

**Groundwater geochemical characteristics and its
suitability for drinking and irrigation in
Ventersdrop, North West Province, South Africa**

Submitted by

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in partial fulfilment of the requirement for the degree of
Master of Science

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March 2019

DECLARATION

I declare that the thesis titled “Groundwater geochemical characteristics and its suitability for irrigation in Ventersdorp, North West Province, 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.

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CONTRIBUTION TO THE BODY OF KNOWLEDGE

The results from this research have been submitted in two peer-reviewed journals and presented an article in International conference.

Article submitted:

1. E. Vetrimurugan and Mubva K.V (2019) Long Term fluctuations of anthropogenic and natural processes on groundwater in Schoonspruit catchment of Northwest Province, South Africa. Environmental Science and Pollution Research (Submitted).
2. E. Vetrimurugan and Mubva K.V (2019) Groundwater chemistry and human health risk assessment in Ventersdorp of Northwest Province, South Africa. Springer African Earth Science (Submitted).

Conference:

E. Vetrimurugan, P. Mthembu, Mubva K.V, “Hydrochemical evaluation of fluoride contamination in fractured rock aquifer in Northern part of Kwazulu-Natal, South Africa” 27th International Union of Geodesy and Geophysics General Assembly - July 8-18, 2019 - Montreal, Canada.

ACKNOWLEDGEMENTS

I would like to send my sincere gratitude to my Supervisor and advisor 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 Hydrology 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. I would like to extend my appreciation to the Department of Water and Sanitation, and South African Weather Services for providing the data of the study area.

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

ABSTRACT

Groundwater is major source of freshwater in regions devoid of surface water resources. The dependence on groundwater is increasing worldwide. South Africa is no exception. Groundwater resource has been identified as the main and reliable water resource for human consumption and agricultural practice in the Ventersdorp area, South Africa. Assessment of groundwater quality is necessary for safe usage for drinking and for irrigation purposes so as to boost the socio-economic wellbeing of the region. One such study was taken in Ventersdorp area, Schoonspruit Catchment, South Africa. The groundwater samples were collected from forty boreholes in 2015 as well as seventy boreholes in 2017 and was analysed for major ions and nitrate. The 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^- during 2015 and 2017 were analysed. The concentration of major ions chemistry in groundwater was within the permissible limits of South African National Guidelines and World Health Organisation and for drinking use. The overall pH values for both sample periods represent slightly acidic to alkaline in the study area. Based on DWAF (1996) approved limit of drinking (EC <450), 45% of groundwater samples in 2015 and 13% samples in 2017 exceeded the limit in the study area. The classification of groundwater based on total hardness (TH) in the study area shows that majority of groundwater samples fall within the hard water category and the major groundwater types were Ca-HCO₃ and Ca-SO₄. The affluence of the major ions in the groundwater of the study area was found to be in the order of Ca>Na>Mg>K and HCO₃>Cl>SO₄>NO₃. Several correlation diagrams between the major ion and other plots like the Gibbs, Chadha, Piper, Durov's were prepared to ascertain the sources of ions in the study area. Gibbs plots have revealed that groundwater in the study area for both year 2015 and 2017 is of rock water interaction dominance. Similar inferences were obtained from Chadha plot. High correlation between calcium and bicarbonate, chloride with sodium, nitrate and sulphate and nitrate and potassium. Further, in order to ascertain the irrigation water quality, Kelly's ratio, Sodium percent, residual sodium carbonate, sodium absorption ratio and permeability index were calculated for the groundwater samples in the study area. The IWQI as well as DWQI was calculated to get a snap shot of the region and it confirmed that most of groundwater samples in the study region fall between the range of suitable for both drinking and irrigation purposes in 2015 and 2017. The impact of heavy metal pollution index (HPI) in groundwater was ascertained. The coefficient variation of Zn was found to be higher than that

of Cu, Cr, Cd, Ni and Pb in groundwater of the study area. The results suggest that Zn concentration has a high probability of being influenced by human activities.

Apart from this groundwater quality, rainfall data and groundwater level data from 1974 to 2014 was collected from National Department of Water and Sanitation of South Africa. The analysis of the data revealed that shallow aquifers are easily affected by local climate changes while deep aquifers are dependent only on regional changes. Thus, shallow aquifers are more vulnerable to climate variability. The recharge of shallow aquifer is brief as compared to recharge of deep aquifer. In the study area, shallow wells are more likely to be affected by irrigation flow compared to deep wells and inferred from high correlation between Ca and HCO₃. Cl was correlated with K and Na. NO₃ and Cl are highly correlated. Variables correlating with Cl, SO₄ and NO₃ are partly derived from agricultural activities. Nitrate concentration in the study area shows strong positive relationship with five major ion and EC for last three decades from 1994 to 2014.

In general, the quality of groundwater is suitable for both drinking and irrigation needs. This study helped to comprehend the present state of groundwater chemical composition in Ventersdorp and to assess its fitness for irrigation and drinking uses.

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LIST OF ABBRIVIATIONS

AgNO ₃	Silver nitrate solution
Al	Aluminium
Ca ²⁺	Calcium ion
CA	Cluster Analysis
CaCO ₃ ⁻	Calcium carbonate
Cd	Cadmium
Cr	Chromium
Cu	Copper
Cl ⁻	Chloride ion
CO ₃ ⁻	Carbonate
CV	Coefficient of variations
MAP	Mean Annual Precipitation
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
F	Fluoride
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
HPI	Heavy Metal Pollution Index
HQ	Hazard Quotient
IAP	Ion Activity Product
ICP-OES	Inductive Coupled Plasma Optical Emission Spectrophotometer
IDW	Inverse Distance Weighted
IWQI	Irrigation water quality index
K ⁺	Potassium ion
K ₂ CrO 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
NH ₄	Ammonium
NO ₃ ⁻	Nitrate ion
NW	North West
NWRS	National Water Resource Strategy
ORP	Oxidation Reduction Potential
PI	Permeability Index
PO ₄	Phosphate
r	Correlation coefficient
RSC	Residual Sodium Carbonate
SANS	South African National Standards
SAR	Sodium Adsorption Ratio
Si	Silica
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

CHAPTER 1

INTRODUCTION

1.1 Introduction

Groundwater is a fundamental component of water resources which is increasingly used to supplement surface water where supplies are unreliable. This resource is regarded as a main factor in local development and poverty alleviation (Glover, 1988). Groundwater constitutes about 97% of all freshwater on the earth (USGS, 2008). It represents a strategic water resource in South Africa which contributes a small amount to bulk water supply (13%). Only 13% of groundwater contributes to South Africa's total water consumption (DWA, 2011). Due to a lack of hydrogeological information, groundwater is not fully developed (DWAF, 1997).

Groundwater geochemistry is described as the science that explores the processes controlling the chemical composition and quality of groundwater. Water quality is referred to as the physical, chemical and biological characteristics of water and can be influenced by either natural or human activities. The geology of formations through which water flows or percolates is the main natural factor that influences water quality and gives rise to sediment load together with mineralization of water. Among various chemical species that contaminate groundwater supplies are nitrates which are generated from animal wastes, human wastes and the large quantities of fertilizers that contain nitrogen used in agriculture (Liyanage *et al.*, 2000). Groundwater quality influences the use of the resource.

In South Africa, industrialization is increasing problems associated with water pollution by metals and manufactured organic components such as herbicides and pesticides. Agricultural pollution is hard to identify measure and monitor and this makes it one of the largest source of non-point water pollution. Changes in the water regime of soil and the transport of possible harmful substances to the ground and surface waters are impacted by irrigation water (Tadic, 2001; Ayers and Wesscot, 1985).

The spread of pollution is as the result of various land use activities like agricultural practices, human settlement as well as precipitation of pollutants from the air. Irrigation water applied concurrently with agrochemicals such as fertilizers and pesticides reach groundwater together with

irrigation return water and affect the quality of groundwater (DWAF, 2004). Agricultural leachates contribute significantly to groundwater pollution. The most sensitive cause of groundwater contamination in agricultural activities is fertilizer and pesticide use (Liyanage et al., 2000). Factors related to hydrogeological and pedologic characteristics of an area contribute to the groundwater quality (Ayers and Wesscot, 1985). A larger proportion (80%) of South Africa's surface area is underlain by shallow, weathered, fractured-rock and relatively low-yielding aquifer systems. The reasonable quantities of groundwater can be extracted from dolomitic and quartzitic aquifer system situated in the northern and southern parts of the country and the primary aquifers situated along the coastline (Thompson *et al.*, 2001 & Midgley *et al.*, 1994).

The inadequate surface water resources, continuous drought conditions, changing environment, natural and man-made pollutions can have direct and indirect effects on both quality and quantity of all water resources especially groundwater resources. Groundwater can be utilized to overcome this adverse situation. The quality assessment of groundwater using various chemical parameters has been identified as most useful, since it can perceive the ongoing changes and conditions of the aquifer system. The standard chemical analysis of groundwater includes TDS, Temperature, ORP, pH, EC and DO, major ions such as, Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , k^+ , CO_3^{2-} , HCO_3^- , SO_4^{2-} , and minor ions such as NO_2^- , NO_3^- , PO_4^{3-} and NH_4^+ . Through this assessment various remedial measures and preservation methods can be adopted to maintain proper groundwater quality. Groundwater pollution pose as a great threat for human life and the extent of which determines the resource usage. Nitrates are among the chemical species that pollute groundwater supplies and originate mainly from human and animal wastes as well as from nitrogenous fertilizers that are often used in large quantities in agriculture (Liyanage *et al.*, 2000).

Fluctuation of groundwater level happens easily in unconfined aquifers as the water from precipitation moves down from the surface until it reaches the water table. Significant water-level changes can be observed during springtime as recharge due to precipitation is greater while evaporation and plant usage rates are low. The disadvantages of climate change on groundwater include groundwater level fluctuation, effects on soil pore water pressure, alteration of groundwater flow regimes, and change in the volume and quality of groundwater resources (Brouyère *et al.*, 2004; Ranjan *et al.*, 2006). The change in precipitation and temperature has influence on recharge rates allowing shifts in water table levels in unconfined aquifers. At higher groundwater elevations (recharge), water level declines are greater whereas at lower elevations (discharge) water levels do not show much of a change (Changnon *et al.*, 1988; Zektser and Loaiciga 1993).

Groundwater extraction, evapotranspiration, water content in unsaturated zones and precipitation rates affect the groundwater level. Long term groundwater change over the period of decades or centuries is due to climate change and anthropogenic activities such as land use, irrigation, pumping, and induced infiltration (Healy and Cook, 2002). In this study, the groundwater levels were only predicted based on groundwater recharge from precipitation, which might result in a simplification in predicting groundwater level change. Groundwater levels from shallow bore wells respond swiftly to recharge driven by rainfall. Groundwater levels in the semi-arid regions can fluctuate due to changes in precipitation regardless to the effect of exploitation. In shallow unconfined aquifers the seasonal and short term rainfall excessively recharges in a short interval. Similarly, the level of groundwater declines significantly in a short term drought period. Water scarcity as results of groundwater levels fluctuation and the incapacity of the bore well yield threatens the sustainability of water management in semi-arid regions (Apaydin, 2010).

1.2 Problem Statement

The demand of fresh water resources is continuously on the rise across the globe, especially to meet the food and fiber needs of the ever increasing human population. The quality of water for specific uses is also crucially important. However, the groundwater quality is vastly affected by many factors such as agricultural, industrial, mining and other human activities. Ventersdorp is most dominantly agricultural lands and the threats on groundwater quality are mostly influenced by agricultural activities.

Agricultural activities affect groundwater quality and pose a significant risk to South Africa's water resources. Failure to manage the impact of human activity on the regional scale will result in the pollution of water resources. The nitrate and pesticide concentration in groundwater caused due to agricultural activities is a worldwide problem. Groundwater is the efficient water resource in the study area since surface water is unreliable. Crop production and animal farming are the major economic source in the study region. These major activities along with improper exploration and maintenance of groundwater deteriorate the groundwater quality in the study region (DEAT, 2009).

The main problem is that, the effects of all these factors on groundwater quality in the study area have not been previously explored. Moreover, surface water has failed to meet the water demand of the Ventersdorp area as stated by the Internal Strategic Perspectives (ISP) and the National Water Resource Strategy (NWRS1) (DWAF, 2004). A study for determining the viability of

groundwater sources and quality is essential. Furthermore, the outcomes will aid to locate suitable sites for developing groundwater resources that could yield a relatively better quality of water. The basis of selecting this catchment was that, the area has high number of agricultural groundwater users. Hence, an attempt is made to explore the groundwater quality and its irrigation suitability in the study area in order to support its economic background.

1.3 Aim of the Study

The Aim of the study is to identify the Groundwater geochemical characteristics and its sustainability for irrigation in Ventersdorp, North West Province, South Africa.

1.4 Objectives

The objectives of the research to be carried out in Ventersdorp, North West Province, South Africa are:

- i. to assess the groundwater chemistry.
- ii. to understand the spatial and temporal variation in groundwater chemistry.
- iii. to determine the causes for spatial and temporal variation in groundwater chemistry.
- iv. to determine the suitability of groundwater for irrigation and drinking purposes.
- v. to assess fluctuation of groundwater level due to climate variation.

1.5. Thesis outline

This report has nine chapters and details are given below:

Chapter 1: Introduction

This chapter will provide introduction and background in line with the subject of the research project. It will further give details on the statement of problem, the main purpose of conducting the study and objectives of the project.

Chapter 2: Literature Review

This chapter will review literature on groundwater quality monitoring, role of agricultural activities on groundwater chemistry as well as the hydrogeochemistry of groundwater. Literature associated with irrigation potential and groundwater level fluctuation will also be reviewed on this chapter.

Chapter 3: Description of the study area

This chapter provides details on the area where the project was undertaken. The location, topography, climate, rainfall, drainage, geohydrology, geology and hydrogeology, land use and irrigational use of the study area will be described on this section.

Chapter 4: Research Methodology

This section will outline various methods used throughout the study when collecting and analyzing data with the aim of achieving the objectives of the study. Information on the types of instruments used to analyze data as well as the software and techniques employed throughout the project will be detailed on this chapter.

Chapter 5: Hydrogeochemical processes

This chapter provides information on the results and discussion from the analyzed data in relation to hydrochemistry of groundwater, hydrochemical facies of groundwater, hydrogeochemical processes, Ion exchange Process and Evaporation. The results and discussion of relation between temporal groundwater level fluctuations as well as the multivariate statistics will be revealed in this chapter.

Chapter 6: Assessment of Groundwater quality and its suitability for drinking and agricultural needs

This section will provide detailed information on the various methods used to assess the suitability of groundwater quality for drinking and irrigation purposes. The results of drinking water quality index and irrigation water quality index techniques will be presented on this chapter and further be compared with those of World Health Organisation as well as South African National Standards (SANS241:2015).

Chapter 7: Response of groundwater to climate variation: fluctuations of groundwater level

The results of how groundwater responds to climate conditions will be presented on this chapter. Information on precipitation, groundwater level and groundwater quality relation will also be presented on this chapter.

Chapter 8: Conclusion and Recommendations

This chapter provides detailed outcomes achieved from the study as well as recommendations which aim to protect water resources in the study area.

Chapter 9: References

This section provides references of reviewed literature.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

In semi-arid areas, groundwater is the main source of drinking, domestic, industrial and irrigation uses which is highly supplying the local and industrial needs. Human health is directly related to groundwater quality and is endangered by poor groundwater quality originating from excessive use of fertilizers and unsanitary conditions. Once groundwater becomes polluted, it is durable to prevent the pollution and reinstate the quality of water. Therefore, the need of regular monitoring of groundwater quality is the key to protect this resource (Rodell, 2009). Groundwater is one of the imperative elements of the global water cycle. The over abstraction of groundwater can lead to water scarcity posing significant adverse impacts on the ecosystem, economic and social developments (Foster and Loucks, 2006; Gleeson *et al.*, 2010).

The water and water-borne solutes movements present within the vadose zone of an aquifer has been strongly influenced by the variety of grasslands, vegetation-forests or agricultural crops. Groundwater contamination by agrochemicals is less in the areas of deep-rooted plants and found mostly in much shallow-root zone of cultivation like corn (Comis, 1990). If the spacing between the individual plants is closer than the potential risk of soil erosion, movement of agrochemicals, groundwater contamination and penetration of soluble nutrients through the root zone to enter the groundwater are also lowered (Raven *et al.*, 1996).

Contaminated water flow is affected by variables like depth of water table, the occurrence and distribution of low-permeability layers and also affect unsaturated zone. Degradation of pesticides occurs through a combination of biological and chemical pathways (Pionke, 1994). Different varieties of soil undergo a physical and chemical reactions with the agrochemicals used in the cultivation land. Certain chemical reactions that require the presence or absence of oxygen or that involve chemical hydrolysis help to breakdown contaminants in the soil. This breakdown can potentially cause even more toxic products higher than the initial compound that it originated from (Cheng, 2000).

Natural formations can either reduce or enhance leaching of agrochemicals into the aquifer and can potentially contaminate the groundwater (Skinner and Porter, 1989). Surface runoff over downward soil seepage can be influenced by local topography and landforms. Vegetation and

climatic factors can also influence on environmental contaminants (Cheng, 2000). The contaminant directly interacts with the sunlight and roots of the vegetation along with the climatic changes which have impacts on the properties of the soil (IDNR, 1992).

2.2. Groundwater quality monitoring

The quality of groundwater is influenced by the quality of water that is recharged to subsurface aquifers as well as the geochemical processes that take place within the aquifer. Li *et al.* (2010) conducted a study on groundwater quality assessment based on improved water quality index and recommended that groundwater requires long term monitoring and protection in vision of future excessive industrial growth. Furthermore, preventive actions on the agricultural non -point pollution sources in the flat area should be considered.

A study on conducted by Vetrinmurugan *et al.* (2017) on heavy metals in groundwater concluded that suitable treatment of the groundwater is needed to for it to be suitable as a public water supply or it could produce serious health issues. The study also recommends that measures to reduce leachate percolation of landfill sites should be exercised.

The study of Long-term groundwater dynamics affected by intense agricultural activities in oasis areas of arid inland river basins, Northwest China suggested that relevant ecosystem refurbishing measures can be recommended, focusing on controlling agricultural land and groundwater exploitation as well as encouraging the water saving awareness. The strong coherence between annual groundwater change and rainfall irregularities shows a close connection between surface climate condition and groundwater storage. This has been concluded on a study conducted in Northwest India on Long-term groundwater variations through satellite gravity measurements by Chen *et al* (2014).

Geochemical assessment study in India has been pursued by Kumar *et al.* (2012) which reveals that the seasonal effect changes in the concentration of various ions present in the groundwater. Dissolution of calcite, dolomite, feldspar and gypsum are the fundamental sources of major ions in groundwater, and the ion exchange reaction has significant effect on the cation substance (Li *et al.*, 2015).

Different studies have been conducted on groundwater quality monitoring worldwide. These ions are normally present at concentrations in the range of a few mg/L to several hundred mg/L

(McArthur *et al.*, 2000). The total dissolved solids (TDS) are the concentrations of all dissolved constituents in a water sample. Total dissolved solids are anticipated by adding the concentrations of analyzed constituents or measuring the electrical conductivity of water using a probe (Allen and Suchy, 2001 & McArthur *et al.*, 2000).

2.3. Role of agricultural activities on groundwater chemistry

Agricultural practices are known to be the source of groundwater pollution globally. For instance, groundwater pollution by nitrate is caused by inadequate management of nitrogen compounds (Ragone, 1990b). Types of agricultural activities that contaminate groundwater quality include the following:

i) Animal feedlots

Animal feeding causes contaminate water quality and causes related health issues due to the quantities of animal manure and wastewater generated by animals. Feedlots have impoundments that cause wastes to infiltrate into the soil and hence to groundwater. The source of nitrate, bacteria, total dissolved solids, and sulfates is due to livestock waste. Confined animal feedlots is a concern contributing to groundwater contamination which resulted by high concentration of manure in feedlot areas (Ragone, 1990a).

ii) Fertilizer, pesticide and chemical application

Shallow aquifers are contaminated from the application of fertilizer on irrigation fields. Agricultural practice contributing nitrate on the environment is crop fertilization. Nitrate has been discovered to be the widespread contaminant of groundwater. The breakdown of pesticides occurs during the exposure to direct sunlight through the process called photochemical degradation (Nesheim, 2012).

Groundwater pollution by salts derived from utilization and pesticides of irrigation water is also a problem nationwide (Newman, 1998). Irrigation water continuously washes nitrate compounds from fertilizers into the shallow aquifers together with high chloride and sodium levels and thereby increasing the concentration of salts of underlying aquifers (Ragone, 1990b & U.S. Congress, 1993).

iii) Agricultural Drainage wells

Agricultural drainage wells are the disposal pathways for irrigation systems or saturated soils. Drainage outflow is achieved through sinkholes while the drainage wells are connected into the subsurface strata (USDA, 1989). Chemicals may remain concentrated in the subsurface in areas with fractured bedrock or slow-moving groundwater (Ragone, 1990a). Agrochemicals and naturally occurring soluble soil minerals such as nitrate and selenium into ground and surface water are commonly carried by drainage outflows and irrigation tail water (U.S. Geological Survey, 2003).

2.4. Hydrogeochemistry of groundwater

Rock water interactions give water its chemical characteristic when water moving through the ground reacts with the surrounding minerals. The silicate minerals which consist of most rocks do not readily react with most groundwater while carbonate minerals readily react with water since they play a pivot role on the evolution of groundwater (McArthur *et al.*, 2000). Heavy metal cations from contaminated water are naturally adsorbed by clay minerals, bearing rocks and sediments. Engineered clay barriers like landfill depend on this principle. Other minerals such as iron-oxides can take part in adsorbing trace elements (Allen and Suchy, 2001). Earle (1982) studied the geochemistry of stream sediments, waters and soils in the Bristol District and indicated that anions and cations play an important role in ion exchange processes. Clay soil is mainly effective at adsorbing cations as their surfaces are consistently negatively charged.

The trace elements are present at some concentration in water samples. Si and F are known to be the most abundant trace elements in the water samples coupled with Ba, Fe B and Sr. Sitakumar (2001) confirms that most trace elements are crucial nutrients while certain trace elements like As, Cd, and Hg are identified as continuous contaminants to the environment and harmful to many forms of life. Health hazards in animals are known to be caused by the potential toxic metal elements like Cr, Pb, Cu and Zn (The Dark Zone, 2003; Nigam Neelam, 2007; National Research Council, 1974). TDS in groundwater is one of the significant parameters to be considered in the irrigation water quality assessment since many of the toxic solid materials may be imbedded in the water, which may construct setback to the plants.

2.5. Irrigation Potential

In South Africa, 24% of the irrigated area is fed by groundwater resources while 76% of the irrigated area is fed by surface water (Perry, 2000). Effects of water quality in irrigated agriculture land depend on irrigation frequency and depth, crop and soil characteristics and the presence of some chemical elements. Salinity depends on how soil water characteristics can be controlled. Increased irrigation water depth is needed to keep salinity at the roots and to flush out excess of salts when salinity in irrigation water increases. Infiltration of return irrigation flows produces related results (Matela, 2001).

Water quality index method (WQI) provides a mechanism for presenting a collective numerical expression defining level of water quality and is the most effective tool which is also a significant parameter to evaluate and manage groundwater quality (Varnosfaderany, 2009). The underlying groundwater level rise is due to excessive irrigated land and this is associated with water-logging in poorly drained soils where groundwater moves closer to the ground surface. The quality of groundwater can also be affected by application of ever-increasing inorganic fertilizers and a wide spectrum of synthetic pesticides (Srinivasamoorthy and Sarma, 2014). Hildebrandt *et al.* (2008) conducted a study and concluded that when pesticides are leached they can be stable for longer periods in the anoxic cold conditions of groundwater, consequently being a more exposed aquatic compartment.

Groundwater is considered as the most dependable water resource for basic human needs. It is extensively used for irrigation, drinking and various industrial purposes globally, especially in arid and semi-arid areas where rainfall and surface runoffs are limited (Delgado et al. 2010; Varis 2014). The first step of sustainable water resources management is through understanding the suitability and status of groundwater quality. Kawo and Karuppanan (2018) constructed a study on groundwater quality assessment and concluded that the correlation analysis discloses that groundwater flow is controlled by cation exchange and rock-water interaction along groundwater flow from high land to rift floor. Consequently, the urban sewages, geogenic process, and fertilizers that are used for agricultural production can possibly affect the groundwater chemistry of the study area.

2.6. Groundwater level fluctuation

Abiye *et al.* (2018) executed a case study in Johannesburg region and suggested that the steady change in the water-level amplitude is a reasonable factor for the long-term recharge variation. It further indicated that the rainfall pattern is inconsistent and the intensity is limited to summer months which could increase the groundwater level. Kotchoni *et al.* (2018) carried out a study on the relationships between rainfall and groundwater recharge and indicated that the recharge of groundwater is estimated from groundwater level fluctuations and uses the values of specific yield derived from magnetic resonance soundings. The study further indicated that recharge varied greatly depending upon the geological environment.

The prediction of long term change of groundwater level with regional climate model in South Korea study was carried out by Jang (2015) concluded that groundwater level responds to many aspects such as the water content in unsaturated zones, evapotranspiration, groundwater extraction and precipitation rates contributing to recharge of groundwater. Gebreyohannes *et al.*, (2013) determined water balance components and groundwater recharge the in Geba basin. Narany *et al.* (2018) conducted a study and revealed that the groundwater chemistry undergoes diverse dramatic changes encouraged by natural and anthropogenic hydrological and geochemical processes throughout its evolutionary path. It also determined the relationship between groundwater quality parameters and types of effective activities and intrinsic factor such as aquifer lithology. Furthermore, the groundwater level during long term monitoring is a very complicated process. The study further concluded that the major negative correlation between areas covered with grass and high contamination of nitrate in the shallow aquifer shows the significant effect of anthropogenic factors on the shallow aquifer.

The study carried out by Acworth *et al.* (2016) concluded that high surface flows are swiftly generated showing that infiltration is low and a high proportion of rainfall is runoff. Under these circumstances, indirect recharge is expected below the creeks. The implications of spatio-temporal rainfall variability on the estimation of groundwater recharge was assessed and revealed that the most likely recharge mechanism is through localised and indirect recharge. According to Apaydin, (2010) groundwater recharge generally depends on nature of intensity, areal and temporal extent of rainfall and climatic parameters. Subsequently, the effective rainfall is more significant than total rainfall and recharge.

CHAPTER 3

STUDY AREA

3.1. Location

Figure 3.1 presents the study area which is situated 28 km north-west of Klerksdorp town and 20 km south-west of Ventersdorp town within the jurisdiction of Vaal Water Management Area in North West Province, South Africa. The catchment covers a total area of 985 km² which lies between the latitudes 26°45'50"S and 26°25'20"S, and longitudes 26°35'50"E and 25°55'10"E.

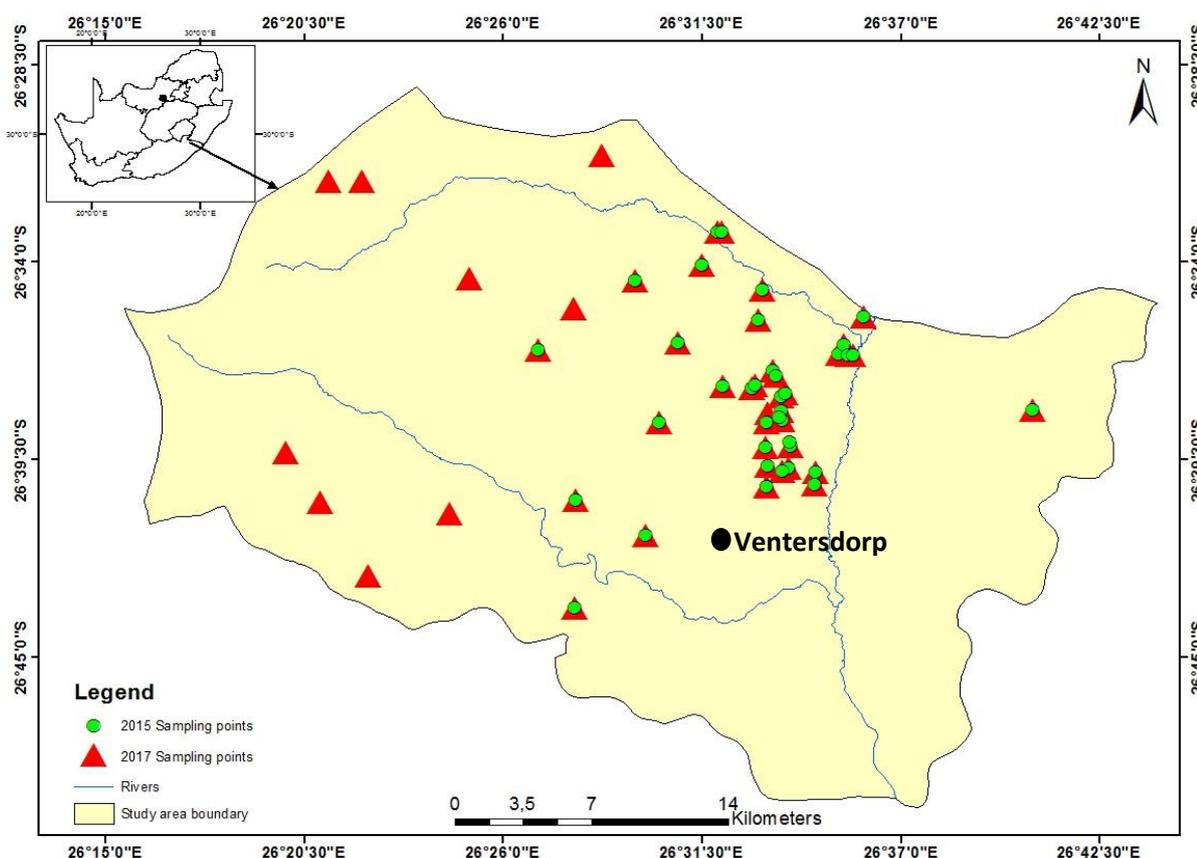


Figure 3.4. Location of study area

3.2. Topography

The topography of the area is generally flat to gently undulating plains with short dry grassland and wood species developing in the bush clumps. The ridges and rocky outcrops are characterized by high spatial variability due to the range of different aspects, slope and altitudes resulting in different soil, light and hydrological conditions. The humidity and temperature regimes of microsites vary on both seasonal and daily basis where moist cool aspects are more conducive to leaching of nutrients than warmer drier slopes (DWAF, 2004).

3.3. Climate and Rainfall

Lohman (1992) reported that, rainfall in Ventersdorp is variable mainly occurring during summer season (from November to March) and decreases from west to east. DWA (2004) and IGS (1994) reported that the area experiences high rainfall during December and January with a mean annual precipitation of 454 mm/year. The mean annual temperature ranges between -9.1°C (minimum) to 36.5°C (maximum) (DWAF, 2004) and mean annual evaporation in the catchment (Schultze 1997) ranging between 2200 and 2400 mm/year.

3.4. Drainage

The area is drained by two tributaries from Schoonspruit River which are Buisfonteinspruit and Kaalspruit Rivers. Buisfonteinspruit River drains the catchment from south to south-west while Kaalspruit River drains the catchment from the north to north-west. About 50% of the flow generated in the Schoonspruit catchment comes from the Schoonspruit Eye, which emphasizes the importance of the correct simulation of the eye flows.

3.5. Geohydrology

The Ventersdorp area is covered by a dolomitic aquifer system. The permeability of dolomites as a result secondary fissures like faults, joints and bedding planes provides easy access to circulate groundwater. Hence this supports the deep weathering of dolomites majorly by carbonate solution. The residues weathering are mainly wad with chert rubble and boulders and brown clay. Darcy (2002) and DWAF (2006) indicated that the most important lithology in terms of groundwater are dolomites of the Malmani Group (Ventersdorp Supergroup, Karoo Sequence and Pretoria Group) which form a broad band across the north of the area. The borehole lithology in the study area (Latitude 26° 37,049' and Longitude 26° 32,046') shows that the unconsolidated quaternary sediments consisting of clay constitute at the upper layer underlain by coarse gravel, fine sand mix with medium sand, fractured hard rock like feldspar, coarse grain sand and weathered rock like charnockite.

3.6. Geology

This area is located on a banded metamorphic rock derived from sedimentary or igneous rocks mineralogical equivalent to granite. It is holocrystalline shale rock consisting of granite, quartz,

potash feldspar, acid plagioclase and mica. The interconnected fractures of granite-gneiss, crystallisation of granite during its formation and interbedded layers of granite provide the properties which enhance groundwater movement. The area is underlain by dolomites and chert of the Malmani Group (Darcy 2002 and DWAF 2006b). Cherts are fine grained silica rich in cryptocrystalline or microcrystalline sedimentary rock that contains tiny fossils. It is formed when microcrystals of silicon dioxide grow within soft sediments that develop limestone or chalk. Dolomites of the Malmani Subgroup of the Transvaal sequence consist of four formations on the basis of chert content and type of algal structures. There occurs a series of cross-cutting lineaments representing faults and dykes. Dykes are not completely impermeable but they are several orders of magnitude less permeable than the dolomite. Though the chert-rich formations form the main aquifers, the Ventersdorp area is located on a dolomitic aquifer (Darcy, 2002).

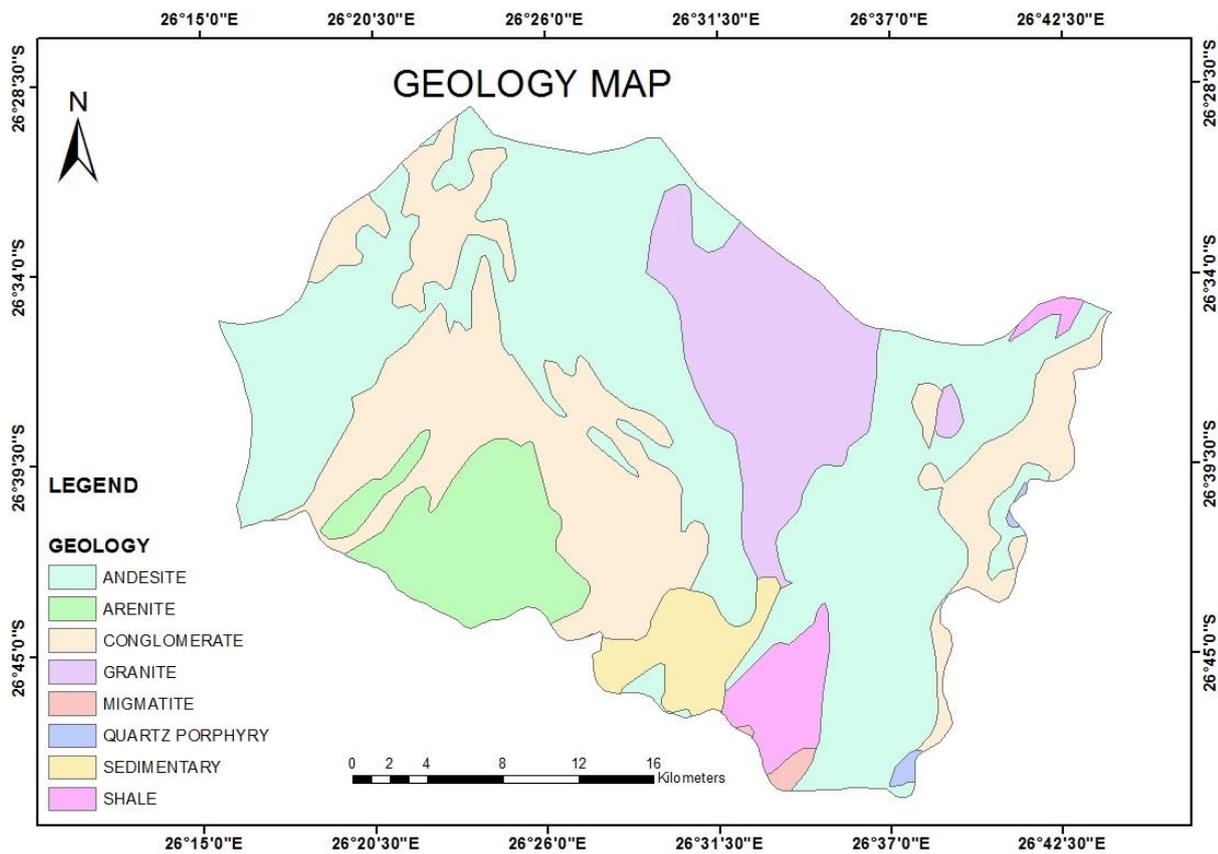


Figure 3.5. Geology of the area

The permeability of the dolomites is mostly due to secondary fissures such as joints, faults, and bedding planes which provides easy access to circulate groundwater. This characteristic causes weathering of the dolomite majorly by carbonate dissolution. Residues of weathering are mainly brown clays and wad with chert rubble and boulders. Borehole logs from the unconsolidated

quaternary sediments consist of clay as the top layer underlain by coarse gravel, fine to medium sand, fractured hard rock such as feldspar and weathered rock like charnockite.

3.7. Land use

The major land uses in the study catchment are agriculture and urbanization (towns and townships). The main land use categories are industries and mining at 0.16%, urban development with 3.41%, agricultural dry land with 41.78%, agricultural irrigation at 10.97%, agricultural intensive livestock at 20.68% and agricultural extensive livestock at 23% (Darcy, 2002 and DWAF, 2006b). Ventersdorp extends to an area of 3 305 km square of which 28.6% or 106 807.13 ha is cultivated land with 87 207.48 hectares of major agriculture land. The greater part of the area consists of unimproved grassland. The available farming unit in Ventersdorp amounts to 4528 farms. The agriculture production of Ventersdorp amounts to R236 558 annually.

3.8. Agriculture and irrigational use

The role of agriculture in the study area is of importance regardless of its small contribution to gross domestic product. Agriculture sector contributes 49% to economy of Ventersdorp and is dominated by large extent commercial farming specializing in producing maize and wheat. The agricultural sector plays a vital role in job creation in Ventersdorp mainly in rural areas and is also a primary earner of the foreign exchange. The sector employs 11% of total population of 56 702 in Ventersdorp. About 70% of agricultural production is utilized as the intermediate products. The study area is known to be the main maize production; maize prices have dropped recently in anticipation of better maize crop. The livestock farming also makes greatest contribution to agricultural production in the area (READ, 2016). This area is mostly covered by the natural grassland (grassveld) of South Africa in the northern and eastern part. There are small areas of tropical woodland (bushveld) on the southern side. Most of the area is under grazing (48%) or cultivated land (47%) with 5% being dry land farming. Maize (70%), sunflower (8%) and sorghum (8%) are the most important crops with the remaining 14% cultivated with other crops such as wheat, lucerne etc (DWAF, 2002).

CHAPTER 4

RESEARCH METHODOLOGY

4.1. Introduction

The objectives of assessing groundwater chemistry are achieved by collecting groundwater chemistry of the area using random sampling method. Groundwater sampling was undertaken in May 2015 and October 2017 to account for seasonal period. The minimum distance allowed between two adjacent boreholes where samples were taken is 1 km.

4.2. Data collection

Data collected include geological maps, groundwater samples, borehole lithology samples and soil samples. Land type maps were obtained from Institute of Soil Water and Climate of the Agricultural Research Council (ARC-ISWC). Groundwater quality data was obtained from National Groundwater Archives of Department of Water and Sanitation. The measured data was analyzed statistically for significant difference between measured parameters and land use classes. Daily rainfall data from 1997 to 2016 of the weather station within the study area was obtained from the South African Weather Services (SAWS). Annual and monthly rainfall totals over the period of 20 years were established from the daily rainfall records.

4.3. Groundwater sampling

Initially, field survey was conducted from where the selected bore wells were chosen for sample collection. Farmers together with farm workers were interviewed during field survey seeking detailed information on the use of anthropogenic activities, types of crops planted, crop yield, availability and utilization of the groundwater resource, the depth of the bore wells, application of fertilizers, and nature of rainfall in the area.

The data collected for the study include 40 groundwater samples collected from shallow boreholes using a bailer to unequipped boreholes and a bucket to equipped boreholes in 2015 and 70 boreholes in 2017. Prior to collection groundwater sample, the bore wells were purged for few minutes in order to remove stagnant water trapped at the bore wells to avoid misinterpretation of data. The groundwater level of the bore well was measured onsite using solinst 101 water level meter-200. The parameters which were measured onsite include ORP, pH, Temperature, TDS and electrical conductivity. These parameters were measured instantly after collecting the groundwater samples with YSI multi-probe digital meter (YSI 6600 V2-4 model). During sample collection, standard procedures of preservation and handling were followed to ensure consistency and data quality. The high-density polyethylene bottles were used to collect groundwater samples, with the samples filled up to the edge, sealed to avoid contact to air and were branded analytically.

4.5. Groundwater analysis

Samples were analysed within 48 hours to obtain analytical results. The major ions, nutrients and trace metals were analysed in the laboratory for various physicochemical parameters. Major cations such as calcium, magnesium, sodium and potassium were analysed using Inductively Coupled Plasma (ICP-MS-41) in the Department of Agriculture, University of Zululand for 2015 groundwater samples. The Inductively Coupled Flex (IC-Flex) from Department of Hydrology, University of Zululand was used to analyse 2017 groundwater samples. The major anions like Cl^- , CO_3^{2-} , HCO_3^- and SO_4^{2-} were analysed by titration using standard methods (APHA, 1998) at the Hydrology Department, of University of Zululand. Apart from sulphate and nitrate, fluoride was also determined using spectrophotometer. The trace metals such as Ni, Cu, Cr, Cd, Al, Pb, Zn, Fe, Mn, B, Si, Li and nutrients like F, NH_4^+ , PO_4^{3-} for year 2017 were analysed using Ion-Chromatography in Hydrology Department. During sample collection and chemical analysis, standard procedures (handling and preservation) were followed to ensure data quality and consistency. The chemical standards for each element were prepared separately and high purity analytical reagents were used throughout the study.

4.6. Software and techniques

The Geographical Information System 10.5 software was used to construct geological map, study area map, sample location map, land use map, drainage map, and spatial variation diagrams. Data was analysed using Microsoft Excel software. Geochemist's Workbench Edition 12.0 software was used to determine Piper and Durov diagrams. The Originlab 2018 64Bit software was used to prepare graphs throughout the study. In this study, XLSTAT 2017 STATISTICA software was used for multivariate statistical.

4.6.1. Multivariate statistical technique

The main principle of factor analysis (FA) is to decrease the contribution of these major variables to simplify the data structure from PCA. In order to achieve this, the axis defined by PCA should be rotated as per the established rules contributing new variables called varifactors (VF). Vega *et al.* (1998) and Helena *et al.* (2000) described VF as hypothetical, unobservable and latent variables while PC is described as a linear combination of observable water quality variables. Correlation analysis of groundwater parameters is an important instrument in hydrogeochemical

studies. This study adopted the factor analysis to extract Eigenvalues and Eigenvectors from covariance matrix to produce orthogonal variables through varimax rotation (Devic *et al.*, 2014). The correlation matrix mainly displays the relations of individual variables, thus revealing interlinks between variables and different controlling factors demonstrating the overall coherence of the data set (Li *et al.* 2011 & 2012). The XLSTAT 2017 software was employed to computed correlation analysis and the pearson correlation matrix.

