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HYDROGEOCHEMICAL ASSESSMENT OF THE JEFFREYS ARCH DOMAIN, EASTERN CAPE, SOUTH AFRICA

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In partial fulfilment for the Master of Science in Hydrogeology

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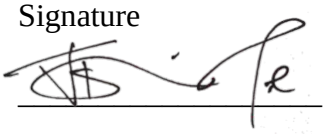
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April 2021

Declaration

I, **VHUTHU TSHISHONGE** declare that the master's degree research report that I herewith submit is my own and ideas from other sources have been duly acknowledged. This work is submitted in partial fulfilment of the Master of Science degree in Hydrogeology at the University of the Witwatersrand, Johannesburg, South Africa. This work has never been submitted before in any university for a degree or examination according to my knowledge.

Signature	Date	Place
	14 APRIL 2021	PORT ELIZABETH

Acknowledgments

I am entirely thankful to the Lord Almighty for His unwavering love and mercy throughout this journey.

I am grateful to my family that has inspired, challenged and supported me from the onset. I dedicate this work to you and the project for knowledge generation and attainment.

I am thankful to my supervisor, Prof. Tamiru Abiye for the guidance throughout the project and the experience obtained from its various phases.

I extend my gratitude to the Department of Water and Sanitation for the provision of resources in undertaking this project as well as my colleagues for the support.

Ndi Mundalamo!

Abstract

The Jeffreys Arch domain consists of groundwater schemes that contribute towards the Algoa Water Supply System through springs and borehole development. The Kabeljous River catchment is subject to over-abstraction for agricultural activities, mainly for commercial irrigation. A hydrogeochemical assessment of the domain is presented using physicochemical, major ion and stable isotopes of oxygen-18 and deuterium methods.

The geology comprises of the Table Mountain Group quartzite, Bokkeveld Group shale, and miniature Grahamstown Formation silcretes. Quartz and feldspar are the main minerals that constitute the rocks. The hydrochemical facies in the study area is represented by the Na-Cl type water. Groundwater is primarily acidic to slightly alkaline leading to accelerated leaching of metals such as iron and manganese prevalent in the domain. The Bokkeveld shale aquifer showed a greater salinity concentration than the TMG aquifers. Elevated salinity and sulphate concentrations downstream of the Kabeljous River signify the contribution of irrigation return flows. The electrical conductivity in the groundwater increases towards the NE-SW in the direction of flow. The Gibbs diagram and ionic relationships (molar ratios) between major ions ascribed the degree of correlation and difference in enrichment to rock-water interaction, ion exchange, and the absence of carbonate minerals in TMG rocks.

Groundwater samples revealed a similar isotopic composition of stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) across the summer and winter seasons. These similarities indicate a hydraulic connection between different aquifers with no seasonal variability. The groundwater isotopic signatures indicated water that recharged prior to an evaporation effect. This is attributed to the circulation of water through fractures, joints, and faults in the form of direct recharge. The Kabeljous River showed an enriched $\delta^{18}O$ and $\delta^{2}H$ composition that was least depleted in the winter season, whereas the upper Kabeljous River revealed a similar isotopic signature to groundwater samples (highly depleted). This confirmed the presence of groundwater-surface water interaction through groundwater discharge into the river channel upstream and its non-existence downstream.

This study showed that hydrogeochemical and stable isotope analyses are effective in the assessment and characterisation of water sources, chemistry, interaction and related processes.

Table of Contents

Declaration i
Acknowledgments ii
Abstract iii
Chapter 1: Introduction 1
1.1. Problem Statement 2
1.2. Research Aims and Objectives 3
1.2.1. Aims 3
1.2.2. Objectives 3
Chapter 2: Site description 4
2.1. Location 4
2.2. Physiography 5
2.3. Climate 6
2.4. Geological Setting 8
2.4.1 Geochemical composition of the Jeffreys Arch domain rocks 9
2.5. Hydrogeological Setting 12
2.5.1 Groundwater discharge 13
Chapter 3: A literature review 16
3.1. Introduction 16
3.1.1. Nature of subsurface and surface water systems 16
3.1.2. Groundwater – surface water interaction mechanisms 17
3.2. Hydrochemical Factors Influencing Groundwater Chemistry 19
3.2.1. Major geochemical controlling processes 20
3.2.2. Major ion chemistry and water types 21
3.3. Salinity as a tracer of groundwater systems and discharge mechanisms 21
3.3.1. Origin and types of salinity 21
3.3.2. Geochemical and isotopic tracers of salinity 22
3.4. Environmental isotopes 22
3.4.1. Nature and application on environmental isotopes 22
3.4.2. Environmental isotopic waters 23
3.4.3. Environmental tracers in recharge and water resource interactions 23
3.4.4. Application of environmental isotopes in TMG aquifers 24
Chapter 4: Methodology 26
4.1 Data Collection 26
4.2 Laboratory Analyses 29

4.2.1 Major ion chemistry 29
4.2.2 Environmental isotopes 29
4.3 Data Analysis 29
4.3.1 Physicochemical parameters 29
4.3.2 Major ion chemistry 30
4.3.3 Environmental isotopes 32
Chapter 5: Results and Discussion 33
5.1 Physicochemical parameters 33
5.1.1 Temperature 33
5.1.2 Electrical Conductivity 35
5.1.3 Hydrogen ion activity (pH) 36
5.2 Major ion chemistry 38
5.3 Mechanisms controlling groundwater chemistry 44
5.4 Environmental Isotopes 48
Chapter 6: Conclusion 54
References 56

List of figures

Figure 1: Locality map showing the Jeffreys Arch domain……...4

Figure 2: Topographical map (Digital Elevation Model) of the Jeffreys Arch domain…….5

Figure 3: Illustration of sandstones (oxidised), fynbos and damming of water along the Kabeljous River for agricultural activities……6

Figure 4: Annual rainfall of Jeffreys Arch (SAWS station: 001723 1)……..7

Figure 5: Evaporation trends of the area (DWS station: K9E002)……7

Figure 6: a) Bokkeveld Shale b) Weathered Peninsula quartzitic sandstone……...10

Figure 7: Quartzite of the Peninsula Formation with jointing plains……....10

Figure 8: Geological setting and cross-section of the Jeffreys Arch……...11

Figure 9: a) Depression spring (JAD114) b) Artesian borehole (JAD115)…….……14

Figure 10: Upstream Kabeljous River spring (KR00)……..14

Figure 11: Distribution of static water levels.....……15

Figure 12: General conceptual illustration of surface and groundwater interaction (Adopted from Tanner, 2013)……..17

Figure 13: 3D Illustration of surface and subsurface interaction
(Source: Brunner et al., 2019)……...18

Figure 14: Sample locations map…….27

Figure 15: Borehole sampling and Field measurements (Eutech Cyberscan PC 10 meter)….28

Figure 16: Spring sampling and measurement of groundwater levels…….28

Figure 17: Piper plot diagram indicating hydrochemical facies (Ravikumar et al., 2011)…..30

Figure 18: Stiff diagram for interpretation of major ion analyses (Stiff, 1951)……...31

Figure 19: Schoeller diagram for analysis of anion and cation concentrations
(Source: Earthsoft.com)……...31

Figure 20: Physico-chemical results (summer)……34

Figure 21: Electrical Conductivity Map of Jeffreys Arch domain……...36

Figure 22: pH Map of Jeffreys Arch domain……...37

Figure 23: DWS historical data for Kruisfontein Spring (ZQMHDP1)……...40

Figure 24: Piper plot indicating major ion results……41

Figure 25: Durov diagram indicating geochemical processes in the domain…..……..42

Figure 26: Stiff diagram indicating major ion results……..43

Figure 27: Schoeller diagram presenting major ion chemistry……44

Figure 28: Gibbs diagrams of groundwater samples……45

Figure 29: Correlation between Na^+ and Cl^- in groundwater samples…….46

Figure 30: Correlation between Na^+ vs Ca^{2+} in groundwater samples…….46

Figure 31: Correlation between Cl^- vs HCO_3^- in groundwater samples……...47

Figure 32: Correlation between EC vs Na/Cl in groundwater samples……...47

Figure 33: Correlation between SO_4^{2-} vs Cl^- in groundwater samples…….48

Figure 34: Stable isotope diagram for Jeffreys Arch domain……..52

List of tables

Table 1: Stratigraphy of the Jeffreys Arch ……..……..…...12

Table 2: Physicochemical results…….……34

Table 3: Major ion composition (mg/L) …….…….38

Table 4: Stable isotope results (Summer & Winter seasons)……..….49

List of abbreviations and notations

DWS	Department of Water and Sanitation
DWAF	Department of Water Affairs and Forestry
TMG	Table Mountain Group
MAP	Mean Annual Precipitation
^{18}O	Oxygen-18
$^{2}H/D$	Hydrogen/Deuterium
d-excess	Deuterium excess
Mbgl	Meters below ground level
Mamsl	Meters above mean sea level
SMOW	Standard Mean Ocean Water
GMWL	Global Meteoric Water Line
LMWL	Local Meteoric Water Line
SAWS	South African Weather Services
EC	Electrical Conductivity
TDS	Total Dissolved Solids
Mbgl	Meters below ground level

Units of measurement

µS/cm	Micro Siemens per centimetre
mS/m	Milli Siemens per centimetre
δ	delta
mm/a	Millimeters per annum
g/l	Grams per litre
mg/L	Milli grams per litre
‰	per mil
meq/l	Milli equivalent per litre
°C	Degree Celsius

Chapter 1: Introduction

The Jeffreys Arch is located along the southern coastline of the Eastern Cape Province, South Africa; about 80 km west of the city of Port Elizabeth between Jeffreys Bay and Humansdorp towns (Figure 1). Goedhart et al. (2004) described the Jeffreys Arch as a hydrogeological domain alongside six other groundwater domains identified as part of a reconciliation investigation of areas between Humansdorp and Alexandria. The arch is a groundwater domain classified in consideration of the underlying bedrock, sequence, thickness, and inferred permeability of the constituent lithologies (Lelliott et al., 2006).

The study area consists of groundwater schemes that contribute towards the Algoa Water Supply System through springs and borehole development to aid bulk surface water supplies to the Jeffreys Bay and Humansdorp towns. Murray et al. (2019) presented municipal plans to expand their dependence on groundwater resources through the development of additional wellfields within the Jeffreys Bay and Humansdorp Table Mountain Group (TMG) aquifers in response to water challenges experienced during the recent drought conditions, gazetted as a National Disaster in February 2018. These towns constitute 48% (Jeffreys Bay: 27 107, Humansdorp: 20 123) of the total population of the Kouga Municipality in the 2011 census. Subsequently, in the Community Survey of 2016, the municipality recorded a population growth of 11.4%.

Groundwater abstractions for the Jeffreys Bay town through the development of additional boreholes increased by 4.7 Ml/day from 3.1 Ml/day to 7.8 Ml/day with borehole yields of about 4.5 – 20 L/s (Murray et al., 2019). In Humansdorp, groundwater supply increased from 2.6 Ml/day to 4.5 Ml/day with borehole yields of 3 – 7 L/s (Murray et al., 2020). These boreholes were largely drilled into the Baviaanskloof and Skurweberg Formation aquifers in Jeffreys Bay and the Goudini, Baviaanskloof and Skurweberg Formation aquifers in Humansdorp. The characteristic occurrence of secondary porosities from the faulting and folding of the Table Mountain Group leads to the interconnection of aquifers.

Groundwater pathways can be interpreted using the classification of groundwater into water types in relation to major ion composition (Somaratne & Frizenschaf, 2013). The chemical composition of water is modified during water circulation through various processes. The main processes defining groundwater chemistry are ion exchange, mineral precipitation and dissolution; salinization and anthropogenic activities (Appelo & Postma, 1993). As a result,

ingress of adjacent and deep aquifers with poor water quality may reconfigure the groundwater chemistry.

The Department of Water and Sanitation (2018; 2019) through the investigations of unlawful water use within the Kabeljous River catchment established the increase in groundwater exploitation to support farming activities probably due to the drought conditions in the region. Additionally, satellite imagery shows the prevalence of the expansion of irrigable land (50 km^2) and farming patterns from livestock to commercial citrus and lucern irrigation. The Kabeljous River and other rivers within the domain experience low flows during periods of little rainfall; base flow is presumed to sustain flow and the associated aquatic life. The Department of Water and Sanitation (2014) National State of Water Resources Quarterly report indicates that freshwater ecosystems in South Africa are threatened by increasing salinity in river channels. Agricultural run-off is one of the anthropogenic factors contributing to the increasing salinity through fertilisers, over-irrigation, incorrect scheduling of irrigation, and regulation of flow resulting in salt accumulation within streams (Wiens, 1980). The interconnectivity of surface water and groundwater results in the infiltration of these salt concentrations into the shallow aquifers (Wiens, 1980).

The National Water Act (Act 36 of 1998) requires, among others, an integrated approach to the management of surface water and groundwater resources as both are public resources (Vegter, 2001). The employment of stable isotopes and hydrochemical methods can reveal the inner processes controlling the groundwater chemistry in an aquifer system for effective groundwater and catchment management (Somaratne & Frizenschaf, 2013; Nolakana, 2016). The hydrochemical characterisation of water within the domain with respect to physical, chemical and isotopic parameters, is essential to improving knowledge of the resources and ensure informed exploitation and management practices.

1.1. Problem Statement

The Jeffreys Arch domain has been subject to bulk groundwater supply developments providing drinking water to the two (semi-) groundwater-dependent towns. Additionally, the area hosts considerable agricultural activities that rely equally on groundwater and surface water resources. The conjunctive use of these resources requires knowledge of their interconnectivity. In view of the increasing demand for limited resources, integrated management of surface water and groundwater resources are necessary. The primary research

question to be addressed by the study is, what are the hydrogeochemical processes that control and influence the groundwater chemistry in the Jeffreys Arch domain?

1.2. Research Aims and Objectives

1.2.1. Aims

The study aims:

- To assess the interaction of groundwater and surface water; and
- To identify the major hydrogeochemical processes and their influence on groundwater chemistry.

1.2.2. Objectives

The objectives of the study are:

- To determine the groundwater-surface water interactions using hydrochemical salinity and environmental tracers and determine groundwater flow direction,
- To characterise and classify groundwater chemistry; and
- To identify hydrochemical processes influencing groundwater chemistry using stable isotopes and hydrochemical or major ion chemistry

Chapter 2: Site description

2.1. Location

The study area is located 80 km west of the city of Port Elizabeth, with an estimated total area of 860 km^2. The Jeffreys groundwater arch domain lies between Jeffreys Bay towards the southeast, Zuurbron to the north and Uitvlucht to the northwest that encompasses the towns of Humansdorp and Kruisfontein to the south (Figure 1). The study area lies within the Kouga Local Municipality, Sarah Baartman District Municipality in the Eastern Cape Province. Groundwater sources are used conjunctively with surface water sources for bulk domestic supply in the Jeffreys Bay and Humansdorp towns. The latter uses on average 6.5 Ml/day (Groundwater: ~2 Ml/d, Surface: ~4.5 Ml/d) and Jeffreys Bay uses about 11 Ml/day (Groundwater: ~3.1 Ml/d, Surface: ~7.9 Ml/d) (Murray et al., 2019; 2020). The dominant economic drivers within these towns are agriculture and tourism. The domain extends across numerous quaternary catchments, namely; L90B (N), K90G (NE), K90D and K90E (S); K90F (SE), K90C (SW), L82G and L82J(W); and L90A (W-N) within the Mzimvubu - Tsitsikamma Water Management Area. The catchments drain into the Kabeljous, Swart, Gheis and Seekoei rivers and their tributaries (Figure 2).

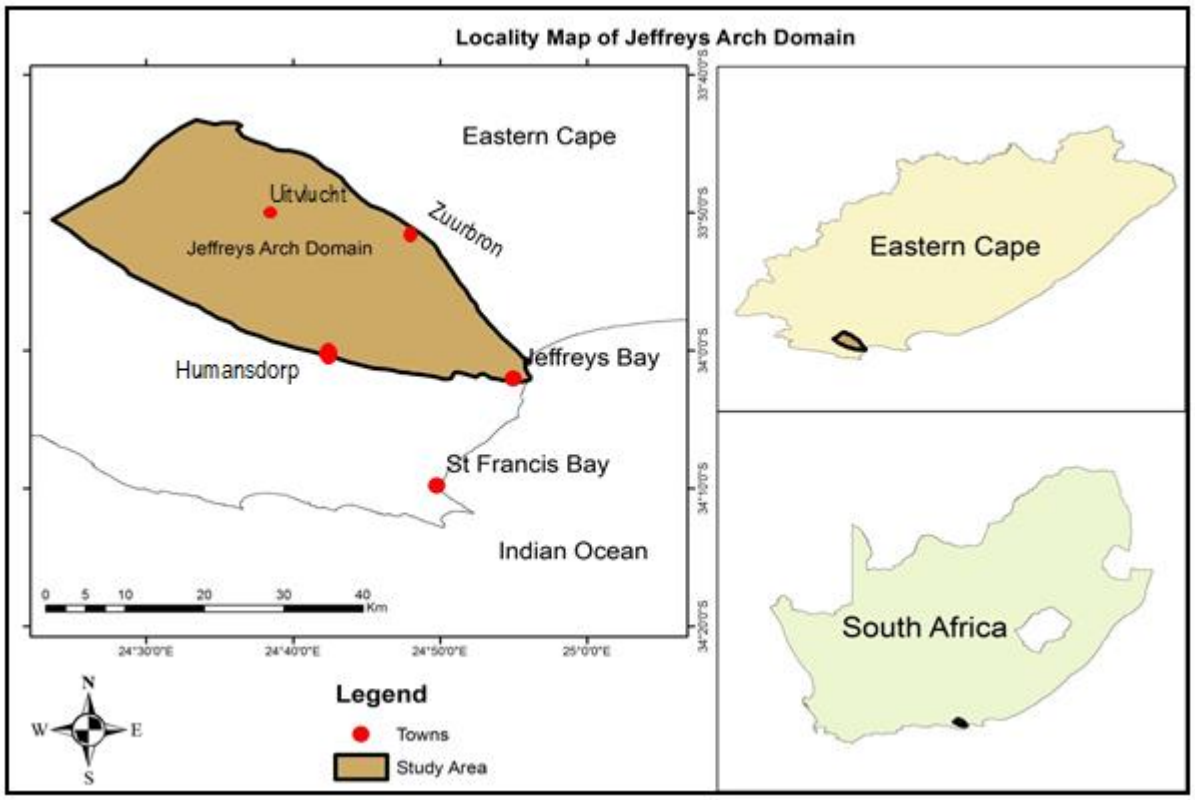


Figure 1: Locality map showing the Jeffreys Arch domain

2.2. Physiography

The Jeffreys Arch constitutes the Baviaanskloof Mountains, intermontane drainage basin and coastal plain. Altitudes increase from sea level along the coast at about 15 m to 785 m above mean sea level (mamsl) inland north-westerly up the Baviaanskloof mountain ranges (Figure 2). Furthermore, differences in elevation are evident in the elevated quartzite ridges and mountains associated with the TMG rocks compared to less elevated areas associated with the Bokkeveld Group rocks. Du Preez (2018) indicates that moderate slopes characterise the Kruisfontein and Humansdorp areas to the south and steeper slopes to the north and northeast. A majority of the area has gentle slopes drained by ephemeral streams in a south-easterly direction (SRK, 2011). The Kabeljous and Swart rivers provide drainage to the Indian Ocean in a NE and SE direction from the centre of the study area, respectively. The Seekoei River drains the southern area whereas the Hol River drains the NW perimeter into the Gamtoos River. The land-cover primarily consists of commercial farms including dairy and crop production; urban settlements and to a lesser extent, wind farms. The vegetation communities prevalent in the area include; secondary grassland, xeric transitional thicket, fynbos (Figure 3), dune slack and strand vegetation (Campbell, 1992). This vegetation is altered in certain areas due to the conversion of livestock farms to extensive irrigation of citrus and lucern.

