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Surface water and groundwater interaction in the Vredefort Dome, South Africa

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A research report submitted in partial fulfilment of the requirements for the degree of

Master of Science in Hydrogeology

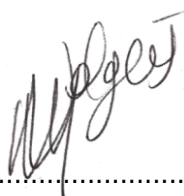
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November 2021

DECLARATION

I hereby declare that this research report titled '*Surface water and groundwater interaction in the Vredefort Dome, South Africa*' is my own, unaided work. It is being submitted to the Degree of Master of Science in Hydrogeology to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University. Information obtained from sources has been indicated and acknowledged by detailed and complete referencing.



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1 November 2021
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Date

ABSTRACT

The growing importance of groundwater as freshwater supply in semi-arid areas such as the Vredefort Dome World Heritage Site (VDHS) demands the judicious management of this vital resource. A comprehensive understanding of the mechanisms operating during hydrological connectivity is, therefore, necessary to achieve sustainable groundwater development. An integrated study based on hydrochemical multivariate statistical techniques, baseflow separation, microorganisms, stable water isotopes, and groundwater level mapping has been conducted to investigate the nature of surface water-groundwater (SW-GW) interaction under the influence of anthropogenic practices, coupled with a structurally complex geological setting.

Surface water loss to the underlying fracture network was observed in the northern and south-western river reaches, underlain by metamorphosed sedimentary and lava units. These areas exhibit declining groundwater levels that are below the riverbed. The continuous wastewater discharge released into the Vaal River coupled with increased groundwater exploitation may be prompting induced recharge conditions. Analysis of seasonal baseflow from 2013 to 2016 indicates that subsurface contribution occurs primarily during the dry season (BFI ~ 7%) as opposed to the wet season (BFI 1%). The limited baseflow that was detected has an isotopic composition consistent with springs and shallow groundwater near the channel in the south-eastern river reach, underlain by the crystalline basement complex.

Principal Component Analysis reveals the combined effect of natural hydrochemical processes and anthropogenic sources as controlling factors of groundwater composition. The microbiological quality of the water shows the prominence of groundwater contamination across the study area, most of which points to faecal sources. The cluster multivariate analysis highlights the multi-source control over the groundwater hydrochemical properties- certain sites proximal to the channel (0 - 500 m) are evidently severely compromised from mixing with river water. In some instances, these sites were found to be additionally polluted by human-derived contaminants; in others, sites were solely contaminated by anthropogenic practices. Sites located further from the river channel (> 1 km) demonstrated improved water quality, however, are susceptible to contamination from localised land-use practices.

Groundwater sites influenced by the river water are characterised by more enriched isotopic signatures, reflecting more recent, shallow groundwater. In contrast, sites located > 1 km from the river were found to have depleted isotopic compositions, representing deep circulating, colder climate groundwater. This may be attributed to recharge originating from high altitude and/or elevation, possibly under cooler conditions. Recharge occurs through direct and indirect modes, where the latter constitutes evaporation prior to infiltration and mixing of water resources.

The results suggest compartmentalisation of the groundwater systems, where certain areas in the vicinity of the channel are not influenced by river-induced contamination, indicating that SW-GW interaction is governed by site-specific hydraulic properties. The interaction weakens gradually with distance and is limited to a maximum distance of 1 km from the channel. This is likely attributed to the topographic controls over groundwater flow direction and the presence of certain barriers governed by the riverbed sediments, as well as regional structural and geological configurations. Regional aquifer connectivity is highlighted by the depleted groundwater isotope signals at various distances from the river. Therefore, it can be deduced that the heterogeneous geological morphology and structure, represented as faults and tectonic zones, facilitate hydrological connection, and serve as significant groundwater drainage systems in the VDHS.

To my mother, Marzenna Śledzińska, and family friend, Zanele Moloi,
In loving memory

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TABLE OF CONTENTS

DECLARATION	i
ABSTRACT.....	ii
ACKNOWLEDGEMENTS	v
LIST OF FIGURES.....	ix
LIST OF TABLES	xii
ABBREVIATIONS.....	xiii
1. INTRODUCTION	1
1.1 Background	1
1.2 Research Problem.....	3
1.3 Research Questions	4
1.4 Research Aim and Objectives.....	4
2. STUDY AREA	5
2.1 Introduction.....	5
2.1.1 Hydrological setting.....	6
2.1.2 Land use and cover.....	10
2.1.3 Physiography and climate	12
2.2 Geological Framework.....	13
2.2.1 Vredefort impact structure	15
2.2.2 Archean crystalline basement core.....	15
2.2.3 Collar and synclinorium	16
2.2.4 Metamorphism, structural deformation, and intrusions	17
2.3 Hydrogeological Setting.....	18
3. LITERATURE REVIEW	22
3.1 Overview of Surface Water-Groundwater Interaction.....	22
3.2 Methods to Monitor Surface Water-Groundwater Interaction	24
3.2.1 Hydrochemistry	26
3.2.2 Hydrograph separation.....	27

3.2.3	Microbes and biological oxygen demand.....	28
3.2.4	Stable water isotopes.....	29
4.	METHODOLOGY	31
4.1	Desk Work and Collation of Data.....	31
4.2	Sampling Sites	31
4.3	Data Collection	33
4.4	Data Analysis	35
4.4.1	Hydrochemistry	35
4.4.2	Hydrograph separation.....	36
4.4.3	Microbes and biological oxygen demand.....	38
4.4.4	Groundwater level measurements.....	39
4.4.5	Stable water isotopes.....	40
4.4.6	Statistical analyses.....	41
5.	RESULTS AND DISCUSSION	43
5.1	Hydrochemistry	43
5.1.1	Major ions and <i>in situ</i> parameters	43
5.1.2	Hierarchical Cluster Analysis (HCA)	47
5.1.3	Principal Component Analysis (PCA)	50
5.1.4	Piper trilinear diagram	53
5.2	Hydrograph Separation.....	54
5.2.1	Seasonal baseflow contribution.....	56
5.3	Microbes and Biological Oxygen Demand	60
5.3.1	Bacterial analysis	60
5.3.2	Canonical Correspondence Analysis (CCA)	63
5.3.3	Biological Oxygen Demand (BOD)	64
5.4	Stable Water Isotopes	65
5.4.1	Surface water-groundwater interaction.....	68
5.4.2	Hydrochemistry and stable water isotopes	71

5.4.3	Geological structure and stable water isotopes	73
5.4.4	Deuterium excess	78
5.5	Groundwater Levels	80
5.5.1	Depth to water level	80
5.5.2	Electrical conductivity and hydraulic head	81
5.5.3	Groundwater levels and geological units	82
5.5.4	Groundwater flow direction.....	83
6.	CONCLUSION.....	85
6.1	Recommendations.....	87
7.	REFERENCES	88
8.	APPENDICES	94
	Appendix A. Details from the hydrocensus survey	94
	Appendix B. Major ion concentrations	102
	Appendix C. Summary of the <i>in situ</i> physico-chemical parameters	103
	Appendix D. Stable isotopes of water and deuterium excess	105

LIST OF FIGURES

Figure 2.1. Location of the Vredefort Dome Heritage Site along with a 30 m resolution digital elevation model. The inset map shows the location of the study site in relation to the provinces of South Africa.....	5
Figure 2.2. Images illustrating (A) an inundated grassland, representing a wetland (site SP 5), and (B) a borehole located on the Vaal Riverbank (site BH 42).....	6
Figure 2.3. Recent pollution in the Vaal River resulting in the death of much wildlife. Image obtained from https://www.exploreparys.co.za/help-stop-the-vaal-river-pollution/	7
Figure 2.4. Images of the Vaal River showing (A) fast and turbulent current under shallow conditions dominated by riffles (27.4463 E; -26.9010 S) and (B) slow current under deep conditions associated with pools (site RV 8).....	8
Figure 2.5. Summary of the borehole status in the Vredefort Dome Heritage Site.....	9
Figure 2.6. Summary of the groundwater use of the utilised boreholes in the Vredefort Dome Heritage Site.....	9
Figure 2.7. Images showing (A) lucerne crop farming situated near the Vaal River (site BH 146), common (B) cattle (site BH 131) and (C) sheep farming (site BH 211), and (D) game present on a conservation farm (site BH 48).	10
Figure 2.8. Simplified map showing the spatial distribution of various land cover classes in the Vredefort Dome Heritage Site (source of data obtained from the Department of Environmental Affairs; https://egis.environment.gov.za/data_egis/data_download/current)	11
Figure 2.9. The undulating landscape of the Vredefort Dome Heritage Site. The outcrop demonstrates the relatively intact and resistant hills in the study area.	12
Figure 2.10. Average monthly rainfall and temperature recorded for the years 2018-2019 in Vredefort (data sourced from the South African Weather Services and World Weather Online; https://www.worldweatheronline.com/vredefort-weather-averages/free-state/za.aspx)	13
Figure 2.11. Simplified geological map and stratigraphy of the Vredefort Dome Heritage Site (source for data is the Council of Geosciences).....	14
Figure 2.12. Cross-section of the Vredefort impact crater shortly after its formation (2.02 Ga), showing the deformation of the rocks, central uplifted region, and present surface. Adapted from https://commons.wikimedia.org/w/index.php?curid=31069486 (By Oggmus - Own work, CC BY-SA 3.0).	15
Figure 2.13. Orientations of the geological structures in the Vredefort Dome Heritage Site (source for data is the Council of Geosciences).....	18
Figure 2.14. Images showing the bedrock outcropping along the riverbank with (A) underlying massive granite (27.4463 E; -26.9010 S), highly fractured (B) quartzite (27.3601 E; -26.8856 S) and (C) lava units (site RV 5), as well as (D) slate bedding plane fractures (27.3599 E; -26.8855 S). (E) Thicker overburden associated with supracrustal rocks (27.2498 E; -26.8791 S) and (F) tilted lava with fracture zones on the riverbank (site RV 5).....	21
Figure 3.1. Surface water-groundwater connectivity that takes place under (A) effluent (<i>gaining</i> stream), (B) influent (<i>losing</i> stream), and (C) disconnected conditions with no interaction taking place (Adapted and modified from Toran, 2019).	23

Figure 3.2. The influence of pumping wells on groundwater levels resulting in induced recharge conditions. Adapted from https://livinghistoryfarm.org/farminginthe50s/water_12.html	24
Figure 4.1. Map showing the geographical location of the borehole, surface water, spring, mine, and waste dam sampling and measuring sites in the study area.	32
Figure 4.2. The spatial distribution of (A) groundwater level measurements, (B) <i>in situ</i> physico-chemical parameters, (C) bacteria, (D) stable water isotopes, (E) biological oxygen demand, and (F) major ion sampling sites in the study area (<i>n</i> = sample size).	33
Figure 4.3. Location of the rain and river gauging stations used for the study area.	37
Figure 5.1. Statistical analysis of the river and groundwater electrical conductivity values at the set distances from the river: 200 m, 500 m, 1 km, 2 km, and > 2 km.	45
Figure 5.2. Spatial distribution map of groundwater electrical conductivity in the study area.	46
Figure 5.3. Dendrogram of the 8 river (RV) and 67 groundwater (BH) sites in the Vredefort Dome Heritage Site classified into five clusters based on electrical conductivity (EC) values, expressed as $\mu\text{S}/\text{cm}$. <i>n</i> = sample size.	49
Figure 5.4. Principal Component Analysis biplot of the hydrochemistry data showing the similarity and dissimilarity among the sites at the set distances from the river.	50
Figure 5.5. Piper trilinear diagram showing the hydrochemical facies of the groundwater and river samples. The ternary plots show the dominance of major cations and anions in decreasing order: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na-K}$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$, respectively.	53
Figure 5.6. (A) and (B) baseflow hydrographs for downstream gauging station C2H018 and (C) and (D) for upstream gauging station C2140 using the Nathan and McMahon (1990) and Chapman (1991) filter algorithms.	59
Figure 5.7. Photographs of (A) Endo (<i>E. coli</i> , <i>E. aerogenes</i> , and <i>P. mirabilis</i>) and (B) Tergitol TTC (<i>S. aureus</i>) nutrient pad discs. For scale, a Petri dish is 5 cm in diameter. <i>E. coli</i> = metallic sheen colonies; <i>E. aerogenes</i> = dark pink-red colonies; <i>P. mirabilis</i> = light pink-red colonies; <i>S. aureus</i> = yellow colonies.	61
Figure 5.8. Canonical Correspondence Analysis (CCA) biplot showing the similarity and dissimilarity between (A) bacteria species and all hydrochemical variables and (B) bacteria species and <i>in situ</i> physico-chemical parameters. Refer to Sections 4.3 and 4.4.1 for the elucidation of abbreviated hydrochemical variables.	63
Figure 5.9. Biological oxygen demand during a 5-day period.	65
Figure 5.10. Stable isotopes of groundwater (boreholes), river, springs, mine, rain, and a waste dam plotted against the Johannesburg Local Meteoric Water Line, Pretoria LMWL, and Global MWL. The inset shows a zoomed-in view of the sites versus the JLMWL and delineation of the groups.	67
Figure 5.11. Stable isotopes of river, springs, and groundwater sites at set distances from the channel plotted against the Johannesburg Local Meteoric Water Line.	69
Figure 5.12. Groundwater level below the ground surface plotted against the stable isotopes of the (A) zones (RV = river; GW = groundwater) and (B) sites at set distances from the river channel.	70
Figure 5.13. Stable isotopes of hydrochemical clusters and springs versus the Johannesburg Local Meteoric Water Line, Pretoria LMWL, and Global MWL.	72

Figure 5.14. Groundwater isotopes of different underlying lithological units plotted against the Johannesburg Local Meteoric Water Line, Pretoria LMWL, and Global MWL (SG = Subgroup). ..	73
Figure 5.15. Images illustrating some of the (A) subparallel lineations in quartzite (137°/50° NW) and (B) south to southeast-dipping bedding planes of the quartzite-dominated successions (northwest of the Vaal River).	74
Figure 5.16. The spatial distribution of zones 1 and 2 groundwater and spring stable isotopes within 1 km distance from the river in relation to the underlying lithological units and Quaternary deposits. Geological lines represent lithological contacts and structural features.....	77
Figure 5.17. Location of the different river reaches in the core boundary of the Vredefort Dome Heritage Site.....	78
Figure 5.18. Deuterium excess plotted against $\delta^{18}\text{O}$ for river, springs, and groundwater in different zones (RV = river; GW = groundwater).	79
Figure 5.19. Interpolated map of the water table depth in the Vredefort Dome Heritage Site.	80
Figure 5.20. Simple regression analysis between hydraulic head and surface elevation ($R^2 = 0.97$).	81
Figure 5.21. Hydraulic head measurements with electrical conductivity values for sites at specific distances from the river channel.	81
Figure 5.22. Box and whisker plot showing the water levels below surface per stratigraphic unit.	82
Figure 5.23. (A) Groundwater contour map in two-dimensions showing (B) the horizontal groundwater flow direction.	84

LIST OF TABLES

Table 3.1. Summary of common methods applied in assessing hydrological interactions.	25
Table 5.1. Mean and standard deviation (σ) values of the hydrochemical parameters for all sites situated at set distances from the river. Concentrations are expressed as mg/L, except for total alkalinity (TAL), pH, electrical conductivity (EC), and temperature (Temp), which are expressed as mg/L as CaCO ₃ , standard units, μ S/cm, and °C, respectively.	43
Table 5.2. The number of groundwater and river sites at the set distances from the river channel in each cluster and their respective percentage (%) contribution to the total.	47
Table 5.3. Varimax rotated principal component loadings for the physical and chemical properties of all water samples.	51
Table 5.4. Descriptive statistics of the streamflow, baseflow, and baseflow index (BFI) for the downstream (C2018) and upstream (C2H140) gauging stations during the 2013 – 2016 period.	55
Table 5.5. Descriptive statistics for the seasonal baseflow index (BFI) for the downstream (C2H018) and upstream (C2H140) gauging stations during the 2013 – 2016 period (cumulative daily average in m ³ /s).	57
Table 5.6. Summary of bacterial count and biological oxygen demand (BOD) for river and groundwater sites located at the set distances (200 m, 1 km, and > 2 km) from the river.	60
Table 5.7. Statistical summary of stable water isotopes for rain, river, springs, waste dam, mine, and groundwater samples located at set distances 200 m, 500 m, 1 km, 2 km, and > 2 km from the river.	66
Table 5.8. The average percentage of river water mixing with groundwater at the set distances from the channel for zone 2 sites.	70

ABBREVIATIONS

BOD	Biological Oxygen Demand
BH	Borehole
CCA	Canonical Correspondence Analysis
ca.	Circa
DEA	Department of Environmental Affairs
DWAF	Department of Water Affairs and Forestry
DWS	Department of Water and Sanitation
DEM	Digital Elevation Model
EC	Electrical Conductivity
GIS	Geographic Information System
Ga	Giga annum
GMWL	Global Meteoric Water Line
GPS	Global Positioning System
HCA	Hierarchical Cluster Analysis
JLMWL	Johannesburg Local Meteoric Water Line
LMWL	Local Meteoric Water Line
Ma	Mega annum
MAR	Mean Annual Runoff
MWL	Meteoric Water Line
MN	Mine
NGIS	National Groundwater Information System
NWA	National Water Act
PLMWL	Pretoria Local Meteoric Water Line
PCA	Principal Component Analysis
RV	River
SAWS	South African Weather Service
SP	Spring
SMOW	Standard Mean Ocean Water
SW-GW	Surface water-Groundwater
TWQR	Target Water Quality Range
TAL	Total Alkalinity
TDS	Total Dissolved Solids
VDHS	Vredefort Dome Heritage Site
WD	Waste Dam
WMA	Water Management Area

1. INTRODUCTION

1.1 Background

Surface water and groundwater form an integral part of the hydrological cycle, and are commonly spatially and temporally interlinked. Development and various contaminant sources can separately affect these systems. Subsequently, due to their dynamic connections, these water resources often impact one another (Sophocleous, 2002). From this perspective, surface water-groundwater (SW-GW) interactions form an important element of water resources management that need to be managed from a holistic viewpoint. In Africa, there has been increased interest in hydrologic exchanges due to their important implications associated with ecosystems and sustainability (Levy and Xu, 2012).

Growing water demand in response to development and population growth is placing water resources under increasing pressure and the functional dynamics of these systems are continuously changing (Rugel *et al.*, 2016). Consequently, this results in the excessive abstraction of groundwater, particularly in arid and semi-arid regions, often reducing baseflow which may have negative impacts on ecosystem integrity and provision of water for basic human needs.

Integrated water resources management forms the foundation of South Africa's National Water Act (NWA; Act 36 of 1998) and emphasises the inherent need to manage surface water and groundwater systems as a single resource. South Africa is afflicted with various challenges related to the inefficient use of water resources, often exacerbated during periods of low flow associated with drought, dry seasons, and anthropogenic influences (Smakhtin and Watkins, 1997). Apart from ensuring that there is sufficient subsurface discharge into surface water to protect ecosystem integrity, NWA strategies also aim to maintain acceptable water quality (Levy and Xu, 2012). It is therefore critical to understand and quantify the dynamic fluxes between these water supplies, to improve understanding of hydrologic behaviour and achieve effective management and sustainable allocation of South Africa's stressed and scarce water resources.

It is projected that by 2030, South Africa will experience a water deficit of about 17%, progressively aggravated by climate change (WWF-SA, 2017). This will inevitably result in the increased development of groundwater reserves to augment surface water supplies, which may have significant implications for SW-GW connectivity. Quantifying and conceptualising SW-GW dynamics as part of achieving the successful implementation of the NWA remains a challenge in South Africa due to the vast dominance of fractured-rock terrain and the historic compartmentalisation of water resources (Smakhtin and Watkins, 1997; Smakhtin, 2001; Murray *et al.*, 2007; Levy and Xu, 2012).

The Vredefort Dome is renowned for being one of the largest, oldest, and most well-preserved meteorite impact structures on Earth's surface. The 2.02 Ga impact represents the single greatest energy release event known on Earth (Kamo *et al.*, 1996). It was declared a World Heritage Site by UNESCO in 2005 (Vredefort Dome Heritage Site; VDHS) to protect approximately a quarter of the dome for its exceptional geological value (IUCN, 2004); however, this has not yet been formally proclaimed in South Africa. The delineated area of the VDHS captures the centre of the astrobleme, located in the Witwatersrand Basin, roughly 120 km southwest of Johannesburg. The perennial Vaal River is the predominant drainage feature in the area and is of national importance (DEA, 2013).

Most anthropogenic activities in the VDHS rely solely on groundwater exploitation due to the rural nature of the area, as well as critical contamination and extensive utilisation of the Vaal River (Walt *et al.*, 2010). As these activities continue to proliferate, there are significant water quality implications associated with chemical and microbial degradation of the water resources.

There is a general shortage of groundwater in the area due to the near-surface location of the bedrock (Brink *et al.*, 2005). Streamflow occurs directly on the exposed bedrock, and coupled with thin soil cover, may result in extremely complex interactions between the two systems along the flow path (Abiye, 2013). Several extensive structural features and geological contacts are present in the lithological units underlying the bedrock along the course of the Vaal River- these may serve as potential conduits and thus preferential pathways for SW-GW connectivity (Oxtobee and Novakowski, 2003). In turn, hydrologic-exchange processes may result in compromised groundwater quality in mixing zones.

The groundwater system is under increasing stress, which has already been evidenced by low water levels in certain areas (Brink *et al.*, 2005; Walt *et al.*, 2010). Considering the current water demand in the VDHS, the Vaal River is relatively limited for future development and thus groundwater resources are increasingly exploited (Pretorius, 2009). However, Walt *et al.* (2010) also warn that under conditions of excessive groundwater abstraction, there is potential for induced recharge to occur from the Vaal River. The primary concerns are, therefore, groundwater availability and potential pollution from the contaminated river.

The hydrology of the VDHS, under the NWA regulatory framework, forms a key component of the *Strategic Environmental Management Plan* that requires specific strategic objectives (DEA, 2013). As such, characterising groundwater resource management units necessitates a thorough understanding of SW-GW linkage.

1.2 Research Problem

Brink *et al.* (2005) assessed the potential impacts of prospective mining in the VDHS and stated that the Vaal River does not infiltrate into the underlying groundwater (though this study was limited to a smaller scale in the north-western section of the region). A study conducted by Walt *et al.* (2010) identified five groundwater resource management units and undertook hydrogeological and social assessments to propose effective management and monitoring strategies in each unit. The authors inferred that recharge from the Vaal River is generally restricted, and some river reaches are characterised by effluent conditions. Furthermore, the groundwater chemistry revealed overall acceptable water quality within the region; the hydrogeological environment was largely unaffected by anthropogenic practices. However, some boreholes within the vicinity of the Vaal River showed compromised groundwater quality. Due to a lack of incorporation of the Vaal River water chemistry and microbiological characteristics, the implications of water quality between these two systems remain poorly understood.

The latest *State of Conservation for the Vredefort Dome World Heritage Site* report was submitted by the Department of Environmental Affairs to the World Heritage Centre in 2013 (DEA, 2013). This investigation emphasised concerns relating to microbial and metal contamination emerging from poorly treated sewage released into the Vaal River. Despite underlining the dire conditions in the Vaal River due to upstream users, the report provided no status of groundwater quality or SW-GW interaction.

No previous hydrogeological studies in the VDHS conducted research explicitly on SW-GW exchange processes, which is an important exercise required to achieve effective management strategies. Moreover, the extent of influence from human activities on the SW-GW interaction has not yet been quantified. Groundwater plays an essential role in sustaining the natural environment and human activities in the area (Brink *et al.*, 2005), so it is imperative to understand the hydrogeological dynamics and character to secure their conservation. It is also critical to maintain the integrity of the Vredefort Dome, especially when considering its significance as a natural and cultural heritage site in accordance with the World Heritage Convention Act (UNESCO, 1999).

The identification of areas that are susceptible to river-induced pollution may prove a useful contribution for the adaptive management of the subsurface system to meet the ever-increasing demand for groundwater supply. Additionally, this insight may help address any environmental issues concerning potential impacts on the underlying aquifers from anthropogenic activities.

1.3 Research Questions

The primary research questions are:

- a) How do the heterogeneous geological features and human activities influence SW-GW interaction in the VDHS?
- b) What are the dominant factors controlling the quality of water resources?
- c) What is the proportion of baseflow contributing to the Vaal River in relation to seasonality?
- d) What are the main mechanisms influencing groundwater recharge conditions?
- e) At what distance from the river channel does the Vaal River interact with the groundwater?
- f) Is the quality of the water resources suitable for their intended purposes?

1.4 Research Aim and Objectives

The aim of this study is to investigate the nature of SW-GW interaction, under the influence of anthropogenic activities using combined techniques in the VDHS. In addition, this study assesses the role of heterogeneous geology and its associated implications for hydrological connectivity, and thus, water quality characteristics within the VDHS.

The objectives of this study are to:

1. Evaluate the relationship between surface water and groundwater systems, and determine the distance from the river channel where hydrologic interaction takes place through hydrochemical, microbial, and stable water isotope methods.
2. Identify the origin and controlling mechanisms of groundwater recharge using stable water isotopes.
3. Characterise the dominant factors controlling the quality of surface water and groundwater, utilising microorganisms and multivariate statistics of hydrochemical data, and evaluate the suitability of water quality for its intended purposes.
4. Determine the quantity of baseflow contributing to the Vaal River using baseflow separation techniques.
5. Conceptualise groundwater flow, and identify recharge and discharge areas through spatial groundwater level mapping.

2. STUDY AREA

2.1 Introduction

The Vredefort Dome is centrally located in the north-eastern section of South Africa, as shown in the inset of Figure 2.1. It forms part of two provinces which are delineated by the Vaal River: the North West Province and Free State Province. The historical mining town of Venterskroon, located in a valley adjacent to the Vaal River, constitutes the only urban cluster within the VDHS. The major urban towns surrounding the designated core area include Potchefstroom, Vredefort, and Parys (Figure 2.1).

The VDHS is surrounded by an outer boundary (in blue) that is situated approximately 5 km away from the demarcated core area (in red), referred to as the buffer zone (Figure 2.1) (DEA, 2013). This zone was outlined during the declaration process to ensure the preservation of the area (Pretorius, 2009). Primary investigations of this study are restricted to the core boundary.