4.6.2. GIS analysis

The Arc-GIS 10.5 software was used in the study to prepare the thematic maps. Sampling locations were noted by Global Positioning System (GPS) and were later transformed to GIS. IDW interpolation method was adopted to map the groundwater suitability for drinking and irrigation purposes. The spatial variation was constructed using Geostatistical analyst module in Arc-GIS 10.5.

4.6.3. Irrigation water quality index

(1) Salinity hazard, (2) permeability hazard, (3) specific ion toxicity and (4) miscellaneous effects are the IWQ parameters given by Ayers and Westcot (1985) which were applied in the study to mark the IWQI. (5) Parameters were assigned in this study with weightage coefficient ranging from 5 to 1, depending on their significance in irrigation, with salinity being the most significant and miscellaneous effects being the least significant. The IWQI was then computed by the following equation:

$$IWQI = \sum_{i=1}^n Gi \quad 4.1$$

Where i is the incremental index and G is the contribution of each of the 5 hazard categories that are significant to evaluate the quality of groundwater for irrigation. G is computed using the following equation 4.2;

$$G = w / N \sum_{i=1}^n rk \quad 4.2$$

where k is the incremental index, N is the total number of parameters, w is the weight value of the selected groups and r represents the rating value of each parameter.

4.6.4 Groundwater for Irrigation Purpose

The quality of groundwater which is utilized for irrigation purposes is essential for, crop yield, environmental and protection maintenance of soil productivity. The suitability of the groundwater for irrigation purposes was determined using various indices. The indices values of Na% (Wilcox 1955), RSC (Eaton 1950; Wilcox 1948), SAR (Todd 1980; Sawyer and MacCarthy 1978, PI (Doneen 1964; Raghunath, 1987), CR (Ryner 1944; Raman 1985) MH (Szaboles and Darab, 1964) and Cl/HCO₃ ratio (Revelle, 1941) in the study area for determining suitability of groundwater for irrigation were computed using equations enlisted in chapter 6 of this report.

CHAPTER 5

HYDROGEOCHEMICAL PROCESSES

5.1 Introduction

In this chapter, the processes responsible for the evaluation of hydrochemical processes of groundwater in study area was brought out based on the analytical results 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^- during 2015 and 2017. World Health Organization (WHO, 2004) standards have been used to check the suitability for drinking water. The geochemical change in groundwater is between the major anions and cations in the Piper (1944) triplot diagram. Cation composition in groundwater is represented as alkaline earths metals for calcium and magnesium, and alkali metals as sodium and potassium while anions are represented as strong acids such as sulphate and chloride, and weak acids such as carbonate and bicarbonate. The major factors influencing suitability of groundwater for various purposes are described as the hydrochemical characteristics of groundwater.

5.2 Hydrochemistry of groundwater

Diversity in 2015 and 2017 on the physical and chemical groundwater parameters (EC, pH TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- , NO_3^-) are presented using Box and whisker plots in Figure 5.1. The major ions vs cations and anions (Ca, Mg, Na, K, CO_3 , HCO_3 , SO_4 , and Cl) and other parameters such as pH, EC and TDS, and its suitability of groundwater in the study area are discussed in detail. Table 5.1 describes the salient statistical ranges of all the parameters in the groundwater of the study area. The pH groundwater of ranges from 6.6 to 8.4 with a mean value of 7.4 during 2015 and pH of groundwater during 2017 ranges from 5.9 to 7.9 with a mean value of 6.5. In general, the pH of the study area during both sampling periods is slightly acidic to alkaline. Ahmed *et al.* (2002) indicated that the salinity hazard is a significant water quality parameter and is estimated using electrical conductivity (EC) and crop production. Water with high EC has negative effects on crop production and also generates physiological drought for crops. In the study area, EC values ranges from 233 to 881 $\mu\text{S}/\text{cm}$ with a mean value of 491 $\mu\text{S}/\text{cm}$ in 2015 and from 155 to 1027 $\mu\text{S}/\text{cm}$ with a mean value of 352 $\mu\text{S}/\text{cm}$ in 2017. On the basis of DWAF (1996) approved limit of drinking (EC <450 $\mu\text{S}/\text{cm}$), the electrical conductivity classification shows that

18 nos (45%) of samples in 2015 and 9 no's (13%) of samples in 2017 exceeds the limit (DWA 1996) in the study area. TDS and EC are indicators of saline water in the absence of non-ionic dissolved constituents (Matthess 1982). TDS in groundwater is one of the important parameters that need to be measured and analysed to identify the suitability of water for irrigation water quality since many of the toxic solid materials may be imbedded in the water, which may construct setback to the plants. Na and Cl varied from 12.9 to 49.4 mg/L and 26.6 to 159.5 mg/L with a mean concentration of 28.4 and 55.4 mg/L. K ranged from 12.6 to 18.9 mg/L in 2015. Ca and Mg concentrations ranged from 2.2 to 67 mg/L and 7.2 to 38.9 mg/L with a mean concentration of 36.3 and 21.5 mg/L. SO₄ and HCO₃ varied from 0.9 to 41 mg/L and 42.7 to 347.7 mg/L. NO₃ concentration in groundwater ranged from 0.9 to 28.9 mg/L with a mean value of 10.1 mg/L. The average concentrations of ions were used to determine the order of major ions in the area. The affluence of the major ions in the groundwater of was used to determine the abundance of the major ions present in the groundwater of the study area was found to be in the order of Ca>Na>Mg>K and HCO₃>Cl> SO₄>NO₃.

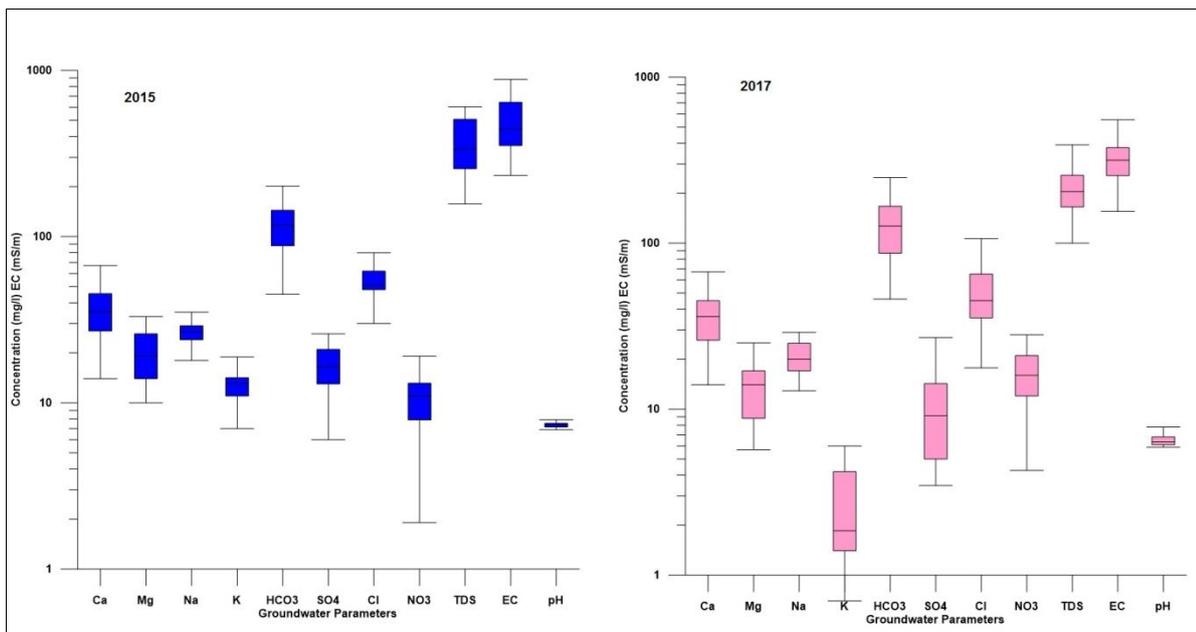


Figure 5.1. Box and whisker plots of groundwater parameters in the year of 2015 and 2017

Table 5.1. Statistical results of physical-chemical characteristics of groundwater in the study area (all in mg/L and EC in mS/m)

Parameter	2015					2017				
	Min	Max	Average	SD	Mean	Min	Max	Average	SD	Mean
pH	6.6	8.4	7.4	0.3	7.4	5.9	7.9	6.5	0.4	6.5
EC	233	881	491	182. 5	490.6	155	1027	347	189. 7	351.5
TDS	157	603	359	133. 3	358.6	100	667	232	129	234.1
Na	12.9	49.4	28.2	6.1	28.2	13	132	30.6	31.1	30.5
K	12.6	18.9	13.4	1.0	13.4	0.7	6	2.9	1.6	2.6
Ca	2.2	67.0	36.3	14.4	36.3	14.0	82.0	33.4	13.1	36.0
Mg	7.2	38.9	21.5	7.8	21.5	5.7	34.0	13.4	6.4	14.6
Cl	26.6	159.5	55.4	31.3	55.4	17.7	212. 7	55.3	35.9	57.6
HCO₃	42.7	347.7	117.9	52.5	117.9	46.0	294. 6	125.8	62.1	138.4
SO₄	0.9	41.0	5.8	7.7	5.8	3.7	91.0	16.7	23.0	16.2
NO₃	0.9	28.2	10.1	5.7	10.1	0.0	47.0	14.7	10.4	8.7

The total hardness (TH) values of groundwater in the study area ranged from 90 to 285 mg/L with a mean value of 179 mg/L during 2015 and during 2017. TH ranges from 35 to 333 mg/L with a mean value of 111. As per the WHO 2011, the maximum permissible limit of TH for drinking purpose is 500 mg/L and the desirable limit is 100 mg/L. The TH classification of groundwater shows that majority of groundwater samples fall within the hard water category. Groundwater with TH more than 300 mg/L is considered to be very hard. The reasons for hardness of the groundwater can be because of the presence of calcium and magnesium. All groundwater samples in the study area are within the permissible range. The range of the TDS in groundwater shows that all groundwater samples in the study area are suitable for drinking and irrigation purpose. The relationship between TDS vs TH is shown in Figure 5.2.

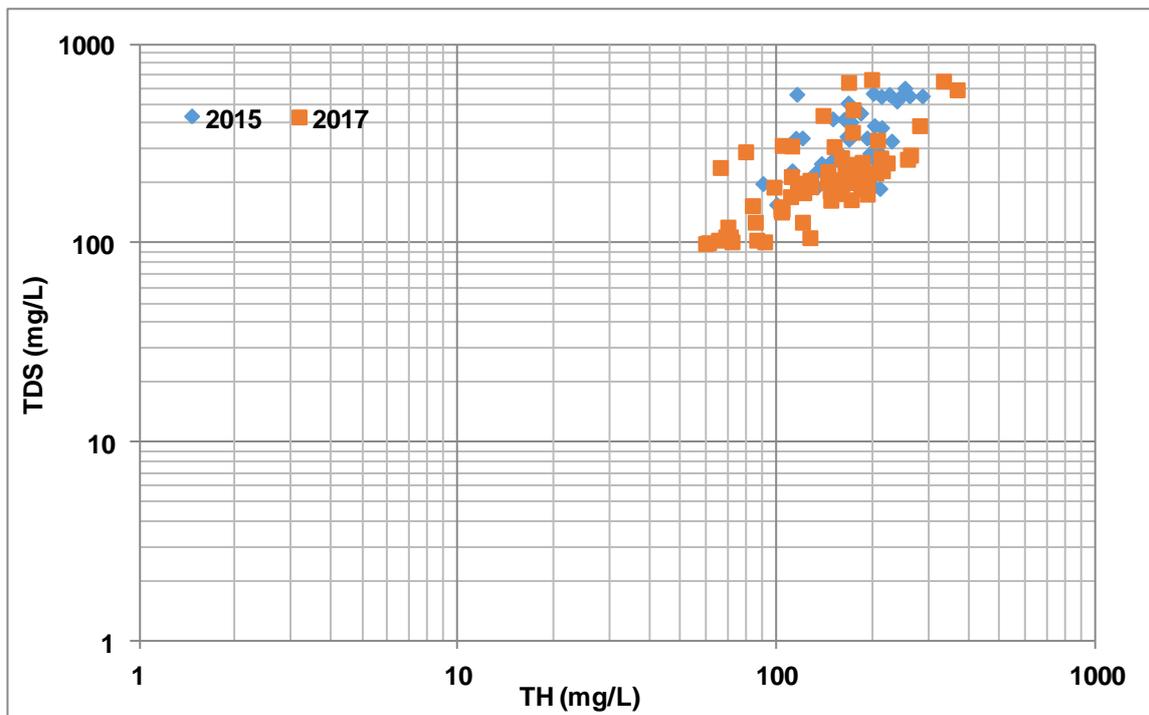


Figure 5.2. Groundwater classification using TH and TDS

The order for domination of cations and anions in the groundwater samples of the study area is $\text{Ca} > \text{Na} > \text{Mg} > \text{K} & \text{HCO}_3 > \text{Cl} > \text{SO}_4$ during the year 2015 and 2017. The mean concentrations of major ions i.e., cations and anions are presented in the diagrams (Figure 5.3) for both years. High concentration of bicarbonate in groundwater clearly indicates recharge to aquifer is from rainfall. Potassium concentrations in groundwater samples in the study area are due to the dissolution of granitic rocks. Sources of chloride in groundwater may be from fertilizers, effluents, human and animal waste in the study area.

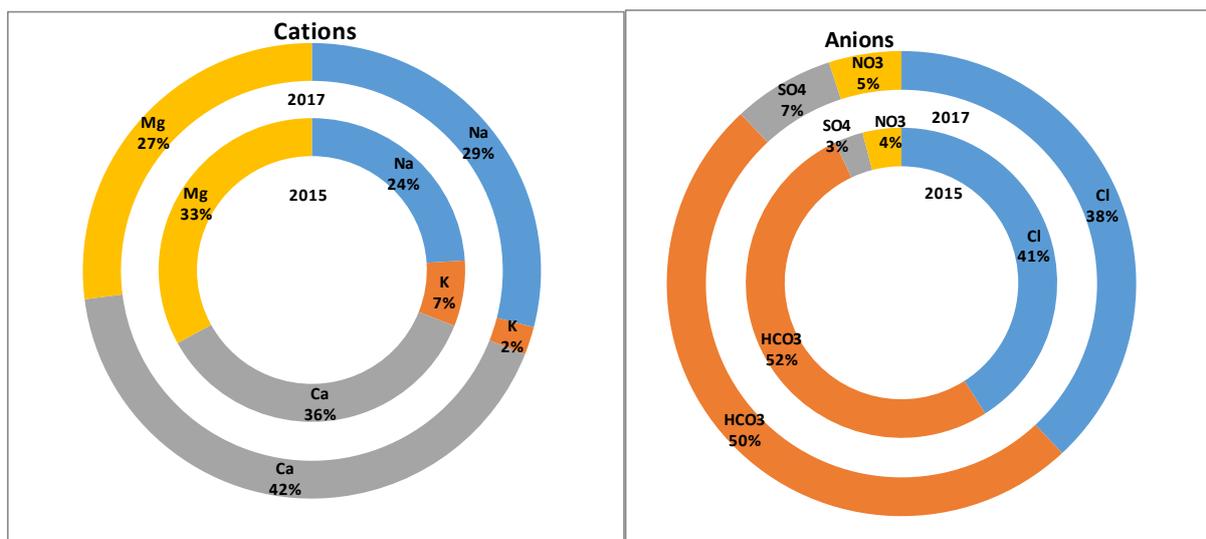


Figure 5.3. Diagrams of the mean concentrations of major cations and anions in the year 2015 and 2017

5.3 Hydrochemical facies of groundwater

Hydrogeochemical facies of groundwater reflects the complete properties of natural chemical processes taking place in between the rock minerals within the aquifers (Varol and Davraz, 2014). In present study, the diagram developed by Chadha (Chadha 1999) was used to infer the hydrochemical facies of the groundwater (Figure 5.6). The hydrogeochemical origin of groundwater can be understood by using a trilinear plot (Piper 1944) wherein the concentrations of major cations and anions (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (HCO_3^- , CO_3^{2-} , SO_4^{2-} , and Cl^-) in meq/L were used. The Geochemist's workbench student Edition software version 12.0 (64-bit) was used to plot the piper diagram. The natural groundwater concentration can be epitomized as solution of cationic and anionic constituents and those contributing towards alkalinity, i.e., CO_3^{2-} and HCO_3^- . A Piper diagram has three distinct fields which consist of two fields in triangle shape and one in diamond shape. The diamond shaped field determines the groundwater types based on the position of the samples plotting. The cations and anions expressed as percentages of total cation & anions and are represented in meq/L. The plot in the right triangle denotes the anion and cations plot on the left side triangle. The piper diagram reveals changes and resemblances among the groundwater samples because those with same origin will incline to plot as same groups (Todd, 2001). The plot shows that most groundwater samples in the study area fall in the field of Ca- HCO_3 type mixed and Ca- SO_4 water type (Figure 5.4). The Ca- SO_4 water type represents the typical of gypsum ground waters and mine drainage and Ca- HCO_3 represents the typical of shallow fresh ground waters. In the anions triangle, most groundwater samples fall within the chloride and bicarbonate type with few samples falling within no dominant type. This plot reveals that only few groundwater samples in the study area are salty in nature.

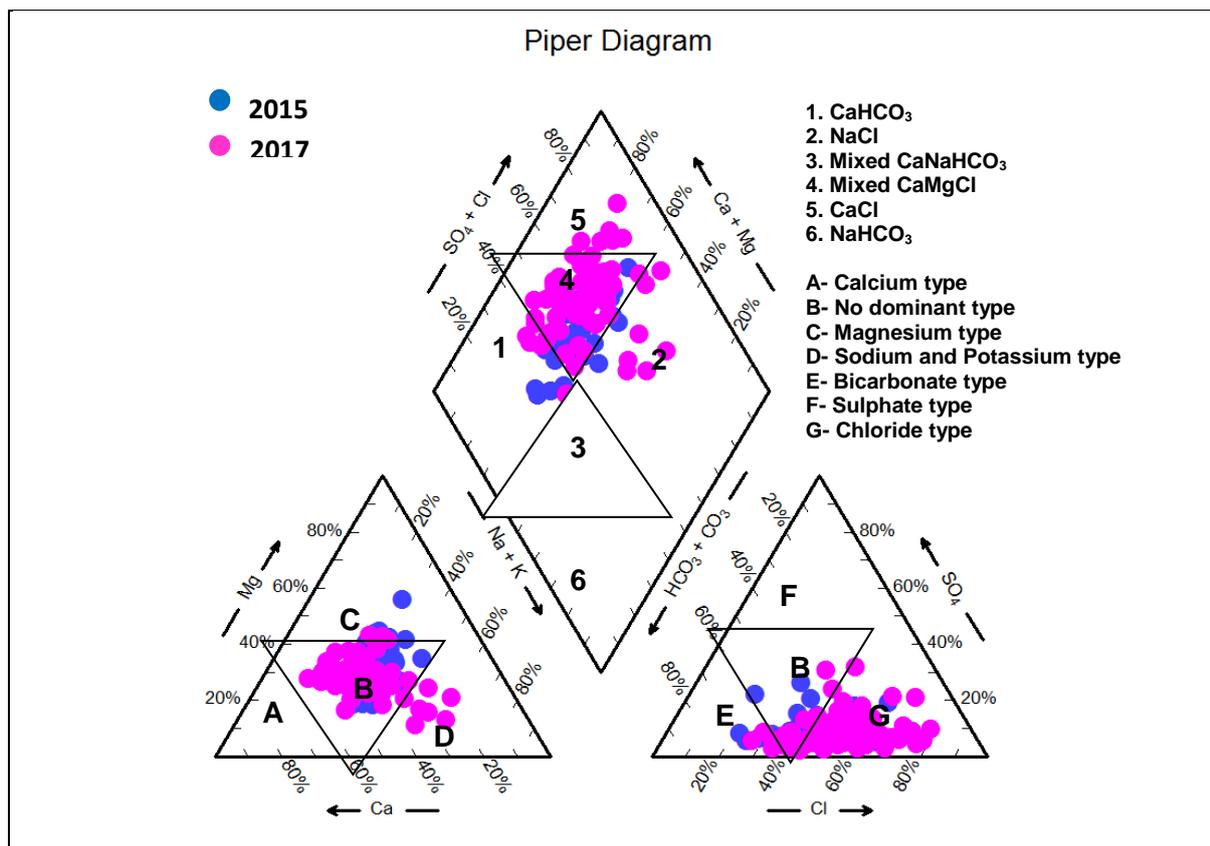


Figure 5.4. Hydrochemical facies of groundwater (Piper 1944)

The groundwater quality in its insitu-state indicates the hydrochemical nature of the groundwater aquifers. The Piper trilinear diagram (Piper 1944) helps in comparing and classifying water types. The diamond-shaped field in the piper diagram is classified into six types: (1) Ca-HCO_3 ; (2) Na-Cl ; (3) mixed Ca-Na-HCO_3 (4) mixed Ca-Mg-Cl ; (5) Ca-Cl ; (6) Na-HCO_3 (Fig. 5.4). The groundwater samples of the study area falls into zones 2, 4 and 5, it is clearly indicating a dominance of NaCl , mixed and CaCl types. The plot clearly shows that most of the groundwater samples fall in the alkaline metals field (Na^+ , K^+) over the alkaline earth metals field (Ca^{2+} , Mg^{2+}). In case of anion Cl^- and HCO_3^- are dominant, followed by sulphate. In the case of major cation sodium is dominant, followed by magnesium and calcium in the groundwater.

Figure 5.4 present 90% of groundwater samples in the study area classified has no dominant type in relation to cations plotted in Zone B. Groundwater types show high variety with classification into CaHCO_3 , NaCl , Mixed CaMgCl and CaCl type. Figure 5.4 shows that groundwater samples fall within the first basic type which is the $\text{SO}_4\text{Cl-CaMg}$ type. The groundwater type indicates that the dissolution of carbonates is the predominant processes that cause the release of large amount of calcium and magnesium into groundwater in the study area. This could be the possible reason for all the samples in the study area to plot in zone 1. The reasons for the groundwater samples of

SO₄Cl–CaMg type may be due to the influence of evaporation and human activity on groundwater hydrochemistry.

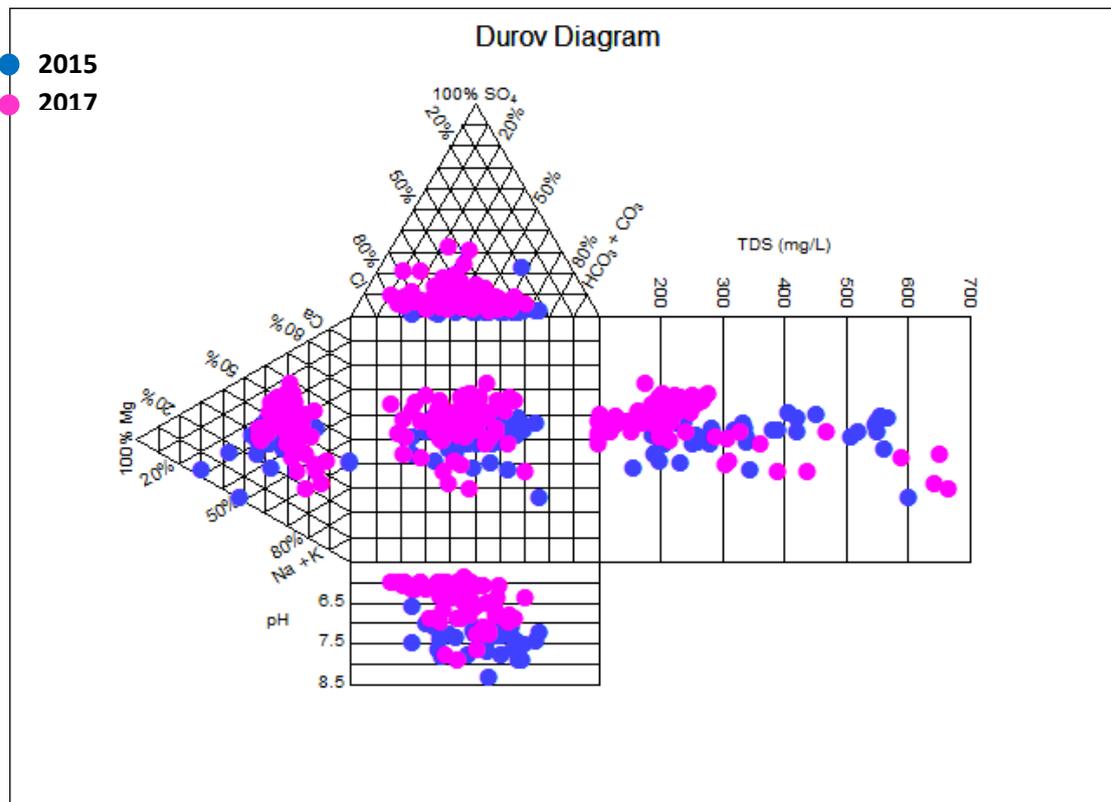


Figure 5.5. Durov plot explains water types and hydrochemical processes

The Durov diagram (Durov 1948) was prepared to understand the hydrogeochemical features of groundwater and as represented in Figure. 5.5. The Durov diagram is more advanced to Piper diagram (Piper 1953) as it can delineate all together the hydrogeochemical facies and also the values of pH and TDS of groundwater samples. Figure 5.5, groundwater samples from different landscapes and aquifers show dissimilar hydrogeochemical characteristics. Figure 5.5 shows that about all groundwater samples of the study area have TDS values of less than 1000 mg/L with bicarbonate as the major anion. Groundwater with TDS greater than 1000 and less than 2000 mg/L (0% samples in the study area) is considered to be brackish water. In case of mixed type of groundwater, the concentrations of anions are close with each other similar to brackish water. None of the groundwater samples in the study area have TDS content greater than 2000 mg/L with high concentrations of SO₄²⁻ and Na⁺. The Durov diagram (Durov 1948), reveals that groundwater in the study area is mainly of HCO₃–Ca–Mg. The pH values in the study area ranges from 6.6 to 8.4 in 2015 and from 5.9 to 7.9 in 2017. The pH of groundwater is generally influenced by several factors like environmental pollution, variation of inorganic salts in water, human activity and geologic transition.

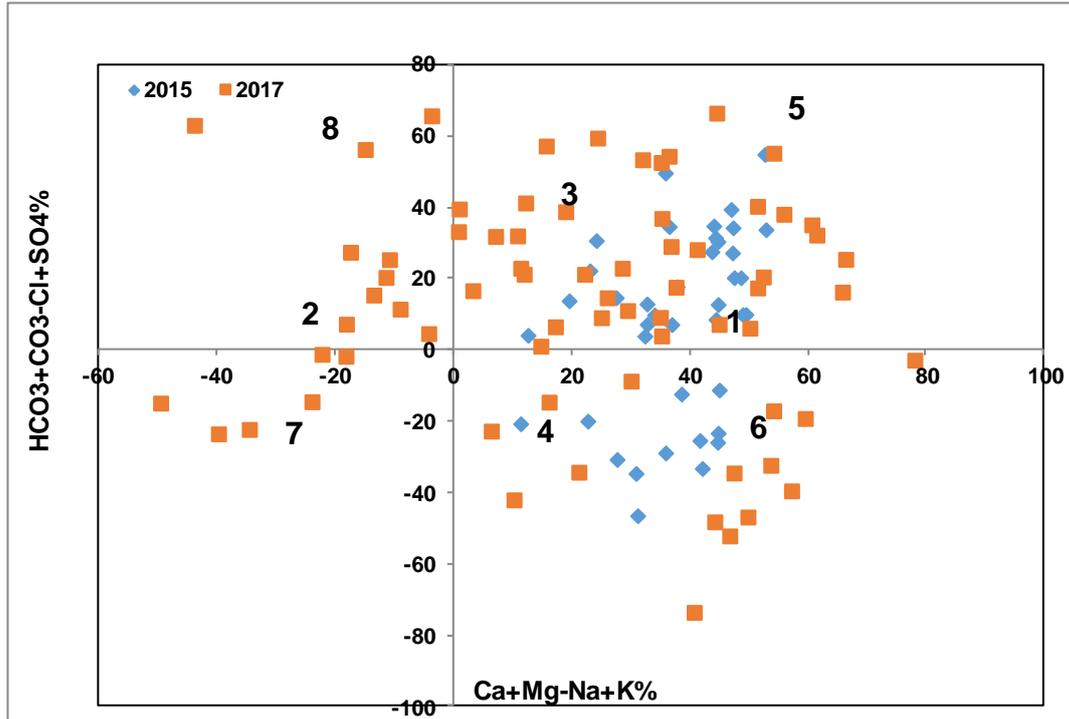


Figure 5.6. Hydrochemical facies of groundwater (Chadha 1999)

The overall effects of natural chemical reactions occurring between the minerals within the aquifers are reflected by hydrogeochemical facies (Varol and Davraz, 2014). The Chadha diagram (Chadha 1999) was used to interpret the hydrogeochemical facies of groundwater in the area of study (Figure 5.6). The Chadha diagram was constructed by plotting the difference in percentage (meq/L) between weak acidic anions ($\text{HCO}_3^- + \text{CO}_3^{2-}$) and strong acidic anions ($\text{Cl}^- + \text{SO}_4^{2-}$) on the Y axis and the difference in percentage (meq/L) between alkaline earths ($\text{Ca}^{2+} + \text{Mg}^{2+}$) and alkali metals ($\text{Na}^+ + \text{K}^+$) on the X axis. The graphical diagram categorizes groundwater into 8 small fields and are as follows: (1) Alkaline earths exceed alkali metals, (2) Alkali metals exceed alkaline earths, (3) Weak acidic anions exceed strong acidic anions, (4) Strong acidic anions exceed weak acidic anions, (5) $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$, $\text{HCO}_3\text{-Ca}$ or $\text{HCO}_3\text{-Mg}$ types, (6) $\text{Cl}\cdot\text{SO}_4\text{-Ca}\cdot\text{Mg}$, $\text{Cl-Ca}\cdot\text{Mg}$ or $\text{SO}_4\text{-Ca}\cdot\text{Mg}$ types (7) $\text{SO}_4\text{-Cl-Na}$, Cl-Na or $\text{SO}_4\text{-Na}$ types, and (8) $\text{HCO}_3\text{-Na}$ type (Chadha, 1999).

Figure 5.6 shows that 90% of groundwater samples in both year 2015 and 2017 fall within sub-field 5 and 6, indicating alkaline earths exceeding alkali metals, and weak acidic anions exceeding strong acidic anions in these water samples. Groundwater for such water is $\text{HCO}_3\text{-Ca-Mg}$ type and has temporary hardness (Chadha, 1999). About 6% of groundwater samples for both year 2015 and 2017 in the study area fall within sub-field 8, and such water is usually due to the deposits of residual sodium carbonate of irrigation use (Chadha, 1999). 4 % of the groundwater

samples in the study area fall within sub-field 7 indicating alkali metals and strong acidic anions exceed alkaline earths and weak acidic anions, respectively. This kind of water generally causes salinity problems for both usage in irrigation and drinking (Chadha, 1999). These samples are characterized as $\text{SO}_4\text{-Cl-Na}$ type.

5.4 Gibbs Plots/ Dissolution of Minerals

In this study, Gibb's plot was used to determine the processes controlling hydrochemistry of groundwater. The diagram has 3 different fields which has major components such as rock water interaction, precipitation and evaporation (Gibb's, 1970). The scatter plot on a semi-log graph between TDS vs. $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and TDS vs. $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ was used to identify the process responsible for the groundwater chemistry. In the study area, groundwater samples fall in the center zone of the plot indicating that rock water interaction is the dominant process in the groundwater hydrochemistry of the study area (Figure 5.7). Gibbs plots revealed that groundwater in the study area for both year 2015 and 2017 is of rock water interaction dominance.

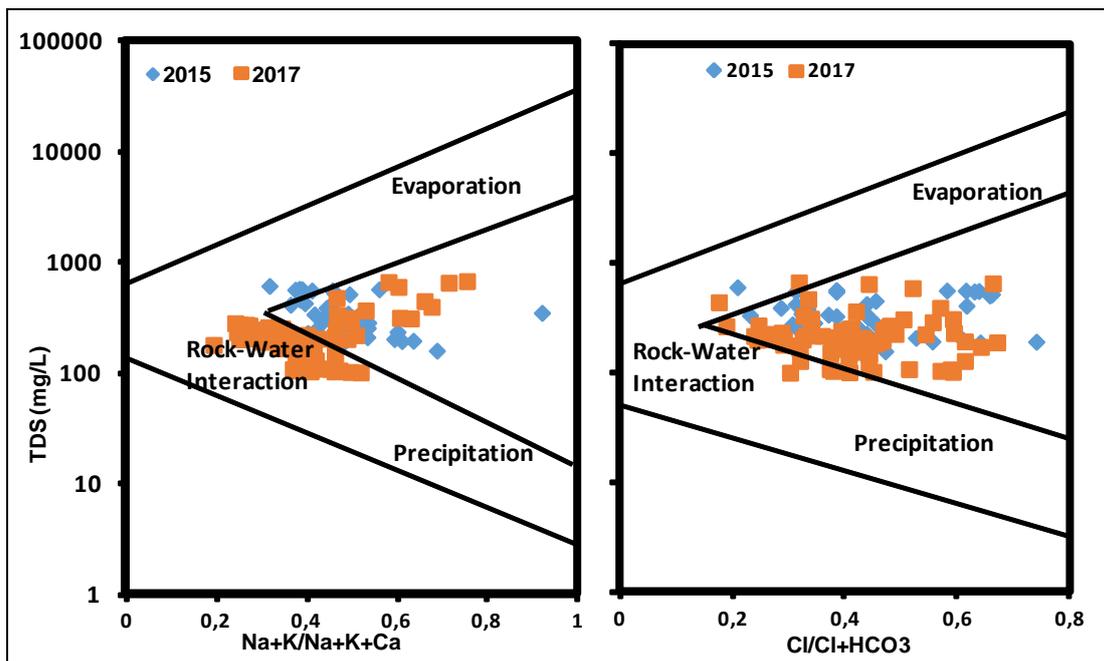


Figure 5.7. Gibbs diagram for groundwater

5.5 Soltan Classification

Groundwater established on Cl , HCO_3 and SO_4 was suggested and categorized by Soltan (1998). The groundwater can be 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 lithology and movement of water influences the water type and concentration of salts in groundwater (Raghunath, 1982).

Figure 5.8a shows the scattered distribution of the groundwater samples of the study area on Soltan's classification. The Figure clearly shows that most of the samples during both years fall in normal bicarbonate type followed by normal chloride and sulfate type. Further, Soltan (1998) equation (eq.5.1) was used to evaluate Base Exchange Indices for grouping of groundwater sources.

$$r1 \frac{Na - Cl}{SO4} \tag{5.1}$$

Where r1 denotes the Base Exchange index. Sodium, chloride and sulphate concentration are in meq/l. If $r1 > 1$, the groundwater is $Na-HCO_3$ type whereas $r1 < 1$ specifies the groundwater is $Na-SO_4$. Groundwater samples of 2015 have 95% $r1 < 1$ which clearly indicates $Na-SO_4$ type water. Groundwater samples of 2017 have 91% $r1 < 1$ which also classifies as $Na-SO_4$ type water (Figures 5.8a&b). About 5 and 9% of samples are $Na-HCO_3$ type ($r1 > 1$) (Figure 5.8a&b) during 2015 and 2017.

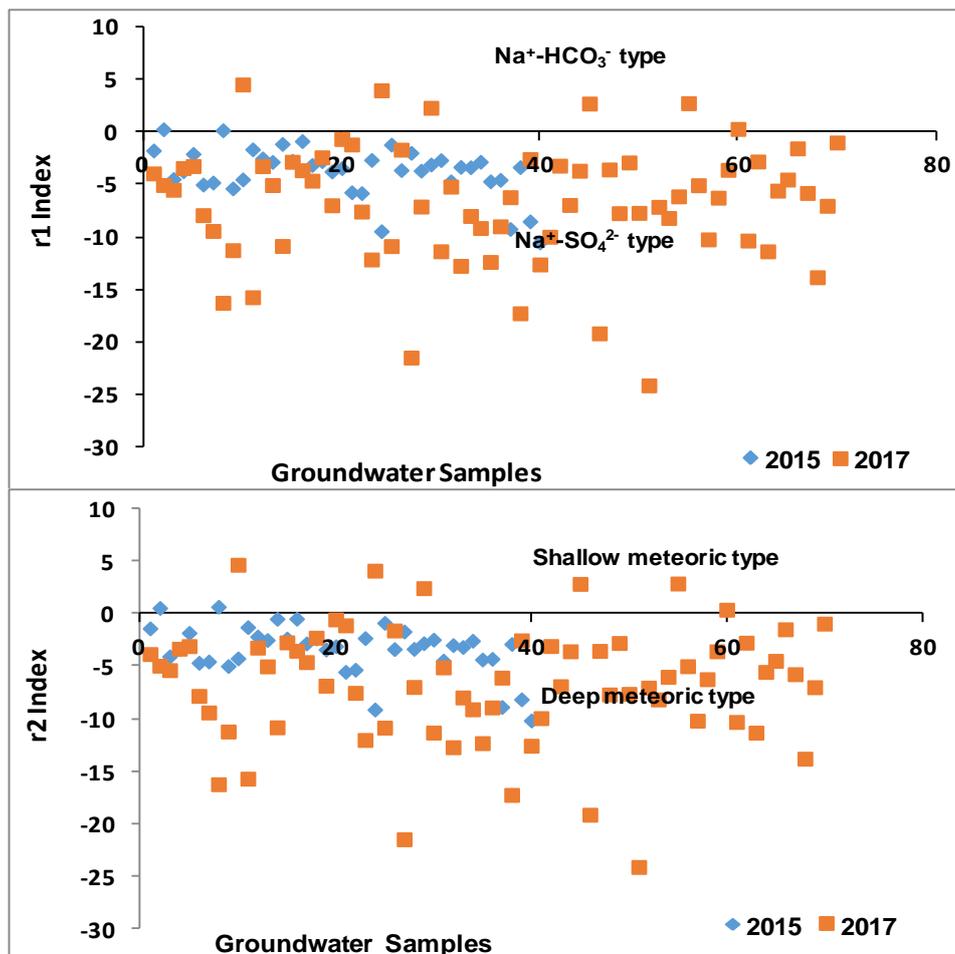


Figure 5.8a, Soltan classification of groundwater samples of the study area Soltan (1998) categorized the sources of groundwater due to meteoric genesis index and this can be determined by using equation 5.2

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

5.2

Where $r2$ denotes meteoric genesis index, concentration of Na, K, Cl and SO_4 are presented in meq/L. If $r2 < 1$ then the groundwater is of deep meteoric water type. If $r2 > 1$, the groundwater can be classified as shallow meteoric water type. On the basis of this categorisation of meteoric genesis index, 95% and 91% of groundwater samples from 2015 and 2017 respectively fall in the deep meteoric water type. 5 and 9% of samples fall in the shallow meteoric water type in 2015 and 2017 respectively (Figure 5.8b). Low rainfall and decline in groundwater levels may be the reasons for deep meteoric type of water (Tamma Rao *et al.*, 2013). Similar results have also been reported by Singh *et al.*, 2006; Reddy *et al.*, 2012; Singh *et al.*, 2014 in India.

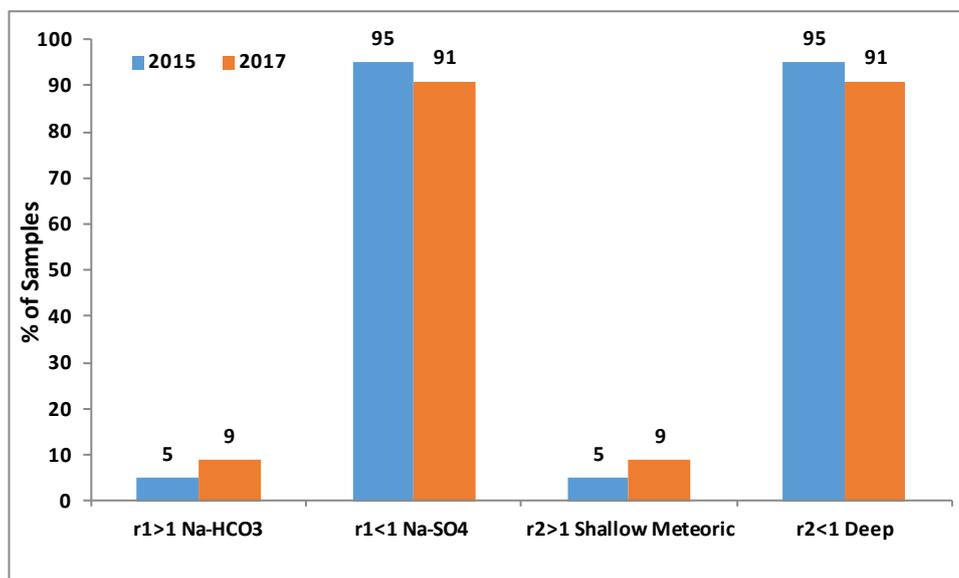


Figure 5.8 b. Percentage of groundwater samples on Soltan classification in the study area

5.6 Hydrogeochemical processes of groundwater

The rock water interaction includes hydrochemical processes such as weathering & dissolution, ion exchange and oxidation-reduction. Hence, it is essential to establish each process in order to determine the major process that controls the concentration of ions within the rock-water interaction. The several graphical diagrams were established to find the processes and the role of the anthropogenic activities functioning in aquifer region. The study area experiences semi-arid climatic conditions wherein evaporation may affect the chemistry of groundwater. If Na/Cl ratio is nearly equal to one, it may be by halite dissolution for sodium. If Na/Cl ratio > 1 then Na gets released due to weathering of silicate reactions (Mayback, 1987). The Na/Cl ratio of the study area ranges from 0.21 to 1.19 during 2015 and 0.12 to 0.55 during 2017. A plot between Na vs Cl was used to understand the role of evaporation processes in the groundwater in the study area. Figure

5.8 for Na vs Cl plot indicates that most groundwater samples in the study area were within the freshwater evaporation line. The plot (Figure 5.9) clearly shows that most of the groundwater samples fall below the freshwater evaporation line, and this clearly indicates that evaporation process is not influencing the chemistry of groundwater.

