconfined aquifer; c and d = Leaky aquifers

Source: Block *et al.* (1995); Kruseman and Ridder (1994).

Figure 3.4: Groundwater occurrences in different aquifer types

3.4 WATER QUALITY

The complexity of the factors that determine the water quality and the quantitative variables used to describe water bodies, make the definition of water quality more complex. Specific or particular water uses have certain requirements and a range of variables in terms of physical, chemical and biological quality of water. As a consequence of this variability, the water quality may be defined in two ways: First, as the suitability of water to sustain multiple or various uses or processes, and second, in terms of the state and concentration of organic or inorganic material that is present in the water, together with certain physical characteristics of water (Meybeck *et al.,*1996; Chapman, 1996).

3.4.1 Water quality and aquifer material

The water quality in igneous, sedimentary and metamorphic rocks has different chemical compositions. The surface water from exposed igneous rocks shows low dissolved solids due to the low process of weathering in this rocks (Rail, 2000).

The sedimentary rocks are consolidated and resistant material (sandstone) and is widely dominated by the clay minerals and particulate matter. There is a considerable range of chemical composition and the cemented material (deposited from water in rocks); interacting with water it may be redissolved (Rail, 2000).

In metamorphic rocks the physical properties and mineral compositions change as a result of heat and pressure. The variation of pressure and heat may release water from different rocks and as a consequence hydrolysates minerals from aqueous solutions. Analysing the composition of natural water quality from metamorphic influence, high concentration of sodium, bicarbonate and boron, as well as low concentration of chloride, can occur. This variability in chemical concentrations is cited as an indicator of metamorphic influence on water (Rail, 2000).

3.4.2 Water quality parameters

The water parameters are the key indicators used to classify the common water uses based on its quality (Meybeck *et al.,* 1996; Gajendran, 2011).

According to the World Health Organization (WHO, 2011), for safe drinking water it is necessary to consider the following aspects or parameters in water quality:

- **Chemicals aspects**: Chemical constituents of water (ionic composition).
- **Microbial aspects**: Contamination of water with faeces from humans or animals (including birds). Pathogenic bacteria, viruses, protozoa and helminths, can be originated from this faeces.
- **Disinfection**: Water treatment for pathogenic microorganisms.
- **Radiological aspects**: Natural presence of radionuclides.
- **Acceptability aspects**: Taste, odour and appearance.

However, in general, both field and laboratory parameters should be taken into consideration to assess the water quality parameters for different purposes (Table 3.1).

TABLE 3.1: WATER USES AND RESPECTIVE EFFECT IN WATER QUALITY

Type of water use	Effect of water use in water quality	
	Consuming	Contaminating
Domestic use	✓	✓
Livestock watering	✓	✓
Irrigation	✓	✓
Aquaculture	✓	✓
Commercial fisheries	✓	✓
Forestry and logging	A	✓
Food processing	✓	✓
Textile industry	✓	✓
Pulp and paper industry	✓	✓
Mining	✓	✓
Water transportation	X	✓
Hydroelectric power generation	X	B
Nuclear power generation	✓	✓
Recreation	✓	✓

A = Alteration of water availability due to changes caused in runoff regimes; B = The water body thermal characteristic may be altered; X = No effect on water consuming.

Source: Meybeck *et al.* (1996).

3.4.2.1 Field parameters

The field measurements of water are carried out for physical and some chemical parameters. Therefore, according to the Environmental Protection Agency (EPA, 2001) and Appelo and Postma (2005), the field parameters are based on the following parameters, measured by electrodes:

- **pH**: Measurement of the effective concentration (or activity) of hydrogen, expressed as the logarithm of the hydrogen ion activity in moles per litre (mol/L), shown in Equation 3.5 below.

$$pH = -Log\left[H^{+}\right] \qquad \text{(Equation 3.5)}$$

- **Electrical conductivity or specific conductance (EC):** Ability of water to conduct electric current and it is expressed in µS/m.
- **Redox potential (Eh) also called Oxidation-Reduction Potential (ORP):** It represents the numerical index on the intensity of the oxidising or reducing conditions within an aqueous solution (surface water or groundwater).

- **Turbidity**: Unlike other field parameters, the turbidity shows the visible presence of suspended mineral and organic particles in water.
- **Electrical conductivity (EC) profiling**: Is a change or variability of electrical conductivity with depth in groundwater. Other parameters that can be measured in the field with EC profiling are water level, well depth and temperature.

3.4.2.2 Laboratory analysis

The laboratory analysis is based on chemical and bacteriological parameters. The chemical parameters are related to major and minor elements (organic and inorganic) in water, and the bacteriological parameters for microorganisms.

The units used to analyse the concentration of dissolved substances in water can be reported in different ways, depending on the purpose of the presentation and also on tradition, as shown in Table 3.2. Generally, it is suggested that milligrams per litre (mg/L) should be the obvious unit to express the chemical analysis. The other common units are parts per million (ppm=1 mg/kg) and parts per billion (ppb=1 µg/kg), which are numerically equal to mg/L and µg/L, respectively, when the density of the water sample is 1 kg/L, as is the case for diluted fresh water (Appelo and Postma, 2005).

TABLE 3.2: CONCENTRATION UNITS FOR DISSOLVED SUBSTANCES IN WATER

Units	Meaning
mg/L	Milligrams per liter sample
µg/L	Micrograms per liter sample
ppm	Parts per million by weight of sample
ppb	Parts per billion by weight of sample
mmol/L	Millimoles per liter sample
µmol/l	Micromoles per liter sample
meq/L	Milliequivalents per liter of sample
epm	Equivalents per million by weight of sample
M	Molality, moles per kg of H_2O
mM	Millimoles per kg of H_2O
N	Normality, equivalents per liter

Source: Appelo and Postma (2005).

3.4.3 Water quality classification

After the laboratory analysis the groundwater quality may be classified based on the Total Dissolved Solids (TDS), hardness and Sodium Adsorption Ratio (SAR).

(i) Total Dissolved Solids

TDS is the measurement of the total mass of dissolved salts in a given mass solution. Generally, in groundwater the relationship between TDS and electrical conductivity (EC) is linear, as shown in Equation 3.6 below (RSA DWAF, 1996; Weaver *et al.,* 2007).

$$\text{TDS} = A \times \text{EC} \qquad \text{(Equation 3.6)}$$

Where, A is the factor that ranges from 5.5 to 7 or 9 and is dependent to the actual chemical composition of the sample. The EC is expressed in µS/m.

According to Abreha (2014), TDS comprises of a dissociated and undissociated substance, but not suspended materials, colloids or gases. The unit used to express TDS is mg/L and mathematically it can also be calculated adding silica to the sum of ions, as shown in Equation 3.7 below.

$$\text{TDS} = \text{SiO}_2 + \text{Sum of ions} \qquad \text{(Equation 3.7)}$$

According to Phocaides (2000) and Rail (2000), the water quality should also be classified for irrigation. The classification is based on the total concentration and composition of salts in water, as shown in Table 3.3 and Table 3.4 below.

TABLE 3.3: CLASSIFICATION OF GROUNDWATER BASED ON TOTAL DISSOLVED SOLIDS

Concentration (mg/L^{-1})	Classification
1 000 – 39 000	Slightly saline
3 000 – 10 000	Moderately saline
10 000 – 35 000	Very saline
>35 000	Brine

Source: Rail (2000).

TABLE 3.4: WATER QUALITY CLASSIFICATION FOR IRRIGATION BASED ON ELECTRICAL CONDUCTIVITY

EC (µS/cm)	Classification
< 700	Non – saline water
700 – 42 000	Saline water
700 – 3 000	Slightly saline
3000 – 6 000	Medium saline
> 6 000	Highly saline
> 14 000	Very saline
> 42 000	Brine

Source: Phocaides (2000).

(ii) Hardness

Hardness is a natural property of water, reflecting the sum of calcium and magnesium, as carbonates, bicarbonates and sulphates (Equation 3.8). Usually it is expressed in terms of mg/L of $CaCO_3$, and classified as shown in Table 3.5 below (Abreha, 2014 and Thompson *et al.,* 2007).

$$Hardness = Ca\left(\frac{mg}{l}\right) \times \frac{M.wt.CaCO_3}{At.Wt.Ca} + Mg\left(\frac{mg}{l}\right) \times \frac{M.wt.CaCO_3}{At.Wt.Mg} \qquad \text{(Equation 3.9)}$$

TABLE 3.5: CLASSIFICATION OF GROUNDWATER BASED ON HARDNESS

Equivalent concentration of $CaCO_3$ (mg/L^{-1})	Classification
0 – 75	Soft
75 – 150	Moderately hard
150 – 300	Hard
>300	Very hard

Source: Rail (2000).

(iii) Sodium Adsorption Ratio (SAR)

According to Chapman (1996), the SAR is a parameter used to evaluate the suitability of irrigation water. This ratio estimates the degree to which sodium will be adsorbed in the soil. If the SAR value is high (more than 10 times greater than EC), the sodium in irrigation water may replace the calcium and magnesium ions in the soil. Therefore, this behaviour of cations exchange is a potential indicator to cause damage in the soil structure as shown in Table 3.6 and Table 3.7 below. As a consequence, the infiltration rate and soil permeability are reduced due to the salt concentration. Mathematically, the SAR can be calculated using Equation 3.9 below:

$$SAR = \frac{Na^{+}}{\sqrt{\left(\frac{Ca^{2+} + Mg^{2+}}{2}\right)}}$$ (Equation 3.9)

Where, the concentration of calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^{+}) are expressed in milliequivalents per litre (meq/L).

TABLE 3.6: WATER CLASSIFICATION FOR IRRIGATION BASED ON SODIUM ADSORPTION RATIO

SAR (meq^{-1})	Water class	Classification
<10	S_1	Excellent
10 – 18	S_2	Good
18 – 26	S_3	Permissible
>26	S_4	Unsuitable

Source: Balachandar *et al.* (2010).

TABLE 3.7: IRRIGATION WATER QUALITY EFFECT ON INFILTRATION RATE BASED ON SODIUM ADSORPTION RATIO AND ELECTRICAL CONDUCTIVITY

Levels of EC in irrigation water (µS/cm)	No reduction	Slight reduction	Medium reduction	Severe reduction
	SAR level	SAR level	SAR level	SAR level
700	<1	1 – 5	5 – 11	>11
700 – 3 000	<10	10 – 15	15 – 23	>23
3 000 – 6 000	<25	>25	No effect	No effect
6 000 – 14 000	<35	>35	No effect	No effect
> 14 000	No effect	No effect	No effect	No effect

Source: Phocaides (2000).

3.5 SOURCE AND OCCURRENCE OF IONS IN GROUNDWATER

The natural composition of groundwater chemistry is described through the relative abundance of the principal constituents dissolved in groundwater. To assess the groundwater quality, besides the minor and trace elements, the standard chemical analysis of groundwater is largely based on major predominate ions. The major cations is represented by Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, and the major anions by Cl^{-}, HCO_3^{-}, NO_3^{-}, SO_4^{2-} (Appelo and Postma, 2005).

According to the Colorado Water and Energy Research Center (CWERC, 2014) and Chapman (1996), the natural source and concentration, as well as the range of mentioned ions in groundwater, are rock minerals. The interaction between this rock mineral with recharge water usually controls the natural quality of groundwater through geochemistry of the lithosphere, the aqueous portions on the earth, the solid portion of the earth and hydrochemistry of the hydrosphere. During interaction between the geological environment and recharge water, the rock minerals is dissolved and transported to groundwater in ionic form through infiltration and percolation.

3.5.1 Sodium

The sodium element (Na) does not occur free in nature, but compounds of this element constitute 2,83% at the earth's crust. Sodium is usually present in freshwater as Na^+ ions within a concentrated solution, such as sodium carbonate, sodium bicarbonate and sodium sulphate. Therefore, sodium salts are extremely soluble in water and when the element is leached from soil or discharged to streams by industrial waste processes, it remains in solution (Rail, 2000).

Source and occurrence: Sodium is a major constituent of igneous rocks. It occurs as plagioclase (soda-lime feldspar-albite), clay minerals, evaporite such as halite, NaCl, industrial wastes (Chapman, 1996; Rail, 2000).

Concentration range in natural groundwater: Generally, is less than 200 mg/L, but in seawater is about 10 000 mg/L and in brines approximately 25 000 mg/L (Chapman, 1996).

According to Rail (2000), concentrations of 10 800 mg/kg, can also occur in seawater and in evaporation deposits where it chiefly shows up in rock salt, NaCl. In sandstones, the element averages a 3 870 mg/kg concentration, either as a constituent of unweathered mineral grains or as a constituent of cement. Sodium in the presence of prolonged or quantitatively lower groundwater movement, can be the cause of higher salt concentrations, which are generally leached out.

3.5.2 Potassium

Potassium (K) is an active metal and reacts vigorously with oxygen and water. This element is abundant in sedimentary rocks and in igneous rocks with an average content of 25 700 mg/kg. The Na^+/K^+ ratio in igneous rocks is 1,09 and in seawater is 27,84 (Rail, 2000).

Source and occurrence: Potassium occurs in potassium feldspars (orthoclase and microcline), micas (muscovite and biotite), and in other minerals (leucite, nepheline) including feldspathoids (Chapman, 1996; Rail 2000).

Concentration range in natural groundwater: The concentration is usually less than 10 mg/L, but up to 100 mg/L in hot springs and 25 000 mg/L in brines (Chapman, 1996).

In farming areas, potassium is intensively used as fertiliser; however, this leads to higher concentrations in groundwater. As potassium is an essential plant nutrient, from its own biological cycle, it can hardly be responsible for the significantly lower potassium content in groundwater relative to sodium. High potassium values are generally associated with comparable levels of human pollution (Rail, 2000).

3.5.3 Calcium

Calcium (Ca) is the principal cation in freshwater and is widely distributed in common minerals of rocks and solids. Calcium ion are relatively large and can be hydrated. Strong alkaline waters also contain hydroxide and carbonate ion pairs with calcium (Rail, 2000).

Source and occurrence: Calcium is an essential constituent of igneous rocks and can occur as silicates, pyroxenes, amphibole and feldspars. Calcium does not occur naturally because it oxidises readily when in contact with air and reacts with water to release hydrogen gas (Rail, 2000).

Concentration range in natural groundwater: Calcium concentration is usually less than 100 mg/L, but in brines may contain up to 75 000 mg/L (Chapman, 1996).

According to Chapman (1996) and Rail (2000), the significant concentration of the element occurs in precipitates, specifically carbonate rocks (272 000 mg/kg). Calcium also forms deposits of carbonates, calcite, aragonite, dolomite, clay minerals and sulphates anhydride and gypsum.

The average content in igneous rocks is 36 200 mg/kg and it is held in plagioclase feldspar, a solid solution series with end members anorthite and albite. However, calcium salts are common in water and may result from leaching of soil and other natural sources, or they may occur in sewage and industrial wastes (Rail, 2000).

3.5.4 Magnesium

In general, the behaviour of magnesium (Mg) is similar to calcium. It is active chemically and does not occur in natural state (i.e., its salts are very soluble). Thus, magnesium and calcium form the property classified as hardness. In spite this similarity, the geochemical behaviour of magnesium is different from calcium. The solubility of magnesium carbonate in water and carbon dioxide is greater than calcium carbonate (so that under normal groundwater conditions, magnesium carbonate is not precipitated). Magnesium levels in freshwater are generally less than those in calcium. This difference is probably because of the lower geochemical abundance of magnesium (Rail, 2000).

Source and occurrence: The minerals containing magnesium are olivine, forsterite, garnets, cordierite, pyroxenes, amphibolite, dolomite, ferromagnesium minerals, mica groups, chrysotile, sepiolite, talc, serpentine, chlorite group and magnesium-bearing clay minerals. Magnesium is a constituent of salt deposits of marine origin (for example, bischofite, kieserite, hexahydrite, epsomite, carnallite), and the salts are also present in terrestrial evaporates and in guano (Chapman, 1996; Rail, 2000).

Concentration range in natural groundwater: The magnesium concentration is usually less than 50 mg/L, about 1 000 mg/L in ocean water and brines may have 57 000 mg/L (Chapman, 1996). According to Rail (2000), the average magnesium content of igneous rocks is 17 600 mg/kg.

3.5.5 Bicarbonate and carbonate

Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), as well as the dissolved carbon dioxide species, have significant influence to produce alkalinity in all natural waters (Hem, 1985).

Source and occurrence: Both carbonate and bicarbonate occur in limestone and dolomite.

Concentration range in natural groundwater: Carbonate is usually less than 10 mg/L, but can exceed 50 mg/L in water highly charged with sodium**.** Bicarbonate is usually less than 500 mg/L, but can exceed 1 000 mg/L in water highly charged with carbon dioxide (CO_2).

3.5.6 Sulphate

Source and occurrence: It occurs in certain igneous rock minerals of the feldspathoids and the expressive occurrences are in evaporative sediments. The sulphates also occur in oxidised states of organic matter (Rail, 2000).

Concentration range in natural groundwater: The concentration is usually less than 300 mg/L, except in wells influenced by acid-mine drainage and up to 200 000 mg/L in some brines (Chapman, 1996).

3.5.7 Chloride

Source and occurrence: The element chloride (Cl) occurs in practically all natural waters. In sedimentary rock it occurs as evaporates and a little in igneous rocks**.** Chloride-bearing minerals occurring in igneous rock include feldspathoids, sodalities, phosphate mineral and apatite. However, igneous rock does not yield high concentrations of chloride to normally circulating natural water. The chloride ion also occurs in terrestrial dust, volcanic emanations, and as human-caused airborne pollutants in the atmosphere (Chapman, 1996; Rail, 2000).

Concentration range in natural groundwater: The concentration of chloride is usually less than 10 mg/L in humid areas, but it is up to 1 000 mg/L^{-1} in more arid regions, approximately 19 300 mg/L in seawater and up to 200 000 mg/L in brines.

According to Rail (2000), chlorides eventually concentrate in marine and terrestrial evaporated deposits. It is the dominant anion in acid groundwater associated with active or recent volcanism. If levels of chloride at the source are high, pollution may be occurring and chloride levels should be further investigated as a cause.

3.5.8 Nitrate

Nitrate (NO_3^-) is the result of the nitrogen association with oxygen (Hem, 1985).

Source and occurrence: The sources are atmosphere, legumes, plant debris, and animal excrements. But in general, the nitrate source is mostly associated with human activities such as agriculture (fertilisers) and discharge of waste from urban areas (Hem, 1985).

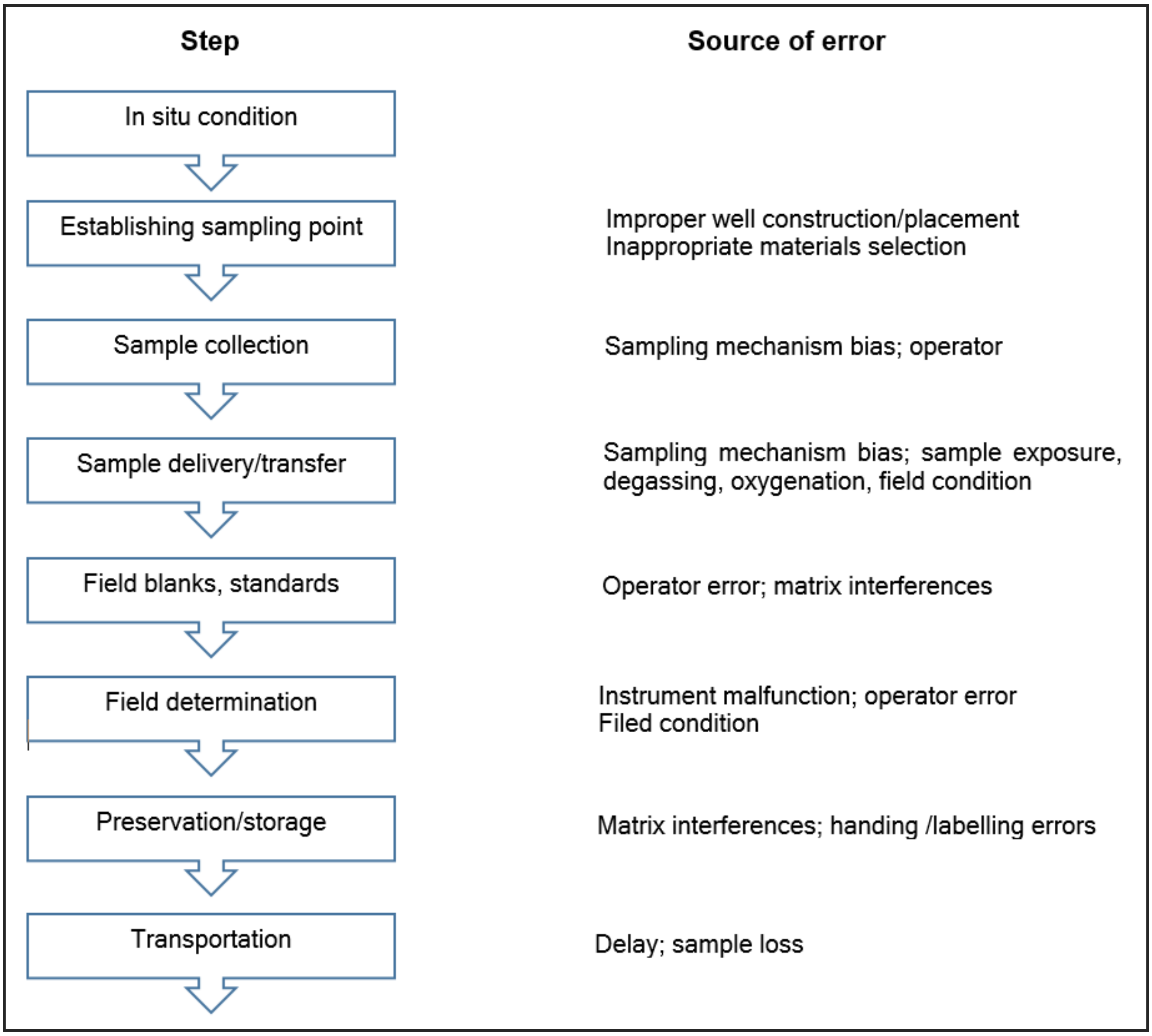
Concentration range in natural groundwater: In general, the concentration is usually less than 10 mg/L.

3.6 GROUNDWATER SAMPLING FOR HYDROGEOCHEMICAL STUDIES

Groundwater sampling is the process through which representative samples are collected in the field for site characterisation. The objective is to obtain groundwater samples with the same chemistry that reflect the original environment where the study is carried out (aquifer). From wells (or boreholes) the groundwater is collected using equipment such as a bailer or pump and saved in containers. Inside the containers, the preservation chemicals are added to counter the chemical changes occurring in water samples (Vivo, Belkin and Lima*,* 2008; Zeman, 2004).

Understanding of the hydrogeology and flow dynamic system of the site is important in groundwater sampling for water quality. Therefore, before the sampling is done, it is necessary to know the density and the frequency of groundwater sampling and also the number of samples needed (Vivo *et al.,* 2008).

According to Schwartz and Zang (2003) in each step of groundwater sampling errors or problems may occur that can invalidate the sample results, as shown in Figure 3.5 below:



Source: Schwartz and Zang (2003).

Figure 3.5: ***Groundwater sampling steps and the source of errors***

3.7 WATER QUALITY ANALYSIS AND INTERPRETATION

The accuracy and reliability of water analysis is the first step required to interpret the chemical data. It is based on the major ions in water, estimating the percentage of Ion Balance (IB) between cations and anions, as shown below in Equation 3.10. If IB is less than 5%, the results and conclusion is acceptable (Appelo and Postma, 2005).

$$IB(\%) = \frac{\sum cations + \sum anions}{\sum cations - \sum anions} \times 100 \qquad \text{(Equation 3.10)}$$

Where the cations and anions are expressed in meq/L.

3.8 METHODS TO ASSESS WATER QUALITY

Graphical and statistical analysis are widely used to assess water quality parameters. The quantitative data are required to use the methods and this can represent advantages to assess qualitative data. In other words, the quantitative methods may need complex interpretations, through computational programs (Andreasi and Azevedo, 2009).

3.8.1 Graphical methods for single data

For a single sample, graphical methods have been developed to display the chemical composition of the main components in groundwater quality. Thus, the analysis can be carried out using the bar diagram, circle diagram histograms, quantile plots, boxplots and probability plots. Therefore, among these diagrams, the bar diagram and circle diagram are the two common diagram types used to recognise waters with similar chemical compositions (Appelo and Postma, 2005; Drever, 1997; Helsel and Hirsch, 2002).

3.8.1.1 Bar diagram

The bar diagram consists of two adjacent columns (cation and anion on the left and right side, respectively). Each column is used to represent the contribution of various ions concentrations expressed in meq/L (Appelo and Postma, 2005). Another use of a bar diagram is to display water quality categories in different geological environments. An example of a bar diagram is shown in Figure 3.6 below.

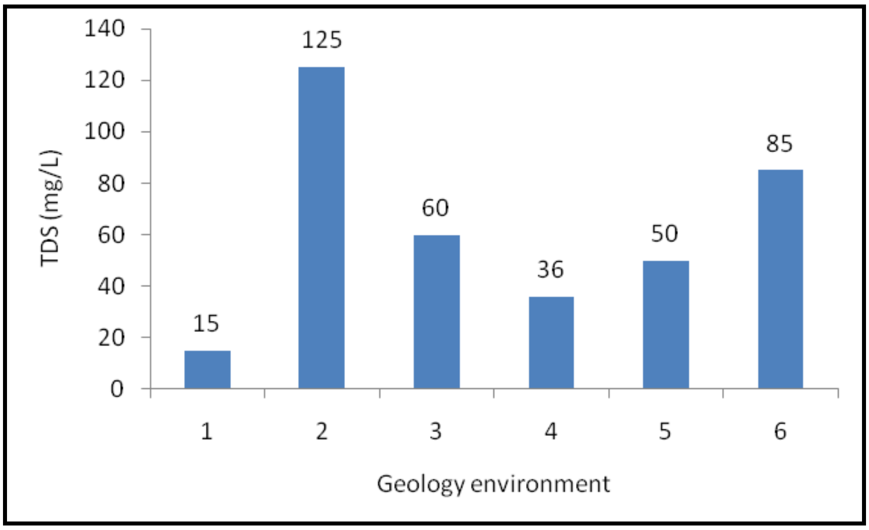


Figure 3.6: Example of bar diagram and its uses in water quality analysis

3.8.1.2 Circle diagram

In the circle diagram, the circle is subdivided in an upper and lower half to show or describe the relative composition in meq/L of the cations and the anions, respectively (Appelo and Postma, 2005). The circle diagram is also called a pie diagram and the analysis of ion composition in water can be displayed as shown in Figure 3.7.

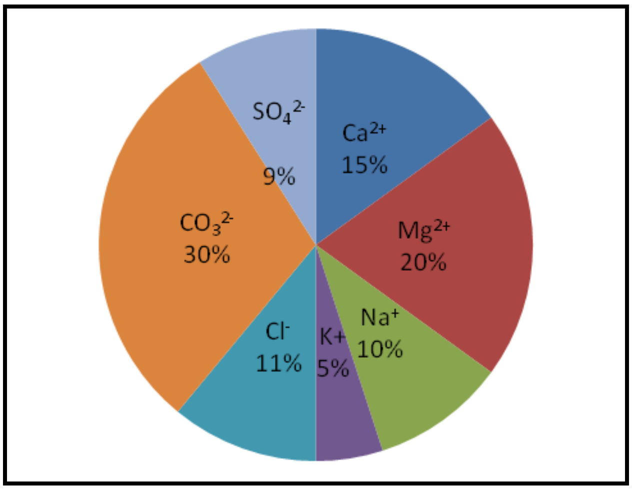


***Figure 3.7:* Example of circle diagram and its uses in water quality analysis**

3.8.2 Graphical methods for multivariate data

Different multivariate methods are used to assess chemical data: profile plots, star plots (kite diagram), trilinear diagrams, Piper diagram, Durov diagram, Stiff diagram and plots of principal components. Therefore, the Piper or Durov diagram as well as the Stiff diagram is widely used to interpret multivariate data.

3.8.2.1 Stiff diagram

A Stiff diagram consists of three to four horizontal axes displaying selected components. On each axis a cation is plotted to the left and an anion to the right again, in meq/L. The variables to be plotted in the fourth axis are dependent and optional from the objective of each study carried out. Using the Stiff diagram method, the predominant ions in water (surface or groundwater) is displayed in a typical shape (for a given water composition) with values in the axes connected by lines. The shape indicates the relative proportions of the different ions, and the size indicates the total concentrations (Appelo and Postma, 2005; Drever, 1997). An example of ion plot in Stiff diagram is shown in Figure 3.8.

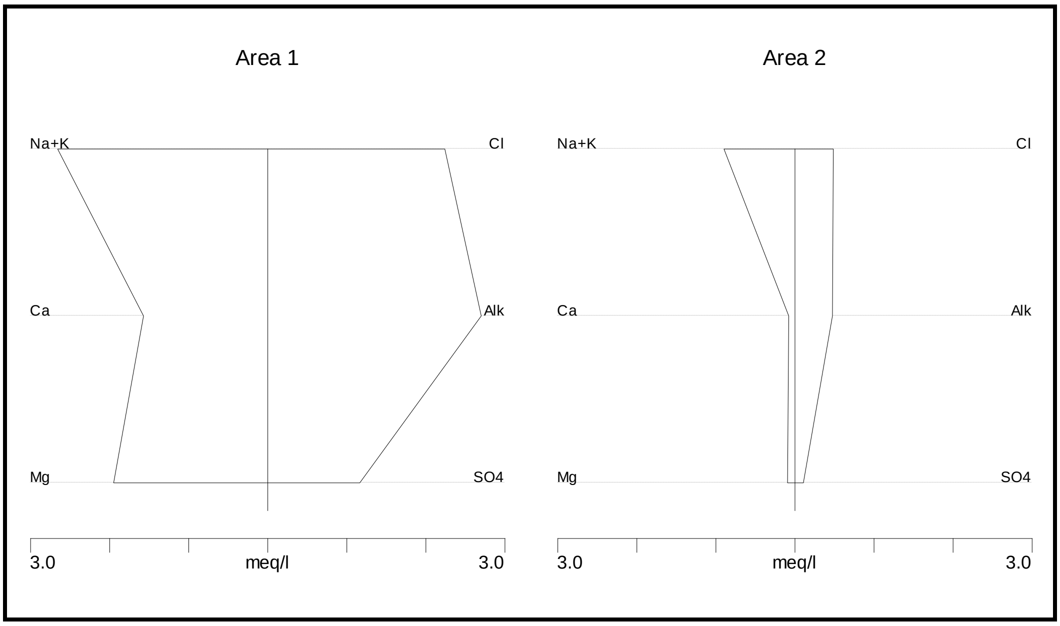


Figure 3.8: Example of water quality analysis using Stiff diagram

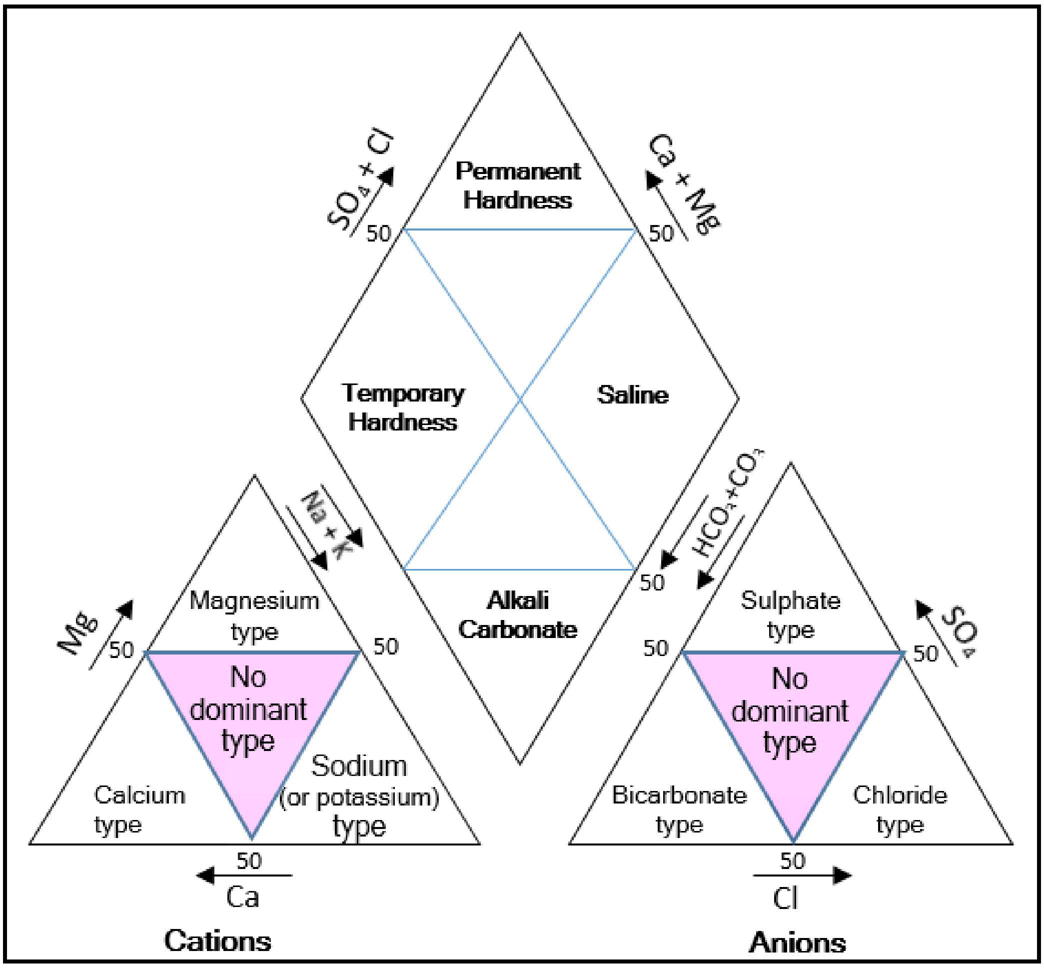
3.8.2.2 Durov and Piper diagrams

A large number of water chemical compositions can be analysed and interpreted using either Durov or Piper diagrams (Appelo and Postma, 2005).

The Piper diagram, also called trilinear diagrams (Figure 3.9 below), is a combination of plotted proportions (in meq/L) of anion (Cl^-, HCO_3^-, CO_3^{2-}, NO_3^-, SO_4^{2-}) and cation (Ca^{2+}, K^+, Mg^{2+}) triangles that lie on a common baseline. These diagrams are used to: (i) make a tentative conclusion about the origin of analysed water sample, (ii) display the type or hydrochemical facies; and (iii) identify the mixing between two end-members. However, the bicarbonate-to-silica ratio must also be considered when making this deduction. Thus, four basic conclusions can be derived from multiple analyses plotted on the Piper diagram, namely:

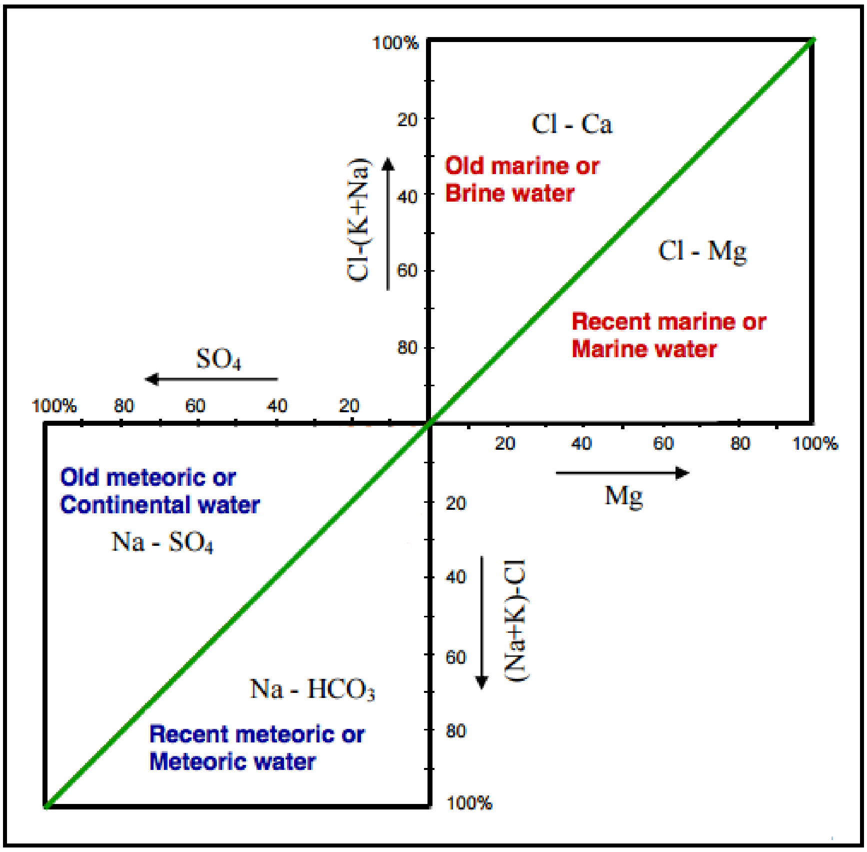
(1) Water type or hydrochemical facies.
(2) Precipitation or dissolution.
(3) Mixing.
(4) Ion exchange (Appelo and Postma, 2005; Drever, 1997).

