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Investigating hydrogeochemical processes of groundwater, Heuningnes Catchment, South Africa

By

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Abstract

This study was conducted to investigate hydrogeochemical processes controlling the evolution of groundwater chemistry and their influence on water quality in the Heuningnes Catchment. The role or influence of hydrogeochemical processes in groundwater quality in aquifer systems remains poorly understood. One of the ways of improving such understanding is to employ different techniques to explore key processes that govern groundwater quality in aquifer systems. Therefore, the present study investigated hydrogeochemical processes of groundwater resources and identified key processes that explained its quality from a spatiotemporal perspective. The quantitative approach that provides the ability to assess relationships between variables both spatially and temporally was applied.

Groundwater sampling was done on four occasions during July 2017, October 2017, March 2018, and July 2018. Identification of hydrogeochemical processes controlling the evolution of groundwater chemistry and quality was done using various complementary tools. These tools included classification of the main water types, evaluation of water-rock interaction by means of stoichiometry analysis and bivariate correlation plots, inverse geochemical modelling, and statistical analysis (hierarchical cluster analysis and factor analysis). Physical parameters were measured *in situ,* while water samples were collected from boreholes, piezometers, springs, and artesian boreholes for laboratory analysis for major ions analysis. Descriptive and bivariate statistical methods were used to summarise and evaluate the strength of the relationship between variables, while multivariate statistical methods were applied to group similar samples based on their chemical compositions. Tri linear Piper diagrams were generated to characterize water type based on double normalizing the proportions of cations and anions, while correlation and stoichiometric analysis were applied to identify hydrogeochemical processes influencing groundwater chemistry.

The results generated from the trilinear Piper diagrams confirmed the dominance of sodium and chloride ions in waters of the Heuningnes Catchment. Groundwater of a Na/Cl type is typical for a coastal aquifer characterised by saline, deep ancient groundwater. The lower parts of the Catchment were characterised by saline groundwater. The results indicated that shallow groundwater samples within the study area were more mineralised as compared to deep groundwater with EC values ranging between 20.8 and 2990 mS/m, with waters within the Table Mountain Group region (TMG), recording the lowest values. Deep groundwater for boreholes and artesian boreholes located upstream in the Catchment was fresh and yielded some of the lowest EC values recorded with an EC value below 50 mS/m. Generally, EC values increased from the upper TMG region of the Catchment towards the Bokkeveld shale region downstream and were highest during the dry season of 2018. The results indicated strong geological influences on water chemistry. Bivariate correlation and stoichiometric analysis identified cation exchange, adsorption, evaporation, weathering of carbonates, sulphates and silicate minerals as processes influencing the chemistry of groundwater in the Heuningnes Catchment. The Saturation Index (SI) results showed a change of calcite, dolomite, aragonite, gypsum, anhydrite, halite, melantinterite, siderite and sylvite from being undersaturated to oversaturated at some areas for the different seasons along the flow path. The mass-balance modelling results indicated that ion exchange and reverse ion exchange processes were more dominant at low elevations along the same flow path during the dry periods. However, at high elevations along the flow path, silicate weathering was the dominant process taking place. The findings of this study demonstrated the influence of hydrogeochemical processes in changing the water chemistry along the flow paths. In conclusion, the study showed the value of utilising various assessment tools as complementary techniques to improve the understanding about hydrogeochemical processes, and its influence on evolution of groundwater chemistry and quality. Based on the findings of the study the following recommendations were made for future studies; the sample points or sample boreholes in the study Catchment should be increased; and to have more sampling trips to enable better comparison between the possible processes.

Abbreviations and Acronyms

μ	Micron
$\mu g/L$	Micrograms per Liter
$\mu S/cm$	Micro Siemens per centimeters
^0C	Degree Celsius
Ca^{2+}	Calcium ion
CA	Cluster Analysis
$CaCO_3$	Calcium carbonate
Cl^-	Chloride ion
CKB	Central Kalahari Basin
CO_2	Carbon dioxide
DOC	Dissolved organic carbon
EC	ElectricalConductivity
FA	Factor Analysis
HCA	Hierarchical Cluster Analysis
HCl (ℓ)	Hydrogen chloride solution
HCO_3^-	Bicarbonate ion
HYB	Hat Yai Basin
K^+	Potassium ion
KAS	Kasserine Aquifer System
Km	Kilometres
mamsl	Meters above mean sea level
meq/L	Milli equivalents per Litre
Mg^{2+}	Magnesium ion
mg/L	Milligrams per Litre
mS/m	MilliSiemens per meter
Na^+	Sodium ion
NH_4^-	Ammonium ion
NO_3^-	Nitrate ion
PHREEQC	PH Redox EQuilibrium
R^2	Coefficient of determination
R	Correlation coefficient
RS	Remote sensing
SO_4^{2-}	Sulphate ion
TA	Total alkalinity

TDS	Total Dissolved Solids
TMG	Table Mountain Group
TZ+	Total Cations

Declaration

I, Abongile Xaza, declare that project title *"Investigating hydrogeochemical processes of groundwater, Heuningnes Catchment, South Africa"* is my own work, that it has not been submitted for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

Full names: **Abongile Xaza**

Signature: A.Xaza

Date: September 2020

This Thesis is dedicated to my late parents, Mr Banguxolo Mbusi and Mrs Thenjiswa Xaza.

HEBREWS 11:1

“Now faith is the substance of things hoped for, the evidence of things not seen”

Acknowledgements

I would like to first thank God for providing me with the strength that was required for the completion of my master’s Thesis. I would also like to thank my supervisor and my co-supervisor, Dr T. Kanyerere and Dr S. Israel respectively for their assistance throughout formulation and execution of this research. To the Non-Perennial River (NPR) project and National Research Foundation (NRF), I am grateful for their financial assistance, without which the research would not be possible. I am deeply grateful to Miss. E. Malijani and Mr. V. Banda for granting access to the required data. To my colleague Miss. S. Nyakeni and the senior students at the Environmental and Water Science department for assisting me where needed. Finally, I would like to thank my family for their encouragement and their continued support.

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Chapter 1: General introduction and background

1.1 Background

Groundwater is vital to the development of most arid and semiarid regions due to limited precipitation and surface water. Rational utilisation and sustainable management of groundwater are particularly important in these areas. Groundwater is one of the important sources of water used for domestic, irrigation and industrial purposes. In natural hydrological cycling, groundwater interacts with the surrounding rocks causing a variety of hydrogeochemical processes that alter groundwater chemical components. Study of the hydrogeochemical processes has been an area of interest in the past few decades, as chemical variation of groundwater can reveal the interaction between groundwater and environment and provide a scientific basis for water resource management (Li *et al*., 2018.

Groundwater chemistry of a region is generally not homogeneous and it is controlled by geochemical processes, flow and recharge processes, evaporation, evapotranspiration and the possible presence of contamination sources (Rajesh *et al*., 2012). Identification of various geochemical processes help to understand the cause of change in water quality due to the interaction with aquifer material, especially in weathered rock formations remains important. These geochemical processes are responsible for the seasonal and spatial variations in groundwater chemistry.

The geochemical properties of groundwater depend on the chemistry of water in the recharge area as well as on the different geological processes that take place in the subsurface (Rajesh, 2012). The chemistry of groundwater is an important factor determining its suitability for use for domestic, irrigation and industrial purposes. Interaction of groundwater with aquifer minerals through which it flows greatly controls the groundwater chemistry. Hydrogeochemical processes that are responsible for altering the chemical composition of groundwater vary with respect to space and time. The hydrogeochemical processes of the groundwater system help to obtain an insight into the contributions of rock/soil–water interaction and anthropogenic influences on groundwater (Kumar *et al*., 2009) (Chebbah and allia, 2016). These geochemical processes are responsible for the spatiotemporal variations in groundwater chemistry (Matthew 1982; Kumar *et al*., 2006).

Groundwater chemistry, in turn, depends on a number of factors, such as general geology, degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources other than water-rock interaction (Domenico 1972; Hem 1985; Schuh *et al*. 1997; Toth 1984). In addition to these processes, water-borne pathogens, toxic and nontoxic pollutants also degrade water quality when they are transported from the recharge to the discharge area through aquifers by groundwater movement or infiltration of polluted surface water anywhere along the flow path. Undesirable and soluble constituents in the water cannot be controlled after entering the ground (Johnson 1979; Sastri 1994). Sami (1992) has explained that leaching of surficial salts, ion-exchange processes, and residence time of groundwater in the aquifer causes the hydrogeochemical variations in the groundwater. Such factors and their interactions result in a complex groundwater quality (Hussein 2004).

Hydrogeochemical studies, in turn, assist in planning management and remedial measures to protect aquifers that are contaminated by natural and anthropogenic activities. Thus, detailed knowledge on the geochemical process that influence groundwater chemistry is essential to understand and deal with the groundwater quality issues.

1.2 Problem statement

On a global scale, the study of hydrogeochemical processes has received much attention as a result of groundwater quality concerns. However, in the current setting, the role of hydrogeochemical processes on groundwater chemistry and quality of different aquifer systems remains poorly understood. The lack of baseline studies on hydrogeochemical processes for comparative purposes in the current study area leads to the poor understanding of these systems. The study argues that improved knowledge of hydrogeochemical processes leads to a better explanation of changes in groundwater chemistry.

1.3 Research question

What is the role of hydrogeochemical processes on groundwater chemistry and quality of coastal aquifers? The current study poses the following hypothesis: Sea-water intrusion processes are dominant in the Heuningnes Catchment, South Africa.

1.4 Aim and Objectives

The aim of the current study was to identify the dominant hydrogeochemical processes that influence the groundwater chemistry along the flow path within the Heuningnes Catchment.

Objectives

In order to achieve the above- mentioned aim, there are three objectives that guide the study into achieving the study aim.

- Objective 1: To determine the hydrogeochemical processes
- Objective 2: To simulate the hydrogeochemical processes
- Objective 3: To evaluate the existing conceptual models of hydrogeochemical processes

1.5 Significance of the study

Knowledge of hydrogeochemical characteristics plays an important role in assessing the groundwater quality to understand its suitability for various purposes. The increased knowledge of geochemical processes can help to understand the groundwater hydrogeochemical systems. Hence this study investigated hydrogeochemical processes of groundwater in the Heuningnes Catchment.

The contribution of the study is to the body of knowledge on hydrogeochemistry through publication of papers in peer-reviewed journals. The planned papers are as follows: 1] Using multi-method approach to determine hydrogeochemical processes in groundwater resources; 2] Using graphical methods and multivariate statistical techniques to investigate hydrogeochemical processes in groundwater resources, Cape Agulhas, South Africa and 3] Using saturation indices and inverse modelling to simulate hydrogeochemical processes in coastal aquifer, Western Cape, South Africa.

1.6 Conceptualisation of the study

This research forms part of the University of the Western Cape's Institute for Water Studies project entitled "Ecologically sustainable management of non-perennial rivers". The overall aim of the study is to improve understanding of the relationships between river flow, ecosystem characteristics and services provided by non-perennial rivers as well as the prediction, decision-making and management related to ecological and social consequences of flow modifications of non-perennial rivers. The factors that determine whether a river is perennial or not are climate, landscapes, land-forming processes at various scales and interactions between surface water and groundwater along these rivers. Since the ecosystems occurring on non-perennial rivers are made up of abiotic (non-living) and biotic (living) elements, the physicochemical characteristics of water along the non-perennial rivers are also being assessed in this bigger project. The main components of the bigger project are hydrology, hydrogeology (groundwater), geomorphology, water quality, aquatic fauna and riparian flora and vegetation. This bigger project has seven objectives in which the second objective is to establish how interactions between surface water and ground water affect the quantity and quality of Non-perennial River flows in different physiographic settings. It is from second objective of the bigger project where the current study is based on. Interaction based on chemistry or quality, requires one to first understand the groundwater chemistry in different parts of the Catchment. However, in order to better understand the system, a study on the processes that influence the groundwater chemistry and concentration of certain parameters in the groundwater was needed. That is how the idea for the current study was conceived as it looks at the system holistically in terms of chemistry and quality.

Scope and nature of the study

Within the scope of hydrogeology, which deals with the movement and distribution of water in the rocks pore spaces, fissures, faults, and lineaments this study focussed on processes that control the chemistry and quality of such waters. The current research study focused on the recharge and discharge components of hydrogeology processes. These include the natural recharge of aquifers from precipitation and surface water bodies such as rivers, streams, and ponds, and the discharge of groundwater to rivers (groundwater recharging surface water bodies). The study focused on establishing the processes that influence groundwater quality through conventional graphical methods together with geochemical modelling techniques and described hydrogeochemical processes through a conceptual model.

The current study used quantitative methods which involved measuring water levels and water quality in the field. A desktop design approach involved the collection of secondary data, such as water levels, climatological, geological, and hydrogeological data from various sources which helped in the development of a hydrogeochemical conceptual model. For the second objective a desktop design approach was used to simulate the possible hydrogeochemical processes through geochemical modelling techniques.

1.7 Study area description and justification

1.7.1 Location of study area

The Heuningnes Catchment is located in the southernmost region of South Africa, in the Cape Agulhas Municipality (Hoekstra and Waller, 2014) and is located at 34º 20" and 34º 50" S latitude and 19º 30" and 20º 30" E longitude. Cape Agulhas is known as the southernmost part of Africa. The Catchment covers five quaternary Catchments: G50B, G50C, G50D, G50E and G50F (Figure 1) and an area of 1 401 km^2. The Heuningnes River, which feeds an estuary has two major tributaries, the Kars River which rises in the Bredasdorpberge and runs for 75 km to its confluence with the Heuningnes River, and the Nuwejaars River that rises from the Bredasdorpberge, Koueberge, and Soetangsberg and runs for some 55 km to the Soetendalsvlei (Heydorn and Grindley, 1984). The Heuningnes Catchment was chosen for groundwater studies by the bigger project.

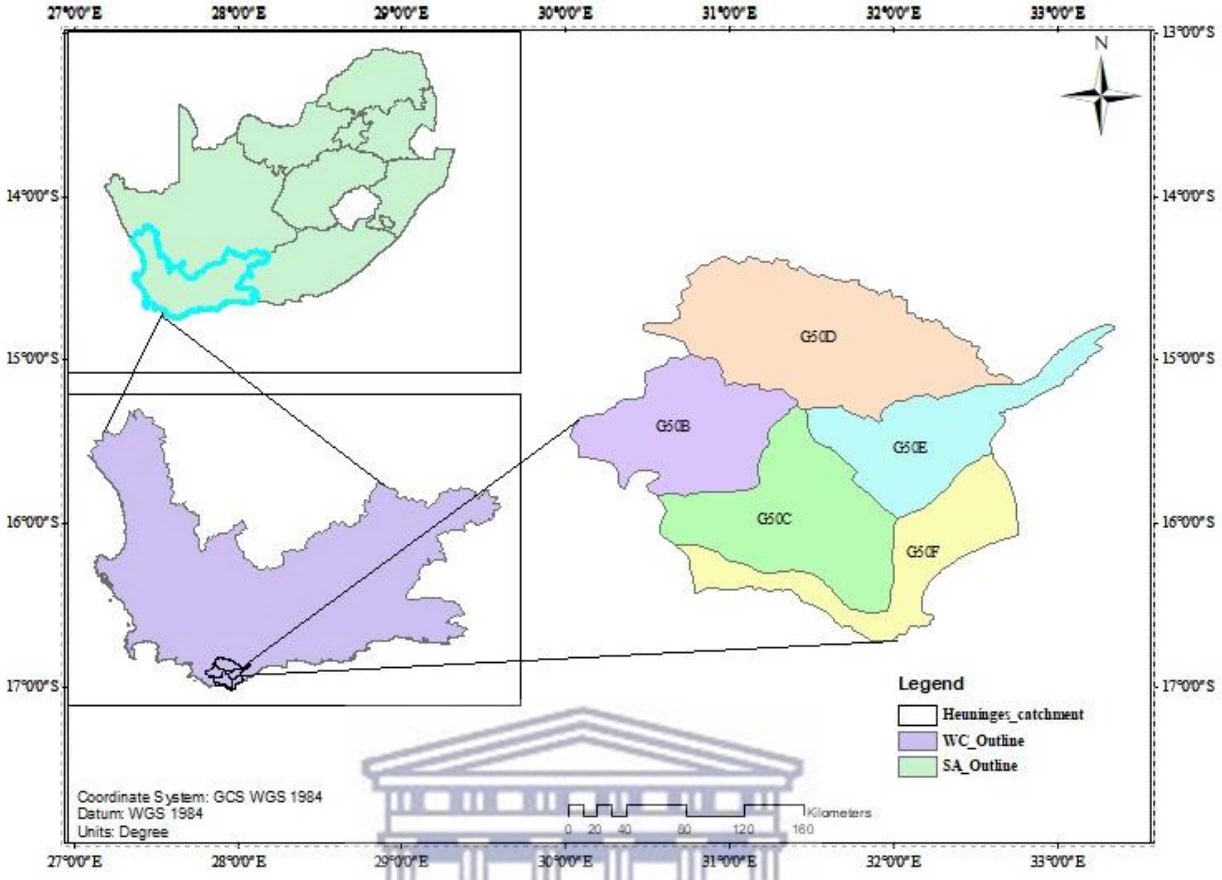


Figure 1: Heuningnes Catchment location in the Western Cape province of South Africa

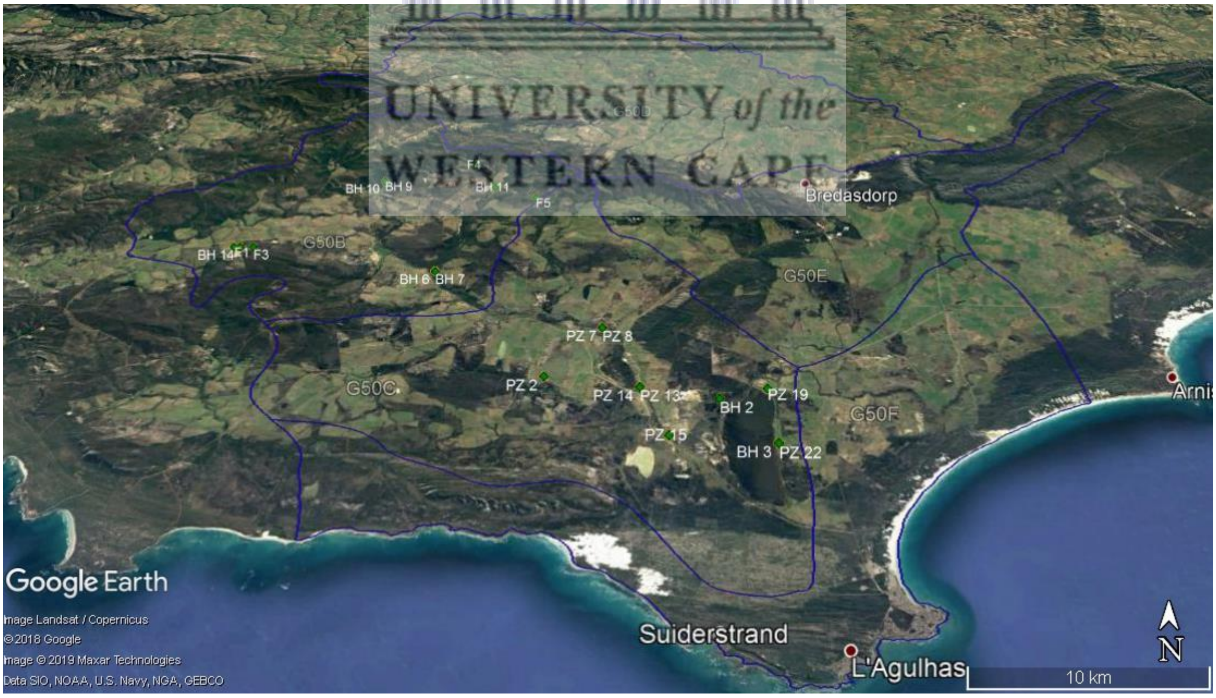


Figure 2: Heuningnes Catchment location and sampling locations in the Western Cape province of South Africa

Influence of soil and lithology on hydrogeochemical processes

The dominant soil types in the study area are leptosols which are very shallow, formed over a hard rock or unconsolidated gravelly material. These are followed by arenosols, which are mainly sand with little clay and humus featuring extraordinarily little or no development. Solonetz has little concentration of organic matter, are characterised by water deficiency and requires age to exhibit weathering and adequate development. Regosols occur on extremely limited shallow, medium to fine-textured unconsolidated parent material while luvisols, found mainly along river channels downstream of the study area are characterised by high activity clays. The soils in the Catchment are shallow with limited or no development (FAO, 1995). The soil and lithology may leach elements into the water as it percolates down to become groundwater thereby influencing the chemistry of the groundwater.

Influence of geology on hydrogeochemical processes

The oldest rocks in the Nuwejaars Catchment are the meta-sediments of the Malmesbury group and Cape Granite Suite which are exposed mainly by faulting. The Malmesbury, formed during the late Precambrian period, consists of alternating layers of greywacke shale and muddy sands. Igneous rocks of the Cape Granite Suite have intruded into the Malmesbury Group, and small outcrops are evident in the Catchment. The Malmesbury and Cape Granite rocks are overlain by the largely arenaceous Table Mountain Group which underlies the argillaceous beds of the Bokkeveld Group (DWS, 2017). The Table Mountain Group comprises the first division of the Cape Supergroup. It consists of quarzitic sandstones deposited during the Ordovician, Silurian and earliest Devonian periods and dominates the upper part of the Catchment (Roets *et al.* 2008). According to Xu *et al*., (2006), the TMG geology is not highly reactive and that gives an indication that chemistry in the upper part may not necessarily be influenced by geology. The Bokkeveld Group constitutes the middle subdivision of the Cape Super Group. It consists of a succession of mudstones, siltstones and fine-grained sandstones deposited early to mid-Devonian. The Bokkeveld shale is a poor aquifer, and the little water produced from it tends to be brackish to salty (Lubke and De Moor, 1998). This formation occurs in the middle section of the Catchment near Elim (Delicado and Banda, 2017). This gives an idea of what the chemistry of groundwater is like in that section of the study area. In the Nuwejaar Catchment, the Bokkeveld formation is overlain by the Bredasdorp Group which occurs downstream around Soetandalsvlei. The Bredasdorp beds consist of Tertiary and Quaternary deposits of unconsolidated to semi-consolidated shelly, calcareous sands. The calcareous sands are rich in calcium bicarbonate this gives an idea of the water type that can be expected in that section of the study area.

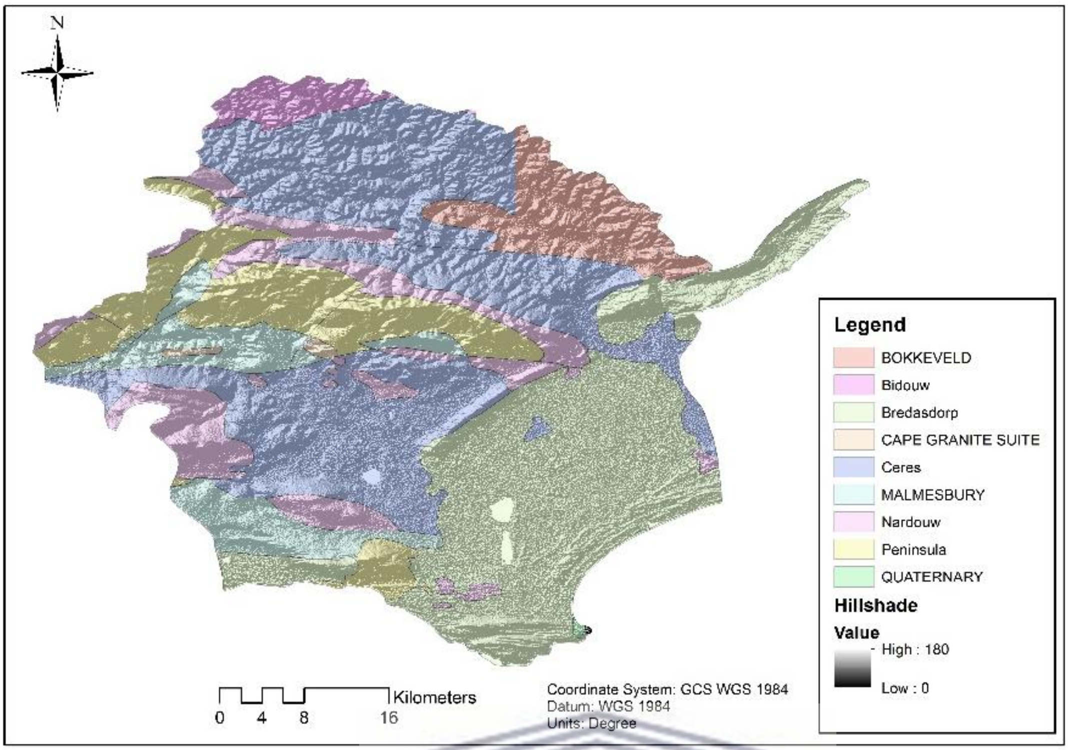


Figure 3: Heuningnes Catchment geology map in the Western Cape province of South Africa

Influence of land cover on hydrogeochemical processes

Land cover is mainly natural and includes shrubland fynbos (limestone and sandplain), grassland, bushland, and wetlands. Wheat, vines, orchards and livestock farming are the main activities in this region (Russell and Impson 2006). Elim town is the only urban development in the study area. Other urban areas in the Heuningnes Catchment include Napier, Bredasdorp, Arnistorn, L'Agulhas, and Struisbaai. Li *et al.*, (2018) listed anthropogenic processes as one of the main influencing factors of groundwater quality thereby land cover provides possible anthropogenic factors that may influence the chemistry of groundwater in the study area. The current study evaluated influence of landcover or the agricultural practices on the groundwater chemistry in the study area.

1.8 Thesis Outline

The present study consists of five chapters. This section presents the general structure of the thesis. Chapter 1 provides the general introduction of the study while contextualizing the study with reference to its main aim. The background, research problem, research aims and objectives, research question, as well as the significance of the study and description of the study area are presented. Chapter 2 provides the theoretical framework and conceptual understanding that guides the study. Chapter 2 also provides a review of studies conducted globally that pertain to the hydrogeochemical processes of groundwater resources. Chapter 3 outlines the research design and methodology used in the present study. In this chapter, commonly used methods are stated with their advantages and disadvantages together with the study variables, sampling design, study approach as well as a study perspective. Chapter 4 provides the conceptual model for the Heuningnes Catchment. This chapter provides main research findings which are discussed for explanations. The final chapter of this study (Chapter 5) provides a conclusion based on obtained results and suggests recommendations for future studies.

Chapter 2: Literature review

2.1 Introduction

This section presents a review of information in relation to the hydrogeochemical processes of groundwater resources. It explores different studies that have been conducted on a global scale on processes that influence groundwater quality. It reviews applicable methods that are used to explore hydrogeochemical processes. The main theoretical model called groundwater flow and the key concept of processes guided the work.

2.2 Previous studies on geochemical and hydrogeochemical processes

2.2.1 Geochemical processes

Senthilkumar *et al.,* (2013), assessed the geochemical processes controlling the groundwater quality in the lower Palar River Basin, southern India. The objectives of the study were to determine the hydrogeochemical nature of the groundwater in this region, to identify the geochemical processes responsible for the present status of groundwater quality and to assess the suitability of groundwater for drinking and irrigational purposes. The study used conventional graphical plots and geochemical modelling techniques. Results showed that cation exchange and silicate weathering are important processes controlling the major ion distribution of the study area. Mass balance reaction model NETPATH was used to assess the ion exchange processes. A high concentration of Ca in groundwater of the study area was due to the release of calcium (Ca) by aquifer material and adsorption of sodium (Na) due to ion exchange processes. The study concluded that the water of the area was suitable for domestic purposes except for certain locations with high EC and pH values. The above study served as a comparison baseline in terms of the expected or possible processes that influence groundwater quality. In the current study as outlined in the geology section, the lower part of the Catchment is dominated by calcareous sands. These sands are dominant in calcium bicarbonate, this gives an idea of a possible water type as well as the likely processes that influence groundwater which are adsorption and ion exchange processes.

Tahoora *et al.,* (2014), evaluated the identification of the Hydrogeochemical Processes in Groundwater Using Classic Integrated Geochemical Methods and Geostatistical Techniques, in Amol-Babol Plain, Iran. The objective of the study was to investigate the major hydrogeochemical characteristics of groundwater chemistry on the Amol-Babol Plain as well as providing an overview of the spatial distribution of the groundwater ionic ratios by using geographic information system (GIS) and interpolation techniques. Geochemical processes and factors controlling the groundwater chemistry were identified based on the combination of classic geochemical methods with GIS and geostatistical techniques. The results of the ionic ratios and Gibbs plots show that water-rock interaction mechanisms followed by cation exchange and dissolution of carbonate and silicate minerals have influenced the groundwater chemistry in the study area. Three classes, namely, C1, C2, and C3, have been classified using cluster analysis. The spatial distribution maps of Na^+/Cl^-, Mg^{2+}/Ca^{2+}, and Cl^-/HCO_3^- ratios and electrical conductivity values indicate that the dissolution of carbonates and weathering of silicate minerals played a significant role in the groundwater chemistry on the southern and western sides of the plain. However, the salinization process had increased due to the influence of the evaporation-precipitation process towards the north-eastern side of the study area. Salinization in the area could have been a result of a combination of different processes, the mixing of seawater intrusion with freshwater is a threat in this area for groundwater especially along the shoreline. The source of salinization was not known in the area due to the limited research available regarding hydrochemical characteristics. The study above has shown that using a multidisciplinary approach was beneficial in understanding the major hydrochemical characteristics of groundwater in Amol-Babol plain, Iran. Therefore, the current study employed a similar multidisciplinary approach like the one used by Tahoora *et al*., (2014), to understand the dominant hydrogeochemical processes that influence the groundwater chemistry of the current study area.

Luo *et al*., (2018), investigated the geochemical processes controlling the groundwater chemistry and fluoride contamination in the Yuncheng Basin, China- an area with complex hydrogeochemical conditions. The study carried out hydrogeochemical and stable isotope analyses and geochemical modelling. The major findings of this case study include the following: 1) Cation exchange and salt effects are vital controls on the enrichment of fluoride in groundwater in the area by reducing the activity of Ca^{2+}/F^- in groundwater via ion complexation. 2) Anthropogenic contamination from pesticide and fertiliser uses and industrial waste discharge is also a main source of fluoride in the groundwater. 3) Evaporation and ion effects favour the enrichment of fluoride in groundwater by encouraging the removal of Ca via precipitation. Lastly, desorption of fluoride from mineral/organic matter surfaces is enhanced under alkaline conditions and high HCO_3^- content in groundwater. The study concluded that human activities (domestic sewage, fertiliser and pesticide application in agriculture) and industries that cause fluoride pollution (aluminium and steel industries) may result in substantial fluoride inputs to the subsurface aquatic environment. The source of salinity is not known, the author argued that the source could be evaporites, dissolution or saline lake water intrusion as reported in previous work. In the current study there are salt lakes/pans in the lower part of the study area. In a study that was done by Mazvimavi (2017) in the study area, it was found that there is interaction between groundwater and surface water. The source of salinity in groundwater of coastal aquifers is often attributed to sea water intrusion but in the current study area the sea is relatively further from the Catchment. The above study and the one by Mazvimavi (2017), offer alternative sources or sites of origin the salinity in groundwater. The current study used the work of both authors to determine whether seawater intrusion, evaporites or the mineralisation processes were the source of the salinity of groundwater in the area.

