ASSESSMENT OF GROUNDWATER QUALITY IN A PART OF MHLATHUZE CATCHMENT OF EMPANGENI AND RICHARDS BAY, KWAZULU-NATAL, SOUTH AFRICA

BY

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DECLARATION

I declare that the thesis titled “Assessment of Groundwater Quality in a Part of Mhlathuze Catchment of Empangeni and Richards bay, KwaZulu-Natal, 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.

Mr. Bongani Sithole ____________________ **Date: 19.03.2018**

APPROVAL

Supervisor: Prof. V.Elumalai________________________Date:_________

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CONTRIBUTION TO THE BODY OF KNOWLEDGE

The results from the research have been submitted in one peer-reviewed journals (impact factor 2.8) and presented an article in International conference on “26 IUGG General Assembly 2015, International Union of Geodesy and Geophysic, Czech Republic”.for which the papers are attached in the APPENDIX:

Article:

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Assessment of groundwater quality in a part of Mhlathuze Catchment of Empangeni and Richards Bay, Kwazulu-Natal, South Africa

ABSTRACT

The study area comprises of a part of Mhlathuze catchment of Empangeni and Richards bay, KwaZulu Natal. This study has revealed the significance of hydrogeochemical studies in understanding the groundwater quality for drinking and irrigation purposes. The study also identified the hydrogeochemical processes and the probable source of toxic metals in the groundwater. About 40 and 33 groundwater samples were collected in the year 2015 and 2016 respectively and they were analysed. The groundwater ranges from acidic to alkaline in nature. The parameters of drinking water quality such as pH, EC, Na, K, Ca, Mg, Cl, HCO_3 and SO_4 exceeds the permissible limits of WHO standard. The USSL salinity classification revealed that the groundwater samples of the study area are unsuitable for irrigation as high salinity and high alkalinity hazards are observed. The hydrogeochemistry of the major ions in the groundwater are in the order of dominance of Na > K > Ca > Mg and Cl > HCO_3 > SO_4 in 2015 and Na > Ca> Mg >K and Cl > SO_4 > HCO_3 in the year 2016. Ca-Mg-Na, Cl-SO_4-HCO_3, Ca-Mg-Cl, and Na-Cl are the dominant hydrochemical facies. The hydrogeochemical processes that have strong influence on groundwater quality are the rock water interaction, ion exchange, and reverse ion exchange, carbonate and silicate weathering processes and evaporation. PI values specified that the quality of groundwater is good for irrigation purposes. The abundance of metals exhibited the sequence in increasing order as follows: Mn < Si < Fe < B < Cu < Zn < Pb < Al < Li < Co < Ni < Cd < Cr and Si < B < Zn < Ag < Li < Pb < Mn < Al < Cr < Fe < Cd < Co. The water quality analysis clearly revealed that the toxic heavy metals such as Mn, Fe, Pb, Al, Ni, Cd and Cr exceeded the permissible limit of WHO and USEPA drinking water standard. Spatial variation of heavy metals also revealed that the overall part of the study area are extremely hazardous and polluted by landfill site, industrial effluents, mining and associated activities, fertilizers and anthropogenic sources in and around the study area. Consumption of groundwater by the public may cause severe health issues. Generally, the study concludes that the high level of contamination is contemporary in the Empangeni and Richard Bay area. The study also suggests that utilising this baseline informations, reconciliation strategies should be formulated to improve and protect the groundwater quality in the study region.

Keywords: Hydrogeochemical processes, rock water interaction, landfill, evaporation, KwaZulu Natal.

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CHAPTER ONE

CHAPTER ONE

1. INTRODUCTION

1.1 GENERAL

Groundwater chemistry is multifaceted due to various hydrogeological conditions, diverse constituents from the formations and several other factors influencing the aquifer system. Globally, the present groundwater quantity and quality are not adequate to cope with the rising urbanization, industrialization and irrigation expansion.

Groundwater is not only an important commodity but also have a strong interlink in the hydrological cycle. Surface water resources, reservoirs and groundwater are the major water sources in South Africa. Due to the indispensable facts like rapid population growth, urbanisation, industrial expansions, depletion of existing water resources and above all the current climate change have pushed the country under severe drought. The Cape Town city is witnessing an ever experienced historical drought where the existing surface water resources have completely depleted. The water management and allocation system of Government of South Africa are looking for the competitive and alternate water source for the surface water resource. Though, the groundwater is also an integral part in the country, a complete exploration of the groundwater resources has not yet been initiated. The studies on the groundwater quality and quantity at this point will have significant impacts on the water usage, preservation, protection and management methods. Groundwater occurs beneath the subsurface of the soils and geological formation. Adequate permeability in the aquifer transmits and yield water through the fractures and the pore spaces. The movement and/ or storage of water in the aquifers occur in two ways. An aquifer in which, the water infiltrates through precipitation and get stored being subjected to fall and rise according to the natural recharge and/ or discharge from high gradient to low gradient or vice versa under atmospheric pressure is called as unconfined aquifer. Whereas, in the other case, two relatively impermeable confining layers store water under pressure taking place at certain portions of the subsurface are called as confined aquifer. Naturally occurring groundwater differs in physical properties and chemical constituents on both spatial and temporal scale. These variations occurs due to various influential factors like climate, geology, hydrogeology, rainfall, drainage pattern, land use, human activities such as irrigation practice, industrial activities etc., The groundwater quality and quantity have to be subjected for assessment in order to avoid negative health impacts and to develop the standard of healthy living. The standards and guidelines of groundwater for drinking, irrigation and was developed and formulated by the WHO and the South African Department of water and sanitation. The numerical values of each chemical constituent of the groundwater are given in the guidelines which are the reflection indicators of the groundwater quality (WHO, 2008). The natural chemical constituents of groundwater such as major ions, minor ions and the trace elements can potentially affect the human health either in the form of deficiency or excessive intake (Frengstad et al. 2001). Ions such Na, K, Ca, Mg, Cl, SO4 and HCO3 are the principle major ions present contributing 90% of the total Dissolved solids (TDS). F, NO3, NO2, PO4 and NH4 are the minor ion constituents while Al, Cd, Co, Cu, Pb, Li, Mn, Ni, Zn, Ag, Fe and Si are the trace elements which constitute the chemical composition of the groundwater. These hydrochemical constituents are the results of the natural hydrogeochemical process taking place in the aquifer and the other anthropogenic sources which determines the geochemical characteristic of the groundwater and explore the groundwater quality.Several methods have been adopted to identify the geochemical process and to assess the groundwater quality. Multivariate statistical approach is widely adopted to identify the hydrogeochemical process and to discriminate the geogenic and anthropogenic sources of such constituents. Several multivariate statistical approaches are adopted in groundwater studies including regression analysis, principal component analysis, varimax analysis, oblimax analysis, key cluster analysis, and object analysis (Wallis. 1965).

However, correlation matrix (CA), Principal component analysis (PCA) and Factor Analysis (FA) are the approaches adopted in the present study. Correlation matrix reveals inter- relationship of the hydrogeochemical data and explore the process responsible for the sources of ion. Principal component analysis (PCA) is used to group the samples of similar classes into separate groups and group the samples of dissimilar classes. Factor analysis is the most reliable method for interpretation of groundwater hydrochemistry. PCA with the combination of HCA reduces large number of parameters into fewer principal components of which the scatter plots can be obtained (Townend, 2002).Due to the necessitate in the groundwater demand in the study area in a part of KwaZulu Natal, South Africa, the statistical approaches to identify the geochemical process and the assessment of groundwater quality for irrigation and drinking purposes have been carried out and the contamination sources for heavy metal has also been revealed with an adequate data set to achieve the aim.

1.2 NEED FOR THIS STUDY

South Africa is witnessing and battling with the crippling effect of the severe drought in the recent years. Previously, in 1995, the province was declared drought. Despite the fact that the KZN province receives highest rainfall than other areas of the country, due to unrelenting drought the KZN cabinet has declared the province as a drought disaster, in December 2014. According to Department of Water Affairs 1996, the population of the study region increase at a rate of 4.2 % which can apparently causes severe drought in future (Kelbe, 1996). The quality of the River water is also desecrating due to various factors such as discharge of domestic and industrial effluent, irrigation return flow and climate change. There are 13 solid landfill sites already existing within the Mhluthuze municipal area which can possibly impose large pollution threat for the groundwater and surface water, as the leachates released from the waste disposal sites can desperately percolate into the aquifer. Landfill site situated in Empangeni and Richards Bay receives only the general waste and the industrial waste has not been disposed in these areas. Currently, the Mhlathuze Municipality distribute water supply to the community through Mhlathuze catchment reservoir. There are several industries, shopping malls, agricultural farming activities and domestic settlements which require large water needs. Due to the climate changing phenomenon and growing population the adequate availability of the surface water have become unreliable as we have evidently witnessed severe drought in neighbouring areas like KwaDukuza in 2017. Future water availability and its use are completely unprecedented due to the present global climate change as we witnessing the Cape Town water crisis. However, the extraction of groundwater from this coastal aquifer will be the alternative and inexpensive method to meet the increasing demand which could be one of the development plans to cope up with the demand on water use (DWAF 2004). Moreover, a rapid growing agricultural and industrial community can be observed in the study region as indicated in previous studies (Steyl et al., 2000). In certain areas the groundwater is being exploited in and around rural and urban areas. For the past few decades the surface water and groundwater is deteriorating in its quality and quantity. There have been several systems that monitor the quality and quantity of the surface water in the study region. But no specific previous research has been carried out on groundwater quality assessment in the study area as the resource has not yet been explored adequately. The groundwater quality criticism would have its direct or indirect impact on the ecosystem and cause severe environmental degradation, hydrological cycle imbalance, other health related risk and the socio-economic under development in and around the study area. Hence, it is crucial to study the quality of groundwater and investigate its suitability for its various utility in human life. The purpose of this research is to know about the groundwater quality for drinking and irrigation purposes and also to identify the hydrogeochemical process adopting multivariate statistical analysis methods with identification of possible heavy metal contaminants in the groundwater due to the irrigation, landfill and natural geogenic process that are primarily taking place in the study region.

In detail, the impact of natural and anthropogenic activities including industrial activities, hydrochemical composition, hydrochemical process, spatial and temporal variations, and presence of other natural elements have been investigated. Demlie and Titus (2015) revealed the importance of the aquifer system as it is one of the major rural water-supply schemes along the eastern KZN province of South Africa

However, no evidence of previous studies on groundwater quality assessment through multivariate statistical approach has been carried out in this area. Thorough investigation on this coastal aquifer can remarkably bring new ideas for proper utilization of groundwater resource where the surface water availability is uncertain. So, it is necessary to study the deterioration of quality on groundwater in detail for this area. Therefore, this study has formulated adequate assessment on groundwater quality and its suitability for drinking purposes and the irrigation purposes

1.3 AIM AND OBJECTIVES

The study was aimed to assess the groundwater quality in a part of Mhlathuze catchment of Empangeni and Richards Bay areas of KwaZulu Natal, South Africa.

The major objectives of this study are

- to determine the seasonal and spatial variations in groundwater quality
- to determine the causes of seasonal and spatial variation in major ion concentration of groundwater.
- to identify the geochemical process that controls the major ion composition of groundwater.
- to assess the suitability of groundwater for irrigation and domestic purposes.

CHAPTER TWO

2 REVIEW OF LITERATURE

2.1 GENERAL

The geology, hydrogeology, climate and anthropogenic activities in an area have great impact on the groundwater hydrochemistry. Studies on hydrogeochemical constituents of groundwater help to identify the hydrogeochemical processes taking place in the aquifer. Globally, significant interest has been shown on studies related to groundwater quality, hydrogeochemical processes and heavy metals analysis in groundwater which are reviewed in this chapter.

2.2 GROUNDWATER QUALITY

There is an urge in obtaining new methods to supply desirable quality of drinking water (Chen and Feng, 2013). The groundwater quality needs special management measures particularly, the areas near the landfill site (Selvam *et al*, 2014 and Masoud, 2014). The groundwater quality around the landfill waste disposal sites is not suitable for drinking and domestic purposes. Whereas, it can be marginally suitable for irrigation purposes. The leachate from waste landfill site creates severe impacts on groundwater causing serious health concerns to human (Deshmukh and Aher 2016). Nageswara Rao *et al* (2015) stated that the groundwater is not suitable for irrigation purposes but it can be utilised for industrial purposes in his study region. The drinking water quality in a part of this study region exceeded the permissible limit (Vetrimurugan *et al* (2017). Venkatramanan *et al* (2015) have reported that the drinking water quality become undesirable due to the influence of unsuitable disposal of effluents from an ore mining, agricultural farming and domestic wastes. Rabeiy (2017) has reported that most of the regions in the Upper Egypt are deteriorated in the groundwater quality which makes it unsuitable for drinking purposes. Zhou *et al* (2016) has reported that more than 70% of the phreatic water samples did not mark up with the drinking water standards due to industrial and irrigational activities. The observed results of the statistical analysis in the Indo-Gangetic alluvial plain revealed that groundwater quality is dominated with attributes of industrial origin (Singh *et al*, 2014). Brindha *et al* (2016) have reported that the results from geochemical assessment pose no threat to drinking purpose based on major and minor ion composition however; the overall quality makes it crucial for regular monitoring. Vetrimurugan *et al* (2015) states that the poor flushing of groundwater and fine- grain sediments in the coastal aquifers are one of the causes for high concentration of ions in the groundwater. Gibrilla et al 2011 states that chemical indices like Na%, SAR, RSC, and PI of the study area reflects the suitability of groundwater for irrigation purposes. Moosavirad *et al* (2013) have reported that the groundwater was highly saline due to the influx of pollutants from the effluents of coal mining and other anthropogenic activities which makes it marginally suitable for agriculture activities. Li et al, (2016) report that the rational usage of irrigation land will have no threat on the rate of salinity and alkalinity hazards in groundwater. Agca (2014) suggest that drip irrigation method is one of the methods when compared to the conventional methods which can effectively reduce the rate accumulation of salt in the groundwater. Zhai et al (2015) suggest that water saving in agricultural sector has a significant role in achieving sustainable water development with the scope of current trending urbanization and ecosystem & groundwater recovery. Li et al (2016) suggest that low and high saline water mixing method can be adopted before irrigation practice which has the potential in minimizing the salinity hazard in local areas. Mahato *et al* (2016) reports the occurrence of higher concentration of saline water and RSC values at few areas which makes the quality unsuitable that needs further development plan in the drainage patterns and new strategies for water management.

2.3 HYDROGEOCHEMICAL PROCESSES

Hydrogeochemical processes are the important natural phenomenon responsible for the chemical constituents of the groundwater. Graphical plots and multivariate statistical approaches were common methods adopted to identify the geochemical process in a region. The main geochemical processes in the Quaternary aquifer reported are reverse ion exchange, evaporation, and dissolution of carbonates, gypsum and soil salts, calcite precipitation, and silicate weathering (Bozdag 2016). In areas of dry seasons carbonate weathering and in areas of wet seasons silicate weathering can be observed (Varol and Davraz, 2015). The other process includes dissolution and/or hydrolysis of minerals (Rodriguez *et al*, 2016), Dissolution of silicate and carbonate minerals were observed by Zhang et al (2016) in northwestern china. The factor analyses imply that silicate weathering is the dominant hydrogeochemical process due to effluents from the tannery and cation exchange processes (Kanagaraj and Elango 2016). Water–rock interaction including dissolution of carbonates and gypsum, calcite precipitation, and de-dolomitization are the major processes in the Neogene aquifer (Bozdag, 2016). The temporal variation in relation to saturation index of minerals implies the presence of evaporation process. The concentration of ions such as calcium, magnesium and sodium indicates that ion-exchange process takes place. (Rajesh *et al*, 2012).

Rock dominance and dissolution/precipitation of minerals and cation exchange are major natural factors governing the formation of groundwater chemistry in the Northwest China. However, stable isotopes and the occurrence of nitrate indicate the inputs of shallow groundwater evaporation and human activities (Li *et al,* 2016). Ahmed (2012) explains that the hydrogeochemical and isotopic methods are excellent exploratory tools for the identification of the main sources of salinization that modify the quality of groundwater. Groundwater can be classified as under 3 groups such as recharge area waters (Group 1), transition area waters (Group 2) and discharge area waters (Group 3). Calculation of Mineral saturation indices obtained from major ions and trace elements, reveals super saturation of carbonate and silicate phases and undersaturation of albite, gypsum, anorthite, halite and anhydrite. Inverse geochemical flow modelling reveal the presence of precipitation of the carbonate minerals, dissolution of the evaporate minerals, and weathering reactions of the silicate minerals (Belkhiri *et al*, 2010).

The water–rock interactions and anthropogenic activities are the major responsible processes in the Celtikci plain. Chemical weathering taking place in different parent rocks such as carbonates, silicates, and evaporites are obtained as a result of different combinations of dissolved cations and anions to solution (Davraz and Ozdemir, 2014). HCA has been broadly applied in groundwater studies to classify it under the 2 major clusters. The four sub-clusters of cold groundwater system explain about the hydrochemical evolution patterns of natural and anthropogenic sources. The positive correlation between the ions such as NO_3, Cl and SO_4 is the indication of the influential anthropogenic factor while the concentration of Na, HCO_3, SO_4 and K is due to groundwater salinity that was assessed by factor analysis. (Demlie *et al*, 2007). The multivariate statistical technique is a useful tool in identification of different hydrochemical processes and to confirm the groundwater contamination factors (Galazoulas and Petalas, 2014)

The geochemical processes like rock – water interaction, ion exchange, dissolution and reduction can modify the hydrochemistry of the source groundwater in the Nurra Region, Sardinia, Italy (Ghiglieri *et al,* 2008). HCA and mass-balance modelling can be combined together and applied to interpret the flow in areas of large uncertianities. (Helstrup *et al*, 2007). Dissolution of minerals, such as halite, gypsum, dolomite, calcite in the sediments results in the chloride, sulphate, bicarbonate, sodium, calcium and magnesium content in groundwater. Cation exchange and the weathering of alumina silicates results in contribution of sodium and potassium (Jalali, 2005). The statistical and mass-balance analyses of major element chemistry of groundwater, the hydro- geochemistry of basaltic aquifers in agricultural land usage underlying Jeju Island was significantly affected by nitrate and acidity during nitrification, and direct input from chemical fertilizers (Koh *et al*, 2007).

Multivariate analysis evidently shows that the evaporation in seawater and the precipitation of gypsum/anhydrite also takes place. PHREEQC geochemical modelling determined the evaporation ratio as 85% (Lu et al 2007). The cation exchange and calcite equilibrium controls the groundwater composition in the Mar del Plata aquifer whereas; in a few areas iron- sulfide precipitation occurs, especially in the seawater/fresh-water mixing zone (Martinez and Bocanegra, 2002). Multivariate statistical analysis clearly explains about hydrochemistry through the interactions between the groundwater and saline/

seawater in coastal aquifers (Mondal *et al,* 2010). The saline/brackish groundwater have been reported due to the dissolution of chloride, evaporation of sulphate and mineral seep of sedimentary Karoo and Cretaceous Lupata sandstones (Monjerezi *et al,* 2011).

Multivariate analysis reveals that the chloride contamination were originated from the salts, animal and domestic waste (Moncoudiol *et al*, 2014). Nguyen *et al* (2014) explains that the factor analysis indicates the sources of dissolved ions in the groundwater is due to rock-water interaction in a part of the study region areas whereas salt water from the sea are the main factors influencing groundwater chemistry in other parts of Red River Delta, Vietnam. The process of reverse ion exchange contributes to the concentration of ions such as calcium, magnesium and sodium in hard rock formations. Dissolution of carbonate and cation exchange of sedimentary formation contribute to the concentration of Ca and Mg. Aquifer hydraulics do not play major role on processes (Reddy and Kumar, 2010).

Na concentration is higher in weathered rocks while concentration of calcium is observed higher in alluvial formations. Hydrogeochemical reaction is the identifying indicators for the release of calcium and adsorption of magnesium and sodium by ion exchange processes. Dissolution and precipitation of minerals are the other two major processes (Senthil kumar and Elango, 2013). Singh et al (2014) reported that the groundwater quality was influenced by industrial origin. Subba Rao et al (2014) shows the usefulness of multivariate statistical model as an effective means of interpretation of spatial controlling processes of groundwater chemistry. Hydrochemistry of Ghatprabha River sub-basin, India exhibits water–rock interaction and influence of aquifer material mineralogy with higher concentration of nitrate due to excess use of fertilisers in the agriculture land. (Tamma Rao *et al*, 2013). Bivariate plots depict the occurrence of silicate weathering, carbonate dissolution and evaporite dissolution. High nitrate concentration was due to intensive agricultural areas. Carbonate minerals were observed predominantly, while they were observed undersaturated with silicate minerals

(Raju *et al,* 2016). The study reports that the combinations of hydrogeochemical tools help us to understand the functioning of the aquifer system. Therefore, it could be utilised to formulate plans to protect and manage the groundwater in Southern Spain (Sanchez *et al*, 2015).

2.4 HEAVY METALS

Higher concentration of heavy metals in the groundwater causes potential health risk to humans (Vetrimurugan *et al,* 2016). The geo-accumulation index revealed that quality ranges from unpolluted to moderately polluted with Cu, Ni, Zn, Pb and As moderately polluted in situation of Cd and heavily to extremely polluted by Cr (Dotaniya *et al,* 2016). Upadhyaya *et al* (2016) suggests that principle component analysis of heavy metals such as Co, Cu, Cd, and Zn in groundwater were due to anthropogenic sources whereas; Pb and Cr may be attributed due to atmospheric deposition. The major hydrogeochemical process identified in watershed of Yaounde, Cameroon-West Africa is weathering and other anthropogenic activities which causes soil and groundwater pollution posing severe threat to the public health.(Defo *et al,* 2015). Multivariate statistical analysis was used to identify the contribution of variables to groundwater pollution. Fe and Mn levels and Al, As, and Cd levels exceeded WHO guidelines for drinking standard (Arslan and Turan 2015). Co–Cr and Fe–Zn were reported with significant correlation. The PCA results reveal the anthropogenic factor contributed to the concentration of Co and Cr while the geogenic factor contributed to the concentration of Zn and Fe. Health risk assessment indicated the adverse impact of industries on Cr concentration which is grouped under non-carcinogenic risk (Bhutiani *et al*, 2016). The concentrations of Al, Fe, Mn, and Ni exceeds the desirable limits with HPI critical pollution index below 100 (Tiwari et al 2016).

Lower concentrations of calcite are reported in Golgohar area which could be due to calcite that neutralizes any acid of sulfide oxidation (Jahanshahi and

Zare, 2015). The health risk assessment HQ indices indicates that the groundwater were safe for drinking purposes (Krishna and Mohan, 2014).

The presence of elements like As, Se, and U in toxic amounts is a matter of serious concern makes it unsuitable for drinking purposes (Kumari *et a*l, 2014). The abundance of metals in the host rocks is the indication of geogenic sources however, other geochemical processes such as oxidation, leaching, and evaporation are the main causes for metal enrichment (Abiye and Leshmo, 2014). HPI, HEI, and Cd pollution indices determines the groundwater contaminations of metals like Be, Cr, Mn, Zn, Mo, Ni, Co, As, Cu, Cd, Pb, and Fe (Chidambaram *et al*, 2014).

The HPI and HEI methods are suitable for evaluation of heavy metal contamination, but, due to the clumsy nature of computation involved with Cd and the HPI, the HEI is preferred for contamination monitoring (Edet and Offiong, 2003). The free ion species of Ba, Cd, Cu, Fe, Mn, Ni and Zn does not pose any contamination risk to the groundwater (Edet *et al*, 2004). Principal Components Analysis report the influence of seawater intrusion and marine and ship breaking as pollution sources(Hasan *et al,* 2013).

Multivariate PCA and CA applied in the study region reveal that the major anthropogenic pollution sources are untreated effluents/waste and agricultural activities processed (Iqbal *et al*, 2013). Integrated pollution indices and multivariate statistical methods are significant approaches and it has been carried out in the surface water of Curtin Lake which exhibits the toxic metals and their sources Prasanna *et al*, (2012).

CHAPTER THREE

3 METHODOLOGY

3.1 SAMPLING AND ANALYSIS

Groundwater samples were collected from Richards Bay and Empangeni areas in August 2015 and July 2016. Additional attention was taken to ensure that the groundwater sampling locations of N=40 and N=33 were scattered to cover the entire area (Fig 3.1). The 500ml polyethylene sampling bottles were rinsed with distilled water and then with the sampling water. The 0.45 µ membrane filter paper was used to filter the water samples. The samples were collected and stored in the bottles. Further, 200ml of samples were collected separately for the Trace metal analysis to which 0.5 ml of concentrated HNO_3 solution was added. Groundwater level was measured using Solinist (101) water level indicator. Temperature, turbidity, oxidation reduction potential, dissolve oxygen, pH, electrical conductivity (EC) and TDS were measured using YSI multiprobe digital meter (YSI Inc. Yellow Springs, OH, USA).

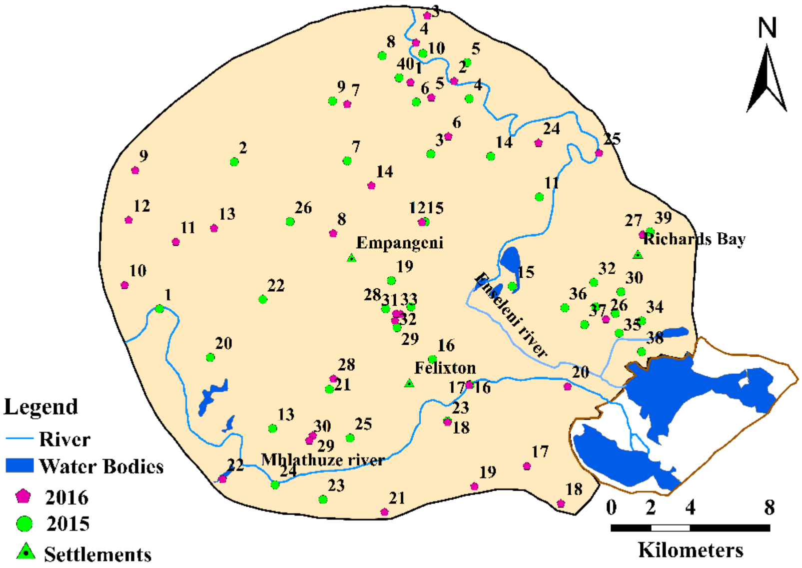


Figure 3.1 Sample location of groundwater in the year of 2015 and 2016 of Richards Bay and Empangeni area

Sulphate, Nitrate, Sodium, Potassium, Carbonate and bicarbonate were measured by titration (APHA 1998). Sodium, potassium, calcium, magnesium, chloride, was analysed using inductively coupled plasma optical emission spectrometry (ICP-OES). Standards and blanks were run repeatedly for confirming the accurate measurement of the concentration of ions. Analytical accuracy was determined by calculating the ion balance error which was within ± 5%.

3.2 GROUNDWATER QUALITY

Groundwater quality in the study area was studied to identify the suitability for drinking and irrigation usage.

3.2.1 Drinking water quality

TDS and total hardness (TH) of water were estimated by the formula suggested by Lloyd and Heathcote (1985) and Sawyer and McCarty (1978) respectively.

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

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

3.2.2 Irrigation water quality

Irrigational water quality were assessed by sodium adsorption ratio (SAR) (Richard, 1954), sodium percentage (Na %) (Wilcox 1955), residual sodium carbonate (RSC) (Eaton 1950), permeability index (PI) (Doneen, 1964) and magnesium ratio (MR) (Szaboles and Darab, 1964).

$$\text{SAR} = \mathrm{Na}/\sqrt{((\mathrm{Ca}+\mathrm{Mg})/2)} \qquad (3)$$

$$\text{Na\%} = (\mathrm{Na}+\mathrm{K}) \times 100/(\mathrm{Ca}+\mathrm{Mg}+\mathrm{Na}+\mathrm{K}) \qquad (4)$$

$$\text{RSC} = (\mathrm{CO_3}+\mathrm{HCO_3}) - (\mathrm{Ca}+\mathrm{Mg}) \qquad (5)$$

$$\text{PI} = (\mathrm{Na}+\sqrt{(\mathrm{HCO\_3})})/((\mathrm{Ca}+\mathrm{Mg}+\mathrm{Na})) \times 100 \qquad (6)$$

$$\text{MR} = Mg/((Ca + Mg)) \times 100 \quad (7)$$

3.3 STATISTICAL ANALYSIS

Statistical analysis methods were adopted in the study in order to identify the contamination sources. Statistical analyses include correlation matrix (CA), hierarchal cluster analysis (HCA) and factor analysis (FA) using STATISTICA version 9 (StatSoft, 2008). Hydrochemical variables such as pH, TDS, Na, K, Ca, Mg, Cl, HCO_3, SO_4 and NO_3 were used in the geostatistical analyses.

3.3.1 Correlation matrix

The Pearson’s CM method was adopted in the study to find the inter-relationships between hydrogeochemical data of groundwater samples. It reveals the source of ions and identifies the hydrogeochemical processes responsible for observed water composition. The results of the correlation analysis reflects high correlation coefficient (r) of 1 or nearly 1 which specifies positive correlation between two variables. If two variables represent r > 0.7, it specifies strong correlation and the ranges between 0.5 and 0.7 specify moderate correlation (Manish et al, 2006).

3.3.2 Hierarchical cluster analysis

Cluster analysis was used for grouping objects into clusters based on the continuity/similarities within a class and dissimilarities between different classes. It plays a significant factor to interprete the data and the specific patterns.

Ward’s method was adopted in the study to classify the samples.

CA is essential to standardize the sample data since each variable has a different unit. Data are standardized to the score (m=0 and S=1) by using the following equation:

$$Z = (X - m)/S \tag{8}$$

Where Z- standardised value, X- value of sample data, m-mean and S-standard deviation.

3.3.3Factor analysis

FA is an important method used to interpret the groundwater hydrochemistry. The factor analysis reflect the relationship in simple terms expressed as a new set of variables called 'factors' (Usunoff and Guzman, 1989)./36+-/69R-mode factor analysis of varimax rotation with Kaiser Normalization is used in the factor analysis. Factor analysis on the collective datasets delivers the factor with Eigen value >1 that can describe the data variability. Liu *et al* (2003) suggested the classification of strong, moderate and weak, according to this classification loading values are >0.75, 0.75-0.50 and 0.50-0.30 respectively.

3.4 HEAVY METALS IN GROUNDWATER

Heavy metals sampling locations N=40 and N=25 in 2015 and 2016 respectively were collected in 1litre polypropylene bottles and were analysed by inductively coupled plasma mass spectrometry (ICP-MS). The heavy metals such as Si, Ag, Al, B, Cd,Co, Cr, Cu, Fe, Li, Mn, Ni, Pb and Zn were studied.

3.5 HEAVY METAL POLLUTION

The assessment of heavy metal pollution in water comprises of Heavy metal pollution index (HPI), heavy metal evaluation index (HEI) and degree of contamination (C_d). The HEI and HPI methods are applied using the ratio of observed concentration of the metals and maximum admissible concentration in drinking water (Siegel, 2002). In the C_d method, the quality of water is assessed as the sum of the contaminated factors of each component exceeding the permissible limit. Hence, Cd indicates the combined effects of a number of quality parameters observed as a risk for drinking water.

3.5.1 Heavy metal pollution index

The water quality and its suitability for drinking purposes can be assessed by heavy metal pollution indeces (Prasad and Kumari, 2008; Prasad and Mondal, 2008; Tiwari *et al,* 2015a). The HPI is an arithmetic based weightage developed in two steps. First step is to establish the rating scale to the individually selected parameters with weightage and secondly the index based pollution parameters are selected. The rating system is an arbitrary value between 0 and 1. The standard permissible value (Si) and the highest desirable (ideal) value (Ii) for each parameter were considered according to the standards of World Health Organization (WHO 2011) (Table 6). The uppermost permissive value is the maximum allowable concentration drinking water in the absence of any alternate water source. The desirable maximum value (Ii) is the standard limits (Prasanna *et al*, 2012 and Bhuiyan et al, 2010). The HPI is determined using the following equation proposed by Mohan et al (1996) is

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} W_i\, Q_i}{\sum_{i=1}^{n} W_i\, Q_i} \tag{9}$$

Where, Qi and Wi are the sub-index and unit weight of the parameter. n is the number of parameters considered.

The sub-index (Qi) is calculated by:

$$Q_i = \sum_{i=1}^{n} \frac{|M_i - I_i|}{|S_i - I_i|} \times 100 \tag{10}$$

Where, Mi, Ii and Si are the monitored heavy metal, ideal and standard values of the parameter, respectively.

The sign (-) indicates numerical difference of the two values, neglecting the algebraic sign.

3.5.2 Heavy metal evaluation index

HEI provides the details on an overall water quality with respect to heavy metals (Edet and Offiong, 2002) and is expressed as:

$$\mathrm{HEI} = \sum_{i=1}^{n} \frac{\mathrm{H_c}}{\mathrm{H_{mac}}} \qquad (11)$$

Wherein, H_C and H_{mac} are the monitored value and maximum admissible concentration (MAC) of the parameter, respectively.

3.5.3 Contamination degree

The contamination index (C_d) summaries the combined effects of several water quality parameters which are analyzed as harmful to the domestic water usage (Backman et al, 1997) and the equation is calculated as follows:

$$\mathrm{C_d} = \sum_{i=1}^{n} \mathrm{Cr_i} \qquad (12)$$

Where

$$\mathrm{Cr_i} = \frac{\mathrm{C_{Ai}}}{\mathrm{C_{Ni}}} - 1 \qquad (13)$$

Wherein,

C_{ri}; C_{Ai} and C_{Ni} represent contamination factor, analytical value and upper permissible concentration of the e component, respectively. N denotes the ‘normative value’ and C_{Ni} is taken as MAC.

3.6 GIS ANALYSISThe base map of Richards Bay and Empangeni area was digitized from the map obtained from the Department of Environmental Affairs using ArcGIS 10.1 software. The GPS was used in the sampling locations and accurate details on longitude and latitude were imported in GIS platform. The ArcGIS 10.1, is the geostatistical analyst tool which was used to prepare the spatial variation for groundwater quality parameters while, Inverse distance weighted (IDW) interpolation technique was used to prepare the spatial modelling.

3.7 AQUEOUS HYROCHEMICAL MODELING

PHREEQC (Version 2.15.0) is a program designed to perform various low-temperature aqueous geochemical calculations (Parkhurst and Appelo, 1999). In this study, PHREEQC was used to calculate the speciation and saturation index calculation of groundwater.

CHAPTER FOUR

4 STUDY AREA

4.1 DESCRIPTION OF THE STUDY AREA

The study area forms a part of Mhlathuze Catchment which surrounds two major towns- Empangeni and Richard Bay of the northern KZN province. It is located 160 Km north of Durban, KZN Province, South Africa. It covers an area of 792Km^2 (Figure 4.1). The Indian Ocean on the south eastern side, Enseleni River on the north eastern side, and the Mhlathuze River in the part of North Western side forms the boundary of the study region.

4.1.1 Climate and Rainfall

The climate of the study region experiences humid and wet weather which is distinct from other African regions. The average temperature in the study area during the month of January – March ranges from 21°C-29°C and during the month of June-August ranges from 12°C-23°C (Vetrimurugan et al, 2017). The KZN coast receives highest rainfall during the month of October to march with an annual rainfall ranging from 850mm in the west and around 1200 mm over the coastal areas (DWAF, 2000).

4.1.2 Land use/Land cover

The Agriculture practised in the study area has significant impact on economic and social status on South Africa due to its diverse natural resources. the Dominant crops cultivated includes sugar, cattle, forestry and staple grains while other minor crops like pineapples, banana, vegetables and nuts are also cultivated substantially and others include commercial plantation of pine and eucalyptus (Department of Agriculture KZN, 2002). A landfill dumping site is active in Empangeni including several industries in Richards Bay, aluminium smelters, fertilizer plants and mining of mineral ores. One of the largest coal export plant is located in Richards bay (Vetrimurugan *et al*, 2017).

4.1.3 Topography

The regional topography of the study area can be categorized as fairly flat to undulating landforms. The hills are low lying and the drainage patterns are present as flat bottom. . The terrain rises slightly towards the west. The greenbelts of coastal dune forest are bordered at 140m above the sea level.

4.1.4 Drainage

Mhlathuze River is one of the largest river in the KwaZulu Natal originating from the Babanago Mountains continue to flow through Empangeni and Richards Bay areas and finally by making an estuary it drains into the Indian Ocean. Most of the drainage in the industrial areas of Richards Bay flows from natural and artificial channels towards the harbour. The Empangeni households and large industrial needs are supplied from the Lake Nsezi. The River Nseleni and River Mposa link with the lake Nsezi supplying the large urban settlement at Enseleni. To meet the demands of industries, Lake Nsezi is supplemented with water from the Mhlatuze River. The entire Richards Bay area completely depends on Mhlatuze Water and a small contribution from Lake Nsezi for all the water requirements. However, a small Stream of Mpisisni River provides the water to the community and also replenishes the Lake Mzingazi which is replenished by groundwater and direct rainfall recharge (Archibald, 1998; Kelbe and Germishuyse, 1999).

