Assessment of Coastal aquifer contamination using geochemical and health risk assessment in Maputaland formations, South Africa

BY

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DECLARATION

I, Philisiwe Promise Mthembu declare that the thesis titled “Assessment of Coastal aquifer contamination using geochemical and health risk assessment in Maputaland formations, South Africa” submitted in fulfilment of the degree of Master of Science (specialising in Hydrology) is my original work duly performed in the Faculty of Science and Agriculture at the University of Zululand. This work has not been submitted before or published by anyone from University of Zululand or any other institution and all the sources I have used have been acknowledged by complete references.

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CONTRIBUTION TO THE BODY OF KNOWLEDGE

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

Article:

1. Philisiwe P Mthembu, Vetrimurugan Elumalai, Brindha Karthikeyan, Peiyue Li (2020). Hydrogeochemical Processes and Trace Metal Contamination in Groundwater: Impact on Human Health in the Maputaland Coastal Aquifer, South Africa. Exposure and Health. https://doi.org/10.1007/s12403-020-00369-2. (Impact Factor: 4.762)
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ABSTRACT

The Maputaland coastal plain of KwaZulu-Natal is among the popular tourist areas in South Africa. Groundwater is the foremost source for drinking and irrigation abstracted from the unconsolidated aquifers where the infiltration rate is very high. This could possibly increase the risk of aquifer contamination. The main objectives of this study is to evaluate the hydrogeochemical processes, identify the intended sources of groundwater contamination, and understanding the extent of trace metal contamination and health risk assessment. In this study, 53 and 42 groundwater samples were collected from bore wells during 2018 and 2019 and were analysed for major ions, minor ions, nutrients and trace metals. Na-Cl water type was dominant in groundwater followed by Ca-HCO_3. Cross plots revealed that ion exchange, reverse ion exchange, silicate weathering, seawater mixing, and anthropogenic inputs from agricultural activities govern the groundwater chemistry. GIS methods were adopted to produce spatial distribution maps of major ions through which locations of groundwater contamination and the intensity of hydrogeochemical processes were identified. The water quality index (WQI) varied from 18.9 to 157.1 with an average value of 45.55. Majority of the samples are classified as good, 22 % as poor, 2 % as very poor and 7% under unsuitable category, which are spatially distributed towards the southern and western parts of the study area. Mean concentration of trace metals were in the order: Zn>Li>Al>Fe>Mn>Cu>Pb>As>Co>Cd in 2018 , Fe>Zn>Mn>Sr>B>Pb>Cu>Co>Cr>Cd>Ag>Al>Ni in 2019. Most of the trace metals were found to be within the WHO standards for drinking water except for Cd, Zn, Pb, Mn, Al and Fe. Health risk assessment of trace elements via ingestion and dermal absorption pathways was carried out. Hazard quotient through dermal absorption (HQ_{dermal}) and hazard index (HI) for Co and Mn were above 1 in adults, children and infants. HQ_{dermal} and HI for Cd was greater than 1 in children and infants. HQ_{dermal} and HI for As and Pb were greater than 1 in infants. This implies that these metals pose serious adverse risk on local people and infants are more vulnerable to health risk than children and adults. The heavy metal pollution index shows that the groundwater samples vary from low to high pollution class and 21% of the samples exceed the critical limit of 100 implying that they are highly polluted with respect to heavy metals and are unfit for human consumption. The heavy metal evaluation index and degree of contamination reveal that all the groundwater samples have low pollution with regards to heavy metals and are suitable for human consumption. Moreover, the results of ecological risk assessment reveal that the studied heavy metals pose low ecological risk. Based on the pollution index of groundwater, majority of the samples fall in the insignificant pollution zone. The synthetic pollution index reveal that 2%, 74% and 24% of the samples are suitable, slightly and moderately polluted respectively with heavy metals. Similarly, the overall index of pollution reveal that majority of the samples are excellent and suitable for drinking purpose. Multivariate statistical analysis were adopted to evaluate sources of heavy metals in groundwater. Correlation matrix and principal component analysis reveal that weathering of aquifer matrix and anthropogenic activities are accountable for the release of heavy metals into groundwater. Furthermore, R-mode and Q-mode cluster analysis revealed two clusters. All the clusters from R-mode and Q-mode cluster analysis are linked to mixed sources including weathering and anthropogenic activities. This study provides the baseline data on hydro geochemistry that can be utilised further in future studies. It is recommended that contaminated groundwater in this region be treated before utilisation in order to maintain the sustainability of public health and recommends for further extended studies.

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List of Abbreviations

Al	Aluminium
As	Arsenic
Ca^{2+}	Calcium ion
CAI	Chloro alkaline index
Cd	Cadmium
C_d	Degree of contamination
CM	Correlation matrix
Co	Cobalt
Cu	Copper
DWAF	Department of Water Affairs and Forestry
EC	Electrical Conductivity
ERI	Ecological risk index
F	Fluoride
Fe	Iron
HCO_3^-	Bicarbonate ion
HDPE	High-Density Polythene
HEI	Heavy metal evaluation index
HPI	Heavy Metal Pollution Index
HQ	Hazard Quotient
HI	Hazard index

IAP	Ion Activity Potential
ICP	Inductive Coupled Plasma
K^+	Potassium ion
KR	Kelly’s Ratio
Ks	Solubility Product
Li	Lithium
Mg^{2+}	Magnesium ion
MHR	Magnesium Hazard Ratio
Meq/L	Milli equivalents per Litre
Mg/L	Milli gram per Litre
Mn	Manganese
mS/cm	MilliSiemens per centimetre
Na^+	Sodium ion
NE	North East
NO_3^-	Nitrate ion
NW	North West
OIP	Overall index of pollution
ORP	Oxidation- Reduction Potential
%Na	Percentage Sodium
Pb	Lead
PI	Permeability Index
PIG	Pollution index of groundwater
PCA	Principal Component Analysis
r	Correlation coefficient
SAR	Sodium Adsorption Ratio
SI	Saturation Index
SO_4^{2-}	Sulphate ion
SE	South East
SMI	Seawater mixing index
SPI	Synthetic pollution index
SW	South West
TC	Total Cations

TDS	Total Dissolved Solids
TH	Total Hardness
USSL	United States Salinity Laboratory
WHO	World Health Organization
WQI	Water Quality Index
Zn	Zinc

CHAPTER ONE

1. INTRODUCTION

1.1 Introduction

Groundwater serves as a vital source of water supply for drinking, domestic, agriculture and industrial purposes, especially in arid and semi-arid countries. Groundwater is usually the most preferred source of human water supply (Ezugwu *et al*., 2019; Çiner *et al*., 2020; Ukah *et al*., 2020). This is because groundwater is generally perceived as safe compared with surface water resources due to its natural filtration of contaminants by the soil as water moves into the groundwater (Sener *et al*., 2017; Wagh *et al*., 2018; Edokpayi *et al*., 2018). However, various researchers have reported several cases of groundwater contamination due to various sources. Contamination of coastal aquifers has been a global concern as these aquifers are more vulnerable to pollution. Coastal aquifers are mostly affected by salinization due to seawater intrusion (Askri *et al*., 2016; Bouzourra *et al*., 2015; Eissa *et al*., 2016; Vetrimurugan *et al*., 2017a; Nair *et al*., 2016; Lotfata and Ambinakudige 2020; Karamouz *et al.*, 2020; Siddha and Sahu 2020). Apart from this, groundwater quality is also influenced by anthropogenic pollution such as agricultural return flow, disposal of domestic and industrial wastes, etc. Assessing the chemistry of groundwater is essential in determining the sources for the composition of ions in groundwater and its suitability for various uses. Various hydrogeochemical processes occur beneath the surface and influence the groundwater chemistry. These hydrogeochemical processes tend to vary temporally and spatially. The chemical composition of groundwater is influenced by several processes which can be natural (e.g. rock-water interaction, evaporation, dissolution of minerals, hydrology) and/or anthropogenic (e.g. industry, agriculture, mining, and urbanization) (Ahmad Dar *et al*., 2011; Ghesquière *et al*. 2015; Gulgundi and Shetty, 2016; Das *et al*., 2016; Di Curzio *et al*., 2017; Liao *et al*., 2017; Aghazadeh *et al*., 2017; Barzegar *et al*., 2017; Adimalla *et al*., 2018; Etikala *et al*., 2019; Ukah *et al*., 2020).

Trace/ heavy metal contamination in groundwater and soil sediments are repeatedly detected with wide attention due to its toxic severity and its potential damage to ecosystem and humans (Burges *et al*., 2015; Abou Zakhem and Hafez 2015; Singh and Kamal 2016; Liao *et al*., 2017;

Tiwari *et al*., 2017;; Rezaei *et al*. 2019; Egbueri and Unigwe 2020; Brindha *et al*., 2020; Chiamsathit *et al*., 2020; Ukah *et al*., 2020). Heavy metals enter groundwater through natural processes i.e. weathering and dissolution of rocks and soils, ion exchange processes, volcanism extruded products, decomposition of living matter and atmospheric matter (Prasanna *et al*., 2012; Rezaei *et al*., 2019; Çiner *et al*., 2020; Panda *et al*., 2020). Mining, industrial, agricultural and solid waste disposal are some of the common anthropogenic activities that lead to the excess concentration of heavy metals in groundwater resources (Rezaei *et al*., 2017; Wagh *et al*., 2018; Giri and Singh 2019; Ahamad *et al*., 2020). However, the accumulation of heavy metals on ecosystems is exacerbated by anthropogenic activities (Ukah *et al*., 2019). These heavy metals are classified as essential (copper, chromium, cobalt, iron, manganese and zinc) and non-essential (arsenic, cadmium and lead) (Çiner *et al*., 2020; Brindha *et al*., 2020). Some trace metals are required for human metabolism as well as the growth of plants and animals. However, the concentration of these metals above the desired limit is known to have toxic effects on human health and may pose threat to the environment (Tamasi and Cini 2004; Brindha *et al*., 2011, 2020; Haloi and Sarma 2012; Chanpiwat *et al*., 2014; Li *et al*., 2014; Boateng *et al*., 2015; Jahanshahi and Zare 2015; Yousaf *et al*., 2016; Vetrimurugan *et al*., 2016, 2018; Wagh *et al*., 2018; Bodrud-Doza *et al*., 2019; Xiao *et al*., 2019; Barzegar *et al*., 2019; Usman *et al*., 2020; Mthembu *et al*., 2020; Rahman *et al*., 2020). For example, elevated Pb concentrations are known to have adverse effects on childhood brain development (Tay and Hayford 2016; Chabukdhara *et al*., 2017). In numerous parts of the world, the risk of As is a major health threat as it relatively cause severe health effects on humans (Kapaj *et al*., 2006; Ravenscroft *et al*., 2009; Mudzielwana *et al*., 2020). Long-term intake of high concentrations of Fe through drinking water may cause kidney, cardiovascular, and liver damage (Usman *et al*. 2020). Exposure to Cd causes acute and chronic diseases such as kidney and skeletal damages (Soleimani *et al*. 2020). Trace metals are reported to be one of the critical contaminants that affect groundwater quality and pose concern to human health as they are persistent, non-biodegradable, stable and toxic in the natural environment (Tay and Hayford 2016; Soleimani *et al*. 2020). Trace metals in groundwater are influenced by weathering of rocks, atmospheric deposition and anthropogenic activities for instance agriculture, disposal of domestic and industrial waste, mining activities etc. (He and Li 2020; Tiwari *et al*., 2017; Prasanna *et al*., 2012; Bhutiani *et al*., 2017; Giri and Singh, 2019; Rezaei *et al*., 2019; Çiner *et al*., 2020; Panda *et al* 2020). The solubility of trace metal is controlled by the pH, content of the trace metal, chemical composition, organic carbon content, and ion exchange (Di Curzio *et al*. 2017; McMahon and Chapelle 2008; Palmucci *et al*. 2016).

Health risk assessment is a process of estimating health effects that may occur from exposure to non-carcinogenic and carcinogenic chemicals (Duggal *et al*., 2017; Zhou *et al*., 2016). The U.S Environmental Protection Agency (USEPA 2004) proposed a four-step method for health risk assessment (hazard identification, exposure assessment, dose-response assessment, and risk characterization) to evaluate the human health risk of pollutants in groundwater (Bodrud-Doza *et al*., 2019; Boateng *et al*., 2015). It is necessary to evaluate the risk to human health owing to groundwater contamination as there may still be possible health hazards, even if the chemical composition of groundwater are consistent with the drinking water standards (Ji *et al*., 2020). Several researchers have carried out health risk evaluations to determine the impact of contaminant toxicity on humans (Zhou *et al*., 2020; He *et al*., 2020; Egbueri, 2020a; Egbueri and Mgbenu, 2020; Edokpayi *et al*., 2018; Panda *et al*., 2020). Previous studies have reported that children are more exposed to non-carcinogenic risk as a result of consumption of groundwater polluted with trace metals as compared to adults (Ukah *et al*., 2019; Zhang *et al*., 2018; Wang *et al*., 2018). Thus, it is not only essential to understand groundwater chemistry concerning to major ions, but trace metals should also be systematically monitored.

South Africa receives an annual average precipitation of approximately 497 mm which is below the world average of 860 mm (Smakhtin *et al*., 2001). The country is regarded as semi-arid with scarce water resources (Smithers *et al*., 2017). Rainfall in South Africa is spatially and temporally dynamic (Ndlovu and Demlie, 2016; Ndlovu and Demlie, 2018). As a result of this, water resources are also scarce and unevenly distributed across the country. Population growth, expansion of agricultural lands, rapid urbanization, industrialization, and climate change are some of the factors that lead to water quality problems in South Africa (Vhonani *et al*., 2019). Surface and groundwater developments are still needed to compensate for the shortage of water supply in rural areas and to meet their basic water needs (Nel *et al*., 2009; Du Plessis, 2017; Vetrimurugan *et al*., 2017). About two-thirds of the population of South Africa rely on groundwater for water supply (Vetrimurugan *et al*., 2017b). About 52% of the 49.4 million of South African population are living in the rural areas (DEAT, 2008) and about 6 million people are without reliable access to drinking water (DWAF, 2000; Wanda *et al*., 2016). According to DWAF (2000), 65% of total water supply in rural areas is derived from groundwater. Direct consumption of groundwater without any form of treatment exposes local residents to various contaminants that may have adverse impact on human health. About 3.6% of deaths per year are linked to water contamination in South Africa (Nel *et al*., 2009). The unique hydrological system and unviability of the existing surface water resources makes it realistic for the people to predominantly rely on groundwater resources for domestic, agricultural, and drinking purposes (Demlie and Titus, 2015; DWAF, 2000). The country is faced with numerous water quality issues (e.g. salinization, eutrophication, microbiological contamination, sedimentation, and silt migration, and acidification) (DWAF, 2002).

Groundwater is an important link for socio-economic and environmental development. The Maputaland coastal aquifer is made of alluvial formation which are more prone for surface contamination further resulting in degradation of underlying aquifers. In general, the coastal aquifers are also commonly affected by sea water intrusion (Vetrimurugan *et al.*, 2017a). Active tourism and continuous extraction of larger volumes of groundwater for domestic and irrigation needs in unconsolidated coastal aquifers could possibly degrade the groundwater quality. The deteriorated and untreated water pose potential threat to ecological and health risk (MOMBA, 2002 & 2003). Groundwater contamination by trace metals is an environmental concern that is often reported in South Africa. Verlicchi and Grillini (2020) reported that arsenic and lead occur in elevated contents in groundwater of South Africa. Demlie *et al.* (2014) stated that the high iron content in groundwater significantly affects the water supply in the region. Increasing population growth, socio-economic development, and anthropogenic activities have exerted much pressure on the country's water resources which further result in deteriorating the water quality.

1.2 Problem statement

South Africa is a semi-arid country with inadequate water resources (Weitz, 2016; Abiye *et al.*, 2018). It receives an average rainfall of approximately 497mm per annum which is below the world annual average of 860mm (Smakhtin *et al.*, 2001). The rapid increase of population, industrialization and urbanization, water supplies are continuously put under pressure hence unable to keep up with the growing demand for water supply. Rural communities rely on groundwater resources for domestic, agricultural as well as industrial purposes. It is important that the quality and quantity of groundwater is monitored in order to ensure an ongoing benefit from the use of groundwater resources. It is essential that water resources are managed in a sustainable manner in order to preserve it for future generations and to sustain the environment (Demlie and Ndlovu, 2016). According to Camp (1999), KZN has more water supplies as compared with the rest of the provinces in South Africa.

Alternative sources of water in South Africa include groundwater abstraction, rainwater harvesting and the re-use of grey water. However, groundwater serves as the main supplier of water for domestic and agricultural purposes when surface water resources are limited especially in rural communities (Demlie & Ndlovu, 2016). Approximately two-thirds of the population relies on groundwater for domestic purposes (DWAF, 2000). Groundwater contributes almost 15% of the bulk volume of water that is consumed. Previous studies show that about 64% of groundwater is utilised for the agricultural sector (Woodford & Rosewarne, 2006) and 8% is utilised for domestic and mining activities (Knuppe, 2011). Groundwater reserves in South Africa are very inadequate and below the world averages (Smakhtin *et al.*, 2001). South Africa is estimated to have 10 343 million m^3/a in a rainfall year or 7500 million m^3/a in a drought year of groundwater to use (DWA, 2010). Woodford & Rosewarne (2006) concluded that the groundwater resource potential of South Africa ranges from 47 727 to 7 536 Mm^3/a. Contamination of groundwater resources instigates problems in communities that largely depend on groundwater. According to Knuppe (2011), groundwater problems in South Africa are attributed to anthropogenic activities. Declining of the quality of water has a negative impact on human health, aquatic organisms and often results in economic losses (DWAF, 2002). Once groundwater has been contaminated, it becomes very difficult and expensive to treat. Groundwater is contaminated by human activities and natural processes that occur within the aquifer. Agriculture, the largest water user sector, requires the application of agrochemicals or fertilisers in order to grow crops. These further leach into groundwater resources leading to contamination of the aquifer system. Industrial effluents also contribute to the contamination of groundwater. Areas with poor sanitation systems, on site sanitation or disposal of sewage pollutes groundwater reserves. Unmonitored and unsustainable disposal of wastes as well as landfills pose threat to the quality of groundwater. It is decisive for effective management of groundwater reserves in order to protect our limited resource.

Rural communities in South Africa lack supply systems and rely on groundwater for water supply (Demlie and Titus, 2015). Groundwater is important for socio-economic and environmental development. As such, it is crucial that it is managed effectively. The Maputaland or Zululand coastal plain is the largest primary aquifer in South Africa. This coastal plain extends from Mtunzini in the south up to the Mozambique border (Smithers *et al.*, 2017). Groundwater remains the sole supplier of water for drinking, domestic and agricultural purposes in rural communities in north-eastern KwaZulu-Natal. The availability of groundwater on the Maputaland coastal plain has been reduced by various land use activities that take place in this aquifer including agriculture, forestry plantations, water supply schemes as well as prolonged periods of drought. Studies on the Lake Sibayi (Nsubuga *et al*., 2019; Smithers *et al*., 2017; Weitz and Demlie, 2014) and impact of land use (Grundling *et al*. 2013) in the Maputaland coastal plain have been reported. Earlier groundwater studies in the region include identifying the sources of iron in groundwater (Demlie *et al*., 2014), the relation between sediments mineral composition and, groundwater quality (Mkhwanazi, 2010) and groundwater modelling to predict the groundwater levels during dry and wet periods (Kelbe *et al*., 2016). Vetrimurugan *et al*., (2018) studied the ecological impact of metals in beach sediments in marine protected areas. They reported that the enrichment of metals in beach sediments were due to the heavy mineral rich coastal dunes and past mining activities. Mthembu *et al*., (2020) conducted a comprehensive study to evaluate hydrogeochemical processes and trace metal contamination in groundwater, and investigated health risks associated with trace metal contamination in groundwater on the Maputaland coastal aquifer. Findings revealed that groundwater samples showed concentrations of cadmium, zinc, lead, manganese, aluminium and iron above the thresholds of the World Health Organization (WHO) standards for drinking water quality (Mthembu *et al*., 2020). The hydrogeochemical processes that govern the chemistry of groundwater, sources of groundwater contamination and health risk assessment have not been studied in detail.

1.3 Aim of the study

The aim of this study is to identify coastal aquifer contamination and its impact due to natural and anthropogenic activities

1.4 Objectives

- To evaluate the hydrogeochemical processes
- To identify the intended sources of groundwater contamination
- Comprehensive understanding of trace metal contamination and health risk assessment

1.5 Research questions

- What are the foremost sources of groundwater contamination in the Maputaland coastal plain?
- How is the sustainability of public health impacted by elevated contents of ions in groundwater of this area?

1.6 Hypothesis

Increasing demand and abstraction of water resource has deteriorate the quality of groundwater in Maputaland coastal plain. High concentration of dissolved ions in drinking water negatively impact human health.

1.7 Thesis outline

Chapter 1: Introduction

The chapter introduces the topic of this study. General information regarding contamination of coastal aquifers is provided in this section. Details pertaining problem statement, aim and objectives, research questions, hypothesis and research outline are all outlined in this chapter.

Chapter 2: Literature review

This chapter provides related literature review used in this study. Literature pertaining groundwater contamination, hydrogeochemical processes, heavy metal pollution as well as health risk assessment is reviewed in this chapter.

Chapter 3: Description of the study area

This chapter provides description of the study area where the research was carried on. Information about the location, topography, climate and rainfall, geology, soils, hydrogeology, land use and agricultural activities of the study area will be described in this section.

Chapter 4: Methodology

This chapter outlines all the various methods adopted to achieve objectives of this study. Methods used for collection of groundwater samples, laboratory analysis as well as interpretation of data is included in this chapter. Information pertaining instruments used for analysis and software used to prepare diagrams will be included in this section.

Chapter 5: Geochemical characterization and assessment of groundwater quality: Impact on potential health risk in coastal aquifers

This chapter entails information of results related to geochemical characterisation and assessment of groundwater quality. Processes controlling groundwater quality, evaluation of groundwater quality and its suitability as well as health risk assessment were covered in this section.

Chapter 6: Hydrogeochemical processes and trace metal contamination in groundwater and health risk assessment

This chapter provides detailed information regarding the identification of hydrogeochemical processes that control groundwater chemistry as well as focusing on trace metal contamination. Health risk assessment of trace metal contaminated groundwater using a four step method provided by USEPA (2004) is also covered in this chapter.

Chapter 7: Extent of metal pollution and groundwater quality assessment using indexical and statistical approach

This chapter provides results and discussion regarding heavy metal pollution in groundwater of the study area. Extent of heavy metal contamination is evaluated using different pollution indices. The suitability of groundwater for drinking is also covered in this section using indexical methods. Information pertaining sources of heavy metals in groundwater is explained in this section.

Chapter 8: Conclusion and recommendations

This chapter includes summary of the overall findings of this study and also include recommendations to enhance the management and sustainable development of groundwater resources in this area.

References

This section includes list of all references of the reviewed literature that was used in this study.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Introduction

Globally, the scarcity of surface water resources has resulted in an increase in the demand for groundwater resources. Groundwater is an important source of freshwater in most arid and semi-arid countries. Rural areas mostly rely on groundwater supply to meet their domestic and agricultural needs. It is therefore important to continuously assess the quality of groundwater that is consumed by local communities. Contaminated groundwater has been reported to lead to various health issues, damage crop yields as well as the environment. Groundwater quality is influenced by various sources including geogenic processes (e.g. rock-water interaction, dissolution of minerals, evaporation etc.) and anthropogenic (e.g. agriculture, industry, mining and urbanization) (Ahmad Dar *et al*., 2011; Ghesquière *et al*. 2015; Gulgundi and Shetty, 2016; Das *et al*., 2016; Di Curzio *et al*., 2017; Liao *et al*., 2017; Aghazadeh *et al*., 2017; Barzegar *et al*., 2017; Adimalla *et al*., 2018; Etikala *et al*., 2019; Ukah *et al*., 2020). Problems of seawater intrusion has led to more interest in researching about the quality of groundwater in these regions. Contamination of coastal groundwater by seawater intrusion remains a global concern (Vetrimurugan *et al*., 2017; Karamouz *et al*., 2020; Siddha and Sahu, 2020). The increasing demand of freshwater in coastal areas has increased pressure on these resources, further resulting in a decline in quality due to seawater intrusion. This review takes into consideration previous written works regarding contamination of groundwater in coastal aquifers from various parts of the world.

Groundwater remains the sole supply of freshwater in the Maputaland coastal aquifer. It is important to understand the various geochemical processes that govern the chemistry of groundwater in this area. Also, appraising the fitness of groundwater for drinking purposes and assessing the related health risk of consuming contaminated groundwater. Previous studies conducted in this area have focused on identifying the sources of iron in groundwater (Demlie *et al*., 2014), the relation between sediments mineral composition, groundwater quality (Mkhwanazi, 2010) and groundwater modelling to predict the groundwater levels during dry and wet periods (Kelbe *et al.*, 2016). This study intends to identify coastal aquifer contamination and its impact due to natural and anthropogenic activities.

2.2 Groundwater quality assessment

It is imperative to evaluate the quality of groundwater as it determines its suitability for various uses such as drinking, irrigation and industrial purposes. Poor water quality is related to human health problems, has a negative impact on aquatic ecosystems and to the economy as well (DWAF, 2000). Li *et al.* (2018) concluded that groundwater quality in most water samples were safe for human consumption although majority of the samples were not acceptable in appearance and taste. Demlie and Titus (2015) reported that groundwater in the NGS was of good quality with regards to major and trace elements. Ahmad and Qadir (2011) concluded that groundwater quality is on the edge of declining. Adimalla *et al*. (2018) reported that groundwater is faced with severe quality problems resulting in serious health concerns to the local residents within the area. Duraisamy *et al*. (2019) concluded that 49% of the groundwater in the area was not potable. Brindha *et al*. (2014) inferred that groundwater quality was affected by the contaminated surface water. Iqbal *et al*. (2018) concluded that groundwater was not suitable for irrigation purposes. Sako *et al*. (2018) reported that groundwater was bacteriologically unsuitable for human consumption. Kalaivanan *et al*. (2018) inferred that groundwater quality was potable for drinking except in few samples that exceed the limit. Alamgir *et al*. (2016) reported that approximately all groundwater samples were unfit for drinking purposes. Batabyal and Gupta (2017) inferred that groundwater was unsuitable for drinking and irrigation in 81 and 16% of the sampling locations. Jangam and Puraji (2017) concluded that the quality of groundwater was influenced by seawater intrusion and impact of on-site sanitation system.

2.3 Drinking water quality

It is imperative to evaluate the quality of groundwater as it determines its suitability for various uses such as drinking, irrigation and industrial purposes. Poor water quality is related to human health problems, has a negative impact of aquatic ecosystems and to the economy as well (DWAF, 2000). Aghazadeh *et al*. (2017) concluded that much of the groundwater was chemically suitable for drinking, industrial and agricultural purposes. Ramakrishnaiah *et al.* (2009) concluded that majority of groundwater samples were poor in quality for drinking purposes. Vetrimurugan and Elango (2015) reported that groundwater was unsuitable for drinking in the coastal part and in few locations in the south-western part of the area. Brindha *et al*. (2017) concluded that groundwater was suitable for drinking purposes based on major ions, minor ions and some heavy metals excluding iron and lead. Zhou *et al*. (2020) reported that the quality of deep and shallow groundwater was suitable for drinking. Mahmud *et al*. (2020) reported that the groundwater quality was safe and suitable for drinking purposes. Brindha *et al*. (2020) inferred that groundwater in the studied area was unfit for drinking purposes. Uddin *et al*. (2018) concluded that groundwater was unsuitable for drinking purposes due to elevated contents of trace metals. Batabyal (2018) concluded that groundwater was unfit for ingestion at 82 and 93% of the wells during the pre-monsoon and post-monsoon seasons. Firat Ersoy and Karaca (2019) reported that groundwater was unfit for consumption purposes owing to elevated concentrations of Na, Al, As, Fe and Fe.

2.4 Seawater mixing

Chandrasekar *et al*. (2014) reported that groundwater quality is highly contaminated by saltwater attributed to the intrusion of seawater, saltpan deposits and beach placer mining activities. Hamzah *et al.* (2017) reported that groundwater was threatened by salinization largely by seawater intrusion. Islam *et al.* (2017) reported that groundwater of Patuakhali District, Southern Coastal Region of Bangladesh was slightly contaminated by seawater. Kanagaraj *et al.* (2018) conducted a study to comprehend the hydrogeochemical processes in groundwater and its impact on seawater intrusion in coastal aquifer of south Chennai, Tamil Nadu, India. They reported that 201 km^2 of the area consisted of groundwater unfit for human consumption owing to the effect of salinization in groundwater. Tran *et al*. (2020) concluded that groundwater salinization in the coastal aquifer was a severe problem that impacts on groundwater quality in the area. Bouderbala *et al*. (2016) concluded that seawater intrusion was owed to overexploitation of water resources, hence, deteriorates groundwater quality in the area. Batayneh and Al-Taani (2016) reported that groundwater quality is influenced by saline water in samples located along the coastline. Ben *et al*. (2018) used GIS and multivariate statistics to evaluate groundwater salinity. Based on principal component analysis, they reported that groundwater contamination was owed to seawater intrusion in factor I.

Mohanty and Rao (2019) conducted a study in Puri District of Odisha, India to evaluate the impact of seawater mixing, and the processes which govern the groundwater evolution along the coastal aquifer. They reported that the coastal aquifer was undergoing continuous influence of seawater mixing. Abdalla (2016) reported that groundwater salinity in Jazan coastal aquifer was predisposed by seawater intrusion and ion exchange processes associated with seawater intrusion. Alfaifi (2019) concluded that the groundwater quality was deteriorated by saline water mixing due to the natural mixing process. Bahir *et al*. (2018) inferred that groundwater mineralization was influenced by processes such as dissolution of minerals, ion exchange, seawater intrusion and sulphate reduction.

2.5 Hydrogeochemical processes

The chemistry of groundwater is influenced by several processes that can be natural (e.g. rock-water interaction, evaporation, dissolution of minerals, hydrology) and anthropogenic (e.g. industry, agriculture, mining and urbanization) (Barzegar *et al*., 2017; Barzegar *et al*., 2018; Narany *et al*., 2014). Thorough understanding of hydrogeochemical processes that take place within the aquifers is indispensable for effective development, protection and management of groundwater resources. Adomako *et al*. (2011) inferred that weathering of silicate minerals, dissolution, ion exchange and evaporation were the dominant hydrogeochemical processes that regulated groundwater quality. Barzegar *et al*. (2017) revealed that mineral weathering and dissolution of rocks, ion exchange, reverse ion exchange and agricultural activities control the hydrochemistry of groundwater. Weathering and dissolution of silicate and carbonate minerals and mixing of domestic waste water with groundwater were the dominant processes that control groundwater chemistry in the area (Batabyal, 2018). Barzegar *et al*. (2018) revealed that weathering and dissolution of evaporitic and silicate minerals, mixing and ion exchange were the dominant hydrogeochemical processes that were influential to the quality of groundwater in the studied area. Ion exchange, weathering, seawater intrusion and anthropogenic activities controlled groundwater chemistry of the coastal region of Cuddalore district, Tamil Nadu (Chidambaram *et al*., 2018).

Brindha *et al*. (2017) reported that weathering, carbonate dissolution, ion exchange and salinization from agricultural fertilizers were the dominant processes in the area. Narany *et al*.

(2014) revealed that groundwater chemistry was governed by rock-water interaction, cation exchange and dissolution of carbonate and silicate minerals. Wagh *et al*. (2019) reported that ion exchange, silicate mineral weathering, evaporation, agricultural runoff, animal and domestic waste were the dominant processes that influence groundwater chemistry. Esmaeili *et al*. (2018) concluded that weathering and dissolution of minerals, water-rock interaction and cation exchange were the dominant processes. Iqbal *et al*. (2018) discovered that groundwater chemistry was controlled by evaporation, weathering of rocks and soil and anthropogenic sources derived from the application of fertilizers. Nethononda *et al*. (2018) reported that groundwater chemistry was governed by mineral weathering, reverse ion exchange and irrigation return flow.

Sivasubramanian *et al*. (2013) conjectured that mixing of freshwater with relict saline water, ion exchange processes, silicate weathering and evaporation controlled the chemistry of groundwater in the area. Pratheepa *et al*. (2015) concluded that reverse ion exchange was the dominant process and that seawater intrusion may be possible for the source of groundwater salinization. Elango *et al*. (2003) concluded that calcium carbonate dissolution, ion exchange processes, halite dissolution, silicate weathering and irrigation return flow control groundwater chemistry of the studied area. Singh *et al*. (2011) reported that dissolution, mixing, weathering of carbonate and silicate minerals and reverse ion exchange govern the groundwater chemistry of the area. Senthilkumar *et al*. (2017) concluded that groundwater chemistry was influenced by surface contamination sources (irrigation return flow, domestic wastewater and septic tank effluents), silicate weathering, ion exchange and evaporation process. Ntanganedzeni *et al*. (2018) revealed that ion exchange, mineral dissolution, saline sources and waste water infiltration controlled groundwater chemistry in the coastal aquifer of Tugela catchment.

2.6 Drinking water quality index

Gaury *et al.* (2018) used water quality index and concluded that the quality of the lake water was unfit for human consumption from pre- monsoon to post-monsoon. Gulgundi and Shetty (2018) conducted a study to assess the spatiotemporal variation in groundwater quality and identify sources with the use of multivariate statistical techniques. From the WQI they concluded that approximately 50% of the samples were regarded as poor, very poor and unfit. Krishna Kumar *et al.* (2015) reported that groundwater samples fall under excellent to good category and are suitable for drinking purposes. Jasmin and Mallikarjuna (2014) used a drinking water quality index and concluded that majority of the samples were of good quality. Kalaivanan *et al*. (2017) used a water quality index and hydrochemical indices to evaluate the quality of groundwater in the Kodavanar sub-basin. They reported that groundwater was suitable for drinking purposes however, there are limited samples that exceeded the limit due to anthropogenic activities. Khan and Jhariya (2017) undertook a study to asses groundwater quality for drinking purposes using a water quality index and GIS. They inferred that 76% of the groundwater samples were classified as excellent, very good and good category with only 24% classified as being poor, very poor and unfit category. Verma *et al*. (2020) concluded that 50.98% and 45.10% of the groundwater samples fell under poor category and were not suitable for drinking purposes during the pre- and post-monsoon seasons.