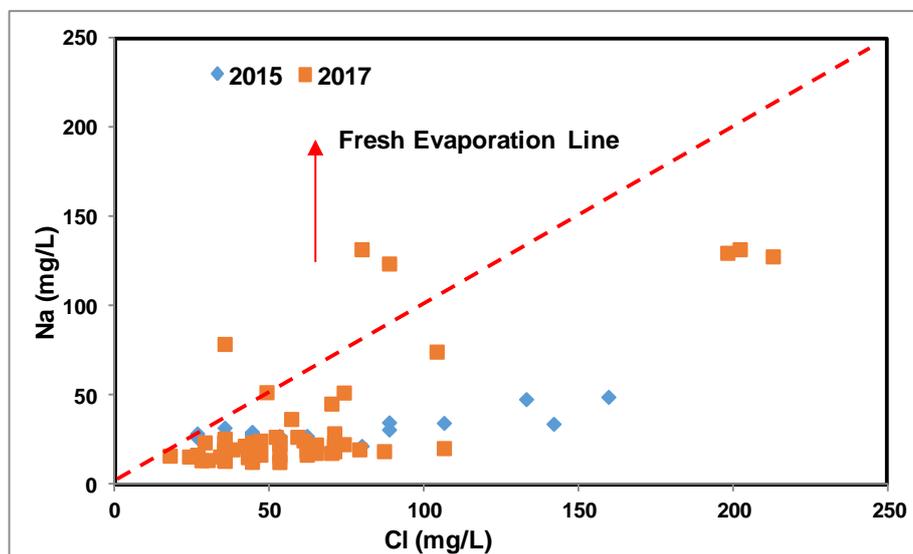
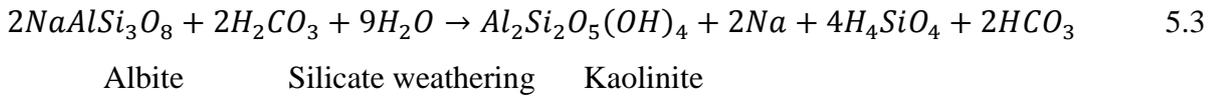


Figure 5.9: Plot of Na vs Cl compared with freshwater evaporation line

In a groundwater system where weathering either carbonate or silicate and dissolution of halite/gypsum and precipitation are the collective mechanism (Elango and Kannan, 2007), graphical representation in form of Na+K vs total cations can be used to understand the influence to the cation concentration to groundwater (Stallard and Edmond, 1983; Elango and Kannan, 2007). The weathering of silicates processes can clearly be represented by the three plots of calcium + magnesium vs bicarbonate, sodium + potassium vs total cations, calcium + magnesium vs total cation and calcium/sodium vs bicarbonate/sodium. The Plot of calcium + magnesium vs bicarbonate is represented in Figure 5.10 and this graph clearly illustrates that most groundwater samples lie above to 1:1 line during 2015 and 2017 with few samples of 2017 lying below 1:1 line. This indicates that the excess of calcium & magnesium over bicarbonate is likely to be released from weathering of carbonate minerals. Similarly, calcium + magnesium vs total cation plot clearly shows that all groundwater sample (Figure 5.10) points fall above the 1:1 line in a linear scattered orientation. The contribution Na+K to the TC is less compared to Ca+Mg as a result of samples which are highly deviated from 1:1 line as indicated on a plot of Na +K vs TC. The Ca/Na is plotted against bicarbonate/sodium in order to understand the role of weathering of silicate and carbonate minerals into groundwater (Figure 5.10). This plot illustrates that basic

mineral sources could be from silicate weathering followed by the dissolution of carbonate minerals. This output of the silicate weathering can be explained by the following reaction;



The pyroxene, amphibole and calcic feldspar which forms the basic composition of the igneous rocks, gets easily weathered. Similar results have been reported by Jacks, 1973; Bartarya, 1993; Rajesh *et al.*, 2012.

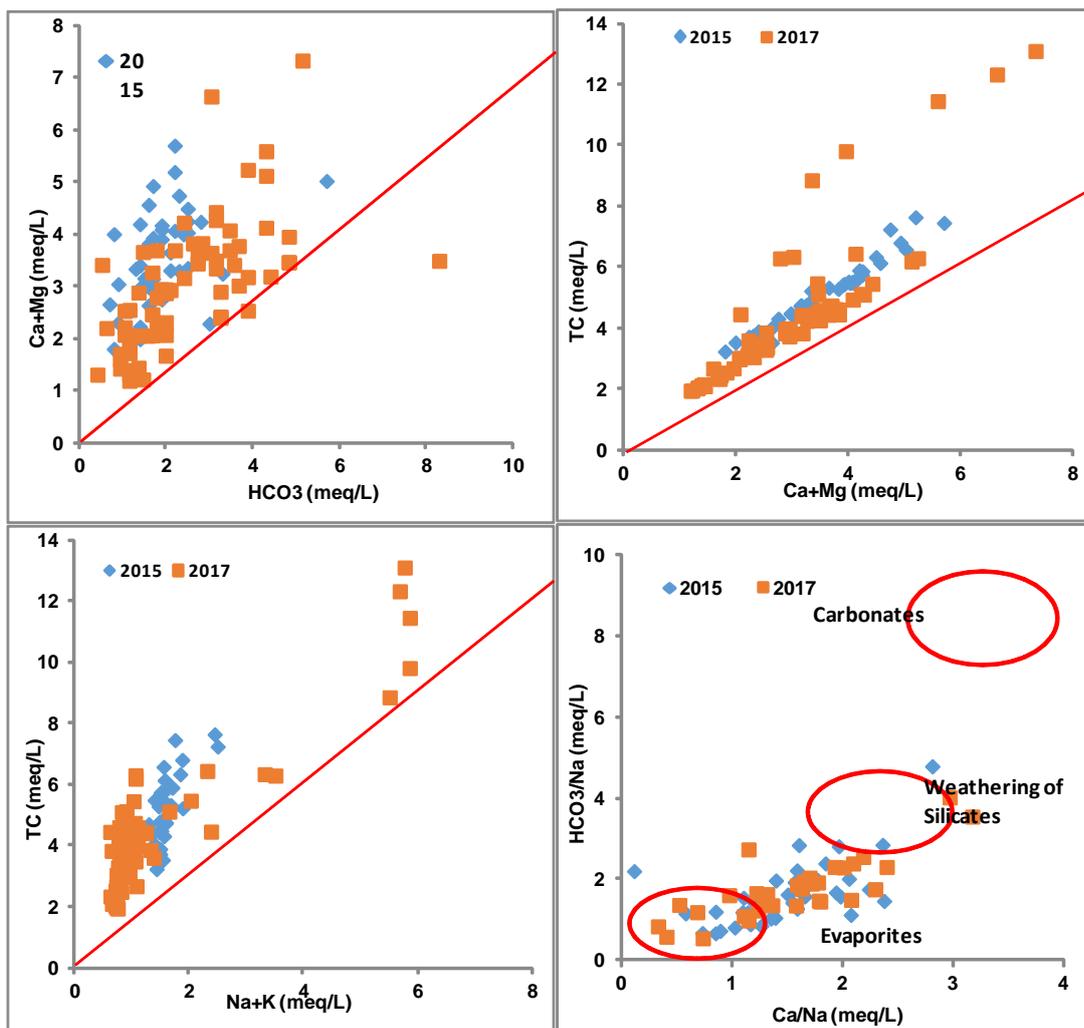


Figure 5.10. Plot of Ca+Mg vs HCO3, Ca+Mg vs TC, Na+K vs TC and Ca/Na vs HCO3/Na explains mineral weathering

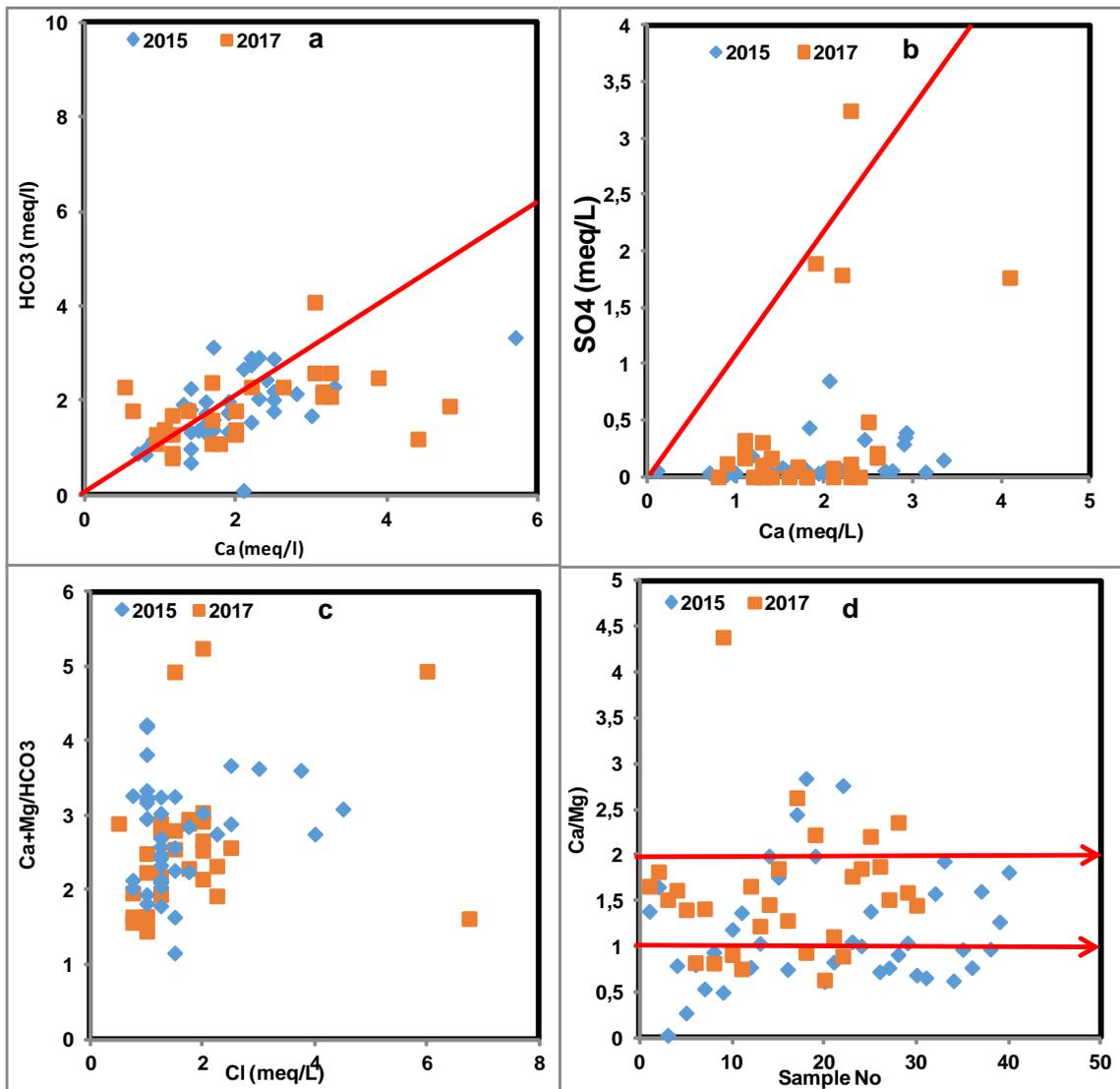
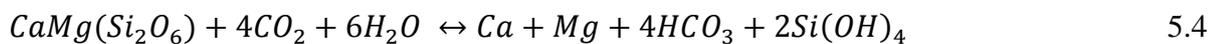


Figure 5.11. Plot of (a) Ca vs HCO₃; (b) Ca vs SO₄; (c) Ca+Mg/HCO₃ vs Cl; (d) Sample location vs Ca/Mg

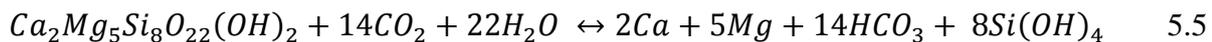
Dissolution of gypsum/anhydrite could be the sources of calcium and sulfate in groundwater. A ratio between $\text{Ca}^{2+}/\text{SO}_4^{2-}$ should be near to the 1:1 line if calcium and sulfate in groundwater is from dissolution of gypsum/anhydrite (Da and Kaur, 2001). The Ca and HCO_3^- in groundwater should be in the ratio of 1:2 if calcite mineral is the source of Ca and HCO_3^- and if the ratio is 1:4 then dolomite weathering should be the source (Subramani *et al.*, 2010). Calcium and magnesium are the main cations with their mean contribution during 2015 of 35 and 34% and during 2017 is 18 and 43% (Figure 5.11) to the total cations of groundwater. HCO_3^- is the most dominant anion compared to other anions while mean contribution of HCO_3^- is 52 and 55% in the year of 2015 and 2017 respectively. Plots between calcium vs bicarbonate (Figure 5.11a) shows that low mineralized waters gets plotted close to the equiline whereas waters with high mineralization gets deviated from the equiline. Calcite dissolution is one of the main processes in the less mineralized

water. Further, calcium vs sulphate (Figure 5.11b) plot shows that all the groundwater points fall below the 1:1 equiline which shows the accumulation of calcium over sulphate. This result shows that dissolution of gypsum is not responsible for the chemistry of the water of the study area. The sources of calcium and magnesium in groundwater can be inferred from the calcium + magnesium/bicarbonate ratio. This ratio clearly shows the reasons for increase in salinity, calcium and magnesium are excess to a solution at a higher rate than bicarbonate. A graphical representation between calcium + magnesium divided by bicarbonate against chloride (Figure 5.11c) clearly shows that this ratio does not change with chloride during 2015 and 2017.

If calcium and magnesium ions in the groundwater are mainly derived from the dissolution of carbonate and the ratio is about 0.5 (Sami, 1992) as the weathering reactions are as follows



Pyroxene



Amphiboles

Figure 11c illustrate that the higher ratio (Ca +Mg/HCO₃) ratio (>1) indicates that calcium + magnesium added to the groundwater due to ion exchange reactions (Rajmohan and Elango, 2004).

The calcium and magnesium molar ratio could be used to verify calcite dissolution and dolomite dissolution in groundwater. If the molar ratio is equal to 1, then this is an indication of dolomite dissolution (Mayo and Loucks, 1995). If the ratio is greater than 1 it signifies dissolution of calcite from rocks. If the calcium/magnesium ratio is greater than 2, this signifies silicate mineral dissolution to the groundwater (Katz *et al.*, 1997). Figure 5.11d clearly shows that most of samples have calcium/magnesium ratio < 2. Sample points that fall between 1 and 2 indicate that calcite dissolution occurs in the study area and only few groundwater sample points the ratio lies above 2 ratio. This clearly shows the effect of silicate minerals (Figure 11d) in the groundwater during the years 2015 and 2017. Jack, 1973; Rajmohan and Elango, 2004; Rajesh *et al.*, 2012; Vetrinmurugan *et al.*, 2013; Varol and Davraz, 2014 noticed similar observations in studies conducted globally.

5.7 Ion exchange Process

Ion exchange process can occur as normal or reverse. Ion exchange is an important hydrogeochemical processes that has main influence on the chemistry of groundwater. A graphical plot of calcium + magnesium vs sulphate + bicarbonate clearly indicates samples plotted close to the 1:1 line (Figure 5.12a). This clearly infers this could be due to the dissolution of dolomite, gypsum and calcite. A plot for calcium + magnesium against sulphate and bicarbonate was used to identify ion exchange process. Further analysis of the plot shows that if the data points fall on the left side it is mainly due to excess sulphate and bicarbonate. If the groundwater sampling points fall in the right side, it is mainly due to the excess calcium and magnesium and it is reverse ion exchange. This can be described using the following equation:



Ca+Mg vs SO₄+HCO₃ plot for year 2015 and 2017 specifies that most samples points fall on the left side of plot due to excess SO₄²⁻+HCO₃⁻ and this shows that the normal ion exchange occurs (Figure 5.12a). About 17.5% and 14% of groundwater samples in 2015 and 2017 shift to the right side due to excess Ca²⁺+Mg²⁺ and this shows that reverse ion exchange process occurs,

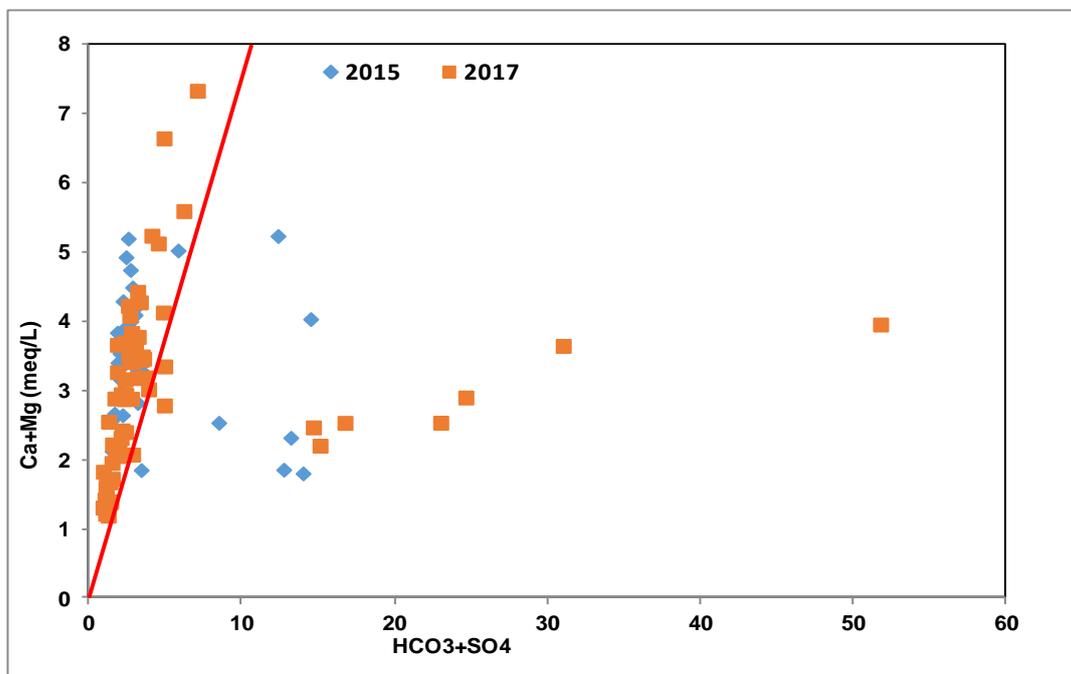


Figure 5.12a. Plot of Ca+Mg vs HCO₃+SO₄

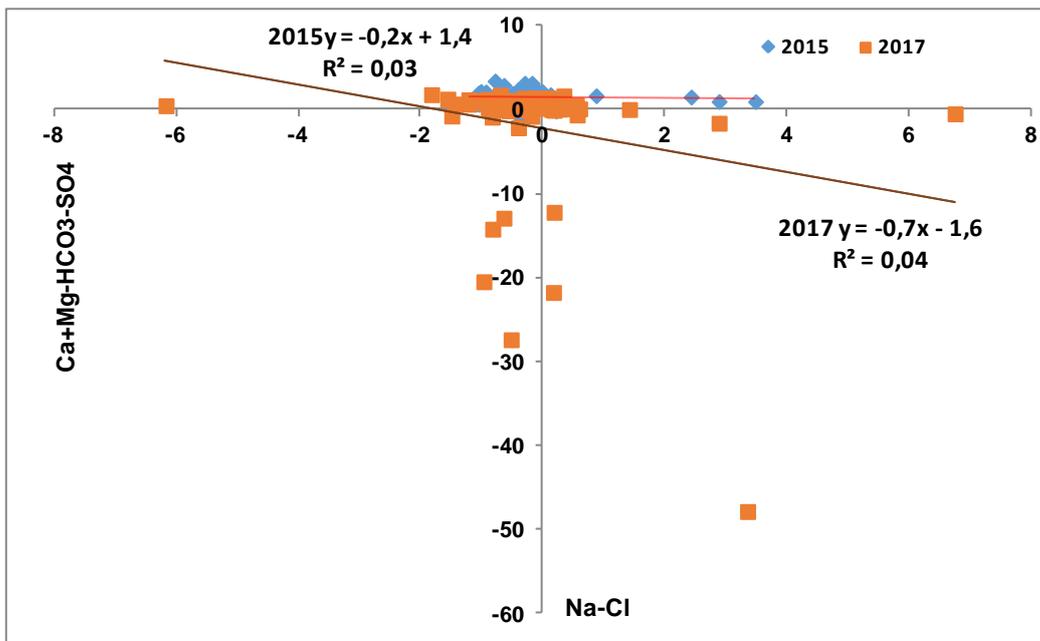


Figure 5.12b, $\text{Ca}+\text{Mg}-\text{HCO}_3-\text{SO}_4$ vs $\text{Na}-\text{Cl}$

A plot between $\text{Na}-\text{Cl}$ vs $\text{Ca}+\text{Mg}-\text{HCO}_3-\text{SO}_4$ was also prepared to establish the ion and reverse ion exchange processes in the study area. In the case of ion exchange was the dominant processes in the study area, data points would have negative trend line with a slope of -1. Groundwater data points during 2015 have a trend line with a slope of 0.2 and during 2017 groundwater samples data points have a trend line with a slope of 0.7 (Figure 5.12b) Fisher and Mulican, 1997; Rajmohan *et al.*, 2017; Li *et al.*, 2016 conducted a study globally and discovered similar results.

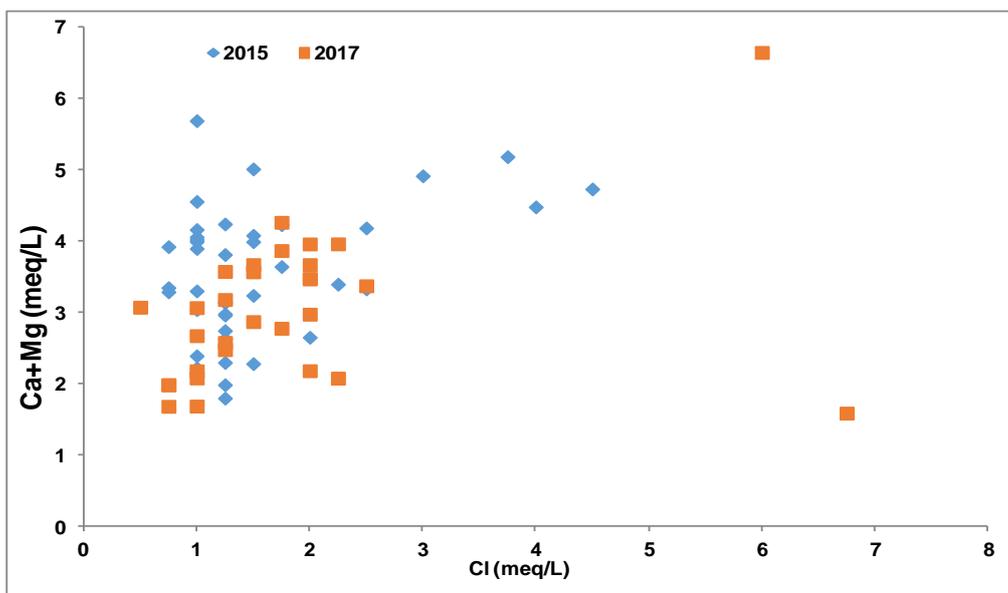


Figure 5.12c, Relation between $\text{Ca}+\text{Mg}$ and Cl

Further to ascertain the ion exchange process a plot between calcium + magnesium against chloride was also used in identify and verify the type of ion exchange occurring in the study area

(Figure 5.12c). In case of calcium & magnesium concentration higher than that chloride it confirms that reverse ion exchange is the dominant process for the ion concentration in an area. In the case of chloride or sodium having high concentration over calcium & magnesium, this infers that normal ion exchange is a dominant process in the area. For the study area $Ca+Mg$ vs Cl plot shows that the calcium & magnesium values tend to increase with increase in chloride (Figure 5.12c). The positive trend between calcium & magnesium against Cl clearly infers that calcium & magnesium is added to the groundwater while increasing salinity is due to the reverse ion exchange process.

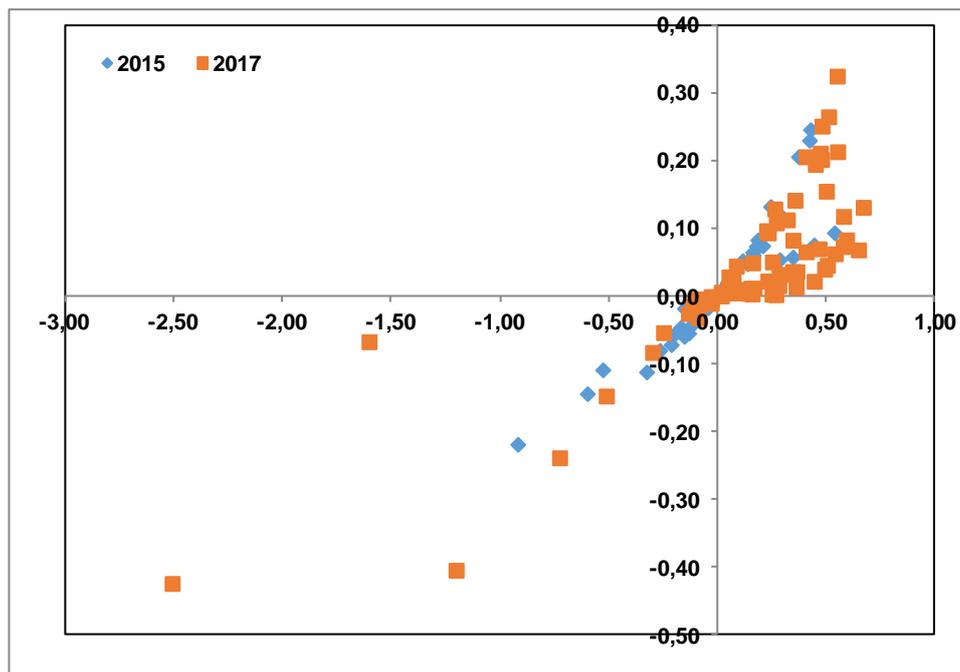


Figure 5.12d, CAI1 vs CAI2

Two chloroalkaline indices (CAI-1 and CAI-2) were used to evidence the occurring of cation exchange in the study area. CAI-1 and CAI-2 represent the relation of $Cl^-(Na^+ + K^+)$ with Cl^- and the total major anions (HCO_3^- , SO_4^{2-} , CO_3^{2-} , and NO_3^-) in groundwater. Ion exchange can also be classified by the chloroalkaline indices of CAI-1 and CAI-2 (Schoellar, 1967). Schoellar indices were estimated using equations 5.7 and 5.8.

$$CAI\ 1 = \frac{Cl - Na + K}{Cl} \quad 5.7$$

$$CAI\ 2 = \frac{Cl - Na + K}{HCO_3 + SO_4 + CO_3 + NO_3} \quad 5.8$$

Schoellar, (1967) defined that the reverse ion exchange is dominant if CAI 1 and 2 have positive values while cation exchange is expressed negative values. Figure 5.11d illustrates that most groundwater samples fall within positive values for both the years, while only few samples have

negative values. Figure 5.11d clearly confirms the reverse ion exchange process on hydrochemistry of the study area.

5.8 Evaporation

Evaporation is another vital process that impacts the hydrochemistry of groundwater. Gibb's plot (Figure 5.13) was used to establish the process. It is observed that there are some data points which fall in the evaporation zone. Subramani *et al.* (2010) suggested that Na⁺/Cl⁻ ratio can also be used to identify the evaporation process in groundwater. Jankowski and Acworth (1997) inferred that if evaporation is the dominant process controlling ionic composition of groundwater in an area, then sodium by chloride ratio should be constantly increases with EC. Figure 5.13 shows that Na⁺/Cl⁻ ratio does not increase with increase in EC. This clearly indicates that evaporation is not a dominant process in the study area.

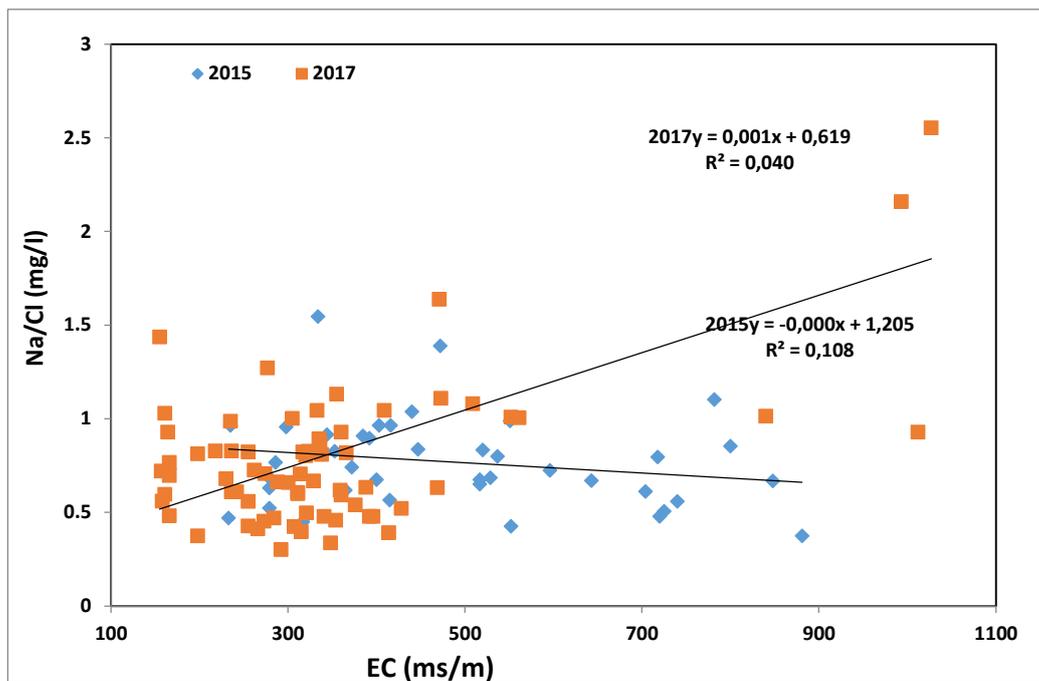


Figure 5.13, Evaporation process-relation between Na⁺/Cl⁻ and EC

5.9 Anthropogenic Activities

Groundwater quality varies due to manmade activities. Involvement of too many factors and uncertainties makes a complex process that is problematic to infer. As nitrate is widely accepted as a contaminant from manmade activities and from fertilizer usage, its relations with physio-chemical index were identified to infer the effects on human activities on groundwater quality (Marghade *et al.*, 2012; Li *et al.*, 2016).

The area of study is an agricultural region and the major ion concentration in groundwater can be altered by agricultural practices such as application of fertilizer. According to field study, wheat and maize are main types of crops practiced; the use of fertilizer and increase in the resistance of crops is a known exercise, and this cause to enrich the concentrations of K^+ , Cl^- , and NO_3^- in groundwater. In order to understand the effect of manmade activities on groundwater, nitrate was plotted against chloride (Figure 5.14). Figure 5.14 clearly shows strong correlation and verifies the role of manmade activities (Li *et al.*, 2016).

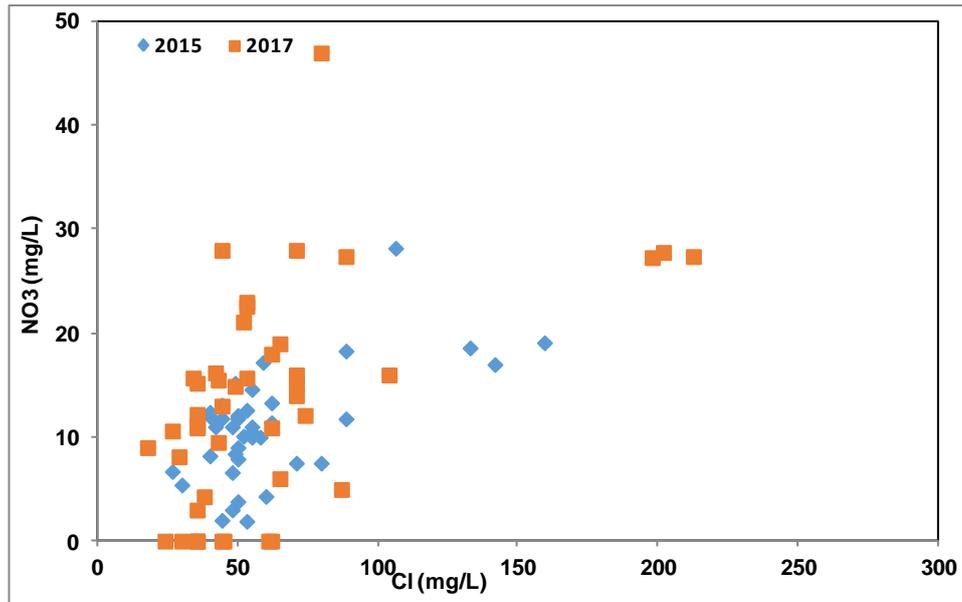


Figure 5.16a. NO3 vs Cl

Nitrate, chloride and sulphate are mainly derived from manmade activities. A plot between sulphate against chloride (Figure 5.14b) clearly shows strong correlation during the years 2015 and 2017. The study area is an intensively irrigated area and application of fertilizers and manures which in return infiltrates due to irrigation return flow impacts the groundwater quality in the study area.

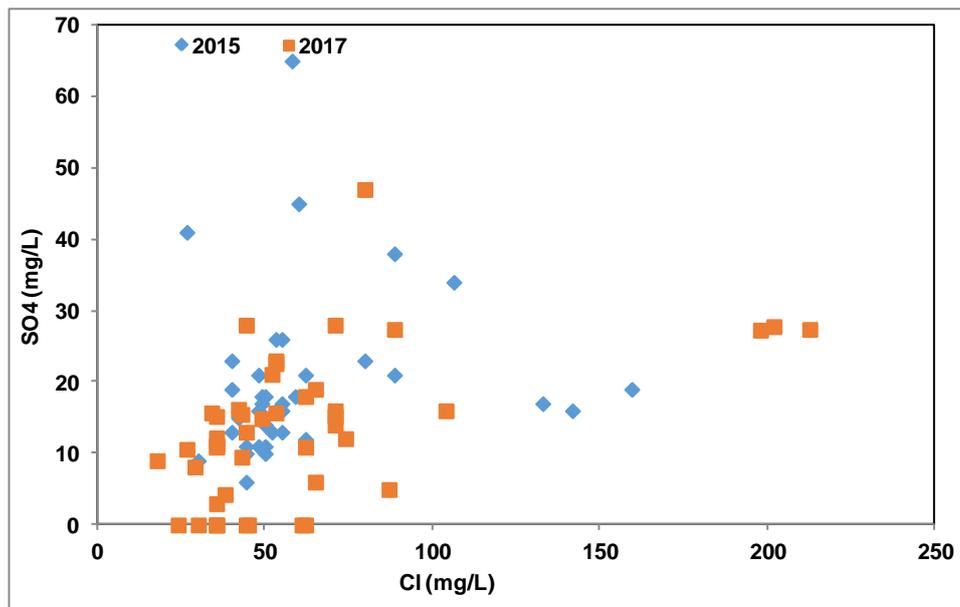


Figure 7.14b. Cl vs SO4

5.10 Relation between temporal groundwater level fluctuations and groundwater quality

Groundwater level fluctuation, effects on soil pore water pressure, alteration in the groundwater flow regimes and changes in the volume as well as the quality of groundwater resources is a result of climate change. Groundwater levels in aquifers is an end product of hydrodynamic balance between inflow i.e., recharge, storage, and outflow i.e., discharge. In the regions where recharge is more than discharge, the volume of water stored will increase drastically and water levels will rise. In the regions where discharge is more than recharge, the volume of water in storage will decrease and groundwater levels will decline. Because recharge and discharge are not spread homogeneously in space and time, that is why ground-water levels are continuously rising or falling to adjust to the hydrodynamic balance (Chen *et al.*, 2004; Brouyère *et al.*, 2004; Bloomfield *et al.*, 2006; Ranjan *et al.*, 2006).

In this study, groundwater dilution occurs through recharge of rainfall. The concentration of ions gets reduced due to the mixing of infiltrating freshwater with groundwater which takes place through the recharge processes. The major ion concentration in the groundwater of the study area changes with respect to the seasonal groundwater level fluctuation (Figure 5.15) during 2015 and 2017. When the groundwater levels decrease, this also increases the concentration of ions due to evaporation during both the years of 2015 and 2017. The increase in groundwater level decreases ion concentrations in groundwater in the study area. Hence it is clear that the recharge processes influence the temporal changes in the groundwater quality of the study area.

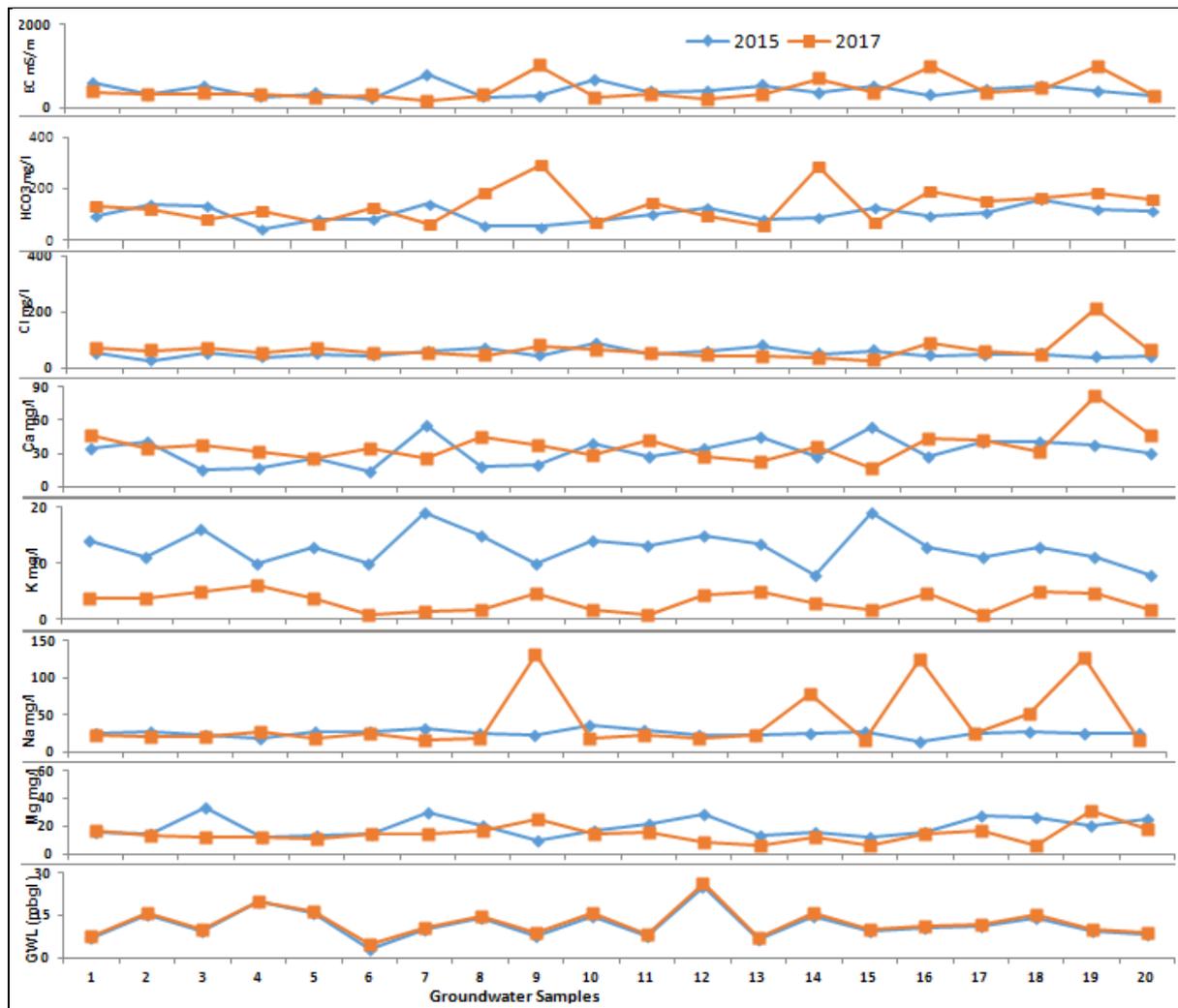


Figure 5.15. Temporal variations in groundwater level and major ions in the study area

5.11. Multivariate Statistics

Correlation analysis between groundwater chemical constituents is a useful tool in the interpretation of hydrogeochemical studies. The correlation matrix can clearly infer the relationship between individual constituents. The correlation analysis clearly establishes the link between individual constituents and various factors that control the ion concentration and also demonstrates the complete unity of the data sets (Li *et al.* 2011 & 2012). In this present study correlation analysis was carried out using the XLSTAT 2017 and the Pearson correlation matrix was calculated (Table 5.2).

The correlations between groundwater chemical constituents provide an insight of the important hydrogeochemical process which controls the hydrochemical constituents of groundwater. The r^2 values greater than 0.7 infers strong correlation, while value of r^2 between 0.5 to 0.7 infers moderate correlation between ions. The correlation of EC and TDS with Ca concentrations is high

during 2015 while during 2017 the correlation between Na, Cl, HCO₃ and SO₄ concentrations is high (Table 5.2).

Table 5.2. Pearson correlation matrix of groundwater in 2015 and 2017

2015	pH	EC	TDS	Na	K	Ca	Mg	Cl	HCO ₃	SO ₄	NO ₃
pH	1	-0,2	-0,2	-0,3	-0,1	0,0	0,0	-0,3	0,0	0,2	0,0
EC	-0,2	1	1,0	0,6	0,6	0,7	0,2	0,6	0,4	0,3	0,3
TDS	-0,2	1,0	1	0,6	0,6	0,8	0,2	0,5	0,5	0,4	0,3
Na	-0,3	0,6	0,6	1	0,3	0,7	0,1	0,7	0,4	0,2	0,3
K	-0,1	0,6	0,6	0,3	1	0,5	0,1	0,2	0,5	0,4	0,0
Ca	0,0	0,7	0,8	0,7	0,5	1	0,2	0,5	0,6	0,4	0,2
Mg	0,0	0,2	0,2	0,1	0,1	0,2	1	0,2	0,2	0,3	0,1
Cl	-0,3	0,6	0,5	0,7	0,2	0,5	0,2	1	0,0	0,1	0,6
HCO ₃	0,0	0,4	0,5	0,4	0,5	0,6	0,2	0,0	1	0,1	-0,4
SO ₄	0,2	0,3	0,4	0,2	0,4	0,4	0,3	0,1	0,1	1	0,0
NO ₃	0,0	0,3	0,3	0,3	0,0	0,2	0,1	0,6	-0,4	0,0	1
2017	pH	EC	TDS	Na	K	Ca	Mg	Cl	HCO ₃	SO ₄	NO ₃
pH	1	-0,2	-0,2	-0,2	0,0	-0,2	-0,2	-0,1	-0,3	-0,1	-0,1
EC	-0,2	1	1,0	0,9	0,3	0,7	0,6	0,7	0,7	0,8	0,7
TDS	-0,2	1,0	1	0,9	0,3	0,7	0,6	0,7	0,7	0,8	0,7
Na	-0,2	0,9	0,9	1	0,4	0,6	0,5	0,7	0,6	0,9	0,7
K	0,0	0,3	0,3	0,4	1	0,0	-0,2	0,3	-0,1	0,5	0,2
Ca	-0,2	0,7	0,7	0,6	0,0	1	0,7	0,7	0,7	0,5	0,5
Mg	-0,2	0,6	0,6	0,5	-0,2	0,7	1	0,6	0,7	0,5	0,4
Cl	-0,1	0,7	0,7	0,7	0,3	0,7	0,6	1	0,4	0,7	0,5
HCO ₃	-0,3	0,7	0,7	0,6	-0,1	0,7	0,7	0,4	1	0,5	0,5
SO ₄	-0,1	0,8	0,8	0,9	0,5	0,5	0,5	0,7	0,5	1	0,7
NO ₃	-0,1	0,7	0,7	0,7	0,2	0,5	0,4	0,5	0,5	0,7	1

This correlation matrix clearly shows the relation between EC and TDS. In the study area, shallow wells show more strong correlation due to the recharge process and irrigation flow when related to deep wells. Chloride concentration is strongly correlated with Na and similar nitrate with sulphate and nitrate with potassium. The Ca ion is highly correlated with EC, TDS and Na in 2015. In the year 2017, EC and TDS are strongly correlated with Na, Ca, Cl, HCO₃, SO₄ and NO₃. The sources of chloride, nitrate and sulphate are derived from agricultural activities.

