

DETERMINATION OF IRRIGATION WATER QUALITY OF SURFACE AND GROUNDWATER IN LUVUVHU CATCHMENT IN LIMPOPO, SOUTH AFRICA



BY

VHONANI G. NETHONONDA

Submitted to

THE FACULTY OF SCIENCE AND AGRICULTURE

in partial fulfillment of the requirement for the degree of

Masters of Science

in the Department of Hydrology at the University of Zululand,

KwaDlangezwa

Supervisor:

Prof. Vetrimurugan Elumalai

March 2018

DECLARATION

I declare that the thesis titled “Determination of irrigation water quality of surface and groundwater in Luvuvhu catchment in Limpopo, South Africa” is the original work duly performed by the author in the Faculty of Science and Agriculture at the University of Zululand. The same work has never been performed and published by anyone from Zululand University and other institutions.

..... Date: 15.03.2018
Vhonani G. Nethononda

APPROVAL:

Supervisor: Prof. V.Elumalai_____Date:_____

HOD: Mr. Brian K Rawlins_____Date:_____

CONTRIBUTION TO THE BODY OF KNOWLEDGE

The results from the research have been submitted in two peer-reviewed journals and presented an article in International conference of which the papers are attached in the APPENDIX:

Article:

1. Chemical constituents in groundwater and multivariate statistical analysis in the upper part of Luvuvhu catchment, Limpopo, South Africa. Springer Chemistry Central Journal.
2. Irrigation return flow induced mineral weathering and ion exchange reactions in the aquifer, Limpopo province, South Africa. Springer Environmental Science and Pollution Research.

Conference:

1. V.G. Nethononda and Vetrimurugan Elumalai “Hydrogeochemical Characterization of groundwater quality in irrigated region of part of Luvuvhu catchment, Limpopo, South Africa” July 9-15, IAHS Scientific Assembly 2017.

ACKNOWLEDGEMENTS

I would like to send my sincere gratitude to my Supervisor Prof.V Elumalai for the unending support in the completion of this thesis. I would also like to acknowledge the Department of Research and Innovation in University of Zululand for financial assistance. The Department of Agriculture in University of Zululand assisted me with chemical analysis. I thank the Department of Hydrology for their extended support in successful completion of this work.

Furthermore, I would like to acknowledge and express my appreciation to my family and friends, who supported me throughout this period.

ABSTRACT

Rapid economic expansion and intensive irrigation activities constitute significant threat to groundwater depletion. This study emphasized on the surface water quality and groundwater quality for irrigation purpose by adopting multivariate statistical methods and the hydrochemical processes and on the probable groundwater contamination in the Luvuvhu catchment Limpopo province. Groundwater samples were collected from 41 wells during 2015 and 2016; and seven samples were collected from Luvuvhu River. The physical parameters pH, EC, TDS, temperature and ORP were measured in the field. Major ion Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- and nitrate were analyzed. The pH values indicate that groundwater is acidic in nature during 2015 and 2016. TDS values indicate that groundwater is fresh in nature. The dominant sequence of cations is presented as $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ while that of anions as $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ in the year 2015 and 2016. The Piper and Chadha plots show that the dominant water types are $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ and $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-$. Gibbs plot reveals that the chemistry of water was influenced by rock-water interaction. Bivariate plots indicate the dissolution of carbonate and silicate minerals, reverse ion exchange and anthropogenic activities influenced the water chemistry in the study area. Groundwater was saturated and oversaturated with respect to calcite and dolomite and undersaturated with gypsum and halite. High nitrate concentration resulted from agricultural and farming activities and leakage of sewage system. Temporal groundwater fluctuations indicates that recharge processes decrease the concentration of ions in groundwater by mixing of infiltrated fresh water with groundwater. Factor analysis revealed that the two main factors of 80.68% and 79.95% of total variance for both years. These factors indicate the impact of irrigation return flows, human disposals and usage of K^+ and NO_3^- fertilizers. Electrical conductivity, pH and the concentration of Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- exceeded the drinking water quality standards prescribed by the DWAF on few samples. DWQI classification results show that 1% and 2% of samples indicate excellent, 49% and 49% specify good, 27% and 29% shows poor, 7% and 10% of very poor, 16% and 10% of unsuitable during 2015 and 2016, respectively. Sodium percentage, residual sodium carbonate and permeability index reveals that surface water and groundwater is suitable for irrigation. USSL diagram suggests that surface water and groundwater is suitable for irrigation with low alkali hazards which represents

excellent water quality for irrigation purpose. This study results revealed the divergent methods are significant for the combined evaluation of the natural processes and groundwater contamination. It contributes a technological basis for the strategic future development where broad organization will be useful for public. However, the study suggest for intensive monitoring to detect the anthropogenic and other contamination elements in the groundwater and surface water to produce quality yield.

Table of Contents

Declaration.....	ii
Acknowledgements.....	iii
Abstract.....	iv
Table of Contents.....	v
List of Figures.....	viii
List of Tables.....	ix
List of Abbreviations.....	x
CHAPTER ONE: INTRODUCTION.....	
.....	1
INTRODUCTION.....	1
1.1 General.....	1
1.2 General Hydrochemistry.....	3
1.3 Surface Water Quality.....	4
1.4 Groundwater Quality.....	5
1.5 Composition of groundwater.....	5
1.6 Aim of the study.....	6
1.7 Objectives.....	6
1.8 Problem statement.....	7
1.9 Thesis outline.....	8
2 Literature Review.....	9
2.1 Introductions.....	9
2.2 Hydrochemistry and groundwater quality assessment.....	10
2.3 Hydrogeochemical processes.....	13
2.4 Previous works attempted from the study area.....	16
3 Study area.....	19
3.1 Location.....	19
3.2 Topography.....	20
3.3 Climate and Rainfall.....	20
3.4 Drainage.....	20
3.5 Geohydrology.....	21

3.6	Geology and hydrogeology	21
3.7	Land use and irrigational use	22
4	Methodology	24
4.1	Introduction	24
4.2	Maps preparation	24
4.3	Field Survey	24
4.4	Water sampling	25
4.5	Water analysis	25
4.6	Software employed	26
5	Hydrogeochemical processes on temporal changes in groundwater quality	27
5.1	Introduction	27
5.2	Multivariate statistical technique	29
5.3	GIS analysis	29
5.4	Hydrochemistry	29
5.4.1	Hydrochemical facies of groundwater	33
5.4.2	Gibbs Plots	36
5.4.3	Soltan Classification	37
5.4.4	Hydrogeochemical processes	38
5.5	Geochemical Modelling	45
5.6	Land use	47
5.7	Relation between temporal groundwater level fluctuations	48
5.8	Multivariate Statistics	49
5.9	Conclusion	53
6	Evaluation of Surface and Groundwater Quality for Drinking and Irrigation purposes ..	55
6.1	Introduction	55
6.2	Water quality Assessment	57
6.3	Spatial Interpolation	58
6.4	Statistical Analysis	58
6.5	General water chemistry	59
6.6	Groundwater suitability assessment	59
6.7	Groundwater suitability assessment using DWQI	66
6.8	Irrigation water quality assessment	70
6.9	Conclusion	76
7	Conclusion	78
8	<u>REFERENCES:</u>	80

List of Figures

Figure 3.1: Location of the Study area	19
Figure 3.2: Geology of the area.....	22
Figure 5.1a, b: Box Whisker plots of groundwater parameters in the year of 2015 and 2016	31
Figure 5.2: Groundwater classification using TH and TDS.....	32
Figure 5.3 a, b: Pie diagram of the mean concentrations of major cations and anions in the year 2015 and 2016.....	33
Figure 5.4: Hydrochemical facies of surface and groundwater (Piper 1944)	34
Figure 5.5: Hydrochemical facies of surface and groundwater (Chadha 1999).....	35
Figure 5.6: Gibbs diagram for both surface and groundwater	37
Figure 5.8: Plot of Na^+ vs Cl^- compared with freshwater evaporation line.....	39
Figure 5.9: Plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs HCO_3^- ; $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs TC, $\text{Na}^+ + \text{K}^+$ vs TC and $\text{Ca}^{2+}/\text{Na}^+$ vs $\text{HCO}_3^-/\text{Na}^+$ explains mineral weathering	40
Figure 5.10a, d: Plot of (a) Ca^{2+} vs HCO_3^- ; (b) Ca^{2+} vs SO_4^{2-} ; (c) $\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^-$ vs Cl^- ; (d) Sample location vs $\text{Ca}^{2+}/\text{Mg}^{2+}$	42
Figure 5.11a: Plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{HCO}_3^- + \text{SO}_4^{2-}$	43
Figure 5.11b: $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- - \text{SO}_4^{2-}$ vs $\text{Na}^+ - \text{Cl}^-$	43
Figure 5.11c: Relation between $\text{Ca}^{2+} + \text{Mg}^{2+}$ and Cl^-	44
Figure 5.11d: CAI1 vs CAI2.....	45
Figure 5.12: Saturation indexes (a) calcite, (b) dolomite, (c) gypsum, (d) halite versus sample numbers of groundwater	46
Figure 5.13: NO_3^- vs Cl^-	47
Figure 5.14: Cl^- vs SO_4^{2-}	48
Figure 5.15: Temporal variations in the major ions and groundwater level in the study area	49
Figure 5.16: Scree Plot of (a) 2015, (b) 2016 of groundwater	51
Figure 5.17: Spatial variation of (a), (b) factor 1 and (c), (d) factor 2 in 2015 and 2016 of groundwater	53
Figure 6.1: Hydrochemical parameters of groundwater based on DWAF (1996) and percentage of samples exceeding the limit	61
Figure 6.2: Spatial distribution of groundwater quality (a, b) pH, (c, d) EC, (e, f) Na^+ , (g, h) K^+ , (i, j) Ca^{2+} , (k, l) Mg^{2+} (m, n) Cl^- in the year of 2015 and 2016 of the study area	65
Figure 6.3: Relationship of water types and percentage of samples	68
Figure 6.4 a, b: Spatial distribution of DWQI during 2015 and 2016 in the study area	69
Figure 6.5 (a-h): Correlation of groundwater hydrochemical parameters with drinking water quality index (DWQI) a) EC versus DWQI b) Na^+ versus DWQI c) K^+ versus DWQI d) Ca^{2+} versus DWQI e) Mg^{2+} versus DWQI f) Cl^- versus DWQI g) HCO_3^- versus DWQI h) SO_4^{2-} versus DWQI in the year of 2015 and 2016	70
Figure 6.6: Wilcox diagram of surface water and groundwater	72
Figure 6.7: USSL diagram for surface and groundwater	74

LIST OF TABLES

Table 5.1	Descriptive statistical results of physicochemical parameters of groundwater in the study are	27
Table 5.2	Pearson correlation matrix of groundwater in 2015 and 2016.....	43
Table 5.3	Varimax rotation factor loadings.....	45
Table 6.1	Descriptive Statistical results of physicochemical parameters of groundwater in the study area.....	52
Table 6.2	Results of <i>t</i> test ($p < 0.05$) values.....	52
Table 6.3	Drinking water quality based on EC, TDS and TH in the year of 2015 and 2016 of groundwater.....	55
Table 6.4	Weights of parameters and DWAF standards.....	58
Table 6.5	Irrigation water quality of groundwater in the year of 2015 and 2016.....	64

LIST OF ABBRIVIATIONS

AgNO ₃	Silver nitrate solution
Ca ²⁺	Calcium ion
CA	Cluster Analysis
CaCO ₃ ⁻	Calcium carbonate
Cl ⁻	Chloride ion
CO ₃ ⁻	Carbonate
CV	Coefficient of variations
MAP	Mean Annual Precipitation
DA	Discriminant Analysis
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
DWQI	Drinking Water quality Index
DWS	Department of Water and Sanitation

EC	Electrical Conductivity
GPS	Global Positioning System
GIS	Geographic Information System
GWB 12	Geochemist's Workbench software
HCA	Hierarchical Cluster Analysis
HCO_3^-	Bicarbonate ion
HDPE	High-Density Polyethylene
IAP	Ion Activity Product
ICP-OES	Inductive Coupled Plasma Optical Emission Spectrophotometer
IDW	Inverse Distance Weighted
K^+	Potassium ion
K_2CrO_4	Potassium chromate
KR	Kelly's Ratio
K_s	Solubility Product
MAP	Mean Annual Precipitation
MR	Magnesium Ratio
meq/l	Milli equivalents per Litre
Mg^{2+}	Magnesium ion
mg/l	Milligrams per Litre
mS/m	MilliSiemens per meter
Na^+	Sodium ion
Na %	Sodium Percentage
NE	North East
NO_3^-	Nitrate ion
NW	North West
NWRS	National Water Resource Strategy
ORP	Oxidation Reduction Potential
PI	Permeability Index
r	Correlation coefficient
RSC	Residual Sodium Carbonate
SANS	South African National Standards
SAR	Sodium Adsorption Ratio
SAWQG	South African Water Quality Guidelines
SI	Saturation Index

SO ₄ ²⁻	Sulphate ion
SE	South East
SSP	Soluble Sodium Percentage
SW	South West
TDS	Total Dissolved Solids
TH	Total Hardness
TWQR	Target Water Quality Range
TZ ⁺	Total Cations
USSL	United State Salinity
WHO	World Health Organization
WMA	Water Management Area
WQI	Water Quality Index
WTW	Water Treatment Work

DETERMINATION OF IRRIGATION WATER QUALITY OF SURFACE AND GROUNDWATER IN LUVUVHU CATCHMENT IN LIMPOPO, SOUTH AFRICA

CHAPTER ONE

1 INTRODUCTION

1.1 General

Surface water and groundwater resources are important fresh water resources worldwide. These resources are being considered as the major component that forms part of the water cycle. Surface water is defined as water that flow/stored above the land or surface namely, rivers, streams, dams, wetland and fountains whereas groundwater is water found underground. Sources of groundwater are recharge from rain, snow, hail and surface water (Hiscock, 2005). The water infiltrates into the ground in perspective of gravity, penetrating the soil and rocks until it accomplishes a significance where the water cannot penetrate any longer and is stored. Aquifer is a geological formation underneath the surface of the earth which contains and permits water to flow. The pore spaces in aquifers are filled with water and are interconnected, so that water flows through them. This type of rocks supplies water for wells and springs. Groundwater is stored in an underground permeable and penetrable rock called an aquifer that allows the permeability of water and permits movement inside the rock. Water is one of the scarce resources in South Africa as compared to other countries. Previous studies denoted that around one third of the populace rely on groundwater for domestic use (Nickson et al, 2005). In many countries, the quality of groundwater is observed to be declining during previous years (Causape et al, 2003). The quality and quantity of groundwater is being affected and disrupted due to overutilization. The deterioration of water quality from several spheres of the world is caused by natural process and anthropogenic impacts (Pophare et al, 2014). Depending upon the types of ions concentration in groundwater, this resource can be used for different purpose.

Worldwide, groundwater resources are over utilized due to limited surface water resource. The groundwater quality is gradually deteriorating and risks to human health are anticipated. Therefore, to guarantee the suitability of water for human utilization, guidelines were produced by international and national organizations namely, Department of Water and Sanitation (DWS) and World Health Organization (WHO) to assess the water suitability for human consumption. The guideline rules are formed with an intention to protect consumer's health and safety. The set principles are numerical values for constituents of water or pointer of water quality (WHO, 2008). A few towns and rural areas of South Africa depend on groundwater for water requirements (i.e. Polokwane Town). Various towns utilize both groundwater and surface water conjunctively depending on water quantity and quality. The quality and quantity of groundwater from Luvuvhu sub-catchment is not known (NWRS, 2004). Due to limited surface water resources within the region, groundwater is viewed as an essential resource to supply the required demand for both human and economic advancements. Groundwater as a fundamental resource should be observed against contamination activities since it is a valuable resource (NJDEP, 2012). The water resources should be utilised sparingly for both economic and social needs in an efficient way for now and future eras (NWA, 1998). Groundwater and surface water resources in South Africa has been severely contaminated and exposed to pollution more especially in the cities (NWQMC, 2007). The main cause of pollution identified is non-point and point sources. The high concentration of ions had an enormous effect in the consumption of the surface water and groundwater assets (Ritchie, 2000). The appraisal and assessment of water resources are essential to observe the suitability of water versus water use. In the Luvuvhu sub-catchment, groundwater resource is mainly exposed to non-point source of pollution due to extensive agricultural practices (Snyder et al, 1998). Farmers apply agrochemicals and fertilizers that seep into groundwater that might pollute groundwater, which discharge into rivers and other waterbodies (Cochran, 2011).

In the Luvuvhu catchment, groundwater resource is the most dependable source of water; hence, farming exercises and residential utilization depend on the previously mentioned resource (NWRS, 2004). The area of study was used for agriculture and settlement for decades (over 50 years) and application of

agrochemicals and pesticides are very common for good crop production. The natural factors such as rainfall, runoff, infiltration and percolation processes are anticipated to influence the major ions in groundwater and widely spread the major ions from irrigated land. The distributions and diversity of the major ions in the study area are presently not identified and similar studies are limited. This study will principally concentrate on surface water and groundwater quality examination.

1.2 General Hydrochemistry

The chemical nature of groundwater is a broad concept, which involves several aspects including precipitation, soil permeability, aquifer formation, geological structure, rock water interaction, mineral occurrence, return flows from agricultural land and industries and domestic waste (Vetrimurugan et al. 2016). In order to use groundwater resource efficiently, effectively and sustainably, geochemical evolution is utmost important and there is a need to emphasize it. The relationship between geology and ionic concentration in the surface water and groundwater should be scientifically studied and recommended to monitor regularly (Srinivasamoorthy et al, 2011).

Groundwater chemistry comprises of large soluble constituents from soil minerals and sedimentary rocks (Water watch, 2005). The lesser part mainly originates from surface water bodies and in the atmosphere. The 95% of groundwater ions are characterized by the negatively charged anions (Cl^- , HCO_3^- , SO_4^{2-} , NO_3^-) and the positively charged cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+). The total cations and anions represent total dissolved solids (TDS) (Bhatt and Saklani, 1996). The undertaking of investigations on hydrochemistry of groundwater through monitoring is a pillar to human health and life as it gives caution more especially in areas that are severely contaminated. Hence, groundwater studies are encouraged for the benefit of now and future generations (Kumar et al, 2006). This study will uncover the geochemical processes dominated in Luvuvhu catchment.

1.3 Surface Water Quality

River water is considered as the most accessible resource and cost effective because it is naturally flowing/stored on the surface and utilised for drinking, irrigation and industries. The surface water run-off from contaminated area that flows to streams connected to main rivers ends up polluting ocean due to contaminated discharges (Trivedi et al, 1990). The complexity of surface water is the chemical system composed of organic substances as well as minerals.

The natural water resources are known to acquire minerals, gases, trace elements, minor ions as well as major ions during precipitation from atmosphere as well as surface soil and this was scientifically proven that it has never been free from ions. Substances dissolved in water reflected the different properties of water such as acidity, alkalinity, salinity, hardness and corrosivity (Daniel et al, 1998). The local geology, topography, hydrology and weather contributed an important part in water chemical compositions (Muller, 2001).

The change in the quality of the surface water resources is becoming a problem due to speedy growing of developments that end-up polluting water. The high standard of living requires increase in developmental activities such as mining, industries, power generation and irrigation, which has impacts on the both quality and quantity of the water resources (Raj, 1997). The flow regime, biota and the structure of rivers and streams vigorously changes due to natural occasion and human activities. Alterations of the characteristics of the bed, banks of the riverine impose alterations in the physical and chemical arrangement of the water resources (Buck and Quadir, 2012). The agricultural activities mainly change the characteristics of water resources due to cultivation on the riverbanks and run-off (Shiklomavon, 1989). Therefore, it is generous to guarantee that the physical and natural attributes of the surface water resource are mainly disturbed through human activities. River health programmes that study the biological life of aquatic ecosystems reflect types of water uses in the catchment and the anticipated impacts. Hence, the quality of freshwaters are being compromised and become scarce due to pollution and overexploitation by the water users. The understanding of natural water chemical composition and related properties are crucial to identify the problems for consumption and irrigational use. The fitness of water to a particular usage is

determined by the water chemical composition and water quality assessment (Stach, 1993).

1.4 Groundwater Quality

The quality of water is influenced by an extensive variety of natural processes and anthropogenic activities that alter the chemical compositions of the water. This variability of the water quality occurs with depth and geographic separations; this is a consequence of a couple of procedures that affect the water in the distinctive situations it experiences (Al-Aboodi, 2008). These components generally consolidate the disintegration of ions in soils, deposit and rocks (Nur et al., 2012). Anthropogenic effects primarily integrate effluents created by manmade activities, rural, urban and manufacturing action (Beamonte et al. 2007).

General consequences for water quality fundamentally relies upon the chemical nature of the initial water, the rock composition underneath and the flow path of the water as it controls the event, grouping, rates and progress of the reaction (Hiscock, 2005). The hydrogeochemical studies provide knowledge and understanding of the influences of rock water association and anthropogenic consequences for groundwater quality. This methodology or geochemical frameworks are in charge of the infrequent and spatial assortments in groundwater chemistry (Matthess, 1982; Kumar et al. 2006). Groundwater chemistry governed by the mixture of water with aquifer minerals or concentrated solute mix among various groundwaters along the stream route in the subsurface (Domenico 1972; Wallick and Toth 1976; Toth 1984).

1.5 Composition of groundwater

There are few components that controls groundwater chemistry namely precipitation , topography, mineralogy of the watersheds, aquifers and land frames inside the aquifer together with impact of external contamination like effluents from agricultural return flows, mechanical and local exercises (Milovanovic, 2007).

An understanding of the geochemical development of groundwater resource is necessary for changes of water resources in the current situation. In the Luvuvhu catchment, the groundwater resource is mainly exposed to non-point source pollution because of high agricultural practices in the province (Snyder et al, 1998). The Luvubu farming land was utilised for agricultural activity for decades and farmers apply pesticides and fertilizers, which percolates in the vadose zone and pollute groundwater, which also pollutes river during discharge. Therefore, the understanding of water quality and hydrogeochemical processes will help for the effective water resource management.

There are four significant measures that are utilized to decide the appropriateness of groundwater for irrigation water namely; sodium hazard, salinity hazard, magnesium ratio and residual sodium carbonate hazard (Michael, 1978). The water utilized for irrigation can likewise shift incredibly in quality relying on dissolved salts quantity and nature. In flooded farming lands, saltwater intrusion is likely a consistent risk. Low quality on water resources turns out to be more worry when climate changes from wet to completely dry conditions (Rowe et al, 1995). The review of previous writings indicated that there are no known studies made to understand the hydrogeochemical processes responsible for groundwater chemistry. Hence, water quality assessment was carried out in the study area.

1.6 Aim of the study

To determine the surface water and groundwater suitability for irrigation uses in Luvuvhu catchment, Limpopo in South Africa. To determine the suitability of irrigation water quality of surface and groundwater in Luvuvhu catchment, Limpopo, South Africa

1.7 Objectives

- To determine the spatial distribution and temporal variation in the major ion chemistry of groundwater.
- Identify the geochemical processes regulate water chemistry in the study site.

- To assess the groundwater suitability - for irrigation and other utilizations.

1.8 Problem statement

The key aspects contributing to the deterioration of groundwater quality in South Africa are salinization, agriculture and acidification (Hoffman, 1980). Groundwater salinity is a major problem in South Africa that reduces crop production specifically to areas with rapid population growth and limited water resources (Balls, 1994). Affected farmers are compelled to use groundwater of poor quality for irrigation. This is a relatively high potential threat that has a limiting factor in crop production (Munns, 2002). Previous studies shows that the large portion of water consumption in South Africa is mainly for farming which probably accounts for 62% of total water uses in the country (DWA, 2004a). Agriculture also influences negative impacts on groundwater quality, specifically through return flows from irrigated land and this contributes to the deterioration of groundwater quality (McArthur et al, 2001). The application of fertilisers in soils results in environmental degradation and elevated uptake of the latter by crops (Balls et al, 1995). Chemical substances are being washed into water bodies via runoff and infiltration process leads to resource contamination (Muchuweti et al, 2006). Water infiltrates into the soil and rocks slowly recharging the groundwater (WRC, 2002). Considering the previous studies, it was found that frequent application of fertilisers result groundwater contamination there by reducing the available quantity of good quality water (Halvorsen et al, 2015).

It is crucial to study the groundwater dynamics and geohydrochemical processes of Luvuvhu catchment because farmers and communities mainly depend on groundwater resource. The poor quality of groundwater will affect the agricultural yield and further reduces economic factor of Limpopo Province. Groundwater use has grown exponentially in scale and intensity in Luvuvhu catchment, which causes aquifer depletion (Giordano, 2009). The groundwater usage in Luvuvhu catchment is high and is mostly utilised for agriculture and domestic purposes. The unmonitored groundwater use has negative impact on agricultural production (DWA, 2004). The studies undertaken in Luvuvhu catchment focused on the water resource management, rainfall and groundwater modelling; hence, the current study will be

able to determine the surface water and groundwater quality and suitability for irrigation practices to understand overall hydrogeochemical processes in this aquifer.

1.9 Thesis outline

This report has seven chapters and details given below:

Chapter 1: Introduction

This section introduces subject and explains the present problems in the study region. It incorporates the general hydrochemistry, background of surface water and groundwater quality, research aim, objectives, problem statement, the importance of the study and research outline.

Chapter 2: Literature Review

This section is more concerned of the literature review associated to the study of groundwater quality for irrigation, hydrochemical facies, hydrogeochemical processes and previous studies conducted in the study area.

Chapter 3: Description of the study area

This chapter describes the study site details namely climate, topography, rainfall, drainage, geology, hydrogeology, land use and irrigation activities.

Chapter 4: Methodology

Methodology utilised for water collection, analysis and data interpretation was elaborated. This includes fieldwork, laboratory analysis (ICP spectrophotometer and titration methods) and data analysis using various methods.

Chapter 5: Hydrogeochemical processes

This chapter entails the data interpretation, presentation of results followed by the discussion. The hydrogeochemical facies, classical hydrochemical methods, correlation matrix and spatial distribution maps application were covered.

Chapter 6: Water quality assessment for various uses

This chapter explore the application of different methods to evaluate water quality for irrigation uses. The outcomes were compared with water quality norms or rules made by the international and national guidelines (World Health Organisation (WHO) and South African National Standard (SANS)).

Chapter 7: Conclusion

This chapter explains over all outcomes obtained from this study followed by the few recommendations to save and protect water resources in the study region.

Chapter 8: References

Concerned literatures were reviewed

CHAPTER TWO

2 Literature Review

2.1 Introductions

Groundwater is an important resource worldwide due to lack of surface water resources. The groundwater movements in the shallow aquifer are generally fast because of recharge and discharge structures (Raghunath, 1987). The groundwater quality is mostly controlled by discharge-recharge design, recharge quality and related rocks and additionally by pollution activities (Walton, 1970). The hydrochemical advancement of groundwater depends on flow regime experiencing consistent variation in the area for a period of time (Karanth, 1987). The appraisal of past written works from global, national and neighbourhood studies about the hydrogeochemical procedures of groundwater were considered in this review. Past examinations in the Luvuvhu catchment incorporate rainfall variability, rainfall runoff modelling, habitat integrity status, crop yielding and hydrological modelling. The studies of groundwater were also done by the Department of Water and Sanitation (NWRS, 2004), but with the limited description on the hydrogeochemical processes of groundwater. Therefore, the current study is significant and necessary to outline

the assessment of several groundwater chemistry procedures and hydrogeochemical processes of the review region.

Studies related to the groundwater quality assessment depict the contaminating sources such as sub-surface rock structure, anthropogenic pollution from farming, sewage, industries and groundwater salinity which were not included in some recent times, in Luvuvhu catchment. Since groundwater is the fundamental resource for domestic water and irrigation water in the catchment, it is important to assess the groundwater suitability. Thus, the present work is endeavoured with the objective of perception to understand the spatial variabilities of hydrogeochemistry of groundwater and in relation to its propriety for drinking and irrigational purposes.

2.2 Hydrochemistry and groundwater quality assessment

Groundwater is the main source of water for drinking in urban and rural areas worldwide. The accessible groundwater resources can be ideally utilized and maintained if the quantity and quality of groundwater are surveyed viably. The groundwater quality and chemistry in a place rely upon the atmosphere, soil, topography, hydrogeology and effects of human exercises. The nature of groundwater depends on considerable number of procedures and responses that follow up on the water from rainfall to discharge to the well (Gupta et al 2004). Administration of water resources is essential to manage the requirements of consistently expanding populace. A clear understanding of the hydrochemical and hydrogeological properties of an aquifer is necessary for sustainable management of groundwater. Pazand et al. (2011) carried out the hydrochemical assessment of groundwater and concluded that dug wells are more contaminated by the anthropogenic activities compared to borewells. Jaysena et al (2007) examined the groundwater flow hydrochemistry in a crystalline territory and reported that climatic change plays a major role on hydrochemistry of groundwater. Ma et al. (2009) identified the high nitrate and salinity in the Wuwei basin of Shiyang river in northwest China and recommended to regular groundwater quality monitoring and assessment to ensure the protection of groundwater sources and administration.