Ntanganedzeni *et al.*, (2018), evaluated coastal aquifer contamination and geochemical processes in Tugela Catchment, South Africa—using Geochemical and Statistical Approaches. The objective of this study was to evaluate the groundwater chemistry and its associated geochemical processes and to evaluate the contamination sources in this coastal aquifer. Durov diagrams, Gibbs plots, ionic ratios, chloro-alkaline indices (CAI1 and CAI2) and correlation analysis implied that groundwater chemistry in the coastal aquifer of Tugela Catchment was regulated by the ion exchange, mineral dissolution, saline sources, and wastewater infiltration from domestic sewage; septic tank leakage and irrigation return flow. Principle component analysis also confirmed the role of saline and anthropogenic sources and carbonates' dissolution on water chemistry. Spatial distributions of factor score also justified the above predictions. The study recommended that a proper management plan was required to protect the coastal aquifer efficiently. Previous studies carried out in the various parts of the world including South Africa do not involve the detailed investigation of geochemical processes and contamination sources in the study area. Therefore, a comprehensive investigation in the coastal aquifer of Tugela Catchment was carried out through an integrated approach with an intention to gain thorough knowledge about the groundwater regime. The purpose of this study was to evaluate the groundwater chemistry and its associated geochemical processes and to evaluate the contamination sources in this coastal aquifer. The setting of the above study is similar to that of the current study; therefore, the current study applied similar methods as the above study to determine if the methods would be beneficial in understanding the processes in a different climatic environment.

2.3 Investigating hydrogeochemical processes in groundwater

Kumar *et al.*, (2009) investigated hydrogeochemical processes in the groundwater environment of Muktsar, Punjab. The objective of the study was to identify the hydrogeochemical processes and their relation with the existing quality of groundwater which was carried out in an intensively cultivated district of Punjab, India. The study adopted a multi-method approach i.e. conventional graphical plots and multivariate analysis of the hydrochemical data to define the geochemical evaluation of the aquifer system based on the ionic constituents, water types, hydrochemical facies and factors controlling groundwater quality. The results of the study suggested that different natural hydrogeochemical processes like simple dissolution, mixing, weathering of carbonate minerals locally known as ‘‘kankar’’ silicate weathering and ion exchange are the key factors in the pre-monsoon, which was superseded by leaching processes loaded with anthropogenic inputs in the post-monsoon. There was evidence of limited reverse ion exchange processes in some areas of the study area. The use of factor analysis in this study was to substantiate the findings of conventional graphical plots and was able to provide greater confidence in data interpretation. The study in its conclusion highlighted the descriptive capabilities of conventional and multivariate techniques as effective tools in groundwater evaluation. The setting of the study is different from the current study environment. Therefore, the current study implemented some of the techniques that were used by Kumar *et al.*, 2009, to see whether they would be effective in determining groundwater evolution of a coastal aquifer.

Rajesh *et al.*, (2012) assessed the influence of hydrogeochemical processes on temporal changes in groundwater quality in a part of the Nalgonda district, Andhra Pradesh, India. The objective of the study was to identify the hydrogeochemical processes that control the groundwater quality in a weathered hard rock aquifer. For the study to complete its objective, it employed the use of conventional graphical plots and modelling approach using phreeqc (saturation index). The study found that the geochemical processes and temporal variation of groundwater in this area are influenced by evaporation processes, ion exchange and dissolution of minerals. Hydrochemical processes such as dissolution, weathering of carbonate minerals and ion exchange are responsible for groundwater quality in Delhi, India. The implication of irrigation activity, evaporation and geochemical processes of granitic aquifers was not understood. The effectiveness of the multiple method approach is well documented for different study environments.

Gomo *et al.*, (2013), investigated hydrogeochemical processes in groundwater resources located in the vicinity of a mine process water dam. The study was aimed at identifying and describing the dominant hydrogeochemical processes and their contribution to the overall groundwater quality of an aquifer situated in the vicinity of a mine process water dam. The study site is in a typical Karoo Basin setting in Southern Africa. The study utilized bivariate plots, expanded Durov diagram and correlation coefficients statistics to analyse groundwater chemistry data. Based on analyses of the groundwater chemistry the study area was divided into two hydrogeochemical zones, the fresh background and contaminated groundwater. The results indicated that there was a positive correlation between major ions; Mg^{2+}, SO_2^{4-} and Ca^{2+} with the conservative Cl indicating that these ions were derived from the same saline source (mine process or water dam). The study identified albite dissolution as the main hydrogeochemical process responsible for the evolution of fresh groundwater chemistry in the background aquifer. The aquifer down gradient of the process water dam is contaminated by saline water that evolved from the dam. Based on the results, a recommendation was to consider decommissioning the facility given that the mine operations had ceased. The influence of surface water bodies on the underlying groundwater chemistry is high more so if there's proven interaction between the two water bodies. In the current study area, there are two salt pans in the lower parts and a study that was done by Mazvimavi, (2017) revealed that there was connection in those lower parts of the study area.

Varol *et al.*, (2014) studied the assessment of geochemistry and hydrogeochemical processes in groundwater of the Tefenni plain (Burdur/Turkey), a semi-closed basin located in the southwest of Turkey. The conceptual hydrogeological model of the plain was prepared for a qualitative description of the underground geology and interpretation of the hydrogeochemical processes of the study area. Various graphical plots and multivariate statistical analysis (Pearson correlation analysis) were used for identifying the occurrence of different geochemical processes. Carbonate weathering in the dry season and silicate weathering in the wet season were the major hydrogeochemical processes in the study area. In addition, ion exchange and reverse ion exchange were two possible processes of water-rock interaction in the basin. The mechanism controlling groundwater chemistry at the Tefenni plain was shown to be regulated by the geogenic process rather than anthropogenic activities. Bivariate correlation is applied to measure the strength of the relationship between two variables. The strength of the relationship is provided by the correlation coefficient value (R^2) between 0 and ±1 based on the generated scatter plot. The current study is set out in coastal rural area with limited agricultural practices taking, therefore, the current study adopted a similar as the above study to determine whether the dominant processes are geogenic or anthropogenic processes in the study area.

Yang *et al*., (2016) investigated the identification of the hydrogeochemical processes and assessment of groundwater quality using classic integrated geochemical methods in the Southeastern part of the Ordos Basin, China. The study was aimed at evaluating the hydrogeochemical processes that probably affect groundwater quality. The study made use of conventional graphical plots and multivariate statistical techniques. The results showed that the ions are derived from the leaching effect, evaporation and condensation, cation exchange, mixing effect and human activities. The study concluded that the integrated methodology applied in this study has proven to have the potential for investigating groundwater chemistry in other areas. Adopting an approach similar to the one used by Yang *et al*., (2016) was vital in identifying the hydrogeochemical processes for the current study.

El Alfy *et al*., (2017), assessed the hydrogeochemical processes affecting groundwater pollution in arid areas using an integration of geochemical equilibrium and multivariate statistical techniques to assess the factors controlling hydrochemistry and potential pollution in an arid region. Fitted variograms were used to map the spatial patterns of nitrate and salinity. The hydrochemical investigations and cluster analysis reveal four significant clusters of groundwater zones. Five main factors were extracted, which explain >77% of the total data variance. These factors indicated that the chemical characteristics of the groundwater were influenced by rock-water interactions and anthropogenic activities. The identified clusters and factors were validated with hydrochemical investigations. The geogenic factors include the dissolution of various minerals (calcite, aragonite, gypsum, anhydrite, halite, and fluorite) and ion exchange processes. The anthropogenic factors include the impact of irrigation return flows and the application of potassium, nitrate, and phosphate fertilizers. The study concluded that over time, these anthropogenic factors will most likely contribute to further decline in groundwater quality. The influence of geogenic processes has been well documented however, the influence of sea-water intrusion in coastal aquifers remains an area that needs to be further explored more so in rural coastal environments.

Pazand *et al*., (2018) studied the identification of the hydrogeochemical processes and assessment of groundwater in a semi-arid region using major ion chemistry in the Ardestan basin in Central Iran. The main objectives were to identify chemical processes that were responsible for the groundwater chemistry based on regional geology and water-rock interaction. The chemical compositions of the groundwater samples were statistically analysed. Multivariate statistical techniques are used to explain the relationship between hydrochemical parameters, statistical relationships between dissolved elements, classify the original data and geochemical data interpretation. The results showed that the factors controlling the water chemistry of the area are chemical weathering, ion exchange, and evaporation. Analysis of the distribution of factor scores shows that the groundwater in the area was influenced by different geochemical processes. Gibbs plot suggests chemical weathering of rock-forming minerals and evaporation are dominant factors controlling the groundwater chemistry. The use of Gibbs plot in groundwater studies has increased although the method was initially designed for surface water studies. The method has proven to be effective in identifying which hydrogeochemical processes were influencing the chemistry of groundwater. The above study has stated that the Gibbs method was originally designed for surface water however, the use of this method has increased in groundwater. Therefore, the current study used the method to determine the hydrogeochemical processes that influence groundwater in the study area.

A comprehensive study was conducted to identify the salinization origins and the major hydrogeochemical processes controlling the salinization and deterioration of the Gaza coastal aquifer system through a combination approach of statistical and geostatistical techniques, and detailed hydrogeochemical assessments, Abu-alnaeem *et al*., (2018). The results of the geostatistical analysis of the groundwater salinity showed that seawater intrusion along the coastline and salt-water up-coning inland highly influenced the groundwater salinity of the study area. The hierarchical cluster analysis (HCA) technique yielded seven distinct hydrogeochemical signature clusters. The box plot shows a wide variation of most of the ions while Chadha's plot elucidates the predominance of Na-Cl (71.6%) and Ca/Mg-Cl (25%) water types. Among the hydrogeochemical processes, the ion exchange process was the most effective process all over the study area. The study concluded that this integrated multi-technique research should be of benefit for the effective utilisation and management of the Gaza coastal aquifer system as well as for future work in other similar aquifer systems. The origin of salinization has been an area of interest more so in the coastal aquifer systems. The study in Iran serves as a good comparative study to the proposed work due to the similarity in setting.

Iqbal *et al*., (2018) investigated the hydrochemical processes determining the groundwater quality and suitability for irrigation use in an arid environment in the Liwa Aquifer, Abu Dhabi, United Arab Emirates. The objective of the study was to determine the hydrochemical processes governing the groundwater chemistry, evaluation of groundwater quality and suitability for irrigation use. The Schoeller diagram was used to study the comparative changes in the concentrations and ratios of water quality parameters for different samples. Gibbs plot was used to determine the mechanism controlling the groundwater chemistry. The factors determined to be governing the groundwater chemistry in the investigated area included evaporation, weathering of rocks and soil as suggested by the Gibbs plot. These factors resulted in increased salinity and therefore the poor quality of groundwater. The study recommended monitoring of agricultural activities with periodic assessment of groundwater quality to prevent further deterioration of groundwater quality in the study area. High salinity of the groundwater in the study area was due to high concentrations of sodium ion and chloride ion in most water samples. High salinity in coastal aquifers has been said to be an issue. The current study considered the relationship of these two major ions in relation to the resultant hydrogeochemical processes.

X. Li *et al*., (2018) assessed how groundwater chemistry is regulated by hydrochemical processes and geological structures in Tongchuan, China. The study aimed to identify the chemical characteristics of groundwater in the area and to identify the hydrochemical processes that control the chemistry of groundwater and to analyse the impact of geologic structures on hydrogeochemistry in the Tongchuan region. Graphical plots of ionic ratios, saturation indices, and ion exchange indices were employed to examine hydrochemical processes that result in different hydrochemical facies of each cluster. Results show the predominance of carbonate and silicate weathering in cluster 1, silicate weathering in cluster 2, and carbonate weathering in cluster 3. Ionic exchange is a ubiquitous process among all clusters. It was concluded that the main driver behind the different hydrogeochemical processes in this study was the Geology. This is one of the aspects that were investigated as part of this study. Therefore, the study contributed to understanding the spatial distribution of the processes in relation to the underlying geology.

Ibrahim *et al*., (2019) investigated the processes of water-rock interactions and their impacts upon the groundwater composition in the Assiut area, Egypt, considering applications of hydrogeochemical and multivariate analysis. Ion exchange, dissolution, and precipitation represent the effective hydrogeochemical processes it is that comprised water-rock interactions. Their influence on groundwater composition was investigated by applying the conventional hydrogeochemical tools and was confirmed with the use of multivariate statistical techniques. The hydrogeochemical indices were used for investigating the actual changes in the chemical composition of the groundwater and their extents. Multivariate statistical analysis of the factors and principal components were used for investigating the effective loading of groundwater. The results indicated that dissolution and precipitation played an essential role in the groundwater composition in the Pleistocene aquifer around the Nile, while ion exchange was effective in controlling the water composition in the Plio-Pleistocene and Eocene aquifers in Assiut area. The study concluded that the multivariate analysis supports the hydrogeochemical analyses and represents a useful and effective tool for the assessment of the geochemical processes that affect the groundwater composition. The study comprised the application of multivariate statistical techniques, factor analysis (FA) and principal component analysis (PCA), to analyse the water quality data set obtained for groundwater samples collected from Assiut area, Egypt. This allowed for better explanation of what the results from the statistical tests reveal about the hydrochemical processes in the current study.

Egbueri (2019), evaluated water quality appraisal of selected farm provinces using an integrated hydrogeochemical, multivariate statistical and microbiological techniques. With increasing use of agrochemicals, inorganic and organic fertilizers in the selected rural farm provinces in Nigeria, the need to assess the quality of their water resources for various purposes became compelling. The study objective was to assess the physicochemical and hydrogeochemical characteristics of water resources and the processes influencing them in the five provinces. This research, therefore, investigated the quality and geochemistry of groundwater and surface water in the area using integrated physicochemical, hydrogeochemical, and multivariate statistical and microbiological approach. Hydrogeochemical investigations showed that the supply of major ions in the waters and the geochemical evolution are mainly controlled by rock–water interactions, silicate weathering, and ionic exchanges. However, multivariate statistical analyses showed that the variations in chemistry and quality of the waters are due to combined influences of geogenic processes and human activities. Despite the lack of baseline data for comparative purposes, the methods used allowed for a better understanding of the hydrogeochemical processes that influenced groundwater chemistry in the area (Egbueri 2019). The current study adopted a similar approach to that used in the above study as in the current study there is lack of baseline on hydrogeochemical processes for comparative purposes.

Ibrahim *et al*., (2019) investigated the processes of water-rock interactions that impacted upon the groundwater composition in the Assiut area, Egypt by the application of hydrogeochemical and multivariate analysis. The hydrogeochemical indices are used for investigating the actual changes in the chemical composition of the groundwater and their extents. Multivariate statistical analysis of the factors and principal components were used for investigating the effective factor loading of groundwater. They confirm the obtained results by applying the hydrogeochemical indices. The results indicated that dissolution and precipitation played an essential control on the groundwater composition in the Pleistocene aquifer around the Nile, while ion exchange is more effective in controlling the water composition in the Plio-Pleistocene and Eocene aquifers in Assiut area. The study concluded that the multivariate analysis supports the hydrogeochemical analyses and represents a useful and effective tool for the assessment of the geochemical processes that affect the groundwater compositions in the Assiut area. Quantification of these geochemical processes based on the numerical simulations using appropriate geochemical modelling codes was recommended for further study. The current study applied geochemical modelling to help further understand and confirm the results from conventional graphical methods and multivariate statistical techniques.

2.4 Modelling approaches for hydrogeochemical processes and source of groundwater parameters

Carucci *et al*., (2012) investigated the interaction between shallow and deep aquifers in the Tivoli Plain (Central Italy) enhanced by groundwater extraction using a multi-isotope approach and geochemical modelling. The main issues were addressed by (i) hydrochemical and statistical clustering techniques in classifying groundwater into hydrochemical facies along different flow paths; (ii) development of a conceptual hydrogeological model regarding their mixing in the travertine aquifer; and (iii) development of inverse geochemical models to support and verify the previous conceptual model. The study used a multi-isotope approach and geochemical modelling. The results showed that the stable isotope data (18O, 2H, 13C and 34S) supports the flow system conceptual model inferred from the geochemical data and represents key data to quantify the geochemical mixing in the different groundwater of the Plain. The results of numerical modelling (PHREEQC) are consistent with the flow paths derived from the hydrogeochemical conceptual model. The inverse models performed generated the main geochemical processes occurring in the groundwater flow system, which also included mixing. Geochemical and isotope modelling demonstrated an increasing influence of groundwater from the deeply buried aquifer in the travertine aquifer, enhanced by the lowering of the travertine aquifer water table due to quarry pumping. Mass-balance indicated different redox states of certain elements as part of the reaction; this may be an indication that there might be redox processes taking place. This approach attempts to indicate the nature and extent of geochemical reactions by defining the minerals that are reacting in the groundwater system, indicating the ones precipitating or dissolving. Additionally, it can define geochemical reactions that played a role in changing the groundwater chemistry. Therefore, the current study adopted the approach used in the above study to understand the extent of the geochemical reactions.

Belkhiri *et al*., (2012) investigated the water-rock interaction and geochemistry of groundwater from the Ain Azel aquifer, Algeria. The main objective of the study was to identify the geologic factors that affect the water chemistry in the region by using multivariate statistical and geochemical modelling techniques to describe the evolution of groundwater. The results showed that cluster analysis based on major ion contents defined 3 main chemical water types, reflecting different hydrochemical processes. The varifactors obtained from R-mode factor analysis indicate that the parameters responsible for groundwater quality variations are mainly related to the presence and dissolution of some carbonate, silicate, and evaporite minerals in the aquifer. Inverse geochemical modelling along groundwater flow paths indicates the dominant processes are the consumption of CO_2, the dissolution of dolomite, gypsum, and halite, along with the precipitation of calcite, Ca- montmorillonite, illite, kaolinite, and quartz. The purpose of inverse modelling is to determine all chemical reactions that lead to chemical and isotopic compositions of the groundwater. This approach uses the measured groundwater compositions to assume the possible geochemical reactions. Besides the groundwater chemistry data, the input data also requires the potential reactive mineral phases along the flow path.

Tahoora Sheikhy Narany *et al.*, (2014), evaluated the identification of the hydrogeochemical processes in groundwater using classic integrated geochemical methods and geostatistical techniques in Amol-Babol Plain, Iran. Geochemical processes and factors controlling the groundwater chemistry are identified based on the combination of classic geochemical methods with geographic information system (GIS) and geostatistical techniques. The results of the ionic ratios and Gibbs plots showed that water-rock interaction mechanisms followed by cation exchange and dissolution of carbonate and silicate minerals have influenced the groundwater chemistry in the study area. The study concluded that special management could be suggested for salinity control in the areas with saline water, which were specified by spatial distribution maps in the ArcGIS environment. The current study adopted a similar approach as the above study for the modelling of the spatial distribution of the processes in the study area.

Jia *et al*., (2017), assessed the application of inverse modelling in a study of the hydrogeochemical evolution of karst groundwater in the Jinci Spring region, northern China. Reaction paths and mineral phases for the hydrogeochemical modelling were determined based on the analysis results and in conjunction with the regional geology and hydrogeology. The PHREEQC hydrogeochemical modelling software was used to perform mass balance and reaction path modelling of the hydrogeochemical evolution. The results from the modelling showed that the hydrogeochemical processes occurring in the karst water vary widely. Additionally, hydrodynamic fields and geological structures were found to have significant control over the hydrogeochemical reactions occurring within the spring region's karst groundwater. A reaction path model can be defined as the assumption of the water chemical composition as the water undergoes reversible (occurring close to equilibrium) and irreversible (not at equilibrium) geochemical reactions in the aquifer system. The principal use of reaction-path modelling is to identify the solubility of certain minerals in solution and identifying the groundwater composition if geochemical reactions took place.

Rajabi *et al*., (2018) assessed hydrogeochemical processes in shallow quaternary aquifers from the northern part of the Datong Basin, China. The problem the study was addressing was that the shortage of water resources was increasingly becoming serious due to the decline of shallow groundwater in urbanized areas and the deteriorating groundwater quality in the urbanized and agricultural areas recently. The study aimed to define the principal hydro-geochemical processes controlling groundwater quality, based on the major ion and trace element chemistry and geochemical modelling. Speciation calculations using the geochemical modelling code PH Redox Equilibrium (PHREEQC) indicated that hydrolysis of bedrock, mainly composed of basalt and metamorphic rocks, is the major hydrogeochemical process controlling groundwater chemistry. Results showed that ion exchange and industrial and/or agricultural contamination contributed to the increase of Na^+ from Zone A to Zone C, where the concentration of NO_3^- is up to 461.5 mg/l with a mean value of 101.5 mg/l, indicating that agricultural practice seriously affects groundwater. Sulphate concentration in groundwater in an alluvial fan at Datong was extremely high, up to 1172.9 mg/l, and showed a directly proportional relationship with the concentrations of trace elements, especially Ni and Co, indicating that coal mining is the main contamination source for groundwater from the alluvial fan, in addition to agricultural activities. Geochemical modelling code PHREEQC has been widely applied and it has proven to be reliable in simulating and determining the possible hydrogeochemical processes that are likely to be influencing groundwater chemistry of different environments. The current study adopted the modelling method used in the above study as one of the possible modelling methods that would be used in simulating the hydrogeochemical processes.

Moran-Ramírez *et al*., (2018), assessed the modelling of groundwater processes in a karstic aquifer of Sierra Madre Oriental, Mexico. The main objective of modelling was to create or devise theoretical reaction models that can provide elements to explain that which is observed in the actual system. The study used a hydrogeochemical analysis of conventional graphical plots and geochemical modelling. Three end members were identified in these regions, one related to local flow, another to intermediate and a third to regional flow. These flows define ternary mixing processes in groundwater. Moran-Ramírez *et al*., (2018) considered the evolution of groundwater, which is important for learning the system performance and hydrogeochemical processes through VISHMOD (Virtual Samples in Hydrochemical Modelling) methodology. The mixing model for the intermountain valleys indicates that recharge occurs, for which local flow contributes 68.3%, intermediate flow 12.3% and regional flow 19.4%. The inverse modelling shows that the water-rock interaction, precipitation and/or dissolution of calcite, gypsum, and dolomite are the main processes occurring in the aquifer system of the intermountain valleys. The study concluded that according to the results, VISHMOD methodology proved to be an excellent tool to understand the evolution of groundwater. With this methodology the evolution could be represented as a mixture of three end members, to identify water-rock interaction processes that occur in the carbonated system which give rise to the chemical signature of water at each site. The use of the modelling method used by Moran-Ramírez *et al*., (2018), is not well documented this could introduce difficulties to execute as well as interpreting the results.

Manoj *et al*., (2019) evaluated hydrogeochemical modelling to understand the surface water–groundwater interaction around a proposed uranium mining site. Groundwater and surface water samples were collected between September 2013 and June 2018 along the groundwater flow path across the uranium mineralised region. The study utilised the geochemical modelling code PHREEQC to determine saturation indices and uranium speciation. The host rock mineralogical composition was considered to perform inverse geochemical modelling along the flow path. The collected groundwater and surface water levels indicated that the rainfall controls the recharge and discharge of this region. The results of the groundwater and surface water levels indicated that there are various scenarios of interaction between groundwater and surface water around the mineralised area based on the saturation indices and the temporal variation of rainfall. Inverse geochemical modelling indicated that the weathering of silicates/carbonates, dissolution of evaporites and the irrigation return flows were the major processes, controlling the hydrogeochemical evolution of water in the area. The study concluded that geochemical modelling was effectively used to understand the temporal changes in the interaction between surface water and the groundwater in a uranium mineralised region. The weakness of a mass-balance approach is that for models to be calculated, the analytical data input should include uncertainty limits (Parkhurst and Appelo, 1999). Because of this weakness, it cannot be easily applied to trace element data. Therefore, this approach is more effective when applied to elements that predominate in solutions. The use of trace element data was not incorporated in the current study.

Akpataku *et al*., (2019) evaluated the hydrochemical and isotopic characterization of groundwater in the south-eastern part of the Plateaux Region, Togo. The study aimed to improve knowledge on the hydrochemical evolution of groundwater from the basement aquifers and used isotopic, hydrochemical and inverse geochemical approaches to evaluate the hydrogeochemical evolution of groundwater. The results indicated that the origin of groundwater was from present-day infiltration. The predominant hydrochemical facies are mixed cations-HCO_3 associated with Ca/Mg-Cl, Na-HCO_3 and Na-Cl water types in equilibrium with kaolinite and Ca/Mg smectites. The identified facies were related to silicate hydrolysis, anthropogenic contamination, nitrification/denitrification, mixing along flow paths and dissolution/precipitation of secondary minerals. Total dissolved solids tend to increase along the flow path toward the potentiometric depression located in the central and southern parts of the aquifer system. Inverse geochemical modelling using the NETPATH-WIN model showed the relative importance of biotite, plagioclase and amphibole weathering and dissolution of secondary carbonate minerals along the flow path, suggesting that an abundance of minerals is not necessarily the main factor controlling the groundwater chemistry evolution. The use of the modelling method used by Akpataku *et al.*, (2019) is not well documented this could mean introduce difficulties to execute as well as interpreting the results. The current study adopted the modelling technique similar as the one above, but the current study used a different modelling code to the one above.

Marghade *et al*., (2019) investigated the application of geochemical and multivariate statistical approaches for the evaluation of groundwater quality and human health risks in a semi-arid region of eastern Maharashtra, India. The study adopted a qualitative approach, including geochemical and multivariate statistical approaches. The results showed a shift of hydrochemical type from $Ca^{2+} – Na^{+} – HCO_3^{-}$ to $Na^{+} – Ca^{2+} - Cl^{-}$ type along different flow paths. The main controlling processes observed from the chemical characterisation of the groundwater are water–rock interactions, de-dolomitization and reverse ion exchange. Inverse modelling showed that there was dissolution of dolomite, gypsum, halite, k-feldspar and CO_2 down the simulated pathways. The first three total variances/components/factors of the PCA accounted for around 77% of the variation. The high positive loadings of EC, TDS, Na^+, K^+, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} of principal Component 1 revealed silicate weathering and reverse ion exchange followed by human activities as the contamination sources. The study suggested that some management measures for protection of groundwater resources.

Roy *et al*., (2020) investigated the geochemical evolution of groundwater in hardrock aquifers of South India using statistical and modelling techniques. Advanced Principal component analysis (PCA) and Q-mode hierarchical cluster (HCA) were utilised to assess the hydrogeochemical characteristics and to classify the samples into three principal groups. The inverse geochemical modelling code PHREEQC and thermodynamic stability diagrams were used to identify the processes controlling hydrogeochemistry of each of the groups obtained from statistical analysis. The model results indicated that only a few geochemical processes governed the water chemistry and the geochemical reactions along the flow path. These were (i) dissolution of evaporite minerals (dolomite, halite); (ii) dissolution of primary silicate minerals (albite, anorthite, K-feldspar, biotite); (iii) precipitation of secondary silicate minerals (kaolinite, quartz, gibbsite, Ca-montmorillonite) along with anhydrite and calcite; and (iv) reverse ion exchange processes. The study concluded that the combined use of major ion chemistry, multivariate statistical analysis, geospatial techniques, saturation indices and inverse geochemical modelling was successfully employed to explain the hydrogeochemical processes operating in the groundwater of this area. Forward modelling is defined as the calculation of water composition from the assumed or specified geochemical reactions. This tool is normally applied in cases where there is no chemical data present. However, in the current study chemical data is present so the best method to use was inverse geochemical modelling.

2.5 Assessing conceptual model for hydrogeochemical processes

Charlier *et al*., (2012), assessed a conceptual hydrogeological model of flow and transport of dissolved organic carbon in a small Jura karst system. This paper aimed at characterizing infiltration and solute transport processes in a karst system during flood events to build a conceptual model of hydrogeological functioning. In this study, coupled hydrodynamic and hydrochemical approaches are used to improve the understanding of karst infiltration and transport. The study used two combined approaches. First, from hydrodynamic and hydrochemical data, a system structure is identified (consistent with a dual-porosity scheme) and characterized the main processes occurring during flood events. Second, based on this scheme, a new conceptual hydrogeological model is built coupled with DOC transport to numerically validate hydrological functioning. The study in its conclusion highlights the need for a quantitative approach to hydrochemical studies of karst systems to understand them better. Due to the complicated nature of groundwater problems, it is usually difficult to thoroughly understand complex hydrogeological systems. Therefore, a conceptual model serves to simplify the field conditions and organize the various flow processes so that the hydrologic system can be analysed with ease. The current study adopted a similar approach in which the conceptual model was used to simplify field conditions and identify the hydrogeochemical processes spatially in the study area.

Francés *et al.*, (2014), evaluated hydrogeophysics and remote sensing for the design of hydrogeological conceptual models in hard rocks – Sardón Catchment (Spain). The main objective of the study was to identify the main hydrogeological features such as high and low hydraulic conductivity zones, their spatial distribution and connectivity and to characterize them in the context of groundwater flow at the Catchment scale. A multi-technique methodology based on a downward approach that combines remote sensing (RS), non-invasive hydrogeophysics and hydrogeological field data acquisition was proposed for the study. The proposed methodology was particularly suitable for data-scarce areas. In line with a general conceptual model of hard rock aquifers, two main hydrostratigraphic layers were identified: a saprolite layer and a fissured layer. Both layers were intersected and drained by fault zones that control the hydrogeology of the Catchment. The spatial discontinuities of the saprolite layer were well defined by RS techniques while subsurface geometry and aquifer parameters by hydrogeophysics. The important step in the development of the model involves integrating all the forms of geological and hydrologic data in the study area, since the groundwater flow model is a form of mass balance. The current study adopted a similar approach in which geologic and hydrologic data would be incorporated together to produce the final conceptual model for the study area.

Montcoudiol *et a*l., (2015), assessed a conceptual model for groundwater flow and geochemical evolution in the southern Outaouais Region, Québec, Canada. A conceptual model was developed for a hydrogeological flow system in the southern Outaouais Region, Quebec, Canada, where the local population relies heavily on groundwater pumped from shallow overburden aquifers and from deeper fractured crystalline bedrock. The results showed that chemical data also allowed the identification of significant mixing zones. Isotope and noble gas data confirmed the hypothesis of remnant water from the Champlain Sea and support the hypothesis of mixing processes between young tritium-rich components with an older component containing high ^{4}He concentrations. It is still unclear if the mixing occurs under natural flow conditions or if it is induced by pumping during the sampling, most wells being open boreholes in the bedrock. It is clear, however, that the hydrogeochemical system is dynamic and still evolving from induced changes since the last glaciation. As a next step, the conceptual model served as a basis for groundwater flow, mass transport, and geochemical modelling to validate the hypotheses developed. Therefore, development of a conceptual understanding is an iterative process such that it should be updated as more data become available and as the understanding is improved. Conceptualization of a groundwater flow system is necessary for future numerical modelling which can be used by decision makers to manage water resources. The current study adopted a similar method to determine groundwater flow which would be used to simulate hydrogeochemical processes in the study area.