4.2 GEOLOGY

The study area lies just in the northern part of the KZN province, South Africa. Geologically, this region consist of five groups namely Cenozoic, Drakensberg, Ecca, Dwyka and Natal group as shown in the Figure 4.1 explained in detail in the following sections. During the Cenozoic periods, most of the areas in the study area underwent deep weathering of old dunes and produced dark red coloured sand known as Berea Red Sand. Recent coastal dunes in the study area contain concentrations of ilmenite, rutile and zircon mined near Richards Bay. Dolerite sills are commonly seen throughout the inland of KZN in the form of sedimentary rocks of the Karoo Super-group. The shales of Pietermaritzburg Formation are easily weathered and often facies slope stability problems**.** Overlying the shale formation a thick sequence of light grey sandstones, called the Vryheid Formation are deposited. The lowermost and the oldest deposit of the karoo supergroup basin is the Dwyka Group. The first sedimentary sequence deposited on the new basement was the Cambrian to Ordovician Natal Group (490 million years ago).The basement rocks of KZN are crystalline granites, gneisses and schists (King,1972).

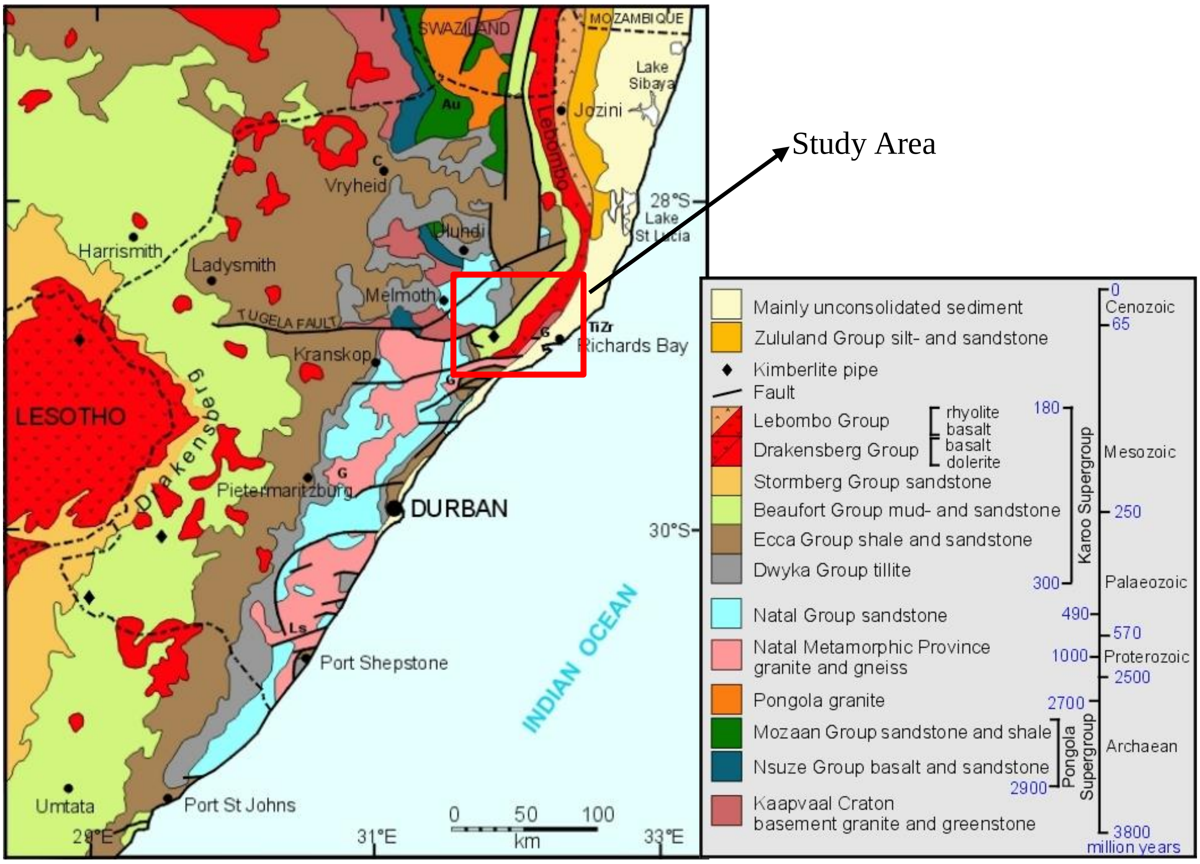


Figure 4.1 Geology of the study area (Geological survey 1984)

The Natal Group, consist of sandstones that are the lowermost and the oldest deposit which overlie the basement rocks. The Karroo Super group covers the Natal Group for thousands of meters with the sedimentary strata which are over-capped by the volcanic lavas. Marine deposits are underlined throughout the entire KZN coastal plain with uniform siltstone and occasional thin clay lenses and thin bands of hardy limestone (Worthington, 1978) The Cretaceous formation is very thick with 1000m under the ocean and tapers out inland towards Lake Nsezi. In the study area, the upper Cretaceous surface elevation varies from approximately -20 m above mean sea level (msl) at the coast to between 20 and 40m msl inland at the Nseleni River. The deepest incision in the study area is the Mhlatuze valley reaching its depths –to 60m msl. The Cretaceous sediments and the overlying Palaeocene deposits have similar hydraulic properties and identical lithology (Maud and Orr, 1975). Botha (1997) also mentions that the lithology of the Palaeocene and Cretaceous siltstones are almost identical.

4.3 HYDROGEOLOGY

Hydrogeology of the study area is characterised by unconfined aquifer. Groundwater level ranges from 1 to 47 m bgl in August 2015 (Fig 4.2) and 2 to 37 m bgl in July 2016, respectively (Fig 4.3). The pore spaces are developed to form potential water-bearing zones due to weathering which creates the weathered portions. Rainfall is the major source of groundwater recharge in this area. Transmissivity value of the study area is 10m^3/day (Martinelli and Associates, 1988). The specific storage of sand ranges from 10^{-3}m to 10^{-4}m (Anderson and Woessner, 1991). The thick impermeable siltstone and mudstone layer of Cretaceous age. Two main aquifers overlying the thick impermeable siltstone and mudstone of cretaceous age forms lower boundary to the Maputuland Group of aquifer while the highly permeable conquina and conglomerate aquifer of the Uloa Formation (Miocene age) is confined by the overlying Port Durnford formation. The unconfined to semi-confined aquifer is found overlying the unconsolidated sands (Kelbe *et al*, 2001). The texture of the grain is coarse and fine in which the layers of unconsolidated sands constitute the localised aquifers and aquitard.

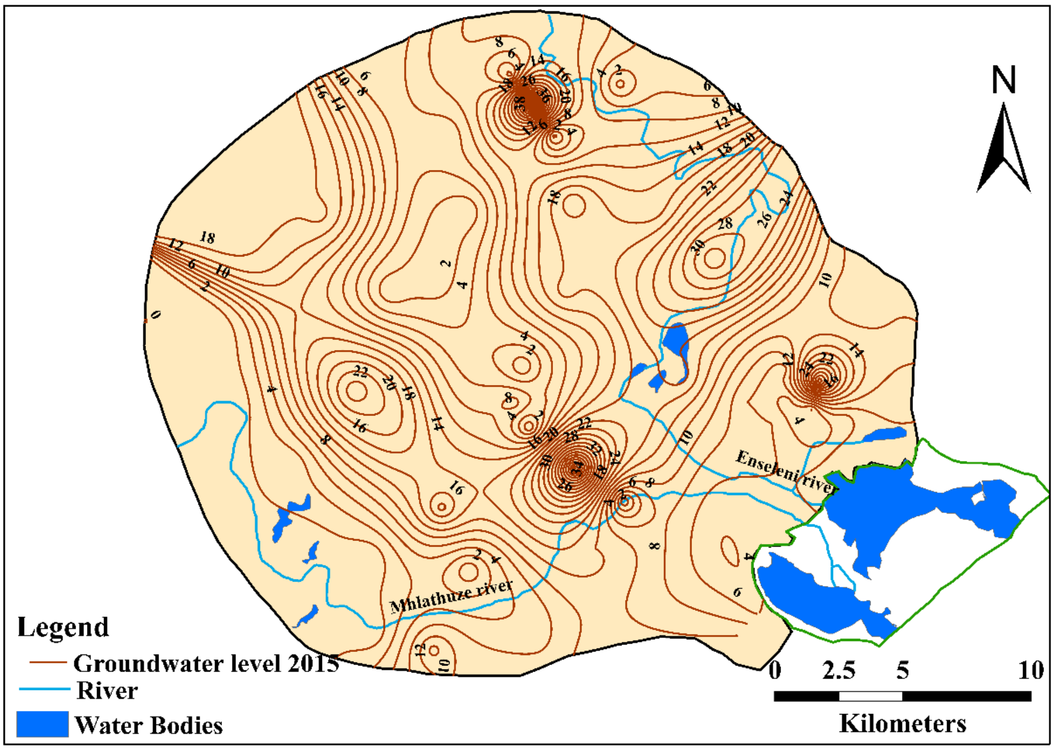


Figure 4.2 Spatial groundwater level of the study area in August 2015

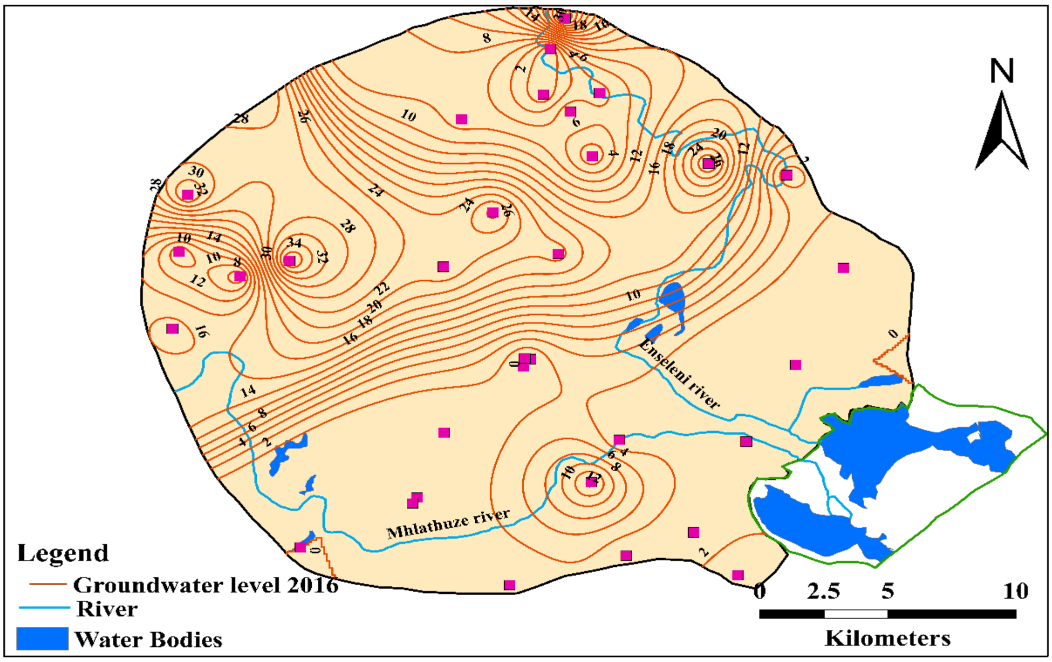


Figure 4.3 Spatial groundwater level of the study area in July 2016

CHAPTER FIVE

5 HYDROCHEMISTRY AND GROUNDWATER QUALITY

5.1 GENERAL

Hydrogeochemical characteristics of groundwater and its spatial variation in a part of Mhlathuze catchment of Empangeni and Richards Bay, Kwazulu-Natal, South Africa was carried out to assess the ground water suitability for drinking and irrigation purposes. The groundwater parameters were pH, TDS, sodium, potassium, calcium, magnesium, chloride, sulphate, bicarbonate, TH, SAR, Na%, PI, RSC and MH. MH is discussed as below.

5.2 TEMPERATURE (C°)

Water temperature controls the metabolic process of the aquatic system. Groundwater temperature varies from 21 to 30 C° with a mean of 25 C° and 17 to 30 C° with a mean of 22 C°. Spatial variation of temperature show that high temperature occurs in N-SE-central part and the low concentration extent in SW-N-SE- central part of the study area in 2015. The temperature variation in 2016 specify that low temperature occurs in southern part and the high concentration covered by NE-S-SE-central part of the area.

5.3 DISSOLVED OXYGEN

DO play an important role for sustaining aquatic life and is considerable to minor changes in the environment (Iticescu et al 2013).Very low DO indicate anaerobic condition and leads to bad odour. High DO level of water is harmful to aquatic life. DO ranges from 0.08 to 137 mg/l with an average mean of 9 mg/l and ranges from 0.27 to 5.2 mg/l with an average mean of 2.7 mg/l of groundwater in 2015 and 2016 respectively. Spatial variation of DO specify high value in central part of the area and the low value in all the other parts except the central part of the study area in 2015. High value of DO is detected in the S-SE-W-central part and low value of DO is detected in the SE-S-central part of the study area in 2016.

5.4 OXYGEN REDOX POTENTIAL

ORP is a measurement of constituent in water that specifies the capable of oxidizing/reducing condition in groundwater. Positive ORP values specified that the substance is an oxidizing agent, the high ORP values indicate more oxidization. Negative ORP value show that substance is a reducing agent, the low value of ORP are indicative of more anti-oxidizing. ORP ranges from -21.6 to 8.23 with an average mean of -0.40 in 2015 and -32 to 6.21 with an average mean of -5 of groundwater in 2016. Spatial variation of ORP show that high value is noticed in the W-NE-S-SE-central part of the area indicated oxidizing condition and low value is observed in the SE-central part of the area indicated reducing condition in 2015. NW-NW part of the study area has high ORP value which indicated oxidizing condition and SE-central part of the area is noticed with low ORP which indicated the reducing condition of groundwater in 2016.

5.5 HYDROCHEMISTRY

The statistical summary such as minimum, maximum and mean concentration of physical and chemical constituents of groundwater in 2015 (Fig 5.1a) and 2016 (Fig 5.1b).

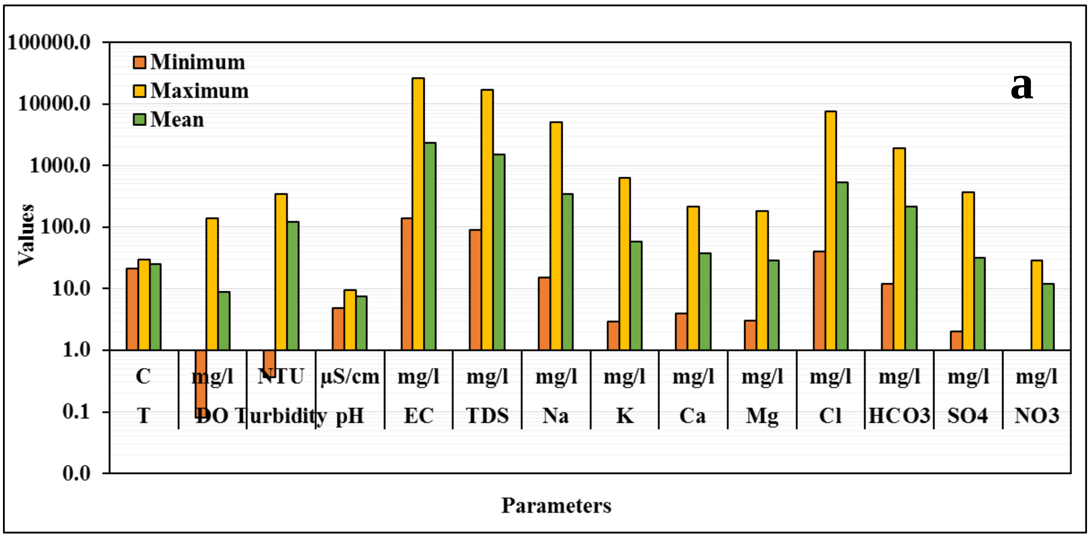


Figure 5.1a Minimum, maximum and mean concentration of various parameters of groundwater in 2015

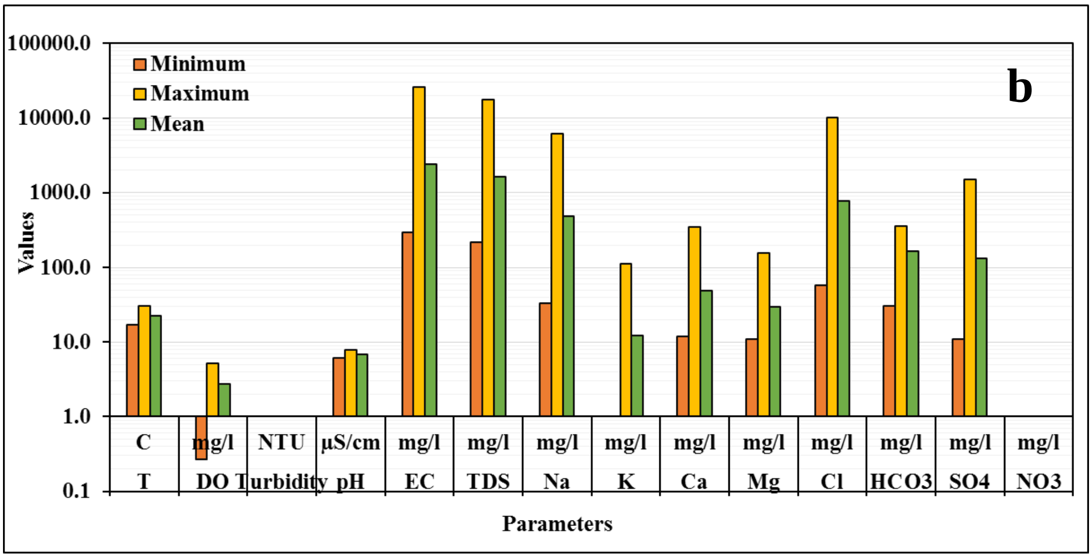


Figure 5.1b Minimum, maximum and mean concentration of various parameters of groundwater in 2016

5.5.1 Major ions

Dominance of major ions in the groundwater of study area was observed in the following order: Na > K > Ca > Mg and Cl > HCO_3 > SO_4 > NO_3 in the year 2015 and the 2016, respectively. Dominance of major cations are Na > Ca > Mg >K and anions are in the order HCO_3 > SO_4 > Cl, respectively. The major ion concentrations of groundwater are explained in detail as following section.

5.5.1.1 Sodium

Sodium value varies from 15 to 5121 mg/l with an average mean of 342 mg/l whereas, ranges from 33 to 6123 mg/l with an average mean of 483 mg/l of groundwater were observed in 2015 and 2016, respectively. About 13% and 21% of groundwater samples exceeds the permissible limit in 2015 and 2016. The Spatial variation of sodium (Fig 5.2a) in the study area indicates that most of the study area falls under permissible limit (200 mg/l) and NW-SE- and central part of the study area fall under unsuitable (>200ml) category in 2015. N-NW-NE-central part of the area are unsuitable and remaining parts of the area are permissible in 2016 (Fig 5.2b). The high concentrations of sodium in the study area are mainly due to industrial effluents and the intensity of weathering of sodium bearing minerals from the rock formation

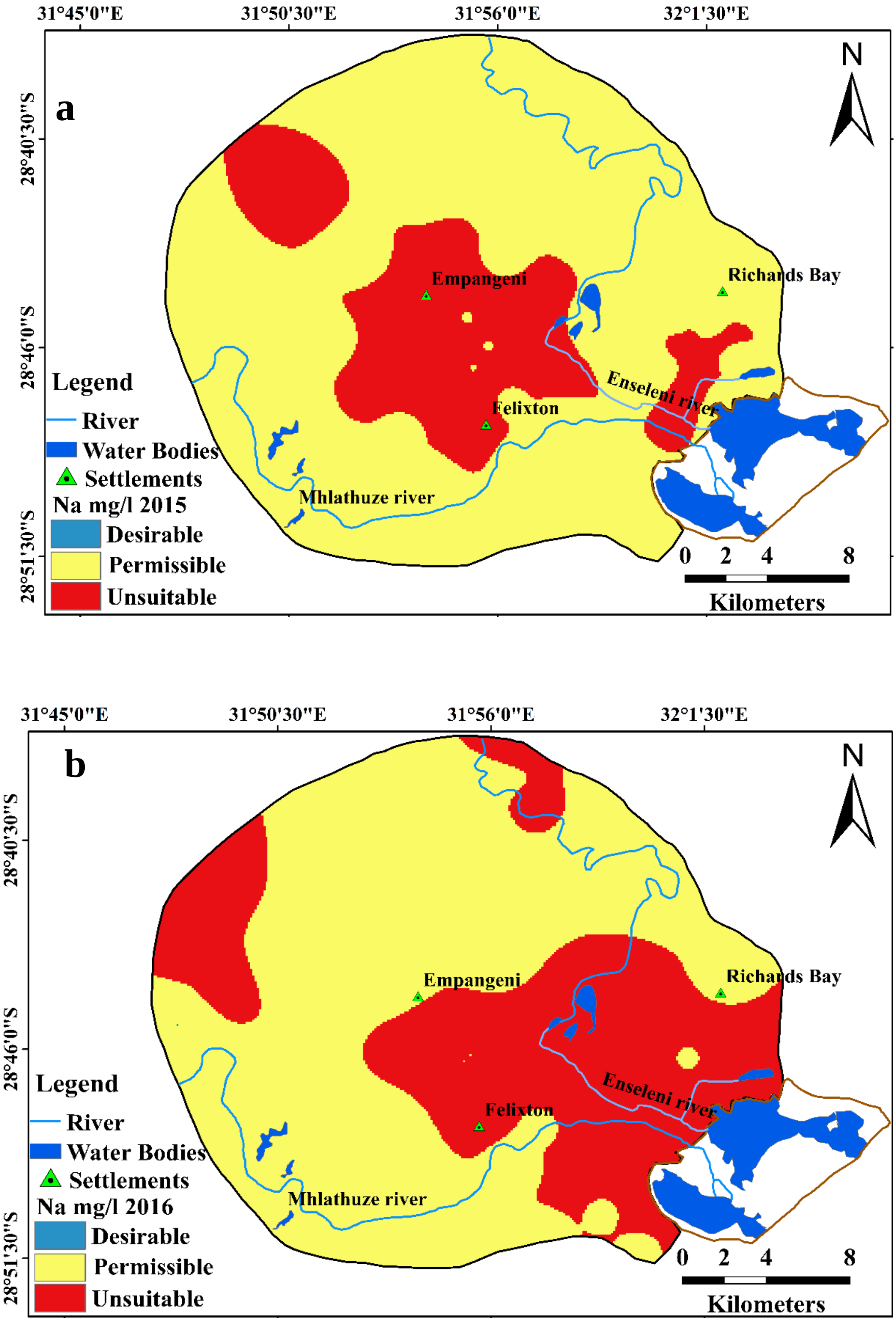


Figure 5.2 a, b. spatial variation of sodium (mg/l) of groundwater in 2015 and 2016

5.5.1.2 Potassium (K)

Potassium is a vital constituent in humans and if ever occurs in drinking water at greater levels (3 mg/l) could create health concerns. Human consumption of potassium level are greater than 3 mg/l. High intake of potassium in human consumption can cause cardiac arrhythmia, muscle weakness, nausea and vomiting (WHO 2004). Potassium concentration varies from 3 to 634 mg/l with an average mean of 58 mg/l in 2015 and ranges from 1 to 112 mg/l with an average mean of 12 mg/l in 2016. About, 18% and 9% of groundwater exceeded the permissible limits of WHO standards (2008) in the year 2015 and 2016 respectively. The Spatial variation of potassium in the groundwater (Fig 5.3a) are categorised as desirable (<12 mg/l) in the NW- N portion, N-NE-NW-S falls under permissible limit (12 mg/l) and the NW-NE-NS-central part are categorised as unsuitable (>12 mg/l) in 2015. SE-NE and central part are categorised as unsuitable, few patches on N-SW are desirable and the remaining part are permissible in 2016 (Fig 5.3b). High concentration of potassium in the study area is as the result of pollution leaching from potassium fertilizers.

5.5.1.3 Calcium (Ca)

Calcium concentration varies from 4 to 217 mg/l, with an average mean of38 mg/l and ranges of value from 12 to 348 mg/l, with an average mean of 49 mg/l were observed in 2015 and 2016, respectively. Around, 5% and 3% of groundwater samples exceeded the permissible limit of WHO standards in the year 2015 and 2016 respectively. Spatial variations of calcium in groundwater of the study area are shown in figure 5.4 a and b. This figure indicates that a few patches on S-NW are desirable (75 mg/l), in NW-SE- central part the quality was unsuitable (>200 mg/l) and the remaining part of the area were observed falling under permissible limits (200 mg/l) in 2015. Generally, calcium moves into the water as $CaCO_3$ (calcium carbonate) and calcium sulphate ($CaSO_4$) in the form of dolomite and limestone. Deficiency of calcium affects severe Osteomalacia and excess intake of human consumption affects kidney and may cause irritation in urinary track (CPCB, 2008).

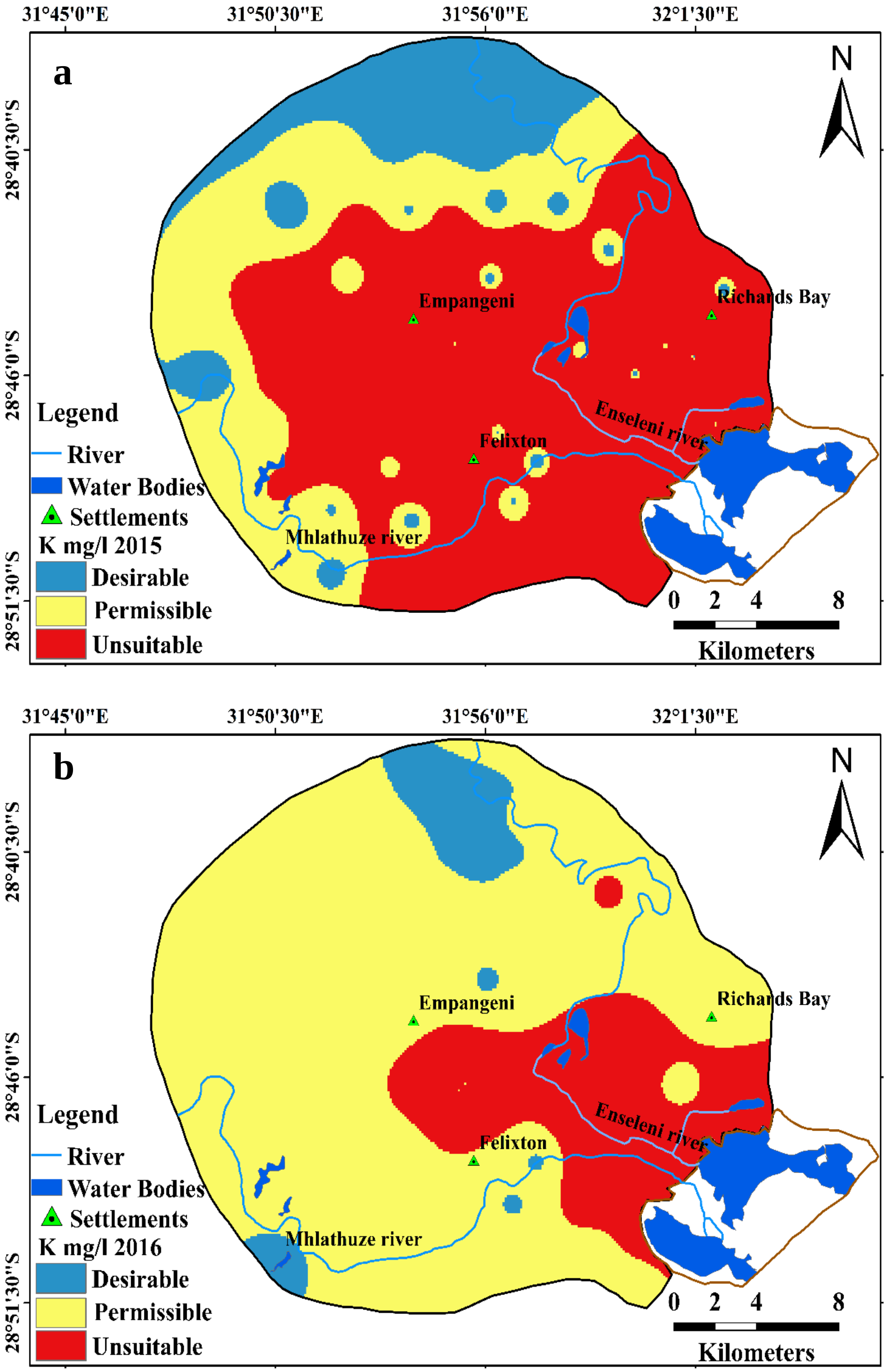


Figure 5.3 a, b. spatial variation of potassium (mg/l) of groundwater in 2015 and 2016

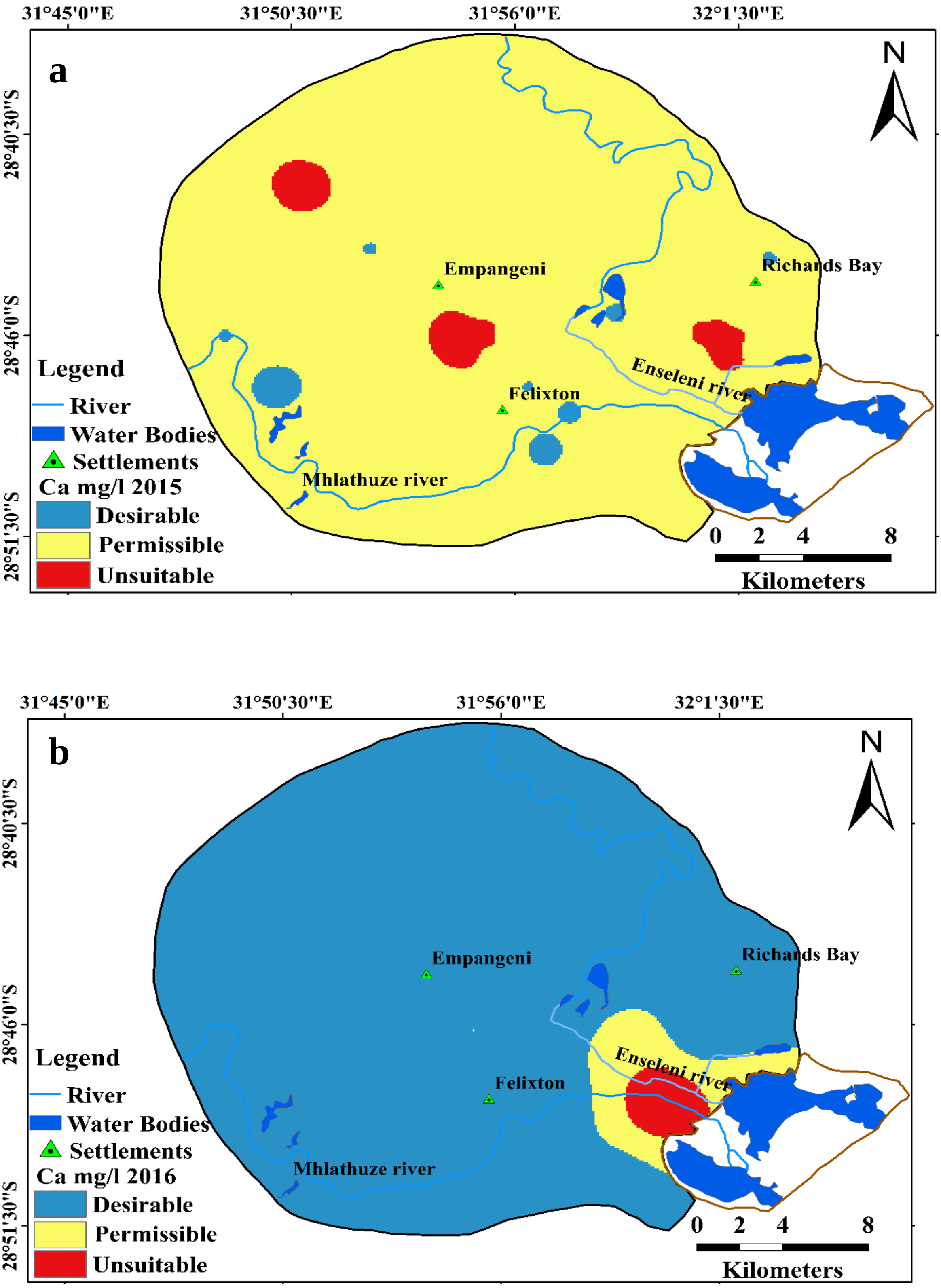


Figure 5.4 a, b. spatial variation of calcium (mg/l) of groundwater in 2015 and 2016

5.5.1.4 Magnesium

Main source of magnesium in the groundwater are the exchange of minerals from rock and soil. Magnesium concentration varies from 3 to184 mg/l, with an average value of 29 mg/l whereas, the ranges from 11 to 156 mg/l, with an average mean value of 30 mg/l were observed in 2015 and 2016 respectively. About 3% of the groundwater samples exceeded the permissible limit of WHO standard in 2015 and 2016. Spatial variation of magnesium of groundwater is noticed in small patches on central part are found unsuitable (>150 mg/l), whereas the SE-N-NW part are observed falling under permissible limit (150 mg/l) and the remaining part of the area fall under desirable limit (30 mg/l) in 2015 (Fig 5.5a). A small patch on the SE part is found unsuitable while the SE-N-central part is observed permissible and the remaining part of the study area is observed to be under desirable limit in 2016 (Fig 5.5b). Magnesium minerals are present in olivine, amphibolite, pyroxene, chlorite groups of rocks and in some clay minerals (Matthess, 1982). Solubility of $MgCO_3$ in water and CO_2 are $>CaCO_3$ therefore normal groundwater condition, $MgCO_3$ are not precipitated (Hem, 1985). The daily human consumption of magnesium is 0.7g (Shohl, 1939). High concentration of magnesium leads to laxative problems (CPCB, 2008).

5.5.1.5 Chloride

Natural water contains low concentration of chloride when compared to other major ions. Chloride concentration ranges from 40 to 7657 mg/l, with an average mean of 531 mg/l and the concentration ranges from 58 to 10250 mg/l of groundwater in 2015 and 2016 respectively. About, 13% and 12% of groundwater samples exceeded the permissible limit of WHO (2008) in 2015 and 2016. Spatial variation of chloride in groundwater (Fig 5.6a) indicate unsuitable (>600 mg/l) water quality in the SE-NW-central part, while in the SE-NW-central part it falls under permissible limit (600 mg/l) and the remaining part of the study area are observed to be under desirable (<600 mg/l) limits in 2015. In the SE-E-N-NW- central part, the quality is categorised as unsuitable while the remaining parts of the area falls under desirable limits in 2016 (Fig 5.6b). High concentrations of chloride in the study area are due to industrial effluents and leaching of salts and Cl bearing minerals from igneous rock. Marine and terrestrial evaporates deposits also contains chloride (Matthess 1982).