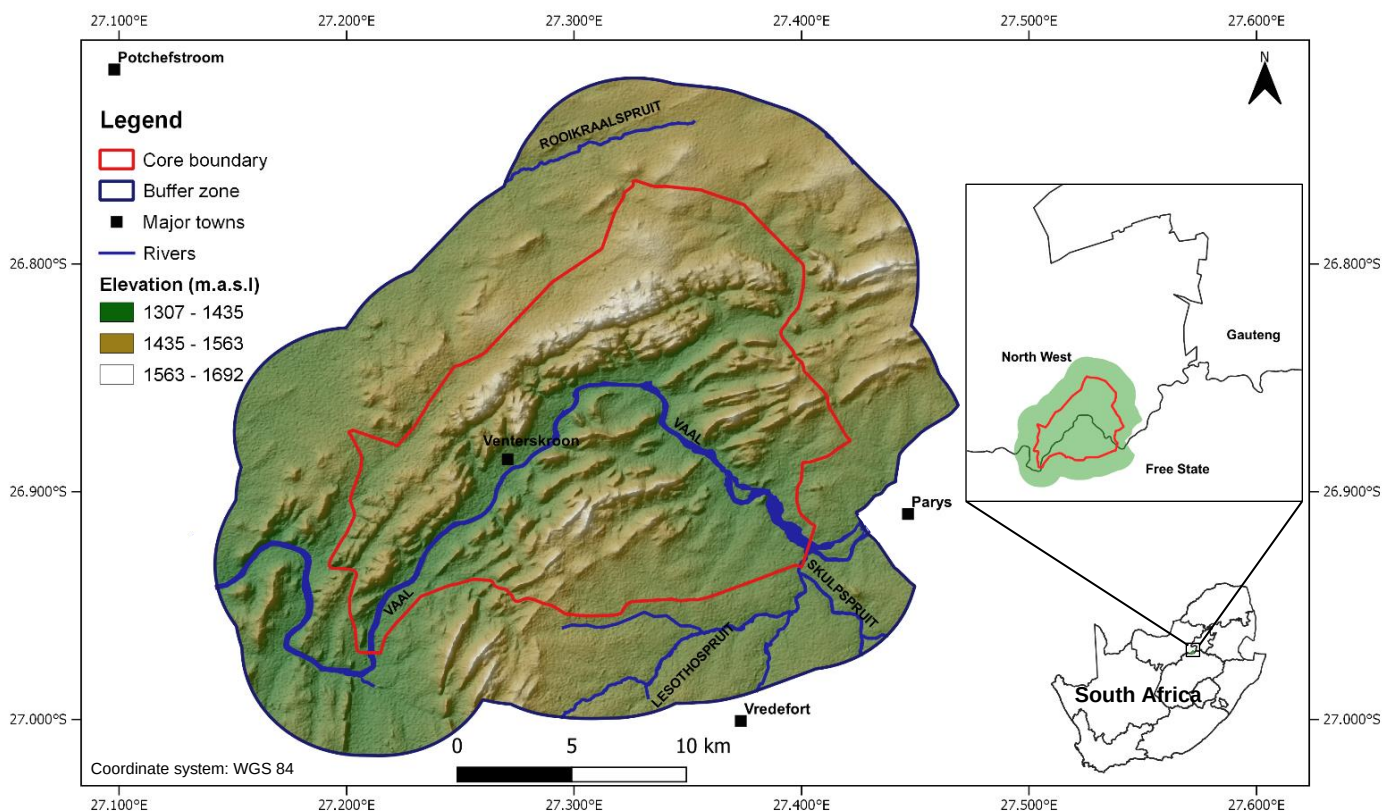


Figure 2.1. Location of the Vredefort Dome Heritage Site along with a 30 m resolution digital elevation model. The inset map shows the location of the study site in relation to the provinces of South Africa.

2.1.1 Hydrological setting

The major surface water bodies in the VDHS include the perennial Vaal River and its non-perennial tributaries, and wetlands (Figure 2.2 A) (DEA, 2013). The Vaal River serves as one of South Africa's major rivers, originating in the Drakensburg escarpment and predominantly drains the central Highveld region, forming the principal tributary of the Orange River (Bezuidenhout *et al.*, 2013).

The Vaal River drains the majority of the VDHS and flows from east to west through the core zone. The confluence of the Skulpspruit and Lesothospruit form a tributary to the Vaal River and drain the southern area outside of the core boundary; the Rooikraalspruit and Ouwertspruit drain the northern and eastern areas, respectively, eventually joining as tributaries to the Vaal River (Figure 2.1). The study area forms part of the C23C and C23L surface quaternary catchments, within the Barrage to Mooi sub-catchments, which fall under the Vaal Water Management Area (WMA)- one of the nine WMAs in South Africa.

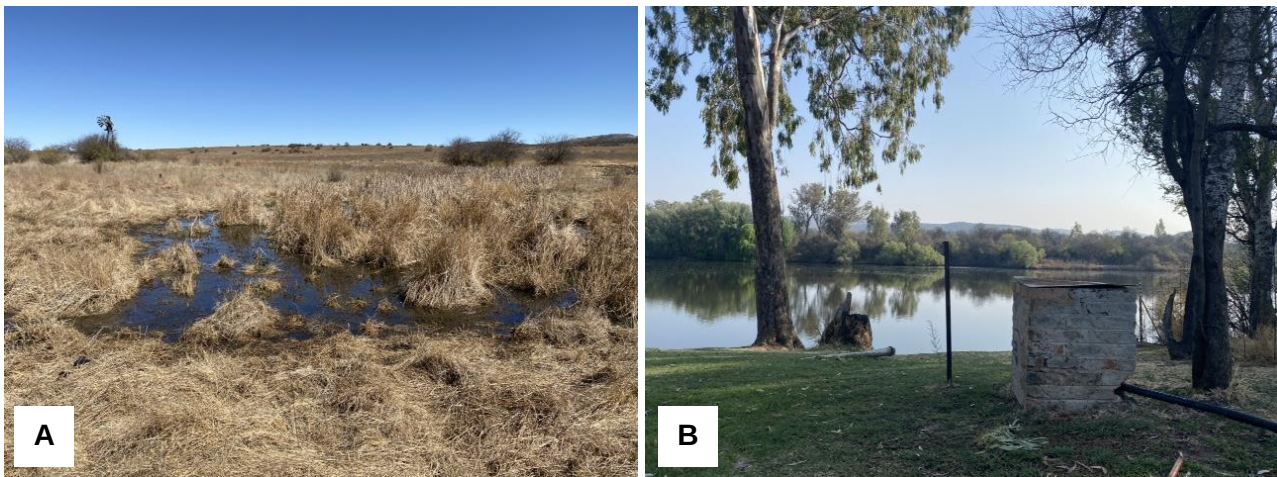


Figure 2.2. Images illustrating (A) an inundated grassland, representing a wetland (site SP 5), and (B) a borehole located on the Vaal Riverbank (site BH 42).

The Vaal system (Vaal River, Barrage, and the Dam) represents national significance as it sustains a high portion of the country's population and economic production. According to the South African Human Rights Commission (SAHRC) (2021) report, the National Treasury advised that roughly 19 million people are dependent on the water from the entire system. As a result, multiple transfer schemes are in effect to supplement the Vaal as the demands exceed the available water supply, particularly during the dry season (DWA, 2004; Mare, 2007). This system receives effluent from wastewater treatment plants and industrial activities along with a substantial amount of surface run-off, dewatering discharge from mines, and agricultural return flows, which mostly occur upstream from the VDHS (Wepener *et al.*, 2011; Bezuidenhout *et al.*, 2013). Consequently, the system is highly stressed and is characterised by poor ecological health and water quality (Pretorius, 2009).

In 2018, the Vaal River was subjected to severe pollution associated with raw, untreated sewage flowing directly into the river and its tributaries as well as into public and private spaces- this served as a tipping point for urgent and comprehensive intervention (Bega, 2018). Consequently, the river became green with scores of dead fish accumulating on the riverbanks (Figure 2.3), representing a serious health risk and environmental crisis. Thereafter, the SAHRC launched an inquiry into the sewage concern and reported that the Vaal system pollution exceeds acceptable standards, and highlighted the violation of constitutional rights (SAHRC, 2021). This was primarily attributed to the lack of maintenance and poor infrastructure development of wastewater treatment plants from local authorities situated upstream from the VDHS (Bega, 2018; SAHRC, 2021). As a result, the pollution has had a detrimental impact on the economy, followed by a noticeable decrease in recreational and tourist activities (SAHRC, 2021). The long-standing challenge of effluent release into the Vaal River persists, further reiterating South Africa's inadequate management of water resources.



Figure 2.3. Recent pollution in the Vaal River resulting in the death of much wildlife. Image obtained from <https://www.exploreparys.co.za/help-stop-the-vaal-river-pollution/>.

In 2004, the Department of Water Affairs and Forestry (DWAF) estimated a natural mean annual runoff (MAR) of 446 million m³/annum downstream of the Vaal Dam. During the field surveys undertaken, there was a foul smell, abundant algae, and foam present in certain areas. The riverbed morphology was characterised by alternating shallow, riffle (Figure 2.4 A) and deep pool (Figure 2.4 B) sequences.

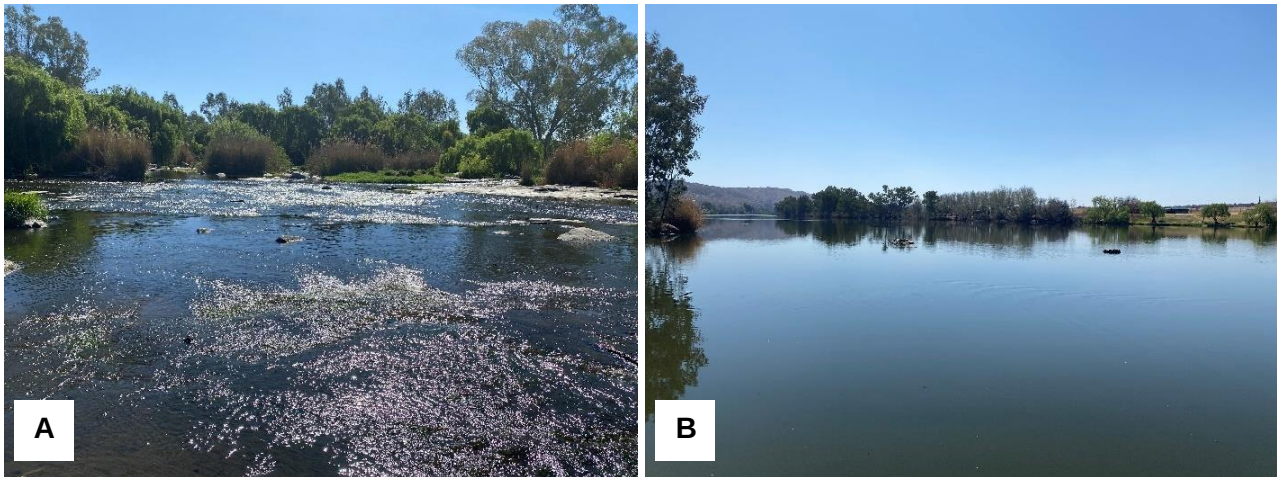


Figure 2.4. Images of the Vaal River showing **(A)** fast and turbulent current under shallow conditions dominated by riffles (27.4463 E; -26.9010 S) and **(B)** slow current under deep conditions associated with pools (site RV 8).

Usage of groundwater is primarily for domestic needs, agricultural practices, and recreational operations such as tourism (Walt *et al.*, 2010; DEA, 2013). The general status of the boreholes and groundwater use in the VDHS from the hydrocensus survey (Appendix A) is shown in Figure 2.5 and Figure 2.6, respectively. Only 170 of the 263 surveyed boreholes are in use (65%), whereas the remaining boreholes are unutilised mainly due to low yields, defective functional infrastructure, and lack of equipment. Of the boreholes that are currently operational, groundwater is largely extracted for domestic, multipurpose (dominated by domestic and livestock use), and livestock uses, representing 42%, 25%, and 9% of the total usage, respectively. An example of a typical borehole is shown in Figure 2.2 B. The well depths (Appendix A) range from 6 m to > 60 m, where the majority of the boreholes are between 21 – 30 m (25%), followed by > 60 m (23%) and 41 – 60 m (21%). The intermediate (31 – 40 m) and shallowest (6 – 20 m) well depths are associated with the lowest occurrence, represented as 16% and 15%, respectively.

Springs are generally rare with low yields and do not provide a regional water supply (Brink *et al.*, 2005; DEA, 2013). Similarly, yields from boreholes are generally low, and groundwater irrigation is limited to a local scale (DEA, 2013). From the hydrogeological investigations, it was apparent that the wetlands are solely sustained by groundwater, suggesting groundwater-dependent ecosystems.

They are predominantly present in the shallow alluvium overlying the granites of the basement complex, forming part of the Vredefort Dome Granite Grassland (Hobbs *et al.*, 2013).

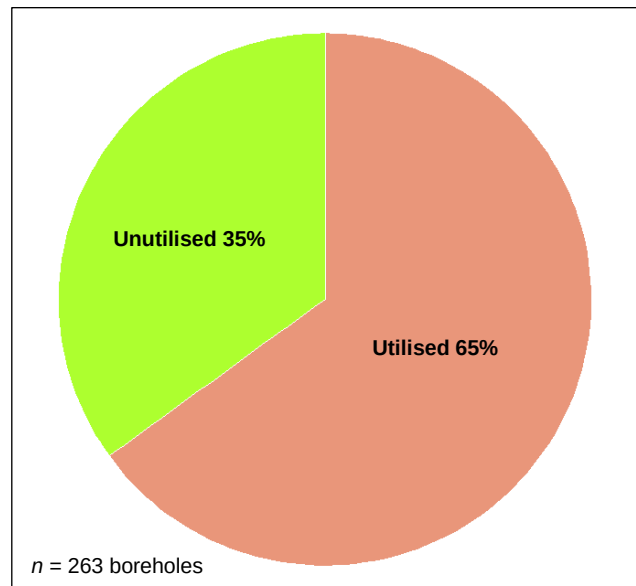


Figure 2.5. Summary of the borehole status in the Vredefort Dome Heritage Site.

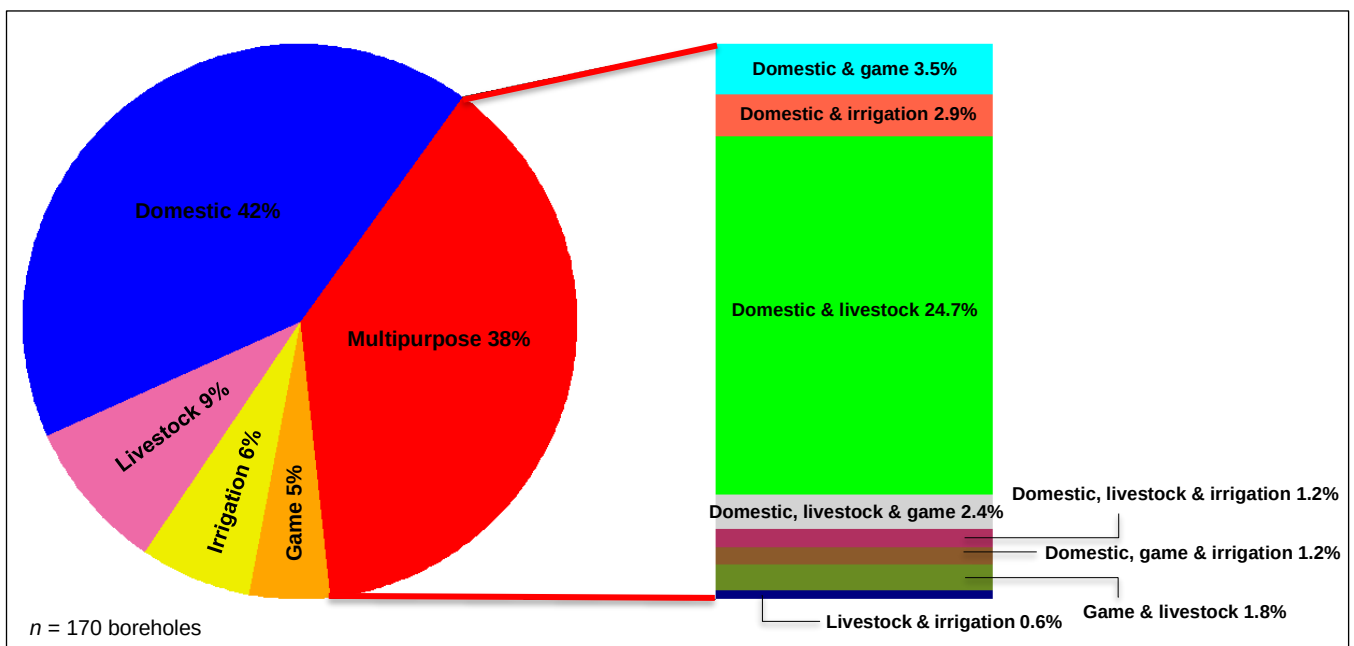


Figure 2.6. Summary of the groundwater use of the utilised boreholes in the Vredefort Dome Heritage Site.

The presence of dry boreholes and decreased surface water from springs points to the unsustainable abstraction of local groundwater. This was particularly noticeable in the windmill-driven groundwater pumps that were mostly dry, forcing residents to drill deeper boreholes. The highly contaminated Vaal River and over-exploitation of groundwater, amongst other factors, threaten the natural value of the heritage site (DEA, 2013).

2.1.2 Land use and cover

The land within the region is largely privately owned and predominantly used for tourism and mixed agricultural purposes. The former includes accommodation and recreational activities; the latter constitutes crop farming (Figure 2.7 A), game, animal husbandry (Figure 2.7 B, C), and to a lesser extent, conservation (Figure 2.7 D) (Pretorius, 2009; DEA, 2013).

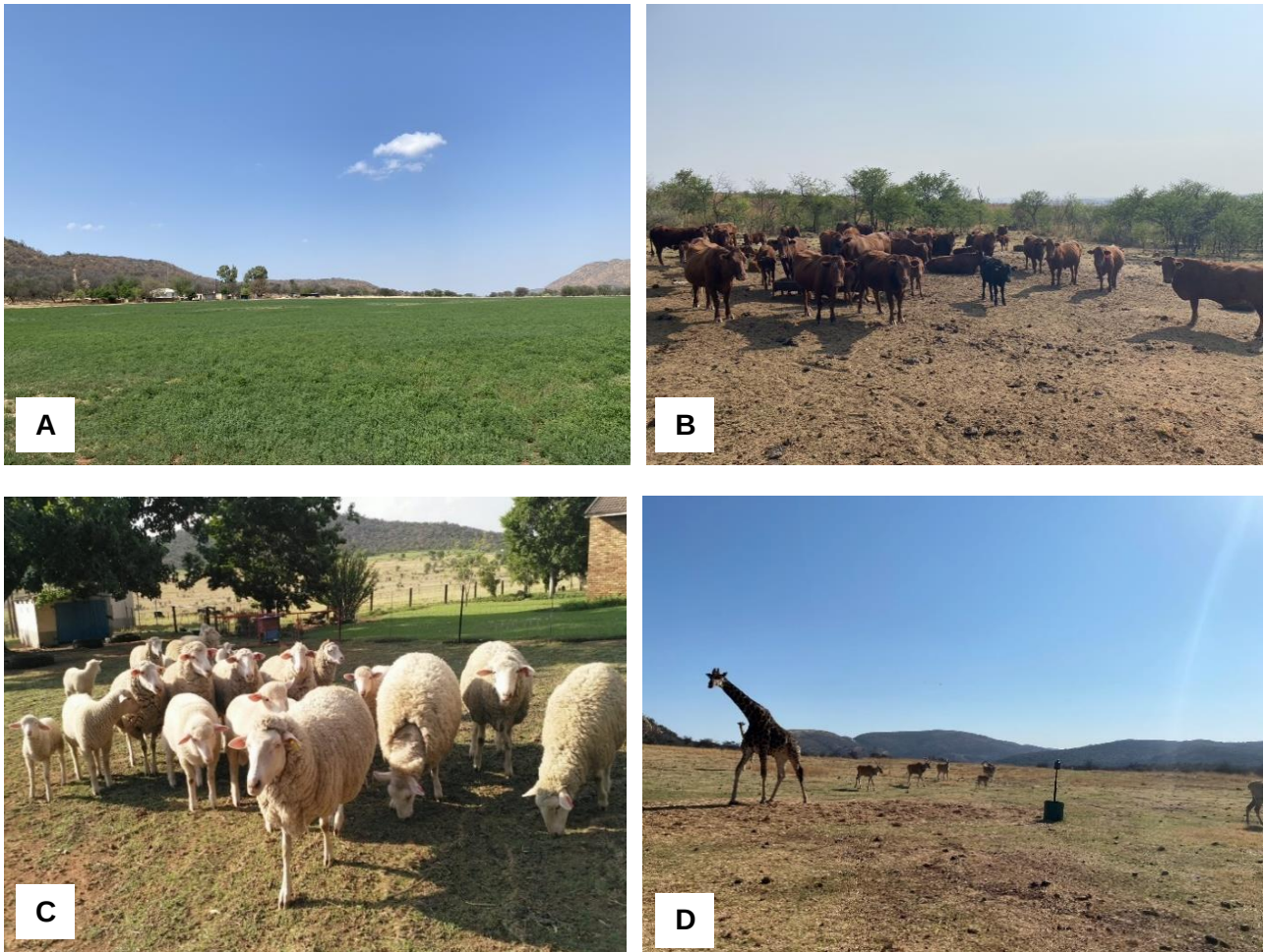


Figure 2.7. Images showing **(A)** lucerne crop farming situated near the Vaal River (site BH 146), common **(B)** cattle (site BH 131) and **(C)** sheep farming (site BH 211), and **(D)** game present on a conservation farm (site BH 48).

The Vredefort Dome serves as a notable tourist attraction and has a high value in the area (Brink *et al.*, 2005). As such, there has been an increase in the development of eco-tourism activities, some in addition to existing agricultural practices (DEA, 2013). Irrigation crop farming is localised, being mostly limited to the floodplains of the Vaal River, and these activities are visibly clustered along the river network.

The general land cover in the VDHS as of 2018 is presented in Figure 2.8. The Vredefort Dome is broadly classified as a grassland biome, hosting dense thorn bushes, shrubs, and trees in the ridges and valleys, whereas the plains are largely dominated by grasses. The natural vegetation often serves as grazing to feed livestock, game, and wild animals.

Grassland, cultivated, and forested land are the dominant land cover classes in the VDHS, covering 55%, 23%, and 20% of the area, respectively. The land cover remains largely natural, particularly in the ridges, supporting the occurrence of dense vegetation; however, landscape fragmentation is driven by expanding agricultural, recreational, and touristic activities (DEA, 2013). Moreover, Brink *et al.* (2005) and DEA (2013) highlight the potential vulnerability of the natural environment due to the overuse of groundwater resources.

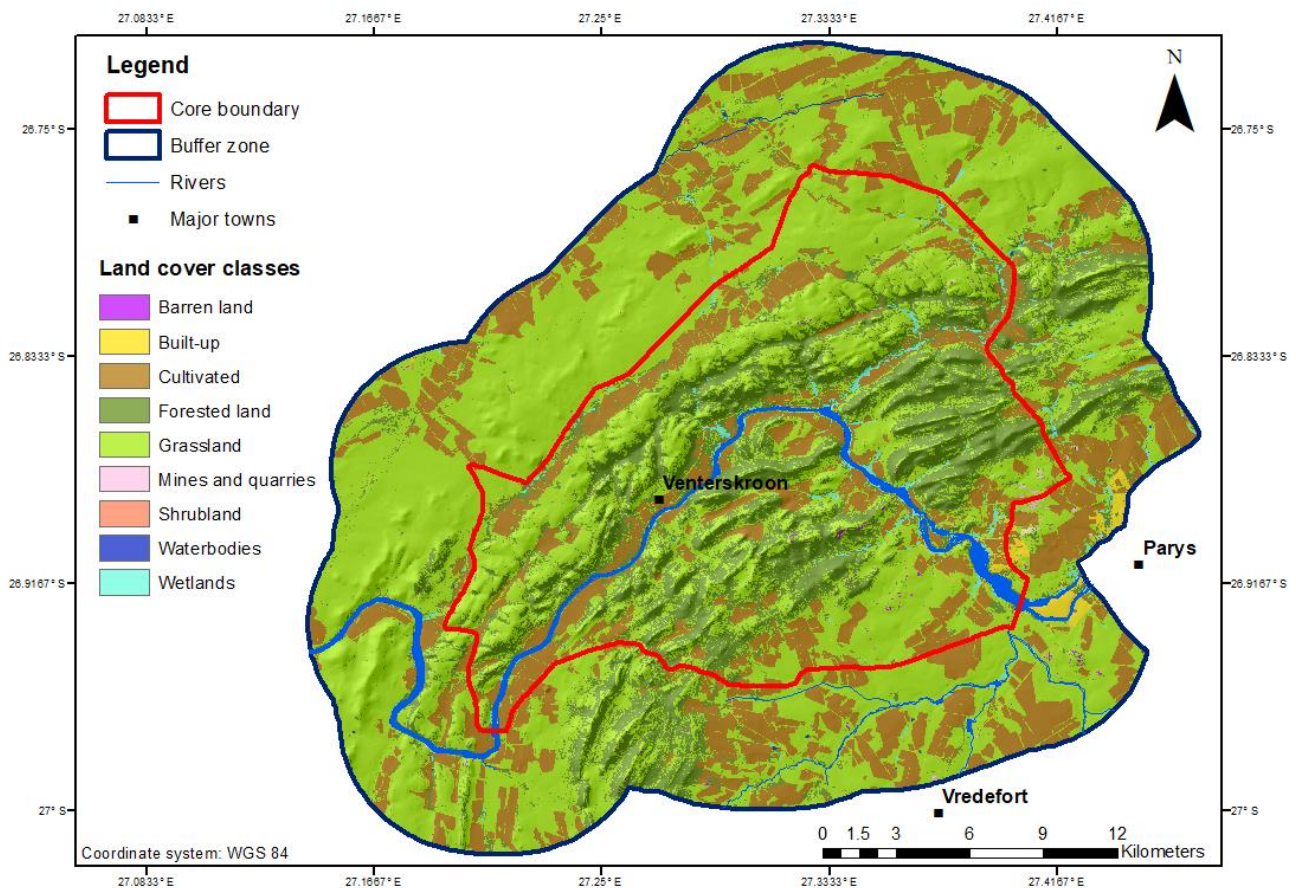


Figure 2.8. Simplified map showing the spatial distribution of various land cover classes in the Vredefort Dome Heritage Site (source of data obtained from the Department of Environmental Affairs; https://egis.environment.gov.za/data_egis/data_download/current)

2.1.3 Physiography and climate

The topography of the Vredefort Mountain Land ranges between ~1300-1700 metres above sea level (m.a.s.l) with moderate to steeply inclined slopes (Figure 2.1). The elevation decreases towards the valleys, thus representing the lowest depressions, whereas the hills are approximately 100 - 400 m higher.