The main principle of factor analysis (FA) is to decrease the influence of these important variables and to simplify the data structure. The objective of the PCA can be obtained by rotating the axis defined by principle component analysis, according to clear demarcated aims and the contributing new variables, also called varifactors (VF). In this study, the scree plot was used to categorize the number of factors measured to establish the configuration of basic data (Liu *et al*, 2003). Procedure was used to identify the variation point on the curve. Scree plot (Figure 5.16), clearly

shows a dip in the slope when two eigenvalue state their dominance of two factors in the groundwater chemistry.

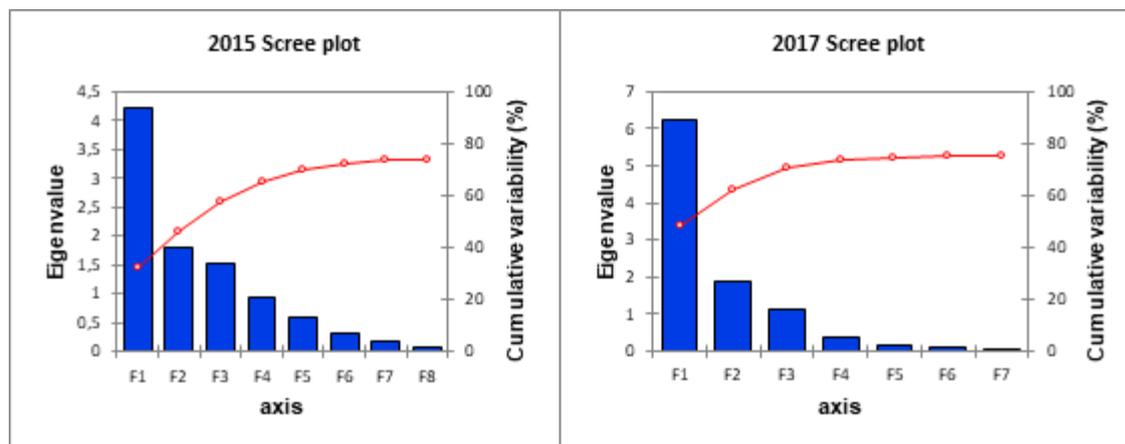


Figure 5.18. Groundwater Scree Plot of 2015 and 2017

Two factors showing the variance of the data as a result of Eigenvalues being ≥ 1 were considered in year 2015 and 2017 with approximately 51.9% and 68.1% of total variance for both years. The results of the factor analysis are tabulated in Table 5.3.

Table 5.3. Varimax rotation factor loadings

Variables	2015		2017	
	F1	F2	F1	F2
pH	-0,2	-0,2	-0,2	0,1
EC	0,9	0,1	1,0	0,1
TDS	0,9	0,0	0,9	0,1
Na	0,8	0,1	0,9	0,3
K	0,6	-0,2	0,2	0,6
Ca	0,9	-0,1	0,8	-0,4
Mg	0,2	-0,1	0,7	-0,5
Cl	0,7	0,6	0,8	0,0
HCO ₃	0,6	-0,6	0,7	-0,4
SO ₄	0,4	-0,1	0,9	0,4
NO ₃	0,3	0,8	0,7	0,1
Eigenvalue	4,6	1,6	6,3	1,2
Variability (%)	38,2	13,7	57,3	10,9
Cumulative %	38,2	51,9	57,3	68,1

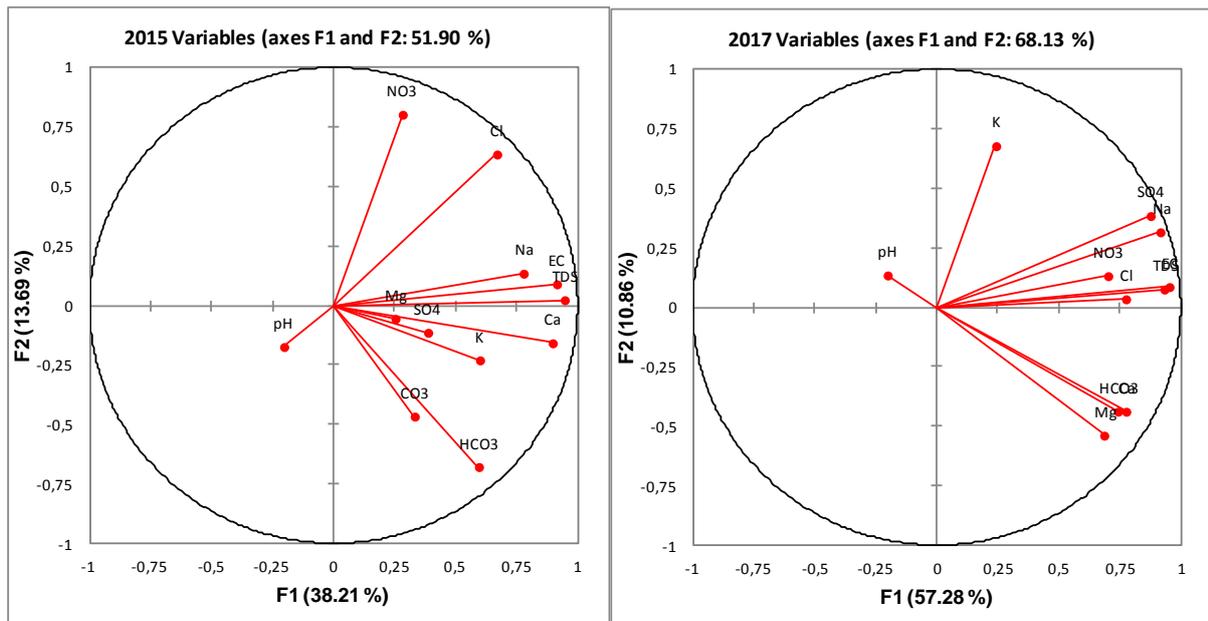


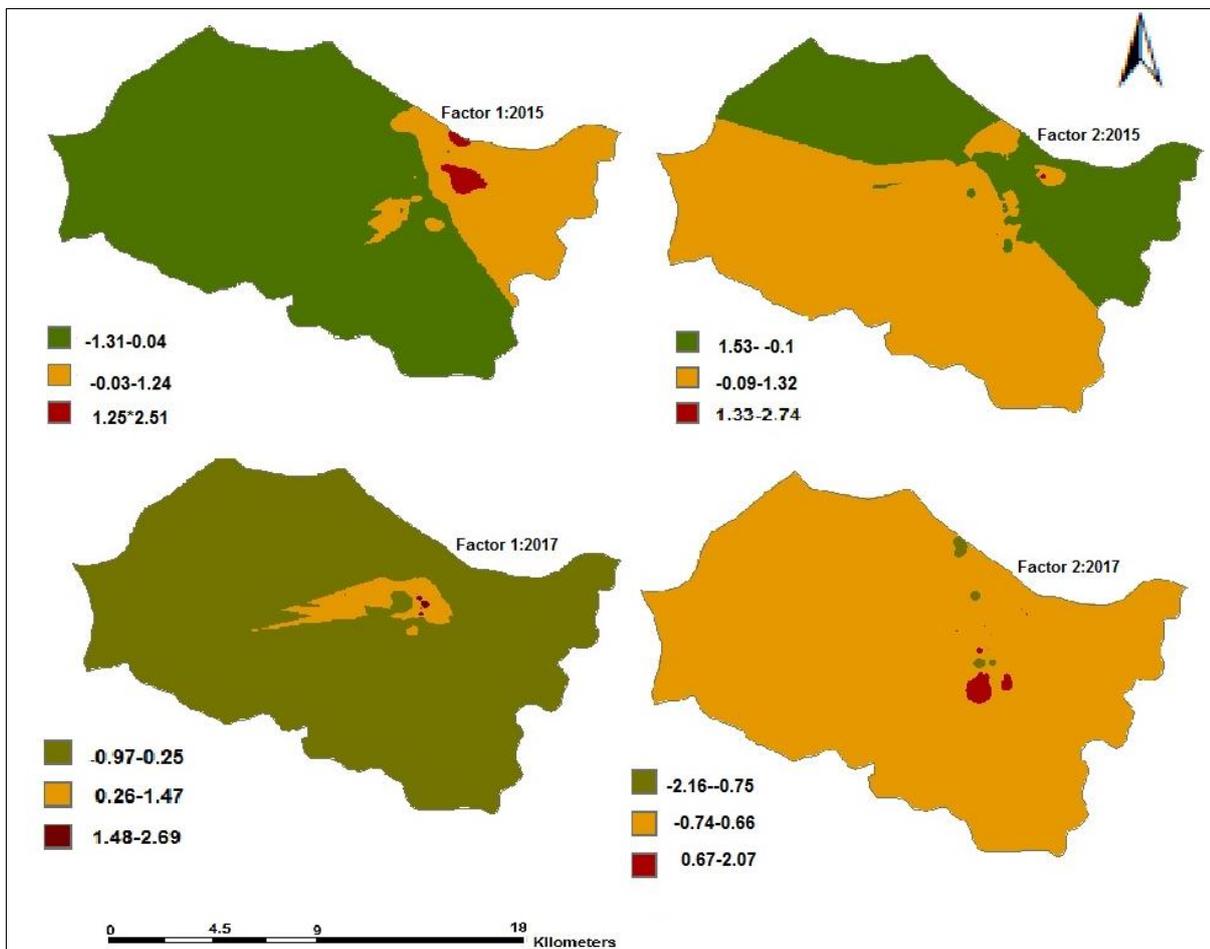
Figure 5.17. Factor Score for 2015 and 2017

The first factors (F1) have highest eigenvalues of 4.6 and 6.3 in 2015 and 2017 respectively. These factors consequently represent the main processes controlling groundwater composition in the study area. Factors clearly illustrate high to moderate loadings with all the parameters. Mineral weathering and ion exchange process caused high loading of sodium and potassium in groundwater in the study area. Carbonate dissolution and reverse ion exchange process has resulted in loading of calcium, magnesium, total dissolved solids and EC and while the sources of chloride and sulphate may be from irrigation return flow (Drever, 1997). The variance contribution rate of factor 1 (Figure.5.17) is mainly composed of electrical conductivity, total dissolved solids, sodium, calcium, chloride and nitrate during 2015 and during 2017. The highest contributor in factor one is TDS, EC and Ca in 2015; and EC and TDS in 2017 which indicate carbonate dissolution and reverse ion exchange processes in the study area.

In the study area, the second factors (F2) (Figure 5.17) accounted for 13.7% and 10.9% of the total variance with the eigenvalues of 1.6 and 1.2 in 2015 and 2017. The variance contribution rate of factor 2 is NO3 and Cl in 2015 which indicates the intense agricultural activities. In 2017, variance contribution rate of factor 2 is Na, K and SO4 which is attributed to carbonate weathering. The impact of this can be defined by the effect of potassium nitrate and potassium fertilizers, which are easily soluble and easily leach into the groundwater (Singh *et al.*, 2017).

Using the regression techniques, the factor score was calculated for the study area (Dalton and Upchurch 1978). The factor scores of each groundwater sample can be related to strength of the processes described in the factors. Where the factor scores indicated negative scores (≤ -1), this show that these are the regions which are not influenced by the process. Regions where the factors indicated positive scores (≥ 1) those areas are most impacted, while regions with near to zero scores are influenced by the medium strength of the processes.

The F1 scores (Figure 5.17) signifies that the high factor scores (≥ 1) occur in the NNE-NE part of the study area during 2015. During the year 2017 (Figure 5.17), F1 scores occur in the NE-E part of the study area, this clearly shows the effect of natural geogenic processes. Factor 1 scores which signify (≤ 1) occur in the ESE-SE and SW part of the study area in 2015 while factor 1 scores of 2017 occur in SE-ESE-SWS part of the study area. F2 scores indicate that high factor scores present in the NW and SE part of the study area during 2015 and occupies major part of the study area during 2017 (Figure 5.18) which signifies that the area is highly affected by manmade processes such as strong agricultural activities and extensive application of fertilizers and pesticides.



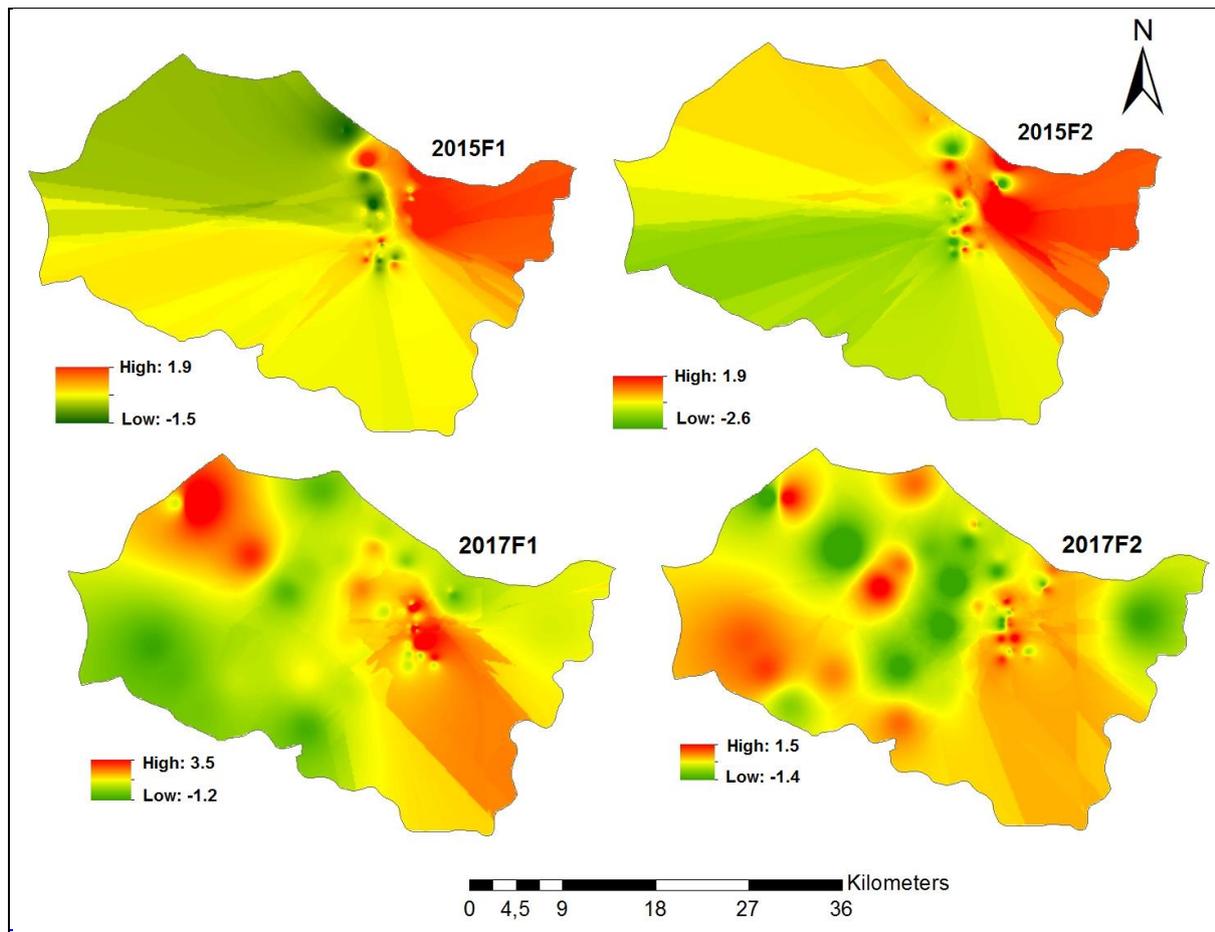


Figure 5.18. Spatial variation of factor scores for 2015 and 2017

Figure 5.18 outlines the spatial variation of factor 1 and 2 for both the years 2015 and 2017. Factor 1 2015 and Factor 2 show higher scores in the Northeastern part and low score is the most dominant centered in the North, East, West and central part of the study area. In the year 2017, Factor 1 and Factor 2 show higher scores at the central part of the study area. Factor 1 2015 shows low score to be dominant covering the full scale of the study area while Factor 2 has moderate scores as the most dominant factor covering almost full scale of the study area. This confirms that Factor 1 and Factor 2 of 2017 are affected by fertilizers and pesticides.

6. Conclusion

- In order to evaluate and categorize the main factors impacting groundwater quality in Schoonspruit Catchment, several relationship diagrams were established since groundwater is the only reliable water source for drinking, industrial and agriculture uses in Ventersdorp.
- Further to achieve the objective, physicochemical properties of groundwater, particularly TDS and major ions concentrations were assessed.

- Hydrogeochemical analysis and multivariate statistical method have been used to categorize and distinguish the quality of groundwater.
- The groundwater samples were collected from forty boreholes in 2015 as well as seventy boreholes in 2017 and was analysed for major ions and nitrate.
- The overall pH values for both sample period represent slightly acidic to alkaline in the study area. Based on DWAF (1996) approved limit of drinking (EC <450), 45% of groundwater samples in 2015 and 13% samples in 2017 exceeded the limit in the study area.
- The classification of groundwater based on total hardness (TH) in the study area shows that majority of groundwater samples fall within the hard water category. Major groundwater types were Ca-HCO₃ and Ca-SO₄ in 2015 and 2017.
- Dissolution of soluble rocks is always under dynamic balance with groundwater flow and precipitation, and if the groundwater recharge decreases there is substantial reduction in the flow of fresh water, this may cause enrichment of groundwater components.
- Gibbs plots have revealed that groundwater in the study area for both year 2015 and 2017 is of rock water interaction dominance. Further, the study also revealed that, groundwater dilution lowers the concentration of ions in groundwater due to mixing of infiltrating freshwater during the recharge processes.
- The temporal groundwater level fluctuation causes changes major ion concentration. In the study area, shallow wells are most affected by the return flow from irrigation compared to that of the deep wells. This is established by the high correlation between calcium and bicarbonate, chloride with sodium, nitrate and sulphate and nitrate and potassium.
- Variables correlating with chloride, sulphate and nitrate may be mainly derived from agricultural activities. The demand for groundwater resource has amplified and immense extraction of groundwater modifies the natural groundwater flow directions and lead to groundwater despair growth in Ventersdorp. The quality in the study area can be attributed to many origins such as dissolution of secondary minerals within the sedimentary formations, anthropogenic contamination, return flow from irrigation water or a combination of some of these processes.

CHAPTER 6

ASSESSMENT OF GROUNDWATER QUALITY AND ITS SUITABILITY FOR DRINKING AND AGRICULTURAL NEEDS

6.1 Introduction

South Africa is the semi-arid country which receives average rainfall of about 495 mm/year (World Bank, 2014). South Africa's rainfall is lower than the world's average rainfall of 1130 mm/year (Barry and Chorley 2010). With a population of 55 million in 2015 (World Bank 2016), South Africa is one among the water scarce country in the world. The country's economy is compelled by mining, agriculture and manufacturing sectors. DWA, (2004) grouped the country's water needs into main sectors like agriculture, mining, power generation, industrial, afforestation, urban and rural uses which are met from surface and groundwater resources. Of the total water requirements, 60% is consumed by agriculture, 23% for urban use and the other four sectors share the remaining 15% (DWA 2004). With surface water reaching the level of non-availability, groundwater is increasingly exploited (DWA 2010). Groundwater plays a crucial role to provide the water demand for industries and domestic use, especially to meet the insufficient supply from surface water resources. Groundwater availability across the country differs due to uneven distribution of rainfall. Not just that, limitation to groundwater availability arises mainly due to the hard rock geology in South Africa (DWA, 2004). Pietersen et al. (2011) reported that, water demand of more than 80% of rural population in KwaZulu Natal and Northwest Provinces and more than 50% of rural communities in Eastern Cape rely on groundwater resources. Apart from groundwater, springs also meet the water requirements to some extent (Pietersen et al. 2011). Since groundwater plays a major role in catering the needs of the country, a complete qualitative study is very much necessary to ascertain its suitability for drinking and agricultural needs. This chapter brings out the various methods for checking the groundwater suitability for drinking and agricultural requirements.

6.2 Suitability for Drinking Purposes

The groundwater quality for drinking uses is primary concern for consumers. The studies have been carried out to assess and classify the groundwater suitability for drinking uses in the study area. The chemical constituents in the water decide the suitability of groundwater for drinking

purposes. According to DWAF (1996), groundwater becomes permissible for drinking purposes when EC and TDS of the groundwater have the mean values of less than 450 mg/L (Table 6.1). The quality of water in the study region has been assessed and classified using major cations and anions and the results were compared with the DWAF (1996) standard guideline. This was done in order to evaluate the suitability of groundwater in the area for human consumption (Figure 6.1).

pH

The pH of groundwater is a degree of the acid base equilibrium. In natural waters pH is inhibited by the carbonate equilibrium system bicarbonate and carbon dioxide. It further presents fundamental information in numerous classes of solubility calculations or geochemical equilibrium. The acceptable range of pH value in drinking water is approved to from a range of 6.5 to 8.5 with the ideal pH value of 7 approved for human health (SANS, 2015; WHO, 2011). The groundwater quality samples collected in 2015 have the pH value varying between 6.6 to 8.4 with a mean value of 7.4 and 5.9 to 7.9 with a mean value of 6.5 in 2017. These results clearly show that the pH value of groundwater in the area study is of normal range in nature and it does not pose any threat to drinking purpose.

Electrical conductivity and TDS

The EC of water is described as degree of dissolved material in water solution and its aptitude to transmit an electric current. The EC is directly proportional to the concentration of dissolved salts in aqueous solution as well as the TDS. The presence of aluminum cations, inorganic dissolved solids as well as the temperature of the area affects the conductivity in water. The suitable limit of the EC of groundwater for drinking water is 450 mS/m (WHO, 2011). The EC rate of groundwater in the area of study shows that 55% is permissible and 45% is not permissible for drinking purposes in 2015 while 87% samples is permissible and 13% samples not permissible for drinking purposes in 2017. WHO (2011) approved the desirable TDS range of <500 mg/L for drinking water and the range of 500-1000 mg/L being permissible for drinking purposes. The approved acceptable range of TDS for irrigation is <3000 mg/L. The range which is >3000 is not suitable for irrigation uses. Table 6.1 shows that 77% of groundwater sample in 2015 are desirable for drinking purposes with 23% being permissible for drinking. The 2017 results show that 94% of samples is desirable for drinking uses with 6% being permissible for drinking uses (Table 6.1).

The quality of groundwater in the study area and its fitness for irrigation and drinking uses was mapped using IDW interpolation method. DWAF 1996 recommended the standards for groundwater suitability for the following parameters, EC (450 $\mu\text{S}/\text{cm}$), pH (6.5 to 7.5), K (50 mg/L), Na (100 mg/L), Ca (32 mg/L), Mg (30 mg/L), Cl (100 mg/L) and SO_4 (200 mg/L). Groundwater suitability maps employed on this study show safe and unsafe zone of groundwater as indicated on Figure 6.1.

The EC of groundwater in 2015 shows the unsafe zone in NW part and the remaining area being safe. In 2017 EC of groundwater shows safe zone with few samples showing unsafe at NE part of the study area. This is influenced by dissolution and weathering of rocks as well as the anthropogenic activities. The pH values of groundwater show unsafe zone at the SW-SE-E part as results the occurrence of HCO_3 ions and the rest of study area being safe zone in 2015. During 2017, the whole study area shows safe zone with few samples of about 2% being unsafe at the central part of the study area (Figure 6.1). Water with low pH value tends to cause increase in the content of heavy metal in water and corrosion of the water supply systems and pipelines.

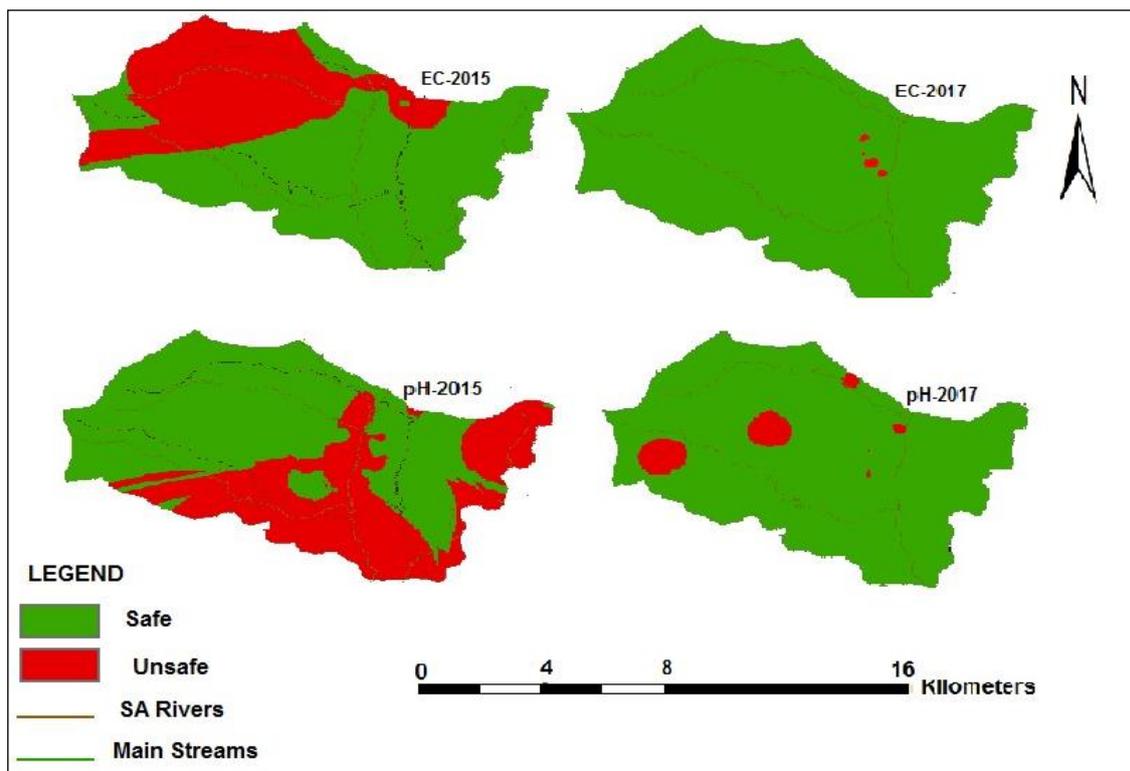


Figure 6.1. Spatial distribution of groundwater quality, pH and EC

Table 6.1. Classification of groundwater based on EC, TDS and TH

EC $\mu\text{S}/\text{cm}$	Range	Classification	% of Samples		Reference
			2015	2017	
	<450	Permissible	55	87	South African National Standards

	>450	Not permissible	45	13	(2006)
TDS mg/L	<500	Desirable for drinking	77	94	Davis and DeWiest (1966)
	500-1000	Permissible for drinking	23	6	
	1000-3000	Useful for irrigation			
	>3000	Unsuitable			
TH mg/L	<75	Soft	-	33	Sawyer and McCarthy, 1987
	75-150	Moderately hard	68	46	
	150-300	Hard	32	20	
	>300	Very hard	-	1	

Total hardness

The categorization of groundwater depending on the total hardness (TH) of water indicates that most of sampling location in the area of study is within the moderately hard water category. Sawyer and McCarthy, (1987) approved limits (Table 6.1) indicate that 33% of samples in 2017 fall within the soft category. About 68 and 46% of groundwater samples in the study region fall within moderately hard category in 2015 and 2017 respectively. The groundwater samples which fall within the hard water category were 32% in 2015 and 20% in 2017 with 1% of sample in 2017 being very hard. This was a result of high concentration of EC in the water sample. The most desirable range of TH in water is 100 mg/L with the maximum acceptable limit of 500 mg/L for purpose of drinking (WHO 2001). The groundwater sample that is greater than the range of 300 mg/L as per Sawyer and McCarthy (1987) is considered to be very hard. The occurrence of alkaline earths like magnesium and calcium influences the hardness of water.

Cations

The most copious constituents in ground and surface water are magnesium and calcium ions which are directly proportional to hardness of water. They mainly exist as bicarbonates and to a less significant degree in the form of sulphates and chlorides. The abdominal ailments in human health are likely to be caused by high concentration of calcium ions, therefore this is not desirable for domestic purposes since it causes scaling and encrustation. The calcium concentration in the study area varies between 2.2 and 67 mg/L with a mean value of 36.3 mg/L in 2015. In 2017, the concentration of calcium ranges between 16 to 82 mg/L with a mean value of 35.8 mg/L. The concentration of magnesium is varied from 7.2 to 38.9 mg/L. The Sodium ion is normally found with a lower concentration than calcium and magnesium in freshwater. In the study area, the

concentration of sodium was found to be varying between 12.9 to 49.4 mg/L with a mean value of 28.2 mg/L in 2015. In 2017, the sodium concentration varied from 4.3 to 178.5 mg/L with a mean value of 34.4 mg/L. The water with the high level of sodium tends to cause arteriosclerosis, increased blood pressure and oedema if consumed. Potassium is a naturally occurring element with its concentration in the study area remaining lower when compared to other cations. The results of the study show that the concentration of potassium varies between 12.6 to 18.9 mg/L with a mean value of 13.4 mg/L in 2015, and in 2017. The concentration of potassium varied from 1.3 to 4.4 mg/L with a mean value of 2.4 mg/L.

Anions

The sulphate ion is among the major dissolved and occurring mechanism of water. The high intake of sulphate concentrations in drinking water might have a laxative effect when combined with magnesium and calcium (Delisle & Schmidt, 1977). The maximum allowable range of sulphate concentration in water is 400 mg/L. The results of the study display the content of sulphate in the study area is ranging between 0.9 to 41 mg/L with a mean value of 5.8 mg/L in 2015 and from a range of 3.7 to 156 mg/L with a mean value of 25.6 mg/L in 2017. The main source of chloride in groundwater could be from various sources including intrusion of saltwater, leaching of sedimentary rocks and soils, industrial waste discharges, weathering, domestic and municipal effluents, and windblown salt in precipitation (Karanth 1987). Prasanth *et al.* (2012) indicated that chloride is very stable in water and is mainly predominant natural form of chlorine element. The range of chloride concentration in groundwater samples is ranging between 26.6 and 159.5 mg/L with a mean value of 55.4 mg/L during 2015, and a concentration of 17.7 to 239.3 mg/L with a mean value of 61.2 mg/L in 2017. The elements like cations, pH, temperature, soluble carbon dioxide, and other dissolved salts influence the concentration of carbonates in natural waters. The concentration of bicarbonate in waters is normally rated as a moderate range by the effects of carbonate equilibrium. The most acceptable limit of carbonate and bicarbonate concentration in groundwater is 500 mg/L. The results show that the concentration of bicarbonate in the area of study is ranged between 42.7 to 347.7 mg/L with a mean value of 117.9 mg/L in 2015, and from a concentration of 25 to 506 mg/L with a mean value of 150.9 mg/L in 2017. The carbonates were absent in the study area. The Bicarbonate ions in the area of study were within the desirable limits for drinking with 1% of sample being not permissible for drinking purposes. The anions were also within the desirable limits for drinking. Nitrates are essential macronutrient in aquatic environments and are the measure of the oxidized form of nitrogen. Pawar, (1995) described the nitrogen compounds as the most extensive pollutants in the environments

developing from non-point agricultural sources. The nitrate nitrogen exposure is associated with diseases like gastric thyroid disease, cancer and diabetes as per the epidemiological evidence by Kumar *et al.* (2011). The increase in nitrogen pollutants threatens the human health and drinking water supply. The concentration of nitrate in the area of study was ranging between 0.9 and 28.2 mg/L with a mean value of 10.1 mg/L in 2015. In 2017, the concentration of nitrate was ranging between 3 to 27.8 mg/L with a mean value of 15.2 mg/L. The groundwater samples in the area of study were not exceeding the acceptable limit of 45 mg/L of WHO (2011) standards.

The concentration of K displays 1% of unsafe zone in Eastern part and the whole area is under safe zone in the year of 2015. In 2017, the concentration of K shows 10% unsafe zone in S-N- SE part and the remaining area being safe zone (Figure 6.1). The source of K in the unsafe part of the study area is as results of weathering of clay minerals and potash feldspar from aquifer system. During the year 2015, the concentration of Na shows 25% unsafe zone in the NW and W part of the area and the remaining area being safe zone; in 2017 the concentration of Na shows 97% of safe zone with 2% and 1% unsafe zone in NW and SE part of the study area respectively. Davis and DeWiest (1996) indicated that Na with high concentrations signify the over exploitation of groundwater and weathering of Na rich plagioclase bearing granitic rocks in the area. The concentration of Ca indicates 10% falls under safe zone in the S, N and at the centre part of the study area and the remaining 90% shows unsafe zone in 2015. In 2017 the concentration of Ca shows 5% unsafe zone at the centre part of the study area with the remaining area being safe zone. DEAT 2008 reported that, the dissolution of minerals in granite region like feldspar, pyroxene and amphiboles are the source of calcium in the unsafe zone. The Mg concentration shows 5%, 3% and 2% unsafe zone in E, NE and S part respectively while the remaining area is safe zone in 2015. In 2017 the concentration shows 9%, 4% and 2 % unsafe zone in N, NW and central part respectively (Figure 6.1). Howari and Banat (2002) illustrated that the unsafe zone of Mg is mostly resulting from Mg-Ca silicates of plagioclase and potash feldspar minerals such as microcline and orthoclase.

In the study region, the concentration of HCO₃ shows 99% safe zone with 1% unsafe zone in the NE part in 2015 while NW-SW-E and central part shows 20% unsafe with the remaining area being safe zone in 2017. The concentration of SO₄ ion shows 15% unsafe zone in E and central part in 2015 with the remaining area being safe zone while in 2017 it shows 96% of safe zone with 4% unsafe zone in NW and central part of the study area. The Cl ion shows 10% of unsafe zone at the centre part of the study area with the remaining being safe zone in 2015 while 97% shows safe zone with 3% unsafe zone in NW and the centre part of the study area in 2017. Cude (2001)

reported that the unsafe zone of Cl and SO₄ ions indicate the pollution sources to be likely from discharges of saline residues in the soil and domestic sewage. The concentration NO₃ ion shows 9 % unsafe in Eastern and central part with the remaining being safe zone in 2015 while 90% shows unsafe zone 2017.

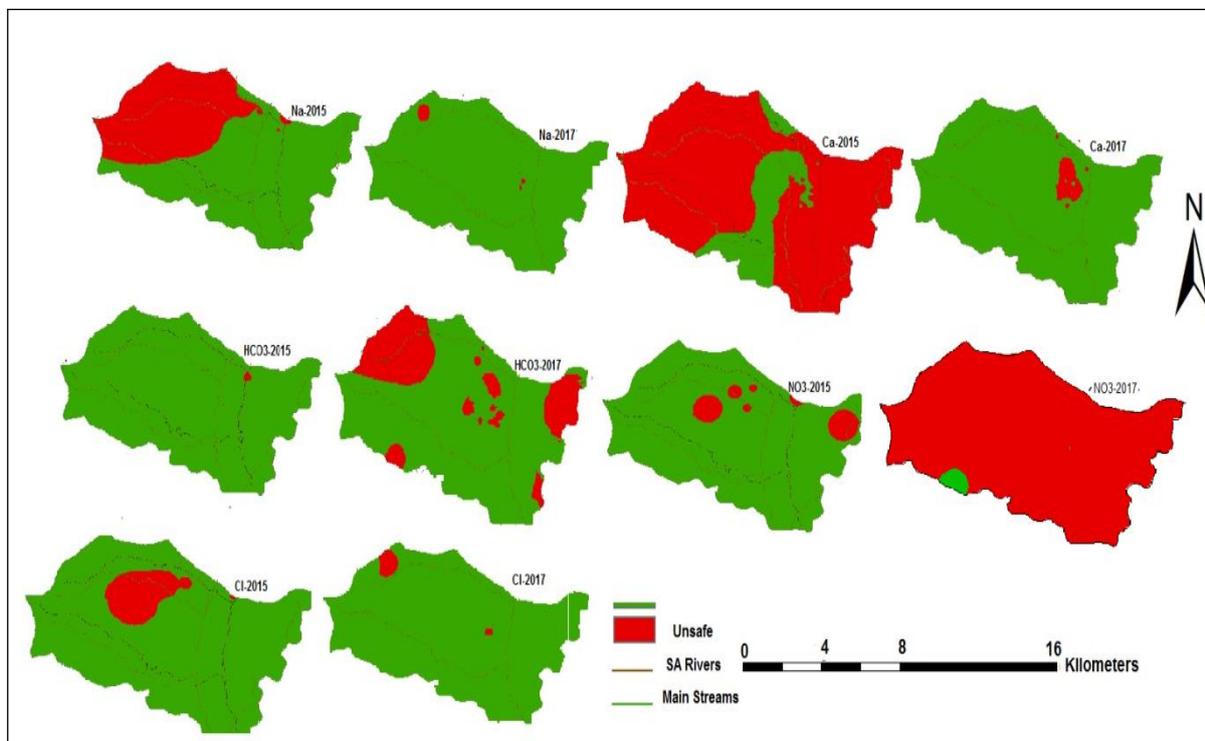


Figure 6.2. Spatial distribution of groundwater quality, NO₃ and major ions maps of the study area

6.3 Groundwater suitability assessment using DWQI

The drinking water quality index (DWQI) methodology was applied in this study to assess suitability of groundwater for drinking purposes. Several studies were conducted around the globe using drinking water quality index (Appelo and Postma 1993, Hem, 1985; Shweta *et al.*, 2013; Howari and Banat 2002; Horton 1965). The WQI was calculated using values outlined in Table 6.2 which provided variation of WQI. The five steps method was employed to compute the drinking water quality index with the initial step being of assigning relevant weight to water quality parameters. Cude (2001) indicated that the weight to a particular parameter was assigned depending on its relative importance in controlling the impact on human consumption and overall drinking water quality. Parameters like Na, K, Ca and HCO₃ were assigned a maximum weight of 5. SO₄ was assigned a minimum weight of 1. Further, Mg and Cl were assigned a weight 3.

Table 6.2. Weights of parameters and DWAF (1996) standards

Parameters	Assigned weight (wi)	DWAF (1996) standard	Relative weight (Wi)
EC	5	700	1
pH	3	9	0.6

Ca	5	32	1
K	5	50	1
Mg	3	30	0.6
Na	5	100	1
Cl	3	100	0.6
SO ₄	1	200	0.2
HCO ₃	5	300	1
	$\sum Wi = 35$		$\sum Wi = 1$

The assignment of relative weights to each parameter is based on equation 6.1.

$$Wi = \frac{wi}{\sum_{i=1}^n wi} \quad 6.1$$

i.e. Wi is the relative weight of the ith parameters. The wi is presented as the weight of the ith parameter and n as the cumulative value of parameters.

The quality rating (qi) calculation for each parameter and sample is computed using equation 6.2.

$$qi = \frac{Ci}{Si} * 100 \quad 6.2$$

i.e. Ci is presented as the concentration of ith parameter, and Si as the acceptable limit of the ith parameter in drinking water as per DWAF (1996).

The equation 6.3 was used to estimate the sub-index of the ith parameter SI_i .

$$SI_i = Wi * qi \quad 6.3$$

SI_i values of the parameters we summed in order to calculate DWQI of the individual water samples using Equation 6.4.

$$WQI = \sum SI_i \quad 6.4$$

Shweta *et al.* (2013) classified the DWQI into 5 categories which are excellent (<50), good (50-100), poor (100-200), very poor (200-300) and unsuitable (>300). The samples percentage and water types in each class are presented in Figure 6.3. The WQI was calculated using values outlined in Table 6.2 which provided variation of WQI from 42 to 271 with a mean value of 117 in 2015 and from 20 to 421 with a mean value of 102 in 2017. This study employed the spatial variation map (Figure 6.4) which categorizes groundwater quality into 5 distinctive types recommended by Ramakrishnaiah *et al.* (2009). At the study area, 8% of groundwater samples fall

within good category in 2015 and 47% excellent category in 2017. About 30 and 10% of groundwater samples fall within good category in 2015 and 2017 respectively (Figure 6.3). The plot also portrays that, 55 and 31% of samples in 2015 and 2017 were within poor category. Figure 6.3 displays that 8 and 10% of samples are within poor category and 7.5% within very poor category in 2015. In year 2017, 2.9% of groundwater samples were found to be in a very poor category in 2017. The small portion of the study of about 1% was found to be with the unsuitable category in 2017, and this is the area where high concentration of EC was detected. These outcomes reveal that the quality of water at the area study is recognised as safe for drinking uses whereas other areas the study are considered to be very poor to not suitable for drinking uses in both year 2015 and 2017.

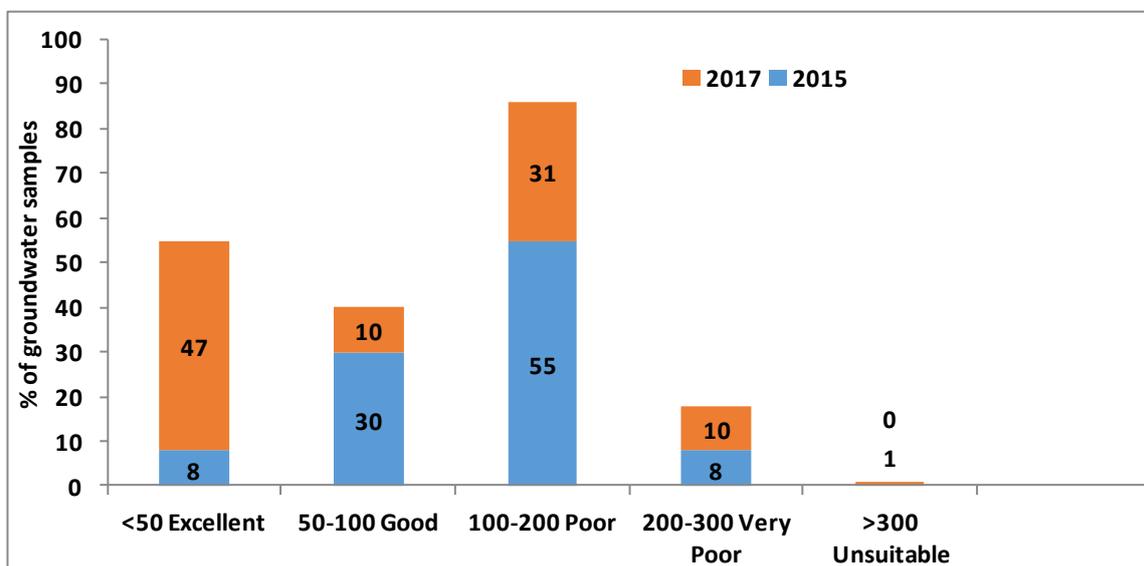


Figure 6.3. Classification of DWQI for 2015 and 2017 in the study area

The plot of spatial distribution of DWQI for 2015 and 2017 samples portray that central part SW and NW part of the study area were within excellent to good zone with the remaining part of the study being poor (Figure 6.4). This plot reveals that a total of 19% of samples are within poor to unsuitable zone for both year 2015 and 2017. The drinking water quality index was confirmed with EC and Na which know as pollutants indicators. The high concentration of Electrical Conductivity, Sodium influences the DWQI which causes display poor quality of groundwater in the study area. The reasons for the poor quality reflected in the DWQI may be due to the effluents discharge, impact of agricultural activity and over extraction of groundwater in the study area.