Nitrate pollution is explicitly identified with land utilization design and detailed in a few investigations throughout the world (Ator and Denis 1997; Elhatip et al. 2003; Jeong 2001; Kalkhoff et al. 1992; Rajmohan et al. 2009). Narayana and Suresh (1989) and Ramesh et al. (1995) directed investigations on the chemical quality of groundwater of Mangalore City in Karnataka State and Madras in Tamil Nadu, India and uncovered that the groundwater quality has been depreciated because of overexploitation. Furthermore, Jalali and Kolahchi (2007) evaluated the groundwater pollution status and reported that fertilizers applications, intensive irrigation, domestic sewage discharge and mineral solubility are prime sources for groundwater contaminations. Vetrimurugan et al 2013 conducted a study on the contamination sources and the groundwater quality assessment in the coastal river delta and reported that groundwater quality is highly unsuitable and suggested for further regular monitoring. Srinivasamoorthy et al. (2009) examined the groundwater quality in Salem area of Tamil Nadu, India and reported that distinguished lithology and anthropogenic sources affected the groundwater chemistry. Vasanthavigar et al. (2010) evaluated the water quality for human consumption utilizing WQI technique for the winter and summer seasons in Thirumanimuttar river basin. They distinguished that the leaching of ions, over usage of groundwater, effluents discharge and agrochemicals are main causes for groundwater quality contamination during summer.

Agricultural practices are considered as predominant sources for groundwater contamination, especially non-point sources (Jones 1997) and reported that nitrate, sodium, calcium, magnesium, ammonia, phosphate and trace element in groundwater are mostly derived from irrigation activities. Sujatha et al. (2003) investigated the groundwater quality in Andhra Pradesh, India and suggested that groundwater quality is affected by the bedrock geology, climate change, agricultural and industrial pollution. Ghana water administration evaluated the groundwater hydrochemistry in the Densu River Basin, Ghana and concluded that there is a possibility for groundwater contamination by the natural and anthropogenic activities. Vetrimurugan et al 2014 has reported that the groundwater quality has been degraded in the deltaic region due to intensive irrigation activities. Oren et al. (2004) examined the groundwater contamination affected by the irrigation return flows and

suggested that contaminated water originating from uplands may cause high salinity if it is utilized downstream Western Iran.

The investigation on groundwater quality was led by Edmunds (2003) and Shanmugam and Ambujam (2011) in Aurangabad, Maharashtra, India, and inferred that impacts of populace development and climate change are making serious pressure to surface water. Rasouli et al. (2012) surveyed the quality and suitability of groundwater and surface water in the Kor-Sivand stream basin. They concluded that one third of river samples tested are not appropriate for irrigation and two third wells are unsafe. Pazand et al. (2011) assessed the groundwater geochemistry in the Meshkinshahr basin, Iran and discovered that the major ions concentrations are under the satisfactory level for drinking water.

Alobaidy et al. (2010) connected WQI in Dokan Lake, Kurdistanregion, Iraq, utilizing ten water quality parameters. The investigation presumed that there is a decline in the quality of water from 1978 to 2009 and brought up the requirement for sustainable monitoring. Sisodia and Moundiotiya (2006) examined WQI for various seasons to assess the effect of industries, agribusiness, and human exercises on Kalakho Lake and documented that man-made process affected the Lake and environment. Vetrimurugan et al 2017 has adopted spatial interpolation methods and multivariate methods to identify and map the groundwater contamination and reported that the groundwater has been severely contaminated due to the industrial activities in the region. Overwhelming metal concentrations were checked in Akpabuya, south-eastern Nigeria, by Offiong and Edet (1998) and viewed higher concentrations of ions in groundwater samples and reported that the corrosion of borehole materials in water or to a different redox environment in the groundwater responsible for high concentrations. Elhatip et al. (2003) announced that the human exercises and farming had immediate and circuitous impacts in tainting of groundwater because of the dissolution and transport of overabundance amounts of compost. Subramani et al. (2005) examined the appropriateness of groundwater for drinking and agricultural uses in Chithar basin and suggested that the groundwater is very hard, fresh to brackish, high to high saline and low alkaline in nature.

Saleh et al. (1999) applied correlation matrix to evaluate the relationship between physical and chemical parameters in the groundwater. Brandl, 2003

announced that the agricultural exercises have influenced the groundwater due to the usage of inorganic chemicals and affected the groundwater quality. Nagarajan et al. (2010) attempt the audit on the evaluation of groundwater quality and its sensibility for utilization and agricultural use. The review inferred that groundwater quality is degraded by non-natural activities, and real organization design is basic to ensure huge groundwater assets in Thanjavur City. Shah and Mistry (2013) considered the groundwater quality appraisal for irrigational use in Vadodara District, Gujarat, India. The investigation disclosed that utilization of compost for agrarian contributing the higher concentration of ions in the aquifer of Vadodara area. As indicated by Sarath Prasanth et al. (2012), the groundwater of Alappuzha District, Kerala, India is very hard to hard and the predominant water type is $\text{Ca}^{2+}\text{-Mg}^{2+}$. Venkatramanan et al. (2015) led the investigation on the appraisal of groundwater quality utilizing GIS and CCME WQI procedure in Thiruthuraipoondi city, India. The investigation prescribes the successful groundwater administration design of artificial recharge to protect significant groundwater resources in Thiruthuraipoondi city. Nitrate concentrations of groundwater in residential areas are gradually increased over the United States (Nolan and Stoner, 2000). The source of contamination is from nonpoint sources, especially turf grass manures and sewage from septic tank/cesspool frameworks. Shahmayur (2008) have investigated the groundwater quality in Gandhinagar Taluk, India with the standard principles recommended by WHO. They documented that the groundwater with low pH value can cause gastrointestinal confusion and this water can't be utilized for the drinking purposes.

2.3 Hydrogeochemical processes

Hydrogeochemical processes are responsible for the chemical composition of groundwater in a place. Groundwater has varying range of chemical composition and this variation is due to the composition of infiltrating surface water, properties of soil and rock in which groundwater moves, contact time and contact surface between groundwater and geological material along its flow path, rate of geochemical rock-water interaction, oxidation/reduction, ion exchange, dissolution, evaporation, precipitation and microbiological processes. Jalali (2005) reported that the dissolution of carbonate minerals, cation exchange and weathering of silicates

control the groundwater chemistry in semiarid region of western Iran. Elango et al (1999) carried out extensive work on the hydrogeochemical nature of groundwater in an intensively irrigated region of Kancheepuram District, Tamil Nadu, South India and identified the need of regular monitoring of groundwater quality. Navarro and Carbonell (2007) studied the groundwater contamination beneath an urban environment in Spain and reported that high concentration of NO_3^- , Ca^{2+} , Mg^{2+} , Ni, Pb, Zn and organic micro pollutants originated from septic tank effluents, domestic sewage and industrial wastewater.

Elango (1992) had studied the hydrogeochemical nature of the multi-layered aquifer of North Chennai, and had brought out the relation of groundwater recharge to flow mechanisms. Pacheco and Szocs (2006) reported that calcium derived from anthropogenic inputs promotes dedolomitization reactions through calcite precipitation in groundwater. Saleh et al (1999) and Muller (2007) reported that the rising water table in the rainy period dissolves more saline matter from the soils and increases the salinity of water. Vetrimurugan et al 2016 has studied and reported the hydrogeochemical studies and solute transport modelling to improve the water quality in intensive irrigation river deltaic region. Raju et al. (2009) have studied groundwater quality in the lower Varuna River basin in Varanasi district and found high nitrate concentrations at few locations due to intense anthropogenic activity and inadequate sewage system. Studies by Edet and Ekpo (2008); Nganje et al. (2010) and Edet and Okereke (2014) in Cross River Basin and Niger Delta Region, Nigeria showed that precipitation through rainfall, water–rock interaction, ion exchange and anthropogenic input are the main controlling factors to water composition.

Aghazadeh and Mogaddam (2011) applied saturation index (SI) to evaluate degree of equilibrium between water and minerals. They concluded that nearly all of the water samples were oversaturated with respect to carbonate minerals and unsaturated with sulfate minerals. Kumar et al. (2014) carried out a hydrochemical study on the groundwater quality in the fast-growing coastal area of South Chennai. Their study indicated that the groundwater quality of South Chennai coastal area had been heavily affected by urbanization and seawater intrusion. The research conducted by Li et al. (2013a) showed that groundwater in a mountainous county of China was suitable for agricultural irrigation and groundwater in this area is

weathering dominated. Kumar et al. 2006) studied the nitrate distribution in a deep, alluvial unsaturated zone and reported that the nitrate concentration is extremely high in the unsaturated zone due to fertiliser application.

Garrels (1976) and Data and Tyagi (1996) had inferred that carbonate weathering process are responsible for Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} in the groundwater, along with silicate weathering which are responsible for Na^+ , K^+ and HCO_3^- . Schuh et al. (1997) indicated that increases in solute concentrations in the groundwater were caused by spatially variable recharge due to microtopography. They concluded that the discharge zones tend to have high mineral concentration compared to recharge zones. Brijraj and Kaur (2007) have concluded that the chemical quality of surface and groundwater of Rawalsar Lake, Mandi district, Himachal Pradesh was controlled by rock weathering, which supplied most of the dissolved constituents to the water. Sarin et al. (1989) reported the significant silicate weathering rather than carbonate weathering for the Son basin, whereas Rai et al. (2010) reported higher carbonate weathering rate than silicate weathering rate based on the water chemistry at Koelwar. Sami (1992) demonstrated that leaching of surficial salts; ion exchange processes, and the residential time have caused the hydrogeochemical variations of groundwater in a semiarid sedimentary basin in Eastern Cape, South Africa.

Apodaca et al (2002) evaluated the water quality in Upper Colorado River Basin, Colorado, where groundwater quality is controlled by various hydrogeochemical processes and residence time. Garrels (1976) and Data and Tyagi (1996) had observed that carbonate weathering process are responsible for Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} in the groundwater, along with silicate weathering which are responsible for Na^+ , K^+ and HCO_3^- . Bocanegra (2002) have identified that cation exchange processes and calcite equilibrium are the important hydrogeochemical processes that control groundwater composition in the Mar del Plata aquifer, Argentina. Mohan et al (2000) reported the lower concentration of potassium in groundwater due to its fixation in the form of clay minerals and greater resistance of potassium bearing minerals to weathering. Many investigations have dealt with the origin of saltwater in coastal aquifer. Araguas Araguas (2003), Bear et

al (1999), Custodio (1997), Ghabayen et al (2006) and several sources have been identified the evaporate dissolution (e.g. Pulido-Leboeuf et al 2003) and downward leakage from surficial saline water through failed or improperly constructed wells (e.g. Aunay et al 2006). Seawater intrusion often occurs due to excessive pumping (e.g. Kim et al 2003) in the coastal region.

2.4 Previous works attempted from the study area

Heerden (2011) studied the geological and anthropogenic impacts on water quality at rural regions in the Limpopo province, South Africa. It was articulated that chloride and sulphate are the fundamental toxins in water resources in the Limpopo region. The review on the evaluation of how water quality and quantity will be influenced by mining of the Waterberg coal stores was embraced by Vermeulen and Bester (2009).

Nkuna and Odiyo (2016) focused on the relationship amongst temperature and rainfall variability in the Luvuvhu catchment, Limpopo, South Africa. The review has discussed that temperature increment is noticed when rainfall reduces, which is probably going to impact water resources accessibility in this area. Further, the study region encounters a high level of yearly precipitation variability with dry spell and wet years exchanging much of the time, which imply that cautious management of water resources is a high need. During fieldwork conducted in November 2016, the water level was low compare to the data collected in August 2015 due to temperature increment (partially drought). Kleynhans (1996) has considered on a subjective technique for the appraisal of the natural surroundings respectability status of the Luvuvhu River (Limpopo framework, South Africa). This method should emphasis the rationality between water amount and quality administration, among surface water and groundwater management and among urban and rustic areas (Schneiders et al, 1993). One of the essential needs in the change of the normal surroundings respectability of the Luvuvhu River can be water storage arrangement (dams), which can be utilized to manage the flow of water to avoid the extreme utilization of low flows and the suspension of flow downstream in the Kruger National Park. Odiyo et al. (2012) lead an examination on rainfall–runoff for assessing Latonyanda River flow responsibilities regarding Luvuvhu River downstream of Albasini Dam. Hydrological

modelling in the Luvuvhu catchment was studied by Jewitt and Garratt (2004) and the modelling exercise experiences the shortage of accurate runoff data. Mpandeli (2014) studied on the assessment of Crop Production Practices by farmers in Tshakhuma, Tshiombo and Rabali in Limpopo Province of South Africa. The review recommends that planters should be advised and empowered to utilize crop variation enhancement.

Recently, several studies were conducted in the Limpopo province including hydrogeological characterization of crystalline basement aquifers and hydrochemical analysis and conceptual hydrogeological models (Holland, 2011). Testing the ability of a coupled linear and non-linear system identification model by estimating the groundwater level in Nzhelele and Luvuvhu area were carried out (Makungo and Odiyo, 2016). Effluents from wastewater treatment facilities are major anthropogenic source of Polycyclic Aromatic hydrocarbons (PAHs) and high level of PAHs are reported in the groundwater (Edokpayi et al. 2016). The chemical composition of the sludge exceeding limits sets out on DWAF guidelines, causes environmental hazard if it applied into soil as fertilizers (Shamuyarira and Gumbo, 2014). Impacts of climate change on water availability and accessibility in the Limpopo River Basin of Southern Africa is examined utilizing a linked modeling system, which comprise of a semi-circulated worldwide hydrological model and water simulation model of the global model for approach examination of agrarian products and exchange (Zhu and Ringler, 2012). Releasing of effluent into a water streams resulted poor quality water and degrade the total region. This action leads to eutrophication due to nitrate enrichment and proliferation of harmful algal blooms and schistomiasis infections in the long term (Gumbo et al. 2016).

All these research studies are mainly focused on hydrogeological characterization of groundwater, estimating groundwater level using model, identification of PAHs concentration in effluents, heavy metal contamination in sewage sludge, climate change and effluent discharge in this region. Concerns about groundwater quality change in Limpopo province is not attracted by the researchers and hence, enough attention from researchers and existing research studies on this objective are not given. Consequently, the present investigation was conducted to evaluate the groundwater quality and its suitability for human utilization

and irrigation use by Drinking Water Quality Index (DWQI) and Geographical data framework (GIS) in Luvuvhu Catchment, Limpopo, South Africa. This will help the local people towards proper management of water resources, and to build up gauge information, which help in future water administration and protection measures.

CHAPTER THREE

3 Study area

3.1 Location

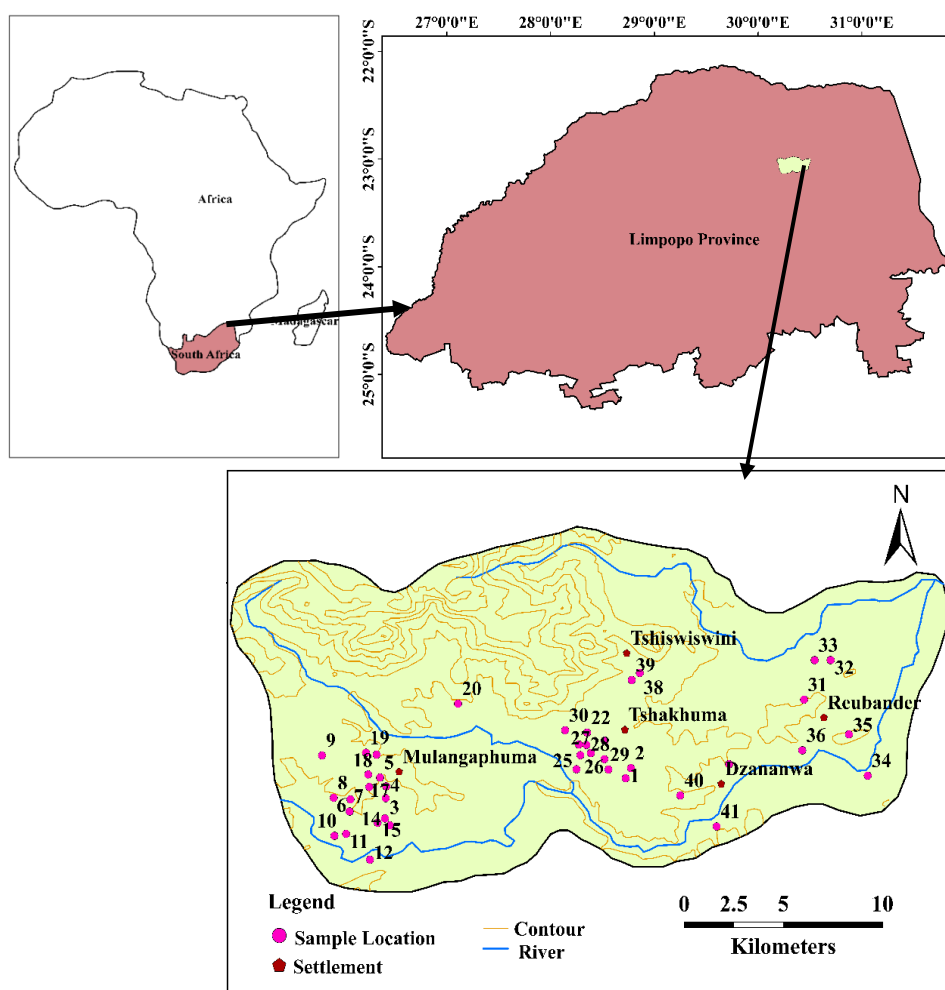


Figure 3.1: Location of the Study area

The present study was carried out in the Luvuvhu catchment, Vhembe District, Limpopo Province of South Africa (Figure 3.1). The study area is located in the Northern side of South Africa and covered by the Zimbabwe in the north and Mozambique in the east. It is the greatest provincial area of South Africa and is usually called the Eden of South Africa due to its high level of agricultural practices and afforestation. Rural groups make up around 90% of the total populace in the region (Busari, 2008). The study region existed between $22^{\circ} 59' 02''$ S and $23^{\circ} 05' 48''$ S and $30^{\circ} 09' 58''$ E and $30^{\circ} 21' 58''$ E and is 30km West of Thohoyandou Town.

3.2 Topography

The Luvuvhu catchment starts as a sharp mountain stream in the south-easterly slope or gradient of the Soutpansberg Mountains. The study area falls in the Lowveld Bushveld, with undulating landscape, hills, and low mountains with moderate relief. Slopes generally 15° and local relief is greater than 1m (DWA, 2006). The altitude ranges from 450 m to 1 425m above mean sea level (MSL). This topography influences the catchment to receive major rainfalls and attributes good results to the hydrology of the area. The unspoiled indigenous forest form shelters in areas of wetlands. The topography of the area is constituted by the Drakensberg Mountainous, which extends to the western part of Limpopo.

3.3 Climate and Rainfall

This catchment usually receives reasonable amount of precipitation as compared to other catchments of Limpopo Water Management Area. Precipitation (95%) occurs during October to March (M'Marete, 2003). During summer (October to February), maximum rainfall is recorded. Normal precipitation is around 450 mm. Daily temperatures of the sub-catchment differ between 25°C and 40°C in summer and between 22°C and 26°C during winter. Extreme temperatures in the Luvuvhu catchment are recorded from October to April (summer) and low temperature is observed from May to August (winter). Region receives rainfall during summer beginning of October and ending in March.

3.4 Drainage

Luvuvhu River is a major drainage for the study area and Latonyanda River is one of the main tributaries to Luvuvhu river. The sub-catchment receives high precipitation compared with other catchments. The Luvuvhu River and its tributaries drain in the Pafuri area, Kruger National Park and joins Limpopo River that drains to Mozambique Channel. The Mean Annual Precipitation (MAP) over the whole catchment is 608mm and mean total evaporation is 1678mm (DWAF, 1996). There is low evapotranspiration (ET) over Soutpansberg Mountains and most noteworthy

precipitation in the upper part of the catchment (western side) and low precipitation with high ET in the bone-dry regions towards Kruger National Park (eastern side).

3.5 Geohydrology

The Luvuvhu catchment is named after Luvuvhu River wherein the catchment is drained into Luvuvhu River and other tributaries (Odiyo et al, 2012). Luvuvhu River is one of the important rivers of the Limpopo Province, with two significant dams namely, Albasin and Nandoni Dam. Previously, Luvuvhu River considered being lasting with deep lakes throughout the year yet recently, sand mining, brick making and agribusiness makes the stream to be non-perennial more particularly in winter months. The accessibility and the amount of groundwater in the catchment are unknown; hence, rural exercises such as agriculture rely on groundwater to supplement surface water (DWA ISP, 2004). Subsequently, the water table is very low and it varies from 4 to 40m in the boreholes.

3.6 Geology and hydrogeology

The study area comes under the extremely faulted Soutpansberg Group of the Mokolian age (Figure 1.1b). The Soutpansberg rocks are not comprised by the economic minerals except Copper mineralization, which is identified in the eastern part (Exxaro coal mining) in Mutale catchment (Brandl, 2003). Volcanic rocks formed substantial part in the Soutpansberg group in the northern Transvaal. The Soutpansberg Group causes part of fractured crystalline basement aquifers of Limpopo province in South Africa.

The study area has fractured aquifers and the yield of bore wells is 0.5-2 l/s (Du Toit et al., 2002). Soutpansberg rock contains Dykes and diabase in high proportions (Brandl, 2003). Semi-confined aquifer (fractured bedrock) is located in the crystalline basement rocks (metamorphic or igneous in origin) and water-table aquifers (the matrix-regolith) situated on top of them (Holland, 2011). The Soutpansberg is an east-west trending mountain range that is made up of an ancient sequence of sedimentary rocks and basaltic lavas (Limpopo State of the

Environmental Report (Phase 1), 2004). East of Louis Trichardt (Levubu-Thohoyandou Town) a thin layer of sedimentary rocks intervenes between the basal lavas and the basement. The thin succession of basal sedimentary rocks east of Louis Trichardt differs in lithology from the entire succession by the presence of feldspathic rocks, and consists of alternating sandstone and shale with feldspathic greywacke and very locally conglomerate and arkoses at base (Jansen, 1975). The latter confirm the geology of the study region, which forms part of the Soutpansberg Mountain Channel.

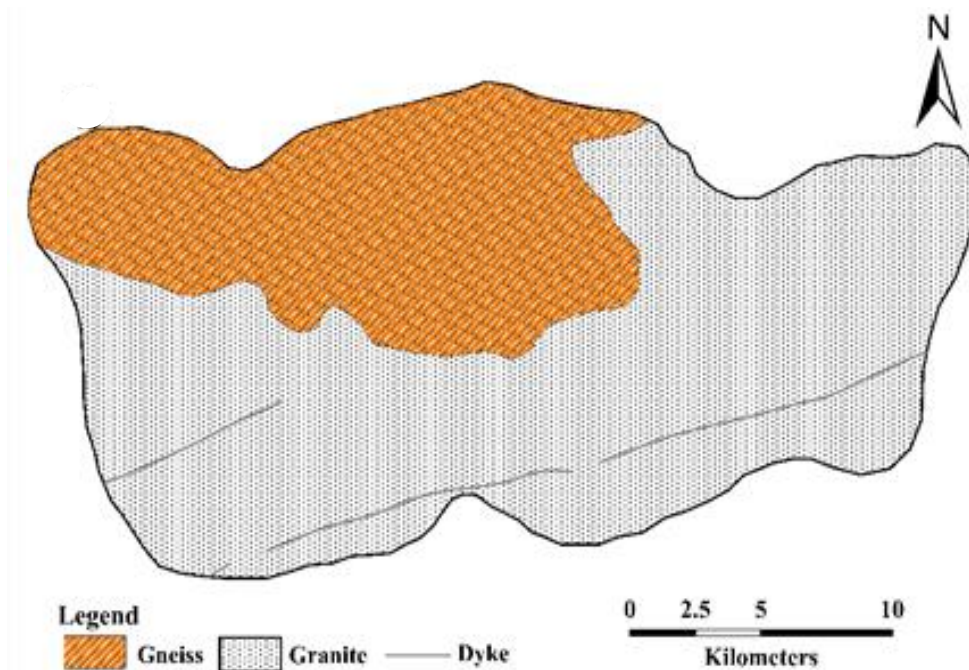


Figure 3.2: Geology of the area

3.7 Land use and irrigational use

The Limpopo Province is usually known as the Eden of South Africa because of its high level of agricultural practices with high production. The economy of Limpopo province is driven by commercial agricultural activities. The dominant land use activities along Luvuvhu catchment include unspoilt indigenous forest, agriculture, commercial plantations (western side towards Makhado Town) and settlement area towards Thohoyandou Town (DWA, 2004). There are no available known industries within the study area however, there is Timberland manufacturing

towards Louis Trichardt Town. The Luvuvhu catchment is blessed with the biggest market operating 24 hours daily called Tshakhuma Fruit Market. The market established for more than 40 years ago situated in 17km west of Thohoyandou Town on the Road to Makhado (Louis Trichardt). The market is surrounded by Levubu farms who constantly supply fresh fruits. The Luvuvhu catchment is known as agricultural area where farmers produces variety of fruits and vegetables namely, bananas, macadamia nuts, oranges, mangoes, avocados, litchis, pawpaw and pecan nuts as well as catch-crops (summer and winter vegetables). Downstream of the catchment is dominated by community gardens and residential areas.

CHAPTER FOUR

4 Methodology

4.1 Introduction

Surface water and groundwater evaluation is performed to understand the hydrochemical characteristics using scientific and standardized methodology. In this study, water samples were obtained from different locations in the study site and investigations were performed based on the major ions and nutrients. The study area is covered by the indigenous timberland and commercial agricultural activities and bore wells have been used for various need. The hydrological investigations require legitimate methodology to precisely discover the geological attributes and contamination rates at research area. The proper selection of the methodology for the study is crucial and applicable to in a wide variety of environmental and hydrological situation.

4.2 Maps preparation

The base map and geology map of Limpopo province study area were prepared using ArcGIS 10.1 software.

4.3 Field Survey

A field survey was undertaken to identify the borewell locations and to assess the usability of groundwater and surface water for irrigation in the upper part of Luvuvhu catchment, Vhembe District. Surface water and groundwater quality evaluations were considered important because extreme farming exercises impose soil and groundwater to more serious danger of pollution (Ackah et al., 2011). The existing Albasin dam deliberately set to serve the irrigation plot; however, the catchment region is modestly dry provoking to low yields. Serious water deficiency experienced in the mid 1990's incited escalated improvement of groundwater to keep up high yielding. Major water uses in the Luvuvhu catchment are cultivation (farming), forestry and residential need (ISP, 2004). The bore wells used for irrigation are considered for sampling purpose and authorization was granted from the agriculturists and yards proprietors.

4.4 Water sampling

In this study, 7 surface water (Luvuvhu River) and 41 groundwater samples were collected from Luvuvhu catchment during August 2015 and 2016 (Figure 3.1a). Groundwater level was measured using automatic water level recorder. Groundwater samples were obtained after the removing substantial quantity of water from borewell to get fresh water from aquifer. High-density polyethylene (HDPE) bottles were employed to collect the water samples. Sampling bottles were rinsed acid washed and pre-cleaned bottles were rinsed with sampling water prior to sampling. Electrical conductivity (EC) and pH were estimated in the field during sampling using portable meters that was pre-calibrated using 84 and 1413 μ S/cm conductivity solutions for EC and 4.01, 7 and 10.1 for pH. Samples were sent to the Agricultural and Hydrology Laboratory, University of Zululand and filtered using 0.45 μ m membrane filter paper.

4.5 Water analysis

Field parameters namely pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) were determined in the field using the portable YSI multiprobe. Major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Nitrate and sulphate were analysed using UV-Visible spectrophotometer as per the standard methods. During analysis, both standard and blanks were run regularly to confirm the accuracy of the ionic concentration. For chloride analysis, 20 ml water pipetted in 250 ml conical flask and titrated against silver nitrate solution (AgNO_3) using indicator (potassium chromate (K_2CrO_4)). To prepare silver nitrate solution, 4.247g of silver nitrate is dissolved and diluted to 500 ml using standard volumetric flask. The silver nitrate solution from a burette was dropped wisely, by swirling the sample constantly till end point (red colour). Red colour indicates that chloride ion is precipitated and titration process continued until the faint persistent reddish brown colour is developed as the end point.

The estimation of carbonate and bicarbonate was achieved through the titration methods. The 20 ml volume of water samples were titrated against dilute sulphuric acid solution with indicators (phenolphthalein and methyl orange). The pink colour was developed at the point when a drop of phenolphthalein introduced to the water if the carbonate is present in the sample. Similarly, pink colour will never develop if there is no carbonate in water; hence, carbonate was absent from the samples showing colourless solution during the titration method. A few drops of methyl orange was added in the same solution and titrated against sulphuric acid until the straw yellow colour changes to pinkish red colour. Burette value gives amount of acid required to neutralizing the bicarbonate originally present and that formed from the carbonates, by subtracting the first value from the second value to get the acid required to neutralize the bicarbonate originally present in the water (APHA, 1998). By calculating the ion balance error, analytical results were rechecked which is within $\pm 5\%$.

4.6 Software employed

- The Piper trilinear was prepared by the use of Geochemist's Workbench (GWB 12) software.
- The Chadha's diagram, bivariate plots and correlation matrix were prepared using Microsoft Excel Spreadsheet.
- The spatial analysis for various physicochemical parameters was performed using the ArcGIS10.2.
- Microsoft Excel 2010 was used for graphical representations and physicochemical factors of the surface and groundwater samples were examined utilizing Microsoft Excel Spreadsheet. This product was used for expressive measurable investigation of the water samples to create a table with descriptive statics namely minimum, maximum, mean, median and standard deviation.