The area is simplistically characterised by resistant, intact hills and weathered valleys, which represent the primary topographical features (Figure 2.9), whilst intrusive rocks constitute subsidiary cross-cutting valleys (Brink *et al.*, 2005). This heterogeneous terrain results in rainwater gravitating towards the valleys, ultimately draining into the Vaal network system.



Figure 2.9. The undulating landscape of the Vredefort Dome Heritage Site. The outcrop demonstrates the relatively intact and resistant hills in the study area.

The Vredefort Dome occupies the Central Highveld climate region. This semi-arid climate experiences hot, wet summers and cold, dry winters; summer months are characterised by highly variable and intense rainfall events and are prone to drought conditions, whereas the winter months are generally dry.

For the years 2018-2019 the average annual temperature in Vredefort was 22°C, and the mean maximum and minimum temperatures were 26°C and 10°C, which are generally experienced in January and July, respectively (Figure 2.10). Groundwater recharge is highly dependent on seasonal rainfall, which typically takes place during the wet season from October to April, with peak rainfall most commonly from February to March. The annual precipitation is approximately 550 mm (Figure 2.10).

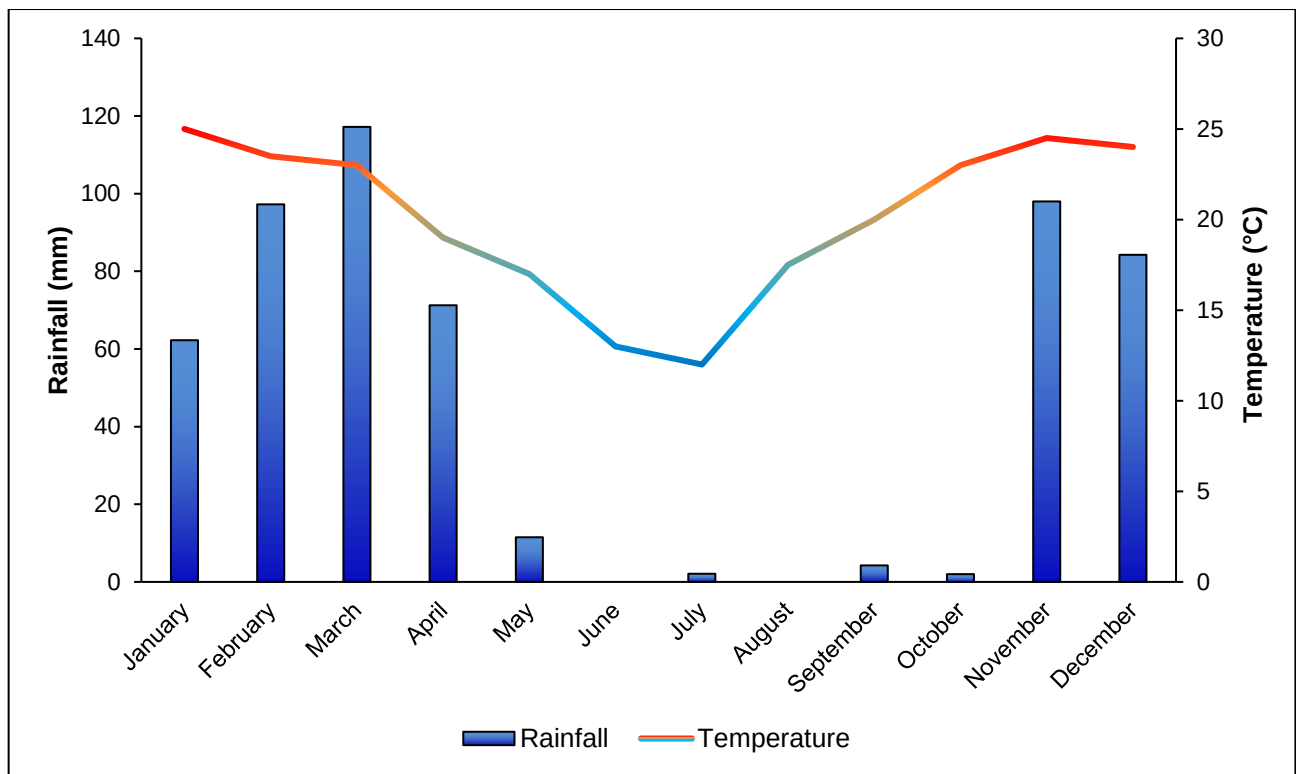


Figure 2.10. Average monthly rainfall and temperature recorded for the years 2018-2019 in Vredefort (data sourced from the South African Weather Services and World Weather Online; <https://www.worldweatheronline.com/vredefort-weather-averages/free-state/za.aspx>)

2.2 Geological Framework

The geological setting and topography serve as important elements that underpin the incentive for listing the Vredefort Dome as a World Heritage Site. The rare configuration represents a wide array of unique outcrops, spanning a vast geological record, demonstrating the various tectonic and geological evolutionary events that have collectively given rise to the complex and dynamic hydrological and hydrogeological nature of the region.

In the VDHS, the central core consists of pre-3.1 Ga Archean crystalline basement rocks, bounded by a prominent collar comprising deep, subvertical to overturned metavolcanics and metasedimentary units of the Dominion Group and Witwatersrand, Ventersdorp, and Transvaal Supergroups (ca. 3.07 - 2.15 Ga; Armstrong *et al.*, 1991) that were exposed on the surface (Reimold *et al.*, 2005; Gibson and Reimold, 2008). This is followed by the Potchefstroom Synclinorium of folded metasedimentary rocks from the Transvaal Supergroup, along with intrusions of varying ages occurring throughout the study area (Reimold *et al.*, 2005). A simplified geological map of the VDHS is shown in Figure 2.11.

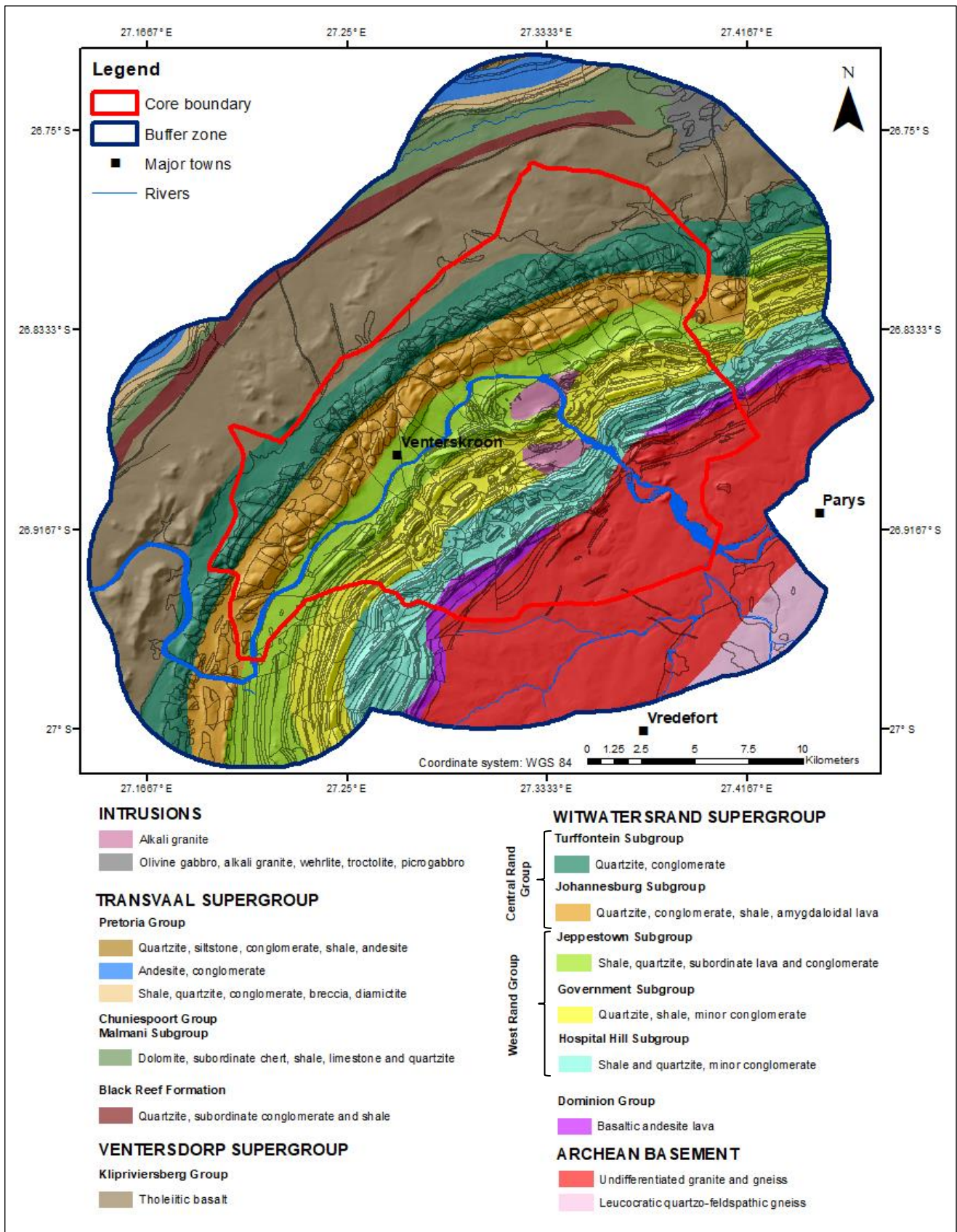


Figure 2.11. Simplified geological map and stratigraphy of the Vredefort Dome Heritage Site (source for data is the Council of Geosciences).

2.2.1 Vredefort impact structure

The Vredefort crater was formed through the impact of an extra-terrestrial object, estimated to be 10 km wide (French and Nielsen, 1990). This impact event exposed the crystalline basement, followed by a complex dome-shaped central uplift, which resulted in the widespread rotation and overturning of originally horizontal supracrustal strata (Figure 2.12) (Lana *et al.*, 2003; Brink *et al.*, 2005; Reimold and Gibson, 2006). The entire astrobleme feature extends approximately 250-300 km in diameter (Reimold and Gibson, 2006).

Much of the multi-ring basin has been deeply eroded, and the geological remnants form the present-day core and collar which constitute the Vredefort Dome (the centrally uplifted region). The dome represents an 80-90 km wide semi-circular structure that is made up of a 45-50 km wide central core enclosed by a 20-25 km wide crescent-shaped feature, surrounded by a 50-70 km wide rim syncline along the northern perimeter of the dome (French and Nielsen, 1990; Reimold *et al.*, 2005; Gibson and Reimold, 2008).

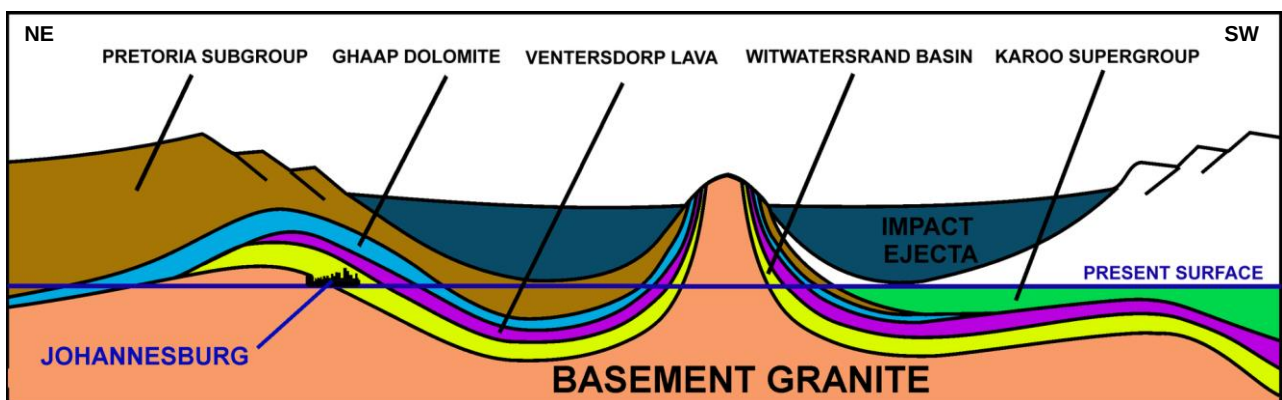


Figure 2.12. Cross-section of the Vredefort impact crater shortly after its formation (2.02 Ga), showing the deformation of the rocks, central uplifted region, and present surface. Adapted from <https://commons.wikimedia.org/w/index.php?curid=31069486> (By Oggmus - Own work, CC BY-SA 3.0).

2.2.2 Archean crystalline basement core

The central core is underlain by the poly-deformed Archean Basement Complex, and is characterised by a granitoid, gneissic, and migmatitic terrain with minor xenoliths consisting of metamorphosed mafic to ultramafic lava, shale, and ironstone (Lana *et al.*, 2003; Reimold and Gibson, 2006), present in the southern portion of the study area. Near the collar-basement boundary, the granites are younger and weakly foliated (Lana *et al.*, 2003).

2.2.3 Collar and synclinorium

The rocks of the Dominion Group occur at the base of the exposed collar and are separated from the basement by an unconformity. The supracrustal volcanic strata consist of metamorphosed andesitic to basaltic lavas that are unconformably overlain by the Witwatersrand Supergroup, which is divided into the West Rand and Central Rand Groups that are separated by an unconformity (McCarthy and Rubridge, 2005; Reimold and Gibson, 2006). The lower West Rand Group constitutes three subgroups; Hospital Hill, Government, and Jeppestown Subgroups, consisting mostly of subordinate meta-conglomerate beds and quartzite units intercalated with slate (generally iron-rich; meta-ironstone), banded iron formation, meta-pelite, and meta-diamictite units.

The Johannesburg and Turffontein Subgroups comprise the younger, auriferous Central Rand Group and are predominantly characterised by interlayered slate, quartzite, and fluvial meta-conglomerate (Reimold and Gibson, 2006). The differential erosion of the strata belonging to the West Rand and Central Rand Groups gave rise to the prominent topographical features associated with the inner and outer collar in the study area, respectively. The amygdaloidal flood basalts of the unconformable overlying Ventersdorp Supergroup constitute the basal Klipriviersberg Group in the study area and are predominantly present in the northern and western portions of the buffer zone. The stratum forms a subparallel zone with the formations of the Witwatersrand Supergroup (Pretorius, 2009).

The metasedimentary rocks of the Transvaal Supergroup encircle the Vredefort structure, defining the Potchefstroom Synclinorium (Reimold *et al.*, 2005). This consists of the lower Black Reef Formation, which represents an unconformity with the Ventersdorp lava and is successively overlain by the Chuniespoort and Pretoria Groups (Manzi *et al.*, 2013). The Black Reef Formation is composed of poorly exposed meta-conglomerate, quartzite, and slate, whereas the Chuniespoort Group is characterised by the carbonate rocks of the Malmani Subgroup, predominantly dolomites with chert fragments (McCarthy and Rubridge, 2005).

The strata of the Pretoria Group form a non-conformity and occur in the outer most northern and western margin of the VDHS; they are primarily composed of shale, quartzite, subordinate meta-conglomerate, andesitic lava, carbonate, and diamictite units (Gibson and Reimold, 2008). The Karoo Supergroup (300 – 180 Ma) strata cover the area southeast of the VDHS (Graham *et al.*, 2005). There are glacial deposits related to the Dwyka Group from the Karoo Supergroup and various Cenozoic Era (< 65 Ma) sediments throughout the study area, occurring as plains and terraces along the Vaal River network and within valleys (Brink *et al.*, 2005; Pretorius, 2009). This material represents a combination of alluvium and colluvium, composed of ferricrete, calcrete, gravel, silt, clay, sand, and lithic fragments.

2.2.4 Metamorphism, structural deformation, and intrusions

It is generally accepted that at least four major regional deformation events have occurred prior to the Vredefort meteorite impact (Lana *et al.*, 2003; Reimold *et al.*, 2005; Wieland *et al.*, 2005; Manzi *et al.*, 2013), followed by multiple post-impact tectonic events. Moreover, at least four metamorphism episodes (pre-impact and impact-induced) have taken place, resulting in a polymetamorphic terrain, ranging from greenschist- to granulite-grade facies (Gibson and Wallmach, 1995; Lana *et al.*, 2003). However, the vast majority of metamorphism and intense structural deformation is attributed to the meteorite impact. Thus, the Vredefort structure demonstrates the complex effects created by the sheer magnitude and force of the impact event, resulting in several characteristic geological features on various scales: these include planar micro-deformation features in minerals, extensive structural deformation, high-pressure polymorphs, shatter cones, pseudotachylite breccia, Vredefort Granophyre, ultramylonite, and chocolate boudinage (French and Nielsen, 1990; Kamo *et al.*, 1996; McCarthy and Rubridge, 2005; Reimold *et al.*, 2005; Reimold and Gibson, 2006; Gibson and Reimold, 2008; DEA, 2013).

The geological orientations of the structures are shown in Figure 2.13. Notably, the lineations largely trend perpendicular to the strike of the geological units and plunge northwest, opposite to the general dip direction (south to southeast) of the rocks due to overturning of the strata.

Several impact-induced kilometre-scale folds are present in the collar and rim synclinorium, predominantly within the West Rand and Pretoria Group strata, respectively (Wieland *et al.*, 2005; Reimold and Gibson, 2006). Pre-impact faults are preserved in the overturned strata and exhibit random orientations in the lithological units, signifying formation prior to the impact under compressive and extensional stress settings (Brink *et al.*, 2005).

Impact-induced faults display crosscutting relationships with the stratigraphic units, and their orientations to the dome vary between oblique and radial (Wieland *et al.*, 2005). The predominant fault displacement is left-lateral strike slip, followed by minor right-lateral strike slip and normal faults (Wieland *et al.*, 2005). Additionally, pre- and post-impact alkali granitic and mafic to ultramafic intrusions include, but are not limited to, dolerite, epidiorite, norite, and gabbro (Reimold and Gibson, 2006).

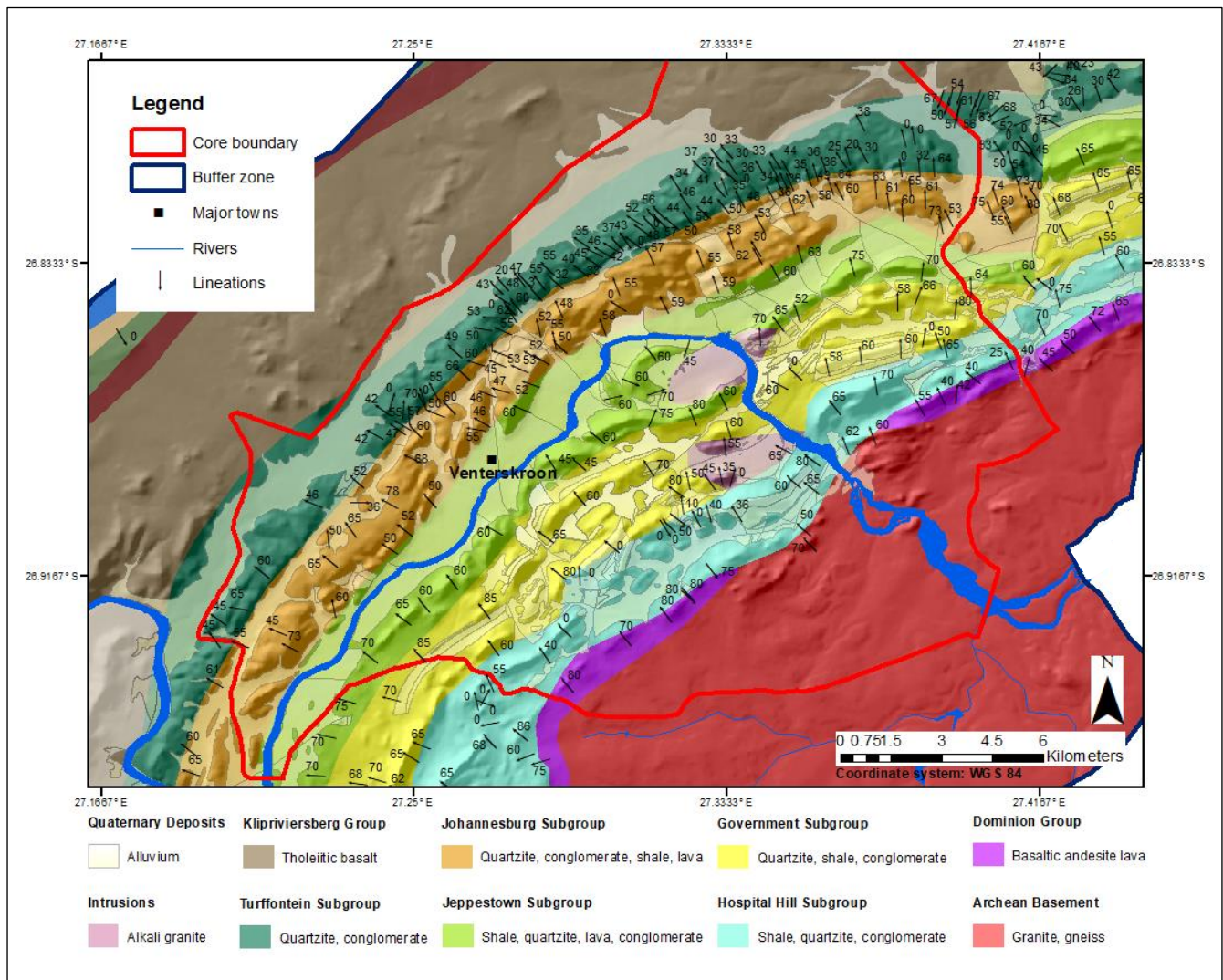


Figure 2.13. Orientations of the geological structures in the Vredefort Dome Heritage Site (source for data is the Council of Geosciences).

2.3 Hydrogeological Setting

The VDHS is predominately characterised by fractured and intergranular aquifer systems, and a combination thereof (Pretorius, 2009; Hobbs *et al.*, 2013): folded, faulted, jointed bedrock with secondary fissure porosity and permeability, and sand and gravel material with primary intergranular porosity and permeability. The former represents the secondary aquifers and consists of metamorphosed sedimentary and igneous rocks of the Basement Complex, Witwatersrand, and Ventersdorp Supergroups and intrusive volcanics; the latter constitutes the primary aquifers and comprise unconsolidated to semi-consolidated deposits associated with the glaciation period and the Vaal River network. In the northern portion of the VDHS, subsidiary fractured karst aquifers are related to the carbonate rocks of the Malmani Subgroup.

The hydrogeological setting is largely attributed to the intense deformation events, resulting in the formation of vast secondary hydrostructures. In the associated weathering processes, much of the groundwater potential largely remains driven by fracture aperture and interconnectivity. The ring-shaped deformation may play a considerable role in restricting and delaying groundwater circulation, thus potentially forming SW – NE elongated trending zones. However, the diverse orientations of the structural features, such as strike-slip faults and dykes, might serve as important conduits for groundwater movement and the occurrence of springs. Additionally, this complex configuration may result in the compartmentalisation of groundwater flow, as evidenced in the Upper Crocodile River Basin (RSA) (Abiye *et al.*, 2015).

Given the structural and geological heterogeneity, there are complex arrangements of faults and fractures along shear zones and dykes in the VDHS. During field surveys, it was noted that there are various sections along the river with exposed bedrock. The outcrops of the basement rocks demonstrate poor hydrogeological properties; they are largely massive (dense), dome-like, poorly jointed, and form tors (Figure 2.14 A) that are weathered in some areas. In these settings, most of the areas have relatively thin soil cover, generally ranging from 0 – 1 m. Wetlands are a common occurrence in these aquifer types (Figure 2.2 A), representing a shallow weathered zone under localised perched aquifer conditions.

Quartzite and metamorphosed lava units are characterised by widespread, randomly oriented, and variable fracture networks which are generally open (Figure 2.14 B, C), whilst the slate units have constrained fractures along inclined bedding planes (Figure 2.14 D) and lithological contacts. These lithologies have thicker overburden which are generally > 1 m (Figure 2.14 E), and are commonly defined by induced secondary permeability, representing deeper groundwater circulation.

The permeability of the metamorphosed sedimentary rocks decreases with increasing depth as it is anticipated that the weathered and fracture zones are mostly limited to the upper surface, where some structural features are possibly present at increased depth. Permeable fracture zones in between the layers of metamorphosed lava units may act as significant pathways for groundwater flow (Figure 2.14 F). The river bedrock units (Figure 2.14 A-D, F) highlight site-specific characteristics, demonstrating the potential of various controls on SW-GW linkage.

Successions dominated by quartzite are commonly characterised by the development of linear aquifers along structural deformation features and intrusions (Brink *et al.*, 2005), potentially serving as important conduits between lithological units and catchment areas (Pretorius, 2009). The highly fractured nature and orientation of these rock units could function as effective pathways for direct recharge (Abiye *et al.*, 2021).

The intergranular aquifer systems are restricted to the alluvial deposits from the Vaal River system, Dwyka sediments, and weathered material above bedrock. These highly heterogeneous coarse sediments can typically store large volumes of groundwater and are expected to be highly productive groundwater resources.

The diverse and complex hydrogeological settings and configurations give rise to manifold groundwater potential. The basement complex and intrusive rocks are generally characterised by low groundwater potential, reflecting a recharge of 3 – 4% of the mean annual precipitation (MAP) (DWAF, 2006). Similarly, igneous strata exhibit low groundwater potential with an estimated recharge of 4% of the MAP (DWAF, 2006). Quartzite successions are defined by low groundwater potential owing to the near-surface occurrence of these rocks (Brink *et al.*, 2005). Recharge for the Witwatersrand quartzites has been approximated to be between 3 – 4% of the MAP (DWAF, 2006). The unconsolidated and semi-consolidated material have moderate groundwater potential, which is characterised by higher transmissivity and storativity. Groundwater potential is often enhanced by structural deformation, dykes, overlying intergranular aquifers, and SW-GW interactions, representing localised areas of higher groundwater potential. The residence time of the groundwater appears to be relatively short (Walt *et al.*, 2010), suggesting a high turnover rate of recharge which is typically associated with mountainous regions.