Another graphical method used to assess the water quality is the Sulin diagram, shown in Figure 3.10. This diagram can be used for genetic classification of water sources (Sharaky *et al*., 2007 and Salman *et al*., 2013).



Source: (Drever, 1997).

Figure 3.9: ***Hydrochemical facies representation on Piper diagram***



Source: Sharaky *et al*. (2007) and Salman *et al*. (2013).

Figure 3.10: Genetic water classification using Sulin diagram

3.8.3 Statistical method

The statistical method of water chemistry is based on a wide range of tools or approaches used in a quantitative analysis. These approaches of the statistical method are: descriptive statistic, regression, correlation and analysis of variance (ANOVA) (Andreasi and Azevedo, 2009; Meier and Zünd, 2000).

3.8.3.1 Descriptive statistical analysis

The descriptive statistic is used to assess the central tendency of the data collected through standard deviation, coefficient of variation (CV), average, median, maximum and minimum.

3.8.3.2 Regression analysis

The regression is used to assess the description and prediction of one quantitative variable from other. The mathematical expression is shown below in Equation 3.11:

$$y = a + bx \qquad \text{(Equation 3.11)}$$

Where y is the dependent variable (predicted or response variable); a is the intercept; b is the slope of the line and x is the independent variable (predictor or input variable).

3.8.4 Correlation analysis

The correlation is used to assess the association between quantitative variables in terms of linear relationship. Mathematically, the correlation analysis can be expressed using Equation 3.12:

$$r = \frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)\left(y_i - \bar{y}\right)}{\sqrt{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2 \sum_{i=1}^{n}\left(y_i - \bar{y}\right)^2}} \qquad \text{(Equation 3.12)}$$

Where *n* is the number of measurement; x_i, y_i is the pairs of measurement and $\bar{x}$, $\bar{y}$ is the average of each measurement. As the correlation coefficient (r), takes values between −1 and +1, the following interpretation may occur:

(a) Perfect correlation – if *r* is −1 or +1;
(b) High negative correlation – if *r* is close to −1;
(c) High positive correlation – if *r* is close to +1; and
(d) No correlation – if *r* is close to zero (0).

3.8.5 Analysis of variance

The analysis of variance (ANOVA) in statistical method used to assess and test the significant variability or difference in terms of chemical concentration. ANOVA tests the significant influence of two-factor or multi-factor (factorial ANOVA) which may affect water quality.

3.9 REVIEWS OF STUDIES AND WORK

Hydrogeochemical studies are widely conducted in the world to investigate the processes that occur in water bodies (surface and groundwater) and affect the water quality.

Elango and Senthilkumar (2013) investigated the geochemical processes in groundwater using the NETPATH program and ratios between chemical parameters. The results show dominance of Ca, HCO_3^- and Na ions in water samples. From this study, it was identified that dissolution, precipitation, silicate weathering and cation exchange are the predominant processes controlling the groundwater quality in the aquifer.

Another investigation conducted by Lakshmanan, Kannan and Kumar (2003), identified the dissolution, precipitation, ion exchange and weathering as the predominant hydrogeochemical processes in the aquifer. The presence of ions in groundwater are dominated by Ca^{2+} cations and HCO_3^- anion, while the water type is Ca-HCO_3 and Ca-Cl-HCO_3.

Skordas *et al*. (2013) used an analytical method to evaluate the groundwater hydrogeochemistry. They concluded that dissolution (of calcite and dolomite) is the main hydrogeological process dominant. The values of EC (higher than 400 µS/cm) and NO_3^- (35 and 40 mg/L) were out of desirable limits, as well as the spatial and temporal variability of water quality which is directly affected by the application of fertiliser.

Sharaky *et al.* (2007) also investigated the hydrogeochemistry of groundwater in the aquifer. Based on the interpretation of chemical data, they concluded that in a quaternary aquifer the hydrochemical composition of water shows a Na-HCO_3 type, while a Na-Cl type in saline area.

Salman *et al*. (2013) investigated the suitability of groundwater for drinking based on physicochemical and hydrogeological analysis. From plotted data on Piper, Durov and Sulin diagrams, as well as Aquachem software, it was concluded that the water is suitable for drinking. However, the oxidation and dissolution are hydrogeochemical processes occurring in groundwater.

In the mining environment (abandoned or in use) the hydrogeochemical processes also have an influence on water quality. Therefore, Jeong (2001) carried out a study to characterise the hydrogeochemistry and mineral water interaction from an abandoned mine. The interpretation from thermodynamic equilibrium and factor analysis of chemical data, shows the presence of Na-HCO_3, Ca-HCO_3 and Ca(Mg)-

$SO_4(HCO_3)$ type of water. Between water and mineral interaction, it was concluded that the dissolution and precipitation are the hydrogeochemistry processes controlling the quality of water in the mine.

Comparing the above studies carried out by Elango and Senthilkumar (2013), Jeong (2001), Lakshmanan *et al*., (2003), Salman *et al*. (2013) and Skordas *et al*. (2013), it is possible to see that the abundance or presence of Ca^{2+} and HCO^{-}_{3} ions in groundwater is significant. Therefore, the water quality in the aquifer is generally controlled by hydrogeochemical processes such as dissolution and precipitation of minerals, including ion exchange and weathering.

The Mineral Resources Centre (MRC, 2009) recently carried out a study of water chemistry in the Limpopo basin between four sharing countries: Botswana, South Africa, Mozambique and Zimbabwe. In these four countries, the salinity, NO_3^- concentration and the presence of heavy metals represent the common problem along the Limpopo basin. Two reasons are attributed for the reported results: (i) the practice of agriculture and mining activities (except Mozambique); and (ii) the evidence of same hydrogeological characteristics in the Limpopo basin. From this study in Mozambique (Chókwè district) the groundwater quality is influenced by mineralisation processes, which differ along areas or sections of the Limpopo River. Also were found the evidence of a sodicity problem, associated with the natural lacustrine and estuarine deposits.

The state Geotechnical company of Mozambique (GEOMOC, 1981) carried out a geotechnical and hydrogeological research in a saline soil area (600 ha) of Chókwè Irrigation Scheme (CIS) located in D13-E and D14-D at a depth of 84.90 m. The research identified hydraulic interconnectivity between the aquifer and the Limpopo River. In a wet season (more rainfall) it is observed losing stream and in a dry season gaining stream. From this research, it was concluded that the groundwater quality is classified as hard and saline water, with EC value ranging from 1 061 to 8 253 μS/cm. High mineralisation and evidence of strong organic pollution due to the nitrite content, were also identified in the area.

Konstapel (1981) investigated the cause of bad rice growth in a new irrigation area of Lionde-Nwachicoluane, and identified the following reasons: The Lionde-

Nwachicoluane soils are saline and calcareous. So because of that in areas where bad rice growth was observed it is caused by high soluble salts and exchangeable sodium. At depth of 150–200 cm all soil layers below 30–80 cm are saline-sodic or sodic. Therefore, 25–50% of soils were saline-sodic or saline in the first layers, through three ways:

- **Primary salinisation**: Through salts and exchangeable sodium accumulation during soil formation.
- **Second salinisation**: Through salts and exchangeable sodium accumulation from salt groundwater located in shallow aquifers.
- **Man-made**: As a consequence of human activities, through spreading saline-sodic and sodic soils from excavated canals of a rice production area.

However, from this study it was concluded that in the Lionde and Nwachicoluane areas the sodicity and salinity problem is the main reason for bad rice growth.

Bouman (1985) characterised the hydrogeology of the Incomati and Limpopo basin south of Mozambique and the results showed that in the Limpopo basin the upper layers are very brackish.

According to Wilson (2009), the soil salinity of the CIS is sensitive to irrigation water management. During irrigation, the soil salinity increases with depth from upstream to downstream up to 3 400 µS/cm and 2 300 µS/cm, respectively. Therefore, from this study it was concluded that the salt is leached downward along the soil profile toward to the water table.

In a dry season, Hakala and Pekonen (2008) carried out a study in the Chókwè district to investigate how the CIS and agricultural production affect the surface water quality. Analysing the water flow of the CIS, they found that the physicochemical parameters from drainage and irrigation channels are different. When the surface water flows along the irrigation system and drainage channels, the EC value increases (salinisation) and pH value decreases (acidification). Based on this variability, the study concluded that the CIS has a significant influence on surface water quality used to irrigate the crops.

Making an analysis of the studies carried out in Mozambique (Chókwè district) to investigate water quality (surface or groundwater) it is possible to see that most of them are focused on farming activities. All studies reported that the salinity affects the water sources. From this reason it is evident that the present research will be conducted in an area with a saline environment.

The previous studies carried out in Mozambique do not specify or identify what and how the chemical processes are affecting the water quality. Unfortunately, there are no studies done to investigate hydrogeochemical processes that affect groundwater quality. Due to this missing information it is expected that form this research the hydrogeochemical process which affect the water quality and their variability in the Chókwè district will be known.

3.10 CONCLUSION

In this chapter, the common approaches used to assess water quality were identified and described. It is shown that the hydrogeochemical investigations in water quality are complex and is dependent on:

- organoleptic parameters (turbidity, colour, odour and taste);
- microbiological parameters (viruses, bacteria and parasitic protozoa); and
- physicochemical parameters (field and laboratory measurements, including inorganic and organic toxic substances).

Different physicochemical water use standards determine the type of hydrogeochemical investigations in groundwater hydrology. The spatial and temporal occurrences of groundwater quality in the Chókwè district is strongly affected by the land use, local geomorphology and semi-arid environment.

From this chapter it can be concluded that in Mozambique there are two main problems regarding groundwater, namely (1) deficit of groundwater research to understand the physical and chemical hydrogeology, and (2) lack of groundwater infrastructure to set up the national monitoring network and database. This lack of information is the most challenging issues to identify and to delineate groundwater potential zones and zones of suitable groundwater quality.

The mentioned problems can be solved proposing the interactive use of different methods and statistical analyses, one of the best options to apply integrated hydrogeological investigations. In addition, detailed geophysics investigations associated to the geochemistry models are needed to know the groundwater pollution sources in the Chókwè district.

Chapter 4
RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter shows and interprets the physicochemical results of groundwater, surface water and rain water quality from the Chókwè district. In addition, it explains and identifies the dominant hydrogeochemical processes, groundwater types as well as their spatial variability in the study area.

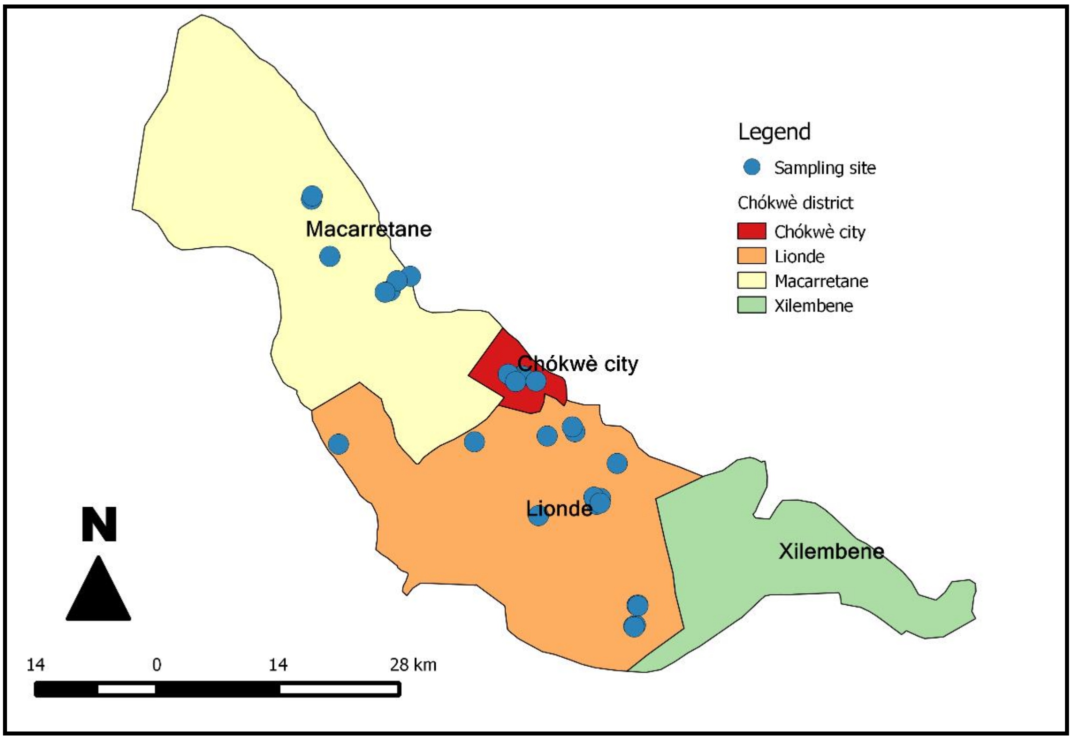
4.2 HYDROCENSUS AND GROUNDWATER LEVEL

The water samples in the study areas were collected in three administrative zone sources of the Chókwè district, namely Chókwè, Lionde and Macarretane. Water source localities, as well as the hydrocensus data, are indicated on the map in Figure 4.1 and summarised in Appendix 4.

The results of the measured water levels and surface topography in Figure 4.2, indicate that Macarretane and Chiaquelane are the elevated areas in the study area. These elevated areas are the driving force for groundwater in the Chókwè district, which contribute to the recharge middle areas such as Lionde and Chókwè administrative zones. The general flow direction is west-east, draining the water into the Indian Ocean, as the dominant flow in most of Mozambique river basins (Tauacale, 2002).

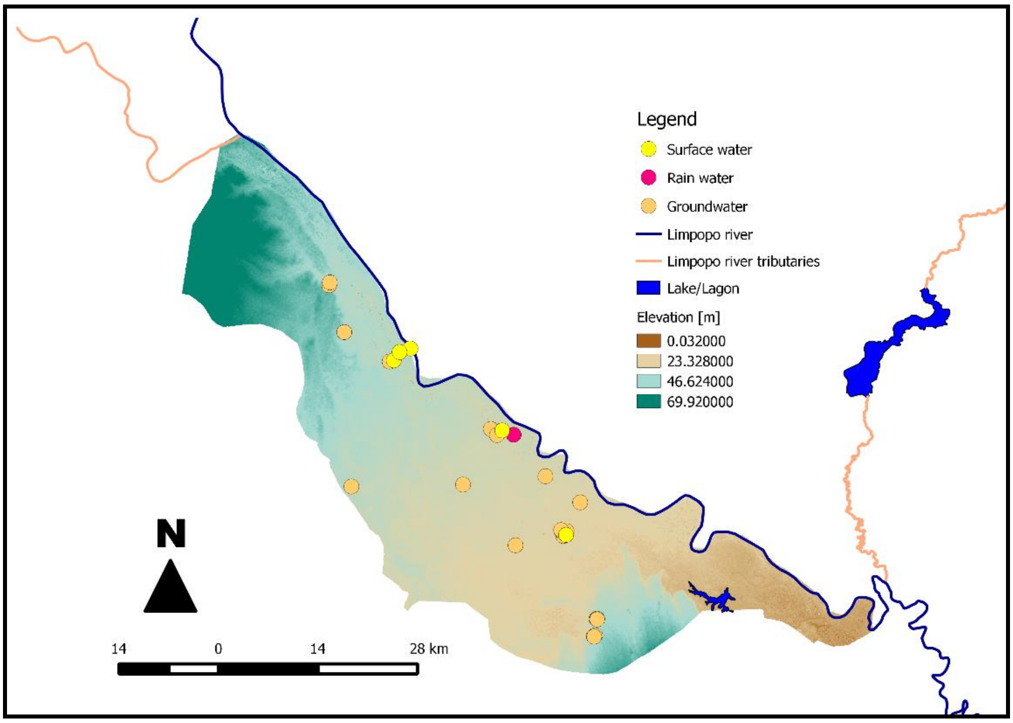
More than 54% of the groundwater sources used in the present study are within the irrigation scheme, where the land use is dominated by intensive agriculture. The irrigation scheme covers an area of 30 000 ha, using a surface irrigation system (Hakala and Pekonen 2008). Chairuca *et al*. (2016) reported that due to the extensive period of surface irrigation (since 1930), the irrigation scheme is known to be a groundwater pollution source. These authors also reported that as a consequence, the local groundwater table has raised and increased soil salinity, affecting the groundwater quality. As expected, the water level in the study area ranged from 4.80 to 12.65 m with a average value of 8.15 m where the high values were observed upstream. Through these water level values, the aquifer is classified as shallow and proximal as shown in Figure 4.3 (Payne *et al*., 2013). The tendency for interaction between the surface water and the shallow aquifer is often increasing the vulnerability to contamination (Meybeck *et al.,*1996). Thus, this may occur in a wide area dominated by unconsolidated material in the study area.

Despite the occurrence of imperfectly drained soils with low hydraulic conductivity and permeability (0.07 to 0.65 m/day) in the CIS reported by Munguambe (2008), referencing Brito (1985) and INIA (1993), the risk of contamination is evident in the aquifer. The dominance of unconsolidated sediments in the study area, with aquifer productivity low to high (Appendix 5 and 6, respectively), often contain brackish to saline water due to decreasing of permeability from the coast inland with increase of clay content in the inland area (Chairuca *et al*., 2016).



Source: ARA-Sul (2015).

Figure 4.1: Sampling site localities and hydrocensus in the study area



Source: ARA-Sul (2015) and CENACARTA (2015).

Figure 4.2: Hydrocensus and surface topography in the study area

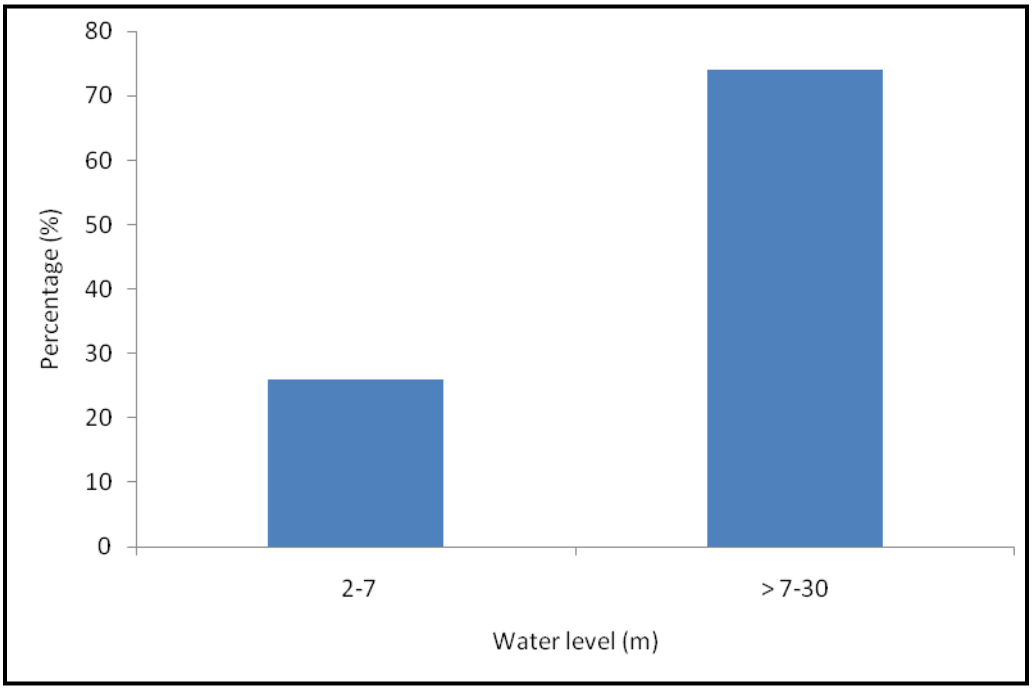


Figure 4.3: Water level and aquifer classification in the study area

4.3 INTERPRETATION OF WATER CHEMISTRY

The interpretation of water chemical composition is a fundamental assessment to determine and understand the water quality through the chemical analysis. Appendix 2 shows the physicochemical parameter results from groundwater and surface water, including the rainfall water in the study area. The results of Ion Balance IB in 79% of water samples range from −5.35 to 1.58 and 21% with values from −10.74 to −5.74. This suggests that in a water sample with an IB between –5 to +5, the total cations and anions are in equilibrium. Non-equilibrium between cations and anions could probably be due to an anthropogenic source that releases ion species or species not included in a laboratory analysis and IB calculation.

4.3.1 Analysis of surface water and rain water chemistry

The statistical analyses of physical and chemical parameters for all surface water and rainfall samples are shown in Table 4.1. In general, all values (minimum, mean and maximum) are within desirable limits, compared with Mozambique standards (MISAU, 2004).

The pH value of the study area shows that the water is basic (pH >7) and ranges from 7.09 to 8.08. Electrical conductivity (EC) and total dissolved solids (TDS) range from 444 µS/cm to 533 µS/cm and 332.108 mg/L to 392.813 mg/L, respectively. Therefore, the surface water is less mineralised and based on equivalent percentage, there is no cation dominant. The bicarbonate ion is the only anion dominant in the water (Table 4.1and Figure 4.4).

Due to a dry season during the present study in Chókwè (low precipitation) only one sample of rain water was collected. Therefore, the rain water tend to be more acidic (pH <7), with a pH value of 6.25. The EC, TDS and hardness have values of 106 µS/cm, 74 mg/L and 9 mg/L, respectively. There is no dominance of anion, but cation combination of $Na^+ + K^+$ is significant in the water.

From the above results, it is evident that the surface water and rain water chemistry are different. During the hydrological cycle different forms of water in the hydrosphere are replenished at very different rates (Babar, 2005). According to

Hounslow (1995), the presence of gases such as SO_3 and SO_2, as well as from nitrogen oxides in the atmosphere, result in acid rain.

TABLE 4.1: STATISTICAL SUMMARY OF SURFACE WATER PHYSICOCHEMICAL PARAMETERS IN THE STUDY AREA

Parameters	Average	Minimum	Maximum	Stdv	MOZNS
pH	7.86	7.09	8.08	0.43	6.5-8.5
EC (µS/cm)	505.20	444.00	533.00	35.34	50-2000
TDS (mg/L)	377.53	332.11	392.81	25.52	1000
TH (mg/L)	160.73	144.76	175.92	12.05	500
Ca (mg/L)	27.72	23.30	31.50	3.05	50
Mg (mg/L)	22.30	21.10	23.70	1.12	50
Na (mg/L)	58.76	53.70	62.20	3.23	200
K (mg/L)	4.85	3.77	7.74	1.62	Nv
HCO_3 (mg/L)	138.40	135.00	146.00	4.39	Nv
F (mg/L)	0.1362	0.01	0.49	0.20	1.5
Cl (mg/L)	78.53	66.50	84.25	7.01	250
Br (mg/L)	0,26	0.19	0.31	0.05	Nv
SO_4 (mg/L)	46.84	13.89	55.90	18.43	250
Al (mg/L)	0.12	0.09	0.17	0.03	0.2
Si (mg/L)	3.68	0.96	4.70	1.54	Nv

TH = Total hardness; Stdv = Standard deviation; MOZNS = Mozambique National Standards;
Nv = No established value

Source: MISAU (2004)

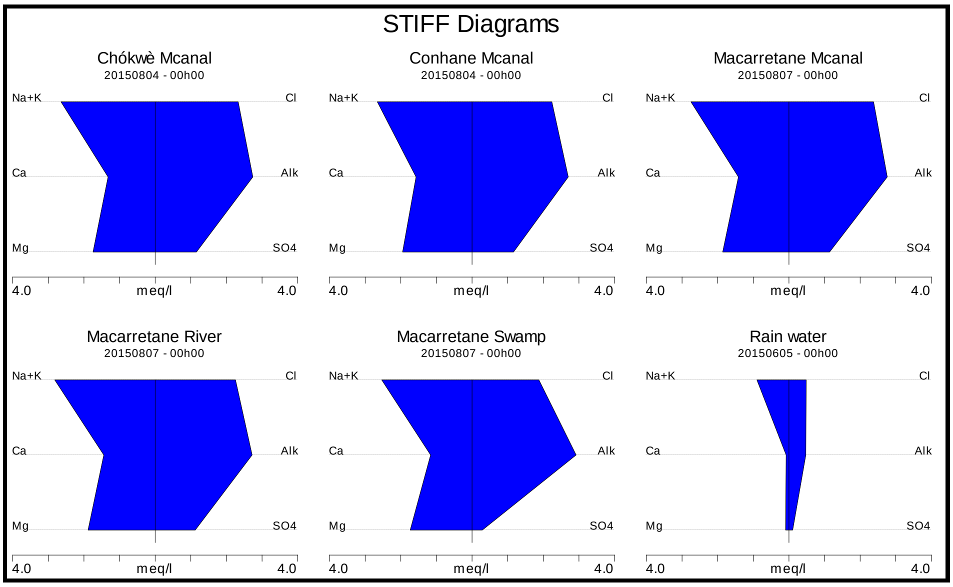


Figure 4.4: Stiff diagram of surface water and rain water chemistry of the Chókwè district

4.3.2 Analysis of groundwater chemistry

The results of the statistical analysis for groundwater samples from Chókwè district are given in Table 4.2. The concentration of Na^+, Mg^{2+}, Ca^{2+} and K^+ ranged from 45.9 to 1 756, 0.58 to 481, 1.61 to 513.98 and 1.31 to 30.39 mg/L with a mean value of 360.67, 45.42, 49.96 and 9.89 mg/L, respectively. The concentration of anions Cl^-, HCO_3^- and SO_4^{2-} ranged from 39 to 3 961, 6.98 to 1 031 and 11.6 to 566 with a mean of 521.36, 217.95 and 97.64 mg/L, respectively.

The order of abundance of the cation concentrations is $Na^+ > Mg^{2+} > Ca^{2+} > K^+$, while those of the anions are $Cl^- > HCO_3^- > SO_4^{2-}$. About 50% and 38% of groundwater samples have a high concentration of sodium and chloride out of desirable limits, respectively (MISAU, 2004). Among sediment deposits in the study area, the pH value in the groundwater samples ranged from 5.9 to 8.17.

TABLE 4.2: STATISTICAL SUMMARY OF GROUNDWATER PHYSICOCHEMICAL PARAMETERS IN THE CHÓKWÈ DISTRICT

Parameters	Average	Minimum	Maximum	Stdv	MOZNS
pH	7.470	5.900	8.430	0.790	6.5–8.5
Ca (mg/L)	49.960	1.608	513.979	107.440	50
Mg (mg/L)	45.420	0.582	480.795	100.870	50
Na (mg/L)	360.672	45.901	1 756.380	388.560	200
K (mg/L)	9.894	1.311	30.386	8.562	Nv
HCO_3 (mg/L)	217.950	6.980	1031.000	203.174	Nv
Cl (mg/L)	521.358	39.479	3 961.430	839.271	250
SO_4 (mg/L)	97.642	11.551	565.836	146.548	250
Si (mg/L)	17.782	9.973	44.579	7.778	Nv
Br (mg/L)	1.543	0.081	11.014	2.444	Nv

Stdv = Standard deviation; MOZNS = Mozambique National Standards; Nv = No established value

Source: MISAU (2004).

The high values of major ions in groundwater has been reported in many hydrogeochemistry studies. Interpretation of an hydrochemical analysis by Aghazadeh and Mogaddam (2010) reveals that in sandstone, limestone and quaternary formations, Ca^{2+} and HCO_3^- are dominant in groundwater and the water is fresh, hard to very hard.

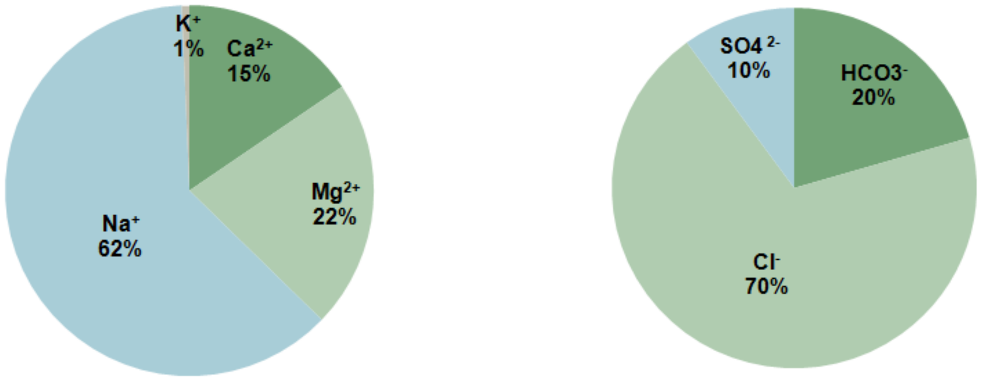
Sayyed and Bhosle (2011) reported that a high chloride content than permissible limits, gives an undesirable taste and indicates heavy pollution. Inorganic fertilizer, landfill leachates and irrigation drainage, are appointed as the key factor. Occurrence of chloride in groundwater originates from both anthropogenic and natural sources. Elevated content of sodium, bromide, bicarbonate and fluoride may be found in stratigraphic units susceptible to marine influences, such as fluvial plains, including swamps and estuaries (Burbery and Vincent, 2009).

The similar geology environment pointed out by Burbery and Vincent (2009). Aghazadeh and Mogaddam (2010), as well as Sayyed and Bhosle (2011), characterises the sampling sites of the Chókwè district. According to Grantham *et al*. (2011), the physiography of the study area in a depression with quaternary deposits (lacustrine, fluvial, aeolian, and marine) is a result of sea level fluctuation owing to the alteration of glacial and interglacial episodes. Therefore, in the Chókwè district similar results of high sodium and chloride concentrations was found, ranging from 202 to 1 756 mg/L and 253 to 1 893 mg/L, respectively.

4.3.2.1 Analysis of variance

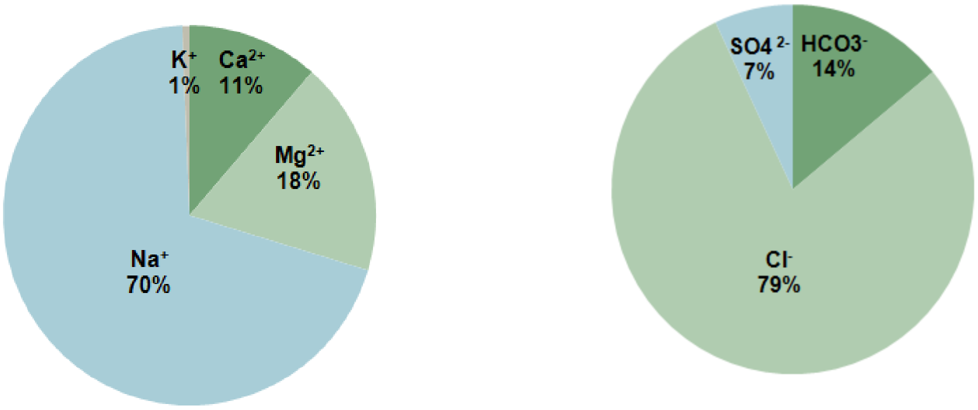
Analysis of variance in groundwater samples from the Chókwè district revealed that at significance level of 5% there is an effect of geology in the groundwater chemistry (Appendix 7). The groundwater from internal dune–red aeolian sand geological deposits has a higher content of Na^+ and Cl^- than an alluvium, sand, silt, gravel geological unit. In internal dune-red aeolian sand geological deposits, both Na^+ and Cl^- ions have 85%, while in alluvium, sand, silt, gravel geological unit is 62% and 70%, respectively (Figure 4.5). The abundance order of cations in internal dune-red aeolian sand geological deposits is $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$ and for anions it is $Cl^- > SO_4^{2-} > HCO_3^-$, which is slightly different from other geological units, both with the follow sequence: $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ versus $Cl^- > HCO_3^- > SO_4^{2-}$.

The relationship of major ions affects the ionic composition and chemical quality of water in the aquifer. According to Hem (1985), a lower concentration of bicarbonate ion (HCO_3^-) than calcium (Ca^{2+}) and magnesium (Mg^{2+}) in groundwater may influence the pH. Carbonate species such as H_2CO_3 may lose protons to from HCO_3^- and CO_3^{2-}. Therefore, the liberated proton will decrease the pH in water.



Groundwater chemistry in alluvium, sand, silt, gravel deposits

Groundwater chemistry in internal dune-aeolian sand deposits



Groundwater chemistry in eluvial floodplain clayey sand deposits

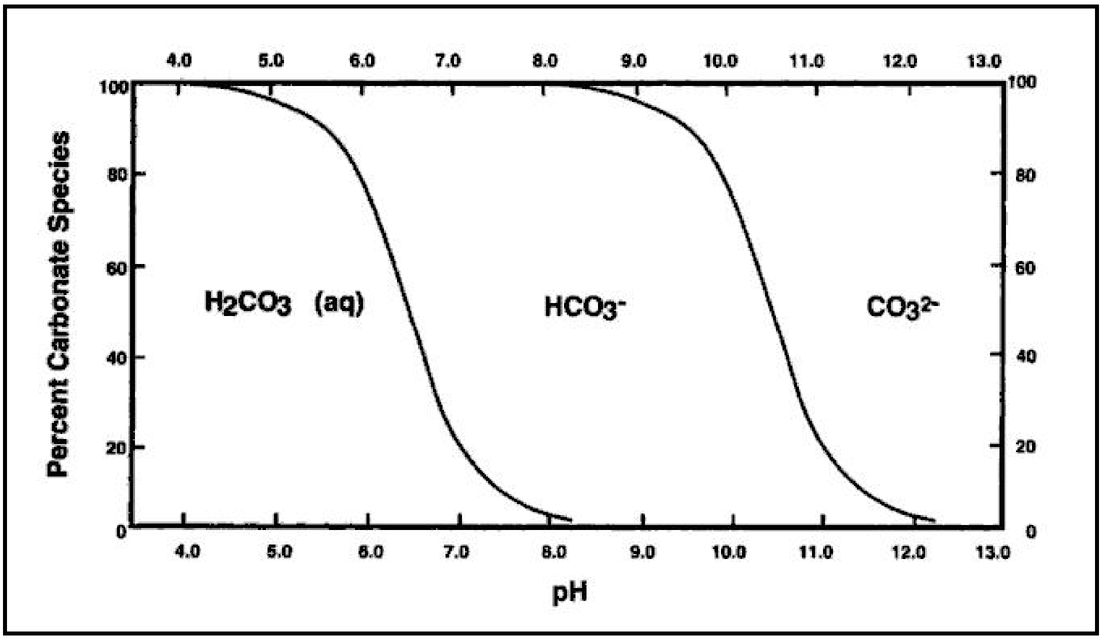
Figure 4.5: ***Distribution of cations and anions in groundwater from different deposits of the Chókwè district***

From the present study, the pH average value of 6.25 indicate acid groundwater in internal dune-red aeolian sand geological, unlike other alluvium–sand–silt–gravel and eluvial floodplain clayey sand geological units with average values of 7.8 and 8, respectively.