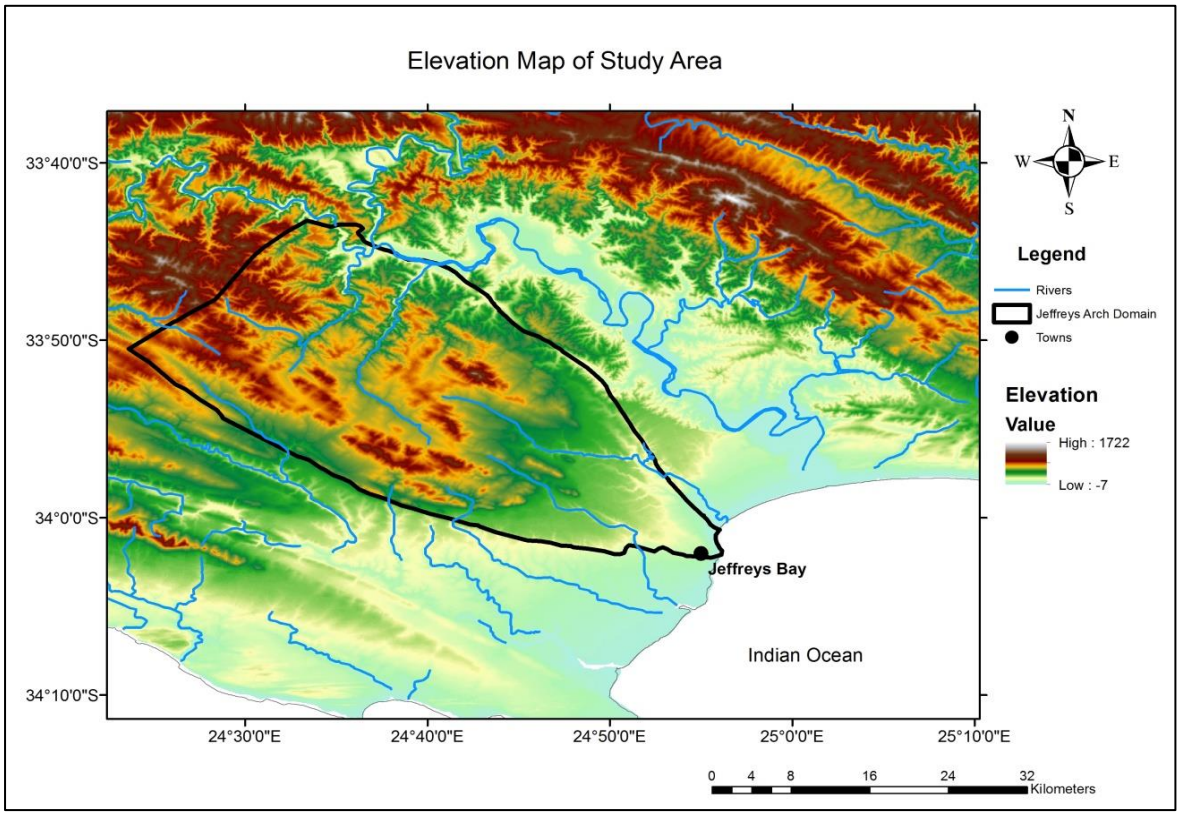


Figure 2: Topographical map (Digital Elevation Model) of the Jeffreys Arch domain



Figure 3: Illustration of sandstones (oxidised), fynbos and damming of water along the Kabeljous River for agricultural activities.

2.3. Climate

The Jeffreys Arch domain area is characteristic of a temperate climate. The area is also known for ever-present windy conditions and predominantly west and north-westerly wind directions (www.weathertoday.co.za). The average annual percentage of humidity for the Jeffreys Bay area is 77.0% with the lowest and highest percentages in March and June, respectively (weatherandclimate.com). Southerly flow from south-westerly airflow after the passage of cold front results in the advection of very cold air and showers to the Eastern Cape coastal regions (SAWB, 1996). Generally, rainfall occurs throughout the year with maximum rainfall volumes recorded in autumn and spring (SRK, 2012). The South African Weather Service (SAWS) station, 0017723 1, in Jeffreys Bay recorded (2007 - 2016) the lowest and highest annual rainfall of 342 mm (2008) and 955 mm (2011), respectively (see Figure 4). The domain's mean annual rainfall is 564 mm. The area has higher evaporation during the summer months (average: 5.55 mm) and lower rates mid-year during the winter months (average: 2.25 mm) characteristic of low temperature and greater rainfall (Figure 5). Temperature variation in the area is influenced by seasonality conditions, where average temperatures are lowest (14.1°C) in the winter and highest (20.8°C) in summer. The

minimum and maximum temperatures range between 9.1 – 9.9℃ and 19.3 – 20.1℃ in June to August and 15.8 – 17.1℃ and 23.3 – 24.5℃ in December to March, respectively.

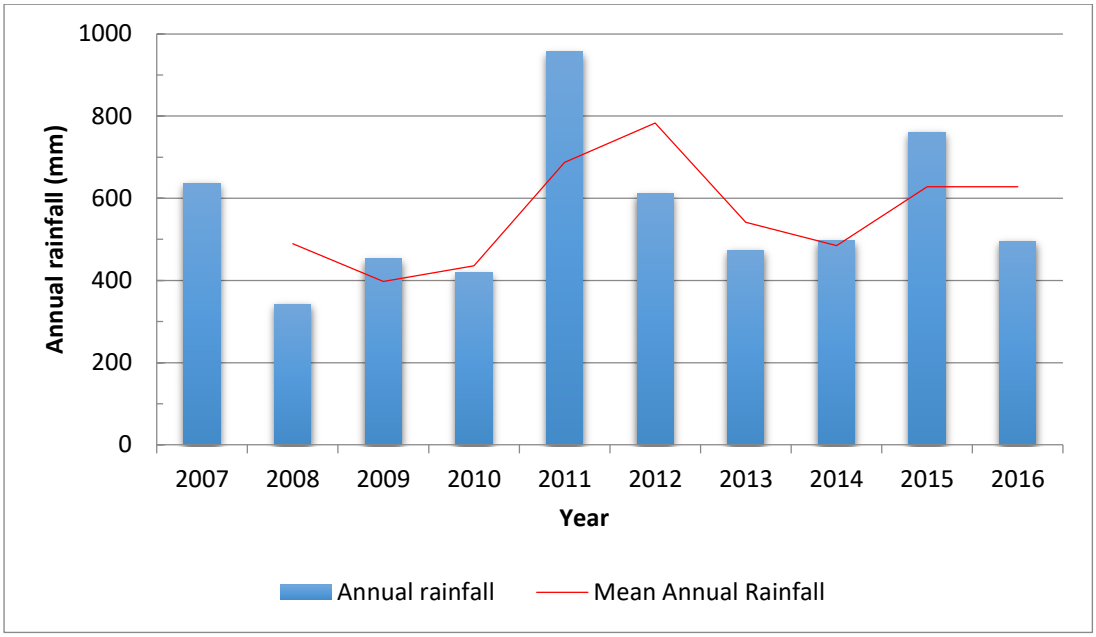


Figure 4: Annual rainfall of Jeffreys Arch (SAWS station: 001723 1)

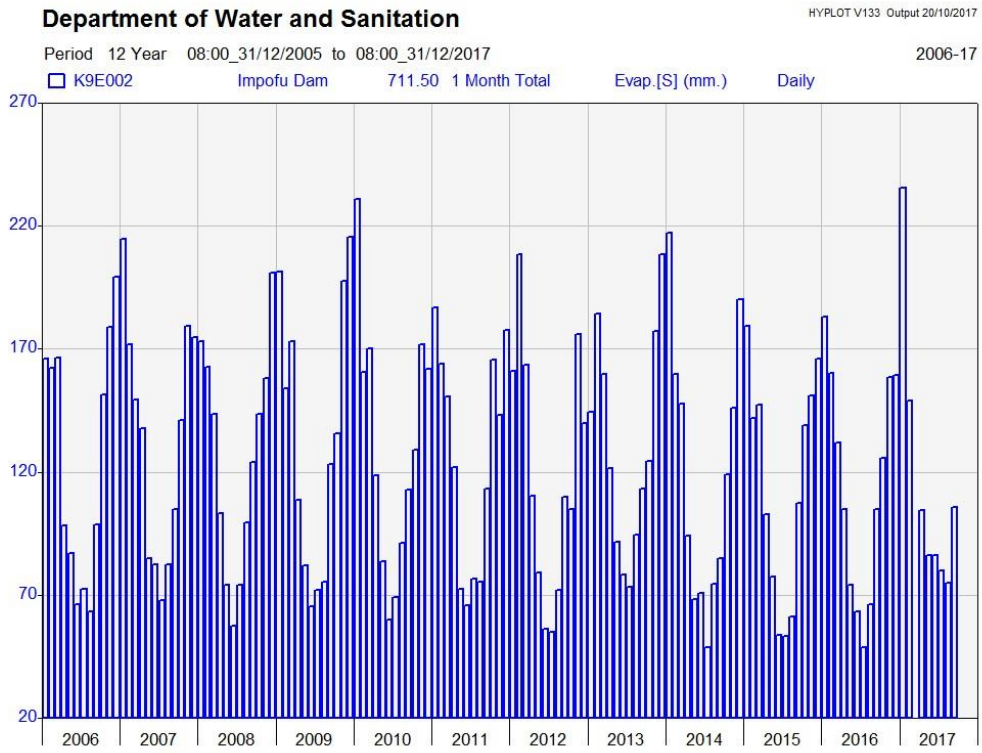


Figure 5: Evaporation trends of the area (DWS station: K9E002)

2.4. Geological Setting

The regional geological setting comprises of the Cape Supergroup meta-sedimentary rocks deposited in the early Ordovician to early Carboniferous ages (Claassen, 2015). The sequence is exposed along the whole length of the Cape Fold Belt, an orogenic belt spanning from the west to south coastlines of South Africa. The nature of deposition ranges from shallow marine environments (tidal, wave and storm influences) and non-marine, braided-fluvial environments (De Beer, 2001). The bedrock of the study area, NW-SE striking (Figure 8), forms part of the siliciclastic Cape Supergroup deposited between 488 Ma (Ordovician) and 359 Ma (Devonian). The coastal Cenozoic sediments were deposited during the Miocene (23 Ma) to Pliocene (1.8 Ma) (De Beer, 2001).

The Jeffreys Arch consists of the Table Mountain Group (TMG) and Bokkeveld Group of the Cape Supergroup (Figure 8). The TMG consists of a predominant succession of quartzitic sandstone, quartzites and shales; stratigraphically defined by the Peninsula, Cedarberg, Goudini, Skurweberg and Baviaanskloof Formations; overlain by the Ceres Subgroup of the Bokkeveld Group. The Peninsula Formation consists of white quartzite interbedded with a red/yellow quartzite indicative of iron oxide, weathering and fractured zones. The Cedarberg Formation constitutes silty shales and shaly siltstone. The overlying Nardouw Subgroup comprises the Baviaanskloof, Skurweberg and Goudini Formations. The Goudini Formation is termed the basal unit of the Nardouw Subgroup and consists of dark grey quartzitic sandstones, quartzites and minor shales. The Skurweberg Formation comprises pale grey cross-bedded and fractured quartzite interbedded with shale units, mylonite and euhedral quartz veins. The Baviaanskloof Formation consists of dark grey quartzitic sandstone and siltstone. The Ceres Subgroup is siliciclastic in nature and comprises a recurring alteration of sandstone and mudstone and shale units (Claassen, 2015). The domain is also minimally characterised by miniature outcrops of the Grahamstown Formation silcrete. These are silica-rich, indurated sedimentary rocks that form on surface or near-surface associated weathering (quartz), precipitation and cementation processes (Summerfield, 1983). The process of silicate weathering is slow, such that its contribution in changing the groundwater chemistry is also very slow (Appelo & Postma, 2005). The dissolution of silicate minerals results in the formation of secondary clay minerals (Van Camp & Walraevens, 2008; Woodford & Chevalier, 2002).

The domain is characteristic of a south-east plunging anticlinorium, with its axis (dip: 110°) directed towards the town of Jeffreys Bay (SRK, 2011). The syncline and anticline folding patterns dominate the structural features of the area. Nakhwa (2005) stated that ductile deformation produces folds and that the magnitude of anticlines and synclines is, therefore, reflective of the different stages of deformation. The extent of deformation and related fracturing and jointing usually informs target areas for groundwater exploitation (Murray et al., 2008). The municipal boreholes in Humansdorp show elements of mylonite within the Skurweberg Formation (Murray et al., 2020). This metamorphic rock is evidence of ductile deformation during folding and faulting of the TMG.

2.4.1 Geochemical composition of the Jeffreys Arch domain rocks

The TMG and Bokkeveld Group rocks of the domain consist mainly of quartzite, sandstone, siltstone and shale. Quartzite is primarily composed of quartz and formed due to metamorphism, pressure and heat exerted on the quartz-rich TMG sandstone during folding and faulting (De Beer, 2001). Meta-sedimentary rocks, quartzitic sandstones, occur within Formations of the Nardouw Subgroup. These usually consist of quartz and feldspars. Feldspars commonly include albite ($NaAlSi_3O_8$), orthoclase ($KAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) (www.geology.com). Shale and silt occur interbedded within the TMG. Shales are composed of clay-size mineral particles like quartz, feldspar and chert; as well as organic particles. These include iron oxide minerals that result in their reddish-brown colour (Figure 6a), carbonate and sulphide minerals. Siltstone occurs to a limited extent. It is composed of silt-sized particles of quartz, feldspars and clay minerals.

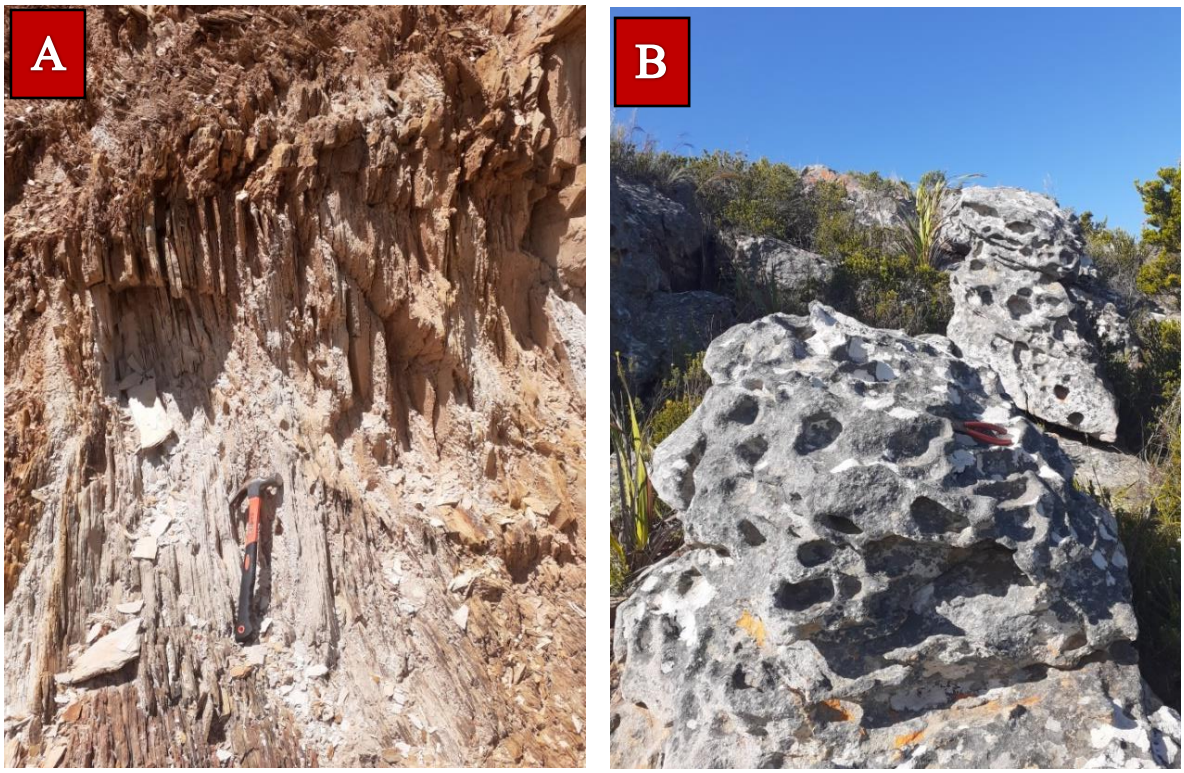


Figure 6 (a, b): a) Bokkeveld Shale b) Weathered Peninsula quartzitic sandstone



Figure 7: Quartzite of the Peninsula Formation with jointing plains

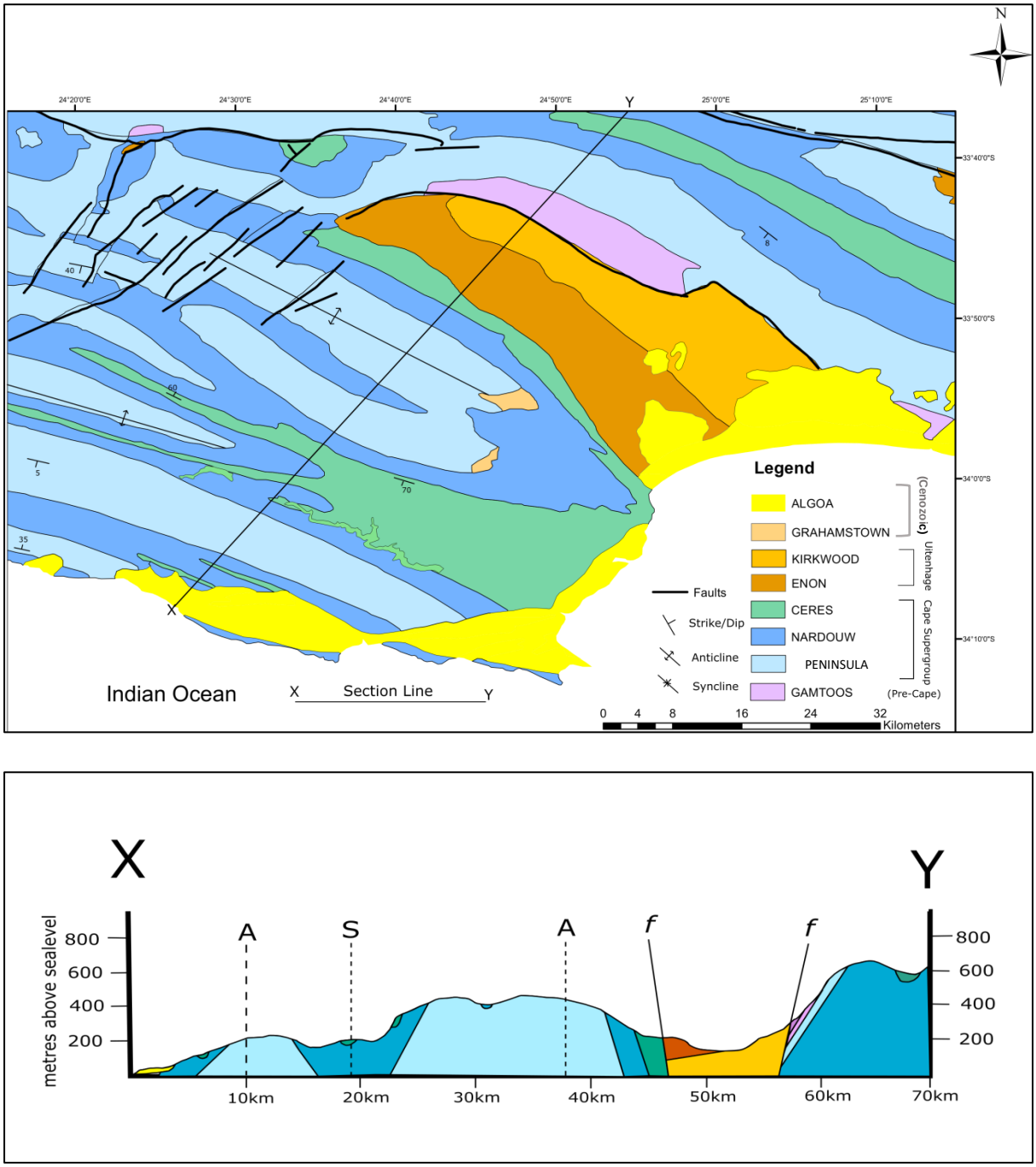


Figure 8: Geological setting and cross-section of the Jeffreys Arch

Age		Supergroup	Subgroup	Group	Formation	Lithological description
Cenozoic (cover sediments)	Pliocene-Miocene 1.8–23 Ma	Cape			Grahamstown	Silcrete
Palaeozioc (Bedrock)	Devonian **359-416 Ma**			Bokkeveld		Shale, sandstone and mudstone
	Silurian **416-444 Ma**		Nardouw	Table Mountain	Baviaanskloof	Dark grey quartzitic sandstone, siltstone minor shale
					Skurweberg	Pale grey quartzite, shale, mylonite and quartz veins
					Goudini	Dark grey quartzitic sandstones, quartzites and minor shales
	Ordovician **444-488 Ma**				Cedarberg	Silty shales and shaly siltstone
					Peninsula	White, red/yellow quartzite

Table 1: Stratigraphy of the Jeffreys Arch

2.5. Hydrogeological Setting

The Jeffreys Arch domain lies within the Southern Cape Ranges groundwater region, composed of Ordo-Devonian strata and water-bearing rocks of the Table Mountain Group (TMG) and Bokkeveld Group (Vegter, 2001). Vegter (2001) further indicates that the region consists mostly of secondary water-bearing formations of meta-sedimentary rock. The Jeffreys Arch domain is located within the Humansdorp hydrogeological unit as mapped out by Xu et al. (2009). In South Africa, the TMG is regarded as one of the major regional aquifers (Jia, 2007). The diversity of the hydrogeological properties of the TMG leads to recharge, flow, and storage influences among other defining systems. Meyer (1998) and SRK

(2012) state that a network of joints and fracture systems of the TMG quartzitic sandstones control recharge and maybe hundreds of metres deep, therefore, facilitates deep groundwater circulation. Murray et al. (2008) and Du Preez (2018) estimate the domain's TMG aquifer recharge rate at 9 - 11% and of MAP, considering the area's rainfall (~600 mm/a) and well-jointed quartzites. Goedhart et al. (2004) note that the domain anticlinorium zone comprising of secondary synclines and anticlines results in increased permeability and groundwater residence time. As a result, oxidising conditions are common resulting in elevated concentrations of iron and manganese that oxidise and precipitate when in contact with the atmosphere (Goedhart et al., 2004; Xu et al., 2009).