According to a generalised borehole yield classification composed by Hobbs *et al.* (2013), the Vredefort Dome was categorised into the moderate yielding boreholes (0.5 – 2 L/s) in the fractured and intergranular aquifers, whereas the fractured aquifers were categorised into the low-moderate yielding boreholes (0.1 – 2 L/s). The Department of Water Affairs and Forestry (DWAF; 2000) estimated mean borehole yield values between 0.5 – 2 L/s for the Witwatersrand, Ventersdorp, and Transvaal strata which predominantly host fractured aquifer systems, whereas intrusive rocks rarely exceed 0.5 L/s despite representing fractured and intergranular aquifer systems (Hobbs *et al.*, 2013).

It was noted during the field investigations that groundwater hosted in the Turffontein Subgroup and Klipriviersberg Group gave rise to the highest borehole yields, while those in the Government and Hospital Hill Subgroups had the lowest borehole yields. A bedding-parallel fault, formed during the Ventersdorp taphrogenesis (involving the stretching and opening of Earth's crust), is located close to the top of Jeppestown Subgroup (Brink *et al.*, 2005). The units overlying this fault were similarly deformed and constitute aquifers that are relatively water-rich (Brink *et al.*, 2005), explaining the observed borehole yields in the strata of the Turffontein Subgroup and Klipriviersberg Group.

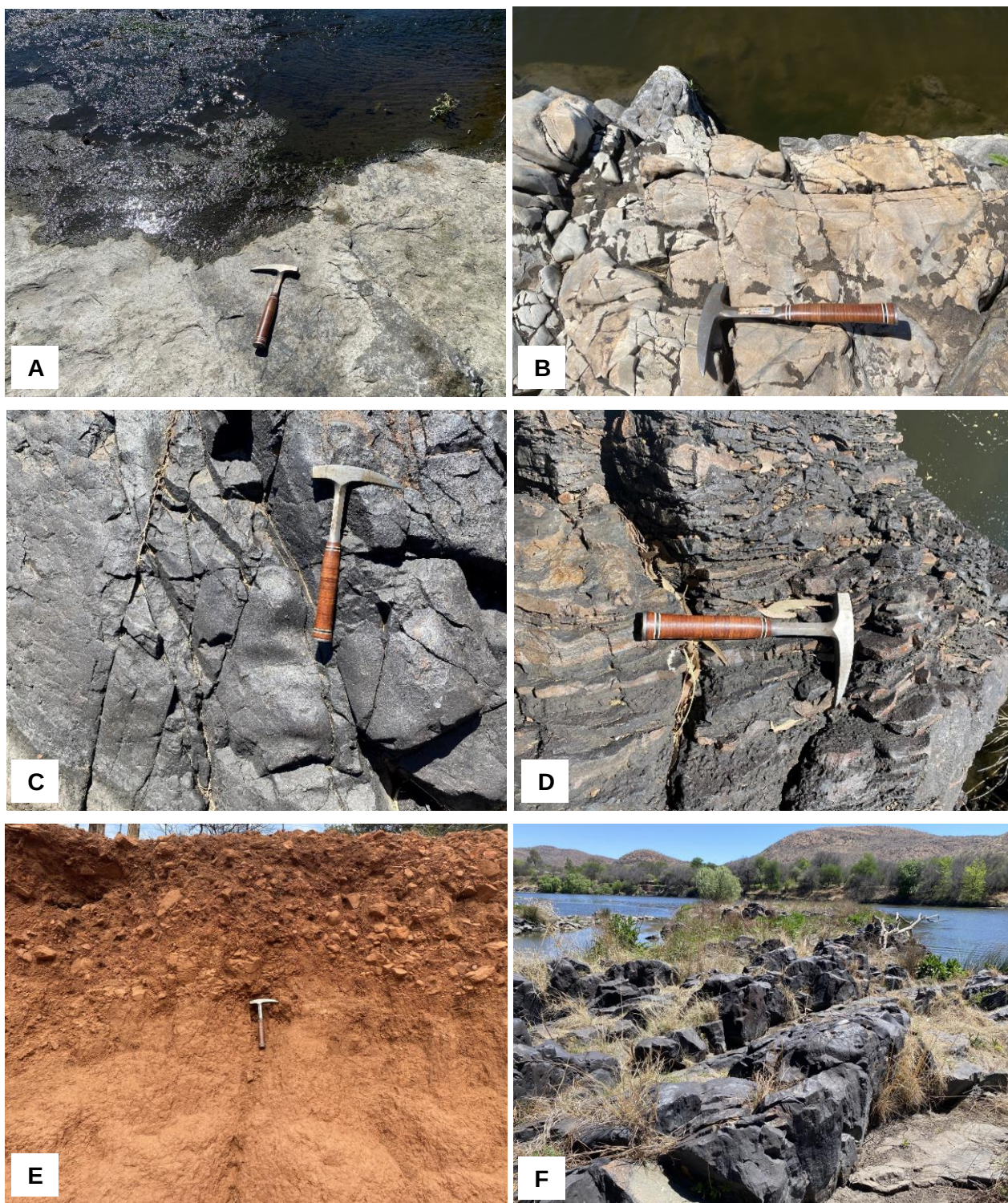


Figure 2.14. Images showing the bedrock outcropping along the riverbank with **(A)** underlying massive granite (27.4463 E; -26.9010 S), highly fractured **(B)** quartzite (27.3601 E; -26.8856 S) and **(C)** lava units (site RV 5), as well as **(D)** slate bedding plane fractures (27.3599 E; -26.8855 S). **(E)** Thicker overburden associated with supracrustal rocks (27.2498 E; -26.8791 S) and **(F)** tilted lava with fracture zones on the riverbank (site RV 5).

3. LITERATURE REVIEW

3.1 Overview of Surface Water-Groundwater Interaction

SW-GW interaction takes place via exfiltration from or infiltrating into the saturated zone (or a combination of both), as well as by lateral subsurface movement through the unsaturated zone. Thus, the flow dynamics are intrinsically multidimensional (Sophocleous, 2002). In fluvial systems, this occurs below the water surface and along the riparian zone and stream banks (Abiye, 2013)- furthermore, the hyporheic zone marks the area where subsurface water and river water locally mix. Subsequently, the chemical and physical seepage fluxes generated by these interactions play a significant role in the hydrologic cycle (Toran, 2019). Evaluating the relationship between these water resources should be a prerequisite to obtain the most effective and sustainable management.

Regional hydrogeological environments have profound control over groundwater systems, and so SW-GW linkage is largely influenced by context-specific settings. These interrelated controlling factors include climate, geology, and surface topography (Sophocleous, 2002; Guggenmos *et al.*, 2011). Climatic factors primarily influence the rates of hydrological processes, which in turn affect the groundwater level and surface water stage; topography influences the groundwater flow systems. The geology exerts significant control over the extent of hydraulic conductivity and connectivity within the rocks and between water resources, respectively (Smakhtin and Watkins, 1997; Levy and Xu, 2012). The latter is more accurately described by local hydrogeological properties of rocks and/or soil media which govern groundwater flow systems.

According to Sophocleous (2002), the exchange direction and magnitude depend on the groundwater level and hydraulic properties of the media, respectively. In parallel, this controls the movement of pollutants between water resources (Khan and Khan, 2019). Infiltrating surface water quality is usually modified and improved through the effective removal of biological and chemical contaminants during its passage through the hyporheic sediments (Sophocleous, 2002; Driehum *et al.*, 2018). Recharge events are generally controlled by seasonal precipitation and are the main factors controlling groundwater levels. These flow directions are differentiated under two conditions: i) effluent conditions associated with the subsurface water discharging into surface water (*gaining* stream; Figure 3.1 A) and ii) influent conditions associated with the subsurface receiving recharge from surface water (*losing* stream; Figure 3.1 B) (Brenot *et al.*, 2015; Toran, 2019). Furthermore, both conditions can arise along different reaches of the same surface water body.

The linkage between water resources is highly dependent on hydraulic properties (e.g., permeability) and unfavourable conditions may result in isolated systems (Xu *et al.*, 2002) (Figure 3.1 C). Streams dictated by structural controls constitute special cases where the interaction with

subsurface water is site-specific (requiring fractures for connection), while in cases of unconsolidated porous media underlying the channel bed, interaction is more gradual and widespread (Oxtobee and Novakowski, 2002, 2003). Generally, during a dry season, river discharge is sustained by baseflow (effluent conditions); during a wet season there is increased input from precipitation, interflow, and surface runoff, which promotes groundwater recharge (influent conditions) (Freeze and Cherry, 1979).

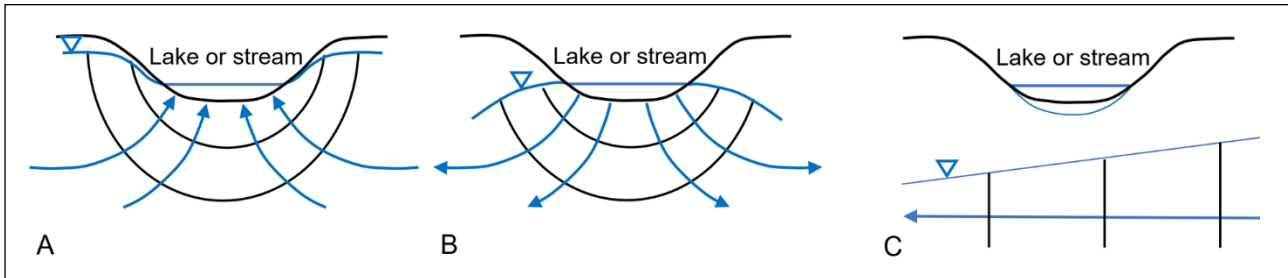


Figure 3.1. Surface water-groundwater connectivity that takes place under **(A)** effluent (*gaining stream*), **(B)** influent (*losing stream*), and **(C)** disconnected conditions with no interaction taking place (Adapted and modified from Toran, 2019).

The nature of SW-GW interaction is often modified by direct and/or indirect anthropogenic activities (Sophocleous, 2002; LaBaugh and Rosenberry, 2008; Levy and Xu, 2012; Yang *et al.*, 2012; Toran, 2019). These include over-abstraction, treated and untreated wastewater discharge, land-use modifications, dams, and water transfer schemes (Smakhtin and Watkins, 1997; Mencia and Mas-Pla, 2008; Zhu *et al.*, 2019). These changes can potentially exert an influence on the hydraulic connectivity between the water resources, subsequently increasing the vulnerability to pollution (Sophocleous, 2002; Kazakis *et al.*, 2017).

Processes such as deposition and erosion have the potential to modify the hydraulic properties at the aquifer-stream boundary (Sophocleous, 2002). Anthropogenic impacts, particularly sewage release, promote algal growth and increase sedimentation which may subsequently exacerbate the clogging at the SW-GW interface (Sophocleous, 2002). The magnitude of these effects is often related to the intensity of various land-use practices (Levy and Xu, 2012). As a result, this may have significant implications on the ecological balance and the extent of SW-GW exchange processes. However, extensive clogging may conversely serve as a barrier that protects the groundwater system from pollution (Younger *et al.*, 1993).

Over-pumping of groundwater results in decreased subsurface discharge to surface water bodies (Sophocleous, 2002; Rugel *et al.*, 2016; Messene, 2017). Consequently, this has considerable impact on the functionality of terrestrial and aquatic ecosystems, as well as downstream users (Brenot *et al.*, 2015). At high pumping rates, the decreased groundwater level induces influent conditions on the surface water body, known as induced recharge (Figure 3.2). In contrast,

wastewater input and water transfers may increase discharge in surface water bodies and can subsequently alter groundwater recharge rates (Zhu *et al.*, 2019).

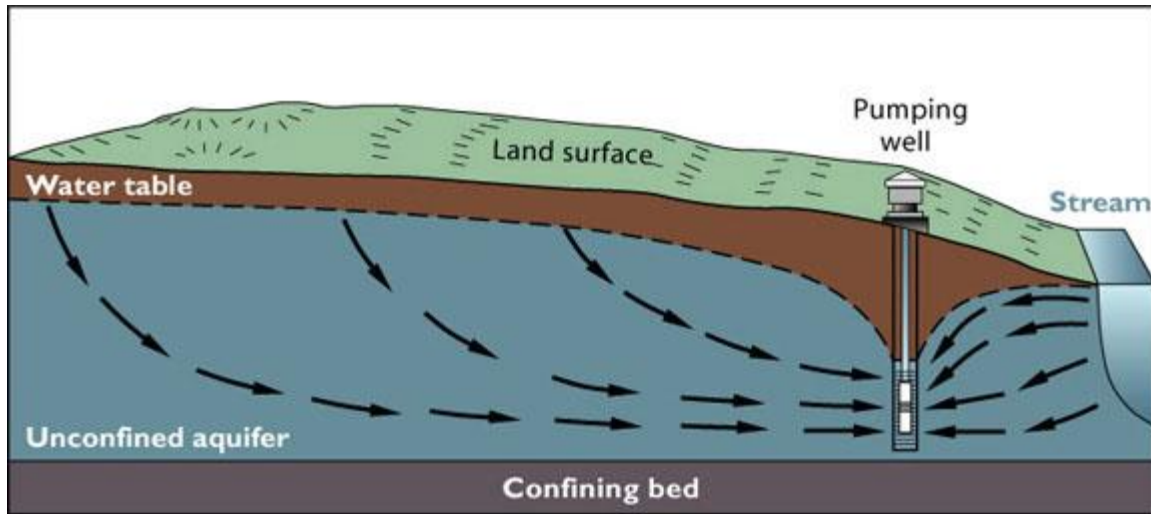


Figure 3.2. The influence of pumping wells on groundwater levels resulting in induced recharge conditions. Adapted from https://livinghistoryfarm.org/farminginthe50s/water_12.html.

Several studies (e.g., Rugel *et al.*, 2016; Zhang *et al.*, 2018; Khan and Khan, 2019; Zhu *et al.*, 2019) have shown the influence of decreasing groundwater levels due to over-abstraction which limit baseflow contributions, and thus induce recharge from surface water. The quality of the artificial water released, however, may degrade the integrity of the surface water, and varying interactions with the underlying aquifer can transfer contaminants. Groundwater depletion coupled with induced recharge (subsurface and surface water loss, respectively) decrease the overall available water for ecosystems and disturb their functionality.

3.2 Methods to Monitor Surface Water-Groundwater Interaction

Understanding and inferring the complex and dynamic mechanisms operating during SW-GW interaction proves to be a difficult task. Globally, numerous conventional methods are available and continuously developed to study the nature of the hydrologic exchanges, but various challenges and uncertainties persist. Quantification of SW-GW linkage does not give fixed values; instead, it is dependent on a range of various spatio-temporal conditions, and not all approaches are suitable for specific hydrogeological settings. Thus, any information relating to this exchange could be useful for adaptive management strategies.

Analyses of SW-GW interchanges are highly dependent on the spatial scale (Sophocleous, 2002; Levy and Xu, 2012; Khan and Khan, 2019) and, therefore, methods are subdivided according to appropriate scale; local (< 10 m), reach (10 - 1000 m) and regional (> 1000 m). The hyporheic zone

characterises small-scale interactions, whereas large-scale interactions are affected by the entire catchment (Khan and Khan, 2019). Site-specific investigations are important to achieve more accurate estimations by accounting for hydrologic spatio-temporal variability and local heterogeneous geology (Levy and Xu, 2012), which subsequently provide a good basis for larger-scale studies. The various scales then demonstrate the nested hierarchy of groundwater flow systems. The most popular tools that are available to investigate hydrologic-exchange processes are summarised in Table 3.1, highlighting their merits and limitations.

Table 3.1. Summary of common methods applied in assessing hydrological interactions.

Technique	Scale	Advantages	Disadvantages
Biological indicators	Local Reach	Useful to locate potential hydrologic exchange areas ⁵	Difficult to apply in humid regions ¹
Differential stream gauging	Reach	Effective in small streams ⁵	All water fluxes need to be known ^{1,5} Difficulty in identifying appropriate reach ² High-flow conditions are difficult to monitor ^{2,5}
Dyes	Reach	Conservative ^{4,5,7}	Equipment and time expense ⁴
Hydrochemical tracers	Regional	Naturally occurring tracers are applicable ⁴ Dyes have a minor impact on the environment ^{5,7}	Difficulty in detecting tracer at transition zone ⁴ Tracer dilution and potential reactivity ^{4,7}
Hydrochemistry	Reach	Can provide insight into contamination from exchanges ¹⁰	Chemical trends lack causation ¹
	Regional	Suitable to identify interactions on a large-scale ¹⁰	Anthropogenic alterations of water chemistry ¹⁰
Hydrograph separation	Reach	Quantitative estimates of flux ^{2,9}	Separation methods are arbitrary ^{1,8}
	Regional		Fails to distinguish sources ^{1,8,9} Potential to ignore spatial heterogeneity ¹
Modeling	Regional	Easily accessible software ⁴ Various modules are available for detailed analyses ⁴	Limited for coupled flow and contaminant transportation ^{3,5} Calibration and time challenges ^{3,4,10}
Remote sensing	Reach Regional	Able to distinguish point and diffuse discharge ⁵	Inaccessible and unreliable during bad weather conditions ²
Seepage meters	Local	Provide direct measurement of hydrologic flow ^{4,5,6}	Poorly account for spatial heterogeneity ^{2,6}
Mini-piezometers		Various modifications available for specific settings ^{4,5,6}	Difficult to use in a fast-flowing stream ^{2,6}
Stable water isotopes	Reach Regional	Conservative ⁴	Fractionation must be significant between water sources ^{5,10}
Thermal profiling	Local Reach Regional	Qualitative and quantitative analytical methods ^{4,10} Inexpensive ^{4,5} Robust natural tracer ⁵	Challenge to detect diffuse discharge ² High contrasts are required ^{2,10}
Water balance/budget	Reach Regional	Useful to distinguish gains and losses on a large-scale ¹⁰	Potential disregard of local impacts ¹ Overlooks seasonal variation ¹ Difficulty in acquiring all relevant data ⁴

¹Levy and Xu (2012) ²Toran (2019) ³Mugunthan *et al.* (2016) ⁴Rosenberry *et al.* (2014) ⁵LaBaugh and Rosenberry (2008) ⁶Rosenberry *et al.* (2008) ⁷Taylor and Greene (2008) ⁸Kilian *et al.* (2019) ⁹Smakhtin (2001) ¹⁰Coluccio and Morgan (2019)

There are various uncertainties and errors associated with the use of single techniques to quantify SW-GW interactions and reliance on one method alone has proven to be futile. In response, numerous authors (Sophocleous, 2002; LaBaugh and Rosenberry, 2008; Levy and Xu, 2012; Brenot *et al.*, 2015; Rugel *et al.*, 2016; Khan and Khan, 2019) encourage the use of a combination approach to evaluate the nature of these interactions accordingly, on a multiscale and multidisciplinary approach. For this study, methods of investigation were selected based on their viability for scale, available resources, and fractured aquifer settings to effectively delineate potential SW-GW exchange zones. The tools used for this study were principally developed for applications in porous media, however, have been found to be useful in fractured aquifer terrains (e.g., Oxtobee and Novakowski, 2002; Madlala *et al.*, 2019). These methods represent those applied in larger-scale contexts, which are more suitable for addressing policy needs (Levy and Xu, 2012), and are briefly discussed in the following subsections.

3.2.1 Hydrochemistry

Hydrochemical parameters serve as naturally occurring tools that are useful to trace water movement along various flow paths and shed light on water quality. Such tracers include dissolved ions, stable and radioactive isotopes, temperature, and *in situ* parameters (Coluccio and Morgan, 2019). This brief overview addresses the use of major dissolved ions and *in situ* variables, whereas stable water isotopes are discussed separately under Section 3.2.4.

Groundwater is often characterised by higher, less variable ionic concentrations relative to surface water, which is more susceptible to diurnal and seasonal variability. This occurs due to the tendency of groundwater to be isolated from the atmosphere and in direct contact with geological material for extended periods. These hydrochemical contrasts and different chemical environments tend to impact redox reactions, precipitation-dissolution conditions, and ion transportation, subsequently altering water quality traits along various flow paths (Toran, 2019). Thus, exchanges between the two systems may be detectable (Mencio and Mas-Pla, 2008; Guggenmos *et al.*, 2011; Abiye, 2013; Coluccio and Morgan, 2019).

Analyses of water quality characteristics are useful to infer any discrete exchange processes and pathways, highlighted by distinct chemical compositions (Levy and Xu, 2012). Zondlo (1998) utilised the hydrochemical approach to identify point groundwater discharge zones close to Oak Ridge, Tennessee (USA). This method was successful where there was direct stream contact with the fractured bedrock; however, the presence of sediment deposits led to indirect contact, and discharge areas were dispersed, making it difficult to delineate these areas.

The hydrochemical character of the water resources elucidates water quality variations relative to the regional geological formations and anthropogenic activities. Therefore, the assessment of the spatial distribution of water quality parameters provides an overview of the origin of water composition. Khan and Khan (2019) studied shallow groundwater contamination in the riparian zone from the Kali River in India. The study showed the negative implications of polluted surface water on groundwater quality, where the Kali River had been identified as a *losing* regime along the study reach. Moreover, the chemistry of the groundwater revealed a limit on SW-GW interaction with distance from the river attributed to potentially clogged riverbed conditions.

Hydrochemical analyses include the use of multivariate statistical methods and graphical techniques to characterise water chemistry and have been applied successfully in numerous studies to describe water quality signatures (e.g., Mencio and Mas-Pla, 2008; Rugel *et al.*, 2016; Masindi and Abiye, 2018; Khan and Khan, 2019). Graphical analyses of major ion chemistry are useful to visually describe and categorise dominant water compositions, but fail to account for physical parameters

and trace elements (Tay *et al.*, 2017). By contrast, multivariate statistical techniques can subdue the above constraint (Kazakis *et al.*, 2017).

Multiple studies have suggested that similarities in chemical characteristics between adjacent surface water and groundwater systems (highlighted by clusters or components) can be used to infer potential hydrological connection (Kumar *et al.*, 2009; Guggenmos *et al.*, 2011). Thus, multivariate statistical methods can be utilised as investigative tools to delineate potential zones of SW-GW interaction. Hierarchical Cluster Analysis (HCA) is a common data reduction technique that uses the statistical similarity of parameters to group monitoring sites into a set number of clusters (Guggenmos *et al.*, 2011). As such, monitoring sites partitioned within the same clusters represent statistical similarity and are illustrated by a dendrogram.

Principal Component Analysis (PCA) is a powerful statistical technique that is increasingly utilised to evaluate variations of hydrochemical constituents. Within a group of observed variables, this approach attempts to delineate underlying factors that best describe the pattern of correlations (Basto and Pereira, 2012). This is achieved by reducing variables and computing new components (referred to as principal components) by using the variances of the manifest variables (Basto and Pereira, 2012). This statistical application reveals hidden structures and aids in the interpretation of complex data matrices, which enhance the understanding of water chemistry and indicate potential factors influencing regional composition (Kazakis *et al.*, 2017; Tay *et al.*, 2017). Varimax rotation is commonly applied to assist the interpretation of the PCA output by clarifying and simplifying the data structure. Rotations highlight the variables with higher contributions to variance by computing rotated orthogonal factor loadings (Mencio and Mas-Pla, 2008).

3.2.2 Hydrograph separation

Hydrograph separation is a quantitative technique that is useful in estimating groundwater inflow into rivers. Natural streamflow generation is assumed to originate from the input of quick flow (surface runoff) and baseflow components. The former refers to eventful surface input (overland flow, direct rainfall, etc.) in response to precipitation events; the latter constitutes subsurface flow occurring from aquifer storage in the saturated zone and other delayed sources (Welderufael and Woyessa, 2009; Kilian *et al.*, 2019) driven by variable response time scales (Lyne and Hollick, 1979). This approach then distinguishes quick flow and baseflow components from time-series discharge data accordingly using recursive digital filters (Nathan and McMahon, 1990). In addition to this, there are various hydrologic processes and anthropogenic contributions that need to be considered which can potentially obscure the results (Welderufael and Woyessa, 2009).

Quick flow contribution to streamflow is highest *during* and *instantly after* precipitation events, but may influence the hydrograph for extended periods (Kilian *et al.*, 2019). This component represents

the peaks in hydrographs and is computed as the difference between baseflow and total stream discharge (Barlow *et al.*, 2015). In between precipitation events, streamflow is commonly sustained by baseflow which is generally derived from the delayed subsurface flow, and thus depends on the rate of subsurface discharge (Smakhtin, 2001; Sophocleous, 2002; Saraiva Okello *et al.*, 2018). Baseflow is computed as the minimum stream discharge over a certain period (Barlow *et al.*, 2015).

In South Africa, baseflow separation methods are most often applied to estimate groundwater fluxes (Xu *et al.*, 2002; Levy and Xu, 2012). However, these techniques are based on several generalised assumptions and limitations which restrict their applicability and appropriateness, as outlined by Barlow *et al.* (2015). Smakhtin and Watkins (1997) indicate that if an aquifer is characterised by a shallow water-table or wide fracture network coupled with sufficient recharge rates, hydraulic connectivity, and storage properties (to maintain flow to the surface water), then SW-GW interaction may be taking place.

The VDHS represents a predominant fractured rock setting with heterogeneous recharge zones in the mountains and alluvial plains, as well as relatively shallow groundwater levels in certain areas (as evidenced by the variety of wetlands and springs). It also exhibits an extensive structural network in the underlying geological units representing direct contact with the channel, which may provide adequate storage and serve as pathways for flow into the river. Thus, it is assumed that the VDHS conforms to the applicability of this method under effluent conditions. However, in fractured aquifer terrains, Levy and Xu (2012) warn that the application of baseflow separation to a single hydrograph can disregard spatial heterogeneity and so potentially overlook implications associated with the spatial arrangement of boreholes.