CHAPTER FIVE

5 Hydrogeochemical processes on temporal changes in groundwater quality

5.1 Introduction

Groundwater as significant resource of water provide for irrigation, domestic and industrial segments in urban and rural areas in various countries throughout the globe. Groundwater of an area was usually heterogenous and it is regulated by the natural processes such as water-rock interactions, evaporation, hydrogeology, dissolution and weathering of minerals and flow path of groundwater. Identification of hydrogeochemical processes that used to know the reasons for variations in groundwater quality depends on aquifer characteristic occurring mainly in weathered granitic formation. Hydrogeochemical studies are used for development, management and safeguard of aquifers, which are polluted by natural and human impact. The reasons for the variation in the groundwater quality are intensive irrigation and human activities, industry, population growth, mining and rapid urbanization, which causes significant problems for water resources in arid and semi-arid areas (Rajesh et al, 2012). Globally, several studies published in the hydrogeochemical topic and researches were carried out to know the hydrogeochemical processes and their correspondence to quality of groundwater (Belkhiri et al 2010; Monjerezi et al. 2011; Rajesh et al. 2012; Li et al 2013; Varol and Davraz, 2014; Venkatramanan et al. 2015; Rajmohan et al. 2017; Vetrimurugan et al. 2017; Barzegar et al. 2017). Understanding the hydrogeochemical processes by graphical methods namely Piper, Chadha, Pie and bivariate plots provided the pictorial representation of hydrogeochemical results, classification of water, sources of groundwater solutes, movements, variations of water quality and composition (Dalton and Upchurch 1978).

Multivariate statistical techniques are mostly applied in recent days and these methods are used to investigate the data and categories groundwater samples and describe the source of pollution (Panagopoulos et al 2016, Guler et al 2002). Factor analyses are used to infer large amounts of groundwater parameters to accomplish a better understanding of the hydrogeochemical processes (Lawrence and Upchurch 1982). Geochemical modelling is perfect technique for computing mass transfer

interface among solution and rock-water interaction (Parkhurst and Appelo 1999; Appelo and Postma 2005; Yidana et al 2008).

South Africa is facing a depletion of water, which is major issue related to quality because of population growths, economic development, climate change and rapid urbanization. Irrigation activities are mostly rely on groundwater in several parts of the region. Two-thirds of population in this country depends on groundwater for home needs (DWAF 2000). In the Limpopo province, Holland (2011) explained the regional hydrogeological characterization of groundwater in combination with the recharge, isotope and hydrochemical investigation. Zhu and Ringler (2012) stated the influence of climate change on groundwater availability using linked model system for agricultural commodities and trade. Shamyarira et al. (2014) evaluated the sewage sludge for heavy metals based on DWAF guidelines and suggested that quality of environment is hazardous and the soil sludge applied as a soil ameliorant in Limpopo province. Makungo and Odiyo (2016) estimated the groundwater level by analyzing the capability of a non-linear and linear coupled method in Nzhelele and Luvuvhu area. Edokpayi et al. (2016) reported that the effluents from wastewater treatment plant as the most important source of high contamination of PAHs in Vhembe district, Limpopo Province. Gumbo et al. (2016) reported that the water supply is unsuitable for human consumption due to discharge of effluent and leads to the schistosomiasis infection in the long-term usage of Limpopo river water. Published research works are mainly focused on subsurface characterization of groundwater, groundwater level estimating by linear models, identification of Polycyclic Aromatic hydrocarbons (PAHs) concentration in effluent discharge, heavy metal contamination in sludge and climate change of groundwater. Nevertheless, no published work was performed to describe the hydrogeochemical processes established on systematic observing of groundwater level over time and space. The current research was conducted in a region of Limpopo province, South Africa with an aim to identify the effect of hydrogeochemical processes on temporal groundwater quality variations.

5.2 Multivariate statistical technique

Multivariate statistical technique is used to reducing and consolidates large conventional data to confirm significant discernment. In this examination, Factor analysis (FA) applies the linear arrangements of action of the factors to frame the variables with a mean of zero and standard deviation of one. In this study, factor analysis was used to extract Eigen values and Eigen vectors from the covariance matrix of original variables to produce new orthogonal variables are varifactors through varimax rotation, which are linear arrangements of the original variables (Devic et al 2014). In the FA, parameters are standardized before calculation to avoid the bias in the results. Varimax rotation is normally used to maximize the variability on the rotated axes (Helana et al 2000). In this study, STATISTICA software package is used.

5.3 GIS analysis

Thematic maps were prepared using ArcGIS 10.1 software. Locations of sampling point are noted by Global Positioning System (GPS) and transformed to GIS. The spatial variation of each parameter was calculated by the support of Geostatistical analyst module in ArcGIS 10.1. Inverse distance weighted (IDW) interpolation method was employed to interpolate the data spatially and to calculate values between measurements. Each value was estimated by IDW interpolation weighted average of the neighboring sample points. A second order polynomial was given in the power field influence the importance of neighboring points on the interpolated value. Weights are calculated by the inverse of the distance from an observation location to location of the point being calculated (Burrough and McDonnell 1998).

5.4 Hydrochemistry

Box and whisker plots describing variation of physical and chemical parameters of groundwater namely EC, pH, TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- and NO_3^- in 2015 and 2016 are shown in the figures 5.1 a, b. The

groundwater pH ranges from 6.0 to 7.6 with a mean value of 6.6 and 6.4 to 7.6 with an average value of 6.8 in the year of 2015 and 2016, respectively (Table 5.1). The overall pH values for both samples represent slightly acidic to alkaline in the study area. Salinity hazard is the influential water quality parameter on crop productivity and estimated using electrical conductivity (EC) (Ahmed et al, 2002). Water with high EC affects crop productivity and also creates physiological drought for plant. EC of surface water ranges from 149 to 168 μ S/cm with a mean value of 159 μ S/cm during 2015 and 187 μ S/cm to 524 μ S/cm with a mena value of 275 μ S/cm during 2016. Groundwater value ranges from 81 to 1206 μ S/cm with a mean value of 358 μ S/cm and from 119 to 900 μ S/cm with an average of 343 μ S/cm during 2015 and 2016 respectively. Based on DWAf (1996), 8 samples exceeded the prescribed limit of drinking (EC <450). Groundwater TDS is one of the important parameters to be considered in the irrigation water quality assessment because many of the toxic solid materials may be imbedded in the water, which may create problem to the plants (Matthess, 1982). TDS and EC are indicative of saline water in the absence of non-ionic dissolved constituents (Michael, 1992). Total dissolved solid (TDS) decided the hydrochemical characteristics of groundwater and is used often to ascertain the groundwater suitability for drinking purpose. TH and TDS are sorted on the grouping by Freeze and Cherry (1979) and Davis and DeWiest (1966).

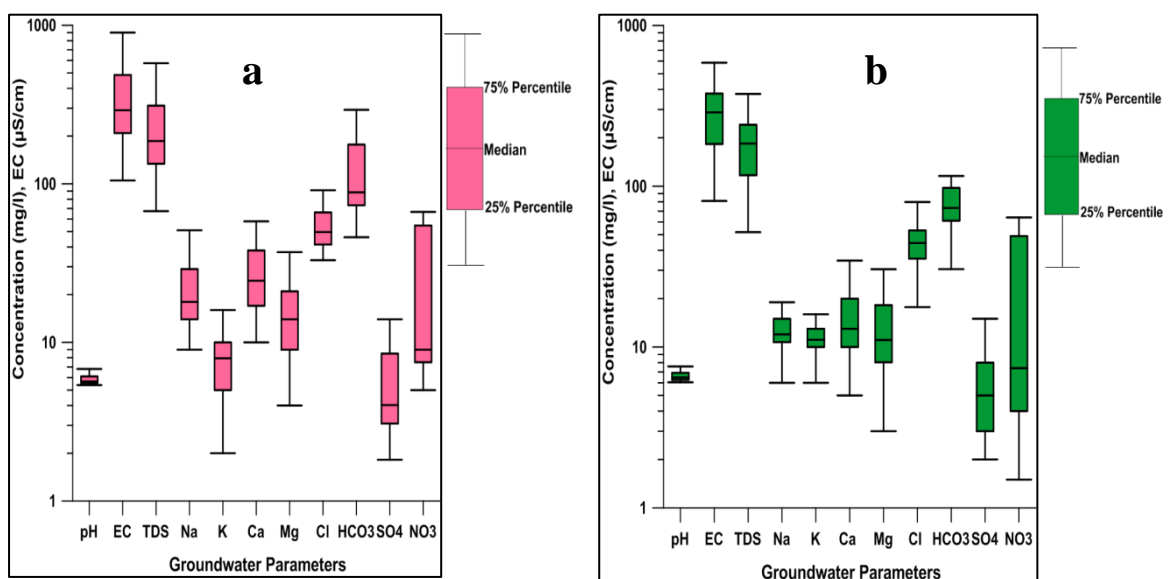


Figure 5.1a, b: Box Whisker plots of groundwater parameters in the year of 2015 and 2016

Table 5.1. Descriptive statistical results of physicochemical parameters of groundwater in the study area

Parameters	2015			2016		
	Minimum	Maximum	Average	Minimum	Maximum	Average
pH	6	7.6	6.6	6.4	7.6	6.8
EC ($\mu\text{S/cm}$)	81	1206	358	119	900	343
TDS (mg/l)	52	772	229	76	576	220
Na ⁺ (mg/l)	6	46	14	9	51	20
K ⁺ (mg/l)	6	18	11	2	15	8
Ca ²⁺ (mg/l)	7	54	18	8	74	24
Mg ²⁺ (mg/l)	3	42	15	4	37	14
Cl ⁻ (mg/l)	18	116	48	23	126	50
HCO ₃ ⁻ (mg/l)	31	266	97	41	293	116
SO ₄ ²⁻ (mg/l)	2	19	6	1.8	24	5

TH of groundwater samples shows that the groundwater samples in the study area are classified as soft (2015 = 13; 2016 = 15), moderately hard (2015=18; 2016=16) and hard (2015=10; 2016=10) (Figure 5.2). Only one sample comes under very hard category. TDS specifies that all samples of groundwater were fresh and suitable for drinking and irrigation purpose (Figure 5.2).

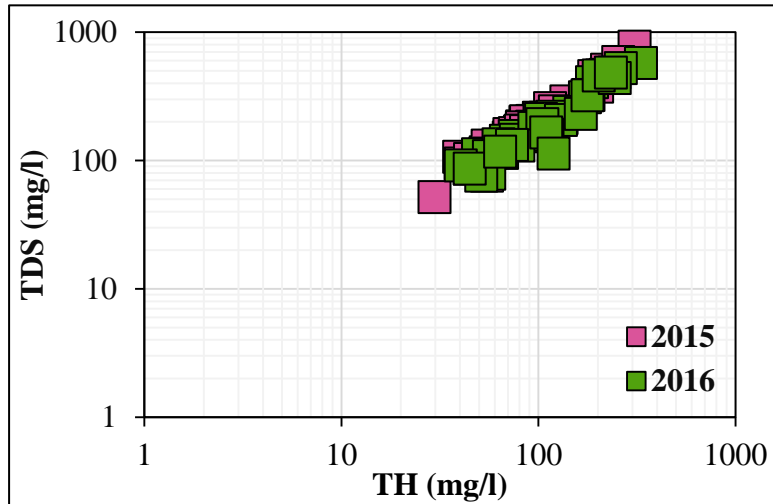


Figure 5.2: Groundwater classification using TH and TDS

The dominant sequence of cations and anions are in the order of $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ in the year 2015 and 2016. The average concentrations of major cations and anions are presented in the Pie diagrams (Figures 5.3 a, b) for both years. High concentration of HCO_3^- indicates freshly recharged aquifer from rainfall and it is resultant of HCO_3^- precipitation in the aquifer. K concentrations in the area are essentially due to the granitic dissolution of rocks. Cl^- was derived from fertilizer, industrial effluents, human and animal waste of the study area.

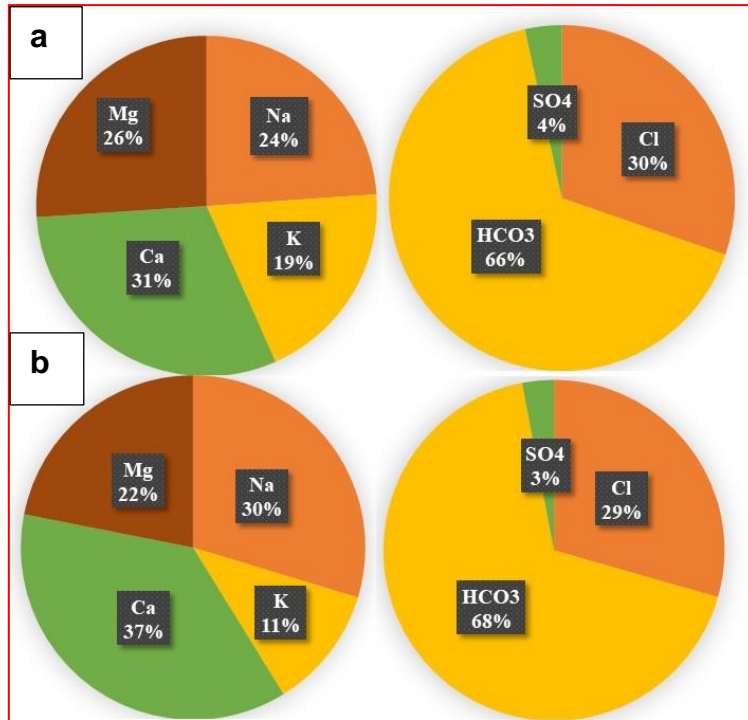
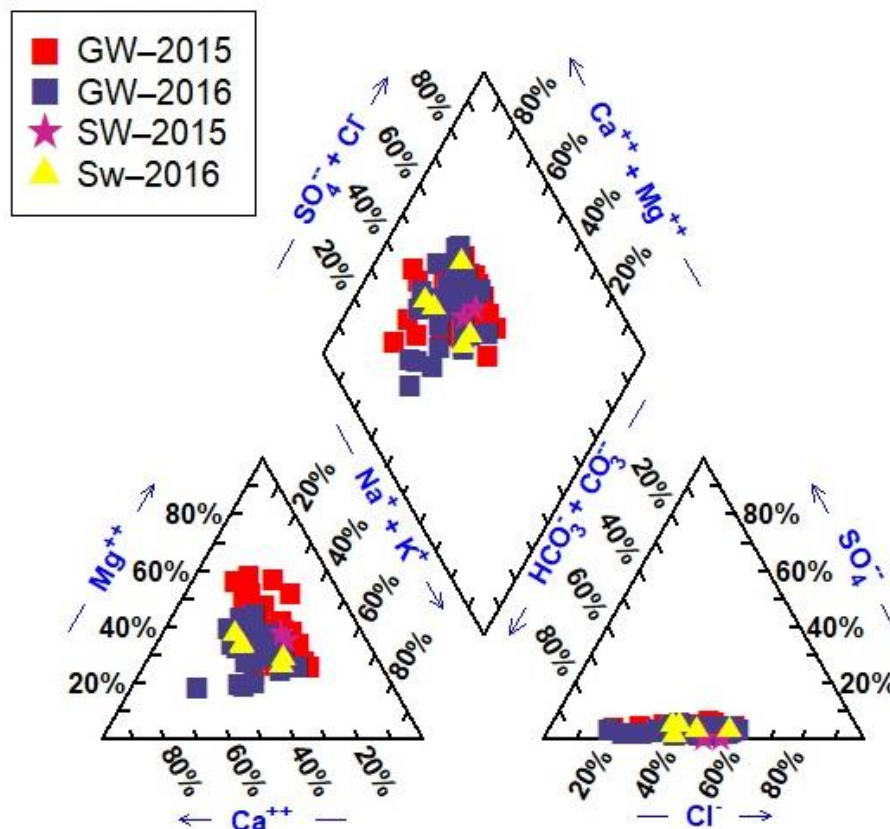


Figure 5.3 a, b: Pie diagram of the mean concentrations of major cations and anions in the year 2015 and 2016.

5.4.1 Hydrochemical facies of groundwater

In order to identify the hydrochemical facies and water types, both surface and groundwater samples were plotted in the Piper trilinear diagram (Piper 1944) (Figure 5.4) using Geochemist's Workbench (GWB 12). Piper diagram will help to identify the water samples with similar characteristics and displays the variations among water samples (Todd 2001). The plot shows that most of the surface water and groundwater samples plotted in the field of $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ and $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-$. Graphical representation of major cations and anions of both surface water and groundwater helps to know the hydrogeochemical processes and areal distribution. Chadha diagram (1999) was used in this study to assess the variation in hydrochemical facies, which specifies the difference in meq/l between Ca^{2+} and Mg^{2+}



(alkaline) and Na and K (alkali). Cations percentage values are plotted on the X-axis. In the Y axis, the difference between $\text{CO}_3^- + \text{HCO}_3^-$ (weak acidic) anions and $\text{Cl}^- + \text{SO}_4^{2-}$ (strong acidic) anions is plotted (Figure 5.5). Chadha diagram is similar to Piper diagram, but there is no need special software to plot the samples. In this diagram, the major cations and anions are plotted in a rectangular plot.

Figure 5.4: Hydrochemical facies of surface and groundwater (Piper 1944)

The eight fields explain eight different water types (Figure 5.5) as follows; (1) alkaline earths exceed alkali metals (2) alkali metals exceed alkaline earths (3) weak acidic anions exceed strong acidic anions (temporary hardness) (4) strong acidic anions exceed weak acidic anions (5) alkaline earths and weak acidic anions (6) alkaline earth exceed alkali metals and strong acidic anions exceed weak acidic anions (permanent hardness) (7) alkali metal exceed alkaline earth and strong acidic anions exceed weak acidic anions and (8) alkali metals exceed alkaline earth and weak acid anions exceed strong acidic anions. During 2015 and 2016, the dominant hydrochemical facies are $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ and $\text{Ca}^{2+}\text{Mg}^{2+}\text{-Cl}^-$ (Figure 5.4). The water types are achieved by the resultant of water-rock interaction likely due to dissolution of carbonate rocks.

The rectangular field explains the overall characteristics of the surface water and groundwater facies. . Hydrochemical facies of surface water and groundwater in the sub-field of $5\text{-Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ and $6\text{-Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-$ are dominant hydrochemical facies of both surface water and groundwater in 2015 and 2016 and this confirms the outcomes of Piper diagram.

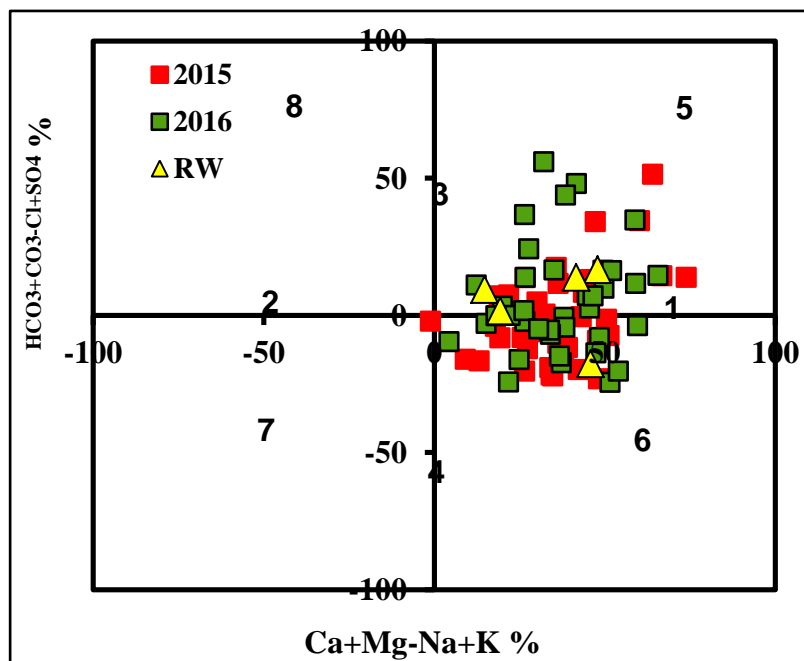


Figure 5.5: Hydrochemical facies of surface and groundwater (Chadha 1999)

5.4.2 Gibbs Plots

Gibbs plots are broadly utilized to identify the inter-relationship of groundwater constituents and aquifer characteristics (Gibbs 1970). Gibbs plots are useful to classify the processes namely precipitation, rock-water interaction and evaporation, and its impact on groundwater chemistry. The ratios $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ are plotted against TDS (Figure 5.6). In this study, both groundwater and surface water samples are clustered on rock-water interaction zone and TDS is <1000 mg/l. In the anion plot, some samples have slightly high TDS and bicarbonate. Figure 5.6 inferred that the water chemistry is predominantly affected by the mineral weathering in the study region.

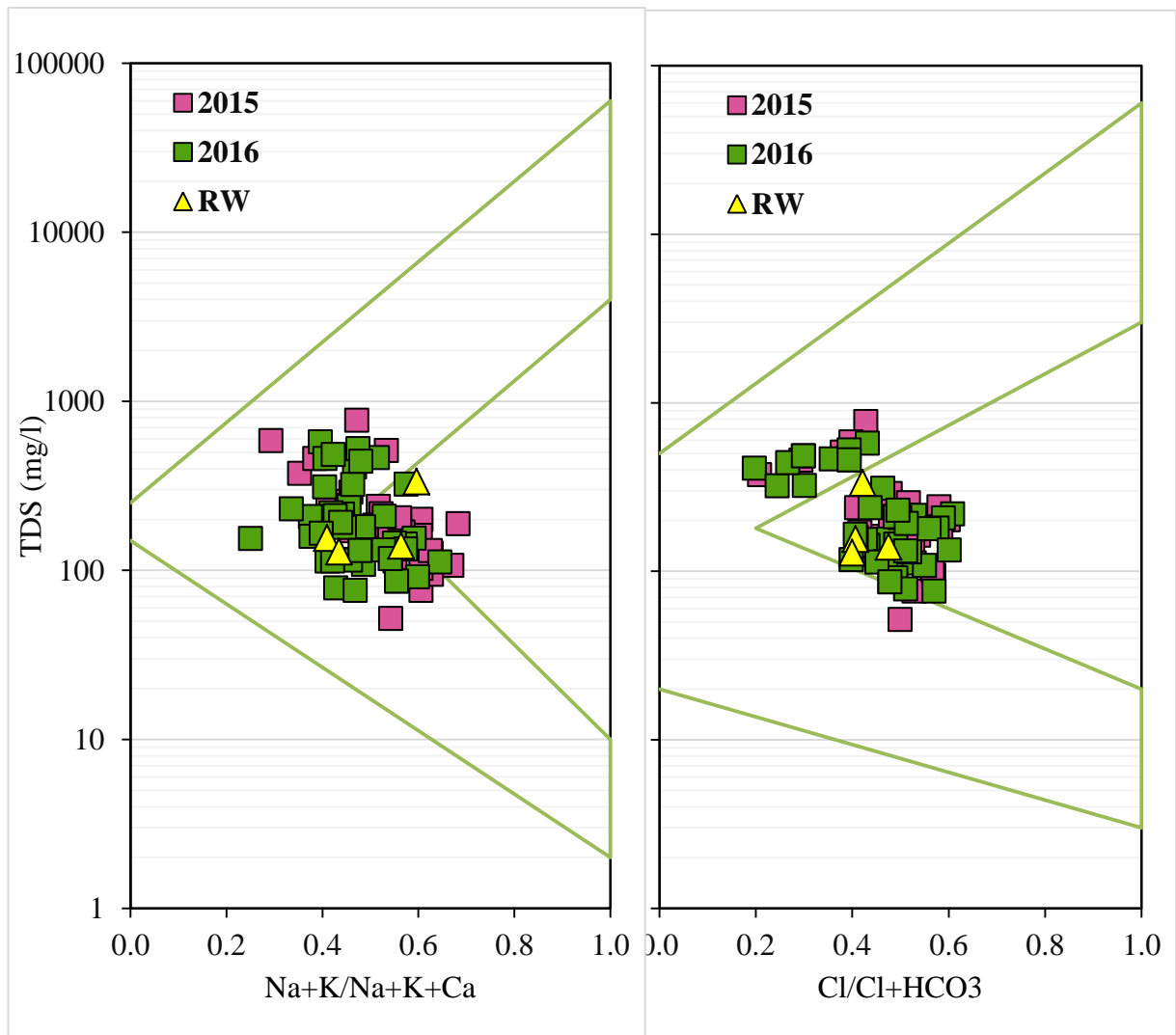


Figure 5.6: Gibbs diagram for both surface and groundwater

5.4.3 Soltan Classification

Soltan (1998) suggested and categorized groundwater established on Cl^- , HCO_3^- and SO_4^{2-} . The groundwater is classified as chloride type ($\text{Cl}^- < 15 \text{ meq/l}$), normal bicarbonate type ($\text{HCO}_3^- 2 - 7 \text{ meq/l}$) and normal sulfate type ($\text{SO}_4 < 6 \text{ meq/l}$). The water type and concentration of salts in groundwater are influenced by lithological and movement of water (Raghunath 1982). Scattering of groundwater established on Soltan's classification signifies most of the samples in both years fall in normal bicarbonate type succeeded by normal chloride and sulfate type.

Base Exchange indices (Soltan 1998) evaluated using the following Eq. 1, which can be useful for the grouping of groundwater sources.

$$r1 = \frac{Na - Cl}{SO_4} \quad 1$$

Where $r1$ - Base Exchange index. Na^+ , Cl^- and SO_4^{2-} concentration are in meq/l. If $r1 > 1$, the groundwater is $\text{Na}^+\text{-HCO}_3^-$ type whereas $r1 < 1$ specifies the groundwater is $\text{Na}^+\text{-SO}_4^{2-}$. During 2015, all the samples have $r1 < 1$ and $\text{Na}^+\text{-SO}_4^{2-}$ type water. During 2016, 90% of samples have $r1 < 1$ and are classified as $\text{Na}^+\text{-SO}_4^{2-}$ type water (Fig 5.7). About 10% of samples are $\text{Na}^+\text{-HCO}_3^{2-}$ type ($r1 > 1$) (Figure 5.7) during 2016.

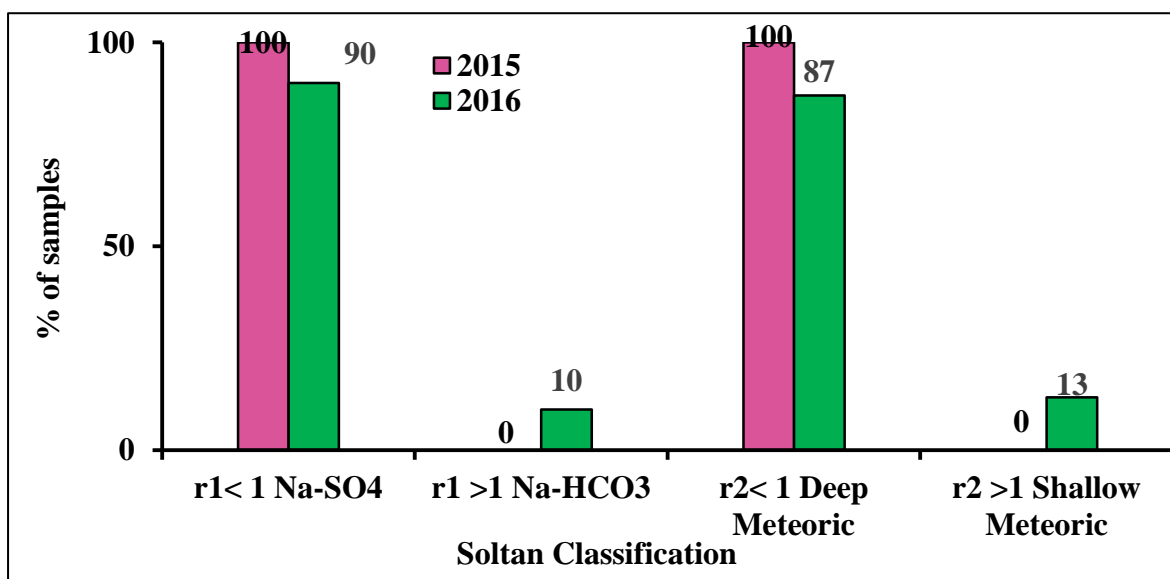


Figure 5.7: Soltan classification of groundwater samples of the study area

The sources of groundwater is able to categorized by meteoric genesis index, which can be determined by using Eq. 2 (Soltan 1998)

$$r2 = \frac{Na + K - Cl}{SO_4} \quad 2$$

Where r2 - meteoric genesis index, concentration of Na⁺, K⁺, Cl⁻ and SO₄²⁻ are termed in meq/l. If r2<1 groundwater is of deep meteoric water type whereas r2>1, the groundwater is shallow meteoric water type. Based on meteoric genesis index, 100% and 87% of groundwater was deep meteoric water type in 2015 and 2016. 13% of samples was shallow meteoric water type in 2016 (Figure 5.7). Low rainfall environments and abrupt fall in water levels causes deep meteoric type of water (Tamma Rao et al 2013). Similar results were observed in the India (Singh et al 2006, Reddy et al 2012, Singh et al 2014).