Groundwater chemistry is characterised by Na-Cl hydrochemical facies, neutral to slightly acidic pH, and Electrical Conductivity at a maximum of 300 mS/m attributed to the presence of meta-sandstones and interbedded shales (Nelson, 2003; Goedhart et al., 2004).

2.5.1 Groundwater discharge

The depth to groundwater levels in the domain ranges from 4.43 to 60.71 mbgl. The location of springs in the area is associated with depression, contact and fracture zones. JAD112 and 114 springs (Figure 9a) are depression springs; characteristic of surface interceptions with the groundwater table, no definite outlet and low yields (~0.03 L/s). JAD106 is a contact spring, where the Goudini and Cedarberg Formations with greater units of impervious material (shale and shaly siltstone) underlie the permeable Skurweberg Formation aquifer allowing the discharge of groundwater along quartzitic sandstone/shale contact zones. Some contact springs discharge into streams as baseflow, like the Kabeljous River spring (KR00) that lies at the contact of Peninsula and Goudini Formations (Figure 9b). The JAD102 and 103 springs are inferred to fracture-type springs with joint sets of the Peninsula and Skurweberg Formations that lead to the discharge of confined water. These springs have greater yields and are responsive to longer recharge events.

Classification of aquifers is determined from drilling logs of municipal production boreholes (Murray et al., 2019; 2020). The area has unconfined aquifers in the domain that constitute highly weathered sandstone and quartzitic sandstone of the Nardouw Subgroup overlain by unconsolidated calcareous sandy soil. These aquifers are characteristic of depth to groundwater levels of 5 – 35 mbgl and overlie the confined aquifers. The thickness of unconfined aquifers ranges from 12 to 181 m (SE) and 10 to 103 m (SW). The Peninsula

Formation constitutes confined aquifers overlain by quartzitic sandstone and shales of the Nardouw Subgroup. The thickness of the confined aquifers is from 119 – 301 m. Boreholes drilled into these aquifers through the overlying Goudini Formation with impervious units (quartzite & shale) have resulted in artesian flows.

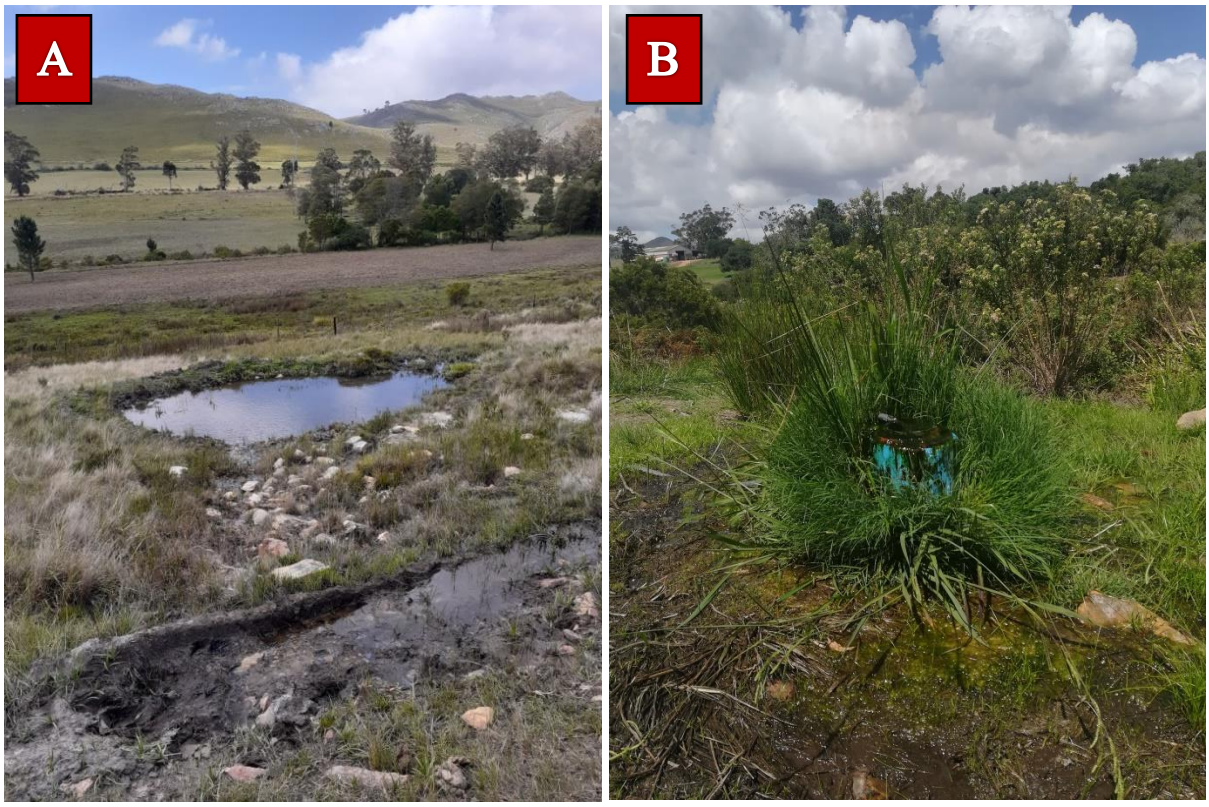


Figure 9 (a, b): a) Depression spring (JAD114) b) Artesian borehole (JAD115)



Figure 10: Upstream Kabeljous River spring (KR00)

Static groundwater levels were measured using an OTT meter, in the effort to collect new data and authenticate DWS continuous database. Figure 11 presents the distribution of static water levels in the domain that suggests the presence of different aquifers. Borehole logs obtained from Kouga Local Municipality borehole development reports were examined to establish aquifer types within the Jeffreys Arch domain.

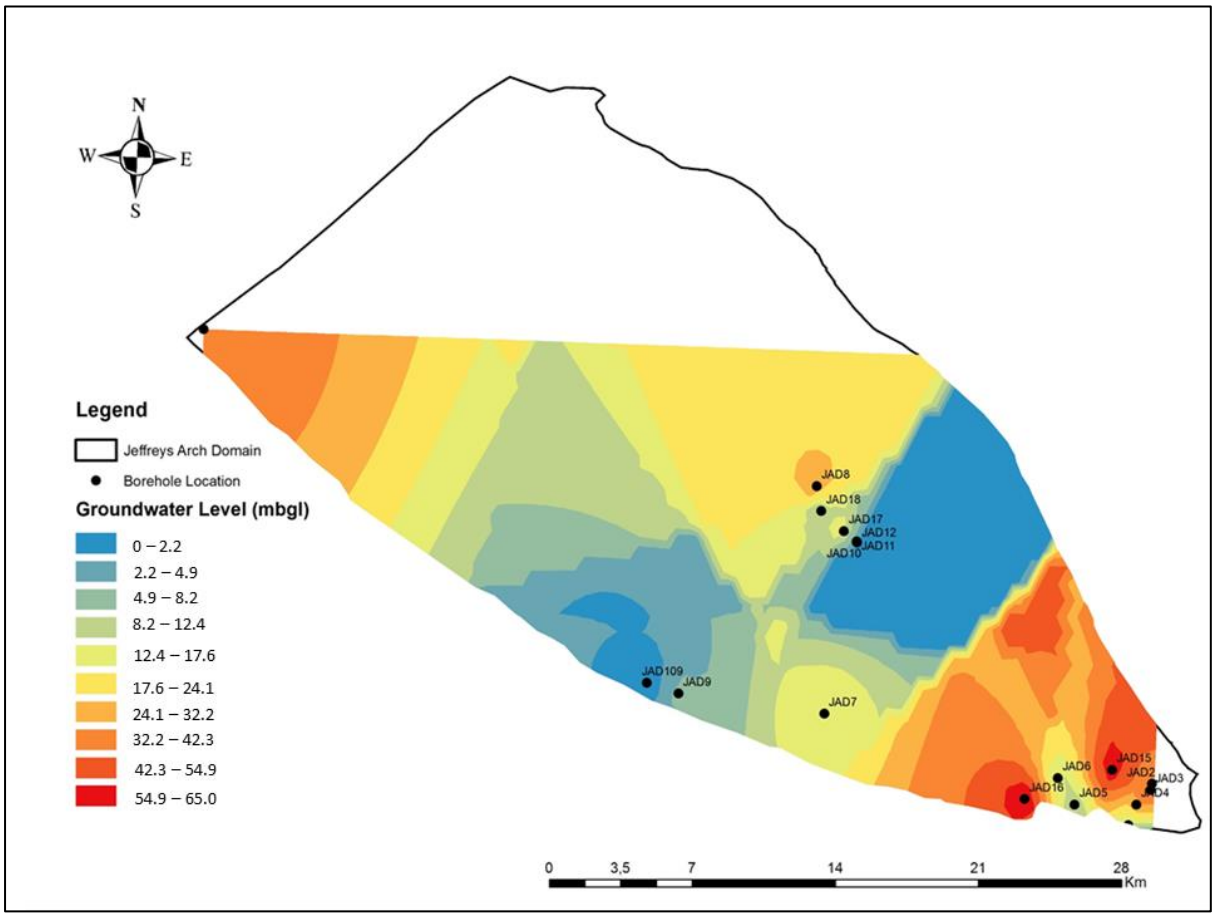


Figure 11: Spatial distribution of static water levels

Chapter 3: A literature review

3.1. Introduction

Winter (1999), Woessner (2000) and Sophocleous (2002) refer to groundwater-surface water interactions as a multidisciplinary field incorporating among others; hydrogeology, hydrology, meteorology, (aquatic) ecology, geochemistry and pedology. Processes involved in surface water and groundwater interactions include surface hydrology and evapotranspiration (Kotze, 2002). The study of groundwater-surface water interaction has received further attention due to its significance for the ecological health of surface water bodies (Woessner, 2000; Winter, 2001) and groundwater ecosystems (Hancock et al. 2005; Humphreys, 2009).

3.1.1. Nature of subsurface and surface water systems

Interaction can generally be described based on hydrological processes, individual resources and the interdependencies, thereof, of specific systems (Kelbe & Germishuyse, 2010). Surface water bodies are typically linked to groundwater (Figure 12). Rivers, lakes, wetlands and estuaries may act as recharge sources for an aquifer or vice versa (Braaten & Gates, 2001). Kelbe and Germishuyse (2010) state that through processes of recharge and discharge inflow or outflow is induced through segments of the aquifer.

In evaluating groundwater contribution to the river system, there is a necessity for reviews of water pathways from the source to discharge points. Abiye (2013) found that sinkholes and fractures enabled the loss of stream water into the dolomite aquifer, proving the connectedness of surface water and groundwater in the area. Kelbe and Germishuyse (2010) illustrate the pathway of water, explaining that considerable amounts of rainfall infiltrate the surface and proceed vertically into the water table. When the water reaches the saturation zone in the subsurface, a lateral flow towards the river is induced, creating a baseflow.

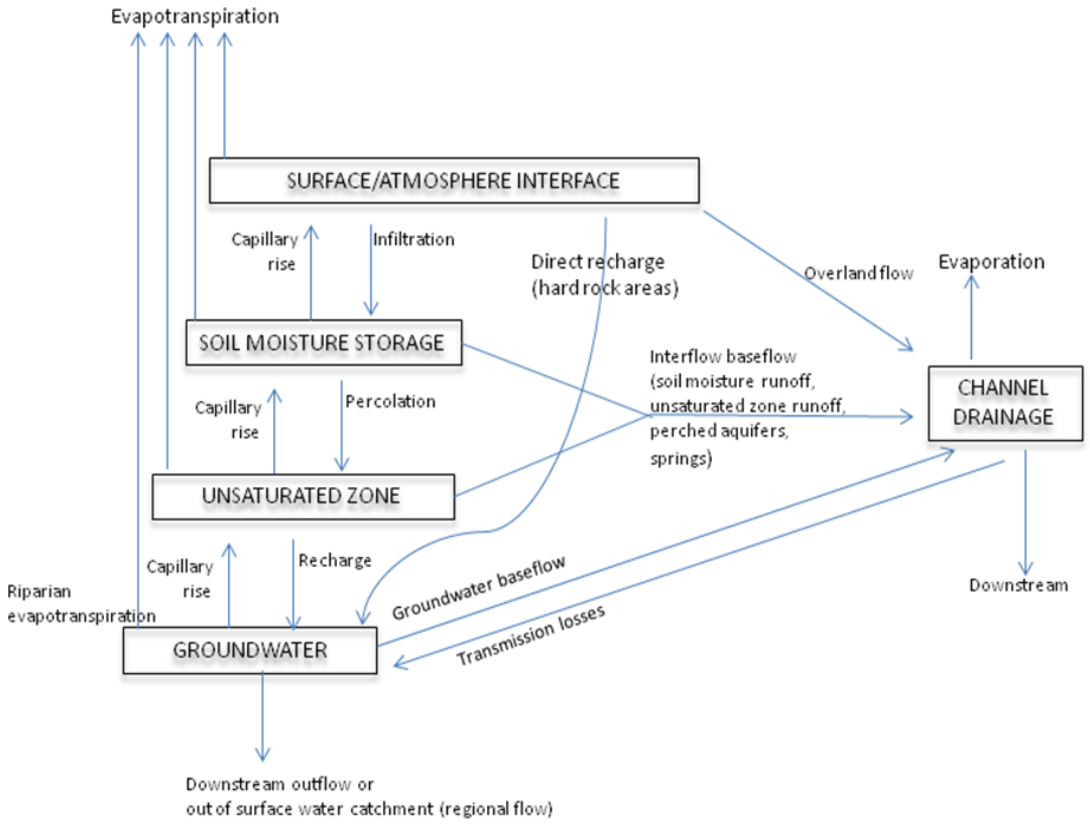


Figure 12: General conceptual illustration of surface and groundwater interaction (Adopted from Tanner, 2013)

3.1.2. Groundwater – surface water interaction mechanisms

The groundwater-surface water connectivity can be a complex assessment to undertake, given the variety of approaches present. Differences in groundwater-surface water connectivity are caused by variations in physiographical catchment characteristics such as variations in topography, geology, climate and stream geomorphology (Madlala, 2015). Braaten and Gates (2001) assert that for interaction between surface water and groundwater systems to occur, the systems need to be hydraulically connected. The identification of the extent of hydraulic connection along the river aids the establishment of whether groundwater discharges into surface water (gaining stream) or surface water recharges groundwater (losing stream) or there is no connection between the two components (neither gaining nor losing).

In order for groundwater to discharge into a stream, the elevation of the water table adjacent to the stream must be higher than the elevation of the riverbed. This setting creates an upward hydraulic gradient, which promotes groundwater inflow to the stream and thus a gaining system. For surface water to seep into groundwater, the elevation of the water table must be lower than the elevation of the riverbed. This creates a downward hydraulic gradient between

the stream and aquifer, promoting the outflow of surface water through the streambed and thus a losing system. In both cases, it is assumed that a permeable structure exists that allows the hydraulic head to move water across the streambed (Braaten & Gates, 2001). Groundwater flow in coastal aquifers is commonly directed towards the ocean because of a positive hydraulic gradient (Campbell et al. 1992).

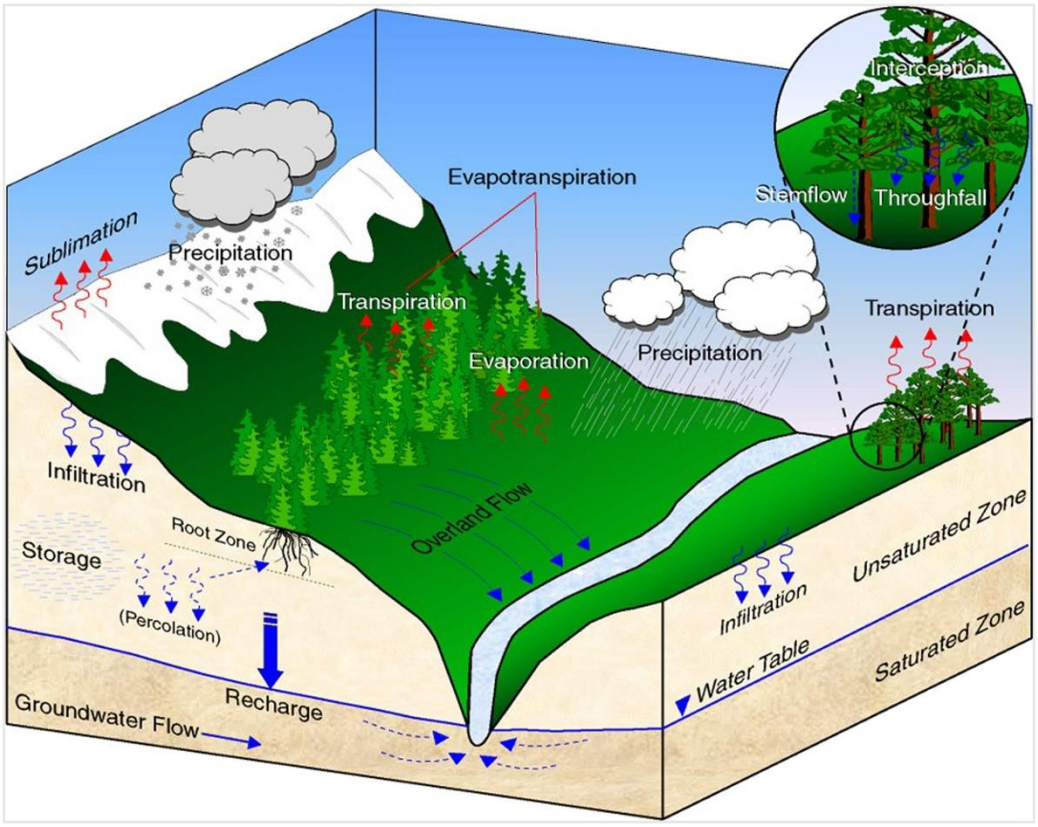


Figure 13: 3D Illustration of surface and subsurface interaction (Source: Brunner et al., 2019)

The investigation and assessment of groundwater-surface water interaction is achieved through different methods such as conceptual models, stream hydrographs (baseflow), geophysics, hydrochemical, environmental isotopes and mass balance.