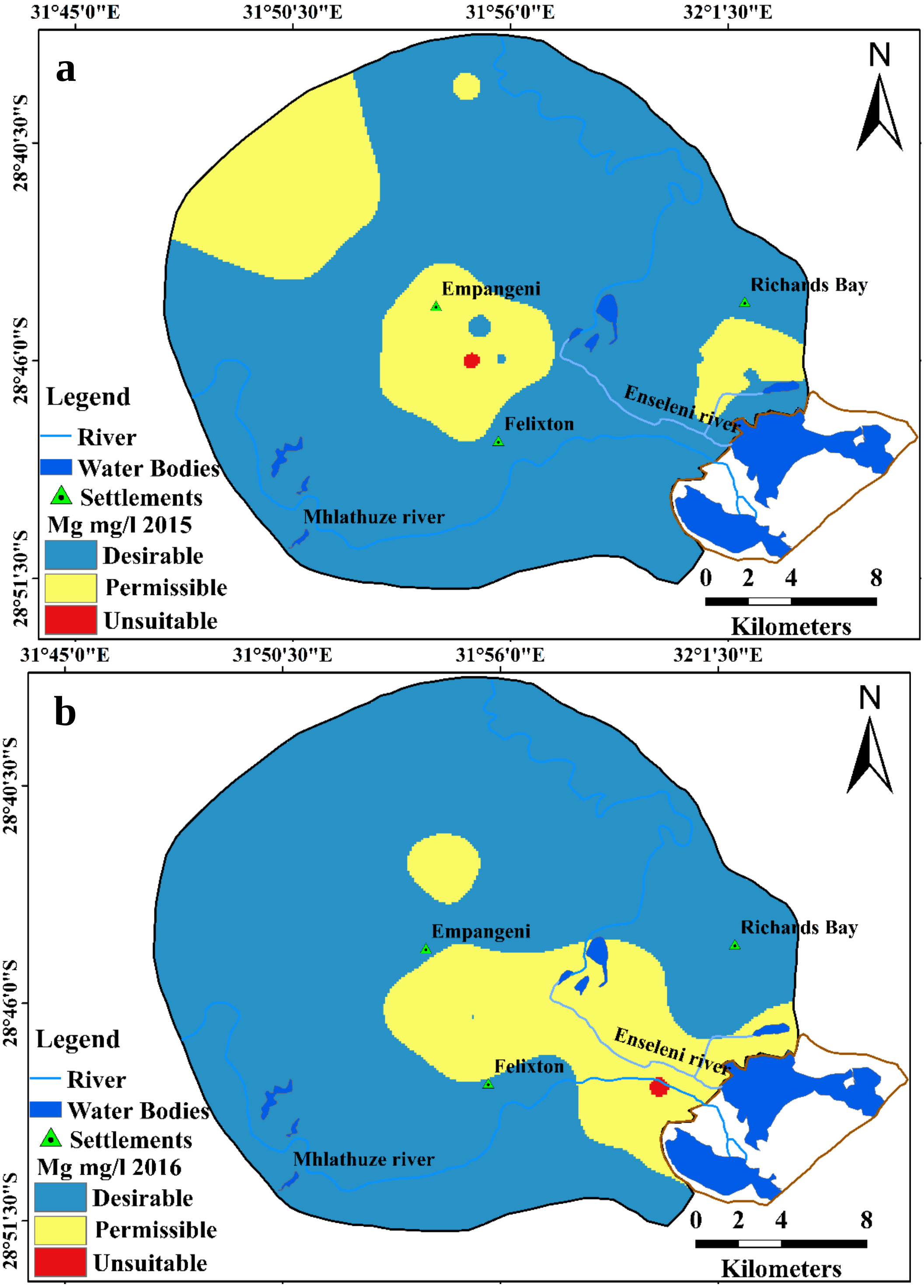


Figure 5.5 a, b. spatial variation of magnesium (mg/l) of groundwater in 2015 and 2016

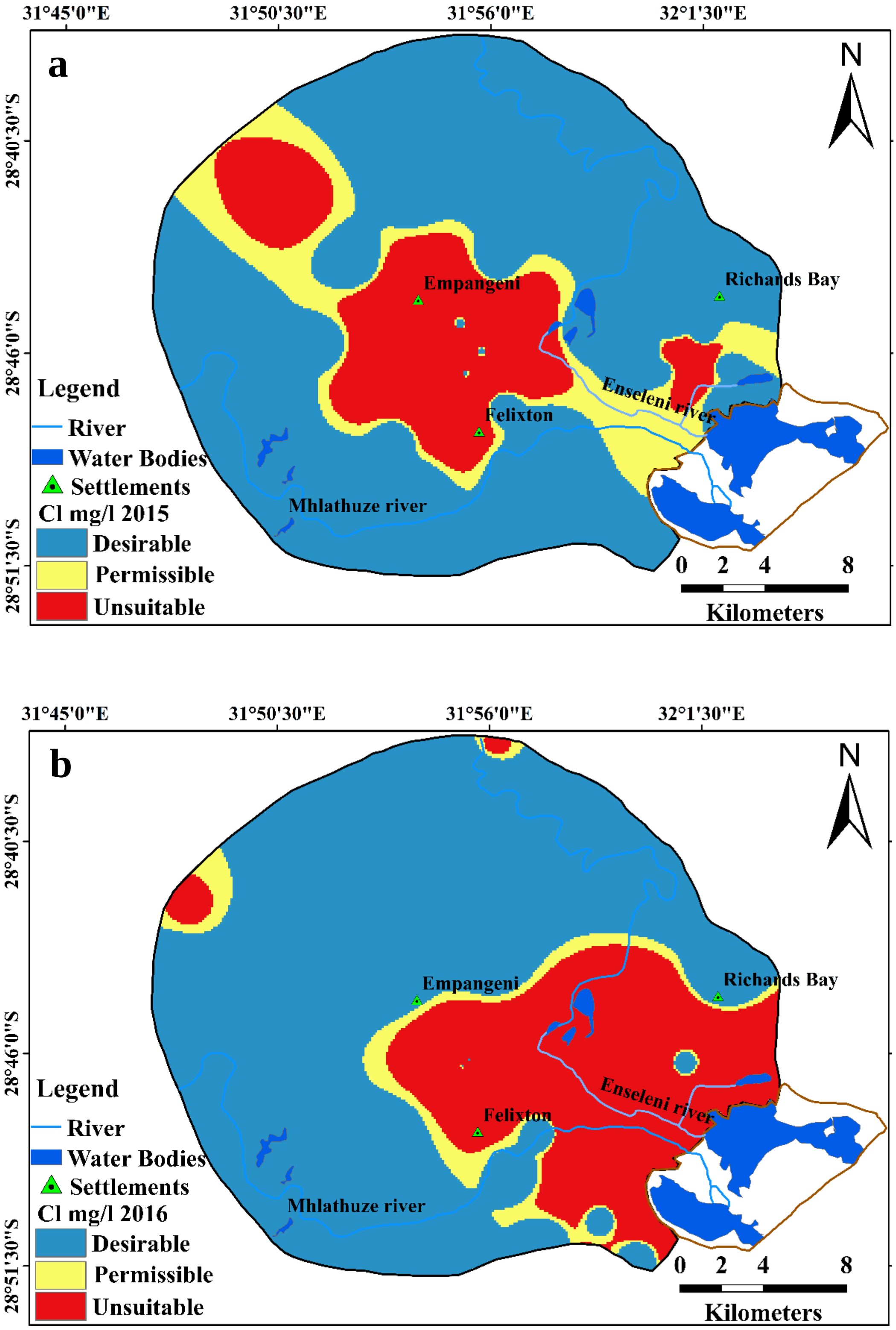
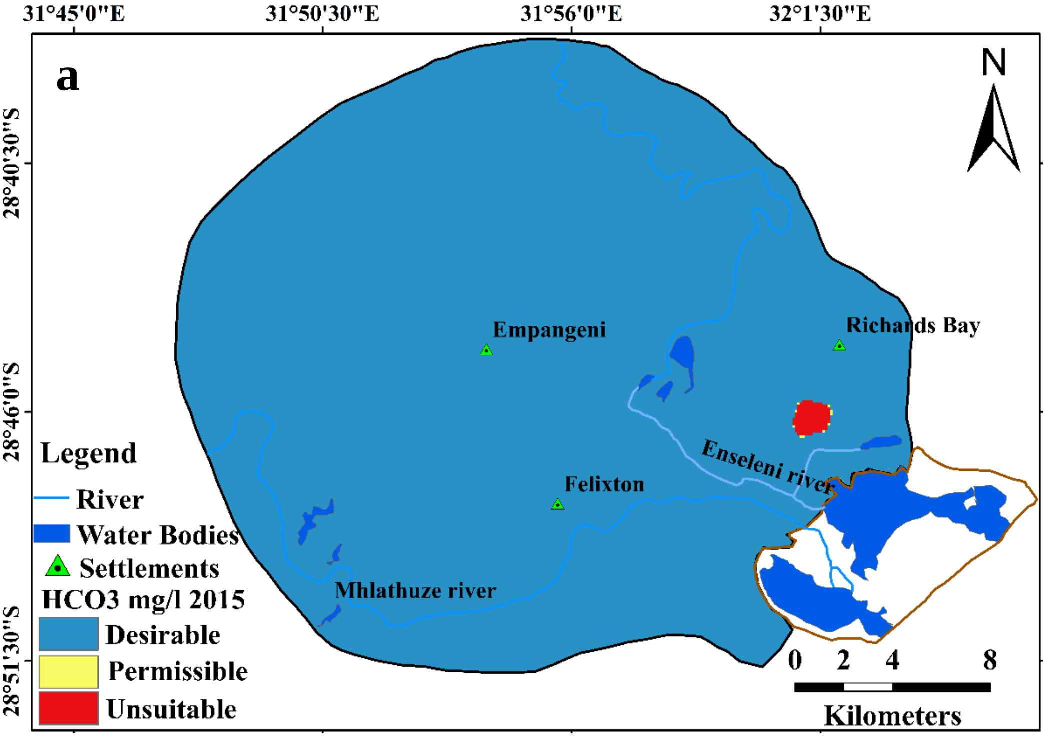


Figure 5.6 a, b. spatial variation of chloride (mg/l) of groundwater in 2015 and 2016

5.5.1.6 Bicarbonate

Bicarbonate concentration of the groundwater (Fig 5.1a) varies from 12 to 1903 mg/l, with an average mean of 218 mg/l and the ranges from 31 to 360 mg/l, with an average mean of 167 mg/l are observed in 2015 and 2016, respectively. About 3% and 2% of groundwater samples exceeded the permissible limits (600 mg/l) of WHO standards (2008) in 2015 and 2016. Spatial concentrations of bicarbonate in groundwater (Fig 5.7a) are permissible (600 mg/l) in the form of patches in the SE and central part of the area. The remaining part of the area are desirable (200 mg/l) while few locations are unsuitable (>600 mg/l) in SE part of the Richard Bay in 2015. NW part of the area are noticed permissible and unsuitable whereas remaining part of the area are observed desirable in 2016 (Fig 5.7b). High concentration of bicarbonate specifies that high intensity of chemical weathering in present in this study area. Bicarbonate can also derive from surface water sources, bacterial degradation of organic matter, anthropogenic CO_2 gas affect from industrial wastes decked in the unlined dumping sites and oxidation of organic matter seeped from old latrines and sewage system (Clark and Fritz, 1997).



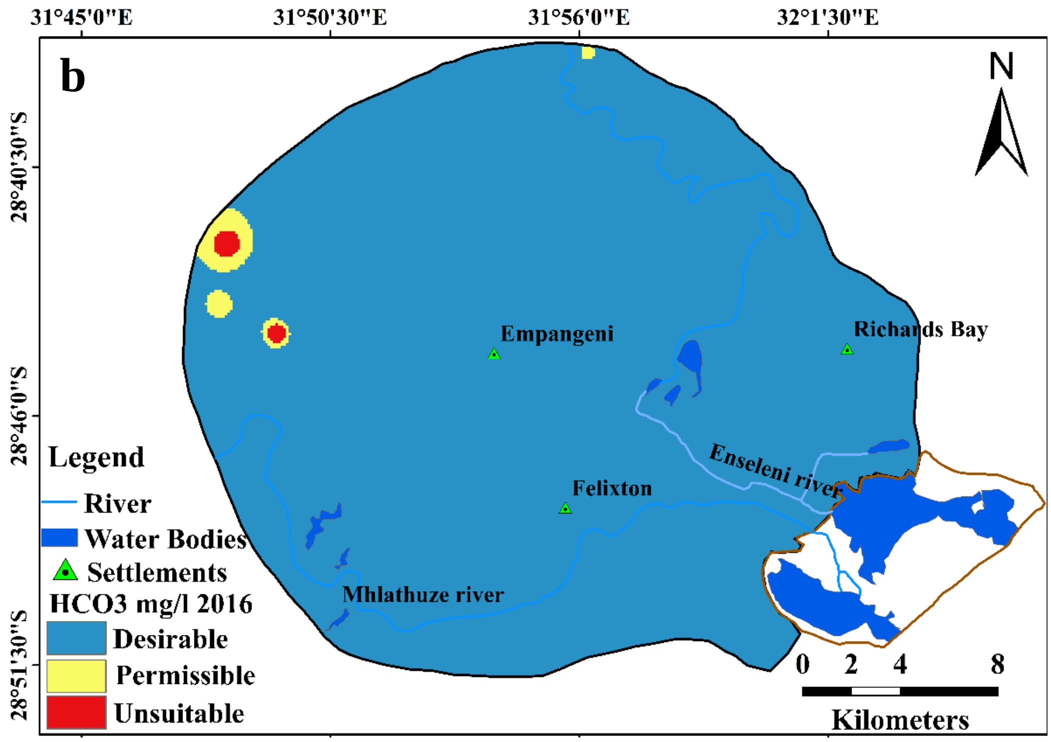


Figure 5.7 a, b. spatial variation of bicarbonate (mg/l) of groundwater in 2015

5.5.1.7 Sulphate

Sulphate concentration of the groundwater ranges from 2 to 374 mg/l, with an average mean of 32 mg/l and the ranges from 11 mg/l to 1514 mg/l, with an average mean of 133 mg/l are observed in 2015 and 2016, respectively. About 3% of groundwater samples exceeded the permissible limits of WHO standards in 2015 and 2016. Spatial variation of sulphate in groundwater (5.8a) revealed high sulphate concentration in the NW-central part of the area making it unsuitable (>400 mg/l) while the NW-central part are observed within permissible limits (400 mg/l) and the remaining part of the study area have desirable sulphate levels (200 mg/l) in 2015. SE part of the study area are unsuitable and the remaining part of the area are observed falling under desirable limits in 2016 (5.8b). High sulphate concentrations are derived from the dissolution of gypsum and halite deposits. Low sulphate concentrations of the study area are controlled by sulphate reduction process. High intake of sulphate concentration in groundwater affects respiratory problems (Maiti, 1982).

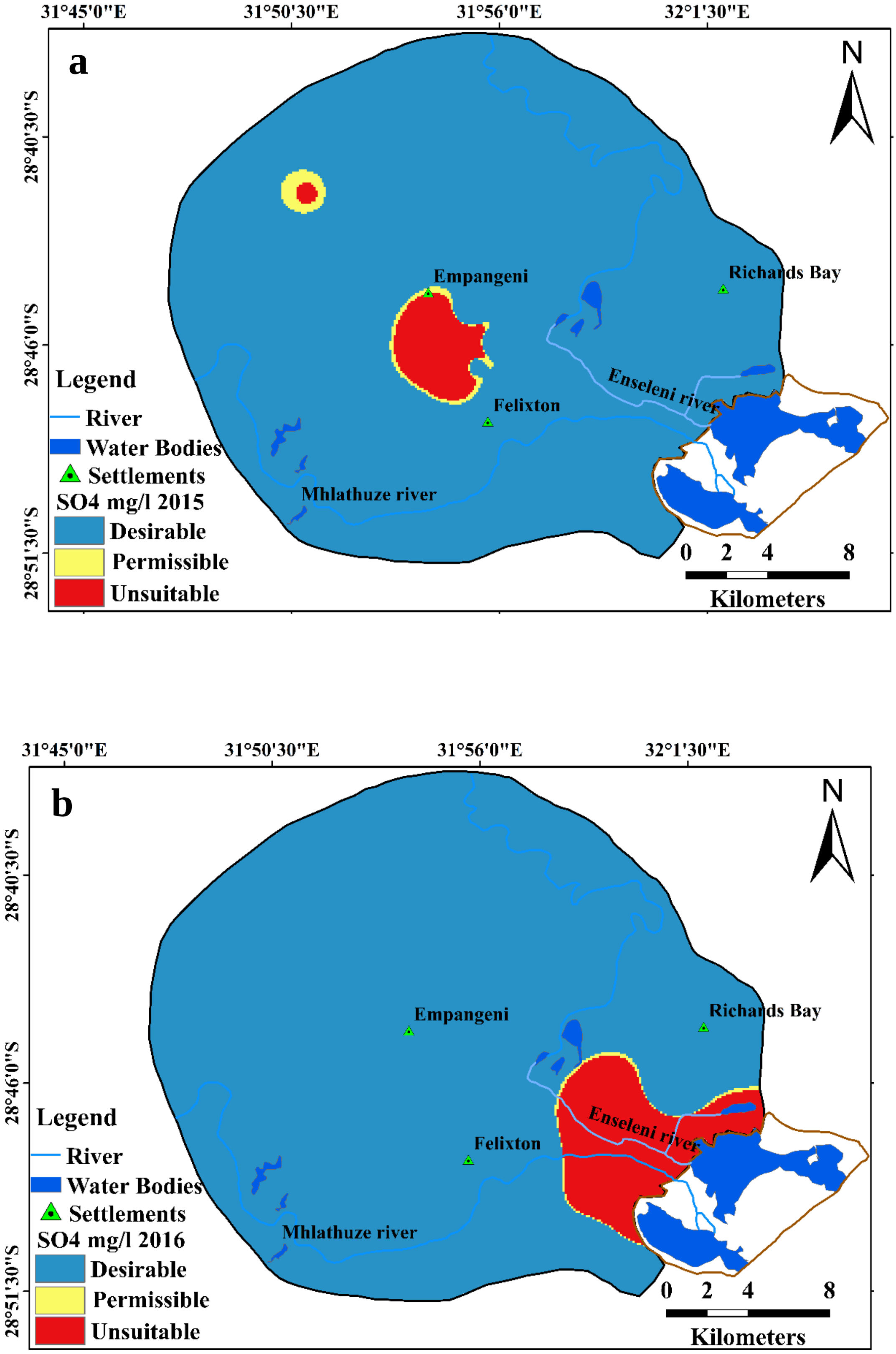


Figure 5.8 a, b. spatial variation of sulphate (mg/l) of groundwater in 2015 and 2016

5.6 DRINKING WATER QUALITY

Water quality for drinking purpose is influenced by its physical, chemical, biological constituents. The groundwater quality with regard to the major ion was assessed. All the required parameters were analysed and compared with the (Fig 5.9) of the World Health Organisation (WHO, 2008) standard guidelines.

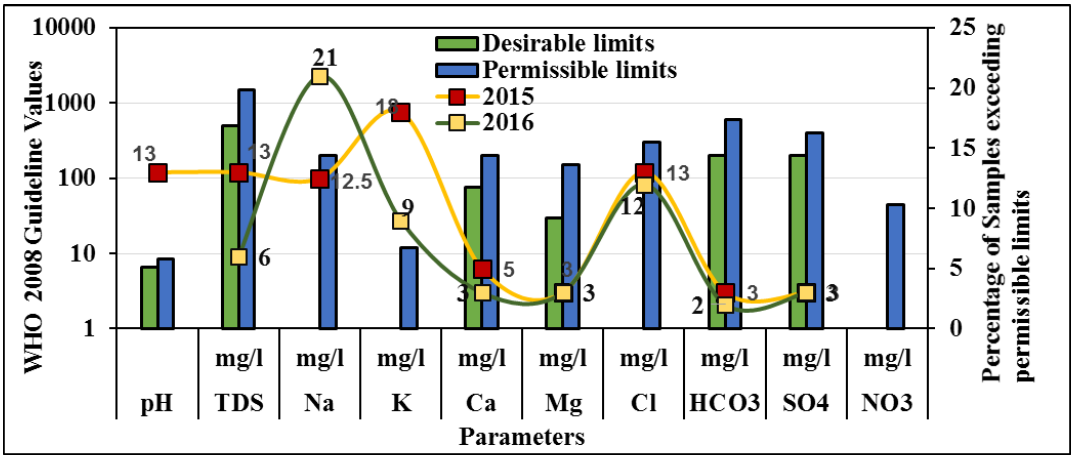


Figure 5.9 Suitability of groundwater for drinking based on WHO (2008) standards

5.6.1 pH

pH is the calculation of the degree of acidity/alkalinity and the estimation concentration of the hydrogen ion in groundwater. pH does not have adverse effect on health. Low value of pH i.e. <4 creates bitter taste and the high value of pH i.e >8.5 causes alkaline taste. The pH of the study area ranges from 4.8 to 9.5 with an average mean of 8 whereas the ranges from 6.05 to 8 with an average mean of 7 in 2015 and 2016, respectively indicated that the water is acidic to alkaline in nature. 13% of the groundwater samples exceeded the permissible limit in 2015 and 2016 as recommended by WHO (2008). Spatial variation of pH in groundwater of the study area are shown in Fig 5.10 a,b 2015 and 2016 respectively.

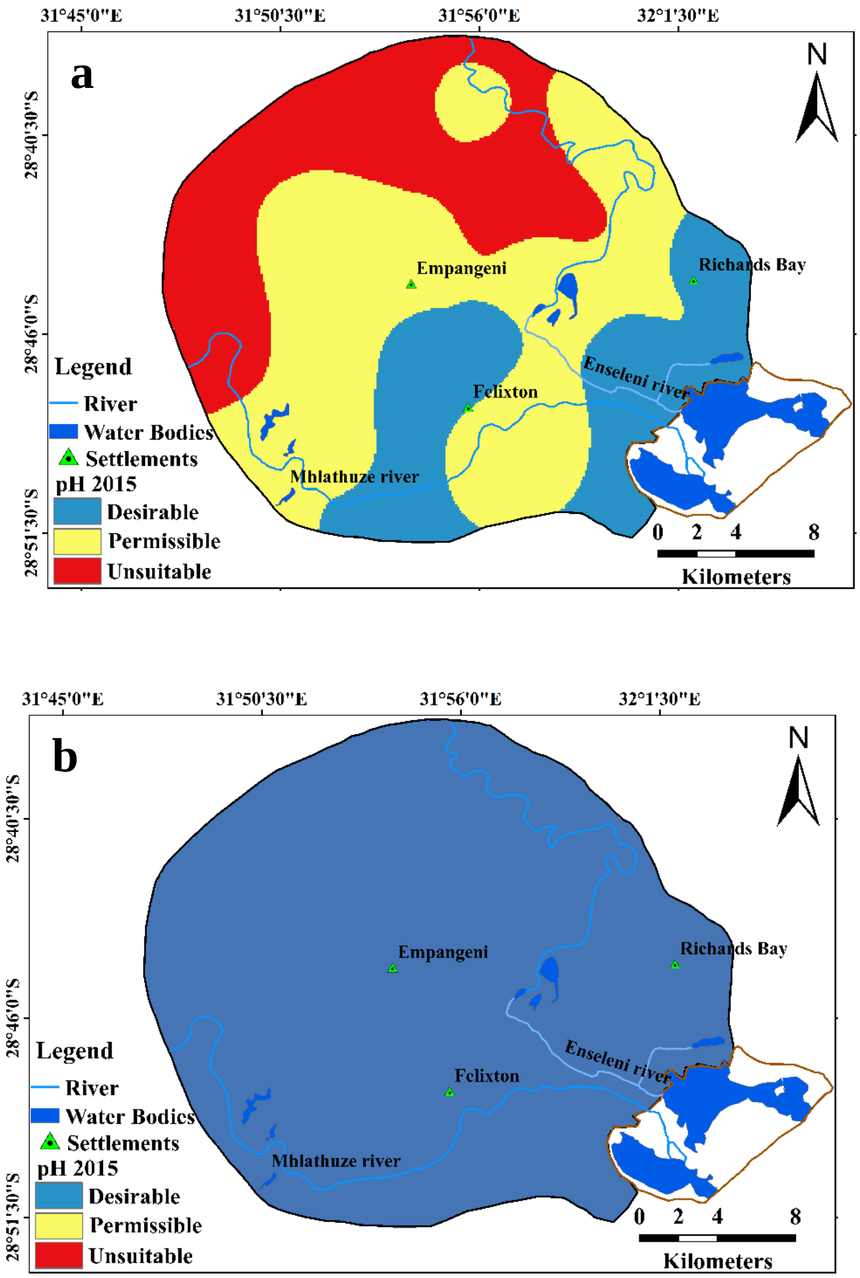
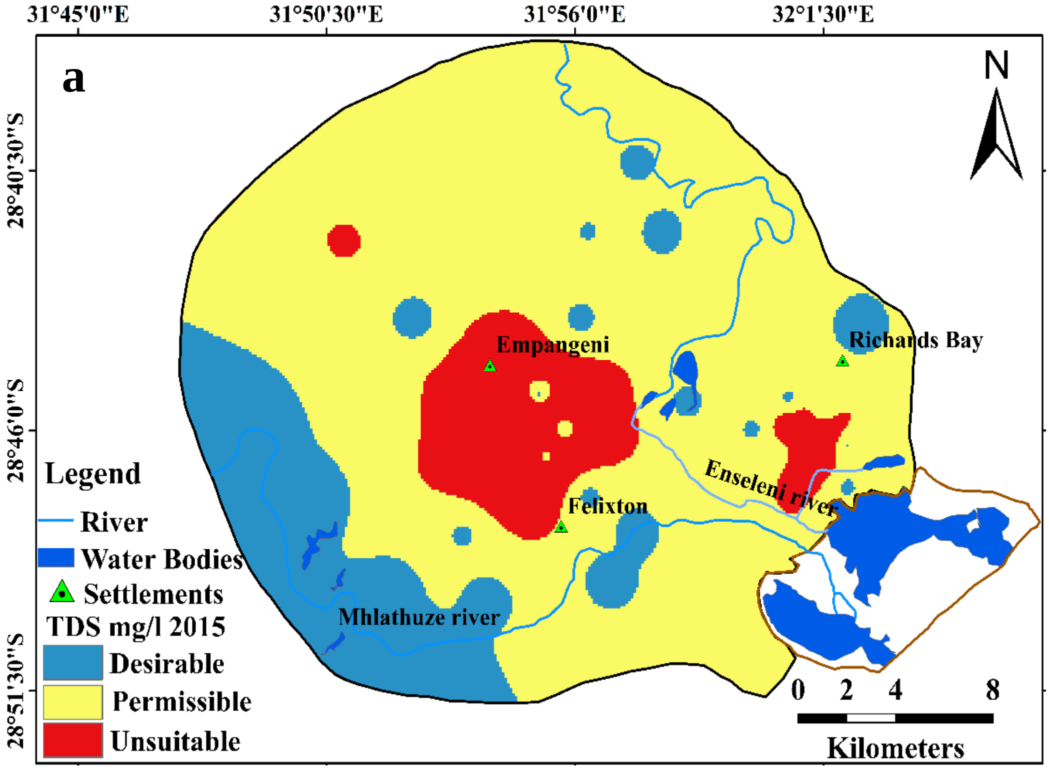


Figure 5.10a,b Spatial variation of pH of groundwater in 2015 and 2016

5.6.2 Total Dissolved Solids

TDS mainly consists of inorganic salts such as sodium, potassium, calcium, magnesium, chloride, sulphate and bicarbonate and minor quantities of organic matter dissolved in water. TDS concentration is the sum of the positively charged ions known as cation and negatively charged ions known as anion in the water. TDS ranges from 90 to 17860 mg/l with an average mean of 1336 mg/l and ranges from 218 to 17860 mg/l with an average mean of 1635 mg/l of groundwater in 2015 and 2016, respectively. About, 13% and 6% of groundwater samples exceeded the permissible limits of WHO (2008) in 2015 and 2016. Spatial Variation of TDS mg/l in groundwater (Fig 5.11a) specifies that SW and few patches of NW part are desirable. NS, NE, NW parts are permissible and SE-central part is unsuitable during the year 2015. SW-S-E-SE-few patches on the central part are desirable. SE-central part are unsuitable and the remaining part of the area are permissible during the year 2016 (Fig 5.11 b). High value of TDS specifies that the salts leach out from the soil and indicates that the sources are from anthropogenic activities. Possible of domestic sewage infiltration into the groundwater may result in increased values of TDS (Ward, 1994).



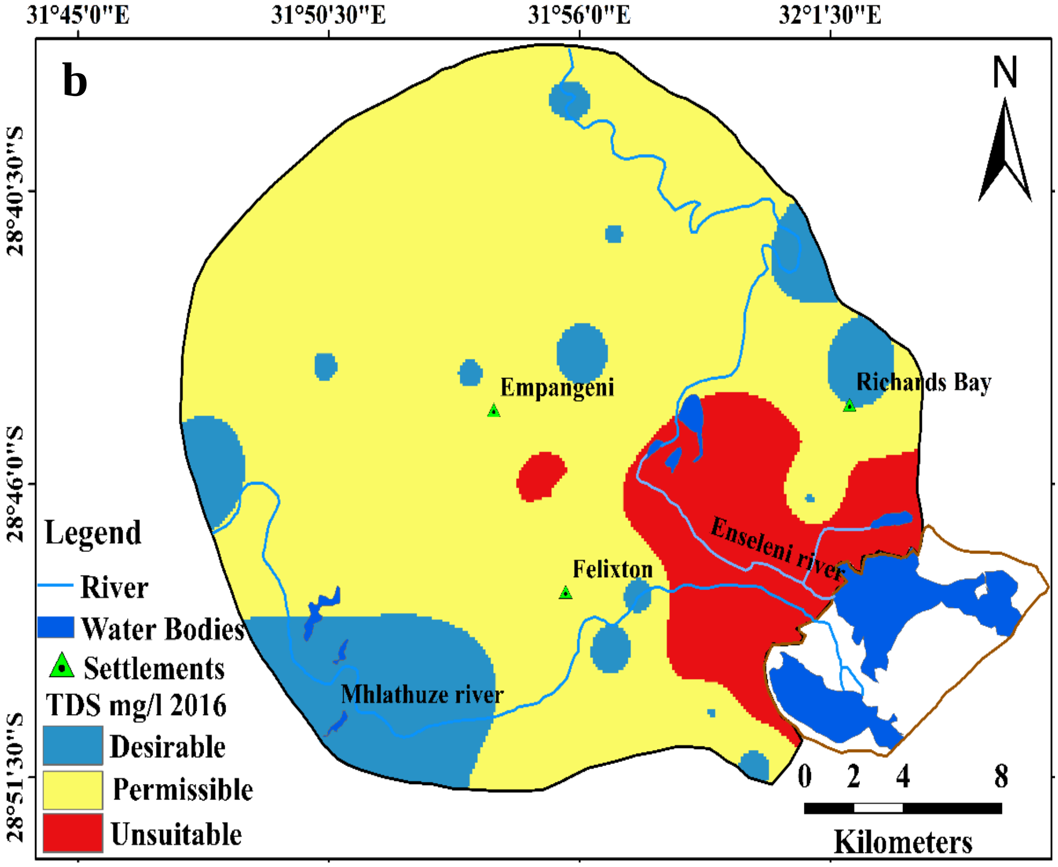


Figure 5.11 a,b. spatial variation of TDS (mg/l) of groundwater in 2015 and 2016

5.6.3 Total Hardness

TH value ranges from 31 to 1297 mg/l with an average mean of 213 mg/l and ranges from 87 to 1510 with an average mean of 246 mg/l of groundwater in 2015 and 2016. TH is classified based on Sawyer and McCarty‘s (1978) classification as shown in figure 5.12. Around, 25% of groundwater samples are soft, 40% and 39% are moderately hard, 23% and 56% are hard and 12% and 5% are very hard in 2015 and 2016, respectively. This TH classification exhibits that the groundwater in the study area fall under soft to very hard. Spatial variation of TH in groundwater indicate that SW-S-few patches on the NE-E part of the area are of desirable (100 mg/l), SE part of TH are unsuitable (>500 mg/l) and NS-EW part of the area fall under the permissible category (500 mg/l) in 2015 (Fig 5.13a). NS-EW-NE-NW-SE-SW part of the area are permissible, SE part of the area and few patches on the central part of the area are unsuitable in 2016 (Fig 5.13b). Raising value of TH may be due to leaching of minerals from geological formation (Ramesh and Elango 2006).

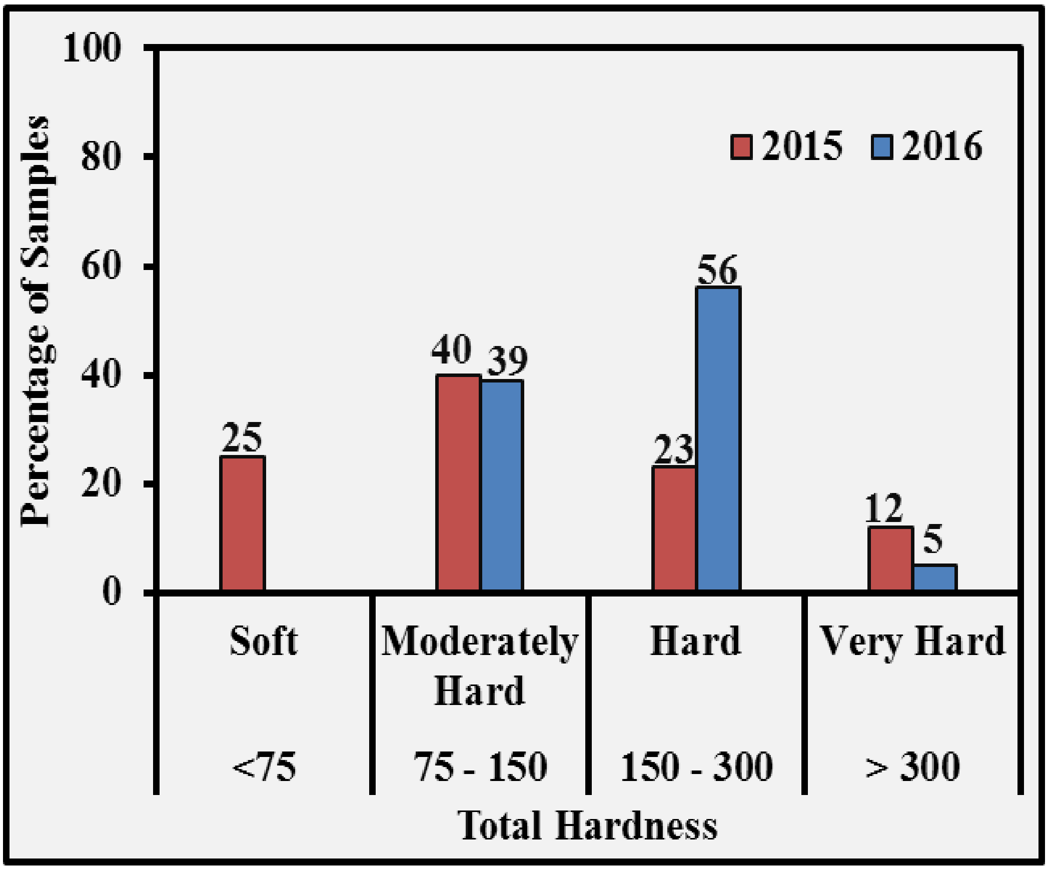


Figure 5.12. Classification of total hardness (TH) of groundwater (Sawyer and McCarty 1978)

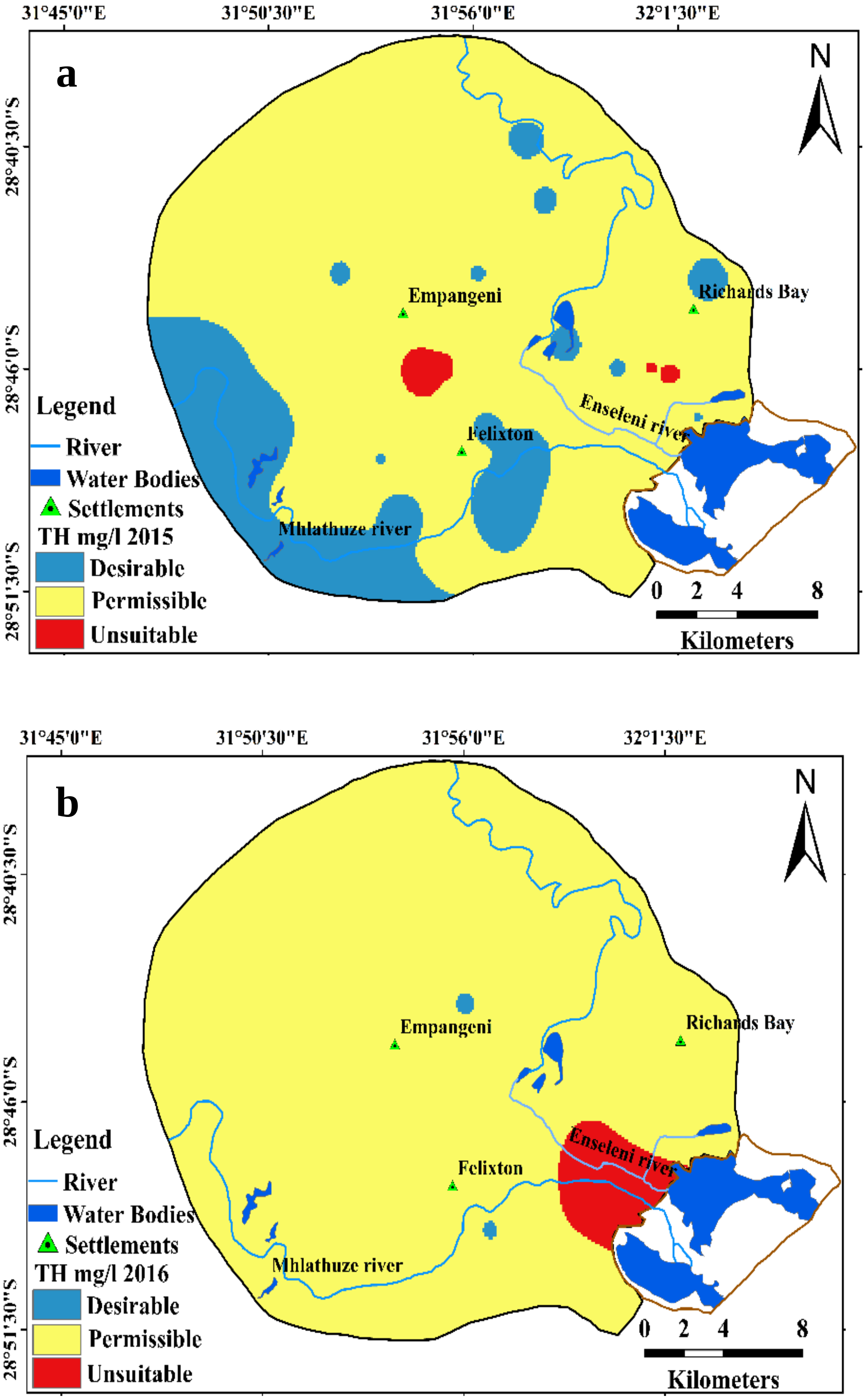


Figure 5.13a,b Spatial variation of total hardness (TH) of groundwater in 2015 and 2016

5.7 IRRIGATION WATER QUALITY

Irrigation water quality is essential for crop yield, sustainability of soil and production (Singh and Singh 2008). Irrigational water quality of groundwater in the study area were assessed by adopting ECEC, SARSAR, USSL classification, Na %, Wilcox diagram, RSC, PI and MR.