Krishna Kumar *et al*. (2014) carried out a study to evaluate the quality of groundwater and its suitability for drinking purposes. Based on the water quality index and Fuzzy membership classification, they reported that majority of groundwater samples fell under excellent and poor water quality classes. Wagh *et al*. (2019) inferred that groundwater samples fell under good quality of water; poor water category, and very poor category during pre-monsoon and post-monsoon seasons, respectively. Berhe (2020) reported that majority of the groundwater samples fell in the excellent category in the wet season. Shaikh *et al*. (2020) concluded that the WQI revealed that 49% of the water samples were unfit for drinking purposes. Derdour *et al*. (2020) concluded that 50 % of the groundwater samples were in excellent category while the remaining 50% was in good category rendering groundwater to be suitable for drinking purposes. Mahmud *et al*. (2020) reported that 11.86% of the samples were excellent, 54.24% were good, 23.73% were poor, 1.69% were very poor, and 8.47% were unfit for drinking purpose. Hamlat and Guidoum (2018) used a WQI and inferred that 36% of groundwater samples fell under good water quality category while 53% was of poor quality.

2.7 Heavy metal pollution index

Zakhem and Hafez (2015) concluded that the HPI was below the critical pollution index value of 100, hence, drinking water was of good quality with regards to heavy metals. Giri and Singh (2014) reported that the HPI varied from 3.55 to 388.9 and high values were found near industries, mining and estuary. Prasanna *et al*. (2012) employed the HPI to evaluate pollution of water with regards to heavy metals. They concluded that the HPI was within the critical limit of 100. Tiwari *et al.* (2016) concluded that HPI values indicated that 21% and 6% of the samples were not suitable for direct consumption throughout the two monsoon seasons, respectively. Rezaei *et al.* (2017) inferred that majority of the samples were categorized as having low pollution levels, 46% was medium pollution level and 3% high pollution levels, respectively. Egbueri (2020b) used HPI and concluded that 45.83% of the groundwater samples were unsuitable for drinking purposes. Bodrud-Doza *et al.* (2016) reported that the HPI revealed that majority of the samples belonged to low level of pollution. Wagh *et al.* (2018a) employed a HPI and reported that majority of the samples were highly contaminated with respect to heavy metals. Rezaei *et al.* (2019) reported that water samples were low and moderately contaminated with respect to heavy metals. Tiwari *et al.* (2017) reported that the HPI was above the critical pollution index of 100 during 2011 and 2012, respectively.

Panda *et al.* (2020) inferred that four samples had HPI above 100 suggesting that groundwater was extremely polluted with heavy metals due to urban activities in the study area. Chiamsathit *et al.* (2020) used HPI to evaluate the seasonal contamination of groundwater by heavy metals and concluded that the HPI values were below the critical limit of 100 suggesting that groundwater quality was not critically polluted with respect to heavy metals. Rahman *et al.* (2020) conducted a study to assess the quality of groundwater using pollution indices. According to the HPI, the reported that 35% of the groundwater samples were unsuitable for human consumption. Venugopal & Giridharan (2020) reported that the HPI revealed that almost all the groundwater samples were unfit for drinking purposes in both monsoons periods. Kumar *et al.* (2019) employed HPI and concluded that groundwater was free from heavy metal contamination except in few locations. Chidambaram *et al.* (2012) reported that 55% of the groundwater samples exceeded the critical limit (HPI> 100) suggesting they are highly contaminated with respect to heavy metals.

2.8 Health risk assessment

Zeng *et al.* (2015) reported that As poses more concern resulting in non-carcinogenic and carcinogenic effects with children being at a higher risk than adults. Wu *et al.* (2009) concluded that hazard quotients (HQs) of all metals were below unity except for As indicating that it may cause serious health concern. Egbueri and Mgbenu (2020) inferred that based on the hazard index (HI), 25% of the samples may cause high chronic health risk and Pb was the major contaminant impacting on the quality of water and rising the human health risk. Mgbenu and

Egbueri (2019) reported that Ni and Pb had hazard index exceeding unity implying that these metals pose high chronic risk to local people. Edokpayi *et al*. (2018) concluded that Mn, Zn, Pb, Cr and Cd were major contributors to non-carcinogenic risk and children were at a higher risk than adults. Zhou *et al*. (2020) reported that non-carcinogenic risk was attributed to F, Fe and As in both adults and children in the shallow groundwater as well as Cr^{6+} in deep groundwater for children. Zhou *et al*. (2016) inferred that risk of non-carcinogens was mainly caused by Zn followed by F while carcinogenic health risk was caused by Cr^{6+}. Zhang *et al*. (2019) reported that non-carcinogenic risk of As was high for children than that of adults.

He *et al*. (2020) inferred that inhabitants of Datong Basin are exposed to high health risk due to elevated contents of As, F, I and NO_3. Tay and Hayford (2016) concluded that HQ/HI was below unity for both adults and children, hence were not very alarming for potential human health risk instigated by exposure to non-carcinogenic elements. Usman *et al*. (2020) concluded that Fe, Mn and As were significant contaminants contributing to non-carcinogenic health risk. Shaikh *et al*. (2020) stated that children were at a higher health risk than men and women in the study region. Wagh *et al*. (2018a) inferred that the HI was greater than one resulting in groundwater being not suitable for drinking in all age groups. Çiner *et al*. (2020) reported that adults had high carcinogenic risk as compared to children due to consumption of arsenic-contaminated groundwater. Adimalla and Qian (2020) conducted a study to assess the potential noncarcinogenic health risk of nitrate contaminated groundwater in Southern India. They concluded that children were at a high non carcinogenic risk of nitrate as compared to adult females and males.

CHAPTER THREE

3. DESCRIPTION OF THE STUDY AREA

3.1 Location

The present study was conducted in the Maputaland coastal plain, KwaZulu Natal, South Africa. The Maputaland coastal plain in northern KwaZulu Natal stretches from Mtunzini in the South up to the Mozambique border in the North (Fig. 3.1). The study area falls under the jurisdiction of the uMkhanyakude District municipality and has a geographical area of approximately 4 400km^2.

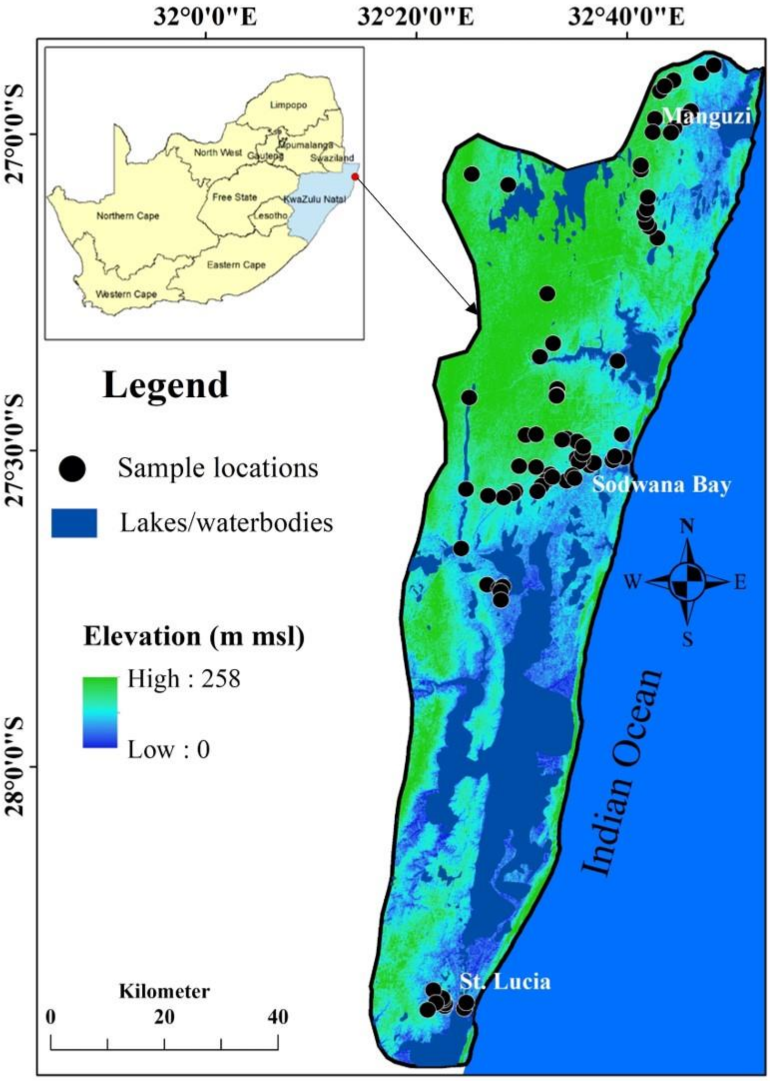

Figure 3.1: Location of the study area

3.2 Topography

The topography of Maputaland coastal plain is characterised by ancient to young sandy dunes with elevated topography and low-lying plains to the east and a series of rugged terraces that are deeply incised by river valleys in the central and western parts (Mkhwanazi 2010; Weitz 2016). Recent, infertile and aeolian sands cover most of the area. This led to the formation of a series of north-south aligned dune ridges oriented parallel to the present coastline. The study area is characterised by flat topography that extends up to 258 meters above mean sea level (m msl) along the Lebombo mountains (Fig. 3.1).

3.3 Climate and rainfall

The area of study is characterised by a humid subtropical climate with warm summers. The annual rainfall ranges from less than 600mm inland to about 1000mm along the coast (Watkeys *et al.*, 1993; Ramsay 1996; Porat and Botha 2008). Highest rainfall occurs during the summer months (November-March) with the eastern side receiving most of the precipitation. Rainfall in this area results from both the tropical and middle latitude weather systems (Weitz and Demlie 2014). Average annual temperature ranges from 21°C along the Lebombo mountains to 23°C inland and approximately 22°C along the coast (Mkhwanazi 2010).

3.4 Geology

Geologically, the Maputaland coastal plain is underlain by unconsolidated to semi-consolidated sediments that are of Cretaceous to Quaternary age. Alluvial deposits, arenite, sandstone, and siltstone cover the study area (Fig. 3.2). Deposits of the Zululand Group consists of Makatini, Mzinene and St. Lucia formations. These sediments are overlain by Miocene aged Uloa formation which is in turn overlain by the cross-bedded calcarenites of the Umkhwelane formation (Meyer *et al.*, 2001). Pleistocene aged Port Durnford and Kosi Bay formations are characterised by loosely consolidated sands, silts, clays and lignite beds (Meyer *et al.*, 2001; Demlie *et al.*, 2014; Ndlovu 2015; Ndlovu and Demlie 2016). Overlying the Kosi Bay formation are the redistributed sands of the KwaMbonambi formation. The Holocene aged Sibayi formation is characterised by high coastal dune cordons (Watkeys *et al.*, 1993). The area is covered by sediments that are highly permeable and promote rapid recharge to the aquifers and strongly interact with the wetlands in the region (Mkhwanazi 2010; Weitz and Demlie, 2014).

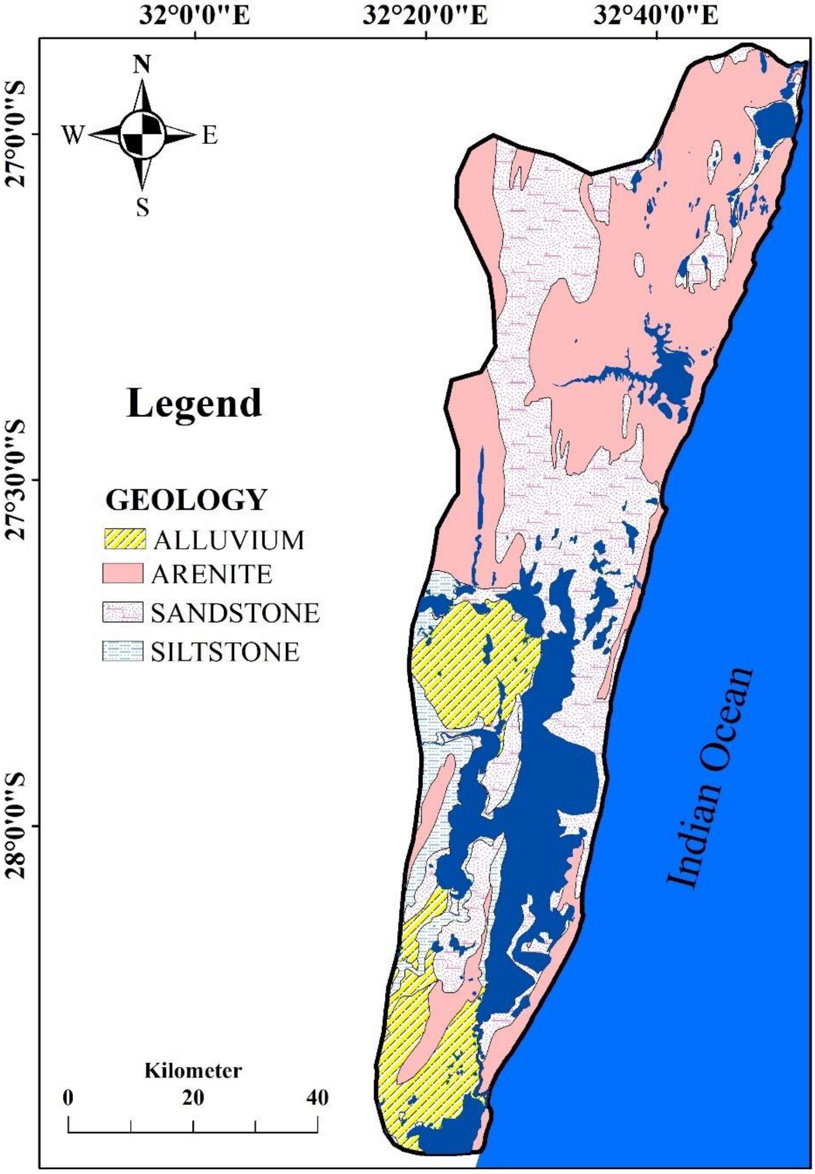

Figure 3.2: Geology map of the study area

3.5 Soils

The type of rocks found in an area influences the nature of soils that will develop. Most of the sediments of the Maputaland Group are infertile, wind-blown distributed sands (Demlie and Ndlovu, 2015; Mkhwanazi 2010). The Maputaland coastal plain consists of poor soils that are unseemly for commercial farming (Kelbe *et al*., 2016). According to Camp (1999), the Maputaland coastal plain consists of recent sands, it is covered by grey Fernwood soils and red soils are also encountered on dune ridges. The sediments of the Maputaland Group consists of fine grained sand and some coarse sand, gravel, silt and clay material (Weitz and Demlie, 2014). The majority of Maputaland is bounded by sandy Tertiary and Quaternary deposits that yield infertile soils (Watkeys, 1993). The easterly dunes consists of poorly developed yellow-orange soils.

3.6 Hydrogeology

The Maputaland coastal plain is regarded as the largest primary aquifer in South Africa, it consists of Cretaceous to Quaternary unconsolidated sediments (Barath, 2015; Mthembu *et al*., 2020). These sediments are highly permeable allowing rapid recharge of the coastal aquifer. According to (Barath, 2015), the aquifer is branded by increased hydraulic conductivity and transmissivity. However, the aquifer is susceptible to contamination as a result of its hydrogeological properties. Occurrence of groundwater is within inter granular aquifer that yields 0.5-5.0 L/s (Demlie and Ndlovu, 2016). The drilling processes revealed that the unconsolidated deposits are of good quality. Sodwana Bay is underlain by an aquifer composed of sediments that consists of sand, silt and clay. The unconfined shallow aquifer of the Maputaland is shaped by the KwaMbonambi formation. It consists of medium to coarse grained sands with a high transmissivity of 150-300m^2/day. Sediments of the Maputaland group is characterized by high hydraulic conductivities which averages to 15.6, 0.87, and 4.3 m/day for the Sibayi, KwaMbonambi and Port Dunford formations (Ndlovu and Demlie 2018). Underlying that is the Kosi Bay formation characterised by sandy silt with moderate clay content. As a result of that, it is regarded as a leaky aquifer and has a transmissivity of 1-3m^2/day. This is because the nature of clay doesn’t allow much water to percolate. The deeper aquifer is composed of the Uloa/Umkwelane formation and it is semi-confined with a high transmissivity of 75-100m^2/day (Nweze, 2016).

3.7 Land use

Land use activities in the area consists of subsistence agriculture, commercial forestry plantations and eco-tourism. The area is covered with dense coastal and swamp forests. Due to the high summer rainfall and high temperatures experienced on the east coast, coastal dunes, tall and dense dune forests are found in areas such as Sodwana Bay. The region is of great importance as it is known for its tourism and ecological diversity. Most areas are under state conservation by the Isimangaliso wetland park. The beauty of this area attracts tourists to visit often to enjoy fishing and scuba diving. According to Barath (2015), forestry is the dominant land use in the Zululand coastal plain. Von Maltitz *et al*. (1996) stated that the natural vegetation of the Zululand coastal plain consisted of mature dune forests, secondary dune forests and grassland. Sodwana Bay lies within the Coast and Coast Hinterland zone (Camp, 1999). Camp (1999) stated that majority of the natural vegetation in this zone has been destructed and replaced with crops mainly sugarcane while the other portion is occupied with forests. According to Nweze (2016), the Sodwana Bay area does not undergo industrialization or large scale agricultural activities other than forestry. Land uses in the Maputaland are subsistence agriculture, conservation and tourism, and plantation forestry (Watkeys *et al*., 1993; Kelbe *et al*., 2016).

3.8 Agricultural activities

Agricultural activities in the study area comprise of subsistence farming of maize, citrus fruits as well as commercial forestry plantations. There’s farming of maize and citrus fruits. Camp (1999) also stated that paw paws, litchis, bananas and vegetables were also dominant in this zone. Forested plantations are also found in this place and timber is also observed along this zone. Sugarcane is the most widely planted crop along the Coast and Coast Hinterland zone (Camp, 1999).

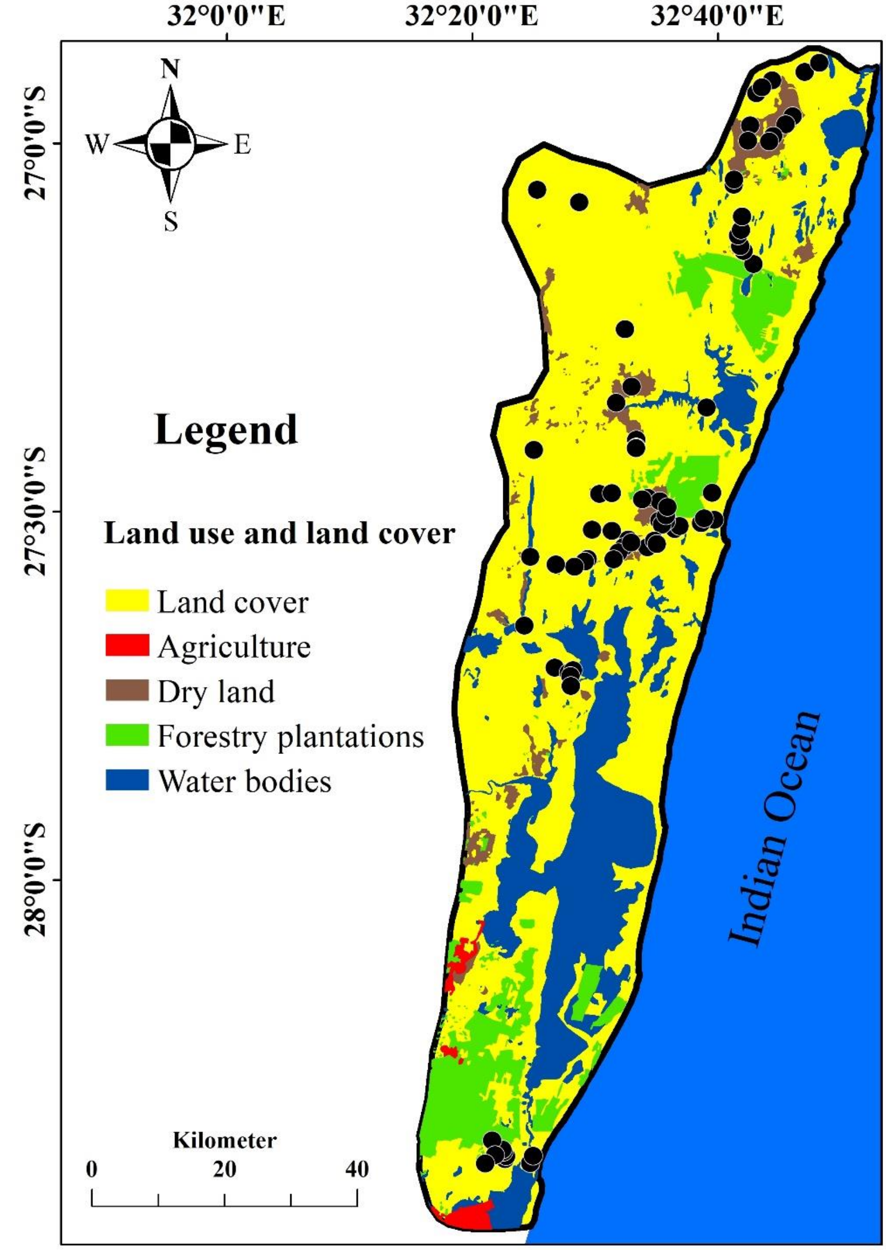

Figure 3.3: Land use and land cover map of the study area

CHAPTER FOUR

4. METHODOLOGY

4.1 Introduction

In order to carry out the objectives of this study, groundwater samples were randomly collected within the study area. Sampling was undertaken during April 2018 and May 2019. The methodologies followed as well as materials used in this study are explained in the following sections.

4.2 Groundwater sampling and analysis

Groundwater samples were randomly collected from borewells within the Maputaland coastal plain based on their availability and accessibility. Sampling was conducted during the months of April 2018 (N=53) and May 2019 (N=42) which represented the autumn season (Fig. 3.1). The difference in the total number of samples collected during 2018 and 2019 resulted from the malfunctioning of some of the borewells. Samples were collected after five minutes of pumping the borewells in order to remove stagnant water. Water from the sampling well was utilised to wash the sample bottles three times prior to sample collection. Groundwater pH and electrical conductivity (EC) were measured in the field using a calibrated Aqua Probe A-700m. Three sets of samples were collected in each sampling point, raw samples were collected in 500ml bottles and the other samples were collected in 200ml high-density polyethylene bottles, filtered in the field using 0.45 µm Millipore membrane filter. Samples were acidified with 0.5ml concentrated nitric acid to avoid precipitation of cations and trace metals. CO_3 and HCO_3 were analysed from the 500ml sampling bottles immediately using standard titration methods (APHA 2012). Collected groundwater samples were analysed for cations (Ca, Mg, Na and K), anions (Cl, SO_4, F), nutrients (NO_3, PO_4, NH_4) and SiO_2 using ion chromatograph (Metrohm 930 IC Compact Flex). A total of 15 trace metal concentrations (As, Ag, Fe, Mn, Al, B, Zn, PB, Ni, Cr, Cu, Cd, Co, Li and Sr) were analysed by inductively coupled plasma-mass spectrometry (NexION 2000 ICP-MS). Ten trace metals including As, Fe, Mn, Al, Zn, Pb, Ni, Cr, Cu, Cd, Co and Li were analysed in 2018 while 13 metals such as Ag, Fe, Mn, Al, B, Zn, Pb, Ni, Cr, Cu, Cd, Co and Sr were analysed in 2019. The ion balance error was calculated to check data quality and was found within ±5%. To ensure the precision of the chemical analysis of trace metals, the standards and blanks were regularly applied to examine the precision of the instrument and to prevent errors.

4.3 Software employed

- ArcGIS software v10.5 was used to prepare study area map, geology map and spatial maps using the IDW (inverse distance weighted) interpolation technique.
- Aquachem v4.0 was utilised to prepare Piper and Durov diagrams.
- Microsoft excel 2016 was used to comprehend the descriptive statistics of the data, prepare bivariate plots and Chadha diagram.
- SPSS v21 was used for multivariate statistical analysis.
- PHREEQC Interactive 3.4 was used to calculate saturation indices.

4.4 Drinking water quality assessment

4.4.1 Drinking water quality index (WQI)

The WQI was first developed by Horton (1965). It is widely used by various researcher scholars to evaluate the quality of water for drinking purposes. Computing the WQI involves five steps; (i) assignment of weights (w_i) to each water quality parameter being analysed, (ii) calculation of relative weights (W_i) of parameters using equation 4.1, (iii) quality rating calculation (q_i) based on equation 4.2, (iv) determining the sub-index value (SI_i) of the analysed parameters based on equation 4.3, (v) calculation of the WQI based on equation 4.4.

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \qquad \text{Eq.4.1}$$

$$q_i = \frac{C_i}{S_i} \times 100 \qquad \text{Eq.4.2}$$

$$SI_i = W_i \times q_i \qquad \text{Eq.4.3}$$

$$WQI = \sum_{i=1}^{n} SI_i \qquad \text{Eq.4.4}$$

where, q_i is the quality rating of each parameter, C_i is the concentration of each chemical parameter in each water sample (mg/L), and S_i is the drinking water standard of each chemical parameter as prescribed by SANS/WHO. Weight values (w_i) ranging from 1 to 5 were ascribed for each parameter according to their relative significance in the overall quality of drinking water and their indebted effects on human health. A maximum weight of 5 was allocated to the most significant parameters while a weight of 1 was assigned to the least significant parameters.

4.4.2 Pollution index of groundwater (PIG)

The pollution index of groundwater (PIG) was proposed by Subba Rao (2012), it is an essential tool for monitoring and assessment of drinking water quality. In PIG assessment, five steps are taken into consideration. The first step includes estimating the relative weight (R_w) of all analysed parameters. This relative weight is on a scale of 1 to 5, depending on the impact of parameters on human health. The second step involves the computation of the weight parameter (W_p) of each water quality variable to evaluate their relative contributions to overall water quality (Eq.4.5). The third step involves estimation of the status of concentration (S_c). S_c is computed by diving the concentration (C) of each water quality variable of every sample by its respective water quality standard limit (D_s) as described by SANS (2015) (Eq.4.6). In the fourth step, the overall quality of groundwater (O_w) is computed by multiplying the W_p by S_c (Eq.4.7). In the fifth step, the pollution index of groundwater is computed by summing all values of O_w contributed by every water quality variable in each groundwater sample (Eq.4.8).

$$W_p = \frac{R_w}{\sum R_w} \qquad \text{Eq.4.5}$$

$$S_c = \frac{C}{D_s} \qquad \text{Eq.4.6}$$

$$O_w = W_p * S_c \qquad \text{Eq.4.7}$$

$$\text{PIG} = \sum O_w \qquad \text{Eq.4.8}$$

4.4.3 Synthetic pollution index (SPI)

SPI is used to evaluate the degree of pollution of groundwater resources (Solangi *et al*., 2019), and their drinking suitability (Egbueri and Unigwe 2019). It is computed by the following equation;

$$\mathrm{SPI}=\sum_{i=1}^{n}\frac{V_o}{V_s}*W_i \qquad \text{Eq.4.9}$$

$$W_i=\frac{K}{V_s} \qquad \text{Eq.4.10}$$

$$K=\frac{1}{\sum_{i=1}^{n}\frac{1}{V_s}} \qquad \text{Eq.4.11}$$

where K, V_s, V_o, n and W_i are the constant of proportionality, each parameter's standard SANS (2015) level, concentration of each parameter, the total number of observed parameters, and the weight coefficient of each parameter, respectively. Based on the SPI values, water is classified into five categories such as suitable for drinking (SPI < 0.2), slightly polluted water (SPI, 0.2-0.5), moderately polluted (SPI, 0.5-1.0), highly polluted (SPI, 1.0-3.0), and unfit for drinking (SPI > 3.0) (Solangi *et al*., 2019; Egbueri and Unigwe 2019; Egbueri *et al*., 2020a).

4.4.4 Overall index of pollution (OIP)

The overall index of pollution (OIP) was developed by Sargaonkar and Deshpande (2003) for the evaluation of the level of contamination in drinking water resources. The OIP is widely used as it provides insight into the suitability of water for drinking purposes. The OIP is computed as follows;

$$\mathrm{OIP}=\frac{1}{n}*\sum_{i=1}^{n}\mathrm{PI} \qquad \text{Eq.4.12}$$

$$PI=\frac{C_s}{C_b} \qquad \text{Eq.4.13}$$

where, PI is the pollution index of the ith parameter defined in equation (Eq.4.13) where C_s is the concentration of the heavy metal in the sample; and C_b is the corresponding background values, and n is the number of analysed heavy metals, respectively.

4.5 Heavy metal pollution assessment

4.5.1 Heavy metal pollution index (HPI)

The heavy metal pollution index (HPI) provides an overall quality of water with regards to heavy metals (Mohan *et al.*, 1996). The HPI is computed by first assigning a rating or a weightage (W_i) to each heavy metal. The rating is an arbitrary value between 0-1 and its selection depends on the relative significance of each water quality parameter. This weightage (W_i) can be defined as inversely proportional to the recommended standard (S_i) for the corresponding parameter (Mohan *et al.*, 1996). In this study, the standard permissible value (S_i) was taken from the SANS standards (SANS, 2015). The HPI is calculated by the following equation (Mohan *et al.*, 1996);

$$HPI=\frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \qquad \text{Eq.4.14}$$

where, Q_i is the sub-index of the ith parameter, W_i is the unit weight of the ith parameter, and n is the number of parameters taken into account. The sub-index (Q_i) is calculated by the equation

$$Q_i=\sum_{i=1}^{n}\frac{\{M_i(-)I_i\}}{(S_i-I_i)} \qquad \text{Eq.4.15}$$

where, M_i is the monitored value of the ith parameter, I_i is the ideal value of the ith parameter and S_i is the standard value of the ith parameter. In this study, the ideal values for all the metals are given as 0 µg/L since their presence in drinking water is not desired (Brindha *et al.*, 2017; Vetrimurugan *et al*., 2017). The negative sign (-) indicates the numerical difference between the two values, ignoring the algebraic sign.

4.5.2 Heavy metal evaluation index (HEI)

The HEI gives an overall quality of water with regards to heavy metals (Edet and Offiong 2002). It is computed as follows;

$$HEI=\sum_{i=1}^{n}\frac{H_c}{H_{MAC}} \qquad \text{Eq.4.16}$$

where H_C and H_{MAC} are the monitored value and maximum admissible concentration (MAC) of the ith parameter taken from SANS (2015).

4.5.3 Degree of contamination C_d

The degree of contamination (C_d) is useful in summarizing the combined effects of various quality parameters regarded as harmful to domestic water (Backman *et al*., 1997; Edet and Offiong 2002; Prasanna *et al*., 2012). It is computed by the following equation;

$$C_d=\sum_{i=1}^{n}C_{fi} \qquad \text{Eq.4.17}$$

where

$$Cf_i=\frac{C_{Ai}}{C_{Ni}}-1 \qquad \text{Eq.4.18}$$

where C_{fi} is the contamination factor for the ith parameter, C_{Ai} is the monitored value and C_{Ni} is the upper permissible concentration of the ith parameter. According to Edet and Offiong (2002), the C_d can be classified into low (C_d<1), medium (C_d=1-3) and high (C_d>3) in order to identify the contaminated areas.

4.5.4 Ecological risks of heavy metals

The ecological risk index (ERI) was computed using the following equations;

$$\mathrm{ERI} = \sum \mathrm{RI} = \sum \mathrm{T_i} * \mathrm{PI} \qquad \text{Eq.4.19}$$

Where RI is the potential ecological risk factor of each heavy metal; T_i is the toxic-response factor of heavy metals, and PI is the pollution index computed by equation 4.13. The toxic-response factor of heavy metals is given as; As=10; Cd=30; Cr, Zn, and Mn=1; Cu, Co, Ni and Pb= 5 (Tiawo *et al*., 2019; Ukah *et al*., 2019; Egbueri and Unigwe 2020)

4.6 Health risk assessment

Health risk assessment estimates health effects that may occur from exposure to non-carcinogenic and carcinogenic chemicals (Duggal *et al*., 2017; Zhou *et al*., 2016; Ji *et al*., 2020; Zhou *et al*., 2020). Human exposure risk of an individual to trace metals in the water occurs in three pathways; direct ingestion, inhalation and dermal absorption through exposure skin (Zeng *et al*. 2015; Duggal *et al*. 2017). For water exposure, ingestion and dermal absorption are common exposure routes. The doses received through ingestion and dermal absorption pathway were computed using Eq.4.20 and 4.21 adapted from USEPA (2004)

$$ADD_{ingestion} = \left(C_W x\ IR\ x\ EF\ x\ ED\right)\ /\ \left(BW\ x\ AT\right) \qquad \text{Eq.4.20}$$

$$ADD_{dermal} = \left(C_W x\ SA\ x\ Kp\ x\ ET\ x\ EF\ x\ ED\ x\ 10^{-3}\right)\ /\ \left(BW\ x\ AT\right) \qquad \text{Eq.4.21}$$

where $ADD_{ingestion}$ and ADD_{dermal} represents the average daily doses from ingestion and dermal absorption of water, given as µg/kg/day, and C_w is the concentration of the trace metal in water (µg/L). IR indicates the ingestion rate of water through drinking (L/day), EF is the exposure frequency (days/year), in this study EF is 350 days/year; ED is the exposure duration (years), BW is the average body weight (kg), AT represents the average time for non-carcinogenic effects (days), SA indicates the exposed skin area (cm^2), ET is the exposure time (h/day), and K_p is the dermal permeability coefficient in water (cm/h) obtained from USEPA (2004).