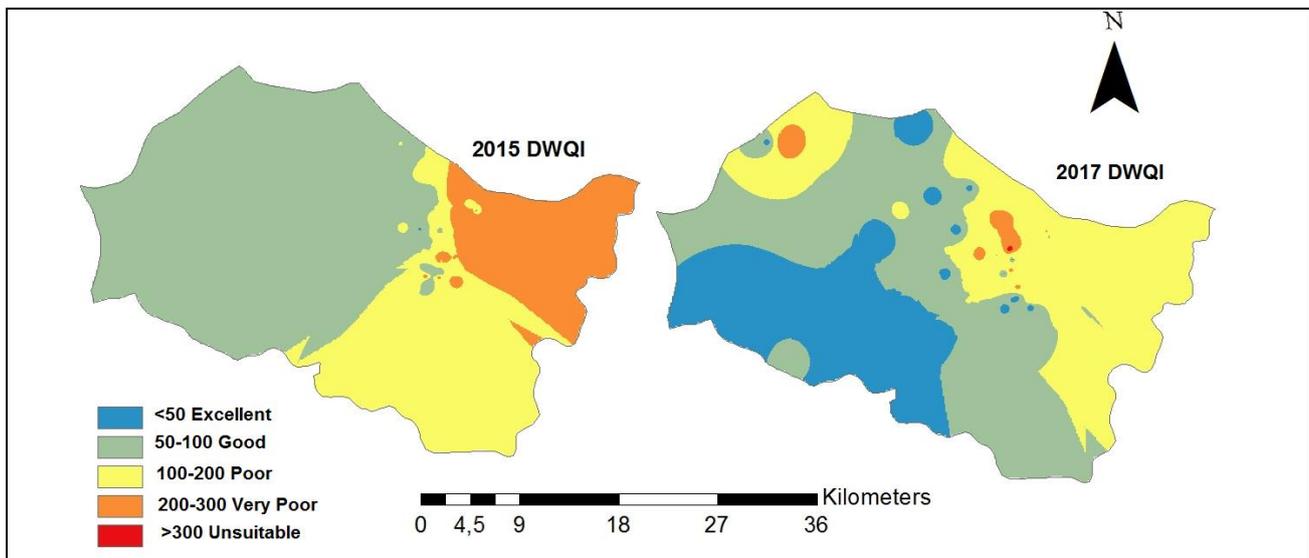


Figure 6.4: Spatial distribution of DWQI during 2015 and 2017 in the study area

The Drinking Water Quality Index (DWQI) for 2015 and 2017 was correlated with physicochemical parameters which are EC, Ca, K, Mg, Na, Cl, SO₄ and HCO₃ (Figure 6.5). DWQI has been correlated with the hydrochemical parameters of groundwater and display strong to moderately correlations as outlined in Figure 6.5. The outcomes of the plot displayed a strong correlation of water quality index with Na, Ca, Cl, NO₃ and SO₄. However, drinking water quality index shows moderate correlation with Mg, EC and HCO₃. Figure 6.5 shows that there was no correlation between K, and F with the drinking water quality index.

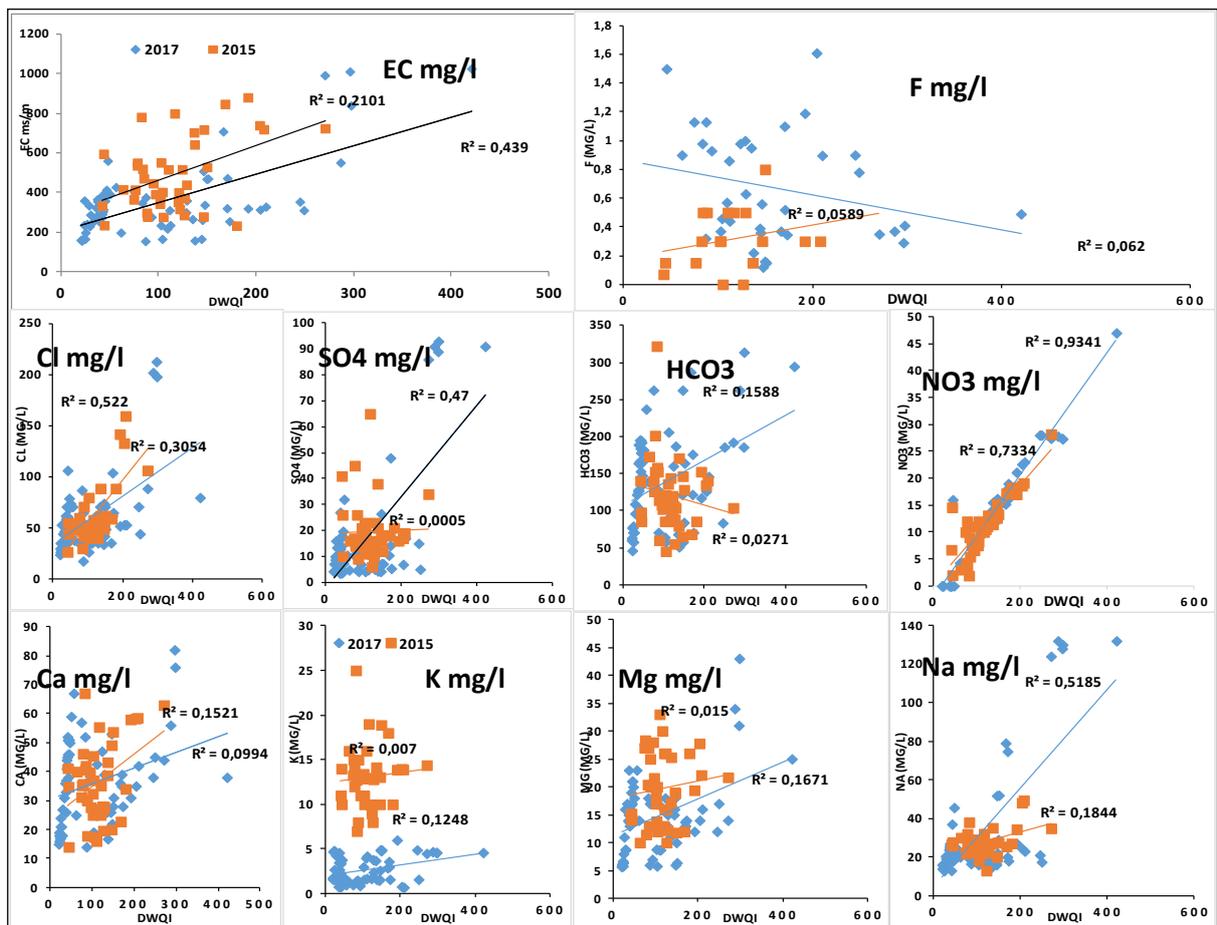


Figure 6.5. Correlation of physicochemical parameters with the water quality index

6.4 Assessment of groundwater for Irrigation Purposes

The groundwater quality which is utilised for agricultural purposes is crucial for crop yield, environmental and protection preservation of soil productivity. An assessment was carried out to check the suitability of water for agricultural purposes using various indices. The indices values of MH (Szaboles and Darab, 1964) eq.6.5, RSC (Eaton 1950; Wilcox 1948) eq.6.6, percent of sodium (Wilcox 1955), eq.6.7, SAR (Todd 1980; Sawyer and MacCarthy 1978) eq.4.8, PI (Doneen 1964; Raghunath, 1987) eq 6.9, KR (Ryner 1944; Raman 1985) eq.6.10 and Cl/HCO₃ ratio (Revelle 1941) in the area of study for determining applicability of groundwater for agricultural purposes were computed using equations listed below:

$$MH = (Mg / (Ca + Mg)) \times 100 \quad 6.5$$

$$RSC = (CO_3 + HCO_3) - (Ca + Mg) \quad 6.6$$

$$Na\% = \frac{(Na+K) \times 100}{(Ca+Mg+Na+K)} \quad 6.7$$

$$SAR = \frac{Na}{\sqrt{\frac{Ca+Mg}{2}}} \quad 6.8$$

$$PI = \frac{Na + \sqrt{[HCO]_3}}{(Ca+Mg+Na)} \times 100 \quad 6.9$$

$$KR = \frac{Na}{Ca+Mg} \quad 6.10$$

Sodium percent

High sodium content in groundwater is not suitable for agricultural purposes and can depreciate the soil, decrease the structure of the soil and permeability of the soil (Todd 1980). The percent of sodium (Na%) mainly represent sodium in irrigation water. Wilcox (1955) indicated that Na% is a main parameter used to define the suitability for irrigation purposes of natural waters in the study area.

Figure 6.6 indicate that about 98 % of groundwater samples at the area of study fall between excellent to good range of Na% in 2015 while 2% of groundwater samples in 2015 fall in the good to permissible range of irrigation. During the 2017, 94% of samples were with the excellent to good with 4% being within good to permissible range and 2% in the permissible to doubtful range for irrigation use (Figure 6.6).

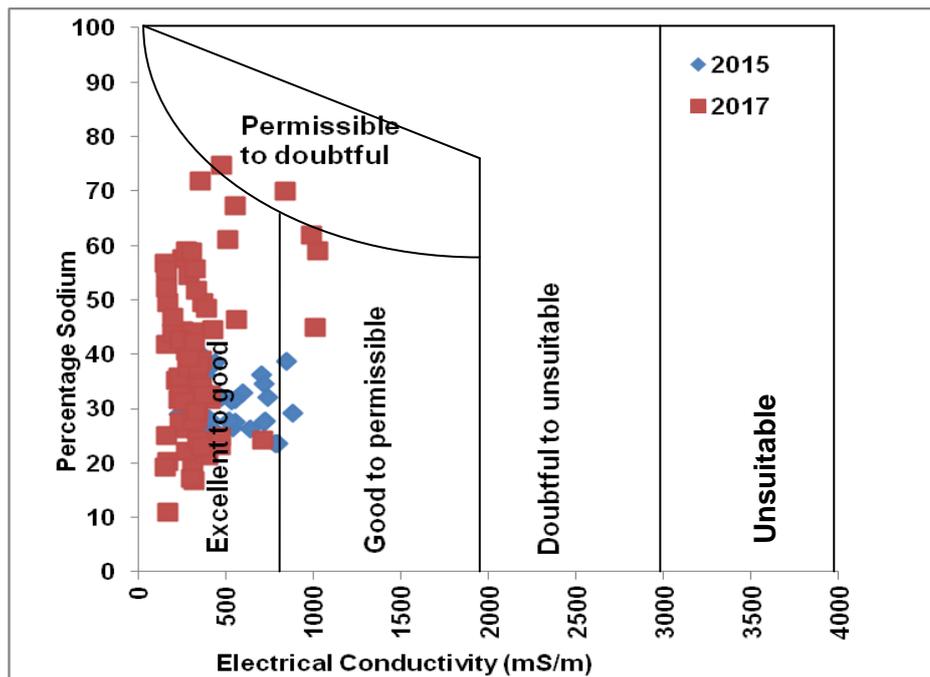


Figure 6.6: Wilcox diagram of groundwater

Sodium Adsorption Ratio

Sodium adsorption ratio (SAR) is described as a quantification of sodium hazard to produced crops or alkali. SAR of water has an important relation with the degree that the sodium is absorbed by the soil. The direct contact of soil with water containing high SAR requires soil amendments to avoid long-term harm on soil since sodium in water display magnesium and calcium in soil.

This will result in decrease in soil capability to loss of soil structure and form steady aggregates. The results of this will also influence the decreased permeability of the soil leading to crop production problems and infiltration rate. The computed SAR values vary from 0.4 to 1.4 and all the samples were found within the excellent range for irrigation purpose (Figure 6.7).

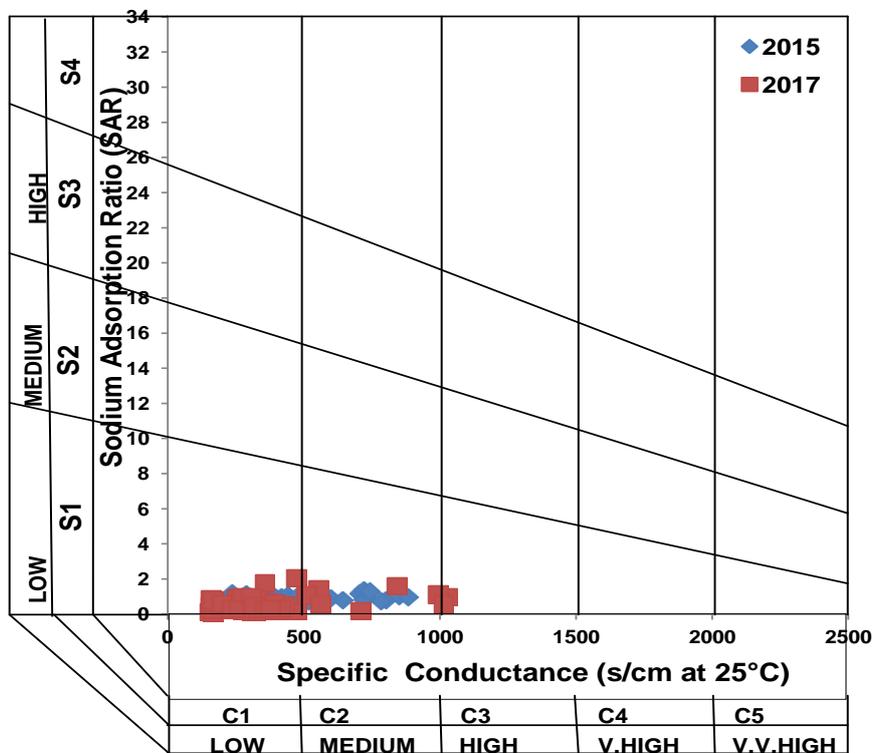


Figure 6.7: USSL diagram for groundwater

The detailed analysis in relation to groundwater irrigation suitability was further completed by plotting the SAR and EC (Figure 6.7). The medium hazard and high salinity water type in fine texture of the soil have a high cation exchange capacity.

However, it may be used on organic soils or coarse textured with good permeability. Chloride combined with sodium produces saline soils, while sodium mixed with carbonate can result to the formation of alkaline soils. Both these soils have adverse impact on plant growth. During 2015, 77.5% of samples fall within C1S1 fields indicating low alkalinity and medium salinity, 22.5% of

samples fall within C2S1 field indicating low alkalinity and medium salinity which can be used for irrigation due to moderate leaching as well as permeability (Figure 6.7). During 2017, 87.5% of samples fall within C1S1 fields indicating low alkalinity and medium salinity, 6.5% of samples fall within C2S1 field indicating low alkalinity and medium salinity which can be used for irrigation. Furthermore, 6% of samples fall under C3S1 indicating low sodium and high salinity, which exempt its suitability for irrigation. Generally, most samples were appropriate for agricultural purposes.

Table 6.3. Classification of irrigation water quality on groundwater

	Range	Classification	% of Samples		Reference
			2015	2017	
EC μS/cm	< 750	Low	92	94	Wilcox [1955]
	750-1500	Medium	8	6	
	1500-3000	High	-	-	
	>3000	Very high	-	-	
SAR	< 10	Excellent	100	100	Richard (1954)
	10-18	Good	-	-	
	18-26	Doubtful	-	-	
	>26	Unsuitable	-	-	
Na%	<20	Excellent		19	Wilcox [1955]
	20-40	Good	99	68	
	40-60	Permissible	1	13	
	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	-	-	Doneen [1964]
	25%-75%	Class II	100	76	
	<25%	Class III	-	24	
Cl/HCO ₃	0-0,5	Not affected	15	1	Revelle, 1941
	0,5-6,6	Slightly Moderately affected	85	99	
	>6,6	Severely affected	-	-	
MH	<50	Suitable	60	94	Paliwal (1972).
	>50	Unsuitable	40	6	
KR	<1	Suitable	100	91	Kelley, 1951
	>1	Unsuitable	-	9	

Magnesium Hazard

The crop yield decreases when soils have more alkaline earths. Mg and Ca uphold the equilibrium state in most waters. Szabolcs and Darab (1964) indicated that high content of magnesium hazard (MH) in water exceeding the value of >50% has an effect on crop yield since soil becomes more alkaline. The MH values of groundwater samples in the study area fall in the range of 27% to 77%. About 40% groundwater samples in 2015 are within the unsuitable category in the study area and are likely to be detrimental on agricultural crop yield and 60% of groundwater samples are found to be good for agricultural crop yield based on MH. In 2017, 91% of groundwater samples in the area of study are good for crop yield with 9% of samples being likely to cause detrimental effect on the crop yield (Table 6.3).

Permeability Index

Long term use of irrigation water which is rich in sodium, calcium, magnesium and bicarbonate affects the permeability of soil. Permeability Index is categorised into three classes where Class I and Class II are water which are considered as good for irrigation with 75% maximum permeability. Class III water is considered as unsuitable (Doneen, 1964; Raghunath, 1987) with maximum permeability of 25%. The PI values in the area of study vary from 44 to 78% with a mean value of 57% in 2015 and from 46 to 94% and a mean value of about 65% in 2017. As per the permeability index values, 100 and 76% of the samples in the study area fall under Class II which is suitable for irrigation in the year 2015 and 2017 respectively (Figure 6.8). About 24% of groundwater samples in 2017 were within Class III which is unsuitable for irrigation.

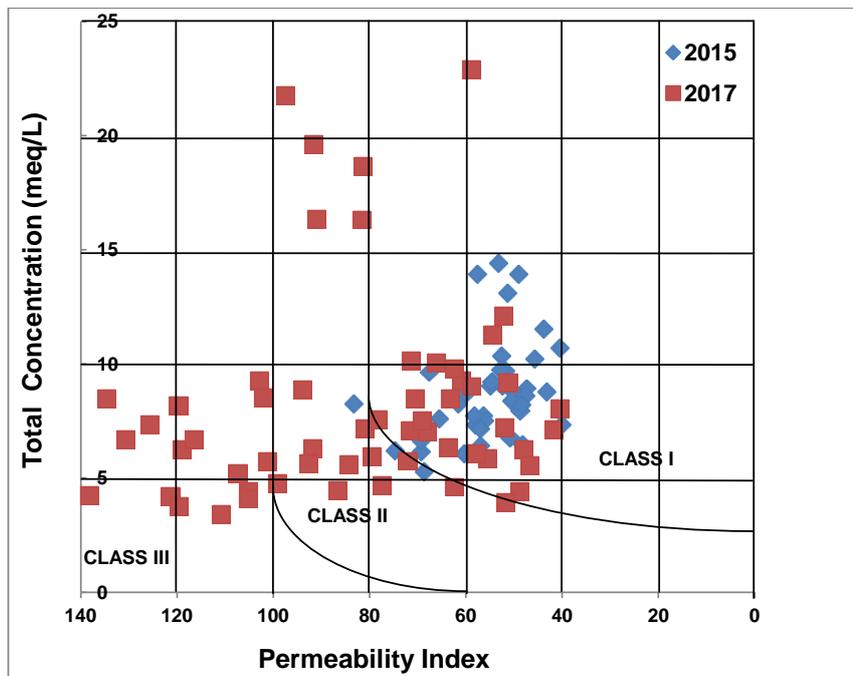


Figure 6.8: Permeability Index

Residual sodium carbonate (RSC)

Eaton, (1950) suggested that the perilous effect of bicarbonates and carbonates on the quality of groundwater for irrigational purpose can be assessed using RSC. Table 6.3 provides classification of RSC where samples with the RSC value of <1.25 are classified as safe for agricultural purpose while the RSC of >2.5 is considered as unsuitable for irrigation. Ramesh and Elango (2012) reported that high RSC value in water result to precipitation of calcium and magnesium. Sadashivaiah *et al.* (2008) indicated that the relative amount of sodium in groundwater is increased in the form of sodium bicarbonate. Reddy and Subba (2011) indicated that deterioration of soil structure, restriction of movement of water and air through the increase in soil alkalinity and shunted of crop yield is caused by higher concentration of RSC in water. The computed RSC ranges between -10.1 and -1.7 meq/L. The study reveals that all groundwater samples in the area of study have negative RSC and fall in the zone of suitable class ($RSC < 1.25$). The negative RSC designates that sodium build up is unlikely since adequate magnesium and calcium are in excess of what can be precipitated as carbonate.

Kelley's ratio

The ratio of calcium to sodium and magnesium in meq/L is identified as Kelley's ratio (Kelley, 1951). Kelley, (1951) classified the water type into two categories where a water sample of $KR < 1$ is classified as suitable for irrigation purposes while a KR value of more than 1 is classified not

suitable for irrigation. The Kelley's Ratio (KR) ranges from 0.2 to 0.7 in 2015 and clearly signifying that water is suitable for irrigation uses. In 2017, the KR ratio ranges from 0.1 to 1.5 with 9% of samples exceeds the ratio of 1, clearly indicating that the groundwater is not suitable for irrigation (Table 6.3).

Cl-/HCO3- ratio

Revelle (1941) indicated that the amount of salinity in groundwater can be categorised using the Cl/HCO₃⁻ ratios. About 19 and 3% of the groundwater samples in 2015 and 2017 have Cl/HCO₃⁻ less than 0.5 indicating that water is not affected by salinity. Groundwater samples of about 81% in 2015 and 97% in 2017 were within the zone of slight to moderate salinity

6.5 Irrigation water quality index

The IWQI is classified into four subgroups namely permeability hazard, salinity hazard, specific ion toxicity and miscellaneous effects (Table 6.4 & 6.5) (Ayers and Westcot, 1985). The irrigation water quality parameters with potential to impact groundwater negatively and yield of crops were considered in order to establish the suitability of groundwater for irrigation purposes. The weight coefficients of 1 to 5 were assigned to parameters depending on their consequence on irrigation purposes.

The IWQI was calculated using equation 6.11.

$$IWQI = \sum_{i=1}^n Gi \tag{6.11}$$

Table 6.4. Infiltration and permeability hazard classification

EC	SAR					Rating	Suitability
	<3	3_6	6_12	12_20	>20		
>700	>1200	>1900	>2900	>5000		3	high
700-200	1200-300	1900-500	2900-1300	5000-2900		2	medium
<200	<300	<500	<1300	<2900		1	low

Table 6.5. Classification of Irrigation Water Quality Index parameters

Hazard	weight	parameter	range	rating	suitability
salinity hazard	5	EC ($\mu\text{S}/\text{cm}$)	EC<700	3	high
			$700 \leq \text{EC} \leq 3000$	2	medium
			>3000	1	low
		TDS (mg/L)	<450	3	high
			$450 \leq \text{TDS} \leq 2000$	2	medium
			>2000	1	low
Specific ion toxicity	3	SAR	SAR<3.0	3	high
			$3.0 \leq \text{SAR} \leq 9.0$	2	medium
			>9.0	1	low
		Boron (mg/L)	B<0.7	3	high
			$0.7 \leq \text{B} \leq 3.0$	2	medium
			>3.0	1	low
		Cl (mg/L)	Cl<140	3	high
			$140 \leq \text{Cl} \leq 350$	2	medium
			>350	1	low
Trace element toxicity	2	Lithium (mg/L)	Li<2.5	3	high
			$2.5 \leq \text{Li} \leq 5.0$	2	medium
			Li>5.0	1	low
		Nickel (mg/L)	Ni<0.2	3	high
			$0.2 \leq \text{Ni} \leq 2.0$	2	medium
			Ni>2.0	1	low
		Zinc (mg/L)	Zn<2	3	high
			$2 \leq \text{Zn} \leq 10$	2	medium
			Zn>10	1	low
		Flouride (mg/L)	F<1.0	3	high
			$1.0 \leq \text{F} \leq 15$	2	medium
			F>15	1	low
Miscellenous effects to sensitive cops	1	HCO ₃ (mg/L)	HCO ₃ <90	3	high
			$90 \leq \text{HCO}_3 \leq 500$	2	medium
			>500	1	low
		NO ₃ -N (mg/L)	NO ₃ -N<5.0	3	high
			$5.0 \leq \text{NO}_3\text{-N} \leq 30.0$	2	medium
			NO ₃ -N>30.0	1	low
		Ph	$7.0 \leq \text{pH} \leq 8.0$	3	high
			$6.5 \leq \text{pH} < 7.0$ or $8.0 \leq \text{pH} < 8.5$	2	medium
			pH<6.5 or pH>8.5	1	low

The irrigation water quality index classification suggested by Islam *et al.* (2018) was employed on this study. The outcomes of the classification shows 87 and 10% of groundwater samples in the area of study were acceptable for irrigation in 2015 and 2017 respectively (Figure 6.9). Figure 6.9 further displayed that about 13 and 90% of groundwater samples were within the zone of

moderately suitable. This study reveals that none of the groundwater samples in the area of study were found to be unsuitable.

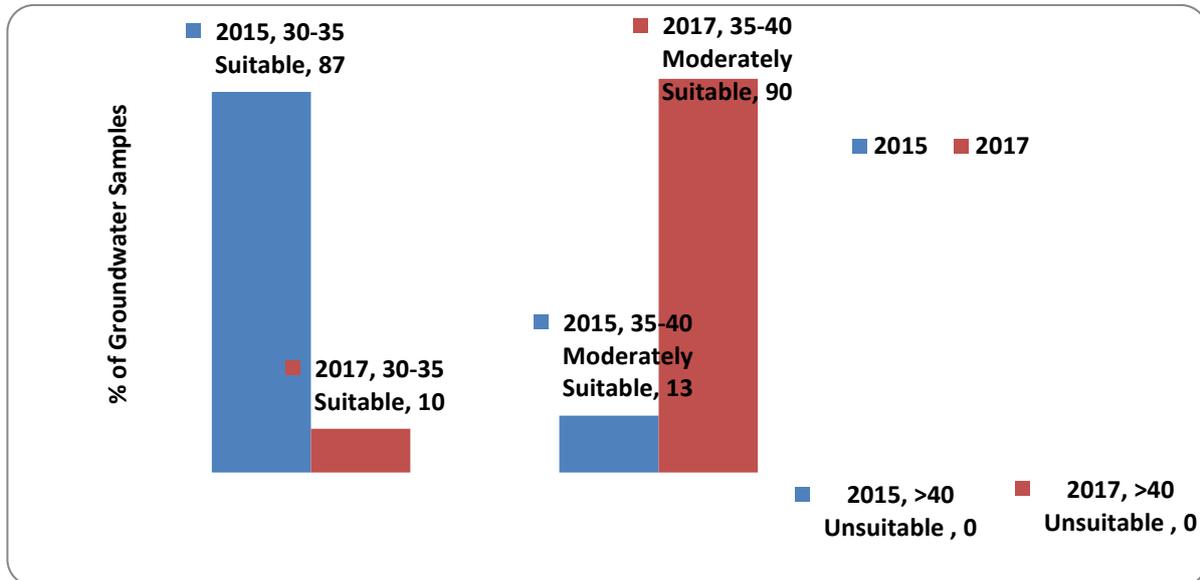


Figure 6.9: Classification of IWQI for 2015 and 2017 in the study area

The spatial distribution of IWQI is valuable in representing suitable conditions for irrigation water quality. Figure 6.10 indicates that most of the groundwater samples fall between the class of suitable and moderately suitable irrigation purposes in 2015 and 2017.

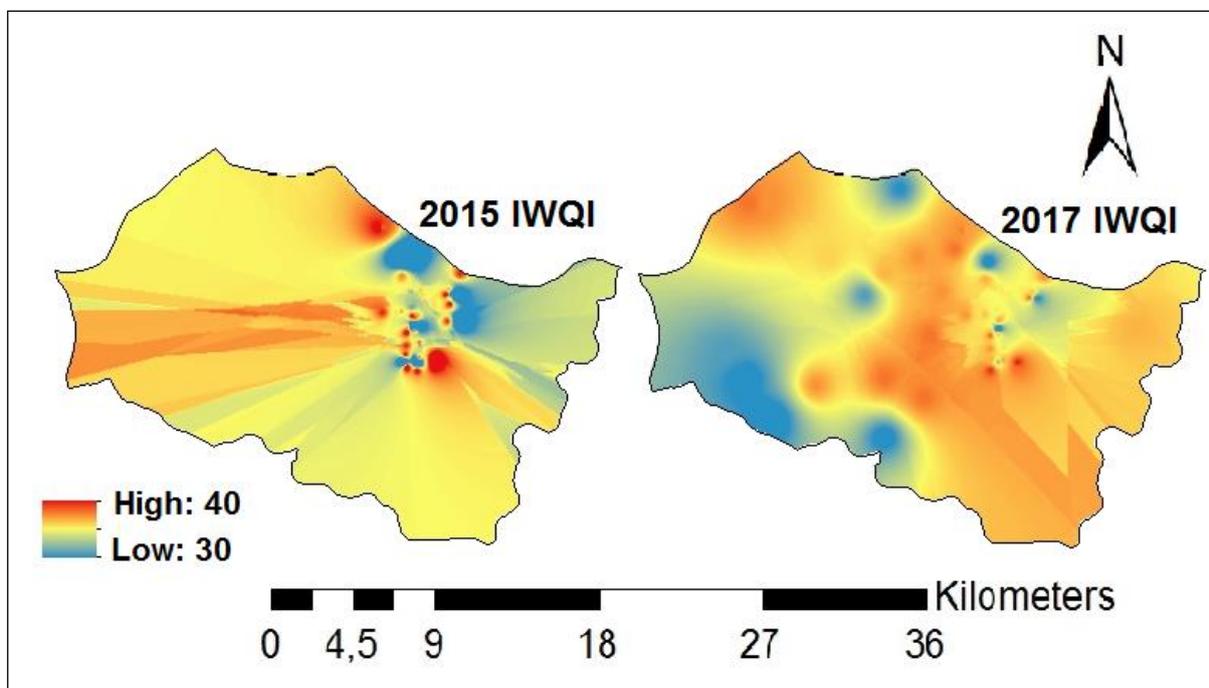


Figure 6.10: Spatial distribution for IWQI of groundwater in the study area.

6.6 Heavy metal pollution index

The heavy metal pollution index (HPI) is extensively utilised by researchers around the globe to assess the influence of heavy metals on groundwater quality. Tiwari *et al.* (2016); Abou Zakhem and Hafez, (2015); Vetricurugan *et al.* (2017) also employed the HPI to assess the influence of heavy metals on the quality of groundwater. The HPI is computed using equation 6.12;

$$HPI = \frac{\sum_{i=1}^n WiQi}{\sum_{i=1}^n Wi} \quad 6.12$$

i.e. Wi is the unit weight of the i th parameter, n is the number of parameters considered. The unit weight (Wi) is computed using equation 6.13

$$Wi = K/Si \quad 6.13$$

i.e. K is the proportionality constant and Si is the standard permissible value of the i th parameter. Sub index (Qi) is computed by equation 6.14

$$Qi = \sum_{i=1}^n \frac{|Mi - Ii|}{|Si - Ii|} \times 100 \quad 6.14$$

i.e. Mi , Si and Ii are the monitored value, the standard and ideal value of i th parameter. The negative sign demonstrate numerical difference of two values, disregarding the algebraic sign. Abou Zakhem and Hafez, (2015) indicated that the high value of HPI is known to cause severe harm on human health.

The range of heavy metals in the area of study measured in groundwater samples is outlined in Figure 6.11. The concentrations of metals in groundwater were compared against the South African and World Health Organization water quality standards for domestic and drinking purposes. The compared target range of water quality for South Africa with the WHO guidelines is outlined in Table 6.6.

Table 6.6: Comparison of World Health Organization (WHO) and South African drinking water quality guidelines.

Heavy metal	Target water quality range (no effect range) of DWAF (1996) ($\mu\text{g/L}$)	Health based guidelines of WHO (1993) ($\mu\text{g/L}$)	Normally found in ground/surface water ($\mu\text{g/L}$)	Percentage of samples exceeding the standards	
				According to WHO (1993)	According to DWAF (1996)
Aluminium	150	200	-	100	100
Copper	1000	2000	-		75
Zinc	3000	3000	-	9	21
Manganese	500	500	-	-	-
Lead	10	10	-	100	100
Iron	100	-	0.5-50	-	-
Cadmium	5	3	<0.001	-	-
Boron	-	300		-	-
Chromium	50	3		-	-
Nickel	No guideline	20	<20	44	-

In the study area, the concentrations of aluminium, cadmium and nickel were exceeding the maximum allowable limits of WHO (1993) and guidelines for South African drinking water quality (DWAF (1996)). The concentration of boron exceeds the WHO (1993) limits with about 75% of groundwater samples, DWAF (1996) does not have guideline limit for boron. The concentrations of zinc, lead, manganese were within the acceptable WHO and DWAF limits. The trace metal such as Ni, Cu, Cr, Cd, Al, Pb, Zn, Mn, Fe, B, Al, Si and Li were used when computing HPI using standard limits classification provided in Table 6.7

Table 6.7: Heavy metal pollution index range in the study area

Range of HPI	Quality range	No. of samples exceeding ideal quality (N=70)	% of samples exceeding ideal quality
<25	Excellent	57	81
25-50	Good	10	14
50-75	Poor	3	5
75-100	Very Poor	0	0
>100	Unsuitable	0	0

The HPI of groundwater in the area of study ranges from 1 to 68 with a mean value of 16. The classification range of groundwater is given on table shows that about 5% of groundwater samples at the area of study fall within poor category with 81% being excellent and 14% being good. This suggests that all samples fall within the critical limit of $\text{HPI} > 100$. The spatial variation of HPI displayed in Figure 6.11 shows that the groundwater samples with poor HPI range is in

Figure 6.11 is located on the Eastern part of the area. Groundwater samples with good HPI range is located in the E-N-S part with the remaining being Excellent HPI range.

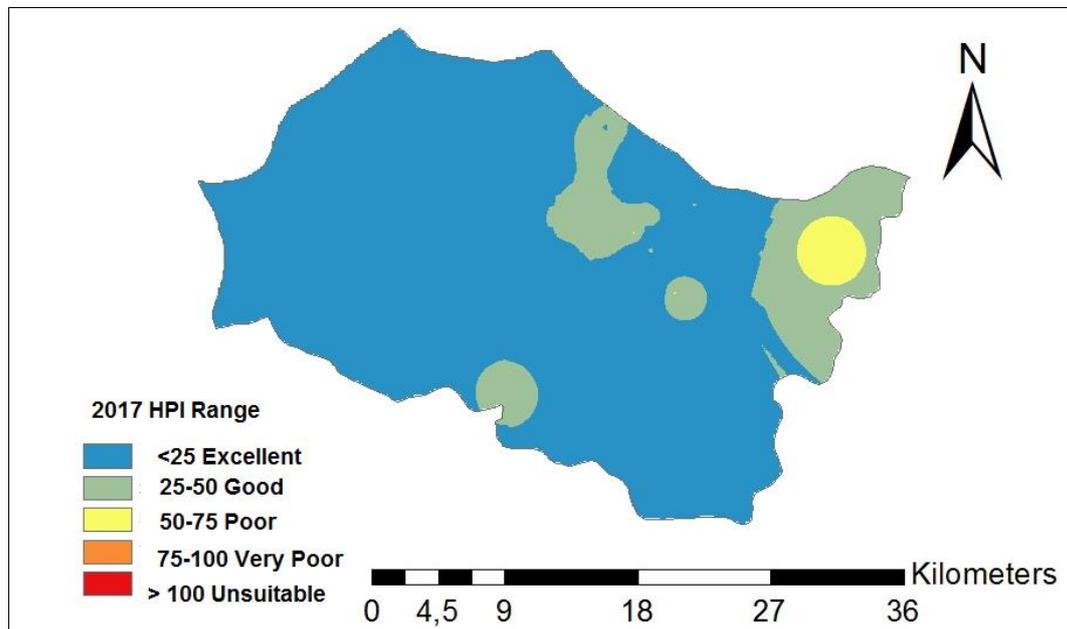


Figure 6.11: Spatial variation of HPI, 2017

6.7 Human health risk assessment

The consumption of contaminated groundwater by human kind poses serious health risk through diverse exposures like dermal contact and direct ingestion (Ahada and Suthar, 2018). The human health risk assessment model is consist four classes which are dose-response assessment, hazard identification, risk and characterization, exposure assessment USEPA (2014). Zhu *et al.* (2017), Vetrimurugan *et al.* (2017), Ahada and Suthar, (2018); Wang *et al.* (2018) conducted a study using the same technique.

The Human exposure risk to heavy metals was computed using equation 6.15;

$$HE_{DW} = (C * IR) / BW \quad 6.15$$

Where HE_{DW} is the human exposure risk from the pathway of drinking water (mg/kg/day), C is the heavy metal concentration in water (mg/L). IR being the intake rate of water (L/day), BW is the weight of the body in kg. The hazard quotient (HQ) was used to assess non-carcinogenic health risk for heavy metal using equation 6.16,

$$HQ = HE_{DW} / RfD$$

6.16

i.e. *RfD* is the reference dosage of heavy metal an individual becomes exposed to (mg/kg/day). The values of heavy metals reference dose are shown in Table 13. HQ value which is more than 1 poses serious risks on human health. The HQ value which is below 1 is considered as satisfactory level of risk in human health (Qasemi *et al.*, 2018; Ahada and Suthar, 2018; Vetrimurugan *et al.*, 2017;).

Table 6.8 outlines the summarised statistics of HE_{DW} . Based on the HE_{DW} values, it was discovered that B, Cu, Cd, Cr, Ni Mn, and Pb were below one in all age groups. However, Li was found to be greater than one in children and Zn was above one in infants and children. Table 6.8 depicts that the HQ values for B, Cd, Cu, Cr, Mn, Ni and Pb are less than one implying that they don't pose any significant health effect in all age groups. HQ values for Li were found to be greater than one in all age groups suggesting substantial health effects. Likewise, Zn had HQ values above one in infants and children.

Table 6.8. Human exposure risk and Non-carcinogenic risk (mg/kg/day) as a result of heavy metals through drinking water pathways

	Human exposure category	Statistical parameter	Heavy metal in groundwater									
			B	Cd	Cu	Cr	Mn	Ni	Pb	Li	Zn	
Human exposure risk (mg/kg/day)	Infant	Min	0	0	0	0	0	0	0	0	0,125	0,00121
		Max	0,0007	3,7E-05	0,0001	0,00018	3E-05	3,4E-05	2,4E-05	0,7207	28,2083	
		Mean	0,0002	9,1E-06	4E-05	2,8E-05	5E-06	1,2E-05	2,6E-06	0,3587	2,01704	
		SD	0,0002	9E-06	3E-05	3,7E-05	7E-06	8E-06	3,1E-06	0,1369	4,99491	
	Children	Min	0	0	0	0	0	0	0	0,225	0,00218	
		Max	0,0013	6,7E-05	0,0002	0,00033	5E-05	6,1E-05	4,4E-05	1,2973	50,775	
		Mean	0,0004	1,6E-05	7E-05	5E-05	9E-06	2,2E-05	4,7E-06	0,6456	3,63067	
		SD	0,0004	1,6E-05	6E-05	6,6E-05	1E-05	1,4E-05	5,7E-06	0,2465	8,99084	
	Adults	Min	0	0	0	0	0	0	0	0,1483	1,4E-06	
		Max	0,0009	4,4E-05	0,0002	0,00021	3E-05	4E-05	2,9E-05	0,8549	0,03346	
		Mean	0,0003	1,1E-05	4E-05	3,3E-05	6E-06	1,4E-05	3,1E-06	0,4254	0,00239	
		SD	0,0003	1,1E-05	4E-05	4,4E-05	9E-06	9,5E-06	3,7E-06	0,1624	0,00592	
Non-carcinogenic risk (mg/kg/day)	Infant	Min	0	0	0	0	0	0	0	6,25	0,00403	
		Max	0,0036	0,07417	0,0264	0,06028	0,0002	0,0017	0,00672	36,035	94,0278	
		Mean	0,0012	0,01821	0,0072	0,00922	4E-05	0,0006	0,00073	17,933	6,72347	
		SD	0,0011	0,01792	0,0064	0,01227	5E-05	0,0004	0,00087	6,8467	16,6497	
	Children	Min	0	0	0	0	0	0	0	11,25	0,00725	
		Max	0,0065	0,1335	0,0476	0,1085	0,0003	0,00306	0,0121	64,864	169,25	
		Mean	0,0022	0,03279	0,013	0,01659	7E-05	0,00109	0,00131	32,28	12,1022	
		SD	0,0019	0,03226	0,0115	0,02208	9E-05	0,00072	0,00157	12,324	29,9695	
	Adults	Min	0	0	0	0	0	0	0	7,4135	4,8E-06	
		Max	0,0043	0,08797	0,0313	0,0715	0,0002	0,00201	0,00798	42,744	0,11153	
		Mean	0,0014	0,02161	0,0086	0,01093	4E-05	0,00072	0,00087	21,272	0,00798	
		SD	0,0013	0,02126	0,0076	0,01455	6E-05	0,00047	0,00104	8,1213	0,01975	

The usage of groundwater that is highly contaminated by heavy metals is known to have negative impact on the health of individuals. Health risk assessment was done in this study to determine the likelihood of adverse health effects in groundwater polluted by heavy metals. Health risk of individuals (infants between 0-6 months, children and adults) exposed to groundwater rich in heavy metals was established by computing human exposure risk through drinking water pathway (HE_{DW}). Values used for IR were assigned as 250mL, 1.5L/day and 3L/day for infants, children and adults. Body weights were taken as 6kg, 20kg and 60.7kg for infants, children and adults. RfD values for the chosen heavy metals are depicted in Table 6.9.

Table 6.9. Heavy metals oral reference dose

Heavy metal	Reference dose (RfD in mg/kg/day)
Boron	2.00E-01
Cadmium	5.00E-04
Copper	5.00E-03
Chromium	3.00E-03
Manganese	1.40E-01
Nickel	2.00E-02
Lead	3.60E-03
Lithium	2.00E-02
Zink	3.00E-01

Vetrimurugan et al., 2017 employed the Non-carcinogenic risk plot to classify the age group that is likely to be affected by health risk in heavy metal and discover that children are at higher health risk from heavy metal than infants and adults. The plot of non-carcinogenic risk in drinking groundwater in Figure 6.12 indicates that children are at a greater risk from heavy metals followed by infants with adults being the least affected. Similar results were observed in a studies conducted by Vetrimurugan et al., 2017 in South Africa. From this, it is concluded that non-carcinogenic health risk through the pathway of drinking water is mainly attributed to Li and Zn in groundwater of this area.