Using hydrograph separation methods, Kilian *et al.* (2019) showed that decreased baseflow was related to areas that experienced water-table declines due to over-abstraction in the Mississippi River Valley alluvial aquifer (USA). Within a South African context, Madlala *et al.* (2019) successfully applied baseflow separation techniques in the upper Berg River (Western Cape Province, RSA) and demonstrated the dependence on groundwater discharge to sustain streamflow.

3.2.3 Microbes and biological oxygen demand

Anthropogenic activities are the predominant cause of poor water quality associated with surface water resources, subsequently compromising human and ecosystem health (Mostafa *et al.*, 2013). Such activities include urban sewage, agricultural return flows, and industrial waste, often resulting in microbial contamination. SW-GW interactions are commonly evaluated by observing changes in hydrochemical variables; however, this gives no clear indication of microbial water quality (Driezum *et al.*, 2018). The dynamics of SW-GW exchange can therefore be determined by evaluating microbial properties of both surface and subsurface components (Driezum *et al.*, 2018).

The interaction that leads to groundwater recharge may provide water enriched in oxygen, creating a habitable environment for various organisms, some of which may colonise the aquifer (Levy and Xu, 2012). As such, it is known that biogeochemical reaction rates tend to increase locally across the hyporheic zone during hydrological exchange processes (Stegen *et al.*, 2016). Furthermore, the deposition of organic matter and sediment during the exchange are often degraded by microbial communities (Levy and Xu, 2012). In this regard, Lin *et al.* (2012a) provide critical evidence relating significant variations in microbial abundance and composition to the intrusion of river water into the underlying aquifer. Bacterial abundance and assemblage in groundwater could then serve as a useful indicator of the extent of SW-GW interaction and in turn any associated contamination from surface water.

Biological oxygen demand (BOD) is defined by the amount of oxygen required to decompose organic waste matter by aerobic bacteria. It essentially serves as a proxy for organic pollution in water resources and is often used in conjunction with bacterial analysis (e.g., Lin *et al.*, 2012b; Mostafa *et al.*, 2013), hence it provides meaningful insight into groundwater pollution.

Driezum *et al.* (2018) assessed SW-GW interactions by analysing bacterial characteristics with water chemistry variables along the Danube River, Austria. During normal discharge conditions, bacterial characteristics in groundwater decreased with increased distance from the river. Different parameters in surface and subsurface components also governed the distribution of bacterial communities; several physico-chemical parameters correlated with bacterial characteristics in the river, whereas hydrogeological dynamics controlled the bacterial characteristics in groundwater (Driezum *et al.*, 2018). Similarly, Stegen *et al.* (2016) investigated spatio-temporal changes in hydrological connectivity within the hyporheic zone and the subsequent influence on microbial communities in the Columbia River (USA). The study revealed the major influence of SW-GW mixing induced by river stage fluctuations, resulting in the increased abundance of microbiological taxa.

3.2.4 Stable water isotopes

The ratios of stable isotopes of water (hereafter referred to as isotopes) act as natural tracers of the hydrological cycle and have been widely utilised as tools to study SW-GW exchanges (LaBaugh and Rosenberry, 2008). This approach has been extensively employed to investigate the dynamics and interconnections of aquifer systems. Isotope labels are used during different phases of the hydrological cycle to provide insight on groundwater flow paths, delineate locations of exchange areas, and confirm and differentiate sources of recharge (Clark and Fritz, 1997; Acheampong and Hess, 2000; Oxtobee and Novakowski, 2002; Abiye *et al.*, 2015). They are also used to identify traces of artificial discharge and quantify the groundwater infiltration into surface water (Brenot *et al.*, 2015; Coluccio and Morgan, 2019).

The isotopic proportions are informative for recognising the variation in source waters and the relative impact of SW-GW processes (Rugel *et al.*, 2016). These compositions are influenced by a variety of environmental processes prior to forming part of the groundwater system, thus generating distinct ratios that can be distinguished from surface processes (Abiye, 2013).

Isotopic signatures differ between surface and subsurface components due to various fractionation pathways that take place during condensation and evaporation (Dansgaard, 1964). Fractionation is primarily controlled by temperature, salinity, and humidity, whereby greater depletion of ^{18}O in precipitation occurs under cooler temperature regimes typical of higher altitude areas (Clark and Fritz, 1997).

The usefulness of stable isotopes lies within their conservative nature (i.e., under the condition of no geothermal effects present) (Acheampong and Hess, 2000)- they do not react with dissolved solutes in the water, but can be altered due to mixing of various water sources. However, isotopes are able to preserve their mixing ratio (Clark and Fritz, 1997; Abiye *et al.*, 2021). As such, stable water isotopes are advantageous in cases of dilution, dissolution, chemical reactions, and cation exchange (Mahlangu *et al.*, 2020) and are, therefore, often jointly used with hydrochemical analyses to evaluate the quality of data (Acheampong and Hess, 2000). The combined stable isotopes and water chemistry approach is useful for inferring discrete localities of hydrologic connections in fractured-rock settings (Levy and Xu, 2012).

Zhu *et al.* (2019) successfully applied water quality parameters and stable water isotopes to investigate anthropogenically modified SW-GW interaction in Xiong'an New Area, China. The study demonstrates the significance of artificial surface water which has changed the nature of the SW-GW connectivity, consequently serving as the dominant source of recharge for the groundwater.

In South Africa, Abiye *et al.* (2015) used an integrated approach to determine the influence of mine water on groundwater quality in the upper Crocodile River Basin. The isotope findings revealed an interconnection between the water resources; subsurface water was contaminated by decanting mine water, subsequently deteriorating the surface water quality through groundwater discharge. Groundwater recharge from surface water is also taking place via dissolution cavities and fractures in the dolomitic settings (Abiye *et al.*, 2015).

4. METHODOLOGY

The SW-GW investigations were largely limited to the core area of the VDHS due to financial and time constraints, covering an area of approximately 314 km² along a 30 km stretch of the Vaal River. Various research strategies were used to ascertain the data required to achieve the outlined objectives. The following subsections present the selected sites for specific sampling along with the collection protocol and associated data analysis for each method.

4.1 Desk Work and Collation of Data

The initial phases of this research involved acquiring, collating, and reviewing any available data and existing literature on the study area. General borehole information was obtained from the National Groundwater Information System (NGIS). A series of GIS based geological data and maps were obtained from the Council of Geoscience. The Department of Water and Sanitation (DWS) and the Department of Environmental Affairs (DEA) have various online repositories storing long-term datasets, including river discharge and GIS land cover data, respectively. Rainfall and digital elevation model (DEM) data were acquired from the South African Weather Services (SAWS) and United States Geological Survey (USGS), respectively. In addition, residents kindly provided information pertaining to historic rainfall and temperature patterns, impacts of droughts, spring occurrence, and local geological characteristics.

4.2 Sampling Sites

Preliminary field investigations took place to verify geological and hydrogeological data from literature and identify sites for sampling. The selection of sites was based on accessibility to boreholes and the river; monitoring wells within the area were inaccessible and unavailable, thus groundwater and surface water measurements and samples were collected from privately owned property. As such, resistance from some landowners restricted accessibility to certain parts of the study area. Field surveys took place during the dry season, in late winter (August) and early spring (September) of 2020. A total of 283 sites were identified, including boreholes (BH; 263), surface water (RV; 8), springs (SP; 10), an abandoned gold mine (MN; 1), and a waste dam (WD; 1) (Figure 4.1). The 'waste dam' was used to store water from processed manure on a dairy farm (site BH 263). For simplicity, springs were defined as wetlands and minor stream channels in the area (sourced solely from springs), with the aid of the information provided by residents. Wetlands were identified through their characteristic vegetation- predominantly inundated grasses and reeds, and less so in combination with shrubs and trees (Hobbs *et al.*, 2013).

4.3 Data Collection

Sites for specific types of sampling were selected based on accessibility, proximity to the Vaal River, and spatial position in the area; preference was given to the boreholes located near the river. Figure 4.2 illustrates the spatial distribution of the site-specific sampling in the study area.

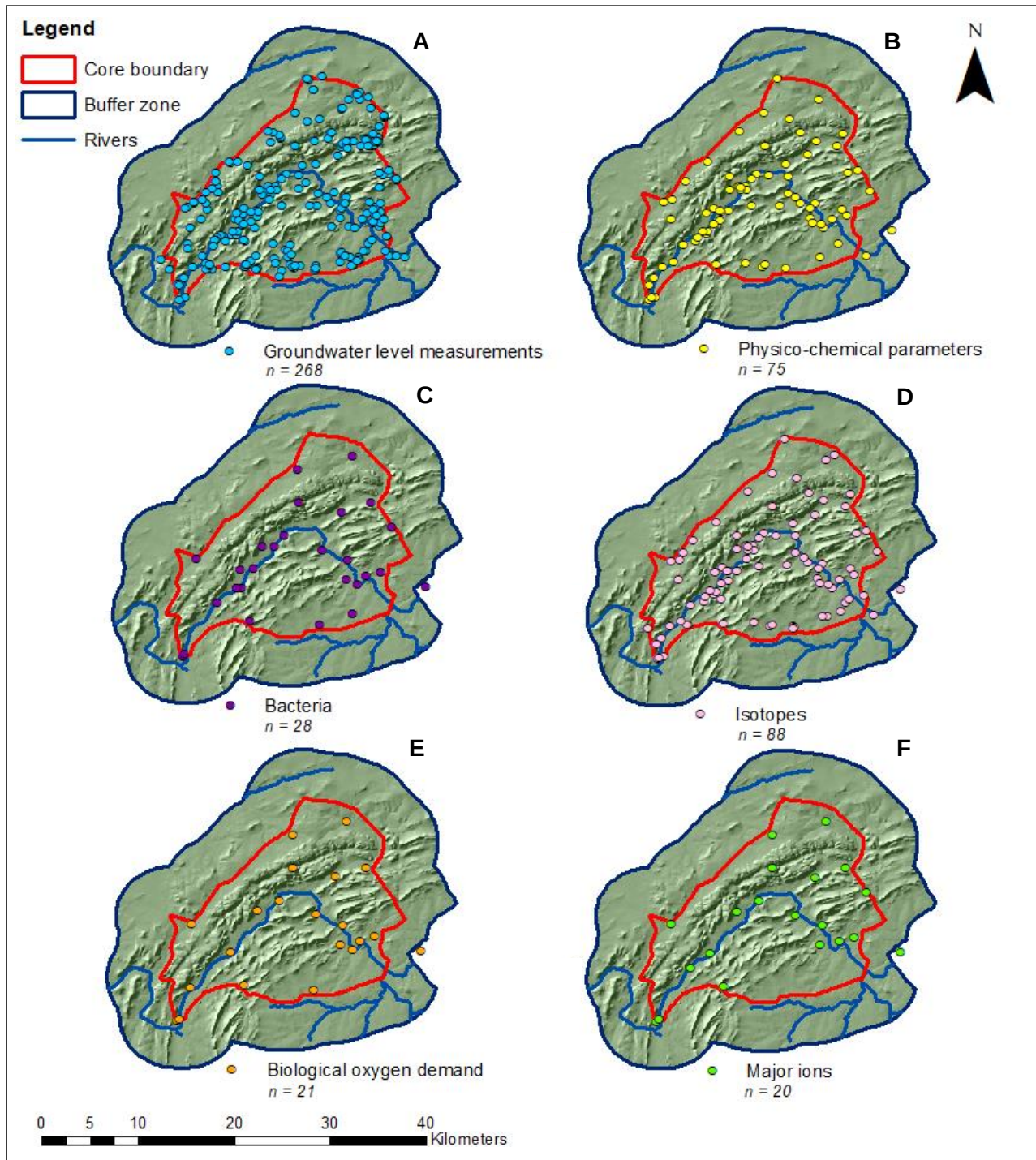


Figure 4.2. The spatial distribution of (A) groundwater level measurements, (B) *in situ* physico-chemical parameters, (C) bacteria, (D) stable water isotopes, (E) biological oxygen demand, and (F) major ion sampling sites in the study area (n = sample size).

During field investigations, there were two rainfall events on the 2nd of September 2020, which were sampled for isotopes at site BH 41. The first rainfall was more intense and took place in the morning for approximately two hours, whereas the second rainfall occurred in the late afternoon for a much shorter period of 10 to 15 minutes. A rain gauge situated at site BH 240 indicated a total of 10 mm precipitation for the specified day.

Groundwater levels were measured using a portable dip metre (Solinst Model 101 P2, Canada Ltd.). Pumps were requested to be switched off for at least 12 hours prior to water level measurements to ensure static conditions in the borehole. 92% of the pumps were switched off for ≥ 12 hours, with the remainder for 3-12 hours. The height of the measuring point below and above the land surface (reference points), and the well depths, were recorded at each site. A global positioning system (GPS) was utilised to locate the sampling positions at each site.

All groundwater samples were collected from boreholes that were equipped with pumps. Direct access to groundwater was provided through outlet pipes or taps located near the well head- this ensured that the groundwater was a true representation of the underlying aquifer. Vaal River samples were collected from bridges and riverbanks using a plastic bucket (rinsed at least three times with the sample water), where possible in the centre of the river, and all samples were taken at a minimum of 0.5 m below the water surface. Care was taken to avoid touching the sides of the outlet pipes, taps, and plastic bucket.

If the boreholes were not being pumped during sampling, groundwater was purged for at least 5 minutes. Physico-chemical parameters including electrical conductivity (EC; $\mu\text{S}/\text{cm}$), temperature (Temp; $^{\circ}\text{C}$), and pH were measured *in situ* using a portable multi-metre (Accsen Series PC 7, Lasec SA) with daily field calibration against fixed buffer solutions in accordance with the ambient temperature. The average from 10 measurements was used for further interpretation of each parameter. Note that the electrode was carefully rinsed with deionised water between sites to prevent contamination.

The recommended sample volumes of 1 L, 500 mL, and 10 mL for major ions, bacteria and biological oxygen demand, and stable isotopes, respectively, were collected. All sample bottles were thoroughly pre-rinsed with sample water at least three times before the final water sample was collected and again, care was taken to not contaminate the inside of the bottle or cap. The sample bottles were filled to the brim and tightly closed, and adhesive tape was used to prevent leakage, contamination, and evaporation. The sample bottles were stored in a cooler box below the temperature range of 15 – 20 $^{\circ}\text{C}$ for the bacteria and biological oxygen demand samples, whereas water chemistry samples were kept in ice below 4 $^{\circ}\text{C}$. Isotope samples were kept in a cool, dark place until delivery to the laboratory.

4.4 Data Analysis

4.4.1 Hydrochemistry

Water quality was measured by the WaterLab (Pty) Ltd, an accredited water laboratory in Pretoria. The samples were analysed for major ions, including bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^- -N), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), as well as total dissolved solids (TDS) and total alkalinity (TAL), as per standard methods. Given feasibility constraints, samples were delivered to the laboratory within 5 days of sampling.

Charge balance error (CBE) was calculated for each sample to ensure quality control of the water analyses. CBE values within a range of $\pm 5\%$ are generally regarded as the standard threshold, however, a CBE range of $\pm 10\%$ serves as an acceptable error (Yang *et al.*, 2012; Masindi and Abiye, 2018). In this study, 90% of the samples were within the $\pm 5\%$ threshold, with the remainder at $\pm 10\%$. The reported TDS values were cross-checked by comparing them to the summed total of the constituents. Values for the groundwater showed similarity and were well within 20% of the summed measured major ions, further confirming the reliability of the dataset. The major ion analyses were performed on a limited sample size whereas *in situ* physico-chemical measurements were taken for a larger sampling size, thus representing a more reliable comparison between water resources. As such, the Hierarchical Cluster Analysis (HCA) was performed only on EC data to maximise the sample size and account for variability. EC values were scaled prior to conducting the HCA and the Euclidean distance method was used.

The fitness of the data for Principal Component Analysis (PCA) was determined using the Kaiser Meyer Olkin (KMO) measure of sampling adequacy and Bartlett's test of sphericity. A KMO value of 0.51 was obtained which represents the minimum requirement for a PCA (Kaiser, 1974), and a significant value ($P < 0.001$) was acquired from Bartlett's test, confirming the suitability of such analysis on the data (Masindi and Abiye, 2018). To facilitate purposeful quantification of variance, the data were log-transformed and auto-scaled prior to the PCA. Component extraction was employed through the well-known Kaiser criterion and scree test; components were retained with eigenvalues larger than one. In addition, parallel analysis based on the Monte Carlo simulation (500 iterations) was used to ascertain retained components. Factor loadings greater than 0.5 were accommodated for interpretation. These loadings were used to aid the identification of primary hydrochemical trends and processes within the study area (Masindi and Abiye, 2018).

A Piper trilinear diagram (Piper, 1944) was utilised to identify the predominant water types and evaluate the hydrochemical evolution of constituents. A spatial interpolation map of groundwater electrical conductivity was constructed using the Kriging technique in the Surfer 19 program, where all values were set to default.

4.4.2 Hydrograph separation

Various empirical separation methods exist to differentiate total streamflow into two primary components. Due to some uncertainties associated with these techniques in fractured aquifer settings, two quantitative hydrograph separation techniques were applied and compared to evaluate the general reliability of the results, in line with the recommendations by Kilian *et al.* (2019) and Barlow *et al.* (2015). Each technique utilises daily averaged time-series data obtained from a river gauge.

Baseflow sources are not differentiated by the hydrograph separation techniques (Hughes *et al.*, 2003; Levy and Xu, 2012); this includes separating baseflow into groundwater, interflow, spring flow, and wastewater components. Therefore, this method must be applied with caution. Xu *et al.* (2002) provide useful criteria to help determine whether the interflow component forms an important part of the hydrograph.

The average daily discharge data (m^3/s) in the DWS database is limited due to inconsistency and paucity, therefore, data were chosen from the most recent, consistent, long-term record available, which was from May 2013 to May 2016. This served to approximate subsurface contribution and identify any effect of seasonality, thus not necessarily reflecting present-day conditions. Based on the available river gauging stations with appropriate data, two gauging stations were chosen: C2H140 (Vaal River at Woodlands) and C2H018 (Vaal River at De Vaal), representing the entry and exit of the Vaal River in the VDHS, respectively (Figure 4.3). Station C2H140 is located outside of the study area, however, it represents the only monitoring point upstream of the VDHS with adequate data for the analysis.

The widely used filtering separation algorithms were adopted from Nathan and McMahon (1990) and Chapman (1991). The analysis and separation were performed in the BFI+ 3.0 module of the HydroOffice 2016 software and by calculations using Microsoft Excel. Note that these separation techniques have no hydrological basis, as they are adapted from signal analysis (Lyne and Hollick, 1979; Smakhtin, 2001; Hughes *et al.*, 2003). Instead, this approach simply computes the proportions of the hydrograph components based on partitioning frequency signals with flow volume, producing repeatable estimated outputs (Nathan and McMahon, 1990).

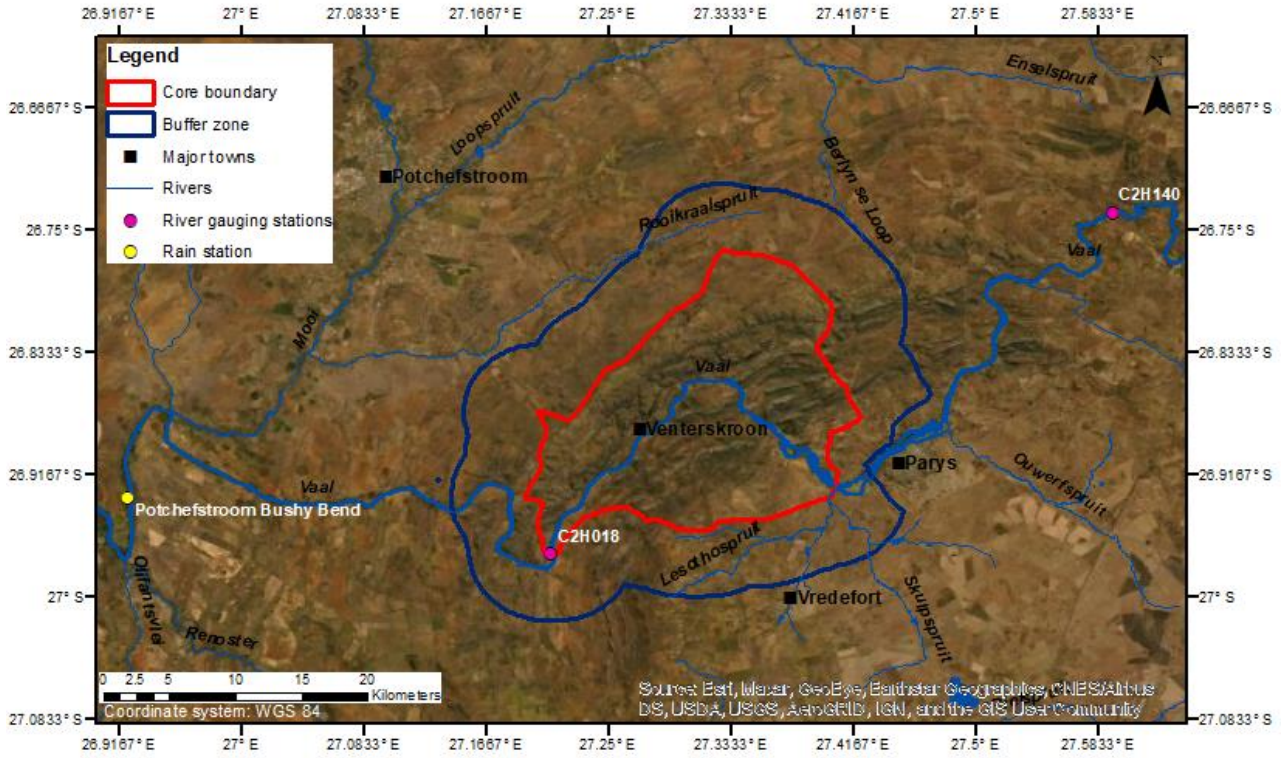


Figure 4.3. Location of the rain and river gauging stations used for the study area.

Smakhtin and Watkins (1997) determined that a value of 0.995 for the alpha filter parameter is acceptable for large daily discharge datasets in South Africa, however, this study utilised a smaller dataset, and thus a value of 0.997 was more appropriate, as proposed by Hughes *et al.* (2003). For the beta filter parameter, a fixed value of 0.5 was used (Smakhtin, 2001; Hughes *et al.*, 2003). Thereafter, the baseflow index (BFI) was calculated, which represents the ratio of groundwater contribution that forms part of the river discharge (Levy and Xu, 2012).

The following digital filter algorithms were used to compute the quick flow component from the total discharge (Equations 1 and 2), followed by the determination of the baseflow component (Equation 3) and index (Equation 4):

Nathan and McMahon (1990); adapted from Hughes *et al.* (2003)

$$q_i = \alpha q_{i-1} + \beta (1 + \alpha)(Q_i - Q_{i-1}) \quad [1]$$

Chapman (1991)

$$q_i = \frac{3\alpha - 1}{3 - \alpha}(q_{i-1}) + \frac{2}{3 - \alpha}(Q_i - \alpha Q_{i-1}) \quad [2]$$

Baseflow calculation

$$Qb_i = Q_i - q_i \quad [3]$$

Baseflow Index

$$BFI = Qb_i / Q_i \quad [4]$$

where q_i and Q_i are the filtered quick flow component and total discharge volume (m^3/s), respectively, at time interval i (days); Qb_i is the baseflow component (m^3/s), and α, β are the filter constants. Owing to the vast anthropogenic input into the Vaal River, the baseflow result may not necessarily represent a reliable estimate. Return flows related to the mining, industrial, and urban sectors were approximated by Mare (2007) for the Vaal River system, amounting to a total of 720 million m^3/annum estimated for the year 2015. This value was subtracted from the baseflow to avoid overestimation and thus provide more reliable results.

4.4.3 Microbes and biological oxygen demand

Microbial analysis of *Salmonella enterica subspecies enterica serotype typhimurium* (*S. enterica*), *Escherichia coli* (*E. coli*), *Enterobacter aerogenes* (*E. aerogenes*), *Proteus mirabilis* (*P. mirabilis*), and *Staphylococcus aureus subspecies aureus* (*S. aureus*) was performed at the University of the Witwatersrand. Given the remoteness of the study area coupled with financial and time constraints, the samples were not delivered to the laboratory for analysis within the recommended 6 hours, and a maximum holding time of 24 hours (Murray *et al.*, 2007). The results must therefore be interpreted with caution.

Sites that were sampled for the microbial assessment were not analysed for all the above-mentioned species due to resource and equipment constraints. As such, bacteria served as indicator organisms of contamination and where possible, a source for the species was identified. The inexpensive and easy to use Membrane Filter method was employed. Sterile cellulose nitrate membrane filters (47 mm) with $0.45 \mu\text{m}$ pore size were used for the isolation and enumeration of bacterial colonies. For *S. enterica* and *S. aureus*, nutrient pad discs (Sartorius) standard TTC and Tergitol TTC were used, respectively, whereas for *E. coli*, *E. aerogenes*, and *P. mirabilis*, the nutrient pad disc Endo was used, for the recovery and differentiation of each species. These selective nutrient media were in Petri dishes and moistened with 3 mL filtered deionised water.

All laboratory equipment was sterilised with boiling water. The beakers were pre-rinsed with sample water, and 100 mL was filtered through the membrane filter held in a stainless-steel filtration system which utilised a negative pressure vacuum. The filter membranes were removed and placed onto the respective nutrient pads. The Petri dishes were closed and placed into the TRAWAS® Portable Water Testing Basic Kit (No. 180.102) incubator. The samples were incubated for 24 hours at

approximately 37.5°C; thereafter, each bacterial species observed on the membrane surface was individually counted (where possible) and recorded as estimated colony forming units per 100 mL (cfu/100 mL).

As in the case of the logistical constraints for the microbial samples, the biological oxygen demand (BOD) samples did not arrive at the laboratory within the suggested 6-hour timeframe. Thus, these results must also be interpreted with caution. BOD was determined using the manometric OxiTop® IS 6 measuring devices over 5 days. The BOD measured value was expected to be in the range of 0 – 40 mg/L, which was paired with a corresponding sample volume of 432 mL, as per manual instructions. The measuring bottles were rinsed with sample water prior to the analysis.