5.7.1 EC and SAR

Sodium and EC are significant to classify irrigation water. Naturally occurring salts in water affects the plant growth and also reduces permeability of the soil matrix and aeration. Freeze and cherry (1979) classified the water into 4 salinity groups- low (< 250µS/cm), medium (250-750 µS/cm), high (750-2250 µS/cm) and very high (2250-5000 µS/cm) figure 5.14. Based on the EC of groundwater samples 5% were low, 46% and 52% were medium, 35% were high, 8% and 3% were very high, 6% and 3% were unsuitable in 2015 and 2016, respectively. Spatial variation of EC in 2015 and 2016 is shown in the figure 5.15 a and b. EC concentrations of groundwater affects the formation of soil in saline and also high sodium concentration in groundwater leads to alkalinity of soil.

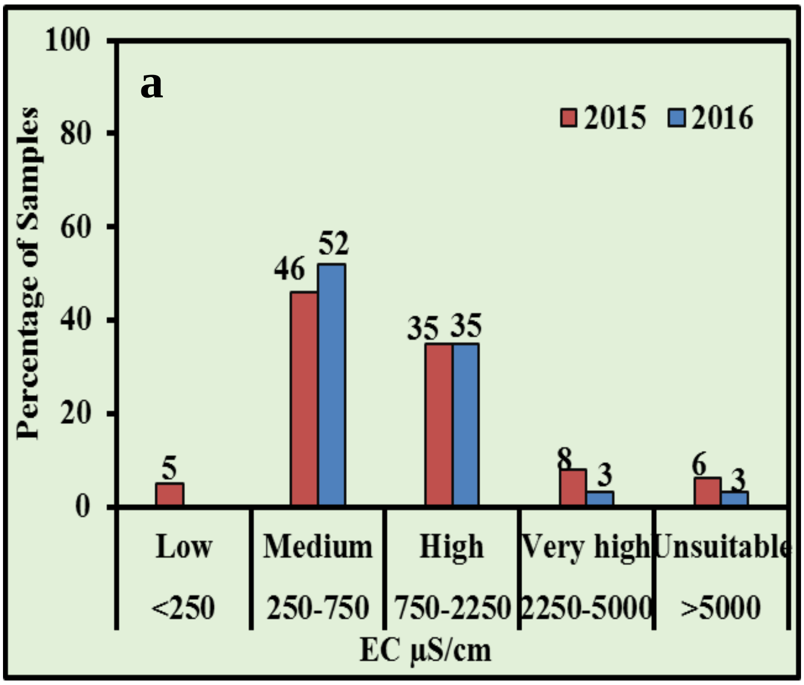


Figure 5.14 Classification of EC based on Wilcox (1955)

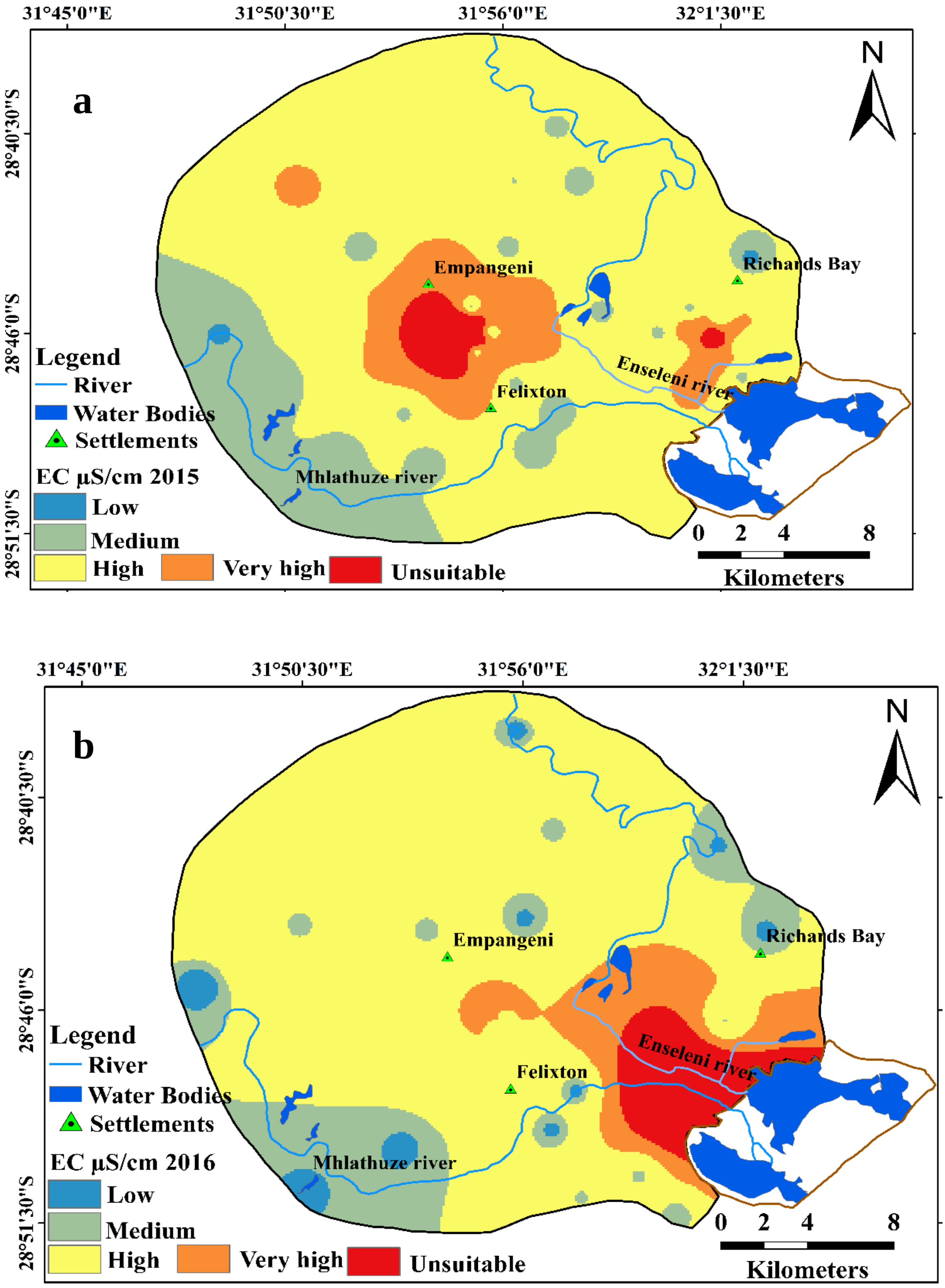


Figure 5.15 ab, spatial variation of EC µS/cm of groundwater in 2015 and 2016

The sodium/alkali hazard is utilized to assess the irrigation water quality as they are influenced by relative and direct concentration of major cations which are termed as SAR. Richards (1954) classified SAR into 4 classes namely, excellent (<250), good (10-18), doubtful (18-26) and unsuitable (>26). According to this classification, SAR concentration of groundwater samples in the study area about 24% and 12% are excellent, 35% and 42% are good, 23% and 18% are doubtful, 18% and 28% are unsuitable in 2015 and 2016, respectively (Fig 5.16). High sodium and low calcium concentrations indicate cation exchange between saturated sodium. This leads to break down of the soil structure due to dispersal of clay particles.

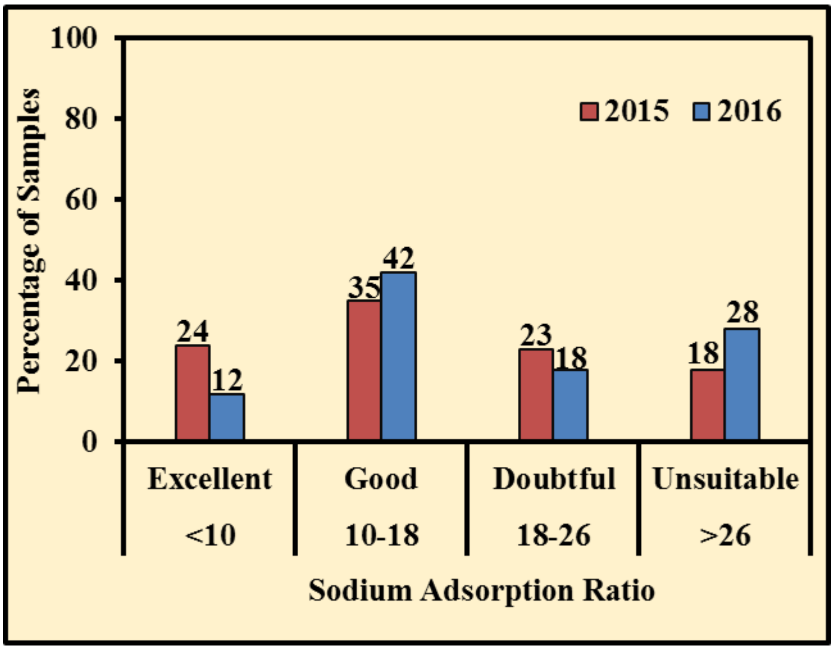


Figure 5.16 Classification of SAR based on Richard (1954) of groundwater in 2015 and 2016

USSL salinity diagram (Fig 5.17) is plotted as EC and are considered as salinity hazard while SAR is considered as alkalinity hazard. This figure indicates that C1S1-low salinity and low sodium hazard are utilised for irrigating all types crop in the soils and low level of Na exchange is a low threat to the soil. C2S2medium salinity and medium sodium hazard indicates moderate leaching and poorly textured fine soils. C2S3- implies medium salinity and high sodium hazard, C2C4 implies medium salinity and very high sodium hazard. C3S1-implies high salinity and low sodium, C3S3-implies high salinity and high sodium which indicate that plants obtain moderate salt tolerance, permeability with leaching of soils and cannot be used on clayey soils of low permeability. C3S4-implies high salinity and very high sodium hazard in water. C4S4 and C5S4- imply very high salinity and very high sodium hazard indicating that the water is unsuitable for irrigation. This classification shows that the groundwater samples of the study area are unsuitable for irrigation in the year 2015 and 2016.

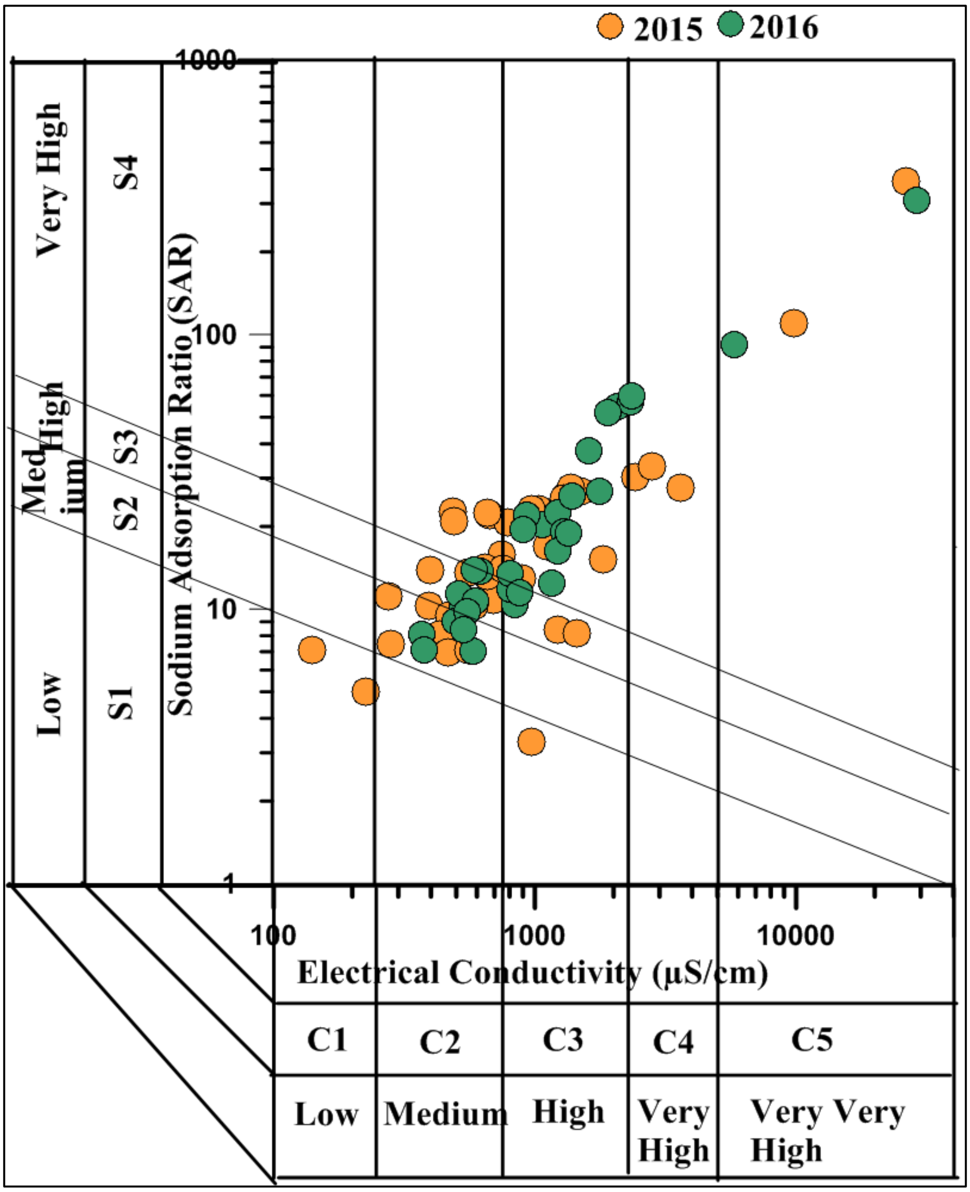


Figure 5.17 USSL diagram for salinity hazard and sodium hazard for irrigation water

5.7.2 Sodium percentage

Na% are analysed to assess the quality of irrigation water. Exchange of sodium in water for calcium and magnesium in soil decreases the soil permeability. With reduced internal drainage it leads to high sodium concentration. Wilcox (1955) classified water into 5 classes based on Na%. In this study area, 2% samples are excellent (<20), 5% and 9% are good (20-40), 57% and 52% are within permissible limits (40-60), 30% and 27% are doubtful (60-80), 6% and 12% are found unsuitable for irrigation in 2015 and 2016, respectively. High Na% leads to long residence time and mineral dissolution from lithological formations, accumulation of chemical fertilizers and affects the irrigation (Subba Rao et al 2002). Wilcox diagram (5.18) interrelating EC and Na% indicate that most of the groundwater samples are excellent to permissible and few samples fall in the doubtful to unsuitable class.

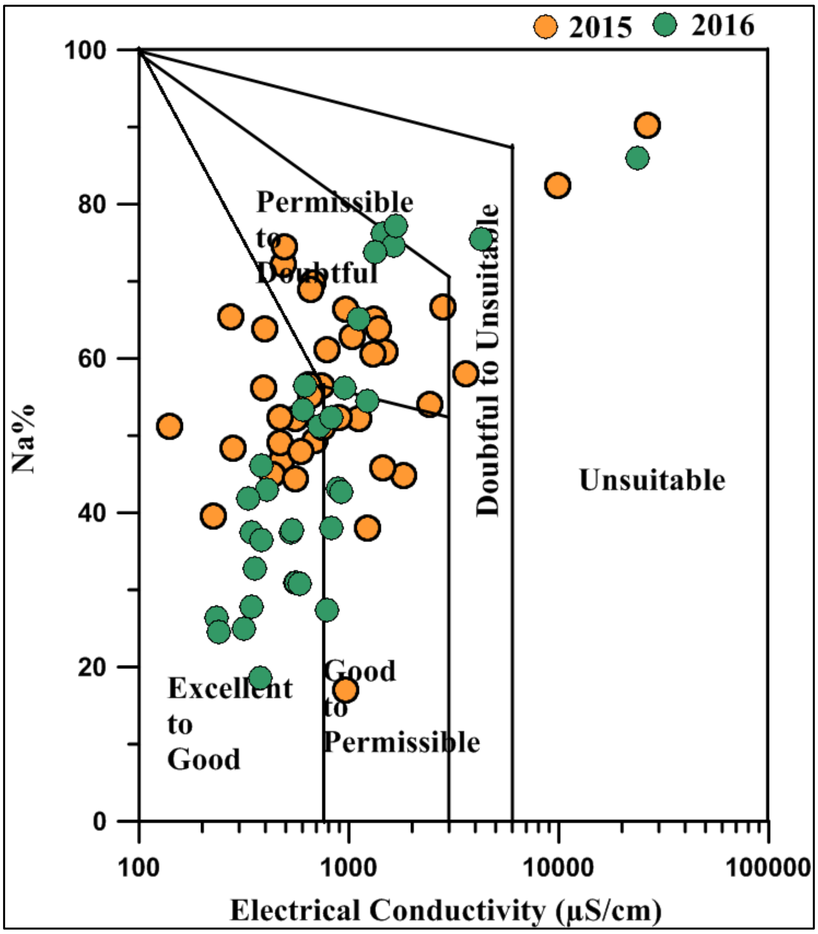


Figure 5.18 Suitability of groundwater for irrigation based on Na% and EC

5.7.3 Residual sodium carbonate

Bicarbonate and carbonate in addition to alkaline elements of calcium and magnesium also accounts for the suitability of the irrigation water. The results of carbonate and bicarbonate and suitability of water for irrigation purposes were analysed to determine the RSC (Fig 5.19). Eaton (1950) classified water into 3 categories based on RSC. In this study area, groundwater samples of about 60% and 30% are good, 25% and 48% are doubtful, 15% and 22% are observed unsuitable in 2015 and 2016, respectively. High value of RSC indicates the raising adsorption of sodium on soil. In this classification, 15 to 22% of groundwater samples were observed falling under doubtful to unsuitable for irrigation.

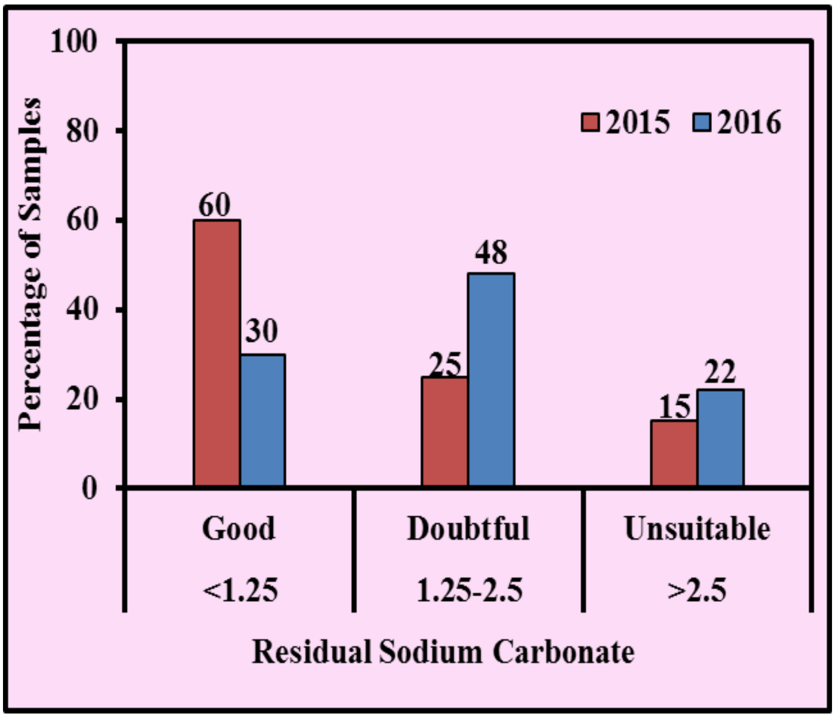


Figure 5.19 Classification of residual sodium carbonate for suitability of irrigation

5.7.4 Permeability Index

Permeability is controlled by sodium, calcium, magnesium, chloride and bicarbonate concentration of the soil. Doneen (1964) classified water into three types based on PI. PI values vary from 44 to 115 and 58 to 96 of groundwater samples in 2015 and 2016, respectively. Class 1 and 2 are suitable for irrigation with a maximum permeability of 75% and class 3 are unsuitable with a maximum permeability of 25% (Fig 5.20). Groundwater samples of the study are 63% and 57% falls under class 1, while 37% and 43% falls under class 2. Based on this classification, groundwater samples are categorised suitable for irrigation in the study area.

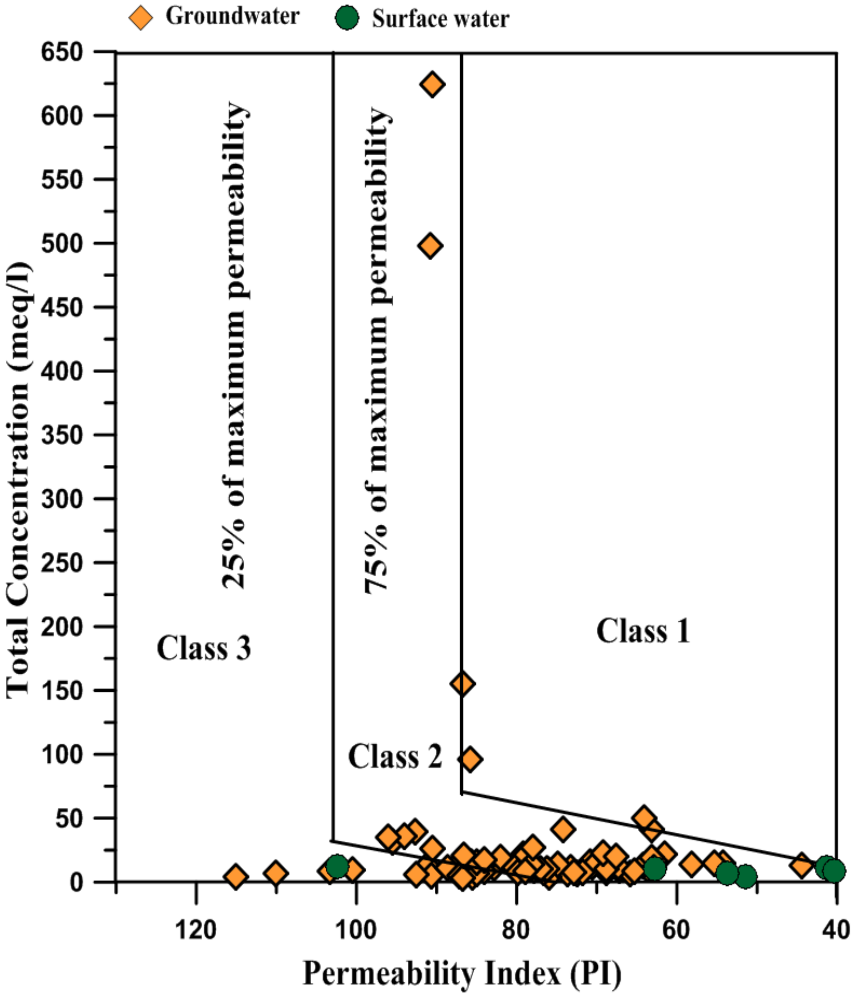


Figure 5.20 Classification of PI of groundwater for irrigation in 2015 and 2016

5.7.5 Magnesium Hazard

Calcium and magnesium are in equilibrium state in groundwater. Szaboles and Darab (1964) classified MH into two categories to assess the suitability for irrigation. Magnesium ratio varies from 21 to 82 and 36 to 67 of groundwater in 2015 and 2016, respectively. MH classified it into 2 categories as suitable (<50) and unsuitable (>50) for irrigation purpose (Fig 5.21). About 17% and 27% are suitable, 83% and 73% of samples are unsuitable for groundwater in 2015 and 2016, respectively. This can affect crop yield and soils can become more alkaline in nature.

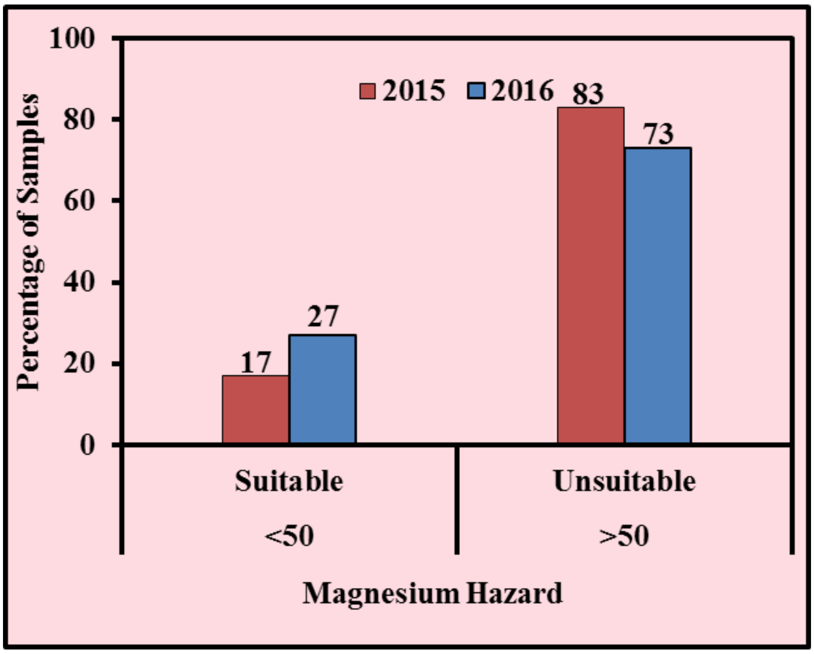


Figure 5.21 Classification of water samples based on MH for irrigation

5.8 INDUSTRIAL WATER QUALITY

Industrial water quality needs vary based on each industry and its specific standards. Industries are often suffered from the common unsuitable effects of incrustation and corrosion.. Incrustation includes deposition of unsuitable element of calcium carbonate on surface of metals, whereas the corrosion is a chemical reaction on metals that result in the erosion of metals. Johnson (1983) suggests that industrial water quality for avoiding the incrusting and corrosive properties as follows;

a. HCO_3 >400 mg/l or SO_4 >100 mg/l indicates the effect of incrustation in water
b. pH < 7 or TDS >1000 mg/l or Cl >500 mg/l indicates the corrosion effect of water

The concentration of bicarbonate (>400 mg/l) exceeded 7%, the limit of bicarbonate of groundwater (Fig 5.22a) in 2015 and all samples are within the limits in 2016. About, 4% and 8% of groundwater (Fig 5.22b) samples exceeded the limit of sulphate (>100 mg/l) in 2015 and 2016. Based on the bicarbonate and sulphate concentration, groundwater is suitable for industrial purpose. About, 4% and 8% are unsuitable which cause the incrustation in water.

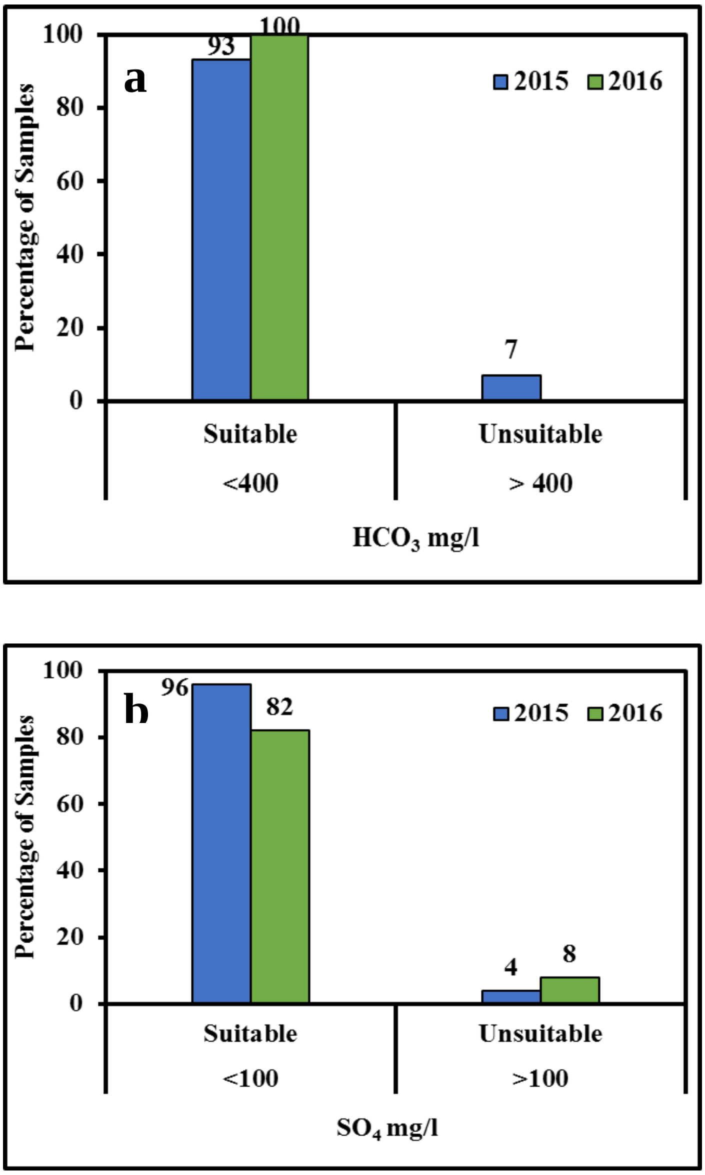


Figure 5.22 a, b. Classification of industrial water based on HCO_3 and SO_4 for incrustation

The pH value <7 in water can cause corrosion. About, 53% and 9% of pH value are observed in the groundwater in 2015 and 2016, respectively. (Fig 5.23a) The groundwater samples are unsuitable and exceed the limit of pH. About, 15% and 8% of groundwater samples exceeded the limit of TDS (>1000 mg/l) (Fig 5.23b). About, 8% and 6% of groundwater samples exceeded the limit of Cl (>500 mg/l) (Fig 5.23c) in 2015 and 2016. Exceeded limit of pH, TDS and Cl indicates the effect of corrosion and is unsuitable for industrial purpose.

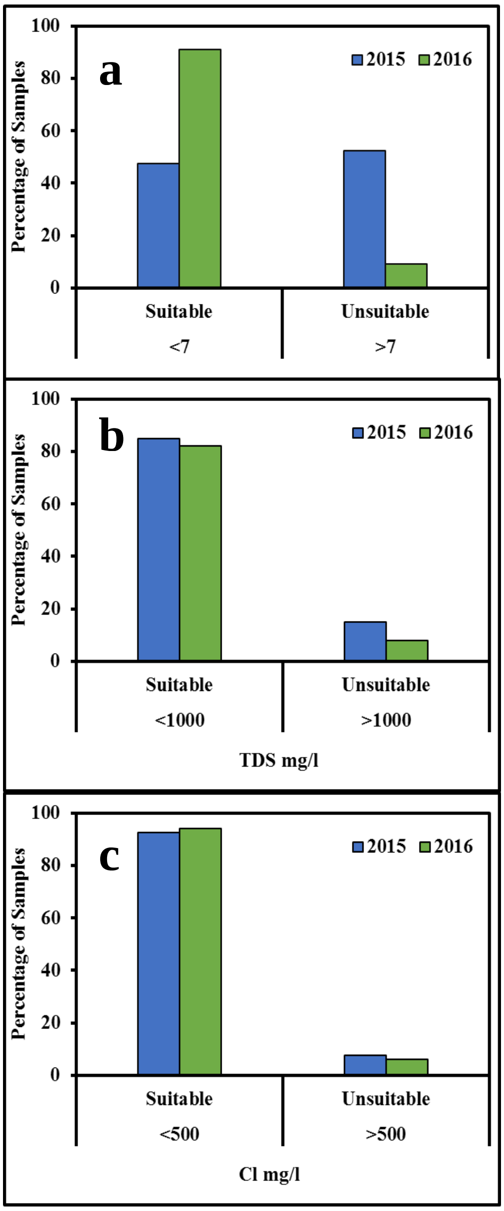


Figure 5.23a, b, c. Classification of industrial water based on pH, TDS and Cl mg/l for corrosion of groundwater in 2015 and 2016

CHAPTER SIX

6 HYDROGEOCHEMICAL PROCESSES

6.1 GENERAL

Groundwater chemistry depends on the constant alteration of the hydrogeological environment. The major ionic concentration depends on the associated aquifer minerals. A special attention on the different geological formations and the seasonal change are crucial. Water penetrates through the soil and into the sub-surface. Chemical constituents of groundwater are controlled by the chemical properties of aquifer, permeability of soil and the residence time of water in the aquifer. Groundwater quality and the chemical constituents are influenced by diverse factors- geology, hydrogeology, topography, drainage system, hydro-metrology and anthropogenic activities. For the efficient water resources management, it is essential to understand the chemical characteristics of the groundwater and their influence on natural processes. Hydrochemical data are represented in different conventional graphical plots in order to find the hydrochemical processes and mechanisms. All the probable identified processes are described in following sections.

6.2 HYDROCHEMICAL FACIES

Hydrochemical facies help to identify the groundwater type. Hydrochemical diagrams are proposed to interpret the evolutionary trends in conjunction with distribution maps and hydrochemical facies. Characterization of hydrochemical data to identify the hydrochemical facies can be done using different diagrams proposed by Durove (1948), trilinear (Piper, 1944), Schoellar (1965) and Chadha (1999). The Chadha diagram suggested as the modified piper diagram as adopted by many researchers for hydrochemical grouping of natural waters and interpretation of chemical data.

The Chadha diagram (Fig 6.1) variance in milliequivalent percentage of Ca + Mg (alkaline earths) and Na + K (alkali metals) showed as percentage reacting values are plotted on the X-axis. The variances in milliequivalent percentage of CO_3 + HCO_3 and Cl + SO_4 were plotted on the Y-axis. The milliequivalent percentage variance of alkaline earth and alkali metals, weak acidic anions and strong acidic anions were plotted on the four possible sub-fields of a rectangle.

The distribution of samples fall under 4 sub-fields- Ca-Mg-Na water type fall under the sub field 1 , Cl-SO_4-HCO_3 water type fall under the sub-field 4 , Ca-Mg-Cl water type fall in the sub-field 6 and Na-Cl water type fall in the sub-field 7. Therefore, the overall dominant hydrochemical facies are Ca-Mg-Na, Cl-SO_4-HCO_3, Ca-Mg-Cl, and Na-Cl. This study area consists of granite, basaltic and sedimentary formation of marine origin which is one of the sources for hydrochemical facies of groundwater. Generally, groundwater is complex in nature and chemical solution is diluted. The chemical constituents resulting from the dissolution of minerals from rocks are contact with sub-surface. Rainfall also acts as diluting factor and contributes significantly to the chemical composition of groundwater.