Non-carcinogenic risk of trace metals was evaluated by calculating the hazard quotients (HQs) using Eq. 4.22

$$HQ_{ingestion/dermal} = ADD_{ingestion/dermal} \,/\, RfD \qquad \text{Eq.4.22}$$

$$RfD_{dermal} = RfD \; x \; ABS_{GI} \qquad \text{Eq.4.23}$$

$$HI = HQ_{ingestion} + HQ_{dermal} \qquad \text{Eq.4.24}$$

Where RfD is the corresponding reference dose of the element (µg/kg/day) and ABS_{GI} is the gastrointestinal absorption factor. These -mentioned values were obtained from Wang *et al*. (2017), Wu *et al*. (2009), Edokpayi *et al*. (2018), and USEPA (2004). The hazard index (HI) is obtained by summing the HQs of individual elements from the different pathways using Eq.4.24. If the HQ/HI is below unity or one, non-carcinogenic risk is not expected to occur; HQ/HI greater than one suggests that there may be a concern for non-carcinogenic risk or adverse effects on human health (Wang *et al*., 2017; Duggal *et al*., 2017; Barzegar *et al*., 2017)

CHAPTER FIVE

Geochemical characterization and assessment of groundwater quality: Impact on potential health risk in coastal aquifers

5.1 Introduction

Coastal aquifers are prone to contamination particularly by salinization. Groundwater is an important source of freshwater in these regions, especially in arid and semi-arid countries. Population growth, expansion of agricultural lands, rapid urbanization, industrialization, and climate change are some of the factors that lead to water quality problems in South Africa (Vhonani *et al*., 2019). An increase in the demand for groundwater has been noted in different parts of the world due to scarcity of surface water resources. An increase in the demand for groundwater leads to a decline in groundwater level. This further results in degradation of groundwater quality. Groundwater that has been contaminated is difficult and expensive to treat. Groundwater is important for socio-economic development. In South Africa, the agricultural sector remains the largest user of water. It is imperative to evaluate the quality of water resources as it directly impact human health and crop yield. Various methods have been developed and used by researchers to evaluate the groundwater quality and its suitability for drinking purposes. Such methods include the WQI method which was developed by Horton (1965). Various researchers have successfully used the WQI method for hydrogeochemical characterisation of groundwater for drinking purposes (Bouderbala *et al*., 2016; Bhuiyan *et al*., 2016; Wanda *et al*., 2016; Şener *et al*., 2017; Adimalla *et al*., 2018; Zahedi *et al*., 2018; Adimalla *et al*., 2019; Solangi *et al*., 2019; Kumari and Rai, 2020). In this chapter, hydrogeochemical characterisation of the aquifer and the processes which determines the chemistry; groundwater quality and its suitability; and the potential human health risk due to contamination in different age groups through ingestion and dermal exposure pathways is carried out based on analysed parameters such as physical parameters (pH, EC, TDS), major cations (Na, K, Ca and Mg), anions (Cl, SO_4, F and NO_3), minor ions (Li, NH_4 and PO_4) and trace metals such as Cu, Zn, Co, Mn, Pb, Al, As, Fe, Cd and Si during 2018. Standards for drinking water prescribed by DWAF (1996) and WHO (2011) were used to carry out WQI and health risk assessment calculations as well as evaluating the suitability of groundwater. Major cations and anions were used to understand the processes that govern the chemistry of groundwater in this area. Various irrigation indices such as KR, PI, MHR, RSC, Na% and SAR were adopted to evaluate the suitability of groundwater for irrigation uses.

5.2 Analysis of groundwater physicochemical parameters

The maximum groundwater level was 25.6 m below ground level (Fig. 5.1). The spatial distribution map of the groundwater level depicts high water level in small patches in the north eastern, central and south western part of the area. Lower water table is distributed mainly in the central part of the study area. Descriptive statistical results of physicochemical parameters are summarised in Table 5.1. The pH of groundwater varied from 5.28 to 8.23 with an average of 6.50. Approximately 25% of the samples are neutral to alkaline (pH>7) and 75% are acidic in nature (pH<7). The pH of groundwater in most of the sample locations are within the permissible limits of DWAF (1996), however, 26% of the groundwater samples have value of pH<6 which is below the permissible limit of DWAF (1996). Similarly, 53% of the sample locations are below the highest permissible limit as proposed by WHO (2011). The EC varied from 115 to 1194 µS/cm with an average of 312.32 µS/cm. The target water quality range for EC in groundwater is 700 µS/cm according to DWAF (1996). The quality of groundwater is within this limit in 92% of the sampling locations and 8% of the samples fall within the permissible limit. Similarly, the TDS of the groundwater samples varied from 74 to 764 mg/L with an average value of 200 mg/L. According to the classification of TDS (Freeze and Cherry, 1979), the groundwater in the study area is fresh (<1000mg/L). The total hardness (TH) of groundwater was estimated using equation 12. In this study, the TH varied from 25 to 464 mg/L with an average of 107 mg/L. Based on the TH value, water can be classified as soft (<75mg/L), moderate (75-150mg/L), hard (150-300mg/L) and very hard (>300) (Sawyer and McCarty 1978). According to the classification of total hardness, 45% of the samples are classified as soft, 38% moderate, 11% hard and 6% very hard.

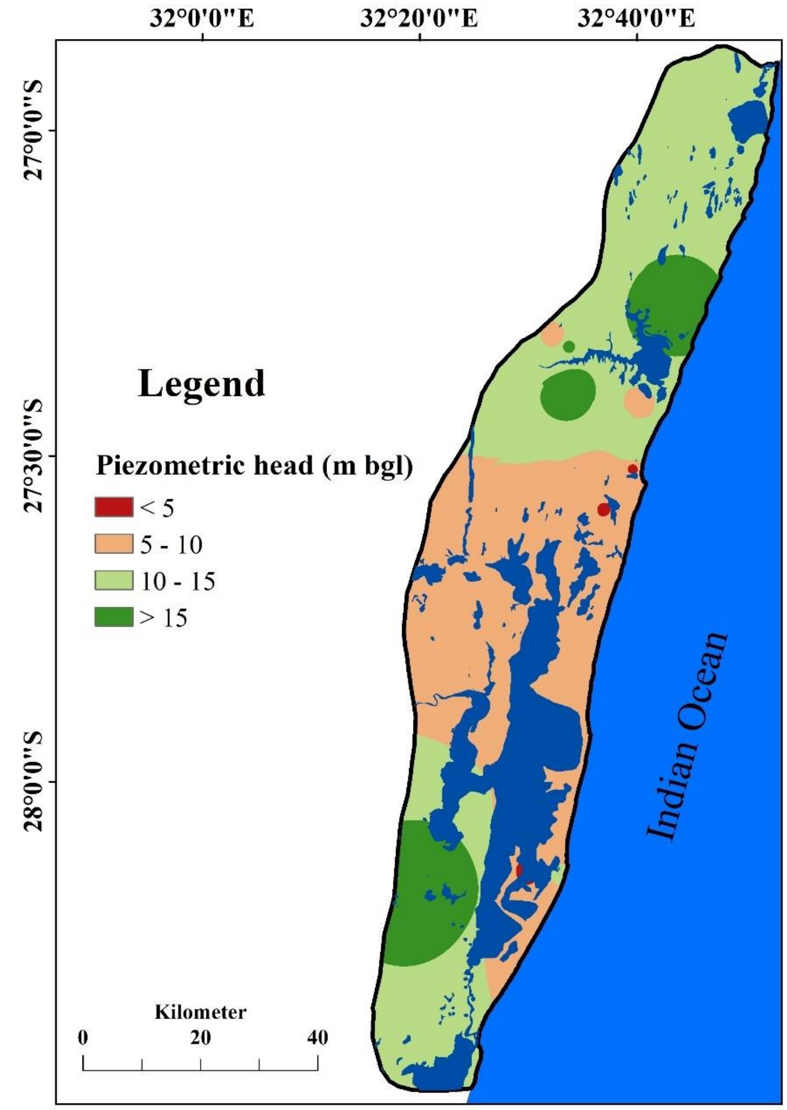

Figure 0.1: Piezometric map of the study area (m below ground level)

Na in groundwater varied from 14 to 126 mg/L with an average concentration of 38 mg/L. Cl concentration in groundwater varied from 27 to 289 mg/L with an average concentration of 83 mg/L. K in groundwater varied from 1 to 15 mg/L with an average concentration of 7 mg/L. Ca and Mg in groundwater varied from 4 to 154 mg/L and from 1 to 56 mg/L with an average concentration of 27 and 10 mg/L, respectively. SO_4 and HCO_3 in groundwater varied from 2 to 65 mg/L and from 18 to 312 mg/L. The average concentration of ions was used to determine the order of major ions in the study area. The affluence of the major ions in groundwater is in the order of Na>Ca>Mg>K>Li and $Cl>HCO_3>SO_4>NO_3>F$.

Nutrients play a significant role in the quality of groundwater and are indicative of the influence of agricultural activities. Ammonia (NH_4) in groundwater varied from 0 to 0.2 mg/L. Phosphate (PO_4) in groundwater varied from 0 to 0.5 mg/L. Nitrate (NO_3) in groundwater varied from 0 to 18.2 mg/L with an average concentration of 1.6 mg/L.

Table 0.1: Descriptive statistics of groundwater physicochemical parameters

Parameters	**Unit**	**Min**	**Max**	**Mean**	**SD**
pH	-	5.28	8.23	6.50	0.67
EC	µS/cm	115	1194	312	222
TDS	mg/L	74	764	200	142
TH	mg/L	25	464	107	85
Na	mg/L	14	126	38	25
K	mg/L	1	15	3	2
Ca	mg/L	4	154	27	25
Mg	mg/L	1	56	10	9
Li	mg/L	BDL*	6	1	1
HCO_3	mg/L	18	312	70	67
Cl	mg/L	27	289	83	45
SO_4	mg/L	2	65	13	14
NO_3	mg/L	BDL	18	2	3
NH_4	mg/L	BDL	0.2	0	0.1
PO_4	mg/L	BDL	0.5	0.1	0.1
F	mg/L	BDL	1	0	0

*BDL= below detection limit.

Trace elements occur in groundwater naturally or due to other anthropogenic activities (Selvam *et al.*, 2017; Mthembu *et al.*, 2020). Silica in groundwater varied from 7.2 to 61.0 mg/L with an average concentration of 21.8 mg/L. Copper in groundwater varied from 0 to 279.5 µg/L with an average concentration of 19.2 µg/L. Zinc and aluminium in groundwater varied from 1.9 to 19964.5 µg/L and 1.6 to 3052.5 µg/L with an average concentration of 501.4 µg/L and 90.0 µg/L, respectively. Manganese in groundwater varied from 0.4 to 84.3 µg/L with an average concentration of 19.8 µg/L. Lead in groundwater varied from 0.2 to 22.1 µg/L with an average concentration of 1.8 µg/L. Arsenic in groundwater varied from 0 to 3.6 µg/L with an average concentration of 0.5 µg/L. Iron in groundwater varied from 2.7 to 770.8 µg/L. Cobalt in groundwater varied from 0 to 4.5 µg/L with an average concentration of 0.4 µg/L. Cadmium in groundwater varied from 0 to 0.2 µg/L. The order of dominance of trace elements in the study area is Si>Zn>Al>Fe>Cu>Mn>Pb>Co>As>Cd. The high concentration of trace metals in groundwater may be owed to the landfill, agricultural activities and seawater intrusion taking place in this area (Mthembu *et al*., 2020). Spatial distribution of trace elements in the study area a) arsenic, b) cobalt, c) lead and d) manganese is represented in Fig. 5.2.

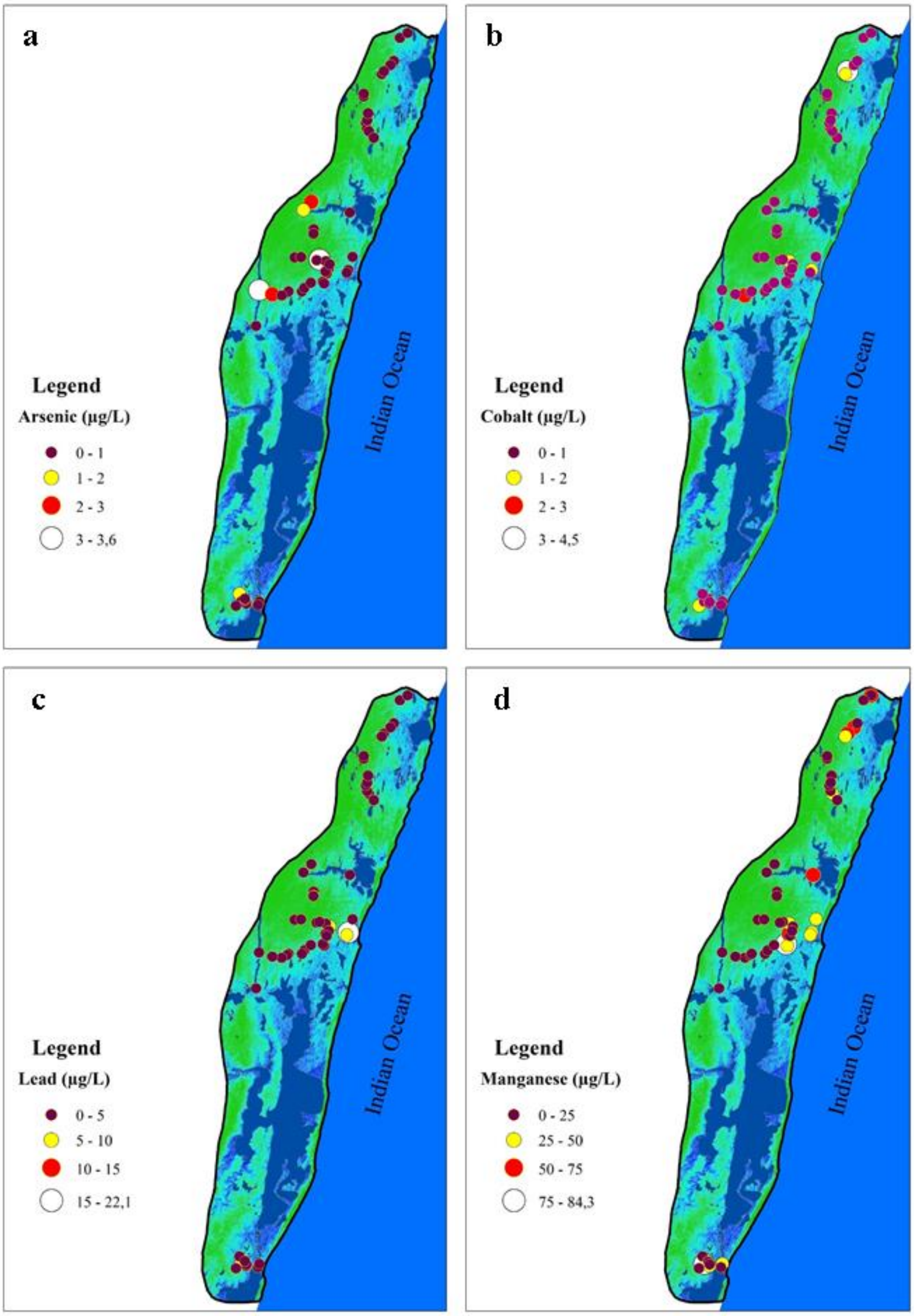

Figure 0.2: Spatial distribution of trace elements in the study area a) Arsenic (µg/l), b) Cobalt (µg/l), c) Lead (µg/l) and d) Manganese (µg/l)

pH is an important parameter that decides the suitability of water for various purposes, the acceptable limit of pH as per WHO (2011) is between 6.5 and 8.5. About 53% of the samples (28 no’s) of the study area have pH values falling less in between 6 to 6.5. Detailed analysis shows that 14 samples have pH values less than 6.0. Water with pH less than 7 is considered as acidic. The samples with pH values less than 6 could be due to exposure of carbon dioxide in the atmosphere and this has led to lowering of equilibrium in the pH value to 5.2 (Discroll, 1986). Eh and pH relationships were established in order to understand the environment. Seawater and rainwater samples were also collected for benchmarking the water environment. The seawater samples recorded a pH of 8 and Eh of 6 volts while the rainwater recorded a pH of 6.5 with Eh value of 5. Majority of the samples in the study area fall in the neutral to acidic condition, with 51% having reducing environment and the rest of the samples have oxidising environment (Fig. 5.3), 13 water samples fall in the neutral to basic condition with reducing environment.

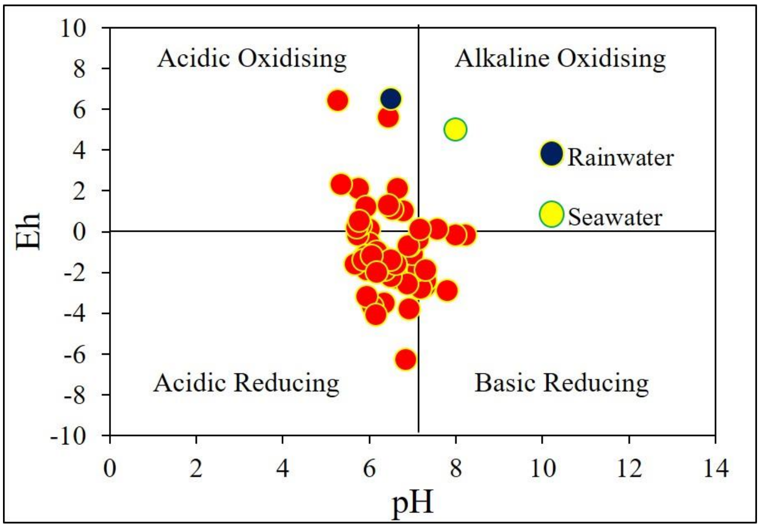

Figure 0.3: Relationship between pH vs Eh

5.3 Process controlling the water quality

5.3.1 Dissolution and precipitation

The composition of the water has to be under balanced or under/over saturated condition in respect of minerals in nature. If the water is under saturated then it is understood that the process of dissolution is still going on, whereas if the water is oversaturated then it is understood that the process of precipitation is ongoing. When the SI is less than zero, it implies that groundwater is undersaturated with respect to a mineral and the mineral will continue to dissolve into solution. When the SI is greater than zero, it indicates that groundwater is oversaturated with respect to a mineral and the mineral may precipitate from solution. If the SI is equal to zero, then groundwater is said to be in equilibrium with respect to the mineral. The saturation index values were calculated and ranked in the order of calcite >gypsum >fluorite >dolomite >halite (Fig. 5.4). The saturation index (SI) of sample number 1 and 6 shows calcite and dolomite values greater than zero whereas the remaining 51 samples shows calcite, dolomite, gypsum, fluorite and halite SI values less than zero. The samples with SI value less than zero clearly indicates that the water is under-saturated with calcite, dolomite, gypsum, fluorite and halite (Li *et al.*, 2016). Transportation of water from higher elevation to lower elevation aided with change in water temperature and carbon dioxide decrease might have caused the removal of carbonate minerals through dissolution (Xiao *et al.*, 2015).

5.3.2 Rock weathering, precipitation and evaporation

Gibbs diagram is prepared in order to ascertain the functional sources of dissolved chemical constituents which resulted due to rock weathering dominance, precipitation dominance and evaporation domination in the study area. TDS values were plotted against (Na + K) / (Na + K + Ca) and Cl / Cl + alkalinity (Fig. 5.5). Most of the groundwater samples falling under the rock dominance zone clearly indicates the influence of rock weathering. The ratio of Cl +SO_4 with HCO_3 was plotted to understand the dominance of anions and their possible sources. Cl + SO_4 values in most of the samples are greater than the HCO_3 concentration. Only 12 samples recorded Cl + SO_4 values lesser than HCO_3 concentration. (Cl + SO_4): HCO_3: SIO_2 has an average ratio of 48: 35: 13. Further in order to ascertain the primary and secondary sources of the solutes in groundwater, two relationships (Ca+Mg) / (Na+Cl) and Na* (Na* = Na–Cl) &SiO_2 were also studied. (Ca+Mg) / (Na+Cl) recorded less than 2 ratios where most of the samples recorded ratios less than 1. This clearly indicates that carbonate weathering and evaporate dissolution are not the primary and secondary sources of the solutes. (Na* = Na–Cl) and SiO_2 ratio recorded some positive relationship in the groundwater samples which indicates that the silicate weathering process cannot be ruled out as one of the sources of the solutes in water (Xiao *et al.*, 2016).

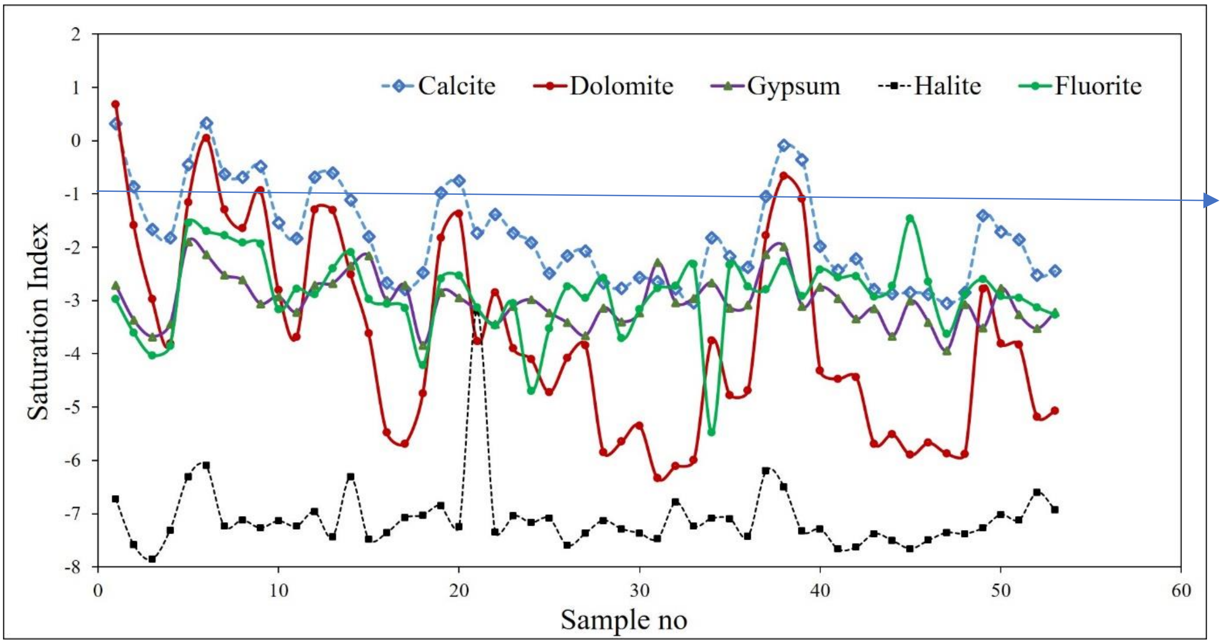

Figure 0.4: Saturation indices of calcite, dolomite, gypsum, halite and fluorite in water samples.

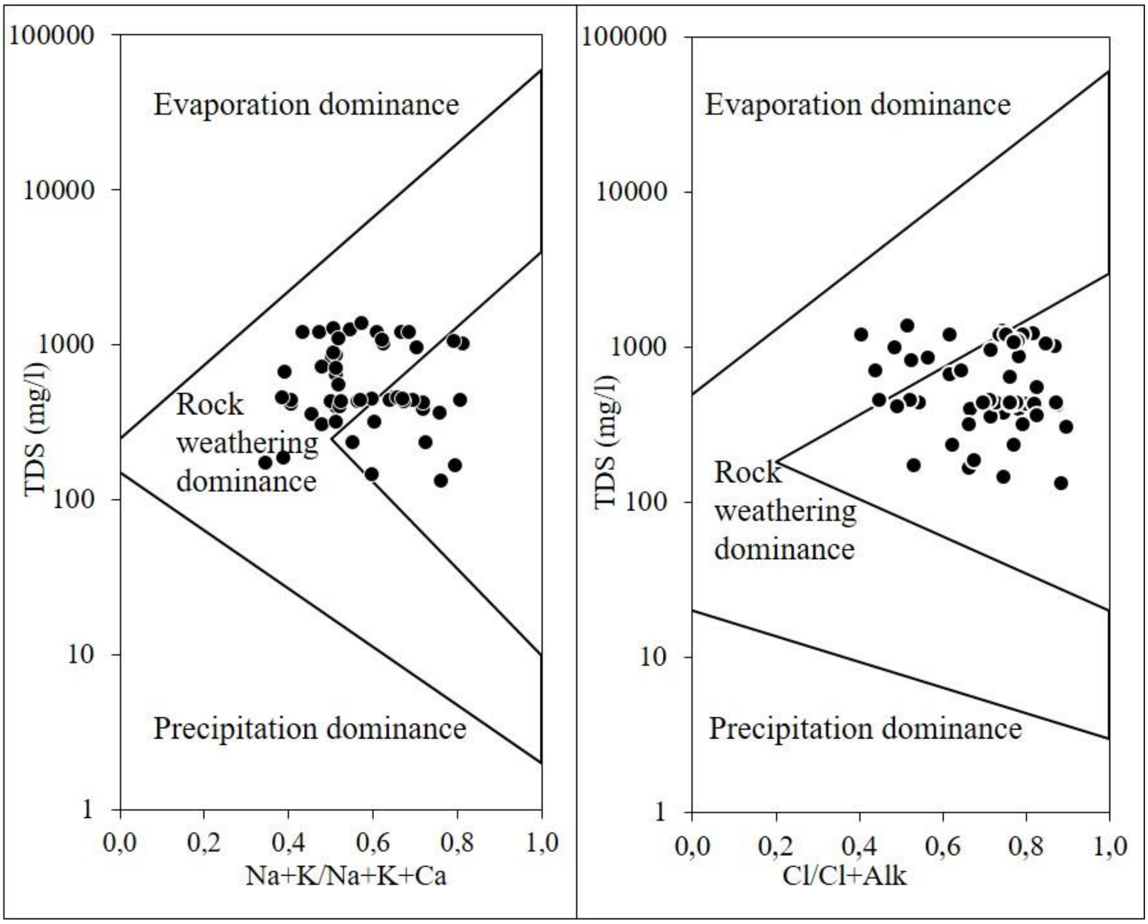

Figure 0.5: Gibbs plot of TDS vs (Na + K) / (Na + K + Ca) and Cl / (Cl +Alk)

5.3.3 Ion exchange

Ion exchange process is the major process that impacts the hydrogeochemistry in an arid and semiarid region. Cation exchange and or calcite, dolomite, gypsum, halite can contribute to Ca and Mg in groundwater. Bonding between these parameters must have a linear relationship with a slope of 1 if ion exchange process is significant (Fisher and Mulican, 1997). In the study area, relationship between Ca +Mg and HCO_3 (Fig. 5.6a) has $R^2 = 0.82$. Most of the samples falling above the 1:1 line clearly indicates excess Ca + Mg, this excess is balanced by Cl and SO_4. Furthermore, if equivalent concentration of Cl is subtracted from Na and the relationship between Ca +Mg +Na + K and HCO_3 (Fig. 5.6b) were plotted, the relationship shows strong linear relation with R^2 of 0.935. Ca + Mg - HCO_3 – SO_4 and Na – Cl (Fig. 5.6c) shows a negative correlation, which indicates cation exchange of Ca and Mg for Na in groundwater (Li *et al.*, 2016; Vetrimurugan *et al.*, 2017b). If Ca + Mg - HCO_3 – SO_4 and Na – Cl ratio were close to -1, then dissolution of calcite, dolomite, gypsum etc., are through rock water interaction (Su *et al.*, 2018). If Ca + Mg - HCO_3 – SO_4 value were less than 0, then Ca or Mg is exchanged by Na & vice versa (Li *et al.*, 2013). If the Na-Cl value is less than 0, then Na in groundwater is exchanged by Ca or Mg and vice versa. The groundwater samples of the study area show -1 ratio value which clearly indicates cation exchange of Ca and Mg for Na in groundwater.

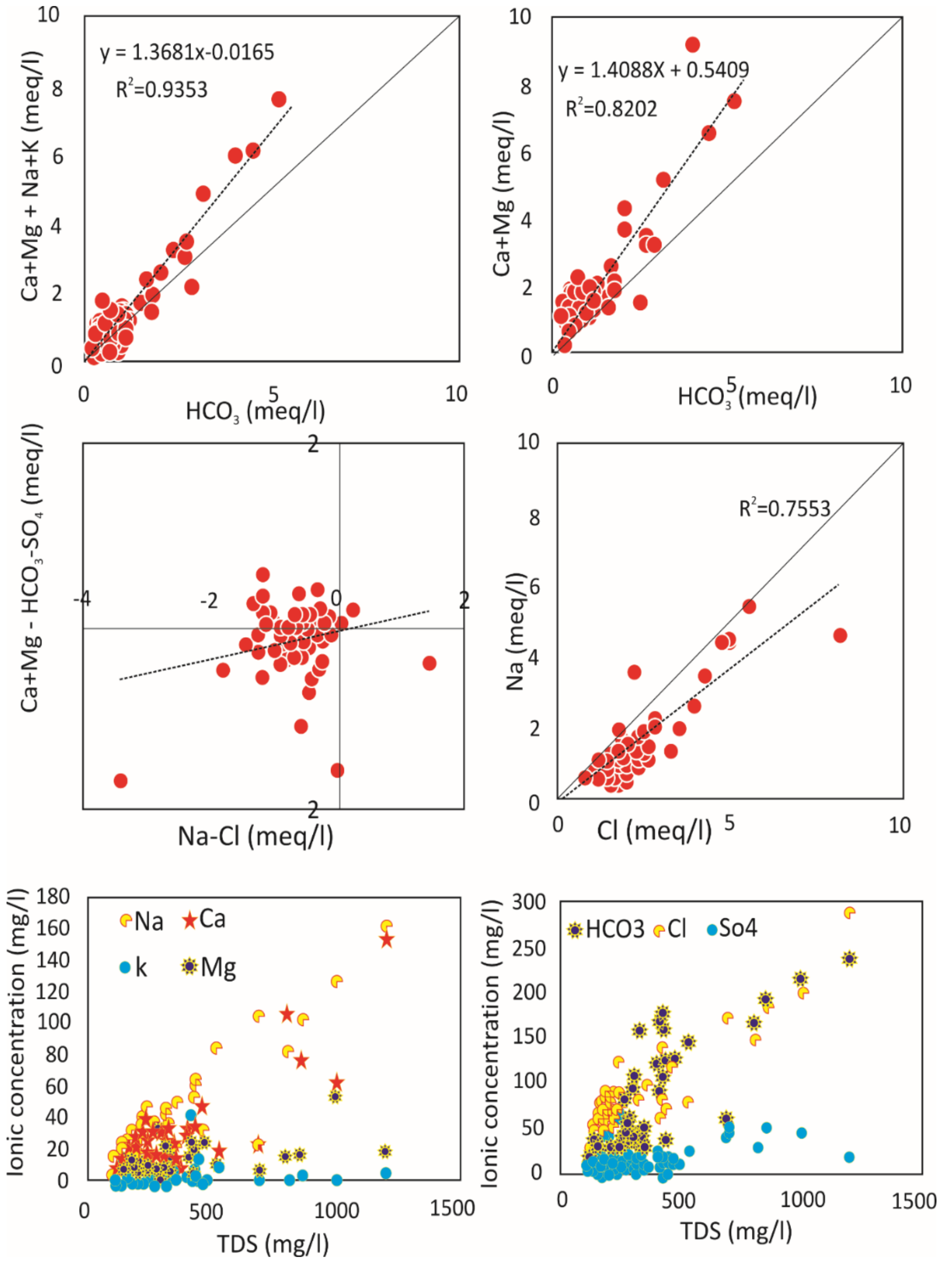

Figure 0.6: Figure 5.6: Plot showing the relationship between major ions like a) cations vs HCO_3, b) Ca & Mg vs HCO_3, c) Ca + Mg- HCO_3- SO_4 vs Na-Cl, d) Na vs Cl, e) Cations (Ca, Mg, Na & K) vs TDS & f) Anions (HCO_3, Cl & SO_4) vs TDS.

Sodium and chloride were plotted (Fig. 5.6d). The correlation of Na vs Cl in most of the samples were falling below the 1:1 line with an R^2 value of 0.755. This clearly indicates that the excess chloride was balanced by calcium and magnesium. Both Ca/Na or Na/Ca exchange is possible, if Ca/Na exchange is active then the concentration of HCO_3 will increase with decrease in Ca and increase in Na (Mande *et al*., 2018). If Na/Ca exchange is active, then the concentration of HCO_3 will decrease with a decrease in Na and increase in Ca. In this region, the concentration of HCO_3 and Na increases with a decrease in Ca concentration. This clearly indicates that the Ca/Na exchange is taking place in the study area.

The molar ratio of Na^+/Cl^- varied from 0.35 to 1.62 with an average value of 0.70. About 95% of samples have Na^+/Cl^- molar ratio < 1, which reflects that the ion exchange process is responsible for the reduction of Na^+. Only 5% of the samples have Na^+/Cl^- molar ratio > 1 which indicates the non-halite source and suggests that the Na^+ release is from silicate weathering.