Lukjan *et al*., (2016), assessed the importance of alternative conceptual model for sustainable groundwater management of the Hat Yai Basin (HYB), Thailand. The objective of this study was to generate the multiple conceptual models by incorporating the uncertainty in hydrogeological interpretations and boundary conditions into the groundwater flow model of the HYB. This study evaluated two sources of conceptual model uncertainty of a groundwater flow model for the HYB. Two hydrogeological interpretations and five boundary conditions were considered. Ten alternative conceptual models were proposed and implemented in a 3D-mathematical model (MODFLOW). Model uncertainty was evaluated through the information criteria-based method. Study results show that the contribution of uncertainty in hydrogeological interpretation has more impact on the groundwater system than the boundary conditions. Additionally, these results strongly indicated the importance of conceptual model uncertainty in groundwater modelling for sustainable groundwater management. The constructing of groundwater conceptual models involves initially defining the geological framework (cross section) and delineating the lithology, aquifer thickness and confining units and these components each introduce a level of uncertainty. The current adopted a similar approach as the study above to construct the conceptual model for the study area.

Matos *et al*., (2016), assessed multivariate statistical analysis of hydrogeochemical data towards understanding groundwater flow systems in granites. The main aim of the study was to assess the use of multivariate statistics to distinguish groundwater from different flow systems, to aid in evaluating the possible infiltration of water from the existing hydraulic circuit into the new one. The results from cluster analysis showed three distinct groups of waters with different physicochemical characteristics and spatial distribution. A hydrogeochemical conceptual model for groundwater flow systems related to infiltration and water–rock interaction in this granite rock mass was proposed based on multivariate statistical analyses and geological information. The conceptual hydrogeological model was prepared for a qualitative description of the underground geology and interpretation of the hydrogeochemical processes of the study area. The current study adopted a similar approach to the one used in the study above as the current constructed the conceptual model as qualitative description illustrating the underlying geology and the resultant hydrogeochemical processes.

Lekula *et al*., (2018), evaluated the hydrogeological conceptual model of large and complex sedimentary aquifer systems – Central Kalahari Basin (CKB). The main objective of this study was to develop an efficient method of integrating data from various sources and scales, to develop a hydrogeological conceptual model of a large and complex multi-layered aquifer system, such as the CKB. Specific objective of their study was to adapt the hydrogeological conceptual model to its smooth conversion into a regional, numerical model. In this study, an efficient data integration method for developing the hydrogeological conceptual model of the large and hydrogeologically complex, Central Kalahari Basin (CKB) aquifer system, was undertaken. In that process, the suitability of 3-D geological modelling with RockWorks code in iterative combination with standard GIS (ArcGIS) was tested. The analysis of the spatial distribution of topological surfaces of the hydrostratigraphic units and hydraulic heads of the aquifers, allowed to identify three flow systems of the three aquifers, Lebung, Ecca and Ghanzi, all three having similar radially-concentric regional groundwater flow patterns directed towards discharge area of Makgadikgadi Pans. As a result of conceptual modelling, a fully 3D, 6 layers numerical model, with shallow, variably saturated, unconfined layer is finally recommended as a transition from conceptual into a numerical model of the CKB. A comprehensive understanding of the hydrogeological characteristics for evaluating and conceptualizing the groundwater flow system is fundamental. The current study used a similar approach as the study above to get a comprehensive understanding of the groundwater and use that knowledge to a better understanding of the groundwater flow path in the study area.

Kpegli *et al*., (2018), investigated the development of a conceptual groundwater flow model using a combined hydrogeological, hydrochemical and isotopic approach: A case study from southern Benin. The main aim of this study was to develop a coherent conceptual groundwater flow model for the research area. In this study, a combined hydrogeological, hydrochemical, and isotopic approach was applied to understand the groundwater flow within this aquifer and to develop a coherent conceptual groundwater flow model. The piezometric results indicated three main groundwater flow directions. Stable isotopes results confirmed the piezometer as the most depleted and enriched values in Oxygen-18 and deuterium were found respectively in downstream areas (southern region) and in the recharge areas (northern region) indicated by the piezometer. The combination of these results with the geologic and topographic data led to a coherent conceptual groundwater flow model. As illustrated in the above study, the current study followed a similar approach in developing a coherent conceptual model.

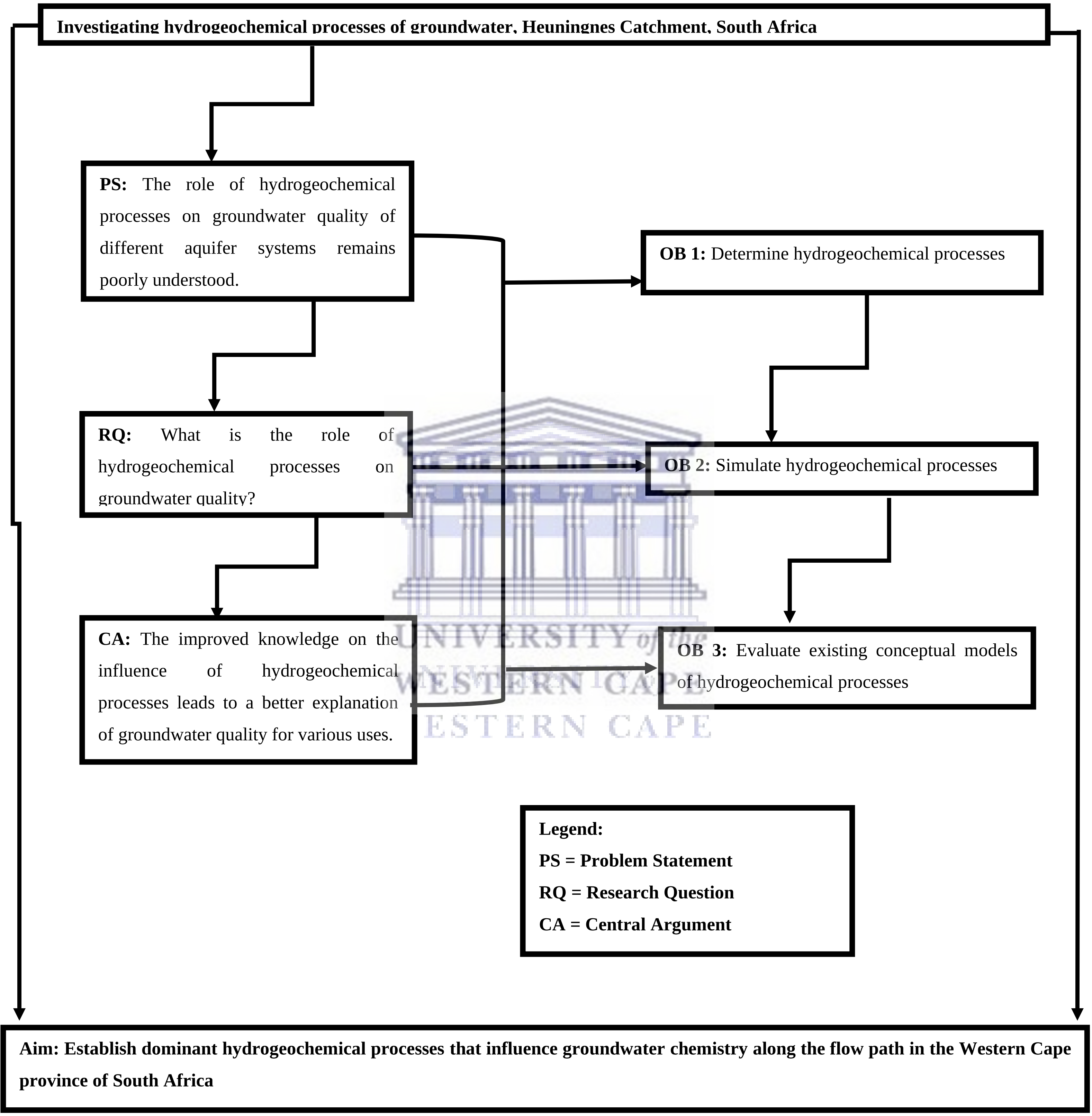
Hassen *et al*., (2018), established complex compartmentalized-aquifers connectivity via geochemical approaches towards a hydrogeochemical conceptual model: Kasserine Aquifer System, Central Tunisia. The objective of the study was to investigate hydrogeochemical and isotopic data to highlight the mechanisms leading to connection between the different compartments of the KAS. The study used geochemical modelling together with conventional hydrogeochemical techniques. The results showed that mixing between the four-groundwater compartments was also highlighted using a binary mixing hypothesis and an End Member Mixing Analysis method including two tracers Cl^- and $\delta^{18}O$ and three endmembers. The integration of these methods made it possible for the estimation of direct recharge ratios in every compartment and the quantification of diffuse and concentrated recharge in the KAS. The study concluded that the main factors affecting the KAS studied in this paper are, mixing, de-dolomitization and cation exchange processes. The conceptual models for karst aquifer systems is complex. A challenge that is often encountered is method selection to study these systems, like karst systems, coastal systems also come with a degree of complexity. Hence, an intergration of different components of the aquifer system are usually considered when developing a comprehensive hydrogeochemical conceptual model. The above study serverd as a guide on how to develop a comprehensive conceptual for coastal systems.

Enemark *et al*., (2019), evaluated the hydrogeological conceptual model building and testing. The study stated that the multi-model approach was the most common when characterising model uncertainty, this provides plausible alternative conceptual models to be evaluated. The aims of the study was to give an overview of how multiple alternative models have been developed, tested and used for predictions in the multi-model approach in international literature and to identify the remaining challenges. The study found that only a few guidelines exist for developing the multiple conceptual models, however, these are rarely followed. The review indicated that finding data that is both suitable to discriminate between conceptual models and relevant to the model objective still remains a challenge when it comes to conceptual model testing. The study argued that a need for an inclusive and systematic approach exists. Where, all aspects relevant to the study objective are covered during the model building process. The study concluded that the multi-model approach is superior to the consensus approach as it is transparent and accounts for conceptual uncertainty. However, to benefit fully from the multi-model approach, challenges remain in being more systematic with regards to both developing and testing alternative models. The current study adopted the alternative model but presented only one.

2.6 Theoretical framework

The theory guiding the study is Henry Darcy’s law, which governs the fluid flow through a porous media. The current study area is made up of fractured rocks. However, for the above law to apply to the current study area. The current study used the argument by Freeze and Cherry (1979), stating that in order for a fractured medium to be considered as porous then an assumption has to be made that fractures are large enough to provide a hydraulic connectivity similar to that of porous media. The law states that the velocity of flow per unit time is directly proportional to the hydraulic flow gradient which is laminar through a saturated mass of rock material. The law is based on the principle of a pressure gradient as well as the difference in head, if there is no pressure gradient then there will be no flow of water. The equation governing the law illustrate that flow occurs where there is a hydraulic head difference between two points across the cross-sectional area, with water flowing from areas of high elevation to areas of low elevation. The law has been based on the assumptions that the material is saturated, the flow is laminar, the flow is steady and continuous, the cross-sectional area of the rock material is considered and the temperature at the time of testing is 27ºC (Kalbus *et al.*, 2006). In the current study, the law was used to understand how the hydrogeochemical processes influence groundwater quality as it flows and interacts with the surrounding lithology. The law in the current study was also used in the development of groundwater flow for the simulation of the processes using difference in head to determine the flow path in the area. The model guided the selection of a modelling technique which relied on understanding the flow path in order to better explain how the processes change from one point of high hydraulic head difference to the next with low hydraulic head difference along the same flow path.

2.7 Research framework for the hydrogeochemical study



Investigating hydrogeochemical processes of groundwater, Heuningnes Catchment, South Africa

PS: The role of hydrogeochemical processes on groundwater quality of different aquifer systems remains poorly understood.

RQ: What is the role of hydrogeochemical processes on groundwater quality?

CA: The improved knowledge on the influence of hydrogeochemical processes leads to a better explanation of groundwater quality for various uses.

OB 1: Determine hydrogeochemical processes

OB 2: Simulate hydrogeochemical processes

OB 3: Evaluate existing conceptual models of hydrogeochemical processes

Legend:
PS = Problem Statement
RQ = Research Question
CA = Central Argument

Aim: Establish dominant hydrogeochemical processes that influence groundwater chemistry along the flow path in the Western Cape province of South Africa

Figure 4: A research framework for the hydrogeochemical study

2.8 Chapter 2 summary

Chapter two reviewed relevant literature on hydrogeochemical processes of groundwater which was done systematically on 1] hydrogeochemical processes and 2] simulation techniques available for hydrogeochemical processes and 3] existing conceptual models in order to better explain the hydrogeochemical processes. The review showed the importance of assessing influence hydrogeochemical processes on groundwater quality. The literature suggests the use of alternative models to limit the level of uncertainty and the biasness associated with relying on a single model.

In summary, tradition methods such as bivariate graphical plots, statistical techniques, isotope techniques as well as stoichiometric ratios remain the most utilised methods when it comes to hydrogeochemical studies. The use of a single method has shown to be less reliable hence the preference to using multi-methods when studying hydrogeochemical processes.

The literature shows that the use of modelling techniques can help to determine the source of cations in the system as well as to determine how the chemistry of the water has changed over time and space. The common modelling code within the reviewed literature was PHREEQC modelling code. Saturation Indices and mass-balance approach are the modelling techniques that are commonly utilised within PHREEQC.

The literature that was reviewed recommends the following: for the adoption of a multi-method approach when investigating hydrogeochemical processes 1], incorporating groundwater flow studies when conducting hydrogeochemical studies 2], long-term monitoring of the changes in groundwater chemistry 3], the use of geochemical modelling software like PHREEQC for future studies 4]. The current study focussed on the first gap which was the use of a multi-method approach coupled with incorporating groundwater flow and geochemical modelling.

Chapter 3: Research design and methodology

3.1 Introduction

This chapter describes the research design, sampling techniques and methods that were followed to collect and analyse the corrected and required data sets. In addition, the procedures for data quality assurance and research integrity that were followed are explained. Limitations that were encountered during the study and how such challenges were addressed to accomplish the set objectives of the study are highlighted. This chapter explains what was done, how it was done and why it was done in that way. The arguments in this chapter are that for results to be reliable and valid, processes which led to such results must be described and explained logically following standard methods and standard procedures. The literature guided the acquisition, preparation, and analysis to inform valid and reliable interpretation of the collected data needed to be reviewed and cited.

3.2 Research design

3.2.1 Research design approach

A field trial experiment was conducted where measurements were acquired at different sites within the study area. The chosen approach was used as it allows for the assessments (quantitative and qualitative) to be done during both dry and wet periods to incorporate possible seasonal variations in the measured data.

The research followed three sub-design methods i.e., Review (Literature review, Systematic review), meta-analytic and experimental design. The first sub-design aided in the completion of objective 1, in which appropriate and current methods were used to help identify the hydrogeochemical processes. The second sub-design aided in the completion of objective 2 where simulation of the hydrogeochemical processes was conducted. Lastly, the third sub-design method aided in the completion of objective 3, in which the systematic review of current and existing conceptual models which better explains the hydrogeochemical process was performed to identify the conceptual model that better explains the processes for the current study setting.

3.2.3 Sampling design

This study used a purposive sampling design, which is the type of nonprobability sampling in which the units to be observed are selected based on researcher’s judgement (Mouton, 2001). The technique is selected based on the characteristics of a sampling population and the study objectives to explain and characterise the possibility of interaction between the aquifer and non-perennial rivers. Therefore, samples from the rivers were collected at points which are close to the boreholes and piezometers.

The current study followed a quantitative approach, which provides the ability to explore relationships between variables, making it possible to characterize water chemistry. Four sampling campaigns were conducted to characterize the chemistry of surface water and groundwater during dry and wet seasons. Groundwater samples collected at depths below 20 m from the surface were collected to represent deep groundwater, while samples collected from piezometers usually at depths less than a maximum of 5 m from the surface were collected to represent shallow groundwater. Samples collected in July 2017 and July 2018 represented the onset of the wet season in each year, while those collected in October 2017 represented the beginning of the dry season and those collected in March 2018, the driest months of summer in the southern hemisphere. Water quality parameters (temperature, electrical conductivity, and pH) were measured while water samples were collected for hydrochemical and isotope analysis. Descriptive statistics were used to summarize large sets of data, while bivariate statistical analysis evaluated the strength of the relationship between variables. Furthermore, multivariate statistical methods were used to identify similarities between groups of samples based on their chemical compositions. Correlation analysis together with bivariate plots were used to infer the source of the elements found in the water samples and the possible processes that could have taken place in the study area, respectively. Inverse geochemical modelling techniques were assessed to determine the prevalent hydrogeochemical processes in the study area.

3.2.4 Data source and data type

The data needed for objective 1 was water quality, which was acquired from the chemical analysis of the sampled water and through secondary data such as chemical and physichemical data (major and minor ions, water level, temperature, and EC). The required data was from boreholes and piezometers.

Geological data needed for objective 2 were acquired from the geological maps, borehole logs of the area and through reports and journal articles. Flow direction data is needed which will be acquired from objective.

The type of data needed for objective 3 was the water levels to determine the flow direction. This data was acquired in the field through measuring depth to water of all the boreholes followed by calculating the water levels. Elevation data was needed as input data using SURFER software to construct the conceptual model; firstly, the data was acquired through Google Earth then confirmed with field measurements using a handheld GPS device.

Geological data was required since the groundwater flows and interacts with the surrounding geology; the data was acquired from geological maps of the area, borehole logs, and reports.

3.3 Research methodology

A research methodology is defined as "a strategy or architectural design by which the researcher maps out an approach to problem‑finding or problem‑solving." A research methodology is a comprehensive strategy "that outlines our choice and use of specific methods relating them to the anticipated outcomes, but the choice of research methodology is based upon the type and features of the research problem". Mixed-method research is "a class of research where the researcher combines quantitative and qualitative research techniques, methods, approaches, theories and or language into a single study". In order to have diverse opinions and views, qualitative findings need to be supplemented with quantitative results. These research methodologies are considered complementary to each other (Jamshed, 2014). Quantitative research was employed in this study for testing objective theories by quantifying variables and examining the relationships between variables. In this study, numerical data were collected and analysed on groundwater levels, geology and hydrogeochemistry.

3.4 Research methods

3.4.1 Methods that were used to determine hydrogeochemical process

Common and current data collection methods to determine hydrogeochemical processes

Field reconnaissance was conducted to identify active boreholes in the Catchment, to get information on the newly drilled ones and to be familiar with the site. Four sampling trips were conducted for the collection of groundwater samples. Sampling dates were selected to account for seasonal change. Samples were collected from selected boreholes on site. Borehole information was collected including borehole depth and groundwater level. The measurements of depth to the water level were measured at the boreholes using a Solonist TLC water level meter. Borehole samples were collected at specific depths within the screen, using a specific depth sampler.

A bailer was used to collect the samples for the piezometers, prior to sample collection, 3 well volumes of water are purged in order to remove the stagnant water, so as to get a sample that is representative of the local water quality of the aquifer. Samples for hydrochemical analysis were stored in 250ml polypropylene plastic bottles, pre-cleaned with 10% hydrochloric acid and phosphate-free detergent from Kimix chemicals and thereafter rinsed with deionized water. Samples for analysis in the laboratory were filtered through a 0.45-µm Munktell filter, kept cool in the field using a cooler box and stored in a refrigerator at a temperature of 6°C until they could be analysed, within a few days after collection.

A HACH HQ40d multi-meter was used to measure temperature, EC and pH in the field. Total alkalinity was titrated in the field using indicator powder pillows, phenolphthalein and bromcresol green-methyl red; the titrant was a standard solution (0.020N) of sulphuric acid.

Common and current data analysis methods to determine hydrogeochemical processes

Conventional graphical methods

Hydrogeochemical facies are generally studied and compared using different graphical representations such as Stiff (Stiff Jr, 1951), trilinear (Piper, 1944) and Durov (1948) diagrams. These methods are useful for visual inspection of hydrochemical data for identifying specific patterns and trends. The grouping of chemical analysis results using these methods helps in identifying hydrochemical facies and understanding the hydrogeological processes that influence groundwater chemistry (Hiscock, 2005). Trilinear diagrams are one of the most commonly and extensively used methods in representing and interpreting groundwater quality trends (Back, 1960, 1961, 1966; Back and Hanshaw, 1965; Hanshaw *et al.,* 1971; Rose, 2008; Zaporozec, 1972). These representations have contributed greatly to the understanding and interpreting of groundwater flow and quality trends. To assess the hydrogeochemistry of the groundwater from the study area, the Piper diagram (Piper, 1944) graphical representation method from AquaChem 3.7.42 was used. The Piper diagram graphical presentation shows the concentrations of individual groundwater samples that are plotted as percentages of the total cation and/or anion concentrations in meq/L, such that the samples with very different total ionic concentrations can occupy the same position in the diagrams. Seven ions namely $Ca^{2+,}$ Mg^{2+}, Na^+ plus K^+, Cl^-, SO_4^{2-} and HCO_3^- were used for this analysis. Such a graphical presentation represents the relative abundance of the ions and is composed of two triangles and a diamond field. The two triangles used in this analysis represent meq percentages of three sets of components, totalling 100%. Typically, components of one triangle are cations (Ca^{2+}, Mg^{2+}, and Na^+ plus K^+) at each corner while components of the other are anions (Cl^-, $SO4^{2-}$ and HCO_3^-). With such trilinear diagrams, groundwater samples that plot on a straight line within the central diamond field represent the mixing of groundwater between two end-member solutions (e.g., Fresh, and saline water).

The chemical reactions involved in the evolution of groundwater chemistry were dependent on the aquifer material or the country rock mineralogy with which the groundwater was associated the method used was the Gibbs plot. The chemical composition of groundwater implies rock–water interaction and the chemical process involved; thus, the groundwater chemistry can be used to identify these processes (Elango and Kannan 2007). Gibbs (1970) plots, and TDS vs $Cl^{-}/(Cl^{-} + HCO_3^{-}$ for anion in which TDS vs $Na^{+}/(Na^{+} + Ca^{2+})$ for cations were plotted to illustrate the groundwater evolution (Reddy and Kumar, 2010).

Bivariate plots are one of the methods used to understand water-rock interactions. Water-rock interactions play a significant role in the variations of groundwater quality, which are also useful to determine the genesis of groundwater. The ratio of the various components of groundwater is often used to analyse the concentration of different major elements and their interrelationship, and to understand and illustrate hydrogeochemical processes and the origin of the chemical compositions (Kumar *et al.*, 2014; Yang *et al.*, 2016). Various conventional graphical plots are often employed to identify the hydrogeochemical processes that occurred in the aquifer (Chebbah *et al*., 2016).

However, mineral weathering, and dissolution can be suggested that a simple plot of Ca^{2+} + Mg^{2+} versus SO_4^{2-} + HCO_3^{-} could provide information on the relative importance of the main minerals contributing to groundwater mineralization. In Ca^{2+} + Mg^{2+} versus SO_4^{2-} + HCO_3^{-}, the points falling along the equiline ($Ca^{2+} + Mg^{2+} = SO_4^{2-} + HCO_3^{-}$) suggest that these ions have resulted from weathering of carbonates and silicates (Datta and Tyagi, 1996; Rajmohan and Elango, 2004; Kuldip-Singh *et al.*, 2011). On the other side, if the ratio Ca/Mg = 1, the dissolution of dolomite should occur, whereas a higher ratio is indicative of greater calcite contribution (Maya and Loucks, 1995). The molar ratio of Ca/ Mg>2 indicates the dissolution of silicate minerals, which contribute calcium and magnesium to groundwater (Chebbah *et al.*, 2016).

Another significant factor affecting the constituents of groundwater is ion-exchange which has become an important topic for hydrogeologists since it regulates the transport of pollutant chemicals in both aquifers and soils (Appelo and Postma 2005). Ion exchange can be studied in terms of the chloro-alkaline indices (CAI-I and CAI-II) as proposed by (Schoeller, 1967; Marghade *et al.*, 2012). When an exchange of Ca^{2+} or Mg^{2+} in groundwater with Na^{+} or K^{+} in aquifer materials takes place, both above indices are negative, while in the instance of reverse ion exchange, both indices are positive (Chidambaram *et al.*, 2012). The Schoeller indices are calculated using the following formulas, where all ions are expressed in meq/L: Check the paper for the formula (Peiyue Li, Wu, and Qian, 2013) The plot of Ca^{2+} + Mg^{2+} versus SO_4^{2-} + HCO_3^{-} will be close to the 1:1 line if the dissolutions of calcite, dolomite, and gypsum are the dominant reactions in a system. Ion exchange tends to shift the points to the right due to an excess of SO_4^{2-} + HCO_3^- (Cerling *et al.*, 1989; Fisher and Mulican, 1997). If reverse ion exchange is the process, it will shift the points to the left due to a large excess of Ca^{2+} + Mg^{2+} over SO_4^{2-} + HCO_3^- (Kumar *et al*., 2009).

In general, it is expected that the evaporation process would cause an increase in concentrations of all species in water (Rajesh *et al*., 2012). If the evaporation process is dominant, assuming that no mineral species are precipitated, the Na^+/Cl^- ratio would be unchanged (Jankowski and Acworth 1997). Hence, the plot of Na^+/Cl^- versus EC would give a horizontal line, which would then be an effective indicator of concentration by evaporation and evapotranspiration. If halite dissolution is responsible for sodium, the Na^+/Cl^- molar ratio should be approximately equal to one, whereas a ratio greater than one is typically interpreted as Na released from a silicate weathering reaction (Kumar *et al*., 2009). Furthermore, sodium versus chloride ratio can be used to identify the evaporation process in groundwater. Evaporation will increase the concentration of total dissolved solids in groundwater, and the Na/Cl ratio remains the same, and it is one of the good indicative factors of evaporation. If evaporation is the dominant process, Na/Cl ratio should be constant when EC rises. Hence, the plot of Na/Cl versus EC would give a horizontal line, which would then be an effective indicator of concentration by evaporation and evapotranspiration (Chebbah *et al*., 2016).

Descriptive and inferential statistical methods

Descriptive statistics

Coefficient of variation (CV) is usually used to characterize the stability of variables. When the 0 < CV < 10 percent this illustrates a weak mutation; 10% < CV < 100% this illustrates moderate variability; CV>100% strong variation (Yang *et al*., 2016). This also includes the mean, minimum, maximum, standard deviation, and range.

Correlation Analysis

Correlation analysis produces pairwise associations from a set of variables and displays them as a matrix. This type of analysis provides information on the strength and direction of the association between two variables. In this context, the null hypothesis asserts that the two variables are not correlated, and the alternative hypothesis asserts that the variables are correlated. In the case of the alternative hypothesis, a small P-value is evidence that the null hypothesis is false, and the variables are, in fact, correlated (Reimann *et al*., 2008). The linear relationship between two variables is measured by the correlation coefficient r, which is also known as the Pearson product-moment correlation coefficient (Cohen *et al*., 2013). The value of r can range from -1 to +1 and is independent of the units of measurement. A value of r near zero indicates little correlation between variables while a value near +1 or -1 indicates a high level of correlation between the variables (Reimann *et al*., 2008). This means when two variables have a positive correlation coefficient, an increase in the value of one variable indicates a likely increase in the value of the second variable while a negative correlation would mean the opposite. A scenario where $r = 0$, then the two variables are not correlated or do not have an apparent linear relationship although it does not mean that they are statistically independent (Reimann *et al.*, 2008).

Hem (1970) pointed out that conventional graphical analysis methods such as the trilinear diagrams (Piper, 1994) are limited to two dimensions in analysing and interpreting groundwater chemistry. Groundwater chemistry is a multivariate dataset involving many variables and multivariate statistical analysis is required for a comprehensive evaluation and interpretation to supplement the conventional methods. Many hidden phenomena and inherent complex groundwater chemistry can be expressed through these statistical methods without losing the original information (Cloutier *et al.*, 2008). There are numerous graphical methods for the classification and interpretation of hydrochemical data and each of them serves a purpose. Although the Piper (1944) diagram is extensively used throughout the literature, it suffers from some serious drawbacks, namely that percentages of various ions are considered and not the actual concentrations of the dissolved solids. This shortcoming was overcome by the Durov (1948) doubled the triangle diagram and the Schoeller (1977) diagram (Zaporozec, 1972). Nevertheless, the Schoeller diagram method has the problem that limited water analyses can be presented in the diagram while the Durov diagram suffers specific drawbacks and a limited number of parameters can be considered (van Tonder and Hodgson, 1986).

Dalton and Upchurch (1978) showed that graphical interpretations (trilinear) of groundwater quality have certain limitations compared to multivariate statistical analysis. These limitations include:

a) A finite number of variables (chemical constituents) can be considered. In the case of the Piper (1944) diagram, only seven to eight variables (Ca^{2+}, Mg^{2+}, Na^{+} + K^{+}, Cl^{-}, SO_4^{2-} and HCO_3^{-} + CO_3^{2-}) are used.

b) The variables are generally limited by convention to major ions. NO_3^{-} for example, is not used in trilinear diagrams.

c) Spurious relationships may be introduced because of the closed-number computing system these methods use.

d) In the case of the trilinear diagram (Piper, 1944); percentages of the meq/L concentrations of the ions are used in comparison to the raw data concentrations (mg/L) which avoid inherent problems of the closed number system.

Multivariate statistical techniques for determining hydrogeochemical processes

Principle component analysis

Principal Component Analysis (PCA) is the most widely used statistical method among the families of multivariate statistics. This method identifies patterns in the data and presents them based on the similarities or dissimilarities in the dataset. Indicating patterns in extensive datasets with complex relations is a difficult task to undertake. Thus, using PCA can provide reliable results on the dominant components. The main aim of PCA is to summarize the multivariate dataset by reducing the statistical noise in the data, exposing the outliers, and then arranging components in descending order. The first few PCA's interpret the variables with the largest variance and contribute equally when the correlation matrix is used. In the present study, a Pearson correlation matrix was used to determine the relationship between variables.

Classification of the correlation matrix is based on Guilford's rule of thumb for the Pearson product-moment correlation.

Table 1: Guilford's rule of thumb for interpreting correlation coefficients r-value (Madlala, 2015)

r-value	**Interpretation**
0.0-0.29	Negligible or little correlation
0.3-0.49	Low correlation
0.5-0.69	Moderate or marked
0.7-0.89	High correlation
0.9-1.0	Very high correlation

The Kaiser-Mayer-Olkin (KMO) measure was applied first prior to the execution of the PCA. This is done to evaluate the suitability of the PCA and to test the adequacy of samples.

According to Kura *et al*., (2013), it is advisable only to proceed to the next level of PCA if the KMO value is 0.5 and above.

Cluster analysis

Cluster analysis is a method used to classify variables into groups called clusters based on their similarities or dissimilarities. This classification is done objectively without prior assumptions regarding the data to uncover the patterns in the original dataset. Cluster analysis can be achieved mainly in three ways, i.e. hierarchical, k-means and two-step clustering. In the first group, Agglomerative hierarchical clustering begins with every case being a cluster unto itself. At successive steps, similar clusters are merged until; finally, few clusters are used to represent the data based on the similarities or differences in variables.

In this study, principal component, factor analysis and hierarchical cluster analysis were used to understand the processes that influence groundwater quality in the Heuningnes Catchment.