Freeze and Cherry (1979) concluded that carbonic acid (H_2CO_3) is the most polyprotic species (Equation 4.1) present in natural or contaminated groundwater, which forms when carbon dioxide (CO_2) combines with water (Equation 4.2). At low pH, the H_2CO_3 is the dominant species, and from a pH value range of 6 to 9 the HCO_3^- species is dominant (Figure 4.6). From the above analysis, it is evident that in the Chókwè district there is variability of dominants species. The alluvial sediments and eluvial floodplains have a dominance of HCO_3^-, while in internal dune it is H_2CO_3.

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad \text{(Equation 4.1)}$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \qquad \text{(Equation 4.2)}$$



Source: Hounslow (1985).

Figure 4.6: Distribution of major dissolved carbon species as a function of pH in water

4.3.2.2 Correlation analysis of major ions

The relationship between the major physicochemical parameter of groundwater is presented in Table 4.3. All major groundwater ions from internal dune-red aeolian sand deposits have a strong correlation with HCO_3^-, except K^+ (0.089). The same correlation was observed between a pH with HCO_3^- (0.990). Therefore, this is the evidence that both HCO_3^- and H^+ are from the same source (H_2CO_3). In contrast with the other geological units, the pH is not correlated with any cation and anion. Thus, the pH can be influenced from oxidation processes and other hydrogeochemical reactions in groundwater which produce H^+ and contribute to acidity in water.

TABLE 4.3: PEARSON CORRELATION MATRIX BETWEEN MAJOR IONS IN DIFFERENT GEOLOGICAL UNITS OF THE CHÓKWÈ DISTRICT

Internal dune; red aeolian sand deposits								
	pH	*Ca*	*Mg*	*Na*	*K*	*HCO3*	*Cl*	*SO4*
pH	1							
Ca	0.820	1						
Mg	0.767	0.932	1					
Na	0.846	0.940	0.989	1				
K	0.070	0.018	0.344	0.324	1			
HCO_3	0.990	0.876	0.839	0.903	0.089	1		
Cl	0.813	0.899	0.986	0.993	0.432	0.869	1	
SO_4	0.858	0.984	0.932	0.946	0.005	0.915	0.901	1
Alluvium, sand, silt, gravel deposits								
	pH	*Ca*	*Mg*	*Na*	*K*	*HCO3*	*Cl*	*SO4*
pH	1							
Ca	-0.328	1						
Mg	-0.267	0.998	1					
Na	-0.144	0.979	0.989	1				
K	-0.222	0.821	0.817	0.828	1			
HCO_3	-0.050	0.088	0.083	0.126	0.103	1		
Cl	-0.221	0.993	0.998	0.994	0.826	0.066	1	
SO_4	-0.202	0.980	0.984	0.991	0.876	0.095	0.990	1
Eluvial floodplain clayey sand								
	pH	*Ca*	*Mg*	*Na*	*K*	*HCO3*	*Cl*	*SO4*
pH	1							
Ca	-0.903	1						
Mg	-0.892	0.9990	1					
Na	-0.489	0.597	0.605	1				
K	-0.747	0.847	0.851	0.900	1			
HCO_3	-0.092	0.308	0.324	0.230	0.430	1		
Cl	-0.768	0.890	0.894	0.893	0.962	0.251	1	
SO_4	-0.520	0.591	0.597	0.707	0.847	0.751	0.678	1

4.3.2.3 Spatial variability of groundwater quality

A detailed investigation of the spatial variability of the groundwater will provide an insight of the current hydrogeological environment and modelling source of pollutants (Hosseinifard *et al*., 2008, referencing Corwin and Lesch, 2005). Groundwater variability in this study has been addressed specifically in terms of concentration distribution of groundwater physicochemical parameters in the Chókwè district.

In general, the spatial distribution of all physicochemical parameters is increasing to the northern part of the Chókwè district. More than 60% of groundwater sampled sites are located in the farming area. In this area the groundwater is used us a main source for drinking water from wells, few hand pumps and pump stations. The abstraction rate per day from all pump stations to supply water is about 590 m^3/h. Due to the elevated volume of water abstracted, high inflow occurs and it can contribute to migrate the pollutant or high mineralised water from the farming area to the aquifer. Therefore, in this study different spatial variabilities of groundwater quality were observed between the farming area and non-farming area (Table 4.4 and Figure 4.7). The farming area has high mineralised water and consequently a high content of ion which affect the EC, TDS and total hardness.

TABLE 4.4: VARIABILITY OF ION CONTENT IN GROUNDWATER BETWEEN FARMING AREA AND NON-FARMING AREA

Ion (mg/L)	Farming area			Non-Faming area		
	Minimum	Maximum	Average	Minimum	Maximum	Average
Ca^{2+}	4.0	514.0	91.5	1.6	20.6	5.4
Mg^{2+}	2.2	480.8	83.0	0.6	30.3	7.8
Na^{+}	97.8	1 756.2	461.5	45.0	629.2	189.9
K^{+}	2.0	20.9	7.2	6.7	30.4	19.9
Cl^{-}	65.0	3 961.0	792.3	39.5	796.3	266.1
HCO_3^{-}	167.0	474.0	263.5	7.0	63.9	22.3
SO_4^{2-}	15.4	565.8	119.2	11.6	204.4	48.5
Hardness	21.0	3 256.0	442.0	9.0	175.0	46.0

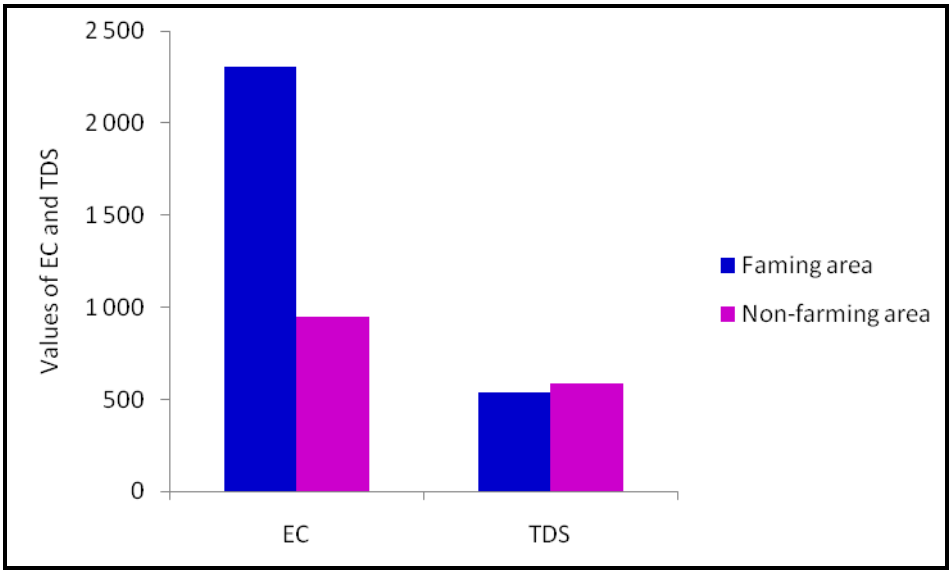


Figure 4.7: ***Variability of groundwater quality between farming area and non-farming area***

The spatial distribution of the surface contour were also analysed in the study area. Diagrammatical spatial variability of Ca (Figure 4.8); Na (Figure 4.9); K (Figure 4.10); Mg (Figure 4.11); Cl (Figure 4.12); SO_4 (Figure 4.13); HCO_3 (Figure 4.14); EC (Figure 4.15); TDS (Figure 4.16) and hardness (Figure 4.17), respectively, are shown below.

In a few groundwater samples from the non-farming area with different sediment deposits (gravel, silt, sand) high mineralised water als was o found. Alemaw *et al*. (2008) reported that the western parts of the Limpopo basin, including the Chókwè district, receive less than 500 mm rainfall per year. Therefore, in this context the fluctuation of water levels due to the arid condition associated with the low volume of recharge water can also contribute to spatial variability of groundwater quality in the shallow aquifer of the study area.

Alley (1993:10) refers to “variations in shallow-ground-water quality due to temporal variations in recharge are most likely to be significant in near-surface water-table aquifers”. Variations of water quality from shallow groundwater can be greatly affected by flushing of constituents during individual recharge events and seasonal periods of recharge. Water table fluctuation that results in up and down movement of the saturated zone into different depth horizons may also have a significant effect on water quality in shallow aquifers.

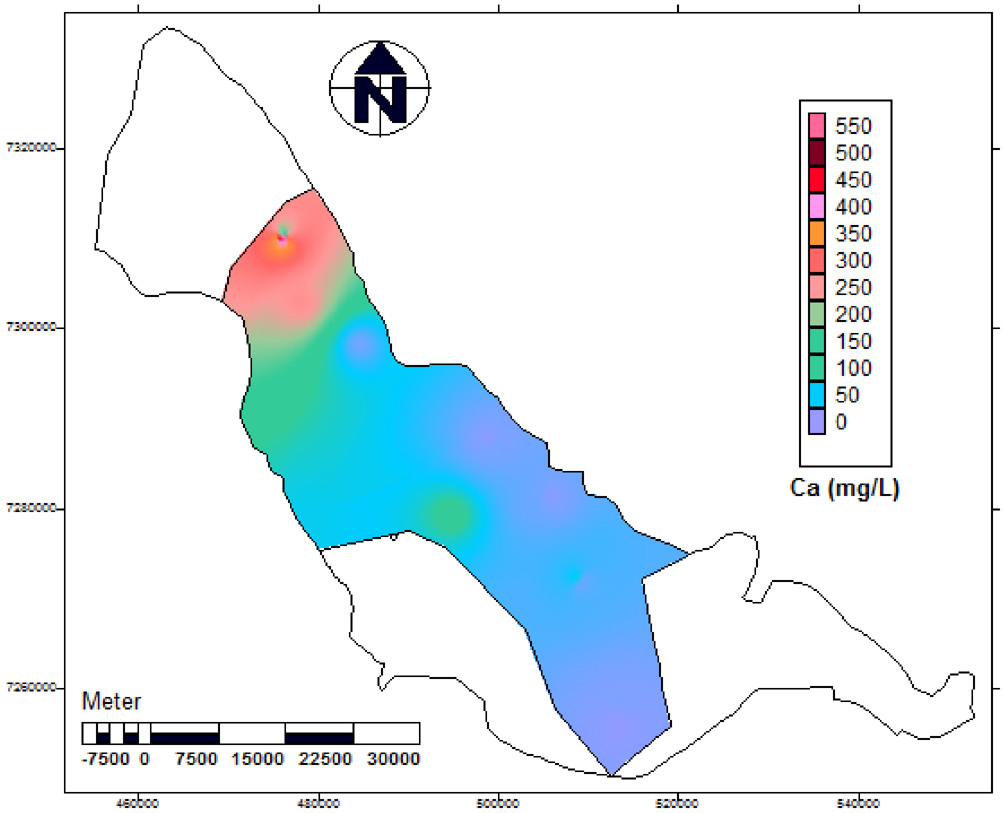


Figure 4.8: *Spatial variability map of calcium in groundwater in the study area*

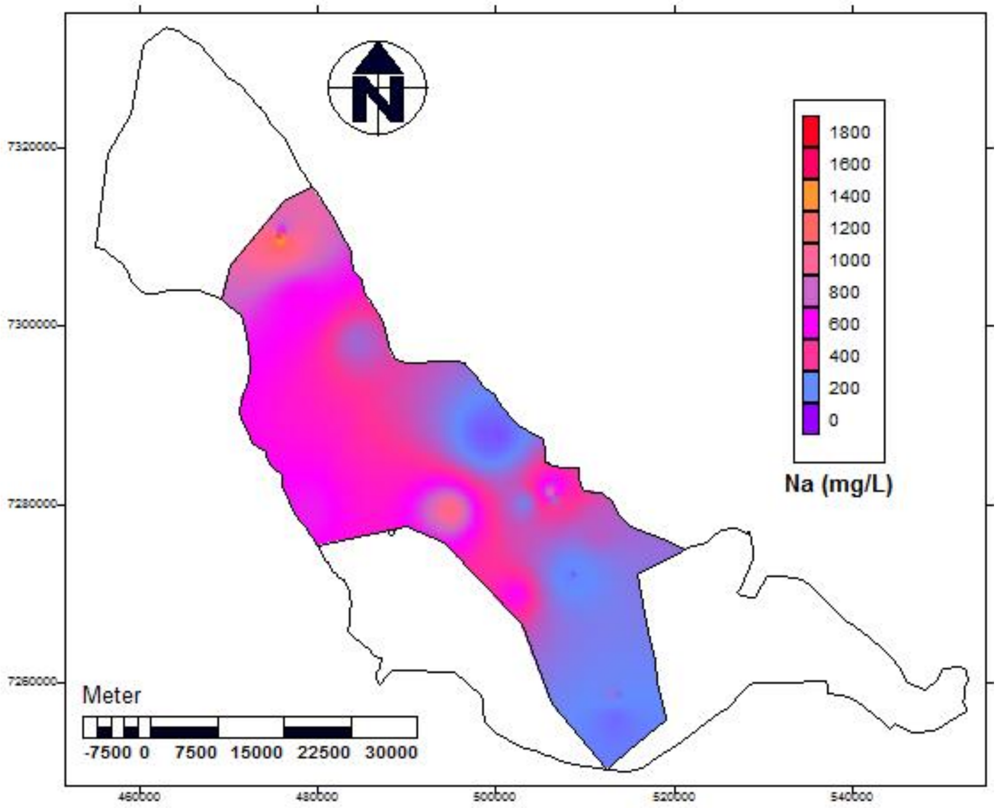


Figure 4.9: *Spatial variability map of sodium in groundwater in the study area*

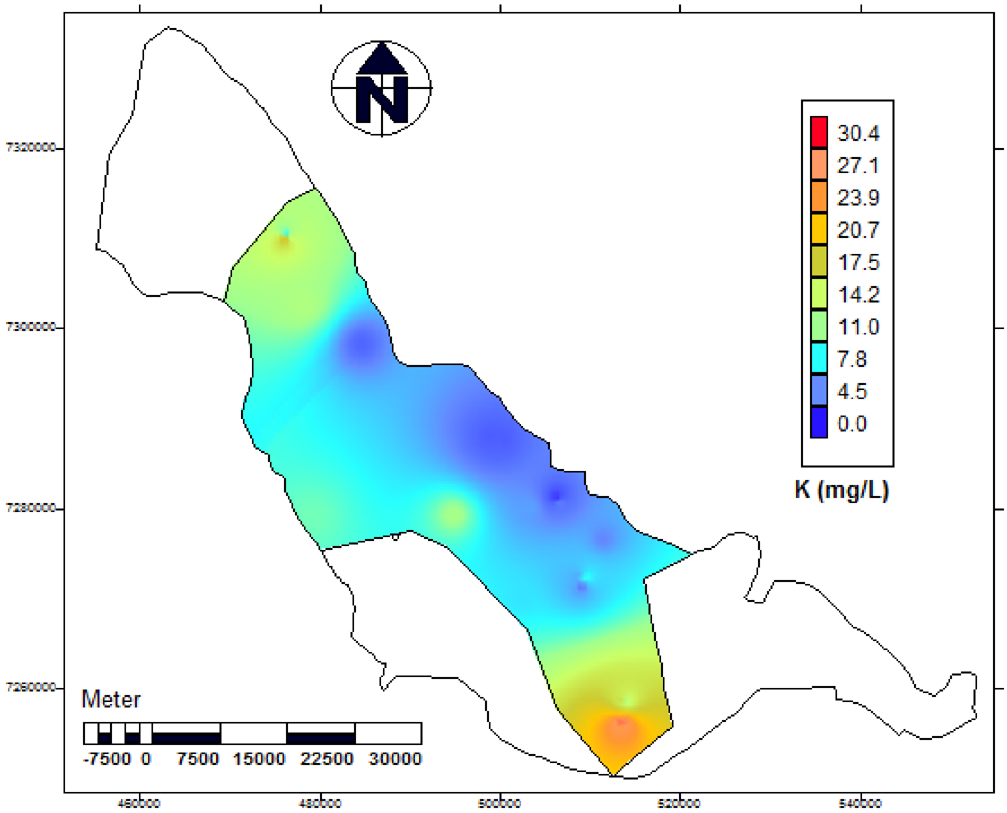


Figure 4.10: Spatial variability map of potassium in groundwater in the study area

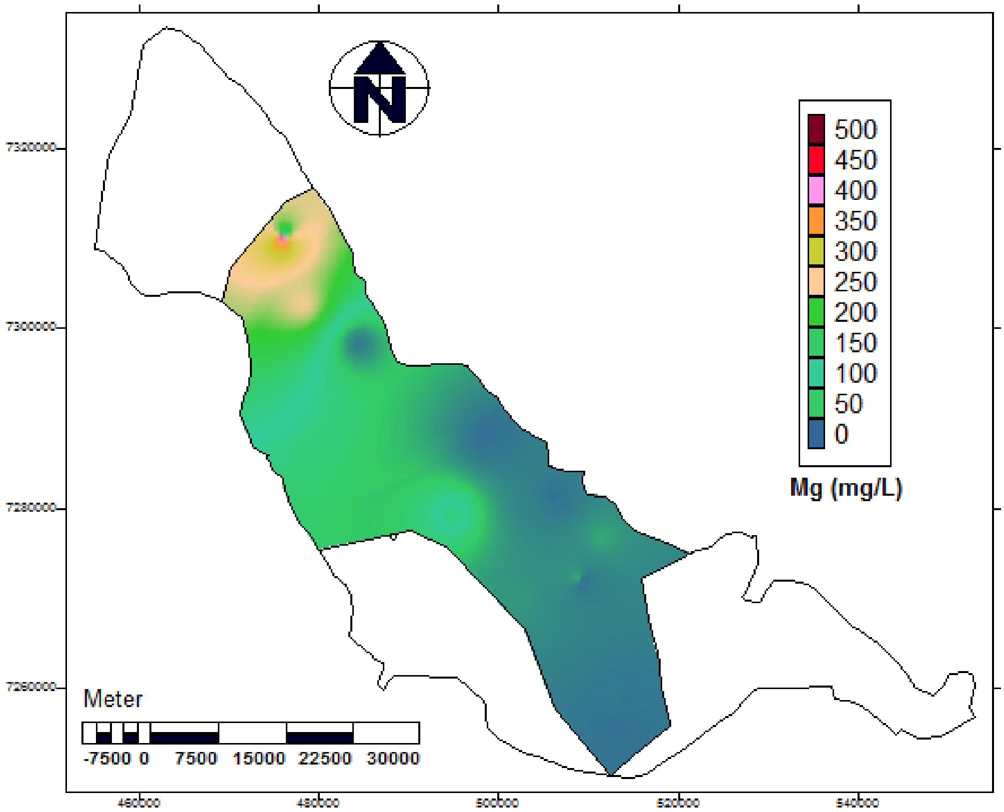


Figure 4.11: Spatial variability map of magnesium in groundwater in the study area

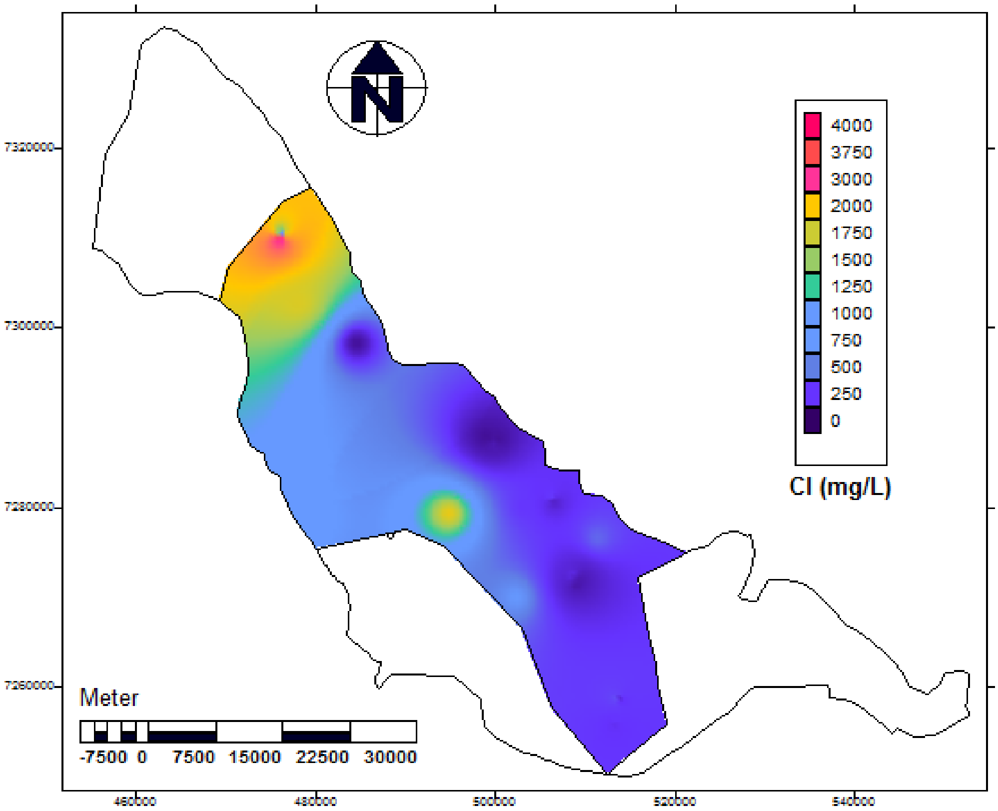


Figure 4.12: Spatial variability map of chloride in groundwater in the study area

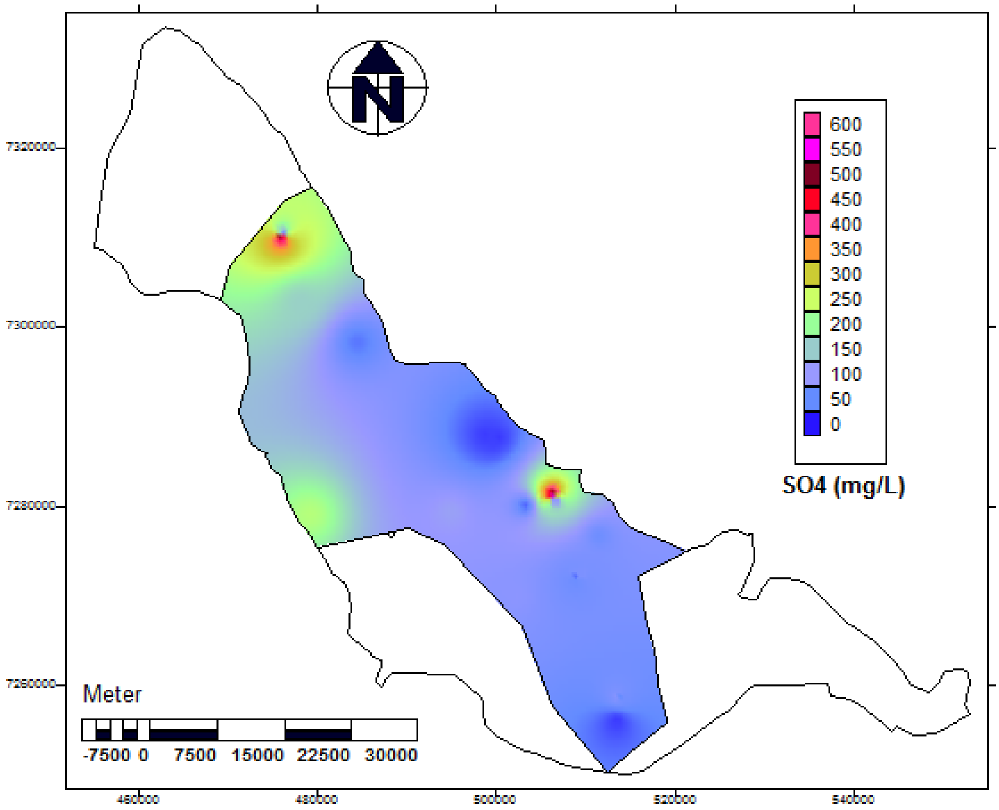


Figure 4.13: Spatial variability map of sulphate in groundwater in the study area

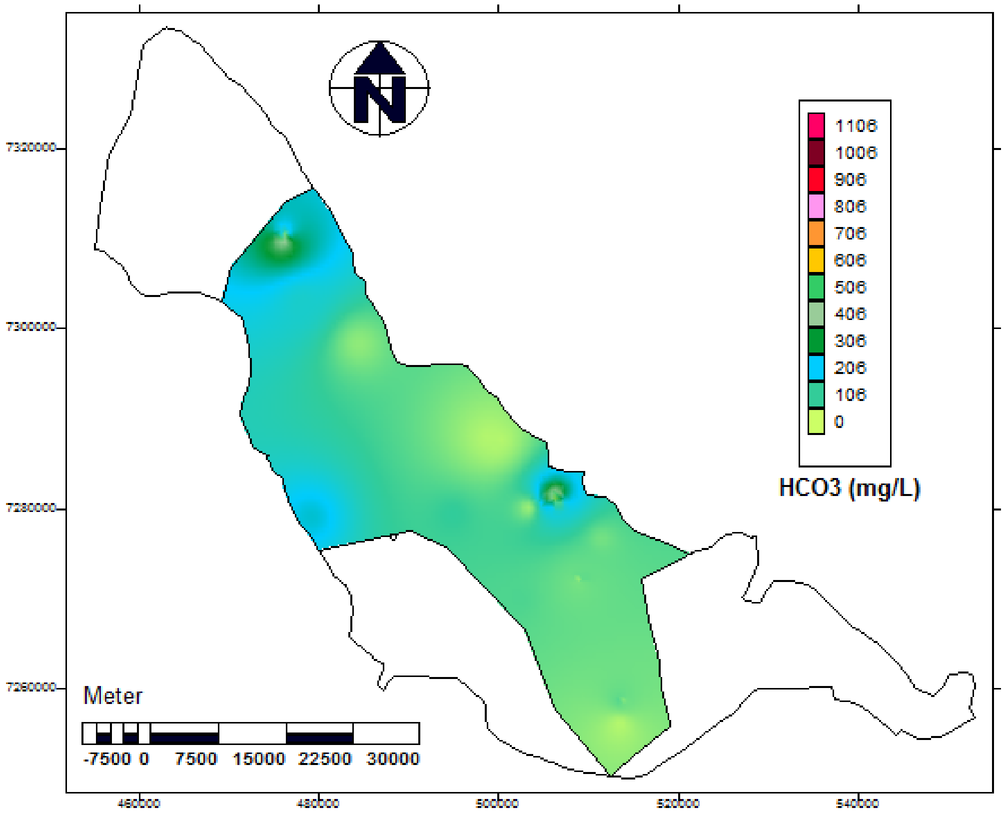


Figure 4.14: Spatial variability map of bicarbonate in groundwater in the study area

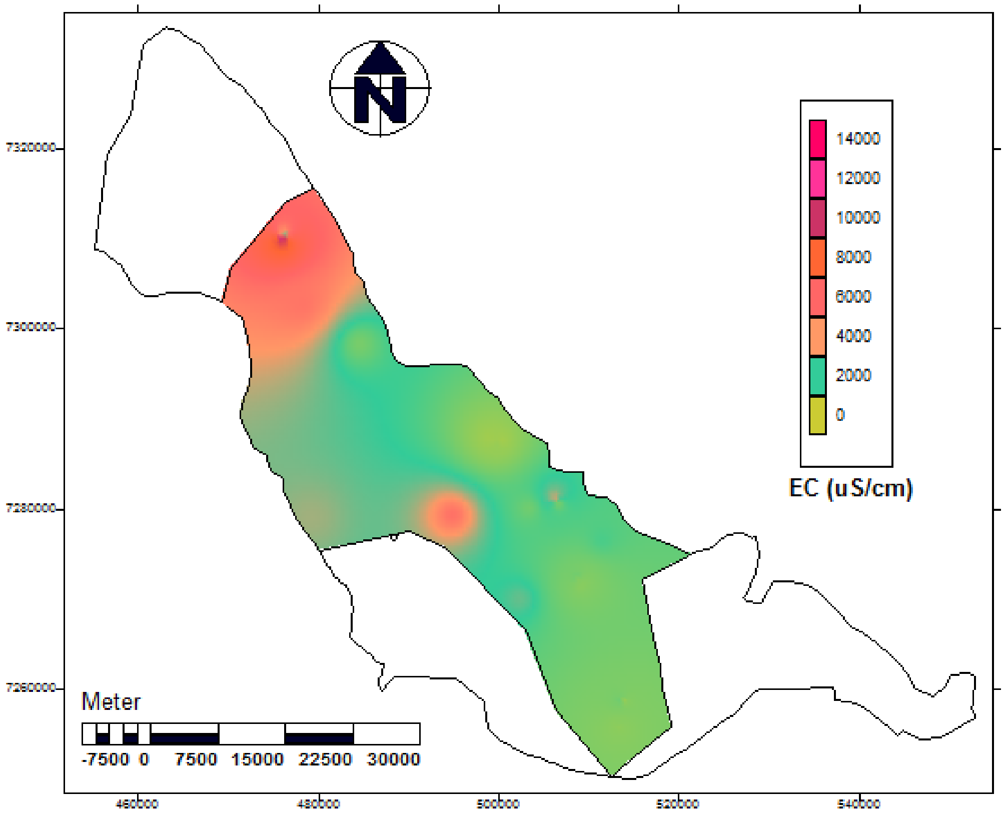


Figure 4.15: Spatial variability map of electrical conductivity in groundwater in the study area

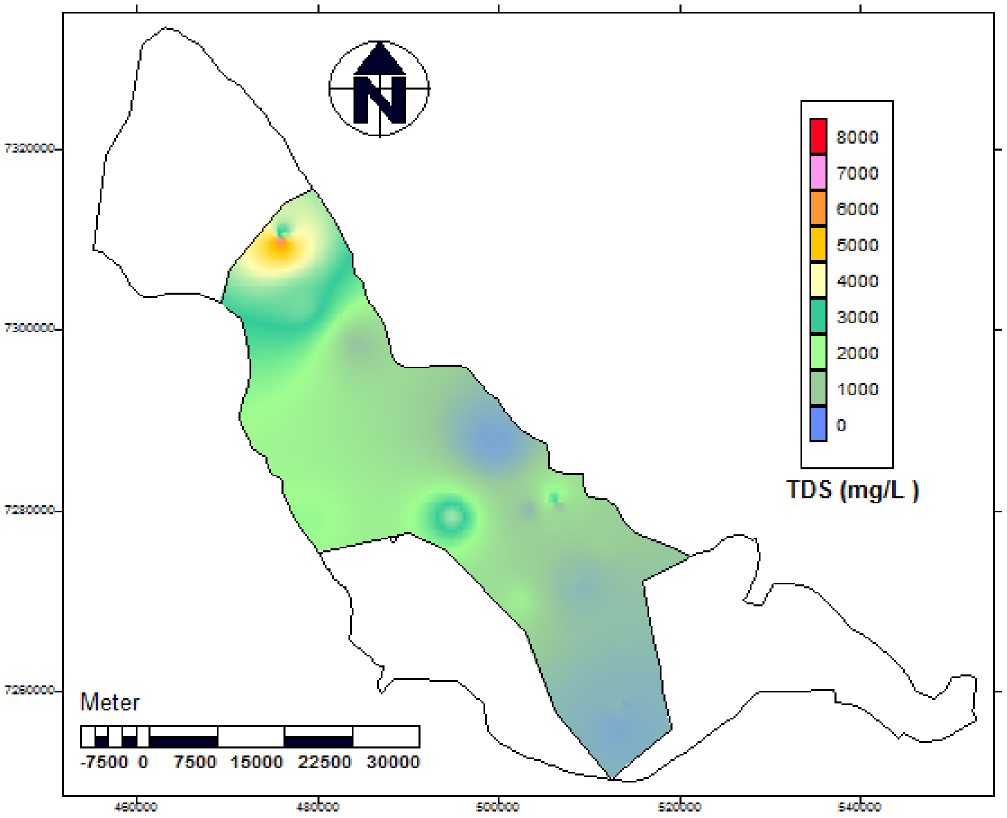


Figure 4.16: Spatial variability map of total dissolved solids in groundwater in the study area

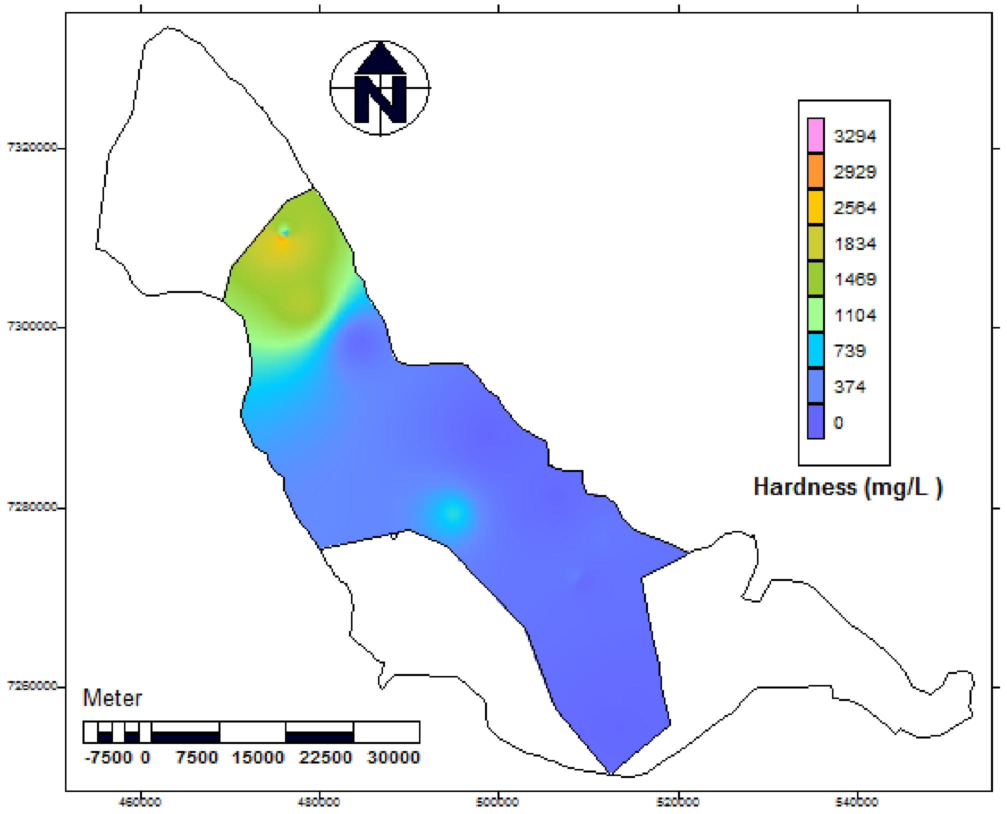


Figure 4.17: Spatial variability map of hardness in groundwater in the study area

4.3.2.4 Analysis of groundwater salinity

The salinity represents the measure of the amount of dissolved particles and ions in water. To analyse and evaluate the salinity in water, the EC and TDS are the two most frequent parameters used.

The groundwater from the Chókwè district has a wide range of salinity. The EC values range from 241 µS/cm to 12 000 µS/cm, with an average of 1 957 µS/cm, while the TDS vary from 163 mg/L to 7 626 mg/L, with a mean of 1 313 mg/L. Both mean values for EC and TDS exceed the limits of the Mozambican standard drinking water. However, 30% of groundwater samples has high EC values (>2 000 µS/cm), while 37% have high TDS values (>1 000 mg/L), as shown in Table 4.5 below. These results indicate that the groundwater quality of those samples is out of Mozambique standards of drinking limits (MISAU, 2004).

TABLE 4.5: DESCRIPTIVE STATISTIC OF ELECTRICAL CONDUCTIVITY AND TOTAL DISSOLVED SOLIDS

Parameters	**Number of sample**	**Range**	**Mean**	**Standard deviation**	**50–2 000**	**>2 000**
Electrical conductivity (µS/cm)	27	241–12 000	1 957	2 450	20	7[a]
Parameters	**Number of sample**	**Range**	**Mean**	**Standard deviation**	**≤1 000**	**>1 000**
Total dissolved solids (mg/L)	27	163–7 626	1 313	1 564	17	10[a]

a = out of desirable limits

Source: MISAU (2004).