5.4.4 Hydrogeochemical processes

Groundwater and aquifer minerals interactions have a substantial influence on chemistry of water and responsible for groundwater solutes. Results of hydrogeochemical data are subjected to different schematic graphical diagrams to find the natural processes and anthropogenic activities functioning in aquifer region. Since the study area receives the semi-arid climatic conditions, evaporation may also affect the chemistry of groundwater. The cause of evaporation processes led to increases the ion concentration in water. Cl⁻ vs Na⁺ is used to know the role of evaporation processes on groundwater in the study area. The plot of Cl⁻ vs Na⁺ (Figure 5.8) shows that most of the samples were deviated from freshwater evaporation line. This observation suggests that evaporation process is not influencing the chemistry of groundwater. The deviation is caused by the excess Cl⁻, which likely derived from anthropogenic activities. If Na⁺/Cl⁻ ratio is nearly equal to one, it is liable for halite dissolution for sodium. If Na⁺/Cl⁻ ratio >1 is usually inferred as Na⁺ released from weathering of silicate reactions (Mayback, 1987). The Na⁺/Cl⁻

ratio ranges from 0.22 to 1.18 and 0.13 to 0.54 of groundwater samples in 2015 and 2016, respectively. Similar results were noticed in several researchers (Appelo and Postma 1993; Rajmohan and Elango 2004; Kumar et al 2008; Li et al 2012; Rajesh et al 2012; Vetrimurugan et al 2017). Silicate weathering processes can be explained by the plots of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs HCO_3^- , $\text{Na}^+ + \text{K}^+$ vs TC, $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs TC and $\text{Ca}^{2+}/\text{Na}^+$ vs $\text{HCO}_3^-/\text{Na}^+$ and employed in the various studies (Mackenzie and Garrells 1965; Rajmohan and Elango 2004; Kumar et al 2008; Rajesh et al 2012).

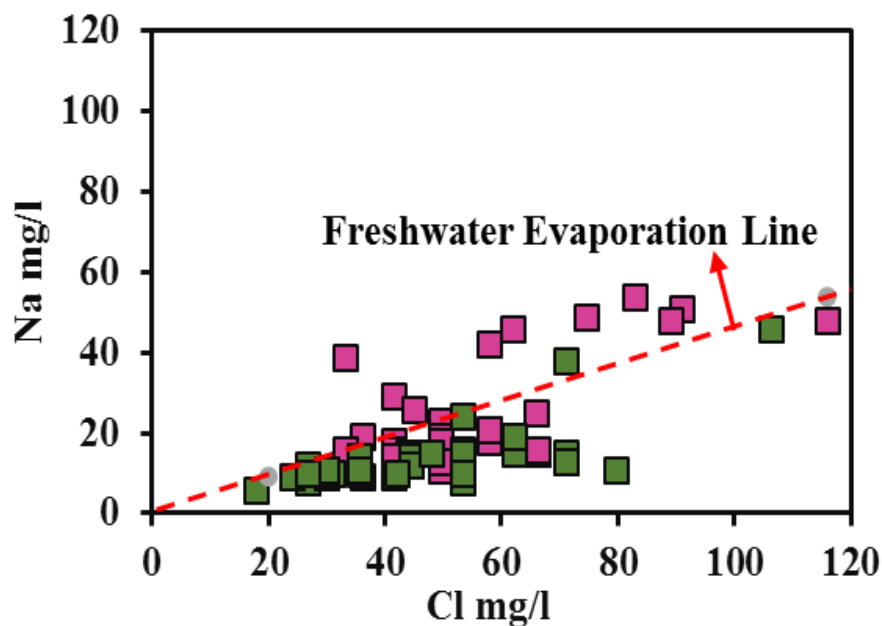
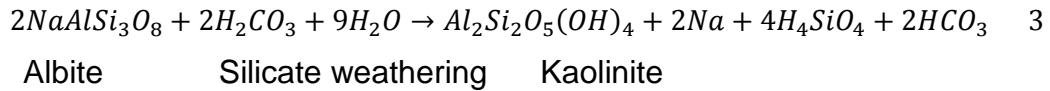


Figure 5.8: Plot of Na^+ vs Cl^- compared with freshwater evaporation line

Plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs HCO_3^- (Fig 5.9) illustrates that all samples lie above to 1:1equiline in both years, indicates excess $\text{Ca}^{2+} + \text{Mg}^{2+}$ over HCO_3^- likely originated from other than carbonate mineral weathering. Likewise, plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs total cation (TC) shows that all sample points lie above the 1:1line in a linearly scattered manner. Plot of $\text{Na}^+ + \text{K}^+$ vs TC expresses that during 2015 and 2016, samples are highly deviated from 1:1line and suggests that contribution $\text{Na}^+ + \text{K}^+$ to the TC is less compared $\text{Ca}^{2+} + \text{Mg}^{2+}$. In order to understand the role of silicate and carbonate minerals weathering on groundwater, $\text{Ca}^{2+}/\text{Na}^+$ is plotted against $\text{HCO}_3^-/\text{Na}^+$ (Figure 5.9). This plot suggests that silicate weathering is basic mineral sources followed by the carbonate minerals dissolution. This resultant silicate weathering was described by the resulting weathering reaction



Calcic feldspar, amphibole and pyroxene, which are present in basic igneous rocks, are easily weathered and governed by the water chemistry in this study area. Similar observations are reported elsewhere (Jacks 1973; Bartarya 1993; Rajesh et al 2012).

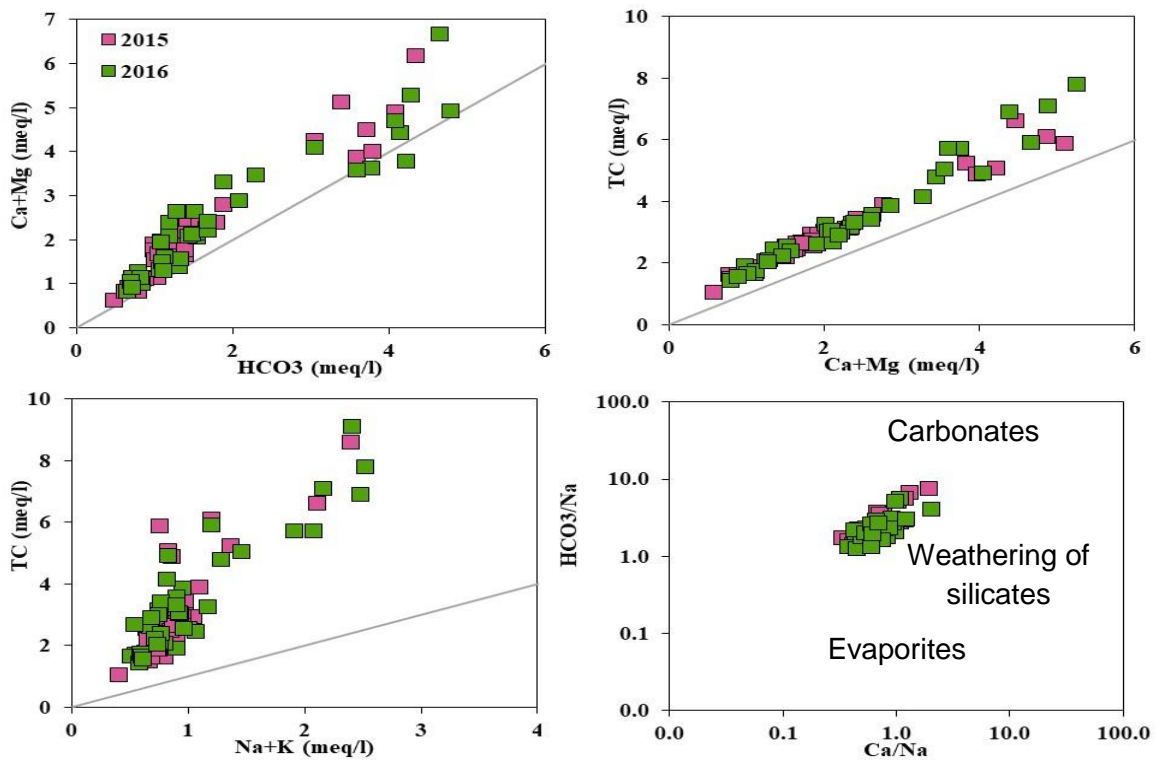
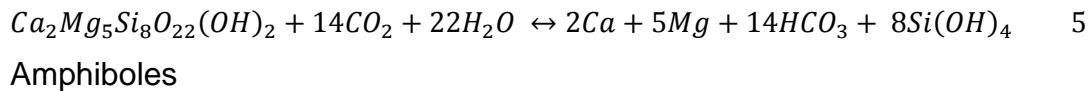
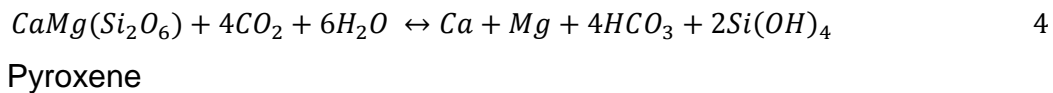


Figure 5.9: Plot of $Ca^{2+} + Mg^{2+}$ vs HCO_3^- , $Ca^{2+} + Mg^{2+}$ vs TC, $Na^+ + K^+$ vs TC and Ca^{2+}/Na^+ vs HCO_3^-/Na explains mineral weathering

Ca^{2+} and Mg^{2+} are the dominant cations with their mean contribution of 29 and 41% in 2015 and 35 and 33% in 2016 (Refer to figure 5.3) to the total cations of groundwater. HCO_3^- is the most dominant anion compared to other anions while mean contribution of HCO_3^- is 51 and 52% in the year of 2015 and 2016. Plot of Ca^{2+} vs HCO_3^- (Figure 5.10a) illustrates that less mineralized waters are plotted close to equiline whereas high mineralized waters are deviated from the line. Dissolution of

calcite is one of the major processes in the low mineralised water. Likewise, Ca^{2+} vs SO_4^- (Fig 10b) plot indicates that all samples lie below the 1:1 line reveals the addition of Ca^{2+} over SO_4^{2-} . This result specifies that gypsum dissolution is not regulating water chemistry. The source of Ca^{2+} and Mg^{2+} in groundwater inferred from the $\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^-$ ratio. As this ratio increases with salinity, Ca^{2+} and Mg^{2+} are excess to a solution at a higher rate than HCO_3^- . Plot $\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^-$ vs Cl^- (Figure 5.10c) show that this ratio do not increases much with Cl^- in 2015 and 2016.

If Ca^{2+} and Mg^{2+} ions are essentially derives from the carbonate dissolution in the groundwater and the weathering of accessory minerals (pyroxene and amphibole) and the ratio of about 0.5 (Sami, 1992) as the weathering reactions are as follows



In the fig 11c, the higher ratio ($\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^-$) ratio (>1) indicates that $\text{Ca}^{2+} + \text{Mg}^{2+}$ added to the water from other sources likely ion exchange reactions (Rajmohan and Elango 2004). $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio of groundwater also evident the carbonate weathering by the dissolution of calcite and dolomite in the area. The ratio of $\text{Ca}^{2+}/\text{Mg}^{2+} = 1$ is dolomite dissolution while between 1 and 2 specifies the calcite impact (Maya and Loucks 1995). $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio is >2 represents dissolution of silicate mineral which leads to Ca^{2+} and Mg^{2+} in groundwater (Katz et al 1998). In the study area, most of the samples have $\text{Ca}^{2+}/\text{Mg}^{2+} < 2$. Sample points lie between 1 and 2 indicate the dissolution of calcite and few sample points lie >2 signifies the influence of silicate minerals (Fig 10d) in the groundwater in the year 2015 and 2016. Similar observations were noticed in several studies globally (Jack 1973; Rajmohan and Elango 2004; Rajesh et al 2012; Vetrimurugan et al. 2013; Varol and Davraz 2014).

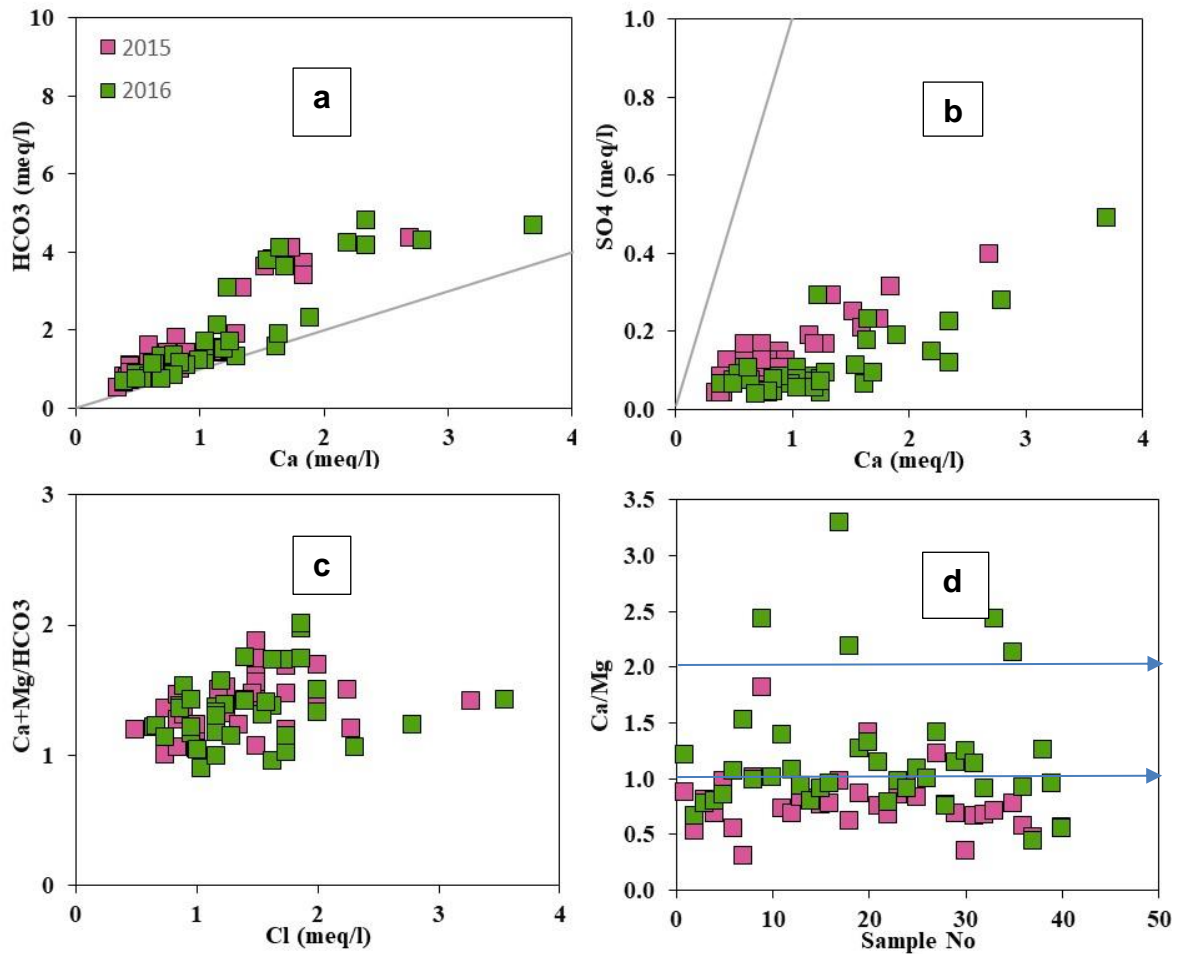
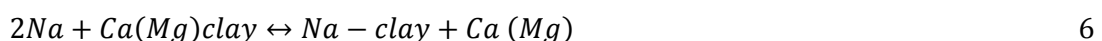


Figure 5.10a, d: Plot of (a) Ca^{2+} vs HCO_3^- ; (b) Ca^{2+} vs SO_4^{2-} ; (c) $\text{Ca}^{2+} + \text{Mg}^{2+} / \text{HCO}_3^-$ vs Cl^- ; (d) Sample location vs $\text{Ca}^{2+} / \text{Mg}^{2+}$

Ion exchange as additional vital hydrochemical processes has major influence on the groundwater chemistry. Plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{SO}_4^{2-} + \text{HCO}_3^-$ shows that samples plotted near to the 1:1 equiline are affected by the calcite, dolomite and gypsum dissolution reactions. The sample points tend to move to the right show the addition of $\text{SO}_4^{2-} + \text{HCO}_3^-$ due to cation exchange (Cerling et al 1989; Fisher and Mulican 1997) while sample points tends to move to the left indicate addition of $\text{Ca}^{2+} + \text{Mg}^{2+}$ over $\text{SO}_4^{2-} + \text{HCO}_3^-$ because of reverse ion exchange, described as follows



Plot of Ca +Mg vs SO₄ +HCO₃ specifies that all samples lie above the 1:1ratio line (Figure 5.11a).

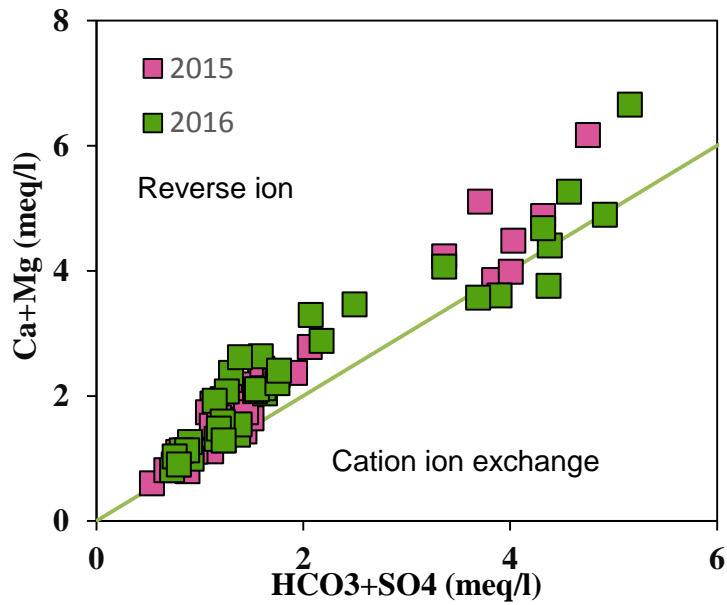


Figure 5.11a: Plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{HCO}_3^- + \text{SO}_4^{2-}$

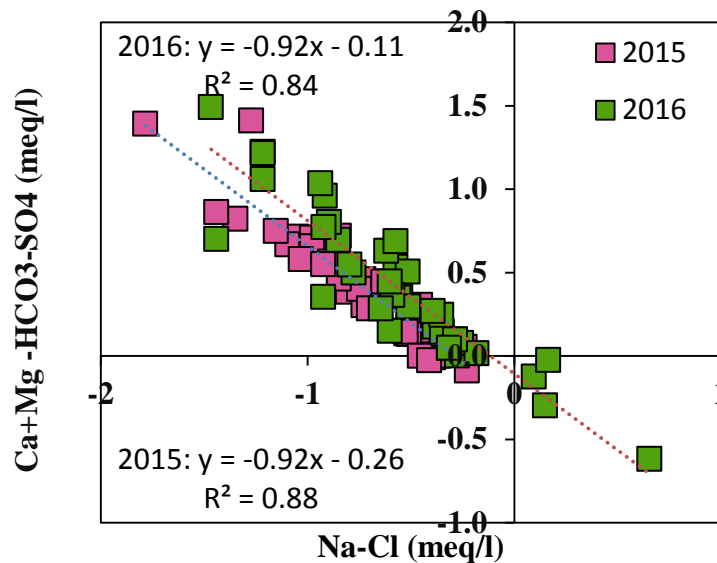


Figure 5.11b: $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- - \text{SO}_4^{2-}$ vs $\text{Na}^+ - \text{Cl}^-$

This results show that addition of $\text{HCO}_3^- + \text{SO}_4^{2-}$ over $\text{Ca}^{2+} + \text{Mg}^{2+}$ indicates the loss of $\text{Ca}^{2+} + \text{Mg}^{2+}$ by cation ion exchange whereas excess $\text{Ca}^{2+} + \text{Mg}^{2+}$ indicates reverse ion exchange processes. $\text{Na}^+ - \text{Cl}^-$ vs $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- - \text{SO}_4^{2-}$ also support the ion and reverse ion exchange processes in the study area. If ion exchange was the dominant processes in the area, groundwater has a trend line with a slope of -1. Based on this plot, both 2015 and 2016 (Figure 5.11b) groundwater samples have a

trend line with a slope of -0.92 and have strong positive correlation ($R^2 = 0.84; 0.88$). This observation confirms the role of ion exchange reactions in this aquifer. Similar results are noticed globally (Fisher and Mulican 1997; Rajmohan et al 2017; Li et al 2016).

Plot of $Ca^{2+} + Mg^{2+}$ vs Cl^- reveals that Ca^{2+} and Mg^{2+} are increase with increasing Cl^- (Figure 5.11c). The positive trend between $Ca^{2+} + Mg^{2+}$ and Cl^- suggests that $Ca^{2+} + Mg^{2+}$ is added to the aquifer while increasing salinity by ion exchange reactions, especially reverse ion exchange reactions.

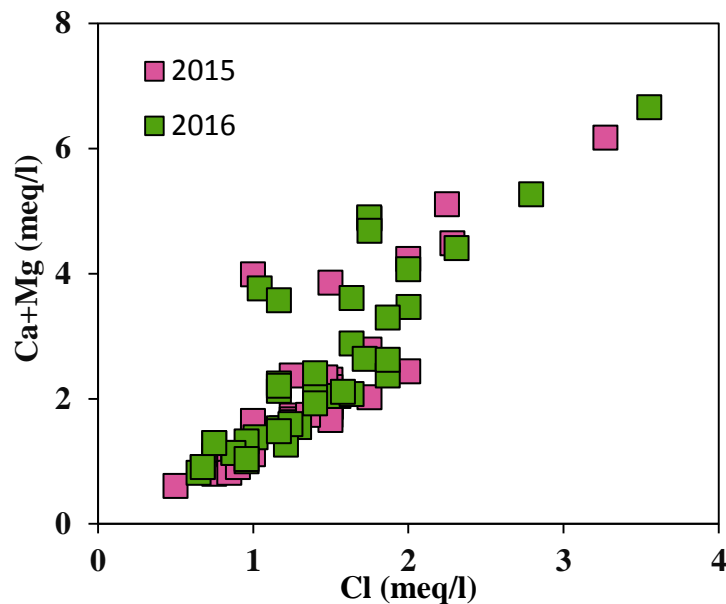


Figure 5.11c: Relation between $Ca^{2+} + Mg^{2+}$ and Cl^- .

Ion exchange can also be evaluated by the chloro alkaline indices of CAI 1 and CAI 2 by Schoellar (1967). Schoellar indices are estimated by using the following equations

$$CAI\ 1 = \frac{Cl - Na + K}{Cl} \quad 6$$

$$CAI\ 2 = \frac{Cl - Na + K}{HCO_3 + SO_4 + CO_3 + NO_3} \quad 7$$

The positive values define reverse ion exchange while negative values express cation exchange. Figure 5.11d illustrates that all samples have positive values irrespective of year. Only few samples have negative values. Hence, figure 5.11d confirm the contribution of reverse ion exchange reactions on water chemistry in the study region.

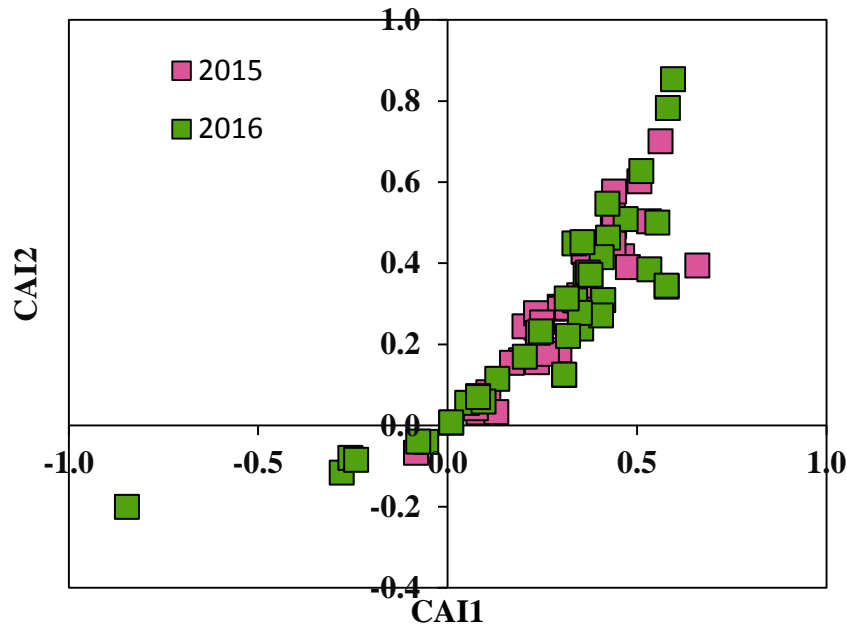


Figure 5.11d: CAI1 vs CAI2

5.5 Geochemical Modelling

Geochemical code PHREEQC, a thermodynamic program was used for speciation calculations (Parkhurst and Appelo 1999). Quality of groundwater was controlled by the occurrence of diverse solutes derived from the rock-soil-water interactions (Saleh et al 1999). Based on the groundwater equilibrium conditions, saturation of specific mineral species is achieved. Groundwater mineral equilibrium calculation was used to inferring the reactive minerals occur in the groundwater aquifer (Deutsch 1997).

Groundwater equilibrium for a specific mineral species is determined by using Saturation Index of minerals using the following equations

$$SI = \log_{10} \frac{IAP}{K_S}$$

8

Where IAP – ion activity product and K_S – solubility product of the mineral

SI = 0 specifies the mineral equilibrium in solution

SI < 0 specifies the mineral was undersaturated (dissolution)

SI > 0 specifies the mineral was oversaturated (precipitation)

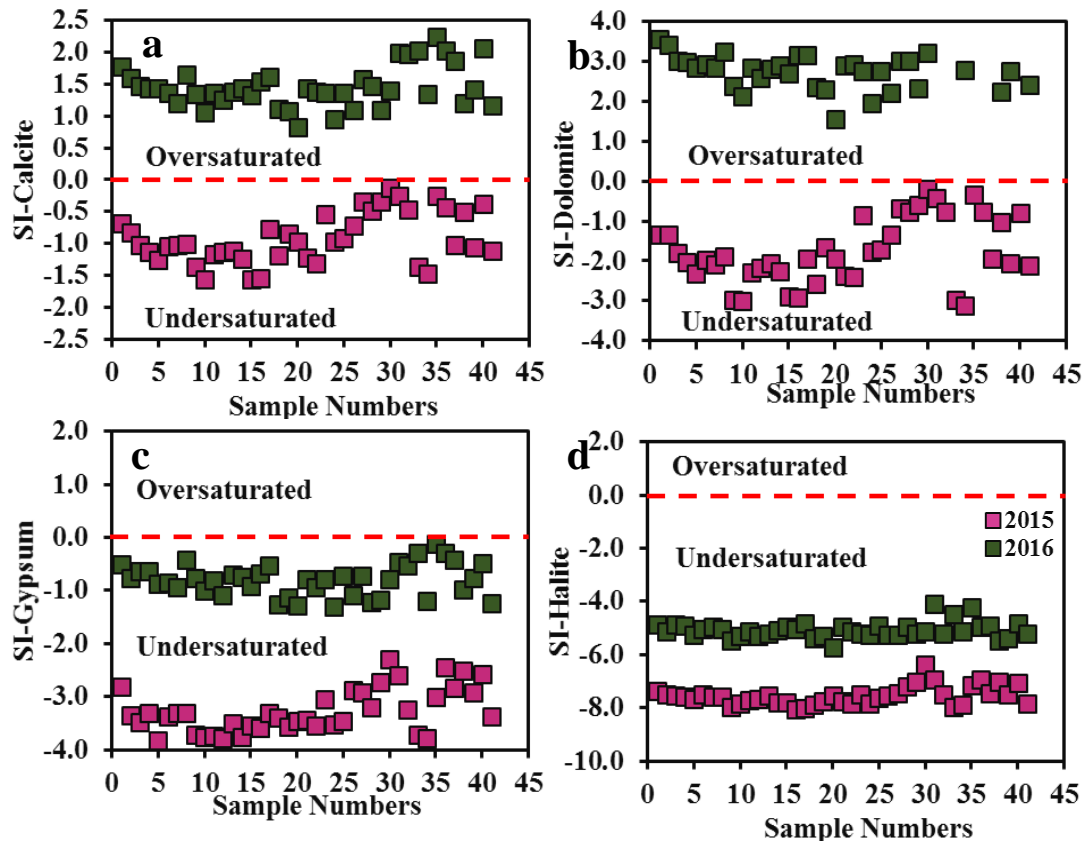


Figure 5.12: Saturation indexes (a) calcite, (b) dolomite, (c) gypsum, (d) halite versus sample numbers of groundwater

Figure 5.12 shows the calculated saturation index of minerals are calcite, gypsum and dolomite. Groundwater samples show that dissolution of carbonate minerals are predominant process in this aquifer. But the water samples are highly undersaturated with respect to gypsum and halite, which ruled out the Cl^- and SO_4^- input from mineral weathering.

5.6 Land use

Separately from the natural/geological controls on groundwater chemistry, land use contributes a significant role in changing the chemistry of groundwater. The correlation between nitrate and chloride can provide indication or evidence the effects of surface contamination, especially irrigation return flows. In case where correlation is strong it is indicative of a possible strong influence of land use (sewer effluent and fertilizers) on groundwater chemistry. NO_3^- was usually identified as a pollutant from anthropogenic activities namely application of fertilizer, domestic sewage and other sources. To understand the impact of land use in groundwater, NO_3^- is plotted against Cl^- (Figure 5.13). Figure 5.13 shows that both have strong correlation and emphasize the role of land use derived from surface input (Li et al 2016). But, there is no NO_3^- data for 2016, hence it is not included in the figure 5.13.