The solutions were poured into the measuring bottles, which have a nominal volume of 510 mL. Magnetic stirring rods and rubber quivers were inserted into the measuring bottles and the neck of the bottles, respectively. Two sodium hydroxide tablets were placed into the rubber quivers using forceps, ensuring that there was no contact with the sample water. OxiTop® measuring heads were tightly screwed on each bottle and placed onto an inductive stirring system to maintain a temperature of approximately 20°C. The measuring heads communicated with a handheld systems controller (OC 100) by utilising an infrared interface, recording a total of 360 measurements for each sample throughout the 5 days, expressed in mg/L.

4.4.4 Groundwater level measurements

Water level measurements in boreholes are useful to investigate groundwater gradients in relation to surface water (Rosenberry *et al.*, 2008). The comparison of groundwater and surface water levels provides insight into the flow direction (Rosenberry *et al.*, 2008). This concept is based on the hydraulic gradients between the water resources. In other words, if an aquifer that is proximal to a surface water body has higher water levels, then the flow direction will be from the groundwater to the surface water and vice versa. Thus, the river is defined as influent or effluent based on hydraulic head information. Groundwater-level measurements were used to evaluate depth to the water table and water table-contours in relation to the geology and surface water, and to construct a flow net to estimate the groundwater flow direction and investigate flow patterns.

The measured reference points were subtracted from or added to the elevation to obtain the true water level in relation to the land surface. Water table elevation maps were constructed from the difference between depth to the borehole water level and surface elevation to obtain the hydraulic head at each site (Appendix A) (Kumar, 2014). Kriging is a common statistical interpolation technique that accounts for the spatial structure of a variable whilst retaining the measured field values (Kumar, 2014). The Kriging interpolation method was applied using Surfer (version 19; Golden Software) to construct a depth to the water table and water table gradient map.

Flow net analysis is a graphical technique that is commonly used to investigate flow direction between water resources. The flow net is composed of equipotential lines (i.e., groundwater contours) and flow lines, where the former are based on hydraulic head data and the latter are constructed perpendicular to the equipotential lines, assuming homogeneous and isotropic aquifer conditions (Geyh, 2000; Rosenberry *et al.*, 2008). These maps provide meaningful insight into groundwater potential (Messene, 2017) by identifying areas of recharge and discharge, and detecting impacts of groundwater pumping (Kumar, 2014); they, therefore, provide invaluable information for conceptualising the hydrogeological model of the study area.

4.4.5 Stable water isotopes

Stable water isotopes were analysed by measuring the isotope ratios ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) using the Liquid Water Isotope Analyser-model 45-EP at the University of the Witwatersrand. The machine comprises a laser analysis system, internal computer, small membrane vacuum pump, liquid auto-sampler, and an intake line that passes room air through a Drierite column to remove moisture. Prior to and periodically during the analysis, five known standard isotopic signatures were used to calibrate the laser machine to ensure quality control.

Sample preparation included pipetting 1.5 mL of sample water into 2 mL vials enclosed with polytetrafluoroethylene septum caps. An estimated 0.75 μL of sample water was collected from the vials by a Hamilton microliter syringe and injected into a preheated (46°C) auto-sampler. The sample is vaporised under vacuum conditions and moves into the pre-evacuated mirrored chamber where analysis takes place. The machine produces results within the accuracy of approximately 0.2‰ for $\delta^{18}\text{O}$ and 1‰ for $\delta^2\text{H}$ in samples up to 1000 mg/L dissolved salt concentration (Leketa *et al.*, 2018). The relative isotopic ratios were calculated and reported in the standard δ -notation ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) in parts per thousand (per mil; ‰) difference from the Vienna Standard Mean Ocean Water (VSMOW) standard reference (Coplen, 2011):

$$\delta^{18}\text{O} (\text{‰}) = \left[\frac{\left(\frac{O^{18}}{O^{16}} \right)_{\text{sample}}}{\left(\frac{O^{18}}{O^{16}} \right)_{\text{standard}}} - 1 \right] * 1000\text{‰} \quad [5]$$

Similarly, $\delta^2\text{H}$ was calculated using $^2\text{H}/^1\text{H}$ values in the sample and standard.

The isotopic signatures ($\delta^{18}\text{O}$ versus $\delta^2\text{H}$) for surface water and groundwater samples were plotted against the Global Meteoric Water Line (GMWL) and Local Meteoric Water Lines of Pretoria (PLMWL) and Johannesburg (JLMWL). The GMWL and PLMWL were obtained from the Global Network of Isotopes in Precipitation (GNIP), whereas the novel JLMWL was adapted from Leketa *et al.* (2018). The use of an LMWL is important in local investigations due to the various ambient

factors that influence isotopic compositions of rainfall (Clark and Fritz, 1997; Levy and Xu, 2012) and has been historically valuable in assessing SW-GW interactions (McGuire and McDonnell, 2007).

Binary mixing between isotopically distinct waters was quantified based on the isotopic proportions (Clark and Fritz, 1997):

$$\delta^{18}\text{O}_{\text{sample}} (\text{‰}) = \chi \delta^{18}\text{O}_A + (1 - \chi) \delta^{18}\text{O}_B \quad [6]$$

where χ constitutes the percentage of the mixing proportion of end member A (river) into end member B (groundwater) for a given sample.

Deuterium excess (*d*-excess) is a function of the isotopic compositions and is useful in characterising the precipitation source and conditions during both vapor transport and in the sub-cloud (Leketa and Abiye, 2020). As such, this approach was undertaken to constrain the potential rainfall source recharging the aquifers. The *d*-excess values were calculated from the LMWL for Johannesburg:

$$d - excess (\text{‰}) = \delta^2\text{H} - 6.7 * \delta^{18}\text{O} \quad [7]$$

4.4.6 Statistical analyses

All statistical analyses were performed using the R Studio i386 (version 3.6.3) and IBM SPSS Statistics (version 19) software. Datasets were examined for normality and homogeneity of variance using the Shapiro-Wilk and Fligner-Killeen tests, respectively. Where necessary, the data were log-transformed to achieve normality. The data were subjected to a one-way analysis of variance (ANOVA) to statistically analyse the means of the response variables. Where normality of data could not be achieved, a non-parametric alternative Kruskal-Wallis test was employed. The validity of regression and ANOVA models were visually checked to ensure the constancy of variance and normality of residuals.

Post hoc tests were conducted to identify where significant differences lay between the explanatory variables. Tukey's Honest Significant Difference (HSD) and Kruskal-Wallis Multiple Comparison post hoc tests were used for parametric and non-parametric analysis, respectively.

Given that most of the data deviated from normality, the Spearman rank-correlation coefficient was used to estimate the strength of the association between two variables. The correlation values were interpreted as: weak ($r = 0.00$ to 0.49), moderate ($r = 0.50$ to 0.69), strong ($r = 0.70$ to 0.79), and

very strong ($r = 0.8$ to 1). Additionally, statistical relationships between variables were examined with simple regression analysis. Statistical significance was set at the standard $P < 0.05$.

Bacterial and water quality data were subjected to statistical multivariate analysis using the Canoco for Windows (version 4.5) software in the interest of identifying, analysing, and visualising the relationship between the communities and environmental variables- as species composition depends on various factors simultaneously (Wang *et al.*, 2012).

A Detrended Correspondence Analysis (DCA) was employed to determine the suitability of the data for linear or unimodal analysis (Ter Braak and Smilauer, 2002). The results indicated that the data were more suitable for a unimodal ordination method: Canonical Correspondence Analysis (CCA). The CCA was run on log-transformed data and significance tests were performed using the unrestricted Monte Carlo permutation tests (499 permutations; $P < 0.05$). Due to the variability of the samples, bacterial species were examined independently with water chemistry data and *in situ* physico-chemical parameters, to include all environmental factors for the former and all bacterial counts for the latter.

5. RESULTS AND DISCUSSION

5.1 Hydrochemistry

5.1.1 Major ions and *in situ* parameters

Mean and standard deviation (σ) for the major ions and *in situ* physico-chemical variables at fixed distances from the river are presented in Table 5.1. The hydrochemical parameters for all sites are presented in Appendix B and C. For the ease of interpretation, reference was made to sample areas that constitute distinct distances from the river; 200 m (0 – 200 m), 500 m (200 – 500 m), 1 km (500 – 1000 m), 2 km (1 – 2 km), and > 2 km.

Table 5.1. Mean and standard deviation (σ) values of the hydrochemical parameters for all sites situated at set distances from the river. Concentrations are expressed as mg/L, except for total alkalinity (TAL), pH, electrical conductivity (EC), and temperature (Temp), which are expressed as mg/L as CaCO₃, standard units, μ S/cm, and °C, respectively.

		Distance from river		
	River	200 m	1 km	> 1 km
Mean ($\pm \sigma$)				
TDS	485 (± 1.41)	597.71 (± 276.02)	636.67 (± 571.39)	347.5 (± 311.96)
TAL	136 (± 5.66)	220 (± 40.99)	149.33 (± 146.22)	161 (± 100.8)
HCO ₃	164 (± 9.9)	268.43 (± 49.85)	182.33 (± 178.27)	196.25 (± 122.9)
Cl ⁻	60 (± 2.83)	70.43 (± 44.07)	104.67 (± 118.95)	40.5 (± 63.68)
SO ₄ ²⁻	131 (± 1.41)	158.43 (± 172.77)	69.67 (± 54.54)	36.13 (± 52.93)
NO ₃ ⁻	5 (± 0.85)	5.97 (± 6.17)	28.23 (± 38.19)	8.31 (± 11.88)
Na ⁺	55.5 (± 0.71)	33 (± 18.93)	43 (± 20.22)	21 (± 14.79)
K ⁺	9.75 (± 0.21)	1.77 (± 0.73)	4.53 (± 3.86)	0.89 (± 0.54)
Ca ²⁺	51.5 (± 0.71)	70.86 (± 50.07)	63 (± 66.78)	43.25 (± 52.61)
Mg ²⁺	21 (± 0)	54 (± 19.82)	39.33 (± 33.02)	25 (± 17.53)
	<i>n</i> = 2	<i>n</i> = 7	<i>n</i> = 3	<i>n</i> = 8
EC	974.51 (± 39.7)	775.61 (± 336.79)	457.24 (± 417.5)	332.98 (± 283.49)
pH	8.7 (± 0.48)	7.52 (± 0.77)	7.47 (± 0.81)	7.78 (± 0.79)
Temp	20.05 (± 1.16)	19.91 (± 1.35)	20.94 (± 1.86)	20.35 (± 1.04)
	<i>n</i> = 8	<i>n</i> = 22	<i>n</i> = 16	<i>n</i> = 29

n = sample size

It is observed that the groundwater sites located furthest from the river (> 1 km) demonstrate the lowest mineralisation, characterised by the lowest EC ($332.98 \mu\text{S/cm}$) and TDS (347.5 mg/L) values as well as almost all other hydrochemical parameters. In contrast, the water characteristics of the sites located in proximity ($0 - 1$ km) to the Vaal River are more variable, expressing the highest mean values for all the parameters, excluding EC and pH. The highest EC ($974.51 \mu\text{S/cm}$) and pH (8.7) values observed for the river are most likely linked to salinity related to pollution (Bezuidenhout *et al.*, 2013) and concentration associated with low flows and high evaporation rates (Saraiva Okello *et al.*, 2018).

The elevated major ion concentration in groundwater was noticed for sites ≤ 1 km from the river. These sites generally exhibit similarity to the river chemistry, particularly the anion trend ($\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$), suggesting a certain degree of linkage between the water resources. However, the mean NO_3^- value (28.33 mg/L) associated with sites 1 km from the river attest to the contribution of land-use activities. This observation agrees with Bezuidenhout *et al.* (2013) that demonstrated the regional vulnerability of groundwater to NO_3^- contamination in the North West Province. Similarities in water characteristics may also be attributed to similar pollution sources, flow paths, or regional lithology (Guggenmos *et al.*, 2011).

The fitness of water for rural domestic purposes was evaluated against the South African Water Quality Guidelines, which serve as the foundation for water quality requirements related to various sectoral uses of water (DWAF, 1996). The water quality criteria are expressed as a Target Water Quality Range (TWQR), representing the most ideal range for each constituent. Values exceeding the TWQR may result in adverse health effects in humans.

The values indicate that the collective sites are within the acceptable range for Na^+ ($< 100 \text{ mg/L}$), K^+ ($< 50 \text{ mg/L}$), SO_4^{2-} ($< 200 \text{ mg/L}$), and pH ($6-9$). All sites are within the TWQR for Cl^- ($< 100 \text{ mg/L}$) except for the 1 km sites which are associated with accelerated corrosion rates but no aesthetic or health effects (DWAF, 1996). The 200 m and 1 km sites are not within TWQR for Mg^{2+} ($> 30 \text{ mg/L}$) whereas the 1 km and > 1 km sites are not within the TWQR for NO_3^- ($> 6 \text{ mg/L}$). The former experience scaling impacts whereas the latter may cause health effects linked to the 1 km sites ($> 20 \text{ mg/L}$) (DWAF, 1996). None of the collective sites were within the TWQR for Ca^{2+} ($> 32 \text{ mg/L}$), reflecting problematic scaling, however, there are no adverse health effects.

The TDS for sites > 1 km is within the TWQR while the remainder of the sites lies within the tolerable range ($450 - 1000 \text{ mg/L}$). The WHO (1996) guidelines for TDS in drinking water indicate that the river, 200 m, and > 1 km sites are classed as good whereas sites 1 km are classed as fair according to the palatability quotient. Overall, there appears to be no regional trend and water quality is deemed tolerable

for domestic purposes, however, particular areas are impacted by local pollution sources and considered unsuitable for certain uses.

Owing to the relatively low sample size and sparse distribution of major ion data, these observations may not necessarily reflect the processes occurring on a large scale as the generalisations made may be biased towards specific sites. Therefore, the following interpretations are made on EC measurements which provide adequate spatial distribution by including a larger and more widespread dataset, representing higher resolution. This is considered appropriate as major ions contribute to EC, and thus it is often used as a proxy to TDS (DWAF, 1996; Lin *et al.*, 2012b). This approach is further validated by a strong and significant correlation ($r = \geq 0.73$; $P < 0.01$) between the EC and TDS, Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} , and Mg^{2+} values from sites in Table 5.1.

Figure 5.1 shows the box and whisker plot for the river and groundwater EC demonstrating the variability at the set distances from the river. There is a significant statistical difference ($P < 0.001$) in EC values between sites situated at various distances from the river, highlighting the highest and lowest values associated with the river and groundwaters located > 2 km from the channel, respectively. This is visualised in Figure 5.2, which shows the spatial variability of the groundwater EC in relation to the position of the Vaal River.

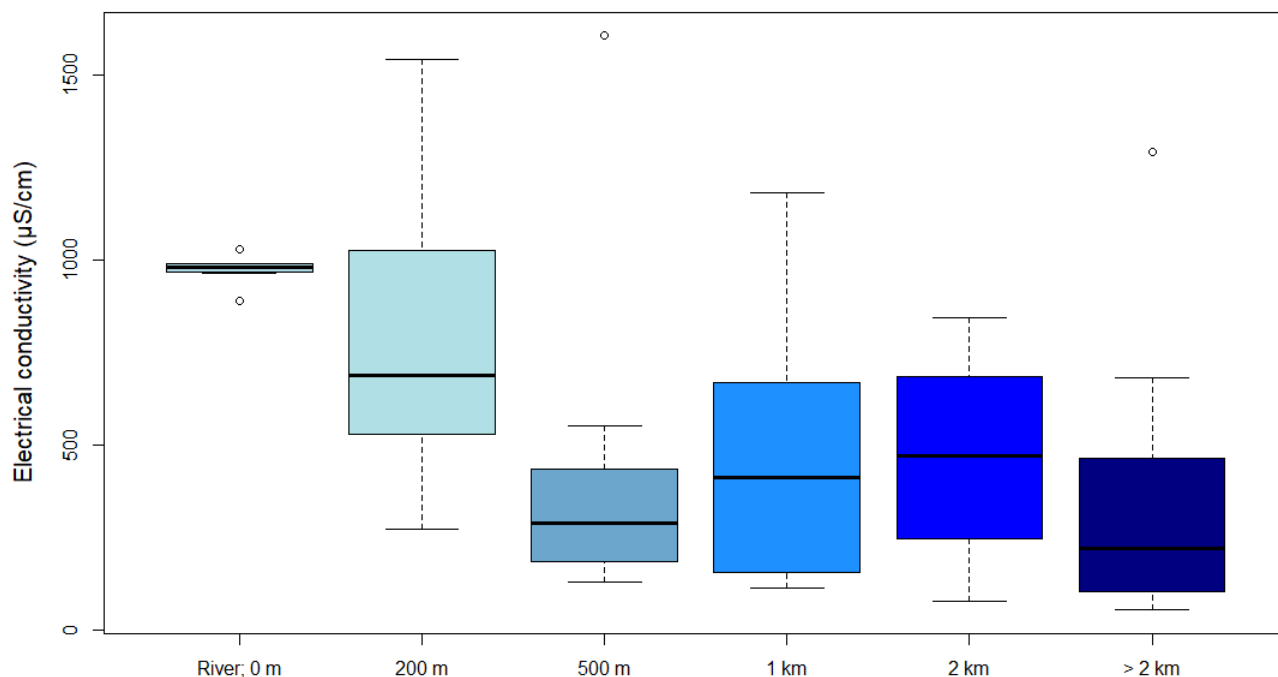


Figure 5.1. Statistical analysis of the river and groundwater electrical conductivity values at the set distances from the river: 200 m, 500 m, 1 km, 2 km, and > 2 km.

The general trend shows that EC values tend to increase towards the Vaal River, wherein some instances, there is a drastic change in EC (Figure 5.2). Some uniform patterns could indicate the influence of similar hydrochemical settings. It appears that the immediate vicinity of the Vaal River system is generally characterised by the highest groundwater EC values, however, it is relatively localised and limited in extent. Moreover, there is no significant statistical difference between the river and groundwater sites located ≤ 200 m from the river ($P > 0.05$). These observations provide evidence for potential linkage across the aquifer-stream boundary in areas near the river channel. The relatively high EC in the northern section of the study area is attributed to local anthropogenic activities.

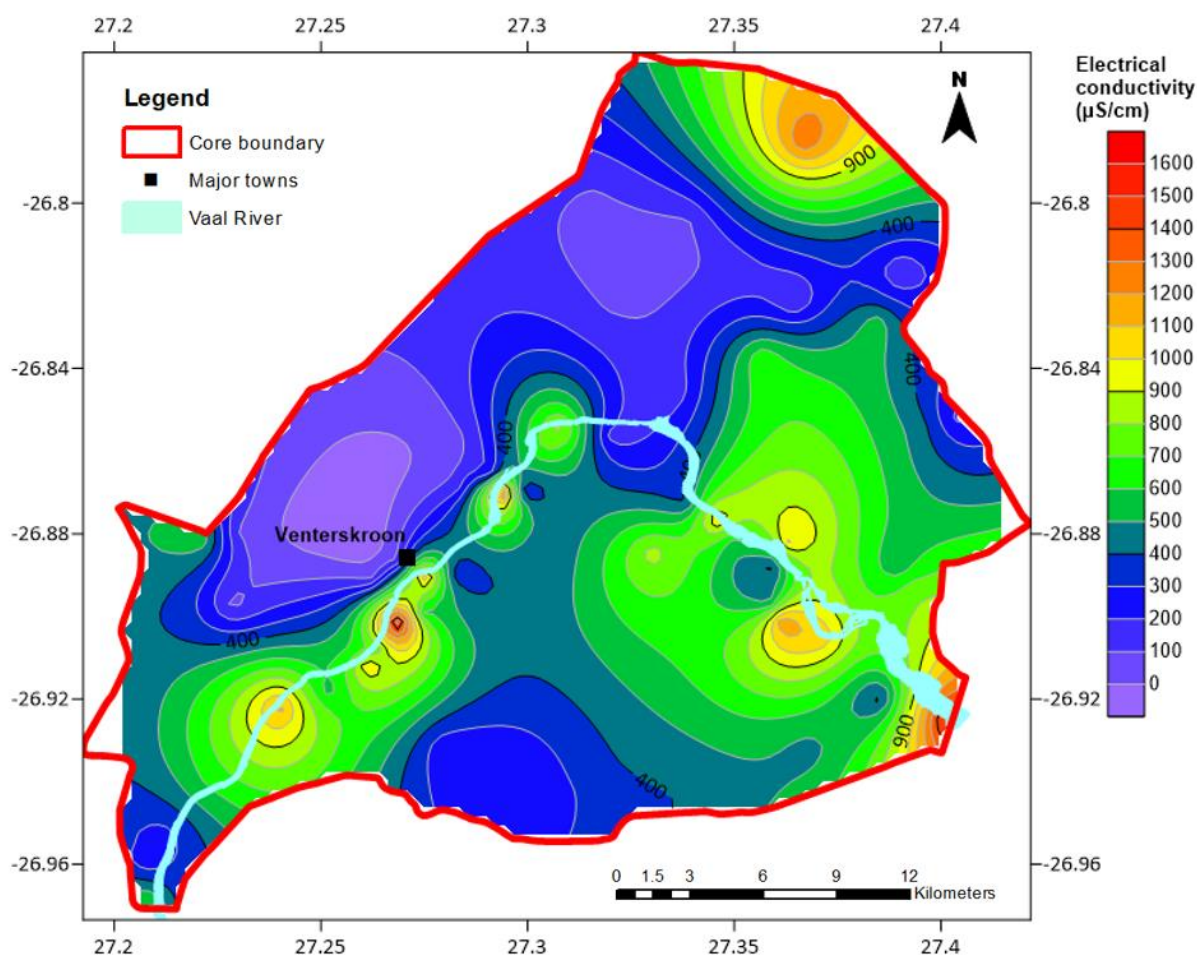


Figure 5.2. Spatial distribution map of groundwater electrical conductivity in the study area.

5.1.2 Hierarchical Cluster Analysis (HCA)

Groundwater and river sites were subjected to the HCA using Ward's linkage method, highlighting the spatial patterns using a single parameter (EC). The resulting dendrogram, presented in Figure 5.3, is subdivided into five major clusters, which shows the number of samples and associated mean EC value for each cluster. Five clusters were considered appropriate and practical for the ease of interpretation and further analysis in this study. River sites were assigned to one of the five clusters, namely cluster A, whereas clusters B-E comprised only groundwater sites, displaying their dissimilarity with river chemical composition (Figure 5.3). EC values progressively decrease in the cluster order of B-A-E-D-C.

Table 5.2 summarises the number of groundwater sites at specific distances from the river and their associated contribution to the total for each cluster. As the river is known to be polluted (Wepener *et al.*, 2011), evidenced by its EC value (mean 947.51 $\mu\text{S}/\text{cm}$), it is expected that any hydrological interaction will be highlighted by mineralised groundwater proximal to the channel (Guggenmos *et al.*, 2011). The groundwater sites belonging to cluster A are predominantly located in the vicinity of the Vaal River (84%), indicating similarity, with the exception of site BH 60 (2 km). Therefore, these sites are likely influenced by the polluted river. This agrees with the Walt *et al.* (2010) findings of low-quality groundwater within the Vaal River drainage system.

Table 5.2. The number of groundwater and river sites at the set distances from the river channel in each cluster and their respective percentage (%) contribution to the total.

Cluster	River	%	200 m	%	500 m	%	1 km	%	2 km	%	> 2 km	%	Total
A	8	57	5	36					1	7			14
B			4	58	1	14	1	14			1	14	7
C			1	4	4	17	3	13	1	4	14	61	23
D			3	30	2	20	1	10	1	10	3	30	10
E			9	43			3	14	1	5	8	38	21

Cluster B is characterised by the highest EC values with the sites situated predominantly (86%) near the river channel (≤ 1 km). The higher EC values associated with these sites could be due to SW-GW interaction exacerbated by land-use activities such as crop (by using fertilisers) and livestock farming. Moreover, this high value may be attributed to the concentration of ions in the soil due to evaporation (Abiye, 2015), possibly related to localised agricultural practices. Therefore, these clusters represent poor water quality due to potential hydrological exchanges and human-induced pollution.

Certain sites (BH 60 and BH 114) that are ≥ 2 km from the channel display similarities to the sites nearby the river. It could be that this high value is attributed to deep circulating, highly mineralised groundwater, or the intense and extensive cattle farming associated with these sites that might be influencing the poor water quality. In comparison with the rest of the sites within these areas, the latter may be a more plausible explanation.

As expected, cluster C primarily comprises sites that are > 1 km from the river (65%), deviating from contaminant gradients, suggesting better water quality associated with these sites. Sites within the vicinity of the river are outliers relative to the surrounding sites (≤ 500 m), and therefore, possibly indicate that there are complex and discrete groundwater flow paths that exhibit variable susceptibility to the influence of the river. This is particularly evident in sites BH 73 and BH 224, which are situated near the contact with the alkali granite intrusion complex and near the periphery of a geological contact, respectively. This hydrochemical observation is confirmed by the general stable isotope depletion (Section 5.4).

Cluster D consists of sites that are situated at various distances from the river. These sites represent moderate to good water quality, likely influenced by a combination of natural and anthropogenic factors. Moreover, the sites located near the channel are unlikely to be affected by the contaminated river; instead, localised human activities may be contributing to the slightly elevated EC. This indicates complex controls on water quality associated with certain reaches of the river.

Sites located 200 m (43%) and > 1 km (43%) from the river dominate cluster E, representing cluster E1 and E2, respectively. The sites located near the channel (≤ 200 m; E1) exhibit EC values lower than the river (mean 614.64 $\mu\text{S}/\text{cm}$) but are higher than those located > 1 km from the channel (mean 526 $\mu\text{S}/\text{cm}$; E2). The groundwater assigned to cluster E1 may exhibit a certain degree of influence from the river and/or human activities that may be contributing contamination to these sites, whereas cluster E2 is likely affected by localised anthropogenic activities.

Overall, the HCA indicated some distinct trends in groundwater characteristics for sites at set distances from the river. However, groundwater quality near the river channel, as represented by the EC, is influenced by different chemical components and therefore, varies along the river reach. This reveals diverse localised controls on hydrochemical properties that may not necessarily be related to direct hydrological exchange, as river EC is dissimilar to some of the ≤ 200 m groundwater sites. It is recognised that localised land-use activities, particularly livestock farming, result in point sources of pollution.