The high values of EC and TDS in groundwater are observed in the Macarretane and Lionde area. Due to the high salinity content in water, 15% and 30% of groundwater sources from these areas is classified as poor and unacceptable for drinking purposes, with TDS ranging from 900–1 200 and higher than 1 200 mg/L, respectively. About 7% and 33% of groundwater sources are classified as excellent and good, respectively, for drinking, as shown in Table 4.6 below.

TABLE 4.6: GROUNDWATER CLASSIFICATION OF CHÓKWÈ DISTRICT BASED ON TOTAL DISSOLVED SOLIDS

Number of samples	Water quality	TDS value (mg/L)
2	Excellent	<300
9	Good	300 – 600
4	Fair	600 – 900
4	Poor	900 – 1 200
8	Unacceptable	>1 200

Source: WHO (2003).

4.3.2.4.1 Groundwater salinity and geology

The groundwater sources with high values of TDS and EC, occur in three dominated geological units of the district. The statistical analysis of variance in Appendix 8, shows that there is a significant effect of the geology on the salinity content in groundwater from the Macarretane to Lionde area. The comparisons between average values of EC and TDS, using the t-Test, at a significant level of 5%, indicate that alluvium, sand, silt, gravel geological unit and eluvial floodplain clayey sand have higher mineralised groundwater than internal dune-red aeolian sand geological unit. Between alluvium, sand, silt, gravel geological unit and eluvial floodplain clayey sand geological unit, there is also a significant difference in the content of EC and TDS in groundwater. From this comparison, it is visible that the groundwater is more highly mineralised in alluvium, sand, silt, gravel geological unit than in eluvial floodplain clayey sand geological unit (Figure 4.18 and Figure 4.19).

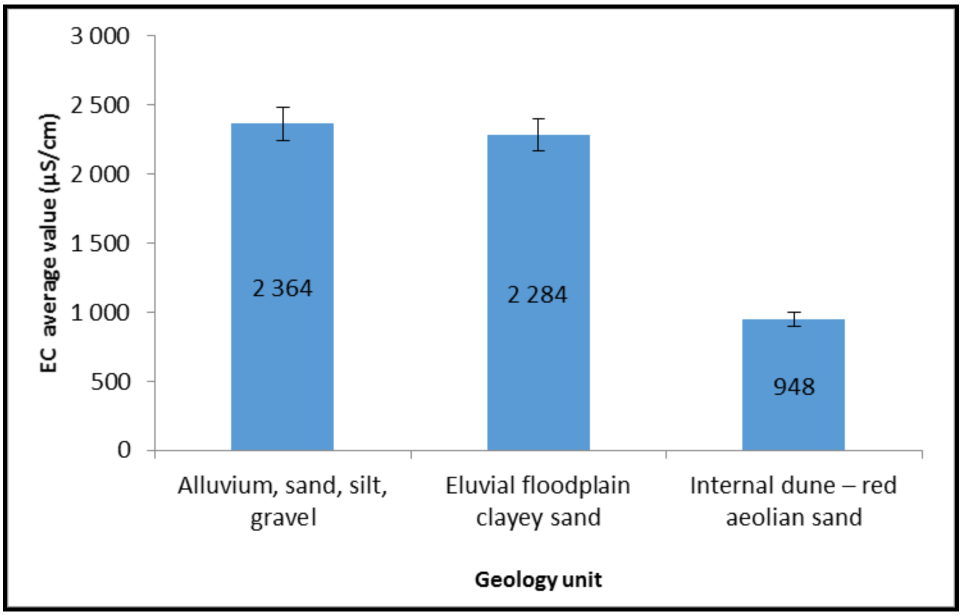


Figure 4.18: Average values of total dissolved solids in groundwater from the main geological units of the study area

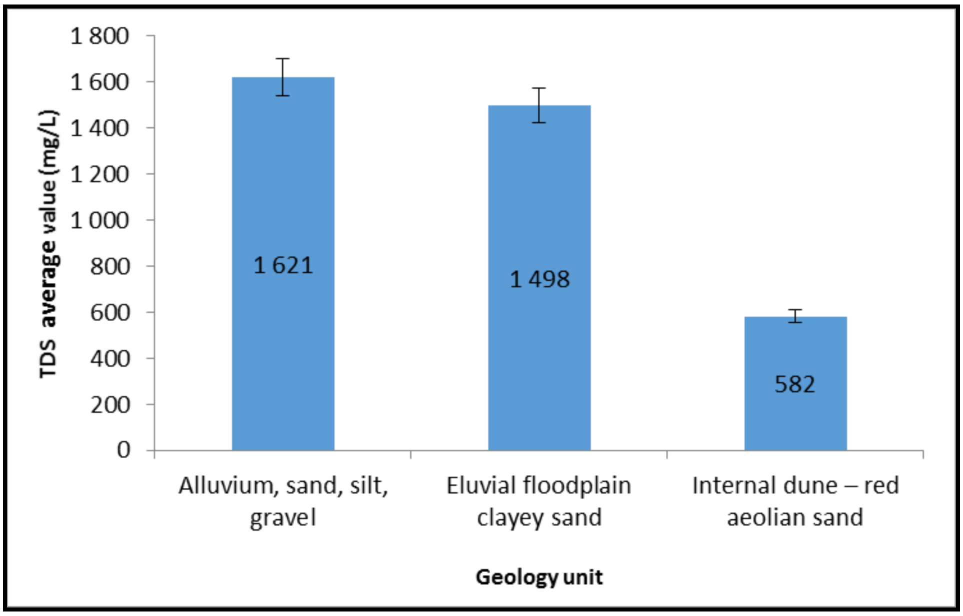


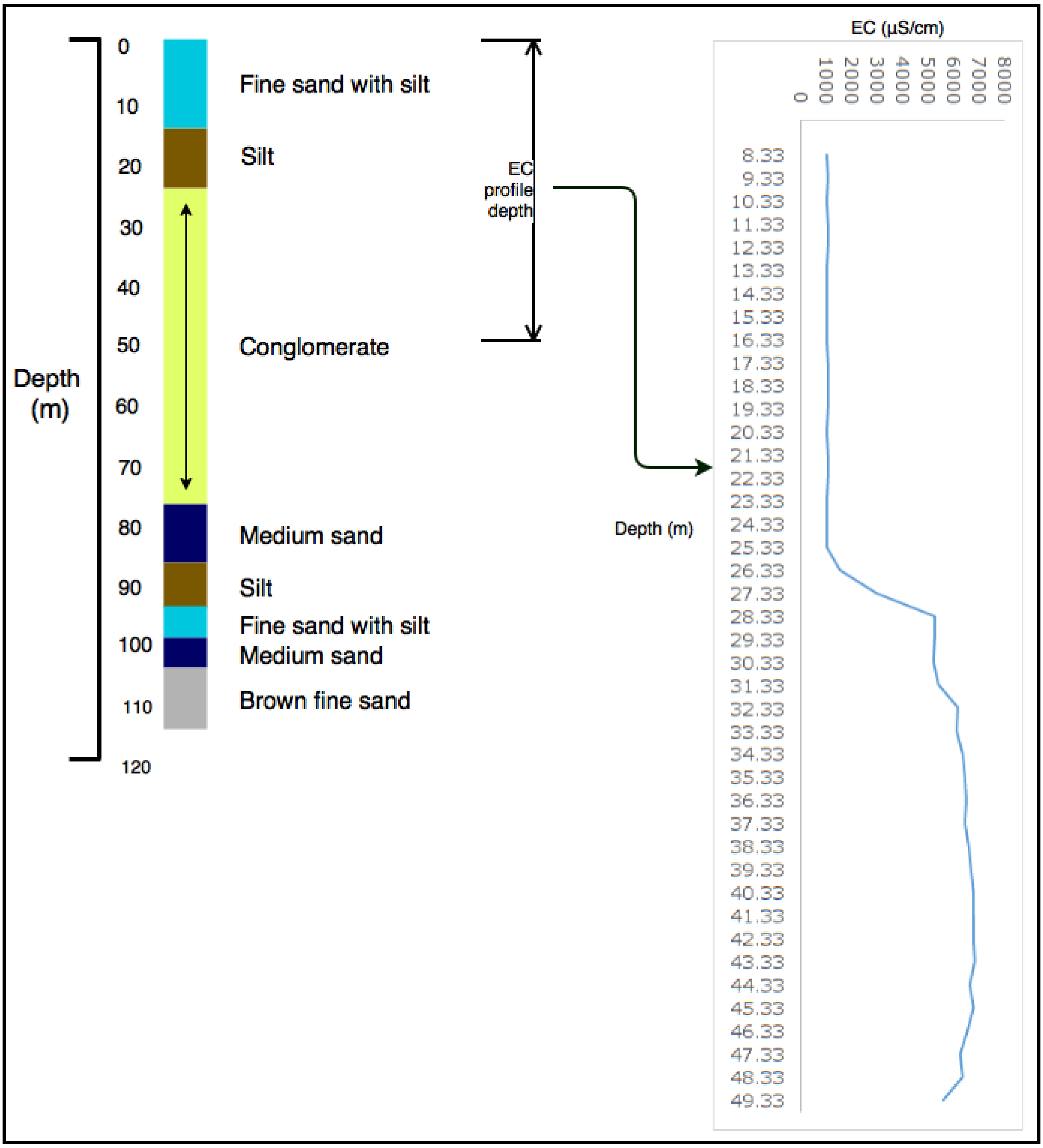
Figure 4.19: Average values of electrical conductivity in groundwater from the main geological units of the study area

4.3.2.4.2 Groundwater salinity and lithology

The Chókwè district is located in the floodplain area of the Limpopo basin and the geology is mainly dominated by quaternary deposits with unconsolidated formations such as sand or sand–clay alluvium, eluvium, conglomerates and gravel. Argillaceous and siliceous sediments are common in different layers in the aquifer. The lithology profile of the district in three geological units show different groundwater qualities from intercalated underlain unconsolidated deposits. The EC profile graph (Figure 4.20) of a monitoring borehole in the Chókwè district up to a depth of 49.33 m, shows that EC values start increasing from a depth of 26.33 m. In the monitoring borehole, from a depth of 24 m up to 76 m, there is an occurrence of conglomerate sediments layer and above fine sand with silt layers. Groundwater occurring over conglomerate (in fine sand with silt layer) has an EC value of less than 2 000 μS/cm.

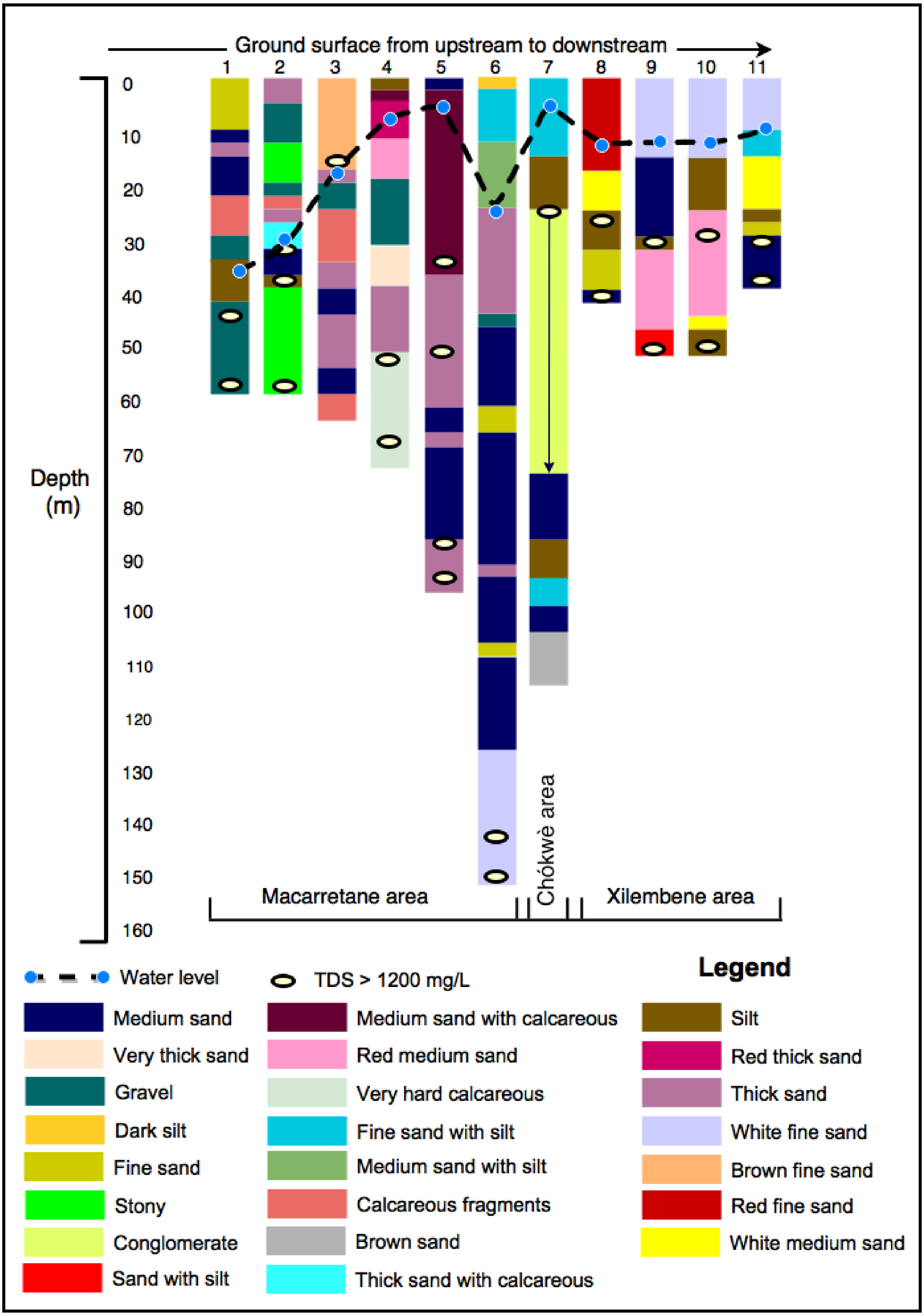
In another borehole, lithological data of the Chókwè district (Figure 4.21), there is also a difference of groundwater quality from stratified layers. Groundwater in a brown fine sand layer is classified as good and in a conglomerate layer is unacceptable. A total of 33% and 50% of layers have poor water quality and fair water quality, respectively (Table 4.7). Most of the unconsolidated layers with different particle size and mineralogy are dominant in the following sequence:

Medium sand > silt > thick sand > gravel. In the upstream area, the dominance sequence of the layers is thick sand > medium sand > gravel, while in downstream the sequence is silt > medium sand > fine sand. Other layers such as calcareous and stony only occur in the upstream area of the district.



Source: ARA-Sul (2015).

Figure 4.20: Electrical conductivity profiling and respective lithology of monitoring the borehole at a depth of 49.33 m



Source: SDPI (2015).

Figure 4.21: Chókwè district lithology view and respective groundwater quality in different layers

TABLE 4.7: GROUNDWATER QUALITY CLASSIFICATION FROM CHÓKWÈ DISTRICT LITHOLOGICAL DATA IN DIFFERENT LAYERS BASED ON THE CONTENT OF TOTAL DISSOLVED SOLIDS

Occurrence area	**Layer name**	**EC** (µS/cm)	**TDS** (mg/L)	**Classification**
Upstream	Gravel	1615.0	1 050.0	Poor
Upstream and Downstream	Medium sand	985.5	640.6	Fair
Upstream and Downstream	Silt	1 132.5	736.1	Fair
Upstream	Stony	1 540.0	1 001.0	Poor
Upstream	Brown fine sand	600.0	390.0	Good
Upstream	Thick sand	1 438.3	934.9	Poor
Upstream	Very hard calcareous	1 126.0	731.9	Fair
Upstream	Medium sand with calcareous	1 672.0	1 087.0	Poor
Upstream	White fine sand	1 022.0	664.3	Fair
Downstream	Conglomerate	4 668.1	3 034.0	Unacceptable
Downstream	Sand with silt	1 000.0	650.0	Fair
Downstream	Red medium sand	1 000.0	650.0	Fair

Source: WHO (2003).

4.3.2.4.3 Groundwater salinity and study area hydrogeology

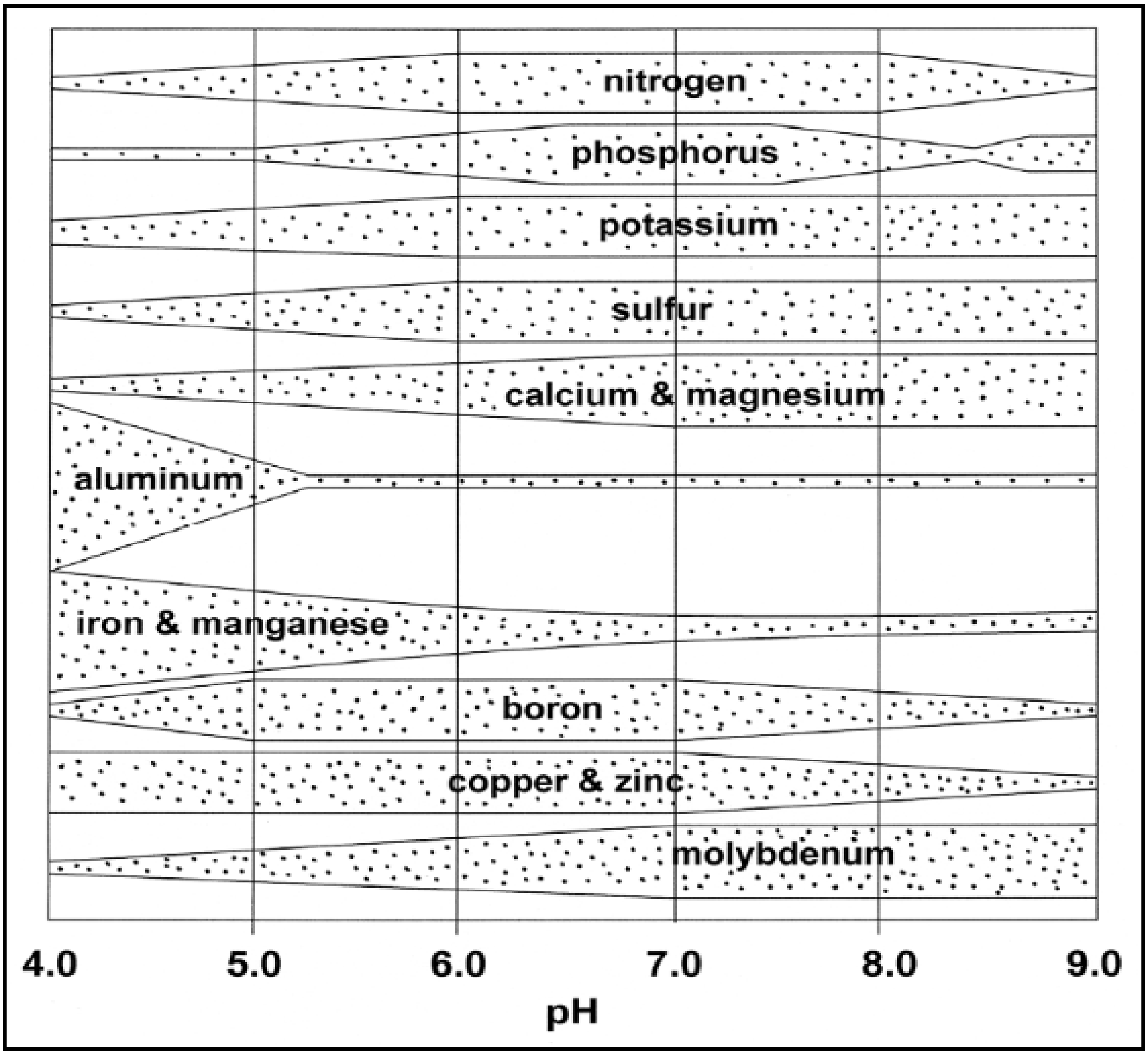
The sedimentary environment of fluvial, alluvial and aeolian deposition is the place of deposition, which includes the interaction of the physical, chemical and biological conditions at the place (Hounslow, 1995). In sedimentary environment, the landform is developed by water flowing from streams or rivers, and through the fluvial processes (sediment transport, sediment entrainment) the deposition and grain distribution of sediments are different.

In Mozambique, the Limpopo basin crosses the plains, including undulating terrain and hill areas upstream. In downstream areas also called lower Limpopo (where the Chókwè district is located) the basin crosses the floodplain areas. The mix of clay and sandy loam, as well as the occurrence of alluvial deposits, makes the soil fertility moderate to good, from upstream to downstream (FEWS NET, 2011).

According to Carvalho *et al*. (2005), alluvial soils are very fertile and it has a high base saturation of more than 50%, comparing to other fluvial deposits. The particle soil surface in soil mineralogy is more filled with the basic cations such as Ca, Mg, and K than hydrogen (H) and aluminium (Al). Wilson (2009) evaluated the effect of irrigation water in soil salinity in the Chókwè district, and found that the pH of soil ranged from 7.9 to 8.9. Mullins and Hansen (2006) studying the soil mineralogy, conclude that there is a strong correlation between mineral availability and pH as a result of chemical reaction in the soil. The Ca, Mg and K elements are most present in soils with pH levels greater than 6.0, as shown in Figure 4.22. From these results it is evident that Ca and Mg ions are more available in the soil profile of the Chókwè district.

Besides the soil mineralogy, another hydrological process that may contribute to the occurrence of high salinity in groundwater can be the floods which are very common in the Chókwè district. According to Hassan (2011), Wang *et al.* (2015), Saeed and Attaullah (2014), the flood has a direct influence on the hydrogeological characteristics of the aquifer. There is considerable increase in the groundwater level, decrease of nitrate (NO_3^-) and chloride (Cl^-) concentration, including the EC in the shallow aquifer close to the river. The same does not happen in intensive farming areas where the concentration increases. Thus, similar results were found in the present study, but the chloride (Cl^-) and EC increased. The equivalent sodium chloride (NaCl) content from major ions in groundwater can be one of the factors for increasing EC and chloride (Cl^-) concentration as shown in Table 4.8 (Moss, 1990).

Nowinski *et al*. (2012) studied the hydraulic interactions between surface water and groundwater in shallow aquifers from flooded areas. Hydraulic conductivity of unconsolidated sediments may contribute to increased ions in groundwater from alluvial aquifers through inflow (recharge) of high mineralised water (Saeed and Attaullah, 2014). As the study area is dominated by unconsolidated material, this is expected to happen.



Source: Mullins and Hansen (2006).

Figure 4.22: Relation between pH and soil mineralogy in the soil profile

TABLE 4.8: THE SODIUM CHLORITE EQUIVALENT FROM MAJOR ION IN GROUNDWATER SAMPLE OF THE CHÓKWÈ DISTRICT

	Ion concentration (mg/L)												E-NaCl (mg/L)
K	0.95		2.0		1.0		1.0		0.5		0.27		
SN	Ca	Ca^a	Mg	Mg^a	Na	Na*	Cl	Cl^a	SO$_4$	SO$_4^a$	HCO$_3$	HCO$_3^a$	
1	3.99	3.79	2.67	5.34	202.00	202.00	94.40	94.40	60.10	30.05	295.00	79.65	**415.23**
2	5.38	5.11	2.20	4.40	152.00	152.00	65.00	65.00	32.50	16.25	228.00	61.56	**304.32**
3	17.60	16.72	7.24	14.48	265.00	265.00	170.52	170.52	115.10	57.55	329.00	88.83	**613.10**
4	65.20	61.94	34.50	69.00	97.80	97.80	150.70	150.70	32.30	16.15	312.00	84.24	**479.83**
5	62.90	59.76	35.40	70.80	229.00	229.00	252.66	252.66	88.90	44.45	343.00	92.61	**749.28**
6	514.0	488.28	480.80	961.59	1756.38	1756.38	3961.43	3961.43	565.84	282.92	329.00	88.83	**7539.42**
7	12.31	11.69	11.50	23.00	279.91	279.91	87.42	87.42	41.52	20.76	474.00	127.98	**550.77**
8	9.78	9.29	8.68	17.36	200.39	200.39	153.30	153.30	37.30	18.65	223.00	60.21	**459.20**
9	2.14	2.03	6.20	12.41	154.88	154.88	245.20	245.20	18.23	9.11	15.20	4.10	**427.73**
10	1.68	1.60	8.71	17.41	160.69	160.69	275.00	275.00	11.55	5.78	6.98	1.88	**462.36**
11	1.61	1.53	2.57	5.13	142.22	142.22	217.20	217.20	19.05	9.52	31.50	8.51	**384.10**
12	5.24	4.98	4.93	9.86	134.17	134.17	198.70	198.70	24.14	12.07	10.30	2.78	**362.56**
13	20.56	19.54	30.25	60.50	629.20	629.20	796.30	796.30	204.36	102.18	63.90	17.25	**1624.96**
14	4.18	3.97	1.79	3.57	62.17	62.17	90.50	90.50	27.53	13.76	15.30	4.13	**178.11**
15	2.50	2.38	0.58	1.16	45.90	45.90	39.48	39.48	34.59	17.29	12.60	3.40	**109.62**
16	28.60	27.17	33.10	66.20	314.00	314.00	423.55	423.55	60.42	30.21	239.00	64.53	**925.66**
17	9.01	8.56	7.41	14.82	108.00	108.00	85.60	85.60	15.39	7.69	177.00	47.79	**272.46**
18	4.98	4.73	4.19	8.38	127.74	127.74	80.20	80.20	18.44	9.22	178.00	48.06	**278.32**
19	4.44	4.22	3.64	7.27	122.58	122.58	80.80	80.80	16.08	8.04	177.00	47.79	**270.70**
20	129.73	123.25	124.84	249.69	1099.01	1099.01	1892.60	1892.60	108.42	54.21	167.00	45.09	**3463.84**
21	57.67	54.79	56.00	111.99	656.67	656.67	832.10	832.10	228.76	114.38	261.00	70.47	**1840.40**
22	258.63	245.70	247.34	494.67	582.74	582.74	1822.70	1822.70	154.98	77.49	235.00	63.45	**3286.75**
23	71.19	67.63	57.00	113.99	314.37	314.37	651.60	651.60	15.07	7.53	120.00	32.40	**1187.53**
24	12.28	11.66	9.55	19.10	134.97	134.97	130.50	130.50	19.47	9.74	183.00	49.41	**355.37**
25	24.12	22.91	25.38	50.76	585.57	585.57	742.90	742.90	87.97	43.98	216.00	58.32	**1504.44**
26	3.96	3.76	4.69	9.38	958.55	958.55	276.14	276.14	564.30	282.15	1031.00	278.37	**1808.35**
27	15.33	14.56	15.33	30.66	222.27	222.27	260.17	260.17	34.06	17.03	212.00	57.24	**601.93**

a = conversion factor for each ion; **K** = conversion factor, **SN** = sample number; **E-NaCl** = equivalent sodium chloride

Source: Moss (1990)

4.3.2.4.4 Groundwater salinity and major ions

The results of a Pearson correlation matrix for both EC and TDS with major ions, revealed that Ca, Mg, Na, Cl and SO_4 have a correlation coefficient close to 1, as shown in Table 4.9 below. This indicates that these ions have a significance influence in groundwater salinity, through hydro-geochemical processes such as dissolution or precipitation. As the coefficient correlation between Ca and SO_4, Na and Cl is close to 1 (0.8775 and 0.9611, respectively), dissolution of gypsum (Equation 4.3) and halite (Equation 4.4) may occur.

$$CaSO_4.\ 2H_2O \longrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \qquad \text{(Equation 4.3)}$$

Gypsum

$$NaCl \xrightarrow{H_2O} Na^{+} + Cl^{-} \qquad \text{(Equation 4.4)}$$

Halite

As the bicarbonate ion (HCO_3^{-}) is not strongly correlated with the calcium (Ca^{2+}) and magnesium (Mg^{2+}), the water will be saturated by dolomite and calcite. In this context, more gypsum is dissolved (unsaturated) in groundwater and the increase of Ca^{2+} concentration will cause precipitation of calcite and dolomite, expressed in Equation 4.5 and Equation 4.6, respectively.

$$Ca^{2+} + HCO_3^{-} + OH^{-} \longrightarrow CaCO_3 \downarrow + H_2O \qquad \text{(Equation 4.5)}$$

Precipitation of calcite

$$Ca^{2+} + Mg^{2+} + 2HCO_3^{-} + 2OH^{-} \longrightarrow CaMg\,(CO_3)_2 \downarrow + 4HCO_3^{-} + H_2O \qquad \text{(Equation 4.6)}$$

Precipitation of dolomite

TABLE 4.9: PEARSON CORRELATION MATRIX BETWEEN MAJOR IONS AND ELECTRICAL CONDUCTIVITY INCLUDING THE TOTAL DISSOLVED SOLIDS IN GROUNDWATER

	EC	TDS	pH	Ca	Mg	Na	K	HCO_3	Cl	SO_4
EC	1									
TDS	0.9989	1								
pH	0.2016	0.2341	1							
Ca	0.9602	0.9577	0.1768	1						
Mg	0.9696	0.9655	0.1679	0.9969	1					
Na	0.9707	0.9744	0.2485	0.8705	0.8845	1				
K	0.2694	0.2416	-0.6724	0.1960	0.2245	0.2594	1			
HCO_3	0.2758	0.3148	0.7972	0.3211	0.2854	0.2775	-0.5405	1		
Cl	0.9962	0.9914	0.1486	0.9576	0.9695	0.9611	0.30273	0.2041	1	
SO_4	0.9204	0.9273	0.2020	0.8775	0.8823	0.9102	0.25236	0.3186	0.8956	1

4.3.3 Analysis of hardness and alkalinity relationship

The concept of hardness is described by the WHO (2011) to understand the behaviour of two dissolved polyvalent cations in water, namely Ca^{2+} and Mg^{2+}. The presence of calcium and magnesium salts in the form of HCO_3^-, Cl^- and SO_4^{2-} in water, makes water hard.

Results of total hardness from the study area, revealed that at least three (11%) groundwater samples exceeded the maximum recommended limit (<500 mg/L) in the Ministry of Health of Mozambique drinking water standards (MISAU, 2004). The percentage of hardness classes in Figure 4.23, shows that 7% and 30% of groundwater samples is classified as hard and very hard, respectively. The categories of hardness distribution were based on four classification classes, listed in Table 4.10.

TABLE 4.10: DISTRIBUTION OF HARDNESS CLASS IN GROUNDWATER AND THE RESPECTIVE CHEMISTRY

Number of sample	Percentage (%)	Hardness class	Total hardness value (mg/L of $CaCO_3$)	Comments
13	48	Soft	<60	Presence of soluble salts, and the water has good taste
4	15	Moderately hard	60 – 120	Slight effect on water taste
2	7	Hard	120 – 180	Presence of insoluble metals and salts and effect on taste
8	30	Very hard	>180	High insoluble salts and effect on water taste

Source: WHO (2011).

Hardness and alkalinity are related through common ions formed in aquatic systems, due to Mg^{2+} and Ca^{2+} associated with the bicarbonate and carbonate fraction of alkalinity (Burton and Pitt, 2002). About 63% of groundwater samples from the Chókwè district have total hardness less than alkalinity. This evidence suggests that Mg^{2+} and Ca^{2+} are associated with SO_4^{2-} and Cl^- and the groundwater presents permanent hardness, as shown in Figure 4.24, Figure 4.25, Figure 4.26, and Figure 4.27 (FAO, 1987).