Further, the correlation between TDS and major ions was established in order to get the reflection of the hydrochemical component of groundwater and formation characteristics (Fig. 5.6e). The TDS vs major cation (Ca, Na, Mg & K) clearly indicates the increase in Ca & Na concentration with increase in TDS. Similarly, anion HCO_3 and Cl increases with an increase in TDS (Fig. 5.6f). Ca, Na, HCO_3 & Cl concentrations were also relatively higher in groundwater and form the main source of the major ions. NaCl forms the main component of halite, $CaSO_4$ forms the main component of gypsum, and other evaporates. Ca, Na & Cl concentrations in groundwater were relatively higher and therefore they could be from the dissolution of evaporates. The relationship between calcium & sodium with chloride & sulphate (Fig. 5.7) shows that most of the samples are falling above the 1:1 line. Higher concentration of Ca & Na against the Cl & SO_4 is attributed to the dissolution of evaporates such as halite & gypsum (Senthilkumar and Elango, 2013; He *et al*., 2019).

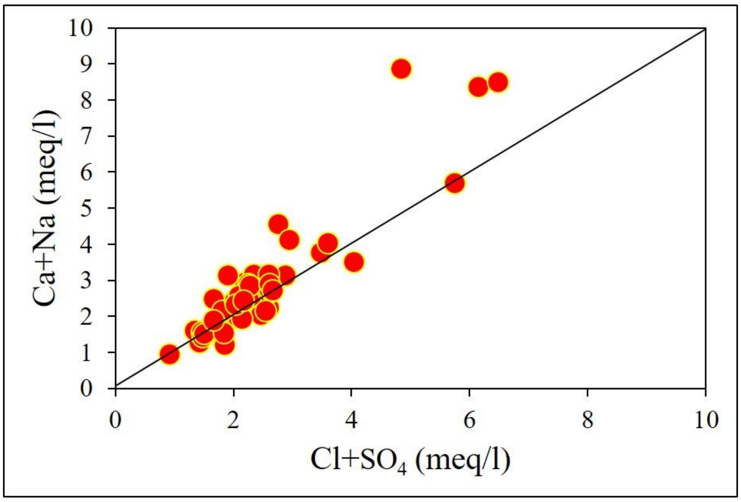

Figure 0.7: Relations between calcium & sodium with chloride & sulphate

5.4 Water quality index for assessment of water for drinking purposes

Groundwater quality was evaluated in an exhaustive approach using the water quality index (WQI). For the calculation of WQI, parameters such as EC, pH, Ca, Mg, Na, K, HCO_3, Cl, SO_4, F and trace elements of each sampling location were taken into consideration. The WQI analysis results from the 53 sampling locations were used to get comprehensive understanding of groundwater quality.

The WQI of each groundwater sample was computed using observed values (C_i), assigned weights (w_i), relative weights and standard limits (S_i) as recommended by DWAF (1996) (Table 5.2). In this study, the WQI varied from 18.9 to 157.1 with an average value of 45.55. Fig. 5.8 shows the results of the water quality assessment in form of spatial distribution of WQI. Water quality index classification (Chatterjee and Raziuddin, 2002) was used to understand the status and type of the water quality in the study area. WQI clearly shows that 2% of the samples belonged to excellent and 67 % of the samples belonged to good water quality (Table 5.3). About 22 % of the groundwater samples belonged to the poor water quality and 2% of the samples belonged to very poor water quality. Only 7 % of the samples are unsuitable for drinking. This is attributed to the rock-water interaction and ion exchange process of Na/Ca as well as anthropogenic activities that occur in the study area. Spatial distribution of the WQI shows that unsuitable water quality samples are located in the western parts (2 samples, no - 5 & 6) and in the southern parts (2 samples no- 37 & 38) of the study area.

Table 0.2: Effective weights of each water quality parameter

Parameters	Assigned weight (wi)	DWAF (1996) standard	Relative weight (Wi)	Effective Weights (Si)			
				Minimum	Maximum	Mean	Standard Deviation
EC	5	700	0.125	2.0536	21.3214	5.5772	3.9704
pH	3	9	0.075	4.4000	6.6667	5.4184	0.5561
Ca	5	32	0.125	1.5625	60.1563	10.4732	9.6881
K	3	50	0.075	0.0708	2.2709	0.4274	0.3690
Mg	3	30	0.075	0.3000	14.0000	2.4604	2.1606
Na	5	100	0.125	1.7500	15.7500	4.7547	3.1833
Cl	5	100	0.125	3.3750	36.1250	10.3303	5.6460
SO_4	1	200	0.025	0.0219	0.8125	0.1673	0.1716
HCO_3	5	300	0.125	0.7625	13.0000	2.8995	2.7840

F	5	1	0.125	0.1788	14.0000	3.0458	2.1326
Al	2	200	0.067	0.054	14.272	1.273	2.6462
As	5	10	0.167	0.053	5.940	0.792	1.2793
Cd	5	5	0.167	0.040	0.613	0.126	0.0855
Co	3	50	0.033	0.000	0.303	0.030	0.0492
Cu	2	1000	0.067	0.000	1.864	0.128	0.3707
Fe	4	300	0.133	0.061	17.129	1.976	3.5060
Pb	5	10	0.167	0.352	36.870	2.941	5.7638
Mn	5	100	0.167	0.060	14.053	3.298	3.7422
Zn	2	1000	0.033	0.006	2.435	0.215	1.1325

The water quality index rating clearly shows that majority of the samples belonged to the good water quality type. Majority of the poor water quality samples are located in the southern part of the study area.

Table 0.3: Results of water quality index

Sl.no	WQI Range	Water Type	Sample locations
1	< 25	Excellent water quality	3
2	25 – 50	Good water quality	2,4,10,11,13,15 to 18, 21 to 31, 33 to 36, 39 to 48, 50,51& 53
3	50 – 75	Poor water quality	1,7,8,9,12,19,20,32,49 & 52
4	75 – 100	Very poor water quality	14
5	> 100	Unsuitable	5, 6, 37 & 38

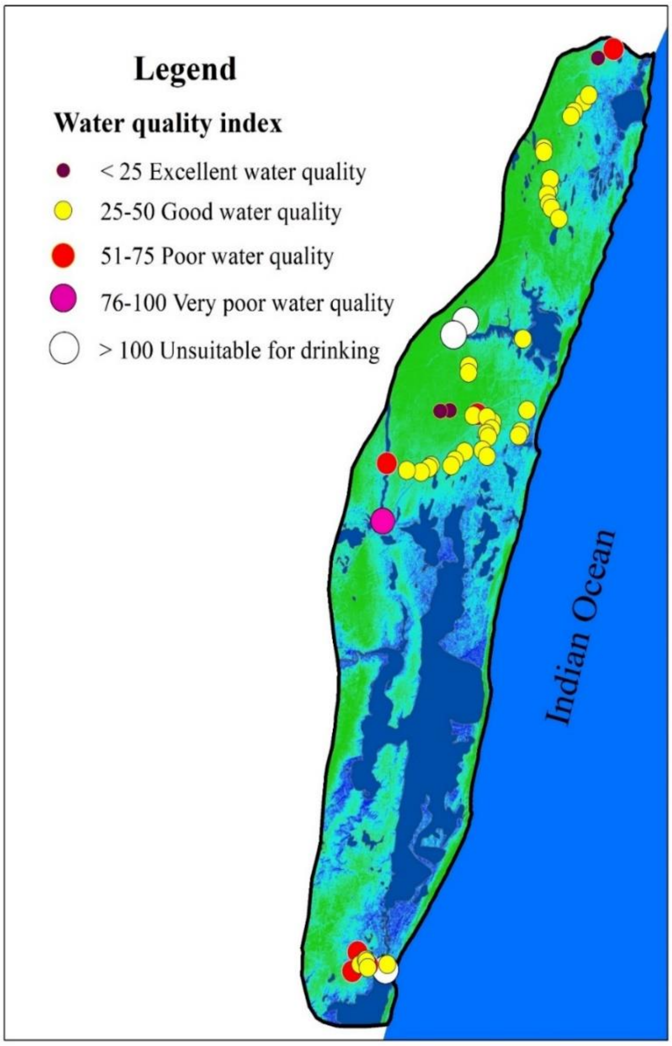

Figure 0.8: Results of groundwater quality assessment based on water quality index

5.5 Water quality criteria for irrigation purposes

Groundwater in this area is also used for irrigation purposes. It is important to evaluate the suitability of groundwater for irrigation purposes as poor irrigation water negatively impact crop yield as well as the quality of the soil. The significant parameters that affect the quality of water for irrigation usability are sodium adsorption ratio (SAR), sodium percent (Na%), Kelly's ratio (KR), permeability index (PI), magnesium hazard ratio (MHR) and residual sodium carbonate (RSC).

Sodium adsorption ratio (SAR) is usually used to represent the relative movement of Na^+ ions in the exchange processes with the soil medium. Replacement of adsorbed calcium and magnesium ions by sodium ions negatively affect the permeability of the soil as well as the soil structure (Gidey, 2018; Kumari and Rai, 2020). SAR is an important factor for understanding the permeability of the soil. Higher sodium concentration lowers the permeability of the soil. SAR was calculated by using the equation

$SAR = Na^{+}/ \sqrt{\ } (Ca^{2+} + Mg^{2+})/2$ (with all ionic concentrations expressed in meq/L) Eq.5.1

In the study area, the SAR value varied from 0.94 to 6.89 meq/L with an average value of 2.36 meq/L. Most of the samples are within permissible limits (<10). The highest SAR value of 6.89 meq/L is observed in sample location 14 falling in the zone of C3S1 with high salinity and low sodium (alkalinity) hazard. This water can be used only to irrigate semi-salt tolerant crops. Remaining samples (52) falling in the C1S1 and C2S1 zone are classified as good quality for irrigation.

Sodium percent (Na%) is one of the important parameter for classification of water for irrigation purposes. The presence of excess sodium in groundwater usually lowers the permeability of the soil and also hinders plant growth (Kumari and Rai, 2020). The sodium percentage (Na%) was calculated using the formula

$Na\% = (Na^{+} + K^{+}) / (Ca^{2+} + Mg^{2+} + Na^{+}+ K^{+}) \times 100$ Eq.5.2

(with all ionic concentrations expressed in meq/L)

In the study area, the calculated Na% in groundwater samples varied from 21.81 to 72.60 meq/L with an average value of 44.75 meq/L (Table 5.4). Except 6 samples, all the groundwater samples are within the permissible limits of < 60. Furthermore, detailed analyses show that 34% of the samples are classified as good (20-40), 55% are classified as permissible (40-60) while 11% are considered as doubtful (60-80). Further, Na% was plotted against EC as Wilcox diagram (Wilcox, 1955) (Fig. 5.9a), which clearly indicates that most of the samples are falling in the zone of excellent to good. Few samples (1,3, 14,21,52 &53) are falling in the permissible to doubtful zone. Excess usage and repeated use of groundwater in this area will increase the sodium percentage and cause reduction or lowering of permeability in the soil thereby hindering plant growth.

Table 0.4: Minimum, maximum, mean and standard deviation for irrigation indices.

	MHR	**%Na**	**PI**	**SAR**	**KR**	**RSC**
Min	7.62	21.81	12.93	0.94	0.28	-5.31
Max	64.11	72.60	469.60	6.89	2.65	0.81
Mean	38.60	44.75	84.66	2.36	0.92	-1.01
S.D	13.73574	12.35518	72.3405	1.18975	0.532144	0.84967

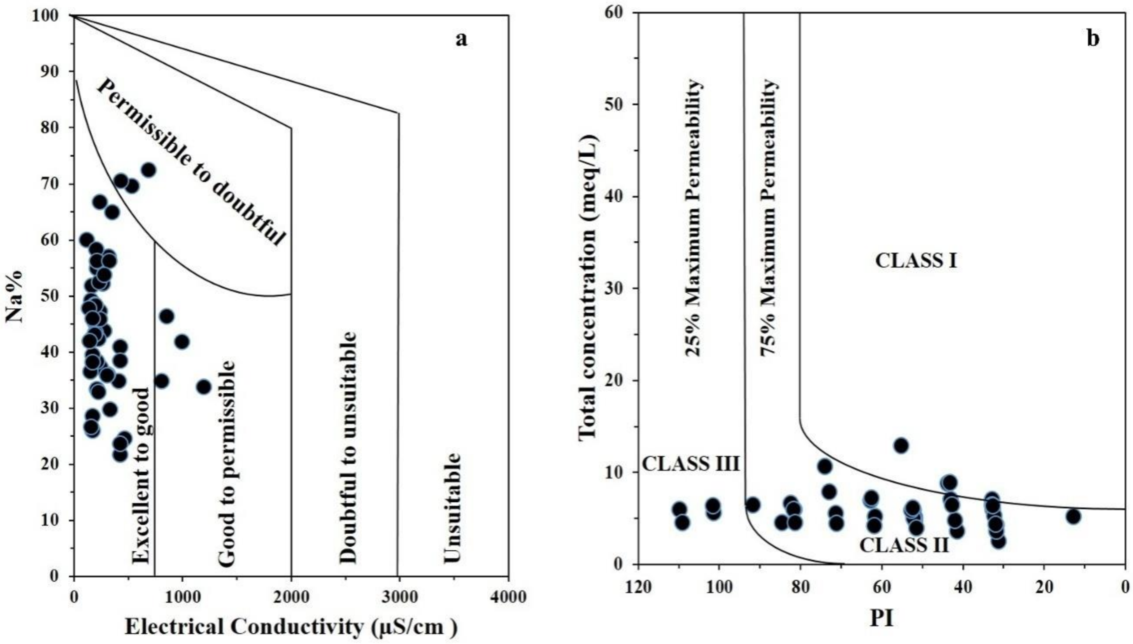

Figure 0.9: Groundwater quality assessment for irrigation based on a)Wilcox diagram and b) permeability index diagram

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

$PI= (Na^{+}+\sqrt{}HCO_3^{-} / (Ca^{2+}+Mg^{2+}+Na^{+}) \times 100$ Eq.5.3

(all ionic concentrations expressed in meq/L)

In the study area, the permeability index values varied from 12.93 to 469.60 meq/L (Table 5.4) with an average value of 84.66 meq/L.

Doneen model classification of irrigation water was classified based on the permeability index represented in (Fig. 5.9b). Class I represents excellent quality for irrigation, 8 % of the samples are falling under class I. 79% of the samples are falling under class II with 75% of maximum permeability. Approximately, 13% of the samples are falling under class III with only 25% of maximum permeability. About 38% of the samples in the study area are falling above the acceptable limits.

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

$KR = Na^{+} / (Ca^{2+} + Mg^{2+})$ Eq.5.4

(all ionic concentrations expressed in meq/L)

Kelly’s ratio above 1.0 in groundwater indicates excess of sodium which is not suitable for irrigation while the ratio less than 1.0 is suitable for irrigation. Kelly's ratio varied between 0.28 and 2.65 meq/L (Table 5.4) with an average value of 0.92 meq/L. About 70% of groundwater samples have KR values less than 1.0 suggesting they are suitable for irrigation purposes. The remaining 30% of the samples have KR values greater than 1.0 and hence are not suitable for irrigation purposes.

Magnesium hazard ratio (MHR) is another indicator used to classify the suitability of irrigation water. In general, calcium and magnesium maintain equilibrium in most water and in those equilibrium conditions magnesium in water will unfavourably impact the crop output (Nagaraju *et al*., 2006). MHR is computed by following equation

$MHR = 100 * (Mg^{2+} / (Ca^{2+} + Mg^{2+})$ Eq.5.5

(all ionic concentrations expressed in meq/L)

Magnesium hazard ratio greater than 50 is considered to be unsuitable for irrigation purposes while MHR below 50 is regarded as suitable for irrigation purposes. In the study area, MHR values varied between 7.62 to 64.11meq/L (Table 5.4) with an average value of 38.60 meq/L, respectively. Approximately 40 groundwater samples (78%) have MHR values less than 50 and are found to be suitable for irrigation purposes. About 11 groundwater samples (22%) have MHR values greater than 50 hence they are unsuitable for irrigation purposes.

Residual sodium carbonate (RSC) was used in order to assess the harmful effects of HCO_3 and CO_3 on the criterion of water quality for agricultural purposes. The RSC was calculated by using the formula

$RSC = (CO_3 + HCO_3 – (Ca + Mg))$ Eq.5.6

(all ionic concentrations are expressed in meq/L)

RSC values below 2.5 suggest that water is suitable for irrigation purposes while RSC values greater than 2.5 meq/L indicates that water is unsuitable for irrigation purposes. RSC values in groundwater varied from -5.31 to 0.81 meq/L with an average value of -1.01 meq/L (Table 5.4). It is observed that groundwater in the study area is suitable for irrigation purposes based on the RSC classification (Table 5.5). About 96 % of the samples recorded RSC values less than 0. It is clear that carbonate and bicarbonate are not the dominant anions and their values are lesser than calcium and magnesium.

Table 0.5: Classification of water quality indices based on irrigation purposes

Water quality indices	Range	Water class	% of groundwater samples
Sodium Adsorption Ratio (SAR)	<10	Excellent	100
	10-18	Good	-
	18-26	Doubtful	-
	>26	Unsuitable	-
Salinity hazard EC (µS/cm)	<250	C1-Excellent (low)	58
	250-750	C2-Good (medium)	34
	750-2250	C3-Permissible (low)	8
	>2250	C4-Unsuitable (Very high)	-
Sodium percent (Na%)	<20	Excellent	-
	20-40	Good	34
	40-60	Permissible	55
	60-80	Doubtful	11
	>80	Unsuitable	-
Magnesium Hazard Ratio (MHR)	<50	Suitable	79
	>50	Unsuitable	21
Permeability Index (PI)	Class 1	Good	8
	Class 2	75% of maximum Permeability	79
	Class 3	25% of maximum Permeability	13
Kelly's Ratio (KR)	<1	Suitable	70
	>1	Unsuitable	30
Residual Sodium Carbonate (RSC)	< 2.5	Suitable	100
	> 2.5	Unsuitable	-

5.6 Health risk assessment

The health risk assessment of trace elements in groundwater and its impact on the human health through different pathways were analysed. Hazard quotient for ingestion & dermal, hazard index of the trace elements and the types of hazard they pose for adult, children and infants were estimated. Direct ingestion and dermal absorption by skin for both adult, children and infants were studied (Zeng *et al*., 2015).

The hazard quotient and hazard index was calculated for adults, children and infants. The reference dose (RfD) for ingestion and dermal values used for this study is tabulated in Table.6. The hazard quotient (HQ) ingestion & dermal and hazard index (HI) for the samples of the study area (Table 5.6) clearly shows the hazard posed on the adults, children and infants. On analysis, some elements posed hazard from little to adverse effects. $HQ_{ingestion}$ values were below one in all age groups (adults, children and infants) for all trace metals (Fig. 5.10a), suggesting that these metals pose little hazard to local communities through the ingestion pathway. Regarding the dermal exposure pathway, for adults the HQ_{dermal} values for Co and Mn exceeded one (Fig. 5.10b). For children, HQ_{dermal} values for Co, Cd and Mn were above one. Regarding infants, trace metals such as As, Co, Cd, Mn and Pb had HQ_{dermal} values greater than one. This suggests that these trace metals pose serious to adverse health effects through the dermal exposure pathway on adults, children and infants, respectively. Likewise, the HI values for Co and Mn exceeded unity in adults (Fig. 5.10c). In children, HI values for Co, Cd and Mn was above one while As, Co, Cd, Mn and Pb was greater than one in infants. This further concludes that these metals pose serious non-carcinogenic health risk in adults, children and infants. HQ_{dermal} and HI values were higher in infants than children and adults, and it clearly indicates that the infants face higher non-carcinogenic health risk than the children and adults. The order of adverse health effect as per the hazard index is infant >children >adult. Similar results have been reported by several international researchers (He and Wu, 2019; He *et al*., 2019; Wu and Sun, 2016) wherein children and infants are at higher non-carcinogenic risk than adults.

Table 0.6: Hazard quotient and hazard index for trace elements

	(µg/kg/day)		Adult			Children			Infant		
Trace metals	**RfD Inges**	**RfD Derm**	**HQ Inges**	**HQ Derm**	**HI**	**HQ Inge**	**HQ Derm**	**HI**	**HQ Inge**	**HQ Derm**	**HI**
Al	1000	200	1.9E-05	2.5E-03	2.5E-03	1.4E-04	1.8E-02	1.9E-02	2.1E-04	5.4E-02	5.4E-02
As	0.3	0.285	1.5E-02	8.6E-02	1.0E-01	1.1E-01	6.4E-01	7.4E-01	1.6E-01	**1.9E+00**	**2.0E+00**
Co	0.3	0.2	3.6E-02	**1.9E+00**	**1.9E+00**	2.6E-01	**1.4E+00**	**2.0E+00**	3.9E-01	**4.1E+00**	**4.5E+00**
Cd	0.5	0.025	7.3E-05	1.5E-01	1.5E-01	5.3E-04	**1.1E+00**	**1.1E+00**	8.0E-04	**3.3E+00**	**3.3E+00**
Cu	40	12	1.4E-04	4.2E-02	4.2E-02	1.0E-03	3.1E-01	3.1E-01	1.5E-03	9.1E-01	9.1E-01
Fe	700	140	1.2E-05	2.2E-02	2.2E-02	8.4E-05	1.6E-01	1.6E-01	1.3E-04	4.7E-01	4.7E-01
Mn	24	0.96	1.8E-03	**4.0E+00**	**4.0E+00**	1.3E-02	**5.9E+00**	**5.2E+00**	2.0E-02	**8.2E+00**	**8.2E+00**
Pb	1.4	0.42	5.1E-04	7.5E-02	7.6E-02	3.6E-03	5.5E-01	5.6E-01	5.5E-03	**1.6E+00**	**1.6E+00**
Zn	300	60	5.7E-04	4.5E-02	4.6E-02	4.1E-03	3.3E-01	3.4E-01	6.3E-03	9.7E-01	9.7E-01

As concentration in the study area varied from 0.03 to 3.542 µg/l falling within the permissible limits. Similarly, high As concentration of 0.51 to 16.7 were reported in loess regions of china and in the waters of southern pampa, Argentina (Xiao *et al*., 2016; Currell *et al*., 2011). As concentration in groundwater is attributed to leaching or anthropogenic sources. As mobilisation in water can increase due to the high concentration of Na and low concentration of Ca (Currell *et al*., 2011). Further, the ORP data reveals that most of the samples have negative values, it clearly indicates that the groundwater in the study region is in reducing environment. Co concentration in groundwater varied from 0.007 to 4.572 µg/l and has a very high gastrointestinal absorption factor (ABS_g) of 40%. The HI of Co for adults varied from 0.008 to 4.5 with an average HI of 1.9. In case of children, the HI of Co varied from 0.05 to 6.8 with an average of 2.0 and in infants the HI of Co varied from 0.172 to 10.6 with an average of 4.5. The HI of manganese in adults varied from 0.03 to 7.1 with an average of 4.0. In children HI of Mn varied from 0.23 to 13.8 with an average of 5.2 and in infants, HI of Mn varied from 0.68 to 23.4 with an average of 8.2.

Exposure of As and Co in drinking water for a longer period may pose potential and adverse carcinogenic effects, hypertension, skin problems, neuropathy etc. Hence the local people including children and infants should be supplied with treated water / after removal of the trace elements.

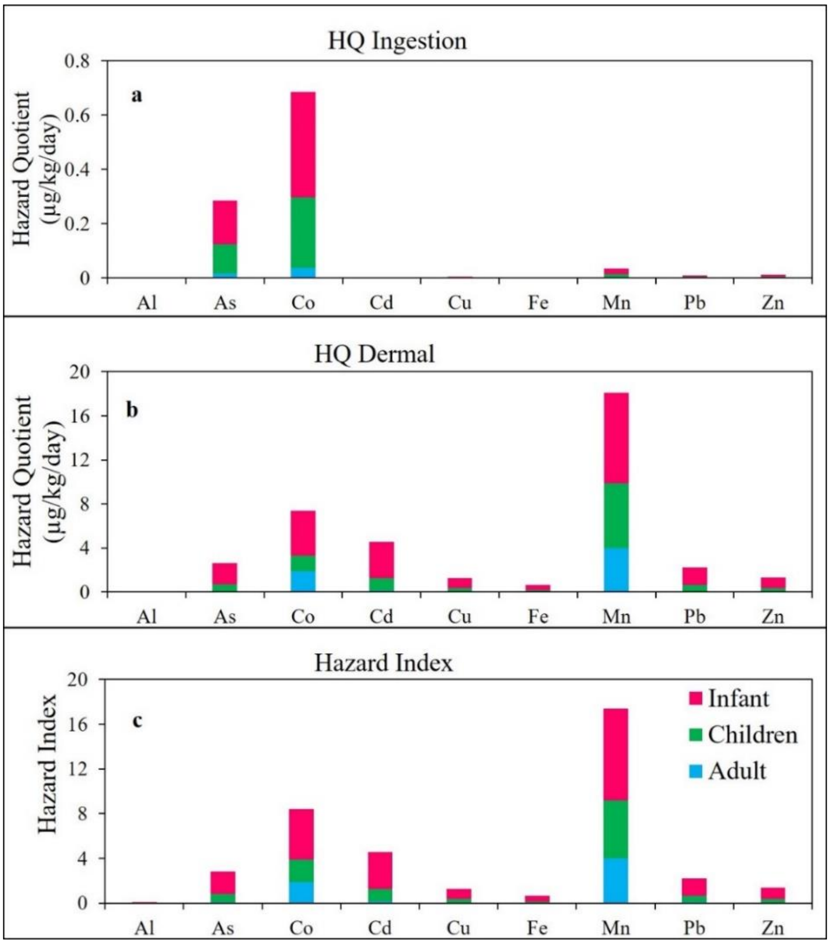

Figure 0.10: Hazard quotient (ingestion & dermal) and hazard index of the study area

Conclusion

Majority of the living population in this region largely depend on groundwater as the primary source. It is important to assess the water quality and the potential health risk as it directly have an impact on the health, socio-economic development and ecosystem. In order to assess the water quality of the Maputaland coastal aquifer, 53 groundwater samples were collected and twenty-nine physiochemical parameters were analysed. The geochemical characteristics of the ions and dissolved trace elements in the groundwater were studied using various interpolation, analytical & graphical methods to understand the suitability for drinking & irrigation purposes and to characterise groundwater quality by understanding the evolution of geochemical processes controlling the groundwater quality. Water quality index and health risk assessment model was applied. The following inferences were drawn from these studies;

- The groundwater is acidic to alkaline, soft to very hard in nature. Na followed by Ca is the major cation and Cl followed by HCO_3 is the major anion. The order of distribution of major ions is Na > Ca > Mg > K and Cl > HCO_3> SO_4> NO_3.The order of dominance of trace elements is Si>Zn>Al>Fe>Cu>Mn>Pb>Co>As>Cd. Fe, Mn, Al, Zn, and Pb were above the limits prescribed by DWAF and WHO in 19%, 13%, 6%, 4% and 2% of the groundwater samples.
- Rock-water interaction and Na/Ca ion exchange are dominant processes that control the groundwater chemistry of the study area. The suitability of irrigation water quality was measured based on EC, SAR, Na%, RSC,US salinity diagram, Kelly's ratio, Wilcox diagram and PI diagrams. Majority of the groundwater samples in the Maputaland region fall in the suitable range for irrigation purposes except in few locations that exceed permissible limits.
- Water quality index (WQI) was carried out to determine the suitability of water by assigning weight factor to major ions and trace metals based on its significance. The computed WQI of the study area varied from 18.9 to 157.1 with an average of 45.55. Most of the samples fall under excellent and good quality, while 22 % of the water samples fall under poor water quality and 2% of the samples fall under very poor water quality. Only 7 % of the samples are unsuitable for drinking which are spatially located on the western and southern part of the study region.
- On the basis of human health risk assessment, it is observed that infants are at higher risk than children and adults with respect to cobalt and manganese concentration in drinking water. Cobalt and manganese have HQ_{dermal} and HI values greater than 1 for infant, children & adult. Cadmium has HQ_{dermal} & HI values greater than 1 for children and infants. As and Pb have HQ_{dermal} & HI values greater than 1 for infants suggesting high non-carcinogenic health risk on infants Exposure of metals such as As and Co for drinking water purposes for a longer period may cause potential and adverse carcinogenic effects, hypertension, skin problems and neuropathy.
- The baseline chemical characteristic of the groundwater and its possible health risk has been determined. The drinking and irrigation water quality has been evaluated.
- This study suggest that water treatment/ water purification is required as the drinking water quality pose health risk to infants. The long-term monitoring of groundwater

quality and dissolved trace elements such as As, Co, Pb & Mn is required. Government and water managers should introduce rainwater harvesting and artificial recharge structures to improve the efficiency of groundwater resources in the study area.

- The results emanated from this preliminary study can be utilised in the future studies.

CHAPTER SIX

5. Hydrogeochemical processes and trace metal contamination in groundwater and health risk assessment

6.1 Introduction

In South Africa, water resources are scarce and unevenly distributed due to the spatial and temporal variability of rainfall the country receives (Smithers et al., 2017; Ndlovu and Demlie 2016, 2018). The country receives an annual average rainfall of about 497mm (Smakhtin *et al*., 2001). Various water quality issues have been reported in South Africa including salinization, eutrophication, microbiological contamination, sedimentation and silt migration, and acidification (DWAF, 2002). Approximately, two-thirds of South Africa's population depend on groundwater resources to meet their daily needs (Nel *et al*., 2009; Vetrimurugan *et al*., 2017b). Groundwater is the main source of water supply that caters the daily needs (drinking, domestic and agricultural activities) of inhabitants in rural communities in north-eastern KwaZulu Natal province. The chemical composition of groundwater is controlled by natural processes (e.g. rock-water interaction, evaporation, dissolution of minerals) and anthropogenic activities (e.g. industry, agriculture, mining and urbanization) (Barzegar *et al*., 2017; Etikala *et al*., 2019). Sound understanding of the hydrogeochemical processes that govern groundwater chemistry is crucial for better management and sustainable development of the available groundwater resources. The quality of water is directly linked to human health. Consumption of contaminated groundwater exposes people to various health issues. Approximately, 3.6% of deaths in a year are associated with water pollution in South Africa (Nel *et al*., 2009). Trace metal contamination remains the major threat to groundwater quality due to its toxicity even at low concentrations. These trace metals have been reported to threaten human health due to their persistent, non-biodegradable, stable and toxic nature in the natural environment (Tay and Hayford, 2016; Soleimani *et al*., 2020). It is therefore necessary to assess the risk to human health due to groundwater contamination. In this area, hydrogeochemical processes that control groundwater chemistry and health risk assessment have not been studied in detail. This chapter focuses on evaluating the hydrogeochemical processes, identifying sources of groundwater contamination and understanding of trace metal contamination and health risk assessment of groundwater using geochemical and geographic information system (GIS) methods. A total of

53 and 42 groundwater samples collected during 2018 and 2019 were considered in this chapter. Graphical techniques (Piper, Chadha diagrams) and scatter plots were used to understand the hydrogeochemical processes controlling groundwater chemistry of Maputaland coastal aquifer. Multivariate statistical analysis was also used to understand the relationship between variables and their sources. Health related risk associated with exposure to trace metals was determined using the concentration of a total of eleven trace metals including As, Cu, Pb, Co, Cd, Mn, Fe, Al and Zn during 2018 and Cu, Pb, Co, Cd, Mn, Fe, Zn, Cr and Ni for 2019, respectively

6.2 Analysis of physicochemical parameters

The statistical results of the physicochemical parameters in groundwater samples measured during 2018 and 2019 are summarised in Table 6.1. The measured groundwater pH values varied from 5.3 to 8.2 and from 7.9 to 8.3 with an average value of 6.5 and 8.0 during 2018 and 2019, respectively. Approximately 75% of the samples have a pH value of less than 7 in 2018 indicating the acidic nature of groundwater. In 2019, all the samples had pH greater than 7 suggesting alkaline conditions (Table 6.1). During 2018, about 53% of the samples had pH below the World Health Organisation (WHO) limit of 6.5 (WHO, 2011) and all the samples were within the WHO limit in 2019. The Department of Water Affairs and Forestry of South Africa (DWAF, 1996) prescribed a limit of 6.0 to 9.0 for pH (Table 6.1), 26% of the samples were below 6.0 during 2018 and all the groundwater samples were within this limit during 2019.

Table 5.1: Statistical parameters of analysed groundwater samples in comparison with WHO and DWAF standards

	2018 (N=53)		**2019 (N=42)**		**Permissible limits**	
Parameters	**Range**	**Average**	**Range**	**Average**	**WHO (2011)**	**DWAF (1996)**
Ph	5.28 - 8.23	6.50	7.9 - 8.3	8.0	6.5-8.5	6.0 - 9.0
EC (µS/cm)	115 - 1194	312	136 - 1450	402.3	1500	<700
Ca (mg/L)	4 - 154	27	5 - 97	21.9	200	<32
Mg (mg/L)	1.2 - 56	9.8	1.8 - 28	6.0	50	<30
Na (mg/L)	14 - 126	38	20 - 167	52.2	200	<100
K (mg/L)	0.5 - 15.1	2.8	1.3 - 18	4.5	12.0	<50

HCO_3 (mg/L)	18 - 312	70	10 - 258	71.2	Not specified	Not specified
Cl (mg/L)	27 - 289	82.64	30 - 297	79.8	250	<100
SO_4 (mg/L)	1.8 - 65	13.4	2.5 - 38	10.3	250	<200
F (mg/L)	BDL* - 1.1	0.2	-	-	1.5	<1.0
NO_3 (mg/L)	BDL - 18	2	2 - 112	14.1	45	<6
NH_4 (mg/L)	BDL - 0.2	0.0	-	-	Not specified	<1.0
PO_4 (mg/L)	BDL - 0.5	0.1	-	-	Not specified	Not specified
As (µg/L)	BDL - 3.6	0.5	-	-	10.0	<10.0
Ag (µg/L)	-	-	BDL - 13.4	3.4	Not specified	Not specified
Fe (µg/L)	2.7 - 770.8	88.9	23.1 – 20 843.2	1 521.9	300	<100
Mn (µg/L)	0.4 - 84.3	19.8	1 – 1 001.4	76	400	<50
Al (µg/L)	1.6 - 3052.5	90.0	0 – 71.1	3.2	900	<150
B (µg/L)	-	-	BDL - 245.5	53.9	2400	-
Zn (µg/L)	1.9 - 19 964.5	501.4	2.5 – 4 253.5	134.1	5000	<3000
Pb (µg/L)	0.2 - 22.1	1.8	0 – 36.5	20	10	<10.0
Ni (µg/L)	-	-	BDL - 9.3	1.7	70	Not specified
Cr (µg/L)	-	-	BDL - 8.4	4.3	50	<50
Cu (µg/L)	BDL - 279.5	19.2	0 – 199.6	20	2000	<1000
Cd (µg/L)	BDL - 0.2	0.0	0 – 4.6	3.5	3	<5
Co (µg/L)	BDL - 4.5	0.4	0 - 9	6	Not specified	Not specified
Li (µg/L)	300 - 6400	1.2	-	-	Not specified	Not specified
Sr (µg/L)	-	-	6.6 - 387.8	70.3	Not specified	Not specified

*BDL= below detection limit.