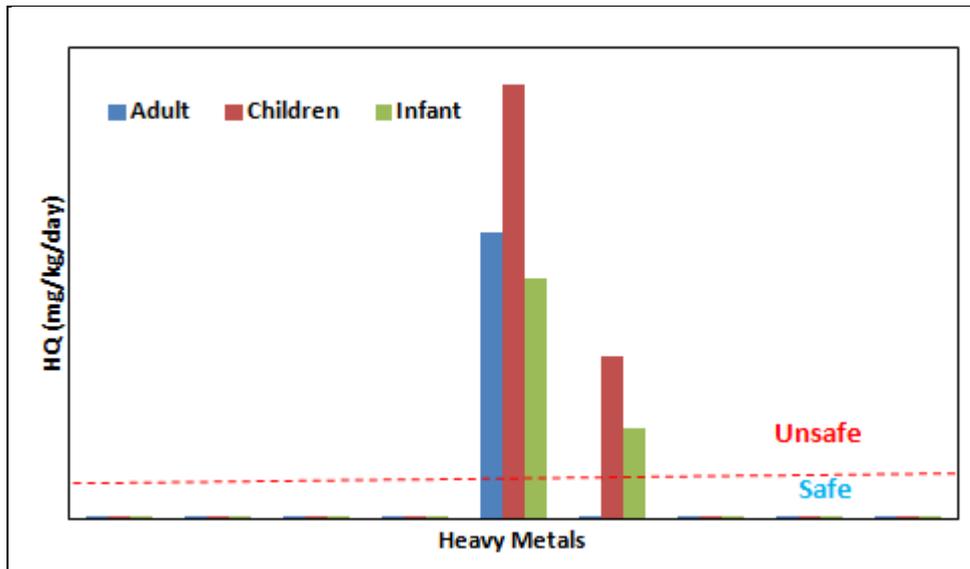


Figure 6.12. Non-carcinogenic risk in drinking groundwater.

Table 6.10. hazard quotient (mg/kg/day) in groundwater

Heavy metals	Hazard Quotient (mg/kg/day)		
	Adult	Children	Infant
Cd	0.021605084	0.032785714	0.018214286
Cu	8.60E-03	1.30E-02	7.25E-03
Mn	4.40E-05	6.68E-05	3.71E-05
Pb	8.66E-04	1.31E-03	7.30E-04
Li	2.13E+01	3.23E+01	1.79E+01
Zn	7.98E-03	1.21E+01	6.72E+00
B	1.44E-03	2.19E-03	1.22E-03
Cr	1.09E-02	1.66E-02	9.22E-03
Ni	7.16E-04	1.09E-03	6.03E-04

6.8 Nutrients and trace metal chemistry on groundwater

Groundwater in the area of study occurs in a shallow aquifer condition where the general groundwater flow follows the topography. This aquifer yield water of good quality which generally acceptable for drinking and irrigation uses. Table 6.11 presents the range of minor ions concentration in groundwater of the study area. The dominant sequence of minor ions order of NO_3 , PO_4 , F, NH_4 , Li and Si based on its average concentration.

Table 6.11: Concentration of groundwater parameters

Variables	Min	Max	STD	Mean	CV
		N=70			
NO ₃ (mg/L)	4.3	49.0	8.5	17.5	0.5
Ni (ug/l)	0.0	0.8	0.2	0.3	0.7
Cu (ug/l)	0.0	3.2	0.8	0.9	0.9
Cr (ug/l)	0.0	4.3	0.9	0.7	1.3
Cd (ug/l)	0.0	0.9	0.2	0.2	1.0
Al (ug/l)	195.0	2654.0	478.3	679.7	0.7
Pb (ug/l)	0.0	0.6	0.1	0.1	1.2
Zn (ug/l)	0.0	677.0	119.9	48.4	2.5
Fe (ug/l)	0.0	29.3	5.7	5.0	1.1
Mn (ug/l)	0.0	0.6	0.2	0.1	1.4
B (ug/l)	0.0	17.2	5.1	5.8	0.9
Si (mg/L)	12.0	64.0	12.3	42.8	0.3
F (mg/L)	0.1	1.6	0.4	0.7	0.6
NH ₄ (mg/L)	0.0	0.4	0.1	0.1	1.3
PO ₄ (mg/L)	0.0	0.5	0.1	0.1	0.9
Li (mg/L)	3.0	17.3	3.3	8.6	0.4

Lithium

The groundwater samples in the study area contains lithium concentration ranging from less than 3 to 17 mg/L with an average value of 8.6 mg/L. Martos *et al.* (1999) described lithium as a conservative tracer which is used to differentiate salinity of water.

Fluoride

Brindha *et al.* (2011); Ayoob and Gupta (2006); described geogenic as the main common sources of fluoride. Evaporation and weathering processes which contribute to the common mechanisms (Yeşilnacar *et al.*, 2016; Brindha *et al.*, 2016). The contribution human kind to fluoride comprises of fertilizers, volcanic and fly ash and industrial wastes. The study conducted by Brindha and Elango (2013) reported the increase fluoride in groundwater in other regions due to impact of fertilizers. The rate of concentration of fluoride in groundwater at the area of study ranges from 0.1 to 1.6 mg/L with a mean value of 0.7 mg/L (Table 6.11). WHO (1996) and SANS241 (2015) recommend the fluoride in drinking water to at maximum value of 1.5 mg/L, therefore groundwater is suitable for drinking purposes.

Phosphate

Phosphate is a crucial nutrient for animal and plant development. The main source of phosphorus in groundwater is as a result of application of fertilizers. Phosphate is mainly utilised in a form of superphosphate as well as nitrogen, phosphorous and potassium fertilizers in the study area. The phosphate is absorbed by fine grained soils and the soil upper layer may possibly be enriched as results of application of fertilizers. Phosphate in groundwater may also be present as results of aquaculture practices that discharge water containing high organic matter and phosphates. The rate of phosphate in groundwater samples ranges from BDL to 0.5 mg/L with an average value of 0.1 mg/L (Table 6.11). The surface pollutants from agricultural activities like the use of farm manure; fertilizers containing phosphate and irrigation return flow which may possibly affect the concentration of phosphate.

Ammonium

Ammonium ion is a significant redox species found in shallow groundwater systems mainly in agricultural areas. Besides anaerobic degradation of organic matter which produces ammonium, sewage disposal plants and landfill also discharge ammonium into the subsurface (Bohlke *et al.*, 2006). The concentration of ammonium in groundwater in the area of study ranges from BDL to 0.4 mg/L with an average value of 0.01 mg/L (Table 6.11). The desirable and maximum permissible limit of ammonium in drinking water is 0.5 mg/L (SANS241, 2015). Therefore, the rate of ammonium concentration groundwater in the area reveals that the water is suitable for drinking purposes. Coefficient of variance is presented in Figure 6.13.

Nitrate

Wakida and Lerner, 2005 indicated that the nitrate has commonly multiple sources which is animal waste, infiltration of inorganic and organic fertilizers from agricultural areas, leakage from sewers and irrigation water. In the area, the nitrate concentration ranges from 5 to 49 mg/L with an average value of 17.5 mg/L (Table 6.11). The nitrate concentration in 18 groundwater samples exceeds the maximum allowable limit of 20 mg/L (SANS241, 2015) which can result to health problems if consumed for longer period. High concentration nitrate in water is also an environmental concern since it affects health of livestock and causes eutrophication. The study

area is an agricultural area, thus contribution of nitrate in groundwater through application of fertilizer cannot be deserted.

Pollution factors of heavy metals in groundwater

The statistical description of NO₃, Ni, Cu, Cr, Cd, Al, Pb, Zn, Fe, Mn, B, Si, F, NH₄, PO₄ & Li is outlined in Table 6.9. The coefficient variations of elements in groundwater also follow the same order. The concentration of heavy metal in groundwater samples significantly varied in the area of study. The coefficient variation value of Zn is higher than that of Cu, Cr, Cd, Ni and Pb in groundwater (Figure 6.13). This is an indication that, the concentrations of Zn to each sampling location were higher than those of Cu, Cr, Cd, Ni and Pb. This illustrates that Cr, Cd, and Pb concentrations are proportionally less in each sampling site when compared to Cu, Cr, Zn and Ni. The results suggest that Zn concentration has a high probability of being influence by human activities (Lv *et al.*, 2014). Comparable results were also observed in a study conducted by Lu *et al.*, (2018). Buchhamer *et al.*, 2012 indicated that heavy metals are usually leach and absorbed by toxic soil in to the shallow groundwater. Figure display the concentration of heavy metal and confirms that Zn concentration is higher than that of other metals.

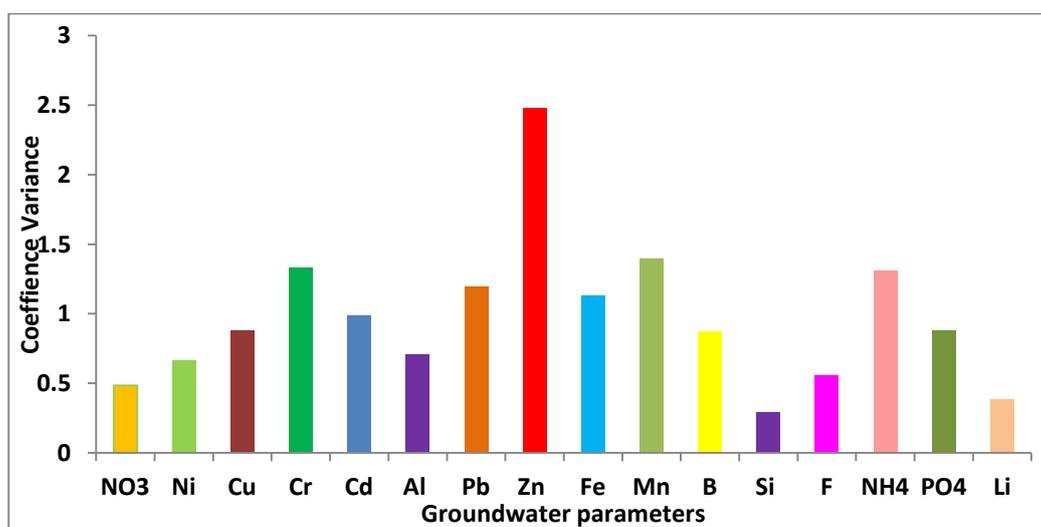


Figure 6.13: Coefficient Variation of Groundwater

7. Conclusion

Groundwater has a significant impact on supplying water for domestic purposes around the globe. Groundwater resource has been identified as the main and reliable water resource for human consumption and agricultural practice in the Ventersdorp area. The groundwater samples were collected from numerous boreholes in the study area and analysed for major ions and nitrate. The

concentration of major ions chemistry in groundwater was within the permissible limits of South African National Guidelines and World Health Organisation and for drinking use. Kelly's ratio Sodium percent, residual sodium carbonate, sodium absorption ratio and permeability index indicate that majority of groundwater samples in the study area within the suitable range of irrigation uses. The application of fertilizers affected the chloride and nitrate contents. Overall, the groundwater quality is good for drinking purposes and suitable for irrigation needs except at few locations. This study helped to comprehend the present state of groundwater chemical composition in Ventersdorp and to assess its fitness for irrigation and drinking uses. The spatial distribution of IWQI as well as DWQI confirmed that most of groundwater samples in the study region fall between the range of suitable for both drinking and irrigation purposes in 2015 and 2017. The constructed correlation of DWQI with major ions displayed a strong correlation of water quality index with Na, Ca, Cl, NO₃ and SO₄. The variables which were correlated with SO₄, NO₃ and Cl were derived from agricultural practices. The spatial variation reveals that the concentration NO₃ ion shows 9 % unsafe in Eastern and central part with the remaining being safe zone in 2015 while 90% shows unsafe zone 2017. The heavy metal pollution index (HPI) is extensively used around the globe to assess the influence of heavy metals on groundwater quality and this was exercised on this study. The concentrations of zinc, lead, manganese were within the acceptable range of WHO (2011) and DWAF (1996) limits. The classification range of groundwater shows that about 5% of groundwater samples in the study area falls within poor category with 81% being excellent and 14% being good. This suggests that all samples are within the critical limit of HPI>100. The consumption of contaminated groundwater by human kind poses serious health risk through diverse exposures like dermal contact and direct ingestion. The non-carcinogenic risk classification in drinking groundwater indicates that children are at a greater risk from heavy metals followed by infants with adults being the least affected in the study area. The coefficient variation of Zn was found to be higher than that of Cu, Cr, Cd, Ni and Pb in groundwater of the study area. This is an indication that, the concentration of Zn to each sampling location was higher than that of Cu, Cr, Cd, Ni and Pb. The results suggest that Zn concentration has a high probability of being influence by human activities.

CHAPTER 7

LONG TERM VARIATION IN GROUNDWATER LEVEL AND QUALITY DUE TO CLIMATE CHANGE

7.1 Introduction

This chapter describes the long-term changes in groundwater level and quality due to the changes in rainfall, temperature and precipitation. Rainfall gradually infiltrates the aquifer and results in increase in the groundwater level. Similarly, the groundwater level lowers significantly in the absence of infiltration during drought period (Apaydin, 2010). Local climate changes affect the shallow unconfined aquifers, while groundwater levels in deeper aquifers can mainly be influenced by supplementary climate changes in a regional scale. Moderately short term climate variability (Figure 7.1) has drastic impact on the shallow aquifer systems than the deeper aquifer systems. In the study area, groundwater level of shallow aquifer varies from 3.4 m to 20 m below ground level and in case of the deeper aquifer it ranges from 22.7 m to 75 m bgl. These changes are mainly attributed to the climate variation such as increase in rainfall intensity, high precipitation rate and changes in the rainy days. These factors can act as positive catalyst for rise in groundwater level.

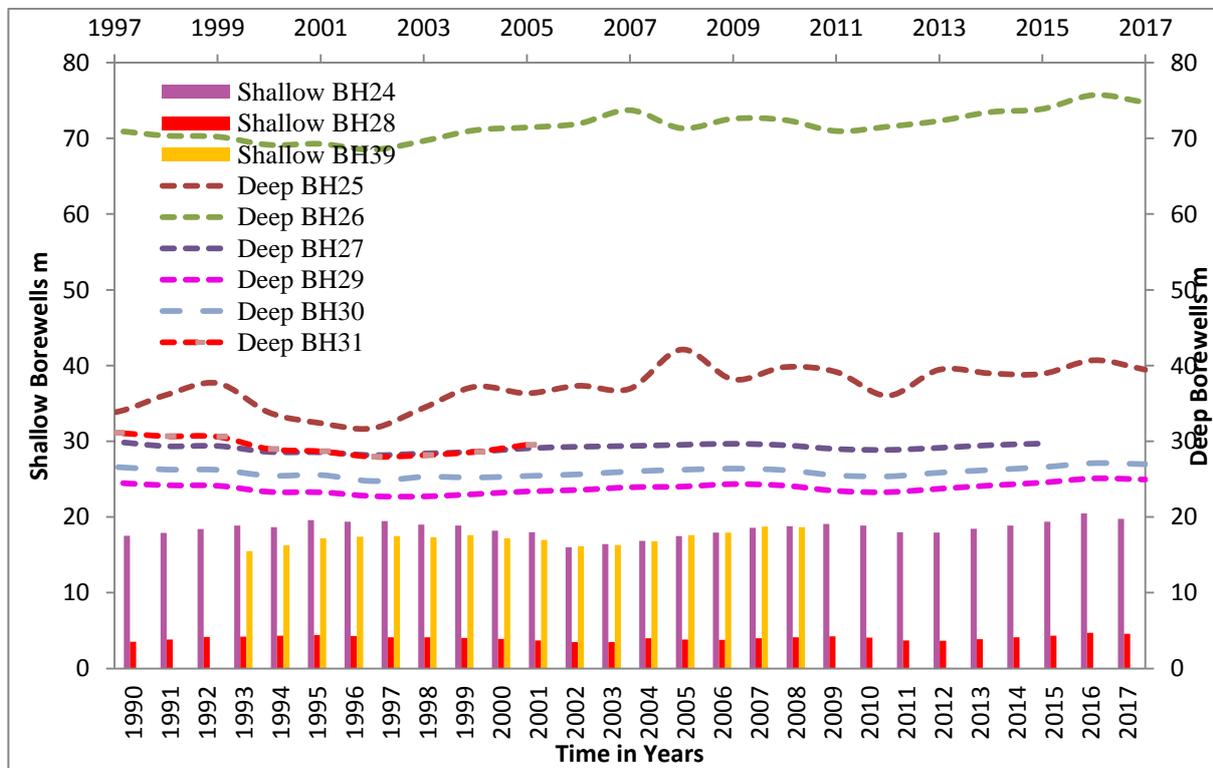


Figure 7.1. Groundwater level analysis

A positive response of fluctuation of groundwater level in shallow bore wells from 1997 to 2018. In the study area (Figure 7.1), the most significant water-level changes in deep aquifer occurred between 1993 and 1998. This may be due to over pumping of groundwater and heavy rainfall which occurred between 1992 and 1996 (see Figure 7.2). High rainfall and hurricanes events may result in runoff than recharge to groundwater as a large amount of the precipitation is lost. Groundwater levels from shallow wells respond more immediately to recharge. For analysis purposes, each station groundwater level data was averaged monthly and annually. The monthly rainfall data was obtained from South Weather Services on a station located in Ventersdorp.

7.2. Groundwater Table and Rainfall Variation

In order to establish the general groundwater level trend in the study area resulting due to the changes in the groundwater-table over a period of 27-years and the yearly dynamics of variation in precipitation, groundwater table data was analysed (Figure. 7.2). Temporal trend in the groundwater regime is clearly influenced by precipitation and withdrawal. During dry period, groundwater table declines and during the rainy period it rises. The long-term relentless exploitation of groundwater results in declining trend as the whole. A detailed perusal of the Figure 7.2 shows that the groundwater table in deeper aquifer declined between 2001 to 2005 and a slight decline between 2011 and 2015. An increase in groundwater table due to increase in annual rainfall was observed between 1990 and 1996 for both deep and shallow aquifers. Annual rainfall decreased between 2001 (118 mm/a), 2002 (304 mm/a) and 2003 (222 mm/a) and again in 2010 (287 mm/a), 2012 (281 mm/a) and 2014 (152 mm/a). In current years, rainfall in the study region drastically decreased compared to previous years (1990 to 1996), and the heavy groundwater withdrawal resulted in decrease in groundwater table. A decrease in rainfall in the study area results in high dependency on groundwater causing an increase in groundwater exploitation. Subsequently, this results in declining trend in the regional groundwater table at a higher rate. For the entire period between 2003 and 2010, decline of 3 m was recorded, that is on an average of nearly 3.5 m/yr.

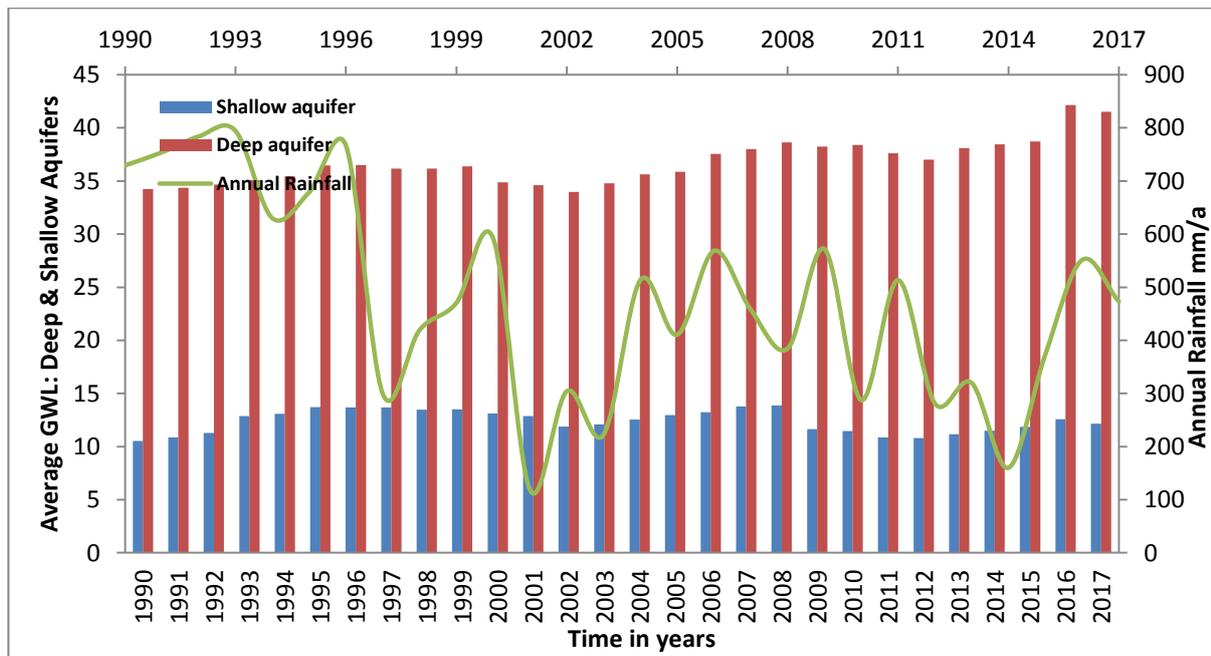


Figure 7.2. Aquifer response of rainfall

7.3. Groundwater Fluctuation in Dry and Wet Seasons

Groundwater withdrawal, unsaturated zone water and moisture content, rainfall and evapotranspiration contribute to recharge of groundwater which ultimately results in changes in groundwater level. Decadal and long-term changes in groundwater level trend can be due to the changes in climate and other manmade activities such as changes in land use pattern, withdrawal of groundwater, change in irrigation pattern, and infiltration rate changes (Healy 2010). In the present study, an attempt is being made to predict the changes in groundwater levels due to groundwater recharge from rainfall. In order to evade inappropriate evaluation of groundwater level change, the groundwater levels from shallow aquifer wells that respond rapidly to recharge influenced by rainfall was analysed (Figure 7.3). Groundwater table starts to rise in wet season with increasing rainfall. This clearly indicates that groundwater level are strongly influenced by rainfall. Perusal of the Figure 7.3 shows that during the years from 2001 to 2003, the study area received low rainfall during the wet season (86 mm/a for 2001, 169 mm/a for 2002 & 211 mm/a for 2003) and has resulted in the decline of ground water level by 5 m. In the study area, majority of rainfall occurs in summer with large number of flood events occurring during this period. Heavy rainfall and flood events have resulted in the increase of groundwater recharge and swallowing of the groundwater level (Figure 7.3). Similarly, when the rainfall decreases the depth of the groundwater level increases. In the study area, ploughing season is between December and February; hence during this period groundwater extraction is more than recharge and groundwater level declined swiftly in shallow aquifer.

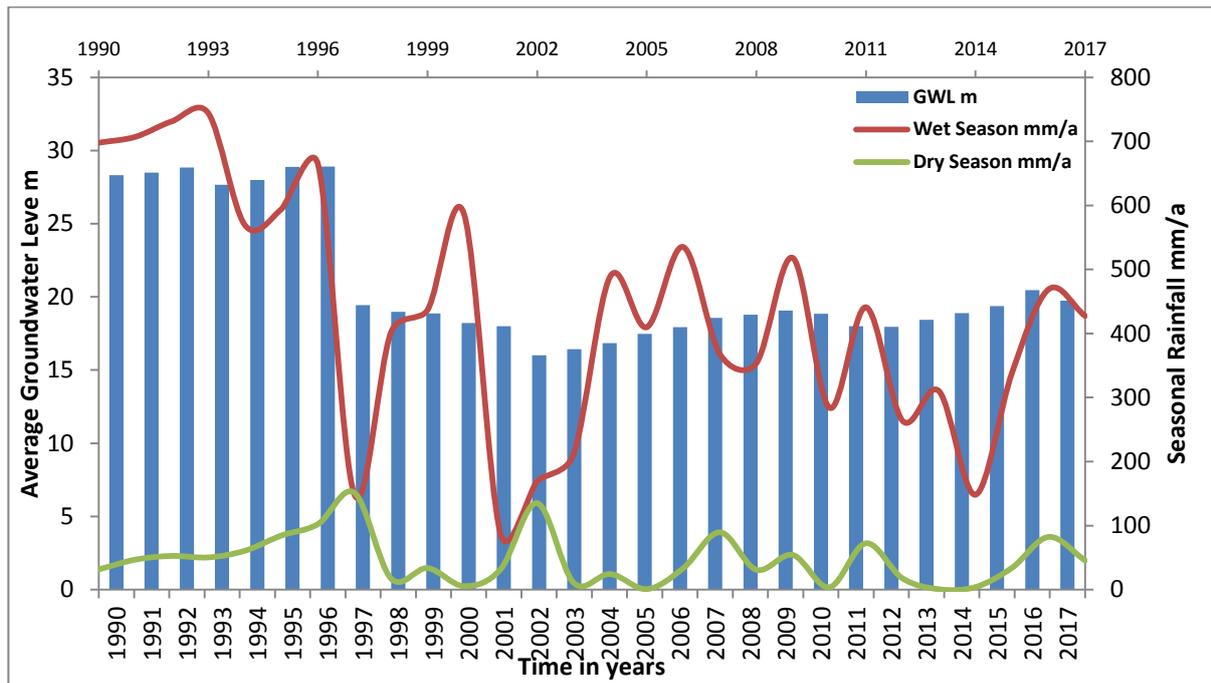


Figure 7.3. Average of groundwater level and seasonal rainfall variation in the study area

7.4 Climate conditions and groundwater response

The average annual rainfall in the study area is around 479 mm/yr. Rainfall includes the rain and secondary snow fall. In the study area, rainfall is mostly experienced during summer (October to February) and in fall season (March to April) and snow falls in winters (generally from December to February). The winters are generally dry and cold, while summers are wet and hot. During winters the temperature and evaporation potential are low while during the summer it is at its peak (Figure 7.4). The amount of groundwater level and rainfall in short and medium term are particularly unstable in the study area. The groundwater system gets replenished from precipitation. Thus, the connection between groundwater level fluctuation and precipitation is significant. The substantial results of this can be outlined from the study of hydrograph between water level and precipitation. In the study area, the period between October and April months is wet season which is generally the potential period for groundwater recharge in the study area (Figure 7.4). Similarly, the groundwater level hydrograph (Figure 7.4) clearly shows the rise in groundwater level between November and March when the rainfall is generally high. Moreover, the impact on the groundwater level due to precipitation appears intricate. Groundwater level shows a clear and linear decline between winter to spring and especially during dry years. This is as a result of minimum recharge to the aquifers taking place during these months. Groundwater also acts as an effluent of water to the streams and springs in the study area. During dry period, the

excess recharge or dejected recharge results in flow in the stream which is mainly from the water from the storage. The decline in groundwater level is highest in the upland recharge areas where groundwater levels are deeper. The discharge areas are the lower elevation regions i.e., valley bottoms where the groundwater levels are shallow and they show only minor change. The groundwater level starts declining from early May to until September (dry season) (Figure 7.4).

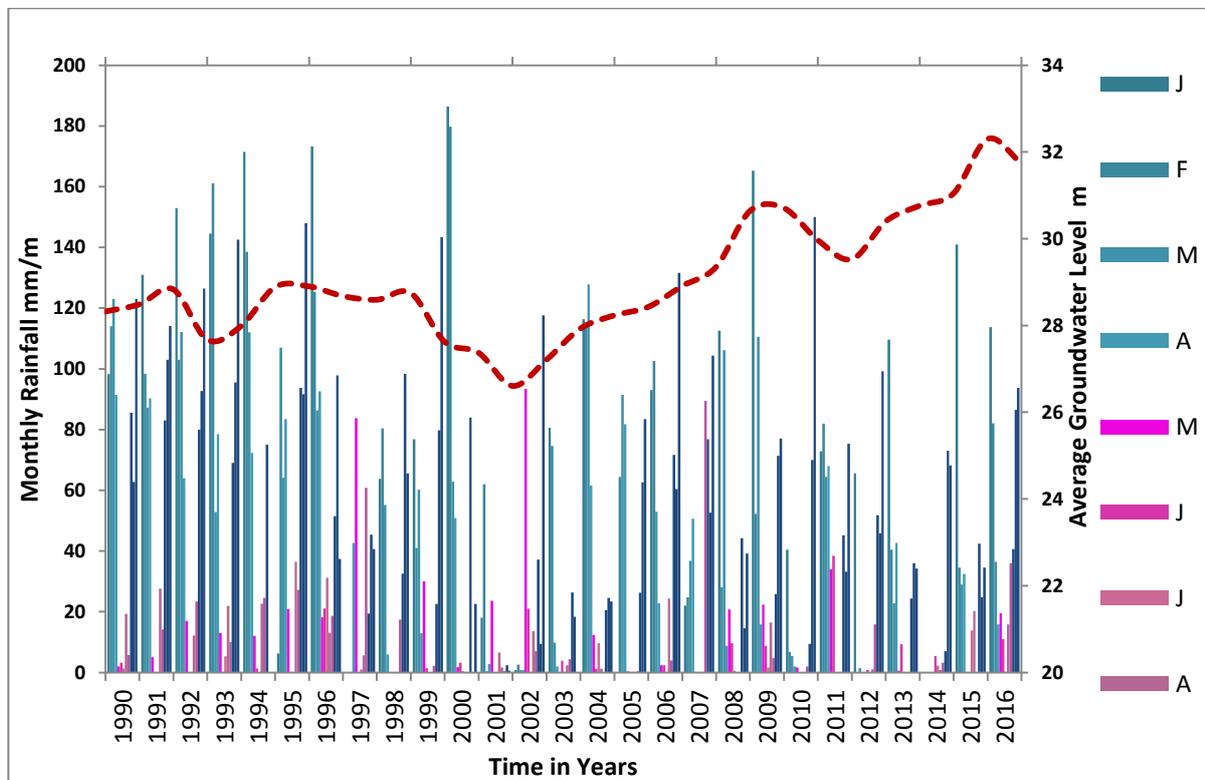


Figure 7.4. Average of groundwater level and rainfall variation in the study area

7.5 Impact of Rainfall on Groundwater quality

Climate change plays a major role in the fluctuation of groundwater level, alteration of soil water pore pressure, changes in groundwater flow regimes and in quality of groundwater resources (Chen *et al.*, 2004 and Ranjan *et al.*, 2006). Local climate changes usually impact the shallow unconfined aquifers while the groundwater of deeper aquifers can only be influenced by regional climate changes. The variability in climate is a brief term when referred with climate change. The highest effect is caressed on the shallow aquifer systems and its groundwater quality. Figure 7.5 brings out the results of chemical composition of the groundwater samples collected during 1994, 2004 and 2014 by the Department of Water and Sanitation. This result brings out clear and detailed scenario of the groundwater quality of the groundwater of the study area. On a perusal of the results, it is clear that there is a comprehensible variation in chemical composition in all bore wells. The concentrations of ion in the study area have increased and the groundwater quality has diluted during 1994. This could be result of decline of groundwater table due to over extraction and reduction in rainfall in the study area. In the present study, the concentration of Na^+ , K^+ , Ca^{2+} ,

Mg^{2+} , Cl^- , HCO_3^- , SO_4^{2-} , and electrical conductivity (EC) has increased with decrease in rainfall in 2004 and 2014 (Figure 7.5). The Electrical conductivity is generally low in 1994 as a result of dilution process that occurred during rainy season through recharge. Groundwater quality in the study area improves with the rise in groundwater level as a result of dilution. Similarly, the quality of groundwater deteriorates with the decrease in rainfall. Therefore, the change in groundwater quality is subjective to groundwater level fluctuation and rainfall variability. In the study area, rainfall recharge contributes to groundwater dilution. This recharge of freshwater due to recharge reduces the concentration of ions due to mixing. The impact on the major ion concentration of the study area is clearly attributed to the groundwater level fluctuation (Figure 7.5) during the years 1994, 2004 and 2014. In contrast, decreasing groundwater levels increases the concentration of major ions due to evaporation. The increase in groundwater level decreases the concentration of major ions in groundwater of the study area. Thus, the temporal changes are mainly influenced by the recharge processes.

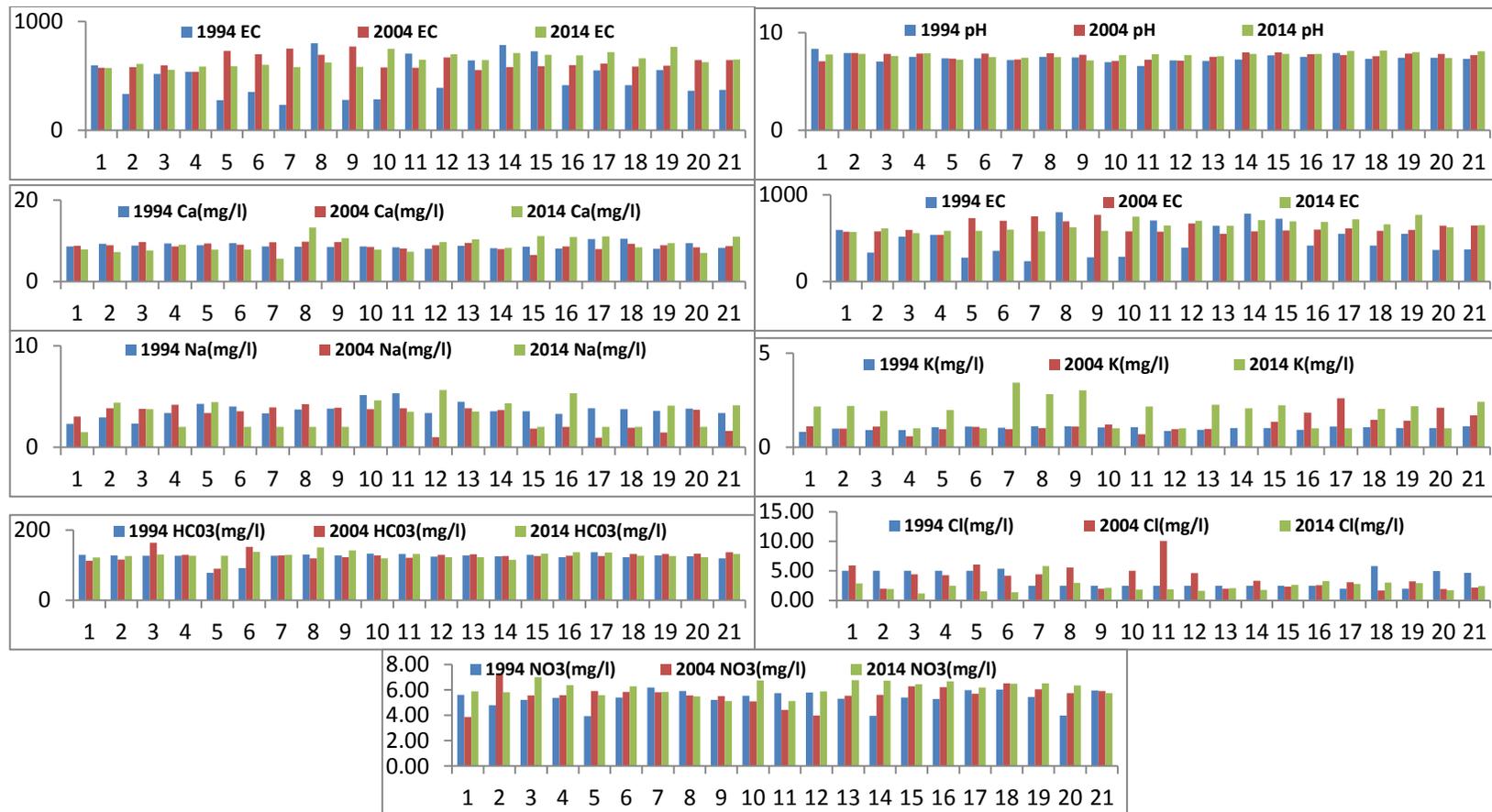


Figure 7.5 Chemical analysis results of groundwater samples for three decades (1994, 2004 and 2014)

7.6 Hydrogeochemical processes in groundwater quality

Hydrogeochemical characterization and assessment of groundwater quality have been a topic of discussion for the past few decades as the attentiveness of groundwater quality protection occurs. Literatures regarding hydrochemical characterization of groundwater and groundwater quality assessment have been carried out and published globally (Vetrimurugan and Elango 2015; Brindha et al. 2014; Bouzourra et al. 2015; Li et al. 2013a, 2014b; Qian et al. 2012; Wu et al. 2014, 2015). Groundwater is considered as the most dependable water resource for basic human needs as it is extensively used for irrigation, drinking and industrial purposes globally, especially in arid and semi-arid areas where rainfall and surface resources are limited (Delgado *et al.*, 2010; Varis 2014). The first step of sustainable water resources management is through understanding the suitability and status of groundwater quality. In recent years, the studies on the hydrochemical characteristics and quality of groundwater are reported worldwide (Currell *et al.*, 2011; Brindha et al. 2014; Li *et al.*, 2014; Mamatha and Rao 2010; Wu *et al.*, 2014). These studies have resulted in the advancement in the field of hydrogeochemistry, making it a useful and decision making tool in water resources management and groundwater pollution regulation. Like South Africa and in the various parts of the globe, several studies have been carried out to evaluate the geochemical characteristics of groundwater (Aghazadeh and Mogaddam 2011; Alexakis 2011; Ahmad and Qadir 2011; Ramesh and Elango 2012) to identify the manmade and geogenic sources affecting groundwater quality. In the study area, agriculture is the main occupation. With this background hydrochemical investigation was carried out to categorize groundwater geochemistry and its irrigation suitability.

7.7 Hydrochemical Facies of groundwater

The geochemical evolution of groundwater may be understood by plotting the concentrations of major cations and anions in the Piper (1944) trilinear diagram. The Geochemist's workbench student Edition software version 12.0 (64-bit) was used to construct the piper diagram. The geochemical evolution of groundwater in the study area was evaluated using the concentrations of major cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (HCO_3^- , CO_3^{2-} , SO_4^{2-} and Cl^-) in meq/L. A Piper diagram has three distinct fields which consists of two fields in triangle shape and one in diamond shape. The diamond shaped field determines the

groundwater types based on the position of the samples plotting. The cations and anions expressed as percentages of total cation & anions and are represented in meq/L. The plot in the right triangle denotes the anion and cations plot on the left side triangle. The piper diagram reveals changes and resemblances among the groundwater samples because those with same origin will incline to plot as same groups (Todd, 2001). The plot (Figure 7.6) shows that 99% of the groundwater samples in the study area fall in the field of Ca-HCO₃ type varied with 1% of groundwater sample falling in the field of Mixed CaMgCl water type. Nethononda *et al.*, 2018 observed similar results on studies conducted in Luvuvhu Catchment of Limpopo Province. The Ca-HCO₃⁻ represents the typical of shallow fresh ground waters.

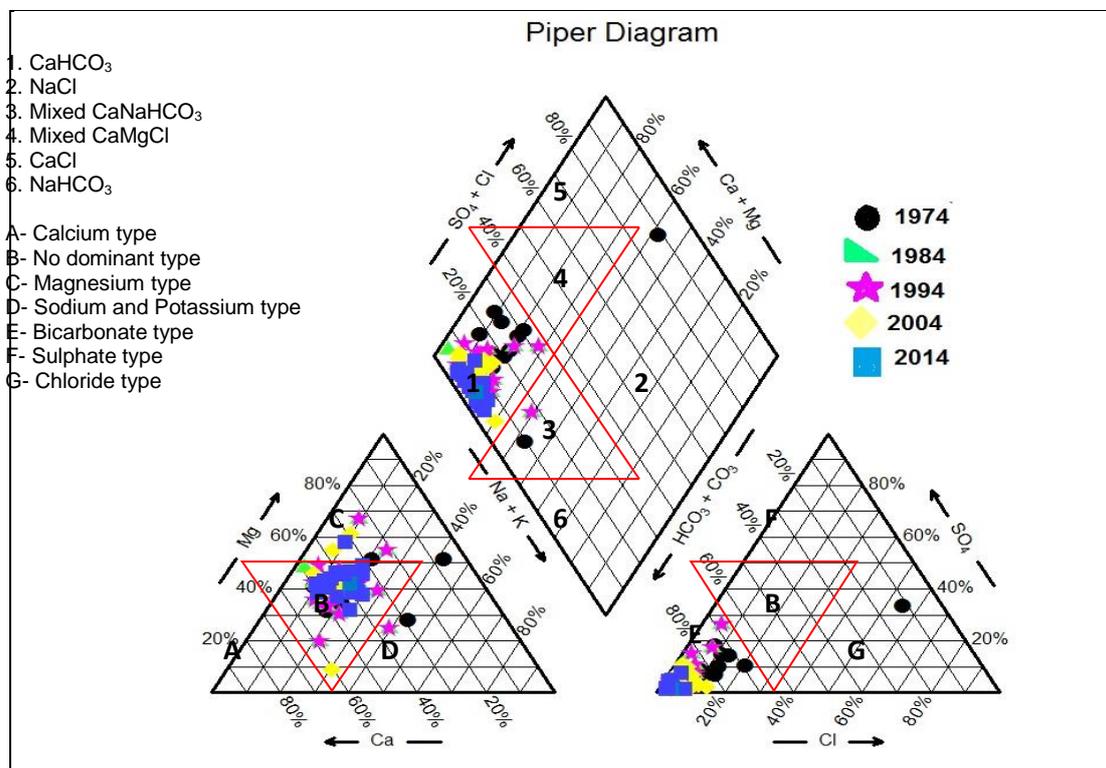


Figure 7.6. Hydrochemical facies of groundwater (Piper 1944)

The groundwater quality in its insitu - state indicates the hydrochemical nature of groundwater aquifers. The Piper trilinear diagram (Piper 1944) helps in comparing and classifying water types. The diamond-shaped field in the piper diagram is classified into six types: (1) Ca-HCO₃; (2) Na-Cl; (3) mixed Ca-Na-HCO₃ (4) mixed Ca-Mg-Cl; (5) Ca-Cl; (6) Na-HCO₃ (Figure 7.6). The groundwater samples of the study area fall into zones 1 clearly indicating a dominance of Ca-HCO₃ type. The plot clearly shows that most of the groundwater samples fall in the alkaline earth metals field (Ca²⁺, Mg²⁺) over the alkaline

metals field (Na^+ , K^+). The plot clearly shows all the samples fall in the zone 1 for all the five years with only one sample of 1974 falls in the mixed zone 4.