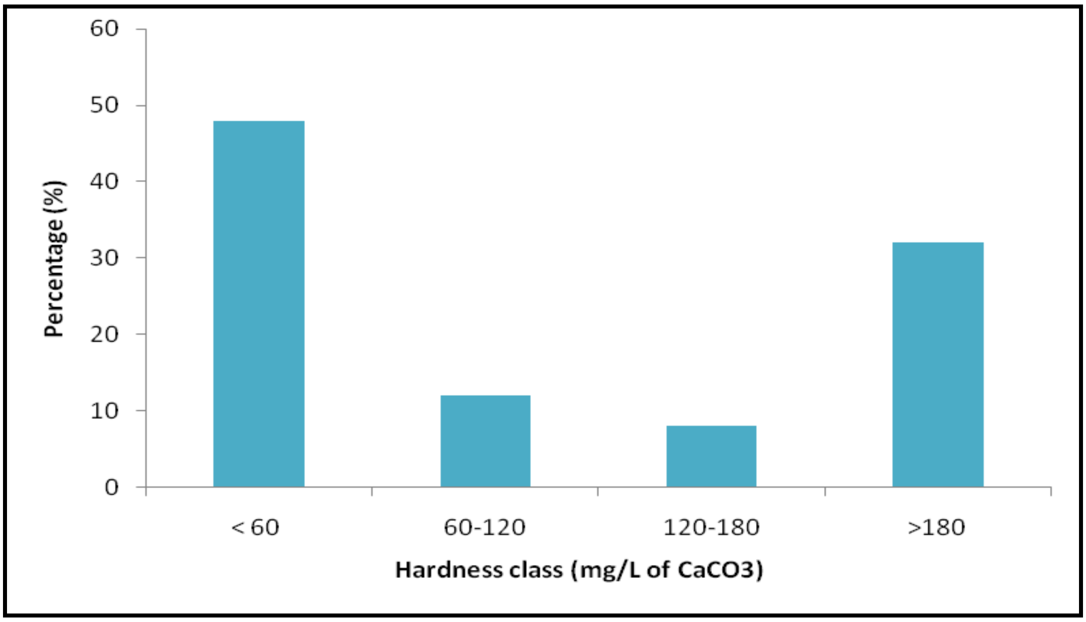


Figure 4.23: Variability of hardness of groundwater in the Chókwè district

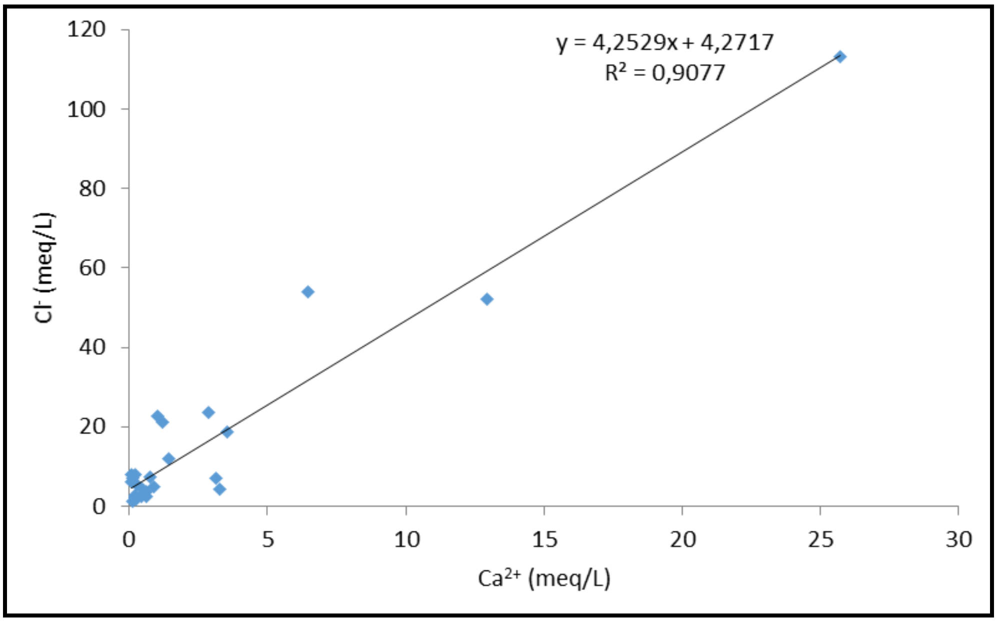


Figure 4.24: Relationship between Ca and Cl in the study area

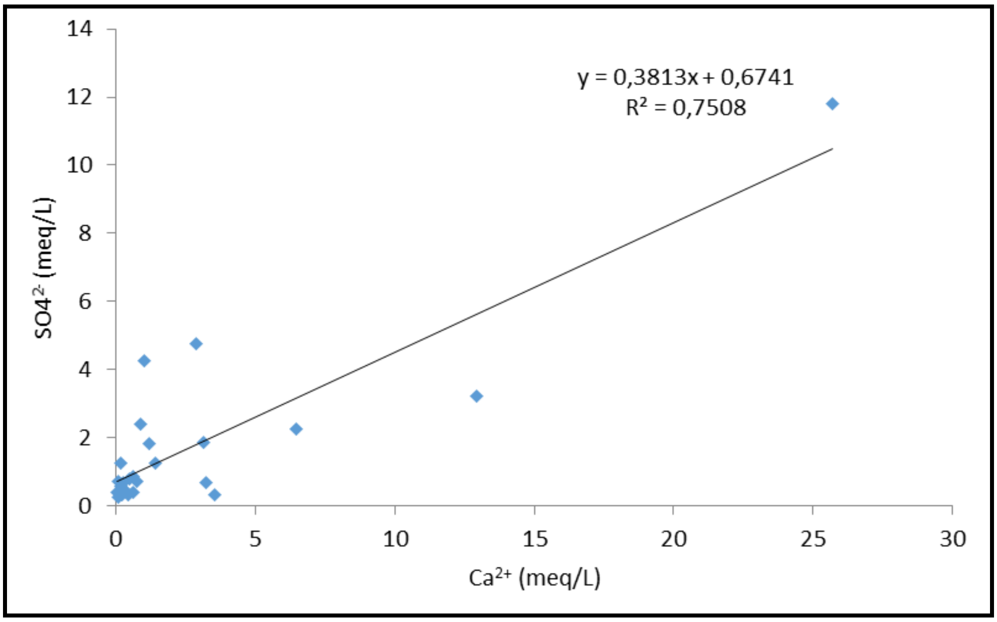


Figure 4.25: Relationship between Ca and SO_4 in the study area

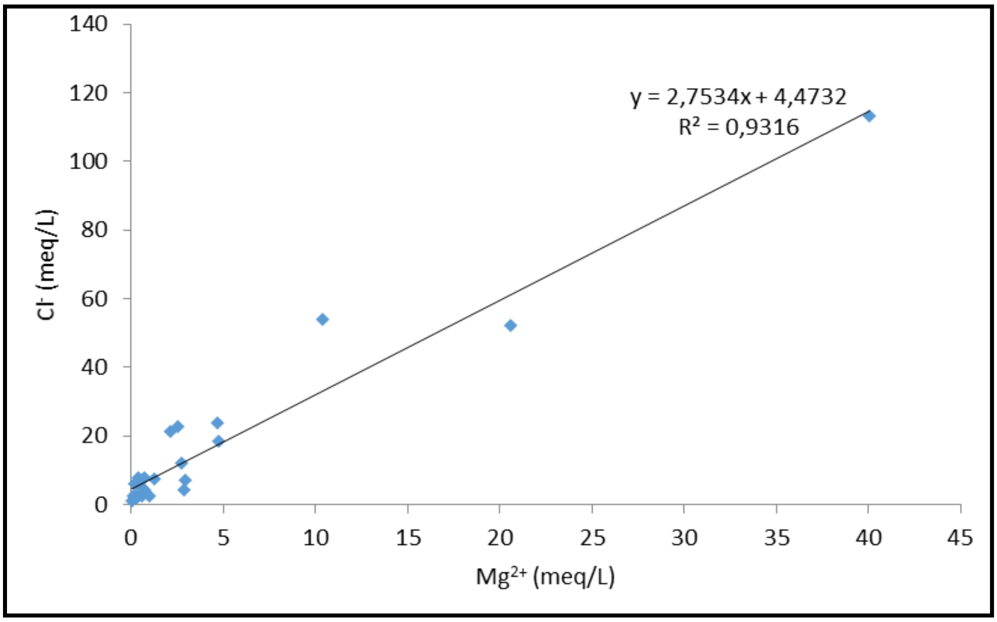


Figure 4.26: Relationship between Mg and Cl in the study area

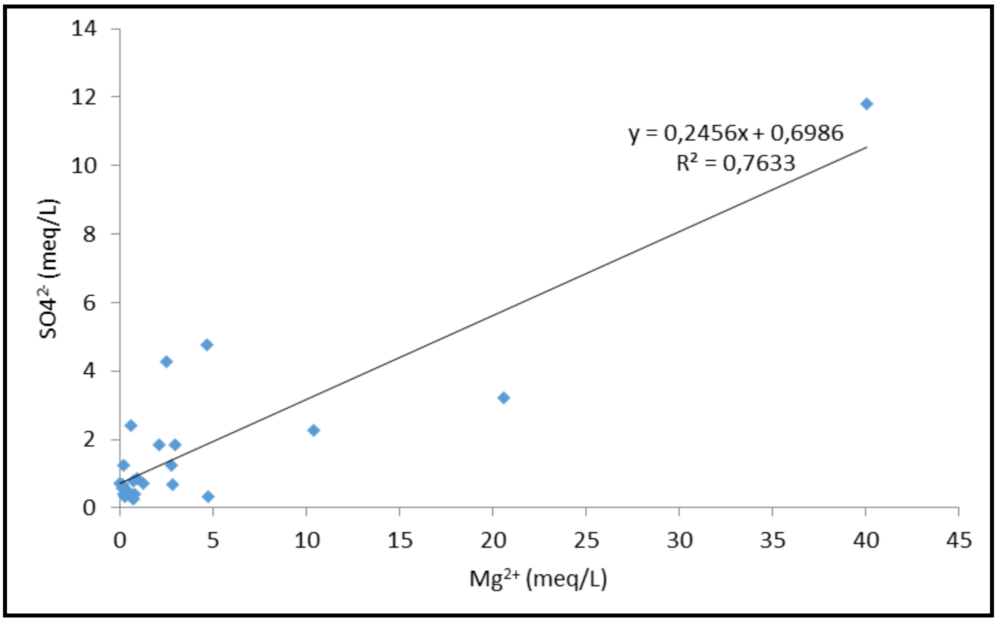
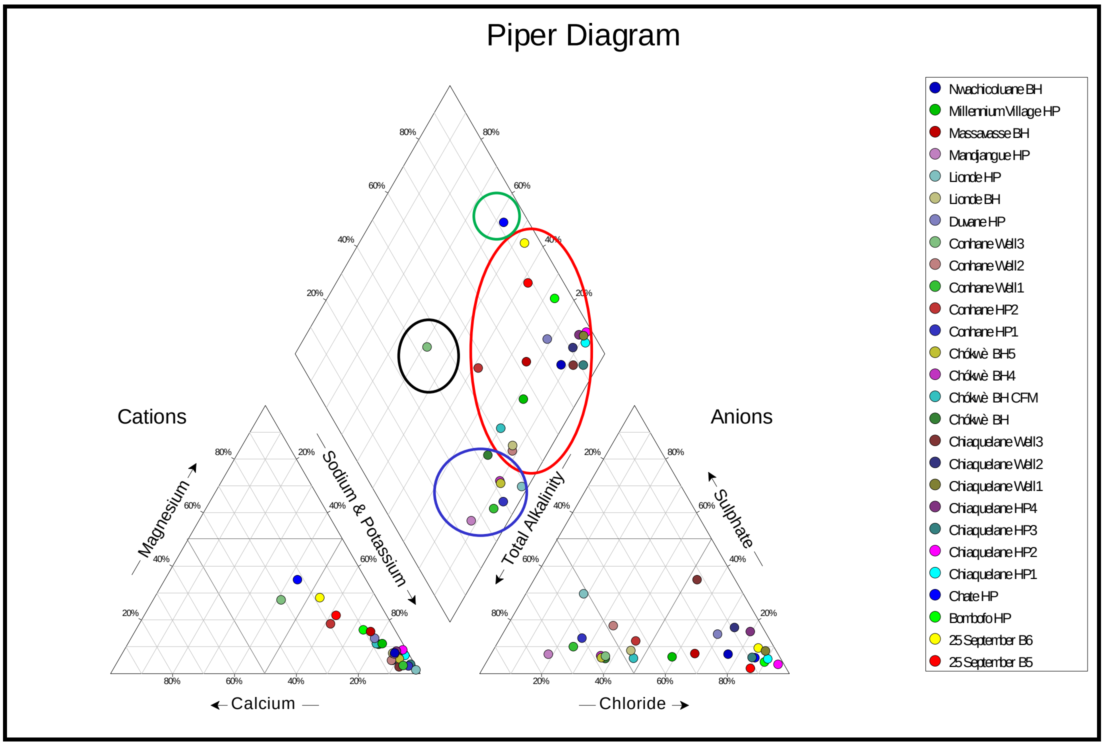


Figure 4.27: Relationship between Mg and SO_4 in the study area

4.4 HYDROCHEMICAL FACIES

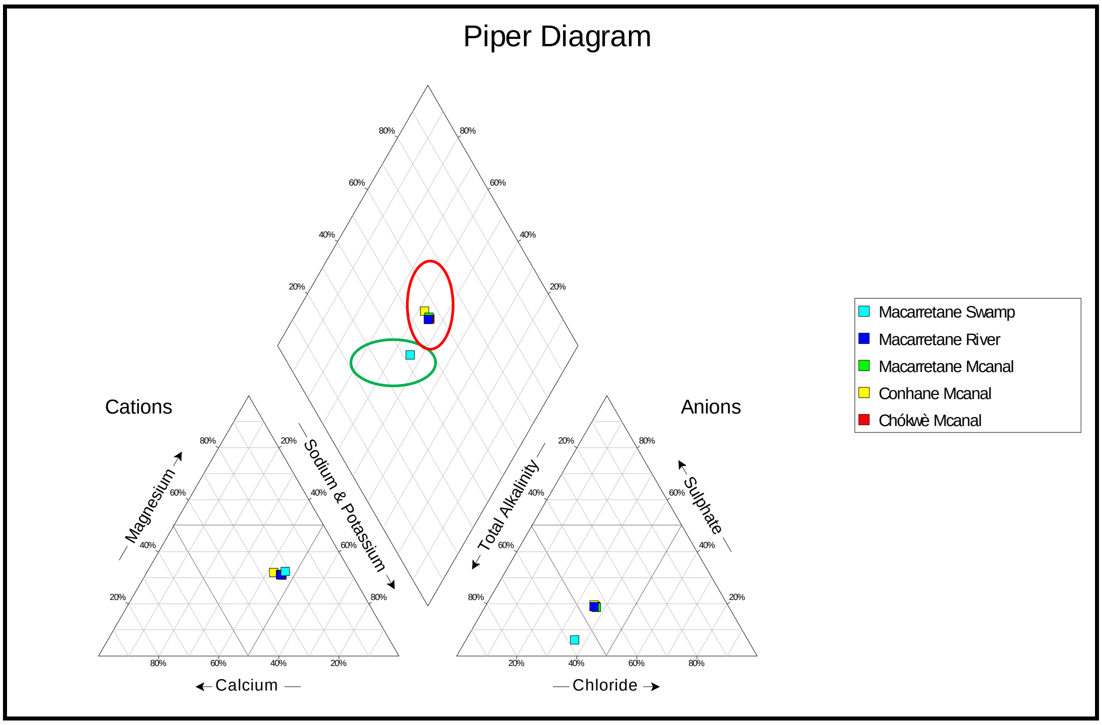
The hydrochemical facies concept has been used to designate the overall chemical character of the water in the hydrogeological system (Back, 1966). According Back and Hanshaw (1965), as cited by Smoor (1967), this concept may provide a model to explain the distribution and origin of the principal chemical types of water. In the present study the hydrochemical facies will be used to define the water type in the Chókwè district.

To identify and classify the hydrochemical facies in the Chókwè district both groundwater and surface water samples were processed and projected on the hydrochemical diagram. From the Piper diagram four types of hydrochemical facies in groundwater and two in surface water were identified, as shown in Figure 4.28 and Figure 4.29, respectively.



Green circle (Ca-SO_4 water); black circle (Ca-HCO_3 water); blue circle (Na-HCO_3 water) and red circle (Na-Cl water)

Figure 4.28: Piper diagram and hydrochemical facies in groundwater samples from the Chókwè district



Red circle (Ca-SO_4 water) and green circle (Ca-HCO_3 water)

Figure 4.29: Piper diagram and hydrochemical facies in surface water samples from the Chókwè district

4.4.1 Type of hydrochemical facies in the Chókwè district

The description and analysis of different types of hydrochemical facies identified in the Chókwè district are presented below.

4.4.1.1 $Na\text{-}HCO_3$ hydrochemical facies

The $Na\text{-}HCO_3$ hydrochemical facies is produced by ion exchange processes and it can result due to an exchange reaction or evolutionary path of groundwater from $Ca\text{-}HCO_3$ type fresh water to Na-Cl mixed sea water (Karmegam *et al*., 2010). Singh *et al.* (2015) state that $Na\text{-}HCO_3$ waters deposit residual sodium carbonate in irrigation use and cause foaming problems.

In the study area, $Na\text{-}HCO_3$ hydrochemical facies constituted about 26% of the groundwater water samples. Their occurrence was observed in two geological units, namely eluvial floodplain clayed sand, and alluvium, sand, silt, gravel geological unity.

4.4.1.2 Na-Cl hydrochemical facies

The Na-Cl hydrochemical facies constitute about 67% of groundwater samples and is dominant in the Chókwè district. Many groundwater samples from most of the major geological units of the study area have an Na-Cl water type. This type of hydrochemical facies is characterised by a water type with permanent hardness and also is a typical of marine and deep ancient groundwater. The occurrence of Na-Cl hydrochemical facies could be attributed to the anthropogenic activities such as application of chemical fertilizers, sewage effluents and also due to the high rate of evapotranspiration (Nur *et al*., 2012).

Inferences from ion ratios between Na^+ and Cl^- in the Chókwè district were determined to understand the chemical changes in the aquifer during the groundwater movement course. The Na^+/Cl^- ratio ranged from 0.49 to 5.28 and groundwater samples having values greater than one, represent 74%. This evidence suggests that the study area is highly enriched with Na and it could be due to human or natural sources of contamination, compared to seawater intrusion with $Na^+/Cl^- < 0.86$ (Moujabber *et al*., 2006; Vengosh, 2014).

4.4.1.3 Ca-HCO_3 hydrochemical facies

The Ca-HCO_3 is typical of shallow, fresh groundwater. This is a type of recharge water and present temporary hardness. Few surface water samples and groundwater samples in the study area have 4% and 20%, respectively. Therefore, it is shown that in groundwater, the Ca-HCO_3 water type occurs in the alluvium, sand, silt, gravel geological unit.

4.4.1.4 Ca-SO_4 hydrochemical facies

Ca-SO_4 hydrochemical facies is a typical of gypsum groundwater and acid mine drainage. In surface water 80% of samples from the river and main canal of the CIS are dominated by a Ca-SO_4 water type, while in groundwater it is only 4%.

The interaction between Ca–Mg–HCO_3 and Na–SO_4–Cl can result in the evolution of the Ca-Mg-SO_4^- Cl water type (Nur *et al*., 2012).

4.4.2 Spatial variability of hydrochemical facies

The spatial distribution of hydrochemical facies is presented in Figure 4.30. In the downstream area, the Na-Cl hydrochemical facies is more dominant in the study area than Ca-HCO_3, Na-HCO_3 and Ca-SO_4 hydrochemical facies. The movement of water from upstream to downstream along different subsurface formations in quaternary alluvium deposits can contribute to the dominant Na-Cl hydrochemical facies. According to Şen (2015), the chemical evolution of groundwater is observed during its travel path from upstream to downstream through the following chain modification:

$$HCO_3^- \Rightarrow HCO_3^- + SO_4^{2-} \Rightarrow + SO_4^{2-} + HCO_3^- \Rightarrow + SO_4^{2-} + Cl^- \Rightarrow Cl^- + SO_4^{2-} \Rightarrow Cl^- + Ca^{2+} \Rightarrow Ca^{2+} + Mg^{2+} + \Rightarrow Ca^{2+} + Na^+ \Rightarrow + Na^+ Ca^{2+} \Rightarrow + Na^+$$

Studies carried out by Vengosh (2014) demonstrated that agricultural practices have caused significant changes in groundwater geochemistry due to mobilisation of natural contaminants and intensification of water–rock interactions that further enhance water mineralisation. Thus, from this evidence, the agriculture activities can also be the main source affecting the chemical composition and groundwater quality in the Chókwè district. As the study area is characterised by an arid/semiarid climate, the natural salinity of soils is high and thus flushing with irrigation water enhances salt dissolution in the soil, as well as the rise of the water table due to infiltrated water.

The occurrence of marine deposits in the Chókwè district can also be one of the reasons for spatial variability in hydrochemical facies. Amer *et al*. (2012) reported that leaching from weathered material and dissolution of marine sediments during recharge of the shallow aquifer is related to an increased amount of ions and salinity.

Evapotranspiration processes mentioned by Nur *et al*. (2012) also can contribute to the spatial variability of hydrochemical facies. In groundwater discharge areas it is an efficient process for changing the water chemistry. Based on the evapotranspiration reference value of 1 580 mm/year reported by FAEF (2001) for the Chókwè district, a high loss of water is expected in groundwater discharging. Thus, the amount of salt is further increased, as evaporation and transpiration exceed recharge (Vengosh, 2014). Ca-HCO_3 water can be converted into either a Na-HCO_3 water or Ca-SO_4, depending on the nature of the excess bicarbonate (Eriksson, 1985). Therefore, probably this change may occur because the three hydrochemical facies (Ca-HCO_3, Na-HCO_3 and Ca-SO_4) were observed in the study area aquifer.

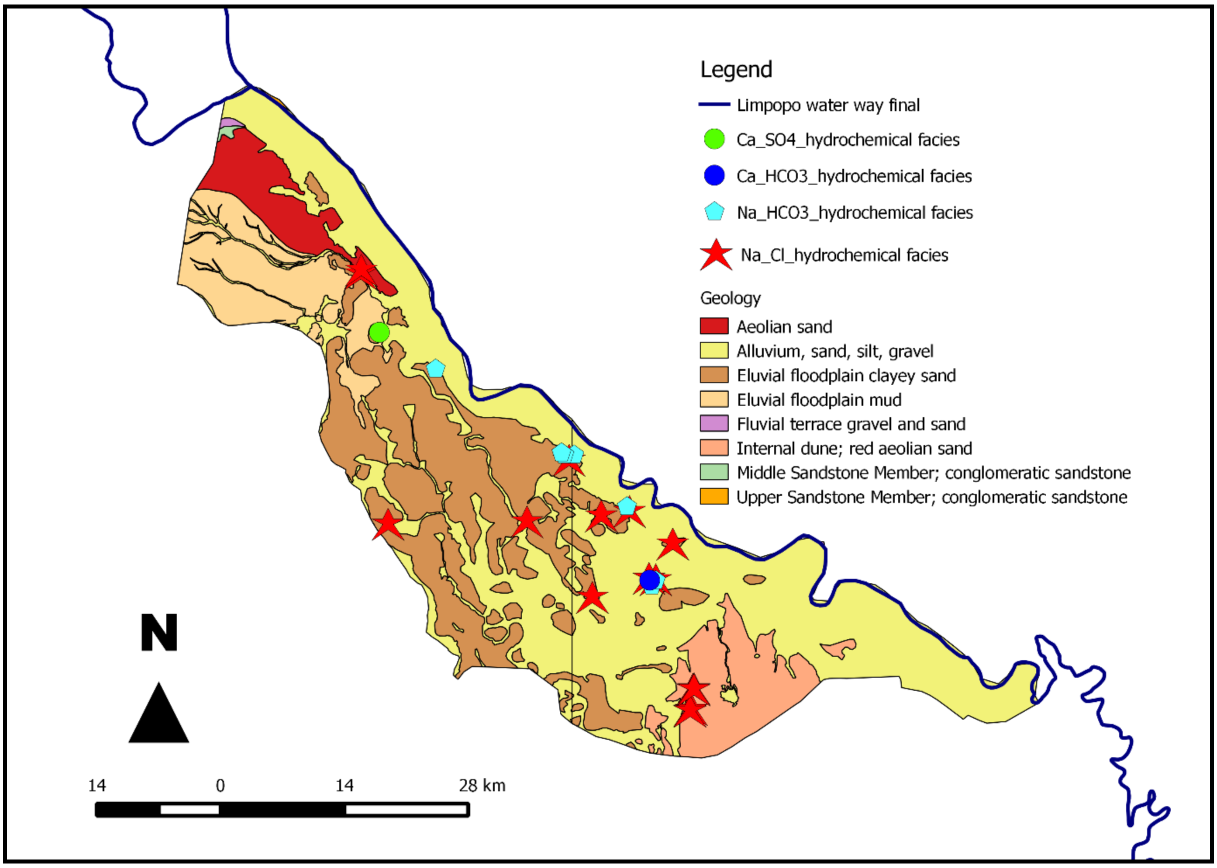


Figure 4.30: ***Spatial variability of hydrochemical facies in the Chókwè district***

4.5 IDENTIFICATION OF HYDROGEOCHEMICAL PROCESSES

Analysis of interaction and reactions between groundwater and aquifer minerals through chemical data, have a significant importance to provide better understanding of water quality. Different approaches such as graphical plots and ratios between the geochemical data are used to identify the hydrochemical processes in the aquifer. For the present study, the hydrogeochemical processes identified are explained below.

4.5.1 Weathering process

Interaction of rocks with the atmosphere and hydrosphere causes a mineral weathering process, which influences and contributes to change the groundwater quality. The type of reactions and their intensity depends to a great extent on climate (Hounslow, 1995; Gibrilla *et al*., 2010). Chemical weathering of minerals is also a dissolution or alteration of minerals present in the bedrock (Drever, 1997).

The silicate and carbonate minerals are the major source of groundwater mineralisation in the Chókwè district. Hounslow (1995) states that the carbonate weathering process occurs when the HCO_3^-/SiO_2 ratio is greater than 10 and TDS more than 500 mg/L. The results from the present study, revealed that only in 63% of groundwater samples there is weathering of carbonate minerals (Appendix 8). The weathering of carbonates and silicates, also can be indicated through the scattered plots of Ca+Mg versus HCO_3+SO_4, when the ionic concentration falling above and below the equiline, respectively (Nur *et al.*, 2012). In Figure 4.31 scattered plots of Ca+Mg versus HCO_3+SO_4 show that in the study area 15% and 85% of groundwater samples lie above and below the equiline 1:1. Therefore, these results reveal the occurrence of carbonate and silicate weathering.

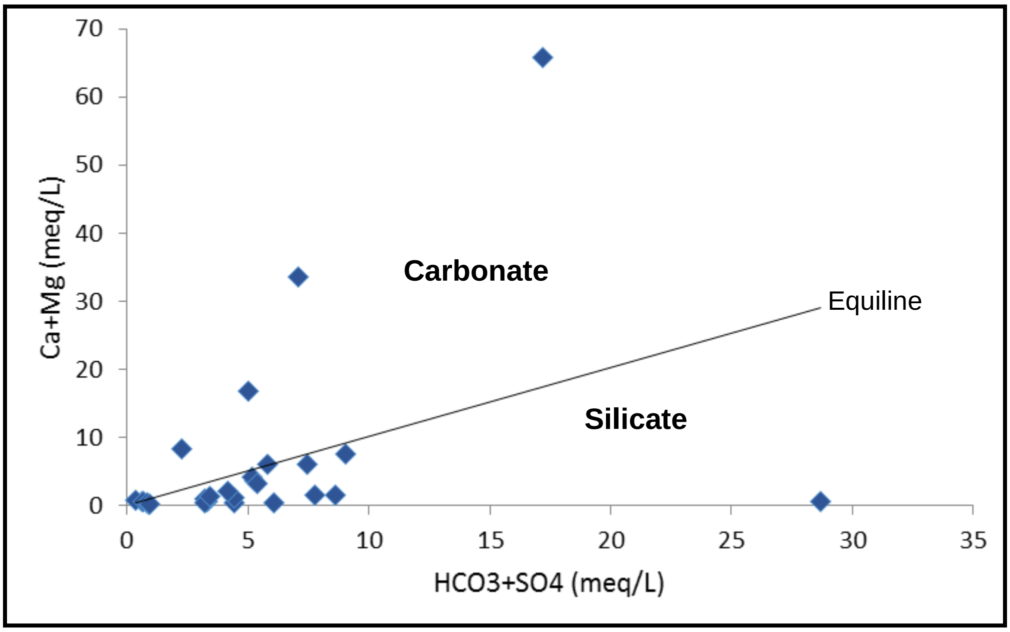


***Figure 4.31:* Diagramatic representation scattered plot of Ca+Mg versus HCO_3+SO_4**

From Figure 4.32, it is clearly shown that plagioclase mineral weathering contributes to the observed dominance of Na and Ca cations in identified hydrochemical facies. The scattered plots of Na+K−Cl versus Na+K−Cl+Ca is >0.2 and <0.8 (Hounslow, 1995). Figure 4.33 shows the relationship between sodium and calcium. The value of R^2 = 0.79 between Na and Ca, indicating that both cations originated from the same source. Sodic plagioclase (Albite) and calcic plagioclase (Anorthite) are probable minerals to weathering and the increase in the concentration of Na and Ca in the study area (Equation 4.7 and Equation 4.8, respectively). The effect of silicate weathering on the water chemistry is primarily the addition of cations and silica. Therefore, the transformation to different weathering products is evident to form clay minerals like Montmorillonite, Kaolinite and Gibbsite (Equation 4.9, Equation 4.10 and Equation 4.11, respectively) (Appelo and Postma, 2005).

$$2Na(AlSi_3)O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4$$ (Equation 4.7)

Sodic plagioclase (Albite) Kaolinite

$$Ca(Al_2Si_2)O_8 + 2H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+}$$ (Equation 4.8)

Calcic plagioclase (Anorthite)

$$3Na(AlSi_3)O_8 + Mg^{2+} + 4H_2O \rightarrow 2Na_{0.5}(Al_{1.5}Mg_{0.5})Si_4O_{10}(OH)_2 + 2Na^+ + H_4SiO_4$$ (Equation 4.9)

Albite Montmorillonite

$$2Na(AlSi_3)O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4$$ (Equation 4.10)

Albite Kaolinite

$$Na(AlSi_3)O_8 + H^+ + 7H_2O \rightarrow Al(OH)_3 + Na^+ + 3H_4SiO_4$$ (Equation 4.11)

Albite Gibbsite

The sequence of weathering products (Montmorillonite – Kaolinite – Gibbsite) reflects the increasing intensity of leaching, removing silica and cations from the rock. The Montmorillonite mineral is preferentially formed in a relatively dry climate, where the rate of flushing of the soil is low. With a longer residence time of water in the soil, the solute concentration becomes higher (Appelo and Postma, 2005). However, greater use of 89% of water in agriculture between the riparian states within the Limpopo basin is observed in Mozambique (Alemaw *et al*., 2008). Thus, most of the groundwater samples from the study area are within the CIS, the largest irrigated area in Mozambique. The poor drainage system of the CIS, waste water through over-irrigation and the poor state of the hydraulic infrastructural network reported by Hakala and Pekonen (2008), will increase the residence time of irrigation water and consequently high concentration of clay minerals as shown in Figure 4.34.

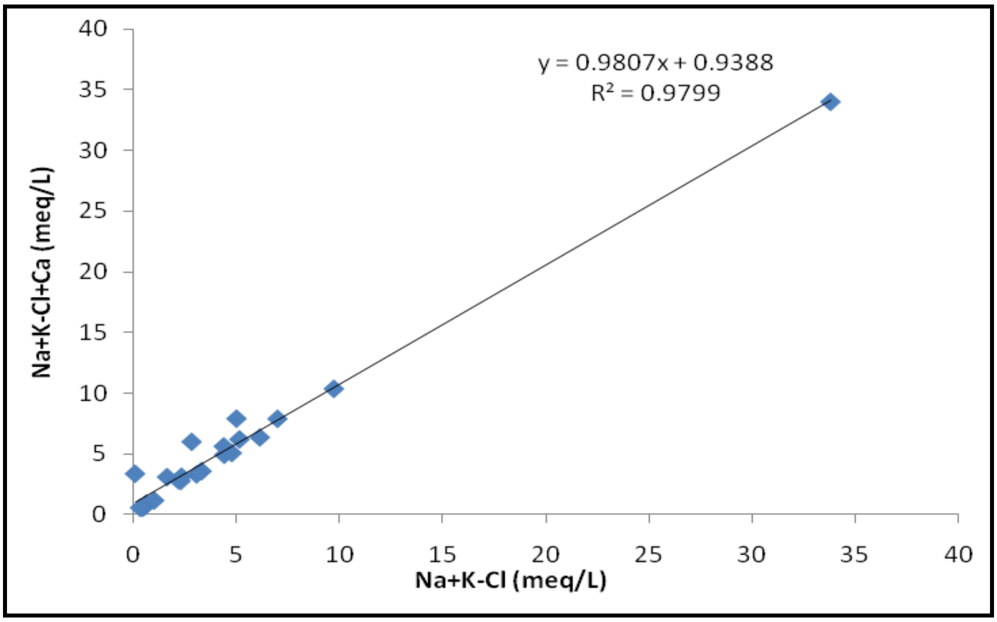


Figure 4.32: Diagrammatic representation ratio for Na+K−Cl versus Na+K−Cl+Ca

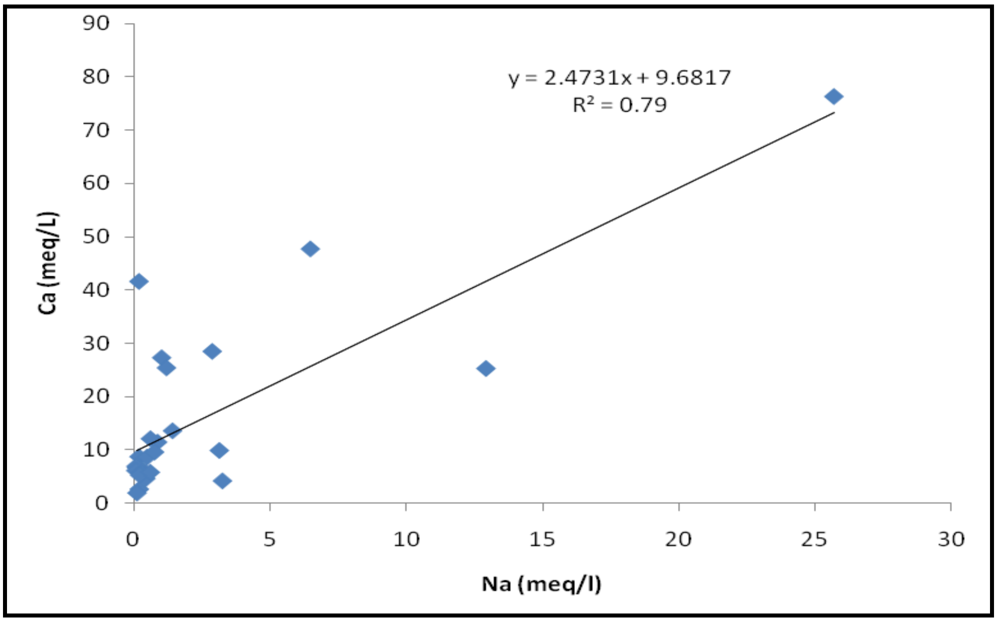


Figure 4.33: Diagrammatic representation of the relationship between Na and Ca

Source: Hakala and Pekonen (2008).

Figure 4.34: Effect of water residence time from the Chókwè Irrigation Scheme in hydrogeochemical processes

4.5.2 Ion exchange process

Changes of chemical composition during residence time and fluid flow in the aquifer can be understood through CAI 1 and 2, presented in Equation 4.12 and Equation 4.13, respectively. Both concentration of cations and anions are in meq/L.

$$CAI_1 = \frac{\left[Cl - \left(Na + K\right)\right]}{Cl} \qquad \text{(Equation 4.12)}$$

$$CAI_1 = \frac{\left[Cl - \left(Na + K\right)\right]}{\left(SO_4 + HCO_3 + CO_3 + NO_3\right)} \qquad \text{(Equation 4.13)}$$

An ion exchange occurs between calcium or magnesium with sodium in groundwater, if both indices are negative, and reverse ion exchange when the indices are positive (Laxman *et al*., 2014; Chebbah and Allia, 2015; Nagaraju *et al*., 2006).

The CAI calculations of the study area are presented in Figure 4.35 and Appendix 8. In the study area the CAI_1 values range from −4.29 to 0.51, while CAI_2 values range from −1.18 to 3.73. The total of 81% groundwater samples shows negative CAI and 19% positive. This result indicates that there is a dominance of ion exchange than the reverse process. Therefore, exchange of Ca and Mg from groundwater with Na and K of the rocks, controls the groundwater quality in the Chókwè district. When the cation exchange is the significant geochemical process controlling the groundwater quality, the relation between Na-Cl versus $Ca+Mg-SO_4-HCO_3$ should be linear, with a slope of −1, and Ca+Mg is less than HCO_3+SO_4 (Fisher and Mullican, 1997). Figure 4.36 and Figure 4.37 show that in most of the groundwater samples from the study area, cation exchange (96%) have occurred, and there is an excess of HCO_3+SO_4 compared to Ca+Mg (77%).

Nur *et al*. (2012) identified that the relation between Na versus Ca, Na versus Mg can also illustrate the evidence of cation exchange when the concentration is plotted below the equiline 1:1. Results of the scattered plot between Na versus Ca, Na versus Mg (Figure 4.38 and Figure 4.39), in the study area indicate that 85% and 88% of the groundwater samples are plotted below equiline 1:1, respectively.