3.4.2 Methods that were used for Simulation of hydrogeochemical processes

Data collection methods

The data collection for the simulation of hydrogeochemical processes has two main data collection method; (1) physical acquisition of geological samples so as to determine its mineralogy and (2) record review together with hydrochemical data. The first method involves going to the field and getting a geological sample either through auguring or drilling in order to get a sample. The sample is then taken to the laboratory to determine its mineralogical make up. The second method involves using geochemical modelling techniques, where hydrochemical data is used as an input. Then based on hydrochemical data, the model gives the likely mineralogical make-up of the host rock. The record review is then used to validate the model results. In the current study, the second method was used to determine the mineralogy of the host rock.

Data analysis methods

Geochemical modelling

The saturation index (SI) approach is used to predict the reactive mineralogy of the litho units from the groundwater data without collecting the samples of the solid phases and analysing the mineralogy. The SI is a widely used indicator in the hydrogeochemical study. It describes the saturation status of minerals in the groundwater. When $S_{\mathrm{I}} = 0$, the minerals in the aqueous solution are in equilibrium status; when $S_{\mathrm{I}} < 0$, the minerals in the aqueous solution have not reached saturation, and bear on a dissolution trend; when $S_{\mathrm{I}} > 0$, a supersaturated status of minerals in the aqueous solution is indicated and mineral deposition will occur (Qian and Ma 2005; Luo *et al*., 2008). The saturation index (SI) is defined as

$$S_{\mathrm{I}} = 1\mathrm{og}\ (I_{\mathrm{AP}}/K) \qquad (1)$$

where IAP (Ion activity product) *I* is the relevant ion activity product in a mineral dissolution reaction, which can be obtained by multiplying the ion activity coefficient and composition concentration; and *K* is the equilibrium constant of mineral dissolution at a certain temperature (Li *et al.*, 2010).

Inverse modelling

Inverse modelling is used to deduce the geochemical reactions that account for the change in the chemical composition of water along a flow path. At least two chemical analyses of water at different points along the flow path are needed, as well as a set of phases that are potentially reactive along the flow path. From the analyses and phases, mole-balance models are calculated. A mole-balance model is a set of mole transfers of phases and reactants that accounts for the change in composition along the flow path (Suma *et al*., 2015).

Inverse geochemical models quantify net solute flux from water-rock interactions. Geochemical reactions (precipitation/dissolution, redox, and surface complexation) between the water and the aquifer material changes the mass of dissolved species, typically in millimol concentrations. Assumptions of inverse models are: (1) initial and final conditions occur along the flow path, which is hydraulically connected, (2) dispersion and dissolution do not affect dissolved concentrations, (3) reactions are at steady state, (4) major reactive mineral phases have been identified in the aquifer material (Zhu and Anderson 2002). A model is a subject of the selected phases that satisfies all the selected mass balance constraints. The model is of the form

Initial water + ‘‘Reaction Phases’’ → Final Water + ‘‘Product Phases’’:

Two prominent pathways A1 and A2 are selected from the identified recharge to discharge (Chidambaram *et al*., 2012).

Mass-balance simulation

Mass-balance simulation, the method is mainly used for studying chemical reactions along groundwater flow paths, in turn it determines the amount of deposited or dissolved minerals and gasses between two points. The method is also used to analyse changes in hydrochemical composition of groundwater based on the reactions that take place (Qian and Ma 2005). The net geochemical mass-balance reactions are constructed using phases, constraints and models as the main concepts and terminologies. (Abu-Jaber and Ismail 2003). The following has been used to describe the mass balance simulation: Two samples collected from two different points along the groundwater flow path are used; the water quality sample at the upstream point is considered the initial water quality, and the water quality sample at the downstream point is considered the end water quality. Then, the following description can be used to describe the principle of geochemical mass-balance reactions: the sum of the initial aqueous components and reactants equals the sum of the end aqueous components and resultants.

Under general circumstances, mass balance simulations are carried out against the elements. If *n* elements in the aqueous solution are considered, the amount of dissolution or deposition of *n* minerals can be determined by the mass balance simulation:

$$a_{ij} X_j = b_i \qquad (2)$$

where a is the stoichiometric number of the *i*th element in relation to the *j*th mineral, a dimensionless value equal to the molar number of *i*th element generated by the complete dissolution of 1 mol of *j*th mineral; *j x* is the molar number that the *j*th mineral precipitates or dissolves (positive for dissolution, and negative for precipitation); and is the increment of the *i*th element in the end water quality. Note that the possible mineral phase identified in the reactions is a set of ambiguous phases; it refers to the selected chemical elements according to the reactants and the resultant in a given hydrogeological system (Li *et al*., 2010).

3.4.3 Methods used to evaluate existing conceptual model for hydrogeochemical processes for groundwater

The following are the common data collection methods for the development of a conceptual model. A conceptual model is a schematization of what is known about the study area and thereby provides a basis for designing the numerical model (Kresic and Mikszewski 2013). "It consists of information on boundary conditions, hydro-stratigraphy and hydro-geological properties, flow directions, sources, and sinks, and preliminary water balance" (Anderson *et al*., 2015).

In this study, two hydro-stratigraphic units were considered. The upper unconfined aquifer consists of Tertiary and Quaternary deposits of unconsolidated and weathered sand and shale with a thickness ranging between 10 to 25m. The second layer is a confined aquifer which extends from the top of the first layer to 100m below the mean sea level. It is composed mainly of sandstone, shale, and quartzite of the Cape Supergroup (Bokkeveld and Table Mountain series). The bottom layer is underlain by an aquiclude comprising meta-sediments of the Malmesbury group at ~100m below the mean sea level. The hydro-stratigraphic units are defined based on geological cross-sections from literature and geologic logs.

When determining groundwater flows and directions, the commonly applied methods are a cross-sectional method, flow nets and three-point method also known as triangulation (Heath, 1983). These standard methods involve determining hydraulic heads by measuring the water levels in boreholes or piezometers installed in alluvial deposits (Freeze and Cherry, 1979).

Several piezometers and boreholes drilled, including existing boreholes in the study area were used.

Methods for the development of the conceptual model

Having collected all the necessary data, hydrogeological conceptual models that explains the role of groundwater on the river systems of the study area is produced using Surfer 11 software. Information from environmental stable isotope and hydrochemical data is incorporated into the conceptual model. The potential groundwater flow direction was determined by creating a groundwater level contour map. The depth to groundwater levels were measured using a water level dip meter while the elevation was determined using the GPS receiver. Therefore, the elevation of the groundwater level (hydraulic head) was calculated by subtracting the depth to water level from the surface elevation. Given this kind of data of more than three points, the groundwater contour map can be produced to deduce the direction of groundwater flow direction. The contours can be drawn manually by connecting points of equal heads (equipotential lines) from a minimum of three wells in a triangular configuration. However, a hand drawn procedure is labour intensive and time consuming, therefore, this study used the Vector Tool in Surfer (version 11) software since the software provides a quick and automated way of analysis and representation.

3.5 Quality assurance

Quality assurance is an especially important aspect of scientific work. Its goal is to identify, quantify as well as document bias and variability in the data that result from the collection, processing, and handling of samples.

3.5.1 Reliability and Validity of the findings

To ensure reliability and validity of the data collection and analysis process for determining the hydrogeochemical processes the following procedures were adhered to (objective 1). All water samples were analysed in an accredited laboratory which is in accordance with the international standards. The field water quality parameters which change during transportation and storage, were measured on site immediately during the sampling. During the measurement of water quality field parameters, the multi-parameter probe was calibrated on each field day. In addition, sample bottles were pre-rinsed for at least three times before collecting the sample for analysis. To ensure that same sites are monitored, a GPS was used locate the site and a permanent mark was placed in sites for easy identification. The reliability of the water quality results was checked by testing the error margin of major ion analysis.

Since the major ions represent most of the dissolved ions, there is almost equal equivalent amounts of major cations and major anions in water in what is known as the principle of electro neutrality (Younger, 2007). This was done by conducting a Charge Balance Error (CBE) using the formula:

$$CBE\ (\%) = \{(\Sigma meq\ cations - \Sigma meq\ anions) / (\Sigma meq\ cations + \Sigma meq\ anions)\} \times 100$$

It has been argued by some authors (Weight, 2008; Younger, 2007; Rajmohan and Elango, 2014) that an ionic balance error of less than 5% is acceptable to be used for scientific investigations whereas errors from 5 – 15 % should be used with caution. The current study CBE values are shown in Table 2.

To ensure the reliability and validity of the data collection and analysis for the simulation of hydrogeochemical processes (objective 2). The process for ensuring the reliability and validity of the hydrogeochemical data that was used in the simulation was already discussed under objective 1. To ensure that the reliabity and validity of the analysis of the data, the models uncertainty levels were set not exceed 5% giving a 95% confidence of the results. The validity of the data was ensured through running the model's multiple times to check if there would be any changes.

The reliability on the data that was collected for the evaluation of existing conceptual models was ensured using peer-reviewed journal articles (objective 3). To ensure that the data was valid cross checks were ran on the data using recent literature detailing the geological structures. The reliability and validity of the hydrogeochemical data illustrated on the conceptual model is discussed under objective 1.

Table 2: Charge Balance Error (CBE) results

Charge Balance Error (CBE) results

Site name	July 2017 CBE	October 2017 CBE	March 2018 CBE	July 2018 CBE
F1	0.05	-2.66	0.70	8.14
F2	-0.97	7.43		3.93
F3	-20.73	-0.03	-3.91	-0.33
F4	-0.61			
F5	-7.40	-5.58	3.47	-6.41
BH1	9.12	-8.29	-10.87	-4.08
BH2			-77.73	-7.47
BH3	2.01		-79.14	0.04
BH4	0.20	-20.58	-4.49	8.82
BH5	1.90	-23.94	-0.22	11.99
BH6	6.04	-11.72	1.68	74.76
BH7	11.72	-8.90	-12.20	12.43
BH8	6.05	-7.43	-11.53	-7.08
BH9	-19.35	-4.86	-16.62	-9.46
BH10	4.44	5.75	-8.73	8.47
BH11	9.73	-28.30	-7.97	0.52
BH12	12.71	-4.71	2.49	30.09
BH13	-17.62	-6.20	-6.49	9.57
BH14	-4.87	2.37	-0.83	7.76
PZ 2		-11.94	-10.81	-5.17
PZ 7	-12.01			
PZ 8	-69.23	-67.42	-2.54	3.62
PZ 13	-37.57			
PZ 14	5.18	-76.24	-10.71	-10.80
PZ 16		-51.23	-3.63	-9.04
PZ 19	6.15			
PZ 26		-79.91	-7.51	1.02

3.6 Research integrity

In this study, some of the study sites were in private boundaries such as farms and a park (SANparks Cape Agulhas), with the area characterized by cropped fields and protected vegetation such as Fynbos and Renos`terveld species. Permission was requested prior to any field visits to the rightful owners of the properties. This was done through writing letters and informing the owners verbally once we were at the site to get access to the sampling sites.

Technical assistance was needed for the collection of field data for the simulation of the hydrogeochemical processes as well as for developing the conceptual model. In terms of objective 2, assistance in the form of coaching and guidance through modelling the processes was required.

All the relevant precautions were adhered to, to ensure that all the legalities and requirements will be met as per the ethics of this study.

3.7 Study limitation

The limitation of the study was the possibility of not being able to acquire geological samples to ascertain which minerals are in the host rock. However, to counter that the study used SI, which is a commonly used method for determining the mineralogy of an area using the water or soil composition without having to physically sample the geology.

Chapter 4: Results and Discussion

4.1 Introduction

In this chapter, deep groundwater refers to groundwater collected from boreholes at sampling depths greater than 20 m from the surface, while shallow groundwater refers to groundwater collected below 20 m. The term groundwater refers to both deep and shallow groundwater sources. The letters inside the figures depict different sampling periods e.g., A-July 2017, B-October 2017, C-March 2018, and D-July 2018. This chapter presents and discusses the results obtained for the three objectives of the study. The first objective was to determine hydrogeochemical processes, the second was to simulate the hydrogeochemical processes, and the third was to evaluate existing hydrogeochemical conceptual models. The intention was to identify the dominant hydrogeochemical processes that influence the groundwater quality in the area. The hydrogeochemical processes were assessed using hydrochemical and geochemical modelling techniques. The chapter argues that unless we assess these hydrogeochemical processes, we cannot improve our understanding of how these processes influence groundwater chemistry. Therefore, the question posed was "What is the role of hydrogeochemical processes in determining the groundwater quality of coastal aquifers?"

4.2 Determination of hydrogeochemical processes

Younger (2007) explained that given the generally low velocities of groundwater flow in the saturated zone, there is normally enough time for even relatively slow geochemical reactions to substantially alter groundwater chemistry through rock-water interactions. In semi-arid environments, the major hydrogeological processes influencing the chemistry of groundwater are usually precipitation, evaporation, and rock-water interactions (Sajil and James, 2016). To understand these complex hydrogeological processes, major ion chemistry and the local geology of the area must be considered. Bivariate plots were used to identify the major geochemical processes influencing the groundwater chemistry in the study area.

4.2.1 Bivariate correlation plots

A. Leaching

The Na-Cl relationship has often been used to identify the mechanisms for acquiring salinity and saline intrusions in semi-arid regions. If sodium comes from only halite dissolution, the Na-Cl ratio is approximately 1 (Pazand *et al*., 2018). Figure 5 shows the relationship between Na^+ and Cl^- in the study area. The Na^+ /Cl^- ratio of most groundwater samples in the four sampling dates is greater than 1, indicating sodium is not only derived from halite dissolution, but also from other processes, such as silicate dissolution, cation exchange, and adsorption, or anthropogenic activity. The samples enriched in Na^+ represented ion exchange or silicate weathering to have been occurring in the system. Furthermore, the high Cl^- over Na^+ in the water could be the result of Na^+ removal from solution during cation exchange (Luo *et al*., 2018); it could also be the result of connate water mixing with the aquifer water (Pazand *et al*., 2018). The Na versus Cl plots further indicates silicate weathering. Thus, for all samples with a Na/Cl of >1 (Appendix 2), a release of Na^+ from silicate weathering could be assumed (Vasu *et al*., 2017), instead of halite dissolution which gives a ratio equal to 1 (Senthilkumar *et al*., 2013). Therefore, albite plagioclase may be one of the significant minerals adding Na^+ in solution because of a Na/Cl >1 (Appendix 2) showing a release of Na^+ (Luo *et al*., 2018).

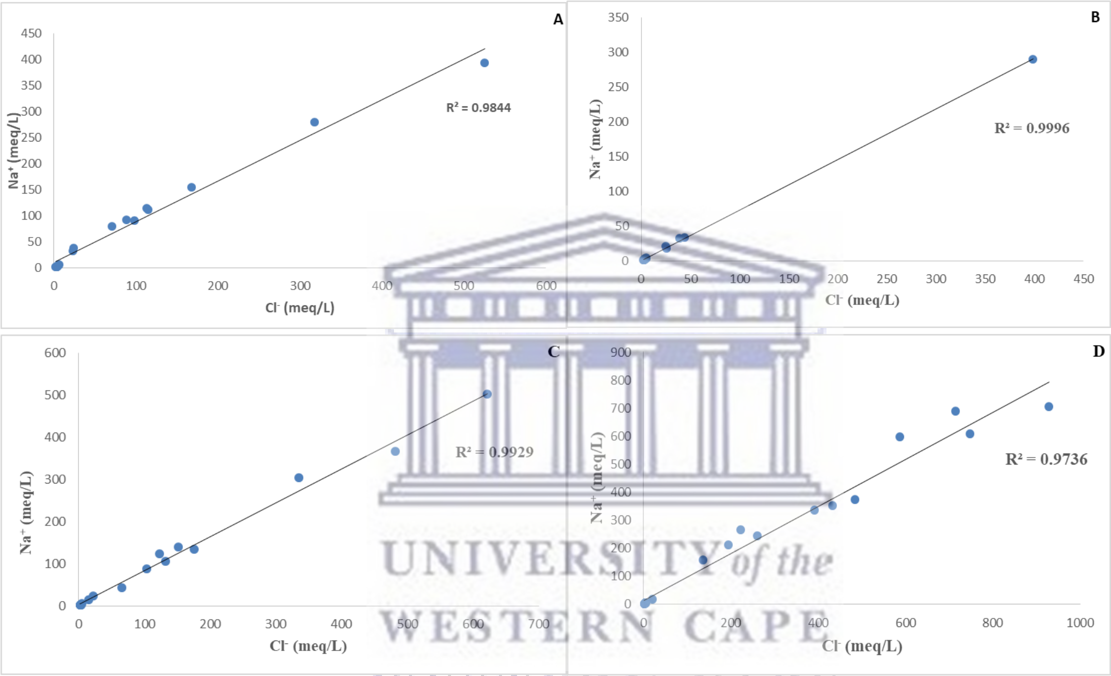


Figure 5: Na vs Cl correlation plot for July 2017 – July 2018

The ratio of Ca^{2+}/HCO_3^- and $(Ca^+ + Mg^{2+})/\ HCO_3^-$ were used to reflect the degree of carbonate dissolution. The ratio of Ca^{2+}/SO_4^{2-} can reflect the degree of sulfate dissolution. If calcium derives only from calcite dissolution, the ratio of Ca^{2+}/HCO_3^- should be approximately 1. If calcium derives only from dolomite dissolution, the ratio of Ca^{2+}/HCO_3^- should be approximately 0.5 and the ratio of $(Ca^{2+} + Mg^{2+})/HCO_3^-$ should be approximately 1. If calcium derives only from gypsum dissolution, the ratio of Ca^{2+}/SO_4^{2-} should be approximately 1. Figure 6 shows that the ratio of Ca^{2+}/HCO_3^- is mainly between 0.5 and 1, the ratio of $(Ca^{2+} + Mg^{2+})/HCO_3^-$ is mainly greater than 1, and the ratio of Ca^{2+}/SO_4^{2-} is mainly less than 1.

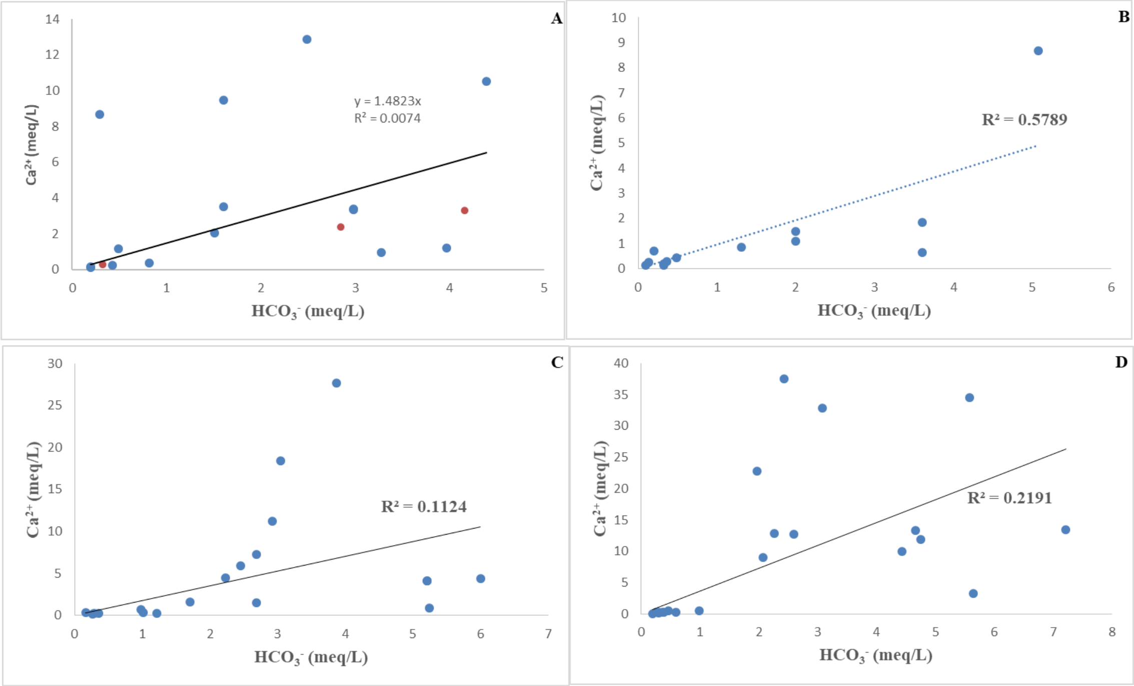


Figure 6: Ca^{2+} vs HCO_3^- bivariate correlation plot for July 2017 – July 2018

The results indicate that the Ca^{2+}/HCO_3^- ratio approaches 1 (F1, F5, BH7 and PZ 19) for July 2017 (Fig.6 A) whereas in other samples the ratio was either greater or smaller than 0.5 with a weak correlation ($R^2 = 0.0074$). Figure 6 (B) indicates that most of the samples approximate 1 and others are below and above 1 with moderate correlation ($R^2 = 0.5789$). In both figures 6 (C) and (D) there is a weak correlation ($R^2 = 0.1124$ and $R^2 = 0.2191$), only a few samples in both sampling dates approximate 1 and the rest are either below or above 1. The results indicate that the source of calcium in the study area is dominantly from calcite dissolution with some parts exhibiting signs of dolomite dissolution.

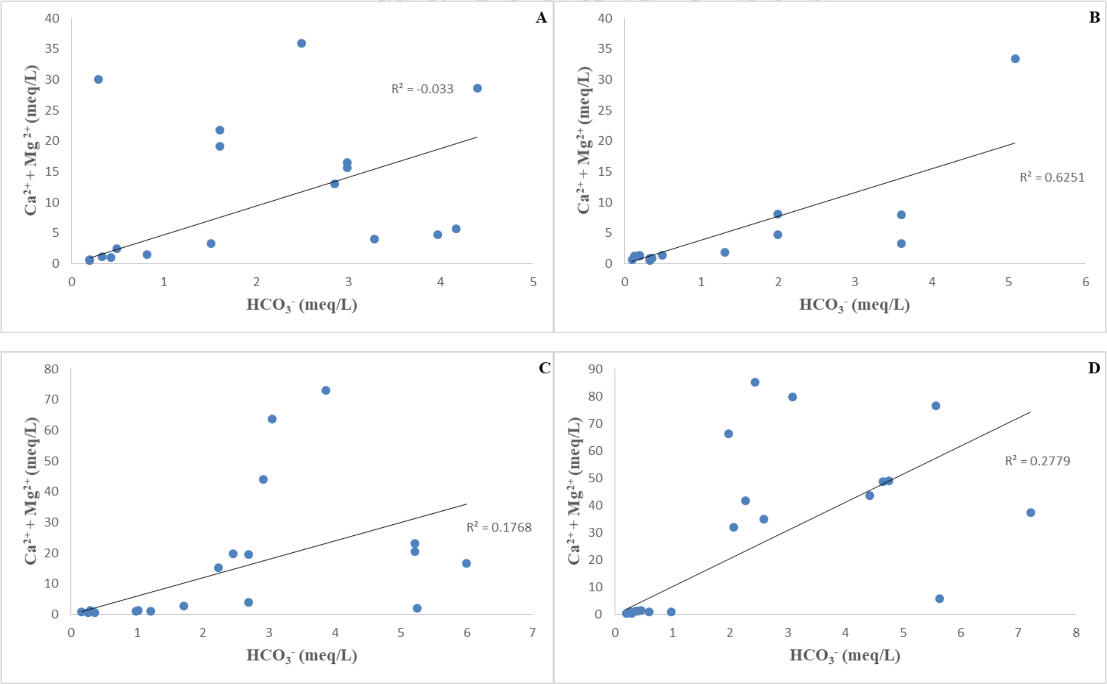


Figure 7: HCO_3^- vs (Ca^{2+} + Mg^{2+}) bivariate correlation plots for July 2017 – July 2018

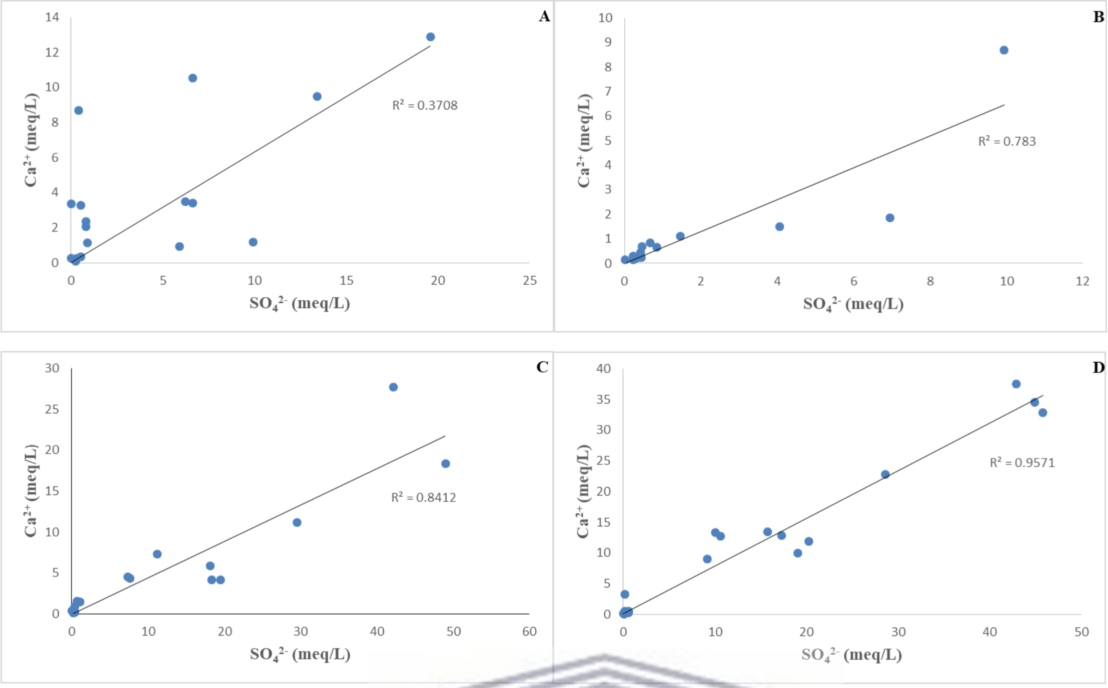
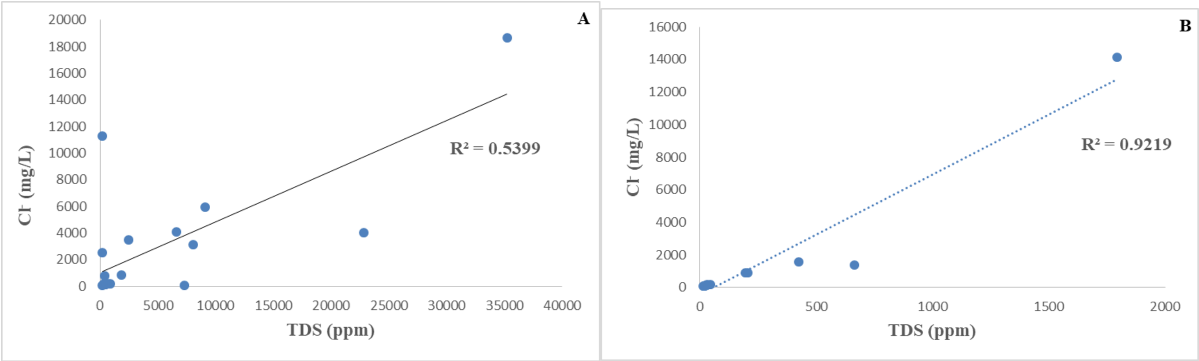


Figure 8: Ca^{2+} vs SO_4^{2-} bivariate correlation plots for July 2017 – July 2018

Figures 6 - 8 show that the ratio of Ca^{2+}/HCO_3^- is mainly between 0.5 and 1, the ratio of $(Ca^{2+} + Mg^{2+})/HCO_3^-$ is mainly greater than 1, and the ratio of Ca^{2+} / SO_4^{2-} is mainly less than 1. According to Rajesh *et al*., (2012), if the sources of Ca^{2+} and Mg^{2+} are carbonate and silicate weathering only, alkalinity should be the only ion to balance their presence.

B. Evaporation and condensation

The correlation between Cl^- and TDS can be used to show the evaporation and condensation effect in groundwater. Figure 9, shows that Cl^- and TDS have strong correlation coefficients in the three groundwater flow systems, especially, fig 9B and C, which indicates there are a strong evaporation and condensation effect over the entire study area.



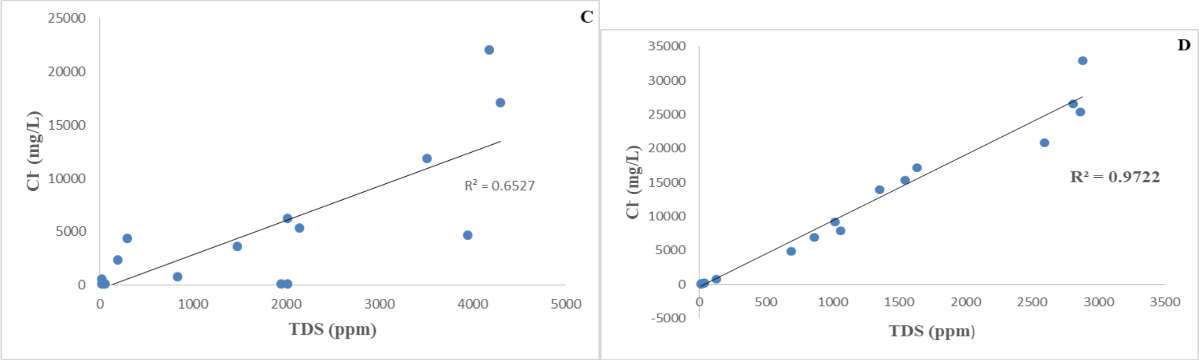
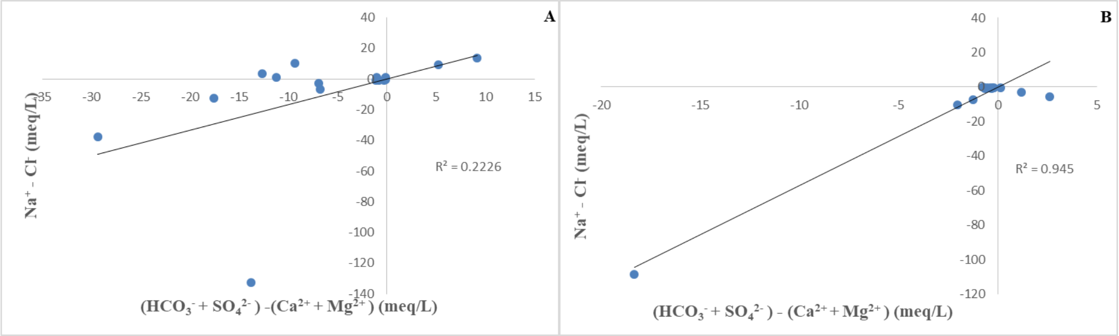


Figure 9: TDS vs Cl- bivariate correlation plots for July 2017 – July 2018

C. Cation exchange and adsorption

The (Na^+ - Cl^-) versus (HCO_3^- + SO_4^{2-} - Mg^{2+} - Ca^{2+}) ratio has been often used to identify the mechanisms for cation exchange and adsorption (An *et al*., 2012). If there is cation exchange and adsorption, the ratio should be approximately 1. Figure, 10 (A) and (D) shows that the (Na^{2+} - Cl-) versus (HCO_3^- + SO_4^{2-} - Mg^{2+} - Ca^{2+}) ratio is greater than 1 and the correlation coefficient (R^2_A = 0.2226 and R^2_D = 0.2046) is very low, indicating cation exchange and adsorption effect is weak. Figure 10, (B) and (C) shows that the (Na^+ - Cl^-) versus (HCO_3^- + SO_4^{2-} - Mg^{2+} - Ca^{2+}) ratio of most groundwater samples is approximately 1 and the correlation coefficients (R^2_B = 0.945 and R^2_C = 0.7091) is strong, indicating there are different degrees of cation exchange and adsorption. A change from ion exchange to reverse ion exchange explains a decrease of HCO_3^- + SO_4^{2-} in solution with an increase of Ca + Mg. Furthermore, a change from reverse ion exchange to ion exchange could be the result of dissolution of gypsum with the removal of Ca^{2+} during exchange or rather silicate weathering dominating in the system (Kumar *et al*., 2009; El Alfy *et al*., 2017). The findings of this study are similar to those of El Alfy *et al*., (2017).