Madlala (2015) studied the upper Berg River catchment using several methods, including the hydrograph, hydrochemical, and differential stream gauging analyses to assess their suitability in fractured rock environments. The study indicated that subsurface discharges dominated stream flows during periods of low flows. This resolved the dependence of the catchment on subsurface discharge to maintain dry season flows.

Saayman et al. (2003) considered the use of isotope, geochemical, hydrograph separation techniques in understanding streamflow generation in the Zachariashoek catchments, Stellenbosch. The study found that upper catchments have little storage capacity contributing to sustained flow, whereas lower catchments have more low flow, and better-sustained low flow.

Heat has become a widely used tracer in surface and subsurface connectivity investigations in the last decade (Schuetz & Weiler, 2011). Groundwater temperature is relatively constant and similar to the average annual air temperature (Deitchman & Loheide, 2009), whereas surface water temperatures change diurnally and seasonally (Kalbus et al., 2006). Conclusively, a considerable temperature difference between surface and subsurface water during various seasons is apparent.

3.2. Hydrochemical Factors Influencing Groundwater Chemistry

Chiles and De Marsily (1993) mentioned that the flow of fluid through fractures is dependent on connectivity. The geological setting of an area influences the changes in natural water chemistry (Somaratne & Frizenschaf, 2013). The permeability of rock masses, including possible pathways in TMG sandstones, is controlled by fracture systems (Xu et al., 2009). The strength of this method possibly lies in the series of hydrogeological processes that may be explored under field conditions (Brodie et al., 2007). Groundwater chemistry is subject to various phases and inputs, including rainfall and recharge conditions, and water-rock interaction. Interpretation of hydrochemistry provides an understanding of important processes that occur during the movement of water through aquifers and streams. These processes include; (i) acid-base reactions, (ii) precipitation and dissolution of minerals, (iii) sorption and ion exchange, (iv) oxidation-reduction reactions, (v) biodegradation and (vi) dissolution and exsolution of gases (Brodie et al., 2007).

Candela and Morell (2004) initially noted that an increase in most major ions and TDS occurs when groundwater moves through the saturated zone. Furthermore, lower amounts of dissolved solids occur in shallow groundwater within recharge areas than shallow groundwater in discharge areas. The groundwater evolution sequence tends to lead to the composition of seawater;

$$HCO_3^- \Rightarrow HCO_3^- + SO_4^{2-} \Rightarrow SO_4^{2-} + HCO_3^- \Rightarrow SO_4^{2-} + Cl^- \Rightarrow Cl- + SO_4^{2-} \Rightarrow Cl^-$$

$Ca^{2+} \Rightarrow Ca^{2+} + Mg^{2+} \Rightarrow Ca^{2+} + Na^{+} \Rightarrow Na^{+}\ Ca^{2+} \Rightarrow Na^{+}$

3.2.1. Major geochemical controlling processes

Generally, the main hydrochemical processes that (re)-define and control groundwater chemistry during the movement of water within the groundwater environment include; water-rock interaction, cation exchange, oxidation-reduction, carbonate and silicate weathering; and gypsum-halite dissolution (Nolakana, 2016).

Silicate dissolution may also release cations such as Na^{+}, Ca^{2+}, and K^{+}, as well as silica in the groundwater (Van Camp & Walraevens, 2008). The process of silicate weathering is slow, such that its contribution in changing the groundwater chemistry is also very slow, as compared to that of carbonates (Appelo & Postma, 2005). The dissolution of these silicate minerals leads to the formation of secondary clay minerals (Woodford & Chevalier, 2002; Van Camp & Walraevens, 2008).

Weaver et al. (1999) studied the TMG Agter-Witzenberg boreholes using the molar ratio of Na/Cl. A significant increase in the concentration was observed as water moved from the TMG quartzites to the Bokkeveld shales. The TMG aquifer showed elevated levels of sodium without an associated increase in chloride, which was attributed to the addition of sodium by ion exchange and mountain recharge.

Christoffel and Retief (2014) indicate that characteristic volume and flow rate within a stream influences water quality through mobilisation, dilution and residence time. Additionally, adsorption and dissolving constituents constitute hydrochemical processes affecting instream water quality. Somaratne and Frizenschaf (2013) indicate the absence of evaporites due to the enrichment of Na-Cl ions via evaporation; dissolution from the Na-Mg-Ca or Na-Ca-Mg water type and identified calcite dissolution from Ca-Na-HCO_3-Cl water indicating recently recharged water. Additionally, Na-Ca-HCO_3-Cl water was associated with Ca-HCO_3 water that underwent cation exchange processes or mixing with Na-Cl water.

3.2.2. Major ion chemistry and water types

The identification and evolution of water types or facies are influenced by the depleted and enriched ionic concentration.

The Du Preez (2018) investigation on the Farm Dieprivier, NE portion of the study area, found that the artesian flows in the borehole drilled into the Peninsula Formation revealed Na-Cl and Ca-HCO_3 type waters showing possible mixing of fresh shallow and old-deep groundwater, although largely characteristic of neutral fresh groundwater with little to no contamination.

Meyer et al. (2001) investigated the Zululand Coastal Plain aquifer using hydrogeochemical methods and established seawater facies evidenced through a chemical pattern of the aquifer similar to that of seawater concerning Na, Cl and SO_4 ratios. The concentration of Cl was observed as decreasing from the coast inland.

3.3. Salinity as a tracer of groundwater systems and discharge mechanisms

Phillips et al. (2003) describe groundwater salinity due to added solutes to groundwater and the concentration of dissolved constituents due to evapotranspiration and water-rock interaction. The sources of solutes may vary from natural to secondary origins. The assessment of groundwater input into streams has been achieved through water quality field parameters such as Electrical Conductivity, pH or redox (Eh) that can be easily measured in the field. It is, therefore, possible to estimate the contribution of groundwater to streamflow based on groundwater salinity and streamflow measurements.

3.3.1. Origin and types of salinity

The origin of groundwater salinity may be classified as; (i) rainfall- contains low salt content, concentrations increased by interaction with atmospheric gases and particles (Richter & Kreitler, 1993), (ii) marine origin- mostly in the coastal zone (connate or intruded), (iii) terrestrial origin – natural, due to evaporation or dissolution; and (iv) terrestrial origin – anthropogenic, irrigation and polluted groundwater (Krishan, 2019).

3.3.2. Geochemical and isotopic tracers of salinity

Guggenmos et al. (2011) focused on the use of chemical tracers to investigate surface water and groundwater interactions. The study indicates higher EC and solute concentrations downstream compared to upstream of the Mangatarere stream catchment, New Zealand. This indicated solute rich groundwater input into stream base flow

The northern flanks of the Hex River Valley, known as the recharge area, in Rosewarne (1984) recorded the least TDS concentrations in relation to downstream concentrations.

The mass balance equation was used to determine the relative contribution of the deeper groundwater, estimated in the order of 10% of streamflow under low flow conditions. Groundwater inflows were identified by a resultant peak in the stream salinity (Oxtobee & Novakowski, 2002).

$$Q_S = Q_G (EC_S - EC_{S+G}) / (EC_{S+G} - EC_G)$$

where Q_G is the relative contribution from the groundwater system
Q_S is the ambient stream discharge
EC_S is the measured ambient electrical conductivity of the stream
EC_G is the measured electrical conductivity of the discharging groundwater, and
EC_{S+G} is the electrical conductivity of the stream resulting from mixing with the groundwater input.

3.4. Environmental isotopes

3.4.1. Nature and application on environmental isotopes

Isotope ratios of oxygen-18 and hydrogen in water may not change substantially because they are the major constituents of water and are conservative. The isotope composition of the water changes only through mixing; which allows the determination of the contribution of end members of a mixed sample (Harris et al., 1999). The difference between a non-reactive isotope of water and a chemical tracer of water is that the isotopic content changes only as a result of mixing, while the chemical composition changes as a result of interaction with the soil or bedrock and residence time in a certain aquifer or rock type (Saayman et al., 2003).

Saayman et al. (2003) explain that stable isotopes (oxygen-18 and deuterium) are widely used in various studies because they form part of the water molecule and therefore, important in tracing the movement of water. Vegter (2001) presents typical environmental isotope applications; understanding hydrochemical and contamination processes, estimating recharge, generating conceptual models, establishing relationships between surface water and groundwater including relationships between groundwater bodies. Stable isotopes can be used to ascertain the hydraulic connection or lack thereof of shallow and deep groundwater through the evaluation of variations in isotopic composition. Evaporation of the water results in a more depleted water molecule compared to the remaining water. Brodie et al. (2007) indicate that stable isotopes are reported relative to an agreed sample of ocean water, known as the Standard Mean Ocean Water (SMOW), and representative of the most expansive and equilibrated water body. The hydrogen ($^{2}H/^{1}H$) and oxygen ($^{18}O/^{16}O$) stable isotope ratios are communicated as units of parts per thousand (per mil, ‰) deviation from SMOW. This relationship ($\delta D = 8\ \delta^{18}O + 10$) is known as the *Global Meteoric Water Line* (GMWL) which offers a valuable benchmark for the comparison and isotopic composition interpretation of the regional or local waters. Water samples falling on the meteoric water line (MWL) are identified as originating from the atmosphere and unaffected by isotopic processes whereas those with isotopic compositions that deviate from the MWL are considered to have undergone various isotopic processes.

3.4.2. Environmental isotopic waters

The IAEA (1981) Technical Reports Series No. 210 categorises groundwater into three (3) groups: meteoric waters, paleowaters and geothermal waters. Meteoric waters are explained as originating directly from precipitation or fresh surface waters. The isotopic composition generally matches that of local precipitation, especially in humid climatic areas. Contrary to meteoric waters, paleowaters refer to meteoric water that originated historically, and its isotopic composition differs from that of present precipitation. Geothermal waters, also known as formation waters are termed waters occurring at great depth and high temperature.

3.4.3. Environmental tracers in recharge and water resource interactions

Abiye (2013) and Abiye et al. (2015) conceptualised groundwater and surface water interaction using environmental isotopes in the upper Crocodile River Basin. The $\delta^{18}O$ and $\delta^{2}H$ of rivers reflected variations of groundwater and precipitation, isotopic compositions of

the sources with time. The study also indicated an extensive interaction of the decanting mine water in the caves around the Sterkfontein area with shallow groundwater and streams. The dolomitic compartments hosting the Malapa area dolomites located away from the mine areas contained unpolluted, old groundwater characteristic of depleted δD and $\delta^{18}O$. This is indicative of a recharge that occurred before evaporation and underwent significant periods of circulation upon recharge.

Meyer et al. (2001) evaluated the interaction between groundwater and lakes, including seawater intrusion in the Zululand coastal plain aquifer using stable isotopes. The piezometric head along the coastal dune cordon is above sea level, and it is unlikely that seawater intrusion occurs. No considerable variation was observed from the ^{18}O dataset analyses in groundwater and rainfall throughout the area. These results indicated a lack of continental effect, which may have been due to the flat topography and episodic rainfall in the area. The water samples from lakes and rivers showed enrichment of ^{18}O and deuterium due to evaporation in the winter and dry summer periods. Groundwater was an unlikely water source as its $\delta^{18}O$ value is lower than other possible water sources. The deuterium values also resulted in plots away from the Meteoric Water Line (MWL) representative of groundwater and rainwater.

West and Bowen (2014) studied hydrogen and oxygen-18 stable isotopes of groundwater and tap water across South Africa to evaluate their compositions, spatial patterns and comparison with precipitation. The study found that extensive areas revealed similar isotopic compositions for tap water and groundwater and significant regions with different compositions. Tap water was more variable than groundwater, given its expected blend of evaporated surface or groundwater. Groundwater and tap water indicated water of meteoric origin by plotting close to the GMWL and evaporated surface waters with low *d* values. The enrichment of tap water compared to groundwater is suggested to be a result of recent seasonal rainfall and its exposure to evaporation during storage (dams) or transportation.

3.4.4. Application of environmental isotopes in TMG aquifers

Diamond (2014) applied stable isotopes on boreholes, springs and rivers around the Cape fold Belt. The isotopic composition of rainfall was negatively correlated with continentality and altitude evidenced in differences between catchments. An amount effect was identified from

the positive correlation of δD and $\delta^{18}O$ values with distance from the mountain. Groundwater mixing was observed from groundwater-fed surface systems showing little variation in isotopic composition.

Weaver et al. (1999) studied the Agter-Wizenberg fractured TMG aquifers with aims to relate groundwater isotopes to hydrogeochemical differences and hydrographs for the estimation of recharge source areas, residence time and resource evaluation. The use of stable isotopes (δD and $\delta^{18}O$) resulted in all the samples plotting close to the Local Meteoric Water Line (LMWL) wherein the mountain and spring samples were much closer than the other samples showing effects of minor evaporation. Some samples plotted along the mixing line, which could suggest a mix of mountain and valley recharge.

Harris et al. (1999) applied stable isotope systems in the greater Cape Town area with a focus on rainwater, groundwater and treated water. The shallow Culemborg-Black River aquifer and Cape Flats aquifer plotted close to the GMWL. The δD and $\delta^{18}O$ data effectively differentiated between groundwater and treated water in the summer and autumn months. Seasonal variability was resembled by higher δD and $\delta^{18}O$ values in the winter months than in summer months in relation to treated water. Additionally, the water treatment process increases the $\delta^{18}O$ of water as observed from the δD and $\delta^{18}O$ values of untreated water that is an offset from the GMWL, whereas treated waters lay closer to the Meteoric Water Line.

Chapter 4: Methodology

A multi-dimensional assessment approach is necessary for the comparison and confirmation of interpretations and findings in space and time. While these methods have benefits and limitations, it is mostly accepted that a multi-method approach, in which various methods are combined, provides the most accurate picture of interaction with the greatest levels of certainty (Kalbus et al., 2006). The approaches used in this research report seek to improve the understanding of the hydrogeochemical characteristics of the area. These include a desktop study, water sample collection, groundwater level measurements and laboratory analysis. The selection of sites for salinity survey, hydrochemistry and environmental isotopic sampling was based on accessibility and even distribution along the river and various characteristic geological formations. The boreholes and springs lie on the Bokkeveld Group, Peninsula, Skurweberg, Baviaanskloof, Goudini and Grahamstown Formations.

4.1 Data Collection

Field sampling for groundwater and river water samples was conducted in December 2017, July and December 2018. Water samples were collected from five (5) springs, thirteen (13) boreholes and three (3) river points in and around the study area. These sampling points were made up of private, farm and municipal production boreholes and springs. Most groundwater points were sampled for physicochemical analysis due to accessibility and financial challenges. The sampling points are spatially distributed and representative of water sources within the study area.

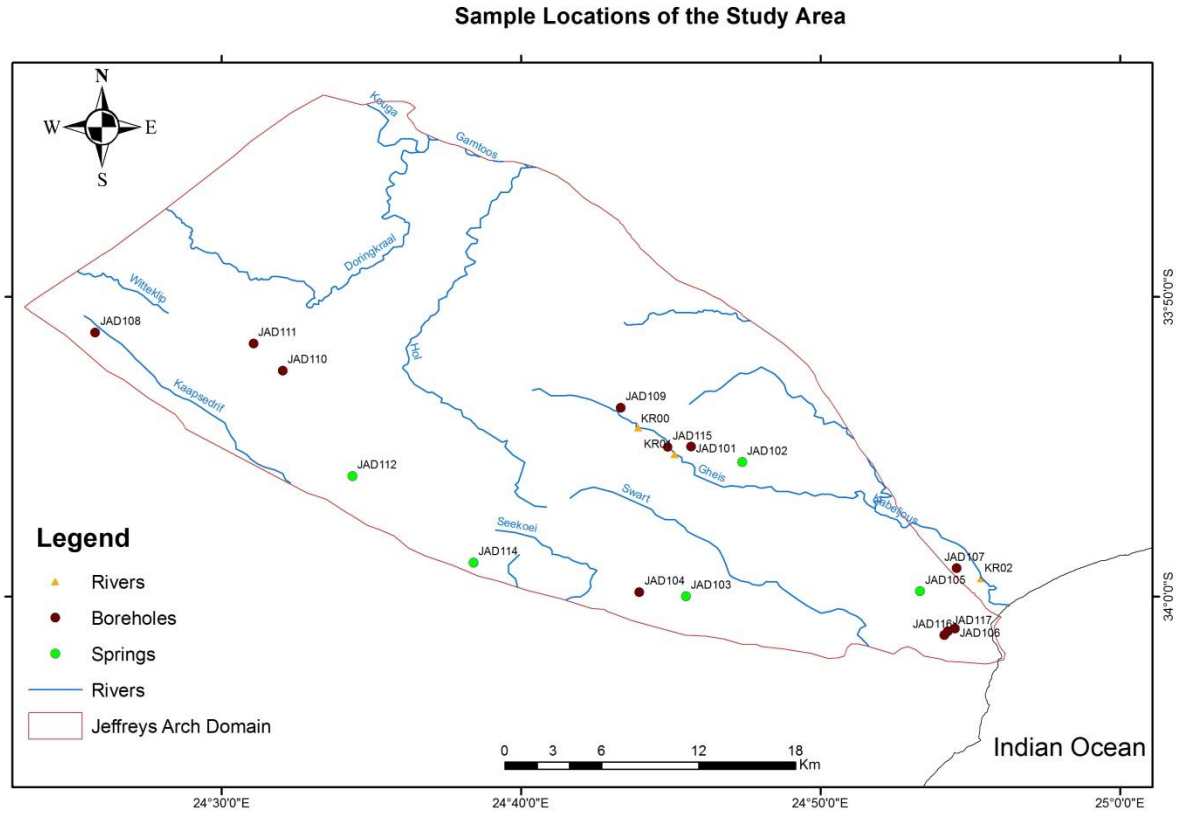


Figure 14: Sample locations map

Boreholes were equipped with electric submersible pumps that are primarily used for production. These were purged for about 20 – 30 minutes before the collection of samples to remove stagnant water from the borehole column. This allows for water to flow from the aquifer into the borehole and thereafter collection of a representative sample. Boreholes such as JAD113 and JAD115 that are artesian were not purged. The surface water samples were collected against the direction of flow below the top surface of the water flow upstream and downstream from the Kabeljous River. Springwater samples were collected along the flow channels towards the collection ponds and earth dams against the direction of flow below the top surface of the water flow. The discharge points or eyes of the springs were inaccessible due to surface terrain and marshy conditions.

The major ion samples were collected in 1L polyethylene bottles and stable isotope samples in 200 ml polyethylene bottles. These sample bottles were labelled, kept away from direct sunlight and stored under cool temperatures. Field sampling included the use of a Eutech Cyberscan PC 10 pH/EC/Temp metre to measure the pH, Electrical Conductivity (EC) and

Temperature. The field information was recorded to enable a precise assessment of the physicochemical parameters.



Figure 15: (a, b): Borehole sampling and Field measurements

(Eutech Cyberscan PC 10 meter)



Figure 16 (a, b): Spring sampling and measurement of groundwater levels

4.2 Laboratory Analyses

4.2.1 Major ion chemistry

A total of nine (9) water samples were collected from various water sources including springs, boreholes, and river points for an analysis of the hydrochemistry in relation to major ions. The samples were analysed for major ions at the Talbot & Talbot laboratories using the inductively coupled plasma - optical emission spectrometry (ICP-OES) and Wet chemistry titration techniques and equipment.