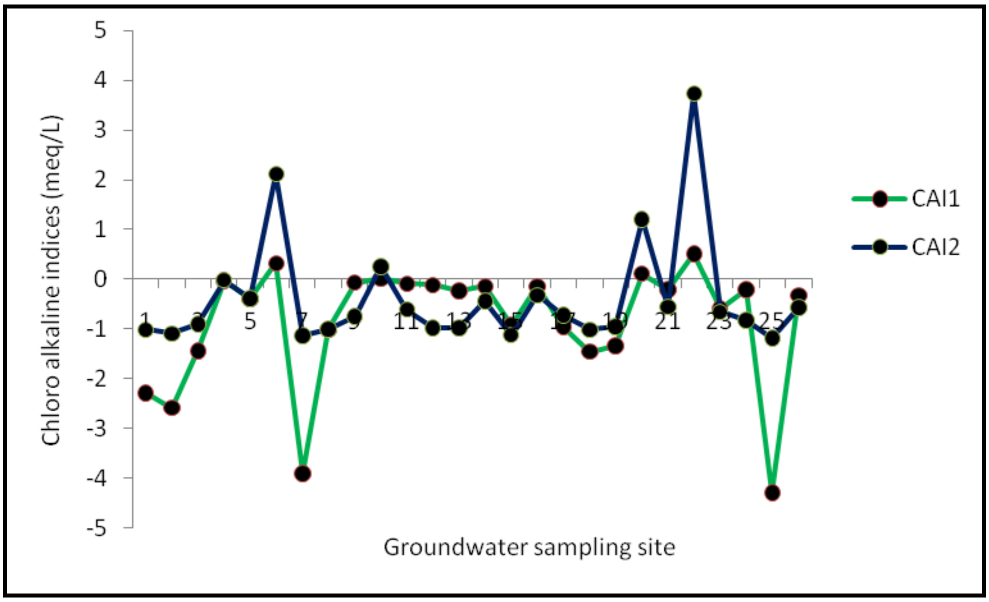


Figure 4.35: Chloro-alkaline indices 1 and 2 for groundwater samples in the study area

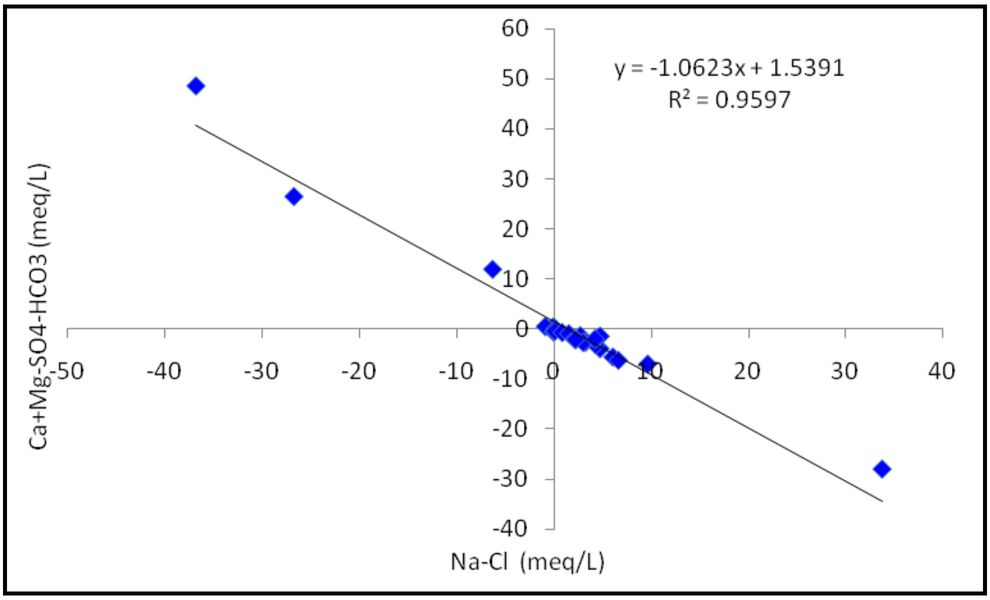


Figure 4.36: Relation between Na−Cl and Ca+Mg−SO_4−HCO_3 for groundwater in the study area

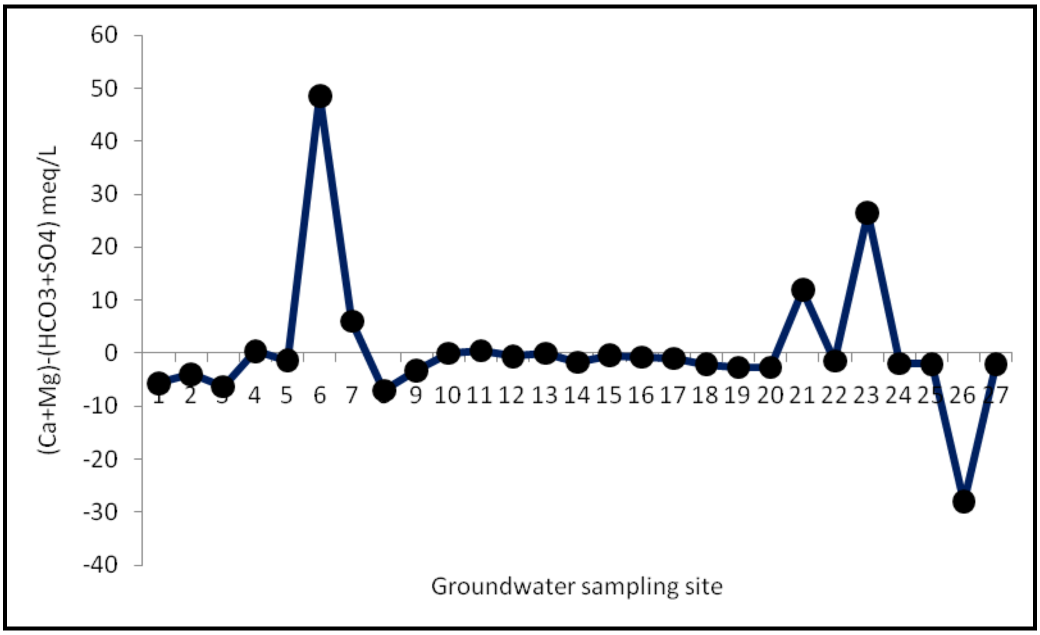


Figure 4.37: Graphical representation of difference between Ca+Mg and HCO_3+SO_4 for groundwater in the study area

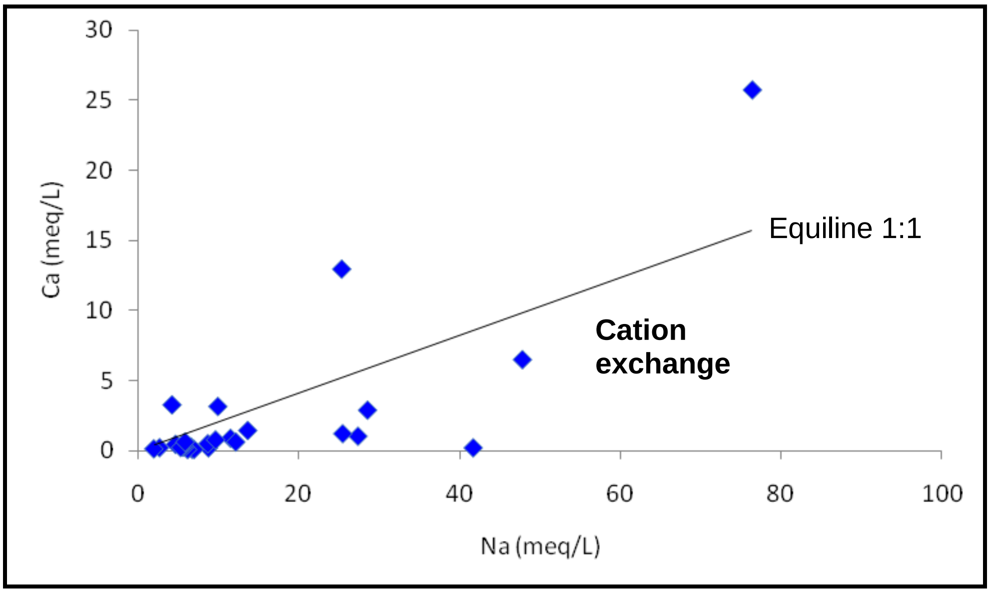


Figure 4.38: Scattered plot between Na versus Ca for groundwater in the study area

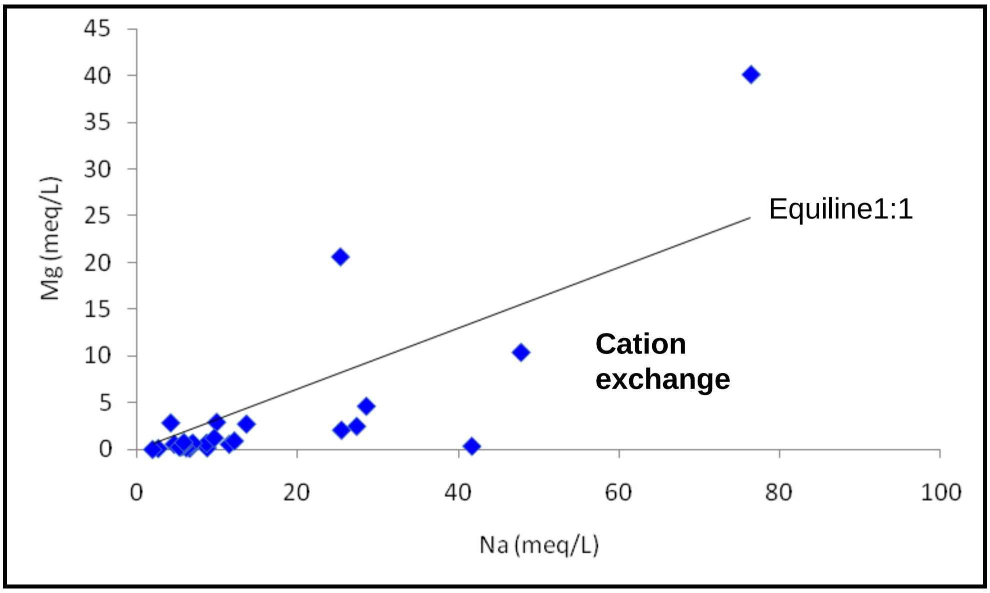


Figure 4.39: Scattered plot between Na versus Mg for groundwater in the study area

4.5.3 Dissolution and precipitation processes

The most important chemical reactions involving groundwater are those of dissolution and precipitation. Dissolved components in groundwater are derived from dissolution of rock-forming minerals in the aquifer. Due to the long-time residence of dissolved components, formation of solid phase (precipitation) in water may occur (Alley, 1993).

The presence of major ions such as Na^+, Ca^{2+}, Mg^{2+}, $Cl^–$, $SO_4^{2–}$ and $HCO_3^–$ in groundwater can contribute to the occurrence of dissolution and precipitation. The results from the correlation matrix show that Ca and Mg are strongly correlated with $R^2=0.99$, close to one (Figure 4.40). A significant correlation is an evidence that both cations originated from the same source, such as carbonate mineral (dolomite or calcite). The Mg/(Mg+Ca) ratio of greater than 0.5 (Figure 4.41), was found in 78% of groundwater samples, as a result of dolomite dissolution and calcite precipitation (Hounslow, 1995). According to Mayo and Loucks (1995), environment aquifers dominated by dolomite dissolutions have a ratio of Ca/Mg=1, whereas higher ratios are indicative of greater calcite contributions. The ratio Ca/Mg>2 indicates a dissolution of silicate minerals, which contribute to Ca and Mg in the aquifer. The study area reveals that 70% of the groundwater samples show a ratio of Ca/Mg close to one, and 15% with a ratio of Ca/Mg greater than two (Figure 4.42). Calcium as well as magnesium in groundwater can be derived from dolomite, calcite and silicate minerals.

The plot of sodium and chloride in Figure 4.43 also shows perfect correlation in the study area. A strong linear correlation between sodium and chloride ($R^2=0.80$) suggests that both evaporite dissolution and effects of evaporation are the most sources of salinity in semi-arid and arid basins (Richter and Kreitler, 1993; Edmunds *et al*., 2003, cited in Monjerezi *et al*., 2012). An Na/Cl approximately equal to 1 is attributed to halite dissolution, whereas a ratio greater than 1 is Na released from silicate weathering. In Figure 4.44, 56% of groundwater samples show an Na/Cl ratio equal to unit as expected for halite dissolution (Monjerezi *et al*., 2012). The dissolution of halite in groundwater released into the aquifer has the same concentration for both sodium and chloride. High values of sodium and chloride observed confirm the significant predominance of saline water (Na−Cl) in the study area.

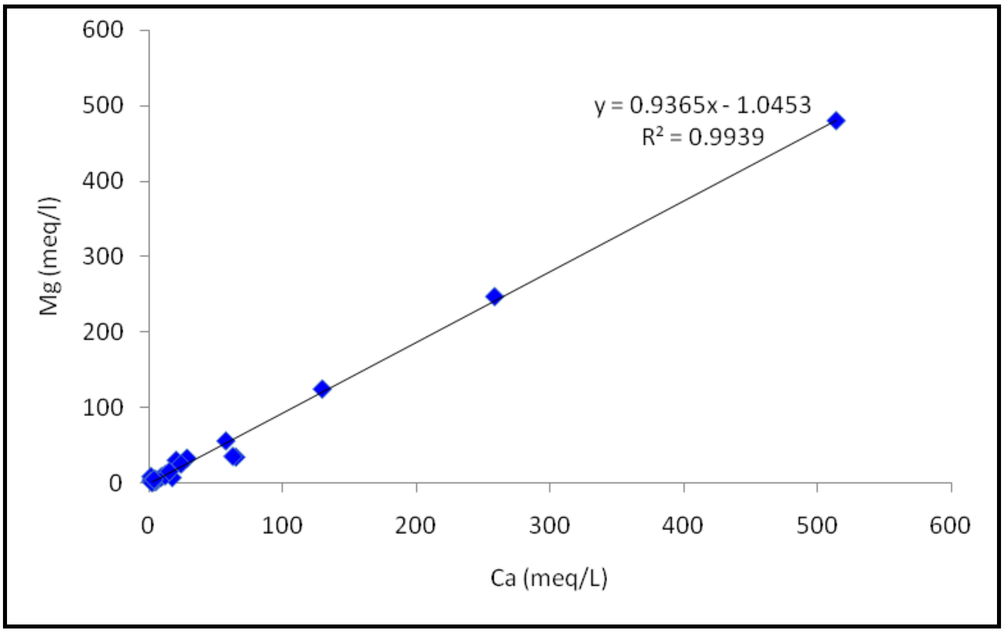


Figure 4.40: Scattered plot between Ca versus Mg for groundwater in the study area

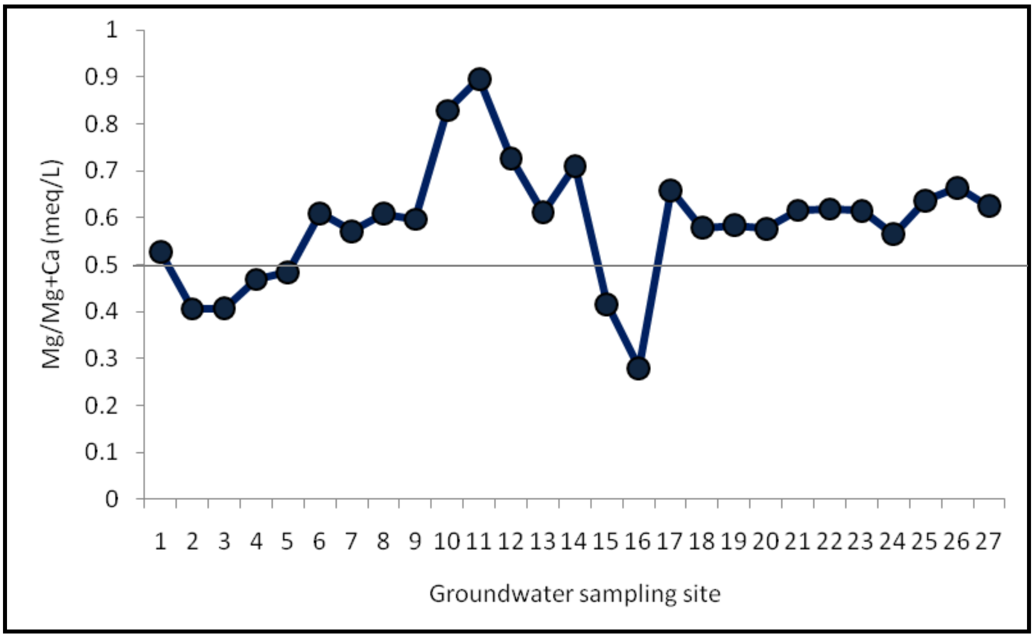


Figure 4.41: Graphical representation of Mg/Mg+Ca ratio for groundwater in the study area

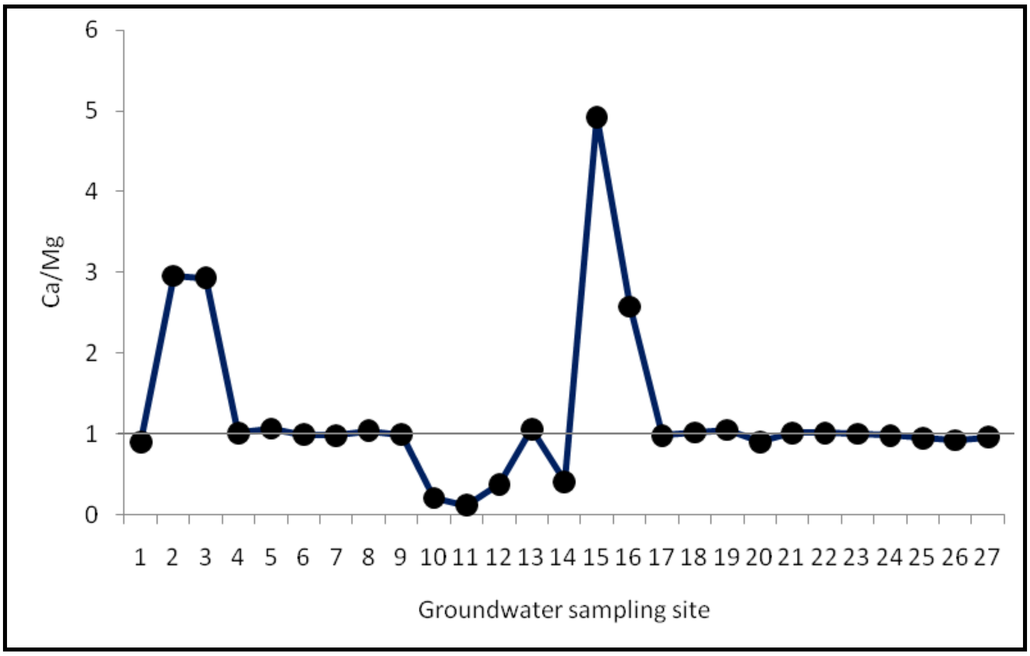


Figure 4.42: Graphical representation of Ca/Mg ratio for groundwater in the study area

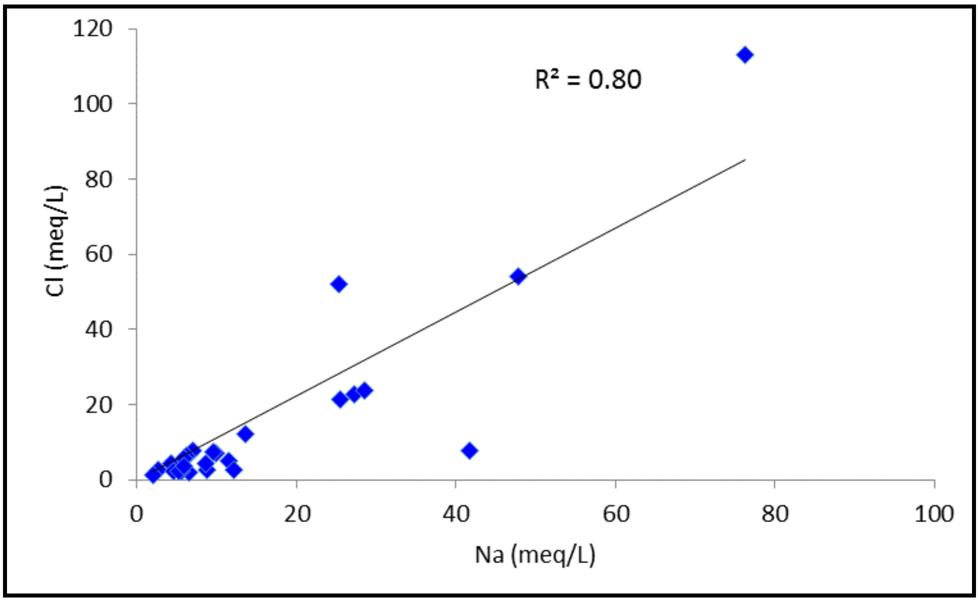


Figure 4.43: Scattered plot between Na versus Cl for groundwater in the study area

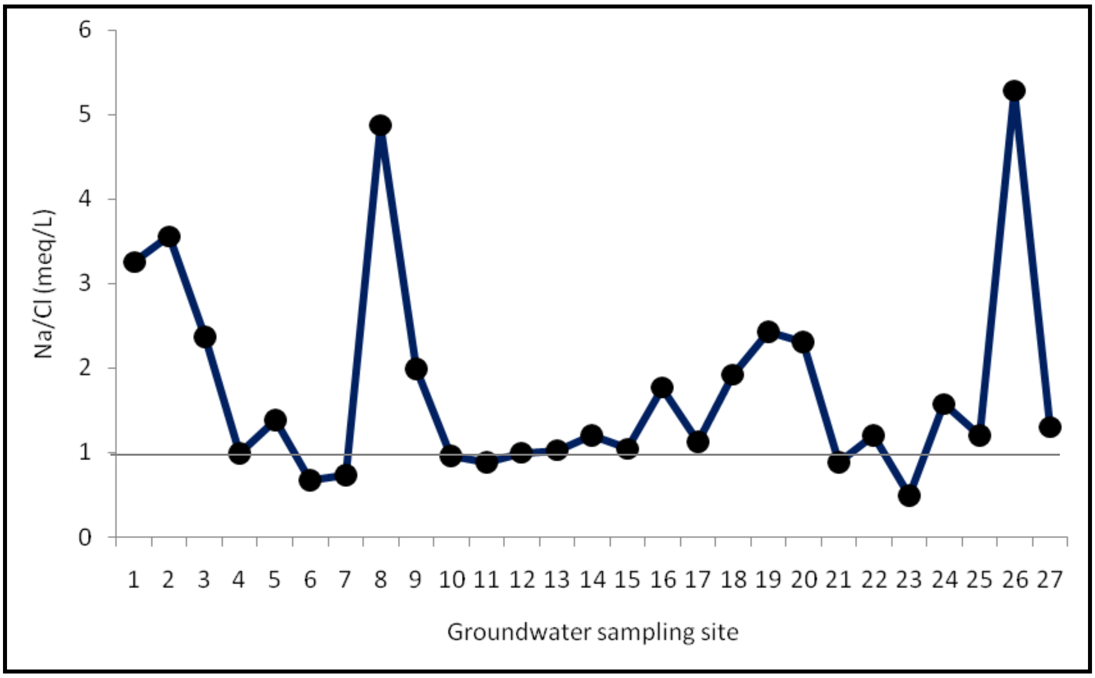


Figure 4.44: Graphical representation of Na/Cl ratio for groundwater in the study area

4.5.4 Spatial variability of hydrogeochemical processes

The spatial characterisation and distribution of identified hydrogeochemical processes in groundwater are displayed in Figure 4.45. All hydrogeochemical processes identified (weathering, ion exchange, dissolution and precipitation) are dominant in the downstream area of the study area. As the Na-Cl hydrochemical facies is also dominant in the downstream area, the groundwater is highly mineralised. A preview investigation carried out by Bouman (1985) and Konstapel (1981) in the Chókwè district, showed that in the new irrigation scheme (Lionde-Nwachicoluane) there is calcareous soils and saline−sodic soils at surface layers, with excess of water periodically (pseudogley environment – hydromorphic soils). The geology has quaternary deposits influenced by marine flooding, and as a consequence, all layers are very brackish, except the deep aquifer along Macia-Chókwè. From this preview studies, it is evident that the environmental characteristics of the downstream area are related to the observed dominance of hydrogeochemical processes. Thus, in an environment dominated by calcareous sediments, the aquifer is a continuously dynamic geochemical system in water–rock interaction due to kinetics of dissolution and precipitation (Hanshaw and Back, 1979, cited by Salem and Horiny (2014). As the carbonate calcium ($CaCO_3$) solubility is strongly influenced by the presence and availability of carbon dioxide (CO_2), the calcium concentration can contribute to the groundwater mineralisation in the downstream area. Therefore, according to Schoeller (1959), in arid areas the dissolved CO_2 will quickly reach the $CaCO_3$ saturation point. In this context, as the Chókwè district is an arid area, the increase of CO_2 will contribute to $CaCO_3$ dissolution and precipitation, when CO_2 decreases in areas with soil permanently flooded from CIS.

Unlike the downstream area, the upstream area (high surface topography) is only dominated by silicate weathering, dissolution and precipitation hydrogeochemical processes. As the upstream area is the recharge area in the study area, this reveals that the dissolved minerals will migrate toward the downstream area, and consequently increase the mineralisation state of the groundwater, as shown in Figure 4.46.

The distribution of hydrogeochemical processes among the dominated geological units in the study area is different. The dissolution and precipitation processes occur in eluvial floodplain clayey sand geological units, while ion exchange and silicate weathering in alluvium, sand, silt, gravel, as well as in internal dune, red aeolian sand geological units. This distribution of hydrogeochemical processes in the study area could be an evidence that the local geology has a significant influence in groundwater quality.

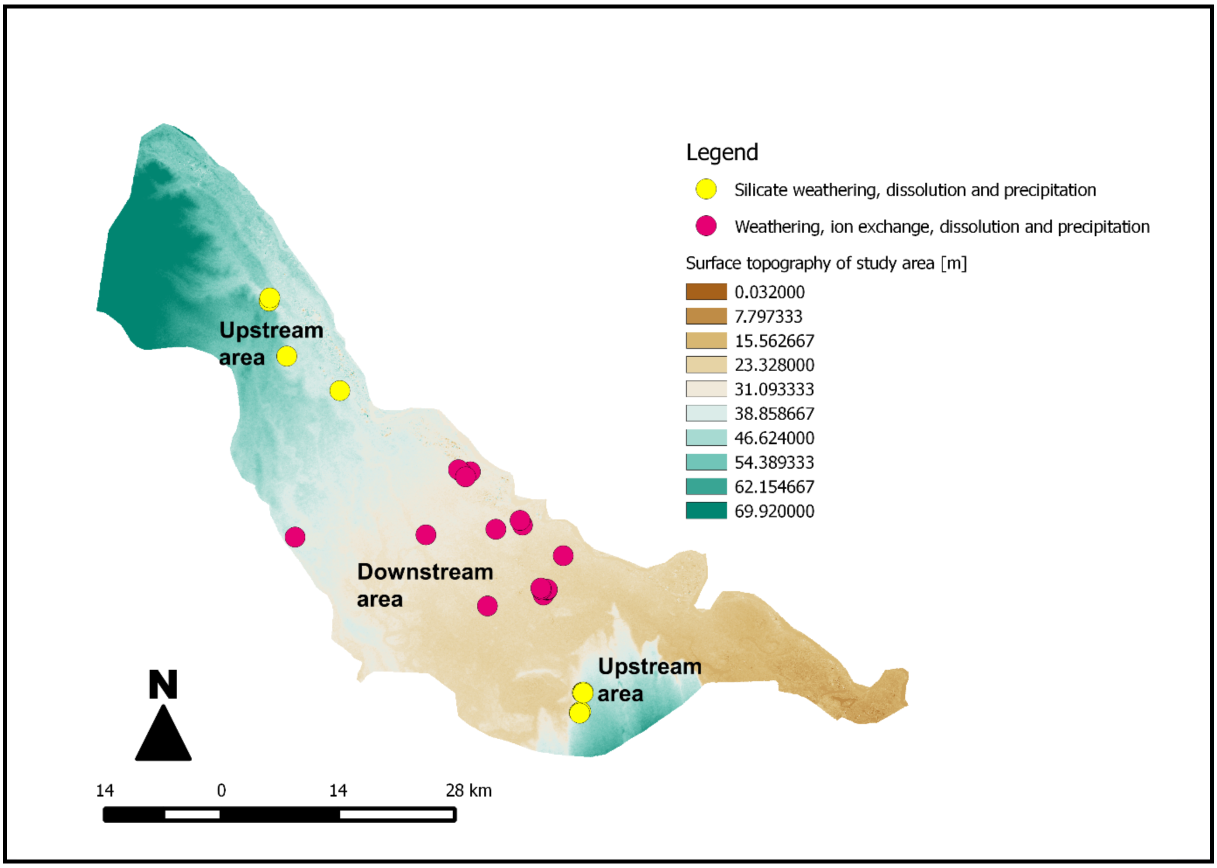


Figure 4.45: Spatial variability o f hydrogeochemical processes in the study area

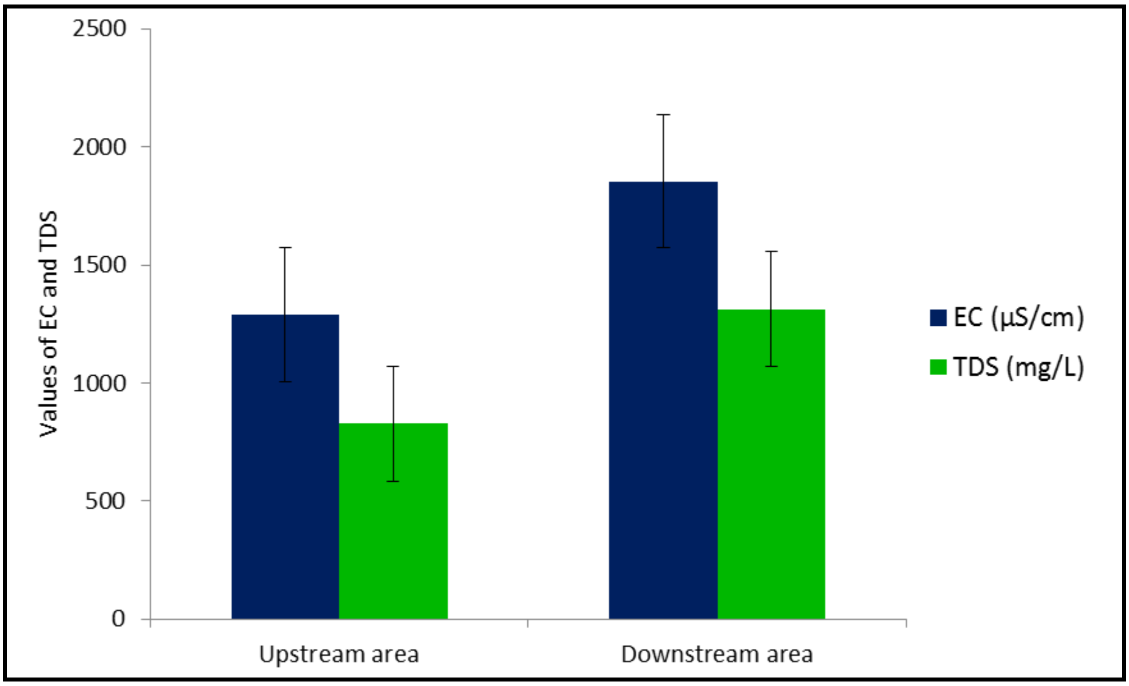


Figure 4.46: Spatial variability of groundwater mineralisation between upstream and downstream in the study area

4.6 SUITABILITY OF WATER SOURCES FOR IRRIGATION

The assessment of water sources for irrigated agriculture gives the degree of the water quality acceptability. The amount of salt, as well as the type of salt, including excessive ions, determine the suitability of water for irrigation. SAR and EC are the two parameters mostly used to determine the suitability of irrigation water. Both SAR and EC have an impact on crop yield, with a significant effect on physical and chemical soil properties (Suarez *et al*., 2006; Yidana *et al.,* 2011).

The results of assessment of the water quality from the Chókwè district are presented in Figure 4.47and Figure 4.48.

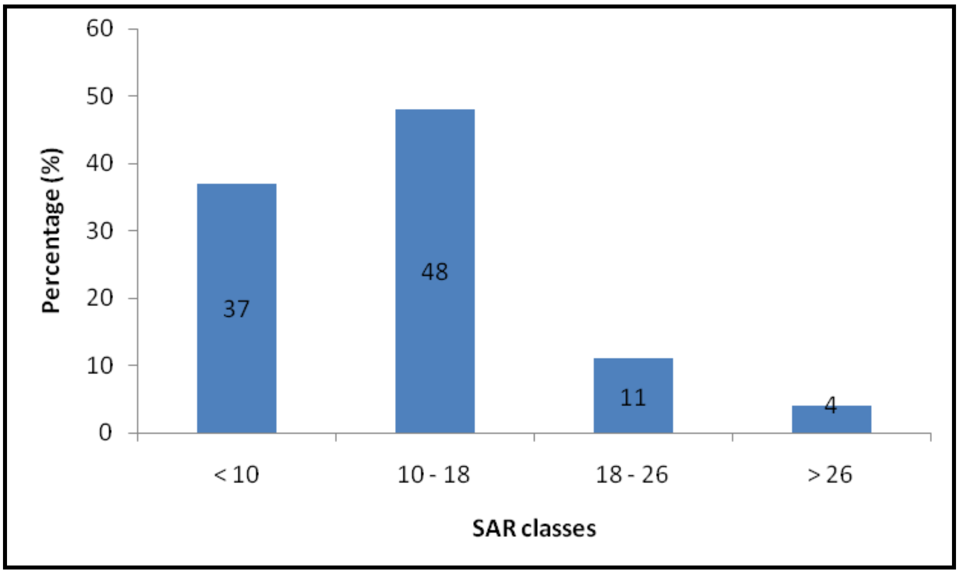


Figure 4.47: Variability of SAR classes in groundwater

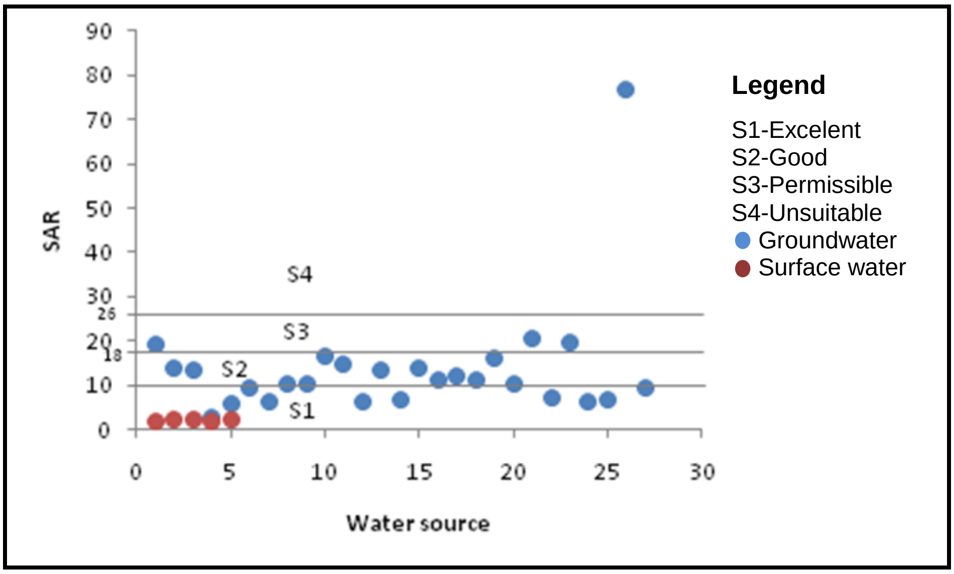


Figure 4.48: Comparision of SAR classes between surface water and groundwater

The SAR values ranged from 2.43 to 76.81 in groundwater and 1.91 to 2.90 in surface water. Four classes of water classification for irrigation were found in the study area. A total of 37% groundwater samples are classified as excellent, 48% good, 11% permissible and 4% unsuitable. Unlike groundwater samples, all surface water sources are classified as excellent and are suitable for irrigation (Balachandar *et al.*, 2010). In general, the results revealed that the water with a SAR from 10 to 26 can be used for irrigation.

In the Chókwè district, the Na percentage of ion is dominant in all geological units and the values ranged from 62% to 85%. This content of Na represents a risk, although many of the groundwater sources have an SAR of <26. According to Joshi *et al*. (2009) and Hakim *et al*. (2009) cited in Naseem *et al*. (2010), irrigation water with an Na percentage higher than 15% may result in deterioration of soil structure, reduce soil permeability and affect the plant growth. In addition, soluble salts contribute to a decrease of soil permeability, as a result of a high Na content in the irrigation water (Phocaides, 2000). Therefore, this evidence suggests that the sodium hazard in the groundwater sources is a significant factor that affects the water quality to be used for irrigation.

Figure 4.49 and Figure 4.50 presents the plot of SAR and EC. In the study area, both a salinity and sodium hazard in groundwater are dominant, with medium and very high categories. About 26% of the samples plot within the medium category, 44% in the high category, 26% in the very high category and 4% plot in the low category region. This result is evidence that if the groundwater is used for irrigation it will have the potential to cause salinity and sodium effects. Poor drainage of soils in the study area can lead to the retention of salts in the root zone, contributing to accumulation of salts in the soil surface.