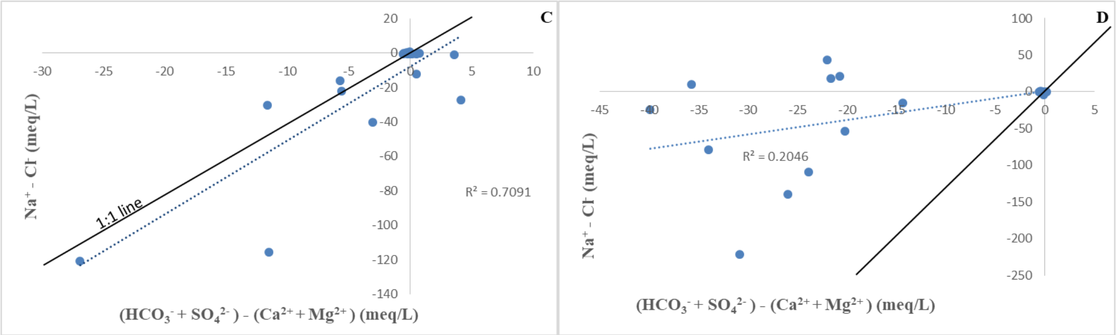


Figure 10: Na^+ - Cl^- vs HCO_3^- +SO_4^{2-} - (Ca^{2+} + Mg^{2+}) bivariate correlation plots for July 2017 – July 2018

4.2.2 Gibbs plot

While the Piper diagram is a method for classifying groundwater based on the distribution of both cations and anions, the Gibbs diagram is a method for estimating the origin of ions in groundwater by focusing on the correlation between the concentration of cations (Na^+, Ca^{2+}) and anions (Cl^-, HCO_3^-), and Total Dissolved Solids (TDS).

Several factors were used in estimating the origin of ions in groundwater by focusing on the correlation between the concentration of cations (Na^+, Ca^{2+}) and anions (Cl^-, HCO_3^-), and TDS (Total Dissolved Solids) control groundwater chemistry, which can be related to the physical situation of the aquifer, bedrock mineralogy, and weather condition. Gibbs (1970) suggested TDS versus Na^+/ (Na^+ + Ca^{2+}) for cations and TDS versus Cl^-/ (Cl^-+HCO_3^-) for anions to illustrate the natural mechanism controlling groundwater chemistry, including the rainfall dominance, rock weathering dominance and evaporation and participation dominance.

Figures 11a, 11b, 11c and 11d below shows the Gibbs diagrams plotted based on TDS and the concentration of cations and anions for the full data for the study.

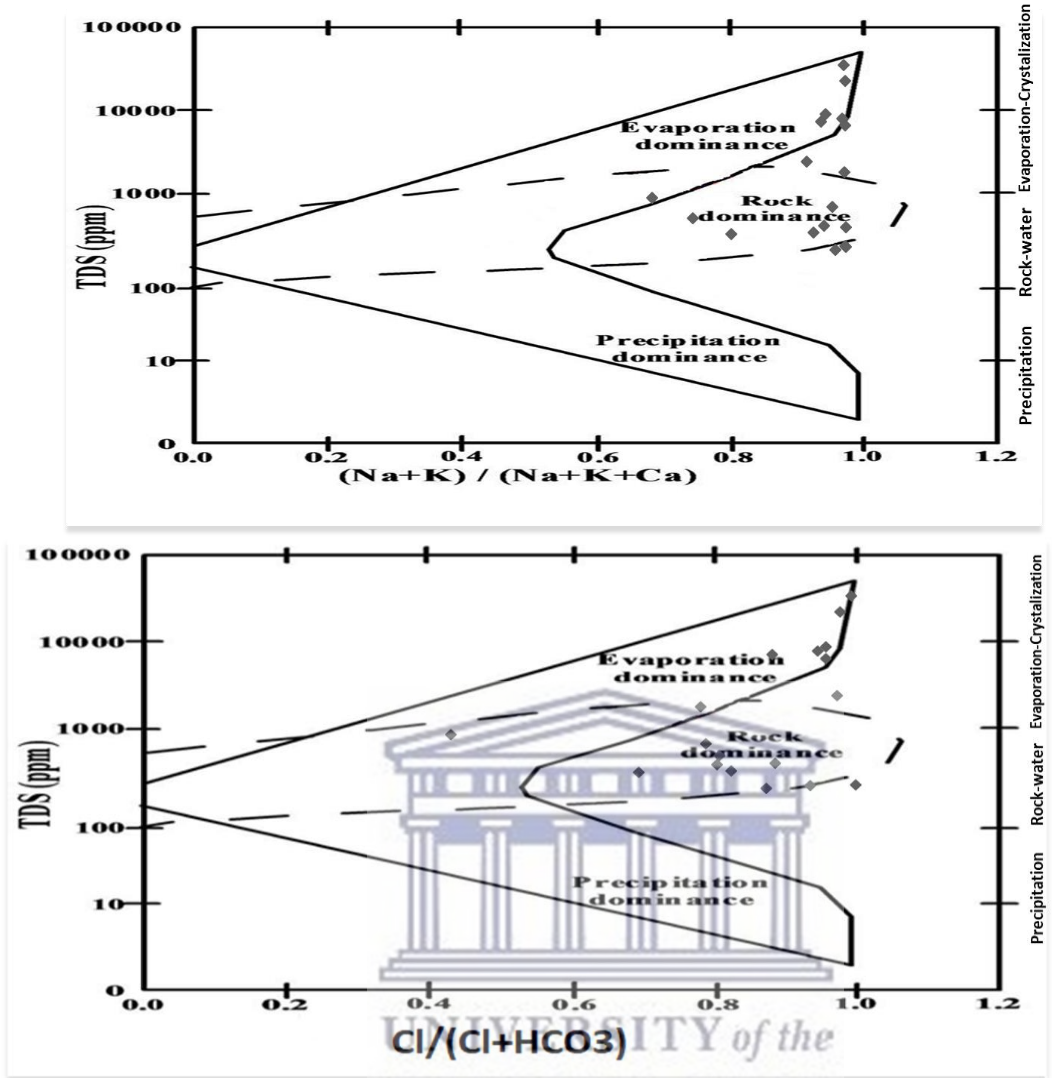


Figure 11(a): Gibbs plot for July 2017

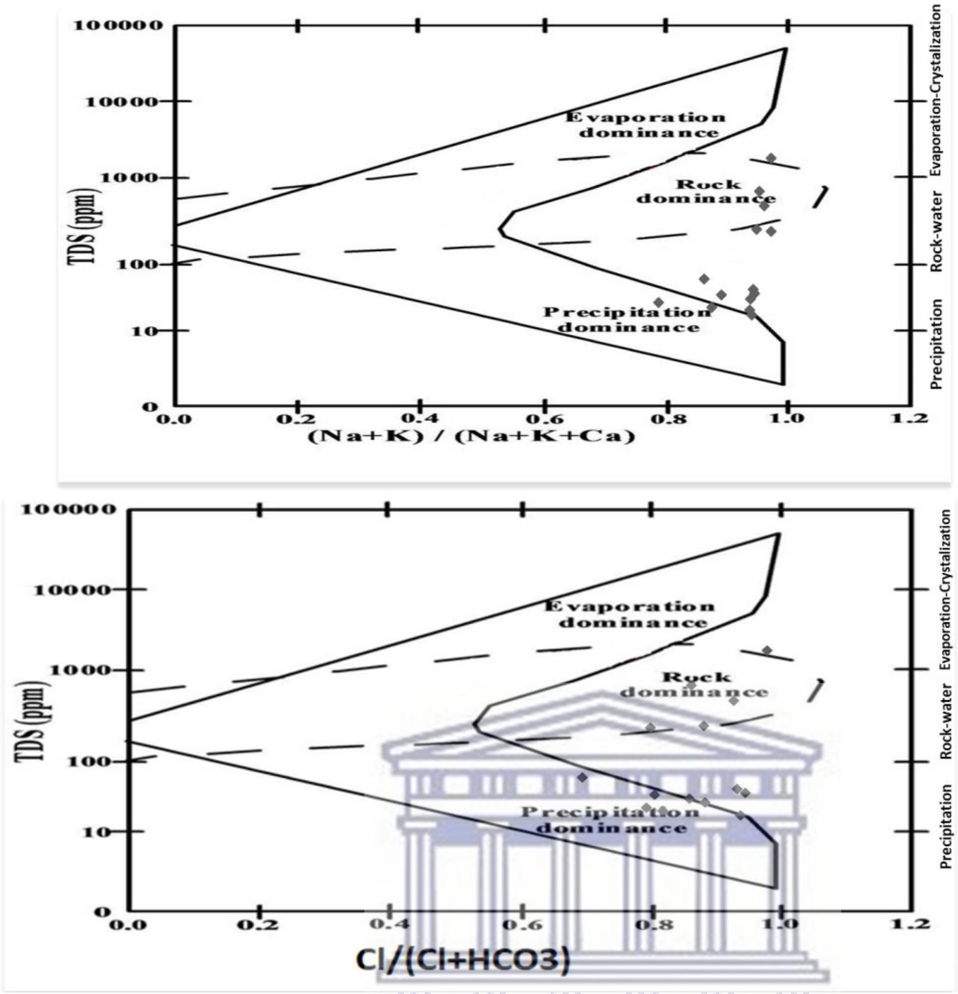
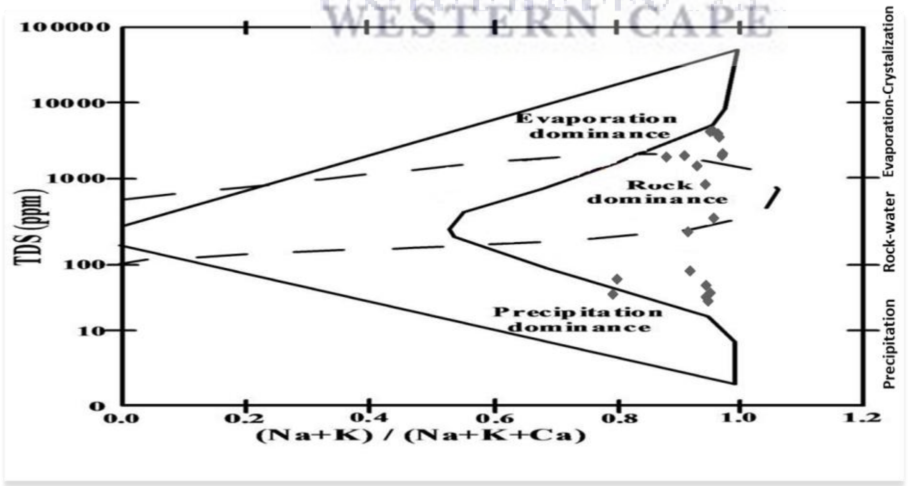


Figure 11(b): Gibbs plot for October 2017



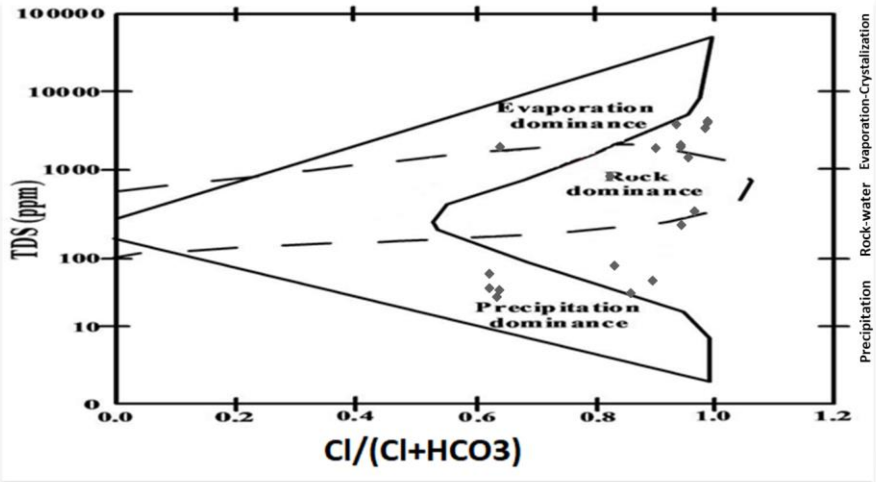


Figure 11(c): Gibbs plot for March 2018

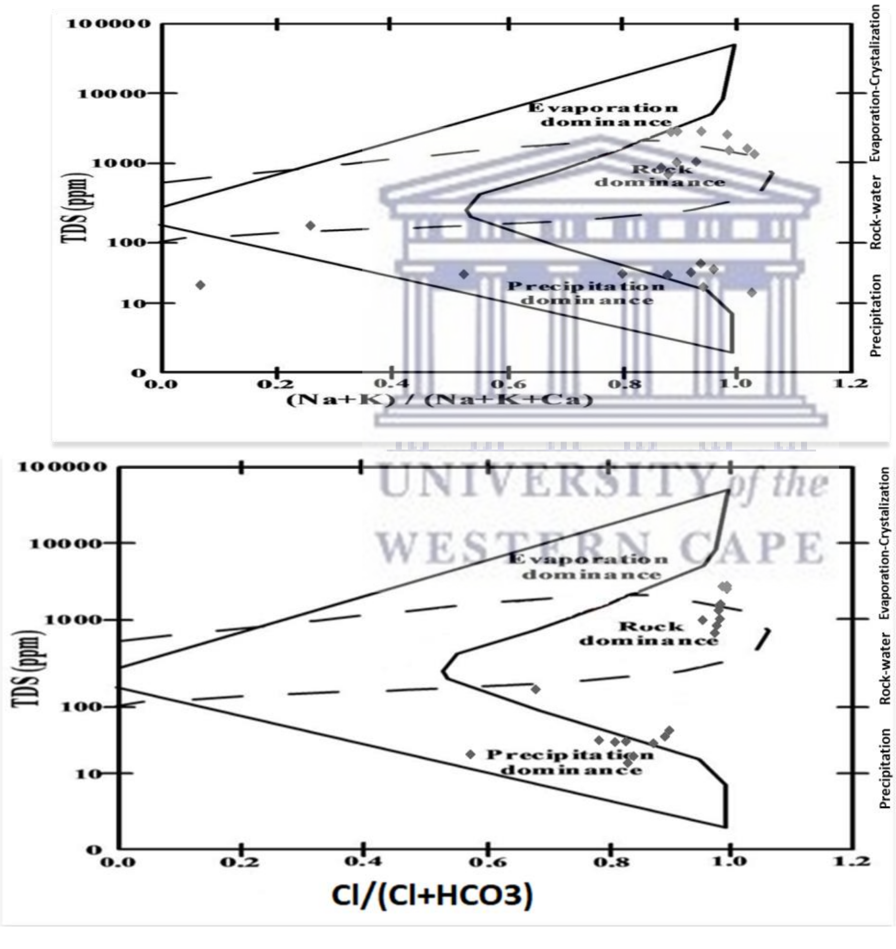


Figure 11(d): Gibbs plot for July 2018

Based on the Gibbs diagram, all the samples for July 2017 plotted into two groups one group that may have been influenced by rock water reaction and the other may have been influenced by evaporative processes. The plots explicitly show that all the cations and anions in groundwater have a rock-water dominance and evaporative dominance origin. This characteristic indicates that the dissolution of ions in groundwater through the interaction between groundwater and matrix is more dominant than any other source such as pollution from various sources. In the other samples, October 2017, March 2018 and July 2018 all showed a dominance of rock-water interaction processes followed by precipitation processes and lastly evaporative processes.

4.3 General hydrochemical characterisation of groundwater

This section makes use of various tools (as discussed in sections 3.4 and 3.5) to understand the hydrogeochemical processes that may be responsible for the resultant water compositions found in the study area. Bicarbonate and others that showed dominance in the samples results from data measured during the study and as shown in the generated Piper plots below. These tools have been tested with respect to their usefulness in improving the understanding of the hydrogeochemical processes as well as prove which amongst the predictive models would be a best suited model of the predominant hydrogeochemical processes in the aquifer system based on the identified species in the study area. Tools that have been used by many researchers include tools such as correlation, bivariate, cluster and principal component analysis tools (as discussed in more detail in Chapter 3). The subsections below apply various proven tools to estimate the dominant hydrogeochemical processes in the system under study.

4.3.1 Descriptive statistics summary for groundwater physicochemical parameters

Physicochemical parameters

pH

The pH values recorded for groundwater during the sampling period are presented in Tables 3 and 4. A gradual decrease in the mean values of pH in groundwater can be observed from season to season. Although groundwater pH values were generally below 7, pH in deep groundwater varied from season to season during the sampling period. The lowest and highest mean ranged from 6.5 to 6.9 in October 2017, July 2017, and March 2018 respectively (See Table 3). Deep groundwater upstream yielded pH values well below 7, even as low as below 5 in artesian boreholes. Shallow groundwater in the mid sections and lower reaches of the Catchment yielded the highest pH values, indicative of near-neutral or slightly alkaline waters. These values were either approaching a pH of 7 or between a pH of 7 and 8.

Electrical conductivity

EC values recorded for groundwater during the sampling period are recorded in Tables 3 and 4. EC values recorded in deep groundwater varied between 20.8 and 2990 mS/m. Deep groundwater from boreholes and artesian boreholes located upstream of the Catchment was fresh and yielded some of the lowest EC values recorded, usually with a EC reading below 50 mS/m. Boreholes BH 1, 2 and 3, which are at the downstream end of the Catchment, exhibited particularly elevated concentrations, generally, recording values higher than 2000 mS/m, and well exceeding this value on occasion. The highest mean value (968 mS/m) for deep groundwater was recorded during the very dry period experienced in March 2018, while the lowest mean (76.7 mS/m) was recorded in October 2017. Shallow groundwater recorded the highest EC values during the study, ranging between a minimum and maximum of 32 and 6620 mS/m. The results indicate that shallow groundwater within the study area is more mineralised as compared to deep groundwater with EC values usually ranging between 20.8 and 2990 mS/m.

Major cations and anions

Results obtained from the hydrochemical analysis conducted on groundwater in the Heuningnes Catchment are presented in Tables 3 and 4. The results indicate that, major ions in waters of the Heuningnes Catchment were present in the following order of abundance, $Cl^- > Na^+ > Mg^{2+} > SO_4^{2-} > Ca^{2+} > HCO_3^- > K^+$, throughout the sampling period. Although the magnitude, pattern, and trends of concentrations of each of the major ions are included within this section, sodium and chloride are discussed in greater detail. This is particularly because sodium and chloride are conservative ions and are usually the dominant ions in waters within the region of the study area (Mazvimavi, 2017). These findings are in agreement to those by (Kanagaraj *et al*., 2018) where sodium and chloride were the most dominant ions.

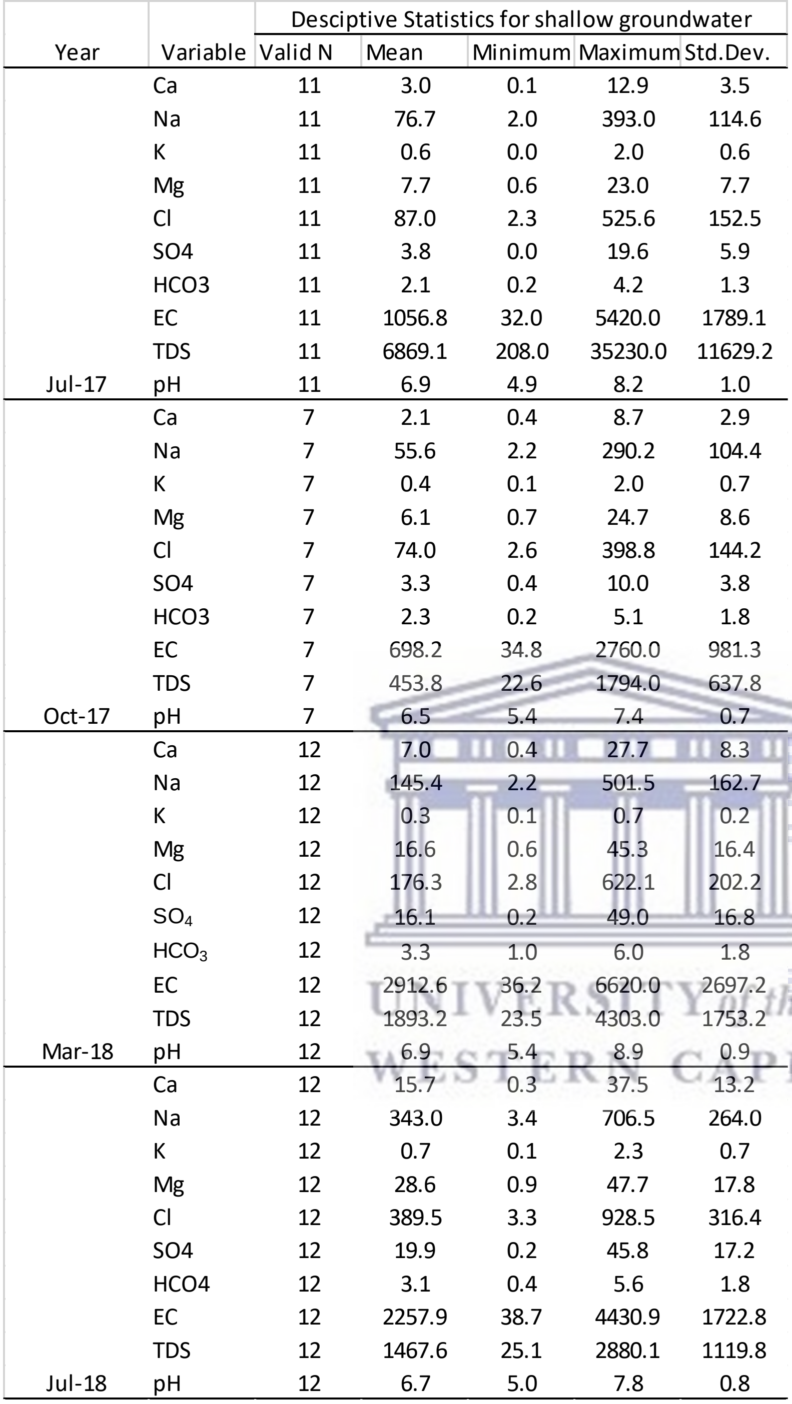
Chloride and sodium concentrations in the Heuningnes Catchment were lower in deep groundwater than in shallow groundwater. Values for chloride ranged between 1.7 and 318 meq/L in deep groundwater and 2.3 and 928 meq/L in shallow groundwater, while values for sodium ranged between 1.6 and 280.4 meq/L in deep groundwater and between 2 and 706.5 meq/L in shallow groundwater. The largest mean of 343 meq/L for sodium and 389 meq/L for chlorine were recorded in shallow groundwater respectively and SD of 264 for sodium and 316.4 for chlorine was recorded for shallow groundwater, respectively. Shallow groundwater recorded higher concentrations of sodium and chloride as compared to deep groundwater. The findings of this study are in agreement with the results found by Argamasilla *et al*., (2017) where the concentration of sodium is lower in the deep groundwater. However, Argamasilla *et al*., (2017) argues that the considering halite dissolution being one of the influencing processes, the sodium concentrations in that coastal area are lower than expected. This is as a result of the fraction of clay being less (Argamasilla *et al*., 2014).

Calcium concentrations ranged between 0.1 and 37.5 meq/L for shallow groundwater, 0.1 and 13.5 meq/L for deep groundwater. Magnesium was more abundant than calcium, with concentrations ranging between 0.6 and 47.7 meq/L for shallow groundwater, 0.3 and 23.9

meq/L for deep groundwater. The highest concentrations of both calcium and magnesium in groundwater were detected in July 2018 during the wet season (see Table 3), while the lowest concentrations were measured in October 2017 at the onset of the dry season. Although not as variable as sodium and chloride, the largest and smallest SD values for all waters were also computed for July 2018 and October 2017, suggesting that concentrations were more variable during the wet season.

Therefore, Ca^{2+} was the most dominant ion in some of the samples whereas Na^{+} was also the most dominant ion in some of the samples. The least concentrated cation in all the samples was potassium. This might be because K^{+} is found in sericite and accessory minerals such as biotite and muscovite, as explained by (Abu-alnaeem *et al.,* 2018). Vasu *et al.,* (2017), as well as Peikam and Jalali (2016), stated that in the geology where there is clay, K^{+} normally appears to be the least dominant ion because it gets attached to the clay minerals as it leaves none, or less K^{+}, in solution. The same case is assumed to be occurring in the study area where the geology comprises mostly of shale and mudstone that are rich in clay minerals.

Table 3: Descriptive statistics for shallow groundwater for July 2017 – July 2018



Year	Variable	Desciptive Statistics for shallow groundwater				
		Valid N	Mean	Minimum	Maximum	Std.Dev.
Jul-17	Ca	11	3.0	0.1	12.9	3.5
	Na	11	76.7	2.0	393.0	114.6
	K	11	0.6	0.0	2.0	0.6
	Mg	11	7.7	0.6	23.0	7.7
	Cl	11	87.0	2.3	525.6	152.5
	SO4	11	3.8	0.0	19.6	5.9
	HCO3	11	2.1	0.2	4.2	1.3
	EC	11	1056.8	32.0	5420.0	1789.1
	TDS	11	6869.1	208.0	35230.0	11629.2
	pH	11	6.9	4.9	8.2	1.0
Oct-17	Ca	7	2.1	0.4	8.7	2.9
	Na	7	55.6	2.2	290.2	104.4
	K	7	0.4	0.1	2.0	0.7
	Mg	7	6.1	0.7	24.7	8.6
	Cl	7	74.0	2.6	398.8	144.2
	SO4	7	3.3	0.4	10.0	3.8
	HCO3	7	2.3	0.2	5.1	1.8
	EC	7	698.2	34.8	2760.0	981.3
	TDS	7	453.8	22.6	1794.0	637.8
	pH	7	6.5	5.4	7.4	0.7
Mar-18	Ca	12	7.0	0.4	27.7	8.3
	Na	12	145.4	2.2	501.5	162.7
	K	12	0.3	0.1	0.7	0.2
	Mg	12	16.6	0.6	45.3	16.4
	Cl	12	176.3	2.8	622.1	202.2
	SO_4	12	16.1	0.2	49.0	16.8
	HCO_3	12	3.3	1.0	6.0	1.8
	EC	12	2912.6	36.2	6620.0	2697.2
	TDS	12	1893.2	23.5	4303.0	1753.2
	pH	12	6.9	5.4	8.9	0.9
Jul-18	Ca	12	15.7	0.3	37.5	13.2
	Na	12	343.0	3.4	706.5	264.0
	K	12	0.7	0.1	2.3	0.7
	Mg	12	28.6	0.9	47.7	17.8
	Cl	12	389.5	3.3	928.5	316.4
	SO4	12	19.9	0.2	45.8	17.2
	HCO4	12	3.1	0.4	5.6	1.8
	EC	12	2257.9	38.7	4430.9	1722.8
	TDS	12	1467.6	25.1	2880.1	1119.8
	pH	12	6.7	5.0	7.8	0.8

Table 4: Descriptive statistics for deep groundwater for July 2017 – July 2018

		Desciptive Statistics for deep groundwater				
Year	Variable	Valid N	Mean	Minimum	Maximum	Std.Dev.
Jul-17	Ca	7	4.4	0.2	10.5	4.9
	Na	7	82.5	2.0	280.4	104.1
	K	7	0.7	0.0	2.2	1.0
	Mg	7	8.3	0.4	21.4	8.9
	Cl	7	88.6	2.5	318.0	118.7
	SO4	7	4.5	0.0	13.4	5.5
	HCO3	7	1.7	0.2	4.4	1.8
	EC	7	483.6	35.7	1398.0	551.1
	TDS	7	3143.7	232.1	9087.0	3582.2
	pH	7	6.4	5.3	8.0	1.1
Oct-17	Ca	7	0.3	0.1	1.1	0.3
	Na	7	4.9	1.8	18.2	5.9
	K	7	0.1	0.0	0.1	0.0
	Mg	7	1.1	0.4	3.6	1.1
	Cl	7	6.4	2.4	25.6	8.5
	SO4	7	0.4	0.0	1.5	0.5
	HCO3	7	0.5	0.1	2.0	0.7
	EC	7	76.7	24.1	319.0	107.3
	TDS	7	49.9	15.7	207.4	69.8
	pH	7	6.0	4.9	7.2	0.9
Mar-18	Ca	7	1.4	0.2	7.3	2.6
	Na	7	17.7	2.3	87.4	31.6
	K	7	0.1	0.0	0.4	0.1
	Mg	7	2.6	0.4	12.3	4.4
	Cl	7	20.3	2.6	103.3	37.3
	SO_4	7	2.0	0.1	11.2	4.1
	HCO_3	7	1.1	0.2	2.7	1.1
	EC	7	968.6	40.8	2990.0	1237.6
	TDS	7	629.6	26.5	1943.5	804.4
	pH	7	6.0	5.0	7.2	0.8
Jul-18	Ca	9	3.1	0.1	13.5	5.7
	Na	9	53.3	1.6	244.6	99.6
	K	9	0.2	0.0	1.4	0.4
	Mg	9	5.7	0.3	23.9	9.9
	Cl	9	53.0	1.7	260.1	100.0
	SO4	9	3.1	0.0	15.7	5.8
	HCO4	9	1.4	0.2	7.2	2.3
	EC	9	350.6	20.8	1571.3	627.1
	TDS	9	227.9	13.5	1021.3	407.6
	pH	9	5.7	4.4	7.7	1.2

4.3.2 Correlation analysis of groundwater parameters

A correlation analysis was done for the hydrogeochemical data collected to understand the relationship among the measured parameters as well as help group the parameters in terms of relevance in the processes under investigation. The degree of linear association between any two-groundwater quality parameters is measured by the correlation coefficient (*r*) value. The Correlation matrix for the different groundwater quality parameters along with the significance level (2 tailed) is shown in Tables 5-8

The significant correlation between EC and the other hydrogeochemical parameters is highly positive apart from K^+ and HCO_3^-. The *r*-value between EC and TDS is 1, which means TDS is highly positively correlated with EC and can be predicted from EC with 100% accuracy. Additionally, the EC value of the groundwater samples has a high positive correlation with Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+} and Na^+ with relative positive coefficient *r* values of 0.735, 0.673, 0.637, 0.572 and 0.705, respectively. Ca^{2+} shows a highly positive correlation with Mg^{2+} compared to Na^+ and strong correlation with Cl^- and SO_4^{2-} compared to HCO_3^-. Na^+ showed a strong positive correlation with Cl^- and SO_4^{2-} besides TDS compared to HCO_3^-. The findings are in agreement to those by Kanagaraj *et al*., (2018), the strong correlation between these elements can attributed to the mineralization of the water.