4.2.2 Environmental isotopes

Stable isotope (^{18}O and ^{2}H) water samples were collected from nine locations; three springs, four boreholes and two river samples. The water samples were analysed in the Hydrogeology Lab at the University of the Witwatersrand using the Liquid Water Isotope Analyser (LWIA) model 45-EP laser machine.

4.3 Data Analysis

A comprehensive interpretation of physicochemical and chemical parameters of water may indicate the degree of surface water and groundwater interaction through a dilution or precipitation process (Abiye, 2013; Abiye et al., 2015).

4.3.1 Physicochemical parameters

This method aims to detect any considerable changes in stream salinity and, from analysis of groundwater salinity data, assess whether these changes are a result of groundwater discharge. The application of this method is based on the key assumption that there is a significant difference between groundwater and surface water salinities (Annan, 2006). This environmental tracer requires readily measured concentration values in the field and does not require sample collection for laboratory analysis. It relies on a significant difference between groundwater and stream salinities, including the absence of spatial variability in groundwater salinities throughout the catchment. Conductivity, Temperature and pH analysis in relation to longitudinal variations, distance, and flow direction are used to interpret data to assess and determine groundwater contribution into the river or vice versa. To determine this phenomenon, the Kabeljous River is used as a case study to measure the interaction within the Jeffreys Arch domain.

4.3.2 Major ion chemistry

The Piper (1944) is a trilinear diagram expressed in concentration percentages of cations and anions plotted on the left triangle and right triangle, respectively. The plotting of cations and anions is further projected onto the centrally placed diamond-shaped field. This diagram allows for the presentation of many water analyses, classification of water types and identification of mixing waters. Wu (2008) highlights that the left-hand corner gives an indication of recently recharged water with high Ca, Mg and HCO_3 concentrations and low Cl and SO_4. The right-hand corner represents stagnant water from the aquifer discharge zone and seawater. Hydrochemical facies or water type relates to categorised zones with certain levels of cations in groundwater (Hiscock, 2005).

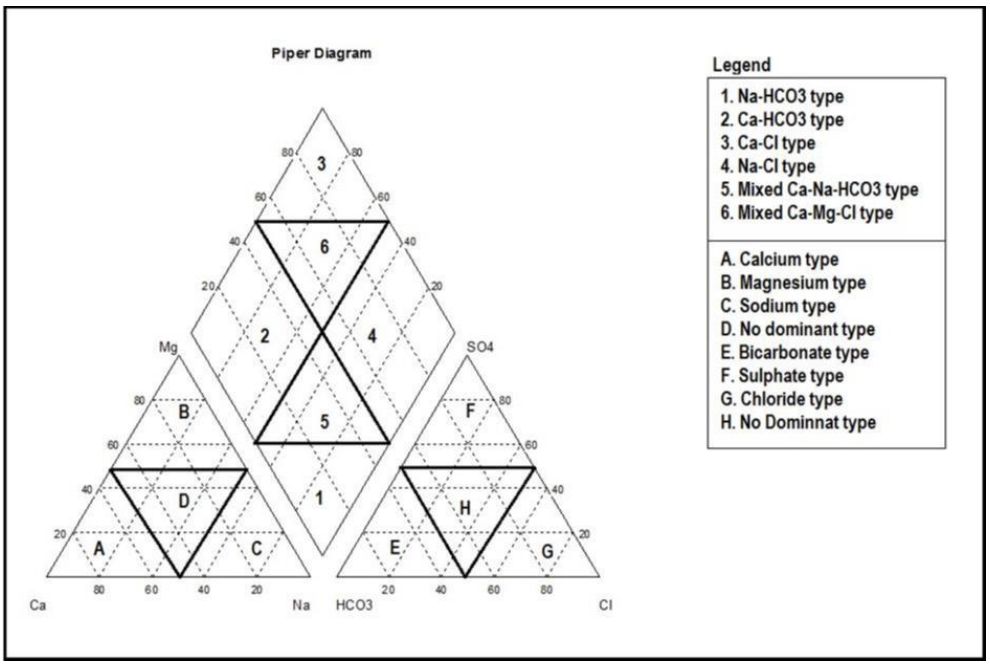


Figure 17: Piper plot diagram indicating hydrochemical facies (Ravikumar et al., 2011)

The Stiff (1951) is characteristic of one vertical axis and four parallel axes. The cation concentrations are plotted on the left and anions on the right of the vertical axis. The values are input in milli equivalent per litre (meq/l). The diagram produces an irregular polygonal pattern that presents waters of similar qualities with a distinctive shape. The concentrations of the different ions are directly reflected by the extent of the polygon towards that ion. This method is useful for the comparison of water from different sources (Dauda & Habib, 2015).

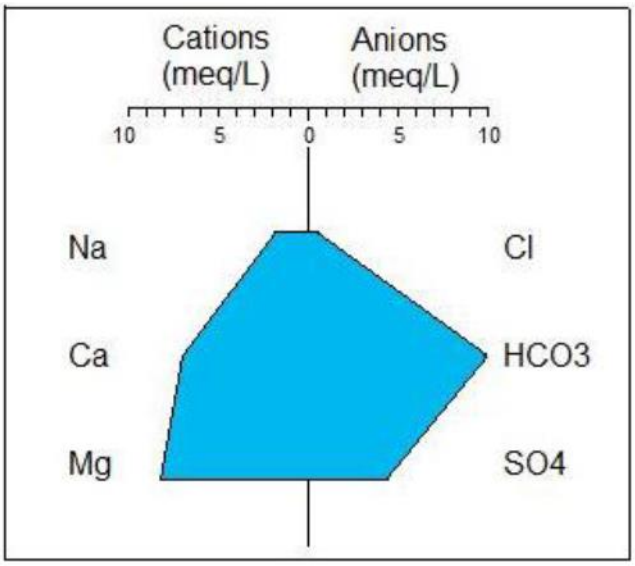


Figure 18: Stiff diagram for interpretation of major ion analyses (Stiff, 1951)

The Schoeller (1962) diagram enables the grouping of water samples with a focus on the relation of the line linking the major ions to each other. The cation and anion values are input in milli equivalent per litre (meq/l). A series of line/scatter plots where the X values are the cation or anion, and the Y values are the concentration of each ion in the sample data. This plot type displays the relative concentrations of various anions and cations from multiple samples on a single graph.

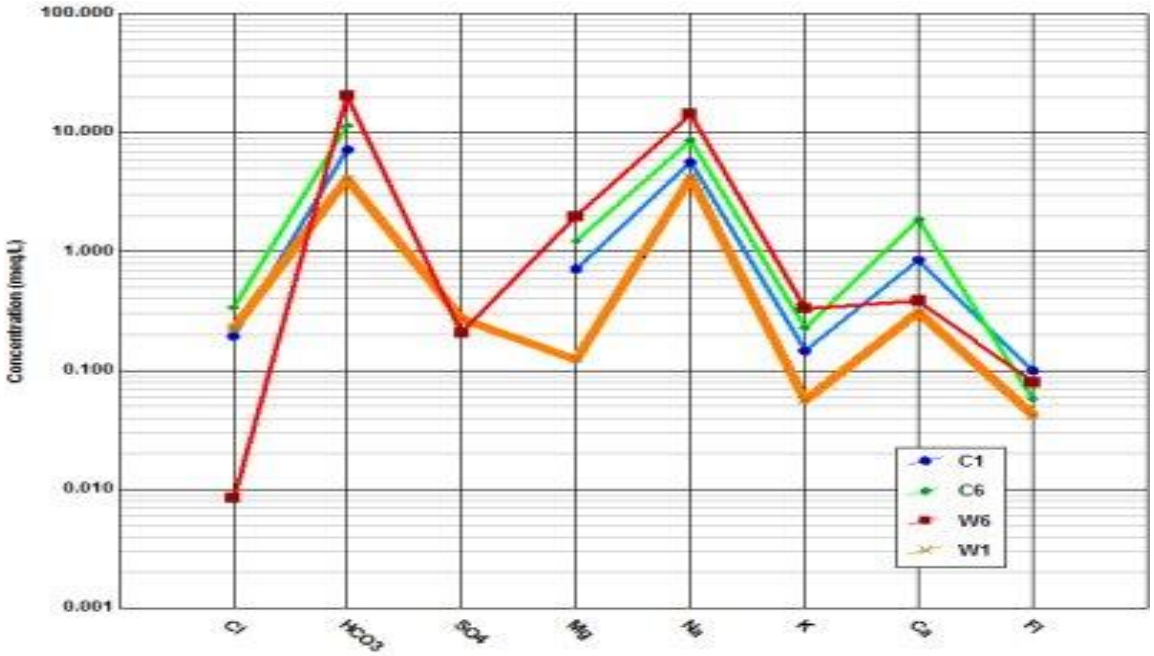


Figure 19: Schoeller diagram for analysis of anion and cation concentrations

(Source: Earthsoft.com)

Gibbs diagram (1970) was used to establish driving mechanisms influencing water chemistry. The diagram utilises Total Dissolved Solids (TDS), and major cations and anions input selections of $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-(Cl^- + HCO_3^-)$. Three distinctive fields indicate the genesis and evolution of water composition; namely, rock dominance, evaporation dominance and precipitation dominance (Kumar, 2015).

Scatter plots are correlation plots that identify the main elements contributing to the groundwater salinity and their tendency to follow a similar trend. Adam et al. (2001) indicated that strong correlations of Na/Cl versus EC were used to identify if evaporation processes occurred. The assumption for evaporation is that the samples must indicate an increasing trend of EC and a constant ratio of Na/Cl (Jankowski & Acworth, 1997). Scatter plots present the effect of one variable on the other and further evaluate their relationship through comparison. The ionic relationships of Na/Cl, Na/Ca, EC vs Na/Cl, Cl/HCO_3 and SO_4/Cl are presented to evaluate the degree of correlation or relationships and the associated chemical processes.

4.3.3 Environmental isotopes

Stable isotopes, oxygen-18 and deuterium, are some of several parameters that offer better guidance in differentiating water sources (Murray et al., 2015). The stable isotopes were assessed in terms of the isotope ratios of the less abundant to the more abundant isotope, $^2H/^1H$ and $^{18}O/^{16}O$. The data were plotted with reference to the Global Meteoric Water Line (GMWL), $\delta D = 8\ \delta^{18}O + 10‰$ (Craig, 1961) and the Local Meteoric Water Line ($y = mx + c$), $\delta D = 5.8\ \delta^{18}O + 5.2‰$ (Van Wyk, 2010). The stable isotopes are usually measured using an isotope ratio mass spectrometer, in terms of the isotope ratios of the less abundant to the more abundant isotope, for example, $^2H/^1H$ and $^{18}O/^{16}O$. The $\delta^{18}O$ and δ^2H ratio is calculated as follows;

$$\delta\ (‰) = \frac{R_{sample} - R_{standard}}{R_{standard}} \text{ x } 1000$$

Chapter 5: Results and Discussion

5.1 Physicochemical parameters

5.1.1 Temperature

Generally, chemical reactions increase as the rate at temperature increases (Dallas, 2008). Warmer temperatures in groundwater stimulate the dissolution of minerals from the surrounding rock (Riedel, 2019). Temperature is a significant feature in the assessment of water quality, which influences other parameters and may modify the physical and chemical properties of water.

The groundwater temperature measured in the field during the summer season from boreholes and springs ranges from 16.7 to 25.1°C (avg. 20.8°C) and 18.7 to 23.6°C (avg. 20.7°C), respectively. The surface water temperatures range between 17.9 – 24.0°C with an average of 20.9°C (Table 2). In contrast, temperatures measured in the winter season averaged at 18.6°C for groundwater samples and 14.7°C for surface water samples. There is a distinctive variation between the summer and winter temperatures in relation to both groundwater and surface water samples. Groundwater records minimal differences in temperature across the seasons primarily due to its isolation from the atmosphere, whereas surface water temperatures recorded considerable variations in temperature because of its direct exposure to the atmosphere. Kalbus et al. (2006) indicate that surface water temperatures change diurnally and seasonally. Surface water temperatures of the lower Kabeljous River (KR02) are higher than those of the upper Kabeljous River (KR01). This may be associated with the effects of turbidity present in greater degrees downstream.

Sample Name	Temperature (°C)		pH		Electrical Conductivity (mS/m)	
	Summer	Winter	Summer	Winter	Summer	Winter
JAD101	19.3	17.8	6.19	6.87	32.1	39.1
JAD102	19.1	18.3	6.15	6.52	33.2	37
JAD103	23.6	14.7	6.61	6.98	23.9	21.3
JAD104	21.5	18.3	6.88	6.48	30	19.4
JAD105	18.7	18.6	6.85	5.96	46	46.6
JAD106	25	23	6.81	7.08	37.3	52.6
JAD107	22.2		7.85		165.8	
JAD108	16.7		5.51		23.9	
JAD109	18.5		5.81		24.3	
JAD110	22.1		5.73		4.03	
JAD111	17.1		5.7		25.8	
JAD112	19.4		5.33		21.3	
JAD113	25.1	19.7	6.6	6.79	73.4	74.5
JAD114	22.8		5.89		0.191	
JAD115	20		5.41		1.3	
JAD116	23.1		5.5		131	
JAD117	22.8		6.2		81	
JAD118	22.6		6.15		40.1	
KR00	21.9		7.13		90.6	
KR01	17.9	12.8	6.45	7.33	45.4	42.2
KR02	24	16.7	6.46	4.98	572	634

Table 2: Physico-chemical results

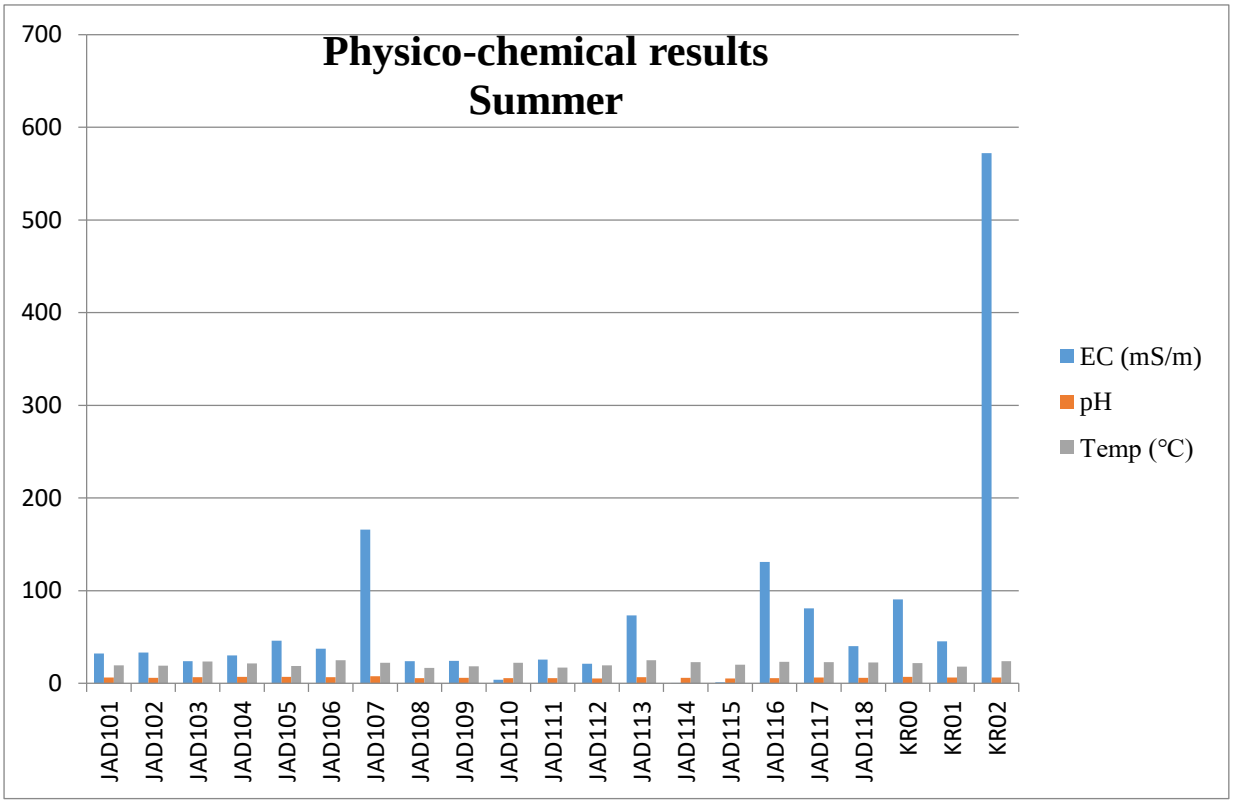


Figure 20: Physicochemical results (summer)

5.1.2 Electrical Conductivity

Electrical Conductivity (EC) refers to the measure of the electrical conductance of water influenced by the presence of charged ions in water (DWAF, 1996). The Electrical Conductivity within the domain ranges between 0.191 and 634 mS/m. There is a positive correlation between EC and temperature; in terms of a decrease during the sampling seasons. The uniform decrease in EC and temperature signifies the seasonality effect, where there are higher EC values in summer compared to winter. In surface water, the summer period is known for higher evaporation rates resulting in increased salinity within the soil profile and subsequently the water resources. In groundwater, higher temperature aids the dissolution of the surrounding rock.

The Kabeljous River originates from a spring discharge that flows onto the surface in an area close to the Baviaanskloof mountains. There is a substantial difference in concentration between KR00, KR01 and KR02 averaging 90.6 mS/m, 45.4 mS/m and 550 mS/m, respectively, indicating longitudinal variations. The higher salinity concentrations downstream suggest input of salts from tributaries, instream dams and agricultural return flows. As rivers flow downstream, salts are continuously added into the water through natural and anthropogenic sources (DWAF, 1996). Sedimentation, adsorption and dissolving constituents are some of the main hydrochemical processes affecting instream water quality (Retief, 2014). KR01 and JAD101 show similar salinity concentrations of 32.1 - 45.4 mS/m indicative of Peninsula groundwater.

The Nardouw sandstone is essentially siliceous and the absence of soluble compounds results in low conductance whereas pellitic rocks of the Bokkeveld Group contain more soluble material, partly indicating higher conductivities of the associated groundwater (Rosewarne, 1984). The highest Electrical Conductivity for groundwater is recorded for JAD107 and JAD116; both boreholes are drilled into the Bokkeveld Group characteristic of high salinity. Furthermore, the salinity of JAD107 is higher than that of the other boreholes located within the Nardouw Subgroup. The confining layer of the Bokkeveld Group in the east and south of the Jeffreys Bay results in poor salinities of 70 - 1000 mS/m whereas salinities of 0 – 70 mS/m may be observed north-west of Jeffreys Bay within the TMG (SRK, 2012).

The Electrical Conductivity of groundwater also shows the increase in the salinity concentration towards the ocean (Figure 21), SE of the domain, possibly due to water-rock interaction and mixing of different waters. Additionally, the increase in salinity correlates

with the NW-SE groundwater flow pattern. The low salinity observed from sampled aquifers, recorded at a maximum of 46 mS/m indicative of fresh water, suggests the absence of the seawater intrusion phenomenon as saline water is identified as greater than 600 mS/m (Talling & Talling, 1965). The longitudinal increase of salinity along the river implies that upstream abstractions offer better water quality than downstream. There exists a need for management of land use in relation to irrigation for commercial purposes and associated return flows that contribute towards the contamination of shallow unconfined aquifers and river flow.