EC ranged from 115 to 1450 µS/cm and groundwater samples were found to be within the WHO limit. However, 8% and 17% of the samples exceeded the limit established by DWAF during 2018 and 2019 respectively. Total dissolved solids (TDS) computed from the EC ranged from 74 to 764 mg/L with an average of 200 mg/L during 2018 and from 87 to 928 mg/L with an average of 258 mg/L during 2019. Total hardness (TH) calculated from calcium and magnesium varied from 25 to 464 mg/L with a mean value of 107 mg/L during 2018 and from 20 to 355 mg/L with a mean value of 79 mg/L during 2019. Bivariate plot of TDS versus TH (Fig. 6.1a) (Vetrimurugan *et al.*, 2017a; Brindha *et al.*, 2017) showed that majority of the samples are freshwater type (i.e. TDS< 1000 mg/L) (Freeze and Cherry, 1979) with hardness ranging from moderate to very hard (Sawyer and McCarty, 1978). Groundwater based on TDS indicates that the samples are moving from fresh to brackish conditions (Fig. 6.1a).

6.3 Evaluation of hydrochemical facies

Hydrochemical facies are crucial in understanding the chemical reactions that take place within the aquifer. The Piper trilinear diagram depicts that Na-Cl is the dominant groundwater type (Fig. 6.1b). This is common in the coastal areas due to seawater intrusion. The physical area with Na-Cl water type had increased from 64% in 2018 to 95% in 2019 (Fig. 6.2a, b). Ca-HCO_3 groundwater type was also noticed. This usually indicates freshly recharging water.

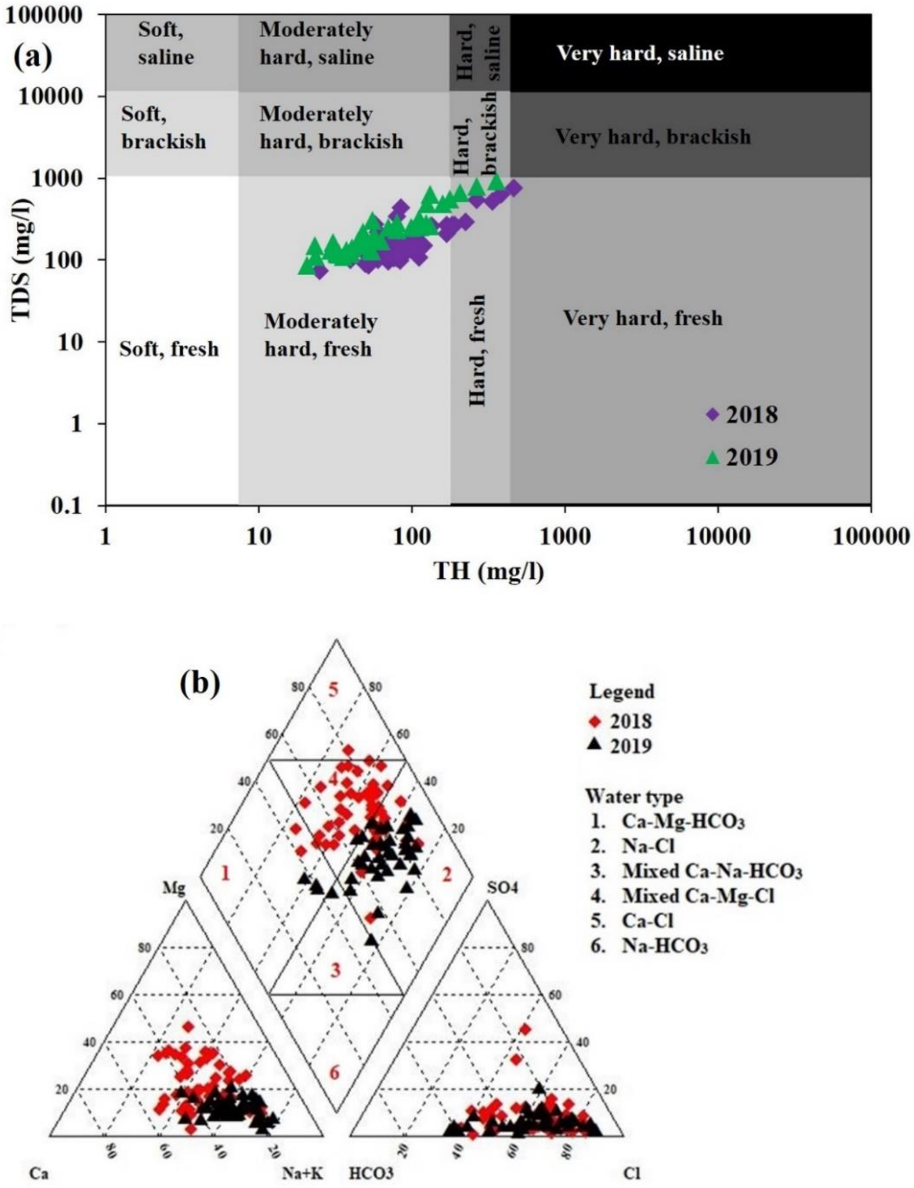

Figure 5.1: (a) Classification of groundwater based on TDS and TH, (b) Hydrochemical facies of groundwater samples

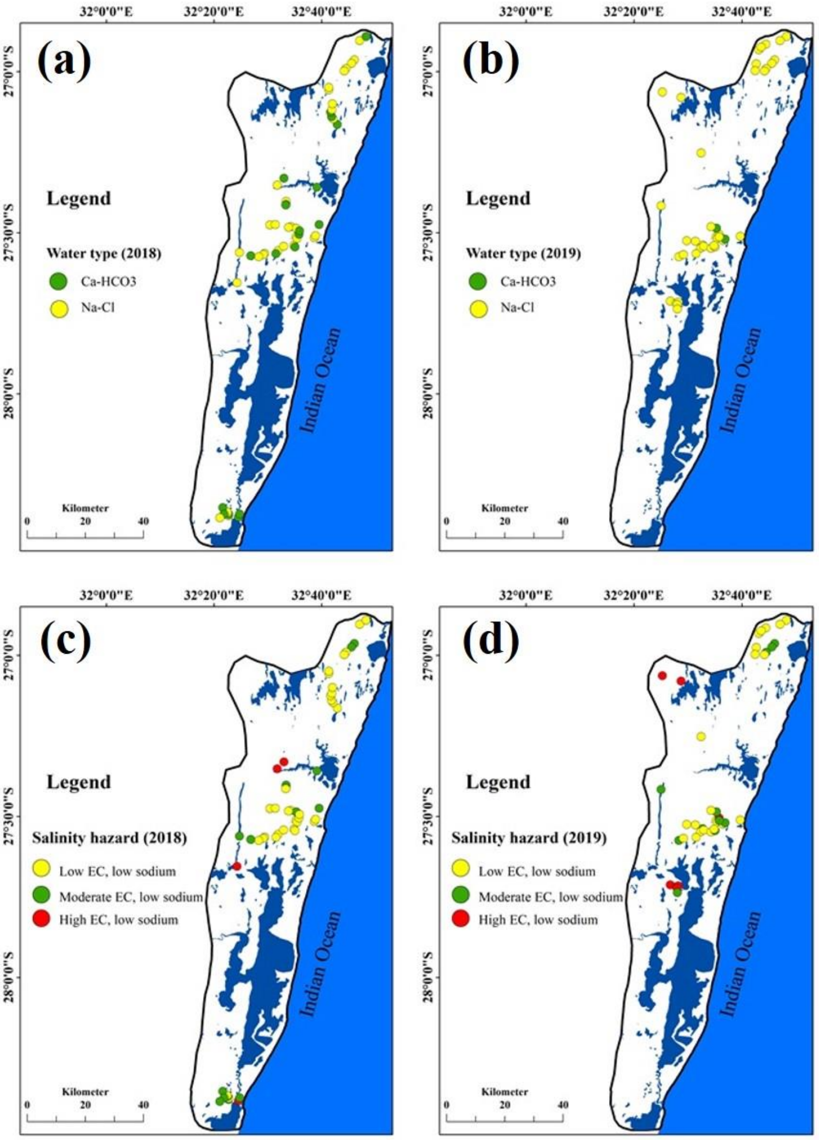

Figure 5.2: Spatial distribution map showing the hydrochemical facies of groundwater samples in (a) 2018, (b) 2019 and the sodium and salinity hazard of groundwater for irrigation use in (c) 2018 and (d) 2019

6.4 Major ion chemistry

Based on the mean concentration of the ions measured in groundwater, the dominant order of cations and anions were Na>Ca>Mg>K and Cl>HCO_3>SO_4 during 2018 and 2019. Sodium did not exceed the recommended limit by WHO (2011). About 8% (2018) and 14% (2019) of the samples exceeded the target water quality range established by DWAF (1996). Except for one location, potassium did not exceed the WHO limits in the study area during both sampling periods (Table 6.1). Calcium concentration was above DWAF (1996) limits in 10% and 24%

of the samples during 2018 and 2019 respectively. All the samples were found to be within the standard limit set by WHO and DWAF for magnesium during 2018 and 2019 except for one location which exceeded the limit during 2018. No limit has been set by DWAF and WHO for bicarbonate. A concentration of bicarbonate below 200 mg/L is regarded as safe for human health (Bhardwaj and Singh, 2011). Approximately 6% (2018) and 7% (2019) of the samples were found to have exceeded the limit. About 15% (2018) and 19% (2019) of the samples had chloride concentrations exceeding the limit recommended by DWAF while 2% (2018) and 2% (2019) of the samples were above the limit established by WHO. Sulphate was within limits throughout the study period.

As groundwater in the study area is used for irrigation purposes, sodium adsorption ratio was plotted against the EC and this information was used to group the irrigation water types. All the groundwater samples had low sodium hazard. Fig. 6.2c&d reveals that 55% and 66% of the groundwater samples fall in the C1S1 category during 2018 and 2019 respectively implying they are suitable for irrigation. About 29% and 26% of the samples fall in the C2S1 category during 2018 and 2019, which indicates medium salinity and low sodium hazard. The remaining 16% and 8% of the samples fall in the C3S1 category i.e. these samples possess high salinity and low sodium hazard and may only be suitable for salt-tolerant crops. The inverse distance weighted interpolation (IDW) method was used to prepare spatial distribution maps of few major ions (Fig. 6.3a-h). Significant positive correlation between the spatial variation in sodium and chloride concentration in groundwater is seen in Fig. 6.3a&e, and Fig. 6.3b&f. Similarly, calcium and bicarbonate concentrations were also high in the same areas (Fig. 6.3c&g, and Fig. 6.3d&h). In general, calcium and bicarbonate predominate in freshwater while seawater is dominated by sodium and chloride. Silicate weathering and dissolution of carbonate minerals increases the concentration of bicarbonate in groundwater (Elango *et al*., 2003; Umarani *et al*., 2019). High bicarbonate concentration in this study may be owed to the weathering of silicate rich sands of the KwaMbonambi and Kosi Bay Formations observed in the study area (Demlie *et al*., 2014). The high values of these four major ions in similar locations suggests that they may be due to seawater intrusion and weathering processes . Western and southern parts of the area usually had higher concentration of all the ions. Temporally, the salinity had increased between 2018 and 2019.

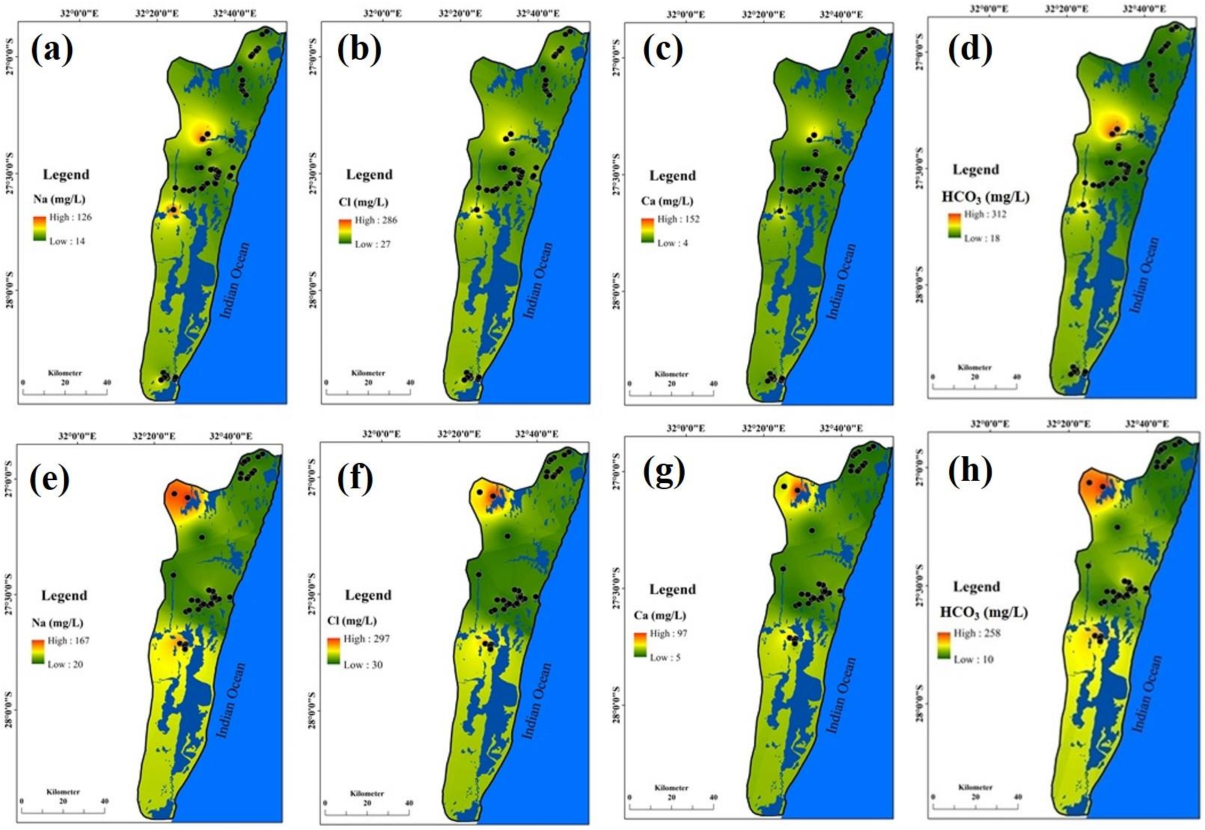

Figure 5.3: Spatial distribution maps for concentrations of major ions in groundwater during 2018 (a-d) and 2019 (e-h)

6.5 Geochemical processes

Groundwater chemistry data was used to identify the geochemical processes and mechanisms in the aquifer.

6.5.1 Rock weathering

Weathering and dissolution processes were identified through various bivariate plots. Fig. 6.4a, b indicates that groundwater chemistry is largely controlled by silicate weathering and evaporation dissolution. The scatter plot of Ca+Mg vs total cations (TC) (Fig. 6.4c) shows that all the samples are plotted below the 1:1 equiline with a strong positive correlation of 0.89 and 0.91 during 2018 and 2019 suggesting that these ions in groundwater are due to the silicate weathering process. The plot of Na+K vs TC (Fig. 6.4d) shows that most samples fall below and closer to the 1:0.5 equiline with a linear trend of 0.76 and 0.94 during 2018 and 2019, respectively. This infers that silicate weathering contributes to the occurrence of Na and K ions in groundwater of this area (Stallard and Edmond, 1983).

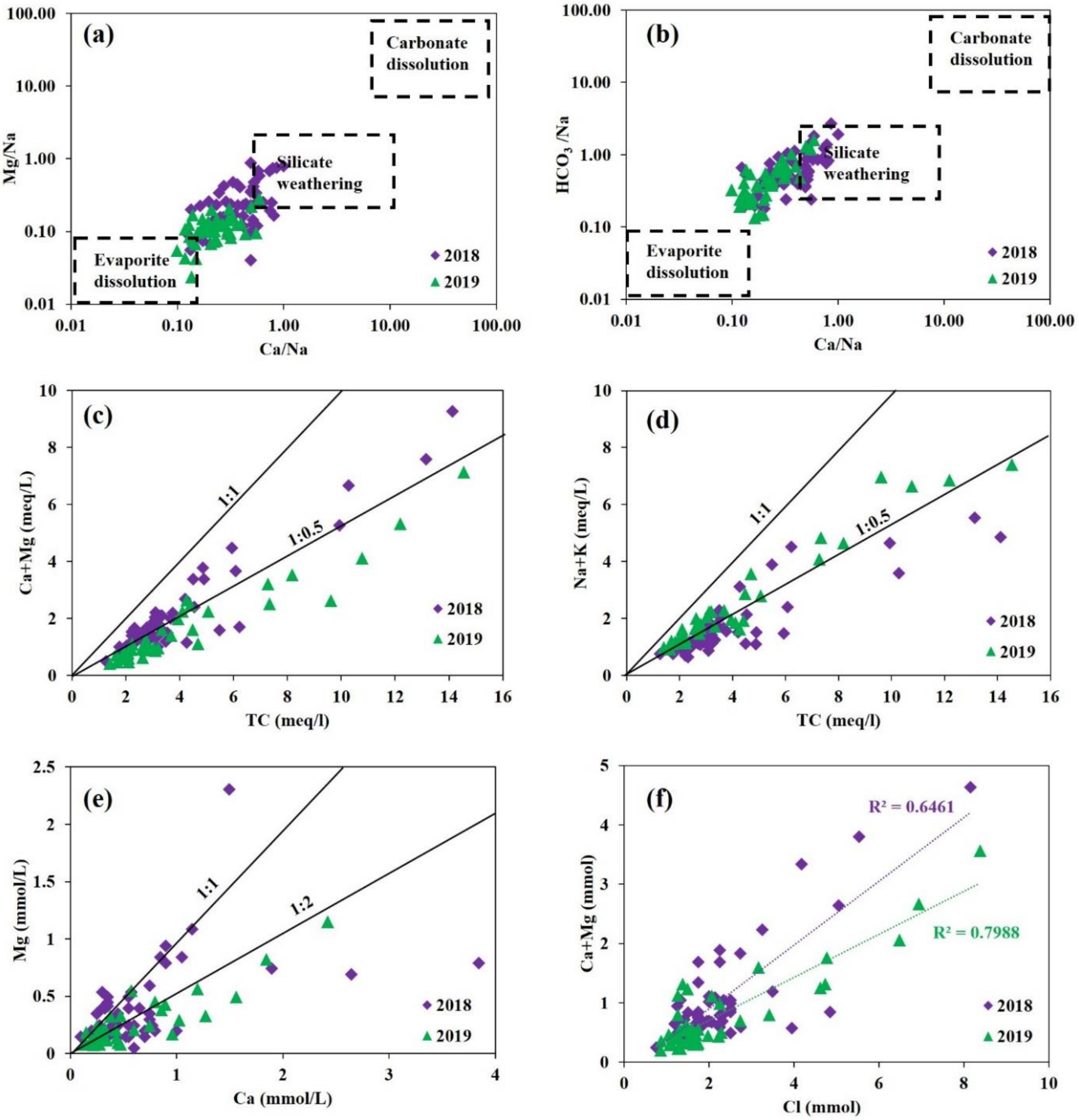

Figure 5.4: Plot of (a) Mg/Na vs Ca/Na, (b) HCO_3/Na vs Ca/Na, (c) Ca+Mg vs TC (d) Na+K vs TC (e) Mg vs Ca and (f) Ca+Mg vs Cl

6.5.2 Ion-exchange

The molar ratio of Ca/Mg is useful in explaining the dissolution of dolomite and calcite. Ca/Mg molar ratio equal to 1 is indicative of dissolution of dolomite (Barzegar *et al*., 2018a). Molar ratio between 1 and 2 reflects calcite dissolution whereas a molar ratio above 2 suggests dissolution of silicate minerals (Paul *et al*., 2019). In this study, the molar ratio of Ca/Mg varied from 0.6 to 12.1 during 2018 and from 0.8 to 5.7 during 2019. Few samples had a molar ratio equal to 1 implying dolomite dissolution. About 42% and 40% of the samples were between 1 and 2 during 2018 and 2019 indicating calcite dissolution. In total, 95% of the samples were greater than 2 suggesting the dissolution of silicate minerals. Fig. 6.4e also shows that most of the samples are plotted between 1:1 and 1:2 line indicating the dissolution of silicate minerals and dissolution of calcite.

Rajmohan and Elango (2004) conveyed that salinity increases with an increase in Ca+Mg and with a decline in Na/Cl ratio as a result of the reverse ion exchange process in the clay or weathered layer. The relationship between Ca+Mg vs Cl (Fig. 6.4f) shows that Ca+Mg increases with an increase in salinity (Zaidi *et al.*, 2015) which is attributed to the reverse ion exchange process that is explained by the following reaction;

$$2Na^{+} + Ca\ (Mg)\ Clay \leftrightarrow Na - Clay + Ca^{2+}\left(Mg^{2+}\right) \qquad \text{Eq.6.1}$$

In a plot of sodium vs chloride, the source of sodium and chloride is explained by halite dissolution if sample points fall along the 1:1 equiline (Iqbal *et al.*, 2018; Zaidi *et al.*, 2015). A Na/Cl ratio above one is indicative of the silicate weathering process (Mayback, 1987). In this study, the sodium vs chloride scatter plot revealed that the majority of the samples fall above the 1:1 equiline (Fig. 6.5a). The excess chloride in groundwater is owed to the cation exchange process. The relationship between sodium vs calcium showed an enrichment of sodium over calcium (Fig. 6.5b) explaining the ion exchange processes (Karroum *et al.*, 2017). Reduction of sodium with respect to chloride and depletion of calcium with respect to sodium suggests that the cation exchange process controls the groundwater chemistry (Thirumurugan *et al.*, 2018). The scatter diagram of Na/Cl vs Cl in Fig. 6.5c shows that in majority of the groundwater samples, the Na/Cl ratio increases with a decrease in chloride concentration and vice versa. This implies that the sodium and chloride concentrations in groundwater of this area are governed by cation exchange processes (Vetrimurugan *et al.*, 2019). Ca/SO_4 ratio closer to the 1:1 line suggests gypsum dissolution is the source of calcium and sulphate in groundwater (Kuldip *et al.*, 2011). Fig. 6.5d shows a scatter plot of calcium vs sulphate which revealed that the majority of the samples fall below the 1:1 equiline. This excess of calcium over sulphate in groundwater suggests that calcium is derived from the dissolution of gypsum.

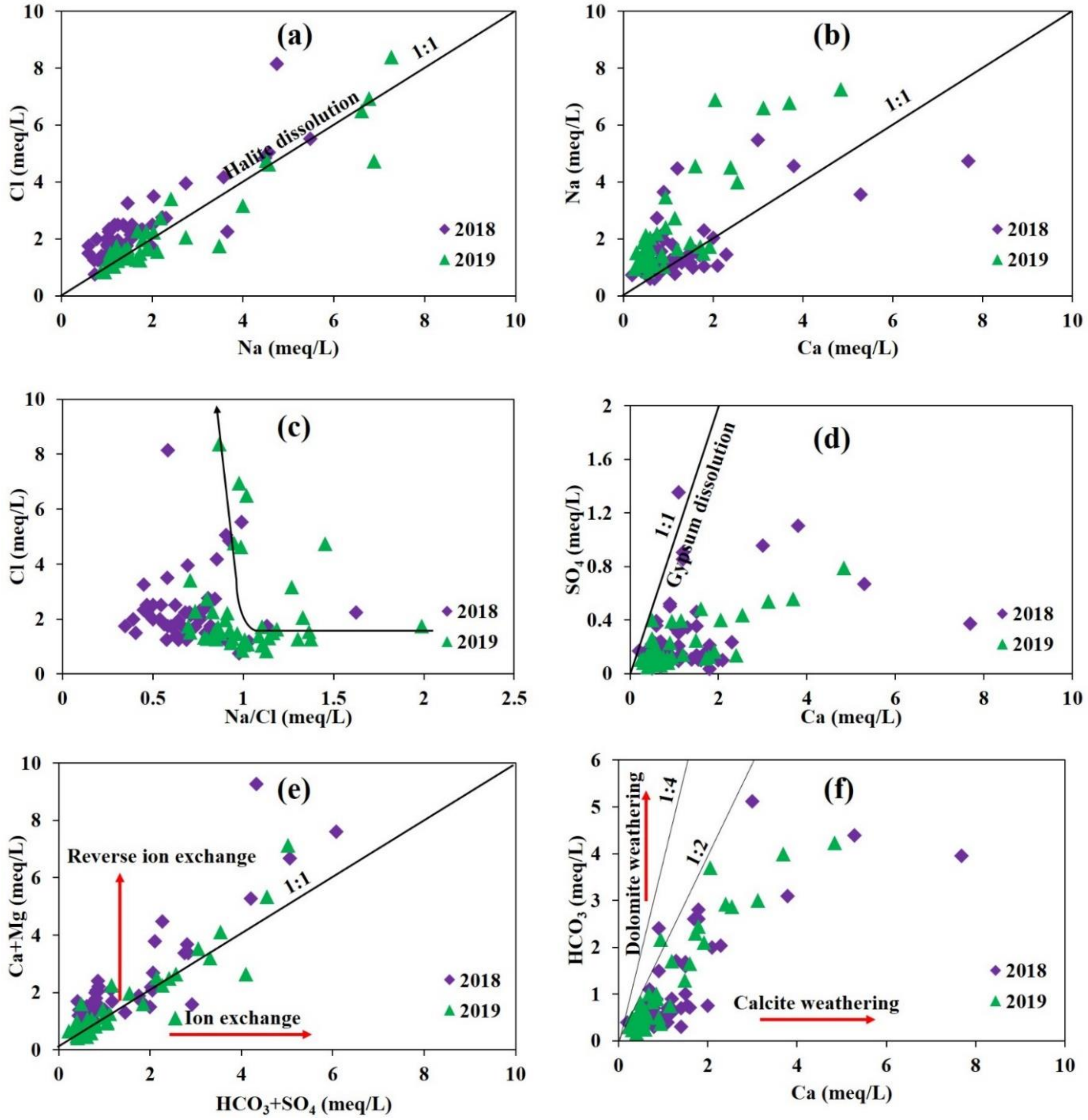

Figure 5.5: Plot of (a) Na vs Cl, (b) Ca vs Na, (c) Na/Cl vs Cl, (d) Ca vs SO$_4$, (e) HCO$_3$+SO$_4$ vs Ca+Mg and (f) Ca vs HCO$_3$

The plot of Ca+Mg vs HCO$_3$+SO$_4$ (Fig. 6.5e) is used to determine the ion exchange process. The 1:1 equiline indicates the dissolution of gypsum, calcite, and dolomite (Paul *et al*., 2019). If sample points are plotted below the 1:1 line (excess HCO$_3$+SO$_4$), it means that ion exchange is the dominant process controlling groundwater chemistry, and samples falling towards Ca+Mg are indicative of the reverse ion exchange. It is depicted that the majority of the samples are plotted along and above the 1:1 line indicating that the enrichment of Ca+Mg is owed to the reverse ion exchange process. The 1:2 ratio between calcium and bicarbonate suggests that calcium and bicarbonate are derived from calcite weathering whereas a 1:4 ratio is indicative of dolomite weathering. The scatter plot of calcium vs bicarbonate revealed that the majority of the samples fall below and closer to the 1:2 line during 2018 and 2019 suggesting the contribution of calcite weathering on groundwater chemistry (Fig. 6.5f).

Schoeller (1965) proposed chloro-alkaline indices (CAI 1 and CAI 2) to identify base ion exchange processes governing groundwater chemistry. The CAIs were computed by the equation;

$$CAI\ 1 = \left[Cl - \left(Na + K\right)/Cl\right] \tag{Eq.6.2}$$

$$CAI\ 2 = \left[Cl - \left(Na + K\right)\right]/\left[Cl + HCO_3 + SO_4 + NO_3\right] \tag{Eq.6.3}$$

A positive CAI is indicative of reverse ion exchange between sodium and potassium in groundwater with calcium and magnesium in the aquifer material. Ion exchange is shown by a negative index which suggests an exchange of sodium and potassium in the aquifer matrix and calcium and magnesium in groundwater. CAIs can also be used to determine the origin of bicarbonate in groundwater. Positive values of CAIs suggest the weathering and the dissolution of silicate minerals and negative values represent dissolution of carbonate minerals. In this study, approximately 94% (2018) and 48% (2019) of the samples were positive for both CAI 1 and CAI 2. Fig. 6.6a shows that reverse ion exchange is the major process governing groundwater chemistry during 2018 while ion exchange is dominant during 2019. Bicarbonate in groundwater results from the weathering and dissolution of silicate minerals during 2018 and by dissolution of carbonate minerals in 2019.

Chadha diagram (Chadha, 1999) was used to comprehend the geochemical processes that influence the chemistry of groundwater (Brindha *et al.*, 2014). It is expressed as the difference between alkaline earths (Ca+Mg) and alkali metals (Na+K) and the difference between weak acids (CO_3+HCO_3) and strong acids (Cl+SO_4) in milliequivalent percentage. Fig. 6.6b, it is depicted that majority of the samples fall in the field of reverse ion exchange and the seawater type during 2018 and 2019, respectively. This further supports that reverse ion exchange and seawater intrusion are the dominant processes in the study area.

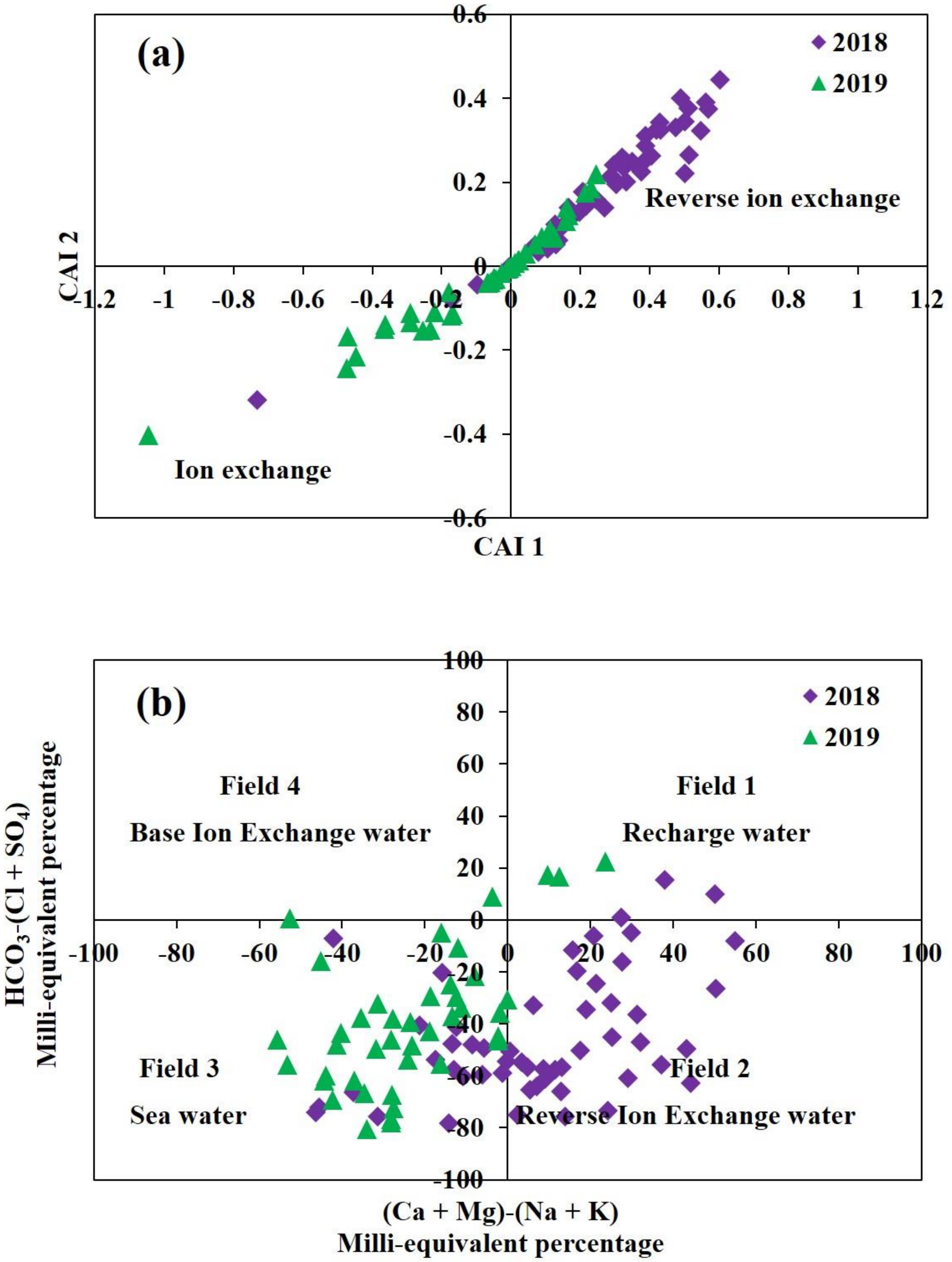

Figure 5.6: (a) CAIs indicating base ion exchange processes in groundwater, (b) Chadha diagram showing hydrogeochemical processes in groundwater

6.6 Impact of seawater intrusion

The Na/Cl molar ratio vs Cl is commonly used to evaluate the influence of seawater into groundwater (Abu-alnaeem *et al*., 2018; Seddique *et al*., 2019; Telahigue *et al*., 2018; Tiwari *et al*., 2019). Values closer to the seawater ratio (0.86) suggest that groundwater is contaminated by seawater. In this study, the Na/Cl ratio varied from 0.3 to 1.6 with an average of 0.7 during 2018 and from 0.7 to 2 with an average value of 1 during 2019. Approximately 6% (2018) and 10% (2019) of the samples fall closer to the seawater ratio due to saline water mixing (Fig. 6.7a). The remaining samples are plotted below and above the seawater ratio suggesting that groundwater is influenced by saline water and anthropogenic activities. The Cl/HCO$_3$ ratio is widely used to examine groundwater salinization due to mixing with seawater (Chidambaram *et al*., 2018; Kanagaraj *et al*., 2018). The Cl/HCO$_3$ ratio can be classified into three categories; unaffected (<0.5), slightly or moderately affected (0.6-6.6), and strongly affected (>6.6) by salinization process (Chidambaram *et al*., 2018). In this study, the Cl/HCO$_3$ ratio varied from 0.7 to 8.3 with an average of 3.02 during 2018 and from 0.6 to 10.7 with an average value of 3.1 (Fig. 6.7b).