Table 5: Correlation matrix for the different groundwater quality parameters for July 2017

Variables	Ca	Na	K	Mg	Cl	SO4	HCO3	EC	TDS
Ca	**1**	**0.864**	**0.700**	**0.872**	**0.854**	**0.686**	0.310	**0.572**	**0.572**
Na	**0.864**	**1**	**0.702**	**0.919**	**0.992**	**0.627**	0.177	**0.705**	**0.705**
K	**0.700**	**0.702**	**1**	**0.816**	**0.646**	0.180	0.368	0.415	0.415
Mg	**0.872**	**0.919**	**0.816**	**1**	**0.873**	**0.559**	0.300	**0.637**	**0.637**
Cl	**0.854**	**0.992**	**0.646**	**0.873**	**1**	**0.645**	0.137	**0.735**	**0.735**
SO4	**0.686**	**0.627**	0.180	**0.559**	**0.645**	**1**	0.386	**0.673**	**0.673**
HCO3	0.310	0.177	0.368	0.300	0.137	0.386	**1**	0.171	0.171
EC	**0.572**	**0.705**	0.415	**0.637**	**0.735**	**0.673**	0.171	**1**	**1.000**
TDS	**0.572**	**0.705**	0.415	**0.637**	**0.735**	**0.673**	0.171	**1.000**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Additionally, the EC value of the groundwater samples has a strong positive correlation with Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+} and Na^+ with relative positive coefficient *r* values of 0.960, 0.955, 0.990, 0.956 and 0.965, respectively. Na^+ showed a strong positive correlation with Cl^- and SO_4^{2-} besides TDS and with HCO_3^-.

Table 6: Correlation matrix for the different groundwater quality parameters for October 2017

Variables	Na	K	Mg	Cl	SO4	HCO3	EC	TDS
Na	**1**	**0.987**	**0.984**	**1.000**	**0.847**	**0.744**	**0.965**	**0.965**
K	**0.987**	**1**	**0.980**	**0.984**	**0.897**	**0.773**	**0.981**	**0.981**
Mg	**0.984**	**0.980**	**1**	**0.982**	**0.914**	**0.804**	**0.990**	**0.990**
Cl	**1.000**	**0.984**	**0.982**	**1**	**0.838**	**0.733**	**0.960**	**0.960**
SO4	**0.847**	**0.897**	**0.914**	**0.838**	**1**	**0.847**	**0.955**	**0.955**
HCO3	**0.744**	**0.773**	**0.804**	**0.733**	**0.847**	**1**	**0.843**	**0.843**
EC	**0.965**	**0.981**	**0.990**	**0.960**	**0.955**	**0.843**	**1**	**1.000**
TDS	**0.965**	**0.981**	**0.990**	**0.960**	**0.955**	**0.843**	**1.000**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

The significant correlation between EC and the other hydrogeochemical parameters is highly positive except for HCO_3^-. The *r*-value between EC and TDS is 1, which means TDS is highly positively correlated with EC and can be predicted from EC with 100%. Additionally, the EC value of the groundwater samples has high positive correlation with Cl-, SO_4^{2-}, Mg^{2+}, Ca^{2+} and Na^+ with relative positive coefficient *r* values of 0.808, 0.824, 0.830, 0.736, 0.875, and 0.804, respectively. Ca^{2+} shows a highly positive correlation with Na^+ compared to Mg^{2+} and strong correlation with Cl^- and SO_4^{2-} compared to HCO_3^-. Na^+ showed a strong positive correlation with Cl^- and SO_4^{2-} besides TDS compared to HCO_3^-.

Table 7: Correlation matrix for the different groundwater quality parameters for March 2018

Variables	Ca	Na	K	Mg	Cl	SO4	HCO3	EC	TDS
Ca	**1**	**0.971**	**0.497**	**0.942**	**0.977**	**0.917**	0.358	**0.736**	**0.736**
Na	**0.971**	**1**	**0.606**	**0.978**	**0.996**	**0.952**	0.443	**0.804**	**0.804**
K	**0.497**	**0.606**	**1**	**0.689**	**0.614**	**0.710**	**0.632**	**0.746**	**0.746**
Mg	**0.942**	**0.978**	**0.689**	**1**	**0.977**	**0.988**	**0.462**	**0.830**	**0.830**
Cl	**0.977**	**0.996**	**0.614**	**0.977**	**1**	**0.952**	0.438	**0.808**	**0.808**
SO4	**0.917**	**0.952**	**0.710**	**0.988**	**0.952**	1	0.435	**0.824**	**0.824**
HCO3	0.358	0.443	**0.632**	**0.462**	0.438	0.435	**1**	**0.478**	**0.478**
EC	**0.736**	**0.804**	**0.746**	**0.830**	**0.808**	**0.824**	**0.478**	**1**	**1.000**
TDS	**0.736**	**0.804**	**0.746**	**0.830**	**0.808**	**0.824**	**0.478**	**1.000**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

The significant correlation between EC and the other hydrogeochemical parameters is highly positive with the exception of K^+ and HCO_3^- The *r*-value between EC and TDS is 1, which means TDS is highly positively correlated with EC and can be predicted from EC with 100%. Additionally, the EC value of the groundwater samples showed a high positive correlation with Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+} and Na^+ with relative positive coefficient *r* values of 0.986, 0.972, 0.964, 0.969 and 0.998, respectively. Ca^{2+} shows a highly positive correlation with Na^+ compared to Mg^{2+} and strong correlation with Cl^- and SO_4^{2-} compared to HCO_3^-. Na^+ showed a strong positive correlation with Cl^- and SO_4^{2-} besides TDS compared to HCO_3^-.

The strong positive correlation between Na^+ and Cl^- indicates the dominance of Na-Cl rich recharge water from coastal origin (Argamasilla *et al*., 2017). Nasher *et al.,* (2013) in their study indicated that Na and Cl provide an indication of deposition and dissolution of halite from atmospherically derived Na-Cl ions in areas close to the coast. The results of the current study in agreement with results from the cited studies, this relationship is further explored in the following sections. Moderate (r = 0.646, r = 0.614 and r = 0.617) and high (r = 0.984) correlations were developed for the K versus Cl plots for spring, summer and autumn. In similar study done by (El Alfy *et al*., 2017), similar results were found and the weathering of sylvite was said to be a possible source of Cl^- and K^+ in the solution.

Table 8: Correlation matrix for the different groundwater quality parameters for July 2018

Variables	Ca	Na	K	Mg	Cl	SO4	HCO3	EC	TDS
Ca	**1**	**0.968**	**0.536**	**0.912**	**0.951**	**0.979**	**0.506**	**0.969**	**0.969**
Na	**0.968**	**1**	**0.574**	**0.967**	**0.987**	**0.972**	**0.512**	**0.998**	**0.998**
K	**0.536**	**0.574**	**1**	**0.629**	**0.617**	**0.580**	**0.780**	**0.599**	**0.599**
Mg	**0.912**	**0.967**	**0.629**	**1**	**0.945**	**0.915**	**0.596**	**0.964**	**0.964**
Cl	**0.951**	**0.987**	**0.617**	**0.945**	**1**	**0.969**	**0.532**	**0.986**	**0.986**
SO4	**0.979**	**0.972**	**0.580**	**0.915**	**0.969**	**1**	**0.491**	**0.972**	**0.972**
HCO3	**0.506**	**0.512**	**0.780**	**0.596**	**0.532**	**0.491**	**1**	**0.525**	**0.525**
EC	**0.969**	**0.998**	**0.599**	**0.964**	**0.986**	**0.972**	**0.525**	**1**	**1.000**
TDS	**0.969**	**0.998**	**0.599**	**0.964**	**0.986**	**0.972**	**0.525**	**1.000**	**1**

Values in bold are different from 0 with a significance level alpha=0.05

4.3.3 Factor components explaining groundwater quality

Factor analysis was performed on 9 variables (EC, TDS, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-} and HCO_3^{-}) of the groundwater samples. Table 9 shows the initially determined factors, their Eigenvalues and the percent of variance contributed to each factor using the Varimax rotation method with Kaiser Normalisation and unrotated factor solution. Only factors with Eigenvalues ≥ 1 were taken into consideration and this resulted in three factors that were sufficient in explaining 88.53% of the variance. The total variance explained by these three factors; factor one, factor two and factor three are 60.45%, 16.52%, and 11.56% respectively. The three factors shown in Table 9 are dominated by certain variables based on the prevailing hydrogeochemical processes and land-use practices.

Table 9: Factor eigenvalues and percentage total for July 2017

	Eigenvalues (Extraction: Principal components)			
Value	Eigenvalue	% Total	Cumulative	Cumulative
1	6.045213	60.45213	6.045213	60.45213
2	1.651878	16.51878	7.697091	76.97091
3	1.155794	11.55794	8.852886	88.52886

Factor analysis was performed on 9 variables (EC, TDS, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-} and HCO_3^{-}) of the groundwater samples. Table 10 shows the initially determined factors, their Eigenvalues and the percent of variance contributed to each factor using the Varimax rotation method with Kaiser Normalisation and unrotated factor solution. Only factors with Eigenvalues ≥ 1 were taken into consideration and this resulted in three factors that were enough in explaining 96.42% of the variance. The total variance explained by these three factors; factor one and factor two are 85.73% and 10.70% respectively. The two factors shown in Table 10 are dominated by certain variables based on the prevailing hydrogeochemical processes and land-use practices.

Table 10: Factor eigenvalues and percentage total for October 2017

	Eigenvalues (Extraction: Principal components)			
Value	Eigenvalue	% Total	Cumulative	Cumulative
1	8.572765	85.72765	8.572765	85.72765
2	1.069716	10.69716	9.642481	96.42481

Factor analysis was performed on 9 variables (EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-} and HCO_3^-) of the groundwater samples. Table 11 shows the initially determined factors, their Eigenvalues and the percent of variance contributed to each factor using the Varimax rotation method with Kaiser Normalisation and unrotated factor solution. Only factors with Eigenvalues ≥ 1 were taken into consideration and this resulted in three factors that were enough in explaining 87.01% of the variance. The total variance explained by these two factors; factor one and factor two is 73.40% and 13.61% respectively. The two factors shown in Table 11 are dominated by certain variables based on the prevailing hydrogeochemical processes and land-use practices.

Table 11: Factor eigenvalues and percentage total for March 2018

	Eigenvalues (Extraction: Principal components)			
Value	Eigenvalue	% Total	Cumulative	Cumulative
1	7.339710	73.39710	7.339710	73.39710
2	1.361109	13.61109	8.700818	87.00818

Factor analysis was performed on 9 variables (EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-} and HCO_3^-) of the groundwater samples. Table 12 shows the initially determined factors, their Eigenvalues and the percent of variance contributed to each factor using the Varimax rotation method with Kaiser Normalisation and unrotated factor solution. Only factors with Eigenvalues ≥ 1 were taken into consideration and this resulted in three factors that were sufficient in explaining 93.27% of the variance. The total variance explained by these two factors; factor one and factor two is 81.05% and 12.21% respectively. The two factors shown in Table 12 are dominated by certain variables based on the prevailing hydrogeochemical processes and land-use practices.

This Factor describes 60.45%, 85.73%, 73.40% and 81.05% respectively of the total variance (Table 9, 10, 11 and 12), and is ascribed to hardness and salinity of the groundwater due to carbonate, silicate, gypsum and halite dissolution as well as infiltration of concentrated saline groundwater resulting from evaporation similar to the findings by Ibrahim *et al*., (2019). The dissolution of these cations with Cl^- and SO_4^{2-} gives rise to the hardness of the groundwater (El Alfy *et al*., 2017) explained by the high TDS contribution to this factor. The high Na^+ loading on the Hardness factor is also an indication of the influence of ion exchange processes in conjunction with carbonate and silicate weathering in the groundwater samples characterized by this factor.

Table 12: Factor eigenvalues and percentage total for July 2018

	Eigenvalues (Extraction: Principal components)			
Value	Eigenvalue	% Total	Cumulative	Cumulative
1	8.105406	81.05406	8.105406	81.05406
2	1.221230	12.21230	9.326636	93.26636

4.3.4 Cluster analysis

The dendrograms generated (Figures 12-15), consists of distinctive groups of clusters. Samples in each group represent waters with similar chemical compositions.

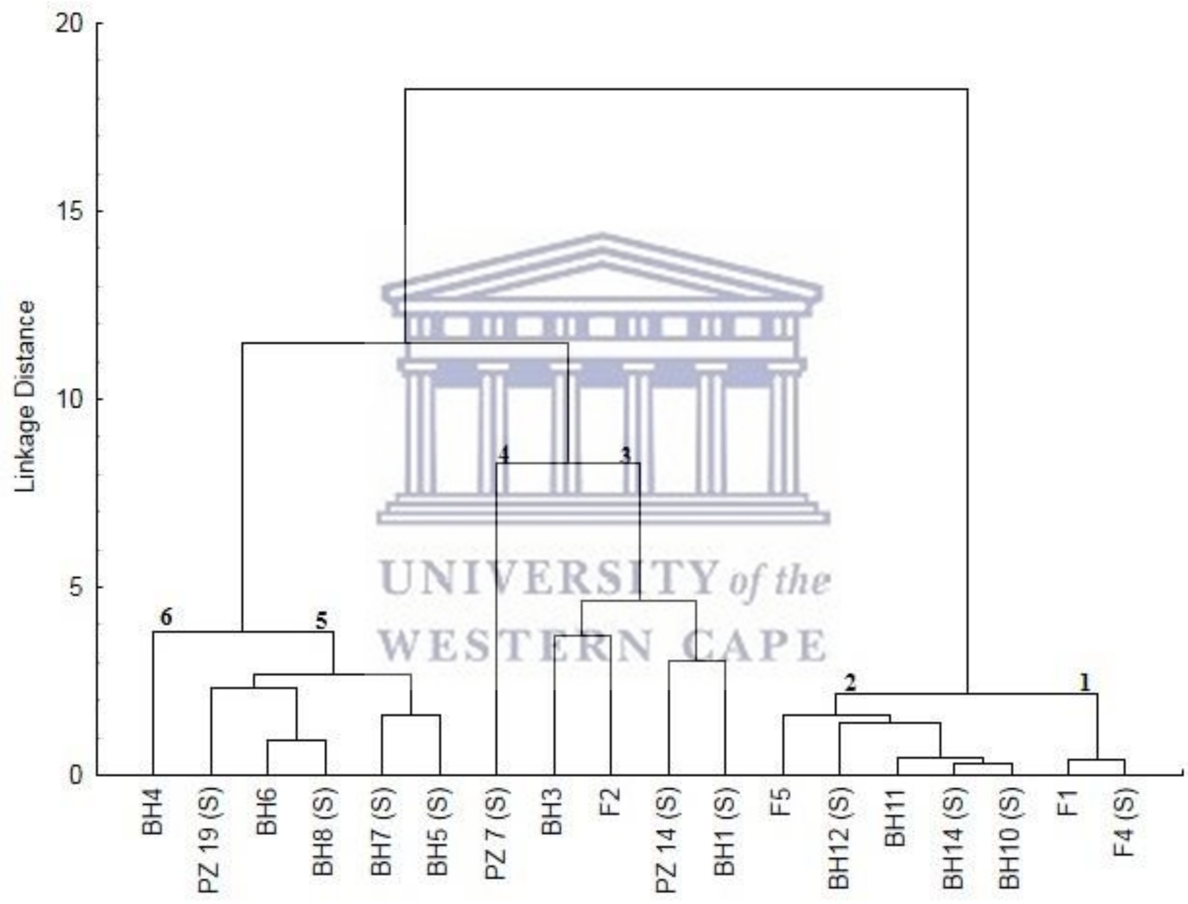


Figure 12: Hierarchal Cluster analysis for July 2017

Cluster 1 consists of a total of two samples, collected from, deep groundwater and shallow groundwater sites, F 1 and F 4. Both samples were collected from the upper section of the Catchment. These samples have low salinity values compared to samples in the lower part of the Catchment. **Cluster 2** consists of a total of 5 samples (F 5, BH 10, BH 11, BH 12 and BH 14)**,** collected mostly from shallow groundwater. This cluster consists of samples with moderate salinities except for F5 which has the highest salinity in this cluster. Similarities in the chemical composition of samples within this cluster could possibly be attributed to similarities in depths at which the samples were collected. These samples were also collected at sites within close proximity to each other, mostly upstream towards the middle of the

Catchment. **Cluster 3** consists of 4 samples, collected from deep and shallow groundwater. These samples were collected downstream of the Catchment except for F2 located furthest from the coast. These include BH1, BH3 and PT 14. These samples are characterized by high salinities except for F2 which has the lowest salinity in this cluster.

Cluster 4 and 6 consists of only 1 sample, PZ 7 and BH 4 respectively, these samples are located downstream closer to the coast, and it is characterized by moderate salinity values considering its proximity to the ocean and the geology of the area. **Cluster 5** consists of 5 samples, (BH5, BH6, BH7, BH8 and PZ 19) located downstream closer to the coast, and it is characterized by moderate salinity values considering its proximity to the ocean and the geology of the area. These samples are all shallow groundwater samples except BH6 and are all located near each other.

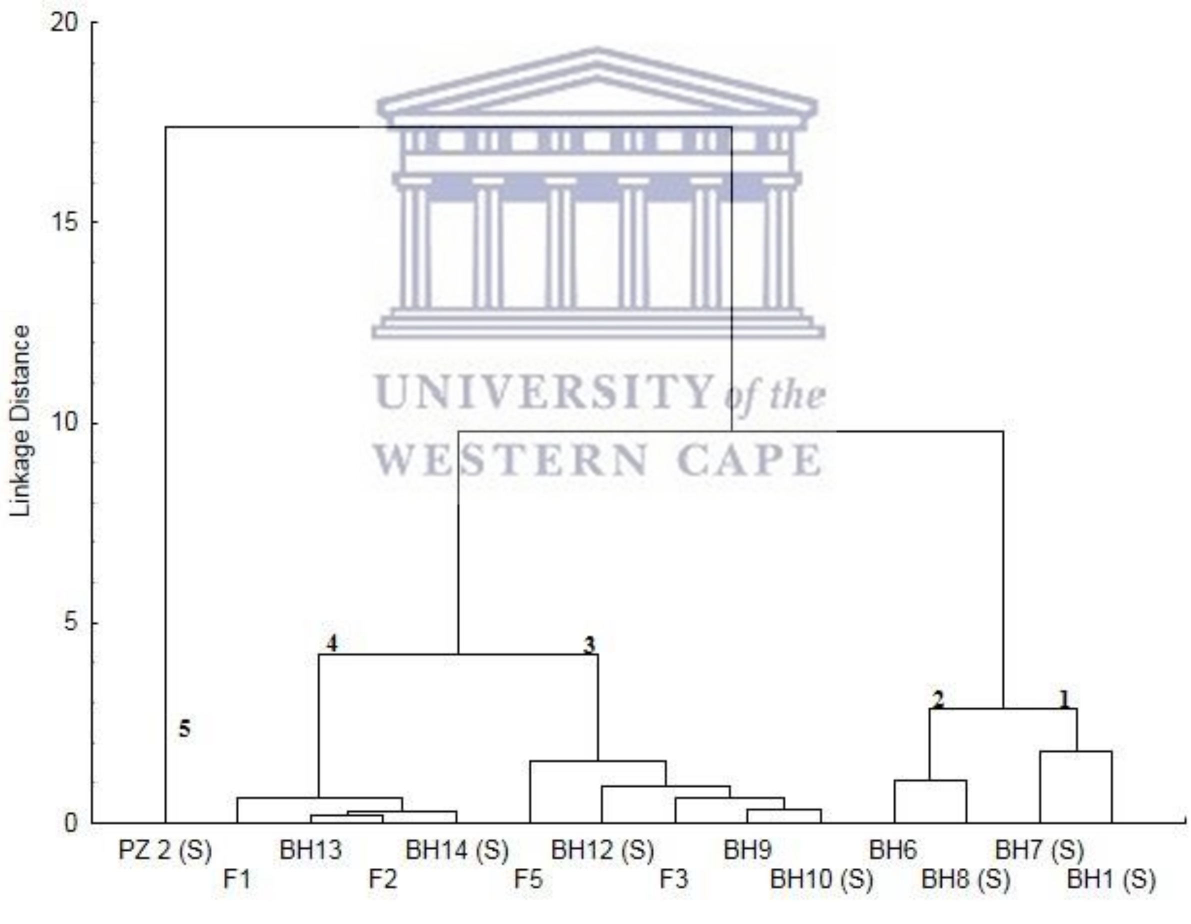


Figure 13: Hierarchal Cluster analysis for October 2017

Cluster 1 and 2 consists of a total of 2 samples each (BH1, BH7, BH8, and BH6), collected from, deep groundwater and shallow groundwater sites. The majority of these samples were collected in the lower sections of the Catchment. No samples from the upper sections of the Catchment fell within this group. Cluster 1 and 2 consists of samples with the highest salinity concentrations. Samples within this cluster are characterised by high chloride and sodium concentrations and therefore high EC values. **Cluster 3** consists of a total of 5 samples (F5, F3, BH12, BH9, and BH10), collected mostly from deep groundwater. This cluster consists of samples with low salinities. Similarities in the chemical composition of samples within this cluster could possibly be attributed to similarities in depths at which the samples were collected. These samples were also collected at sites within proximity to each other, mostly upstream. **Cluster 4** consists of 4 samples, primarily collected from deep groundwater apart from BH14. These samples were collected upstream of the Catchment, furthest from the coast. These include BH14, BH13, F1, and F2. These samples are characterized by low salinities and are generally fresh. **Cluster 5** consists of only 1 sample, PZ2, located downstream near the coast. The sample in this group is characterized by the highest salinity compared to any sample during this sampling trip.

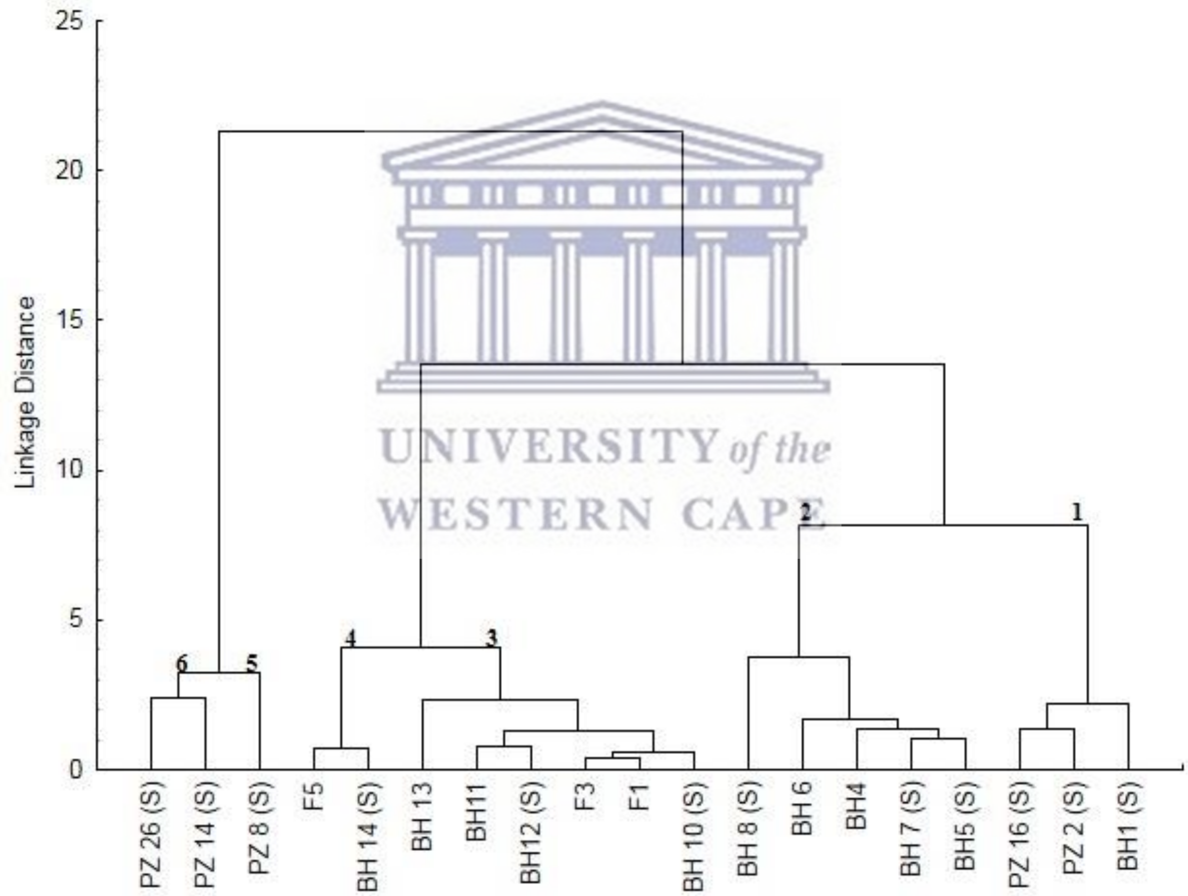


Figure 14: Hierarchal Cluster analysis for March 2018

Cluster 1 consists of a total of 3 samples, collected from shallow groundwater sites, BH1, PZ 2 and PZ16. These samples were all collected in the lower sections of the Catchment. No samples from the upper sections of the Catchment fell within this group. Cluster 1 consists of samples with the highest salinity concentrations. Samples within this cluster are characterised by high chloride and sodium concentrations and therefore high EC values. The clustering of these groundwater samples gives an indication of waters that are influenced by the same hydrological processes. **Cluster 2** consists of a total of 5 samples (BH4, BH5, BH6, BH7, and BH8)**,** collected mostly from shallow groundwater from the same sampling site. This cluster consists of samples with the highest salinities coming from the deep groundwater samples and those from shallow groundwater are characterized by low salinities. Similarities in the chemical composition of samples within this cluster could possibly be attributed to similarities in depths at which the samples were collected and the geology. These samples were also collected at sites within proximity to each other, mostly downstream.

Cluster 3 consists of 6 samples, mostly collected from deep groundwater with only two from shallow groundwater. These samples were collected upstream of the Catchment, furthest from the coast. These include BH12, BH11, BH10, BH13, F1, and F3. These samples are characterized by low salinities and are generally fresh. **Cluster 4** consists of only 2 samples, F5 and BH14, located upstream. Waters in this group are characterized by low salinities. Similarly, to cluster 3, low salinity concentrations in this group can be attributed to the geology type (weathered sandstones), that dominates in the upper sections of the Catchment.

Cluster 5 consists of 1 sample, collected from shallow groundwater. This sample was collected downstream of the Catchment, which is in close proximity to the coast. The samples were characterized by high salinities and were generally saline. **Cluster 6** consists of only 2 samples, PZ14 and PZ26, located downstream. Waters in this group are characterized by high salinities. Similarly, to cluster 5, low salinity concentrations in this group can be attributed to the geology type (greywackle shale), that dominates in the lower sections of the Catchment.

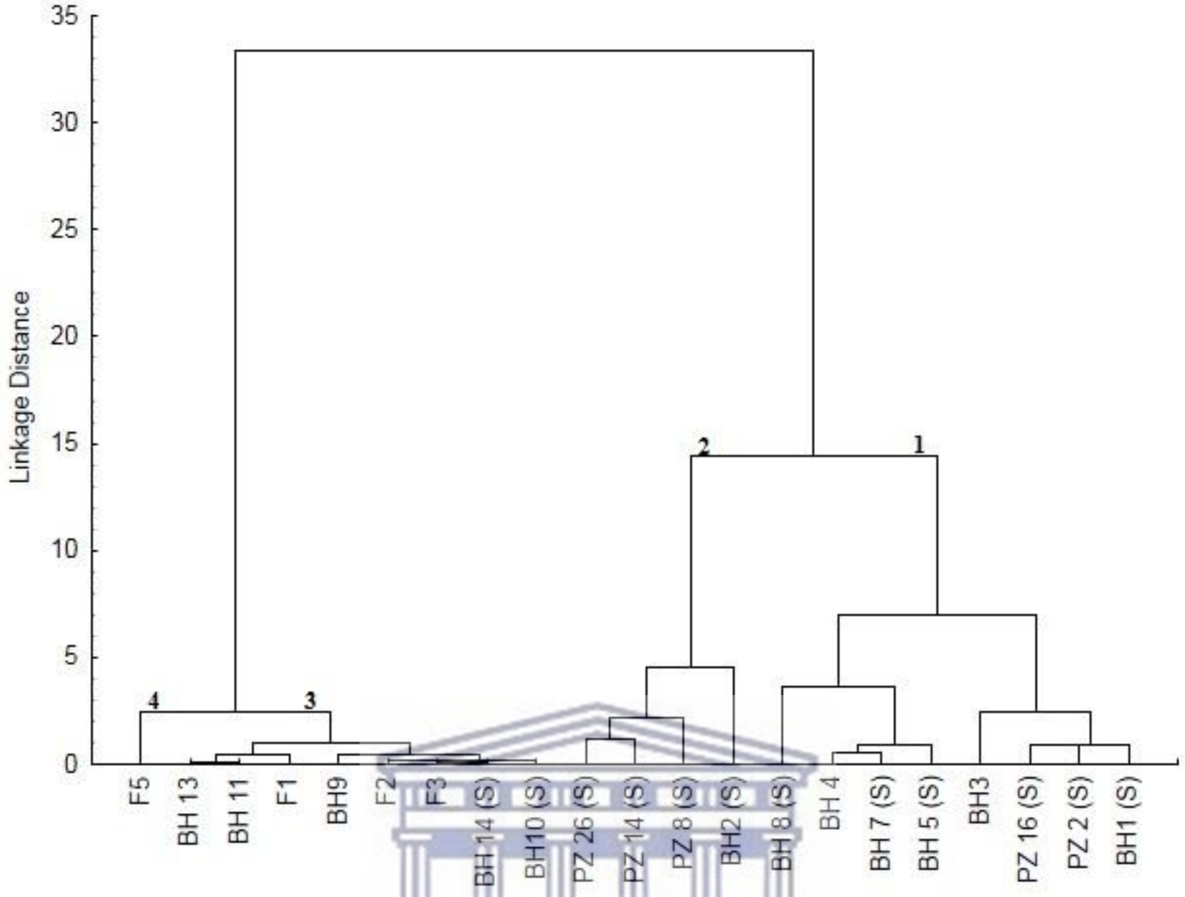


Figure 15: Hierarchal Cluster analysis for July 2018

Cluster 1 consists of a total of 8 samples, collected from, deep groundwater and shallow groundwater sites, BH1, BH3, BH4, BH5, BH7, BH8, PZ 2 and PZ16. The samples were all collected in the lower sections of the Catchment. No samples from the upper sections of the Catchment fell within this group. Cluster 1 consists of samples with the highest salinity concentrations except for BH8 which has low salinity. Samples within this cluster are characterised by high chloride and sodium concentrations and therefore high EC Values. **Cluster 2** consists of a total of 4 samples (PZ26, PZ8, PZ14, and BH2), all collected from shallow groundwater. This cluster consists of samples with some of the highest salinities. Similarities in the chemical composition of samples within this cluster could possibly be attributed to similarities in depths at which the samples were collected. These samples were also collected at sites within proximity to each other, mostly downstream. **Cluster 3** consists of 8 samples, mostly collected from deep groundwater and only two from shallow water. These samples were collected upstream of the Catchment, furthest from the coast. These include BH13, BH 14, BH11, BH10, BH9, F1, F2, F3, and F5. These samples are characterized by low salinities and are generally fresh. **Cluster 4** consists of only 1 sample, F5, located upstream. Waters in this group are characterized by low salinities. Similarly, to cluster 3, low salinity concentrations in this group can be attributed to the geology.