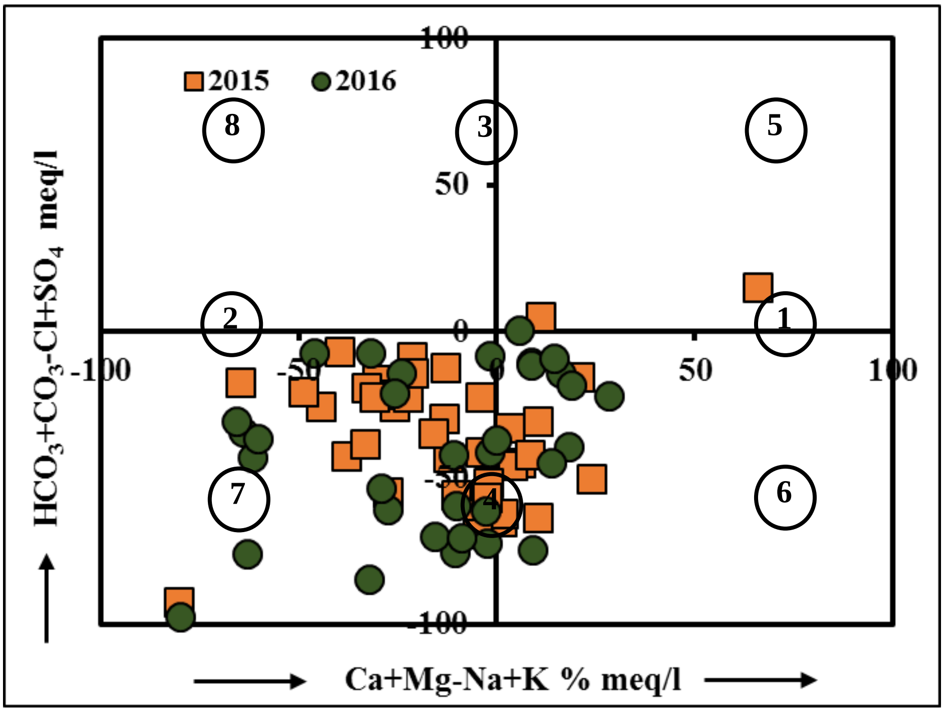


Figure 6.1 Hydrochemical facies of groundwater (Chadha 1999)

6.3 ION EXCHANGE

Hydrogeochemical difference in the ion concentrations of groundwater can simply be understood by plotting on a graph along the X-Y axis (Aghazadeh and Mogadam 2011). Results obtained from the hydrochemical data were used to identify the hydrogeochemical processes in the aquifer system. Ion exchange between the groundwater and its host environment can be understood by studying the chloro-alkaline indices (CAI) (Schoellar, 1967). The following equations are used to identify the ion exchange of the study area;

$$CAI\ 1 = [Cl – (Na + K)]/ Cl \qquad (14)$$

$$CAI\ 2 = [Cl – (Na + K)]/ (SO_4 + HCO_3 + CO_3 + NO_3) \qquad (15)$$

The positive indices indicate ion exchange and the negative indices indicate reverse ion exchange (Schoellar, 1967). The groundwater samples of the study area specify both ion exchange and reverse ion exchange. About, 60% and 40% of the groundwater samples show CAI 1 and CAI 2 in 2015. Whereas, 76% and14% of the groundwater samples indicates CAI 1 and CAI 2 in 2016 (Fig 6.2 a,b). The plot of Na – Cl versus Ca + Mg – HCO_3 – SO_4 with a linear slope of -1 indicates reverse ion exchange. Figure 6.3 shows the relationship between Na – Cl versus Ca + Mg – HCO3 + SO4 and indicates that the groundwater samples of the study area follow a straight line (R^2 = 0.72) with a slope of -0.7, which supports the reverse ion exchange process.

The plot of Ca + Mg versus SO_4 + HCO_3 (Fig 6.4) show that the sample points lie close to the equiline i.e. 1:1 which specifies the dissolution of carbonate and silicate minerals in the aquifer system. If the sample point fall above the equiline 1:1 line indicates the reverse ion exchange (Datta and Tyagi 1996). If the sample points fall below the equiline, it indicates ion exchange process. In this study area, the sample points fall above and below the equiline 1:1 indicating both ion exchange and reverse ion.

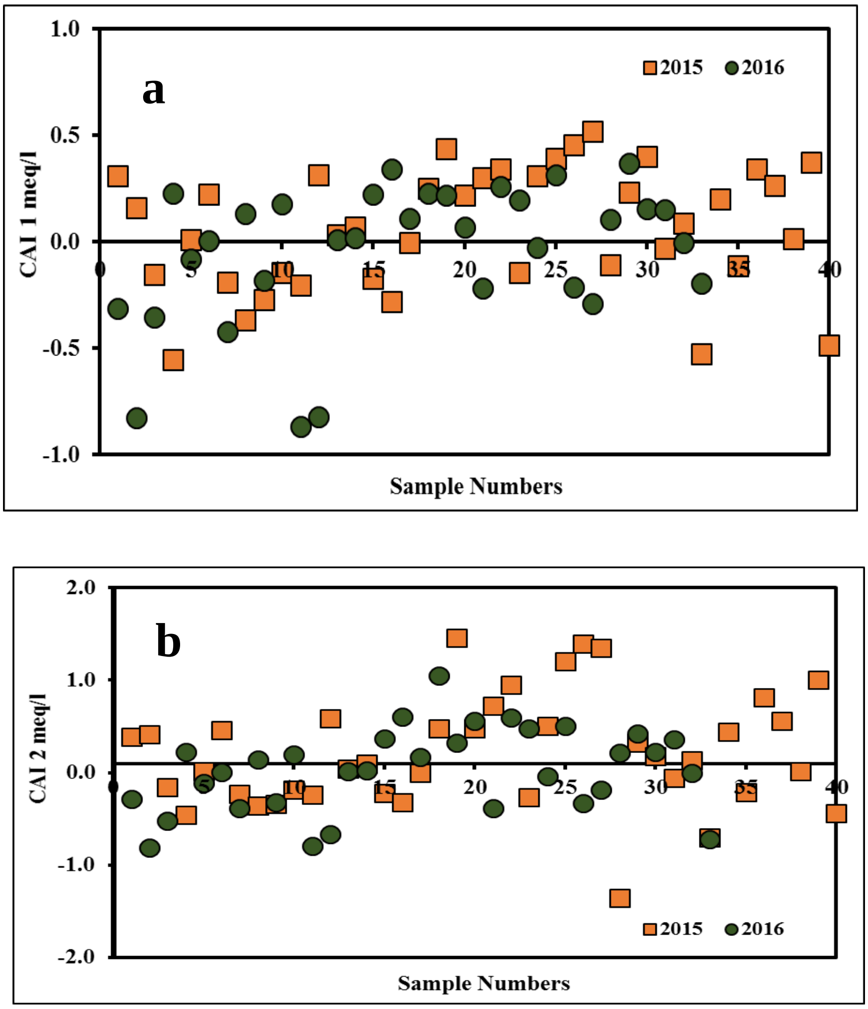


Figure 6.2 a and b, Chloroalkaline indices of groundwater in 2015 and 2016

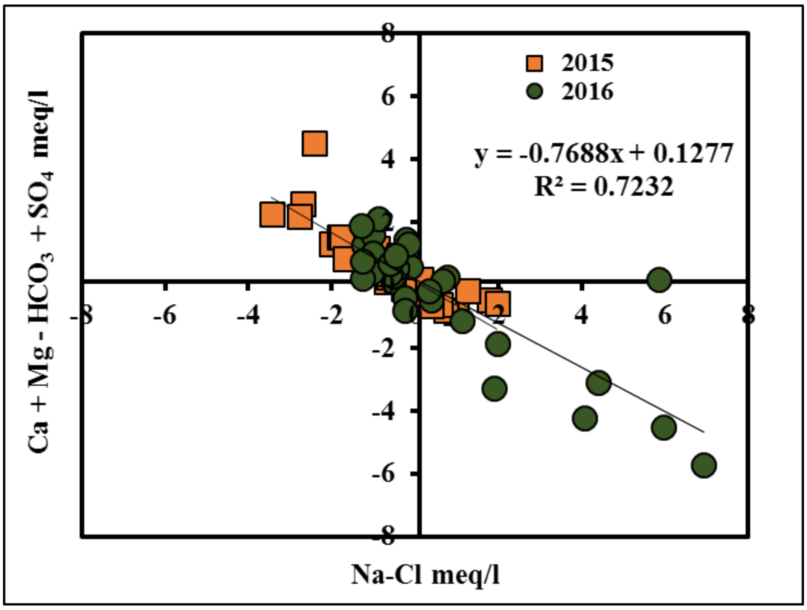


Figure 6.3 Relationship between Na – Cl versus Ca + Mg – HCO_3 + SO_4

A plot of Ca + Mg versus Cl (Fig 6.5) indicates that Ca +Mg concentration increases with increasing Cl concentration in few samples in 2015 whereas majority of samples which does not represent the increasing Ca +Mg with increasing Cl indicated that reverse ion exchange. The difference in the two time periods indicates the contribution is also from anthropogenic activity.

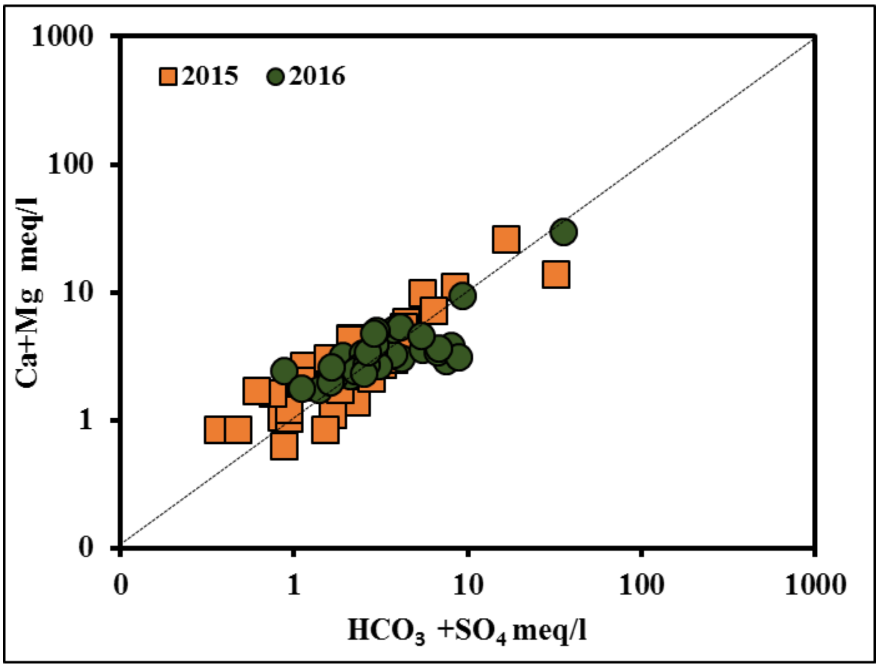


Figure 6.4 Relationships between Ca + Mg versus HCO_3 + SO_4

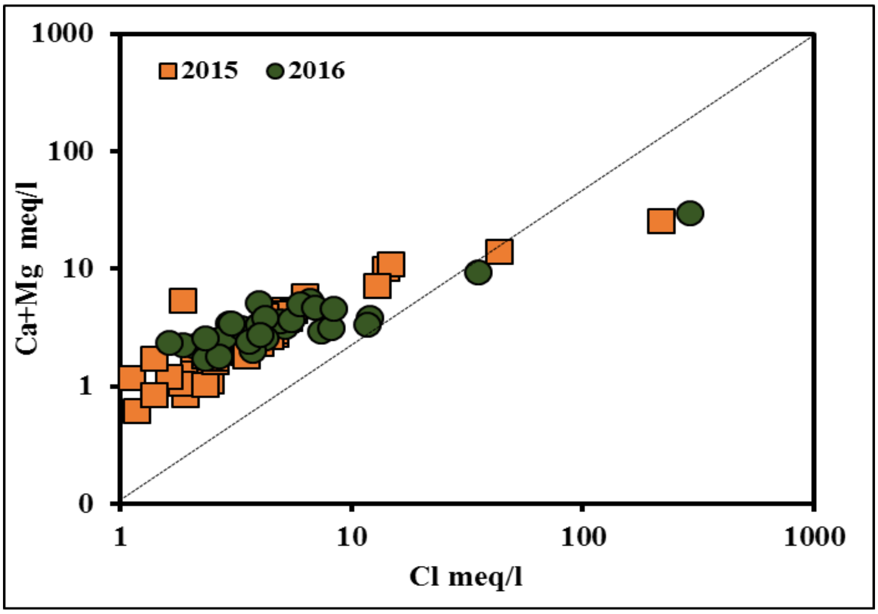


Figure 6.5 Relationships between Ca + Mg versus Cl

6.4 CARBONATE WEATHERING AND DISSOLUTION

In the study area, calcium and magnesium are the dominant cations while the bicarbonate is the dominant anion in groundwater. The sample points plotted on the line Ca/Mg = 1 indicates that the groundwater is influenced by dolomite dissolution. The Ca/Mg ratio varies from 1 to 2 indicates the dissolution of calcite (Maya and Louks, 1995). In natural groundwater, Ca/Mg is >2 mainly due to the dissolution of silicate minerals (Elango *et al*, 2003; Rajesh *et al*, 2012).

The ratio of Ca/Mg of groundwater in the study area varies from 0.2 to 3 and from 0.4 to 1.7 meq/l (Fig 6.6) in 2015 and 2016 respectively. About, 78% and 72% of the samples of groundwater are Ca/Mg = 1 which indicates dolomite dissolution, 15% and 27% of groundwater samples indicates calcite dissolution in 2015 and 2016, respectively and 7% of groundwater are >2 indicate that silicate dissolution in 2015. The dolomite weathering by carbonic acid imposes the chemical composition of the groundwater in the study area. The Carbonate weathering by rainwater saturation with CO_2 enriches carbonic acid. Dissolution process is important for the increase in the concentration of calcium, magnesium and bicarbonate constituents of groundwater. Source of carbonate minerals in the recharge area and silicate minerals are the main factor which leads to raising carbonates and bicarbonate concentration in the groundwater

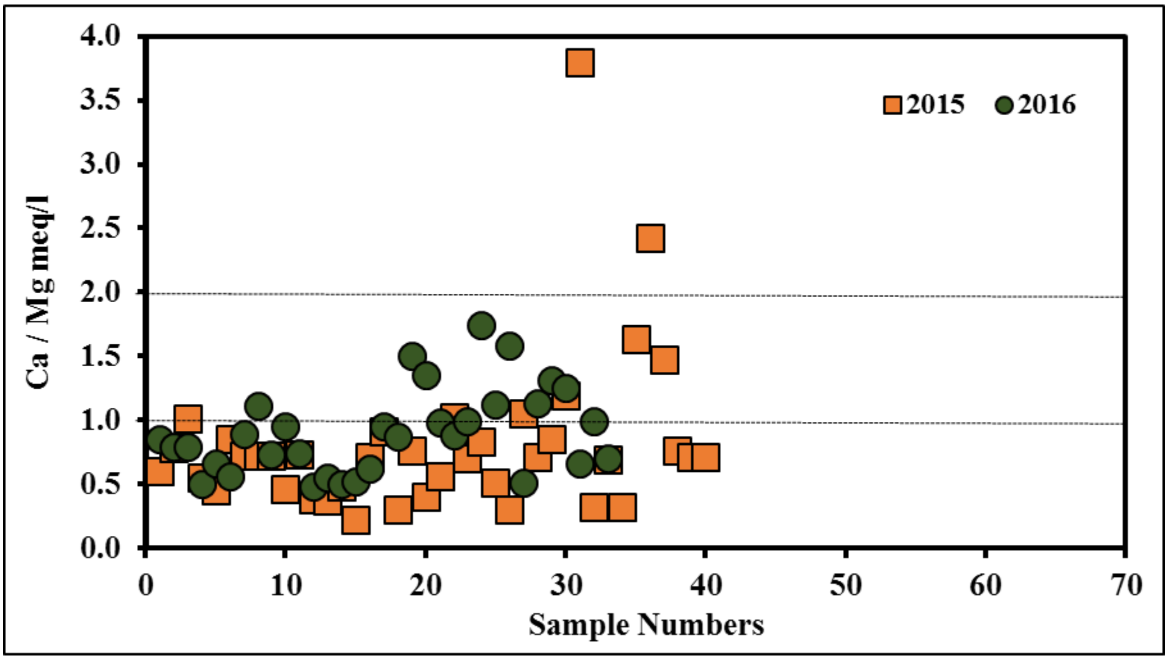


Figure 6.6 Relationship between Ca/ Mg versus sample numbers

6.5 SILICATE WEATHERING

Silicate weathering directly influences the major ion chemistry. Contribution of silicate weathering in the hydrogeochemical processes indicates the presence of sodium and potassium in the groundwater (Stallard and Edmond 1983;). Understanding the silicate weathering is by the relationship between Na + K versus TC (total cations) (Fig 6.7). All sample points fall above equiline 1:1 line of groundwater in both sampling period. Weathering of soda feldspar containing albite and potash feldspar containing orthoclase and microcline contributes the Na and K ions to the groundwater. Feldspar is subjected to weathering than quartz in silicate rocks. The Ca + Mg versus HCO_3 (Fig 6.8) ratio >3 indicates the silicate weathering more than carbonate dissolution. Majority of the sample points fall above the 1:1 equiline indicating silicate weathering in excess of carbonate dissolution. The plot of Ca +Mg versus TC of groundwater show that the sample points fall above the 1:1 equiline indicating silicate weathering. In the study area, potassium is not abundant as that of sodium act as fixation in the formation of clay minerals. A plot of Na versus HCO_3 (Fig 6.9) of groundwater show that the sample points fall below the line also indicate the silicate weathering of minerals in the below equation

$$\underset{\text{Albite}}{2NaAlSi_3O_8} + 2H_2CO_3 + 9H_2O \longrightarrow \underset{\text{Kaolinite (Silicate weathering)}}{Al_2SiO_5 (HO)_4 + 2Na + 4H_4SiO_4 + 2HCO_3} \quad 15$$

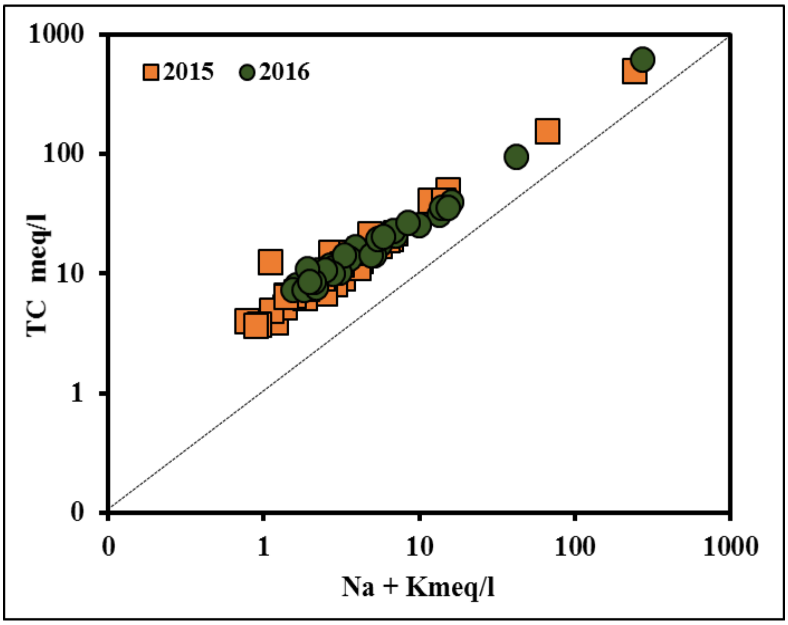


Figure 6.7 Relationship between Na + K versus TC meq/l

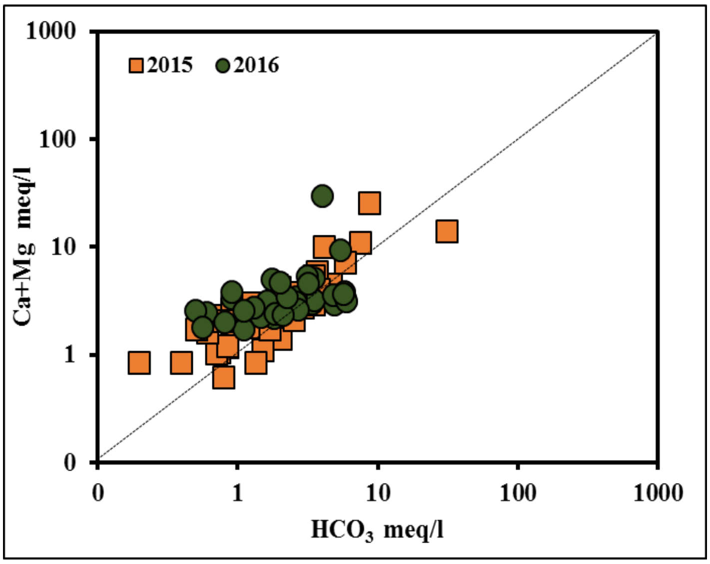


Figure 6.8 Relationship between Ca + Mg versus HCO_3 meq/l

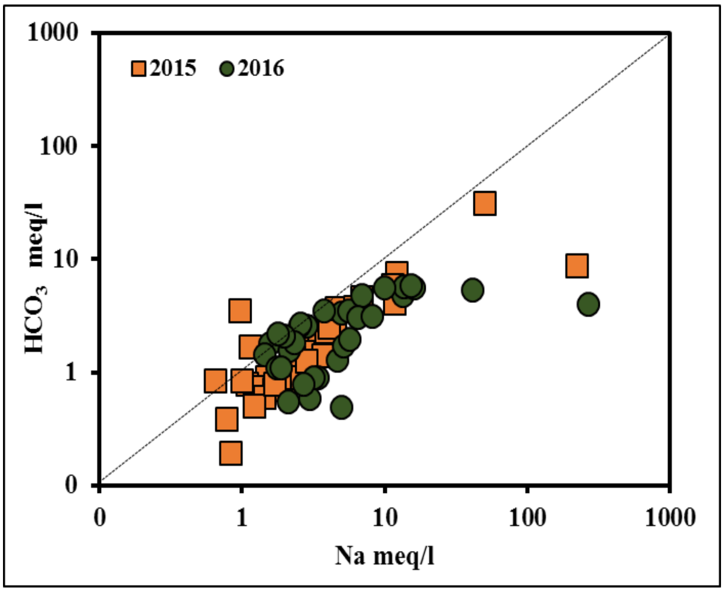


Figure 6.9 Relationship between Na versus HCO_3 (meq/l)

6.6 EVAPORATION

The evaporation process affects the concentration of all minerals in groundwater. Evaporation process is dominant, if none of the minerals are precipitated, the ratio Na/Cl do not change (Jankowski and Acworth 1997). The plot of Na/Cl versus EC (Fig 6.10) specifies that the horizontal line is an efficient indicator of evaporation process. The sample points indicate an horizontal line. Na/Cl ratio is equal to 1 indicating that halite dissolution is responsible for sodium, Na/Cl ratio are >1 indicating that sodium may be released from silicate weathering process (Mayback

1987). The Na/Cl ratio ranges from 0.3 to 1.8 and 0.58 to 1.84 of groundwater in 2015 and 2016 respectively. About, 67% and 63 % of groundwater samples are equal to 1 indicating halite dissolution. 33% and 36 of groundwater samples are >1 indicating silicate weathering in 2015 and 2016 respectively. The plot of Na versus Cl (Fig 6.11) the groundwater samples fall above the equiline 1:1 ratio line specify that silicate weathering. Few samples fall along the equiline 1:1 ratio may be source of halite dissolution are responsible for high chloride and low annual rainfall are probable source of halite for dissolution in the soil zone (Elango and Kannan, 2007).

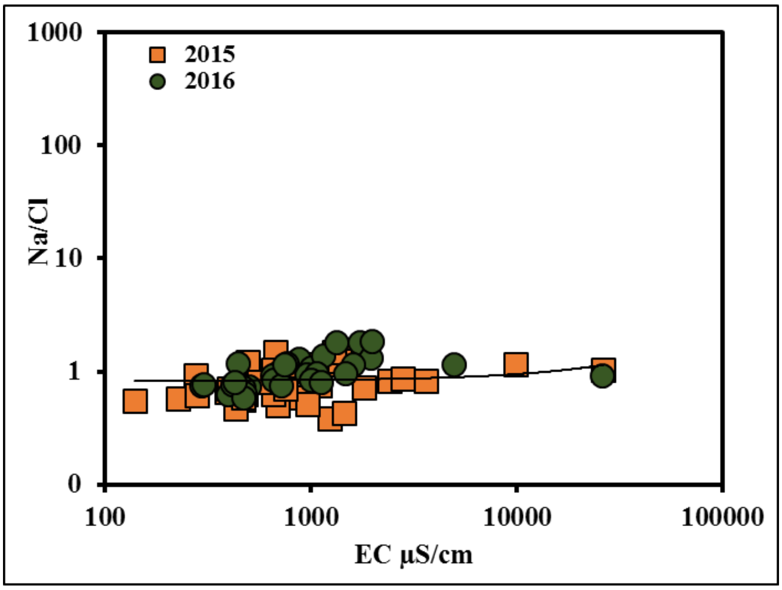


Figure 6.10 Relationship between Na/Cl versus EC (µS/cm)

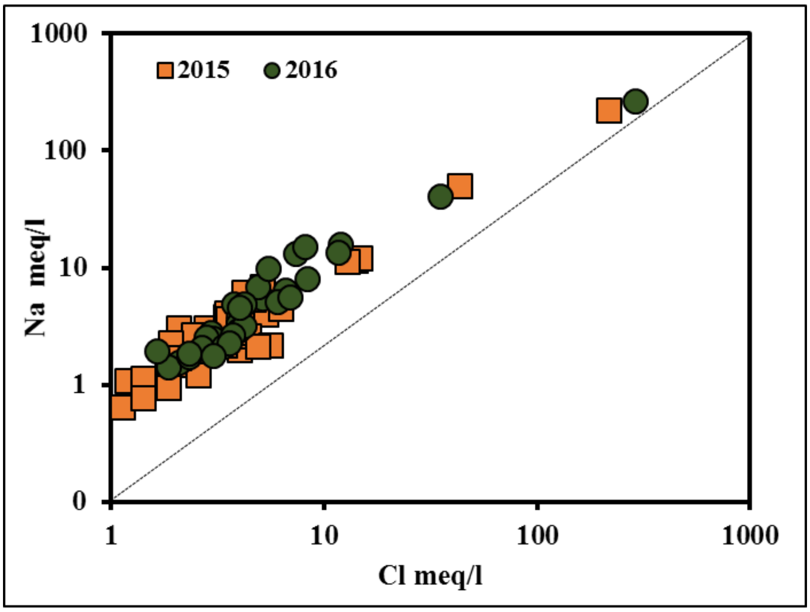


Figure 6.11 Relationship between Na versus Cl meq/l

6.7 Gibbs Plot

Gibbs (1970) plot identifies the geochemical processes and mechanisms such as rock-water interaction, evaporation and precipitation. The plot of TDS versus cations and TDS versus anions is shown in Figure 6.12. This diagram shows that the groundwater of the study area is largely influenced by weathering of minerals and evaporation process. This implies the increase in ionic concentration and the precipitation of the soluble minerals in the groundwater. Precipitation of Calcium carbonate under evaporation occurs by losing Ca and HCO_3 indicating groundwater as alkaline nature. The modified piper diagram Chadha (1999) and Gibbs diagram indicates that the rock water interaction, evaporation, carbonate weathering, silicate weathering, and ion exchange processes control the groundwater chemistry.

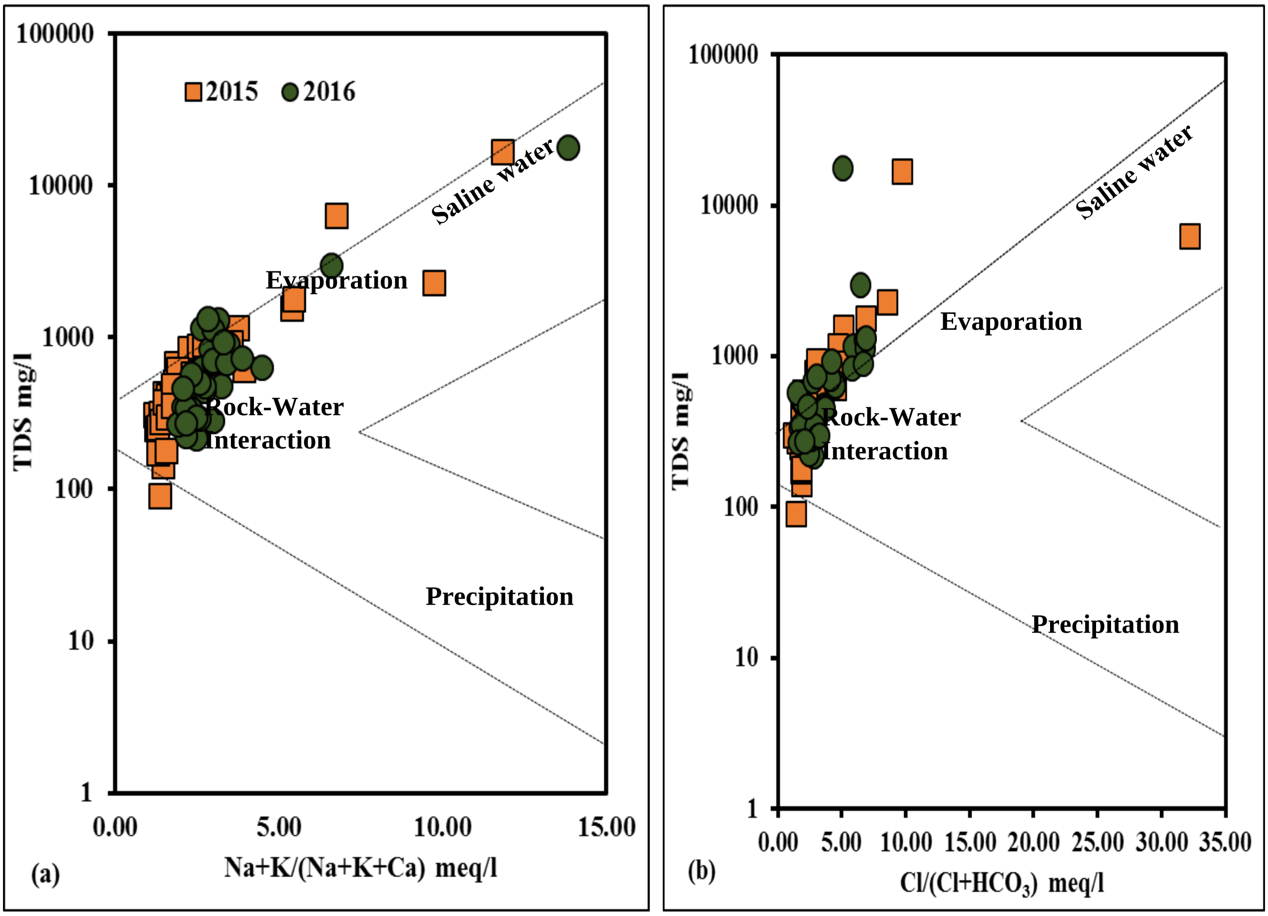


Figure 6.12 Gibbs diagrams showing the mechanism of controlling groundwater chemistry of (a) TDS vs cations and (b) TDS versus anions

6.8 AQUEOUS GEOCHEMICAL MODELLING

Phreeqc software is used to calculate the chemical reactions and transport processes in the natural groundwater. The software is used to identify the chemistry of aqueous solutions relating with minerals, gases, solid solutions, exchangers and sorption surface.

SI indicates that the degree of chemical equilibrium between water and mineral phases in the aquifer matrix and help to measure the dissolution/precipitation processes are responsible rock water interaction (Derver 1997). The SI of minerals indicates the capacity of the mineral to thermodynamically precipitate or dissolve. The SI value < 0, then implies that the water is undersaturated, if SI=0, then it implies that water is in equilibrium with the mineral and if the SI is > 0, the n it implies that the water is oversaturated. Figure 6.13 indicates the TDS versus calcite, dolomite, gypsum and halite. Calcite ($CaCO_3$) (Fig 6.13a) varies from -2.86 to 1.4 and from -2.06 to 0.103 in groundwater in 2015 and 2016 respectively. Dolomite ($MgCO_3$) (Fig 6.13b) varies from -5.61 to 3.02 and from -3.97 to 0.41 of groundwater in 2015 and 2016 respectively. Plot of TDS versus calcite and dolomite shows that increasing TDS concentration with SI of calcite are oversaturated with respect to precipitated minerals and does not contain calcium and magnesium in the groundwater. It also explains that ion exchange processes, simultaneously decreasing TDS. SI of calcite and dolomite are undersaturated indicating dissolution. Gypsum ($CaSO_4.2H_2O$) varies from -4.03 to -1.41 and -3.08 to -0.68 in groundwater in 2015 and 2016 respectively. Halite (NaCl) varies from -7.76 to -3.18 and from -7.22 to -2.99 of groundwater in groundwater in 2015 and 2016 respectively. Gypsum (Fig 6.13c) and halite (Fig 6.13d) of samples are undersaturated . Dissolution of gypsum is due to anthropogenic activity, calcium enrichment in groundwater and also responsible for the groundwater sulphate concentration. Dissolution of halite a source are mainly contributed by Na and Cl and involves atmospheric deposition, rock-water interaction, brine water and anthropogenic activity (Panno et al 2006). Cation exchange processes with clay can also result increasing sodium concentration in water.

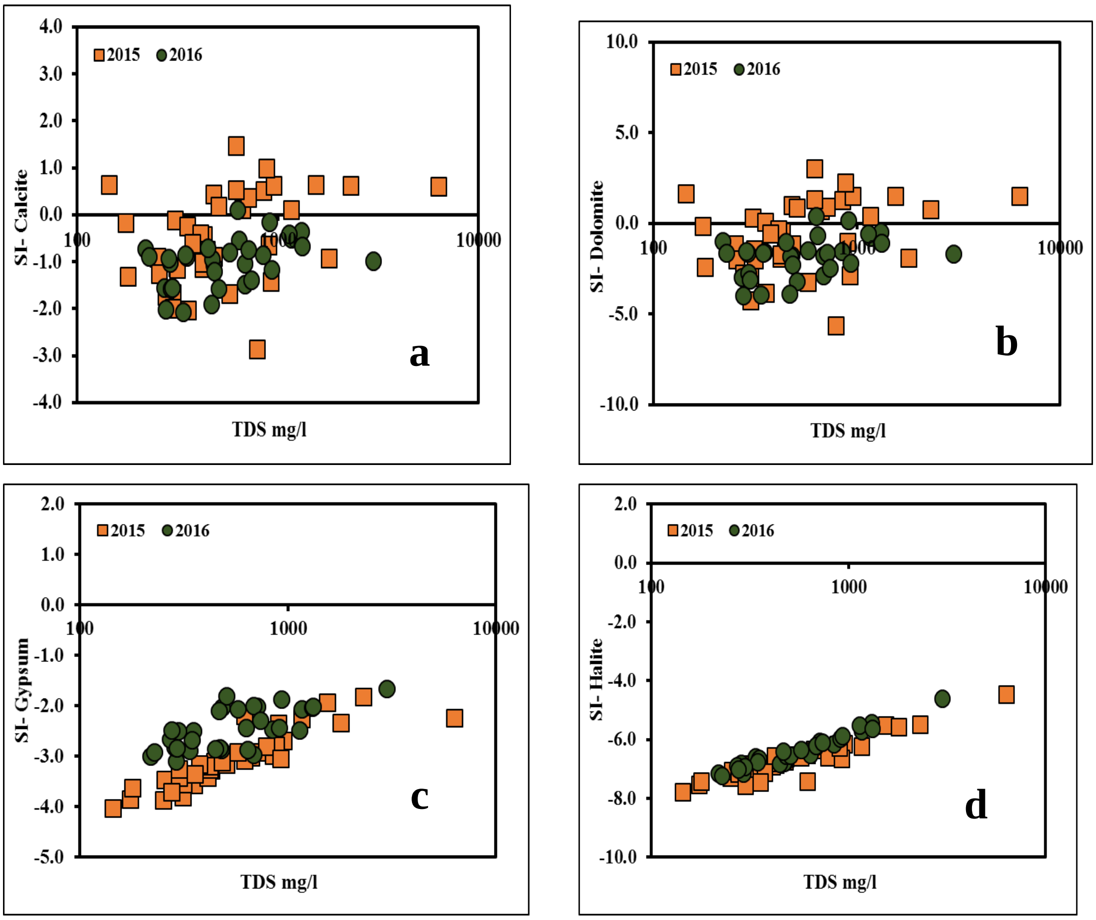


Figure 6.13 SI indicates the TDS versus (a) calcite, (b) dolomite, (c) gypsum and (d) halite.