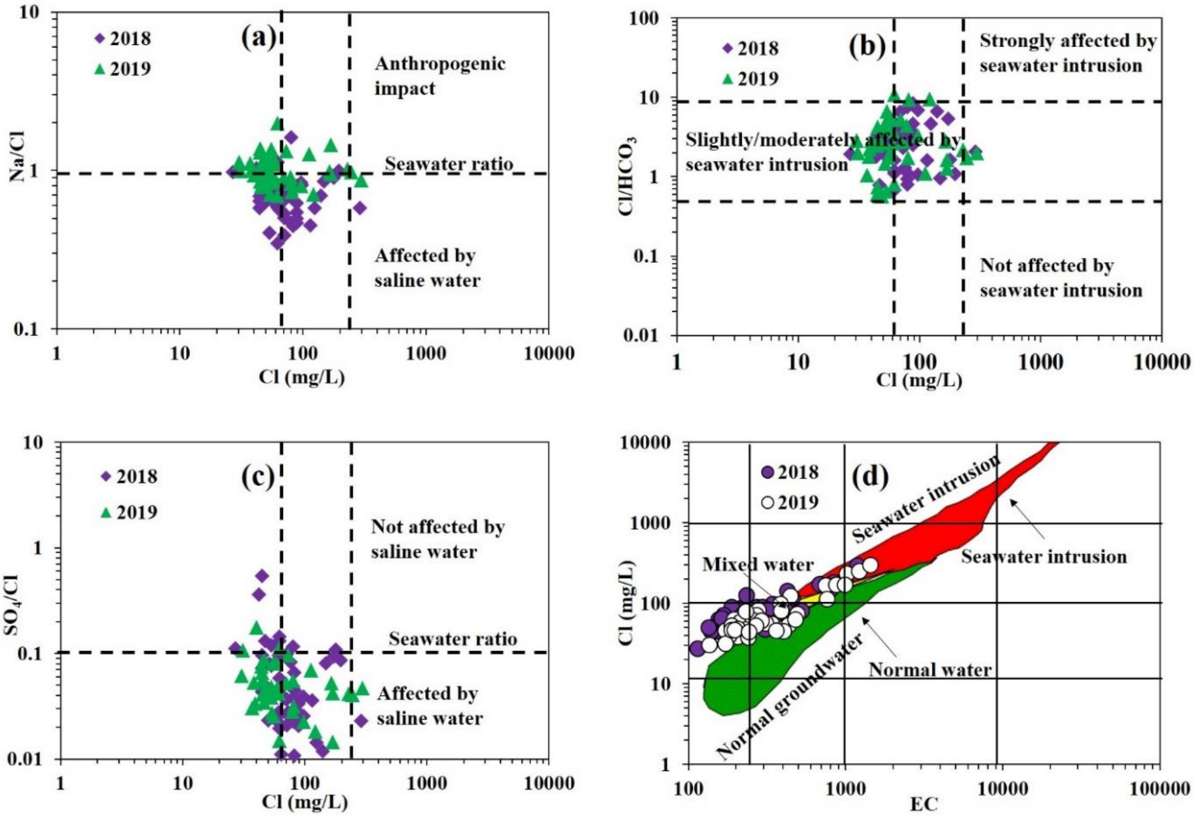

Figure 5.7: Plots explaining the seawater intrusion (a) Na/Cl vs Cl, (b) Cl/HCO$_3$ vs Cl, (c) SO$_4$/Cl vs Cl and (d) Cl vs EC

A plot of SO$_4$/Cl vs Cl with values above 0.1 implies that groundwater is not affected by seawater and samples with values below 0.1 are affected by seawater intrusion (Kanagaraj *et al*., 2018). About 23% (2018) and 10% (2019) of the samples had SO$_4$/Cl values greater than 0.1 suggesting that they are not contaminated by seawater while 77% (2018) and 90% (2019)

of the samples were below 0.1 indicating the influence of seawater intrusion (Fig. 6.7c). Most of the groundwater samples were slightly or moderately affected by seawater intrusion. The scatter diagram of EC vs chloride indicates that the majority of the samples fall in the mixed and few in the seawater zone during 2018 and 2019 (Fig. 6.7d).

6.7 Seawater mixing index

The seawater mixing index (SMI) which was established by Park *et al.* (2005) is widely employed to identify seawater mixing based on four major ions such as Na, Mg, Cl and SO_4 (Vetrimugan *et al*. 2017a; Kanagaraj *et al*. 2018; Seddique *et al*. 2019). It is computed using the following equation;

$$SMI = a * \frac{C_{Na}}{T_{Na}} + b * \frac{C_{Mg}}{T_{Mg}} + c * \frac{C_{Cl}}{T_{Cl}} + d * \frac{C_{SO_4}}{T_{SO_4}} \qquad \text{Eq.6.4}$$

Where the constants a, b, c and d represent the relative concentration proportions of the four major ions in seawater with Na (a= 0.31), Mg (b= 0.04), Cl (c= 0.57) and SO_4 (d= 0.08). C is the measured concentration of ions in mg/L and T is the regional threshold value. Cumulative probability curves plotted against log concentration of ions is used to estimate the regional threshold values of the ions. Regional threshold values estimated in this study are indicated by the inflection points in Fig. 6.8a-d. Regional threshold values such as Na= 53 mg/L, Mg= 20 mg/L, Cl= 97 mg/L and two inflection points were identified as 3 and 19 mg/L for SO_4 during 2018 and Na= 80 mg/L, Mg= 14 mg/L, Cl= 121 mg/L and SO_4 was 4 and 23 mg/L during 2019. In this study, the highest value of the inflection point was chosen for SO_4, i.e. 19 and 23 mg/L for 2018 and 2019. A SMI value greater than one suggests the impact of seawater mixing with fresh water. In this study, the SMI varied from 0.3 to 2.5 during 2018 and from 0.3 to 2.3 during 2019. About 15% and 14% of groundwater have a SMI above one during 2018 and 2019, respectively. This suggests that groundwater chemistry is influenced by mixing with saline water.

6.8 Nutrients

Nitrate occurs naturally at very low concentrations in groundwater and is regarded as an important plant nutrient. Common sources of nitrate in groundwater are from inorganic fertilizers and manures, wastewater disposal on land for irrigation, and oxidation of nitrogenous waste products in human or animal excreta (He *et al*., 2020). In this study, nitrate ranged up to 112 mg/L with an average of 2 and 14 mg/L during 2018 and 2019, respectively. The nitrate concentration in groundwater has increased in 2019 at two locations which is due to anthropogenic sources such as the application agricultural fertilizers This led to nitrate concentrations exceeding the WHO limit in 5% of the locations. Nitrate contamination is usually associated with shallow groundwater (He *et al*., 2020). Still and Nash (2002) reported that pit latrines and public water points have been observed to influence nitrate concentrations in groundwater of Maputaland. This may also be another reason for an increase in nitrate concentration in groundwater of the study area.

Natural levels of ammonia in groundwater are usually below 0.2 mg/L (WHO, 1996). However, elevated concentrations are indicative of bacterial, sewage, and animal waste pollution. In this study, ammonia ranged from 0 to 0.2 mg/L. Phosphate is another essential element for plant life. In the study area, it ranged up to 0.5 mg/L with an average of 0.1 mg/L. Both ammonia and phosphate were in low concentrations and were not a threat to groundwater quality (Table 6.1). Sources of phosphate include decomposition of rocks and minerals, agricultural runoff, sewage, industrial runoff, aquaculture activities, etc. (Vetrimurugan *et al*., 2013, 2017c; Sharma and Bhattacharya, 2017).

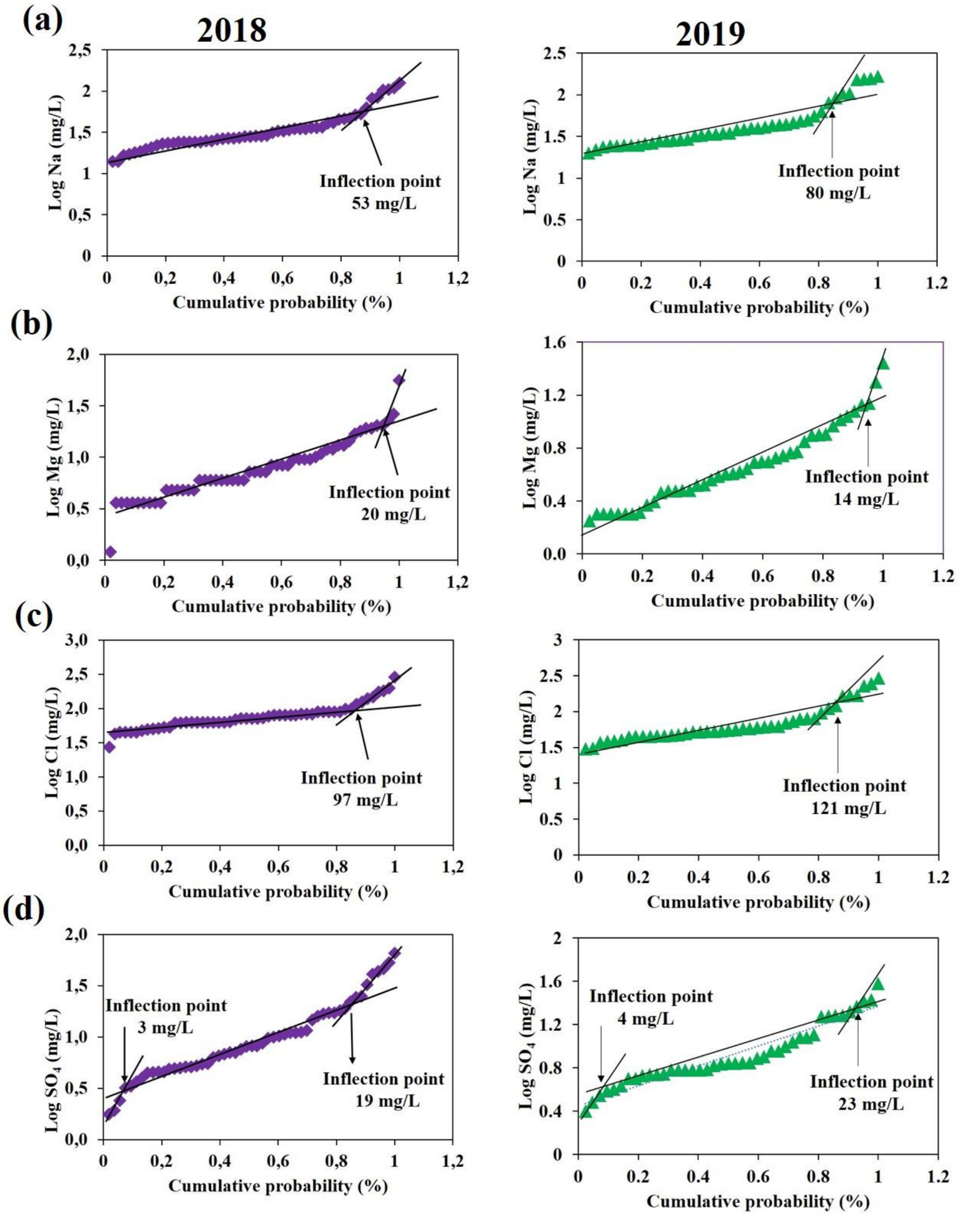

Figure 5.8: (a-d) Cumulative probability distribution during 2018 and 2019

6.9 Trace metals in groundwater

The concentrations of analysed trace metals are summarised in Table 6.1. A total of ten and thirteen trace metals were analysed during 2018 and 2019, respectively. Trace metals such as As, Ag, B, Ni, Cr, Cu, Cd and Co recorded minimum values below detection limit in some sample locations. Based on the mean concentrations of the trace metals in groundwater, they were found in the following order during 2018: Zn>Li>Al>Fe>Mn>Cu>Pb>As>Co>Cd and the following descending order during 2019:

Fe>Zn>Mn>Sr>B>Pb>Cu>Co>Cr>Cd>Ag>Al>Ni. Iron in groundwater of this area was found to have exceeded the DWAF limit in 19% and 48% of the samples during 2018 and 2019, respectively. Likewise, 9% and 24% of the samples were found to have exceeded the WHO limit during 2018 and 2019, high iron content resulting from the leaching of iron-rich sediments (Demlie *et al.*, 2014). Concentrations of manganese were found to be above the standard limit proposed by DWAF in 13% and 26% of the samples during 2018 and 2019. Likewise, manganese concentration exceeded the WHO standard limit in 7% of the samples during 2019. About 6% and 2% of the samples had aluminium concentrations above the limit established by DWAF and WHO for drinking water during 2018 while all the samples were within the limit during 2019. The concentration of zinc in groundwater was found to have exceeded the DWAF and WHO standard limit in 4% and 2% of the samples during 2018. Approximately 2% of the samples had zinc in groundwater above the DWAF limit during 2019. Lead in groundwater of this area was above the limit of DWAF and WHO in 2% and 86% of the samples during 2018 and 2019, respectively. The concentration of cadmium in groundwater of this area was found to be within the DWAF/ WHO limits during 2018. However, 86% of the samples had cadmium concentration above the limit of 3µg/L proposed by WHO during 2019. Contents of copper, arsenic, boron, chromium, and nickel were found to be below the established WHO and DWAF standard values. The Mbazwana landfill lying within the study area is used for the disposal of domestic wastes and garden refuse. Hence, landfill, and seawater intrusion use of agricultural fertilizers may be the source of high trace metal concentrations in groundwater of this area. The difference noticed between the results of the two years owed to the increased contribution of these processes in groundwater of the area during 2019.

6.10 Anthropogenic activities

Subsistence farming and commercial forestry plantations are widely practised in the study area. The plot of HCO_3 vs TC is used to evaluate the influence of anthropogenic activities on groundwater quality. Samples plotting on the 1:1 line are indicative of the dominance of the dissolution of silicates and carbonates. Sample points plotted below the 1:1 line suggest the influence of anthropogenic activities. Fig. 6.9a reveals that all the samples are plotted below the 1:1 line. This indicates the influence of anthropogenic activities such as waste disposal and agricultural activities on the groundwater of this area. The plot of TDS vs NO_3+Cl+SO_4/HCO_3 was also employed to further evaluate the contribution of anthropogenic activities (especially from agricultural activities) on groundwater chemistry. A high correlation between NO_3+Cl+SO_4/HCO_3 and TDS is attributed to the use of agricultural fertilizers (Barzegar *et al.*, 2018a). Fig. 6.9b shows a strong correlation of R^2 =0.96 (2018) and R^2 =0.99 (2019). These further reveal that groundwater chemistry in the study are is impacted by agricultural activities which mainly results from excessive application of fertilizers. This could also be the source for the presence of trace metals in groundwater due to the use of agrochemicals in the farming land.

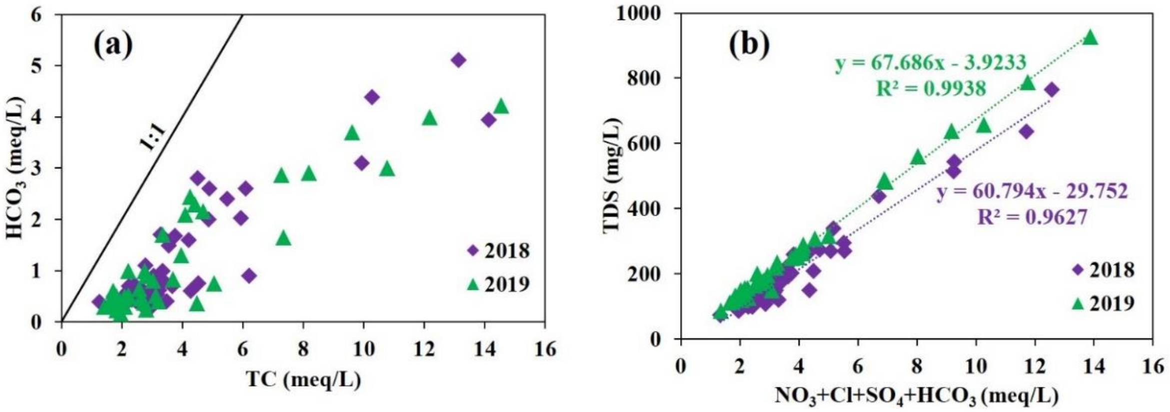

Figure 5.9: Plot of (a) HCO_3 vs TC and (b) TDS vs NO_3+Cl+SO_4/HCO_3

6.11 Correlation matrix

The correlation matrix was used to evaluate the interrelationship between parameters. Values >0.7 indicate a strong positive correlation, values between 0.5 and 0.7 indicate moderate correlation, and values between 0.5 and 0.3 indicate a weak correlation. The correlation matrix of measured variables is outlined in Table 6.2. Strong and moderate correlations between EC and most major ions. The strong positive correlation of EC with the other major ions suggests that the major processes controlling the groundwater chemistry of this area are ion exchange and seawater intrusion. Hence, these ions contribute to groundwater salinity. The strong correlation between sodium and chloride is indicative of a common source of origin which is from excessive evaporation process, dissolution of halite rock, and anthropogenic activities. Calcium strongly correlates with chloride and bicarbonate during 2018 and showed strong correlation with magnesium (r= 0.9), chloride (r= 0.9), bicarbonate (r= 0.9), sulphate (r= 0.8) during 2019. The strong correlation between calcium and bicarbonate indicates that calcite dissolution is a possible source of calcium in groundwater of this area (Barzegar *et al.*, 2017).

The good correlation between calcium and magnesium is owed to the dissolution of calcium-magnesium bearing minerals such as calcite, aragonite, dolomite, and clays (Papazotos *et al.*, 2019). The strong correlation between calcium and sulphate suggests a contribution from sulphate minerals such as gypsum (Soltani *et al.*, 2017; Esmaeili *et al.*, 2018) and correlation between calcium and chloride is indicative of the reverse ion exchange process. Chloride showed strong positive correlation with bicarbonate (r= 0.81) during 2018 and a strong correlation with bicarbonate (r= 0.78) and sulphate (r= 0.79) during 2019. The high chloride concentration when compared to sulphate suggests sulphate reduction (Elango *et al.*, 2003) (Table 6.2).

Table 5.2: Correlation matrix of groundwater quality variables during 2018 and 2019

2018	***pH***	***EC***	***Na***	***K***	***Ca***	***Mg***	***Cl***	***HCO_3***	***SO_4***	***NO_3***
pH	1									
EC	0.32	1								
Na	0.22	**0.91**	1							
K	0.04	0.18	0.29	1						
Ca	0.19	**0.85**	**0.65**	0.04	1					
Mg	0.10	**0.64**	**0.50**	-0.05	0.49	1				
Cl	0.10	**0.90**	**0.87**	0.26	**0.82**	0.49	1			
HCO_3	0.27	**0.87**	**0.71**	0.07	**0.78**	**0.81**	**0.66**	1		
SO_4	0.22	**0.53**	**0.57**	-0.07	0.33	0.32	0.33	0.40	1	
NO_3	0.08	0.19	0.26	0.09	0.09	-0.01	0.28	-0.04	-0.01	1
2019	***pH***	***EC***	***Na***	***K***	***Ca***	***Mg***	***Cl***	***HCO_3***	***SO_4***	***NO_3***
pH	1									
EC	0.10	1								
Na	0.09	**0.97**	1							
K	0.09	0.11	0.08	1						
Ca	0.11	**0.95**	**0.86**	0.05	1					
Mg	0.06	**0.88**	**0.79**	0.15	**0.89**	1				
Cl	0.11	**0.95**	**0.94**	0.18	**0.87**	**0.87**	1			
HCO_3	0.03	**0.91**	**0.86**	-0.01	**0.93**	**0.76**	**0.78**	1		
SO_4	0.09	**0.83**	**0.83**	-0.04	**0.77**	**0.74**	**0.79**	**0.69**	1	
NO_3	0.15	0.26	0.25	-0.02	0.22	0.37	0.15	0.15	0.39	1

Bold significant correlation (p 0.05)

6.12 Health risk assessment

Health risk assessment was used to evaluate the health risk that trace metals may pose on humans through oral ingestion and dermal absorption. Table 6.3&6.4 shows the values of parameters used for health risk assessment in this study. Health related risk associated with exposure to trace metals was determined using the concentration of a total of eleven trace metals including As, Cu, Pb, Co, Cd, Mn, Fe, Al and Zn during 2018 and Cu, Pb, Co, Cd, Mn, Fe, Zn, Cr and Ni for 2019, respectively. The average HQs and HI values of the trace metals via ingestion and dermal absorption pathways are presented in Table 6.5 , respectively. The calculated mean values of $HQ_{ingestion}$ and HQ_{dermal} in the study area decreased in the order of Zn>As>Co>Pb>Mn>Cu>Fe>Al>Cd and Mn>Zn>Co>Cu>As>Cd>Fe>Al>Pb, for both adults and children during 2018, respectively. The $HQ_{ingestion}$ and HQ_{dermal} was in the order of Co>Pb>Cd>Mn>Fe>Cr>Zn>Cu>Ni and Cd>Mn>Cr>Co>Fe>Pb>Cu>Zn>Ni, for both adults and children during 2019. This suggests that arsenic, cobalt, lead, and zinc are major contributors to the ingestion exposure for both age groups in the study area. Regarding the dermal exposure, manganese, cadmium, and zinc were observed to have more potential non-carcinogenic concerns for both age groups. The $HQ_{ingestion}$ values for both adults and children were less than one for all trace metals during 2018 (Fig. 6.10a), indicating that they pose little hazard. The mean $HQ_{ingestion}$ values for lead and cobalt were greater than one for children during 2019 (Fig. 6.10b). This implies that these metals pose serious to adverse health effects on children and are major contributors to ingestion exposure. The HQ_{dermal} values for both adults and children in all trace metals were below one during 2018 and 2019, respectively. This suggests that the concentration of these metals pose a minimum hazard to people through dermal exposure pathway. For children, the total hazard index (HI) values ranged from 8.9E-2 to 8.35E+0 and from 1.2E-2 to 1.3E+1 with average values of 9.3E-1 and 6.0E+0, during 2018 and 2019, respectively. The HI average values for the study area were higher than the acceptable limit of one during 2019, indicating that trace metal concentrations may pose non-carcinogenic health risks for children. The HI values for adults ranged from 2.3E-2 to 2.2E+0 and from 3.1E-3 to 3.3E+0 with average values of 2.4E-1 and 1.6E+0, during 2018 and 2019, respectively. The HI average values exceeded the acceptable limit during 2019, implying that the concentration of trace metals in groundwater may cause serious to adverse health effects on adults. Similarly, Fig. 6.10c shows that the average HI of all the trace metals were below unity in both adults and children in 2018 whereas the average HI values for lead and cobalt exceeded unity in children during 2019 (Fig. 6.10d).

Table 5.3: Human exposure parameter values

	IR (L/day)	**ED (years)**	**BW (kg)**	**AT (days)**	**SA (cm^2)**	**ET (hours/day)**
Adults	2.2	70	70	25 550	18 000	0.58
Children	1.8	6	15	2 190	6 600	1

Table 5.4: Kp and RfD for the analysed trace metals

Trace metal	**Kp[c] (cm/hr)**	**$RfD_{ingestion}$ (μg/kg/day)**	**RfD_{dermal} (μg/kg/day)**
As[a]	$1 * 10^{-3}$	0.3	0.285
Cu[b]	$1 * 10^{-3}$	40	8
Pb[b]	$1 * 10^{-4}$	1.4	0.42
Ni[b]	$2 * 10^{-4}$	20	0.8
Co[b]	$4 * 10^{-4}$	0.3	0.06
Cr[b]	$1 * 10^{-3}$	3	0.075
Cd[b]	$1 * 10^{-3}$	0.5	0.025
Mn[b]	$1 * 10^{-3}$	24	0.96
Fe[b]	$1 * 10^{-3}$	700	140
Al[b]	$1 * 10^{-3}$	1000	200
Zn[b]	$6 * 10^{-4}$	300	60

[a] Wu et al. (2009)

[b] Wang et al. (2017)

[c] USEPA (2004)

Table 5.5: Non-carcinogenic health risk of trace metals by ingestion and dermal absorption pathway

Trace metal	**$HQ_{ingestion}$ (μg/kg/day)**				**HQ_{dermal} (μg/kg/day)**				**HI**	
	2018		**2019**		**2018**		**2019**		**2018**	
	Adult	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Chil**
As	4.98E-2	1.90E-1	-	-	2.49E-4	7.34E-4	-	-	5.00E-2	1.9
Cu	1.51E-2	5.77E-2	9.82E-3	3.75E-2	3.58E-4	1.06E-3	2.33E-4	6.87E-4	1.55E-2	5.8
Pb	3.96E-2	1.51E-1	4.48E-1	**1.71E+0**	6.27E-5	1.85E-4	7.09E-4	2.09E-3	3.97E-2	1.5
Ni	-	-	2.60E-3	9.92E-3	-	-	6.17E-5	1.82E-4	-	-
Co	4.64E-2	1.77E-1	6.31E-1	**2.41E+0**	4.41E-4	1.30E-3	5.99E-3	1.77E-2	4.69E-2	1.7
Cr	-	-	4.54E-2	1.73E-1	-	-	8.61E-3	2.54E-2	-	-

Cd	2.39E-3	9.11E-3	2.19E-1	8.35E-1	2.26E-4	6.68E-4	2.08E-2	6.12E-2	2.61E-3	9.7
Mn	2.59E-2	9.90E-2	9.95E-2	3.80E-1	3.07E-3	9.07E-3	1.18E-2	3.48E-2	2.90E-2	1.0
Fe	3.99E-3	1.52E-2	6.83E-2	2.61E-1	9.47E-5	2.79E-4	1.62E-3	4.78E-3	4.09E-3	1.5
Al	2.83E-3	1.08E-2	-	-	6.71E-5	1.98E-4	-	-	2.90E-3	1.1
Zn	5.25E-2	2.01E-1	1.41E-2	5.37E-2	7.48E-4	2.21E-3	2.00E-4	5.90E-4	5.33E-2	2.0

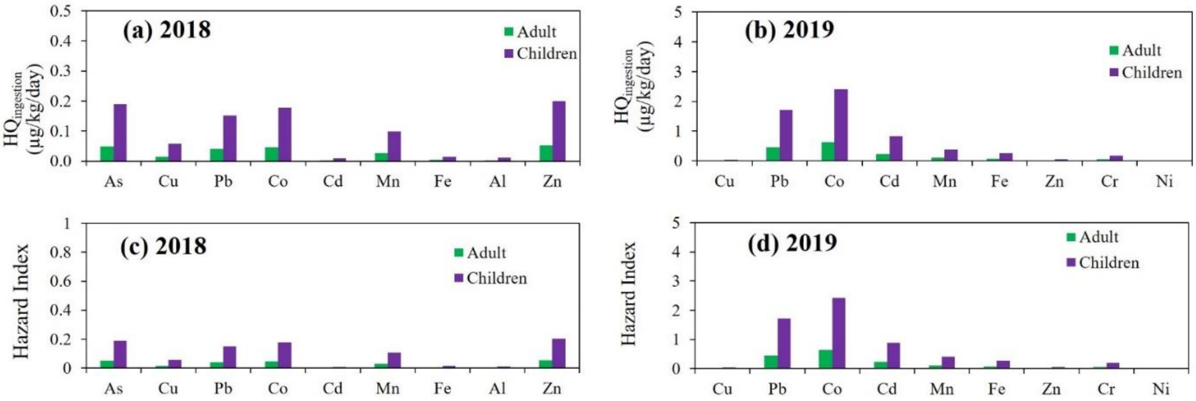

Figure 5.10: Human health risk based on $HQ_{ingestion}$ (a-b) and hazard index (c-d) during 2018 and 2019

Fig. 6.11(a-d) shows the spatial distribution of HI values for children and adults during 2018 and 2019. The HI values for adults during 2018 and 2019 were classified into two levels of chronic risk comprising low (96% and 14% samples during 2018 and 2019) and medium (4% and 86% samples during 2018 and 2019, respectively) (Table 6.6). HI values for children were classified in terms of three levels including low (84% and 12% of samples), medium (14% and 2% of samples), and high (2% and 86% of samples) during 2018 and 2019, respectively. This implies that chronic risk level is high in children as compared to adults. This also concludes that children and adults face higher non-carcinogenic health risk during 2019 as compared to 2018. This is due to the rise in concentrations of trace metals found in 2019.

Table 5.6: Classification of chronic (non-carcinogenic) risk (USEPA 1999)

Risk level	**HI**	**Chronic risk**
1	< 0.1	Negligible
2	≥ 0.1 < 1	Low
3	≥ 1 < 4	Medium
4	≥ 4	High

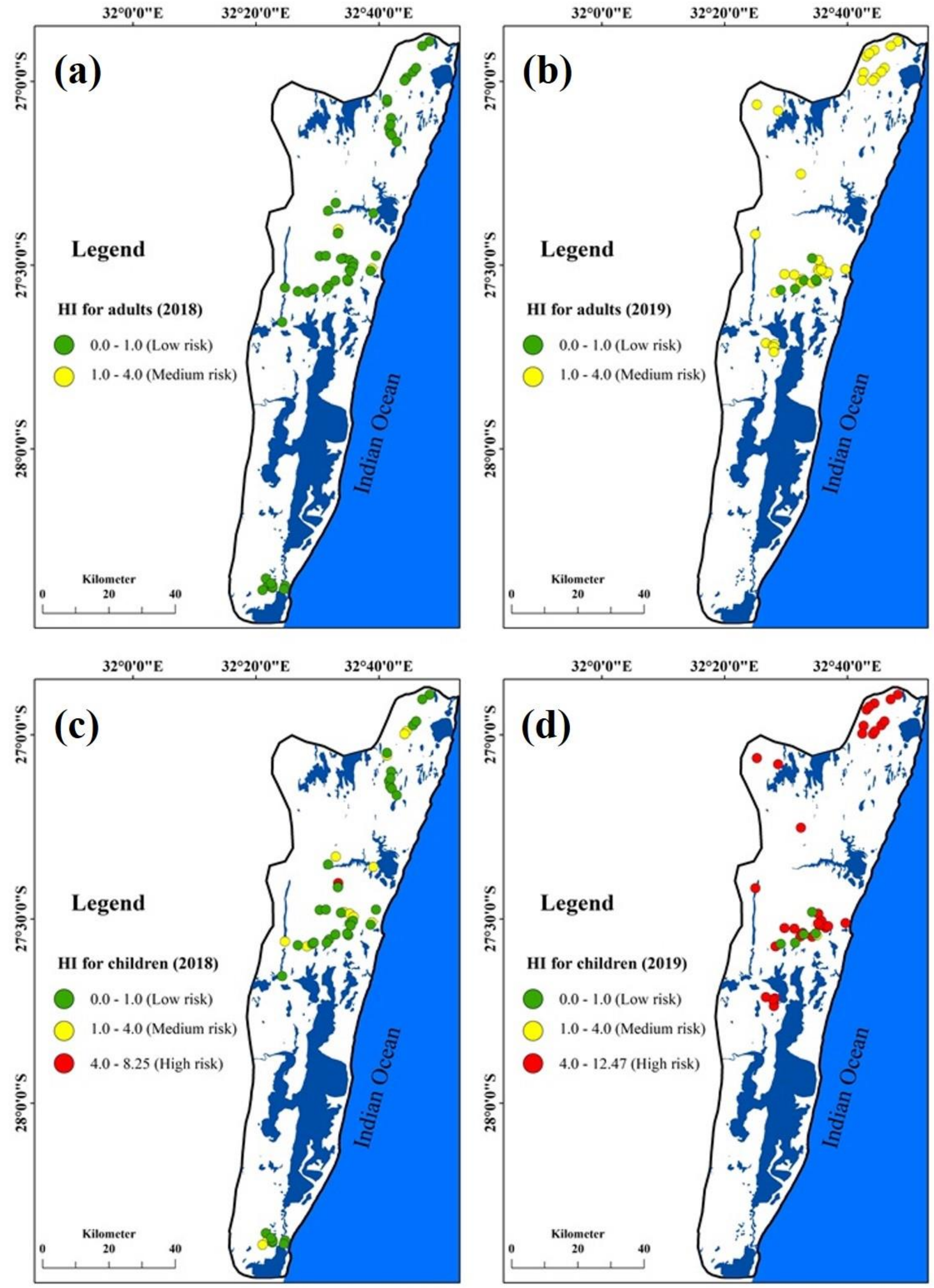

Figure 5.11: Spatial variation of hazard index of trace metals in groundwater during 2018 and 2019

Conclusion

In this study, groundwater samples were collected from the Maputaland coastal plain, South Africa and analysed. Geostatistical and GIS methods were applied to identify the hydrogeochemical processes that control the groundwater chemistry of the study area. The potential non-carcinogenic health risk of trace metals through the ingestion and dermal absorption pathways was assessed. The following conclusions are summarised:

- Groundwater is acidic to alkaline in nature. Based on the TDS and TH classification, groundwater belongs to soft and hard freshwater type. In general, the groundwater quality is suitable for drinking purposes except in few locations that exceeded the DWAF and WHO drinking water limits for Na, Cl, Ca, and Mg. All trace metals were within the WHO standards for drinking water except for Cd, Zn, Pb, Mn, Al, and Fe . Na-Cl water type is the dominant groundwater type followed by Ca-HCO_3.