4.3.5 Predominant water types

Water type was characterized using Piper diagrams (Piper 1944). Piper diagrams in this section have also been applied to gain insight into the chemical evolution or origin of groundwater in the Heuningnes Catchment. The ionic proportions, expressed in meq/L, of groundwater in the Heuningnes Catchment are presented in figures 16-19. Results indicate that groundwater is confined to the sodium-chloride type (Na-Cl type) and these are therefore the dominant ions in all waters within the Catchment. Calcium, magnesium, potassium, and bicarbonate were present in less significant amounts. The Piper diagrams do not give an indication of recently recharged or fresh groundwater within the Heuningnes Catchment. Instead, the Piper diagram gives an indication of a coastal aquifer; consisting of deep ancient groundwater that is expected to be saline that was expected in this Catchment given that it is a coastal Catchment. The Piper diagram generated for all the sampling trips shows that BH 8 and BH 9 tend to deviate from the clustering of the other samples.

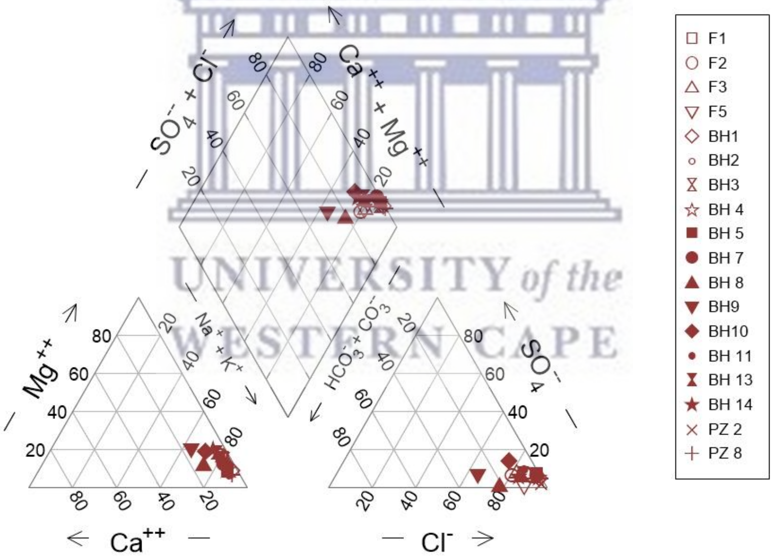


Figure 16: Piper diagram for groundwater samples in July 2017

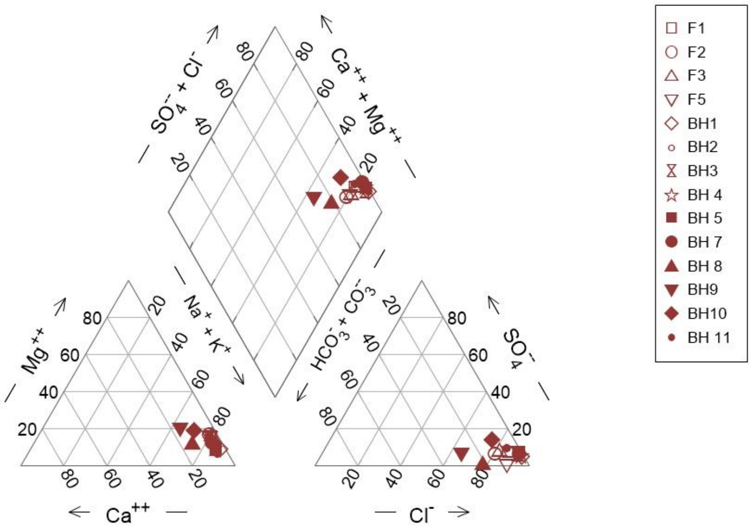


Figure 17: Piper diagram for groundwater samples in October 2017

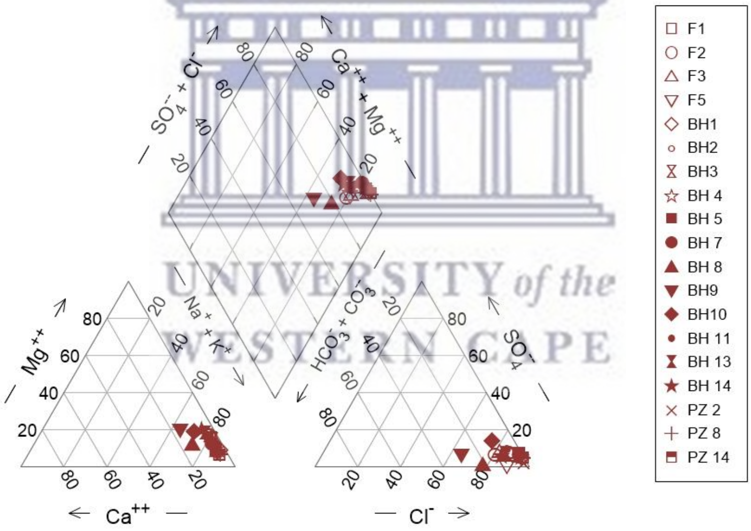


Figure 18: Piper diagram for groundwater samples in March 2018

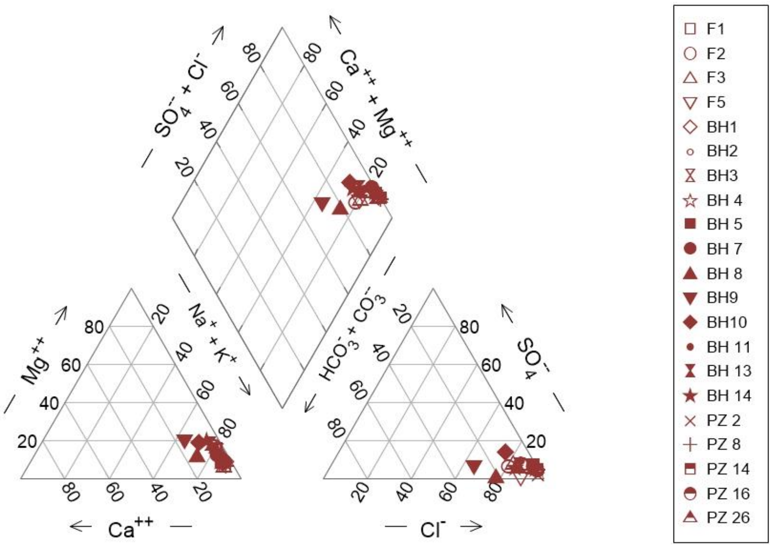


Figure 19: Piper diagram for groundwater samples in July 2018

4.4 Hydrogeochemical modelling

Several approaches were used to help in identification of hydrogeochemical processes that led to the water types at the study area. The measured ion concentrations and stoichiometry of reactions were used together to improve the understanding of the hydrogeochemical processes. Furthermore, the type of rocks and their linked mineralogy of aquifers were deduced from the literature review.

4.4.1 Saturation Indices

Table 13-16 show the saturation indices that were calculated using the PHREEQC hydrogeochemical program (Parkhurst and Appelo, 1999), making use of the July 2017, October 2017, March 2018, and July 2018 groundwater chemistry data. The SI was calculated to determine how saturated the solution at a certain point was, relative to specific minerals. Variations in processes that took place within the groundwater system leading to the change of the chemistry were indicated by SI (Roy *et al*., 2020) as presented for each borehole.

4.5.1.1 July 2017

Table 13 shows that all the sampling boreholes were oversaturated with respect to the following minerals: anhydrite, aragonite, calcite, dolomite, gypsum, melanterite and siderite. However, for the same sampling trip, all the sampling boreholes were under-saturated with respect to halite and sylvite, respectively.

Table 13: Saturation indices for all the boreholes in July 2017

BH #/PZ #	Phases												
	Anhydrite	Aragonite	Calcite	CO_2 (g)	Dolomite	Gypsum	H_2 (g)	H_2O (g)	Halite	Melanterite	O_2 (g)	Siderite	Sylvite
F1	0.446	0.260	0.253	0.426	0.239	0.417	0.847	-	-0.692	0.777	1.228	0.180	-1.047
F2	0.346	0.214	0.207	0.478	0.194	0.316	0.860	-	-0.413	0.730	1.319	0.168	-0.853
F4 (S)	0.419	0.278	0.271	0.364	0.254	0.390	0.831	-	-0.721	0.748	1.241	0.193	-1.059
F5	0.414	0.246	0.238	0.572	0.225	0.384	0.890	-	-0.720	0.723	1.185	0.147	-1.057
BH1 (S)	0.412	0.139	0.132	0.550	0.114	0.382	0.919	-	-0.508	0.769	1.151	0.091	-0.888
BH3	0.278	0.181	0.174	0.341	0.163	0.248	0.854	-	-0.465	0.734	1.221	0.181	-0.869
BH4	0.260	0.118	0.111	0.601	0.101	0.231	0.932	-	-0.506	0.000	1.134	0.000	-0.936
BH5 (S)	0.300	0.114	0.107	0.604	0.087	0.271	0.942	-	-0.492	0.726	1.121	0.111	-0.913
BH6	0.308	0.125	0.117	0.592	0.100	0.278	0.941	-	-0.581	0.732	1.122	0.120	-0.977
BH7 (S)	0.349	0.128	0.121	0.587	0.101	0.320	0.934	-	-0.521	0.734	1.131	0.097	-0.941
BH8 (S)	0.323	0.122	0.115	0.616	0.097	0.293	0.949	-	-0.587	0.678	1.111	0.063	-0.976
BH10 (S)	0.354	0.227	0.220	0.474	0.212	0.324	0.865	-	-0.703	0.722	1.211	0.168	-1.033
BH11	0.385	0.226	0.219	0.494	0.204	0.356	0.879	-	-0.673	0.752	1.197	0.171	-1.044
BH12 (S)	0.345	0.175	0.168	0.522	0.164	0.315	0.899	-	-0.668	0.767	1.175	0.165	-1.023
BH14 (S)	0.400	0.244	0.237	0.498	0.222	0.371	0.872	-	-0.706	0.751	1.204	0.176	-1.029
PZ 7 (S)	0.255	0.133	0.126	0.540	0.114	0.226	0.912	-	-0.373	0.636	1.160	0.083	-0.854
PZ 14 (S)	0.302	0.167	0.160	0.530	0.141	0.272	0.902	-	-0.492	0.646	1.171	0.092	-0.900
PZ 19 (S)	0.344	0.140	0.133	0.513	0.128	0.315	0.911	-	-0.679	0.757	1.161	0.130	-0.981

4.5.1.2 October 2017

The table below shows that all the sampling boreholes were super-saturated with respect to the following minerals: anhydrite, aragonite, calcite, dolomite, gypsum, melanterite and siderite. However, for the same sampling trip, all the sampling boreholes were under-saturated with respect to halite and sylvite, respectively. There was an exception with siderite and halite. Siderite was under-saturated for the following sampling points; F5, BH 1 and BH 7 but was super-saturated for the rest of the other sampling points. There was only one exception for halite which was PZ 2, which was super-saturated while the rest of the sampling points were under-saturated.

Table 14: Saturation indices for all the boreholes in October 2017

BH #/PZ #	Phases												
	Anhydrite	Aragonite	Calcite	CO_2 (g)	Dolomite	Gypsum	H_2 (g)	H_2O (g)	Halite	Melanterite	O_2 (g)	Siderite	Sylvite
F1	0.237	0.190	0.183	0.185	0.169	0.207	0.829	-	-0.489	0.625	1.243	0.135	-0.872
F2	0.234	0.187	0.179	0.269	0.166	0.205	0.841	-	-0.495	0.569	1.232	0.099	-0.850
F3	0.258	0.153	0.145	0.450	0.131	0.228	0.890	-	-0.530	-	1.185	-	-0.902
F5	0.313	0.107	0.100	0.464	0.088	0.283	0.913	-	-0.532	0.611	1.159	0.000	-0.902
BH1 (S)	0.133	0.023	0.016	0.369	0.000	0.103	0.917	-	-0.293	0.548	1.153	-0.004	-0.734
BH6	0.182	0.045	0.037	0.388	0.021	0.153	0.914	-	-0.346	0.561	1.157	-0.005	-0.805
BH7 (S)	0.155	0.064	0.057	0.331	0.039	0.125	0.898	-	-0.284	0.547	1.176	0.018	-0.766
BH8 (S)	0.210	0.031	0.024	0.385	0.006	0.180	0.922	-	-0.338	0.556	1.147	-0.039	-0.792
BH9	0.243	0.142	0.135	0.317	0.126	0.214	0.870	-	-0.540	0.527	1.206	0.024	-0.890
BH10 (S)	0.204	0.129	0.122	0.382	0.119	0.175	0.879	-	-0.529	0.559	1.197	0.056	-0.888
BH12 (S)	0.194	0.098	0.091	0.256	0.087	0.165	0.876	-	-0.478	0.626	1.200	0.081	-0.851
BH13	0.246	0.173	0.165	0.220	0.152	0.217	0.845	-	-0.513	0.622	1.229	0.112	-0.861
BH14 (S)	0.220	0.151	0.144	0.209	0.134	0.191	0.849	-	-0.507	0.581	1.225	0.081	-0.867
PZ 2 (S)	0.114	0.019	0.012	0.305	-0.004	0.085	0.902	-	0.096	0.617	1.171	0.052	-0.586

4.5.1.1 March 2018

The table below shows that all the sampling boreholes were super-saturated with respect to the following minerals: anhydrite, gypsum and melanterite. However, for the same sampling trip, all the sampling boreholes were under-saturated with respect to sylvite, respectively. In this sampling trip there were some minerals (aragonite, calcite, dolomite, siderite and halite) that were under-saturated in some sampling points and super-saturated in others.

Table 15: Saturation indices for all the boreholes in March 2018

BH #/PZ #	Phases											
	Anhydrite	Aragonite	Calcite	CO_2 (g)	Dolomite	Gypsum	H_2 (g)	H_2O (g)	Halite	Melanterite	O_2 (g)	Siderite	Sylvite
F1	0.238	0.182	0.175	0.167	0.161	0.209	0.832	-	-0.490	0.606	1.240	0.115	-0.874
F3	0.257	0.179	0.172	0.243	0.158	0.227	0.846	-	-0.525	-	1.228	-	-0.899
F5	0.271	0.149	0.142	0.373	0.137	0.241	0.873	-	-0.528	0.566	1.203	0.039	-0.901
BH1 (S)	0.098	0.024	0.017	0.313	-0.001	0.069	0.906	-	-0.132	0.558	1.166	0.020	-0.684
BH4	0.091	0.009	0.002	0.387	-0.007	0.062	0.916	-	-0.166	0.536	1.155	-0.002	-0.757
BH5 (S)	0.088	0.017	0.010	0.396	-0.003	0.058	0.917	-	-0.124	0.482	1.154	-0.031	-0.747
BH 6	0.179	0.040	0.033	0.347	0.024	0.150	0.908	-	-0.342	0.576	1.164	0.004	-0.832
BH 7 (S)	0.111	0.031	0.024	0.364	0.012	0.083	0.908	-	-0.245	0.498	1.165	-0.021	-0.770
BH 8 (S)	0.218	-0.061	-0.068	0.526	-0.075	0.189	0.969	-	-0.378	0.675	1.079	-0.010	-0.826
BH 10 (S)	0.214	0.132	0.125	0.161	0.123	0.185	0.851	-	-0.527	0.521	1.224	0.029	-0.886
BH11	0.233	0.148	0.141	0.305	0.132	0.204	0.867	-	-0.518	0.576	1.209	0.068	-0.897
BH12 (S)	0.178	0.084	0.076	0.234	0.077	0.149	0.875	-	-0.472	0.605	1.201	0.063	-0.857
BH 13	0.248	0.138	0.130	0.196	0.115	0.218	0.862	-	-0.508	0.595	1.214	0.062	-0.818
BH 14 (S)	0.241	0.122	0.115	0.249	0.104	0.212	0.871	-	-0.513	0.553	1.205	0.023	-0.852
PZ 2 (S)	0.127	0.002	-0.006	0.350	-0.021	0.097	0.918	-	-0.083	0.521	1.153	-0.038	-0.693
PZ 8 (S)	0.070	0.021	0.014	0.358	-0.001	0.042	0.907	2.176	0.075	0.496	1.166	-0.011	-0.678
PZ 14 (S)	0.042	0.008	0.001	0.372	-0.013	0.013	0.910	2.176	0.155	0.543	1.162	0.022	-0.635
PZ 16 (S)	0.104	0.033	0.026	0.289	0.006	0.075	0.900	-	-0.096	0.475	1.173	-0.031	-0.684
PZ 26 (S)	0.0360092	-0.009476	-0.01671	0.371759	-0.027	0.008451	0.912959	2.176	2.61E-01	5.60E-01	1.16E+00	2.22E-02	-6.55E-01

4.5.1.1 July 2018

The table below shows that all the sampling boreholes were super-saturated with respect to the following minerals: anhydrite, gypsum and melanterite. However, for the same sampling trip, all the sampling boreholes were under-saturated with respect to sylvite, respectively. In this sampling trip there were some minerals (aragonite, calcite, dolomite, siderite, and halite) that were under-saturated in some sampling points and super-saturated in others.

The SI results showed a change of calcite, dolomite, aragonite, gypsum, anhydrite, halite, melantinterite, siderite and sylvite from being undersaturated to oversaturated at some areas for the different seasons. All the evaporites and plagioclase minerals were undersaturated in all samples for different seasons. The undersaturation of evaporites might have been the result of fewer occurrences of these minerals along certain flow paths (Manoj *et al*., (2019). A seasonal variation was indicated between the results. Most of the samples appeared to be supersaturated in carbonates during July 2017 and October 2017, whereby ions, Ca^{2+}, Mg^{2+} and HCO_3^-, were abundant in solution. This could be an indication that carbonate weathering took place in the absence of silicate weathering and vice versa.

4.4.2 Mass balance approach

The saturation indices were used to constrain the possible mineral phases that were identified to either precipitate or dissolve. The mean values for the ions were taken as initial and final solution compositions. Simulations were performed from BH 9 to BH 8, from BH 8 to BH 6, BH 6 to BH 1 and F5 to BH 4. The conceptual inverse model was formulated where phases such as quartz, kaolinite, gibbsite, Ca-montmorillonite and calcite were constrained to precipitate and minerals such as anorthite, albite, biotite, plagioclase, kfeldspar, dolomite, halite and fluorite were constrained to dissolve based on the SI values. Cation exchange reactions were also included in the simulations since the hydrochemical inferences point to ion exchange (Fig. 10 (b)–(c)). Model outputs are shown in Tables 17-20. The results only show models with minimum statistical error (sum of residuals, sum of delta/uncertainty limit and maximum fractional error in element concentrations) are included in the tables.

Table 16: Saturation indices for all the boreholes in July 2018

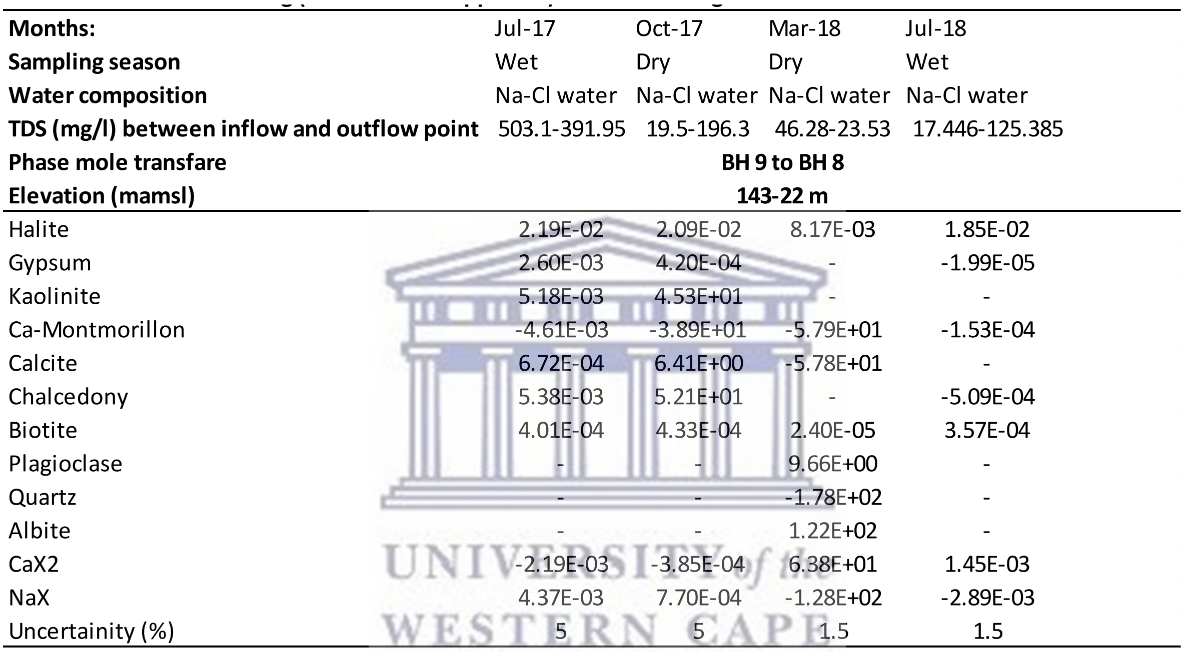
BH #/PZ #	Phases												
	Anhydrite	Aragonite	Calcite	CO_2 (g)	Dolomite	Gypsum	H_2 (g)	H_2O (g)	Halite	Melanterite	O_2 (g)	Siderite	Sylvite
F1	0.245	0.203	0.195	0.023	0.181	0.216	0.809	0.000	-0.484	0.617	1.259	0.136	-0.875
F2	0.249	0.168	0.160	0.153	0.146	0.220	0.841	0.000	-0.495	0.578	1.232	0.078	-0.879
F3	0.291	0.204	0.197	0.224	0.180	0.261	0.838	0.000	-0.554	0.658	1.235	0.141	-0.912
F5	0.322	0.135	0.128	0.416	0.113	0.292	0.896	0.000	-0.529	0.589	1.179	0.004	-0.886
BH1 (S)	0.091	0.022	0.015	0.311	-0.002	0.063	0.901	0.000	0.113	0.565	1.173	0.026	-0.602
BH2 (S)	0.028	-0.059	-0.066	0.437	-0.073	0.001	0.935	2.176	0.351	0.597	1.130	0.018	-0.550
BH3	0.080	-0.047	-0.054	0.406	-0.066	0.051	0.933	0.000	0.017	0.585	1.133	-0.003	-0.624
BH 4	0.091	0.009	0.002	0.382	-0.009	0.062	0.912	0.000	-0.032	0.598	1.160	0.041	-0.722
BH 5 (S)	0.080	0.021	0.014	0.372	0.001	0.050	0.907	0.000	0.008	0.596	1.166	0.053	-0.704
BH 7 (S)	0.103	0.022	0.015	0.383	0.001	0.073	0.910	0.000	-0.094	0.575	1.162	0.029	-0.728
BH 8 (S)	0.209	-0.022	-0.029	0.380	-0.031	0.180	0.927	0.000	-0.360	0.597	1.140	-0.049	-0.811
BH9	0.233	0.142	0.135	0.136	0.129	0.204	0.846	0.000	-0.540	0.546	1.228	0.043	-0.891
BH10 (S)	0.209	0.165	0.158	0.136	0.149	0.179	0.834	0.000	-0.501	0.579	1.239	0.098	-0.862
BH 11	0.228	0.184	0.176	0.129	0.162	0.199	0.828	0.000	-0.468	0.598	1.244	0.116	-0.882
BH 13	0.250	0.192	0.185	0.140	0.171	0.221	0.825	0.000	-0.507	-	1.246	-	-0.883
BH 14 (S)	0.252	0.173	0.166	0.173	0.153	0.222	0.838	0.000	-0.506	0.565	1.235	0.074	-0.882
PZ 2 (S)	0.105	0.000	-0.007	0.353	-0.023	0.076	0.912	2.176	0.135	0.621	1.160	0.045	-0.609
PZ 8 (S)	0.059	0.035	0.028	0.343	0.016	0.031	0.895	2.176	0.287	0.524	1.180	0.022	-0.643
PZ 14 (S)	0.0322572	0.0077416	0.000512	0.351197	-0.00795	0.005653	0.902915	2.176091	4.64E-01	5.94E-01	1.17E+00	5.88E-02	-6.13E-01
PZ 16 (S)	0.0862267	0.0277357	0.020506	0.279841	0.003795	0.057636	0.894423	2.176091	1.62E-01	6.17E-01	1.18E+00	6.88E-02	-6.12E-01
PZ 26 (S)	0.0294217	-0.006294	-0.01352	0.404391	-0.02082	0.001892	0.913985	2.176091	3.70E-01	5.64E-01	1.16E+00	3.00E-02	-6.96E-01

4.4.3 Inverse geochemical modelling

Table 17 indicates the mass-balance modelling results that were generated for flow path from the BH 9 to BH 8. Model simulations were obtained for the periods July 2017, October 2017, March 2018, and July 2018. Uncertainty values of 5% and 1.5% were used to conduct the simulation. The sample for all the sampling periods indicated a Na-Cl water composition as displayed in the Piper diagrams (Figures 16-19). The results indicated by these simulations showed that for July 2017, October 2017, March 2018, and July 2018 there was dissolution of halite, kaolinite, and biotite. In addition, Ca-montmorillonite was precipitating for all the sampling periods (Table 17). On the other hand, there was dissolution of gypsum and chalcedony during July 2017 and October 2017 but during July 2018 there was precipitation for the same minerals. In March 2018, there was dissolution of plagioclase and albite, however there was also precipitation of quartz. The dissolution of gypsum for both periods has been excluded as one of the processes to having taken place in the study area (Figure 10), however the mass balance results indicate that gypsum dissolution to be an active process in the study area.

Ion exchange along this flow path was occurring around this area down-gradient in the Catchment. The occurrence of ion exchange was indicated by a negative CaX2 value with a positive NaX. During ion exchange, Na^+ detaches from the sediments to replace Ca^{2+} in solution. On the other hand, Ca^{2+} is removed to fill in the void Na^+ spaces on the rock surface (Li *et al*, 2010). Conversely, the transfer of moles during March 2018 and July 2018 indicated the occurrence of cation exchange instead. This was indicated by a positive value of CaX2 with a negative value of NaX along the same flow path. The occurrence of cation exchange at the same area during these two periods was as a result of high recharge such that sodium ions were flushed out of the system as they were replaced by calcium.

Table 17: Inverse modelling (modelling-approach) results showing mole transfer between two boreholes



Months:	Jul-17	Oct-17	Mar-18	Jul-18
Sampling season	Wet	Dry	Dry	Wet
Water composition	Na-Cl water	Na-Cl water	Na-Cl water	Na-Cl water
TDS (mg/l) between inflow and outflow point	503.1-391.95	19.5-196.3	46.28-23.53	17.446-125.385
Phase mole transfare	**BH 9 to BH 8**			
Elevation (mamsl)	**143-22 m**			
Halite	2.19E-02	2.09E-02	8.17E-03	1.85E-02
Gypsum	2.60E-03	4.20E-04	-	-1.99E-05
Kaolinite	5.18E-03	4.53E+01	-	-
Ca-Montmorillon	-4.61E-03	-3.89E+01	-5.79E+01	-1.53E-04
Calcite	6.72E-04	6.41E+00	-5.78E+01	-
Chalcedony	5.38E-03	5.21E+01	-	-5.09E-04
Biotite	4.01E-04	4.33E-04	2.40E-05	3.57E-04
Plagioclase	-	-	9.66E+00	-
Quartz	-	-	-1.78E+02	-
Albite	-	-	1.22E+02	-
CaX2	-2.19E-03	-3.85E-04	6.38E+01	1.45E-03
NaX	4.37E-03	7.70E-04	-1.28E+02	-2.89E-03
Uncertainity (%)	5	5	1.5	1.5

Table 18 indicates the mass-balance modelling results that were generated for flow path from the BH 8 to BH 6. Model simulations were obtained for the periods July 2017, October 2017, March 2018, and July 2018. Uncertainty values of 5% and 1.5% were used to conduct the simulation. The sample for all the sampling periods indicated a Na-Cl water composition as displayed in the Piper diagrams (Figures 16-19). The results indicated by these simulations showed that for July 2017, there was dissolution of halite, kaolinite, biotite, and quartz, though there was also precipitation of Ca-montmorillonite and sylvite. In October 2017, there was precipitation of halite, kaolinite, and biotite however there was dissolution of gypsum and plagioclase. In March 2018, there was dissolution halite, biotite, plagioclase, and albite but there was also precipitation of Ca-montmorillonite, calcite, and quartz. In October 2017, there was dissolution of halite, gypsum, chalcedony, and plagioclase, however there was precipitation of biotite.

The results indicated that ion exchange along this flow path was occurring. The occurrence of ion exchange was indicated by a negative CaX2 value with a positive NaX for October 2017 and July 2018. During ion exchange, Na^+ detached from the sediments to replace Ca^{2+} in solution. On the other hand, Ca^{2+} was removed to fill in the void Na^+ spaces on the rock surface (Li *et al.*, 2010). Conversely, the transfer of moles during March 2018 indicated the occurrence of reverse ion exchange instead. This was indicated by a positive value of CaX2 with a negative value of NaX along the same flow path. The occurrence of cation exchange at the same area during these two periods was as a result of high recharge such that sodium ions were flushed out of the system as they were replaced by calcium.