6.9. MULTIVARIATE STASTICAL ANALYSIS

Multivariate statistical analyses were used for sample classification which permits the grouping of water samples and the creation of correlations between the hydrochemical data (Cloutier 2008). Multivariate statistical analysis carried out includes CM, CA and FA

6.9.1 Correlation Matrix

The Pearson's CM was used to find the inter-relationships between hydrogeochemical data. It reveals the source of ions and identifies the hydrogeochemical processes responsible for the observed chemical composition. The results of the correlation analysis reflected the following interpretation. A high correlation coefficient equal to 1 or nearly 1 specifies good positive correlation between two variables. If two variables represent r > 0.7, then it specifies strong correlation and the r between 0.5 and 0.7 specifies moderate correlation (Manish et al 2006).

In 2015, groundwater samples of Pearson's CM obtained strong correlation (> 7) between TDS, Na, K, Ca, Mg, Cl, SO_4 and moderate correlation between HCO_3 and $NO_{3.}$ This is shown in Table 6.1a. Strong correlation of r= 0.99, r=0.89, r=0.81, r=0.95, r=0.98, r=0.96 obtained between TDS and Na, K, Ca, Mg, Cl and SO_4 and moderate between r=0.53 of $HCO_{3.}$ This indicates high weathering of basaltic rocks, dissolved silica in groundwater and major ions, humid wet climate where rainfall inputs dominate evaporation and evapotranspiration processes (Appelo and Postma, 1999). Moderate correlation of r=0.30, r=30 obtained between NO_3 of Na and Cl which specify that source of NO_3 in natural water are atmospheric contribution. Correlation between NO_3 and Na-Cl derives from dissolution of sodium sulphate and leaching of excreta of animals dung are the main source of nitrate in the study area.

In 2016, groundwater samples had strong correlation (> 7) between TDS, Na, K, Ca, Mg, Cl, SO_4 and moderate correlation between HCO_3 and Mg. This is shown in Table 6.1b.Comparison between 2015 and 2016 correlation, there exist some similarity. Strong correlation of r= 1, r=0.98, r=0.98, r=0.95, r=1, r=0.99 obtained between TDS and Na, K, Ca, Mg, Cl and SO_4 specify that simultaneous increase and decrease in the cations effects mainly of dissolution of minerals, ion exchange and evaporation processes, anthropogenic activities and irrigation return flow. This area is probably influenced by paints, dying bleaching and manufacturing of chemical industries.

Table 6.1a Pearson's CMof groundwater in 2015

Variables	pH	TDS	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3
pH	1.00									
TDS	-0.14	1.00								
Na	-0.10	**0.99**	1.00							
K	-0.20	**0.89**	**0.82**	1.00						
Ca	-0.22	**0.81**	**0.74**	**0.76**	1.00					
Mg	-0.12	**0.95**	**0.92**	**0.88**	**0.83**	1.00				
Cl	-0.12	**0.98**	**1.00**	**0.81**	**0.75**	**0.91**	1.00			
HCO_3	-0.11	**0.53**	0.40	**0.82**	**0.59**	**0.62**	0.38	1.00		
SO_4	-0.08	**0.96**	**0.98**	**0.75**	**0.78**	**0.91**	**0.98**	0.33	1.00	
NO_3	-0.08	0.29	0.30	0.25	0.16	0.22	0.30	0.07	0.25	1.00

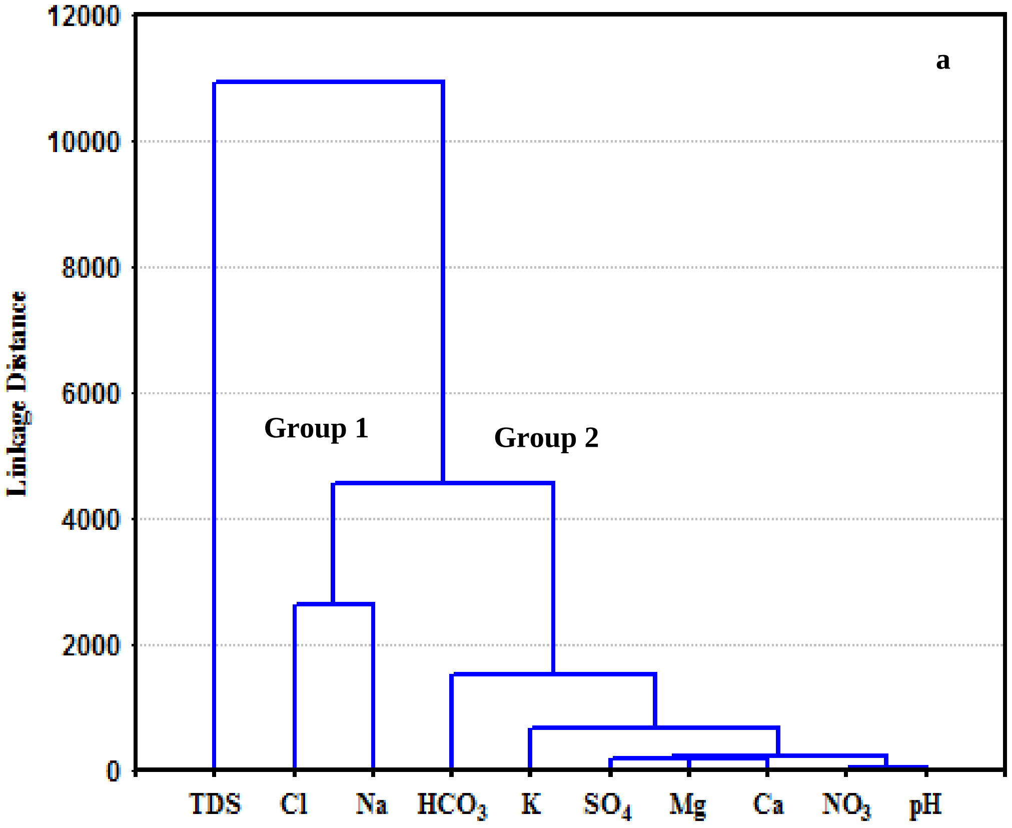
Table 6.1b Pearson's CMof groundwater in 2016

Variables	pH	TDS	Na	K	Ca	Mg	Cl	HCO3	SO4
pH	1.00								
TDS	0.02	1.00							
Na	0.03	**1.00**	1.00						
K	-0.06	**0.98**	**0.98**	1.00					
Ca	-0.09	**0.98**	**0.98**	**0.98**	1.00				
Mg	-0.05	**0.95**	**0.95**	**0.97**	**0.95**	1.00			
Cl	0.02	**1.00**	**1.00**	**0.98**	**0.98**	**0.94**	1.00		
HCO^3	0.06	0.26	0.24	0.23	0.20	0.34	0.20	1.00	
SO^4	0.03	**0.99**	**0.99**	**0.97**	**0.98**	**0.93**	**0.99**	0.21	1.00

6.9.2 Cluster analysis

Hierarchal CA with the Euclidean distance measure and the Wards linkage method were applied to classify the variables and identification of additional parameters contributing to the main hydrogeochemical processes in the groundwater system. CA are applied for the grouping of 40 and 33 samples of groundwater in

2015 and 2016 respectively for10 parameters. The groundwater variables are pH, EC, Na, K, Ca, Mg, Cl, HCO_3, SO_4 and NO_3. The results are derived from the application of the R-mode hierarchal cluster are given in the Figures 6.14a, b. This diagram indicates two groups of clusters. Group 1 represents EC, Na and Cl and are characterised with ion exchange, reverse ion exchange and evaporation are the major dominant hydrochemical processes. Group 2 represented HCO3, SO_4, K, Ca, Mg, NO_3 and pH are characterised with carbonate weathering, silicate weathering and dissolution of minerals due to rock-water interaction. . Figure 6.14b contains 2 groups for the year 2016. Group 1 consists of TDS, Na and EC and HCO_3, SO_4, K, Ca, Mg, NO_3 and pH comprises of group 2. This was similar to the year 2015. Thus the same processes influence the groundwater chemistry at both time periods. Hierarchal CA are also supports the hydrogeochemical processes of the study area.



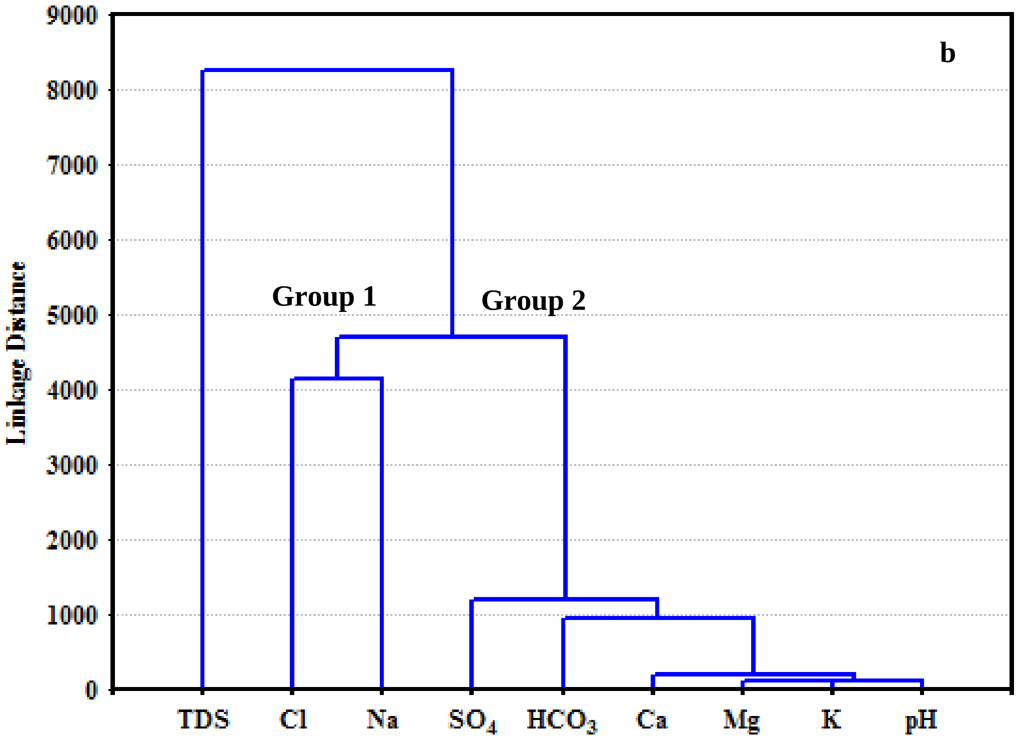


Figure 6.14a, b R- mode hierarchal cluster analysis of groundwater of 2015 and 2016 respectively

6.9.3 Factor analysis

. In this study, the factors are classified with the relative absolute loading values as strong>0.75, moderate 0.75-0.5 and weak 0.5-0.3 to identify the hydrogeochemistry of the groundwater. FA of 2015 and 2016 respectively groundwater samples on the combined hydrochemical data provided 2 factors with eigenvalue >1 that describe the variance are 67% and 10% of the data variation of the groundwater.

Strong loadings of EC, Na, Ca, Mg, Cl and SO_4 indicate that factor 1 (Fig 6.15a) specifies rock-water interaction and dissolution of minerals and anthropogenic activities which are contributed due to occurrence of granite, basaltic and sedimentary formation (marine origin) in the study region. The sources of SO_4 are derived from the atmospheric deposition, sulphate fertilizers and bacterial oxidation of sulphur constituents (Siddle et al 2000). Sulphate source can also come from breakdown of organic substance of weathered soil and human influences are the causes for the sulphuric salts from domestic wastewater (Craig and Anderson 1979).

Factor 2 (Fig 6.15b) describes that strong loadings for K, HCO_3 and moderate loading of NO_3 which specifies that dissolution of carbonate and silicate minerals and also non-point source pollution. Strong loadings of K derived from the potash feldspar in the host rock formation. Strong loadings of HCO_3 indicate that dissolution of carbonate minerals, soil CO_2, and from the bacterial degradation of organic contamination. Moderate loadings of NO_3 are derived from nitrogenous fertilizers and the courses of water obtained nitrate leaching from groundwater. The occurrence of NO_3 in the study area is mainly by industrial effluents. Positive loadings of pH described the groundwater chemistry are influenced by pH variations in the study area. This specifies that they are resulting from rock-water interaction.

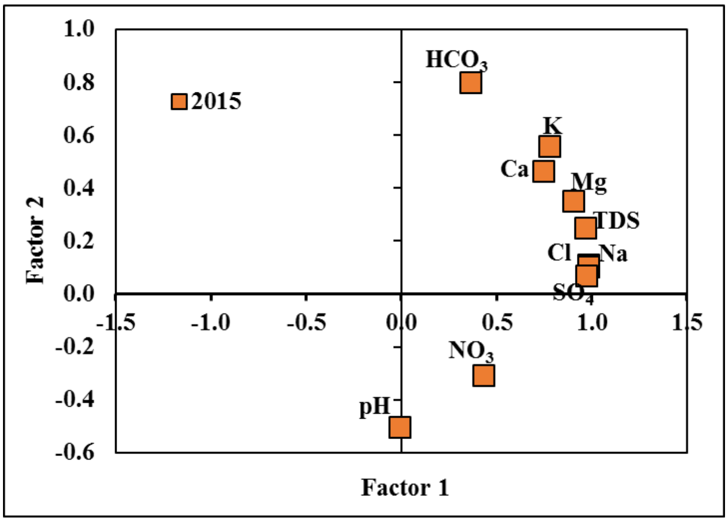


Figure 6.15a Factor analysis of groundwater in 2015

Factor 1 (Fig 6.14b) of groundwater in 2016 explains that 76% of variance has strong negative loading of TDS, Na, K, Ca, Mg, Cl and SO_4. Strong negative loadings of this variable are mainly from anthropogenic pollution sources such as effluents of domestic origin, fertilizers and industrial effluents. In this factor, negative loadings of TDS are from the leaching of industrial effluents and from the landfill sites of the study area. Na is released from anthropogenic source such as residential water softeners and agricultural activities. Potassium is mainly released from potash fertilizers used in agricultural land areas. Strong negative loading of Ca is also related to anthropogenic induced calcite dissolution. Excess of calcium is contributed by cation exchange and the calcite equilibrium. Significant contribution of metallic ions from metallic scraps and dumps are the reason for negative loading of Mg. Chloride and bicarbonate negative loadings are mainly from anthropogenic, industries and atmospheric pollution. Dissolution of gypsum and halite minerals increases the concentration of the sulphate as strong negative loadings.

Factor 2 (Fig 6.14b) of groundwater describe that 11% of variance imply strong positive loading of pH and moderate loading of HCO_3 in 2016. Strong loading of pH is due to biogenic control of the pH value as the values decreases with increasing salinity due to the calcium cation exchange results in calcite saturation. Dissolution of carbonate minerals and dissolution of atmospheric, soil CO_2 gas could be the responsible mechanism for the contribution of HCO_3 and CO_3 to the groundwater.

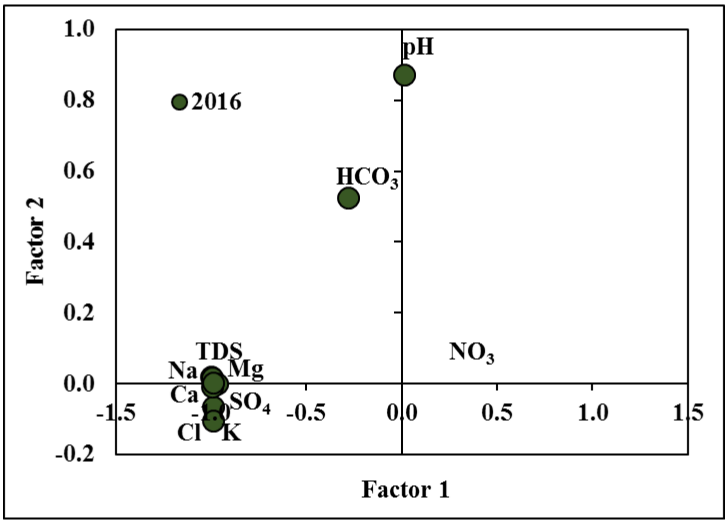


Figure 6.15b Factor analysis of groundwater in 2016

CHAPTER SEVEN

7 HEAVY METALS

7.1 GENERAL

Heavy metals occur in trace concentration and act as a significant part in the metabolism of plants, animals and human beings. The increased concentration causes numerous toxicological problems to human beings. Source of heavy metals are two types- natural and anthropogenic. Natural sources are the metals derived from weathering and leaching of rocks by rock-water interaction. Anthropogenic sources in the atmosphere are derived by burning the fossil fuels and in the streams by rainwater, industrial waste disposals, sewage water, surface water bodies and other activities. Rapid urbanization and industrialization has contributed to heavy metals contamination in groundwater. . Due to urbanization, soil quality is strongly controlled by anthropogenic sources which differs from natural soils. Groundwater quality deteoration is the significant problem in the study area.

7.2 METALS IN GROUNDWATER

Quality of water is influenced by the EC and TDS of groundwater for drinking purpose which was explained in more detail in chapter 5. However, further study on the heavy metal concentration in groundwater of this area was carried out. Fourteen heavy metals were analysed and the order of dominance of heavy metals in 2015 and 2016 are given as follows Mn < Si < Fe < B < Cu < Zn < Pb < Al < Li < Co < Ni < Ca < Cr and Si < B < Zn < Ag < Li < Pb < Mn < Al < Cr < Fe < Cd < Co . The statistical summary of heavy metals of groundwater is specified in the Table 1. Significance of heavy metal occurrence should be considered as an important criteria according to the recommended guideline values for drinking water by WHO (2011), USEPA (2014) and FOA. Spatial variation of heavy metals of groundwater in 2015 and 2016 are classified as safe and risk based on above guideline values.

Table 7.1 Statistical summary of heavy metals of groundwater in the study area

Heavy Metals	Groundwater						Guideline values
	2015 (N=39)			2016 (N=25)			
	Minimum	Maximum	Mean	Minimum	Maximum	Mean	
Si	BDL	15310	8226	207	15470	2475	-
Ag	421	506.5	463	105	152	130	100[b]
Al	276	453	346	53	112	69	200[a]
B	BDL	1655	68	4	701	180	2400[a]
Cd	BDL	11	1	23	59	26	3[a]
Co	BDL	233	26	23	30	26	50[c]
Cr	BDL	BDL	BDL	24	110	103	50[a]
Cu	10	1265	138	11	107	23	2000[a]
Fe	21	5488	333	16	104	97	300[a]
Li	311	422	380	20	120	36	-
Mn	BDL	16815	549	22	113	101	100[a]
Ni	51	225	89	91	107	94	70[a]
Pb	30	582	354	91	117	109	10[a]
Zn	BDL	732	39	83	221	104	5000[a]
All units in µg/l BDL - Below detectable limit							
[a] WHO (2011)							
[b] EPA (2012)							
[c] FAO http://www.fao.org/DOCREP/003/T0234E/T0234E06.htm							

7.2.1 Toxic Heavy Metals

The toxic heavy metals of groundwater are lead (Pb) and cadmium (Cd) in the study area. Naturally occurring lead (Pb) are associated with sulphides, galena (PbS), clausthalite (PbSe), pyrite (PbS_2), alminosilicates and carbonate minerals. Concentration of lead in 2015 ranges from 30 to 582µg/l with an average mean of 354µg/l and in 2016 it ranges from 91 to 117µg/l with an average mean of 109µg/l. 100% of groundwater samples in 2015 (Fig 7.1a) and 2016 (Fig 7.2b) exceeded the permissible (10µg/l) limit of WHO standard. Spatial variation of lead concentration in groundwater samples in 2015 and 2016 are identified falling under risk category. High concentration of lead hazard in the study area are mainly attributed due to the industrial effluents, runoff from contaminated landfill areas, atmospheric pollution, sewage effluents and corrosion from household plumbing system. It affects the physical and mental problems to children and induces the high blood pressure to adults (USEPA 2014).

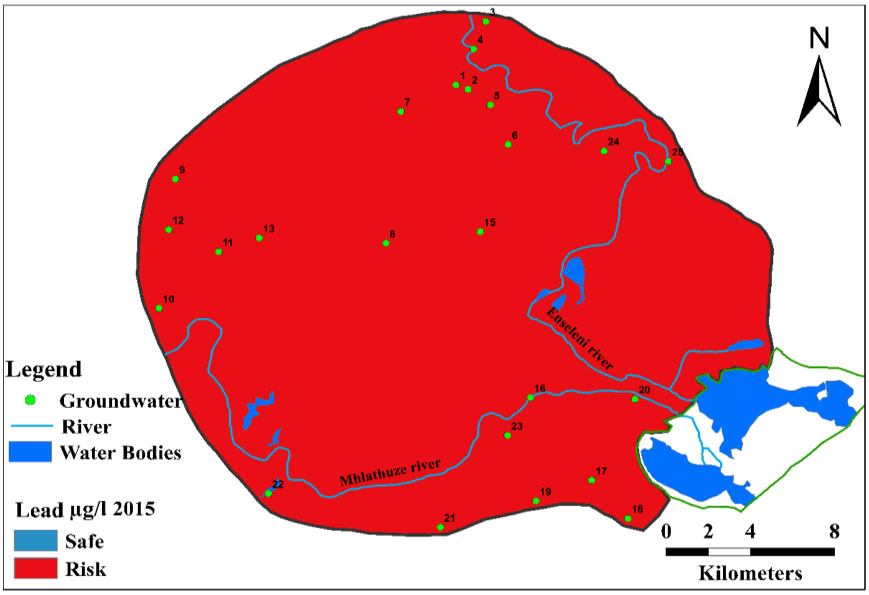


Figure 7.1a. Spatial variation of lead µg/l of groundwater in 2015

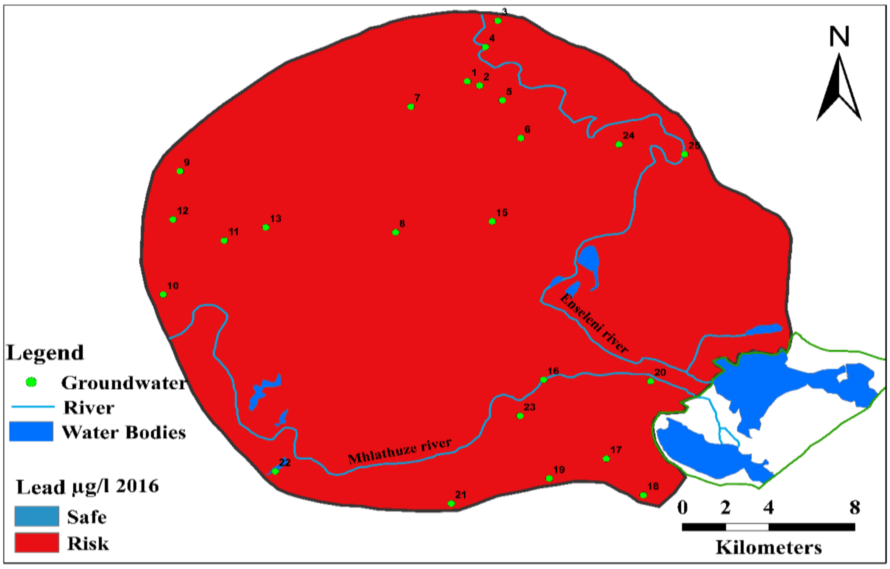


Figure 7.1b. Spatial variation of lead µg/l of groundwater in 2016

Cadmium (Cd) is one of the most toxic metals in the groundwater. It occurs as a rarely dispersed element and natural cadmium are present in greenockite, cadmium sulphide and is usually associated with zinc. Cadmium concentration ranges from below detection limit (BDL) to 11µg/l with an average mean of 1 µg/l of groundwater in 2015 while the ranges from 23 µg/l to 59 with an average mean of 26 µg/l is observed in 2016. Groundwater samples of cadmium concentration in 2015 to 2016 are observed in increasing trend. About 5% and 100% of samples exceeded the permissible (3 µg/l) limit of WHO standard in 2015 (Fig 7.2a) and 2016 respectively (Fig 7.2b). Spatial variation of groundwater in the study area are observed to fall under safe category and few samples are observed under risk category in 2015 and the variation of cadmium concentration in 2016 groundwater samples are observed to fall under risk category. High concentration of cadmium in groundwater samples indicates that corrosion of galvanized pipes, erosion of natural deposits, metal refineries effluents, waste battery and paints through runoff of surface water. High cadmium of groundwater leads to damage the kidney of human beings (USEPA 2014).

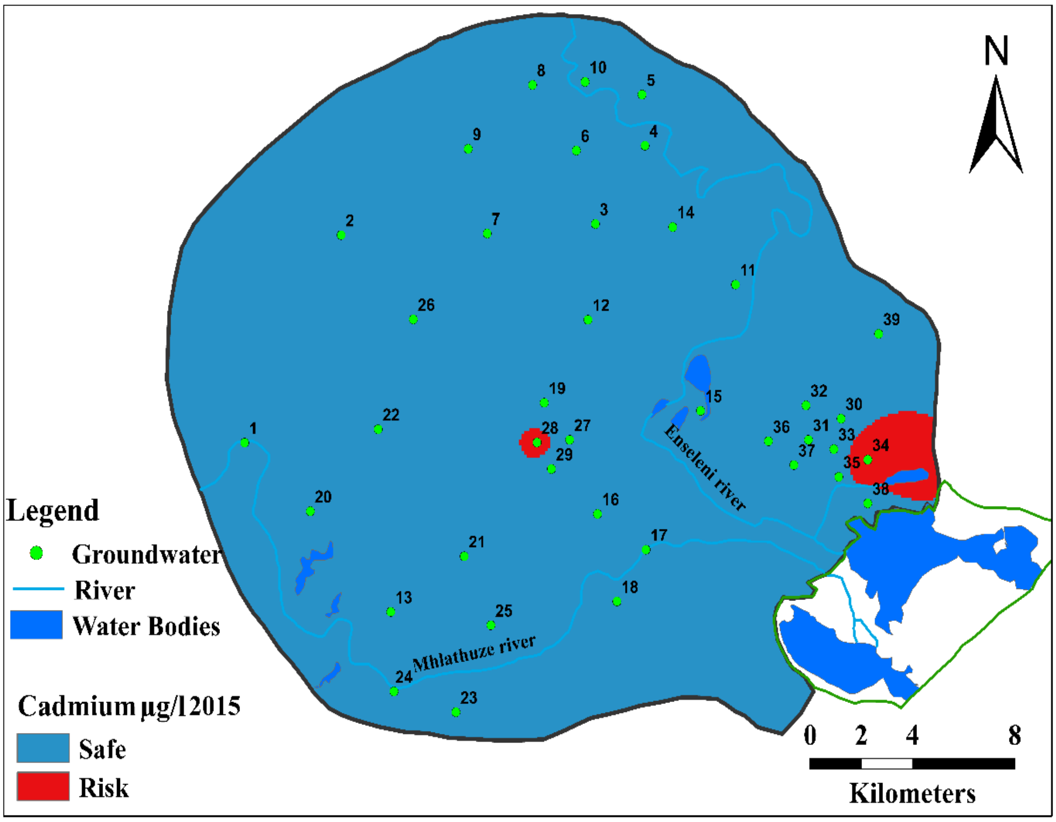


Figure 7.2a. Spatial variation of cadmium µg/l of groundwater in 2015

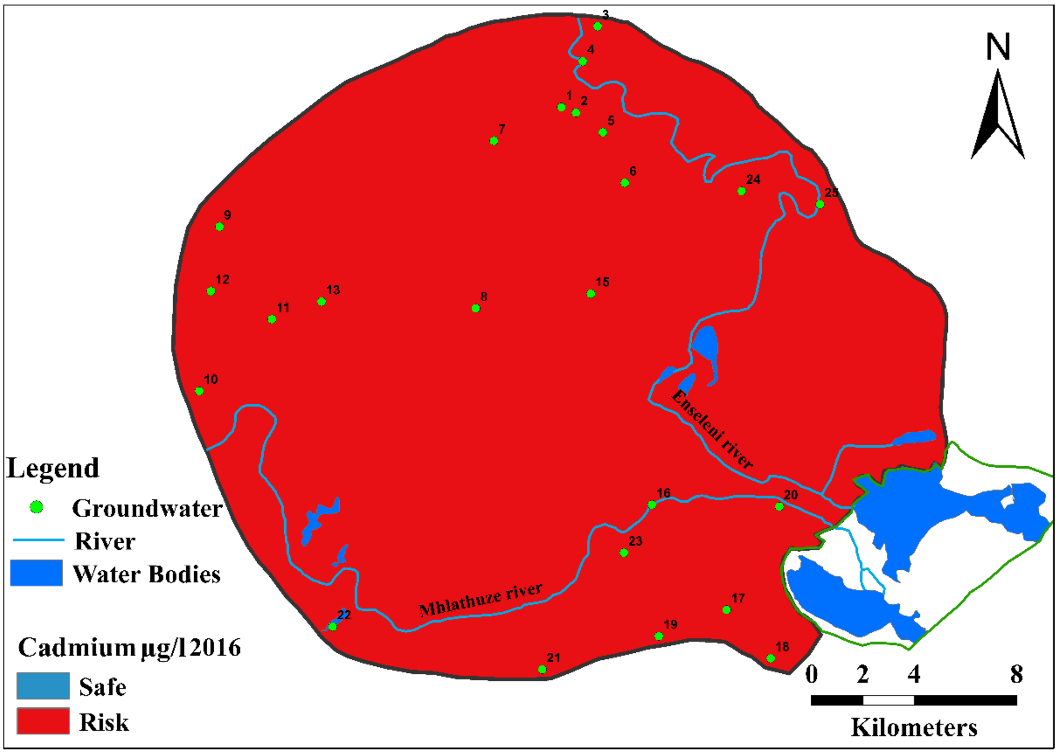


Figure 7.2b. Spatial variation of cadmium µg/l of groundwater in 2016

7.2.2 Transition Heavy Metals

Chromium (Cr) occurs naturally in ultramafic and serpentine rocks/soils and geologically derived Cr (VI) are widely distributed in groundwater. Chromium in the groundwater are BDL in 2015 and range from 24µg/l to 110 µg/l with an average mean of 103 µg/l in groundwater in 2016 (Fig 7.3). About, 96% of chromium concentration in the groundwater samples exceeded the permissible limit (50 µg/l) of WHO standard in 2016. High chromium hazard in the year 2016 specifies the influence of electroplating, tanning of leather and textile industries effluents, chromate processing and improper disposal of landfills. . Chromium affects the allegeric dermatitis, but it is used for insulin secretion to the human body and helps to maintain normal glucose level (USEPA 2014).

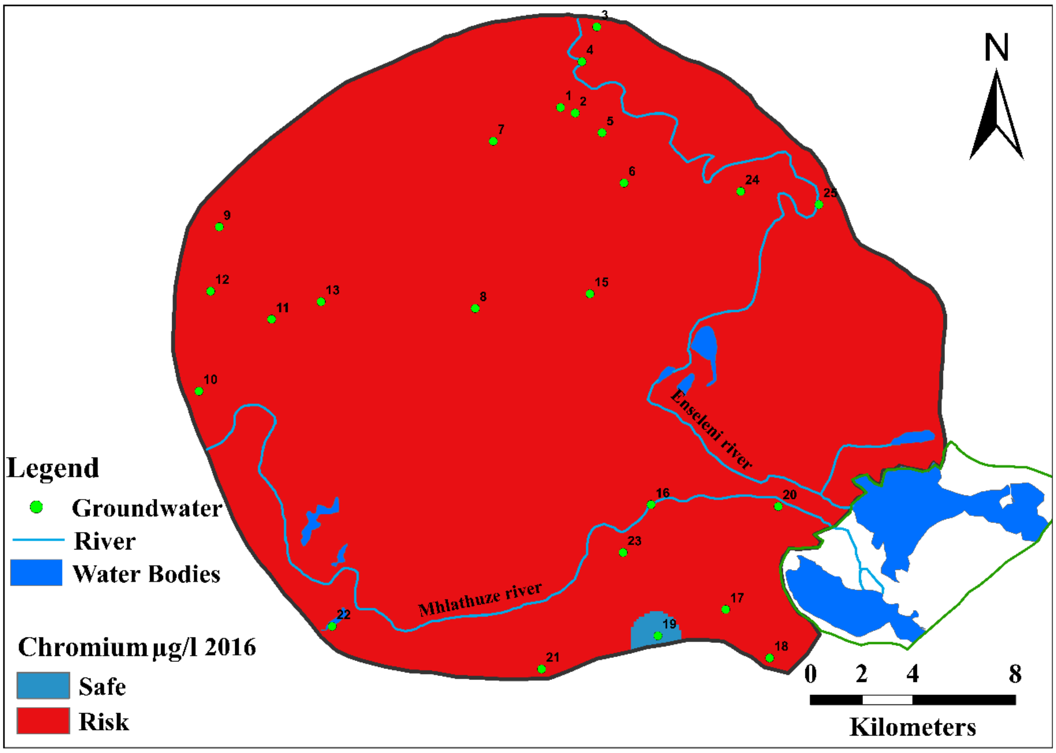
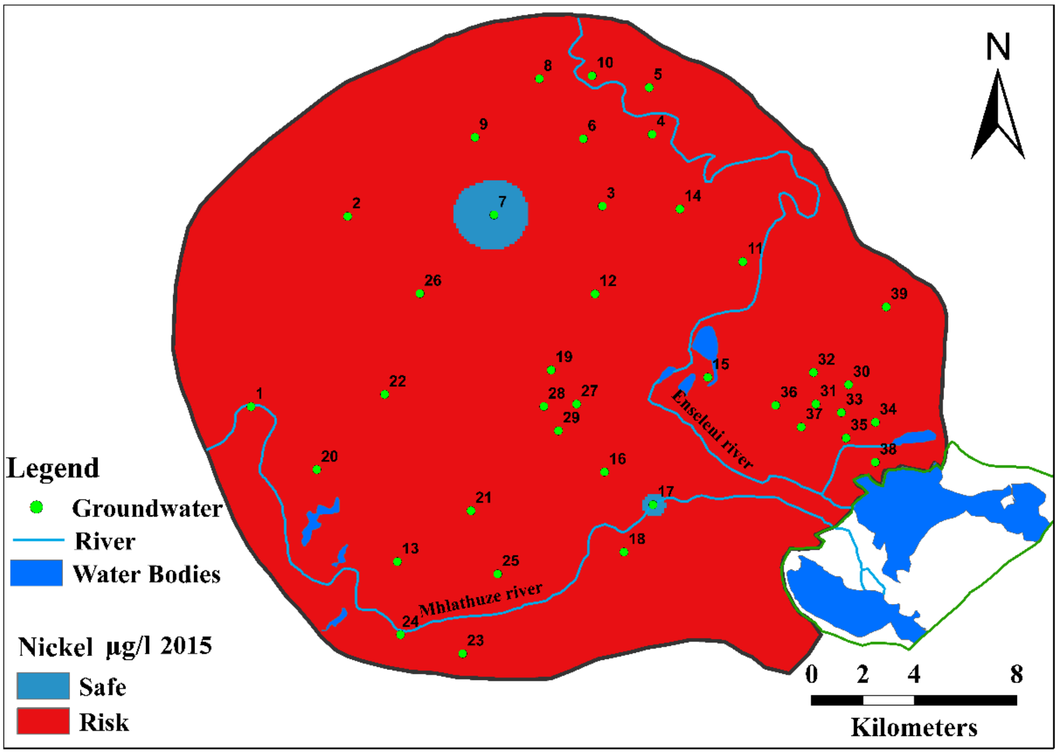


Figure 7.3. Spatial variation of chromium µg/l of groundwater in 2016

Nickel is one of the transition metal in the environment and being released from natural and anthropogenic source. Concentration of nickel ranges from 51µg/l to 225 µg/l with an average mean of 89 µg/l and the ranges from 91 µg/l to 107 µg/l with an average mean of 101 µg/l are observed in 2015 and 2016 respectively. About 96% and 100% of samples exceeded the permissible limits (70 µg/l) of WHO in 2015 (Fig 7.4a) and 2016 (Fig 7.4b) respectively. Spatial variation of nickel concentration of groundwater in 2015 and 2016 are observed to fall under risk category. A few samples fall under safe category in 2015. Sources of nickel are from sewage sludge, wastewater from sewage treatment plant which infiltrates through groundwater near landfill areas. In this study area, large amount of industrial effluents discharge tends to increase nickel hazard. High contamination from nickel causes different pathological effects like skin allergies, lung infection, cancer of the respiratory pathway, nickel poisoning and also causes toxicity to the kidney, cardiovascular system and immune system.