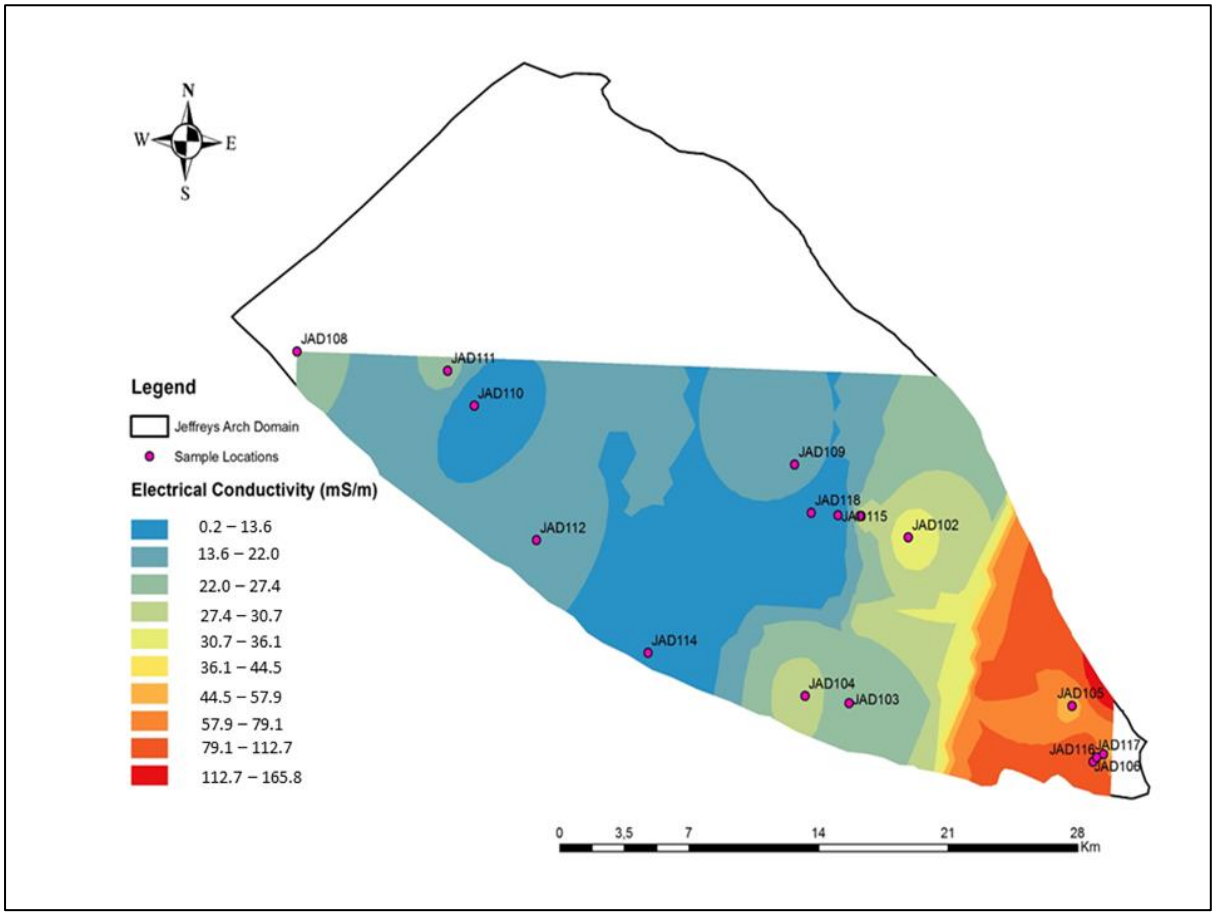


Figure 21: Electrical Conductivity Map of Jeffreys Arch domain

5.1.3 Hydrogen ion activity (pH)

pH is an essential water quality parameter that shows the degree of water acidity. Additionally, pH controls the solubility of chemical constituents (nutrients and metals) in water and the amount that may be used by aquatic life (Nienie et al., 2017). Water with a pH <7 is generally considered to be acidic and pH >7 as basic. Groundwater is primarily known to exhibit pH values between 6 – 8.5 and surface water pH values between 6.5 – 8.5. Water

with pH <6.5 indicates soft and corrosive water, whereas pH>8.5 indicates hard water. The pH of water depends on the nature of the water collected within the drainage basin. Therefore, the geological composition and mineralogical nature of the rocks considerably impact the pH (Mihu-Pintilie et al., 2014).

The pH values in the groundwater vary from 5.33 – 7.85 in the summer period and 5.96 – 7.08 in the winter period. No significant seasonal differences were found. The surface water pH ranges between 6.45 – 6.46 and 4.98 – 7.33 in summer and winter, respectively. Groundwater is primarily acidic to slightly alkaline leading to accelerated leaching of metals, in the case of the domain, iron and manganese are the most prevalent and problematic in relation to treatment for urban water supply. Smart and Tredoux (2002) state that the TMG groundwater is commonly acidic, corrosive and contains low calcium and bicarbonate, translating to poor buffering. The lower Kabeljous River indicates greater acidity compared to the upper Kabeljous River, which largely identifies with groundwater. The acidic nature of the lower Kabeljous River may be attributed to agricultural run-off, creating a hostile environment for aquatic life.

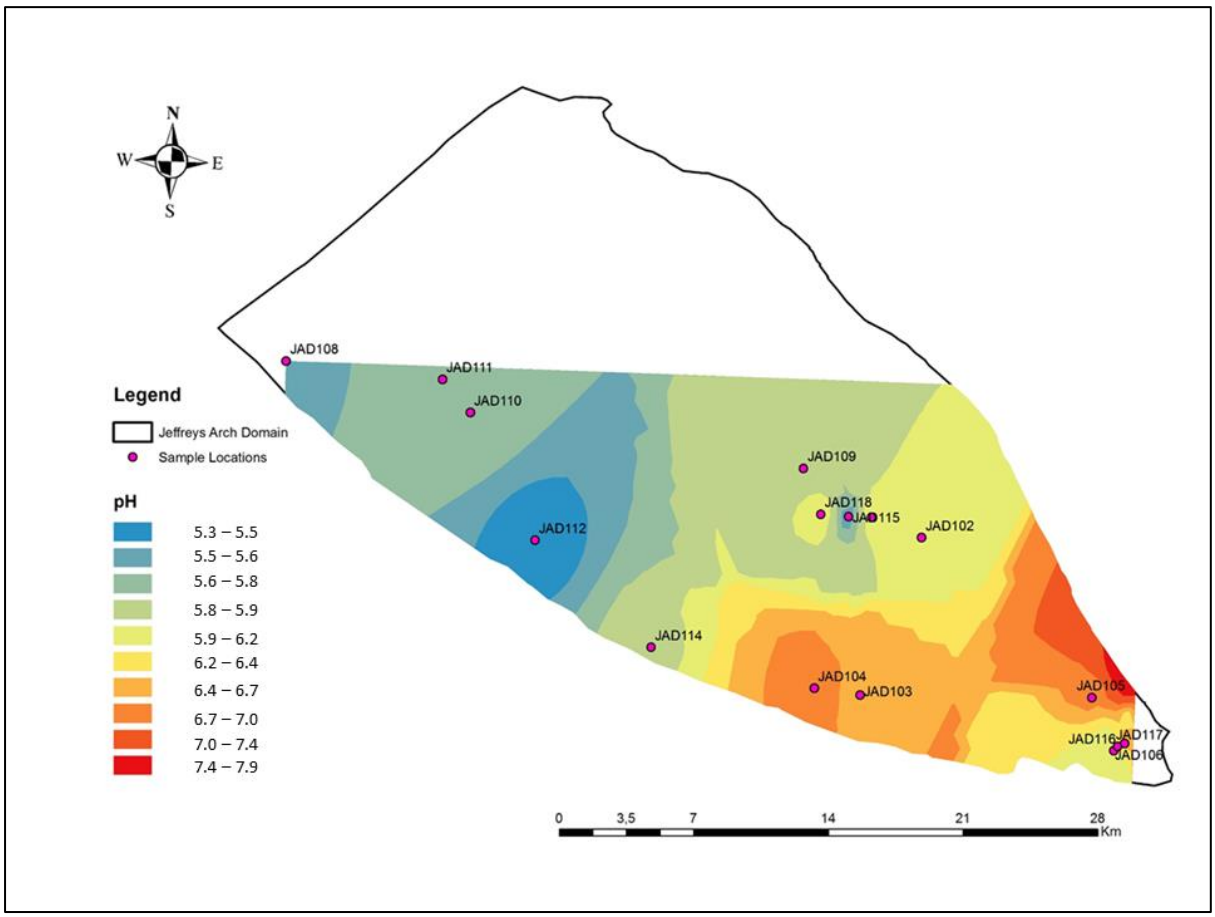


Figure 22: pH Map of Jeffreys Arch domain

5.2 Major ion chemistry

The major ion chemistry data is presented using the Piper, Durov, Stiff, Gibbs and Schoeller diagrams to determine the water types or hydrochemical facies present within the Jeffreys Arch. The July 2018 chemical results are not considered due to ionic balances outside ±5%.

Sample	**Ca**	**Mg**	**K**	**Na**	**Cl**	**SO_4**	**HCO_3**
JAD101	4.17	8.55	0.88	67	119	10.7	13
JAD102	20	32	797	220	382	57	40
JAD103	2.91	5.88	0.17	49	90	10.4	7
JAD104	7.94	7.94	1.13	58	107	10.4	11
JAD105	6.97	11.5	0.55	96	170	12.3	12
JAD106	8.50	14.9	4.65	111	205	16.2	24
JAD113	9.72	18.2	4.67	164	303	44	22
KR01	6.04	11.6	0.90	99	182	10.2	14
KR02	48	120	35	893	1624	279	7

Table 3: Major ion composition (mg/L)

The chemical order of concentration of cations in borehole water is Na>Mg>Ca>K and anions concentration of $Cl>HCO_3>SO_4$ except for JAD113 ($Cl>SO_4>HCO_3$). In the spring water, the order of concentration for cations and anions is Na>Mg>Ca>K and $Cl>SO_4>HCO_3$, respectively. The range of concentrations between borehole and spring water is closely related to differences of 9 – 17 mg/L for Na and Cl. In the river water, the order of concentration is Na>Mg>Ca>K for cations and $Cl>HCO_3>SO_4$ and $Cl>SO_4>HCO_3$ for anions. The latter order of anions refers to the lower Kabeljous River (KR02).

The general chemical order of abundance is observed as follows;

$Cl>Na + K>Mg>HCO_3 + CO_3>SO_4>Ca$

It is evident that the variation in the order of concentration among borehole, spring and river water occurs within anions than cations. Na and Cl are the dominant ions for groundwater and surface water.

The Piper diagram classified groundwater in the domain as Na-Cl type water (Figure 24). This is supported by the results of the Durov (Figure 25), Stiff (Figure 26) and Schoeller diagrams (Figure 27). Similarly, Nelson (2003), Goedhart (2004), Du Preez (2018) and SRK (2012) also determined Na-Cl hydrochemical facies in the area. Sodium and chloride contributions are possibly mainly from the Bokkeveld shale. Weaver et al. (1999), using a molar ratio of Na/Cl, found that significant increases occur in Bokkeveld shale samples compared to TMG quartzites. High chloride concentrations could be a result of the deposition of chlorine from rainfall originating from the ocean and irrigation return flows. The high Na concentrations and low Ca suggest an ion-exchange geochemical process leading to Na–Cl type water (see Figure 25).

The higher concentration of HCO_3 than SO_4 for the upper Kabeljous River (KR01) is probably due to carbonic acid forming during the decomposition of plants along the river catchment. In contrast, the higher sulphate concentrations in KR02 can be ascribed to irrigation return flows concentrated with mineral salts from among others, ammonium sulphate fertilisers used for crop production. This indicates contamination of the water resource (DWAF, 1996). Borehole, JAD113 has a similar order of concentration to that of KR02 although at lower concentrations suggesting contamination from a similar source. This may suggest the percolation of excess return flows that have not been lost through evapotranspiration or surface drainage.

KR01 shows a similar order of chemical abundance with boreholes, JAD101, 104 and 106. This correlates with the spring-fed nature of the river flow upstream. Figure 23 shows the results of historical data (24-year period) of the DWS bi-annual chemical water quality monitoring of the spring, JAD103 (ZQMHDP1) since the early 1990s. The historical data and sampled data are compared to ascertain the evolution, change of water facies and groundwater quality with time. Both datasets show the same chemical signature and hydrochemical facies. The Na-Cl hydrochemical facies indicate the ionic stability of the water source. The historical data also shows a change of plots over time suggesting the influence of regional groundwater circulation. The spring is located along the Peninsula and Skurweberg Formation contact zone. Additionally, a negligible effect of the Grahamstown Formation outcrop (overlie the TMG) is evident due to no significant bicarbonate concentrations.

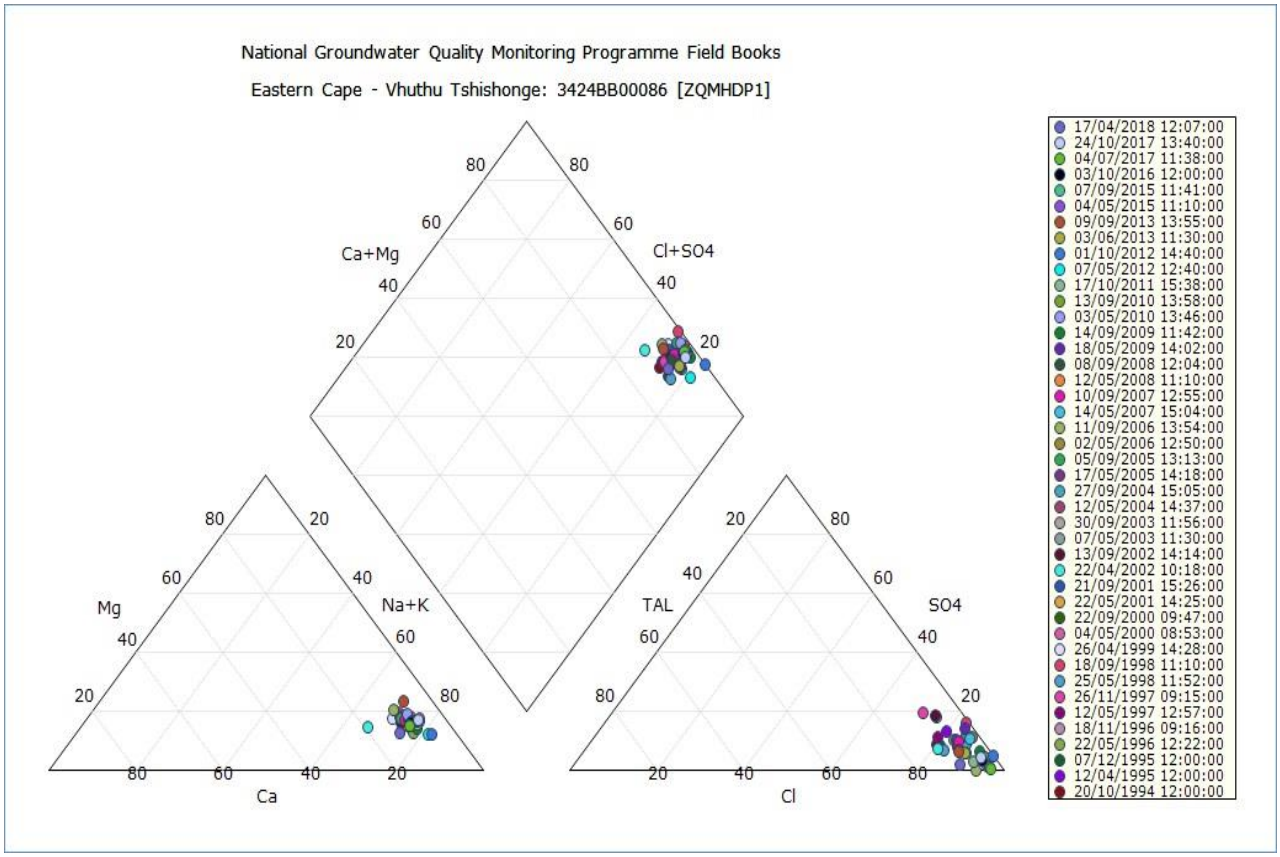


Figure 23: DWS historical data for Kruisfontein Spring (ZQMHDP1)

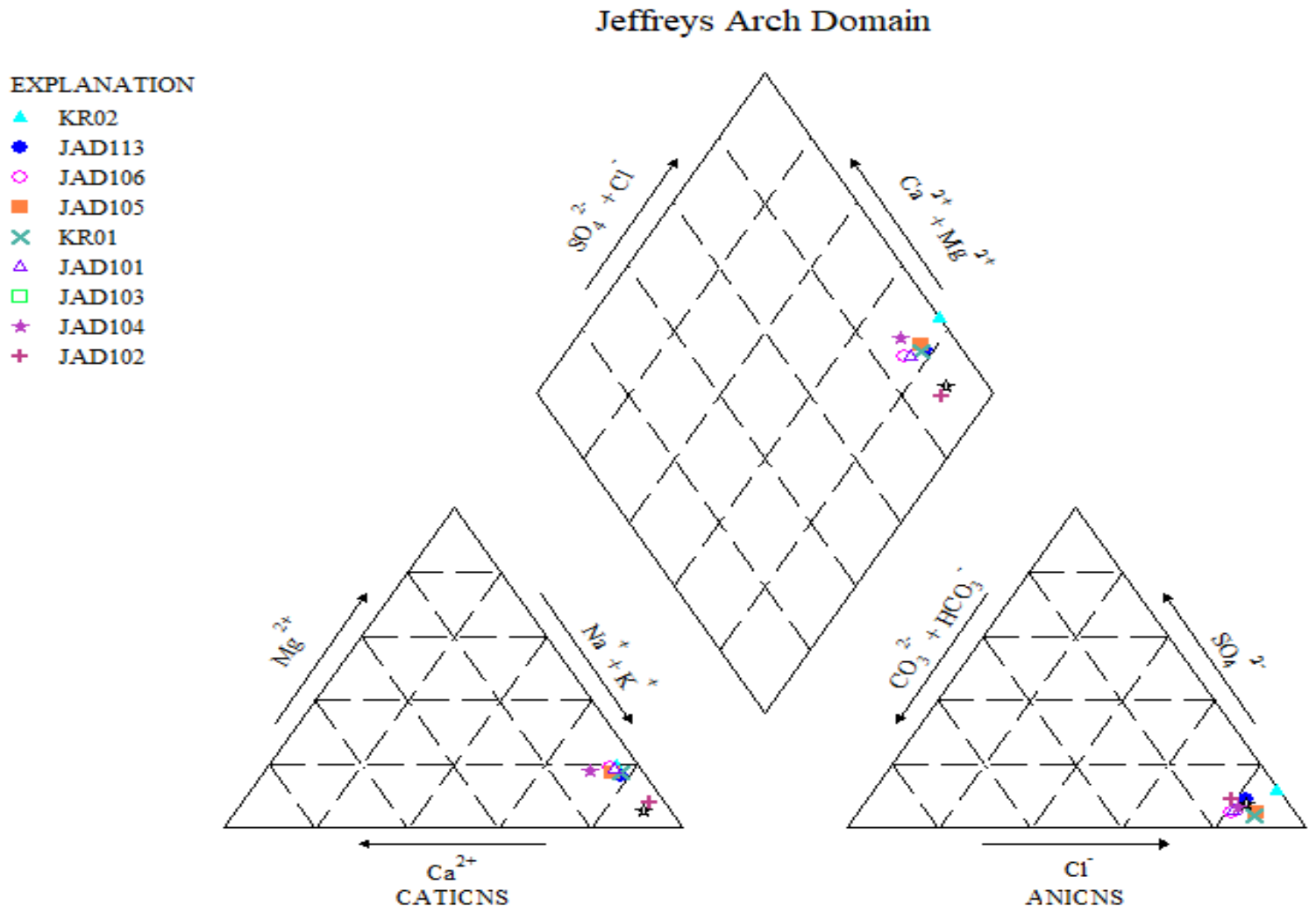


Figure 24: Piper plot indicating major ion results

The Durov diagram indicated ion exchange as one of the geochemical processes controlling the groundwater chemistry within the domain (Figure 25). The Ca^{2+}/Na^{+} exchange is generally driven by the strong adsorption tendency of calcium ions onto surfaces.