- Hydrogeochemical processes controlling groundwater chemistry were rock-water interaction, silicate weathering, reverse ion exchange, seawater intrusion, and anthropogenic activities. Increasing concentrations of some major ions with an increase in salinity owing to the reverse ion exchange process was also identified. The SMI ranges from 0.3 to 2.5 and from 0.3 to 2.3 during 2018 and 2019, respectively. Approximately 29% of groundwater had high SMI values suggesting contamination by seawater intrusion. Statistical analysis also confirmed the geochemical processes identified.
- Trace metal analysis showed arsenic, cobalt, cadmium, lead, manganese, and zinc as the main contributors to non-carcinogenic risk through the oral ingestion pathway. The mean values of $HQ_{ingestion}$ and HI values for cobalt and lead has the highest contribution to the total non-carcinogenic risk in the study area. The HQ_{dermal} was less than unity implying that trace metal pose less significant health risk to adults and children through dermal absorption pathway. According to the classification of chronic risk, adults in the study area fall into two levels of risk including low and medium; children fall into three levels of risk including low, medium and high risk. This concludes that the chronic risk level is high in children than adults.
- Long term monitoring and assessment of trace metals is necessary to minimize health effects from consuming groundwater on local people. These findings will help improve

understanding of the hydrogeochemistry of this area and assist decision-makers with the management and development of groundwater resources.

CHAPTER SEVEN

6. Extent of metal pollution and groundwater quality assessment using indexical and statistical approach

7.1 Introduction

In most parts of the world, groundwater serves as a vital source of water supply for drinking, domestic, agriculture and industrial purposes. Naturally, groundwater is free from pollution when compared with surface water resources. However, anthropogenic activities have been reported to negatively impact groundwater quality. Contamination of groundwater by heavy metals is a major threat to groundwater quality. Heavy metals are introduced into groundwater through natural processes (e.g. weathering and dissolution of minerals, ion exchange processes, volcanism extruded products) (Prasanna *et al*., 2012; Rezaei *et al*., 2019; Çiner *et al*., 2020) and anthropogenic activities (e.g. mining, industrial, agricultural and disposal of solid wastes) (Rezaei *et al*., 2017; Wagh *et al*., 2018; Giri and Singh, 2019; Ahamad *et al*., 2020). Some heavy metals are required in minor quantities for human body building as well as the growth of plants and animals. However, when these metals are consumed at concentrations above the desired limits, they can be detrimental to human health and pose threat on the environment (Tamasi and Cini, 2004; Brindha *et al*., 2011; Haloi and Sarma, 2012; Chanpiwat *et al*., 2014; Li *et al*., 2014; Boateng *et al*., 2015; Jahanshahi and Zare, 2015; Yousaf *et al*., 2016; Wagh *et al*., 2018; Vetrimurugan *et al*., 2018; Xiao *et al*., 2019). Groundwater in South Africa has been reported to be contaminated by arsenic and lead (Verlicchi and Grillini, 2020). High iron in groundwater of Maputaland coastal aquifer has been reported by Demlie *et al*. (2014). This chapter focuses on evaluating the extent of heavy metal pollution in groundwater using HPI, HEI and C_d; assessing groundwater quality for drinking purposes using PIG, SPI and OIP indices; and evaluating the potential sources of heavy metals in groundwater using multivariate statistical tools such as PCA and HCA. The pH and heavy metals such as As, Fe, Mn, Zn, Pb, Ni, Cr, Cu, Cd and Co from 53 samples collected in 2018 were used in this chapter.

7.2 Heavy metal contamination

Table 7.1 presents summary of statistical results of physicochemical parameters and their comparison with drinking water standards (WHO, 2011; SANS, 2015). The groundwater pH varied from 5.3 to 8.3 with an average value of 7.1. Hence, groundwater is acidic to alkaline in nature. The pH of the samples indicated that all the samples were within the standard limits of SANS (2015) but 30% of the samples were found below 6.5 as prescribed by WHO (2011). Groundwater arsenic varied from below detection limit to 3.6 µg/L (mean 0.5 µg/L). In the present study, the measured concentrations of cadmium in groundwater is below the detection limit of 4.6 µg/L (mean 0.9 µg/L). The measured concentrations reveals that approximately 23% of the samples exceed the SANS (2015) and WHO (2011) standard limits. Zinc ranged from 1.9 to 19 964.5 µg/L (mean 499.9 µg/L). 2% of the samples exceeded the SANS (2015) and WHO (2011) standard limits in 2% of the samples. Iron concentrations in groundwater ranged from 2.7 to 1 848.6 µg/L with an average value of 140 µg/L. It was observed that 11% of the samples have iron concentrations higher than the SANS (2015) and WHO (2011) standard limits for drinking water, respectively. The high iron concentrations may be owed to the leaching of iron-rich sediments in the study area (Demlie *et al*., 2014). In this study, lead contents varied from below detection limit to 26 µg/L (mean 6.6 µg/L). Approximately,25% of the samples have lead concentrations exceeding the SANS (2015) and WHO (2011) standard limits. Hence, these samples are unfit for human consumption. Manganese concentrations ranged from 0.4 to 116 µg/L (mean 19.1). About 2% of the samples have manganese concentrations above the SANS (2015) standard limit. Nickel contents in groundwater of this area varied from below detection limit to 9.3 µg/L (mean 2.1 µg/L). Chromium concentrations ranged from below detection limit to 8.4 µg/L with an average value of 3.4 µg/L, respectively. Copper contents ranged from below detection limit to 279.5 µg/L (mean 22.7 µg/L), respectively. Cobalt contents in groundwater varied from below detection limit to 8.4 µg/L with an average value of 1.8 µg/L. It was also observed that arsenic, chromium, copper, cobalt and nickel concentrations are low in groundwater samples and are within the prescribed standard limits of drinking water as prescribed by SANS (2015) and WHO (2011). Furthermore, iron, lead and cadmium were recognised to be dominant heavy metal contaminants in this area. Fig. 7.1a-d shows the spatial distribution of selected heavy metals in the study area. In this study, high iron concentrations are observed on the north western and south eastern part of the area (Fig. 7.1a). High manganese are observed in eastern, northern, and south eastern part (Fig. 7.1b). High lead concentrations are recorded on the south eastern, northern, central and south western part of the area (Fig. 7.1c). The spatial distribution of cadmium illustrates that high concentrations are recorded on the central, northern and south western part of the area (Fig. 7.1d).

Table 6.1: Statistical summary of physicochemical parameters of groundwater and water quality standard limits values in µg/L except for pH

	(N=53)				**Standard limits**	
Parameter	**Minimum**	**Maximum**	**Average**	**SD**	**SANS (2015)**	**WHO (2011)**
pH	5.30	8.3	7.1	0.9	5-9.7	6.5-8.5
As	BDL	3.6	0.5	0.8	≤10	10
Fe	2.70	1848.6	140.1	303.4	≤300	300
Mn	0.40	116.1	19.1	23.1	≤100	-
Zn	1.9	19964.5	499.9	2775.0	≤5000	5000
Pb	BDL	26.0	6.6	9.4	≤10	10
Ni	BDL	9.3	2.1	2.2	≤70	70
Cr	BDL	8.4	3.4	2.7	≤50	50
Cu	BDL	279.5	22.7	61.2	≤2000	2000
Cd	BDL	4.6	0.9	1.7	≤3	3
Co	BDL	8.4	1.8	3.0	≤500	-

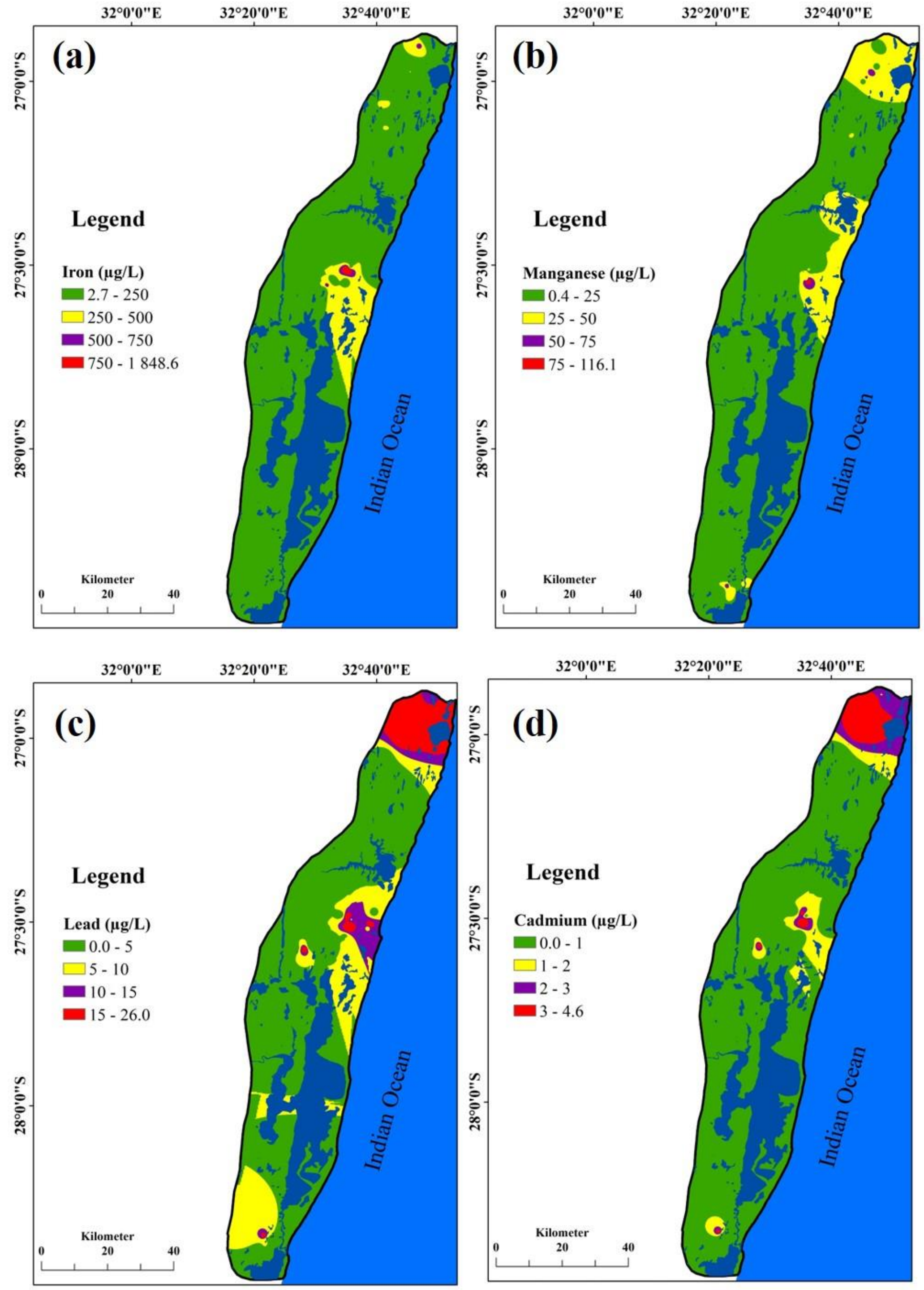

Figure 6.1: Spatial distribution of heavy metals (a) iron, (b) manganese, (c) lead and (d) cadmium

7.3 Heavy metal pollution assessment

7.3.1 Heavy metal pollution index (HPI)

The computed HPI varied from 0.28 to 128.08 with a mean value of 30.65, respectively (Table 7.2). The critical value for HPI for drinking water is 100 (Mohan *et al*., 1996; Prasad and Bose, 2001). In this study, 21% of the samples exceeded the critical value of 100 indicating that these samples are unfit for consumption with respect to heavy metals. The HPI can be classified into three categories such as low class (< 15), medium class (15-30) and high class (> 30) (Edet and Offiong, 2002; Tiwari *et al*., 2016). Table 7.3 and Fig. 7.2 demonstrates that the HPI was categorised into low (71%), medium (4%) and high (25%). The high HPI values were spatially located in the northern, central and south western part of the area.

Table 6.2: Results of the various quality indices

S.No.	HPI	HEI	C_d	ERI	PIG	OIP	∑SPI
BH1	5.618	0.607	-9.393	3.473	0.137	0.061	0.307
BH2	3.141	0.184	-9.816	1.173	0.097	0.018	0.282
BH3	1.310	0.081	-9.919	0.506	0.083	0.008	0.254
BH4	1.801	0.156	-9.844	0.723	0.081	0.016	0.228
BH5	3.038	0.317	-9.683	1.529	0.097	0.032	0.242
BH6	2.240	0.143	-9.857	0.918	0.086	0.014	0.252
BH7	3.260	1.060	-8.940	1.909	0.164	0.106	0.260
BH8	3.087	0.711	-9.289	1.524	0.133	0.071	0.255
BH9	2.466	0.189	-9.811	1.210	0.090	0.019	0.250
BH10	7.127	0.525	-9.475	2.532	0.123	0.052	0.286
BH11	1.440	0.254	-9.746	0.676	0.092	0.025	0.236
BH12	118.446	3.883	-6.117	54.646	0.486	0.388	1.195
BH13	19.342	2.263	-7.737	7.257	0.286	0.226	0.387
BH14	4.936	0.440	-9.560	2.396	0.112	0.044	0.268
BH15	128.081	10.252	0.252	63.245	1.031	1.025	1.275
BH16	112.857	7.054	-2.946	52.772	0.755	0.705	1.151
BH17	1.158	0.781	-9.219	1.218	0.147	0.078	0.272
BH18	126.213	4.300	-5.700	57.242	0.527	0.430	1.256
BH19	7.196	0.469	-9.531	4.056	0.114	0.047	0.271
BH20	4.733	0.510	-9.490	2.703	0.116	0.051	0.258
BH21	111.338	4.168	-5.832	49.480	0.515	0.417	1.149
BH22	3.814	0.328	-9.672	1.395	0.102	0.033	0.261
BH23	5.354	0.613	-9.387	2.010	0.121	0.061	0.249
BH24	2.862	1.405	-8.595	2.079	0.182	0.140	0.219

BH25	10.827	0.946	-9.054	3.586	0.157	0.095	0.296
BH26	97.673	3.303	-6.697	44.609	0.424	0.330	1.030
BH27	1.675	1.238	-8.762	1.963	0.188	0.124	0.299
BH28	12.946	1.912	-8.088	4.614	0.255	0.191	0.363
BH29	4.366	2.271	-7.729	3.526	0.252	0.227	0.219
BH30	1.330	0.420	-9.580	1.071	0.116	0.042	0.271
BH31	0.275	0.100	-9.900	0.213	0.087	0.010	0.257
BH32	42.433	3.146	-6.854	14.472	0.368	0.315	0.505
BH33	17.246	1.091	-8.909	5.430	0.166	0.109	0.309
BH34	3.194	4.261	-5.739	5.211	0.428	0.426	0.229
BH35	3.129	0.260	-9.740	1.384	0.084	0.026	0.220
BH36	1.985	0.154	-9.846	0.888	0.073	0.015	0.207
BH37	4.657	0.302	-9.698	2.481	0.091	0.030	0.235
BH38	6.177	0.489	-9.511	3.407	0.117	0.049	0.271
BH39	1.966	0.175	-9.825	0.830	0.093	0.018	0.266
BH40	5.073	0.685	-9.315	2.013	0.127	0.068	0.249
BH41	4.484	0.969	-9.031	2.230	0.149	0.097	0.240
BH42	4.930	1.794	-8.206	3.273	0.218	0.179	0.239
BH43	1.959	0.109	-9.891	0.794	0.070	0.011	0.206
BH44	1.425	0.328	-9.672	0.793	0.084	0.033	0.193
BH45	4.677	2.062	-7.938	3.286	0.237	0.206	0.227
BH46	3.103	0.394	-9.606	1.333	0.095	0.039	0.215
BH47	124.671	6.028	-3.972	58.155	0.674	0.603	1.247
BH48	127.831	4.639	-5.361	57.151	0.562	0.464	1.271
BH49	2.269	0.637	-9.363	1.102	0.116	0.064	0.216
BH50	114.772	4.443	-5.557	51.002	0.539	0.444	1.175
BH51	113.164	5.428	-4.572	50.326	0.622	0.543	1.160
BH52	124.125	4.617	-5.383	57.545	0.551	0.462	1.251
BH53	101.346	3.976	-6.024	44.413	0.494	0.398	1.067

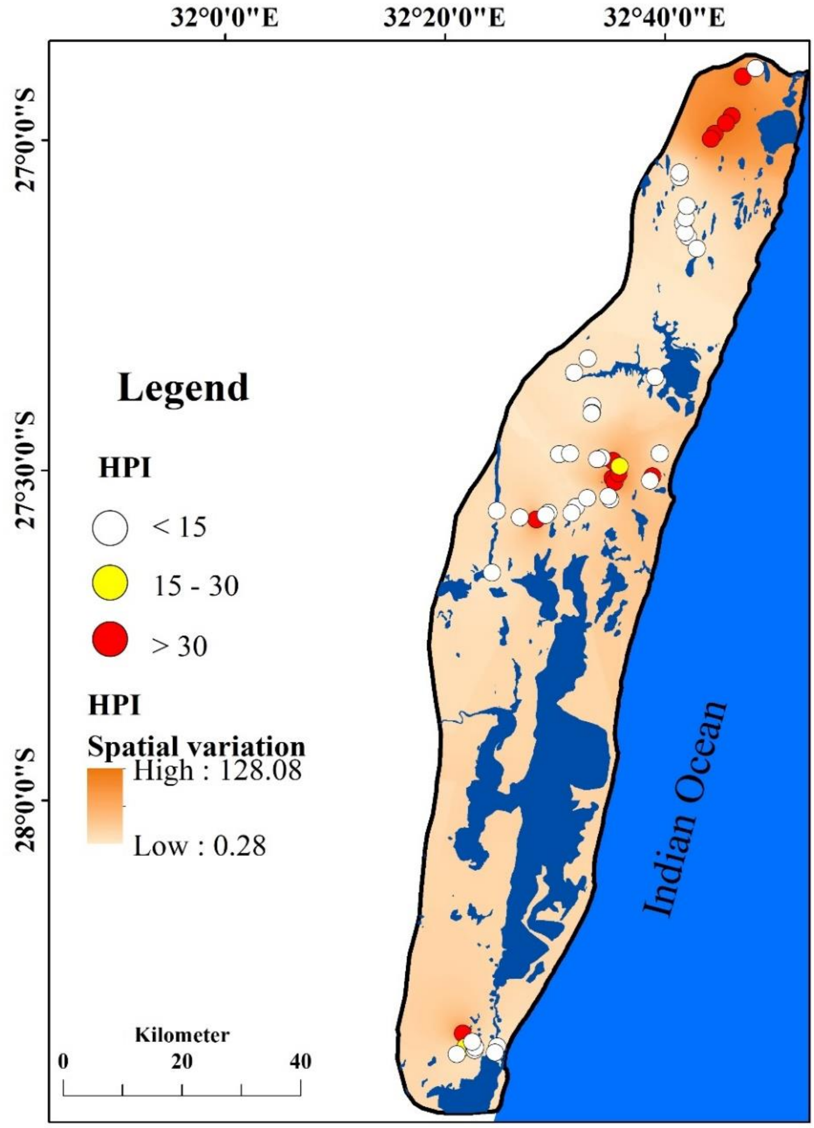

Figure 6.2: Spatial distribution of HPI values

7.3.2 Heavy metal evaluation index (HEI)

The values of HEI ranged from 0.08 to 10.25 with an average value of 1.83 (Table 7.2), respectively. The HEI can be classified as low (< 400), medium (400-800) and high pollution (> 800) (Edet and Offiong, 2002). In this study, all the groundwater samples were found below the 400 (Table 7.3; Fig. 7.3), respectively. This suggests that the groundwater has low pollution with respect to heavy metals and is safe for human consumption.

Table 6.3: Classification of pollution indices

Index method	Class	Extent of pollution	% of groundwater samples
HPI	< 15	Low	71.6
	15 - 30	Medium	3.7
	> 30	High	24.5
HEI	< 400	Low	100
	400 - 800	Medium	-
	> 800	High	-
C_d	< 1	Low	100
	1 - 3	Medium	-
	> 3	High	-

7.3.3 Degree of contamination (C_d)

The calculated C_d values ranged from -9.92 to 0.25 with a mean value of -8.18 (Table 7.2) , respectively. C_d values may further be categorized into three categories (Backman *et al.*, 1997; Edet and Offiong, 2002) as follows: low (< 1), medium (1-3) and high (> 3). In this study, all of the groundwater samples have C_d values below one suggesting low contamination by heavy metals (Table 7.3; Fig. 7.4). A similar trend at various sampling locations was observed between the three indices (HPI, HEI and C_d) (Fig. 7.5). Furthermore, the indices were compared with each other and it shows that there is a strong association between HEI and C_d, similar findings were inferred by Paul *et al.* (2019); Jahanshahi and Zare (2015).

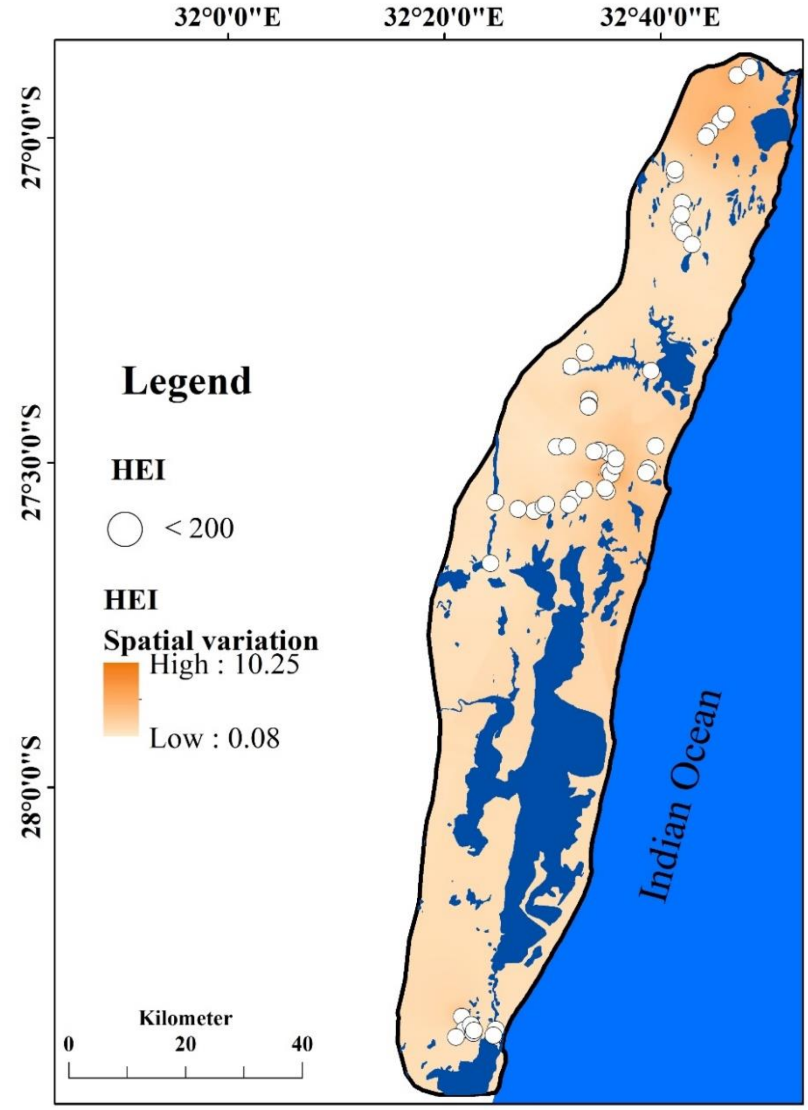

Figure 6.3: Spatial distribution of HEI values

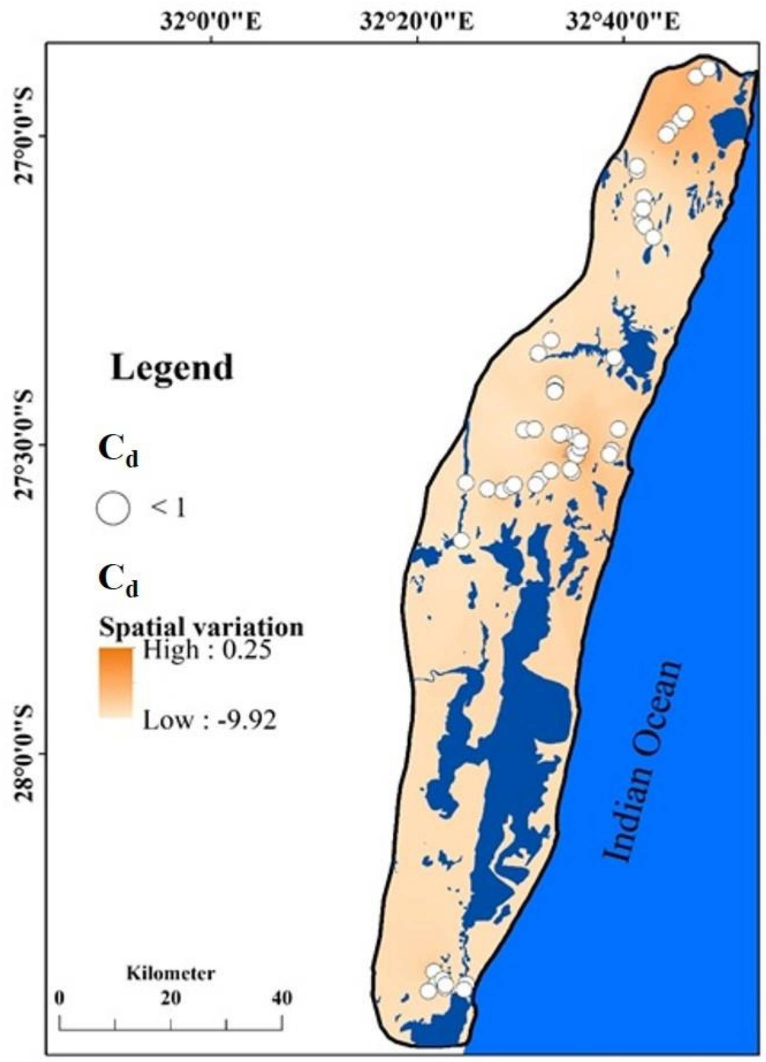

Figure 6.4: Spatial distribution of C_d values

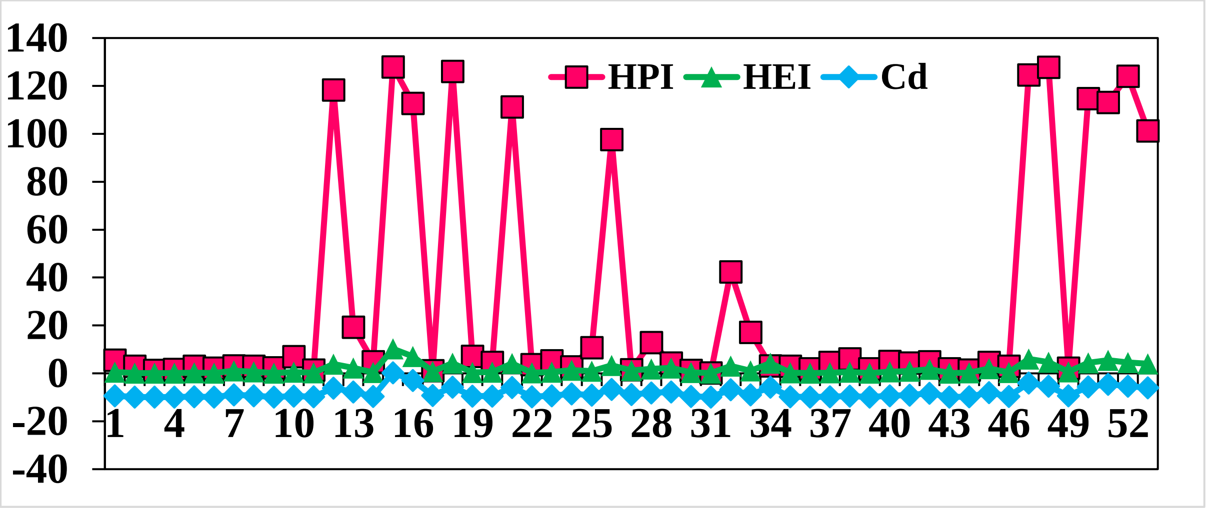

Figure 6.5: Comparison between pollution evaluation indices

7.3.4 Ecological risks of heavy metals

The potential ecological risk factor (RI) was first determined prior to the computation of the ERI. RI may be classified as follows; RI< 40 (low potential ecological risk), 40<RI<80 (moderate potential ecological risk), 80<RI<160 (considerable potential ecological risk), 160<RI<320 (high potential ecological risk), RI>320 (very high potential ecological risk) (Bhuitani *et al*., 2017; Tiawo *et al*., 2019; Egbueri 2020a,b). Based on this classification, the RI was found to be less than 40 for all the heavy metals in all groundwater samples except for cadmium which could pose moderate potential ecological risk in 11% of the samples. The final ERI ranged from 0.21 to 63.24 with an average value of 14.03 (Table 7.2). Furthermore, the ERI can be classified as follows; ERI <150 indicates low ecological risk, 150<ERI<300 indicates moderate ecological risk, 300<ERI<600 indicates considerable ecological risk, and ERI>600 indicates very high ecological risk (Tiawo *et al*., 2019, Ukah *et al*., 2019; Egbueri 2020a). In the current study, the ERI was found below 150 suggesting low ecological risks.

7.4 Drinking water quality assessment

7.4.1 Pollution index of groundwater (PIG)

Table 7.4 outlines values used to compute PIG calculations. Computed PIG values are presented in Table 7.2. In PIG assessment, the relative contribution of chemical parameters of each groundwater sample is considered. When the overall chemical quality of water (O_w) is above 0.1, it contributes 10% of the value of 1.0 of PIG (Subba Rao, 2012). This provides a clear and precise evidence on the impact of groundwater pollution. PIG values can be classified into five categories as follows; PIG < 1.0 (insignificant pollution), 1.0-1.5 (low pollution), 1.5-2.0 (moderate pollution), 2.0-2.5 (high pollution) and PIG > 2.5 (very high pollution) (Subba Rao, 2012; Subba Rao *et al*., 2018; Egbueri and Unigwe, 2019). The PIG values varied from 0.07 to 1.03 with an average value of 0.25, respectively (Table 7.2). According to the classification of PIG, 98% of the samples have PIG less than 1.0 (0.23) which falls under insignificant pollution zone, and 2% of the samples have PIG between 1.0 and 1.5 (1.03) which comes under low pollution zone (Table 7.5).The spatial distribution of PIG shows that insignificant pollution zone is spread throughout the study area (Fig. 7.6). The low pollution zone is predominant observed mainly in the central part of the study area (Fig. 7.6).