Table 18: Inverse modelling (modelling-approach) results showing mole transfer between two boreholes

Months:	Jul-17	Oct-17	Mar-18	Jul-18
Sampling season	Wet	Dry	Dry	Wet
Water composition	Na-Cl water	Na-Cl water	Na-Cl water	Na-Cl water
TDS (mg/l) between inflow and outflow point	391.95-1826.5	196.3-207.35	23.53-834.6	125.385-407.03
Phase mole transfare	**BH 8 to BH 6**			
Elevation (mamsl)	**23-22 m**			
Halite	5.90E-03	-5.63E-03	8.17E-03	2.66E-02
Gypsum	-	3.63E-04	-	1.13E-03
Kaolinite	7.86E-03	-1.81E-04	-	-
Ca-Montmorillon	-6.78E-03	-	-5.79E+01	-
Calcite	-	-	-5.78E+01	-
Chalcedony	-	-	-	5.61E-04
Biotite	7.04E-05	-2.97E-04	2.40E-05	-5.11E-04
Plagioclase	-	4.77E-04	9.66E+00	3.70E-04
Quartz	8.94E-03	-	-1.78E+02	-
Albite	-	-	1.22E+02	-
CaX2	-	-3.14E-04	6.38E+01	-1.43E-03
NaX	-	6.27E-04	-1.28E+02	2.85E-03
Sylvite	-1.00E-04	-	-	-
Uncertainity (%)	5	5	1.5	5

Table 19 indicates the mass-balance modelling results that were generated for flow path from the BH 6 to BH 1. Model simulations were obtained for the periods July 2017, October 2017, March 2018, and July 2018. Uncertainty values of 5% and 1.5% were used to conduct the simulation. The sample for all the sampling periods indicated a Na-Cl water composition as displayed in the Piper diagrams (Figures 16-19). The results indicated by these simulations showed that for July 2017, there was only dissolution of plagioclase, though there was precipitation of kaolinite and biotite. In October 2017, there was precipitation of Ca-montmorillonite, calcite, and chalcedony, however, there was dissolution of halite, gypsum, and biotite. In March 2018, there was dissolution halite, biotite, plagioclase, and albite but there was also precipitation of Ca-montmorillonite, calcite, and quartz. In October 2017, there was dissolution of halite and biotite, however there was precipitation of gypsum, Ca-montmorillonite, and chalcedony.

The results indicated that ion exchange along this flow path was occurring. The occurrence of ion exchange was indicated by a negative CaX2 value with a positive NaX for October 2017. During ion exchange, Na^+ detached from the sediments to replace Ca^{2+} in solution. On the other hand, Ca^{2+} was removed to fill in the void Na^+ spaces on the rock surface (Li *et al*., 2010). Conversely, the transfer of moles during July 2017, March 2018 and July 2018 indicated the occurrence of cation exchange instead. This was indicated by a positive value of CaX2 with a negative value of NaX along the same flow path. The occurrence of cation exchange at the same area during these two periods was as a result of high recharge such that sodium ions were flushed out of the system as they were replaced by calcium.

Table 19: Inverse modelling (modelling-approach) results showing mole transfer between two boreholes

Months:	Jul-17	Oct-17	Mar-18	Jul-18
Sampling season	Wet	Dry	Dry	Wet
Water composition	Na-Cl water	Na-Cl water	Na-Cl water	Na-Cl water
TDS (mg/l) between inflow and outflow point	1826-8034	207.35-664.9	834.6-3952	407.03-1354.73
Phase mole transfare	**BH 6 to BH 1**			
Elevation (mamsl)	**23 - 18 m**			
Halite	-	1.18E-02	8.17E-03	1.85E-02
Gypsum	-	2.76E-03	-	-1.99E-05
Kaolinite	-1.23E-04		-	-
Ca-Montmorillon	-	-1.77E-04	-5.79E+01	-1.53E-04
Calcite	-	-6.10E-04	-5.78E+01	-
Chalcedony	-	-5.89E-04	-	-5.09E-04
Biotite	-2.03E-04	4.13E-04	2.40E-05	3.57E-04
Plagioclase	3.26E-04	-	9.66E+00	-
Quartz	-	-	-1.78E+02	-
Albite	-	-	1.22E+02	-
CaX2	9.61E-04	-1.74E-03	6.38E+01	1.45E-03
NaX	-1.92E-03	3.48E-03	-1.28E+02	-2.89E-03
Uncertainity (%)	5	5	1.5	1.5

Table 20 indicates the mass-balance modelling results that were generated for flow path from the F5 to BH 4. Model simulations were obtained for the periods July 2017, October 2017, March 2018, and July 2018. Uncertainty values of 2.5%, 5% and 1.5% were used to conduct the simulation. The sample for all the sampling periods indicated a Na-Cl water composition as displayed in the Piper diagrams (Figures 16-19). The results indicated by these simulations showed that for July 2017, there was only dissolution of gypsum and calcite, though there was no precipitation taking place. In October 2017, there was no precipitation taking place, however, there was dissolution of gypsum and calcite. In March 2018, there was dissolution halite and calcite but there was no precipitation taking place. In October 2017, there was dissolution of halite, gypsum, and calcite, however there was no precipitation taking place. The results indicated that ion exchange along this flow path was occurring. The occurrence of ion exchange was indicated by a negative CaX2 value with a positive NaX for July 2017, October 2017, and July 2018. During ion exchange, Na^+ detached from the sediments to replace Ca^{2+} in solution. On the other hand, Ca^{2+} was removed to fill in the void Na^+ spaces on the rock surface (Li *et al*., 2010). Conversely, the transfer of moles during March 2018 indicated the occurrence of cation exchange instead. This was indicated by a positive value of CaX2 with a negative value of NaX along the same flow path. The occurrence of cation exchange at the same area during these two periods was as a result of high recharge such that sodium ions were flushed out of the system as they were replaced by calcium.

Table 20: Inverse modelling (modelling-approach) results showing mole transfer between two boreholes

Months:	Jul-17	Oct-17	Mar-18	Jul-18
Sampling season	Wet	Dry	Dry	Wet
Water composition	Na-Cl water	Na-Cl water	Na-Cl water	Na-Cl water
TDS (mg/l) between inflow and outflow point	7319-2450.5	1781-664.5	1943.5-3952	1641.9-1354.73
Phase mole transfare	**F5 to BH 4**			
Elevation (mamsl)	**218-25 m**			
Halite	-		9.02E-02	1.94E-01
Gypsum	6.65E-03	4.06E-03	-	5.38E-03
Calcite	7.10E-04	9.72E-04	1.27E-03	1.16E-03
CaX2	-2.65E-03	-1.87E-03	2.22E-03	-1.73E-04
NaX	5.31E-03	3.74E-03	-4.44E-03	3.46E-04
Uncertainity (%)	2.5	5	1.5	1.5

4.5 Hydrogeochemical conceptual model development

This section integrates different hydrogeological data to develop a hydrogeochemical conceptual model for the study area. Geology, hydrogeology, recharge/discharge, groundwater flow and hydrology data are used to construct the conceptual model while chemistry data was used to improve and verify the conceptual understanding of the model (Kpegli *et al.,* 2018). The conceptual model provides information on how groundwater flows within the aquifer system. A discussion of how the different hydrogeologic settings influence hydrogeochemical processes in the study area also ensues. Developing an accurate conceptual model is an essential step in the process of a groundwater modelling (Izady *et al*., 2014).

The lithological logs show that the boreholes (BH 9, BH 11 and BH 13) located upstream are all drilled into the sandstone formation. The boreholes that are drilled in the upper part of the Catchment are drilled in a more mountainous part of the Catchment compared to the lower part of the Catchment. Whereas all the boreholes (BH 4 and BH 6) that are located downstream of the Catchment are drilled primarily into shale and clay except for borehole 3 which is largely drilled into a sand formation. The lithological formation that this drilled into is not surprising given its proximity to the coast and that the area is dominated by sand dunes.

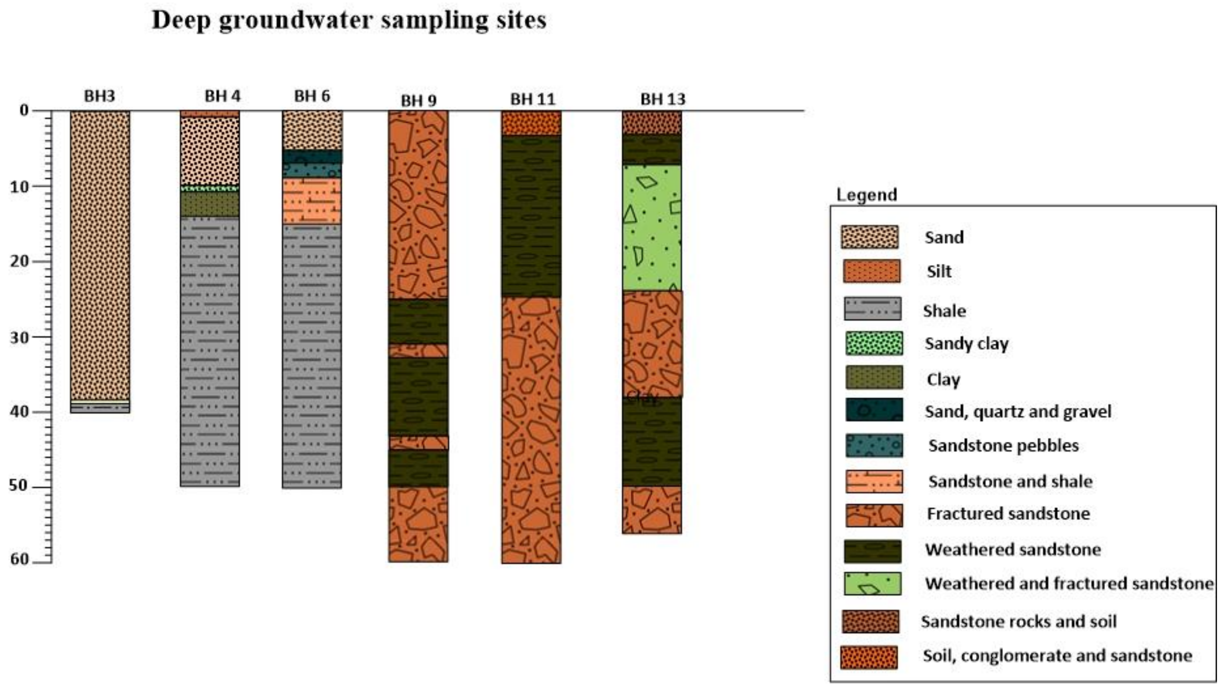


Figure 20: Lithological logs for deep groundwater boreholes in Heuningnes Catchment

The marine clay in the lower part of the study area tends to impede flow (Montcoudiol, 2015), this together with gentle slope of the area can attributed to the high salinity levels. Flow in the lower parts maybe slow as result of the above-mentioned factors, leading to increased contact time with host geology.The argument by Montcoudiol (2015) support the results that were found in the current study area, where the low lying areas with clay in the host geology exhibit high salinity levels compared to those that were recorded in the upper areas of the study area.

The cross-sectional (not drawn to scale) conceptual model (figure 21) for the lower part of the Catchment shows the general flow direction of the groundwater, the lithologies it flows in and the faults in the area.

The groundwater flows from point c to d which is from the middle part of the Catchment towards the coast. The water table in this area is generally close to the surface and during the wet season, this area is usually waterlogged (Mazvimavi, 2018). The boreholes that are in the area mostly drilled into the Bokkeveld series (shale and sandy shale formation). The elevated salinity levels can be attributed to the weathering of the shale formation (Tahoora *et al*., 2014).

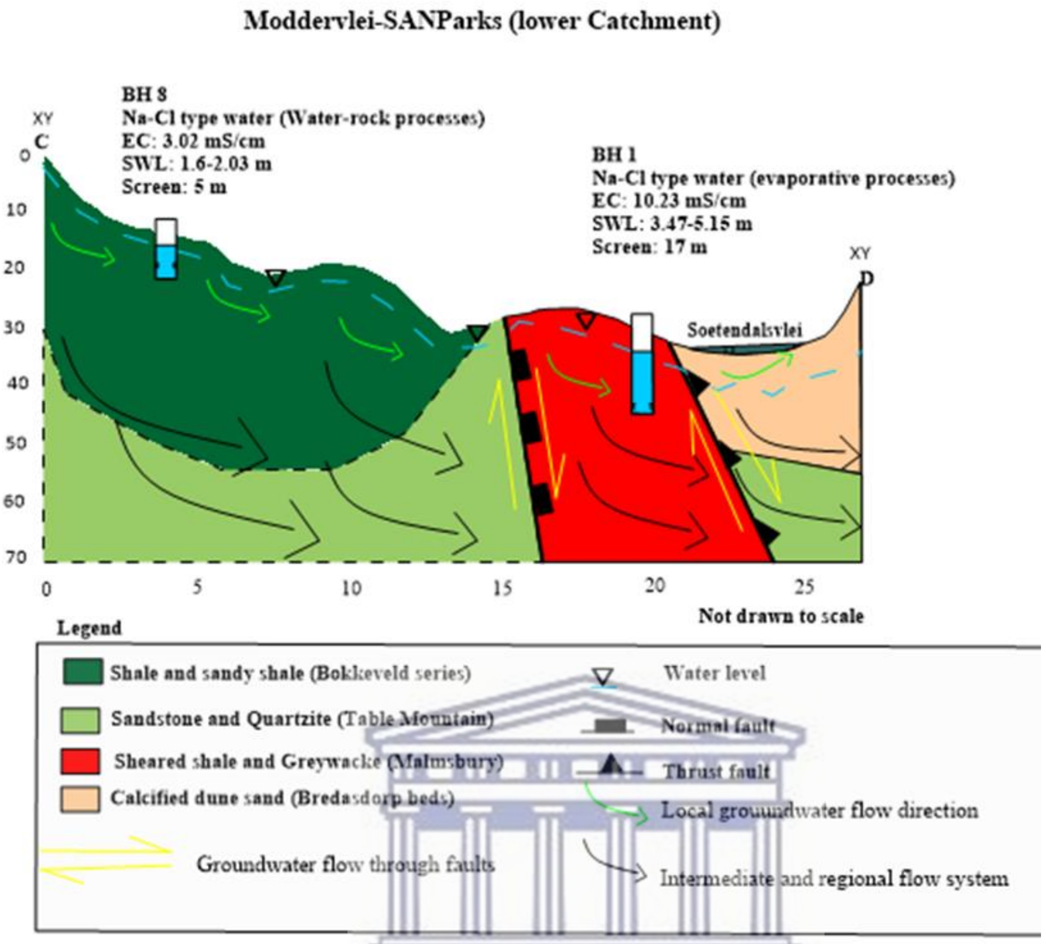


Figure 21: Cross-sectional conceptual model for the Heuningnes Catchment

Figure 22 below shows the major formations in which the aquifer(s) in the study are found in.

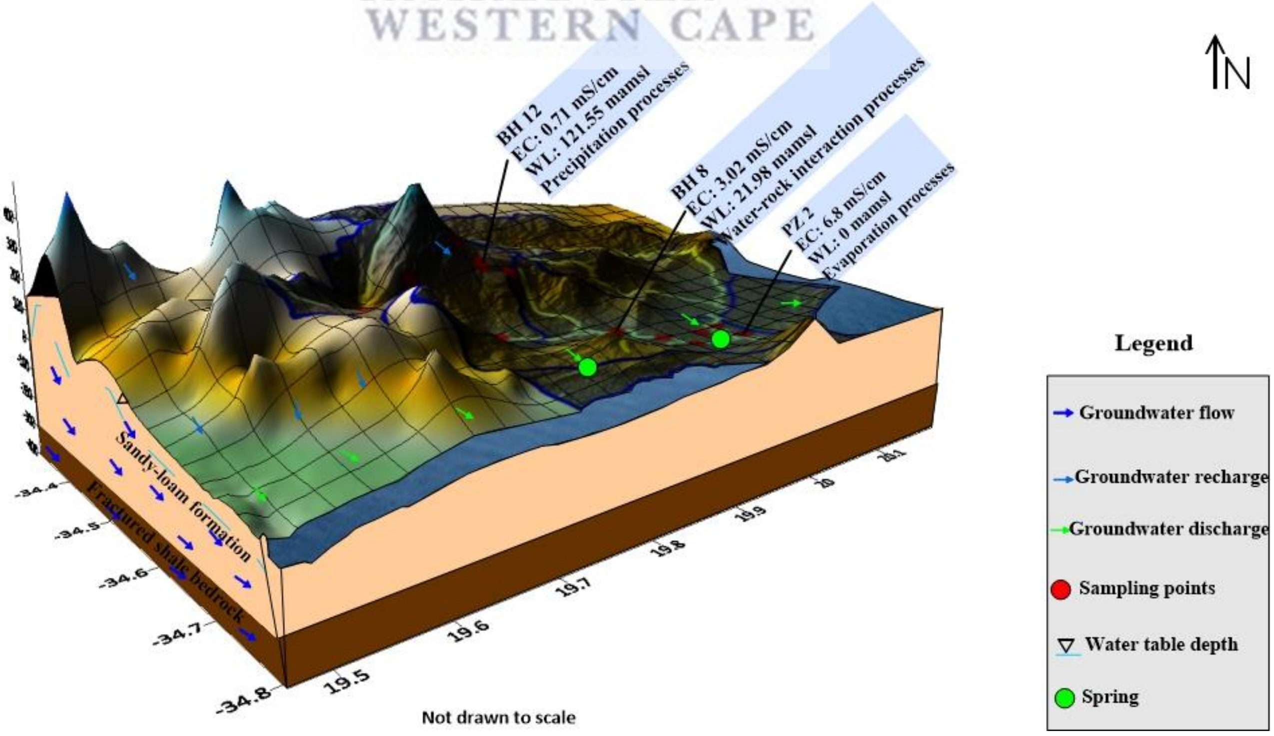


Figure 22: A 3D conceptual model for the Heuningnes Catchment

The boreholes that are drilled in the high altitudes are characterized by low salinity levels but towards the low altitudes in the middle reaches towards the coast salinity begins to rise (0.71 mS/cm, 3.02 mS/cm, and 6.8 mS/cm) as shown in the figure 22. As reported by Mazvimavi (2017), the hydrogeology of the area is influenced by the changes in geology resulting in the main flow not being across the geological boundaries but along the faults. The elevated levels of salinity were expected in the study area and were possibly derived from weathering of the geologic material (rock-water interaction) and/or salinization processes (Tahoora *et al.*, 2014) and given that the shale geology and the calcified dune sands which formed under marine environments (Mazvimavi, 2017).

Implication of hydrogeochemical studies in coastal environments

The results from this study can be used as a base line study for future research in coastal environments. In this way the results will shed light on the likely or possible processes that can be expected in coastal aquifers in turn contributing to the knowledge of these systems. The results can be used by water resources managers, when planning protection and management strategies of coastal aquifer systems.

Chapter 5: Conclusion and Recommendations

5.1 Introduction

This study focused on investigating the hydrogeochemical processes of groundwater within the Heuningnes Catchment by, firstly determining the hydrogeochemical processes using different techniques. The second part was to simulate the hydrogeochemical processes based on the spatiotemporal variation of the parameters using a modelling technique. The last part was to evaluate the existing conceptual models of hydrogeochemical processes through literature review.

5.2 Investigation of the dominant hydrogeochemical process in groundwater

The first objective was to determine hydrogeochemical processes. Water type within the Catchment was characterised as belonging to the Na-Cl water type, during all 4 sampling campaigns. The results generated from the Piper diagrams confirm the dominance of sodium and chloride ions in waters of the Heuningnes Catchment. Despite having different concentrations, the same ions were dominant in the whole Catchment. Groundwater of a Na/Cl type is typical for a Costal aquifer characterised by saline, deep ancient groundwater. No differences in major ion dominance in groundwater could be established during the duration of the study. Based on the results from Gibbs plots, it was concluded that the dominant processes in July 2017 were evaporation and water-rock interaction, during October 2017, March 2018 and July 2018, the dominant processes were water-rock interaction, evaporation and precipitation, respectively. It was concluded based on bivariate correlation and stoichiometric analysis that cation exchange, adsorption, and evaporation, weathering of carbonates, sulphates and silicate minerals are processes influencing the chemistry of groundwater in the Heuningnes Catchment. Therefore, the first objective of the study focusing on determining hydrogeochemical processes was achieved and the research question was answered with valid reliable data sets.

5.3 Modelling approaches for hydrogeochemical processes and source of groundwater parameters

The process of ion exchange and reverse ion exchange happened at low elevations at the same flow path, although during different periods, and this was related to high recharge in summer. Silicate weathering was experienced at high elevations along the flow path. The major silicate weathering that took place was either releasing montmorillonite or kaolinite. Carbonate and gypsum dissolutions were also experienced at some areas along the flow paths. Meanwhile, dissolution of other minerals such as sylvite and halite were also experienced at random areas along the flow path. The mass-balance modelling results indicated that if more minerals were precipitated from solution, the resulting solution would have a TDS concentration smaller than that of the initial solution. This was assumed to be happening in areas where Solution 1 was mineralised or had a higher TDS than Solution 2. However, if more minerals were dissolved, the resultant solution becomes more mineralised and its TDS increased. Therefore, the second objective of the study focusing on simulating hydrogeochemical processes was achieved and the research question was answered with valid reliable data sets.

5.4 Assessment of conceptual model for hydrogeochemical processes in groundwater

The third objective was to evaluate the existing conceptual models of hydrogeochemical processes. This was done in order to develop a comprehensive hydrogeochemical conceptual model for the study area. The model was developed based on secondary data from records review and hydrochemical data. The conceptual model for the hydrogeochemical processes in the study area has been supported by the following evidence: The study area has a shallow water table (less than 10 m) both in upstream and downstream areas. The Table Mountain Group (TMG) formation dominant in upstream areas has low salinity values this is as a result of the reduced time of interaction between the water and the host material. Generally, the Bokkeveld series in the study area is characterised by high salinity values due to the layer of shale. Deeper groundwater in the upstream parts of the study area indicates influence of direct recharge without significant evaporation while in the lower areas the dominant process points to evaporation processes. Low surface elevation (gradient) and poor hydraulic conductivity due to the clay layer in the downstream portion of the study area cause slow groundwater flows resulting in high salinization due to the increased residence time. Therefore, the third objective of the study focusing on the evaluation of existing hydrogeochemical conceptual models was achieved and the research question was answered with valid reliable data sets.

Recommendations

The following recommendations were made for future studies:

Sampling should cover a larger area for further studies; thus, more boreholes should be sampled so that there would be no data shortage during the interpretation of results. This will also assist in determining any link on the hydraulic behaviour for different Catchments around the area.

Sample collection may be done for at least four seasons of the year or more in order to make better comparisons of the data; also, to determine any variations in the hydrochemistry of the area.

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Appendix 1

Table 21(c): Major Ion concentration of groundwater March 2018 (meq/L)

Site name	Calcium	Sodium	Pottasium	Magnisium	Chloride	Sulphate	Bicarbonate
F1	0.25	3.87	0.05	0.99	4.42	0.37	0.30
F2							
F3	0.15	2.30	0.03	0.58	2.79	0.25	0.26
F4							
F5	0.35	2.26	0.03	0.41	2.62	0.06	0.16
BH1	4.14	105.13	0.66	16.45	132.48	19.53	5.21
BH2	25.45	2.00	2.25	41.14	506.60	52.36	6.26
BH3	5.19	1.30	0.51	9.05	112.84	17.40	7.64
BH4	7.29	87.39	0.13	12.34	103.30	11.22	2.69
BH5	5.89	123.26	0.15	13.99	123.30	18.15	2.46
BH6	1.50	22.83	0.05	2.39	22.06	1.12	2.69
BH7	4.49	43.78	0.13	10.70	65.92	7.37	2.23
BH8	0.90	14.91	0.08	1.15	15.84	0.40	5.25
BH9	0.30	1.83	0.03	0.49	2.54	0.21	0.95
BH10	0.65	2.22	0.05	0.58	2.82	0.35	0.98
BH11	0.25	2.52	0.03	0.49	3.10	0.40	0.36
BH12	1.60	5.30	0.08	1.07	5.26	0.69	1.70
BH13	0.20	2.96	0.41	0.82	3.47	0.31	1.21
BH14	0.35	2.91	0.15	0.90	3.15	0.23	1.02
PZ 2	4.34	135.13	0.41	12.34	175.52	7.62	6.00
PZ 7							
PZ 8	11.18	304.78	0.36	32.91	335.00	29.50	2.92
PZ 13							
PZ 14	18.36	366.30	0.69	45.25	481.80	49.03	3.05
PZ 16	4.14	139.57	0.59	18.92	151.96	18.34	5.21
PZ 19							
PZ 26	27.69	501.48	0.36	45.25	622.10	42.16	3.87

Table 21d: Major Ion concentration of groundwater July 2018 (meq/L)

Site name	Calcium	Sodium	Pottasium	Magnisium	Chloride	Sulphate	Bicarbonate
F1	0.20	4.61	0.05	0.90	4.25	0.35	0.30
F2	0.20	3.91	0.05	0.82	3.73	0.29	0.59
F3	0.05	1.61	0.03	0.33	1.68	0.15	0.20
F4							
F5	0.10	2.09	0.05	0.41	2.70	0.02	0.30
BH1	9.98	336.96	1.53	33.73	391.20	19.07	4.43
BH2	34.58	608.70	2.33	41.96	748.10	44.95	5.57
BH3	13.47	244.57	1.38	23.86	260.10	15.74	7.21
BH4	12.67	211.96	0.20	22.21	193.76	10.64	2.59
BH5	12.82	266.30	0.28	28.79	222.60	17.34	2.26
BH6	2.89	347.83	0.10	6.17	46.75	2.41	2.39
BH7	9.03	157.61	0.23	23.04	136.64	9.22	2.07
BH8	3.24	17.04	0.10	2.71	20.80	0.19	5.64
BH9	0.45	1.83	0.05	0.58	2.30	0.23	0.98
BH10	0.50	3.70	0.10	0.99	3.40	0.60	0.46
BH11	0.25	5.30	0.03	1.07	5.62	0.60	0.36
BH12	1.10	6.57	0.08	1.23	3.14	0.67	1.02
BH13	0.20	3.39	0.05	0.82	3.15	0.27	0.26
BH14	0.25	3.35	0.05	0.90	3.30	0.21	0.39
PZ 2	13.32	353.26	1.23	35.38	432.40	10.06	4.66
PZ 7							
PZ 8	22.75	597.83	0.49	43.60	587.60	28.62	1.97
PZ 13							
PZ 14	32.88	706.52	0.61	46.89	928.50	45.82	3.08
PZ 16	11.93	375.00	1.07	37.02	484.50	20.30	4.75
PZ 19							
PZ 26	37.52	690.22	0.13	47.72	714.60	42.91	2.43

Appendix 2

Table 22(a): Stoichiometric analysis results for groundwater, July 2017

Site name	Na/Cl	Ca/HCO$_3$	Ca/Ca+SO$_4$	Na/Na+Cl	(Ca+Mg)/(HCO$_3$+SO$_4$)
F1	0.81	1.31	0.92	0.45	3.31
F2	0.88	0.03	0.96	0.47	43.54
F4	0.88	1.97	0.29	0.47	1.51
F5	0.78	1.31	0.40	0.44	1.32
BH1	1.04	0.89	0.99	0.51	5.22
BH3	0.93	0.42	0.61	0.48	2.60
BH4	0.93	0.17	0.41	0.48	1.45
BH5	0.98	0.88	0.34	0.49	1.72
BH6	1.57	3.31	0.11	0.61	0.34
BH7	1.14	1.22	0.74	0.53	3.56
BH8	1.39	3.46	0.14	0.58	0.44
BH10	0.80	0.43	0.57	0.44	1.80
BH11	1.24	2.35	0.39	0.55	1.10
BH12	1.21	0.74	0.72	0.55	1.46
BH14	0.76	1.71	0.44	0.43	1.45
PZ 7	0.75	0.19	0.40	0.43	1.63
PZ 14	1.01	0.46	0.36	0.50	2.44
PZ 19	0.94	1.26	0.86	0.49	1.21

Table 22b: Stoichiometric analysis results for groundwater, October 2017

Site name	Na/Cl	Ca/HCO$_3$	Ca/Ca+SO$_4$	Na/Na+Cl	(Ca+Mg)/(HCO$_3$+SO$_4$)
F1	0.79	1.27	0.39	0.44	2.09
F2	0.96	1.90	0.36	0.49	2.32
F3	0.83	1.52	0.40	0.45	2.22
F5	0.79	0.46	0.88	0.44	1.61
BH1	0.86	0.51	0.21	0.46	0.75
BH6	0.71	0.55	0.43	0.41	1.36
BH7	0.76	0.75	0.27	0.43	1.33
BH8	0.88	0.18	0.43	0.47	0.74
BH9	0.74	0.83	0.57	0.43	1.48
BH10	0.86	3.55	0.60	0.46	2.07
BH12	0.88	0.65	0.56	0.47	0.93
BH13	0.74	0.61	0.39	0.43	1.47
BH14	0.89	0.91	0.52	0.47	1.58
PZ 2	0.73	1.71	0.47	0.42	2.22

Table 22c: Stoichiometric analysis results for groundwater, March 2018

Site name	Na/Cl	Ca/HCO$_3$	Ca/Ca+SO$_4$	Na/Na+Cl	(Ca+Mg)/(HCO$_3$+SO$_4$)
F1	0.88	0.85	0.40	0.47	1.85
F3	0.83	0.57	0.37	0.45	1.42
F5	0.86	2.13	0.85	0.46	3.36
BH1	0.79	0.79	0.17	0.44	0.83
BH4	0.85	2.71	0.39	0.46	1.41
BH5	1.00	2.39	0.24	0.50	0.96
BH6	1.03	0.56	0.57	0.51	1.02
BH7	0.66	2.01	0.38	0.40	1.58
BH8	0.94	0.17	0.69	0.48	0.36
BH10	0.79	0.66	0.65	0.44	0.92
BH11	0.81	0.69	0.39	0.45	0.98
BH12	1.01	0.94	0.70	0.50	1.11
BH13	0.85	0.16	0.39	0.46	0.67
BH14	0.93	0.34	0.60	0.48	1.01
PZ 2	0.77	0.72	0.36	0.43	1.22
PZ 8	0.91	3.83	0.27	0.48	1.36
PZ 14	0.76	6.02	0.27	0.43	1.22
PZ 16	0.92	0.79	0.18	0.48	0.98
PZ 26	0.81	7.16	0.40	0.45	1.58

Table 22d: Stoichiometric analysis results for groundwater, July 2018

Site name	Na/Cl	Ca/HCO$_3$	Ca/Ca+SO$_4$	Na/Na+Cl	(Ca+Mg)/(HCO$_3$+SO$_4$)
F1	1.08	0.68	0.36	0.52	1.70
F2	1.05	0.34	0.41	0.51	1.16
F3	0.96	0.25	0.26	0.49	1.11
F5	0.77	0.34	0.83	0.44	1.62
BH1	0.86	2.25	0.34	0.46	1.86
BH2	0.81	6.20	0.43	0.45	1.52
BH3	0.94	1.87	0.46	0.48	1.63
BH4	1.09	4.89	0.54	0.52	2.64
BH5	1.20	5.67	0.43	0.54	2.12
BH7	1.15	4.37	0.49	0.54	2.84
BH8	0.82	0.58	0.95	0.45	1.02
BH9	0.80	0.46	0.66	0.44	0.85
BH10	1.09	1.09	0.45	0.52	1.40
BH11	0.94	0.69	0.29	0.49	1.37
BH13	1.08	0.76	0.42	0.52	1.92
BH14	1.02	0.63	0.55	0.50	1.92
PZ 2	0.82	2.86	0.57	0.45	3.31
PZ 8	1.02	11.57	0.44	0.50	2.17
PZ 14	0.76	10.67	0.42	0.43	1.63
PZ 16	0.77	2.51	0.37	0.44	1.95
PZ 26	0.97	15.47	0.47	0.49	1.88