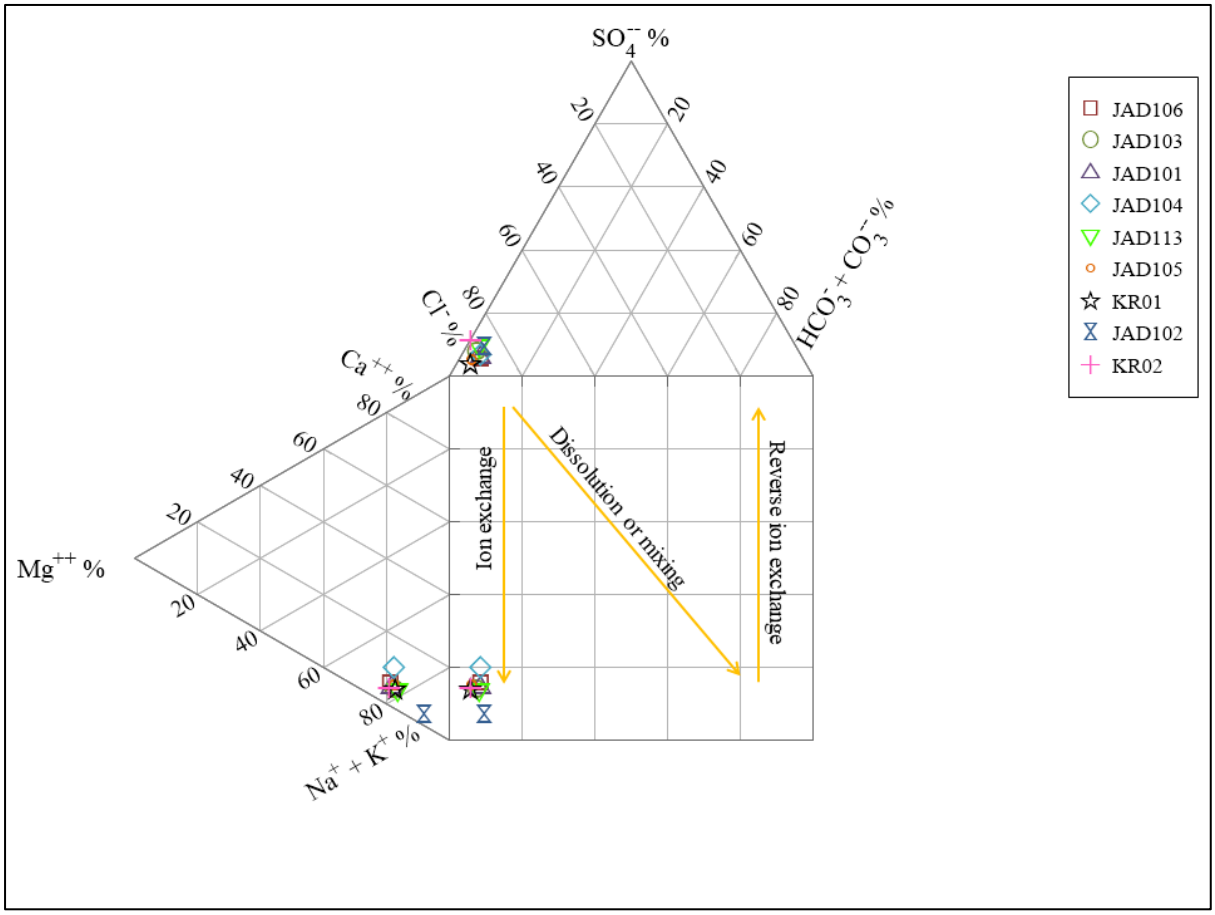


Figure 25: Durov diagram indicating geochemical processes in the domain

The Stiff diagram revealed Na-Cl hydrochemical facies across the domain (Figure 26). The water types were interpreted based on the respective shapes per sample. The groundwater and KR01 samples presented a funnel shape, whereas the river sample, KR02 presented a ribbon shape. The chemical composition of groundwater samples is indicative of water-rock interaction with a similar source of origin. The upper Kabeljous River, KR01 shows concentrations similar to those of groundwater samples that may be associated with the observed spring-fed streamflow at the origin of the river.

The JAD102 spring shows greater concentrations of Na-Cl and to a lesser extent Mg and SO_4, indicative of other sources such as sodium from soils and sulphate from return flows. The sample was collected upon considerable surface flow suggesting the effects of the surface environment.

The lower Kabeljous River, KR02 shows a significantly greater concentration of Na and Cl with enriched Mg and SO_4 concentrations. These are probably a result of anthropogenic activities, tidal influence and low flows.

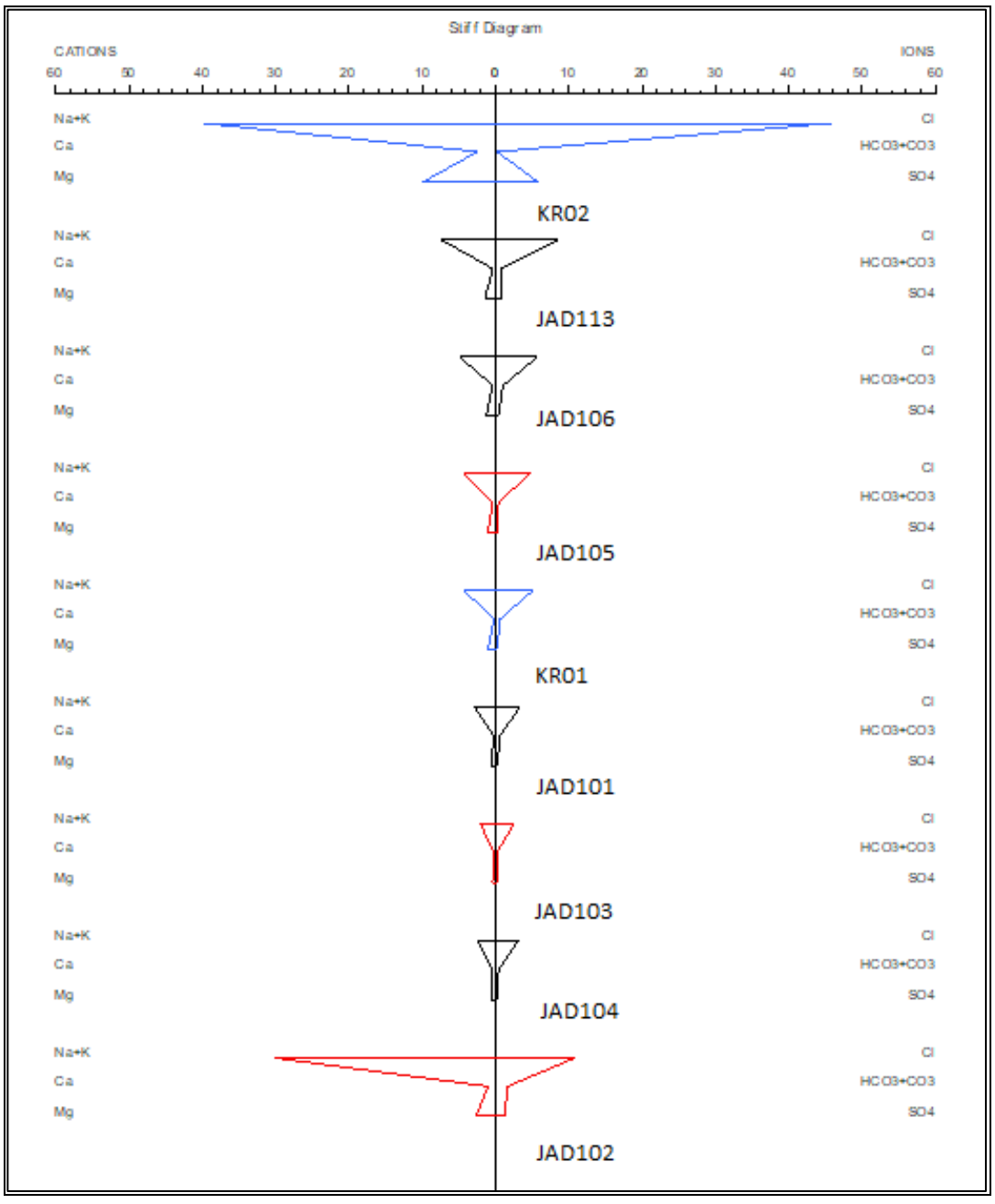


Figure 26: Stiff diagram indicating major ion results

The Schoeller diagram shows the dominance of Na^+ and Cl^- ions across the domain (Figure 27). A majority of the samples resemble a similar pattern of abundance with notable differences of Ca^{2+} and SO_4^{2-}concentrations, either causing an ascending or descending trendline. The depiction of a similar pattern suggests a common water source, recharge

mechanism and geochemical processes. Borehole, JAD101 shows the highest concentration of Na^+ and Cl^- indicating additional input sources. The groundwater is classified as Na-Cl type water.

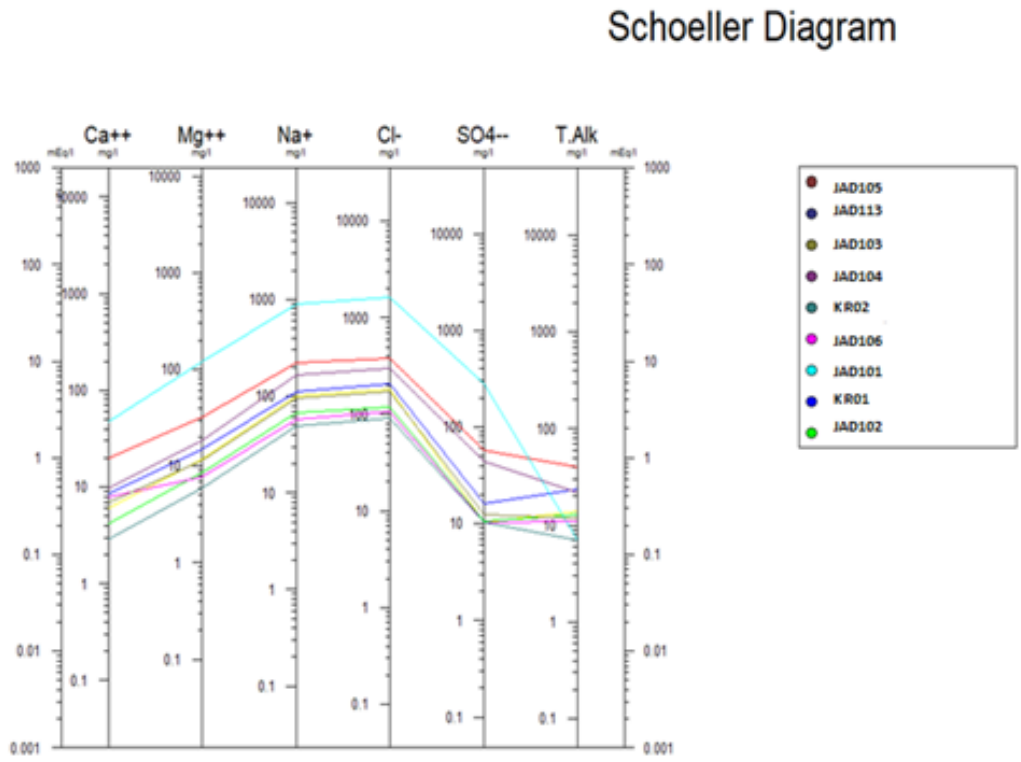


Figure 27: Schoeller diagram presenting major ion chemistry

5.3 Mechanisms controlling groundwater chemistry

The Gibbs diagrams distinguish natural processes controlling geochemical compositions of water. These are categorised into precipitation dominance, rock-water dominance and evaporation dominance. Figure 28 shows that the main factors controlling groundwater chemistry are rock-water interaction and evaporation. Samples fall in and between the evaporation and rock dominance fields. Furthermore, most springs and the artesian borehole, JAD113 indicate the influence of evaporation whereas boreholes and JAD103 spring show rock-water interaction as the major geochemical process. The rock dominance field indicates chemical interaction between the host rock and percolated water in the subsurface typical of ion exchange reactions. Evaporation leads to the concentration of water from the surface and unsaturated zone resulting in the precipitation and deposition of evaporites. These leach into the saturated zone and increase the concentration of ions (Mohamed & Zineb, 2015).

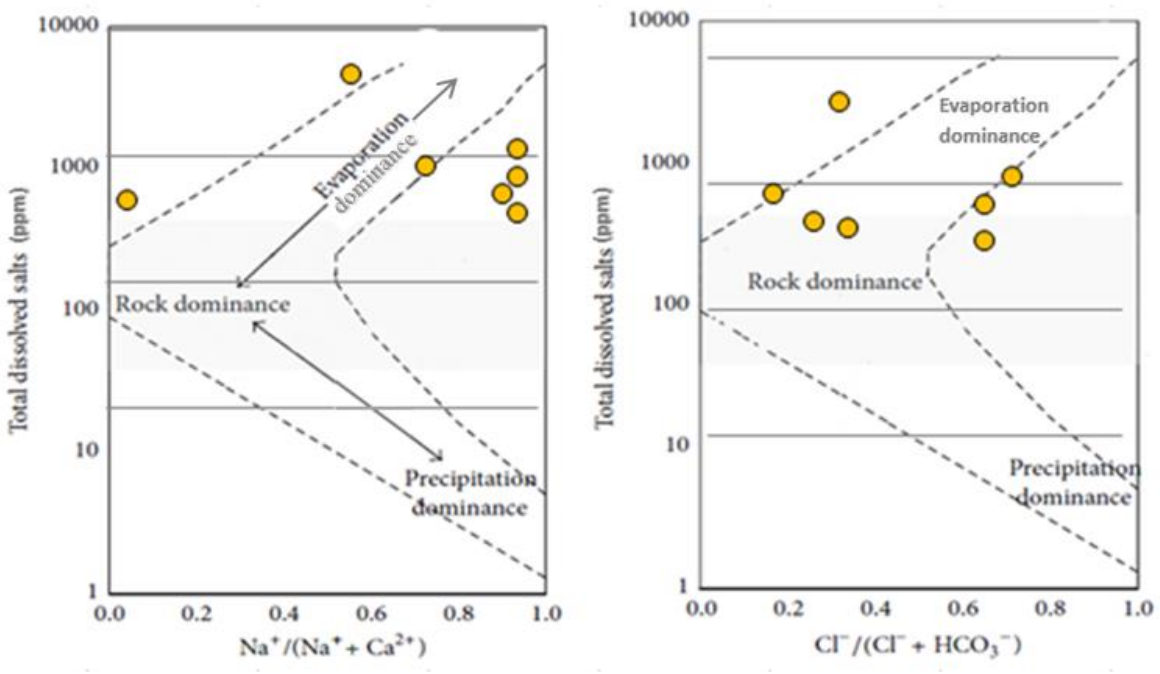


Figure 28: Gibbs diagrams of groundwater samples

The groundwater chemical constituent ratios are compared to explore their ionic relationship, degree of correlation and related chemical processes. The depleted and enriched ionic concentrations support and explain the identification and evolution of certain water types or facies. The geochemical signature is influenced by water-rock interaction, ion exchange and evaporation.

The Na-Cl water type characterised by a high concentration of Na^+ and Cl^- ions, may be ascribed to ion exchange and the geochemistry of the host rocks (Weaver et al., 1999).

The Na/Cl ionic relationship in Figure 29 portrays a strong correlation that exists between the two ions. The ratio of Na to Cl in groundwater is just about equal to 1 (R^2 = 0.9967), suggesting the common origin and/or the addition of seawater into groundwater.

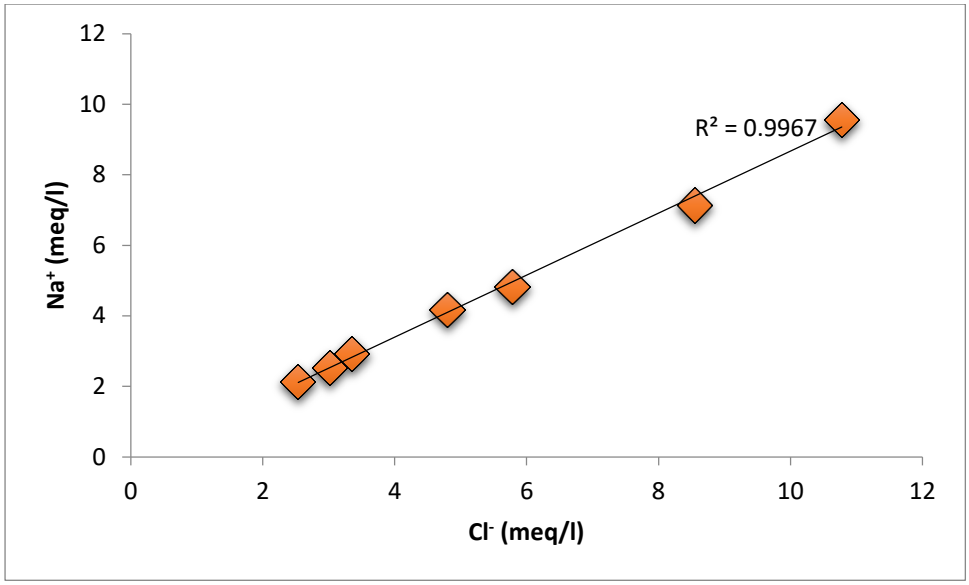


Figure 29: Correlation between Na^+ and Cl^- in groundwater samples

The elevated Na^+ concentration compared to Ca^{2+} in Figure 30 indicate the influence of the chemical composition of the host rocks: TMG sandstones and Bokkeveld shales. Calcium may be reduced or lost through precipitation of calcite and to a lesser extent by ion exchange.

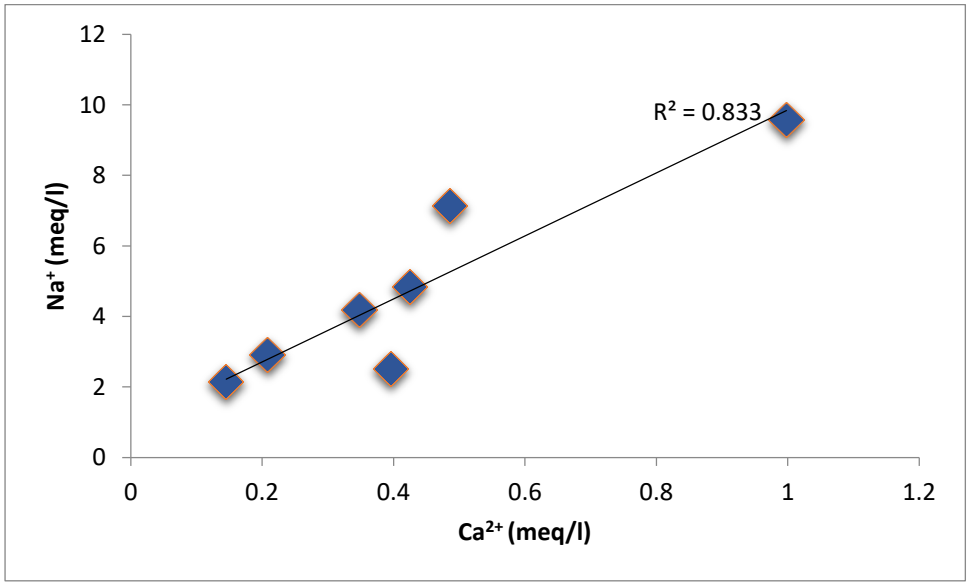


Figure 30: Correlation between Na^+ vs Ca^{2+} in groundwater samples

Figure 31 shows a strong correlation between the concentration of Cl and HCO_3. This suggests the input of chloride and bicarbonate in the aquifer system from the soil through the infiltration of water. Furthermore, the lower concentrations of bicarbonate reveal the low carbonate mineral content of rocks within the TMG (Weaver et al., 1999).