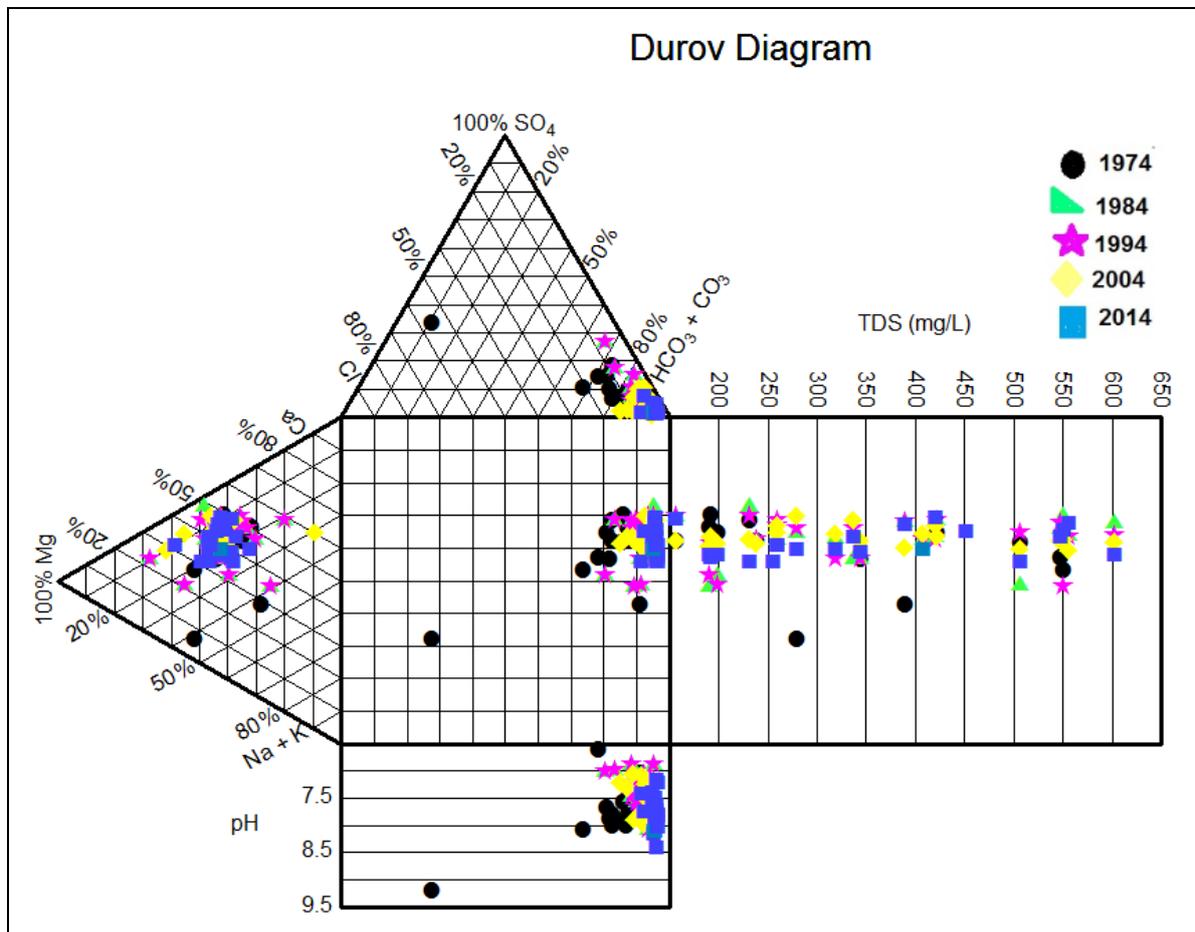


Figure 7.7. Durov plot explains water types and hydrochemical processes

The Durov diagram (Durov 1948) was prepared to understand the hydrogeochemical features of groundwater and as represented in Figure 7.7. Figure 7.7, groundwater samples from different landscapes and aquifers show dissimilar hydrogeochemical characteristics. Figure 7.7 shows that about all groundwater samples of the study area have TDS values of less than 1000 mg/L with bicarbonate as the major anion. Groundwater with TDS greater than 1000 and less than 2000 mg/L (0% samples in the study area) is considered to be brackish water. In case of mixed type of groundwater the concentrations of anions are close with each other similar to brackish water. None of groundwater samples in the study area have TDS content greater than 2000 mg/L with high concentrations of SO_4^{2-} and Na^+ . The Durov diagram (Durov 1948), reveals that groundwater in the study area is mainly of HCO_3 -Ca-Mg. The pH values in the study area ranges from 6.6 to 8.4. The pH of groundwater is generally

influenced by several factors like environmental pollution, variation of inorganic salts in water, human activity and geologic transition.

Figure 7.8 shows that 91% of groundwater samples in the year 1974 to 2014 fall within sub-field 5, indicating that alkaline earths exceeding alkali metals and weak acidic anions exceed strong acidic anions in these water samples. Groundwater for such water is $\text{HCO}_3\text{-Ca-Mg}$ type and has temporary hardness (Chadha, 1999).

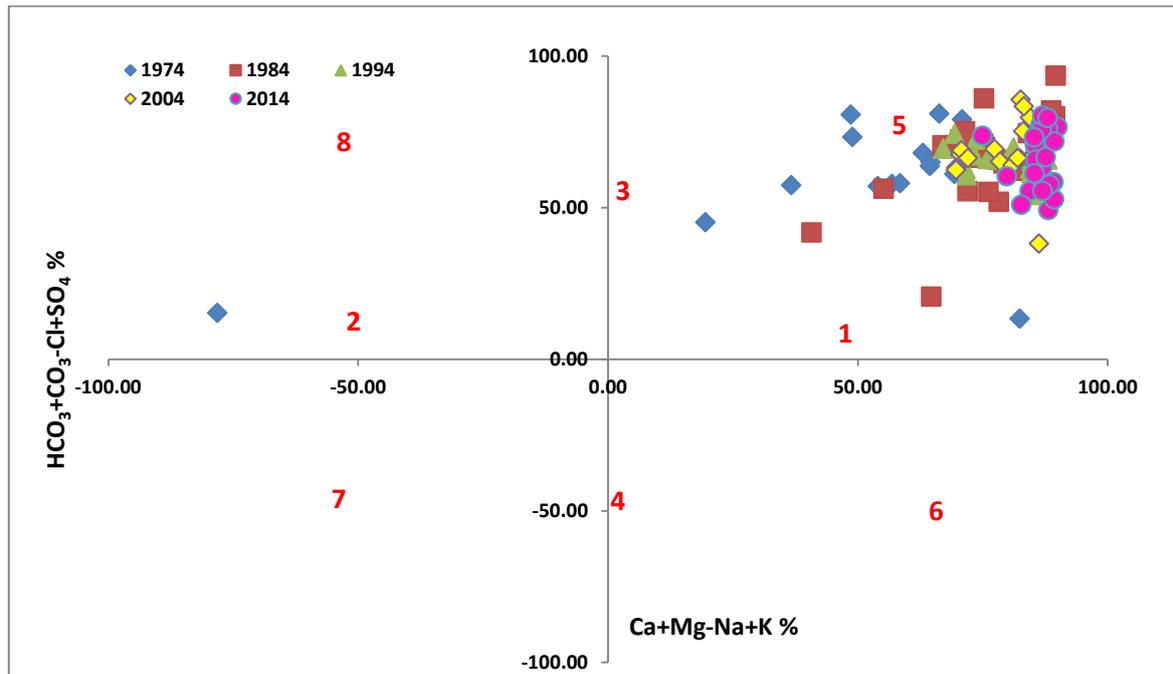


Figure 7.8. Hydrochemical facies of groundwater (Chadha 1999)

The overall effects of natural chemical reactions occurring between the minerals within the aquifers are reflected by hydrogeochemical facies (Varol and Davraz, 2014). The Chadha diagram (Chadha 1999) was used to interpret the hydrogeochemical facies of groundwater in the area of study (Figure 7.8). The Chadha diagram was constructed by plotting the difference in percentage (meq/L) between weak acidic anions ($\text{HCO}_3^- + \text{CO}_3^{2-}$) and strong acidic anions ($\text{Cl}^- + \text{SO}_4^{2-}$) on the Y axis and the difference in percentage (meq/L) between alkaline earths ($\text{Ca}^{2+} + \text{Mg}^{2+}$) and alkali metals ($\text{Na}^+ + \text{K}^+$) on the X axis. The graphical diagram categorizes groundwater into 8 small fields and is as follows: (1) Alkaline earths exceed alkali metals, (2) Alkali metals exceed alkaline earths, (3) Weak acidic anions exceed strong acidic anions, (4) Strong acidic anions exceed weak acidic anions, (5) $\text{HCO}_3\text{-Ca-Mg}$, $\text{HCO}_3\text{-Ca}$ or $\text{HCO}_3\text{-Mg}$ types, (6) $\text{Cl-SO}_4\text{-Ca-Mg}$, Cl-Ca-Mg or $\text{SO}_4\text{-Ca-Mg}$ types (7) $\text{SO}_4\text{-Cl-Na}$, Cl-Na or $\text{SO}_4\text{-Na}$ types, and (8) $\text{HCO}_3\text{-Na}$ type (Chadha, 1999).

Figure 7.8 show that 94% of groundwater samples in 1974, 1984, 1994, 2004 and 2014 fall within sub-field 5. Groundwater for such water is $\text{HCO}_3\text{-Ca-Mg}$, $\text{HCO}_3\text{-Ca}$ or $\text{HCO}_3\text{-Mg}$ types and has temporary hardness (Chadha 1999). About 3% (2% 1974 & 1% 1984) of groundwater samples are falling under sub-field 3 which is an indication that weak acidic anions exceed strong acidic anions in these water samples. In 1974 and 1984, 2% of groundwater samples were falling under sub-field 1 which shows that alkaline earths exceed alkali metals and 1% of 1974 groundwater sample falling within sub-field 2 resulting to an indication of alkali metals exceeding alkaline earths (Chadha 1999). This kind of water generally causes salinity problems for both usage in irrigation and drinking (Chadha, 1999). The hydrochemical facies of groundwater in the sub-field of 5-Ca-Mg- HCO_3 are dominant hydrochemical facies all decades from 1974 to 2014 and this confirms the outcomes of Piper and durov diagrams

7.8 Gibbs Plots/ Dissolution of Minerals

In this study, Gibb's plot was used to determine the processes controlling hydrochemistry of groundwater. The diagram has 3 different fields which has major components such as rock water interaction, precipitation and evaporation (Gibb's, 1970). The scatter plot on a semi-log graph between TDS vs. $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and TDS vs. $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ was used to identify the process responsible for the groundwater chemistry. In the study area (Figure 7.9) samples fall in the centre zone of the plot indicating that rock water interaction is the dominant process in the groundwater hydro chemistry of the study area. Gibbs plots revealed that groundwater in the study area is that of rock water interaction dominance in all decades from 1974 to 2014.

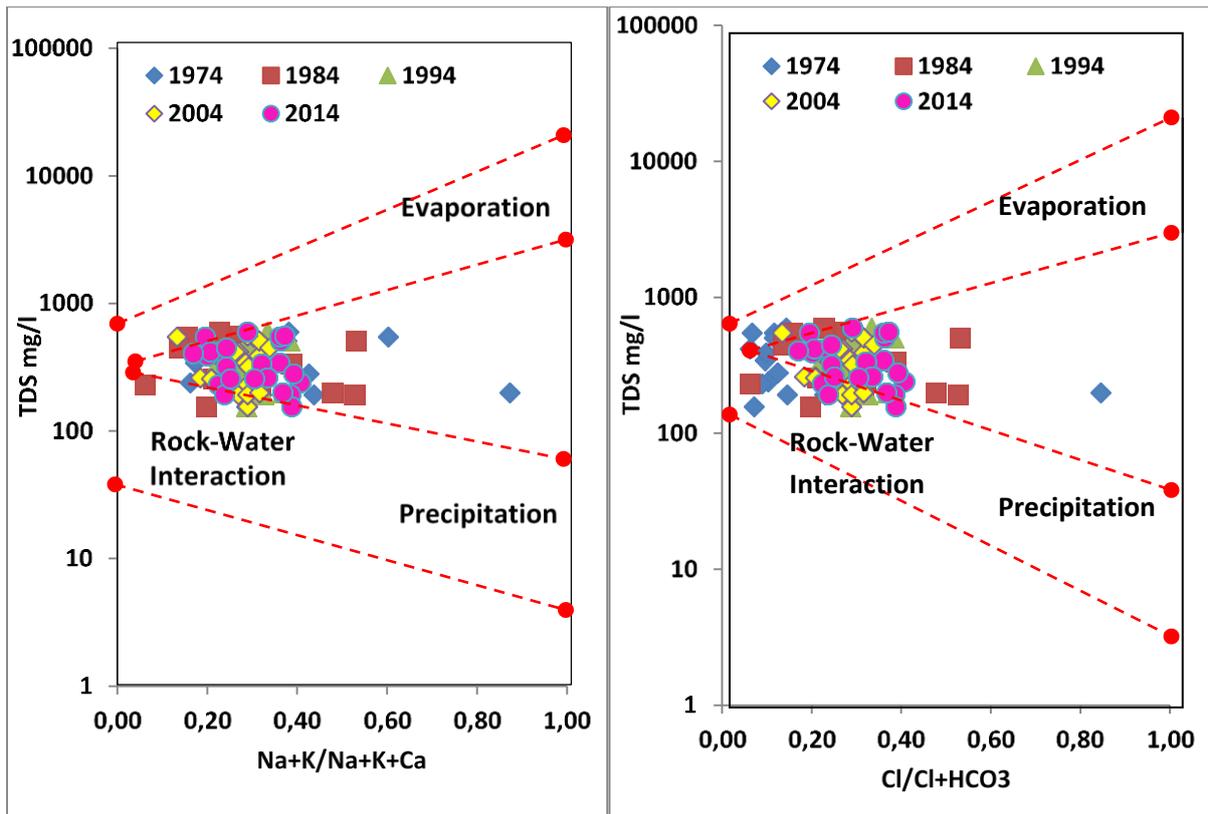


Figure 7.9: Gibbs diagram of groundwater from 1974 to 2014

7.9 Soltan Classification

Groundwater established on Cl, HCO₃ and SO₄ was suggested and categorized by Soltan (1998). The groundwater can be classified as chloride type (Cl <15 meq/L), normal bicarbonate type (HCO₃²⁻ < 7meq/l) and normal sulfate type (SO₄<6 meq/L). The lithology and movement of water influences the water type and concentration of salts in groundwater (Raghunath, 1982). Figure 7.9 showing the scattered distribution of the groundwater samples of the study area on Soltan's classification. The Figure clearly shows that most of the samples during both years fall in normal bicarbonate type followed by normal chloride and sulfate type. Furthermore, Soltan (1998) equation (eq.7.1) was used to evaluate Base Exchange Indices for grouping of groundwater sources.

$$r1 = \frac{Na - Cl}{SO4} \quad 7.1$$

Where r1 denotes the Base Exchange index. Sodium, chloride and sulphate concentration are in meq/L. If r1>1, the groundwater is Na-HCO₃ type whereas r1<1 specifies the groundwater is Na-SO₄. During 1974, 87% of samples have r1<1 and are classified as Na-

SO₄ type water (Figure 7.10a & b). About 13% of samples are Na-HCO₃ type ($r_1 > 1$) (Figure 7.10b) 1974. In 1984, 92% of groundwater samples have $r_1 < 1$ and are classified as Na-SO₄ type water; and about 8% of samples are Na-HCO₃ type ($r_1 > 1$). About 100% of groundwater samples in 1994, 2004 and 2014 have $r_1 < 1$ and are classified as Na-SO₄ type water.

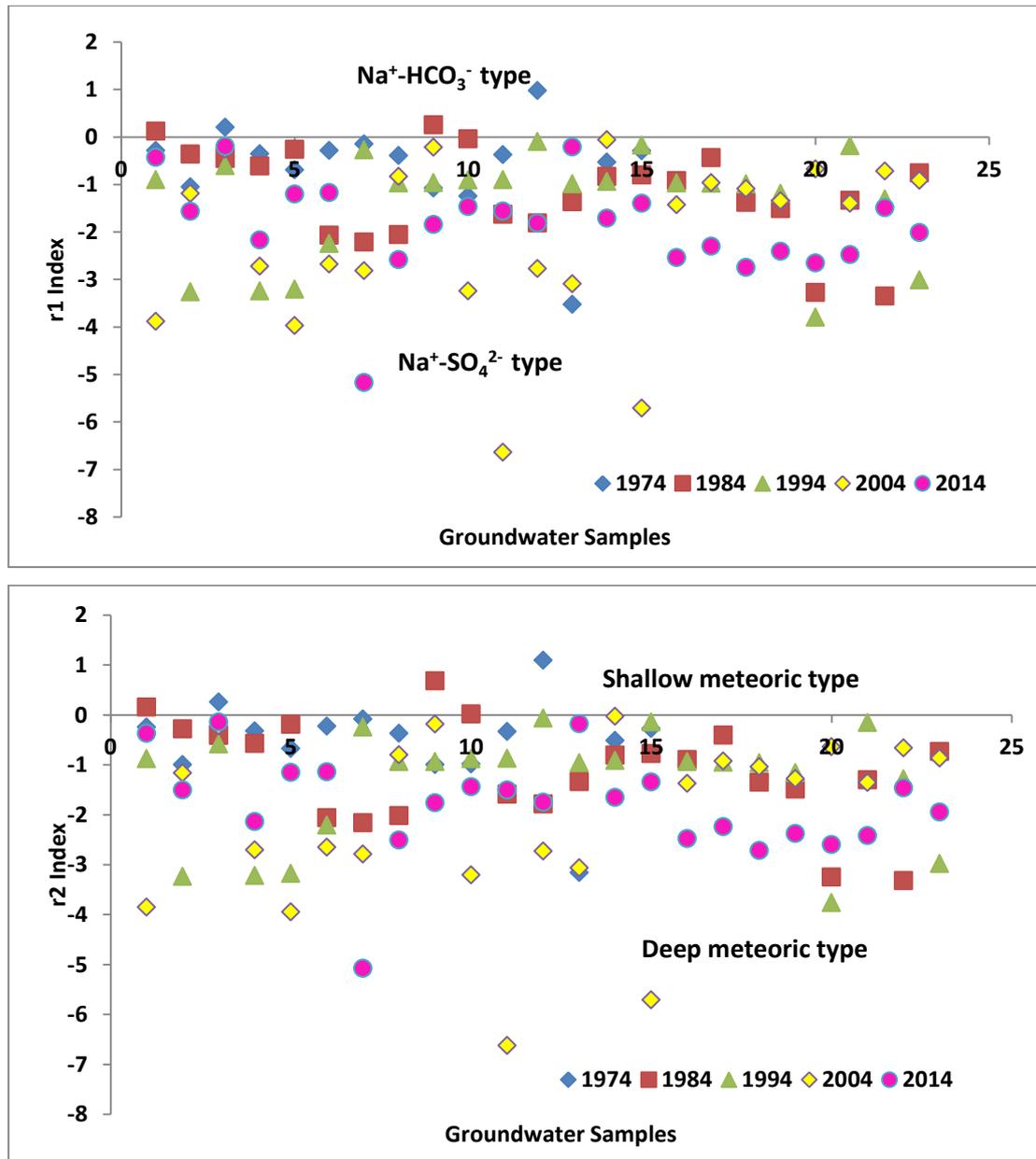


Figure 7.10a: Soltan classification of groundwater samples of the study area

Soltan 1998 categorized the sources of groundwater by meteoric genesis index which can be determined by using equation 7.2

$$r_2 = \frac{Na+K-Cl}{SO_4}$$

7.2

Where r_2 denotes meteoric genesis index, concentration of Na, K, Cl and SO_4 are presented in meq/L. If $r_2 < 1$ then the groundwater is of deep meteoric water type. If $r_2 > 1$, the groundwater can be classified as shallow meteoric water type. Based on meteoric genesis index, 87% of groundwater was deep meteoric water type with 13% being shallow meteoric water type in 1974 and 1984 (Figure 7.10b). Low rainfall environments and abrupt fall in water levels causes deep meteoric type of water (Tamma Rao et al 2013). The studies conducted by Singh *et al.* (2006), Reddy *et al.* (2012), Singh *et al.* (2014) in India shows similar results. About 100% of groundwater was deep meteoric water type in 1994, 2004 and 2014 (Fig 7.10 a & b).

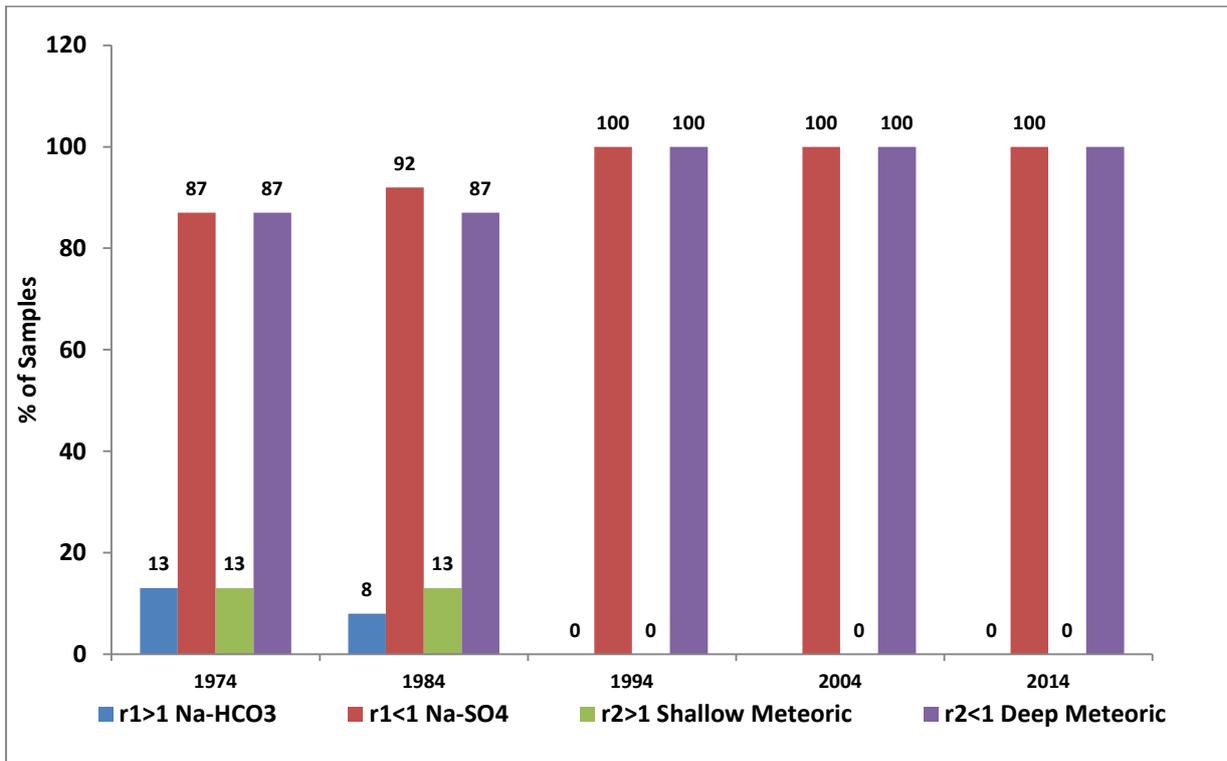


Figure 7.10b: Percentage of groundwater samples on Soltan classification in the study area

7.10 Hydrogeochemical processes

The rock water interaction includes hydrochemical processes such as weathering and dissolution, ion exchange and oxidation-reduction. Hence, it is essential to establish each process in order to determine the major process that controls the concentration of ions within

the rock-water interaction. The several graphical diagrams were established to find the processes and the role of the anthropogenic activities functioning in aquifer region. The study area experiences semi-arid climatic conditions wherein evaporation may affect the chemistry of groundwater. If Na/Cl ratio is nearly equal to one, it may be by halite dissolution for sodium. If Na/Cl ratio >1 then Na gets released due to weathering of silicate reactions (Mayback, 1987). In the study region, Na/Cl ratio of groundwater samples range from a value of 0.03 to 2.5 in 1974; 0.6 to 4.9 in 1984; 0.5 to 2.1 in 1994; 0.2 to 1.9 in 2004 and 0.3 to 3.5 in 2014 (Table 7.1). During 1974, 27% of groundwater samples have Na/Cl ratio <1 which means it is liable for halite dissolution for sodium while 73% of groundwater samples have Na/Cl ratio >1 and is usually deduced as Na released from weathering of silicate reactions. In 1974, 61% of groundwater samples have Na/Cl ratio <1 while 39% of groundwater samples have Na/Cl ratio >1 . Table 7.1 also shows that 39 of groundwater sample have Na/Cl ratio <1 whereas 61% of groundwater samples have Na/Cl ratio >1 in 1994. About 70% of groundwater samples in 2004 have Na/Cl ratio <1 as 30% of groundwater samples have Na/Cl ratio >1 . Groundwater samples of about 39% in the study area have Na/Cl ratio <1 which indicates that it is liable for halite dissolution for sodium while 61% of groundwater samples have Na/Cl ratio >1 in 2014.

Table 7.1: Na/Cl ratio in the study area from 1974 to 2014

Decades	Range of Na/Cl ration			
	Minimum	Maximum	Na/Cl ratio <1 (%)	Na/Cl ratio >1 (%)
1974	0,03	2,5	27	73
1984	0,6	5,0	61	39
1994	0,5	2,1	39	61
2004	0,2	1,9	70	30
2014	0,3	3,5	39	61

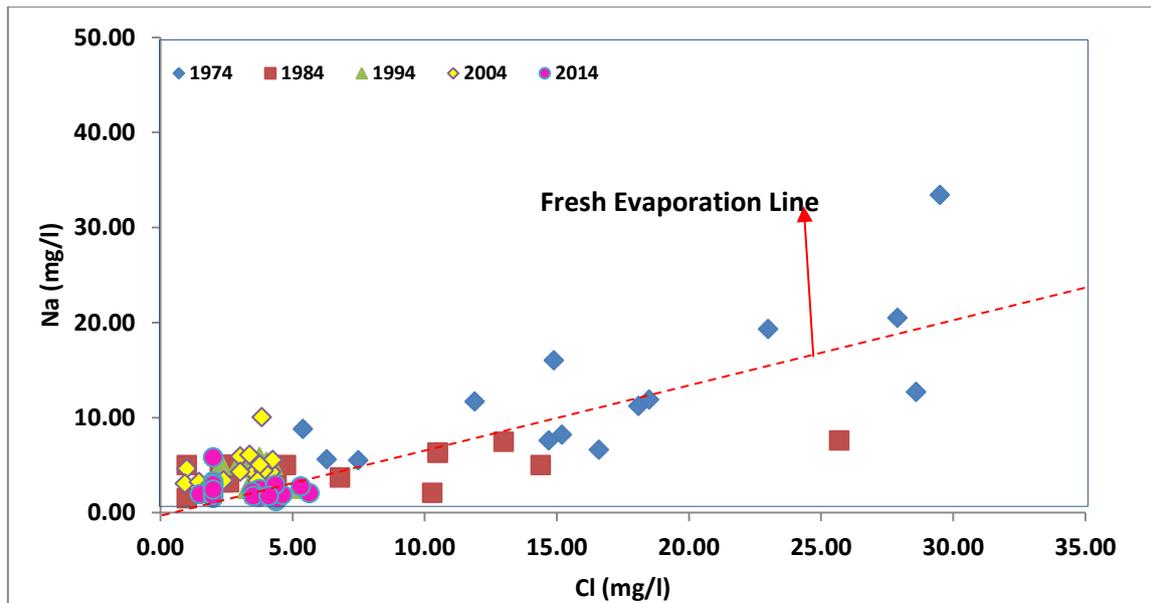
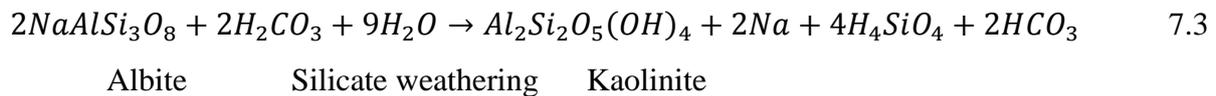


Figure 7.11: Plot of Na vs Cl compared with freshwater evaporation line

The Na vs Cl plot is used to understand the role of evaporation processes on groundwater in the study area. Figure 7.11 for Na vs Cl plot indicates that most groundwater samples in the study area are within the freshwater evaporation line. The plot (Figure 7.11) also shows that few groundwater samples are deviated from freshwater evaporation line, and 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.

In a groundwater system where weathering either carbonate or silicate and dissolution of halite/gypsum and precipitation are the collective mechanism (Elango and Kannan, 2007), graphical representation in form of Na+K vs total cations can be used to understand the influence to the cation concentration to groundwater (Stallard and Edmond, 1983; Elango and Kannan, 2007). The weathering of silicates processes can clearly be represented by the three plots of calcium + magnesium vs bicarbonate, sodium + potassium vs total cations, calcium + magnesium vs total cation and calcium/sodium vs bicarbonate/sodium. Figure 7.12 of Ca + Mg vs HCO₃ illustrates that most groundwater samples lie above to 1:1equiline in 1974, 1984, 1994, 2004 and 2014 with few samples of 1984, 2004 and 2014 lying below 1:1equiline. This indicates that the excess of Ca + Mg over HCO₃ is likely originated from carbonate mineral weathering. Similarly, Ca + Mg vs total cation (TC) plot shows that all groundwater sample points lie above the 1:1line. Figure 7.12 of Na + K vs TC shows that samples are extremely deviated from 1:1line, therefore the contribution of Na + K to TC is less weigh

against the Ca + Mg. The Ca/Na is plotted against HCO₃/Na in order to know the role of silicate and carbonate minerals weathering on groundwater as shown in Figure 7.12. This plot demonstrates that silicate weathering is basic mineral sources followed by the carbonate minerals dissolution. This resultant silicate weathering was described by the resulting weathering reaction



The pyroxene, amphibole and calcic feldspar which are present in basic igneous rocks, are easily weathered and governed by the water chemistry. Jacks (1973); Bartarya (1993); Rajesh et al (2012) discovered similar observations in the studies conducted worldwide.

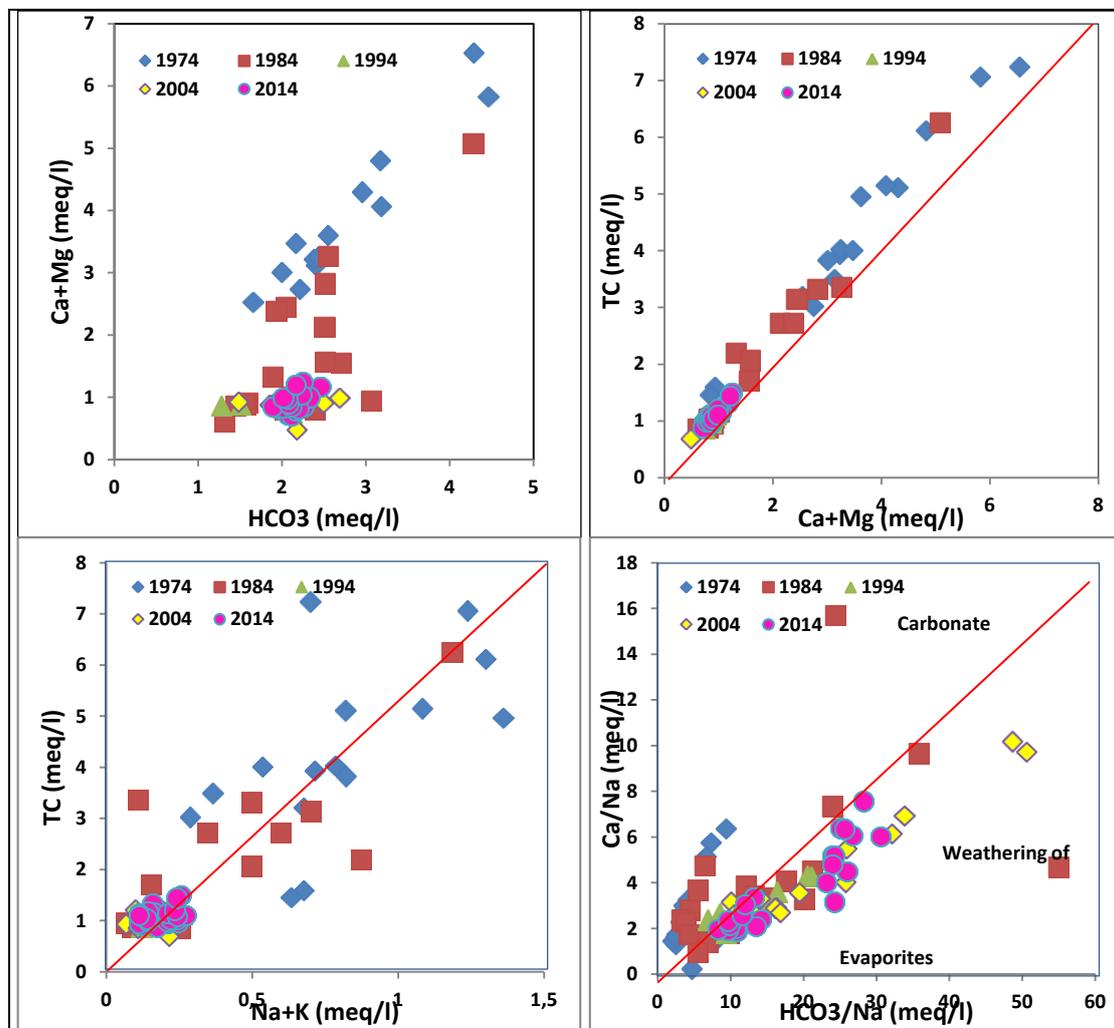


Figure 7.12: Plot of Ca +Mg vs HCO₃, Ca +Mg vs TC, Na +K vs TC and Ca/Na vs HCO₃/Na explains mineral weathering

Calcium and sulfate in groundwater systems are likely to originate from gypsum/ anhydrite dissolution. If calcium and sulfate on groundwater is from gypsum/anhydrite dissolution, therefore the $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio should be 1:1 (Da and Kaur, 2001). Consequently, if calcium and bicarbonate originated from calcite mineral then the ratio of dissolved Ca and HCO_3^- in groundwater should be 1:2, but if is from dolomite weathering, then it should be 1:4 (Subramani et al., 2010). The mean contribution of Ca and Mg as the dominant cations is 87% in 1974 and 22% in 1984 (Figure 7.12). HCO_3^- is the most dominant anion compared to other anions while mean contribution of HCO_3^- is 78% in 1984, 88% in 1994, 72% in 2004 and 64% in 2014.

Figure 7.13a of Ca vs HCO_3^- illustrates that water with less mineralized are plotted close to line whereas water with high mineralized are deviated from the line. Calcite dissolution is one of the main processes in the waters with low mineralisation. Similarly, calcium against sulphate (Fig 7.13a) plot shows that all samples fall below the 1:1 line and this shows enrichment of calcium over sulphate. This result reveals that dissolution of gypsum is not controlling groundwater chemistry of the study area. The source of calcium and magnesium in groundwater is deduced from the $\text{Ca} + \text{Mg}/\text{HCO}_3^-$ ratio. While ratio of $\text{Ca} + \text{Mg}/\text{HCO}_3^-$ increases with salinity, Calcium and magnesium are excess to a solution at a higher rate than bicarbonate. Figure 7.13c of $\text{Ca} + \text{Mg}/\text{HCO}_3^-$ vs Cl illustrate that this ratio is likely to increase with Cl in all decades.

If calcium and magnesium ions are basically derived from the dissolution of carbonate in the groundwater and the minerals get weathered (pyroxene and amphibole) and the ratio is equal to 0.5 (Sami, 1992) as the weathering reactions are as follows

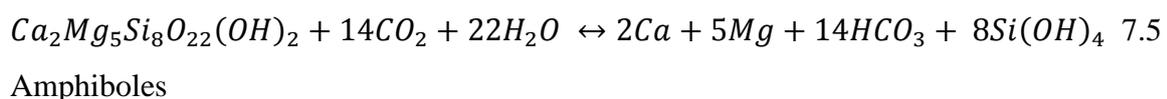
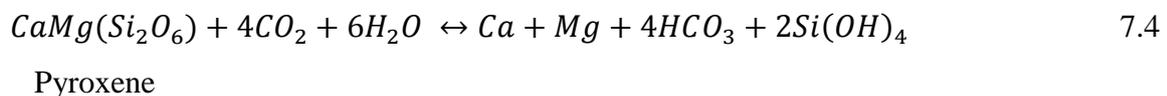


Figure 7.13a illustrate that the higher ratio ($\text{Ca} + \text{Mg}/\text{HCO}_3^-$) ratio (>1) indicates that Ca+Mg added to the water from other sources likely ion exchange reactions (Rajmohan and Elango 2004).

The molar ratio of calcium against magnesium can be used to verify the calcite and dolomite dissolution in groundwater. The molar ratio is near to 1 and is an indication of dolomite rock dissolution whereas if the ratio is greater than 1 it suggested that dissolution of calcite from rocks (Mayo and Loucks, 1995). If the calcium/magnesium ratio is greater than 2 it may be due to silicate mineral dissolution into the groundwater (Katz et al. 1997). Figure 7.13 of Ca/Mg plot shows most of samples in the study area have $\text{Ca/Mg} < 2$ ratio. Sample points fall between 1 and 2 indicate the dissolution of calcite and in the study area. This Figure also shows that 47%, 30%, 39%, 26%, 48% of groundwater samples in 1974, 1984, 1994, 2004 and 2014 respectively have Ca/Mg ratio of less than 1, this clearly indicates that dissolution of dolomite for the presence of calcium and magnesium in the study area. The plot of Ca/Mg ratio also show that 53%, 69%, 74% and 52% of groundwater samples have molar ratio of equal to or greater than 1 of respective decades from 1974 to 2014. This clearly indicates that dissolution of dolomite mineral is not responsible for the occurrence of calcium and magnesium in the study area. About 1% of groundwater sample in 1984 falls above Ca/Mg ratio of 2. This indicates the impact of silicate minerals in the groundwater. Rajmohan and Elango (2004); Rajesh et al (2012); Vetrimurugan et al. (2013); Varol and Davraz (2014) detected related observations in studies conducted globally.

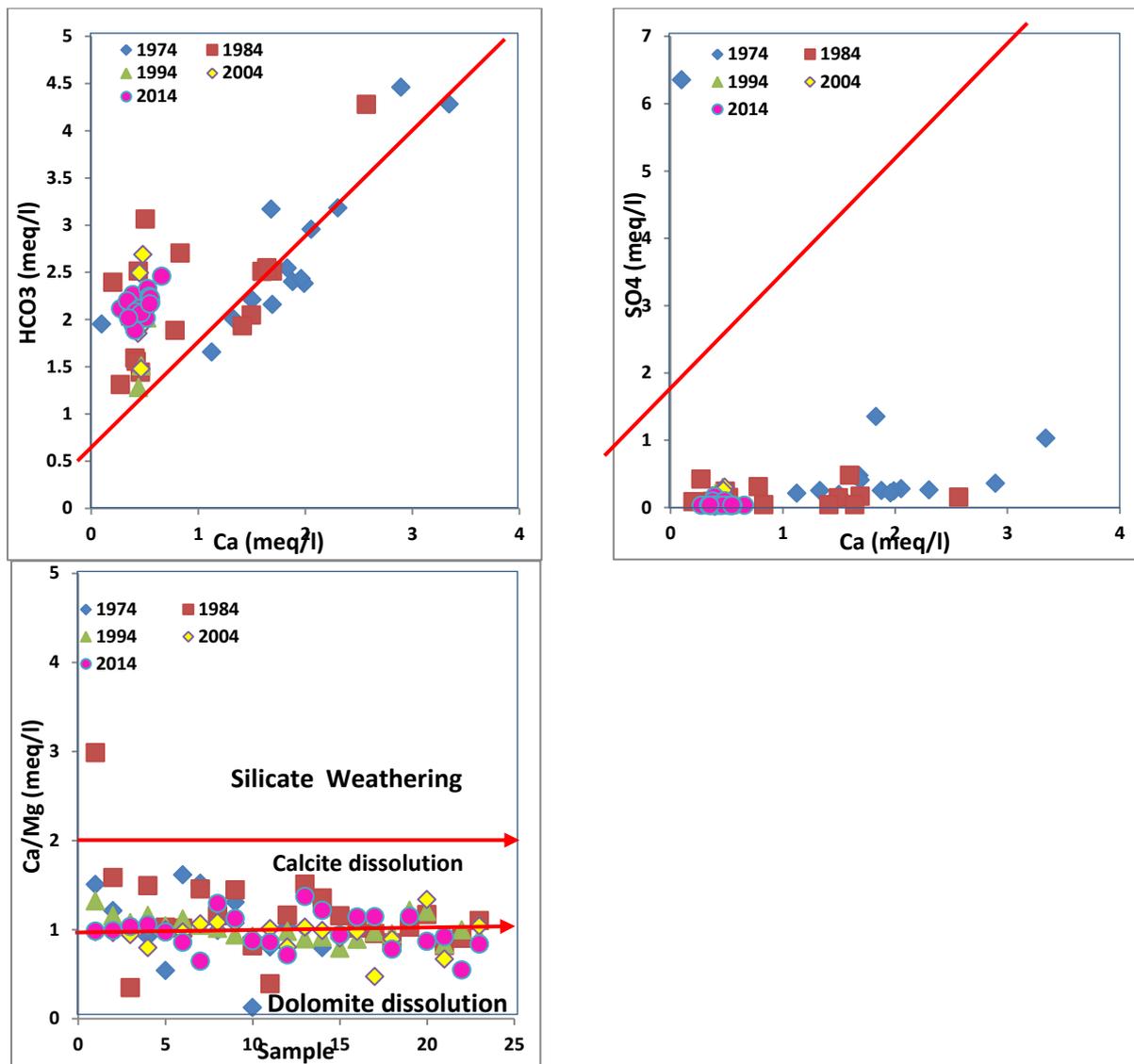
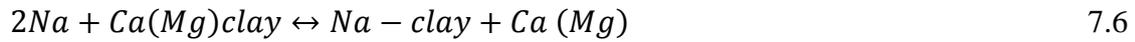


Figure 7.13 : Plot of (a) Ca vs HCO₃; (b) Ca vs SO₄; (c) Ca +Mg/HCO₃ vs Cl; (d) Sample location vs Ca/Mg

Ion exchange Process

Ion exchange process can occur as normal or reverse. Ion exchange is an important hydrogeochemical processes that has main influence on the chemistry of groundwater. A graphical plot of calcium + magnesium vs sulphate + bicarbonate clearly indicates that samples plotted close to the 1:1 line. This clearly infers this could be due to the dissolution of dolomite, gypsum and calcite. A plot for calcium + magnesium against sulphate & bicarbonate was used to identify ion exchange process. Further analysis of the plot shows that if the data points fall on the left side it is mainly due to excess sulphate and bicarbonate. If the groundwater sampling points fall in the right side, it is mainly due to the excess calcium and

magnesium and it is reverse ion exchange. This can be described using the following equation:



The Ca+Mg vs SO₄+HCO₃ Plot for five decades from 1974 to 2014 specifies that 16% of groundwater sample points are located on the left side of plot due to excess SO₄²⁻+HCO₃⁻ and this demonstrates that the normal ion exchange occurs while 84% of groundwater sample points are located on the right side of the plot due to excess Ca²⁺+Mg²⁺ and this shows that reverse ion exchange is the process (Figure 7.14a). This results show that excess Ca+Mg indicates reverse ion exchange processes while addition of HCO₃+SO₄ over Ca+Mg signifies the loss of Ca+Mg by cation ion exchange.