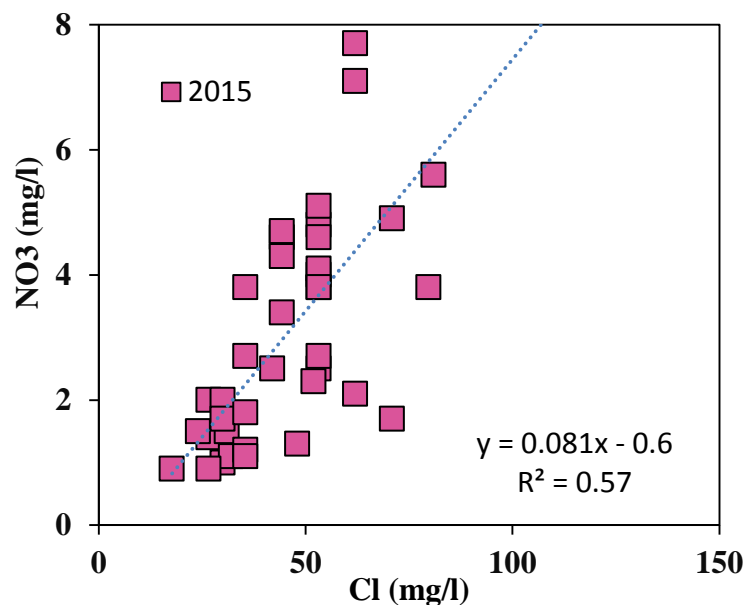


Figure 5.13: NO_3^- vs Cl^-

Cl^- is mostly derived from sewage effluents in addition to dissolution of halite. But figure 5.14 ruled out the geological sources of Cl^- and SO_4^{2-} in the study site. Hence, NO_3^- , Cl^- and SO_4^- are mainly derived from anthropogenic activities. Plot of SO_4^- vs Cl^- (Fig 5.14) also shows strong correlation between them during 2015 and 2016. The study area was intensively irrigated with fertilizers and hence, irrigation

return flow, manures and fertilizers affected the groundwater quality and responsible for high NO_3^- in groundwater.

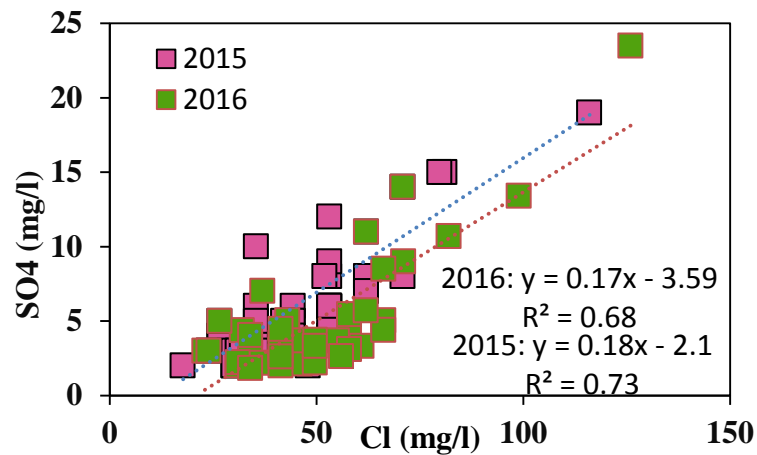


Figure 5.14: Cl^- vs SO_4^{2+}

5.7 Relation between temporal groundwater level fluctuations

Temporal changes in the chemistry of groundwater in a region are significantly related to changes in pumping, well lithology, recharge of groundwater and hydrogeochemical reactions (Scheytt, 1997). Recharge of rainfall was the main source for changes in chemistry of groundwater. The infiltrated water composition was influenced by the soil environ, rainfall, agriculture practice and the unsaturated zone thickness (Scheytt, 1997). Major ion concentration of groundwater of this region changes with respect to temporal groundwater level fluctuation (Figure 5.15) in 2015 and 2016.

In this study, increasing groundwater level decreases ions concentration in groundwater. Groundwater dilution occurs through recharge of rainwater. During the recharge processes, concentration of ions is decreased in groundwater due to mixing of infiltrating freshwater with groundwater. In contrast, decreasing groundwater levels increases the concentration of ions in groundwater due to evaporation in 2015 and 2016. Thus, the temporal changes are mainly influenced by the recharge processes.

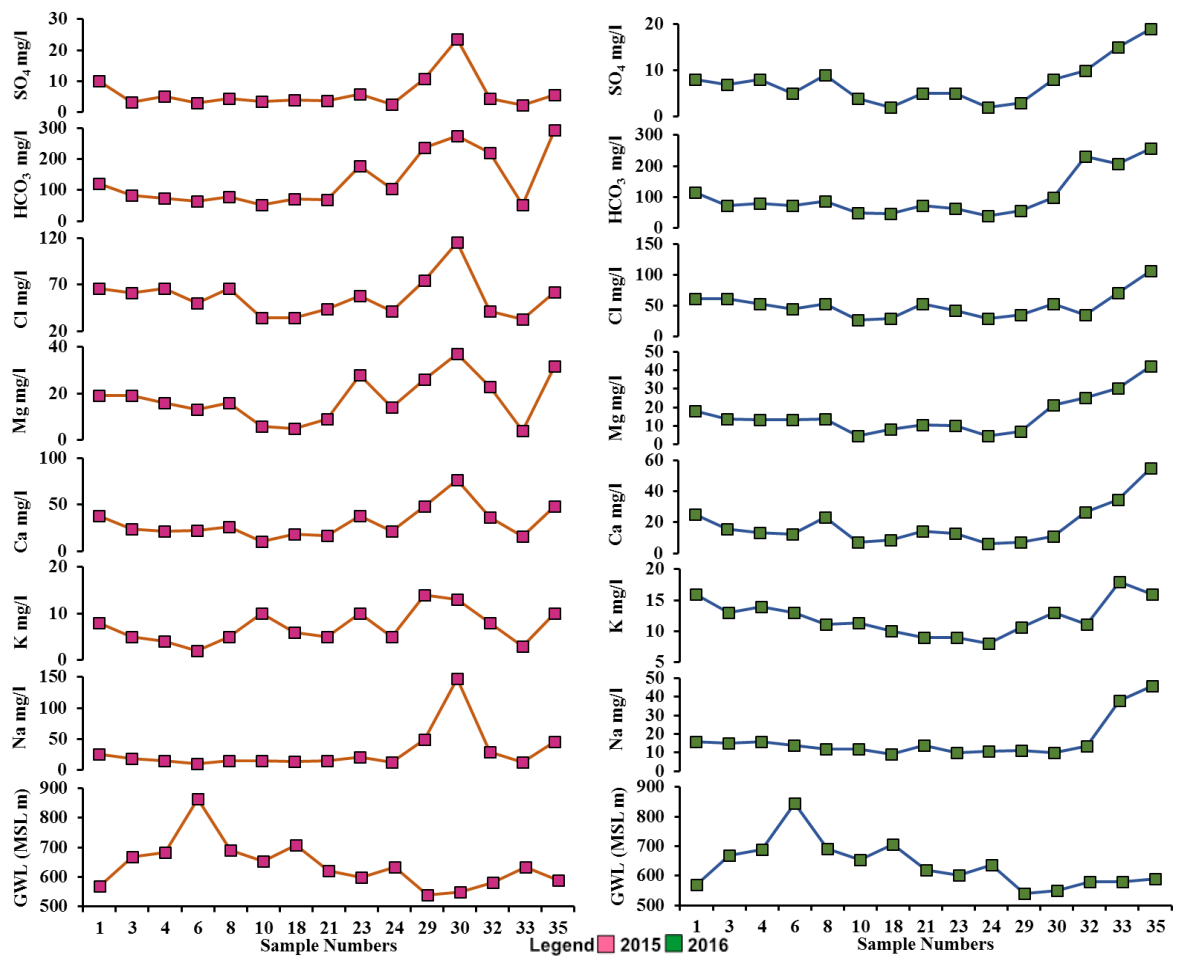


Figure 5.15: Temporal variations in the major ions and groundwater level in the study area

5.8 Multivariate Statistics

Correlations between groundwater variables provide understanding of the significant hydrogeochemical process, which operates the chemical constituents of groundwater. The value of $r^2 > 0.7$ shows high correlation, whereas r^2 value 0.5-0.7 shows medium correlation between parameters. EC and TDS are highly correlated with Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- and SO_4^{2-} concentrations in 2015 (Table 5.2) and Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- and SO_4^{2-} concentrations in 2016 (Table 5.2).

Table 5.2 Pearson correlation matrix of groundwater in 2015 and 2016

2015	pH	EC	TDS	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻
pH	1.00										
EC	0.41	1.00									
TDS	0.41	1.00	1.00								
Na ⁺	0.37	0.81	0.81	1.00							
K ⁺	0.19	0.63	0.63	0.58	1.00						
Ca ²⁺	0.39	0.90	0.90	0.84	0.61	1.00					
Mg ²⁺	0.34	0.84	0.84	0.74	0.58	0.87	1.00				
Cl ⁻	0.37	0.77	0.77	0.76	0.57	0.80	0.79	1.00			
HCO ₃ ⁻	0.35	0.86	0.86	0.75	0.65	0.89	0.89	0.60	1.00		
SO ₄ ²⁻	0.45	0.76	0.76	0.77	0.63	0.80	0.66	0.85	0.59	1.00	
NO ₃ ⁻	0.70	0.44	0.44	0.42	0.72	0.49	0.37	0.42	0.42	0.61	1.00
2016	pH	EC	TDS	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻
pH	1.00										
EC	0.20	1.00									
TDS	0.20	1.00	1.00								
Na ⁺	0.06	0.50	0.50	1.00							
K ⁺	0.01	0.61	0.61	0.34	1.00						
Ca ²⁺	0.24	0.96	0.96	0.49	0.62	1.00					
Mg ²⁺	0.24	0.96	0.96	0.44	0.61	0.89	1.00				
Cl ⁻	0.10	0.85	0.85	0.32	0.61	0.81	0.81	1.00			
HCO ₃ ⁻	0.25	0.94	0.94	0.53	0.58	0.91	0.94	0.68	1.00		
SO ₄ ²⁻	0.11	0.96	0.96	0.47	0.66	0.92	0.93	0.84	0.89	1.00	
NO ₃ ⁻	0.43	0.58	0.58	0.35	0.80	0.55	0.64	0.32	0.66	0.56	1.00

Units: EC(μS/cm), TDS (mg/l)

This correlation established between EC and TDS indicate the amount of total dissolved solids in groundwater. In the study area, shallow wells are likely affected by the irrigation flow compared to deep wells and inferred from high correlation between Ca²⁺ and SO₄²⁻. Cl⁻ was highly correlated with Na⁺, Ca²⁺, Mg²⁺ and SO₄²⁻. NO₃⁻ and K⁺ are highly correlated. Variables correlating with Cl⁻, SO₄²⁻ and NO₃⁻ are partially/completely derived from agricultural activities.

Factor analysis obtain the relative importance of each ion in describing the samples changes in each other are applied to investigate the probability of chemical equilibrium between the aqueous and solid mineral phases of the study area. The scree plot was applied to categorize the amount of factors consider to know the basic data configuration (Liu et al, 2003). It was applied to identify the inflection point on the curve. In this scree plot, a dip in the slope was observed once two eigenvalue specify the dominance of two factors in the chemistry of groundwater (Figure 5.16a, b).

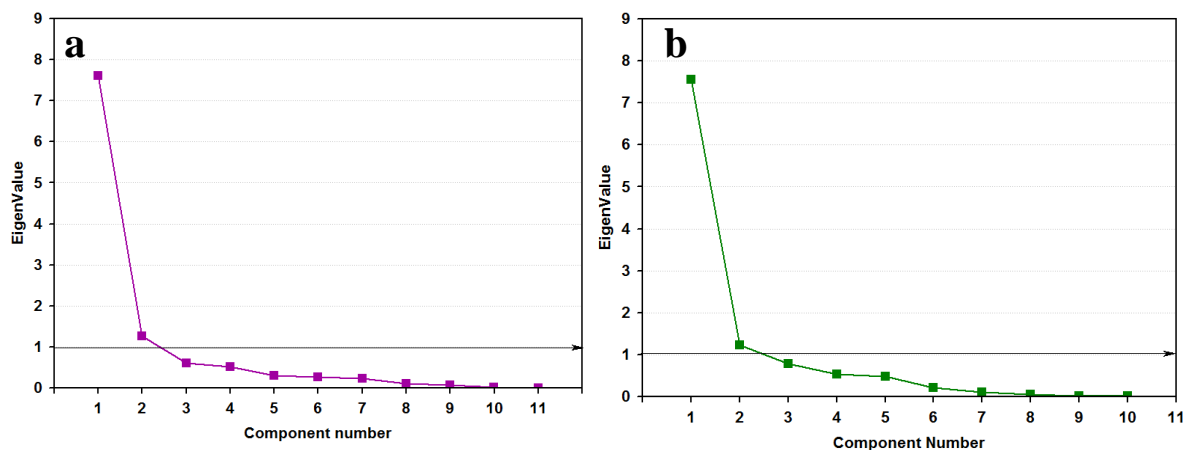


Figure 5.16: Scree Plot of (a) 2015, (b) 2016 of groundwater

Therefore, an overall of two factors were noticed each in 2015 and 2016, which describes approximately 80.68% and 79.95% of total variance for both years. The factor analysis produced two important factors each in 2015 and 2016 with eigenvalues >1. Factor results are shown in the Table 5.3.

F1 accounted for 69.17% and 68.75% of the total variance; the eigenvalues are 7.60 and 7.56 in 2015 and 2016. High to moderate loadings with EC, TDS, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻, SO₄²⁻ and NO₃⁻. High loading of Na⁺ and K⁺ specifies the mineral weathering and ion exchange reactions in the groundwater (Drever 1997). Ca²⁺, Mg²⁺, TDS and EC resulted from dissolution of carbonate and reverse ion exchange processes while Cl⁻ and SO₄²⁻ are derived from irrigation return flow.

F2 accounted for 11.50% and 11.20% of the total variance with the Eigen values of 1.26 and 1.23 in the study area. Significant high loadings of pH, K⁺ and

NO₃⁻ are obtained in 2015 and 2016. High loadings of pH can rely to organic and biogenic processes. pH K⁺ and NO₃⁻ show the high loadings, which indicate the intense agricultural activities. These effects can be described by the influence of potassium nitrate and potassium fertilizers, which are easily soluble and leaching into the groundwater (Singh et al, 2017).

Table 5.3 Varimax rotation factor loadings

Variables	2015		2016	
	Factor 1	Factor 2	Factor 1	Factor 2
pH	-0.175	0.895	-0.057	0.890
EC (µS/cm)	0.919	0.250	0.974	0.164
TDS (mg/l)	0.919	0.250	0.974	0.164
Na ⁺ (mg/l)	0.841	0.258	0.536	0.099
K ⁺ (mg/l)	0.737	0.709	0.731	-0.167
Ca ²⁺ (mg/l)	0.916	0.272	0.942	0.184
Mg ²⁺ (mg/l)	0.895	0.163	0.938	0.232
Cl ⁻ (mg/l)	0.813	0.285	0.874	-0.068
HCO ₃ ⁻ (mg/l)	0.883	0.172	0.912	0.284
SO ₄ ²⁻ (mg/l)	0.747	0.061	0.968	0.076
NO ₃ ⁻ (mg/l)	0.265	0.879	0.511	0.673
Eigenvalue	7.609	1.265	7.563	1.232
% Variance	69.176	11.504	68.757	11.200
Cumulative %	69.176	80.679	68.757	79.957

Dalton and Upchurch (1978) explained the factor scores calculated by the regression technique were applied. Factor scores for individual sample can be correlated to intensity of the processes explained by the factors. Factor scores indicated that positive scores (≥ 1) areas are utmost impacted and negative scores (≤ -1) area are uninfluenced by the process signified by the factors, while areas with near zero scores influenced by the average intensity of the processes.

The spatial variation of F1 scores (Figure 5.17a) indicates that the high factor scores (≥ 1) present in the SW-NW-W-SE-E-central part of the study area in 2015. During 2016 (Figure 5.17b), F1 scores occur in the SE-NE-E part of the area, which shows the impact of natural geogenic processes.

F2 scores (Figure 5.17c) indicate that high factor scores present in the western and central part of the area in 2015. In 2016 (Figure 5.17d), F2 scores

present in the eastern part of the area, which is affected highly by anthropogenic processes such as intense agricultural activities and applied fertilizers and pesticides.

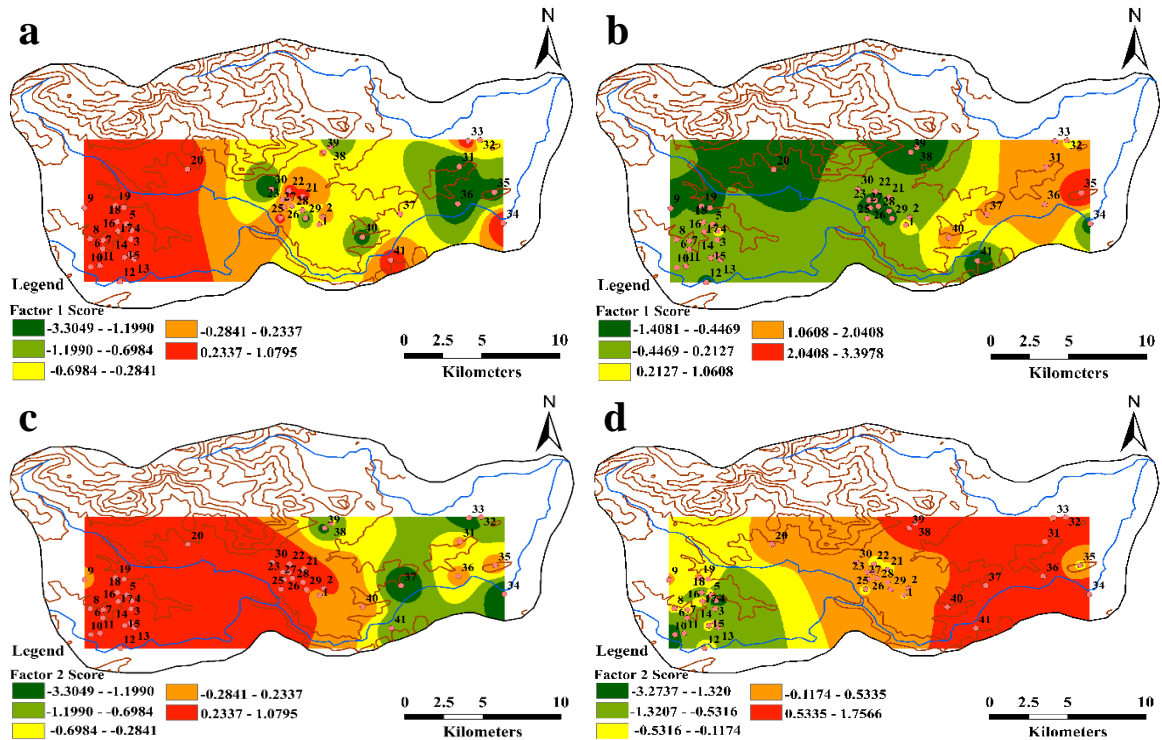


Figure 5.17: Spatial variation of (a), (b) factor 1 and (c), (d) factor 2 in 2015 and 2016 of groundwater

5.9 Conclusion

Development of economic growth is serious effect in the fast draining of groundwater in arid areas. The impact of groundwater pollution was significantly high in areas wherever the water table was relatively shallow. In this study, a comprehensive approach was applied to including hydrogeochemical studies with statistical and geostatistical methods to evaluate the natural and anthropogenic impact on groundwater in the Limpopo province. The pH values indicate the acidic nature of groundwater during 2015 and 2016. TDS suggests that groundwater is fresh in nature. The dominant sequence of cations presented as $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ while that of anions as $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ in the year 2015 and 2016. The Piper and Chadha plots show that the dominant water types are $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$

and $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-$. Gibbs plot reveals that the chemistry of water was influenced by rock-water interaction. Bivariate plots suggest that dissolution of carbonate and silicate minerals, reverse ion exchange and anthropogenic activities (especially agricultural activities) influenced the water chemistry in the study area. Groundwater was saturated and oversaturated with respect to calcite and dolomite and undersaturated with gypsum and halite. High nitrate concentration resulted from agricultural and farming activities and leakage of sewage system. Temporal groundwater fluctuations indicates that recharge processes decrease the concentration of ions in groundwater by mixing of infiltrated fresh water with groundwater. Decreasing the groundwater levels while increasing the concentration of ions are likely by the evaporation processes. Factor analysis reveals that the two main factors describe about 80.68% and 79.95% of total variance for both years. These factors explain hydrogeochemical processes (evaporation, ion and reverse ion exchange, weathering of silicate and carbonate minerals) and impact from irrigation return flows, human effects and usage of K^+ and NO_3^- fertilizers. The water quality in the study region is affected by the natural and man-made activities.

CHAPTER SIX

6 Evaluation of Surface and Groundwater Quality for Drinking and Irrigation purposes

6.1 Introduction

Due to the expanding demand for drinking and irrigation water and inadequacy of surface water, significant of groundwater is drastically expanding over the globe. In the developing countries, around 80% of the diseases and deaths are associated with water contamination (UNESCO 2007). South Africa has a population of 49.4million and 52% of people are estimated to be living in rural areas (DEAT 2008). Six million people do not have access to a good quality drinking water. In recent years, industrial expansion, utilization of synthetic composts for farming and utilization of pesticides and bug sprays have caused a major thread for groundwater and groundwater is more vulnerable for these contaminants. Generally, quality of groundwater is influenced by precipitation, climate, geology, irrigation practices, anthropogenic sources and a few different reasons (Rajesh et al. 2015). Similarly, toxic and nontoxic pollutants are the major contaminants of water that are transported from recharge to discharge zone by the groundwater flow (Manish et al 2006). The hydrochemical attributes of groundwater have a fundamental part in evaluating its quality for different purposes. It is also responsible for groundwater quality changes in the aquifer additionally in charge of a superior understanding of likely changes in groundwater quality.. Globally several researchers have studied and reported the groundwater quality related problems (Yidana and Yidana 2009; Stamatis et al. 2011; Ketata et al. 2012; Li et al. 2013; Mohebbi et al 2013; Agca 2014; Varol and Davran 2014; Venkatramanan et al 2015; Zhou et al 2016; Rabeiy 2017; Faniran et al 2004). In South Africa, few studies have been carried out to assess the drinking water quality using Drinking Water Quality Index (DWQI) (Faniran et al. 2004; Mpenyana-Monyatsi et al 2012; Nephalama and Muzarengi 2016; Ntokozo 2017; Vetricurugan et al. 2015).

Water Quality Index method was applied to determining the groundwater quality. The index was computed for assessing influence of natural and anthropogenic exercises in light of some key parameters in the groundwater chemistry. To compute the WQI, the weight has been allocated out for the each physico-chemical parameters as indicated by the parameters relative significance in the general quality of drinking water. The allocated weight varies from 1 to 5 (Horton 1965). Weighting and analysis method have improved by the presence of artificial neural networks, Fuzzy theory, etc. Fuzzy approach has been widely used in DWQI in recent times (Li and Qian, 2014; Venkatramanan et al, 2015). All these methods influence on their individual manner and the results of these methods are not always be similar. The Inverse Distance Weighted (IDW) method was used for 3D maps, contours preparation and groundwater quality assessment (Cong et al, 2014).

Recently, several studies were conducted in the Limpopo province including hydrogeological characterization of crystalline basement aquifers and hydrochemical analysis and conceptual hydrogeological models (Holland 2011). The application of coupled linear and non-linear system identification model was tested to estimate the groundwater level in Nzhelele and Luvuvhu area (Makungo and Odiyo 2017).

Effluents from wastewater treatment facilities are major anthropogenic sources for groundwater contamination (Edokpai et al. 2016). Sludge with high metals and other ions over limits recommended by the DWAF guidelines, causes environmental hazard if applied in soil as fertilizers (Shamuyarira and Gumbo 2014). Climate change impacts on water availability and utilizations in the Limpopo River Basin of Southern Africa is studied using a linked modeling system, which consist of a semi-distributed global hydrological model and water simulation model for policy analysis of agricultural commodities and trade (Zhu and Ringler 2012). Discharging of effluent into a water resource gives poor quality water and makes it unsuitable for consumption. Effluent discharge resulted eutrophication because of nitrate enrichment and proliferation of harmful algal blooms and schistomiasis infections in the long term (Gumbo et al 2016). All these research studies are mainly focused on hydrogeological characterization of groundwater, estimating groundwater level using model, heavy metal contamination in sewage sludge, climate change and effluent

discharge in this region. Concerns about groundwater quality change in Limpopo province is not attracted by the researchers and hence, enough attention from researchers and existing research studies on this objective are not given. Therefore, the present study was carried out to assess the changes in groundwater quality and its suitability of human consumption and irrigation usage by Drinking Water Quality Index (DWQI) and Geographical information system (GIS) in Luvuvhu Sub-Catchment, Limpopo, South Africa. This will help the local people towards proper management of water resources, and to build up gauge information, which help in future water administration and protection measures.

6.2 Water quality Assessment

Total dissolved solids (TDS) and total hardness (TH) of groundwater were estimated using the following equations (Loyd and Heathcote 1985; Szaboles and Darab 1964)

$$\text{TDS (mg/l)} = \text{EC } (\mu\text{S/cm}) \times 0.64 \quad (1)$$

$$\text{TH (mg/l)} = 2.497 \text{ Ca (mg/l)} + 4.115 \text{ Mg (mg/l)} \quad (2)$$

Irrigation water quality was assessed using different indices namely magnesium hazard (MH) (Szaboles and Darab 1964), sodium percent (Na %) (Wilcox 1955), residual sodium carbonate (RSC) (Eaton 1950), Kelly's ratio, sodium adsorption ratio (SAR) (Sawyer and MacCarthy 1978) and permeability index (PI) (Doneen 1964).

$$MH = (Mg / (Ca + Mg)) \times 100 \quad (3)$$

$$RSC = (CO_3 + HCO_3) - (Ca + Mg) \quad (4)$$

$$Na\% = \frac{(Na + K) \times 100}{(Ca + Mg + Na + K)} \quad (5)$$

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}} \quad (6)$$

$$PI = \frac{Na + \sqrt{[(HCO)_3]}}{(Ca + Mg + Na)} \times 100 \quad (7)$$

$$KR = \frac{Na}{Ca + Mg} \quad (8)$$

6.3 Spatial Interpolation

Surface interpolation techniques in a geographical information system (GIS) are very powerful tools for predicting surface values. The IDW method was used for spatial interpolation in this study for groundwater quality assessment with the help of geostatistical analyst modules in ArcMap 10.1 (2012). IDW is a method used to interpolate spatial data between measurements. In the IDW interpolation, each value calculated is a weighted average of the surrounding sample points. A second order polynomial was assigned in the power field, which controls the significance of surrounding points on the interpolated value. Weights are computed by taking the inverse of the distance between observation locations of the points being calculated (Cong et al 2014).

6.4 Statistical Analysis

Descriptive statistical analysis such as range, mean, median, standard deviation, co-efficient of variation and skewness was carried out as a first step to explore the physicochemical data. Correlation analysis was employed to assess the probable relationship between ionic concentration of groundwater in the year 2015 and 2016. The independent t test analysis was also used to evaluate the difference in 41 data sets between sampling years. The t-test formula is given below

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}} \quad (9)$$

Where \bar{X}_1 – mean of first set of values, \bar{X}_2 – mean of second set of values, S_1 - Standard deviation of first set of value, S_2 – Standard deviation of second set of value, n_1 – total number of first set of values and n_2 - total number of second set of values. All statistical analysis was completed by using STATISTICA 8 (2007).

6.5 General water chemistry

The results of descriptive statistics for physicochemical data of groundwater in 2015 and 2016 in the study area are given in Table 6.1. Coefficient of variations represent low variability ($CV < 10\%$), moderate ($10\% \leq CV \leq 100\%$) and high ($CV > 100\%$) variability. Low CV values show a homogenous distribution of variables whereas high CV values suggest a non-homogenous distribution of variables. According to this classification of groundwater in the year 2015, pH values are weak variability while Na^+ values are the strong variability. Moderate CV variability is noticed in the K^+ , Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- and SO_4^{2-} . In the year of 2016, CV indicates that pH and Na^+ have weak and strong variability whereas other ions have moderate variability. Coefficient of variance of 2015 and 2016 indicates heterogeneous distribution of variables in the study area. The t-test is the most common method for determining the differences in means between two variables or season in groundwater. There is a difference in the most of the variables namely Na^+ , Ca^{2+} , Cl^- and HCO_3^- during 2015 and 2016. t-test implies that there is a difference in the major ion chemistry during 2015 and 2016 and the difference is statistically significant ($p < 0.05$) except EC, TDS, Mg^{2+} and SO_4^{2-} (Tables 6.2).

6.6 Groundwater suitability assessment

The groundwater suitability for drinking uses depends on the chemical constituents in the water. If the mean values of EC and TDS of the groundwater is less than 450, the groundwater is suitable according to DWAF (1996) (Table 6.1 and 6.3). In the present study, the quality of water is evaluated using major ions. Results of chemical analysis are compared with the standard guideline values proposed by

the Department of Water Affairs and Forestry (DWAF, 1996), South Africa (Figure 6.1) to assess the suitability for human consumption.