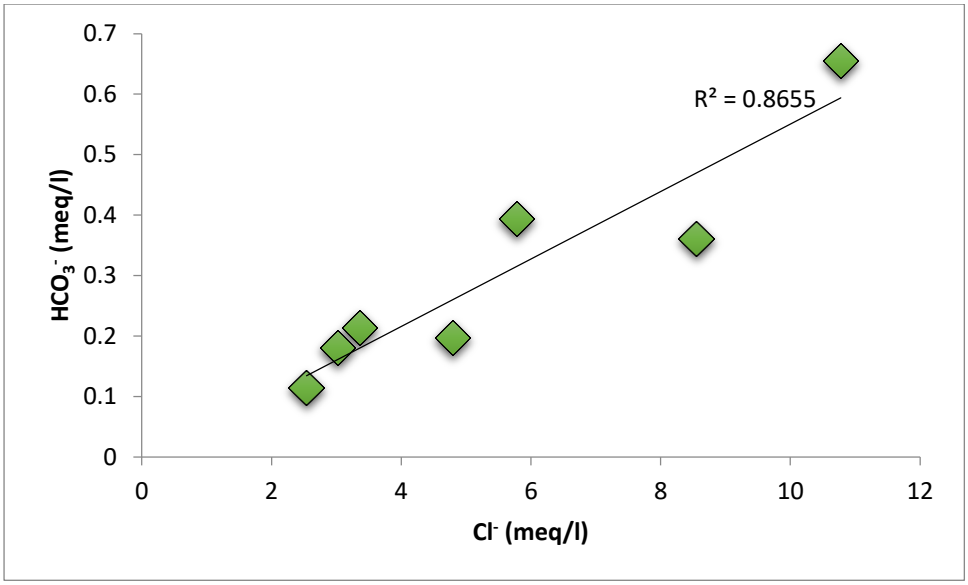


Figure 31: Correlation between Cl^- vs HCO_3^- in groundwater samples

Evaporation is an important process affecting groundwater chemistry as supported by the Gibbs diagrams (Figure 28). The Na^+/Cl^- ratio shows a constant and slightly decreasing concentration with increasing EC indicating the evaporation factor (Figure 32). The sodium/chloride ratio has to be constant when EC rises, where evaporation is a dominant process (Jankowski & Acworth, 1997).

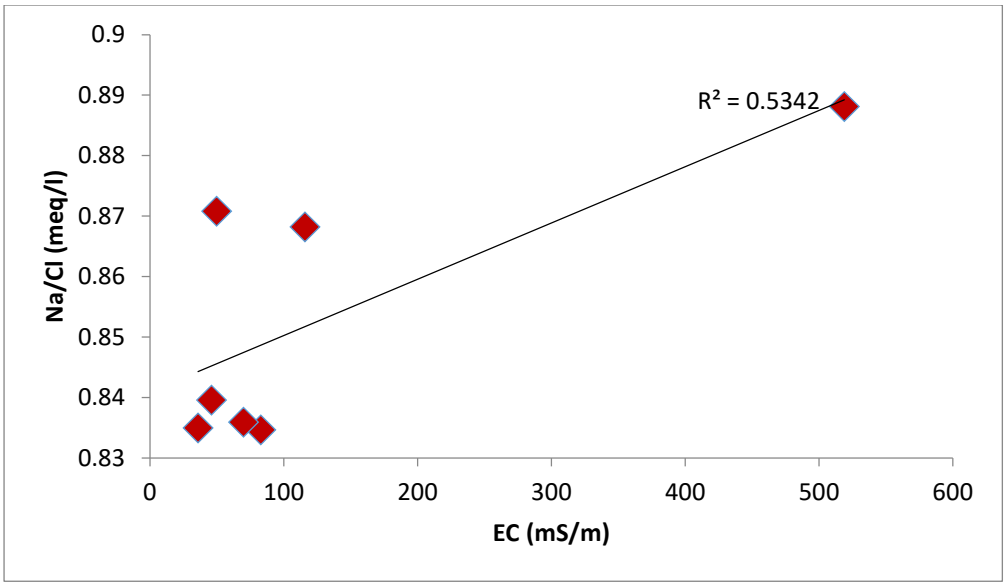


Figure 32: Correlation between EC vs Na/Cl in groundwater samples

Although geological processes influence groundwater chemistry, anthropogenic activities (i.e. irrigation return flows) contribute to the chemical signature of groundwater. The ionic relationship (see Figure 33) shows a strong correlation between SO_4^{2-} and Cl^- indicating

possible surface contamination sources (irrigation return flows) and land use patterns as major factors controlling geochemical composition.

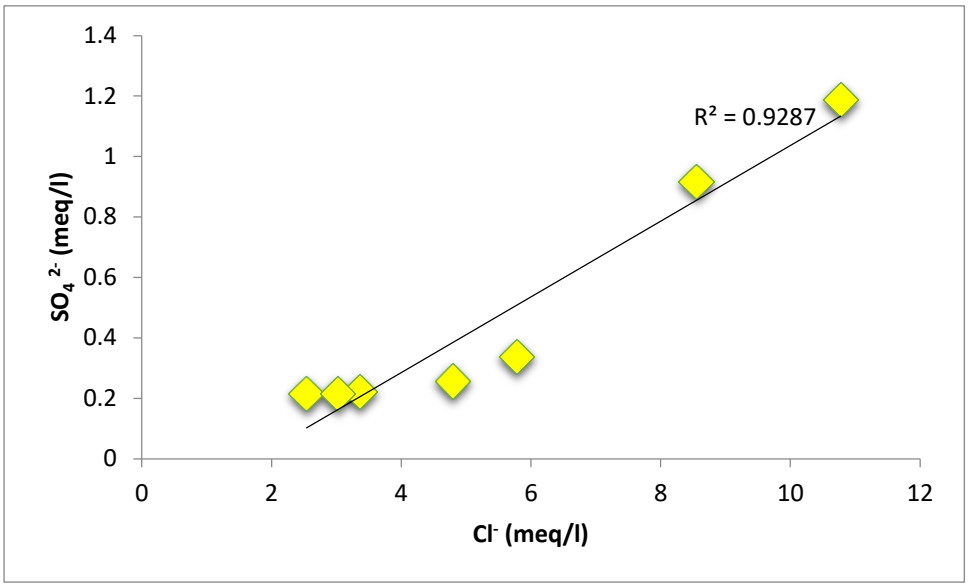


Figure 33: Correlation between SO_4^{2-} vs Cl^- in groundwater samples

5.4 Environmental Isotopes

Stable isotope analyses of seven (7) groundwater samples and two (2) surface water samples are presented in Figure 33. The results, $\delta^{18}O$ and δD, are presented in Tables 4 and 5. The December 2017 results refer to summer season data and the July 2018 results are winter season data. The Local Meteoric Water Line ($\delta D = 5.8\ \delta^{18}O + 5.2‰$) is determined from Sandveld station data by Van Wyk (2010) and the Global Meteoric Water Line ($\delta D = 8\ \delta^{18}O + 10‰$) are referenced in these analyses. The Local Meteoric Water Line (LMWL) correlates $r^2 = 1$. The $\delta^{18}O$ and δD signatures were used to identify the origin and characteristics of groundwater; and the interaction of groundwater with surface water.

Saayman et al. (2003) indicate that water with an isotopic composition that falls on the meteoric water line is assumed to have originated from the atmosphere and is to be unaffected by other isotopic processes. In contrast, deviations from the meteoric water line result from other isotopic processes. Samples that deviated from the MWLs plotting under the MWLs are interpreted as signifying water that underwent evaporation and was subject to indirect recharge mechanisms.

The $\delta^{18}O$ and δD stable isotope results for groundwater varied from -5.91 ±0.3 ‰ and -28.6 ±1.9 ‰ to -0.20 ±0.1 ‰ and 2.2 ±0.5 ‰ across the Jeffreys Arch area, respectively. The $\delta^{18}O$

and δD stable isotope results for surface water varied from -5.35 ±0.3 ‰ and -26.4 ±3.5 ‰ to -0.99 ±0.2 ‰ and -2.7 ±1.6 ‰ across the Jeffreys Arch area, respectively. The results show a categorisation of three (3) groups; Group A comprises of KR02 and a spring (JAD102); Group B consists of KR02 and borehole JAD104 and Group C comprises of boreholes (JAD101, 106 & 113), springs (JAD103 & 105) and KR01.

Sample ID	**δ ^{2}H (‰)**	**± ^{2}H StDev**	**δ ^{18}O (‰)**	**± ^{18}O StDev**
JAD101	-26.6	1.8	-5.68	0.2
	-28.6	1.9	-5.91	0.3
JAD102	2.2	0.5	-0.20	0.1
	-25.6	2.1	-5.78	0.2
JAD103	-18.6	0.5	-4.87	0.1
	-22.7	3.9	-5.38	0.4
JAD104	-9.3	0.5	-2.84	0.1
	-24.4	5.3	-5.48	0.5
JAD105	-21.0	0.6	-5.07	0.1
	-24.0	1.2	-5.32	0.1
JAD106	-22.4	0.8	-5.31	0.1
	-24.0	1.5	-5.17	0.5
JAD113	-23.1	0.5	-5.12	0.0
	-26.4	2.1	-5.44	0.2
KR01	-24.3	2.8	-5.15	0.2
	-26.4	3.5	-5.35	0.3
KR02	-11.9	1.0	-3.03	0.1
	-2.7	1.6	-0.99	0.2

Table 4: Stable isotope results (Summer & Winter seasons)

The surface water (river) samples plot on the fourth quadrant. The summer and winter season results are plotted on the LMWL and below the LMWL, respectively. The winter results indicate water that has undergone evaporation by plotting below the LMWL and GMWL whereas the summer results show water originating from the atmosphere or direct recharge.

The upper Kabeljous River (KR01) sample plots in Group C characterised by groundwater samples with highly depleted $\delta^{18}O$ and δD. The seasonal effect influenced mainly by rainfall and evaporation levels is considered minimal to non-existent given the insignificant difference in isotopic signature between the summer and winter season results. The origin of the water at this station infers to the groundwater recharge from the spring discharging on the riverbed. Generally, mountain springs recharge rivers at the upper-end of the catchment before the collection of catchment run-off. The JAD101 borehole samples collected about 250 metres adjacent to the KR01 show similar stable isotope compositions of $\delta^{18}O$ and δD, supporting the interaction of groundwater and surface water. Most of the other groundwater sample results indicate similar stable isotope signatures.

The lower Kabeljous River (KR02) enriched in δ18O and δD and plots within Group A and B indicating seasonal variation in the isotopic signature. The winter sample is least depleted and plots below both the LMWL and the GMWL indicating the evaporation signature. The KR02 samples show a distinct isotopic signature that suggests hydraulic disconnection and no occurrence of surface water and groundwater interaction. Similarly, Harris et al. (1999) differentiated between different groundwater systems and treated across various seasons using $\delta^{18}O$ and δD analysis.

Most groundwater samples show depleted isotope signatures that indicate water recharged during a colder season or from high latitude sources. These samples have identical isotopic signatures suggesting similar sources or interconnections of different aquifers. Some of the samples plotted above both the Meteoric Water Lines (MWL) and on the LMWL indicating water resulting from direct recharge or negligible to no surface or subsurface residence time. These are representative of water of meteoric origin emanating directly from precipitation. All the groundwater and surface water signatures bear no relevance to the typical seawater isotope signature suggesting no seawater intrusion.

The sampled boreholes and springs plotted on the fourth quadrant except for JAD102 (spring) that plotted on the first quadrant and below the meteoric water lines indicating water that had undergone evaporation prior to infiltration. The summer results show that JAD102 was highly enriched in $\delta^{18}O$ and δD with positive δD values (2.2 ‰) identified under Group A compared to most groundwater samples identified under group C. Other spring samples, JAD103 and 105 show no seasonal variability in stable isotope composition. The $\delta^{18}O$ and δD values are notably more positive in the winter than the summer season indicative of high

temperature and relative humidity. These springs plot above the MWLs indicating water that experienced no evaporation.

Borehole, JAD104 plotted in Group B and C in summer and winter seasons, respectively. This shows a considerable difference in depletion of 2‰ for ^{18}O and 14‰ for ^{2}H reflective of rainfall amount and humidity. The summer and winter season results for boreholes, JAD104 and 106 plotted above the MWLs signifying water that underwent no evaporation prior to infiltration. Some boreholes (JAD101 & 113) in winter suggest water from direct recharge that experienced minimal to no evaporation by plotting on the LMWL. Generally, no significant groundwater isotopic composition difference exists across the summer and winter sampling periods. Gat and Gonfiantini (1981) suggest that this indicates the non-occurrence of surface water input.

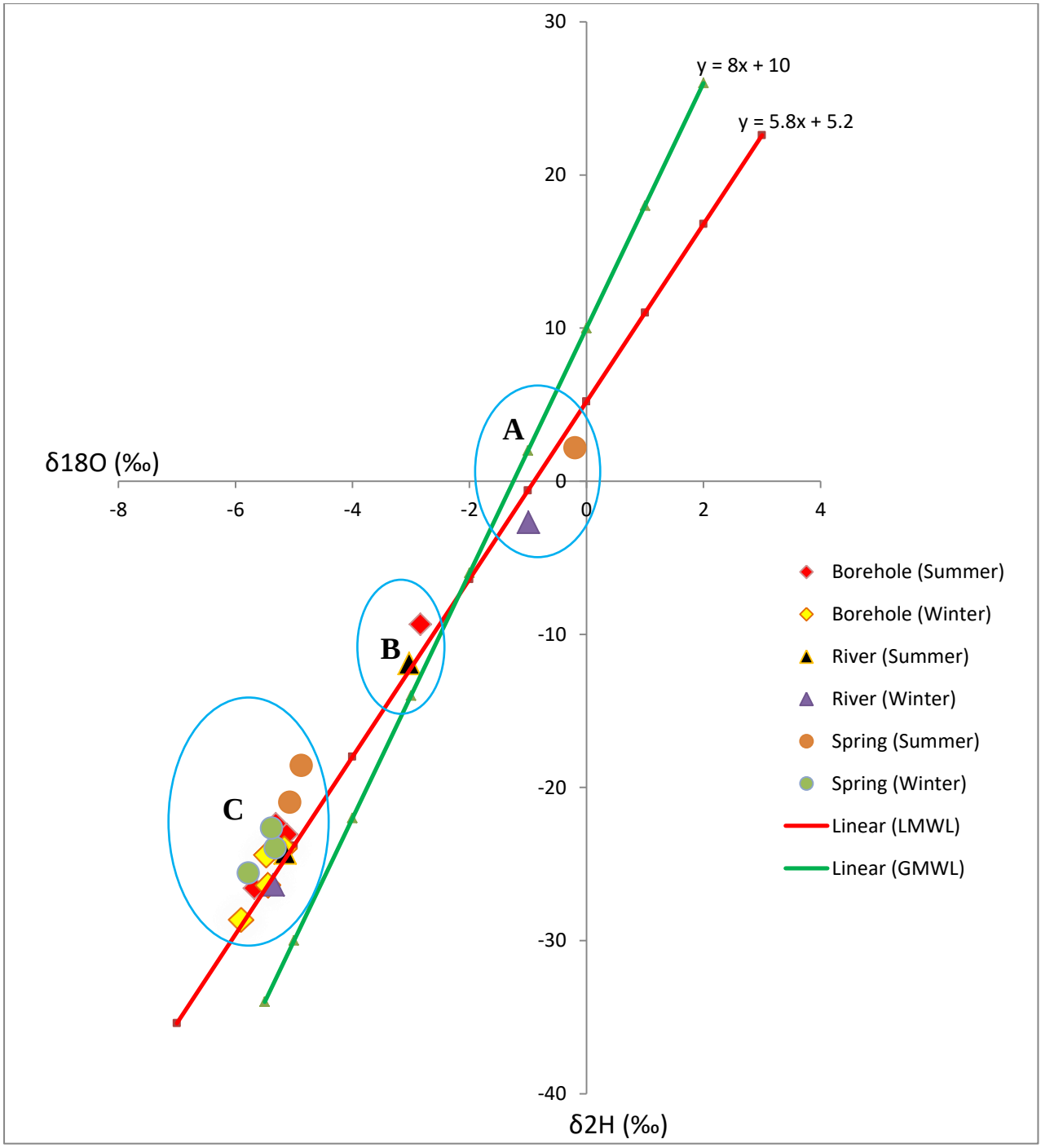


Figure 34: Stable isotope diagram for Jeffreys Arch domain

The river flow consisting of baseflow shows enriched water that has undergone evaporation. Seasonal variation is also evidenced by isotopic and salinity differences in concentration. The river spring source shows highly depleted water originating from the atmosphere and no distinct effect of evaporation. Electrical Conductivity and isotopic concentrations indicate no seasonal variation showing constant values across the seasons. The Stiff diagram also presents lower Na-Cl-SO_4 concentrations.

Borehole, JAD101 drilled at depth into the confined Peninsula Formation aquifer show highly depleted stable isotopes of deuterium and oxygen-18 that indicate no evaporation prior to infiltration. This is supported by the Gibbs diagram that presents water-rock interaction as a dominant factor influencing the geochemical signature. Additionally, characteristics of deeper-lying groundwater of high Na-Cl, and low Ca, SO_4 and HCO_3 concentrations are shown in the Schoeller and Stiff diagrams, respectively.

On the contrary, unconfined aquifers represented by boreholes, JAD106 and 113 (Skurweberg Formation and Bokkeveld Group) are characterised by slightly enriched water originating from the atmosphere. Similarly, the role of evaporation is supported by the Gibbs diagram. Higher bicarbonate from soil transported through water percolation and high salinity and SO_4 concentrations symbolic of contamination sources at surface identify with shallow groundwater circulation.

Chapter 6: Conclusion

The integrated approach applied in this study met the set objectives to: assess the interaction of groundwater and surface water, characterise the groundwater chemistry and identify its preceding hydrogeochemical processes within the Jeffreys Arch domain.

The physicochemical analyses indicated acidic to slightly alkaline waters. The highly acidic and saline Kabeljous River may be attributed to agricultural run-off. The salinity survey indicated a positive correlation between Electrical Conductivity and Temperature signifying the seasonality effect with higher conductivity values in summer than winter seasons. The Bokkeveld shale presented higher conductivity concentrations than the Nardouw Subgroup TMG aquifer. The lower Kabeljous River recorded elevated conductivity and sulphate concentrations compared to upstream proving the contribution of irrigation return flows. Similarly, a strong ionic correlation between SO_4^{2-} and Cl^- indicated possible surface contamination sources and land use patterns as major factors controlling geochemical composition.

The major ion diagrams showed a dominance of Na^+ and Cl^- concentrations indicating Na-Cl hydrochemical facies. Sodium and chloride contributions are possibly mainly from the Bokkeveld shale. Borehole, JAD113 presented a similar order of concentration to the lower Kabeljous River (KR02) at lower concentrations indicative of the Bokkeveld shale or contamination from a similar source. The upper Kabeljous River (KR01) showed a similar order of chemical abundance with boreholes suggesting groundwater and surface water interaction. The assessment of JAD103 spring historical data indicated ionic stability of the water source and a change of plots overtime suggesting the influence of regional groundwater circulation.

The major driving factors of groundwater chemistry include ion exchange, water-rock interaction and evaporation. The latter was confirmed by the Gibbs diagram. The elevated Na^+ concentration compared to Ca^{2+} in Na/Ca ionic ratios and the Durov diagram indicated the influence of the chemical composition of the host rocks: TMG quartzites/sandstones and Bokkeveld shales; and to a lesser extent ion-exchange.

The stable isotopes dataset indicated similarities and a distinction between surface water and groundwater samples. The lower Kabeljous River showed an enriched $\delta^{18}O$ and δ^2H composition, which was least depleted in the winter season. The upper Kabeljous River

revealed a similar isotopic composition to groundwater samples (highly depleted) and no seasonal changes. This highlighted evidence of surface-groundwater interaction attributed to groundwater discharge into the river channel. The groundwater isotopic signature indicates water that underwent no evaporation prior to filtration as most samples plotted above both the Meteoric Water Lines. These similarities suggest water of the same origin and the hydraulic connectivity of aquifers. The geochemical variation within aquifers suggests that the Peninsula Formation aquifer with lower shale content and less vulnerability to contamination occurring at the surface present better water quality that may require lesser water treatment in relation to supply.

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