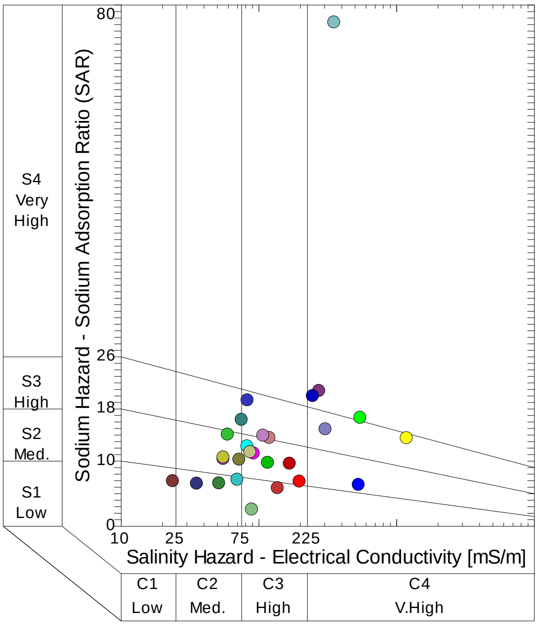


Figure 4.49: Plot of SAR and EC for groundwater samples in the study area

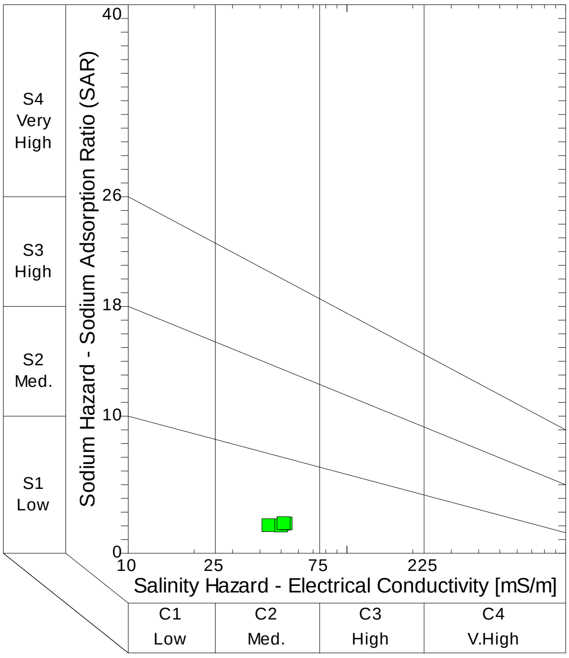


Figure 4.50: Plot of SAR and EC for surface water samples in the study area

4.7 CONCLUSION

The groundwater quality and hydrogeochemical processes in the Chókwè district are conditioned by the local environmental characteristics (semi-arid area). Water–soil and rock–water interactions determine the chemical interactions between solutes in groundwater. The significant main surface water bodies, through which surface water and groundwater interact, are the Limpopo River and the CIS. Sodium and chloride are the major ions dominant in groundwater, which make the water too saline and not suitable for drinking. The study area is characterised by a shallow aquifer underlined by unconsolidated quaternary and tertiary sediments.

In conclusion, the general overview summary of the interaction between the physical and chemical hydrogeology, as well as the water composition, is presented in the conceptual flowchart scheme (Figure 4.51).

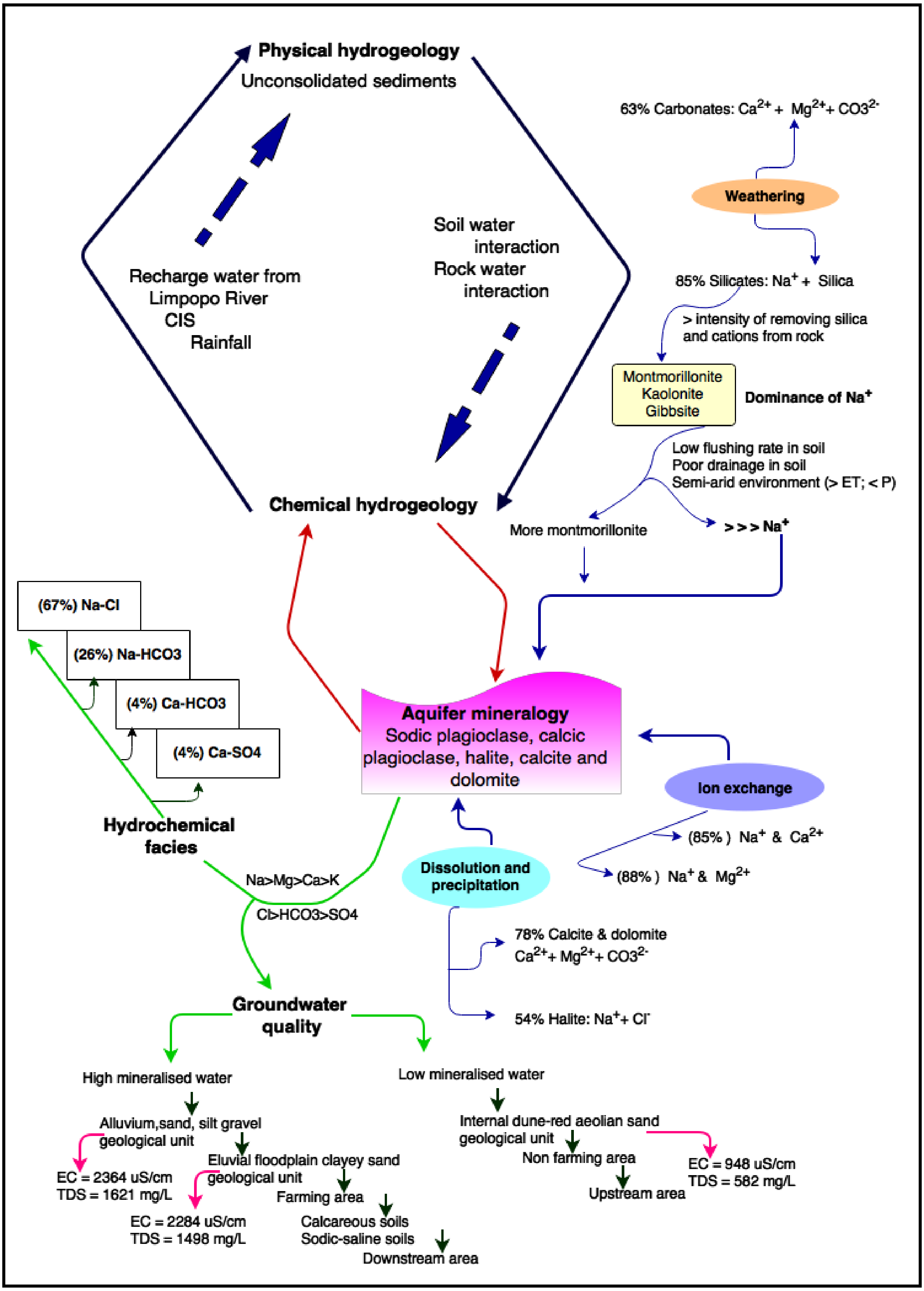


Figure 4.51: Conceptual interaction between physical and chemical hydrogeology of the study area

Chapter 5
CONCLUSION AND RECOMMENDATIONS

5.1 INTRODUCTION

This chapter concludes the interpretation and analysis carried out from groundwater physicochemical parameters in the study area. General overview of groundwater quality, dominant hydrochemical facies and the dominant major ions will be summarised. In addition, hydrogeochemical processes contributing to the groundwater quality will be summarised and its relation with the local environment. Furthermore, from this research, future recommendations will be addressed for better understanding and management of groundwater in the Chókwè district.

5.2 CONCLUDING REMARKS

The main aim of this study was to analyse the groundwater chemistry of the Chókwè district and its influence on water quality, which was achieved through identification of the dominant hydrochemical facies, hydrogeochemical processes and major ions in the aquifer. Spatial variability and input factors for groundwater mineralisation were also identified.

According to this research, the groundwater quality in the study area is dominated by Na-Cl hydrochemical facies, with cations in the order of Na > Mg > Ca > K and anions Cl > HCO_3 > SO_4.

The water level from sampled sources ranged from 4.80 to 12.65 m and the aquifer is classified as shallow within the CIS and proximal in the non-farming area.

Analysis of variances between physicochemical parameters revealed that the local geological units have a significant effect on groundwater quality. High mineralised groundwater occurs in aquifers underlined by alluvium, sand, silt, gravel geological units and eluvial floodplain clayey sand geological units. The TDS and EC in alluvium, sand, silt, gravel geological units ranged from 488 to 7 626 mg/L, with an average value of 1 621 mg/L, and 603 to 12 000 µS/cm, with an average value of 2 364 µS/cm, respectively. For eluvial floodplain clayey sand geological units, the values ranged from 406 to 3 537 mg/L, with an average value of 1 562 mg/L, and from 522 to 5 530 µS/cm, with an average value of 2 300 µS/cm. Low mineralised groundwater was observed in internal dune-red aeolian sand geological units. The TDS and EC values ranged from 163 to 1 806 mg/L, with an average value of 582 mg/L, and from 241 to 2 780 µS/cm, with an average value of 582 mg/L and 948 µS/cm, respectively.

Analysis based on the Mozambique standards indicated that 37% of groundwater samples with an EC >2 000 µS/cm and 26% with TDS >1 000 mg/L are not suitable for drinking purposes. However, from WHO standards, 15% and 30% of groundwater samples are classified as poor and unacceptable for drinking. Hard and very hard groundwater was observed in 7% and 30% of the water samples. Unlike groundwater, the physicochemical parameters in surface water are within desirable limits. From the suitability analysis of the water source, groundwater would not be safe to use for irrigation over the long term, due to a possible sodium and salinity hazard.

The aquifer mineralogy shows that there is a dominance of sodic plagioclase (Albite), calcic plagioclase (Anorthite), halite, dolomite and calcite, which through hydrogeochemical processes, are released in groundwater. Weathering, ion exchange, dissolution and precipitation are the main hydrogeochemical processes affecting the mineralisation of groundwater in the study area. Therefore, the mineralisation is reinforced by chemical evolution of groundwater, as well as spatial distribution of hydrochemical facies and hydrogeochemical processes. The release of major ions into the aquifer through hydrogeochemical processes, are significantly related with the high concentration of Na and Cl in groundwater. Results from the contribution of each major ion in the groundwater, revealed that Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and HCO_3^{-} have halite equivalent values of 1 282, 2 453, 9 738, 14 077, 1 318 and 1 589 mg/L, respectively. This is evidence that all major ions in the aquifer are strongly correlated to the halite mineral and consequently dominant of Na-Cl hydrochemical facies.

Besides the spatial variability and chemical evolution, the land use in the study area is another main factor influencing the groundwater quality. All hydrogeochemical processes identified, occur in the downstream area where the CIS is located, while in the upstream area only silicate weathering and dissolution/precipitation occur. However, due to intensive use of surface irrigation, the groundwater is highly mineralised water in downstream. Occurrence of saline-sodic soils and calcareous sediments in the area, significantly influence the release of ions in groundwater.

5.3 RECOMMENDATIONS

The recommendations arising from this research are related to scientific and technical approaches in the study area.

5.3.1 Scientific approaches

More studies should be done to investigate and determine the impact of CIS in groundwater management (quality and quantity).

Investigation to identify other groundwater sources of pollution (natural and anthropogenic) in the Chókwè district will help to design the local groundwater conceptual model which is very important and crucial in a semi-arid area such as the Chókwè district, to understand the aquifer dynamics (physical and chemical).

Setup of a local and provincial data base for groundwater management, to implement spatial and temporal assessing of groundwater quality and quantity, is also recommended.

5.3.2 Technical approaches

The lack of infrastructure for groundwater monitoring in the district represents a challenge to manage the quality and quantity of groundwater. Therefore, the public water sector institutions should adopt local strategies to link and share the little information available in groundwater. Additional information from reports of drilled boreholes in the Chókwè district is needed. The future reports should contain the following detailed technical information of the aquifer in each borehole: (i) EC profiling, (ii) pump test (step test and constant rate, including sustainable borehole yield).

Establishment and design of local or provincial groundwater monitoring network is needed in order to implement interdisciplinary management from existing interactions between all surface water bodies and groundwater in the district. As the

Chókwè district is part of the Limpopo basin in the floodplain area of Mozambique, flood and drought events are very common. However, the design of a local and provincial monitoring network should consider the regional hydrogeology environment between the sharing countries in the basin (South Africa, Botswana and Zimbabwe).

Training in groundwater quality management should be done for public water institutions. This will help them to:

- improve the technical skills which will be used to understand the characteristics of the local aquifer; and
- define and identify different water treatment plans for drinking water, taking into account the four hydrochemical facies (Na-HCO_3, Na-Cl, Ca-HCO_3 and Ca-SO_4) and the dominant hydrogeochemical processes, as well as aquifer mineralogy.

.

REFERENCES

Abreha, A.G. 2014. *Hydrogeochemical and water quality investigation on irrigation and drinking water supplies in the Mekelle region northern Ethiopia*. MSc thesis, Faculty of Geo-science and Earth, University of Twente.

Aghazadeh, N. and Mogaddam, A. A. 2010. Assessment of groundwater quality and its suitability for drinking and agricultural uses in the Oshnavieh area, northwest of Iran. Journal of Environmental Protection, (1): 30 – 40.

Alemaw, B.F., Scott, K. and Merrey, D. 2008. *Limpopo River basin focal project: Literature on Work Package 2 – Water availability and access*. Challenge Program for Water and Food, CPWF.

Alley, W.M. 1993. General design considerations. In: Alley, W.M. (Ed.) *Regional ground-water quality*. New York: Van Nostrand Reinhold, 3-22.

Amer, R., Ripperdan, R., Wang, T. and Encarnación, J. 2012. Groundwater quality and management in arid and semi-arid regions: Case study, Central Eastern Desert of Egypt. *Journal of African Earth Sciences*, (69):13-25.

Andreasi, W.A.M. and Azevedo, A.A.P. 2009. *Introduction to statistical tool analysis of Excel2007 applied to engineering assessment.* Brazil: Federal University of Mato Grosso do Sul.

Appelo, C.A.J. and Postma, D. 2005. *Geochemistry groundwater and pollution.* (2nd ed.). Amsterdam, Netherlands: A.A. Balkema.

Araújo, J.C. 2012. Capítulo 2 - Recursos hídricos em regiões semiáridas In: Gheyi, H. R., Paz, V. P. S., Medeiros, S. S. e Galvão, C. O. (Eds). *Recursos hídricos em regiões semiáridas: Estudos e aplicações.* Governo do Basil.

Babar, M. 2005. *Hydrogeomorphology, fundamentals, applications and techniques*. New India publishing agency, Pitam Pura-New Delhi.

Back, W. 1966. *Hydrochemical facies and ground-water flow patterns in northern part of Atlantic Coastal Plain*. Geological Survey Professional Paper 498-a. U.S. Geological Survey.

Balachandar, D., Sundararaj, P., Rutharvel, M.K. and Kumaraswamy, K. 2010. An investigation of groundwater quality and its suitability to irrigated agriculture in Coimbatore District, Tamil Nadu, India – A GIS Approach*. International Journal of Environmental Sciences*, 1(2):176-190.

Block, L.V., Burnett, R.P., Cunningham, A.J., Didricksen, K.D., Hamilton, J.L., Lacey, J.E., Matuska, P.J., Prince, N.W., Pruitt, T.D., Rappmund, R.A., Reeves, C.R., Sanders, G.D., Shadix, S.J., Bianchi, R., Talbot, W.R. and Watt, D.E. 1995. *Groundwater manual: A water resources technical publication. A guide for the investigation, development, and management of ground-water resources* (2nd ed.). United States Department of the Interior/Bureau of Reclamation.

Bouman, D.1985. *Revista da Hidrogeologia do baixo Limpopo e do baixo Incomati.* Instituto-Série: DNA/Geohidrologia.

Bouman, D. and Ferro, B.P.A. 1987. *Explanatory notes to the hydrogeological map of Mozambique: Scale 1:1000 000*. Project of the Hydrogeological map of Mozambique, sponsored by UNICEF. National Directorate for Water Affairs, Maputo-Mozambique.

Burbery, L. and Vincent, C. 2009. *Hydrochemistry of the south Canterbury tertiary aquifers*. Technical report: Investigations and Monitoring Group. (Report R09/34). Christchurch: Environment Canterbury.

Burton, G.A. Jr. and Pitt, R.E. 2002. *Storm effects handbook: A toolbox for watershed managers, scientists, and engineers*. Boca Raton, FL: Lewis Publishers.

Carvalho, J.C.R., Sousa, C.S. and Sousa, C.S. 2005. *Fertilizantes e fertilização*: Universidade Ferderal da Bahia. Escola de Agronomia, Departamento de Química Agrícola e Solos.

Chairuca, L., Naafs, A., Van Haren, I., Upton, K. and Dochartaigh, B.Ó. 2016. *Africa groundwater atlas: Hydrogeology of Mozambique*. British Geological Survey. Available from: http://earthwise.bgs.ac.uk/index.php/Hydrogeology_of_Mozambique [Accessed at 5 May 2016].

Chapman, D. 1996. *Water quality assessments: A guide to use of biota, sediments and water in environmental monitoring.* (2nd ed.). Cambridge: Cambridge University Press.

Charbeneau, R.J. 2000. *Groundwater hydraulics and pollutant transport.* United States of America: Prentice-Hall.

Chebbah, M. and Allia Z. 2015. Geochemistry and hydrogeochemical process of groundwater in the Souf valley of low Septentrional Sahara, Algeria. *African Journal of Environmental Science and Technology*, (9)3: 261-273.

Clifton, C., Evans, R., Hayes, S., Hirji, R., Puz, G. and Pizarro, C. 2010. *Water and climate change: Impacts on groundwater resources and adaptation options*. Washington: The World Bank.

CWERC (Colorado Water and Energy Research Center). 2014. *Groundwater quality interpretation guide: Understanding your water quality results*.

Davis, S.N. and Wiest, R.J.M. 1966. *Hydrogeology.* (3rd ed.). New York: John Wiley & Sons.

DNG (National Directorate of Geology – Nacional de Geologia). 2006. *Explanatory notes, scale 1:250 000*. Volume 1. Maputo-Mozambique.

Drever, J.I. 1997.*The geochemistry of natural waters: Surface and groundwater environments.* (3rd ed.). United States of America: Prentice-Hall.

Eaton, A.D., Clesceri, L.S., Rice, E.W. and Greenberg, A.E. 2005. *Standards methods for the examination of water and wastewater*. (21st ed.) Baltimore, Maryland: Port City Press.

Elango, L. and Senthilkumar, M. 2013. Geochemical processes controlling the groundwater quality in lower Palar river basin, southern India. *Indian Academy of Sciences*, 122(2):419-432.

EPA (Environmental Protection Agency). 2001. *Technical guidance manual for groundwater investigations. Groundwater sampling.* United States: Washington, D.C.

Eriksson, E. 1985. *Principles and applications of hydrochemistry*. Department of Hydrology, Uppsala University, Sweden.

FAEF (Faculdade de Agronomia e Engenharia Florestal). 2001. Programa Competir: região agrícola do Chókwè diagnóstico da fileira agrícola, Faculty of Agronomy and Forestry Engineering – Eduardo Mondlane University, Maputo.

FAO (Food and Agriculture Organization). 1987. Site selection for aquaculture: Chemical features of water. Nigerian institute for oceanography and marine research. Project RAF/82/009. Available from: http://www.fao.org/3/contents/71f37a4b-429c-5f42-8cad-8e05710d67e0/AC175E00.htm [Accessed on 13 May 2016].

Ferro, B.P.A. and Bouman, D. 1987. *Explanatory notes to the hydrogeological map of Mozambique: Scale 1:1 000 000.* National Directorate for Water Affairs. Maputo, Mozambique.

FEWS NET (Famine Early Warning Systems Network). 2011*. Livelihoods baseline profiles: Limpopo basin, Mozambique.* http://www.fews.net/sites/default/files/documents/reports/mz_baseline_rural%20limpopo_en.pdf [Accessed on 4 April 2016].

FEWS NET (Famine Early Warning Systems Network). 2014. *Mozambique livelihood zones description. Map of livelihood zones in Mozambique*. Available from: http://reliefweb.int/sites/reliefweb.int/files/resources/MZ%20LHdescriptions%202013%20en2-7_0.pdf [Accessed on 23 October 2015].

Fisher, R.S. and Mullican, W.F. 1997. Hydrochemical evolution of sodium-sulphate and sodium-chloride groundwater beneath northern Chihuahuan desert, trans-pecos, Texas, USA. *Hydrogeology Journal*, 5(2):4-16.

Freeze, R.A. and Cherry, J.A. 1979. *Groundwater*. Englewood Cliffs, Prentice Hall.

Gajendran, C. 2011. *Water quality assessment and prediction modelling of Nambiyar River basin, Tamil Nadu, India.* PhD thesis, Faculty of Civil Engineering, Anna University, Chennai.

GEOMOC (Geotecnia de Moçambique). 1981. *Complemento ao relatório dos trabalhos de prospecção hidrogeológica e geotécnica na Vala 5, piezometros entre Rio Limpopo e Lagoa Chinhanga.*

Gibrilla, A., Osae, S., Akiti, T.T., Adomako, D., Ganyaglo, S.Y., Bam, E.P.K. and Hadisu, A. 2010. Hydrogeochemical and groundwater quality studies in the Northern part of the Densu river basin of Ghana. *Journal of Water Resource and Protection*, 2(12):1071-1081.

Grantham, G.H., Marques, J.M., Wilson, M.G.C., Manhiça, V. and Hartzer, F.J. 2011. *Explanation of the geological map of Mozambique, scale 1:1 000 000*. National Directorate of Geology, Maputo-Mozambique.

Hakala, A. and Pekonen, L. 2008. *The Impact of the irrigation system and agricultural production on water quality in Chókwè Irrigation Scheme*. Eduardo Mondlane University, Maputo, Mozambique.

Hassan, S.S. 2011. *Impact of flash floods on the hydrogeology aquifer system at Delta Wadi El-Arish (North Sinai)*. Fifteenth International Water Technology Conference, IWTC–15, Alexandra, Egypt.

Heath, R.C. 1987. *Basic groundwater hydrology*. Department of Interior: United State Geological Survey.

Helsel, D.R. and Hirsch, R.M. 2002. *Statistical Methods in Water Resources.* Techniques of Water-Resources Investigations of the United States Geological Survey.

Hem, J.D. 1985. *Study and interpretation of the chemical characteristics of natural water.* (3rd edition). U.S. Geological Survey Water-Supply Paper 2254.

Hosseinifard, J., Salehi, M.H., Esfandiarpour, I. and Mohammadi, J. 2008. Spatial variability of groundwater and its relationship with pistachio yield in Anar region, Iran. *Journal of Applied Sciences*, 8(20):3697-3705.

Hounslow, A.W. 1995. *Water quality data: Analysis and interpretation*. Boca Raton, Lewis Publisher, New York.

INE (Instituto Nacional de Estatística). 2012. *III Recenseamento Geral da População e Habitação 2007*. Indicadores Socio-demográficos distritais - Província de Gaza.

INE (Instituto Nacional de Estatística). 2013. Cartaz de dados sobre a população de Moçambique. Maputo-Mozambique.

Janardhana, R.D., Hari, B.B., Swami, A. and Sumithra, S. 2013. Physico-chemical characteristics of ground water of Vuyyuru, part of east coast of India. *Journal of Environmental Research and Technology*, (3)2:225-232.

Jeong, C. 2001. Mineral water interaction and hydrogeochemistry in the Samkwang mine area, Korea. *Geochemical Journal*, 35:1-12.

Karmegam, U., Chidamabram, S., Sasidhar, P. Manivannan, R., Manikandan, S. and Anandhan, P. 2010. Geochemical characteristics of groundwater are of shallow coastal aquifer in and around Kalpakkam, South of India. *Research Journal of Environmental and Earth Sciences*, 2(4):170-177.

Konstapel, C.D. 1981. Problemas de salinidade-sodicidade no novo regadio de Lionde-Nwachicoluane vale do Rio Limpopo.

Kottek, M., Grieser, J., Beck, C., Rudolf, B. and Rubel, F. 2006. World map of the Köppen-Geiger climate classification updated. *Meteorologische Zeitschrift,* 15(3):259-263.

Kruseman, G.P. and Ridder, N.A. 1994. *Analysis and evaluation of pumping test data*. (2nd revised edition). International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands. (ILRI Publication 47).

Lakshmanan, E., Kannan R., and Kumar, M.S. 2003. Ion chemistry and identification of hydrogeochemical processes of ground water. *Environmental Geosciences*, 10(4):157-166.

Laxman, K.D., Sundariah, R., Sudhakar, A., Kamal, D.K and Saxena, P.R. 2014. Hydrochemical characteristics and groundwater quality assessment in the South eastern part of Ranga Reddy district, Andhra Pradesh, India. *Indian Journal of Applied Research*, 4(6):231-235.

Mathias, S. A. and Wheater, H. S. 2010. Groundwater Modelling in arid and semi-arid areas: an introduction In: Wheater, H. S., Mathias, S. A. and Li, X (Eds). *Groundwater Modelling in arid and semi-arid areas*. International Hydrology series, Cambridge University Press.

Mayo, A. L. and Loucks, M.D.S 1995. Solute and isotopic geochemistry and groundwater flow in the central Wasatch range Utah. *Journal of Hydrology*, 172(1-4):31-59.

Meier, P.C. and Zünd, R.E. 2000. *Statistical methods in analytical chemistry.* (2nd edition). New York: John Wiley & Sons.

Meybeck, M., Kuusisto, E., Mäkelä, A. and Mälkki, E. 1996. Chapter 2 – Water Quality. In: Bartram, J. and Ballance, R. (Eds.) 1996. *Water quality monitoring: A practical guide to the design and implementation of freshwater quality studies and monitoring programmes*. United Nations Environment Programme and the World Health Organization (UNEP/WHO).

Mihajlovich, D. and Gomes, F. 1986. *Áreas de rega: Inventário e possibilidades futuras. Instituto nacional de Investigação agronómica*. Série terra e água, comunicado nº 53. Maputo Moçambique.

MISAU (Ministério da Saúde). 2004. *Regulamento sobre a qualidade de água para o consumo humano. Boletim da República*, I série, nº 37. Publicação oficial da República de Moçambique. diploma ministerial nº 180/2004 de 15 de Setembro.

Monjerezi, M., Vogt, R. D., Aagaard, P. and Saka, J. D. K. 2012. The hydro-geochemistry of groundwater resources in area with prevailing saline groundwater, lower Shire valley, Malawi. *Journal of African Earth Sciences*, 68:67-81.

Moss, R. 1990. *Handbook of groundwater development*. John Wiley & Sons.

Moujabber, M., Samra, B.B., Darwish, T. and Atallah, T. 2006. Comparison of different indicators for groundwater contamination by seawater intrusion on the Lebanese coast. Water Resource Management, 20: 161-180.

MRC (Mineral Resources Centre). 2009*. Baseline Study of the water chemistry of the Limpopo Basin: Country studies from Botswana, Mozambique, South Africa and Zimbabwe*. Mineral Resources Centre, University of Zimbabwe.

Mullins, G. And Hansen, D. J. 2006. Chapter 4-Basic Soil Fertility In: Haering, K.C and Evanylo, G.K. (Eds.), *The Mid-Atlantic nutrient management handbook*. Mid-Atlantic Regional Water Program. U.S. Department of Agriculture, 256.

Munguambe, P.D.A. 2007. *Nitrogen and salt leaching management on irrigated salt-effected soils in Chókwè irrigation Scheme, Mozambique*. PhD thesis, Faculty of Natural and Agricultural Sciences, University of Pretoria.

Nagaraju, A., Suresh, S., Killham, K. and Edwards, K.H. 2006. Hydrogeochemistry of waters of mangampeta barite mining area, cuddapah basin, andhra pradesh, India. *Turkish Journal of Engineering and Environmental Sciences*, 30(4):203-219.

Naseem, S., Hamza, S. and Bashir, E. 2010. Groundwater geochemistry of winder agricultural farm, Balochistan, Pakistan and assessment for irrigation water quality. *European Water Resources Association*, 31: 21-32.

NEPAD (New Partnership for Africa's Development). 2004. *Small-scale irrigation project II: Inhambane, Manica, Tete and Nampula Provinces*. Government of the Republic of Mozambique.

Nowinski, J.D., Cardenas, M.B., Lightbody, A.F., Swanson, T.E. and Sawyer, H. 2012. Hydraulic and thermal response of groundwater-surface water exchange to flooding in an experimental aquifer. *Journal of Hydrology*, 184-192.

Nur, A., Ishaku. J. M. and Yusuf, S.N. 2012. Groundwater flow patterns and hydrochemical facies distribution using geographical information system (GIS) in Damaturu, Northeast Nigeria. *International Journal of Geosciences*, 3, 1096-1106.

Ostovari, Y., Shahram, Z., Harchegani, H.B. and Asgari, K. 2003. Effects of geological formation on groundwater quality in Lordegan region, Chahar-mahal- va-Bakhtiyari, Iran. *International Journal of Agriculture and Crop Sciences*, (5)17:1983-1992.

PANESA (Pastures Network for Eastern and Southern Africa). 1988. African forage plant genetic resources, evolution of forage germplasm and extensive livestock production system. Proceedings of the Third Workshop held at the International Conference Centre, Arusha, Tanzania, 27-30 April 1987. ILCA, Addis Ababa.

Payne, S.M., Magruder, I.A. and Woessner, W.W. 2013. Application of a groundwater classification system and GIS mapping system for the lower Ruby valley watershed, southwest Montana. *Journal of Water Resource and Protection*, 5:775-791.

Phocaides, A. 2000. *Technical handbook on pressurized irrigation techniques.* Rome: Food and Agriculture Organization of the United Nations.

Rail, C.D. 2000. *Groundwater contamination: Contamination, sources and hydrology* (Volume 1). Florida: Technomic Publishing.

Ravichandran, V.1999. Regional land cover changes, sustainable agriculture and their interaction with global change. Proceedings of an International Workshop, Maputo, Mozambique, 28-30 July 1997. Universities Press.

RSA DWAF (Republic of South Africa. Department of Water Affairs and Forestry).1996. South African water quality guidelines. Volume 1, Domestic water use. (2nd ed.). Pretoria: Department of Water Affairs and Forestry.

Sadashivaiah, C., Ramakrishnaiah, C. R. and Ranganna, G. 2008. Hydrochemical analysis and evaluation of groundwater quality in Tumkur Taluk, Karnataka state, India. *International Journal of Environmental Research and Public Health*, 5(3):158-164.

Saeed, T.U. and Attaullah, H. 2014. Impact of extreme floods on groundwater quality in Pakistan. *British Journal of Environment & Climate Change*, 4(1):133-151.

Salem, Z. E. and Horiny, M. M. 2014. Hydrogeochemical evaluation of calcareous eolianite aquifer with saline soil in a semiarid area. Environmental Science and Pollution Research International Journal, 21(13):8294–8314.

Salman, S.A., Melegy, A.A., Shaban, A.M., and Hassaan, M.M. 2013. Hydrogeochemical characteristics and classification of groundwater in sohag governorate, Egypt. *Journal of Applied Sciences Research*, 9(1):758-769.

Sayyed, J.A. and Bhosle, A.B. 2011. Analysis of chloride, sodium and potassium in groundwater samples of Nanded City in Mahabharata, India*. European Journal of Experimental Biology*, 1(1):74-82.

Schoeller, H. 1959. Arid zone hydrology, recent developments. Arid zone research – XII, UNESCO.

Schwartz, F.W. and Zang, H. 2003. *Fundamentals of groundwater.* New York: John Wiley & Sons.

Şen, Z. 2015. *Practical and applied hydrogeology*. Istanbul Technical University. United Kingdom: Elsevier.

Sharaky, A.M., Atta, S.A., Hassanein, A.S. and Khallaf, K.M.A. 2007. *Hydrogeochemistry of groundwater in the western Nile Delta aquifers, Egypt.* 2nd International Conference on the Geology of Tethys, Cairo University.

Shaw, R. and Gordon, I. 2011. *Salinity management handbook*. (2nd ed.) Department of Environment and Resource Management, Brisbane: Queensland Government.

Sharaky, A.M., Atta, S.A., Hassanein, A.S. and Khallaf, K.M.A. 2007. *Hydrogeochemistry of groundwater in the western Nile Delta aquifers, Egypt.* Second International Conference on the Geology of Tethys, Cairo University.

Shaw, R. and Gordon, I. 2011. *Salinity management handbook*, 2nd edition. Department of Environment and Resource Management, Brisbane- Queensland government.

Singh, V.K., Pandey, G. and Singh, R. 2015. Interpreting groundwater chemistry and identifying water type of Dehrdun City, Uttarakhand. *International Journal for Scientific Research & Development*, 3(7):851-854.

Skordas, K., Papastergios, G., Tziantziou, L., Neofitou, N. and Neofitou, C. 2013. Groundwater hydrogeochemistry of Trikala municipality, central Greece. *Environmental Monitoring and Assessment*, 185(1):81-94.

Smedley, P.L. 2002. *Groundwater quality: Mozambique*. British Geological Survey.

Smoor, P. B.1967. *Hydrochemical facies study of groundwater in the Tucson Basin*. Faculty of the Department of Geology, University of Arizona.

Suarez, D. L., Wood, J. D. and Lesch, S. M. 2006. Effect of SAR on water infiltration under a sequential rain-irrigation management system. *Agricultural Water Management Journal*, 86(1-2):150-164.

Sundaram, B., Feitz, A., Caritat, P., Plazinska, A., Brodie, R., Coram, J. and Ransley, T. 2009. *Groundwater sampling and analysis – A field guide.* Australian Government, Geoscience Australia.

Tauacale, F. 2002. *Water resources of Mozambique "and the situation of the shared rivers".* River Basin Information Systems Meeting, Nairobi – Kenya, 13-14 February 2002. Department of Geography, Eduardo Mondlane University, Mozambique.

Timberlake, J. and Chidumayo, R. 2011. Miombo ecoregion vision report. Occasional publications in biodiversity nº 20. Biodiversity Foundation for Africa, Bulawayo – Zimbabwe.

Thompson, T., Fawell, J., Kunikane, S., Jackson, D., Appleyard, S., Callan, P., Bartram, J. and Kingston, P. 2007. *Chemical safety of drinking-water: Assessing priorities for risk management:* Geneva: World Health Organization.

UNEP (United Nations Environment Programme). 2008. *Water quality for ecosystem and human health.* (2nd ed.). Canada: United Nations Environment Programme Global Environment Monitoring System (GEMS)/Water Programme.

Vengosh, A. 2014. *Salinisation and saline environments*. Duke University, Durham, United States of America.

Vivo, B., Belkin, H.E. and Lima, A. 2008. *Environmental geochemistry. Site characterization, data analysis and case histories*. Amsterdam: Elsevier.

Wang, X., Zhang, G. and Xu, Y.J. 2015. Impacts of the 2013 extreme flood in Northeast China on regional groundwater depth and quality. *Water,* 7(8):4575-4592.

Weaver, J.M.C., Cave, L. and Talma, A.S. 2007. *Groundwater sampling. A comprehensive guide for sampling methods*. (2nd ed.). Water Research Commission, South Africa.

Wilson, T.L. 2009. *Gestão da água de rega e sua implicação na salinização de solos no regadio de Chókwè.* Honours script, Faculdade de Agronomia e Engenharia Florestal, Universidade Eduardo Mondlane, Moçambique.

Winter, T. C., Harvey, J. W., Franke, O. L. and Alley, W. M. 1998. *Ground water and surface water a single resource*. United State Geological Survey. Circular 1139, Denver, Colorado.

WHO (World Health Organization). 2003. *Total dissolved solids in drinking-water. Background document for development of WHO guidelines for drinking-water quality*. Geneva, Switzerland. Available from: http://www.who.int/water_sanitation_health/dwq/chemicals/tds.pdf [Accessed on 19 April 2016].

WHO (World Health Organization). 2011. *Guidelines for drinking water quality*. (4th ed.) Geneva, Switzerland.

Yidana, S. M., Sakyi, P. A. and, Stamp, G. 2011. Analysis of the suitability of surface water for irrigation purposes: The Southwestern and coastal River systems in Ghana. *Journal of Water Resource and Protection*, 3(10): 695-710.

Zektser, I.S. and Everett, L.G. 2004. *Groundwater resources of the world and their use*. IHP-VI, Series on Groundwater No. 6. UNESCO.

Zeman, J. 2004. *Introduction to environmental hydrogeochemistry.* Masaryk University in Brno, Faculty of Science.