Table 6.1 Descriptive Statistical results of physicochemical parameters of groundwater in the study area

Parameter s	2015 (n=41)				2016 (n=41)			
	Range	Mean	SD	CV%.	Range	Mean	SD	CV%.
pH	6-7.6	6.6	1.0	16	6.4-7.6	6.8	0.4	6
EC (μ S/cm)	81- 1206	358	241	69	119- 900	343	204	58
TDS (mg/l)	52-772	229	154	69	76-576	220	131	58
Na ⁺ (mg/l)	6-46	14	18.6	114	9-51	20	23.1	92
K ⁺ (mg/l)	6-18	11	2.5	22	2-15	8	3.4	44
Ca ²⁺ (mg/l)	7-54	18	10	62	8-74	24	14.8	52
Mg ²⁺ mg/l)	3-42	15	10	69	4-37	14	8.4	54
Cl ⁻ (mg/l)	18-116	48	17.5	38	23-126	50	18.6	34
HCO ₃ ⁻ (mg/l)	31-266	97	62	66	41-293	116	69.6	59
SO ₄ ²⁻ (mg/l)	2-19	6	4.1	65	1.8-24	5	5.3	86

Table 6.2 Results of *t* test ($p < 0.05$) values

Parameters	Significance
pH	0.00
EC (μ S/cm)	0.94
TDS (mg/l)	0.94
Na ⁺ (mg/l)	0.04
K ⁺ (mg/l)	0.00
Ca ²⁺ (mg/l)	0.00
Mg ²⁺ (mg/l)	0.51
Cl ⁻ (mg/l)	0.03
HCO ₃ ⁻ (mg/l)	0.03
SO ₄ ⁻ (mg/l)	0.89

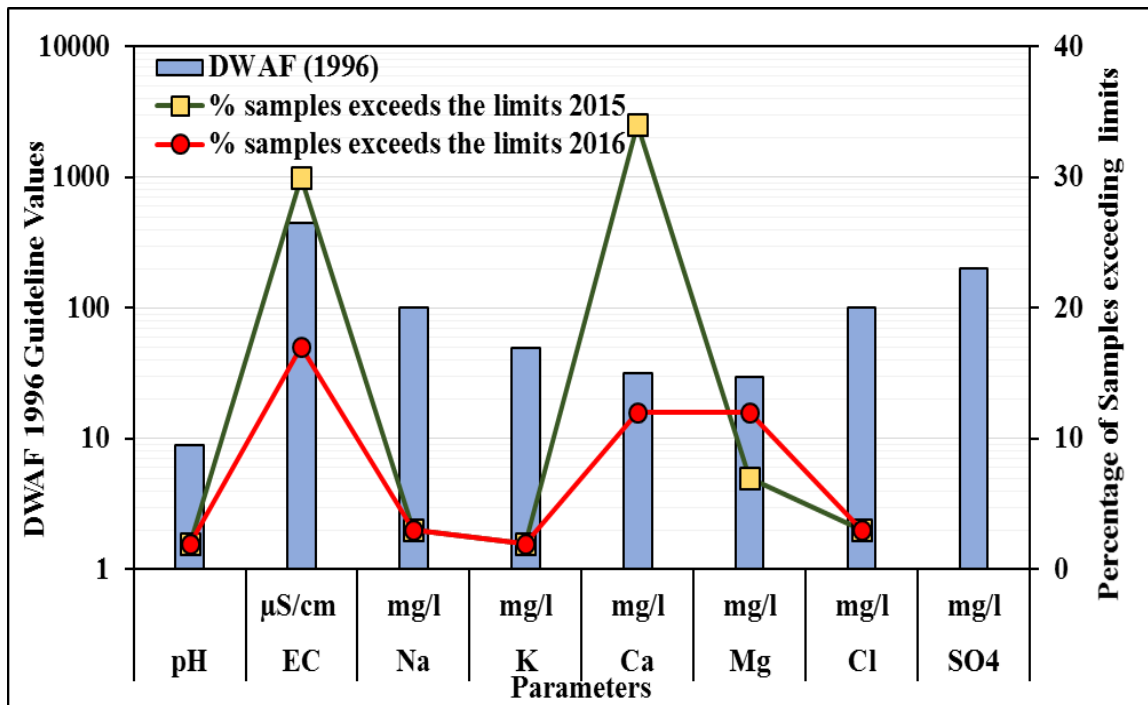


Figure 6.1: Hydrochemical parameters of groundwater based on DWAF (1996) and percentage of samples exceeding the limit

The pH value of groundwater varies from 6 to 7.6 with a mean value of 6.6 and 6.4 to 7.6 with an average value of 6.8 in the year of 2015 and 2016, respectively (Tables 6.1) which indicates that the water is slightly acidic to alkaline in nature in both years. The high EC water reduces plant water availability even though the soil may appear wet. Groundwater EC ranges from 81 to 1206 $\mu\text{S}/\text{cm}$ with a mean of 358 $\mu\text{S}/\text{cm}$ and 119 to 900 $\mu\text{S}/\text{cm}$ with a mean of 343 $\mu\text{S}/\text{cm}$ during 2015 and 2016, respectively. Based on DWAF (1996) water quality guideline value of EC (<450), 33 and 32 water samples are within the acceptable limits and 8 samples recorded above the limits for both years. Total dissolved solid (TDS) decided the hydrochemical characteristics of groundwater and is used often to ascertain the groundwater suitability for drinking purpose. TH and TDS are together used to assess the suitability of water for drinking and other uses. TH of groundwater samples indicate that 18 and 7 (mg/l) samples are soft, 16 and 21 (mg/l) samples fall moderately hard, 6 and 11 under hard and 1 is very hard in both years. TDS indicates that all groundwater samples are fresh.

According to these classifications, the groundwater is suitable for drinking without any major health threat to human. The hard water is classified and describe as water with high concentration of magnesium and calcium (Brian Oram, 2014). There is no danger to human health due to hard water; however, it gives poor performance with soap and bad smell. High level of hardness water affects and its reaction with soap can cause scale and incrustation accumulation in the water supply system. Long-term consumption of very hard water can cause an increased incidence of kidney problems, anencephaly, prenatal mortality, cardio-vascular disorders and cancer (Kumar et al. (2014). Calcium is significant element, which is important to aquatic plants. The concentration of total hardness in the groundwater ranges from 25 to 311mg/l and 50 to 345mg/l and with mean value of 100mg/l and 128mg/l during 2015 and 2016, respectively. Sawyer and McCarty (1978) classification (Table 6.3) of TH suggests that 44 and 18 % of samples are soft (<75mg/l), 39 and 52 % are moderately hard (75-150mg/l), 15 and 28 % are hard (150-300mg/l) and 2 and 2% are very hard (>300) in the year of 2015 and 2016, respectively. According to TH classification, the groundwater is soft to hard in nature in the study area.

Groundwater quality mapping was employed and created by the IDW interpolation method. In this study, the South African Water Quality standards DWAF (DWA, 1996) are used to assess the drinking water quality. The suitability of groundwater is assessed using DWAF (1996) for the following parameters, pH (6.5 to 7.5), EC (450 μ S/cm), Na^+ (100mg/l), K^+ (50 mg/l), Ca^{2+} (32 mg/l) and Mg^{2+} (30 mg/l), respectively. The same standards are applied in Cl^- and SO_4^{2-} limits which is 100 and 200mg/l. Carbonate was absent in the groundwater during 2015 and 2016. Suitability maps indicate the safe and unsafe zones for groundwater usage and future development. Based on pH values, NE-SE of the study area is unsafe and safe zone is NW-SW of the area in the year 2015 and 2016 (Figure 6.2a, b). Unsafe part of the pH spatial map values are due to the occurrence of HCO_3^- ions, which affects the pH of the water. Low pH causes metal corrosion in the water supply pipes and increases the heavy metal content in water.

EC of groundwater indicates the unsafe zone in NE-SE part and rest of the area are safe in the year of 2015 (Figure 6.2c). In the year of 2015 and 2016, EC (Figure 6.2d) shows same pattern but few unsafe zones are extent to the central part of the area. Spatial map of EC shows that unsafe part of the area are mainly comprises of granitic basement rocks, which are due to the influence of dissolution and weathering of rocks and also anthropogenic activities.

Table 6.3 Drinking water quality based on EC, TDS and TH in the year of 2015 and 2016

EC μS/cm	Range	Classification	% of Samples		Reference	
			2015	2016		
	<450	Permissible	80	75	South African National Standards (2006)	
	>450	Not permissible	20	25		
TDS mg/l	< 1000	Fresh water	100	100	Freeze and Cherry (1979)	
	1000-10000	Brackish water	-	-		
	10000-100000	Saline water	-	-		
	>100000	Brine water	-	-		
		<500	Desirable for drinking	93	95	Davis and DeWiest (1966)
		500-1000	Permissible for drinking	5	7	
		1000-3000	Useful for irrigation			
		>3000	Unsuitable			
TH mg/l	<75	Soft	44	18	Sawyer and McCarthy, 1987	
	75-150	Moderatly hard	39	52		
	150-300	Hard	15	28		
	>300	Very hard	2	2		

In the study region, Na⁺ ranges from 6 to 46mg/l and 9 to 51mg/l with a mean of 14mg/l and 20mg/l during 2015 and 2016, respectively. The results denote that 3% of samples exceeded the DWAF limit (DWAF, 1996). In the year of 2015 (Figure 6.2e), Na⁺ concentration are unsafe in NE-SE part and rest of the area are safe. The spatial pattern of Na⁺ appears differently during 2016 and small portion of NE-SE is unsafe (Figure 6.2f). Likewise, K⁺ ranges from 6 to 18mg/l with a mean of 11mg/l and 2 to 15mg/l with a mean of 8mg/l in the year 2015 and 2016, respectively. Concentration of K⁺ indicates unsafe zone in N-S, SE and few parts in the central part of the area and rest of the area are safe in the year of 2015 (Figure 6.2g). Similar spatial trends occurs in the year of 2016 (Figure 6.2h). High concentrations of

Na⁺ in the area specify the weathering of Na⁺ rich plagioclase bearing granitic rocks and over exploitation of groundwater (Davis and DeWiest 1996). Weathering of potash feldspar and clay minerals from aquifer system are the source of K⁺ in the unsafe part of K⁺ spatial map in the area.

Calcium (Ca²⁺) ranges from 7 to 54mg/l with a mean of 18mg/l and 8 to 74mg/l with a mean of 24mg/l during 2015 and 2016, respectively. The samples exceeded the DWAF limits accounts 34 and 12% (Figure 6.1) in the year 2015 and 2016, respectively. The direction of N-S, NE, SE and central part of the area are unsafe and NW-SW are safe in the year 2015 (Figure 6.2i). During the year 2016 (Figure 6.2j), water is unsafe in the NE-SE part of the study area. Hence, groundwater is severely contaminated in the year 2015 as compared to 2016. Magnesium (Mg²⁺) ranges from 3 to 42mg/l with a mean of 15mg/l and 4 to 37mg/l with a mean of 14mg/l in the year 2015 to 2016, respectively. Seven percent (7%) and twelve (12%) of samples exceed the standard value (Figure 6.1). NE-SE part of the area are unsafe and rest of the area are safe in the year 2015 (Figure 6.2k) and 2016 (Figure 6.2l). Dissolution of minerals in granitic area namely pyroxene, amphiboles and feldspar are the source of Ca²⁺ in the unsafe zone (DEAT 2008). Unsafe part of Mg²⁺ spatial map is mainly derived from Ca²⁺-Mg²⁺ silicates from plagioclase and potash feldspar minerals namely orthoclase and microcline (Howari and Banat 2002).

In this study, Cl⁻ ranges from 18 to 116mg/l with a mean of 48mg/l and 23 to 126mg/l with a mean of 50mg/l during 2015 and 2016, respectively. The samples of 3% (Figure 6.1) exceeded standards values recommended by the DWAF. The central part and NE-SE of the area are unsafe and the rest of the area are safe in the year 2015 (Figure 6.2m). The portion of NE-SE of the area are unsafe and other parts of the area are safe in the year of 2016 (Figure 6.2n). Spatial maps of Cl⁻ and SO₄²⁻ indicate the pollution sources like domestic sewage and leaching of saline residues in the soil (Cude (2001).

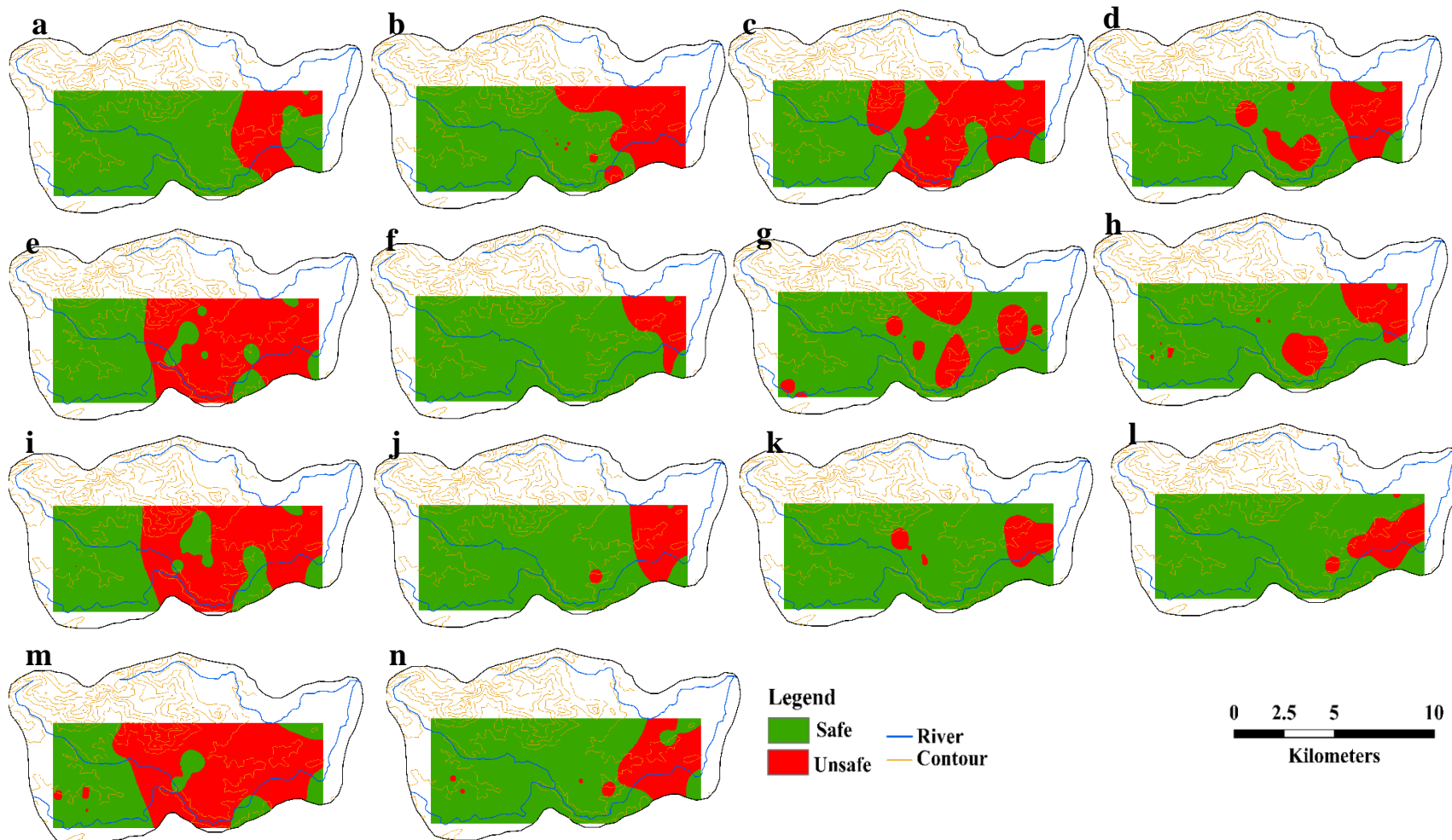


Figure 6.2: Spatial distribution of groundwater quality (a, b) pH, (c, d) EC, (e, f) Na⁺, (g, h) K⁺, (i, j) Ca²⁺, (k, l) Mg²⁺ (m, n) Cl⁻ in the year of 2015 and 2016 of the study area

6.7 Groundwater suitability assessment using DWQI

The drinking water quality in the study area is assessed using the drinking water quality index (DWQI) employed by several researchers (Hem, J.D 1985; Howari and Banat 2002; Appelo and Postma 1993; Horton 1965; Shweta et al, 2013). WQI is a dimensionless number and indicates the overall water quality in a study area using compiling different water quality variables in a single number (Shweta et al, 2013). The permissible limits (Table 6.4) for drinking water recommended by the DWAf (1996) used for this calculation. Eight groundwater parameters namely, EC, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻ and HCO₃⁻ are selected.

The calculation of the DWQI includes five steps. In the 1st step, a relevant weight is given to selected water quality parameters. The assignment of the weight to a particular parameter (Table 6.4) depends on its relative importance in controlling the overall drinking water quality and its impact on human consumption (Cude, 2001). Maximum weight of 5 was assigned to parameters namely Na⁺, K⁺, Ca²⁺ and HCO₃⁻. Minimum weight of 1 was assigned to SO₄²⁻. Further, weight 3 was assigned to Mg²⁺ and Cl⁻.

Table 6.4 Weights of parameters and DWAf standards

Parameters	Assigned weight (Wi)	DWAf	Relative weight (Wi)
Ca ²⁺ (mg/l)	5	32	0.15625
Mg ²⁺ (mg/l)	3	30	0.09375
K ⁺ (mg/l)	5	50	0.15625
Na ⁺ (mg/l)	5	100	0.15625
HCO ₃ ⁻ (mg/l)	5	300	0.15625
SO ₄ ²⁻ (mg/l)	1	200	0.03125
Cl ⁻ (mg/l)	3	100	0.09375
EC (μS/cm)	5	450	0.15625
	∑ Wi =32		∑ Wi =1

The 2nd step indicates the assignment of relative weights to each parameter based on the following equation

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (10)$$

Where W_i is the relative weight of the i th parameters, w_i is the weight of the i th parameter and n is the total number of parameters.

The third step indicates the quality rating (q_i) calculation for each parameter for each sample (Eq 11).

$$q_i = \frac{C_i}{S_i} * 100 \quad (11)$$

Where C_i is the concentration of the i th parameter, and S_i is the permissible limit of the i th parameter in drinking water based on DWAF (1996).

In the fourth step, sub-index of the i th parameter SI_i is estimated using the equation 12

$$SI_i = W_i * q_i \quad (12)$$

Finally DWQI of the individual water samples are calculated by summing SI_i values of all the parameters (Eq 13).

$$WQI = \sum SI_i \quad (13)$$

The DWQI values in the study area ranges from 23 to 134 and 20 to 147, with a mean value of 58 in the year of 2015 and 2016, respectively. DWQI can be divided into 5 types are excellent (<25), good (25-50), poor (50-75), very poor (75-100) and unsuitable (>100) (Shweta et al. 2013). The water types and samples percentage in each class is shown in figure 6.3.

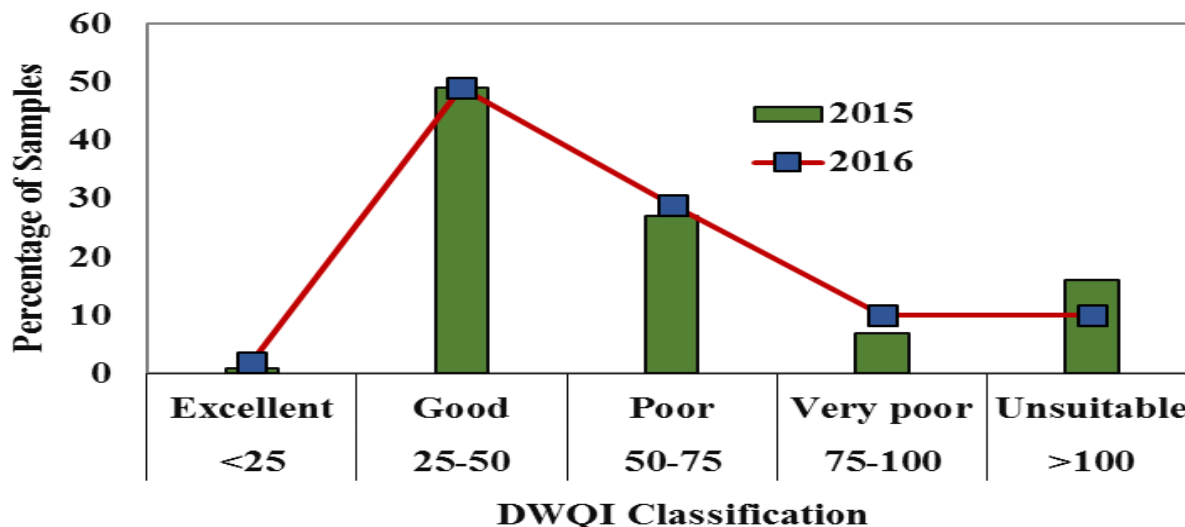


Figure 6.3: Relationship of water types and percentage of samples

Spatial distribution of DWQI map of 2015 (Figure 6.4a, b) and 2016 depict that NW- SW and central part of the area were excellent to good and the remaining parts of the area was poor to unsuitable. Spatial variation of DWQI maps (Figure 6.4 a, b) indicate that approximately 50% of area shows poor to unsuitable class of groundwater in the year 2015 and 2016. DWQI was verified with Na^{2+} and EC, which are selected as pollution indicators. The observed high values of Na^+ , EC and DWQI suggest the poor quality of groundwater in the study area. The high value of DWQI has been found to closely relate to the high values of Ca^{2+} , Mg^{2+} , K^+ and Cl^- . Poor quality of water in the area is mainly due to over exploitation of groundwater, direct discharge of effluents and agricultural impact. DWQI was plotted with various parameters. Results suggest that there is a strong correlation during 2015 compared to 2016. Hence, DWQI is reasonable applicable for groundwater quality assessment in addition with other parameters.

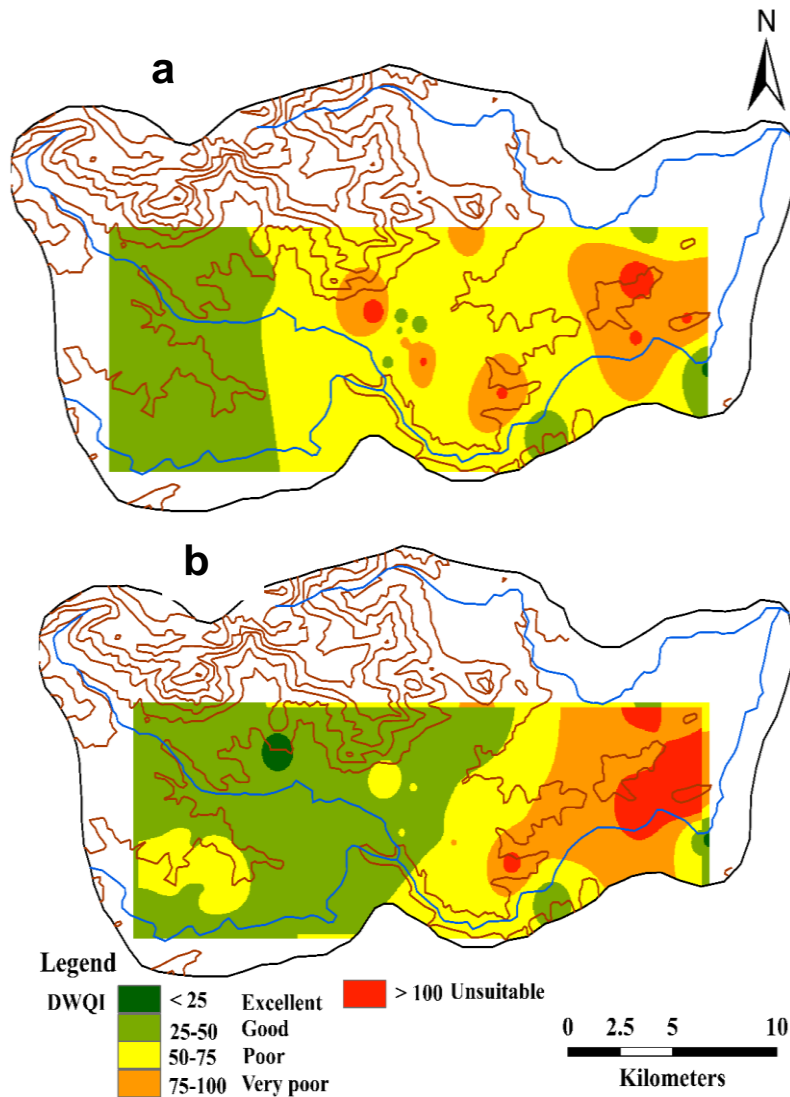


Figure 6.4 a, b: Spatial distribution of DWQI during 2015 and 2016 in the study area

Hydrochemical parameters of groundwater show strong to moderately correlations with DWQI outlined in the figure 6.5. During the year of 2015, parameters such as EC, Na^+ , Ca^{2+} , Mg and SO_4^{2-} (Figure 6.5 a, b, d, e, h) have strong correlation with the DWQI (>0.9). However, Cl^- and HCO_3^- (Figure 6.4f, g) have moderate correlation (0.7 and 0.8). K^+ shows positive correlation (0.5 to 0.6) with DWQI. EC, Na^+ , Ca^{2+} , Mg^{2+} and HCO_3^- (Figure 6.4 a, b, d, e, g) express moderately correlation with DWQI. Nevertheless, K^+ , Cl^- and SO_4^{2-} show positive correlation of 0.5 to 0.6 with the DWQI.

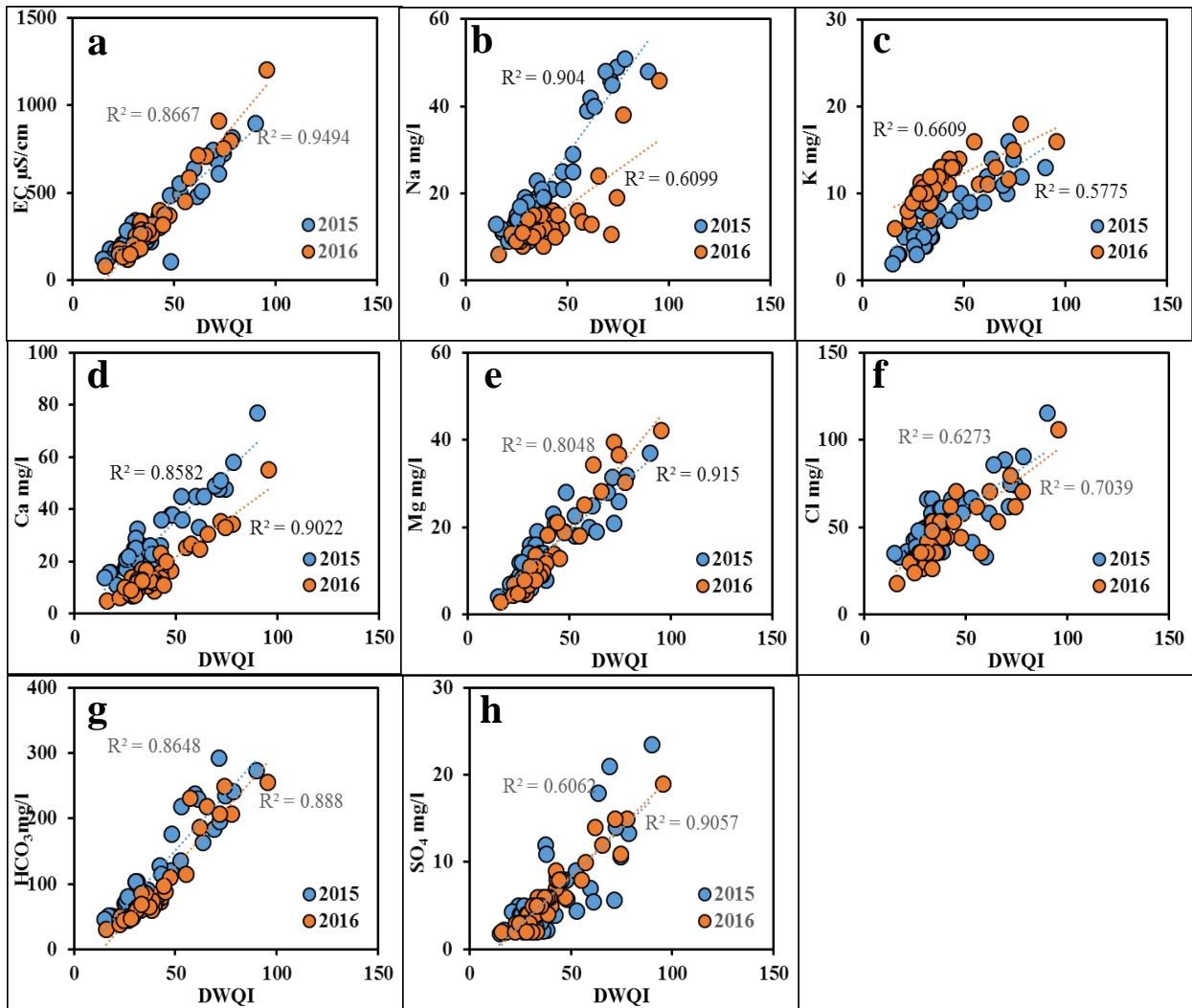


Figure 6.5 (a-h): Correlation of groundwater hydrochemical parameters with drinking water quality index (DWQI) a) EC versus DWQI b) Na^+ versus DWQI c) K^+ versus DWQI d) Ca^{2+} versus DWQI e) Mg^{2+} versus DWQI f) Cl^- versus DWQI g) HCO_3^- versus DWQI h) SO_4^{2-} versus DWQI in the year of 2015 and 2016

6.8 Irrigation water quality assessment

Evaluation of the appropriateness of groundwater for irrigation depends on the assessment of sodium concentration compared with total cations in the aquifer framework. High sodium water is not appropriate for irrigation utilization on the grounds because it increases cation exchange process. This process affects soil permeability followed by the crop production (Cued 2001). Groundwater suitability for

irrigation in the investigation zone was evaluated using EC, SAR, RSC, Na%, USSSL, Wilcox, KR, MH and PI.