7.2.3

Figure 7.4a. Spatial variation of nickel (µg/l) in groundwater in 2015

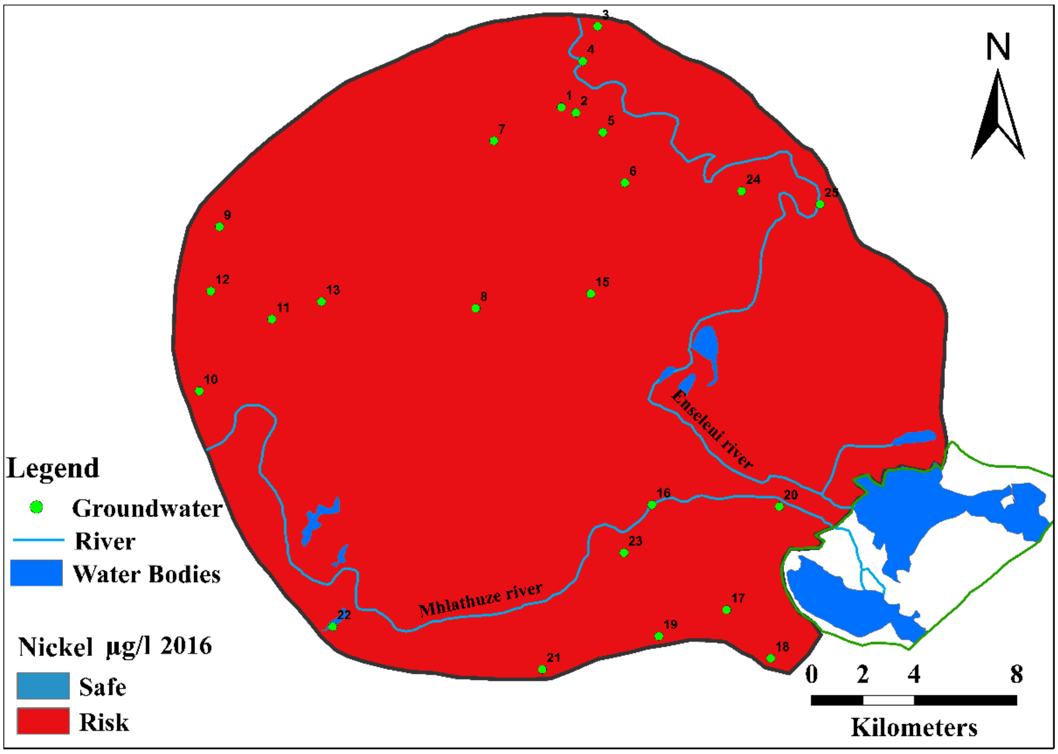


Figure 7.4b Spatial variation of nickel (µg/l) in groundwater in 2016

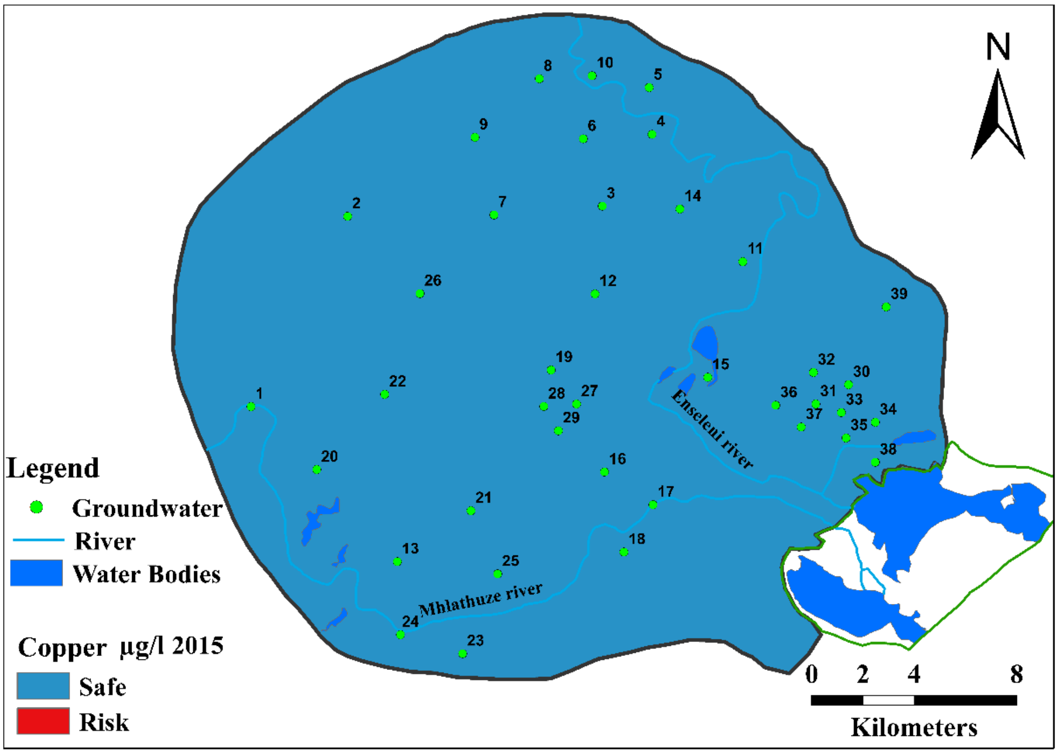


Figure 7.5b. Spatial variation of copper (µg/l) in groundwater in 2015

7.2.3 Metallic Heavy Metals

Copper (Cu) occurs naturally in magmatic and hydrothermal activity as insoluble sulphides. Most common copper mineral is chalcopyrite ($CuFeS_2$) and it is also associated with sulphide oxides as cuprite (Cu_2O), carbonates as azurite ($2CuCO_3.Cu\ [OH]\ _2$) and malachite ($CuCO_3$. Cu [OH] $_2$). Copper concentration (Table 7.1) ranges from the value 10 µg/l to 1265 µg/l with an average mean of 138 µg/l in 2015 and the ranges from 11 µg/l to 107 µg/l with an average mean of 23 µg/l is observed in 2016. About, 100% of groundwater samples are observed falling within the permissible limit (2000 µg/l) of WHO standards. Spatial variation of copper concentration of groundwater in 2015 (Fig 7.5a) and 2016 (Fig 7.5b) are observed to fall under safe category. Sources of copper are metal plating, industrial and domestic waste, mining processing waste and leaching of effluents. Copper is an essential element for life in plants, animals and human beings in which the increasing concentration affects the stomach and intestinal distress, liver and kidney damage, deficiency anaemia (USEPA 2014).

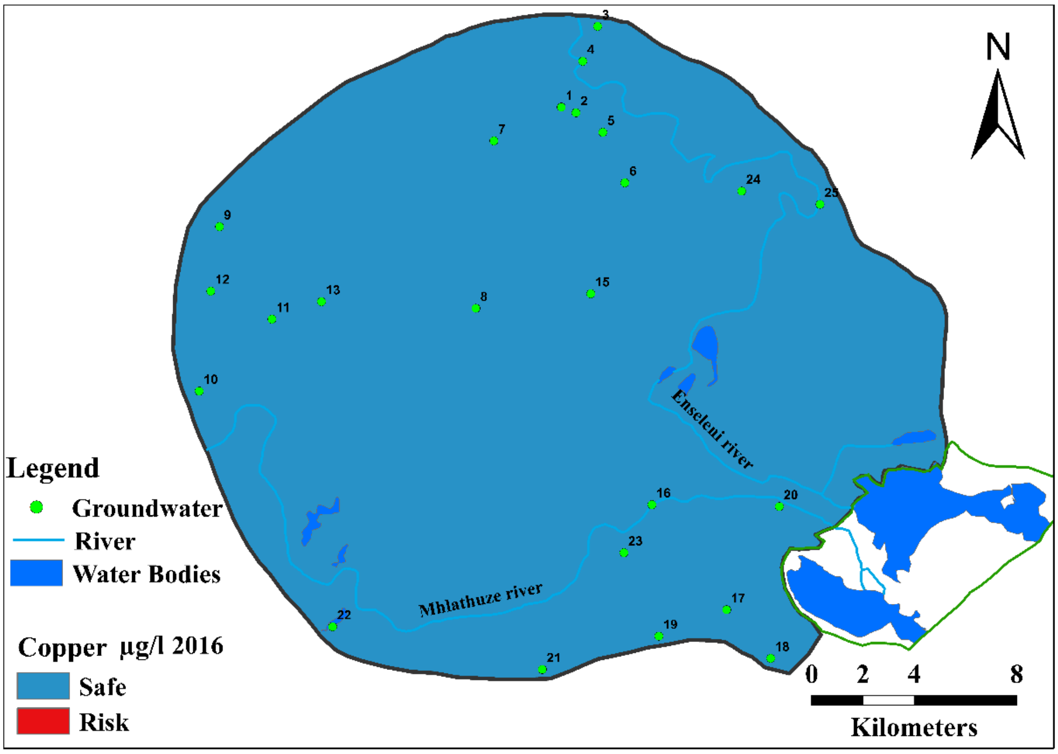


Figure 7.5b. Spatial variation of copper µg/l of groundwater in 2016

Iron (Fe) is the common heavy metal in the earth, naturally occurs as pyroxene, amphiboles, biotite and neosilicate olivine. Iron minerals are magnetite, hematite, goethite and siderite. Iron concentration (Table 7.1) ranges from 21µg/l to 5488 µg/l with an average mean of 333 µg/l in 2015 and the ranges from 16 µg/l to 104 µg/l with an average mean of 97 µg/l is observed in 2016. About 15% of iron concentration in groundwater samples exceeded the permissible limit (200µg/l) in 2015. Spatial variation of iron concentration in groundwater in 2015 (Fig 7.6a) are observed to fall under safe category in NS and NW- SW. SE part of the study area are observed to be falling under risk category. Variation of iron concentration in groundwater in 2016 (Fig 7.6b) are observed to be falling under safe category. High iron concentration in groundwater specifies the interaction of oxidized iron minerals with organic matter and dissolution of iron carbonate at a low pH and removal of DO in organic matter under reduced condition. Increasing the solubility of iron bearing minerals leads to enrichment of dissolved iron in the groundwater under reducing condition (White et al 1991). Iron, an important element of red blood cells (haemoglobin) and muscle cells (myoglobin) plays a major role in carrying oxygen from liver to the tissue. Uses of iron are disagreeable in food and beverage processing and cause stains in laundry and utensils (USEPA, 2014)

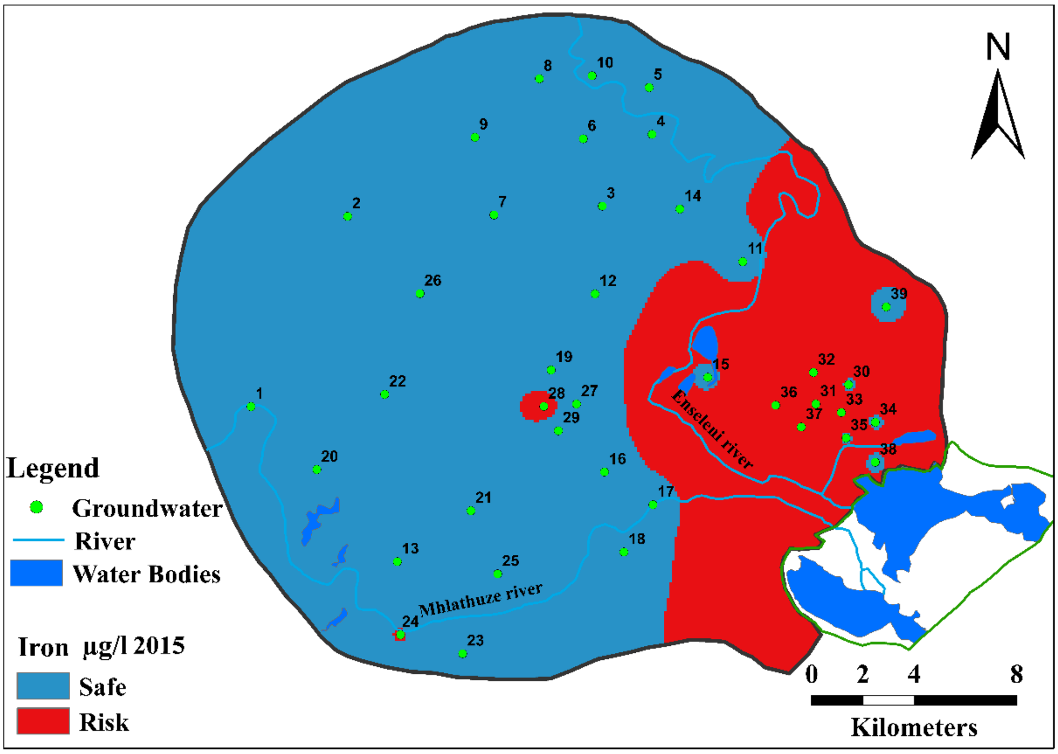


Figure 7.6a. Spatial variation of iron (µg/l) in groundwater in 2015

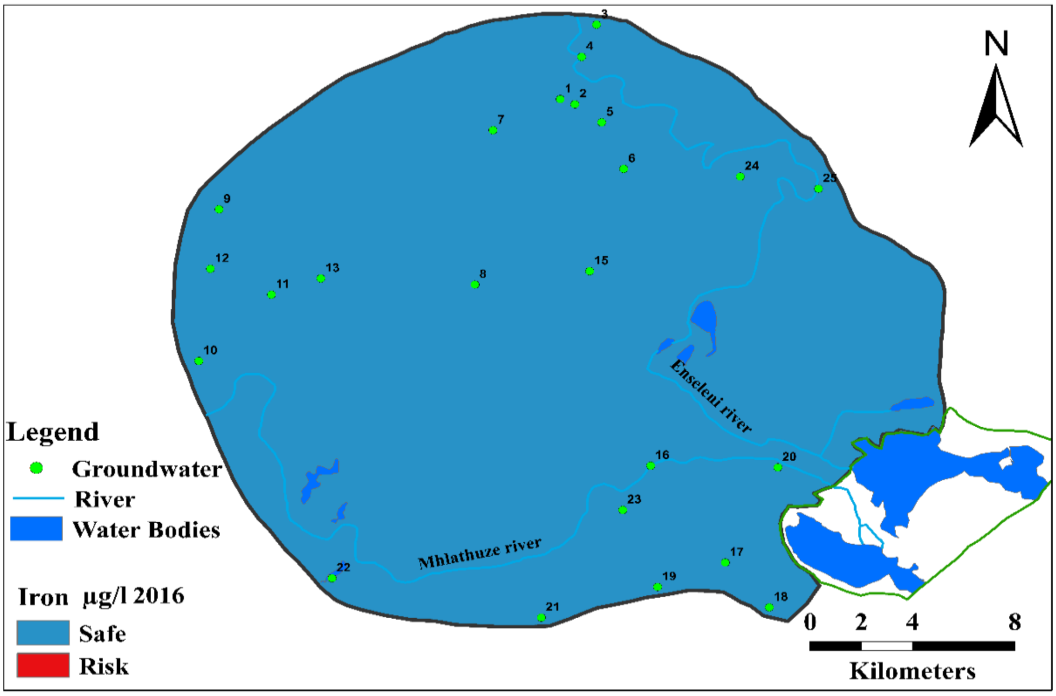


Figure 7.6a. Spatial variation of iron µg/l of groundwater in 2016

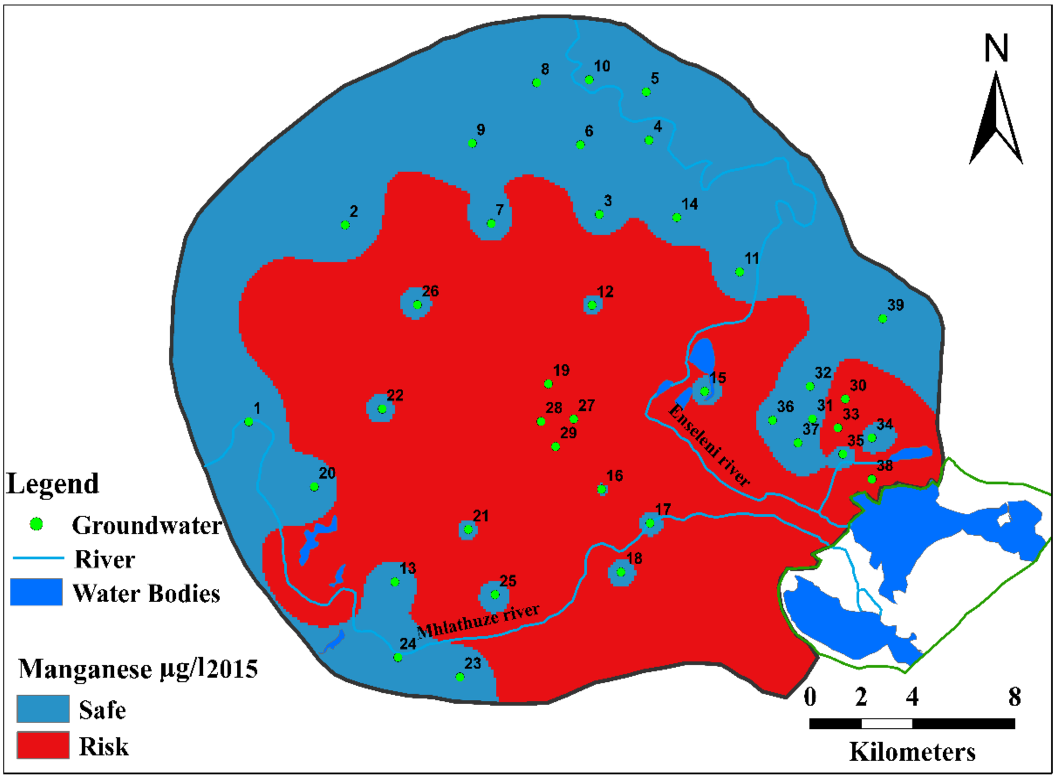


Figure 7.7a. Spatial variation of manganese µg/l of groundwater in 2015

Manganese (Mn) occurs in igneous and metamorphic rocks and it is present as the minor constituents. Significant compositions of basaltic rocks are olivine, pyroxene and amphibole. Minor amount of manganese occurs in dolomite and limestone. Manganese concentration ranges (Table 7.1) from BDL to 16,815 µg/l with an average mean of 549 µg/l in 2015 and the ranges from 22 µg/l to 113 µg/l with an average mean of 101 µg/l is observed in 2016. About 13% and 100% of groundwater samples exceeded the permissible limit (100 µg/l) of WHO standard in 2015 and 2016 respectively. Spatial variation of manganese concentration in groundwater in the year 2015 (Fig 7.7a) in the S-SE, NW and central part are observed falling under risk category and other parts are observed falling under safe category. Manganese concentration variation in groundwater in the year 2016 (Fig 7.7b) are observed falling under risk category. Source of manganese specifies that microorganism play an essential role in the oxidation and reduction of manganese (Matthess 1982). Deficiency of manganese results the abnormal growth, central nervous system problems, anaemia and problem with reproductive functions (Rothstein, 1949).

Manganese cause brownish stains to cloths and affects taste of water and causes black stains on plumping pipes (USEPA, 2014).

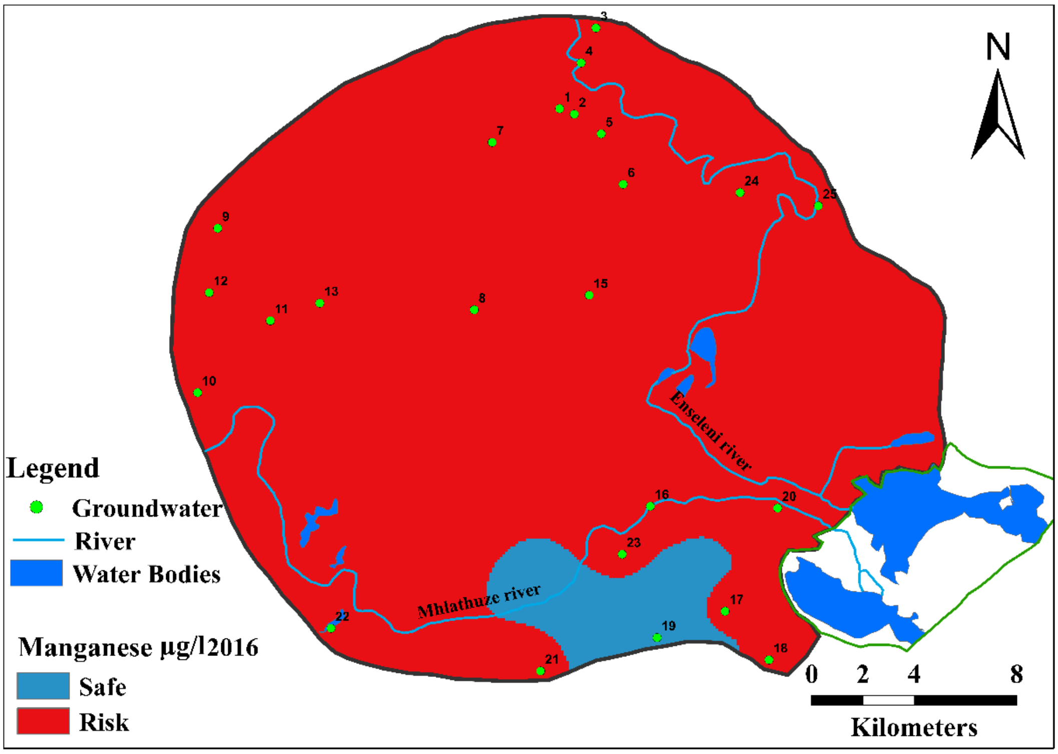


Figure 7.7b Spatial variation of manganese µg/l of groundwater in 2016

Zinc is an abundant element and constitutes the earth crust. Zinc mineral is sphalerite (ZnS) and it is associated with sulphide and other metallic elements. It occurs naturally in volcanic exhalation. Concentration of zinc ranges (Table 7.1) from BDL to 732 µg/l with an average mean value of 39 µg/l is observed in 2015 and the ranges from 83 µg/l to 221 µg/l with an average mean of 104 µg/l is observed in 2016. In 2015 and 2016 groundwater samples are observed falling within the permissible limits (5000 µg/l) of WHO standards. Spatial variation of zinc concentration in groundwater samples in 2015 (Fig 7.8a) and 2016 (Fig 7.9b) are observed to fall under safe category. Zinc is used as an anti-corrosion agent to protect corrosion on pipes, while construction of the boreholes, galvanized pipelines. Corrosion pumps leads to increasing zinc into groundwater. Zinc is important to execute normal metabolic activities and deficiency in children (Vetrimurugan et al 2016).

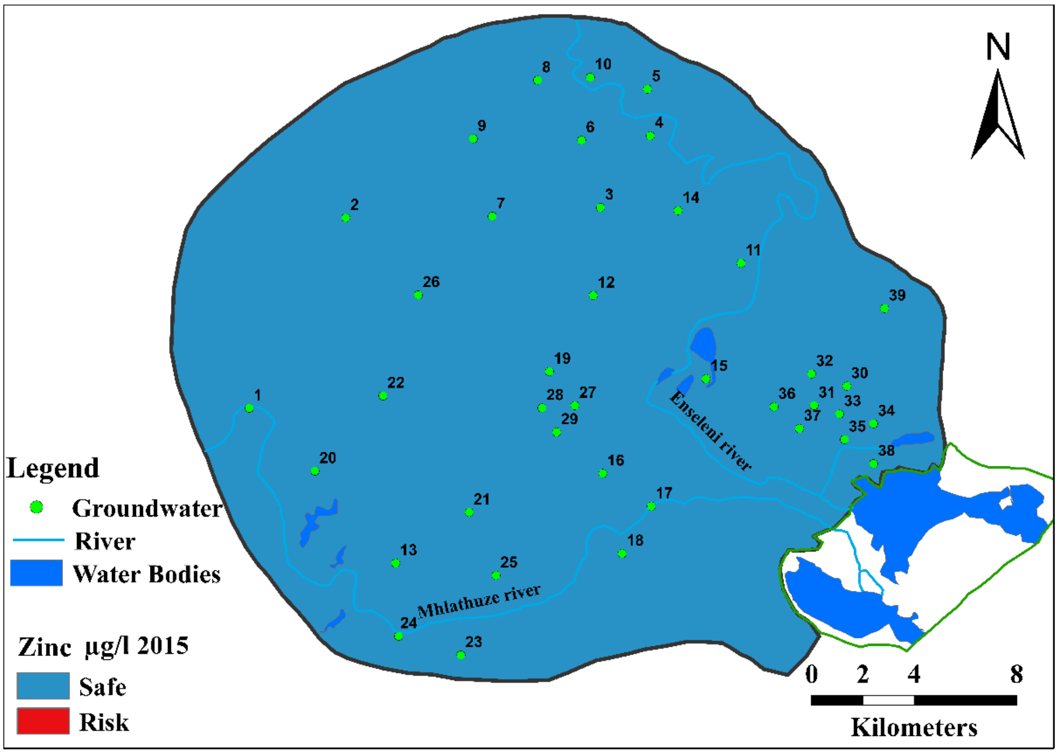


Figure 7.8a Spatial variation of zinc µg/l of groundwater in 2015

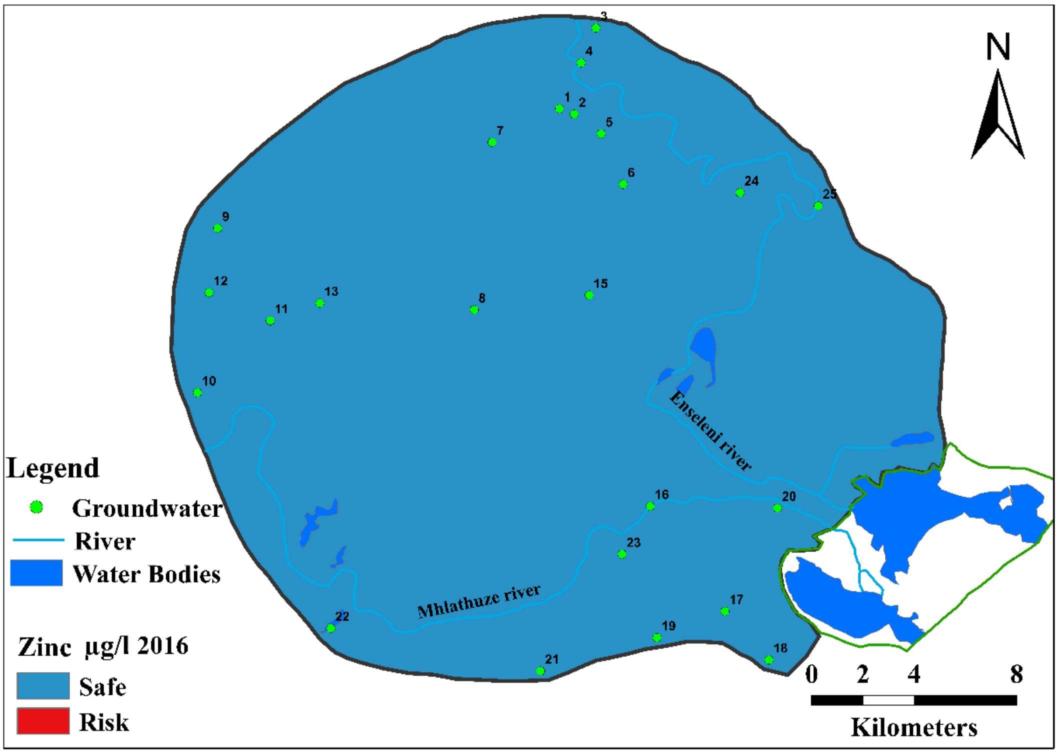


Figure 7.8b Spatial variation of zinc µg/l of groundwater in 2016

Aluminium (Al) is the third most abundant element in the earth. Aluminium occurs at low concentration level which indicates low solubility of the aluminium bearing minerals at the neutral pH values of groundwater (Nordstorm and Ball, 1986). Aluminium ranges (Table 1) from 276 µg/l to 453 µg/l with an average mean of 346 µg/l in 2015 and the ranges from 53mg/l to 112 µg/l with an average mean of 69 µg/l is observed in 2016. About 100% of samples exceeded the permissible limit (200 µg/l) of WHO standard in 2015 and 100% of samples are observed falling within the permissible limit in 2016. Spatial variation of aluminium concentration are at risk category in 2015 (Fig 7.9a) and in 2016, (Fig 7.9b) groundwater samples are under safe category. High concentration of aluminium specifies anthropogenic sources, sewage seepage and atmospheric deposition. Aluminium released into groundwater are due to effluent from bauxite processing and aluminium manufacturing industries are toxic to aquatic life (Trieff et al, 1995).

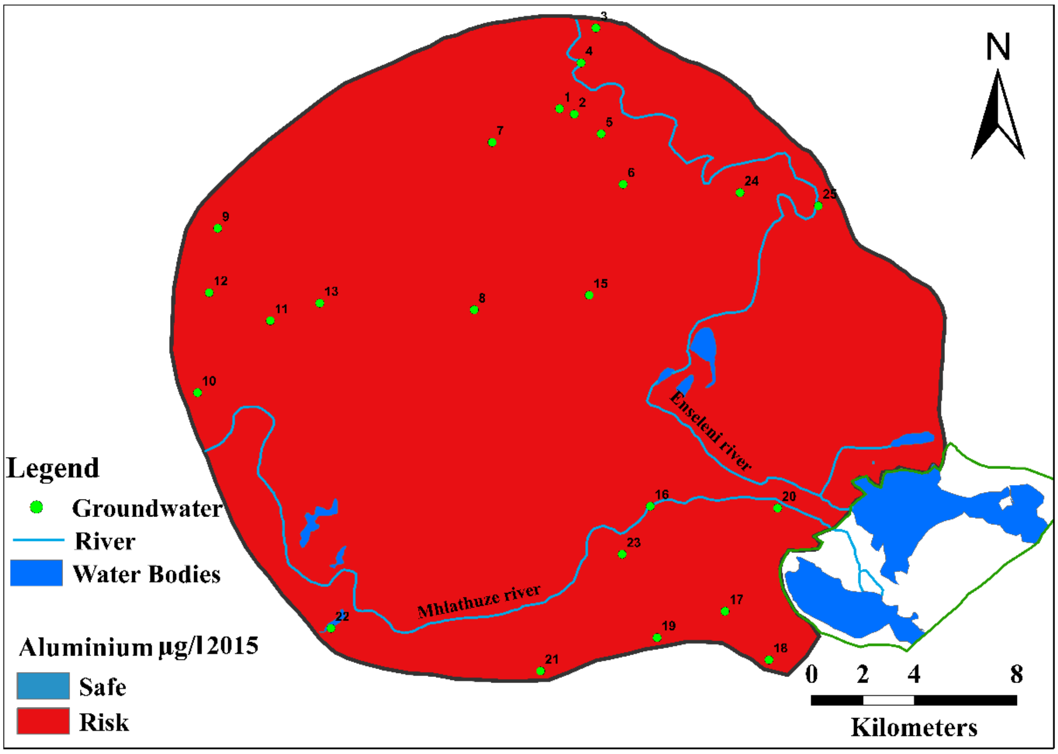


Figure 7.9a. Spatial variation of aluminum µg/l of groundwater in 2015

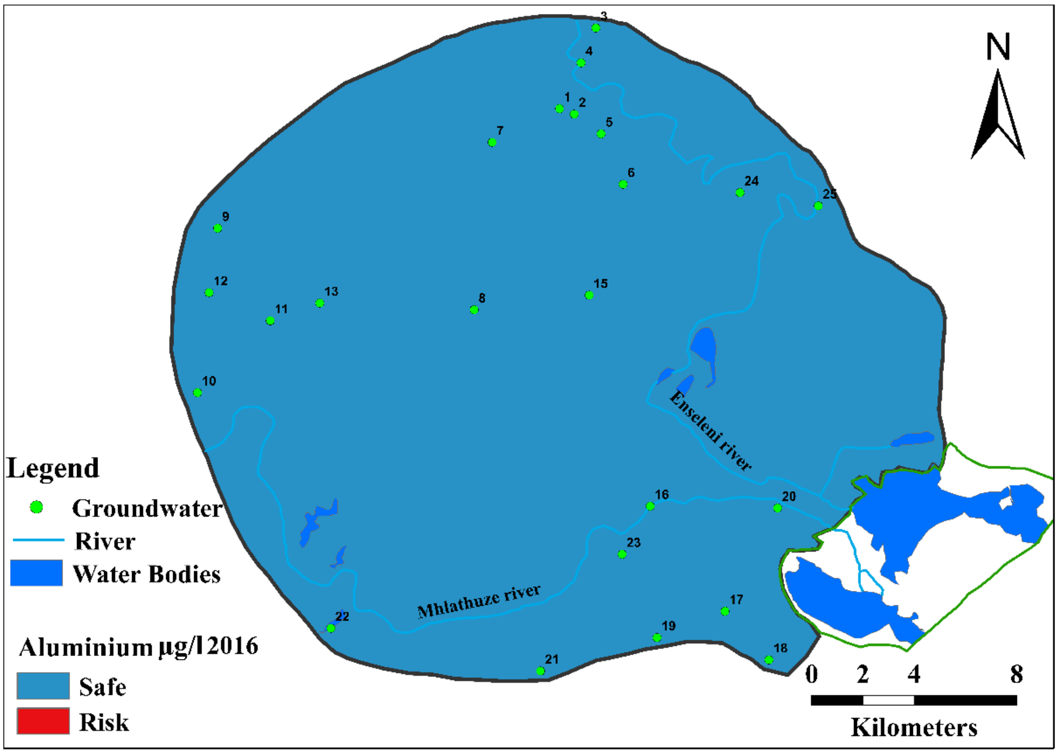


Figure 7.9b. Spatial variation of aluminum µg/l of groundwater in 2016

Cobalt is a naturally occurring element and has similar properties of nickel and iron. The most common minerals are arsenide $CoAs_2$ (smeltite), arsenosulfide, CoAsS (Cobaltine) and sulphides Co_3S_4 (linneite). Cobalt ranges (Table 7.1) from BDL to 223 µg/l with an average mean of 26 µg/l in 2015 and the ranges from 23 to 30 µg/l with an average mean of 26 µg/l is observed in 2016. About 3% of samples exceeded the permissible limit of FOA in 2015. About 100% of aluminium concentration in groundwater samples is observed to fall under safe category in 2016. Spatial variation of cobalt concentration in groundwater samples are falling under safe category in 2015 (Fig 7.10a) and in 2016, (Fig 7.10b) and a few samples are at risk. The natural sources of cobalt include wind- blown dust, seawater spray, volcanoes, continental and marine biogenic emissions. Burning of fossil fuels, sewage sludge, phosphate fertilizers, mining and smelting of cobalt ores and industries are driven factors (WHO 2008). Occupational contact to cobalt and tungsten carbide are problem of lung cancer. Cobalt is used to treat anaemia as it increases the red blood cells production.