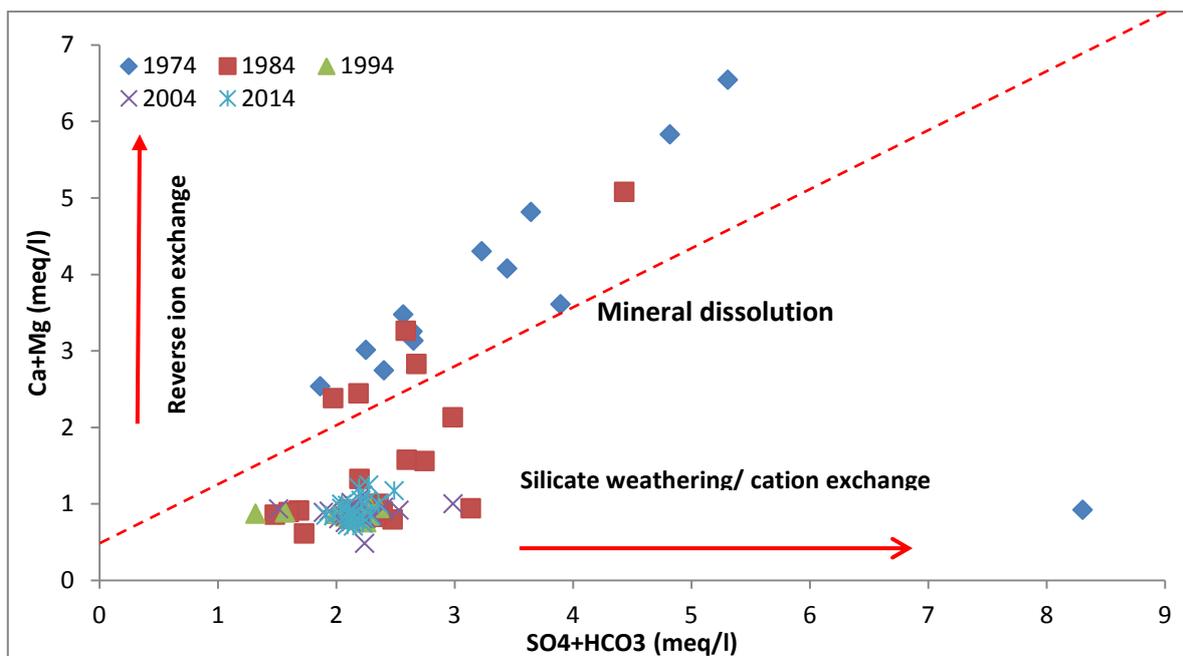


Figure 7.14a: Ca+ Mg vs SO₄+HCO₃

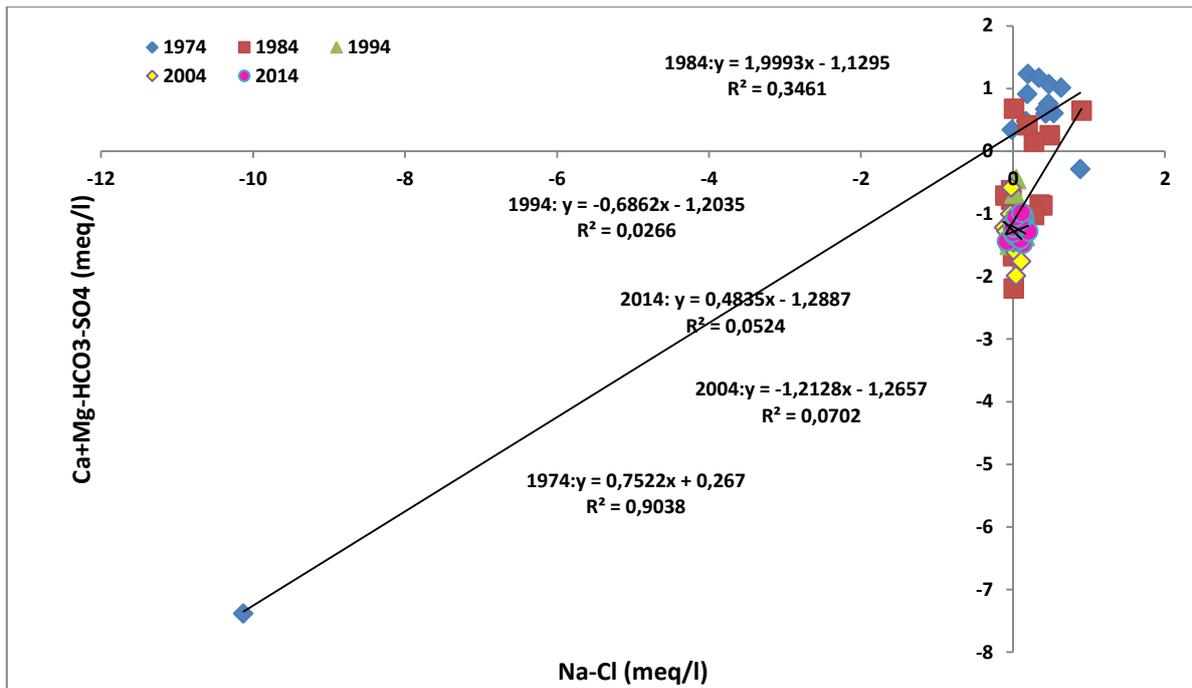


Figure 7.14b: Ca+ Mg-HCO₃-SO₄ vs Na-Cl

The plot of Na-Cl vs Ca+Mg-HCO₃-SO₄ also support the dominant of reverse ion exchange followed by normal ion exchange process in the study area. Groundwater demonstrates a trend line with a slope of -1 when ion exchange is the dominant processes in the area. Figure 7.14b shows that groundwater samples in 1974 have a trend line with a slope of 0.75 and a strong correlation of R²=0.9. During 1984, groundwater samples had a trend line with a slope of 1.9 with a strong correlation of R²=0.3 while 1994, 2004 and 2014 decades had weak correlation of R²=0.02, R²=0.04, R²=0.05 respectively. This observation confirms the role of ion exchange reactions in the aquifer and related results were observed globally by Rajmohan et al 2017; Li et al 2016.

Figure 7.14c of Ca+ Mg vs Cl reveals that Ca and Mg are increase with increasing Cl. The positive trend between Ca+Mg and Cl suggests that Ca+Mg is added to the aquifer while increasing salinity by ion exchange reactions, especially reverse ion exchange reactions.

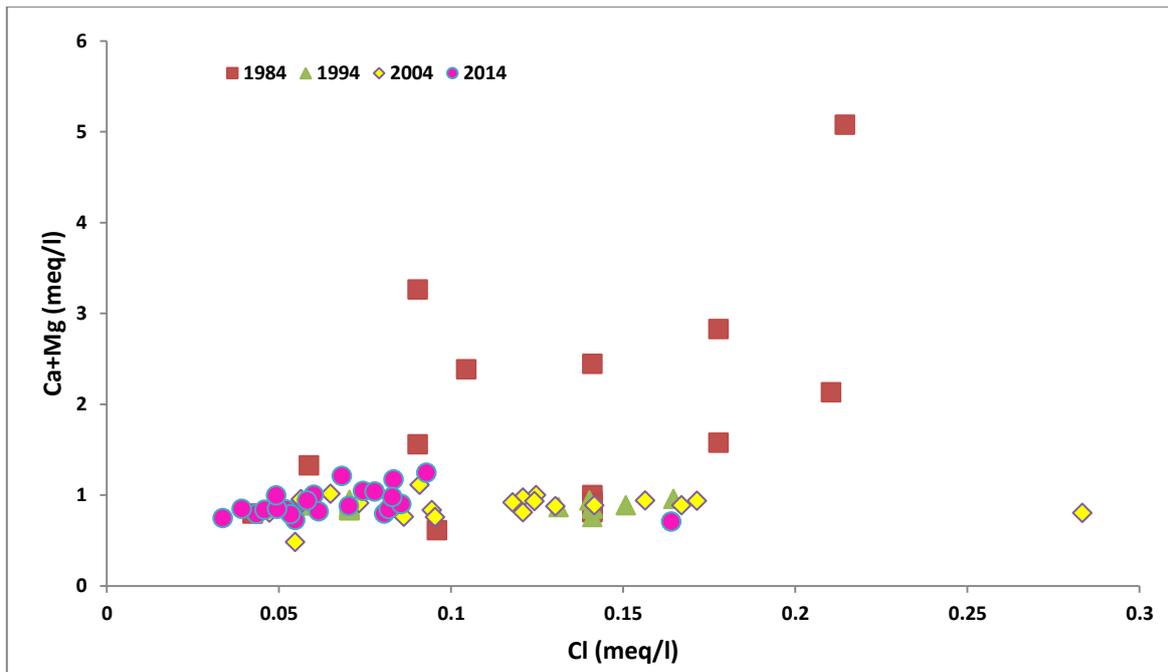


Figure 7.14c: Relation between Ca+ Mg and Cl

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

$$CAI\ 1 = \frac{Cl - Na + K}{Cl} \quad 7.7$$

$$CAI\ 2 = \frac{Cl - Na + K}{HCO_3 + SO_4 + CO_3 + NO_3} \quad 8.8$$

The negative values define cation exchange whereas positive values express reverse ion exchange. Figure 7.14d illustrates that 96% of samples have positive values irrespective of year. During 1974 and 1984, only 1% shows negative values, and 2% of samples in 2004 also display a negative value. Consequently, Figure 7.14d confirm the contribution of cation exchange reactions on water chemistry in the study region.

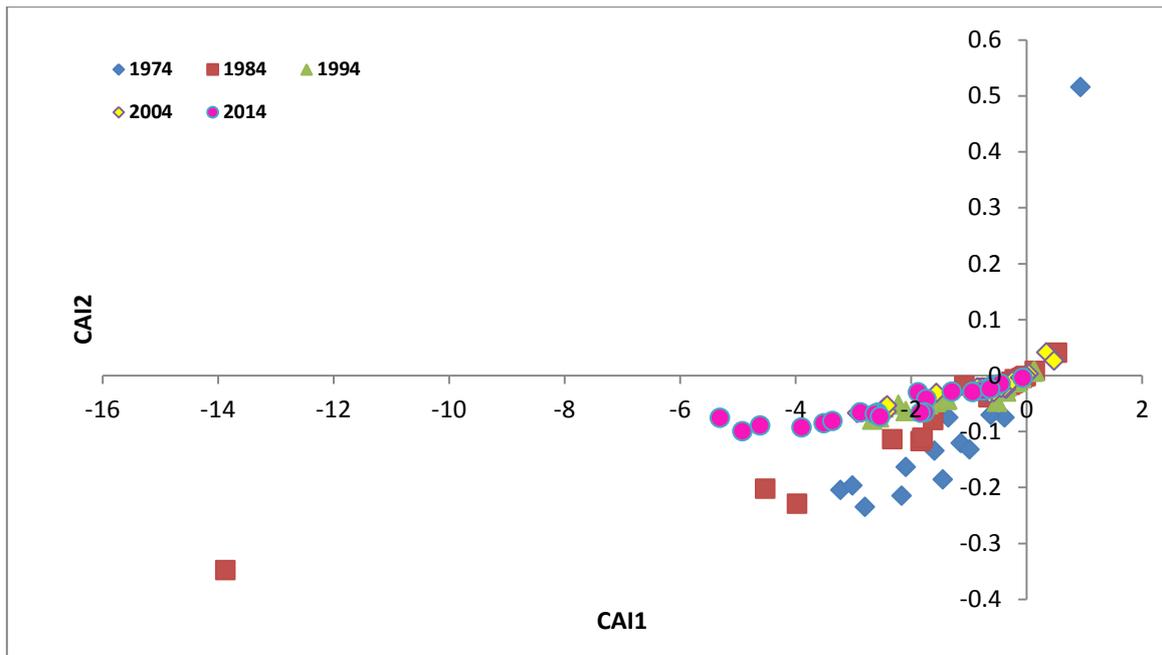


Figure 7.14d. Plot of CAI1 Vs CAI2 from 1974 to 2014

7.11 Anthropogenic Activities

Groundwater quality varies due to manmade activity. Involvement of too many factors and uncertainties makes a complex process that is problematic to infer. As nitrate is widely accepted as a contaminant from manmade activities and from fertilizer usage, its relations with physio-chemical index were identified to infer the effects on human activities on groundwater quality (Marghade *et al.*, 2012; Li *et al.*, 2016).

The area of study is an agricultural region and the major ion concentration in groundwater can be altered by agricultural practices such as application of fertilizer. According to field study, wheat and maize are main types of crops practiced; the use of fertilizer and increase in the resistance of crops is a known exercise, and this cause to enrich the concentrations of K^+ , Cl^- , and NO_3^- in groundwater. In order to understand the effect of manmade activities on groundwater, nitrate was plotted against chloride (Figure 7.15a). Figure 7.15a clearly shows strong correlation and verifies the role of manmade activities (Li *et al.*, 2016).

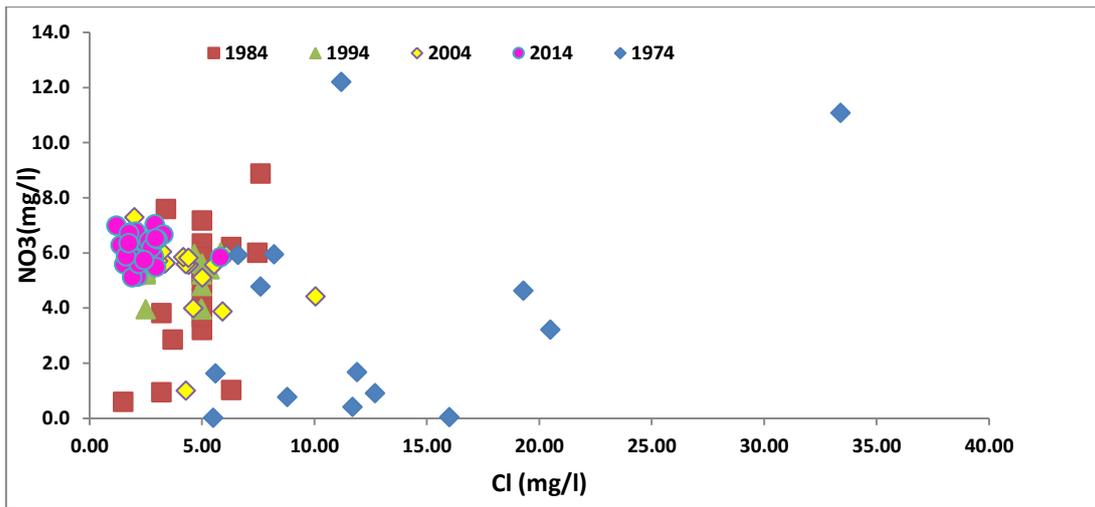


Figure 7.15a: NO₃ vs Cl

NO₃, Cl and SO₄ are mainly derived from anthropogenic activities. SO₄ vs Cl Plot in Figure 7.15b shows strong correlation between them during all decades from 1974 to 2014. The study area was intensively irrigated with fertilizers and hence, irrigation return flow and fertilizers affected the groundwater quality and responsible for high NO₃ in groundwater.

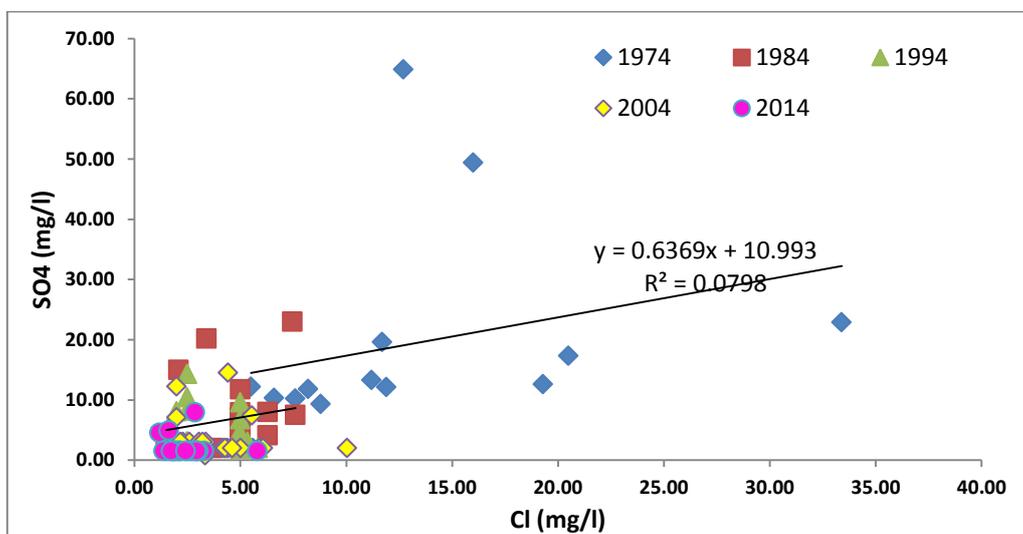


Figure 7.15b: Cl vs SO₄

Nitrate concentration in groundwater

Groundwater pollution due to high concentration of nitrate is rapidly increasing throughout the world due to the various agricultural practices. High nitrate concentration in groundwater has caused several medical disorders like the neoplastic changes in stomach & stomach cancer (Xu et al 1992). In this study an attempt was made to create a connection between

nitrate and other constituents present in the groundwater of the study area. Figure 7.16a shows the relationship diagram between nitrate and five major ion and EC for last three decades from 1994 to 2014. The relationship diagram was developed only for those parameters which fall in the nitrate zone and which have strong correlation. Weak or negative correlated parameter were omitted. The relationship between nitrate vs major ions (Ca, Na, HCO_3 , K and Mg) and EC are positive. Nitrate shows strong bonding with positive correlation with all the six parameters.

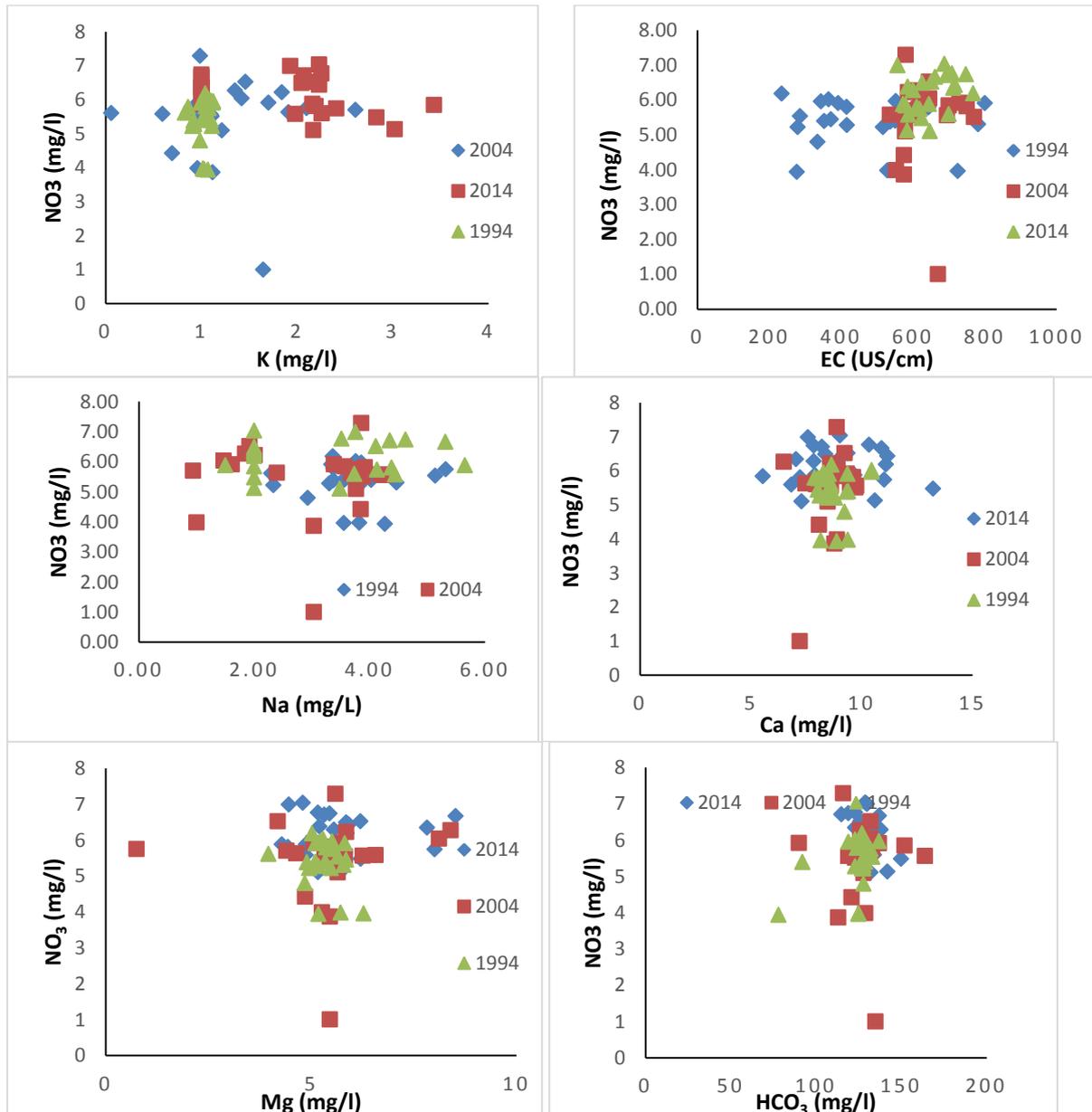


Figure 7.16a Relationship diagram between nitrate and other constituents

Correlation diagram between nitrate and minor ions like ammonia, silicate, phosphate and fluoride was plotted (Figure 7.16b) to understand its strong relationship for five decades from 1974 to 2014. Silicate and ammonia relationship with nitrate shows increase in silicate & ammonia values with lower nitrate values. Whereas the phosphate and fluoride against nitrate shows a reverse correlation i.e., increase in nitrate values against the low values of fluoride and phosphate.

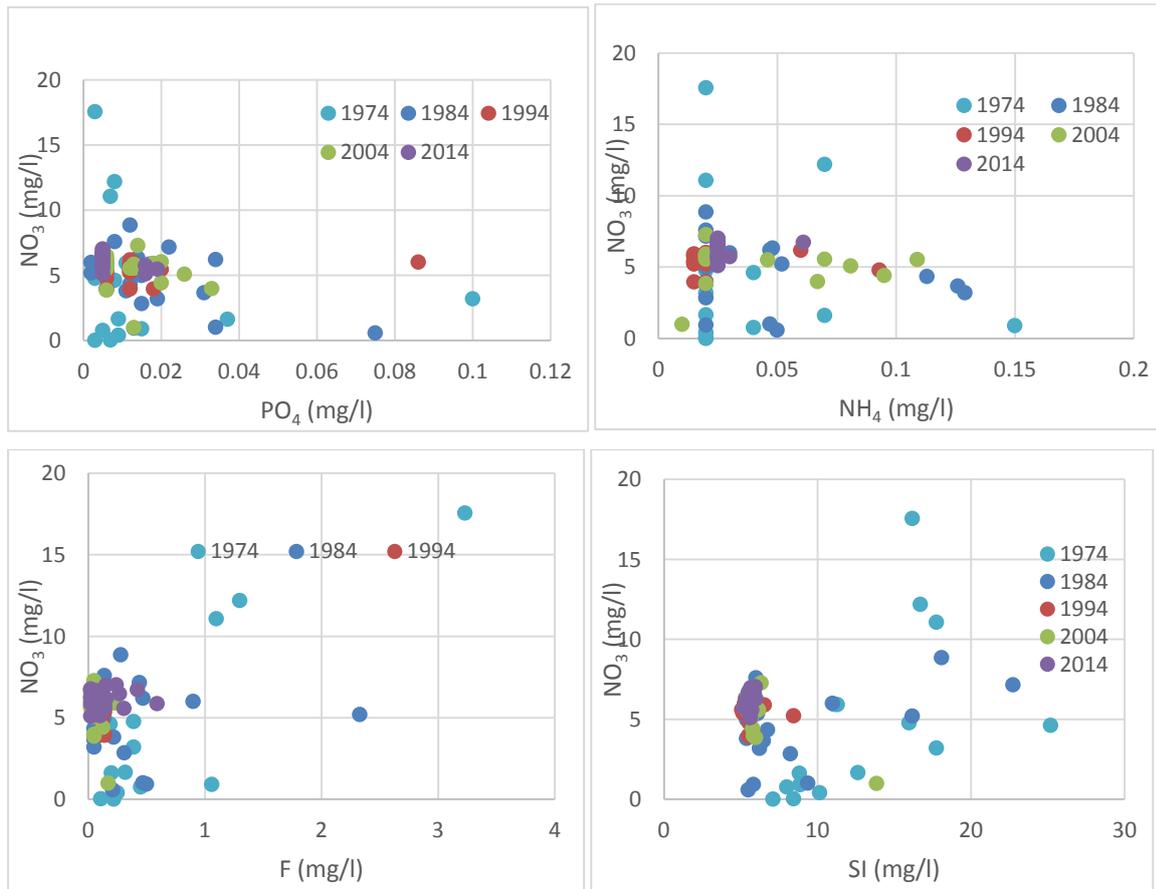


Figure 7.16b Relationship diagram between nitrate and minor ions

7.12 Long term Groundwater quality criteria for Irrigation purposes

The significant parameters that affect the quality of water for irrigation usability are percent sodium (%Na), sodium absorption ratio (SAR), Kelly's ratio (KR), permeability index (PI), and Hazardous Magnesium ratio (HMR). Sodium Absorption Ratio (SAR) is usually used to represent the relative movement of Na⁺ ions in the exchange processes with the soil medium. It is a very important factor for understanding the permeability of soil. Higher sodium

concentration lowers the permeability of the soil. SAR is usually determined by using the equation

In the study area, the SAR value ranged from 0.22 to 0.49 meq/L with a mean value of 0.34 meq/L (Table 7.1). All the samples were within safe limits (<10). All the samples of 1994, 2004 and 2014 fall in the C1 S1 and C2 S1 are considered as good quality water for irrigation (Figure.7.17).

Sodium Percent (Na%) is one of the important parameter for classification of water for irrigation purposes. The presence of excess sodium in groundwater usually lowers the permeability of the soil and also hinders the plant growth. The sodium percentage (Na%) is calculated using the formula.

In the study area, the observed value of ranged from 4.82 (1994) to 25.12 (2004) meq/L with an average value of 15.04 meq/L (Table.7.1). All the samples fall in the range of 20-40 and hence are categorized as good. Further Na% is plotted against the EC values representing through the Wilcox diagram (Figure.7.18) clearly shows that most of the samples fall in the zone of excellent to good. Only Few samples fall in good to permissible zone

Permeability index (PI) is used for assessing the groundwater suitability of water for irrigation purposes. Long term use and reuse of water for irrigation purpose leads to influence of Na, Ca, Mg and HCO_3 on the soil and thereby reduces the permeability of the soil property Doneen (1964). Permeability index is calculated using the formula

In the study area, the Permeability Index values ranged from 15.41 to 90.22 meq/L (Table 7.1) with an average value of 59.79 meq/l.

Doneen model classification of irrigation waters into three classes based on the Permeability Index for the study area is represented in (Figure 7.19). 93% of the samples of the study area belong to class II wherein there is 75% of maximum permeability. 7% of the samples of the study area fall in Class III where there is only 25% of maximum permeability.

Kelly's ratio (KR) is used for classifying the irrigation water quality based on the hazardous effects of sodium. Kelly (1951) ratio can be calculated using the formula.

The water with Kelly's ratio above 1.0 indicates excess of sodium in water and is not suitable for irrigation and the ratio less than 1.0 is suitable for irrigation. Kelly's ratio in the study area ranged between 0.04 and 0.33 meq/L (Table 7.1) with an average value of 0.15 meq/l.

100% of water samples of the study area have KR values less than 1.0 and were found suitable for irrigation.

Magnesium Hazard ratio (MHR) is another indicator used to classify the irrigation water suitability. In general Calcium and Magnesium maintain equilibrium in most water and in those equilibrium conditions magnesium in water will unfavorably impact the crop output (Nagaraju et al 2006).

Magnesium Hazard ratio greater than 50 percent is considered to be unsuitable for irrigation purposes. In the study area MHR values of waters ranges between 12.82 to 68.07meq/L(Table 7.1) with an average value of 51.34 meq/l. 89% of the water samples in the study area have MHR values less than 50 and are found to be suitable for irrigation purposes. About 11% of the samples of the study area have MHR values greater than 50 hence they are unsuitable for irrigation.

Table.7.1. Minimum, Maximum, Average ranges for Irrigation indices.

Year	Ranges	MHR	Na%	KI	PI	SAR
1994	MINIMUM	43.13453	10.70397	0.119871	49.34734	0.220584
	MAXIMUM	55.91599	21.01604	0.26608	61.45249	0.496135
	AVERAGE	49.94759	15.3043	0.181547	54.02235	0.340201
	ST.DEV	3.203954	2.302724	0.032696	2.869701	0.062976
2004	MINIMUM	12.82708	4.727583	0.049622	15.8984	0.090552
	MAXIMUM	68.07617	25.12785	0.33561	90.22581	0.384885
	AVERAGE	49.92358	12.9339	0.151959	59.06824	0.28027
	ST.DEV	9.446832	4.813884	0.064648	14.41383	0.09402
2014	MINIMUM	42.19517	6.917858	0.07432	41.77001	0.14632
	MAXIMUM	64.69347	22.72444	0.29407	81.10312	0.537663
	AVERAGE	51.34161	13.16979	0.155511	59.79558	0.292099
	ST.DEV	5.458092	5.065902	0.068838	10.38162	0.121338

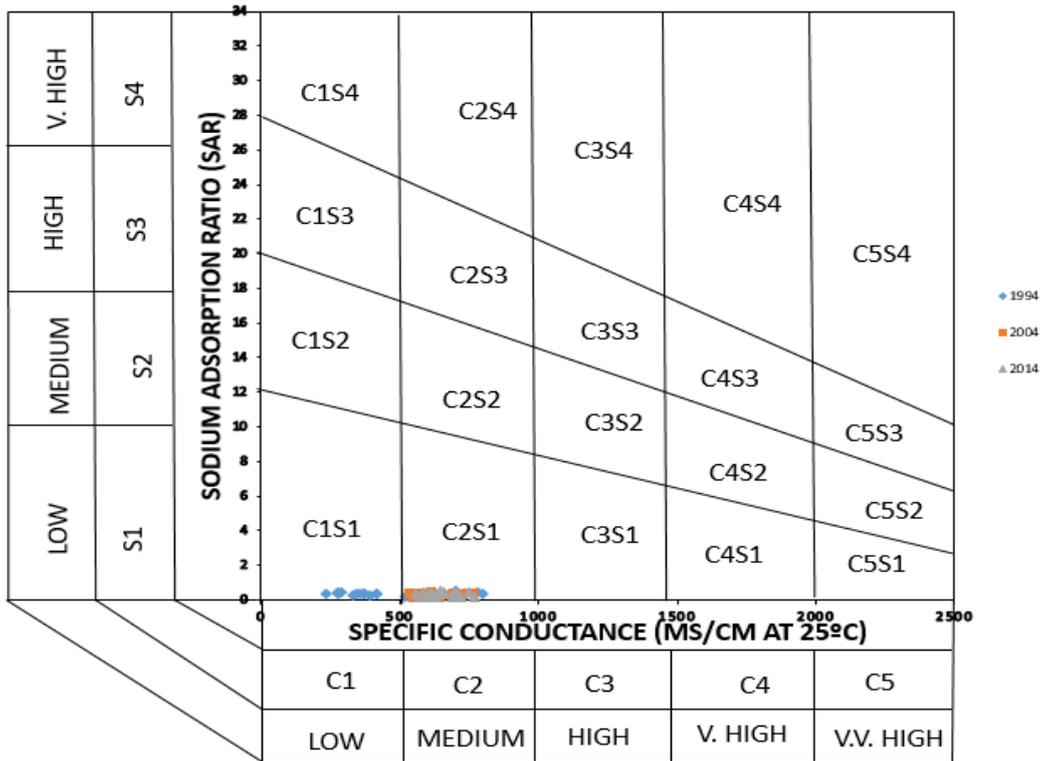


Figure.7.17 USSL diagram

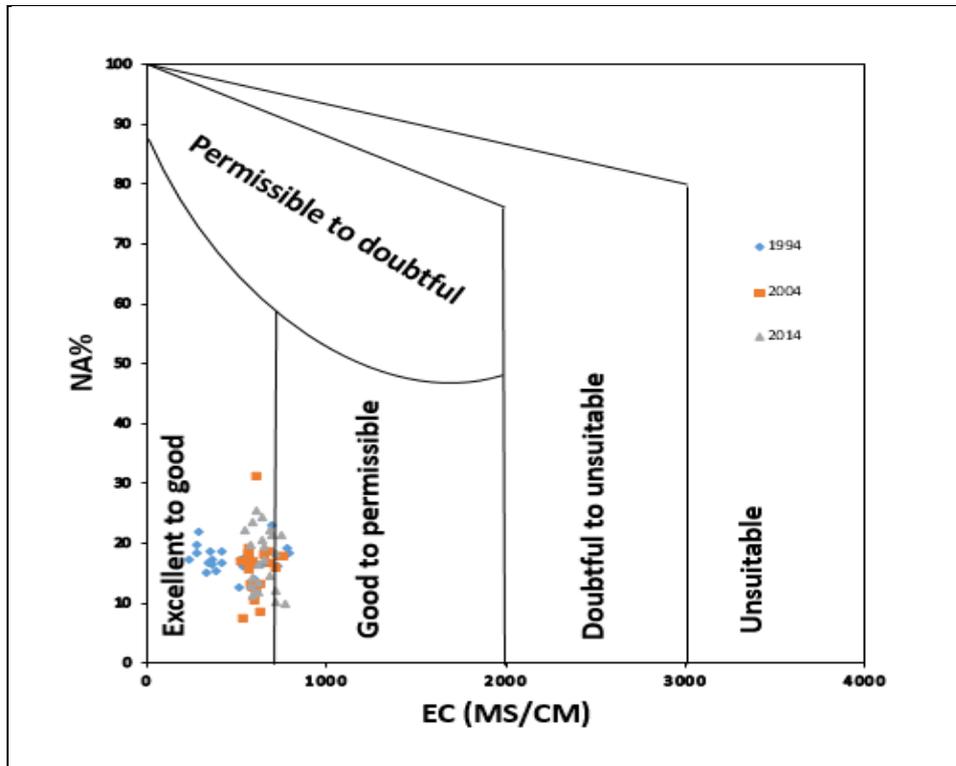


Figure.7.18 Wilcox diagram

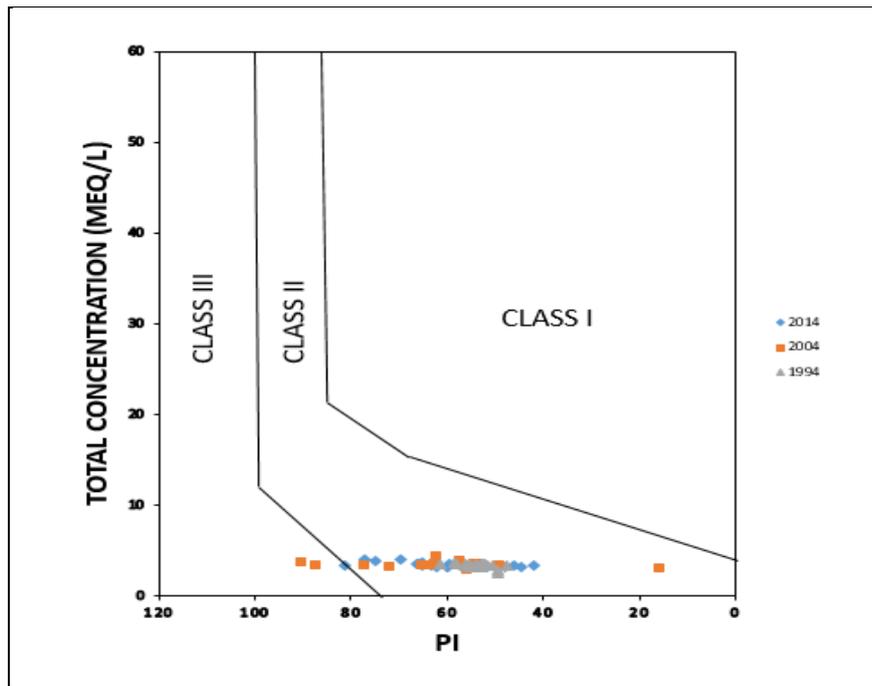


Figure.7.19 Wilcox diagram

8. Conclusion

- Shallow aquifers are easily affected by local climate changes while deep aquifers are dependant only on regional changes. Thus, shallow aquifers are more vulnerable to climate variability.
- The study area is comprised of shallow and deep aquifers. Therefore, the recharge of shallow aquifer is brief as compared to recharge of deep aquifer. In shallow aquifer, rainfall and snow melts can swiftly infiltrate the groundwater as a result of the vadose zone being thin and made of coarse materials.
- Consequently, groundwater system responds well to the short-term recharges by raising its level. Groundwater levels in the study area have declined from 1993 to 1998 when groundwater exploitation/ utilization are more.
- The rainfall variability in the study area was observed to be from 0-151 mm/a during dry season and 86 to 744 mm/a during wet season. The introductory evaluation of groundwater levels demonstrates that the regional water table is moderately deeper mainly when considering the amount of localised and indirect recharge.
- On the groundwater quality in the study area improves with the rise in water level as a result of dilution which influenced/ driven recharge from rainfall. Therefore, the

change in groundwater quality is subjective to groundwater level fluctuation and rainfall variability.

- The natural or man-made effects generally contribute to groundwater level fluctuations. This problem can be conquered by recording the behaviour of groundwater level and discharges of bore wells and informing water users about the current condition and the possible development in the future of the system.
- The piper plot shows that 99% of the groundwater samples in the study area fall in the field of Ca-HCO₃ type which represent the typical of shallow fresh ground waters. The Durov diagram (Durov 1948), support that groundwater in the study area is mainly of HCO₃-Ca-Mg. The Chadda plot shows that 94% of groundwater samples in 1974, 1984, 1994, 2004 and 2014 fall within sub-field 5. Groundwater for such water is HCO₃-Ca·Mg, HCO₃-Ca or HCO₃-Mg types and has temporary hardness (Chadha 1999).
- In the study area, shallow wells are more likely to be affected by irrigation flow compared to deep wells and inferred from high correlation between Ca and HCO₃. Cl was correlated with K and Na. NO₃ and Cl are highly correlated. Variables correlating with Cl, SO₄ and NO₃ are partly derived from agricultural activities.
- Nitrate concentration in the study area shows strong positive relationship with five major ion and EC for last three decades from 1994 to 2014.
- Long term irrigation water quality suitability was established using percent sodium (%Na), sodium absorption ratio (SAR), Kelly's ratio (KR), permeability index (PI), and Hazardous Magnesium ratio (HMR).

CHAPTER 8

SUMMARY AND CONCLUSION

- Groundwater has a significant impact on water supply for domestic purposes around the globe. Groundwater resource has been identified as the main and reliable water resource for human consumption and agricultural practice in the Ventersdorp area.
- In order to evaluate and categorize the main factors impacting groundwater quality in Schoonspruit Catchment several relationship diagrams were established since groundwater.
- The groundwater samples were collected from forty boreholes in 2015 and seventy boreholes in 2017 respectively. The samples were analysed for major ions and nitrate.
- The long term water quality data, rainfall data and water level data since 1974 to 2014 was collected from DWAS.
- The concentration of major ion chemistry in groundwater was within the permissible limits of South African National Guidelines and World Health Organization and for drinking use.
- The overall pH values for both sample periods represent slightly acidic to alkaline in the study area. Based on DWAF (1996) approved limit of drinking (EC <450), 45% of groundwater samples in 2015 and 13% samples in 2017 exceeded the limit in the study area.
- The classification of groundwater based on total hardness (TH) in the study area shows that majority of groundwater samples fall within the hard water category. Major groundwater types were Ca-HCO₃ and Ca-SO₄ in 2015.
- Dissolution of soluble rock is always under dynamic balance with groundwater flow and precipitation, and if the groundwater recharge decreases there is substantial reduction in the flow of fresh water, this may cause enrichment of groundwater components.
- Gibbs plots have revealed that groundwater in the study area for both year 2015 and 2017 is of rock water interaction dominance. Further, the study also revealed that, groundwater dilution lowers the concentration of ions in groundwater due to mixing of infiltrating freshwater during the recharge processes.

- The temporal groundwater level fluctuation causes changes in major ion concentration. In the study area, shallow wells are mostly affected by the return flow from irrigation compared to that of the deep wells. This is established by the high correlation between calcium and bicarbonate, chloride with sodium, nitrate and sulphate and nitrate and potassium.
- Variables correlating with chloride, sulphate and nitrate may be mainly derived from agricultural activities. The demand for groundwater resource has amplified and immense extraction of groundwater modifies the natural groundwater flow directions leading to groundwater despair growth in Ventersdorp.
- The quality in the study area can be attributed to many origins such as dissolution of secondary minerals within the sedimentary formations, anthropogenic contamination, return flow from irrigation water or a combination of some of these processes.
- Kelly's ratio Sodium percent, residual sodium carbonate, sodium absorption ratio and permeability index indicate that majority of groundwater samples in the study area are within the suitable range of irrigation uses. The application of fertilizers affected the chloride and nitrate contents.
- Shallow aquifers are easily affected by local climate changes while deep aquifers are dependent only on regional changes. Thus, shallow aquifers are more vulnerable to climate variability.
- The recharge of shallow aquifer is brief as compared to recharge of deep aquifer. In shallow aquifer, rainfall and snow melts can swiftly infiltrate the groundwater as a result of the vadose zone being thin and made of coarse materials.
- The rainfall variability in the study area was observed from 0-151 mm/a during dry season and 86 to 744 mm/a during wet season. The introductory evaluation of groundwater levels demonstrates that the regional water table is moderately deeper mainly when considering the amount of localized and indirect recharge.
- In the study area, shallow wells are more likely to be affected by irrigation flow compared to deep wells and inferred from high correlation between Ca and HCO₃. Cl was correlated with K and Na. NO₃ and Cl are highly correlated. Variables correlating with Cl, SO₄ and NO₃ are partly derived from agricultural activities.
- Nitrate concentration in the study area shows strong positive relationship with five major ion and EC for last three decades from 1994 to 2014.
- Overall, the groundwater quality is good for drinking purposes and suitable for irrigation needs except at few locations. This study helped to comprehend the present

state of groundwater chemical composition in Ventersdorp and to assess its fitness for irrigation and drinking uses.

- The spatial distribution of IWQI as well as DWQI confirmed that most of groundwater samples in the study region fall between the range of suitable for both drinking and irrigation purposes in 2015 and 2017.
- The constructed correlation of DWQI with major ions displayed a strong correlation of water quality index with Na, Ca, Cl, NO₃ and SO₄. The variables which were correlated with SO₄, NO₃ and Cl were derived from agricultural practices. The spatial variation reveals that the concentration of NO₃ ion falls 9 % unsafe in Eastern and central part while the remaining falls under the safe zone during 2015 and 90% falls under unsafe zone during 2017.
- The impact of heavy metal pollution index (HPI) in groundwater was ascertained. The concentrations of zinc, lead, manganese were within the acceptable range of WHO (2011) and DWAF (1996) limits. The classification range of groundwater shows that about 5% of groundwater samples in the study area fall within poor category with 81% being excellent and 14% being good. This suggests that all samples are within the critical limit of HPI>100.
- The consumption of contaminated groundwater by human kind poses serious health risk through diverse exposures like dermal contact and direct ingestion. The non-carcinogenic risk classification in drinking groundwater indicates that children are at a greater risk due to heavy metals followed by infants with adults being the least affected in the study area. The coefficient variation of Zn was found to be higher than that of Cu, Cr, Cd, Ni and Pb in groundwater of the study area. This is an indication that, the concentration of Zn to each sampling location was higher than that of Cu, Cr, Cd, Ni and Pb. The results suggest that Zn concentration has a high probability of being influenced by human activities.

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