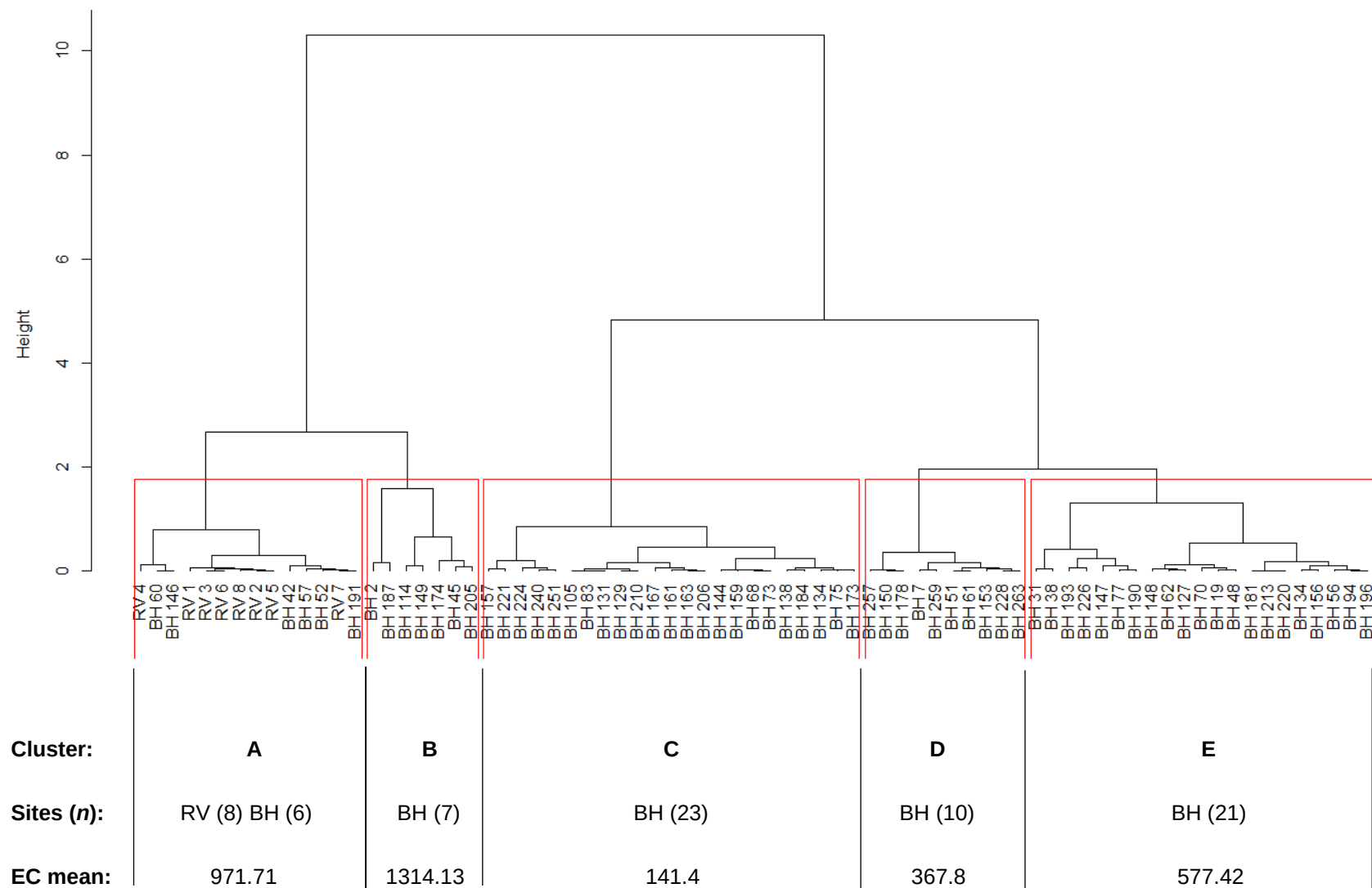


Figure 5.3. Dendrogram of the 8 river (RV) and 67 groundwater (BH) sites in the Vredefort Dome Heritage Site classified into five clusters based on electrical conductivity (EC) values, expressed as $\mu\text{S}/\text{cm}$. *n* = sample size.

5.1.3 Principal Component Analysis (PCA)

The PCA ordination plot for the hydrochemistry data, indicating the similarity and dissimilarity between sites located at various distances from the river, is shown in Figure 5.4. The PCA biplot describes two principal components (PCs) that were retained, where 52.6% from PC 1 is shown on the first axis and 19.8% from PC 2 is shown on the second axis- these account for 72.4% of the total variance.

Notably, sites are separated along the PC 1 axis based on water quality associated with lower and higher ion concentrations that are located at various distances from the channel. This indicates that the water quality at sites nearest to the channel (200 m) is not limited to contamination from the river water. Instead, it appears that other local factors, such as land-use activities, could be influencing the hydrochemical properties. Such activities are also likely responsible for the poorer water quality observed at sites furthest from the river (e.g., BH 114). Moreover, it is apparent that the 200 m sites exhibit variable water quality characteristics, supporting the findings from the HCA. Overall, the PCA biplot displays no significant separation along the PC axes between sites situated at different distances from the channel, which signifies spatial similarity and dissimilarity in water quality at various distances.

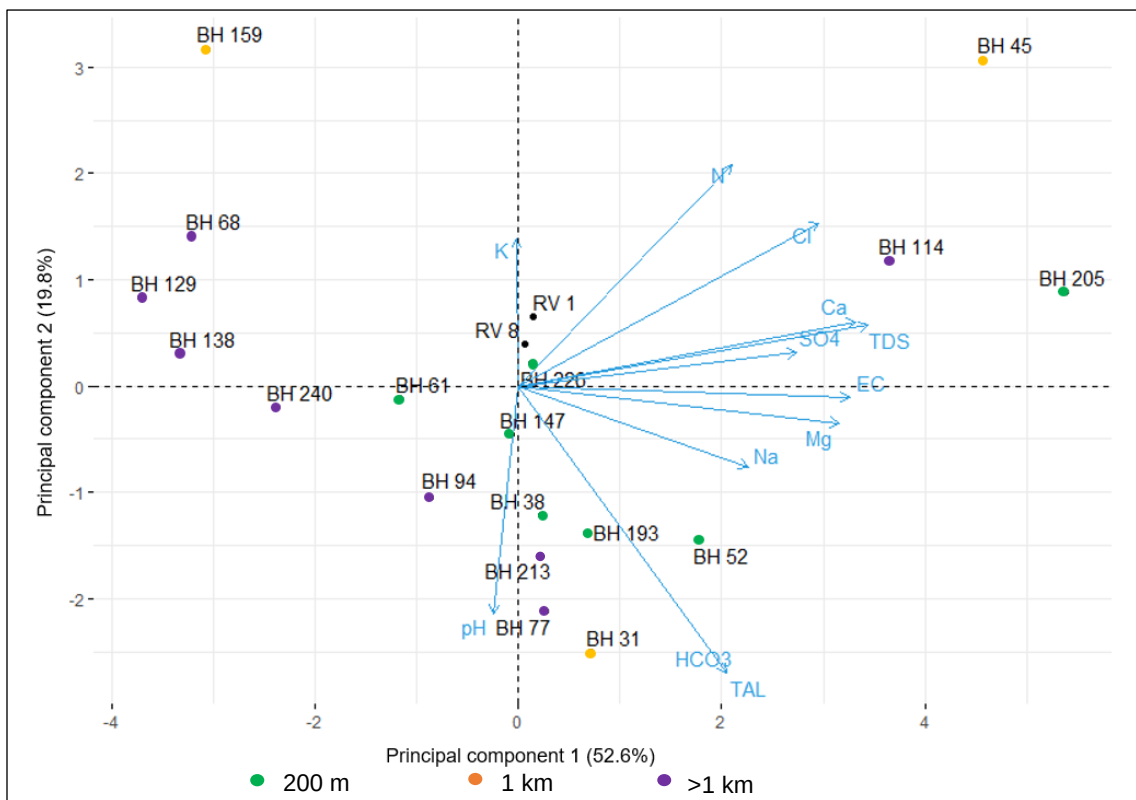


Figure 5.4. Principal Component Analysis biplot of the hydrochemistry data showing the similarity and dissimilarity among the sites at the set distances from the river.

The summarised PCA results after varimax rotation are shown in Table 5.3, indicating the highest loadings (≥ 0.5), eigenvalues, percentage of variance explained by each component, and the cumulative percentage of variance. The highest loadings explicate the contribution of each variable to each component. Three PCs were extracted, delineating the contributions involved in determining the water characteristics, which explain 84.72% of the total variance in the hydrochemical data.

Table 5.3. Varimax rotated principal component loadings for the physical and chemical properties of all water samples.

Variables	Component		
	1	2	3
TDS	0.970		
Cl ⁻	0.953		
Ca ²⁺	0.952		
Mg ²⁺	0.834		
NO ₃ ⁻	0.799		
EC	0.798		
SO ₄ ²⁻	0.721		
TAL		0.921	
HCO ₃ ⁻		0.920	
pH		0.560	
K ⁺			0.911
Na ⁺			0.681
Eigenvalue	6.31	2.38	1.48
Variance explained (%)	52.57	19.84	12.31
Cumulative variance (%)	52.57	72.41	84.72

The first PC contributed 52.57% to the variance with the loading of TDS, Cl⁻, Ca²⁺, Mg²⁺, NO₃⁻, EC, and SO₄²⁻. The loading of these ions with EC and TDS suggests that they predominantly contribute to water salinity, further justifying the use of EC for interpretations. Natural mineral dissolution (e.g., salt-rich minerals, feldspars, micas, amphiboles, pyroxenes), ion-exchange processes, as well as the chemical evolution of groundwater are all possible sources for the enrichment of Cl⁻, Ca²⁺, and Mg²⁺. Moreover, a common source of anthropogenic origin includes urban sewage, industrial discharge, and agricultural runoff.

Anthropogenic disturbances are often highlighted by the presence of NO_3^- (Kumar *et al.*, 2009; Lin *et al.*, 2012b; Tay *et al.*, 2017), and so this loading suggests pollution sources originating primarily from sewage discharge and agricultural return flows. Natural sources such as organic decomposition, atmospheric deposition, and oxidation of ammonia could be contributing to a lesser extent. The loading of SO_4^{2-} is likely an indication of anthropogenic sources related to mining activities. The exposure of sulphide ores (e.g., pyrite, pyrrhotite) in tailing dumps and abandoned mines (which are prevalent in the VDHS) subsequently result in oxidation, releasing SO_4^{2-} into the environment.

The groundwater system can largely be interpreted as an open system due to the presence of NO_3^- and SO_4^{2-} , revealing the occurrence of oxidising conditions. Moreover, highly evolved groundwaters tend to be anoxic and therefore lack NO_3^- and SO_4^{2-} (Guggenmos *et al.*, 2011). Despite this, the high loading of TDS, NO_3^- , and SO_4^{2-} suggests evidence for human-induced contamination of the water bodies. Overall, this component indicates that both natural and anthropogenic factors influence the quality of the water resources- however, the latter may be more prevalent.

The second PC explained 19.84% of the variance with the loading of TAL, HCO_3^- , and pH. During water-rock interactions in the aquifers, carbon dioxide charged water can result in silicate weathering, which may give rise to HCO_3^- (Tay *et al.*, 2017). Alternatively, this ion may be attributed to the natural dissolution of the carbonates related to calcrete, as well as the dissociation of carbonic acid. Additionally, sewage effluents discharged into the Vaal River, subsequently infiltrating into the underlying aquifer, could be a source. The release of HCO_3^- influences the pH and primarily contributes to the TAL.

The third PC accounted for 12.31% of the variance with the loading of K^+ and Na^+ . These ions are commonly associated with the chemical weathering of minerals such as salts, feldspars, and micas (Masindi and Abiye, 2018). Owing to the semi-arid climate in the study area, high evaporation rates may result in soil salinity, possibly exacerbated by irrigation return flow, and thus giving rise to K^+ , Na^+ , and Cl^- enrichment. Alternatively, other human-induced activities may be linked to these ions, particularly effluent release (Kumar *et al.*, 2009).

The components above demonstrate various controls on the chemical status of the water resources, including both natural and human-derived sources. The lack of single dominance from any variable in each component implies the mixing of waters from different sources (Kumar *et al.*, 2009). Approximately 15.28% of the total variance was not explained by the PCA. Other constituents such as minor ions, heavy metals, and pesticides may be contributing to the unknown factor.

5.1.4 Piper trilinear diagram

The major ions were plotted on the Piper trilinear diagram, shown in Figure 5.5. The water chemistry is dominated by weak acids (HCO_3^-) over strong acids (Cl^- and SO_4^{2-}), and alkaline earth metals (Ca^{2+} and Mg^{2+}) exceed alkalis (Na^+ and K^+). The water samples are broadly categorised into three primary water types: Ca-Mg-HCO_3^- (60%), $\text{Ca-Mg-Cl-SO}_4^{2-}$ (35%), and Na-K-Cl-SO_4^{2-} (5%).

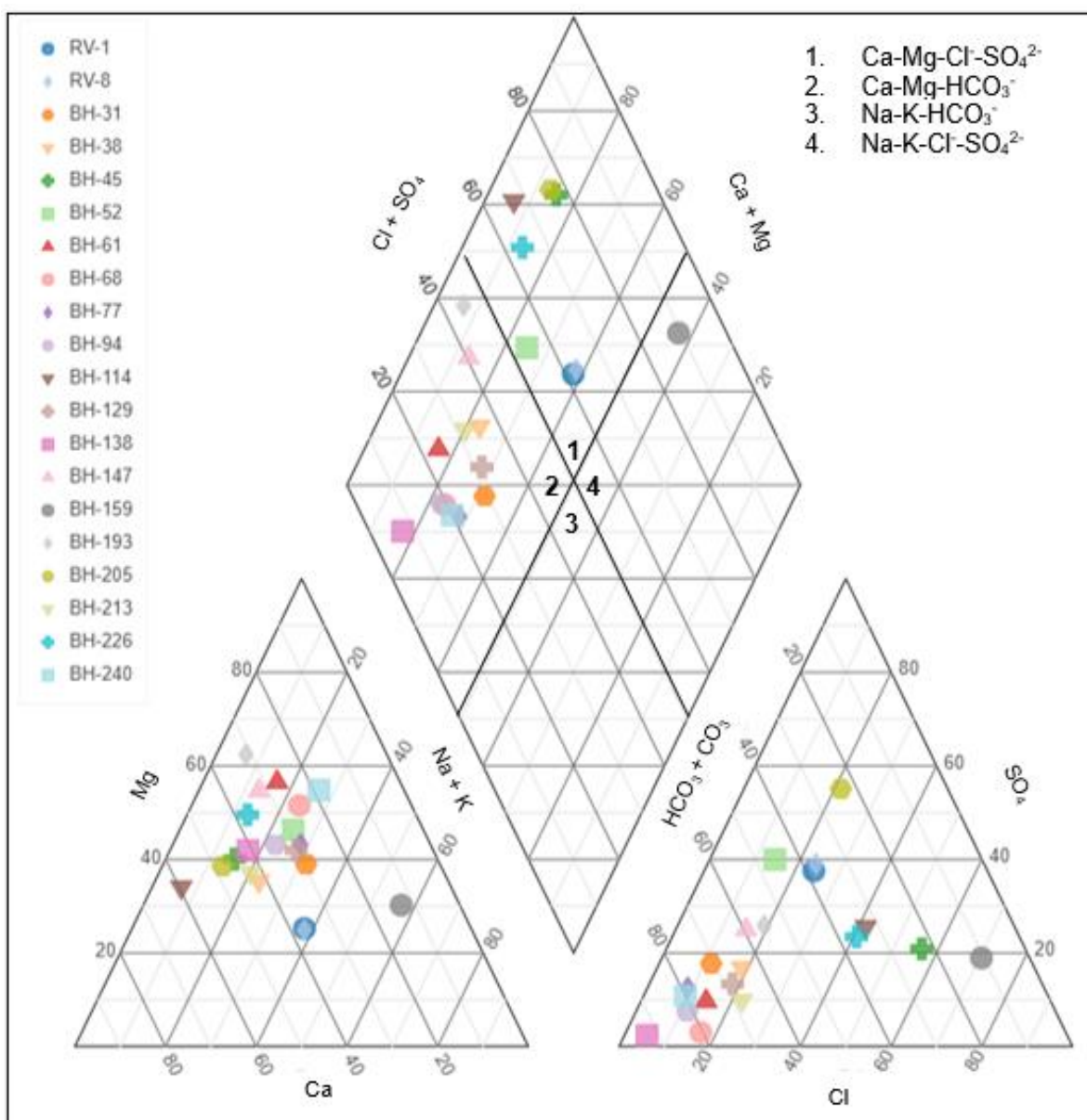


Figure 5.5. Piper trilinear diagram showing the hydrochemical facies of the groundwater and river samples. The ternary plots show the dominance of major cations and anions in decreasing order: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na-K}$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$, respectively.

The predominant Ca-Mg-HCO_3^- water type consists of sites that are associated with moderate to good water quality, corresponding to the clusters C-E detected by the HCA. These water samples are primarily located > 1 km from the river (67%), providing evidence that groundwater quality increases with distance. Moreover, these sites delineate the dominance of natural processes controlling chemical composition, where certain areas are more impacted by human-induced activities than others.

The second dominant $\text{Ca-Mg-Cl-SO}_4^{2-}$ water type comprised of samples associated with highly mineralised water, which form part of the moderate to poor water quality clusters A and B identified by the HCA. The river sites are likely polluted from domestic waste, industrial effluent, and agricultural practices, which subsequently impact shallow groundwater quality through interaction at discrete areas along the reach. The surface water pollution sources likely originated from outside the study area, as there is a substantial number of extensive anthropogenic activities taking place upstream of the VDHS. Sites that are located outside the 500 m radius of the river are most likely influenced by local human-induced activities, particularly agricultural practices. This water type shows the manifestation of negative effects from anthropogenic activities on the water quality.

Only one sample (BH 159) belonged to the least dominant Na-K-Cl-SO_4^{2-} water type, part of cluster C. Despite being situated within 1 km of the channel, this site displays very good water characteristics, similar to those of sites situated furthest from the river. It is located at the foot of a quartzite-dominated sequence and demonstrates minimal anthropogenic influence on its water quality. Thus, the hydrochemical properties are likely influenced by natural controls (e.g., weathering, ion exchange processes, etc.), giving rise to the Na-Cl water composition from the ternary plots.

The absence of cation and anion dominance coupled with the overlap of the Ca-Mg-HCO_3^- and $\text{Ca-Mg-Cl-SO}_4^{2-}$ water types may indicate a certain degree of mixing between the waters. This describes the possibility of certain areas being affected by both natural hydrochemical processes and anthropogenic activities.

5.2 Hydrograph Separation

As the data used for the baseflow separation techniques did not temporally correspond with the data utilised for the other approaches, the comparison between these results is solely based on potential seasonal influences. A total of 1127 daily streamflow datapoints were analysed for the 2013-2016 period, and the results from the filter algorithms are presented as composite hydrograph-hyetographs in Figure 5.6, and as a statistical summary in Table 5.4. Despite the efforts to account for the artificial wastewater component (which contributes $> 50\%$ of the total streamflow), the filtered streamflow results

should be interpreted with caution. Additionally, the upstream river gauging station is located ~ 27 km from the core boundary, which may be subjected to various factors that influence streamflow and subsequent baseflow calculations; interpretation of these results should thus be approached with caution.

The average baseflow over the three years from Nathan and McMahon (1990) for the upstream and downstream gauging station was 2.81 m³/s and 2.39 m³/s, respectively, which was significantly different ($P < 0.001$) from the Chapman (1991) method that generated 0.74 m³/s and 0.66 m³/s for the same gauging stations, respectively. However, upstream and downstream baseflow from Chapman (1991) were not significantly different ($P > 0.05$), whereas there was a significant difference between the two gauging stations for Nathan and McMahon (1990) ($P < 0.05$). Furthermore, there is a strong positive association between the river discharge from the upstream and downstream gauging stations, displaying significant similarity ($r = 0.7$; $P < 0.001$). The higher downstream river discharge value is most likely attributed to the confluence of various tributaries to the Vaal River (refer to Figure 4.3), and to a lesser extent, baseflow.

Table 5.4. Descriptive statistics of the streamflow, baseflow, and baseflow index (BFI) for the downstream (C2018) and upstream (C2H140) gauging stations during the 2013 – 2016 period.

	Surface flow	Nathan and McMahon (1990)		Chapman (1991)	
	(m ³ /s)	Baseflow (m ³ /s)	BFI	Baseflow (m ³ /s)	BFI
C2H018 (D)					
Minimum	7.99	0	0	0	0
Maximum	1297.33	39.13	1	31.24	1
Mean ($\pm \sigma$)	39.45 (± 101.17)	2.39 (± 6.03)	0.18 (± 0.36)	0.66 (± 3.89)	0.03 (± 0.17)
C2H140 (U)					
Minimum	7.8	0	0	0	0
Maximum	1008.07	33.57	1	25.6	1
Mean ($\pm \sigma$)	39.16 (± 81.8)	2.81 (± 5.59)	0.24 (± 0.43)	0.74 (± 3.6)	0.05 (± 0.21)

σ = Standard Deviation; D = downstream; U = upstream

Chapman (1991) modified and improved the Nathan and McMahon (1990) algorithm to account for the incorrect baseflow or streamflow constant once the quick flow component had ceased (see Chapman, 1991). This may serve as an explanation for the significantly higher baseflow associated with the Nathan and McMahon (1990) algorithm. Brink *et al.* (2005) and Walt *et al.* (2010) inferred low contributions from the subsurface water in the study area; therefore, this study gives preference to the Chapman (1991) values. In a fractured aquifer system, Welderufael and Woyessa (2010) reported more consistent

results from Chapman (1991) in comparison to other separation algorithms, further affirming the reliability of these values.

The BFI serves as an indicator of the proportional dependency of streamflow on the subsurface discharge (Kilian *et al.*, 2019). High groundwater dependence tends to have a BFI approaching 1 while low contribution is close to 0, generally characteristic of ephemeral streams (Smakhtin and Watkins, 1997). The Chapman (1991) algorithm shows that the river exhibits overall low dependence (3 - 5%) on water derived from the subsurface system to sustain streamflow. The baseflow patterns suggest interflow as one of the possible sources of subsurface storage (Xu *et al.*, 2002).

In the semi-arid Upper Modder River Basin, located in the Free State Province (RSA), Welderufael and Woyessa (2010) reported a relatively high baseflow proportion of the total streamflow (69%) between the years 1999 to 2007 using the Chapman (1991) method, demonstrating the large dependence of streamflow on the groundwater discharge obtained from the underlying fractured aquifer network. This implies that local geological, hydrological, and anthropogenic features have considerable influence over the magnitude of the baseflow component.

5.2.1 Seasonal baseflow contribution

The seasonal BFI was determined by subdividing the values into wet (October – March) and dry (April – September) periods, presented in Table 5.5. As expected, there is a significant difference between the upstream and downstream seasonal BFI values from both methods ($P < 0.001$). Disregarding the significantly mismatched values from Nathan and McMahon (1990), the BFI values from Chapman (1991) indicate that the dry season receives subsurface discharge represented as 5% and 8% of the total streamflow for the downstream and upstream gauging stations, respectively. Saraiva Okello *et al.* (2018) similarly found higher baseflow during the dry season in a semi-arid South African catchment. The different baseflow values between the gauging stations can be a result of local characteristics such as topography, geology, land-use, rainfall, and hydrogeological characteristics (Zhang *et al.*, 2013).

The average daily streamflow for the upstream and downstream gauging stations during the wet season was 54.8 m³/s and 57.62 m³/s, respectively. In contrast, the dry season was characterised by corresponding values of 22.72 m³/s and 20.36 m³/s. This seasonal variability is highlighted in Figure 5.6, where the river discharge generally increases and peaks in response to summer rainfall events. It is apparent that when the wet season begins, the streamflow is generally driven by meteoric water as opposed to delayed subsurface input. The low baseflow component during the start of the wet season

may imply that the subsurface reserves respond slowly to precipitation events. This is also highlighted by the low BFI (1%) associated with the wet season (Table 5.5).

Table 5.5. Descriptive statistics for the seasonal baseflow index (BFI) for the downstream (C2H018) and upstream (C2H140) gauging stations during the 2013 – 2016 period (cumulative daily average in m³/s).

	Nathan and McMahon (1990)		Chapman (1991)	
	Dry	Wet	Dry	Wet
C2H018 (D)				
BFI ($\pm \sigma$)	0.15 (± 0.36)	0.12 (± 0.36)	0.05 (± 0.22)	0.01 (± 0.11)
Total	409.83	2227.83	180.42	558.38
C2H140 (U)				
BFI ($\pm \sigma$)	0.27 (± 0.44)	0.20 (± 0.41)	0.08 (± 0.28)	0.01 (± 0.10)
Total	810.37	2349.01	345.96	486.36

σ = Standard Deviation; D = downstream; U = upstream

Both gauging stations demonstrate a rapid and abnormal increase ($> 1000 \text{ m}^3/\text{s}$) in March 2014 that does not correspond to precipitation, and it is unreasonable to suggest that baseflow peaks in late summer. Thus, it can only be explained by a large amount of artificial input into the Vaal River. Moreover, the first two dry periods (2013-2014) tend to exhibit a consistent low flow pattern while the dry period in 2015 experienced more variable streamflow, which could be attributed to the increased contribution of anthropogenic discharge.

Baseflow and streamflow reveal considerable spatio-temporal variability across the study area. Although minimal, the greatest subsurface contribution to streamflow was found to occur during the dry season. This was evidenced by the presence of springs and groundwater-dependent wetlands during field investigations, particularly in the crystalline basement rocks, where some springs were situated $\leq 200 \text{ m}$ from the river (e.g., SP 1 and SP 2), and assumed to be contributing to surface water flow. According to anecdotal information provided by multiple landowners, springs are usually only present during the dry period, indicating a rise in the water table. This is attributed to the subsurface storage of antecedent wet season precipitation, which subsequently discharges onto the surface or into a water body during the dry season (Alley *et al.*, 2002). This would, therefore, suggest the presence of permeable vertical and/or horizontal fractures that facilitate the direct or indirect interconnection between the bedrock river and transient subsurface stores (Oxtobee and Novakowski, 2003).