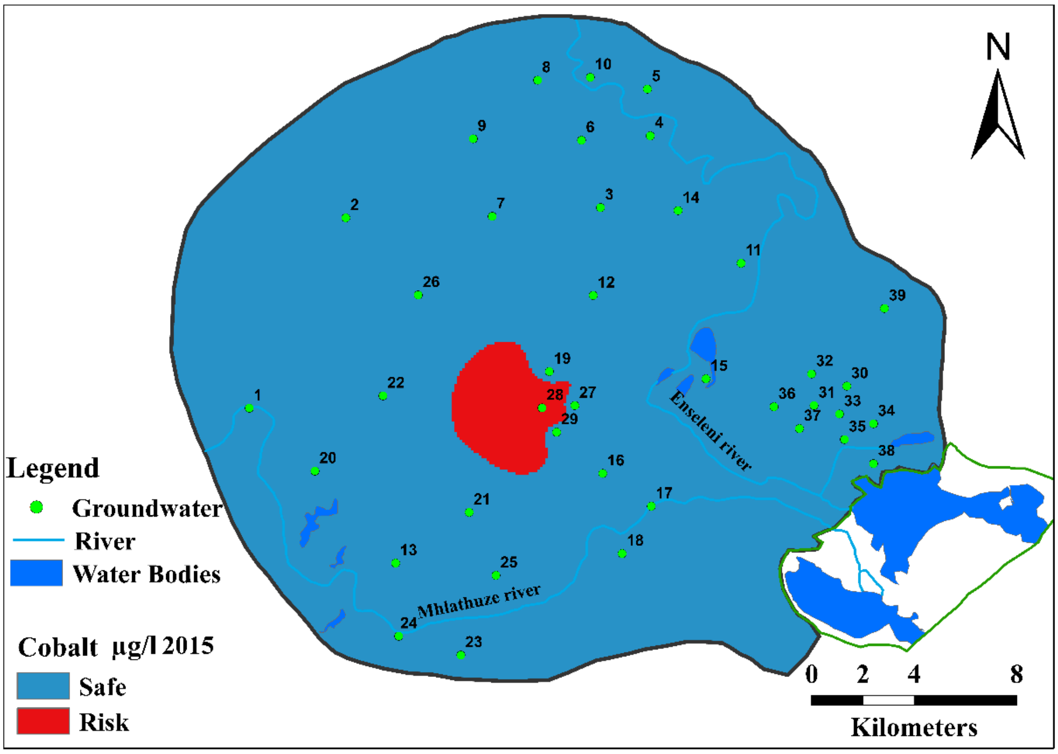


Figure 7.9a. Spatial variation of cobalt µg/l of groundwater in 2015

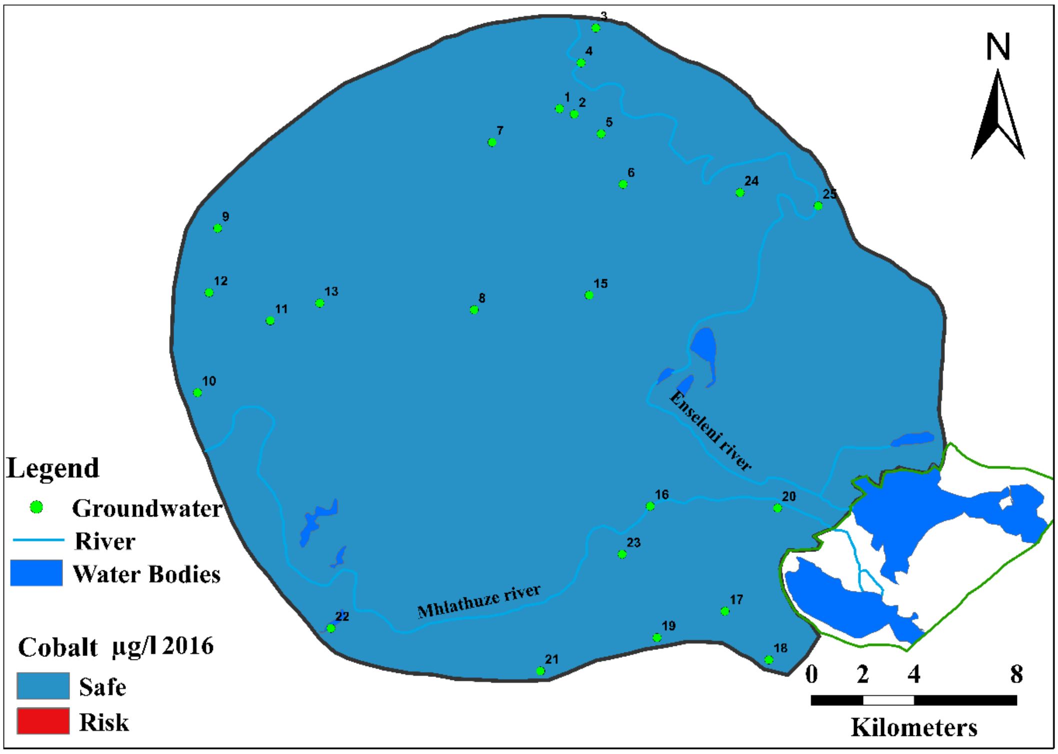


Figure 7.9b. Spatial variation of cobalt µg/l of groundwater in 2016

Silver (Ag) occurs as sulphides and associated with pyrite, galena, tellurides and gold. Silver ranges from 421 to 506 µg/l with an average mean of 346 µg/l in 2015 and the ranges from 105 to 152 µg/l with an average mean of 130 µg/l is observed in 2016. About 100% of samples exceeded the permissible limit (100 µg/l) of USEPA. Sources of silver are from ore mining and processing and disposal of ore waste. Silver is used for electric and electronic equipment sterling, electroplating, alloy and solder. High concentration of silver is toxic and affects eyes and skin.

7.2.4 Non -Metallic Heavy Metals

Boron occurs in a non-ionized form as H_3BO_3 in soils at pH< 8.5, if it exists above this pH, it exists as an anion B (OH) $_4$ (Miller and Donahue 1995). Boron ranges from BDL to 1655 µg/l with an average mean of 68 µg/l in 2015 and the ranges from 4 to 701 µg/l with an average mean of 180 µg/l is observed in 2016 (Table 1). About 100% of samples are within the permissible limit (2300 µg/l) of WHO standard. Boron spreads in the environment through fertilizer usage. Boron concentrations are important to plant growth, but, in higher concentration can be toxic.

Silicon (Si) ranges from BDL to 15310 µg/l with an average mean of 8226 µg/l in 2015 and the the ranges from 207 to 15470 µg/l with an average mean of 2475 µg/l is observed in 2016. WHO (2011) and USEPA (2014) did not recommend any standard limit for silicon concentration in groundwater. High concentration of silicon specifies the potential therapeutic effects.

Lithium (Li) is an alkali metal that occurs in rock and soil in the form of minerals and ionic salts. Lithium ranges from 311 to 422 µg/l with an average mean of 380 µg/l in 2015 and the ranges from 20 to 120 µg/l with an average mean of 36 µg/l is observed in 2016. WHO (2011) and USEPA (2014) have not recommended any standard limit for lithium concentration in groundwater.

7.3 HEAVY METAL POLLUTION INDEX

. The Heavy metal pollution indices for drinking water suitability comprises of HPI, HEI and C_d. The HEI and HPI methods utilise the ratio of observed concentration with WHO (2011) standards and the maximum admissible concentration in drinking water (Siegel, 2002).

7.3.1 Evaluation Indices

The pollution indices of HPI, HEI and Cd are computed by using WHO standard. Edet and Offiong (2002) suggested that approach of pollution indices values are shown in the Table 7.2.

Table 7.2 Classification of water quality using modified pollution indice (Edet and Offong 2002)

Indexing Method	Pollution Class	Percentage of samples	
		2015	2016
HPI	Low (<5)	3	82
	Medium (5-10)		18
	High (>10)	97	-
HEI	Low (<10)		-
	Medium (10-20)		100
	High (>20)	100	-
C_d	Low (<15)	3	97
	Medium (15-25)	-	-
	High (>25)	97	3

HPI ranges from 1 to 56 with an average mean value of 29 in 2015 while the ranges from 3 to 6 with an average mean value of 5 is observed in 2016. Classification of HPI (Fig 7.10a) results indicates that 3% of low index (<5), and 97% of high risk (> 10) is observed in 2015. HPI values of about82% fall in low index and 82% fall in medium index class in 2016.

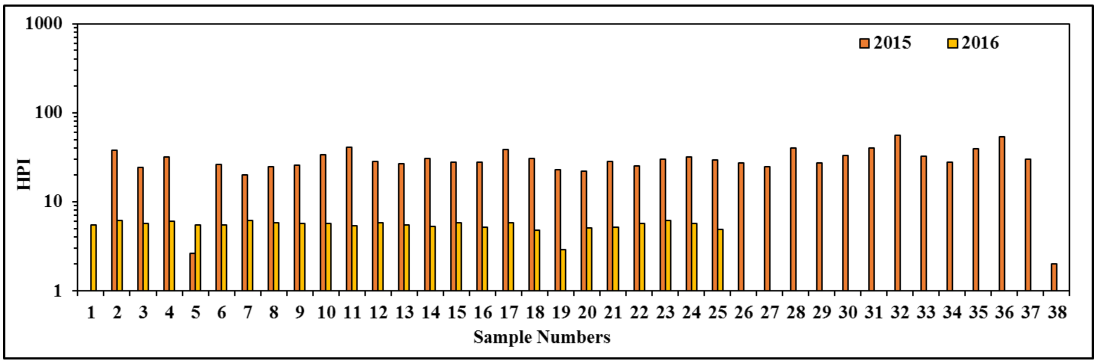


Figure 7.10a. Classification of groundwater quality on modified categories of HPI pollution indices in 2015 and 2016

HEI ranges from 13 to 76 with an average mean of 42 is observed in 2015 and the ranges from 11 to 14 with an average mean of 14 is observed in 2016. HEI classification (Fig 7.10b) show that 3% fall in low (<10) index class and 97% (>20) fall in high index in 2015 and 100% fall in medium index class in 2016.

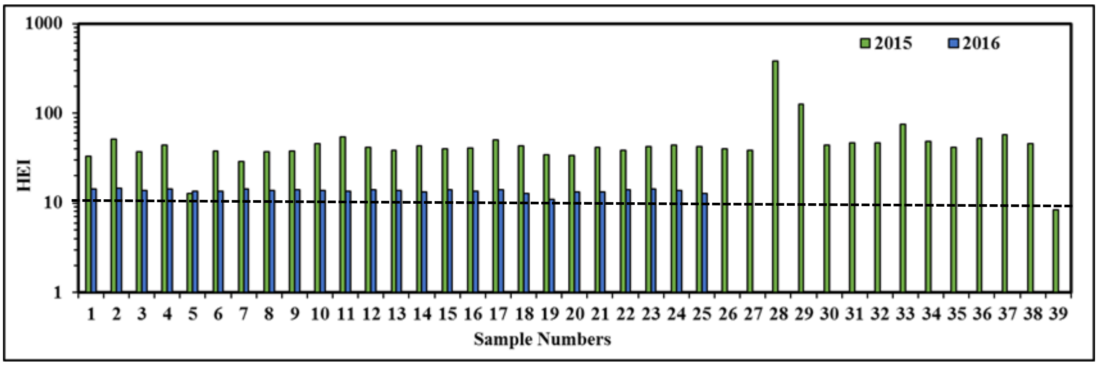


Figure 7.10b. Classification of groundwater quality on modified categories of HEI pollution indices in 2015 and 2016

C_d ranges from 21 to 70 with an average mean of 37 in 2015 and the ranges from 10 to 14 with an average mean of 13 is observed in 2016. Classification of C_d specifies that 3% fall in low (<15) index and 97% fall in high (>25) index class in 2015 and 97% fall in low and 3% fall in high index classification.

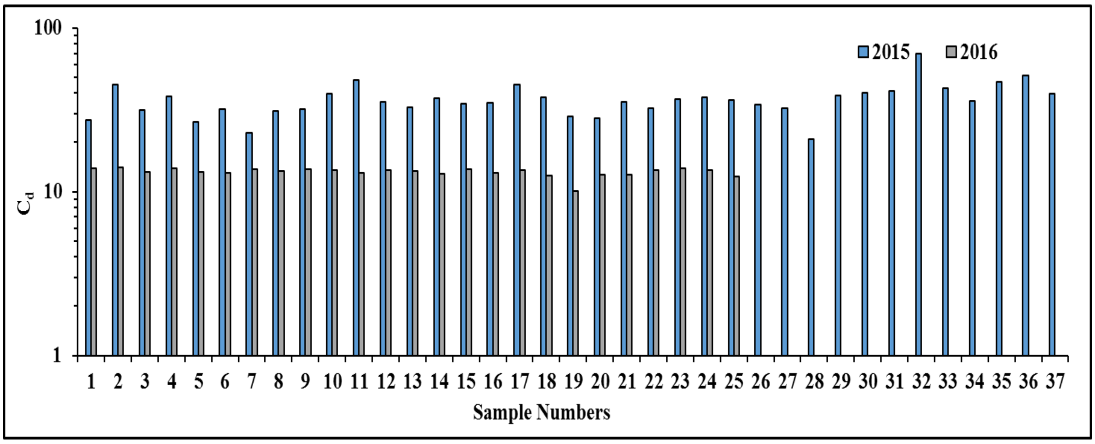
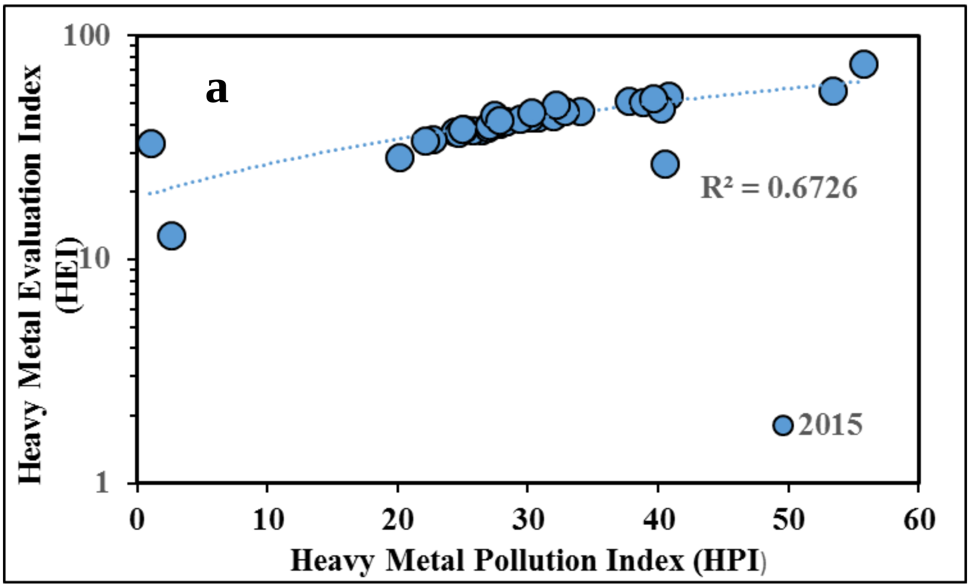


Figure 7.10c. Classification of groundwater quality on modified categories of C_d pollution indices in 2015 and 2016

Regarding the above classification of the indices (Edet and Offiong 2002) and considering the percentage samples have high contamination index value of 2015 and 2016. Further, plot of HPI versus HEI (Fig 7.11a,b), HPI versus C_d (Fig 7.12a,b) and HEI versus C_d (Fig 7.12c,d) indicates strong correlation i.e. R^2= 0.67, R^2= 0.58 and R^2=0.89 in 2015 and R^2= 0.94, R^2= 0.95 and R^2 =0.94 in 2016.



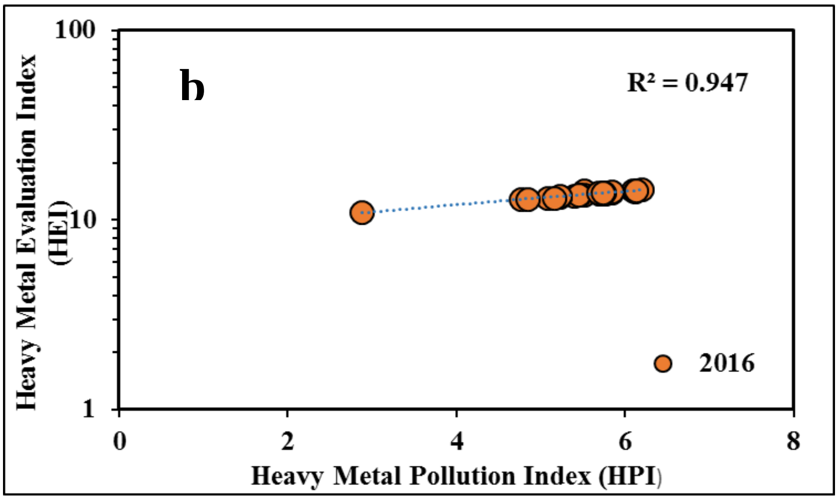
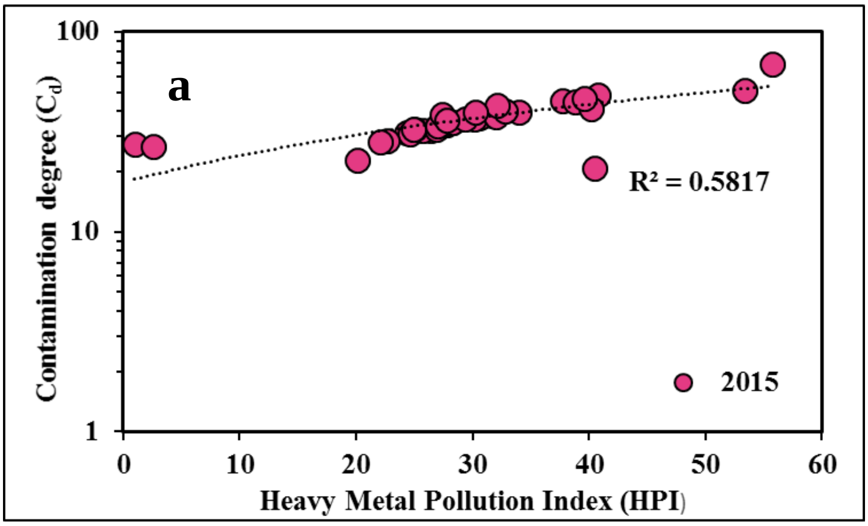
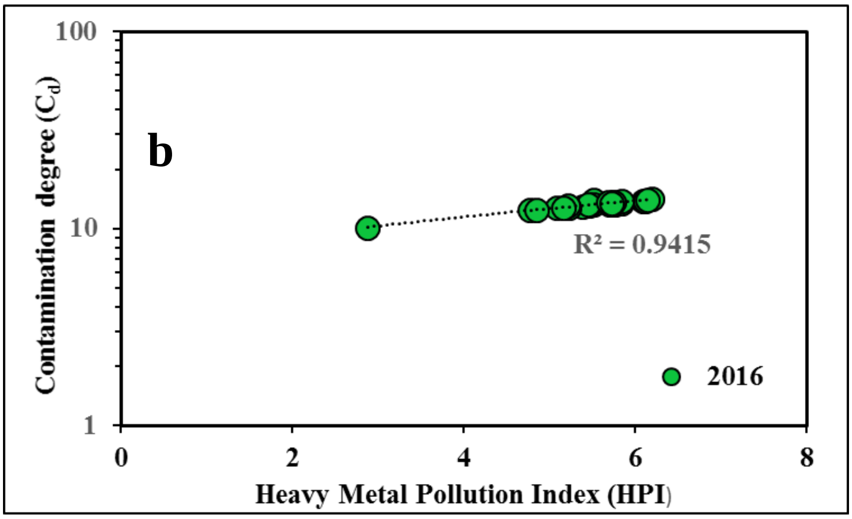


Figure 11a,b. HPI versus HEI





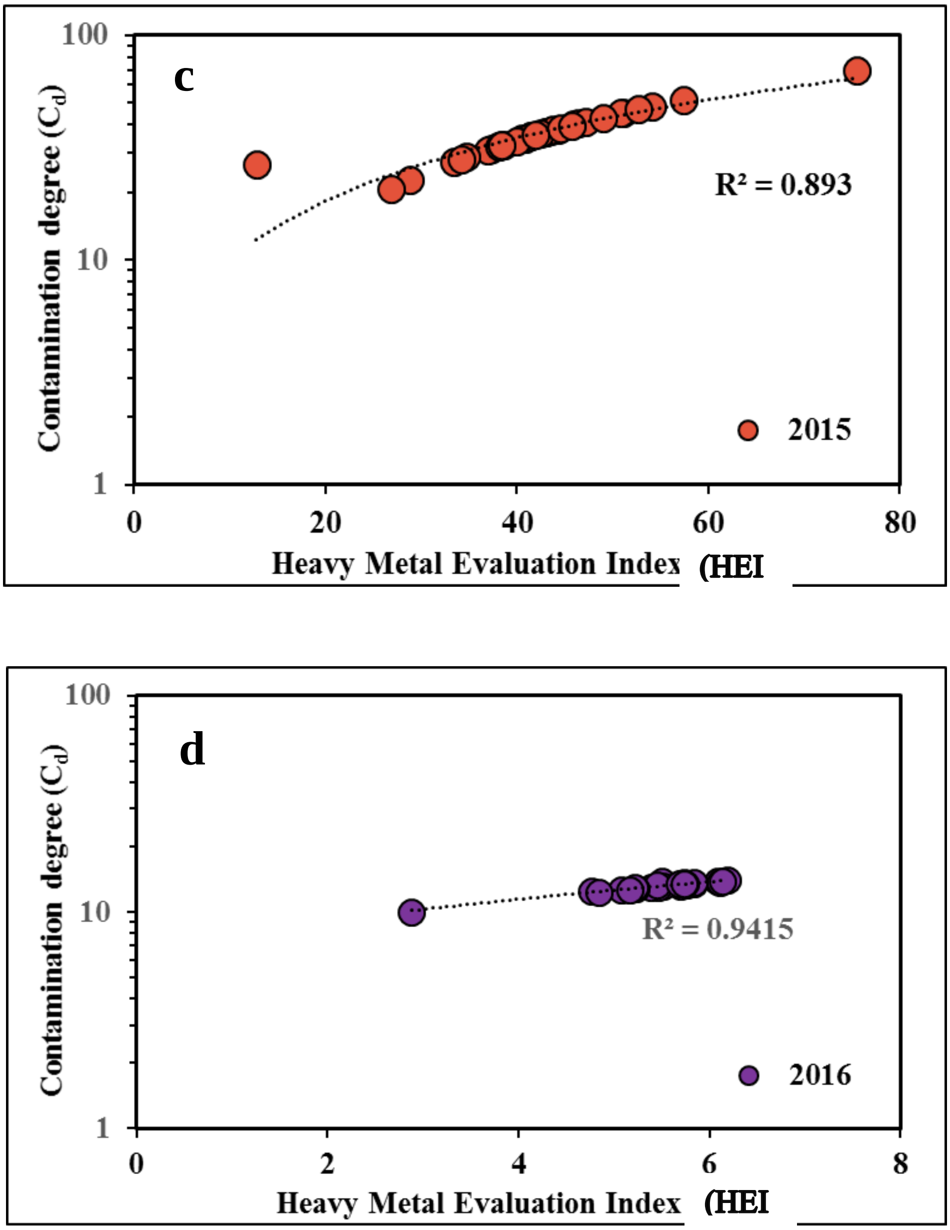


Figure 7.12. Correlation of HPI, HEI and C_d pollution indices in 2015 and 2016

The pollution indices method of HPI, HEI and Cd indicates two extreme results during 2015 and 2016 while the values also specify significant strong correlation of the study area with influence of industrial activity. This study indicates the high level of heavy metal contamination in the Empageni and Richard bay area.

7.4 METAL SPECIATION

The chemical species of the different species are shown in the figure 7.13 and 7.14 in 2015 and 2016.The major species of aluminium in the groundwater are aluminium hydroxide. Al (OH) $_2$ ranges from -2.54 to 0.28 with an average mean of -0.81 in 2015 and the ranges from -0.88 to-0.56 with an average mean of 0.78 is observed in 2016. Gibbsite value ranges from 0.14 to 2.97 with an average mean of 1.84 in 2015 and the ranges from 1.80 to 2.13 with an average mean of 1.91 is observed in 2016. Aluminium hydroxide in the groundwater are undersaturated and gibbsite are oversaturated in 2015 (Fig 7.13) and 2016 (Fig7.14). Dissolution and precipitation of Al bearing minerals specify the undersaturated and oversaturated in the aluminium hydroxide and gibbsite mineral species.

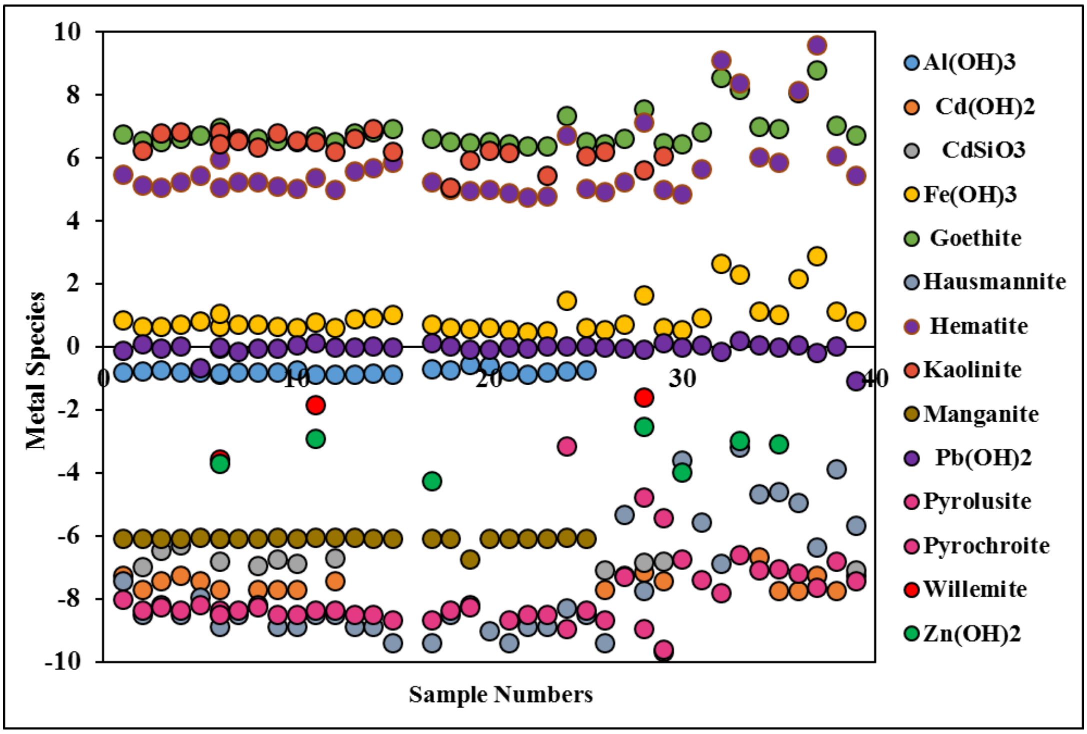


Figure 7.13 Metal speciation versus sample numbers in groundwater in the year 2015

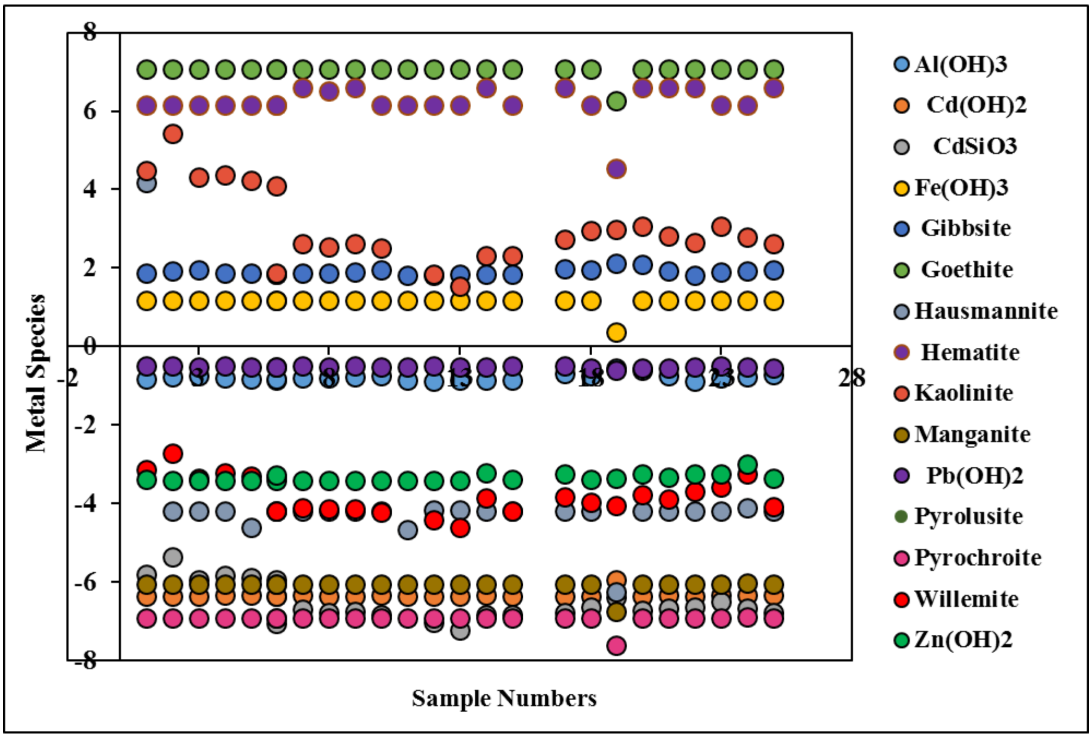


Figure 7.14 Metal speciation versus sample numbers in groundwater in the year 2016

Cadmium species in the groundwater are cadmium hydroxide and cadmium metasilicates in the groundwater of the study area. Cadmium hydroxide (Cd (OH) $_2$) ranges from -7.71 to -7.43 with an average mean of -6.67 in 2015 and the ranges from -6.34 to -5.9 with an average mean of -6.31 is observed in 2016. Mineral species of cadmium species are undersaturated. Cadmium metasilicates ranges from -7.06 to -6.67 with an average mean of -7.43 in 2015 and the ranges from -7.22 to -5.34 with an average mean of -6.50 is observed in 2016 (Fig 7.13 and 7.14). Mineral species of cadmium hydroxide and cadmium metasilicate species are undersaturated in groundwater.

The oversaturation and undersaturation of the mineral phases comprising iron contains iron hydroxide (Fe (OH) $_3$), goethite (FeOH), hematite (Fe_2O_3), magnetite (Fe_3O_4) and hausmanuite (Mn_2O_4). This is consistent with the high iron concentration in the groundwater. Iron hydroxide species ranges from 0.48 to 2.89 with an average mean of 1.05 and the ranges from 0.37 to 1.18 with an average mean of 1.12 is observed in r in 2015 and 2016 respectively. Geothite species ranges from 6.37 to 8.78 with an average mean of 6.89 in 2015 and the ranges from 6.26 to 7.07 with an average mean of 7.01 is observed 2016. Hematite species ranges from 4.7 to 9.5

with an average mean of 5.80 in 2015 and the ranges from 4.5 to 6.6 with an average mean value of 6.19 is observed 2016. Magnetite species ranges from -8.09 to -3.9 with an average mean of -6.97 in 2015 and the ranges from -6.74 to -6.03 with an average mean of -6.10 is observed 2016. Hausmanuite ranges from -6.24 to 4.18 with an average mean of -3.74 in 2015 and the ranges from -6.24 to 4.18 with an average mean of -3.78 is observed in groundwater in 2016. Iron hydroxide, goethite and hematite species are oversaturated; magnetite and hausmanuite species are undersatured in the groundwater in 2015 and 2016 (Fig 7.13) and (Fig 7.14). Iron species are immobile in the groundwater. Mobility might be controlled in the area by precipitation as iron oxides of hematite, magnetite, oxyhydroxides of goethite and co-precipitating and dissolution with other metals.

Manganese is non-toxic and more than 90% of manganese is in the ionic form as Mn^{2+} in the groundwater. Manganese contains pyrolusite and phyrochroite species in the groundwater of the study area. Pyrolusite ranges from -12.83 to -3.13 with an average mean of -11.61 while -11.78 to -11.07 with an average mean value of -11.14 are observed in 2015 and 2016, respectively. Mineral speciation of pyrolusite (Fig 7.13) and (Fig 7.14) phyrochroite of groundwater in the study area are undersaturated. Manganese is also immobile in groundwater. Zinc mineral species contains zinc hydroxide and willemite in the groundwater of the study area. Zinc hydroxide ranges from -3.57 to -1.60 with an average mean of -2.43 in 2015 and the ranges from -4.25 to -2.50 with an average mean of -3.34 of willemite is observed 2016. Zinc hydroxide and willemite mineral species were undersaturated in 2015 (Fig 7.13) and 2016 (Fig 7.14).

CHAPTER EIGHT

8 SUMMARY AND CONCLUSION

The present study was carried out to assess the groundwater quality in a part of Mhlathuze catchment of Empangeni and Richard Bay areas, KZN, South Africa. In this study, 44 and 33 groundwater samples were collected during 2015 and 2016 and were analysed. Drinking water suitability of groundwater in the study area was assessed based on pH, TDS, TH and major ions. The pH of the study area is acidic to alkaline in nature. Based on pH, 13% of groundwater samples exceeded the permissible limits (> 8.5) of WHO standard in 2015 and 6 % of samples exceeded the permissible limit in 2016. Based on TH, 25% of groundwater samples are soft, 40% are moderately hard, 23% are hard, 12% are very hard in 2015 and 39% are moderately hard, 56% are hard, 5% is very hard in 2015 and 2016. This TH classification exposes that the study area has soft to very hard water types in different time period. Total hardness of groundwater values increased from 2015 to 2016. The major ions in the study area also exceeded the limits in few samples: 12.5% and 13% of sodium, 18% and 9% of potassium, 5% and 3% calcium, 3% and 3% of magnesium, 13 and 12% of chloride, 3% of bicarbonate, 3% and 3% of sulphate exceeded the permissible limits of WHO standard in 2015 and 2016 respectively. Spatial variation of groundwater for the parameters such as pH, TDS, TH and major ions (Na, K, Ca, Mg, Cl, HCO_3, SO_4 and NO_3) indicated the high concentration in SE part of Richard Bay and central part of the Empangeni region. This is due to the weathering and dissolution of minerals, domestic wastewater disposal and industrial effluents. Large numbers of industries are present in the Richard bay area which is the main sources of high concentration of various ions in groundwater. Overall drinking water quality of the study area is safe except in the SE and central part of the study area.

Suitability of groundwater for irrigation in the study area are appraised by EC, SAR, RSC, PI, MR, USSL classification, Na% and Wilcox diagram. The EC values of groundwater samples are good to permissible in 2015 and 2016 respectively. SAR values in 2015 and 2016 specify that 18% and 28% of samples are unsuitable for irrigation. US salinity diagram specifies that groundwater samples are not suitable.

Na% of groundwater samples signify 65% as excellent to permissible, 35% as unsuitable to doubtful in 2015 and 61% as good to permissible, 39% as unsuitable to doubtful in 2016. The results from the Wilcox diagram imply that most of the groundwater samples in the study area are categorised under excellent to permissible, a few samples fall under doubtful to unsuitable class, a few samples fall under excellent to permissible and a few other samples fall under doubtful to unsuitable for irrigation. RSC classification signifies groundwater samples are suitable for irrigation. PI indicates that the groundwater is suitable for irrigation in the study area. MH specifies that groundwater is not suitable for irrigation. Overall, groundwater quality for irrigation is not suitable in the study area. Based on the industrial water quality limits, groundwater samples are suitable, but it differ for drinking water quality and irrigation water quality.

Hydrogeochemistry of groundwater in the order of dominance of cations and anions are Na > K > Ca > Mg and Cl > HCO_3 > SO_4 in 2015 and Na > Ca> Mg >K and Cl > SO_4 > HCO_3 in 2016. Modified Piper diagram is used to identify the dominant hydrogeochmical facies of groundwater in the study area. Ca-Mg-Na, Cl-SO_4-HCO_3, Ca-Mg-Cl, and Na-Cl are the dominant groundwater types. The study area consists of granite, basaltic and sedimentary formation of marine origin which are the sources for the present hydrochemical characteristics of groundwater. The hydrogeochemical processes of groundwater are strongly influenced by rock water interaction, ion exchange, reverse ion exchange, carbonate and silicate weathering processes and evaporation. The groundwater samples of the study area specify ion exchange and reverse ion exchange of CAI 1 and CAI 2. CAI 1 and CAI 2 of groundwater samples is 60% and 40% in 2015 and 76% and 14% in 2016 indicating the ion exchange and reverse ion exchange processes. High concentration of Na and Cl are mainly due to evaporation processes. Gibbs plot was used to identify the mechanism controlling the water chemistry. Groundwater samples largely fall in rock dominance zone. Aqueous geochemical modelling explains ion exchange processes, simultaneously decreasing TDS concentration, oversaturated calcite and dolomite and undersaturated with respect to minerals of gypsum and halite are dissolution.

Strong correlation was obtained between TDS and Na, K, Ca, Mg, Cl and SO_4 and moderate correlation with HCO_3 in 2015. Comparison between correlation in 2015 and 2016 show some similarity. In 2016, strong correlation exists between TDS and Na, K, Ca, Mg, Cl and SO_4. Group 1 obtained from the cluster analysis of groundwater samples represent EC, Na and Cl and indicate ion exchange, reverse ion exchange and evaporation as the major dominant hydrogeochemical processes. Group 2 consisting of HCO_3, SO_4, K, Ca, Mg, NO_3 and pH are due to carbonate and silicate weathering and dissolution of minerals to groundwater. Factor analysis also helped to assess the sources of chemical ions in groundwater. According to the factor analysis results, Factor 1 represents the natural hydrogeochemical processes as rock-water interaction. Factor 2 represented the contribution of nonpoint source pollution from agriculture areas, industry effluents and anthropogenic sources. The heavy metals such as lead, cadmium, silver, aluminium, cobalt, iron, manganese, nickel and zinc exceeded the permissible limit. Boron, chromium and copper are within the permissible limits of WHO in 2015. Silver, chromium, cadmium, manganese, nickel and lead exceeded the permissible limits and aluminium, boron, cobalt, copper, iron and zinc are within the permissible limits in 2016. The pollution indices such as HPI, HEI and C_d indicates two extreme results in 2015 and 2016 even though the values specifies significant strong correlation with the influence of industrial activity. Thus, the methods are very useful to assess the heavy metal contamination of the study area. This study indicates that the high level of contamination occurs in the Empageni and Richard Bay area. This study has revealed the significance of hydrogeochemical studies in understanding the variation in groundwater quality and helped in the identification of hydrogeochemical processes and finding the probable source of toxic heavy metals in the groundwater. This study serves as baseline information of groundwater quality in Empangeni and Richard Bay region of the Mhlathuze catchment.

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