The suitability of groundwater for irrigation is affected by the the total concentration of soluble salts namely Na^+ , Ca^{2+} , Mg^{2+} and its relative proportions. Suitability of irrigation water of groundwater quality in high EC value in water resulted the formation of saline soil whereas high Na^+ concentration in water affects alkaline soil. The EC and Na^+ concentration are important parameters in the classification of irrigation water. Wilcox (1955) (Figure 6.6) classified the irrigation water into four classes using EC namely, low ($\text{EC} < 250 \mu\text{S/cm}$), medium ($250-750 \mu\text{S/cm}$), high ($750-2250 \mu\text{S/cm}$) and very high ($2250-5000 \mu\text{S/cm}$) salinity (Table 6.5). In the year of 2015 and 2016, 90 and 95% of samples are medium and 10 and 5 % of samples are high salinity classes in the study area. Sodium concentration is widely used in terms of percentage sodium. The percentage sodium was calculated by equation (5). This method is mainly used for suitability of groundwater for irrigation depends on the mineralization of water and its effects on plants and soil. Wilcox (1955) classification of Na% indicates 5 classes of irrigation water namely excellent (<20), good ($20-40$), permissible ($40-60$), doubtful ($60-80$) and Unsuitable (>80) (Table 6.5). Based on this classification, 100% of samples fall in excellent class and suitable for irrigation in the year of 2015 and 2016. Figure 6.6 displays the behavior of Na% vs EC and it shows that both surface water and groundwater are permissible for irrigation purposes.

SAR and EC are used to assess irrigation water quality. SAR value of groundwater in the study area ranges from 9 to 80 and from 6 to 76 during 2015 and 2016, respectively. SAR is used to classify the samples as excellent (<10), good ($10-18$), doubtful ($18-26$) and unsuitable (>26) (Table 6.5). According to the SAR classifications, all samples are considered as excellent ($\text{SAR} < 10$).

A more detailed analysis of water quality data was carried out to assess the irrigation suitability of surface and groundwater in the study area using United States Salinity Laboratory (USSL) (1954) classification. According to USSL classifications, C1S1 represents low salinity and low sodium and C2S2 represents the medium salinity and medium sodium water. Both groups are good for irrigation with soil having good

permeability as well as salt tolerant and semi tolerant crops with suitable drainage condition. C2S3 shows medium salinity and high sodium water, which are usually doubtful for irrigation and it may produce harmful levels of exchange Na in soils. It will require soil management such as good drainage, leaching and addition of organic matter. C2S4 represents the medium salinity and very high sodium water. C3S2 is high salinity and medium sodium water and suitable for moderate salt tolerant crops and soil with moderate permeability. C3S3 is high salinity and high sodium water. C3S4 is high salinity and very high sodium water and are unsuitable for irrigation.

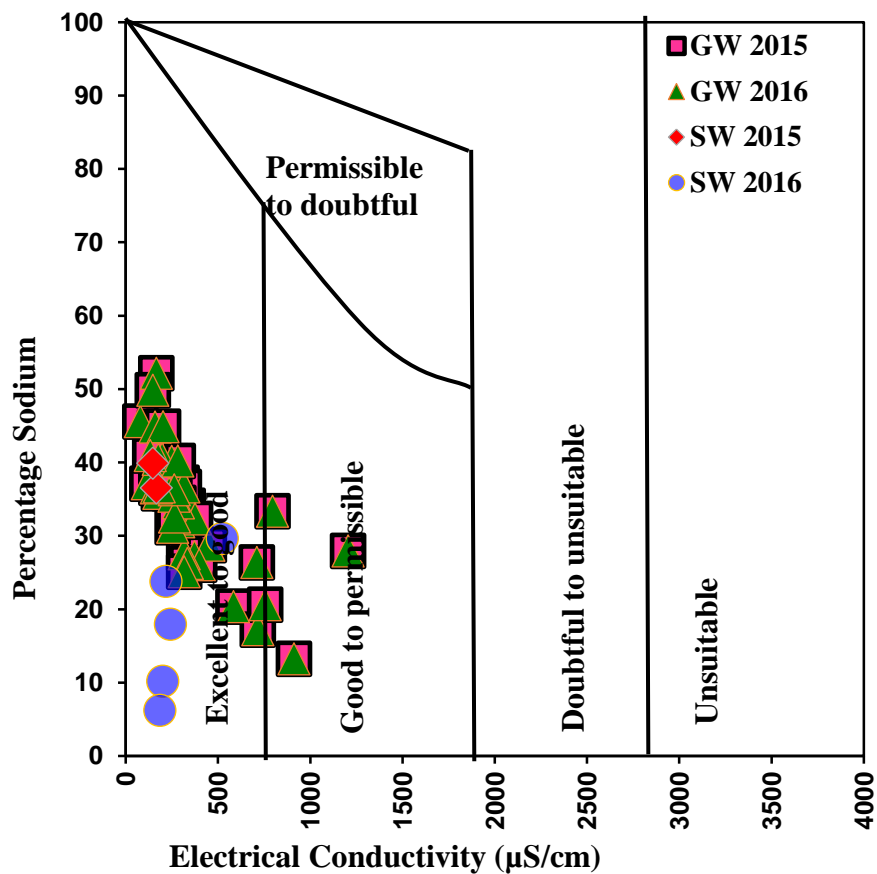


Figure 6.6: Wilcox diagram of surface water and groundwater

Based on USSL diagram (Figure 6.7), water samples fall in C1S1 classes, which shows that the water samples has low salinity and sodium. The water can be utilised in various soil and several crops. Samples plotted on C2S1 class indicate that these are medium salinity and low sodium water, which are suitable for major crops and fine textured soils. C3S1 is high salinity and low sodium water in both 2015 and 2016. According to the USSL classification (Figure 6.7), all water sample collected in 2015 and 2016 from both water resources fall into category C1-S1,C2-S1 and C3-S1, indicating low alkali hazards and excellent irrigation water.

Table 6.5 Irrigation water quality of groundwater in the year of 2015 and 2016

	Range	Classification	% of Samples		Reference
			2015	2016	
EC μS/cm	< 750	Low	90	95	Wilcox [1955]
	750-1500	Medium	10	5	
	1500-3000	High	-	-	
	>3000	Very high	-	-	
SAR	< 10	Excellent	5	4	Richard (1954)
	10-18	Good	32	29	
	18-26	Doubtful	3	6	
	>26	Unsuitable	1	2	
Na%	<20	Excellent	5	-	Wilcox [1955]
	20-40	Good	68	88	
	40-60	Permissible	27	12	
	60-80	Doubtful	-	-	
	>80	Unsuitable	-	-	
RSC	<1.25	Safe	100	100	Eaton [1950]
	1.25-2.5	Moderate	-	-	
	>2.5	Unsuitable	-	-	
PI	>75%	Class I	54	30	Doneen [1964]
	25%-75%	Class II	46	70	
	<25%	Class III	-	-	

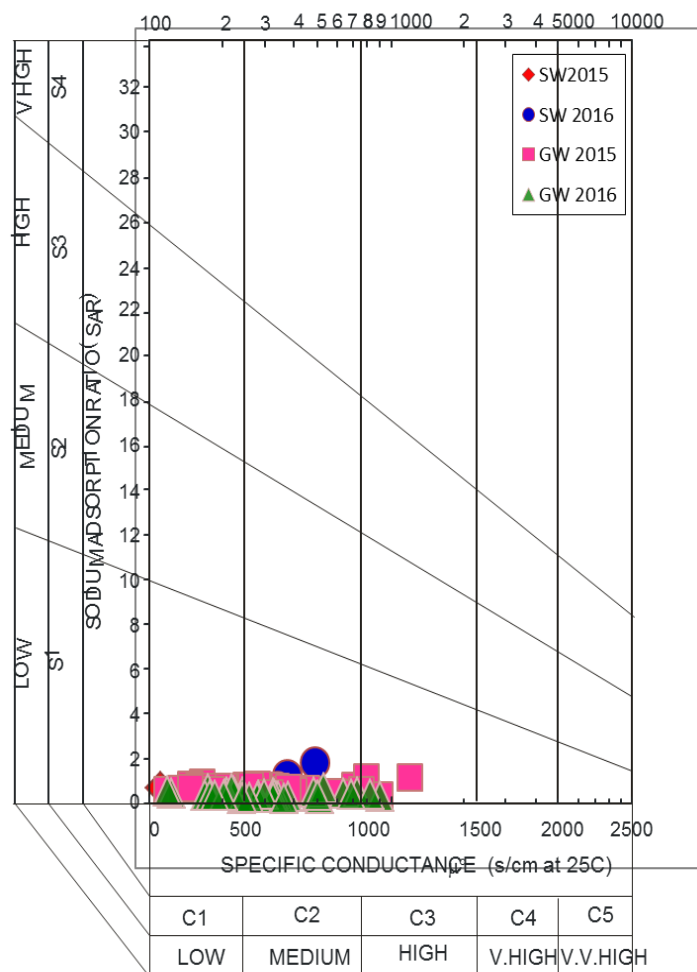


Figure 6.7: USSL diagram for surface and groundwater

RSC was calculated to evaluate the role of CO_3^- and HCO_3^- on the surface and groundwater quality for irrigation usage. Excess CO_3^- and HCO_3^- in the water over the total of Ca^{2+} and Mg^{2+} affect the irrigation suitability of groundwater. High concentration of HCO_3^- having the tendency to precipitate Ca^{2+} and Mg^{2+} and increases Na^+ and K^+ in the water and soil. Hence, the land irrigated with such water affects infertile owing to deposition of sodium carbonate (Eaton 1950). RSC was calculated using the equation (4). The high RSC in groundwater was significantly hazard for plant growth. Eaton (1950) classified the RSC into 3 classes, safe (<1.25), moderate (1.25-2.5) and unsuitable (>2.5) (Table 6.5). Based on this classification, 100% of samples fall in safe class in the year of 2015 and 2016, respectively.

A modified criterion has been evolved based on the solubility of salts and the reaction occurring in the soil solution from cation exchange for estimating the quality of agricultural waters (Gupta and Gupta 1987). The soil permeability is affected by the long-term use of irrigation water mainly due to sodium, calcium, magnesium and bicarbonate content. Irrigation water with high concentration of Na^+ , Ca^+ , Mg^{2+} and HCO_3^- affects soil permeability and it reduces crop yield. Permeability index (PI) was calculated using the equation (7). Doneen (1964) classified the PI of groundwater into Class I (>75%), Class II (25-75%) and Class III (<25%) (Table 6.5). Class I and Class II waters are good for irrigation with >75% of maximum permeability. Class III waters are unsuitable for irrigation with <25% of minimum permeability. The PI value plotted on the Doneen diagram (Figure 6.8). According to Doneen classification of groundwater, 39 (95%) samples plotted in Class I and Class II in the year of 2015 and 2016 in the study area. Surface water samples plotted in Class I and Class II, which represents maximum permeability. The results indicate that water samples are moderately good for irrigation.

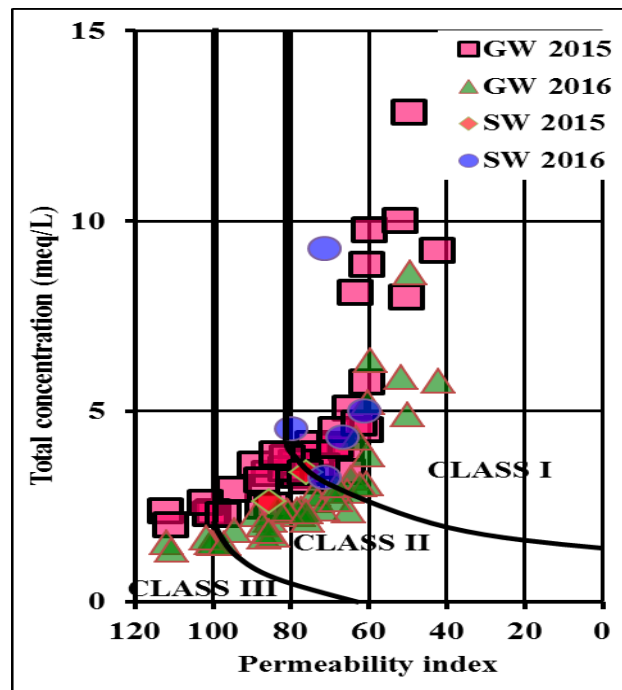


Figure 6.8: Permeability Index

Szaboles and Darab (1964) proposed an MH for evaluating the suitability of water for irrigation. MH was calculated by the equation (3). Szaboles and Darab

(1964) classified into two classes namely suitable (<50) and unsuitable (>50). Based on this classification, 12 and 55% (Table 6.5) of samples fall in suitable category and 88 and 45% of samples fall in unsuitable in the year of 2015 and 2016, respectively. Magnesium hazard is high in the groundwater samples collected during 2016.

Kelley's Index is expressed as the level of sodium ion estimated against calcium and magnesium ions, and it is applied to assess the irrigation waters (Kelley, 1940). Kelly's ratio was calculated by the equation (8). Kelly (1940) provided two classes to assess irrigation water suitability namely safe (<1) and unsafe (>1) (Table 6.5). In this study, all samples fall within the suitable limit of less than one (<1), indicating the good quality of the surface and groundwater and suitable for irrigation uses.

6.9 Conclusion

Groundwater quality and its suitability for human consumption and irrigation uses in the Limpopo province were assessed as the groundwater is a major source of water for drinking and irrigation activities in the study area. In the study area, 41 groundwater samples were taken from Limpopo province in the year of 2015 and 2016. Hydrochemical analysis reflect the dominant sequence of major cations are in the order of $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and anions are $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. The groundwater samples are acidic in nature. Dominant water types are $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ and $\text{Ca}^+\text{-Mg}^{2+}\text{-Cl}^-$. TDS classification reveals that the groundwater is good to permissible category. TH results show that the groundwater is soft to very hard in nature. pH, EC, Na^+ , Ca^{2+} , Mg^{2+} , K^+ , and Cl^- in few samples exceeded the permissible limits for drinking water recommended by the DWAF. Groundwater quality mapping illustrates that NE-SE part of the study are unsafe. DWQI classification results show that 1% and 2% of samples indicate excellent, 49% and 49% specify good, 27% and 29% shows poor, 7% and 10% of very poor and 16% and 10% of unsuitable during 2015 and 2016, respectively. Spatial distributions of DWQI maps indicate that groundwater in the 50% of area are poor to unsuitable for drinking. DWQI shows strong positive correlation with major ions. Irrigational suitability of groundwater in the study area was assessed by EC, SAR, Wilcox,

USSL, Na%, RSC, PI, MH and KR. According to the SAR values that 10% of samples indicate excellent in 2015 and 2016, 78% and 71% specify good, 7% and 15% of doubtful, 2% and 5% of unsuitable during 2015 and 2016. Na%, RSC, PI and KR suggest that the groundwater is suitable for irrigation. According to MH, 12 to 55% samples are suitable and 88 to 45% are unsuitable for irrigation during 2015 and 2016, respectively. USSL diagram reveals that groundwater is mostly suitable salt tolerant crops due to high sodium and salt content, so certain measures for the salinity control is required. The overall groundwater quality is partially suitable for both consumption and irrigation purposes. Approximately 50% of areas, the groundwater is severely contaminated. The study recommends that the strategic plan pertaining to resource protection and use generated and adhered. Further researches within the study region are encouraged and information dissemination to local communities about the groundwater status is necessary to prevent high magnitude of water pollution. Generate a strategic plan to aware the local people about the contamination that produce them and how we can prevent and save our environment from this important groundwater quality issue.

This study recommends to strictly monitor and control the groundwater quality in the study area and to confirm the sustainable safe use of the groundwater. Rainwater harvesting should be encouraged to stored rainwater, which will be useful to recharge the aquifer and reduce the salinity in the groundwater. Regular monitoring of the groundwater quality and water level as well as environmental protection of groundwater resources is recommended.

CHAPTER SEVEN

7 Conclusion

The study was conducted to assess the irrigation water quality of surface and groundwater and to determine the hydrogeochemical processes responsible for the major ion chemistry of groundwater and the probable contamination in Luvuvhu catchment, Limpopo, South Africa. To attain this objectives, the WHO (2011) and SANS (2006) water quality guidelines were utilised as the basis to assess the groundwater quality for drinking and irrigation purposes. The study revealed that most of the groundwater samples were within the standards recommended by WHO (2011) and SANS (2006) for drinking uses. The groundwater samples found to be acidic to alkaline and ranging from soft to hard in nature. The order of the abundance of the major cation and anion is $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ and $Cl^- > HCO_3^- > NO_3^-$ during 2015. During 2016, the order of abundance of major cations and anions are $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and $Cl^- > HCO_3^- > SO_4^{2-}$.

The hydrogeochemical facies identified using piper trilinear diagrams are $Ca^{2+}-Mg^{2+}-Cl^-$, $Ca^{2+}-HCO_3^-$ and Na^+-Cl^- water types. These water types indicate GW-SW mixing, mineral weathering and ion exchange reactions. The examination of the major ions and their spatial distribution suggested the dominance of rock-water interaction as the fundamental procedure controlling groundwater chemistry in the study area. Overall, water chemistry is regulated by the silicate weathering, carbonate dissolution and ion exchange (both reverse and cation) reactions. In addition, the impact on the application of fertilizers and sewer effluent is also noticed in the study area. Apparently, a spatial distribution result indicates that the central part and NE-SE of the area are unsafe and the rest of the areas are safe in the year 2015 and 2016, respectively.

Groundwater suitability assessment was carried out using various parameters. Based on TDS classifications, all the groundwater samples are suitable for drinking purposes whereas Na%, RSC, SSP, PI and KR values shows that most of the samples are suitable for irrigation purposes. According to the SAR values that 10% of samples indicate excellent in 2015 and 2016, 78% and 71% specify good,

7% and 15% of doubtful, 2% and 5% of unsuitable during 2015 and 2016. The results of TH and MR show that there are certain samples that exceeded the standard classifications values. Groundwater with $MR > 50$ assumed to be less permeable and reduce crop production. Around 13 and 16 water samples have $MR > 50$ during 2015 and 2016, respectively. These water samples are not suitable for irrigation because these water samples have a potential to cause alkaline soil resulting in low penetration capability. The eastern part (downstream of Albasin Dam) towards Thohoyandou Town of the study area has high concentration of all ions. A very strong correlation is observed between Ca^{2+} and Mg^{2+} and Ca^{2+} and Mg^{2+} with HCO_3^- and SO_4^{2-} ($r^2 > 0.8$). The irrigation water quality assessment was done using the following irrigation parameters, namely, sodium percent (Na%), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), soluble sodium percentage (SSP), total hardness (TH), magnesium ratio (MR), permeability index (PI) and Kelly's ratio (KR).

This study shows the importance of multivariate statistical methods of vast and complex dataset keeping in mind the end goal to get better data and translation concerning groundwater water quality. Principal component analysis indicates that the groundwater quality is regulated by two major factors. The percentages of the total variances of the two extracted components are 76.59% in 2015 and 84.35% in 2016, Variables loaded in the factors indicate that apart from geological origin, anthropogenic activities might have great influence to the groundwater quality.

In view of the findings of the study, it is recommended that the water from the study area is suitable for different purposes. Programs should implement on how to improve the protection of groundwater from anthropogenic impact. In perspective of the discoveries of the study, it is suggested that the groundwater quality status should be kept within the limits of WHO (2011) standards and SANS (2006) guidelines. The water resource managers such as Geohydrology specialist from the Department of Water and Sanitation should develop scientific techniques to monitor the groundwater quality. Groundwater quality should be monitored for more especially for minor ions and trace elements. The anthropogenic impact should also be closely monitored.

8 REFERENCES:

REFERENCES:

1. Abudaya, M., Tayeh, A., Ramlawi, A., 2014. Assessment of chemical characteristics of the desalinated water used in household facilities in Gaza Strip: *Journal of Natural Sciences Research*, vol. 4, no. 1, pp. 72-83.
2. Agca, N., 2014. Spatial variability of groundwater quality and its suitability for drinking and irrigation in the Amik Plain (South Turkey): *Environ Earth Sci*, 72(10), 4115–4130.
3. Aghazadeh, N., Mogaddam, A.A., 2010. Assessment of groundwater quality and its suitability for drinking and agricultural uses in the Oshnavieh Area, Northwest of Iran: *J Environ Prot* 1:30–40.
4. Alobaidy, A.H.M.J., Abid, H.S., Maulood, B.K., 2010. Application of Water Quality Index for assessment of Dokan Lake ecosystem, Kurdistan Region, Iraq. *J Water Res Prot* 2:792–798.
5. Ambujam, N.K., Shanmugam P. A., 2011. Hydrochemical and geological investigation on the mambakkam mini watershed, Kancheepuram District, Tamil Nadu: *Environmental Monitoring Assessment*, DOI 10.1007/s10661-011-2189-1.
6. American Public Health Association, 1998. Standard methods for the examination of water and wastewater, 20th ed. American Public Health Association/American Water Works Association/ Water Environment Federation, Washington DC.
7. Andrade E., Palacio, H.A.Q., Souza, I.H., Leao, R.A., Guerreio, M.J., 2008. Land use effects in groundwater composition of an alluvial aquifer by multivariate techniques. *Environ Res* 106:170–177, *Water and Wastewater*, 19th ed., p. 1100.
8. Appelo, C.A.J., Postma, D., 2005. *Geochemistry, Groundwater and Pollution*. Second edition. A.A. Balkema, Rotterdam.

9. Appelo, C. A., Postma, D., 1993. *Geochemistry, groundwater and pollution*. Rotterdam: Balkema.
10. Ator, S. W., Denis, J. M., 1997. Relation of nitrogen and phosphorus in ground water to land use in four subunits of the Potomac River Basin. USGS Water Resources Investigations Report, 97–4268. Reston: US Geological Survey.
11. Ayers, R. S., Bronson, R. L., 1975. Guidelines for interpretation of water quality for agriculture, Uni . of Calif ornia, Ex en sion Mimeographed, 13p .
12. Ayers, R.S., Westcot, D.W., 1985. Water quality for agriculture fao irrigation and drain: paper No. 29, 1-109.
13. Balls, P.W., Edwards, A.C., MacDonald, A., Pugh, K., 1995. Long-term nutrient enrichment of an estuarine system, Ythan, Scotland. *Environmental Pollution* 90:31-321.
14. Balls, P.W., Edwards, A.C., MacDonald, A.M., Pugh, K.B., 1994. Soluble nitrogen and phosphorus in the River Ythan system, annual and seasonal trends. *Water Resources* 29: 837-846
15. Balls, P.W., Edwards, A.C., MacDonald, A.M., Pugh, K.B., 1996. Soluble nitrogen and phosphorus in the River Ythan system in annual and seasonal trends. *Water Resources* 29: 837-846
16. Bartarya, S.K., 1993. Hydrochemistry and rock weathering in a sub- tropical lesser Himalayan river basin in Kumaun, India: *J Hydrol* 146:149–174
17. Barzegar, R., Moghaddam, A.A., Tziritis, E., Fakhri, M.S., Soltani, S., 2017. Identification of hydrogeochemical processes and pollution sources of groundwater resources in the Marand Plain, Northwest of Iran. *Environ. Earth Sci.* 76, 1–16.
18. Bauder, J., Bauder, T., Waskom, R., Scherer, T.F., 2008. Assessing the suitability of water (quality) for irrigation-salinity and sodium: *Western Fertilizer Handbook*.
19. Belkhiri, L., Boudoukha, A., Mouni, L., Baouz, T., 2010. Application of multivariate statistical methods and inverse geochemical modelling for characterization of groundwater—a case study: Ain Azel plain (Algeria). *Geoderma* 159:390–398.
20. Bhatt, K.B., Saklani, S., 1996. Hydrgeochemistry of the upper Ganges river. *India Journal Geology Soc. India*, 48: 171-182.

21. Birke, M., Rauch, U., 1993. Environmental aspects of the regional geochemical survey in the southern part of East Germany, *J Geochem Explor* 49(1–2):35–61
22. Brandl, G., 2002. The geology of the Alldays area. Explain sheet geological Survey South Africa, 2228 (Alldays), 71pp.
23. Busari, O., 2008. Environment, development and sustainability of groundwater in the Limpopo basin: occurrence, use and impact. *Earth and Environmental Science*, 10(6):943-957.
24. Causapé, J., Quílez, D., Aragüés, R., 2006. Groundwater quality in CR-V irrigation district (Bardenas I: Spain): alternative scenarios to reduce off-site salt and nitrate contamination. *Agric. Water Manage.* 84, 281–289.
25. Central Pollution Control Board, 2008. Guideline for water quality management, Parivesh Bhawan.
26. Chadha, D., 1999. A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data, *Hydrogeology Journal*, vol. 7, no. 5, pp. 431-439.
27. Cochran, B., Logue, C.A., 2011. Watershed approach to improve water quality: case study of clean water services Taulatin River Program. *Journal of the American Water Resources Association: Vol 47-No 1.*
28. Cude, C.O., 2001. Water quality index: a tool for evaluating water quality management effectiveness, *J. Am. Water Resour. Assoc.*, 37, 125 – 137.
29. Dalton, M.G., Upchurch, S.B., 1978. Interpretation of hydrochemical facies by factor analysis: *Ground Water* 16(4):228–233.
30. Daniel, T.C., Sharpley, A.N., Lemunyon, J.L., 1998. Agricultural phosphorus and eutrophication: a symposium review. *J. Environ. Qual.* 27, 251–257.
31. Datta, P., Tyagi, S., 1996. Major ion chemistry of groundwater in Delhi area: chemical weathering processes and groundwater flow regime, *Geological Society of India*, vol. 47, no. 2, pp. 179-188.
32. Davis, S.N., 1966. DeWiest, R.J. *Hydrogeology*, Wiley, New York.
33. Department of Environmental Affairs and Tourism, 2008. State of the environment report: Republic of South Africa.
34. Department of Environmental Affairs and Tourism, 2008. State of the environment reporting. <http://soer.deat.gov.za/themes.aspx?m=45>. Date of access 04 Mar 2010.

35. Department of Water Affairs and Forestry, 1996. South African Water Quality Guidelines (2nd ed.). Vol. 1: Domestic Use. Pretoria: Department of Water Affairs and Forestry, In Holmes S. (Ed.).
36. Department of Water Affairs and Forestry, 1996. South African water quality guidelines agricultural use irrigation. Republic of South Africa, 2nd Edition: Volume 4
37. Department of Water Affairs and Forestry, 2000. Strategic environmental assessment for water use: Mhlathuze Catchment—KZN; Report No. SEA-01/2000; DWAF: Pretoria, South Africa.
38. Department of Water Affairs and Forestry, 2003. Luvuvhu/Letaba water management Area: water resources situation assessment; Department of Water Affairs and Forestry, South Africa.
39. Department of Water Affairs and Forestry. 1996. South African water quality guidelines (second edition). Volume 1: domestic use, Pretoria. Pp. 214.
40. Department of Water Affairs and Forestry: 2004a. National Water Resource Strategy. First Edition of September, Pretoria South Africa.
41. Devic, G., Djordjevic, D., Sakan, S., 2014. Natural and anthropogenic factors affecting the groundwater quality in Serbia: *Sci Total Environ* 468–469:933–942.
42. Domenico, P.A., 1972. The concepts and models in groundwater hydrology in McGraw-Hill, New York.
43. Doneen, L.D., 1964. Water quality for agriculture, department of irrigation: University of California, Davis.
44. Drever, J.I., 1997. The Geochemistry of natural waters, 3rd edn: Prentice Hall, Englewood, p 436.
45. Duraiswamy, R. A., Patankar, V., 2011. Occurrence of fluoride in the drinking water sources from Gad River, Basin, Maharashtra. *Geol. Soc. India*, 77 , 167 - 174.
46. Du Toit, W. H., Mullin., Jonck F., 2002. 10:500 000 Hydrological Map series of the Republic of South Africa, Mussina 2230. First ed. DWA, Pretoria.
47. Department of Water Affairs and Forestry (DWAF), 2004, Internal Strategic Perspective: Levubu Letaba Water Management Area. Version 1.