Appendix 1

FIELD NOTE FORM

Field note form used to describe the physical environment of sampled water sources in the study area

Site name	**Coordinates**		**Filed parameters**				**Surface water sources**			**Groundwater sources**			**Observation**		
	Latitude	Longitude	pH	EC	TDS	WL	River	M canal	Swamp	BH	HP	Well	FA	Non-FA	Other

FA = farming area; Non-FA = Non farming area; M canal = Main canal

Appendix 2

LABORATORY ANALYSIS OF WATER SAMPLES

Table 1: Laboratorial physicochemical analysis of groundwater samples part 1

Site Name	pH	EC	Ca	Mg	Na	K	HCO_3	F	Cl	NO2(N)	Br	NO3(N)	PO4	SO4
Site name 1	8,17	838	3,99	2,67	202	2,91	295	0,91	94	0,01	0,30	2,07	-0,1	60,1
Site name 2	7,93	603	5,38	2,2	152	2,01	228	0,84	65	-0,01	0,46	-0,05	-0,1	32,5
Site name 3	7,95	1210	17,6	7,24	265	14,3	329	0,13	171	-0,10	0,43	1,16	-1	115,1
Site name 4	7,31	902	65,2	34,5	97,8	6,36	312	0,02	151	-0,01	0,47	-0,05	-0,1	32,3
Site name 5	7,35	1390	62,9	35,4	229	4,5	343	0,33	253	-0,10	0,66	-0,50	-1	88,9
Site name 6	8,10	1700	28,6	33,1	314	4,35	239	0,44	424	-0,10	1,18	0,76	-1	60,4
Site name 7	8,00	522	9,01	7,41	108	2,77	177	0,19	86	-0,01	0,37	0,07	-0,1	15,4
Site name 8	7,97	561	4,98	4,19	127,74	2,91	178	0,21	80	-0,01	0,39	-0,05	-0,1	18,4
Site name 9	7,93	561	4,44	3,64	122,58	2,74	177	0,13	81	-0,01	0,44	-0,05	-0,1	16,1
Site name 10	7,81	5530	129,73	124,84	1099,01	11,62	167	0,11	1893	-0,1	4,67	0,18	-1	108,4
Site name 11	7,9	3090	57,67	56,00	656,67	9,79	261	0,29	832	-0,1	2,34	0,05	-1	228,8
Site name 12	7,63	5380	258,63	247,34	582,74	12,21	235	-0,10	1823	-0,1	5,45	0,28	-1	155,0
Site name 13	7,65	12000	513,98	480,80	1756,38	20,87	329	-1,00	3961	-1	11,01	0,35	-10	565,8
Site name 14	7,9	2000	71,19	57,00	314,37	6,65	120	0,50	652	-0,1	1,89	0,04	-1	15,1
Site name 15	8,07	1090	12,31	11,50	279,91	3,08	474	0,55	87	-0,1	0,45	0,00	-1	41,5
Site name 16	8,04	878	9,78	8,68	200,39	4,16	223	0,27	153	-0,01	0,46	0,22	-0,1	37,3
Site name 17	6,14	836	2,14	6,20	154,88	28,76	15,2	0,01	245	-0,01	0,65	2,83	-0,1	18,2
Site name 18	5,9	930	1,68	8,71	160,69	30,39	6,98	0,01	275	-0,01	0,71	6,98	-0,1	11,6
Site name 19	6,51	761	1,61	2,57	142,22	22,42	31,5	0,02	217	-0,01	0,61	0,01	-0,1	19,0
Site name 20	6,02	731	5,24	4,93	134,17	19,50	10,3	0,01	199	-0,01	0,53	9,50	-0,1	24,1
Site name 21	6,99	2780	20,56	30,25	629,20	22,07	63,9	-0,10	796	-0,1	2,31	8,81	-1	204,4
Site name 22	8	708	12,28	9,55	134,97	3,08	183	0,09	131	-0,01	0,49	-0,05	-0,1	19,5
Site name 23	8,05	2500	24,12	25,38	585,57	7,04	216	0,28	743	-0,1	2,36	0,13	-1	88,0
Site name 24	6,16	360	4,18	1,79	62,17	9,49	15,3	0,03	91	-0,01	0,20	1,13	-0,1	27,5
Site name 25	6,04	241	2,50	0,58	45,90	6,70	12,6	0,03	39	-0,01	0,08	4,63	-0,1	34,6
Site name 26	8,43	3570	3,958	4,691	958,549	1,311	1031	5,3434	276,1427	-0,1	1,0631	21,3233	-1	564,3
Site name 27	7,83	1180	15,329	15,331	222,269	5,182	212	-0,1	260,1677	-0,1	-0,4	0,6405	-1	34,062

Observation: All ions including TH and TDS are expressed in mg/L while EC in µS/cm.

Table 2: Laboratorial physicochemical analysis of groundwater samples part 2

Site name	Ca H	Mg H	TH	TDS (sum)	Al	As	Cr	Cu	Fe	Mn	Pb	Zn	Si
Site name 1	10	11	21	671	0,040	0,030	<0.01	<0.01	<0.01	0,010	<0.01	<0.01	25,600
Site name 2	13	9	22	488	0,030	0,010	<0.01	<0.01	0,010	0,020	<0.01	<0.01	28,500
Site name 3	44	30	74	923	0,060	<0.01	<0.01	<0.01	<0.01	0,020	<0.01	<0.01	24,500
Site name 4	163	141	304	699	0,050	<0.01	<0.01	<0.01	<0.01	2,360	<0.01	0,010	11,900
Site name 5	157	145	302	1014	0,070	<0.01	<0.01	<0.01	<0.01	2,680	<0.01	0,010	11,600
Site name 6	72	136	207	1107	0,070	<0.01	0,030	<0.01	<0.01	0,020	<0.01	0,010	14,300
Site name 7	23	30	53	406	0,070	<0.01	<0.01	<0.01	<0.01	0,020	<0.01	<0.01	12,100
Site name 8	12	17	30	417	0,010	<0.010	0,019	0,006	<0.010	<0.010	<0.010	<0.010	10,39
Site name 9	11	15	26	407	<0.010	<0.010	0,017	0,004	0,023	<0.010	<0.010	<0.010	9,97
Site name 10	324	512	836	3537	<0.010	<0.010	0,025	0,031	<0.010	0,014	0,023	0,035	13,53
Site name 11	144	230	374	2103	<0.010	<0.010	0,020	0,015	0,022	0,015	<0.010	<0.010	13,62
Site name 12	647	1014	1661	3319	<0.010	<0.010	0,021	0,022	<0.010	0,017	0,017	<0.010	16,54
Site name 13	1285	1971	3256	7626	<0.010	<0.010	0,017	0,050	<0.010	0,046	0,025	0,128	15,10
Site name 14	178	234	412	1237	<0.010	<0.010	0,017	0,029	0,055	0,040	0,026	<0.010	11,37
Site name 15	31	47	78	909	0,012	<0.010	0,017	0,012	<0.010	0,115	<0.010	<0.010	21,63
Site name 16	24	36	60	638	<0.010	<0.010	0,029	<0.010	<0.010	0,011	<0.010	<0.010	11,47
Site name 17	5	25	31	484	0,012	<0.010	0,015	<0.010	<0.010	0,297	<0.010	<0.010	23,25
Site name 18	4	36	40	526	0,012	<0.010	0,016	0,019	0,053	0,455	<0.010	<0.010	24,38
Site name 19	4	11	15	437	0,012	<0.010	0,015	0,015	0,154	0,207	<0.010	<0.010	19,75
Site name 20	13	20	33	439	0,028	<0.010	0,018	0,019	0,025	0,073	<0.010	<0.010	23,31
Site name 21	51	124	175	1806	<0.010	<0.010	0,021	0,034	0,018	0,173	0,085	<0.010	22,13
Site name 22	31	39	70	493	<0.010	<0.010	0,020	0,015	0,011	0,011	0,027	<0.010	10,11
Site name 23	60	104	164	1691	<0.010	<0.010	0,027	0,017	<0.010	<0.010	0,024	<0.010	12,06
Site name 24	10	7	18	216	0,042	<0.010	0,022	0,020	0,071	0,017	<0.010	<0.010	18,77
Site name 25	6	2	9	163	0,055	<0.010	0,018	0,013	0,116	0,018	<0.010	<0.010	18,33
Site name 26	564,3	9,895	19,2331	2939,319	0,033	0,215	<0.010	0,015	0,029	<0.010	<0.010	0,013	44,579
Site name 27	34,062	38,3225	62,8571	765,2475	0,019	<0.010	<0.010	0,013	0,026	<0.010	<0.010	0,017	11,327

Observation: All ions including TH and TDS are expressed in mg/L while EC in µS/cm.

Table 3: Laboratorial physicochemical analysis of surface water and rain water samples

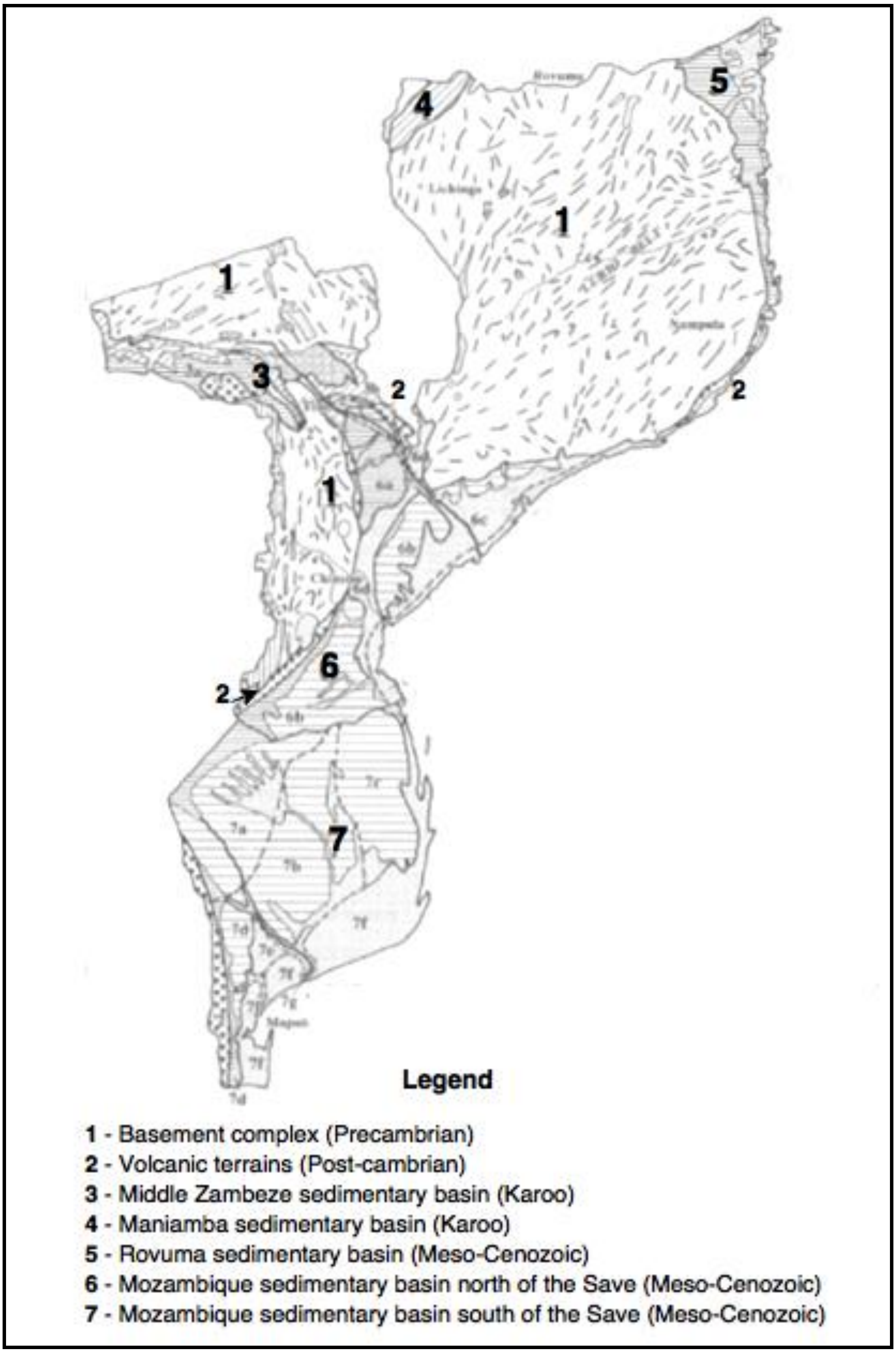
Site name	pH	EC	Ca	Mg	Na	K	HCO_3	F	Cl	NO2(N)	Br	NO3(N)	PO4	SO4
Site name 1	7,09	444	23,3	21,1	53,7	7,74	146	0,0436	66,5	-0,01	0,1906	-0,05	-0,1	13,8977
Site name 2	8,02	521	28,9	22,9	62,2	4,38	136	0,1001	79,9	-0,01	0,3108	0,059	-0,1	54
Site name 3	8,04	533	28,4	22,6	60,8	4,07	138	0,0097	84,25	-0,01	0,247	-0,05	-0,1	54,8
Site name 4	8,08	508	31,5	23,7	58,7	4,08	135	0,0386	79,4	-0,01	0,277	-0,05	-0,1	55,9
Site name 5	8,06	520	26,5	21,2	58,4	3,97	137	0,489	82,6	-0,01	0,2859	-0,05	-0,1	55,6
Rain water	6,25	10,6	1,58	1,148	19,722	1,5755	23,7	0,0269	17,1953	-0,01	0,0407	0,8793	-0,1	5,109

Site name	Ca H	Mg H	TH	TDS (sum)	Al	As	Cr	Cu	Fe	Mn	Pb	Zn		Si
Site name 1	58,25	86,51	144,76	332,1077	0,11	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0,96	
Site name 2	72,25	93,89	166,14	388,8092	0,17	<0.01	<0.01	0,01	0,05	0,03	<0.01	0,01	4,23	
Site name 3	71	92,66	163,66	392,8125	0,12	<0.01	<0.01	<0.01	0,01	0,03	<0.01	0,01	4,13	
Site name 4	78,75	97,17	175,92	388,2314	0,09	<0.01	<0.01	<0.01	0,02	<0.01	<0.01	<0.01	4,38	
Site name 5	66,25	86,92	153,17	385,6807	0,1	<0.01	<0.01	<0.01	0,02	0,02	<0.01	<0.01	4,7	
Rain water	3,95	4,7068	8,6568	73,84687	0,015	<0.010	0,018	0,013	0,017	0,01	<0.010	<0.010	2,056	

Note: All ions including TH and TDS are expressed in mg/L while EC in µS/cm.

Appendix 3

MOZAMBIQUE HYDROGEOLOGICAL PROVINCES MAP



Source: Adapted from Bouman and Ferro (1987).

Appendix 4

STUDY AREA HYDROCENSUS DATA

Table 1: Water source and hydrocensus data part 1

Site name	Coordinates[(1)]		Filed parameters				Surface water sources			Groundwater sources			Observation		
	Latitude	Longitude	pH	EC	TDS	WL	River	M canal	Swamp	BH	HP	Well	FA	Non-FA	Other
Site name 1	-24.42635	32.85309	7,56	512	364	-			x				x		
Site name 2	-24.40986	32.87623	8,35	600	425	-	x						x		
Site name 3	-24.41488	32.86105	8,61	607	430	-		x					x		
Site name 4	-24.67097	33.08926	8,33	969	685	5,9					x		x		
Site name 5	-24.66496	33.09367	8,44	698	497	5,55						x	x		
Site name 6	-24.66421	33.09378	7,66	1377	967	7,4						x	x		
Site name 7	-24.66458	33.08686	6,88	1040	736	4,8						x	x		
Site name 8	-24.66276	33.08618	6,80	1632	758	6,2					x		x		
Site name 9	-2462420	33.11279	7,97	1514	812	7,5				x				x	
Site name 10	-24.66945	33.09317	8,45	594	424	-		x					x		
Site name 11	-24.52446	33.00236	8,15	616	439	8,17				x				x	
Site name 12	-24.52398	33.00422	8,19	609	429	-		x					x		
Site name 13	-24.52425	32.99131	8,15	632	448	9,15				x				x	
Site name 14	-24.52201	32.98817	8,17	629	448	7,7				x				x	

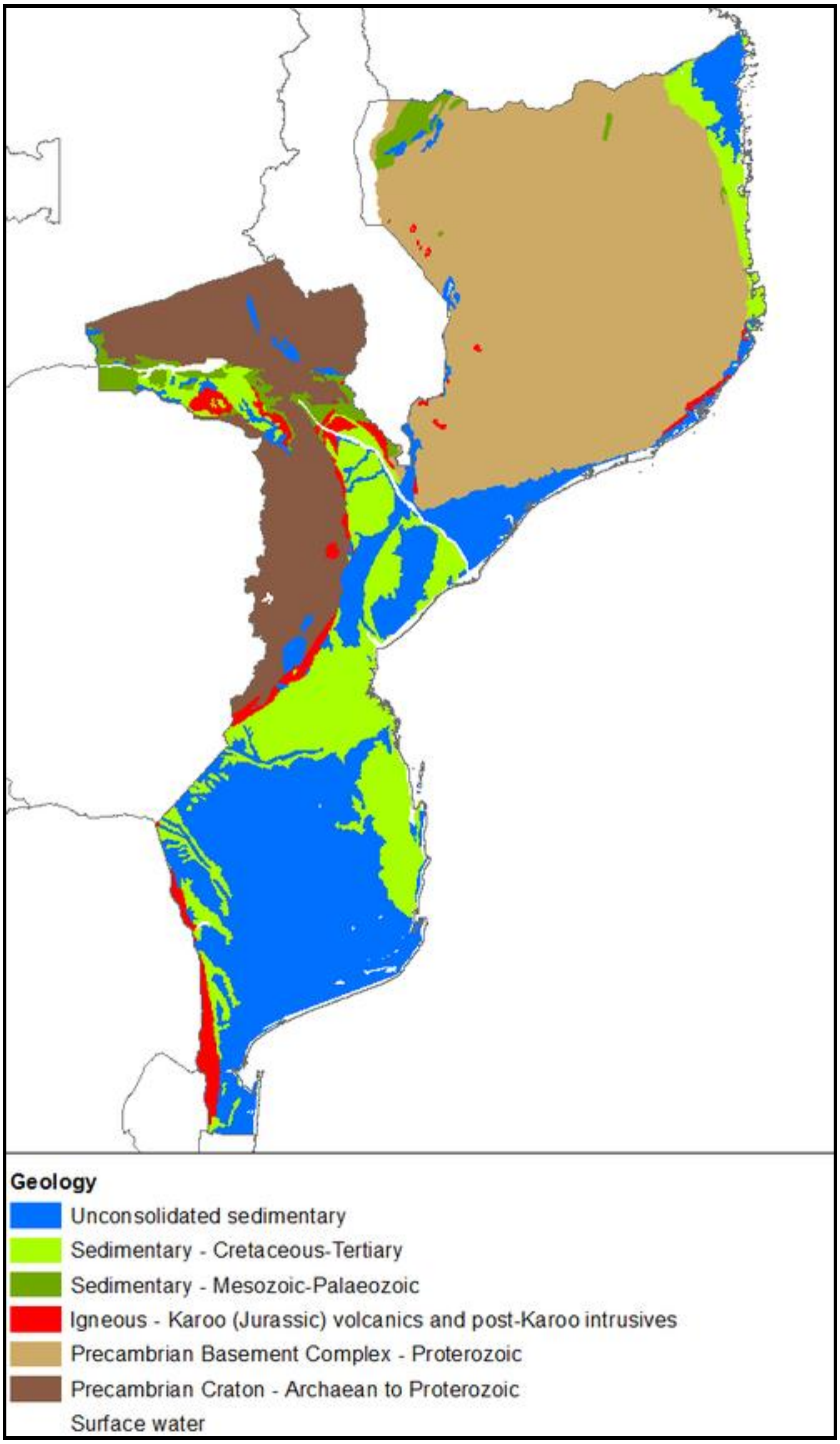
Note: (1) = the coordinates are in decimal degrees; FA = farming area; Non-FA = Non farming area; M canal = Main canal

Table 2: Water source and hydrocensus data part 2

Site name	**Coordinates**		**Filed parameters**				**Surface water sources**			**Groundwater sources**			**Observation**		
	Latitude	Longitude	pH	EC	TDS	WL	River	M canal	Swamp	BH	HP	Well	FA	Non-FA	Other
Site name 15	-24.59943	32.94955	7.49	5460	3830	9.00					x			x	
Site name 16	-24.60213	32.79399	7.30	3250	2280	8.60					x			x	
Site name 17	-24.38711	32.78412	6.77	5310	3,75	12.65					x			x	
Site name 18	-24.32168	32.76311	6.46	10400	7330	10.50					x			x	
Site name 19	-24.31783	32.76396	7.58	2180	1550	9.75					x			x	
Site name 20	-24.42812	32.84720	7.43	1243	880	11.00					x		x		
Site name 21	-24.58791	33.06437	8.17	989	708	6.80				x			x		
Site name 22	-24.81068	33.13171	6.96	942	666	10.35					x			x	
Site name 23	-24.8094	33.13360	5.46	1058	750	8.10					x			x	
Site name 24	-24.81137	33.13228	5.78	856	609	11.10					x			x	
Site name 25	-24.80514	33.13248	5.63	824	589	9.58					x			x	
Site name 26	-24.78663	33.13548	5.87	3000	2120	6.85					x			x	
Site name 27	-24.53050	32.99670	7.95	812	578	7.12				x				x	
Site name 28	-24.68399	33.02271	7.21	2570	1810	5.60				x			x		
Site name 29	-24.78633	33.13656	5.98	427	303	6.91						x			
Site name 30	-24.78733	33.13648	5.75	285	204	7.43						x			
Site name 31	-24.53000	33.02000	-	-	-	-									
Site name 32	-24.58224	33.06148	7.95	3760	2640	7,76					x				
Site name 33	-24.59279	33.03267	7.60	1296	921	8.59					x				

Appendix 5

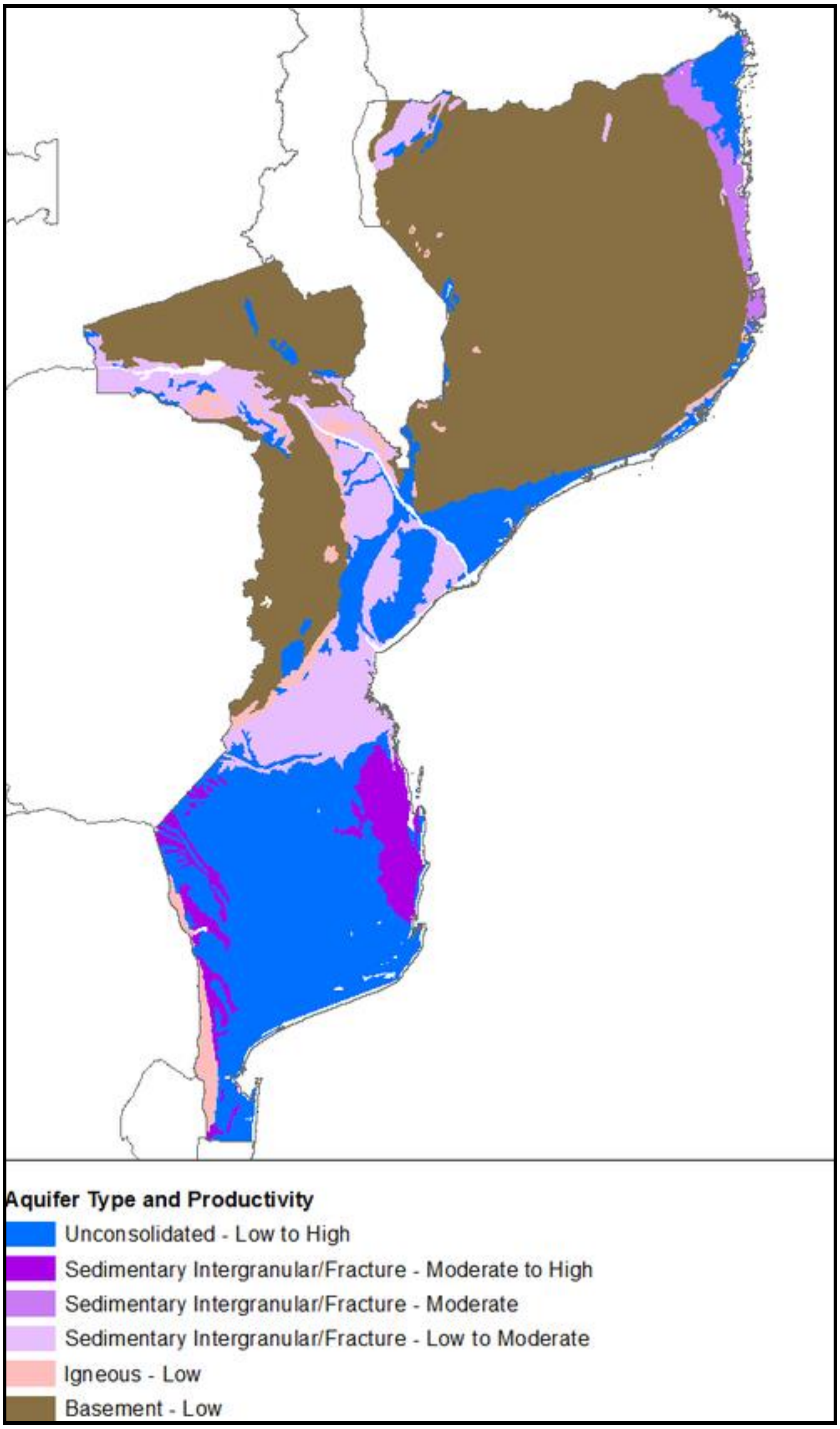
GEOLOGY MAP OF MOZAMBIQUE



Source: Chairuca *et al*. (2016)

Appendix 6

AQUIFER PRODUCTIVITY OF MOZAMBIQUE



Source: Chairuca *et al*. (2016)

Appendix 7
RESULTS OF ANOVA AND T-TEST

Table 1: ANOVA for EC between ASSG and EFCS geological unit

F-Test Two-Sample for Variances		
	Variable 1	*Variable 2*
Mean	2363.875	2283.555556
Variance	15218771.55	4085619.528
Observations	8	9
Df	7	8
F	**3.724960548**	
P(F<=f) one-tail	0.042552854	
F Critical one-tail	**3.500463855**	

Table 2: ANOVA for EC between ASSG and IDRAS geological unit

F-Test Two-Sample for Variances		
	Variable 1	*Variable 2*
Mean	2363.875	948.4285714
Variance	15218771.55	716123.619
Observations	8	7
Df	7	6
F	**21.2515984**	
P(F<=f) one-tail	0.000781574	
F Critical one-tail	**4.206658488**	

Table 3: ANOVA for EC between EFCS and IDRAS geological unit

F-Test Two-Sample for Variances		
	Variable 1	*Variable 2*
Mean	2283.555556	948.4285714
Variance	4085619.528	716123.619
Observations	9	7
Df	8	6
F	**5.705187511**	
P(F<=f) one-tail	0.023905464	
F Critical one-tail	**4.146804162**	

Table 4: t-Test for EC mean value between ASSG and EFCS geological unit

t-Test: Two-Sample Assuming Unequal Variances		
	Variable 1	*Variable 2*
Mean	2363.875	2283.556
Variance	15218772	4085620
Observations	8	9
Hypothesized Mean Difference	0	
Df	10	
t Stat	**0.052324**	
P(T<=t) one-tail	0.47965	
t Critical one-tail	**1.812461**	
P(T<=t) two-tail	0.959301	
t Critical two-tail	2.228139	

Table 5: t-Test for EC mean value between ASSG and IDRAS geological unit

t-Test: Two-Sample Assuming Unequal Variances		
	Variable 1	*Variable 2*
Mean	2363.875	948.4286
Variance	15218772	716123.6
Observations	8	7
Hypothesized Mean Difference	0	
Df	8	
t Stat	**0.99971**	
P(T<=t) one-tail	0.173363	
t Critical one-tail	**1.859548**	
P(T<=t) two-tail	0.346725	
t Critical two-tail	2.306004	

Table 6: t-Test for EC mean value between EFCS and IDRAS geological unit

t-Test: Two-Sample Assuming Unequal Variances		
	Variable 1	*Variable 2*
Mean	2283.556	948.4286
Variance	4085620	716123.6
Observations	9	7
Hypothesized Mean Difference	0	
Df	11	
t Stat	**1.790124**	
P(T<=t) one-tail	0.050482	
t Critical one-tail	**1.795885**	
P(T<=t) two-tail	0.100965	
t Critical two-tail	2.200985	

Table 7: ANOVA for TDS between ASSG and EFCS geological unit

F-Test Two-Sample for Variances

	Variable 1	*Variable 2*
Mean	1621.024	1497.781
Variance	5916950	1574009
Observations	8	9
Df	7	8
F	**3.759159**	
P(F<=f) one-tail	0.041542	
F Critical one-tail	**3.500464**	

Table 8: ANOVA for TDS between ASSG and IDRAS geological unit

F-Test Two-Sample for Variances

	Variable 1	*Variable 2*
Mean	1621.024	581.6971
Variance	5916950	310478.7
Observations	8	7
Df	7	6
F	**19.05751**	
P(F<=f) one-tail	0.001061	
F Critical one-tail	**4.206658**	

Table 9: ANOVA for TDS between EFCS and IDRAS geological unit

F-Test Two-Sample for Variances

	Variable 1	*Variable 2*
Mean	1497.781	581.6971
Variance	1574009	310478.7
Observations	9	7
Df	8	6
F	**5.06962**	
P(F<=f) one-tail	0.031629	
F Critical one-tail	**4.146804**	

Table 10: t-Test for TDS mean value between ASSG and EFCS geological unit

t-Test: Two-Sample Assuming Unequal Variances		
	Variable 1	*Variable 2*
Mean	1621.024	1497.781
Variance	5916950	1574009
Observations	8	9
Hypothesized Mean Difference	0	
Df	10	
t Stat	**0.128875**	
P(T<=t) one-tail	0.450006	
t Critical one-tail	**1.812461**	
P(T<=t) two-tail	0.900011	
t Critical two-tail	2.228139	

Table 11: t-Test for TDS mean value between ASSG and IDRAS geological unit

t-Test: Two-Sample Assuming Unequal Variances		
	Variable 1	*Variable 2*
Mean	1621.024	581.6971
Variance	5916950	310478.7
Observations	8	7
Hypothesized Mean Difference	0	
Df	8	
t Stat	**1.173821**	
P(T<=t) one-tail	0.137113	
t Critical one-tail	**1.859548**	
P(T<=t) two-tail	0.274225	
t Critical two-tail	2.306004	

Table 12: t-Test for TDS mean value between EFCS and IDRAS geological unit

t-Test: Two-Sample Assuming Unequal Variances		
	Variable 1	*Variable 2*
Mean	1497.781	581.6971
Variance	1574009	310478.7
Observations	9	7
Hypothesized Mean Difference	0	
Df	12	
t Stat	**1.956462**	
P(T<=t) one-tail	0.037044	
t Critical one-tail	**1.782288**	
P(T<=t) two-tail	0.074088	
t Critical two-tail	**2.178813**	

Appendix 8
HYDROGEOCHEMICAL PROCESSES RATIOS

Table 1: Hydrogeochemical ratios in groundwater part 1

Site Name	TDS (mg/L)	HCO_3/SiO_2	CAI_1	CAI_2	Na/Cl	Ca/Mg
Site name 1	671.4147	5.289	-0.218	-0.096	3.256	0.897
Site name 2	487.977	3.672	-2.586	-1.088	3.559	2.957
Site name 3	923.054	6.164	-1.440	-0.901	2.365	2.923
Site name 4	698.988	12.035	-0.025	-0.019	0.988	1.010
Site name 5	1013.680	13.573	-0.395	-0.382	1.379	1.066
Site name 6	7625.560	10.002	0.321	2.112	0.675	0.990
Site name 7	1237.025	4.843	0.257	2.095	0.734	0.980
Site name 8	909.326	10.061	-3.904	-1.129	4.872	1.040
Site name 9	638.195	8.922	-1.014	-1.001	1.989	0.990
Site name 10	483.656	0.300	-0.066	-0.740	0.961	0.207
Site name 11	526.467	0.131	0.012	0.258	0.889	0.116
Site name 12	437.091	0.732	-0.089	-0.605	0.996	0.376
Site name 13	439.430	0.203	-0.116	-0.977	1.028	1.058
Site name 14	1806.393	1.326	-0.227	-0.975	1.202	0.408
Site name 15	216.040	0.374	-0.139	-0.438	1.045	4.926
Site name 16	162.803	0.316	-0.922	-1.121	1.769	2.577
Site name 17	1106.564	7.672	-0.137	-0.321	1.128	0.980
Site name 18	405.930	6.715	-0.949	-0.720	1.920	1.015
Site name 19	416.681	7.866	-1.456	-1.010	2.424	1.050
Site name 20	407.475	8.147	-1.339	-0.955	2.309	0.900
Site name 21	3537.373	5.664	0.111	1.200	0.884	1.010
Site name 22	2103.418	8.798	-0.211	-0.556	1.201	1.010
Site name 23	3318.743	6.521	0.507	3.732	0.487	1.000
Site name 24	493.066	8.309	-0.595	-0.651	1.574	0.980
Site name 25	1690.778	8.220	-0.208	-0.821	1.199	0.950
Site name 26	2939.31948	10.616	-4.287	-1.180	5.282	0.920
Site name 27	765.247	8.591	-0.318	-0.565	1.300	0.960

Table 2: Hydrogeochemical ratios in groundwater part 2

Site Name	Ca/Ca+SO4	Ca+Mg/HCO3+SO4	Na+K-Cl/Na+K-Cl+Ca	Na-Cl/Ca+Mg-SO4-HCO3
Site name 1	0.137	0.069	0.969	-1.074
Site name 2	0.284	0.102	0.947	-1.199
Site name 3	0.268	0.190	0.889	-1.054
Site name 4	0.829	1.060	0.033	-0.154
Site name 5	0.629	0.815	0.476	-1.984
Site name 6	0.686	3.828	3.428	-0.758
Site name 7	0.919	3.643	3.921	-0.821
Site name 8	0.416	0.182	0.941	-1.370
Site name 9	0.386	0.273	0.901	-1.345
Site name 10	0.220	0.992	0.813	54.510
Site name 11	0.259	2.280	12.260	-1.916
Site name 12	0.168	0.322	0.873	0.036
Site name 13	0.342	1.002	0.715	143.766
Site name 14	0.195	0.669	0.834	-2.622
Site name 15	0.267	0.434	0.633	-0.252
Site name 16	0.148	0.187	0.893	-1.151
Site name 17	0.532	0.809	0.538	-1.569
Site name 18	0.584	0.331	0.837	-1.044
Site name 19	0.393	0.181	0.931	-1.206
Site name 20	0.399	0.162	0.933	-1.114
Site name 21	0.742	3.381	-12.147	-0.529
Site name 22	0.377	0.835	0.636	-3.196
Site name 23	0.800	4.737	1.958	-1.011
Site name 24	0.602	0.414	0.783	-1.072
Site name 25	0.397	0.618	0.785	-2.062
Site name 26	0.017	0.021	0.994	-1.204
Site name 27	0.519	0.488	0.755	-1.042

Table 3: Hydrogeochemical ratios in surface water and rain water part 1

Site name	TDS (mg/L)	HCO_3/SiO_2	CAI_1	CAI_2	Na/Cl	Ca/Mg
Site name 1	332.108	69.809	-0.539	-0.509	1.229	0.663
Site name 2	388.809	14.758	-0.471	-0.455	1.185	0.757
Site name 3	392.813	15.338	-0.280	-0.267	1.098	0.754
Site name 4	388.231	14.148	-0.330	-0.315	1.125	0.797
Site name 5	385.681	13.380	-0.222	-0.209	1.076	0.750
Rain water	73.847	5.291	-0.448	-0.448	1.745	0.826

Table 4: Hydrogeochemical ratios in surface water and rain water part 2

Site name	$Ca/Ca+SO_4$	$Ca+Mg/HCO_3+SO_4$	Na+K-Cl/Na+K-Cl+Ca	$Na-Cl/Ca+Mg-SO_4-HCO_3$
Site name 1	0.801	1.090	0.352	1.809
Site name 2	0.562	1.000	0.270	-358.757
Site name 3	0.554	0.970	0.194	-2.349
Site name 4	0.575	1.051	0.198	1.646
Site name 5	0.534	0.908	0.175	-0.573
Rain water	0.426	0.353	0.837	-1.143