Table 6.4: Parameters considered in PIG evaluation

Parameter	**Relative weight (R_w)**	**Weight parameter**	**SANS (2015) and WHO (2011)**
pH	3	0.06	6.5
As (µg/L)	5	0.11	10
Fe (µg/L)	4	0.06	300
Mn (µg/L)	4	0.06	100
Zn (µg/L)	4	0.06	5000
Pb (µg/L)	5	0.11	10
Ni (µg/L)	5	0.11	70
Cr (µg/L)	5	0.11	50
Cu (µg/L)	4	0.06	2000
Cd (µg/L)	5	0.11	3
Co (µg/L)	3	0.06	500
	∑Rw=47	∑Wp=1	

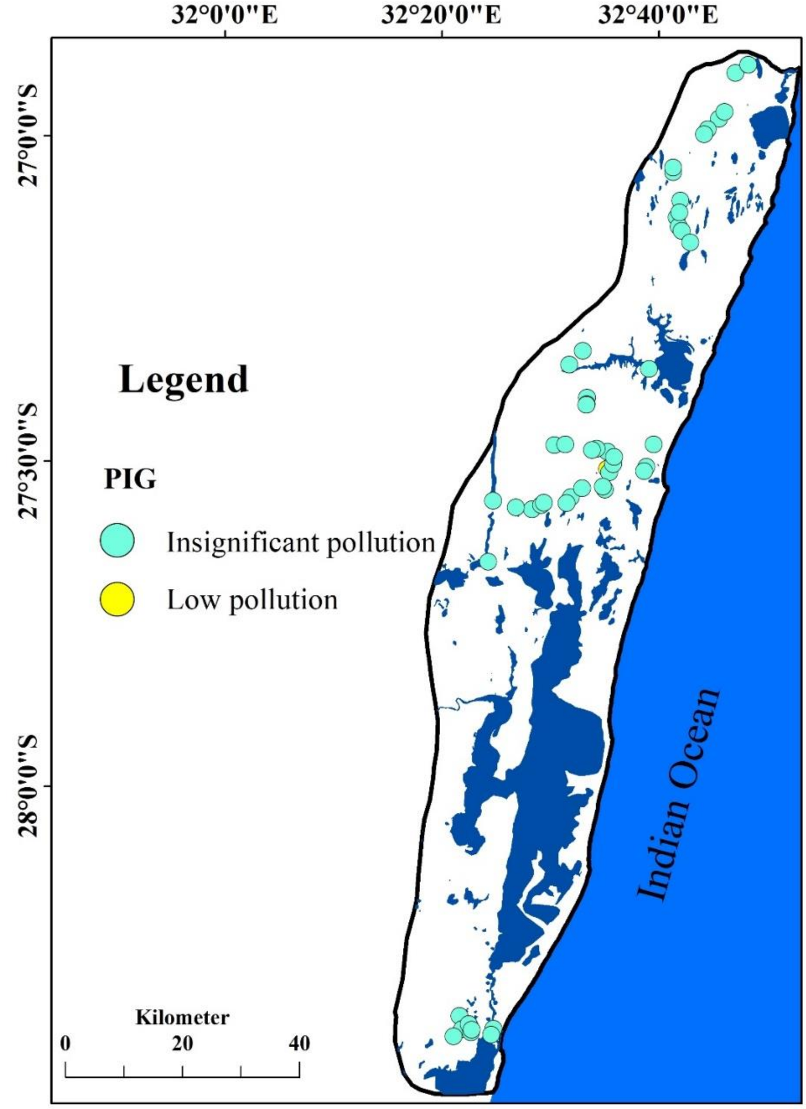

Figure 6.6: Spatial distribution of groundwater pollution zones based on PIG

The pH (0.07), As (0.01), Fe (0.03), Mn (0.02), Zn (0.01), Pb (0.07), Ni (0.00), Cr (0.00), Cu (0.00), Cd (0.03) and Co (0.00) show the values O_w less than 0.1 in the insignificant pollution zone. These values are therefore regarded as natural contributors of groundwater quality. In the low pollution zone, the Cd (0.16), Fe (0.52), and Pb (0.23) have the O_w values higher than 0.1 (Table 7.5). Thus, these high values in the low pollution zone indicate the influence of anthropogenic sources in the aquifer system.

Table 6.5: Average values of Ow & PIG

pH	As	Fe	Mn	Zn	Pb	Ni	Cr	Cu	Cd	Co	PIG	Pollution zone
O_w	O_w	O_w	O_w	O_w	O_w	O_w	O_w	O_w	O_w	O_w		
0.07	0.01	0.03	0.02	0.01	0.07	0.00	0.00	0.00	0.03	0.00	0.23	Insignificant pollution
0.08	0.00	0.52	0.02	0.00	0.23	0.00	0.01	0.00	0.16	0.00	1.03	Low pollution

7.4.2 Synthetic pollution index (SPI)

The SPI is employed to categorize drinking water into five categories: suitable for drinking (SPI<0.2), slightly polluted water (SPI= 0.2-0.5), moderately polluted water SPI= 0.5-1.0), highly polluted water (SPI= 1.0-3.0), and unfit for drinking (SPI>3.0) (Solangi *et al*., 2019; Egbueri and Unigwe, 2019; Egbueri *et al*., 2020a). In this study, the SPI values ranged from 0.19 to 1.28 with an average value of 0.47 (Table 7.2). According to the SPI classification, 2% of the samples are classified as suitable for drinking, 74% of the samples are classified slightly polluted with heavy metals while 24% of the samples are classified as moderately polluted (Fig. 7.7).

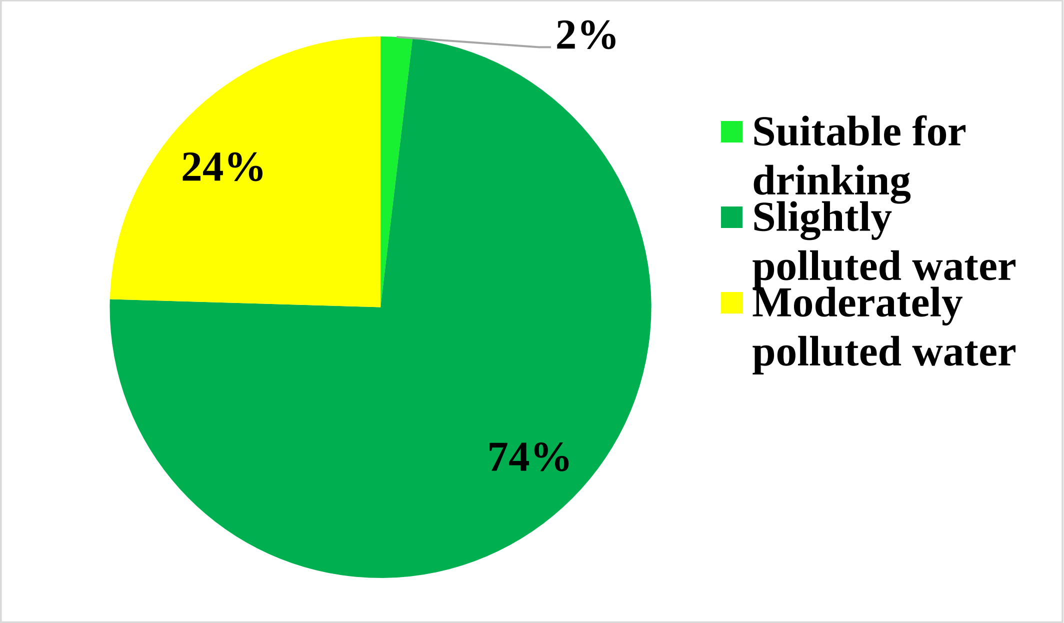

Figure 6.7: Classification of groundwater based on SPI

7.4.3 Overall index of pollution (OIP)

Computation of the OIP first requires calculation of the pollution index (PI). The PI can be classified as follows; PI < 1 indicate low pollution, 1-2 indicate low-moderate pollution, 2-3 indicate moderate pollution, 3-4 indicate moderate-high pollution, 4-5 indicate high pollution , and PI > 5 indicate very high pollution (Adimalla *et al*., 2019). According to the PI classification, majority of the samples are classified as low to moderately low pollution with respect to heavy metals. However, iron at one location (sample 15) has PI value greater than five. This suggests that this sample is very highly polluted with respect to the heavy metal iron Furthermore, this implies that iron is the predominant heavy metal in groundwater of this area.

All the trace metals had PI average values below one indicating low pollution (Fig. 7.8). According to Sargaonkar and Deshpande (2003), the OIP model further categorizes water quality into five categories as follows: OIP < 1.9 (Class C_1; excellent water quality, OIP < 3.9 (Class C_2; acceptable water quality), OIP < 7.9 (Class C3; slightly polluted), OIP < 15.9 (Class C4; polluted water), and OIP > 16 (Class C_5; heavily polluted water). In this study, the OIP values varied from 0.01 to 1.03 with an average value of 0.18 (Table 7.2). Based on the OIP scores obtained in this study, it was revealed that all the samples were identified to be excellent water quality and are suitable for drinking purposes.

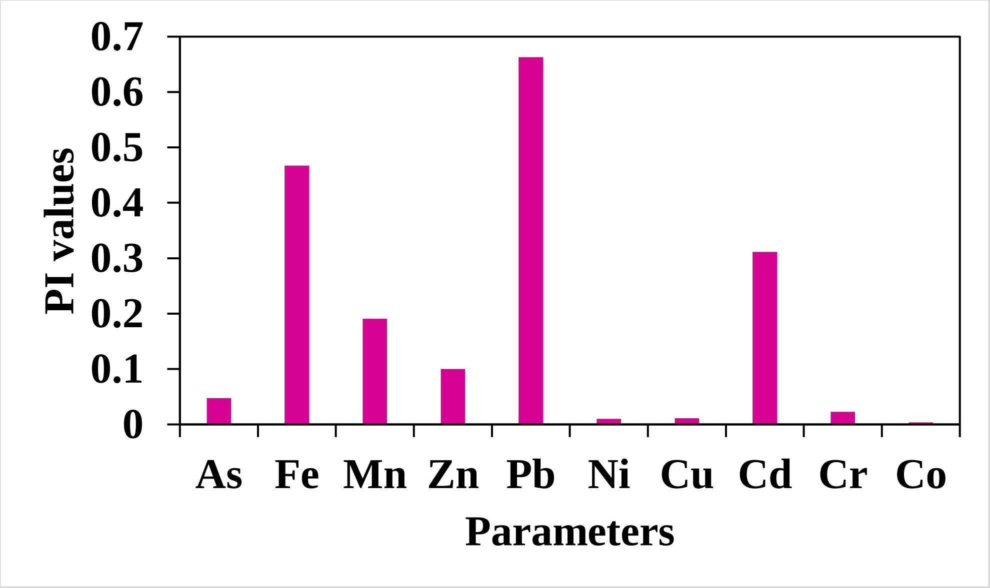

Figure 6.8: Average PI values

7.5 Multivariate statistical analysis for identification of pollution source

7.5.1 Correlation matrix (CM)

Correlation matrix was employed to recognize the interrelationship between parameters and their possible sources in groundwater. Correlation coefficients r>0.7, 0.7>r>0.5 and <0.5 were regarded as strong, moderate and weak, respectively (Egbueri and Mgbenu, 2020). The correlation matrix (Table 7.6) was used to demonstrate the interrelationship between the analysed parameters and to identify their source of origin. The groundwater pH showed a moderate correlation with cadmium (r= 0.57), cobalt (r= 0.55) and HPI (r= 0.55) (Table 7.6). Iron showed a strong relationship with HEI and C_d, this suggests that iron has a key role in determining groundwater quality. Lead showed significant correlation with chromium (r= 0.90), cadmium (r= 0.92), cobalt (r= 0.94), HPI (r= 0.96), HEI (r= 0.84) and C_d (r= 0.84). High concentration of lead and cadmium may be indicative of anthropogenic sources such as agrochemicals (Arslan and Ayyildiz Turan, 2015). Chromium strongly correlated with cadmium (r= 0.89), cobalt (r= 0.94), HPI (r= 0.90), HEI (r= 0.71) and C_d (r= 0.71). Furthermore, cadmium showed a strong positive correlation with cobalt (r= 0.97), HPI (r= 0.99), HEI (r= 0.86) and C_d (r=0.86). Heavy metals such as lead, chromium, cadmium and cobalt showed a significant strong correlation with HPI, HEI and C_d. The correlation among heavy metal pollution indices reflected good relation between HPI, HEI (r= 0.87) and C_d (r= 0.87). Similarly HEI is strong correlated with C_d (r=1) . This indicates that HEI and C_d can be used to evaluate the risk and contamination of heavy metals in groundwater of this area.

Table 6.6: Pearson correlation matrix of analysed parameters

	pH	*As*	*Fe*	*Mn*	*Zn*	*Pb*	*Ni*	*Cr*	*Cu*	*Cd*	*Co*	*H*
pH	1											
As	0.00	1										
Fe	0.14	-0.07	1									
Mn	0.15	-0.22	0.06	1								
Zn	-0.15	-0.09	-0.06	-0.04	1							
Pb	0.46	-0.18	0.33	0.21	-0.09	1						
Ni	-0.02	-0.07	0.08	0.24	-0.09	-0.28	1					
Cr	0.00	-0.25	0.19	-0.11	0.29	**0.90**	-0.23	1				
Cu	0.00	-0.12	-0.10	0.25	-0.05	0.35	-0.34	0.18	1			
Cd	**0.57**	-0.13	0.41	0.10	-0.09	**0.92**	-0.25	**0.89**	0.09	1		
Co	**0.55**	-0.14	0.28	0.09	-0.09	**0.94**	-0.28	**0.94**	0.17	**0.97**	1	
HPI	**0.55**	-0.12	0.40	0.14	-0.09	**0.96**	-0.26	**0.90**	0.18	**0.99**	**0.97**	
HEI	0.41	-0.16	**0.71**	0.24	0.16	**0.84**	-0.10	**0.71**	0.15	**0.86**	**0.79**	
C_d	0.41	-0.16	**0.71**	0.24	0.16	**0.84**	-0.10	**0.71**	0.15	**0.86**	**0.79**	

Significant correlation (p 0.05) are in bold

7.5.2 Principal Component Analysis (PCA)

Principal component analysis was employed to identify the sources of heavy metals in groundwater of this area. Varimax rotation was used with Kaiser normalization. Component loadings, Eigen values, percentage of variance and cumulative percentages of the identified principal components (PCs) are presented in Table 7.7. Fig. 7.9a-c shows the spatial distribution maps of the principal components that were extracted. PCA revealed three principal components that accounted for 70.18% of the total variance. PC1 which explains 37.59% of the total variance has strong positive loadings of lead, chromium, cadmium and cobalt. The presence of these heavy metals in PC1 revealed the contribution of anthropogenic sources such as the application of agricultural fertilizers and pesticides, leaching or infiltration of domestic wastes and garden refuse from the Mbazwana landfill site (Mthembu *et al*., 2020). Highest values of PC1 are situated in the northern, central and southern part of the study area, especially in sample BH12, BH15-16, BH26, BH47-53 (Fig. 7.9a). PC2 accounted for 19.65% of the total variance and has significant loadings of pH and cobalt, and moderate loading of zinc. This suggests that the groundwater pH is accountable for the release of cobalt and zinc into groundwater. Moderate PC2 values are distributed throughout the study area with highest values seen at the central part of the study area at sample BH21 (Fig. 7.9b) The presence of zinc is owed to the use of agricultural fertilizers (Razei *et al.*, 2019). PC3 explains 12.9% of the total variance with a negative moderate loading of arsenic, strong positive loading of manganese and moderate loading of nickel. The negative loading of arsenic suggests a different source of origin. The strong and moderate loadings of manganese and nickel may be due to the weathering of manganese and nickel bearing minerals. Landfill leachate may also contribute to the occurrence of manganese in groundwater of this area. For PC3, the distributed loadings were high on the eastern and north western part of the study area for samples BH27-28, BH51-52 (Fig. 7.9c). For better understanding, the three principal components were overlaid into a single map using fuzzy overlay (Fig. 7.9d). Highest loadings are observed in the northern and central part of the study area with moderate values spread throughout the study area. This indicates that the samples in the northern and central part of the study area are highly influenced with anthropogenic and weathering processes. This also corresponds with the high values of heavy metals observed in these locations (Fig. 7.1a-d).

Table 6.7: Varimax rotated principal component analysis

	Principal components (initial eigenvalue= 1)		
Quality parameter	PC 1	PC 2	PC 3
pH	-0.002	**0.911**	0.089
As	-0.397	0.014	**-0.587**
Fe	0.345	-0.492	0.186
Mn	-0.069	0.072	**0.777**
Zn	0.232	**0.607**	0.042
Pb	**0.965**	0.191	0.042
Ni	-0.278	-0.175	**0.628**
Cr	**0.941**	0.031	-0.075
Cu	0.229	**0.785**	-0.14
Cd	**0.972**	0.035	-0.042
Co	**0.953**	0.17	-0.091
Total	4.134	2.161	1.424
% variance	37.586	19.648	12.941
Cumulative %	37.586	57.235	70.176

Significant component loadings ate in bold

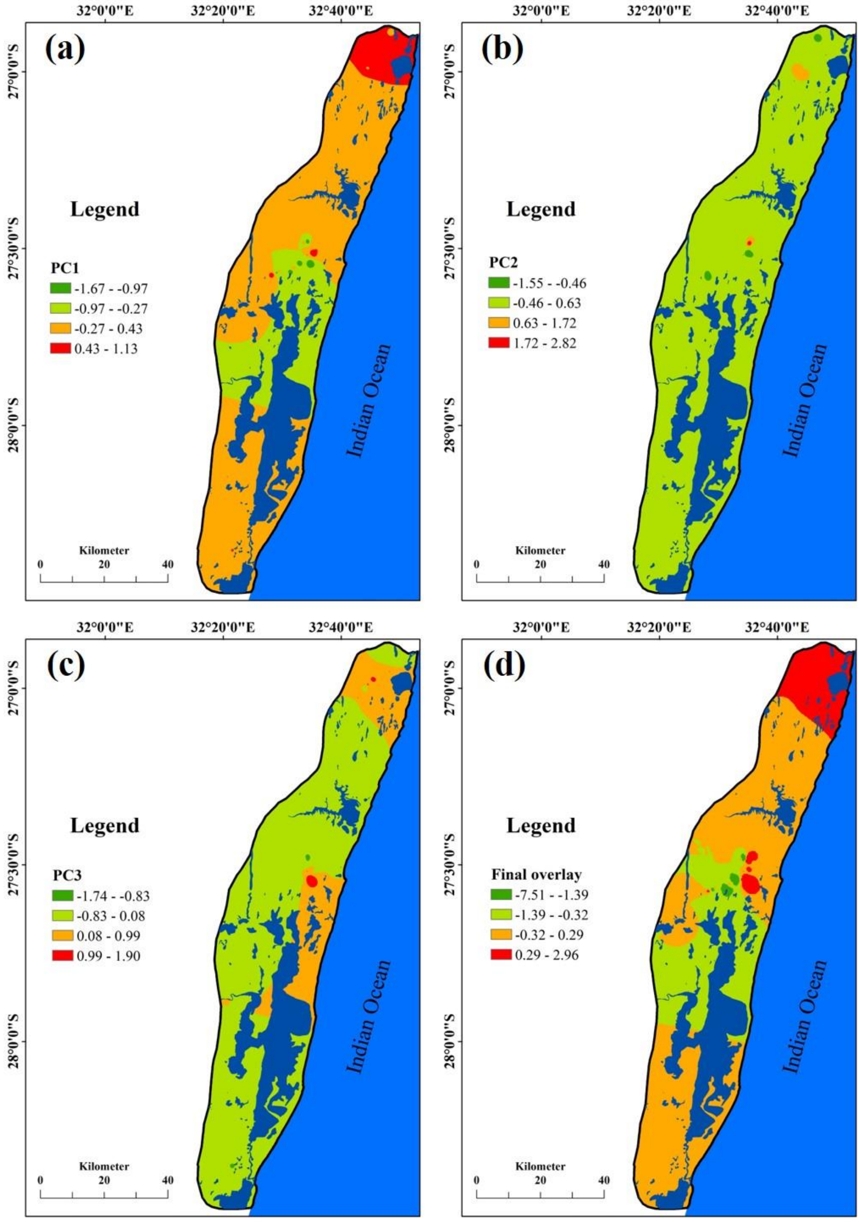

Figure 6.9: Spatial distribution of principal components in the study area (a) PC1, (b) PC2, (c) PC3, (d) final overlay map of principal components

7.5.3 Hierarchical cluster analysis (HCA)

The possible sources of pollutants in groundwater of this area was further investigated by carrying out cluster analysis. R-mode cluster analysis was used to examine the sources of heavy metals in groundwater of this area. R-mode cluster analysis revealed two groups of clusters (Fig. 7.10). Cluster 1 consists of pH, chromium, cadmium, cobalt, arsenic, nickel and lead. This cluster indicates the influence of both geogenic (weathering of rock minerals) and anthropogenic sources (domestic wastes and agricultural fertilisers) in the study area. Cluster 2 comprises of manganese, copper, iron and zinc and is due to the impacts of geogenic and anthropogenic sources. Q-mode cluster analysis was also used to determine the similarities that exists between sampling points. Two groups of clusters were identified by Q-mode cluster analysis (Fig. 7.11) Cluster 1 consisted of 46 sampling locations. These sampling locations are BH1-BH14, BH17-BH23, BH25-BH33, BH35-BH41, BH43, BH44, BH46, BH48-BH53. The samples of this cluster are mainly located throughout the entire study area and its characteristics may be linked to the rocks found in this area such as arenite, sandstone, siltstone and alluvium. Furthermore, these sample locations are characterised by elevated average concentrations of iron, zinc, copper and manganese(Fig. 7.11). These high levels are associated with PC2 and PC3, respectively. This cluster is associated with pollution by mixed sources e.g. weathering of soil or rock minerals and anthropogenic sources (agrochemicals). Based on average concentrations, pH, arsenic, nickel and copper were elevated in cluster 1 than in cluster 2. Cluster 2 included 7 sampling locations BH15, BH16, BH24, BH34, BH42, BH45 and BH47. Cluster 2 samples are spatially situated in the southern, central and north western part of the study area. This cluster is characterised by rocks such as arenite, sandstone and alluvium These sampling locations have highest concentrations of zinc, iron, manganese, and lead. These high levels correspond to PC1, PC2, and PC3, respectively. This cluster is also linked to mixed sources i.e. weathering of soil or rock minerals and anthropogenic sources. According to average values, iron, manganese, zinc, lead, chromium, cadmium and cobalt were greater in cluster 2 than those in cluster 1.

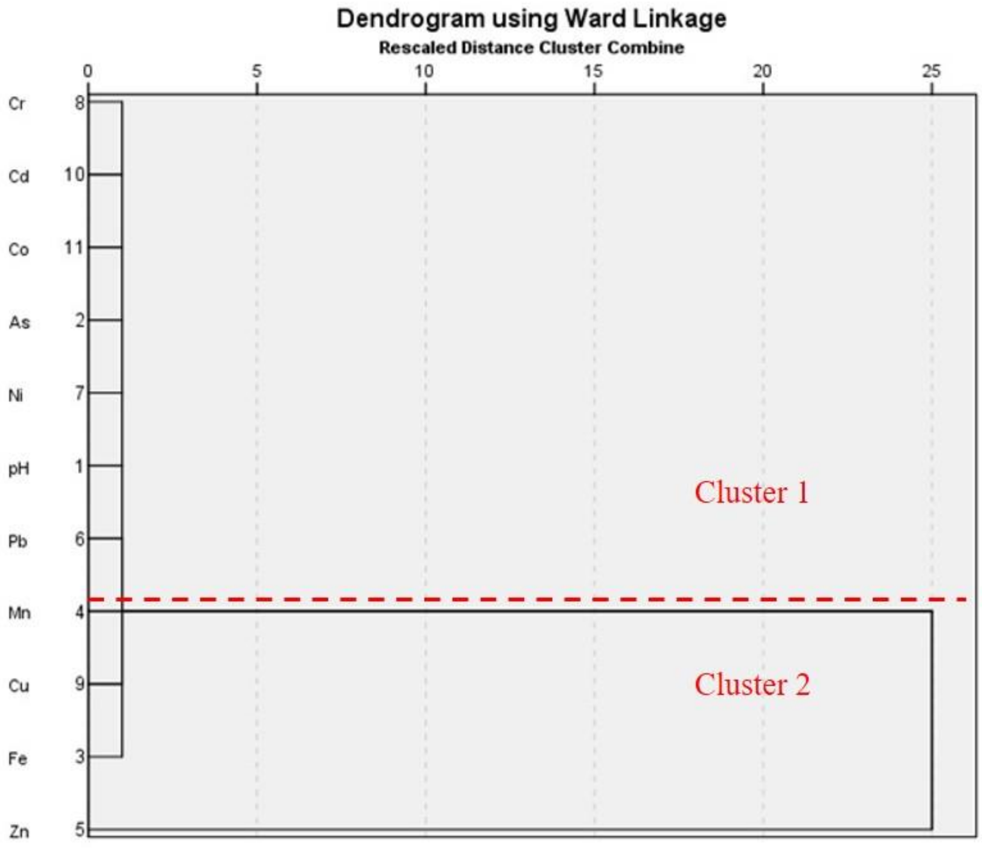

Figure 6.10: Dendogram grouping of analysed parameters

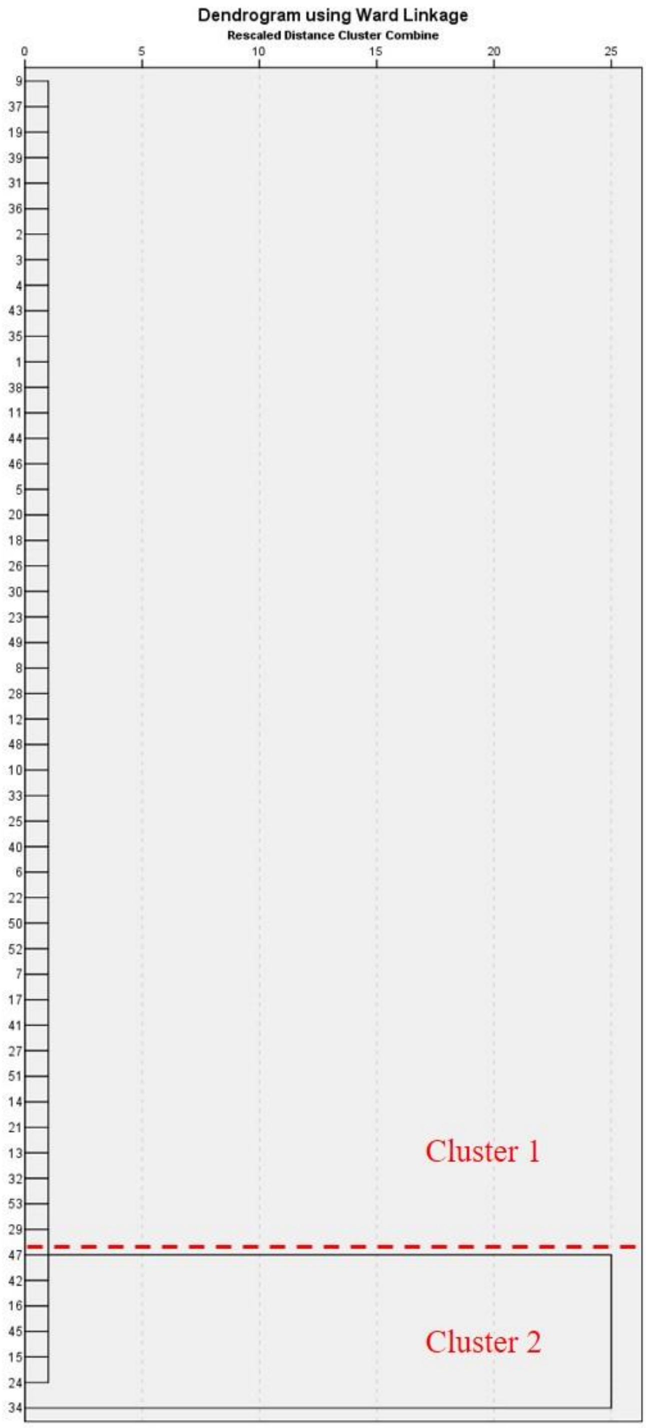

Figure 6.11: Dendogram grouping groundwater samples with respect to their heavy metal concentrations

Conclusion

The present study focused on evaluating the extent of heavy metal contamination and their source of origin in groundwater of Maputaland coastal aquifer using indexical and statistical analysis. The following conclusions were made:

- Groundwater is acidic to alkaline in nature. The dominance of heavy metals is in the order; Zn>Fe>Cu>Mn>Pb>Cr>Ni>Co>Cd<As. Of all the heavy metals, lead, cadmium and iron exceeded the WHO and SANS standard limits for drinking water in 25%, 23% and 11% of the samples.
- The HPI varied from a minimum of 0.28 to a maximum of 128.08. Based on the HPI classification, the samples varied from low to high pollution class. About 21% of the samples have HPI values greater than the critical limit of 100, suggesting that they are critically contaminated with respect to heavy metals and are unfit for human consumption.

  According to the classification of HEI, all the groundwater samples have low pollution with regards to heavy metals. Similarly, the C_d results revealed all the groundwater samples have low contamination with respect to heavy metals and are suitable for human consumption. The ERI revealed low ecological risk due to heavy metal contamination in this area.
- The PIG, SPI and OIP were employed to evaluate the drinking water suitability of groundwater in this area. Based on PIG results, 98% of the samples fall in the insignificant pollution zone. However, a total of 2% of the samples fall in the low pollution zone, respectively. Moreover, metals such as cadmium, iron and lead had O_w values greater than 0.1 in the low pollution zone suggesting the influence of anthropogenic sources in groundwater of this area.
- The SPI classified 2% of the samples as suitable while 74% and 24% were classified as slightly and moderately polluted with heavy metals, respectively.
- The OIP results revealed that majority of the samples are identified as excellent water quality and are suitable for drinking purposes. However, one sample showed to be very highly polluted with heavy metal especially iron.
- Multivariate statistical analysis (correlation analysis, principal component analysis and hierarchical cluster analysis) were utilized to assess the sources of heavy metals in groundwater of the study area. CM and PCA revealed that the release of heavy metals

into groundwater is governed by geogenic (weathering of rocks and minerals) and anthropogenic sources (domestic wastes and agricultural fertilizers).

- From HCA, R-mode cluster analysis showed two clusters. Cluster 1 consisted of pH, chromium, cadmium, cobalt, arsenic, nickel and lead which indicates the influence of geogenic and anthropogenic sources. Cluster 2 comprised of manganese, copper, iron and zinc which is due to geogenic and anthropogenic sources in the study area. Q-mode cluster analysis grouped groundwater samples into two clusters. Samples in cluster 1 have high levels of iron, zinc and copper and correspond to PC2 and PC3. Similarly, samples in cluster 2 have high levels of zinc, iron, and manganese. These samples correspond to PC, PC2 and PC3. Both samples in cluster 1 and cluster 2 are linked to mixed sources including weathering of parent material and anthropogenic sources.
- This study recommends treatment if contaminated groundwater prior to consumption by local residents to ensure the sustainability of public health . Regular monitoring of groundwater quality is also advised in this area to prevent further contamination of this precious aquifer.

CHAPTER EIGHT

7. CONCLUSION AND RECOMMENDATION

- The inhabitants of Maputaland coastal aquifer solely depend on groundwater for freshwater supply. It is crucial to assess groundwater quality as it directly influences human health, socio-economic development and ecosystem. This study was conducted to evaluate the hydrogeochemical processes, identify sources of groundwater contamination as well as evaluating the extent of heavy metal contamination and health risk assessment.
- Groundwater samples were randomly collected from 53 and 42 borewells during 2018 and 2019. Samples were analysed for major and minor ions, nutrients and trace metals.
- Groundwater is acidic to alkaline in nature. Based on TDS and TH classification, groundwater belongs to soft and hard freshwater type. NaCl water type is the dominant groundwater type followed by $CaHCO_3$.
- Groundwater is suitable for drinking purposes except in few locations that exceeded the DWAF and WHO standards for drinking limits for Na, Cl, Ca and Mg. Trace metals were above the WHO standards for drinking water for Cd, Zn, Pb, Mn, Al and Fe.
- EC, SAR, Na%, RSC, US salinity diagram, KR, Wilcox and PI diagrams revealed that groundwater is in the suitable range for irrigation purposes except in few locations.
- WQI revealed that majority of the groundwater samples fall under excellent and good quality. However, 22, 2 and 7% of the groundwater samples fall under poor water quality, very poor water quality and unsuitable water quality for drinking which are spatially situated on the western and southern part of the study area.
- Rock-water interaction, silicate weathering, reverse ion exchange, seawater intrusion, and anthropogenic activities are dominant processes that control groundwater chemistry of the study area. SMI confirmed that 29% of the samples are contaminated by seawater intrusion. Statistical analysis also confirmed the geochemical processes identified.
- Trace metal analysis showed that arsenic, cobalt, cadmium, lead, manganese and zinc as the main contributors to non-carcinogenic risk through the oral ingestion pathway. Mean value of $HQ_{ingestion}$ and HI value for cobalt and lead had highest contribution to the total non-carcinogenic risk in the study area. HQ_{dermal} and HI for cobalt and

manganese were above 1 in adults, children, and infants. HQ_{dermal} and HI for cadmium was greater than unity in children and infants. HQ_{dermal} and HI for arsenic and lead exceeded 1 in infants suggesting that these metals pose serious to adverse risk on local people.

- Based on the HPI classification, the samples varied from low to high pollution class. About 21% of the samples have HPI values greater than the critical limit of 100, suggesting that they are critically contaminated with respect to heavy metals and are unfit for human consumption.
- Based on the classification of HEI, all the groundwater samples have low pollution with regards to heavy metals. Similarly, the C_d results revealed all the groundwater samples have low contamination with respect to heavy metals and are suitable for human consumption. The ERI revealed low ecological risk due to heavy metal contamination in this area.
- The PIG, SPI and OIP were employed to evaluate the drinking water suitability of groundwater in this area. Based on PIG results, 98% of the samples fall in the insignificant pollution zone. However, a total of 2% of the samples fall in the low pollution zone, respectively. Moreover, metals such as cadmium, iron and lead had O_w values greater than 0.1 in the low pollution zone suggesting the influence of anthropogenic sources in groundwater of this area.
- The SPI classified 2% of the samples as suitable while 74% and 24% were classified as slightly and moderately polluted with heavy metals, respectively. The OIP results revealed that majority of the samples are identified as excellent water quality and are suitable for drinking purposes. However, one sample showed to be very highly polluted with heavy metal especially iron.
- Multivariate statistical analysis (correlation analysis, principal component analysis and hierarchical cluster analysis) were used to evaluate the sources of heavy metals in groundwater of the study area. CM and PCA revealed that the release of heavy metals into groundwater is governed by geogenic (weathering of rocks and minerals) and anthropogenic sources (domestic wastes and agricultural fertilizers). R-mode and Q-mode cluster analysis showed two groups of clusters that confirms the influence of geogenic and anthropogenic sources as major sources of heavy metals in groundwater of this area.

- This study recommends treatment if contaminated groundwater prior to consumption by local residents to ensure the sustainability of public health. Government and water managers should introduce rainwater harvesting and artificial recharge structures to improve the efficiency of groundwater resources in the study area.
- Long term monitoring and assessment of trace metals is necessary to minimize health effects from consuming groundwater on local people. These findings will help improve understanding of the hydrogeochemistry of this area and assist decision-makers with the management and development of groundwater resources.

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