48. Department of Water and Sanitation (DWAS)
<https://www.dwa.gov.za/thukela/Background.htm> (Accesses 2015-03-04)
49. DWAF, 2004. National Water Resource Strategy. Department of Water Affairs and Forestry, Pretoria.
50. Department of Water Affairs and Forestry (DWAF)., 1998, National Water Act No. 36 version: www.dwaf.gov.za.
51. Eaton, E.M., 1950. Significance of carbonates in irrigation waters: *Soil Sci*, 69, 123–133.
52. Edmunds, W.M., Shand, P., Hart, P., Ward, R.S., 2003. The natural (baseline) quality of groundwater: a UK Pilot Study. *Sci Total Environ* 310:25–35.
53. Edet, A. E., Okereke, C. S., 2014. Hydrogeological and hydrochemical character of the regolith aquifer, northern Obudu Plateau, southern Nigeria. *Hydrogeology Journal* Vol 13 No 2: 391-415.
54. Edet, A. E., Ekpo, B. O., 2008. Hydrogeochemistry of a fractured aquifer in the Ogoja/Obudu area of SE Nigeria In *Applied groundwater studies in Africa* (Eds Adelana S, MacDonald A) IAH Selected papers on Hydrogeology, Vol 13 391-403
55. Edokpayi, N.J., Odiyo, O.J, Popoola, O., Msagati, M.A.T., 2016. Determination and distribution of polycyclic aromatic hydrocarbons in rivers, sediment wastewater effluents in Vhembe District, South Africa: *Int. J. Environ. Res. Public Health*, 13(4), 387.
56. Elhatip, H., Afsin, M., Kuscu, L., Dirik, K., Kurmac, A., Kavurmac, M., 2003. Influences of human activities and agriculture on groundwater quality of Kayseri–Incesu–Dokuzpinar springs, central Anatolian part of Turkey. *Environmental Geology*, 44, 490–494.
57. Environmental Systems Research Institute, 2012. ArcGIS Desktop: release 10, Redlands, CA.
58. Faniran, J., Ngceba, F., Bhat, R., Oche, C., 2004. An assessment of the water quality of the Isinuka Springs in the Transkei Region of the Eastern Cape, Republic of South Africa, *Water SA*, 27, 241–250.
59. Freeze, R.A., Cherry, J.A., 1979. *Groundwater*: Prentice Hall Inc., New Jersey.

60. Garratt, J.A., Jewitt, G.P.W., 2004. Water resource planning and modelling tools for the assessment of land use change in the Luvuvhu Catchment South Africa.
61. Garrels, R. M. A., 1976. Survey of Low Temperature Water Mineral Relations, in Interpretation of Environmental Isotope and Hydrogeochemical Data in Groundwater Hydrology: Vienna, International Atomic Energy Agency, pp. 65–84.
62. Gibbs, R.J., 1970. Mechanisms controlling world water chemistry, science (New York, N.Y.), vol. 170, no. 3962, pp. 1088-1090.
63. Giordano, M., 2009. Global Groundwater Issues and Solutions Annual Review of Environment and Resources, Volume 34:153-178.
64. Gleick, P.H., 1996. Basic Water requirements for human activities: Meeting Basic Needs. Water International 21: 83-92.
65. Gomo, M., Steyl, G., van Tonder, G. J., 2013. Investigation of the hydrogeochemical processes in an alluvial channel aquifer located in a Typical Karoo Basin of Southern Africa. Environmental Earth Sciences, Volume 70: pp 227-238.
66. Gomo, M., Vermeulen, D., 2013. Investigation of hydrogeochemical processes in groundwater resources located in the vicinity of a mine process water dam. Journal of African Earth Sciences, Volume 86, p. 119-128.
67. Guler, C., Thyne, G.D., McCray. J.E., Turner, A.K., 2002. Evaluation of graphical and multivariate statistical method for classification of water chemistry data. Hydrogeol J 10(4):455–474
68. Gumbo, J.R., Dzaga, R.A., 2016. Nethengwe. Impact on water quality of Nandoni water reservoir downstream of municipal sewage plants in Vhembe District, South Africa, Sustainability, 8(7), 597.
69. Gupta, S., Mahato, A., Roy, P., Datta, J.K., Saha, R.N., 2004. Geochemistry of groundwater, Burdwan district, West Bengal, India. Environmental Geology 53, 1271–1282. <http://dx.doi.org/10.1007/s00254-007-0725-7>.
70. Halvorsen, A.S., Jones, T., Kolka, K.E., Mayer, K.W., Saenz, R.K., 2015. Self-assessing impacts of payments for watershed services on sustainability in coupled human and natural systems Bioscience 65: 579-591.

71. Hem, J. D., 1985. Study and interpretation of the chemical characteristics of natural water, USGS, Water Supply paper no. 2254 264, 117-120.
72. Hiscock, K., 2005. Hydrogeology. Principles and Practice. xvi + 389 pp. Malden, Oxford, Carlton: Blackwell Publishing. ISBN 0 632 05763 7.
73. Holland, M., 2011. Hydrogeological characterisation of crystalline basement aquifers within the Limpopo Province, South Africa, Ph.D Thesis, University of Pretoria, Pretoria, South Africa, 1-162 <http://hdl.handle.net/2263/25713>.
74. Horton, R.K., 1965. An index number system for rating water quality: *J Water Pollut Control Fed*, 37(3), 300–306.
75. Howari, F. M., Banat, K. M., 2002. Hydrochemical characteristics of Jordan and Yarmouk River Waters: Effect of Natural and Human Activities. *J Hydrol Hydromech*, 50(1), 50.
76. Institute of Medicine, 1997. Dietary reference intakes for calcium, phosphorus, magnesium, vitamin d and fluoride: prepared by the standing committee on the scientific evaluation of dietary reference intakes, food and nutrition board: National Academy Press, Washington, DC.
77. Jacks, G., 1973. Chemistry of groundwater in a district in southern India: *J Hydro* 18:185–200.
78. Jalali, M., Kolahchi, Z., 2007. Effect of water quality on the leaching of potassium from sandy soil. *Journal of Arid Environment* 68,624–639.
79. Jansen, H., 1975. The Soutpansberg trough (Northern-Transvaal): an aulacogen. *Transaction geological Society South Africa*, 78, pp.129–36.
80. Joeng, C.H., 2001. Effect of land use and urbanization on hydrochemical and contamination of groundwater from Taejon area, Korea. *Journal of Hydrology*, 253(1-4), 194-210. Doi: [http://dx.doi.org/10.1016/S0022-1694\(01\)00481-4](http://dx.doi.org/10.1016/S0022-1694(01)00481-4)
81. Jewitt, G.P.W., Garratt, J.A., Calder, I.R., Fuller, L., 2004. Water resources planning and modelling tools for the assessment of land use change in the Luvuvhu catchment, South Africa. *Phys. Chem. Earth* 29, 1233–1241.
82. Jones, B.F., 1997. Geochemical investigation of groundwater quality, In *Seawater intrusion in coastal aquifers concepts methods and practices*. Kluwer, Netherlands, pp. 1–71.

83. Kalkhoff, S. J., Detroy, M. G., Cherryholmes, K. L., Kuzniar, R. L., 1992. Herbicide and nitrate variation in alluvium underlying a cornfield at a site in Iowa County, Iowa. *Water Resources Bulletin*, 28(6), 1001–1011.
84. Katz, B.G., Coplen, T.B., Bullen, T.D., Davis, J.H., 1998. Use of chemical and isotopic tracers to characterize the interaction between groundwater and surface water in Mantled Karst: *Groundwater* 35(6):1014–1028.
85. Kelly, W.P., 1957. Adsorbed sodium cation exchange capacity and percentage sodium sorption in alkali soils: *Science*, 84, 473–477.
86. Kelley, W.P., 1940. Permissible composition and concentration of irrigation waters. In: proceedings of the ASCE 66, pp 607.
87. Ketata, M., Gueddari, M., Bouhlila, R., 2012. Use of geographical information system and water quality index to assess groundwater quality in El Khairat deep aquifer (Enfidha, Central East Tunisia): *Arab. J. Geosci*, 5, 1379–1390.
88. Kim, T.H., Chung, S.Y., Park, N., Hamm, S.Y., Lee, S.Y., Kim, B.W., 2003. Combined analyses of chemometric and kriging for identifying Groundwater contamination sources and origins at the Masancoastal area in Korea. *Environ Earth Sci*. doi:10.1007/s12665-012-1582-6.
89. Kleynhans, C.J., 1996. A qualitative procedure for the assessment of the habitat integrity status of the Luvuvhu River (Limpopo system, South Africa): *Journal of Aquatic Ecosystem Health* 5: 41-54.
90. Kumar, M., Kumari, K., Singh, U.K., Ramanathan, A., 2008. Hydrogeochemical processes in the groundwater environment of Muktsar, Punjab: conventional graphical and multivariate statistical approach. *Environ. Geol.* 57, 873–884. doi:10.1007/s00254-008-1367-0.
91. Kumar, M., Ramanathan, A.L., Rao, M.S., Kumar, B., 2006. Identification and Evaluation of Hydrogeochemical Processes in the Groundwater Environment of Delhi, India, *Environmental Geology*, 50, 1025-1039. <http://dx.doi.org/10.1007/s00254-006-0275-4>
92. Kumar, P.S., Elango, L., James, E.J., 2014. Assessment of hydrochemistry and groundwater quality in the coastal area of South Chennai, India. *Arab. J. Geosci*, 7 (7), 2641-2653.
93. Lawrence, F.W., Upchurch, S.B., 1982. Identification of recharge areas using geochemical factor analysis. *Ground Water* 20:680–687.

94. Li, P., Qian, H., Wu, J., Zhang, Y., Zhang, H., 2013a. Major ion chemistry of shallow groundwater in the Dongsheng Coalfield, Ordos Basin, China. *Mine Water Environ* 32(3):195–206.
95. Li, P., Wu, J., Qian, H., 2012. Assessment of groundwater quality for irrigation purposes and identification of hydrogeochemical evolution mechanisms in Pengyang County, China: *Environ. Earth Sci.* 69, 2211–2225.
96. Li, P., Wu, J., Qian, H., Zhang, Y., Yang, N., Jing, L., Yu, P., 2016. Hydrogeochemical characterization of groundwater in and around a wastewater irrigated forest in the southeastern edge of the Tengger Desert, Northwest China. *Expo. Heal.* 8, 331–348.
97. Loyd, J.W., Heathcote, J.A., 1985. *Natural inorganic hydrochemistry in relation to groundwater.* Clarendon Press, Oxford.
98. M'MARETE CK., 2003. *Climate and water resources in the Limpopo Province, Agriculture is the Cornerstone of the Economy in the Limpopo Province. A study commissioned by the Economic Cluster of the Limpopo Provincial Government under the leadership of the Department of Agriculture.*
99. Ma, J., Ding, Z., Wei, G., Zhao, H., Huang, T., 2009. Sources of water pollution and evolution of water quality in the Wuwei basin of Shiyang River, Northwest China. *Journal of Environmental Management*, 90, 1168–1177.
100. Mackenzie, F.J., Garrells, R.H., 1965. Silicates: reactivity with water. *Sci J* 1505:57–58.
101. Makungo, R., Odiyo, J.O., 2016. Estimating groundwater levels using system identification models in Nzhelele and Luvuvhu areas, Limpopo Province, South Africa, *Physics and Chemistry of the Earth, Parts A/B/C*, doi.org/10.1016/j.pce.2017.01.019.
102. Manish, K., Ramanathan, A., Rao, M.S., Kumar, B., 2006. Identification and evaluation of hydrogeochemical processes in the ground- water environment Of Delhi, India. *J Environ Geol*, 50, 1025–1039.
103. Matthes, G., 1982. *The properties of groundwater.* Wiley, New York, 498.
104. Maya, A.L., Loucks, M.D., 1995. Solute and isotopic geochemistry and groundwater flow in the Central Wasatch Range, Utah. *J Hydrol* 172:31–59.
105. Mayback, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. *Am J Sci* 287:401–428.

106. McArthur, P.J.M., Ravenscroft, D., Safiullah, M.F., 2001. Testing pollution mechanisms for sedimentary aquifers in Bangladesh Water Resource Thirlwall Arsenic in groundwater Resources 37: 109–117
107. Michael, A.M., 1978. Irrigation theory and practice: Vikas Publishing House Private Limited, New Delhi, pp. 713-71.
108. Milovanovic, M., 2007. Water quality assessment and determination of pollution sources along the Axios/Vardar River, Southeast Europe. Desalination 213:159–173.
109. Mohan, R., Singh, A. K., Tripathi, J. K., Choudhry, G. C., 2000. Hydrochemistry and quality assessment of ground water in Naini industrial area Allahabad District, Uttar Pradesh. Journal of Geological Society of India, 55: 77–89.
110. Mohebbi, M.R., Saeedi, R., Montazeri, A., Azam Vaghefi, K., Labbafi, S., Oktaie, S., Abtahi, M., Mohagheghian, A., 2013. Assessment of water quality in groundwater resources of Iran using a modified drinking water quality index (DWQI); *Ecol. Indic*, 30, 28–34.
111. Monjerezi, M., Vogt, R.D., Aagaard, P., Saka, J.D.K., 2011. Hydro-geochemical processes in an area with saline groundwater in lower Shire River valley, Malawi: An integrated application of hierarchical cluster and principal component analyses. *Appl. Geochemistry* 26, 1399–1413.
112. Mpandeli, S., 2014. Evaluation of Crop Production Practices by Farmers in Tshakhuma, Tshiombo and Rabali Areas in Limpopo Province of South Africa: *Journal of Agricultural Science*; Vol., No. 8.
113. Mpenyana-Monyatsi, L., Onyango, M.S., Momba, M.N.B., 2012. Groundwater quality in a South African rural community: A possible threat to public health. *Polish J. Environ. Stud*, 21, 1349–1358.
114. Muchuweti, M., Birkett, J. W., Chinyanga, E., Zvauya, R., Scrimshaw, M. D., 2006. Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: implications for human health. *Agriculture Ecosystem and Environment*, 112(1): 41–48.
115. Muller, M., 2001. Transforming Water Law to Achieve South Africa's Development Vision: A Case Study in National Law. Speech delivered on 16 March 2001 by Mike Muller, Director General, Department of Water Affairs and

- Forestry, South Africa. URL: www.dwaf.gov.za/communications (Accessed 19 February 2008).
116. Munns, R., 2002. Comparative physiology of salt and water stress. *Plant, Cell and environment*: 25, 239–250
 117. National Water Quality Monitoring Council, 2007. Glossary of water quality monitoring terms: Advisory Committee on Water Information.
 118. Nephalama, A., Muzerengi, C., 2016. Assessment of the influence of coal mining on groundwater quality : Case of Masisi Village in the Limpopo Province of South Africa, Proceedings IMWA, Freiberg/Germany.
 119. New Jersey Department of Environmental Protection, 2012. Integrated Water Quality Monitoring and Assessment Overview.
 120. New Jersey Department of Environmental Protection, 2012. Integrated Water Quality Monitoring and Assessment Overview.
 121. Nickson, R.T., McArthur, J.M., Shrestha, B., Kyaw-Nyint, T.O., Lowry, D., 2005. Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan: *Appl Geochem* 20:55–68.
 122. Nkuna, T.R., Odiyo, J.O., 2016. The relationship between temperature and rainfall variability in the Levubu sub-catchment, South Africa: *International Journal of Environmental Science*.
 123. Ntokozo, M., 2017. Hydrogeochemical assessment of groundwater quality in the Soutpansberg Basin around Tshikondeni, Limpopo Province, South Africa, *Geochem: Explo, Environ, Analysis*, doi: 10.1144/geochem2016-433.
 124. Nur, A., Ishaku, J., Taiyib, A., 2012, Spatial distribution of chemical facies using geographical information system (GIS) in Michika, northeastern Nigeria, *Res J Eng Appl Sci*, vol. 1, no. 2, pp. 102-109.
 125. Offiong, O. E., Edet, A. E., 1998. Water quality assessment in Akpabuyo, Cross River basin, South-eastern Nigeria. *Environmental Geology*, 34(2/3), 167–174.
 126. Paliwal, K.V., 1972. Irrigation with saline water, Water Technology Centre, Indian: Agricultural Research Institute New Delhi, NO.02 (New Series), pp. 198.
 127. Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2)—a computer program for speciation, batch-reaction, one-dimensional

transport, and inverse geochemical calculations. Water Resources Investigation Report, pp 99–4259.

128. Pazand, K., Hezarkhani, A., Ghanbari, Y., Aghavali, N., 2011. Groundwater geochemistry in the Meshkinshahr basin of Ardabil province in Iran. *Environ Earth Sci*. doi:10.1007/s12665-0111131-8.
129. Piper, A.M., 1994 A graphic procedure in the geochemical interpretation of water analyses. *Am Geophy Union Trans*, 25, 914–923.
130. Pophare AM, Lamsoge BR, Katpatal YB, Nawale VP (2014) Impact of over-exploitation on groundwater quality: a case study from WR-2 watershed, India. *J Earth Syst Sci* 123(7):1541–1566
131. Rabeiy, R.E., 2017. Assessment and modeling of groundwater quality using WQI and GIS in Upper Egypt area, *Environ Sci Pollut Res*, doi:10.1007/s11356-017-8617-1.
132. Rangunath, H.M., 1987. *Groundwater*. Wiley Eastern Ltd, New Delhi, pp 563.
133. Rahman, M.A.T., Rahman, S.H., Majumder, R.K., 2012. Groundwater quality for irrigation of deep aquifer in southwestern zone of Bangladesh, *Songklanakarin J Sci Technol*, vol. 34, no. 3, pp. 345-352.
134. Rajesh, R., Brindha, K., Murugan, R., Elango, L., (2012) Influence of hydrogeochemical processes on temporal changes in groundwater quality in a part of Nalgonda district, Andhra Pradesh, India. *Environ Earth Sci*. 65, 1203-1213.
135. Rajesh, R., Brindha, K., Murugan, R., Elango, L., 2012. Influence of hydrogeochemical processes on temporal changes in groundwater quality in a part of Nalgonda district, Andhra Pradesh, India. *Environ Earth Sci*. 65, 1203-1213.
136. Rajesh, R.; Brindha, K.; Elango, L. Groundwater Quality and its Hydrochemical Characteristics in a Shallow Weathered Rock Aquifer of Southern India, *Water Qual Expo Health*, 2015, 7(4), 515–524.
137. Rajesh, R.; Brindha, K.; Elango, L., 2015. Groundwater quality and its hydrochemical characteristics in a shallow weathered rock aquifer of southern India: *Water Qual Expo Health*, 7(4), 515–524.

138. Rajeshwara, R. B., Sujatha, D., 2003. Quality characterization of groundwater in the south-eastern part of the Ranga Reddy district Andhra Pradesh, India. *Environmental Geology*, 44, 579–586.
139. Rajmohan, N., Al-Futaisi, A., Al-Touqi, S., 2009. Geochemical process regulating groundwater quality in a coastal region with complex contamination sources: Barka, Sultanate of Oman. *Environmental Earth Sciences* . 59(2), 385-398.
140. Rajmohan, N., Elango, L., 2004. Identification and evolution of hydrogeochemical processes of groundwater environment in an area of the Palar and Cheyyar River Basins, Southern India. *J Env Geo* 46,47–61.
141. Rajmohan, N., Patel, N., Singh, G., Amarasinghe, U., 2017. Hydrochemical evaluation and identification of geochemical processes in the shallow and deep wells in the Ramganga Sub-Basin, India. *Environmental Science and Pollution Research* 24(26), 21459-21475.
142. Raju, N. J., 2009. Hydrogeochemical Parameters for Assessment of Groundwater Quality in the Upper Gunjanaeru River Basin, Cuddapah District, Andhra Pradesh, South India *Environmental Geology*, Vol. 52, pp. 1067-1074. doi:10.1007/s00254-006-0546-0.
143. Ramesam, V., 1982. Geochemistry of groundwater from a typical hard rock terrain. *J Geol Soc India* 23:201–204.
144. Ramesh, K., Elango, L., 2012. Groundwater quality and its suitability for domestic and agricultural use in Tondiar river basin, Tamil Nadu, India, *Environmental monitoring and assessment*, vol. 184, no. 6, pp. 3887-3899.
145. Reddy, A.G.S., Saibaba, B., Sudarshan, G., 2012. Hydrogeochemical characterization of contaminated groundwater in Patancheru industrial area, southern India: *Environ. Monit. Assess.* 184, 3557–3576.
146. Rasouli F, Kiani Pouya A, Cheraghi SAM (2012) Hydrogeochemistry and water quality assessment of the Kor-Sivand Basin, Fars province, Iran. *Environ Monit Assess* 184:4861–4877. doi:10. 1007/s10661-011-2308-z
147. Richards, L. A., 1954. Diagnosis and improvement of saline alkali soils: *Agriculture, Handbook*, US Department of Agriculture, Washington DC, Vol. 160, pp. 60.

148. Ritchie, J.C., 2000. Soil Erosion, Remote Sensing in Hydrology and Water Management: (Schultz GA, Engman ET, editors) Springer-Verlag Berlin in Germany: 271– 286 and 349–350.
149. Rowe, D.R., Abdel-Magid, I.M., 1995. Handbook of wastewater reclamation and reuse: CRC Press, Inc. p. 550.
150. Saleh, A., Al-Ruwaih, F., Shehat, M., 1999. Hydrogeochemical processes operating within the main aquifers of Kuwait. *J. Arid Environ.* 42, 195-209.
151. Saleh, A., Ruwaih, F., Shehata, M., 1999. Hydrogeo-chemical processes operating within the main aquifers of Kuwait. *Journal of Arid Environment*, 42: 195–209.
152. Sami, K., 1992. Recharge mechanisms and geochemical processes in a semi-arid sedimentary basin, Eastern Cape, South Africa. *J Hydrol* 139:27–48.
153. Sarath Prasanth, S.V., Magesh, N.S., Jitheshlal, K.V., Chandrasekar, N., Gangadhar, K., 2012. Evaluation of groundwater quality and its suitability for drinking and agricultural use in the coastal stretch of Alappuzha District, Kerala, India. *Appl Water Sci* 2:165–175
154. Sawyer, C.N., McCarty, P.L., 1978. Chemistry of environmental engineering, In: Series in water resources and environmental engineering, 3rd edn. McGraw–Hill, NY.
155. Sarin, M. M., Krishnaswamy, S., Dilli, K., Somayajulu, B. L. K., Moore, W. S., (1989). Major-ion chemistry of the Ganga–Brahmaputra river system: Weathering processes and water quality assessment. *Environment Geology*, 48, 1014–1028.
156. Scheytt, T., 1997. Seasonal variations in groundwater chemistry near Lake Belau, Schleswig-Holstein, northern Germany: *Hydrogeology Journal*, 5, 86–95.
157. Schuh, W.M., Klinekebiel, D.L., Gardner, J.C., Meyar, R.F., 1997. Tracer and nitrate movements to groundwater in the Norruem Great Plains. *J Environ Qual* 26:1335–1347.
158. Shamuyarira, K.K., Gumbo, R.J., 2014. Assessment of heavy metals in municipal sewage sludge: A Case Study of Limpopo Province, South Africa, *Int. J. Environ. Res. Public Health*, 11(3), 2569-2579.
159. Shweta, T., Bhavtosh, S., Prashant, S., Rajendra, D., 2013. Water quality assessment in terms of water quality index: *Am. J. Water Res*, 1 (3), 34–38.

160. Singh, C.K., Kumar, A., Shashtri, S., Kumar, A., Kumar, P., Mallick, J., 2017. Multivariate statistical analysis and geochemical modeling for geochemical assessment of groundwater of Delhi, India: *J. Geochemical Explor.* 175, 59–71.
161. Singh, K. P., Malik, A., Mohan, D., Singh, V. K., Sinha, S. 2006. Evaluation of groundwater quality in Northern Indo-Gangetic alluvium region. *Environ Monit Assess*, 112,211–230.
162. Singh, K.P., Gupta, S., Rai, P., 2014. Investigating hydrochemistry of groundwater in Indo-Gangetic alluvial plain using multivariate chemo metric approaches: *Environ. Sci. Pollut. Res. Int.* 21, 6001–15.
163. Snyder NJ, Mostaghimi S, Berry DF, Reneau RB, Hong S, McClellan PW, et al. Impact of riparian forest buffers on agricultural nonpoint source pollution. *J Am Water Resour Assoc* 1998;34:385–95
164. Soltan, M. E., 1999. Evaluation of groundwater quality in Dakhla Oasis (Egyptian Western Desert): *Environ Monit and Assess*, 57, 157–168.
165. Srinivasamoorthy, K., Chidambaram, S., Vasanthavigar, M., 2009. Application of multivariate statistical techniques in elucidation of hydrogeochemical data: a case study. *International Journal of Ecological and Environmental Statistics*, 14(S09): 98-109.
166. Srinivasamoorthy, K., Nanthakumar, C., Vasanthavigar, M., 2011. Groundwater quality assessment from a hard rock terrain, Salem district of Tamilnadu, India. *Arabian Journal of Geosciences*, 4(1): 91-102.
167. Stamatis, G., Alexakis, D., Gamvroula, D., Migiros, G., 2011. Groundwater quality assessment in Oropos-Kalamos basin, Attica, Greece: *Environ Earth Sci*, 64, 973–988.
168. STATISTICA, 2007. Version 8. StatSoft, Oklahoma, USA.
169. Subramani, T., Elango, L., Dhamodarasamy, S. R., 2005. Groundwater quality and its suitability for drinking and agricultural use in Chithar River Basin, Tamil Nadu, India; *Environ. Geol.*47 1099–1110.
170. Sujatha, D., Rajeshwara Reddy, B., 2003. Quality characterization of groundwater in the south-eastern part of the Ranga Reddy district, Andhra Pradesh, India. *Environmental Geology*, 44, 579–586.

171. Szaboles, I., Darab, C., 1964. The influence of irrigation water of high sodium carbonate content of soils, in proceedings of 8th international congress of ISSS, Trans, II, 803–812.
172. Tamma Rao, G., Gurunadha Rao, V.V.S., Srinivasa Rao, Y., Ramesh, G., 2013. Study of hydrogeochemical processes of the groundwater in Ghatprabha river sub-basin, Bagalkot District, Karnataka, India. *Arab. J. Geosci.* 6, 2447–2459.
173. Todd, D.K., 1995. *Groundwater Hydrology*: 3rd Ed, John Wiley and Sons Publications, New York.
174. Toth, J., 1984. The role of regional gravity flow in the chemical and thermal evolution of groundwater. Proceedings of the first Canadian/American conference on hydrogeology, Banff, Alta.
175. Trivedi, R.K., 1990. Chemical and biological methods for water pollution studies. Environmental Publications Karad, India, 213.
176. United Nations Education, Scientific and Cultural Organization, 1995. Discharge of selected rivers of Africa, Studies and Reports in Hydrology No. 52. Paris, UNESCO Publishing. Pp. 166.
177. United Nations Education, Scientific and Cultural Organization, 2007. Water portal newsletter no. 161: Water-related diseases. <http://www.unesco.org/water/news/newsletter/161.shtml>.
178. United States Salinity Laboratory, 1954. Diagnosis and Improvement of Saline and Alkaline Soils: US Department of Agriculture, Washington, Hand Book No. 60, 160p.
179. Varol, S., Davraz, A., 2014. Evaluation of the groundwater quality with WQI (Water Quality Index) and multivariate analysis : a case study of the Tefenni plain (Burdur / Turkey). *Environ Earth Sci*, 73 (4), 1725–1744.
180. Vasanthavigar, M., Srinivasamoorthy, K., Vijayaragavan, K., R., Ganthi, R., Chidambaram, S., Sarama, V.S., Anandhan, P., Manivannan, R., Vasudevan, S., 2010. Application of water quality index for groundwater quality assessment: Thirumanimuttar Sub-basin, Tamil Nadu, India; *Environ. Monit. Assess* 171(1–4) 595–609.
181. Venkatramanan, S., Chung, S.Y., Rajesh, R., Lee, S.Y., Ramkumar, T., Prasanna, M.V., 2015. Comprehensive studies of hydrogeochemical processes

- and quality status of groundwater with tools of cluster, grouping analysis, and fuzzy set method using GIS platform: a case study of Dalcheon in Ulsan City, Korea. *Environ Sci Pollut Res*, 22(15), 11209–11223.
182. Vermeulen, D., Bester, M., 2009. Assessment of how water quality and quantity will be affected by mining of the Waterberg coal reserves Institute for Groundwater Studies. University of the Free State.
183. Vetrimurugan, E., and Elango, L., 2014. Groundwater quality in an intensively cultivated river delta. *Water Quality, Exposure and Health*. 7:125–141
184. Vetrimurugan, E., Brindha, K., Bongani Sithole., Elango, L., 2017. Spatial interpolation methods and geostatistics for mapping groundwater contamination in a coastal area. *Environ. Sci. Pollut. Res*, doi:10.1007/s11356-017-8681-6.
185. Vetrimurugan, E., Elango, L., Rajmohan, N., 2013. Sources of contaminants and groundwater quality in the coastal part of a river delta. *International Journal of Environmental Science and Technology* 10(3), 473–486.
186. Wallick, E.I., Toth, J., 1976. Methods of regional groundwater flow analysis with suggestions for the use of environmental isotope and hydrochemical data in groundwater hydrology, IAEA, Vienna, 37–64.
187. Walton, W.C., (1970) Groundwater resources evaluation. McGraw Hill Book Co, New York
188. Wilcox, L.V., 1955. Classification and use of irrigation waters: USDA, Washington, DC Circular 969.
189. World Health Organization (WHO), 2003. Sodium in drinking water. Background document for development of WHO guidelines for drinking-water quality.
190. World Health Organization (WHO), 2011. Guidelines for drinking-water quality (4th ed.). WHO Library Cataloguing-in-Publication Data, 564 pages.
191. World Health Organization, 2004. Guidelines for drinking water quality: Recommendations, vol 1, 3rd edn. WHO, Geneva, 515.
192. Yidana, S.M., Yidana, A., 2009. Assessing water quality using water quality index and multivariate analysis: *Environ. Earth Sci*, 59, 1461–1473.
193. Yidana, S.M., Ophori, D., Yakubo, B.B., 2008. Hydrochemical evaluation of the Voltaian system- the Afram Plains area, Ghana: *J. Environ. Manag.* 88, 697–707.

194. Zhu, T, Ringler, C., 2012. Climate change impacts on water availability and use in the Limpopo River Basin: *Water*, 4(1), 63-84.