Due to the differences in temporal scale associated with this method, baseflow contribution may have decreased over the years as a result of increased groundwater extraction, which explains the position of the observed water table levels below the riverbed in the northern and south-western reaches during the study period (Section 5.5). As groundwater extraction may lead to reduced groundwater discharge rates (Seward *et al.*, 2006), the continuous release of artificial discharge may prompt induced recharge conditions within the underlying aquifer. The electrical conductivity along the river reach remained relatively consistent with no sharp fluctuations, suggesting low baseflow inputs into the Vaal River.

Increased abstraction of river water for irrigation may explain the apparent small quantity of baseflow observed during the dry months whereas the water demand decreases during summer rainfall; therefore, the quick flow component is not heavily impacted (Saraiva Okello *et al.*, 2018). The baseflow contribution is deemed negligible during the rainy periods as the river responds rapidly to precipitation events.

Overall, these results indicate that subsurface water does not contribute significantly to streamflow. Instead, much of the streamflow is sustained by precipitation routed as surface runoff, wastewater discharge, irrigation return flows, and industrial effluents, subsequently maintaining flow persistency.

It is worthy of note that the filter algorithms cannot differentiate between sources of baseflow as it may not be limited to groundwater storage (Saraiva Okello *et al.*, 2018). Moreover, the potential over- and under-estimation of baseflow is ever more present, due to the selected algorithms and the vast dynamic anthropogenic discharge that is fed into the Vaal River. Hughes *et al.* (2003) note that baseflow may be under- and over-represented during the beginning and end of wet seasons, respectively, using daily discharge data for the separation. The limitation of applying this method in a fractured aquifer terrain is also noted.

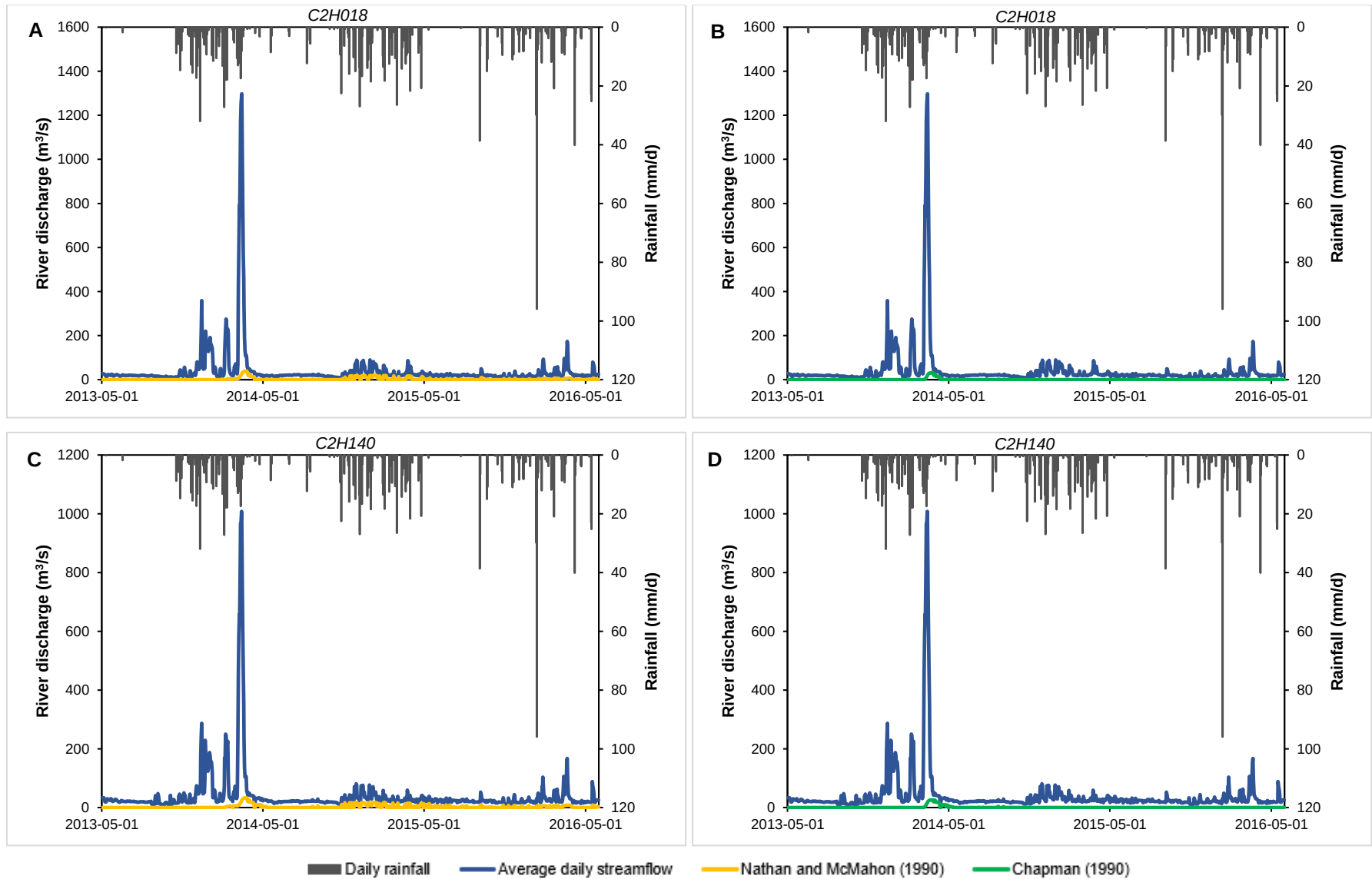


Figure 5.6. (A) and (B) baseflow hydrographs for downstream gauging station C2H018 and (C) and (D) for upstream gauging station C2140 using the Nathan and McMahon (1990) and Chapman (1991) filter algorithms.

5.3 Microbes and Biological Oxygen Demand

5.3.1 Bacterial analysis

A count of biological parameters and measured BOD from all sites at given distances from the river are shown in Table 5.6. All the sites were characterised by the existence of at least one bacterial species; almost all sites (82%) recorded the presence of *P. mirabilis* (74%) and/or *E. aerogenes* (44%) and/or *E. coli* (11%), whereas all the sites analysed for *S. enterica* and *S. aureus* had these microorganisms present. Given that the samples were not analysed within the recommended holding time, interpretation of results should be exercised with caution.

Table 5.6. Summary of bacterial count and biological oxygen demand (BOD) for river and groundwater sites located at the set distances (200 m, 1 km, and > 2 km) from the river.

Site	<i>S. enterica</i>	<i>E. coli</i>	<i>E. aerogenes</i>	<i>P. mirabilis</i>	<i>S. aureus</i>	BOD (mg/L)
(cfu/100 mL)						
RV 1	80	0	0	22	-	1.4
RV 8	11	0	2	24	-	1.4
200 m						
BH 38	215	0	0	36	-	3.4
BH 42	-	20	42	137	8	5.6
BH 52	37	0	0	0	-	5.3
BH 61	-	0	190	30	38	7.6
BH 147	-	0	746	4	647	2.8
BH 149	-	0	587	3	560	-
BH 174	-	1	> 10000	0	> 1000	-
BH 190	-	0	0	123	159	-
BH 193	40	0	0	3	-	0.8
BH 205	-	0	178	322	631	-
BH 220	-	2	108	52	-	7.3
BH 226	11	0	0	1	-	10.9
1 km						
BH 31	5	0	0	0	-	0.6
BH 45	21	0	0	0	-	5.9
BH 159	59	0	0	4	-	4.5
BH 184	-	0	92	> 1000	-	-
> 2 km						
BH 19	-	0	> 1000	20	-	-
BH 68	-	0	11	> 1000	-	-
BH 77	1	0	0	0	-	3.1
BH 94	14	0	0	0	-	4.5
BH 114	-	1	38	> 1000	-	4.8
BH 129	160	0	0	30	-	0.6
BH 138	106	0	0	0	-	3.4
BH 213	80	0	0	75	-	0.3
BH 240	1	0	0	65	-	3.4
BH 263	-	0	2	230	368	2.2

The bacterial content in the river water was much lower than expected, possibly attributable to the prolonged holding time and human error during sampling and analysis. However, the relatively high bacterial presence in groundwater reflects some degree of contamination, despite the questionable results. Figure 5.7 illustrates the content from some of the groundwater sites that were characterised by high bacterial count.

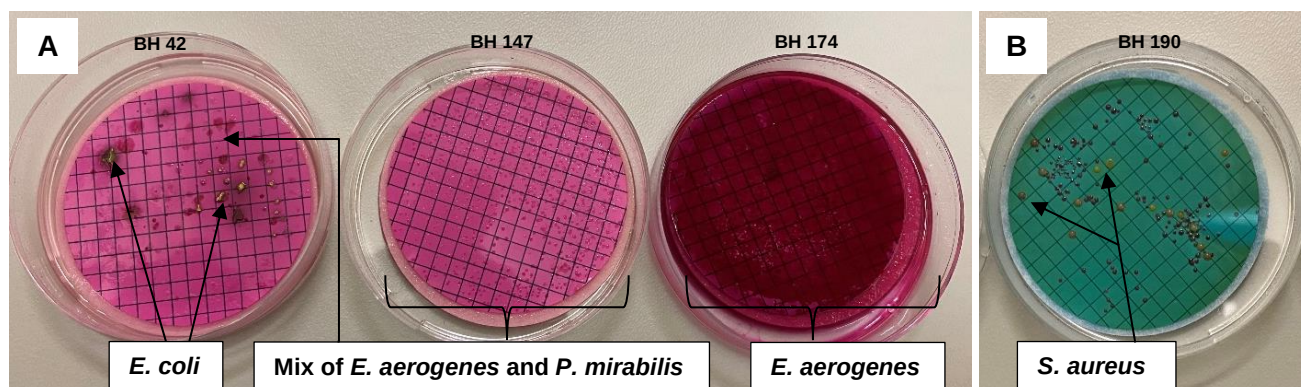


Figure 5.7. Photographs of **(A)** Endo (*E. coli*, *E. aerogenes*, and *P. mirabilis*) and **(B)** Tergitol TTC (*S. aureus*) nutrient pad discs. For scale, a Petri dish is 5 cm in diameter. *E. coli* = metallic sheen colonies; *E. aerogenes* = dark pink-red colonies; *P. mirabilis* = light pink-red colonies; *S. aureus* = yellow colonies.

E. coli are characterised as coliforms which are widely used to identify faecal contamination (Taka and Quay-Ballard, 2018). Opportunistic pathogens *E. aerogenes* and *P. mirabilis* are utilised to evaluate the hygienic quality of water (Lin *et al.*, 2012b) and form part of the group of total coliforms (DWA, 1996). Moreover, these species are commonly found in the mammalian intestinal tracts and thus serve as additional indicators of faecal pollution; however, they do not necessarily cause serious infections in humans (Drzewiecka, 2016). *S. enterica* is found in the gastrointestinal tracts of numerous animals (e.g., birds, reptiles, mammals) and is a renowned pathogen resulting in foodborne diseases (Liu *et al.*, 2018). Therefore, this pathogen is directly affiliated with faecal origins. *S. aureus* is commonly found on nasal cavities, skin, and in animal faeces, amongst others (LeChevallier and Seidler, 1980), and thus can be detected in sewage (WHO, 2011). This pathogen does not transmit through the consumption of polluted water and instead health effects arise through direct contact with food (LeChevallier and Seidler, 1980).

According to the DWA (1996) compliance guidelines for drinking water, 100 mL of water should not contain any faecal indicator species and restricted numbers (0 – 5 cfu/100 mL) of total coliforms are considered to have negligible risk. Most sites failed to meet the Target Water Quality Range (TWQR) and certain sites recorded extremely high bacterial counts (> 1000 cfu/100 mL).

The transport of microbes is mainly facilitated by the bulk movement of water, however, these organisms are immobilised and filtered in varying degrees by the media through which they migrate (Murray *et al.*, 2007; Driezum *et al.*, 2018). As such, soil, aquifer, and microbial properties influence the occurrence and survival of these waterborne pathogens. The general concept of relatively slow groundwater flow rate gives rise to localised impacts (Murray *et al.*, 2007). The overall deeper hydraulic head associated with sites > 2 km from the river (Section 5.5) may provide more unfavourable conditions for bacterial migration and colonisation; nonetheless, the severe contamination affiliated with certain sites draws attention to the localisation concept as proposed by Murry *et al.* (2007).

Livestock animals seem to be the primary source of bacterial contamination in the VDHS. Animal waste is widely known as a significant factor contributing to groundwater pollution (Cho *et al.*, 2000). In many instances, the disturbed area in the immediate radius of the borehole can serve as an entry point for bacteria (Murray *et al.*, 2007). During field surveys, it was noted that several boreholes are located in close proximity to the grazing areas, watering points, and/or barns/stables of farm animals, proving little doubt that these practices contributed to the elevated counts.

Poorly designed and managed septic tanks may promote bacterial occurrence. Takal and Quaye-Ballard (2018) found that bacterial counts in groundwater were associated with septic tank pollution in the Ashanti region, Ghana. Furthermore, surface runoff and the release of poorly treated wastewater discharge into surface water contribute to microbial contamination (Lin *et al.*, 2012b; Bezuidenhout *et al.*, 2013). Therefore, in some instances relating to boreholes near the river, interaction through readily open geological structures and unconsolidated material could account for the bacterial presence.

Due to the uncertainty associated with the results, it cannot be said with confidence that there was SW-GW interaction taking place. However, owing to the unnatural count of microorganisms in the groundwater near the Vaal River, which is relatively shallow (Section 5.5), it is a good possibility that a certain degree of interaction was contributing to bacterial contamination. Lin *et al.* (2012a) identified a greater influence on bacterial structure from infiltrating river water in the shallow groundwater zone as opposed to deeper areas in an aquifer. Moreover, the predominant occurrence of alluvial aquifers in the vicinity of the river system (which are defined by unconfined coarse material) serve as ideal porous pathways for bacterial movement, and are more likely to reach the saturation zone (Murray *et al.*, 2007).

The presence of microbes at every site suggests that bacteria could be ubiquitous in the VDHS. The findings demonstrate that human or animal consumption of groundwater may be exposed to a certain degree of bacterial contamination. Moreover, the results indicate that other harmful microbiological

pathogens could be co-existing with the bacterial species identified in this study (DWAF, 1996; Lin *et al.*, 2012b; Bezuidenhout *et al.*, 2013). Bezuidenhout *et al.* (2013) similarly found high bacterial counts in groundwater in the North West Province. Their study also highlighted the influence of seasonality on the abundance of bacterial populations, which favoured warm and wet conditions (Bezuidenhout *et al.*, 2013). Temporal dynamics of bacterial communities have been documented in numerous studies (Lin *et al.*, 2012a; Driezem *et al.*, 2018; Liu *et al.*, 2018).

5.3.2 Canonical Correspondence Analysis (CCA)

The similarity and dissimilarity between the bacterial species in relation to the water chemistry and *in situ* physico-chemical data are shown in the CCA ordination plots (Figure 5.8). Both CCA biplots describe > 90% of the total variance in the data, suggesting a high correlation between the water quality parameters and bacterial species data. The physico-chemical water quality variables are represented by the red arrows whose length is proportional to the rate of change (Liu *et al.*, 2012).

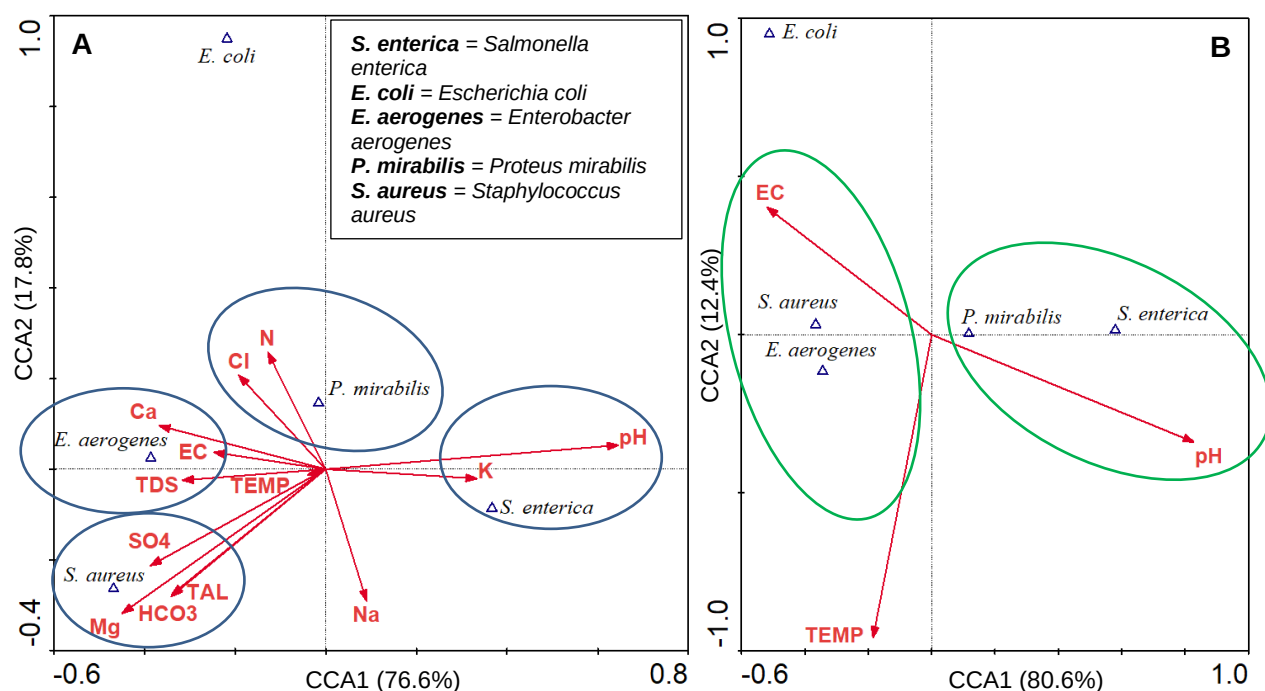


Figure 5.8. Canonical Correspondence Analysis (CCA) biplot showing the similarity and dissimilarity between **(A)** bacteria species and all hydrochemical variables and **(B)** bacteria species and *in situ* physico-chemical parameters. Refer to Sections 4.3 and 4.4.1 for the elucidation of abbreviated hydrochemical variables.

In Figure 5.8 A, the CCA biplot reveals strong relationships between environmental variables and microbial species, distinguishing communities along both CCA1 and CCA2 axes. These associations are highlighted by the blue circles, which demonstrate the strongest correlations between bacterial species and water quality variables. Interestingly, *E. coli* is weakly correlated with the water quality variables and other microbes. This is likely attributed to the relatively low counts associated with this species. Figure 5.8 B shows that *S. aureus* and *E. aerogenes* have a stronger relationship with EC while *P. mirabilis* and *S. enterica* correlate with pH in the environment, separating these groups along the CCA1 axis, as delineated by the green circles.

The ordination plots show that significant environmental relationships exist between the microbes and measured parameters. These observations suggest that bacterial community structures are influenced by contaminated water associated with higher ion concentrations, representing the source for higher counts. This was further noted in Figure 5.8 B, where moderate to strong correlations were present between the bacterial species and EC.

5.3.3 Biological Oxygen Demand (BOD)

BOD concentrations over time are illustrated in Figure 5.9. Almost all the sites show linear growth in the first 1000 minutes, followed by variable increases, and decreases in BOD concentration. These observed fluctuations confirm the presence of microorganisms that consume oxygen at the expense of organic matter decomposition, providing evidence for groundwater contamination. Moreover, these results confirm the possibility of a largely open groundwater system in the VDHS.

Approximately 62% of the sites were found to exceed the universal BOD water quality index of 3 mg/L (Boyacioglu, 2007), with the highest mean value (5.68 mg/L) observed for BH 226, reaching the maximum value of 10.9 mg/L (Table 5.6; Figure 5.9). BOD was lower for the > 2 km sites relative to the sites in closer proximity to the river, further suggesting that deeper water levels are less favourable for organic matter decomposition, or less affected unless there are significant local pollution sources.

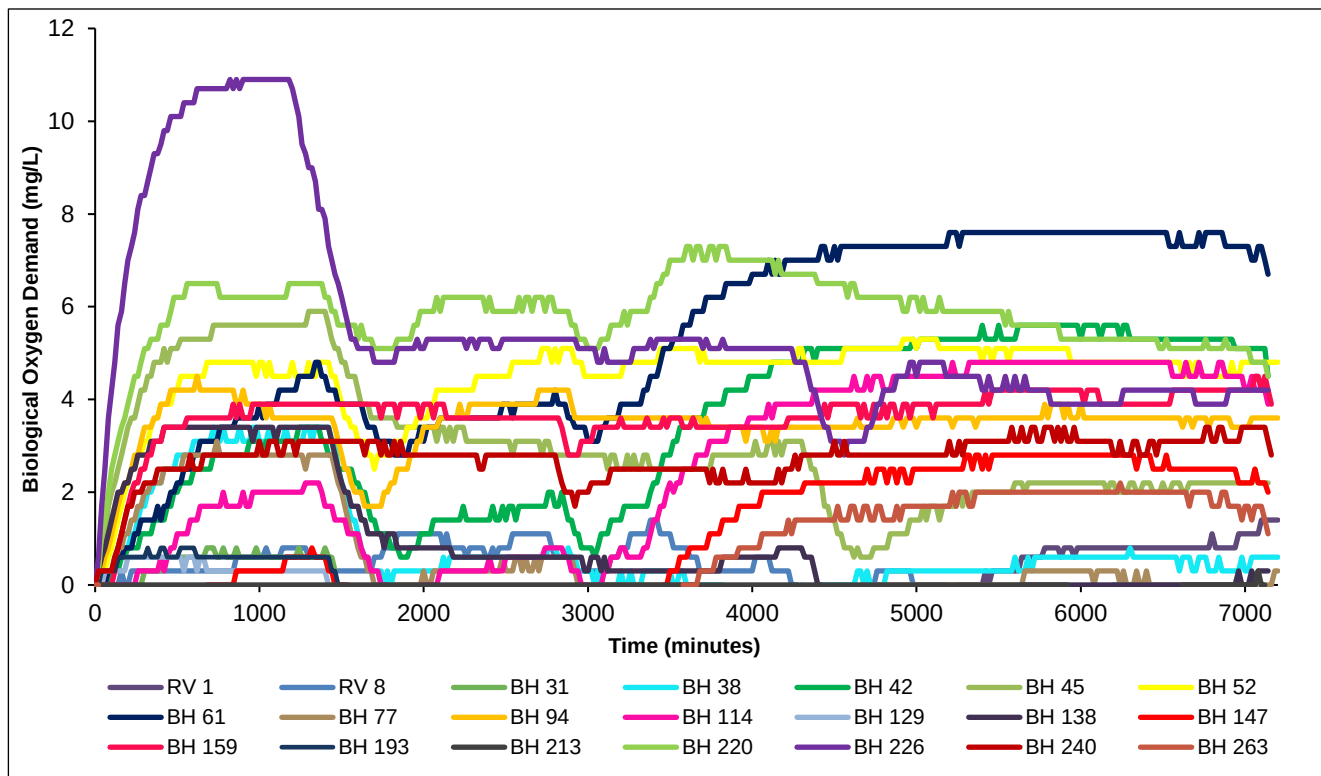


Figure 5.9. Biological oxygen demand during a 5-day period.

5.4 Stable Water Isotopes

A statistical summary of the stable water isotopes associated with different sites is described in Table 5.7. The stable isotope results for all sites are presented in Appendix D and were plotted on a $\delta^{18}\text{O}$ - $\delta^2\text{H}$ graph (Figure 5.10). Relations are expressed as enrichment or depletion with respect to the heavier isotope ($\delta^{18}\text{O}$). The most depleted mean values were observed for groundwater sites 2 km from the river ($\delta^{18}\text{O}$: -5.57‰) while the most enriched value was associated with the waste dam ($\delta^{18}\text{O}$: 4.16‰).

The relationship between the isotopic content and Meteoric Water Line (MWL) can provide invaluable information pertaining to groundwater flow paths, origin, and physical post-precipitation processes (Geyh, 2000). This includes atmospheric (e.g., condensation, evaporation) and recharge processes (e.g., water-media interactions, mixing) (Gupta and Deshpande, 2005; Abiye *et al.*, 2021).

The Local Meteoric Water Lines of Pretoria (PLMWL) and Johannesburg (JLMWL) were plotted in addition to the Global Meteoric Water line (GMWL) (Figure 5.10). While useful for interpretation, the GMWL is associated with conditions that are too broad for application in the study area (e.g., relatively high slope; humidity). The JLMWL (Leketa *et al.*, 2018) represents a closer proximity to the study area

and hence a more reliable environmental setting. Therefore, the JLMWL was primarily used as a reference for tracing and understanding water origin.

Table 5.7. Statistical summary of stable water isotopes for rain, river, springs, waste dam, mine, and groundwater samples located at set distances 200 m, 500 m, 1 km, 2 km, and > 2 km from the river.

	<i>n</i>	$\delta^{18}\text{O}$ (‰)				$\delta^2\text{H}$ (‰)			
		Mean	Min	Max	C.V. (%)	Mean	Min	Max	C.V. (%)
Rain	2	-2.78	-3.39	-2.16	-31.40	1.90	-6.91	10.72	654.74
River	8	-1.34	-1.65	-1.07	-12.80	-2.97	-6.19	-1.16	-52.07
Springs	8	-0.28	-4.87	7.60	1689.25	2.29	-24.93	46.16	1176.19
Mine	1	1.41				8.45			
Waste dam	1	4.16				20.21			
Boreholes									
200 m	22	-3.95	-6.25	0.87	-42.47	-17.70	-30.02	2.10	-51.16
500 m	8	-5.09	-6.00	-3.81	-19.20	-24.77	-31.58	-18.33	-20.25
1 km	8	-5.10	-6.16	-3.43	-16.79	-25.29	-29.44	-16.67	-16.79
2 km	5	-5.57	-6.47	-4.95	-10.28	-26.03	-27.67	-23.06	-7.34
> 2 km	26	-5.53	-6.41	-4.67	-8.18	-27.18	-33.61	-23.13	-8.82

n = sample size; Min = minimum; Max = maximum; C.V. = coefficient of variation

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of the surface water and groundwater samples exhibit variation in relation to the JLMWL. Three fundamental groups were broadly identified from the plotted isotopic data: (1) data points plotted above the JLMWL, (2) data points plotted along the JLMWL, and (3) data points plotted below and semi-parallel to the JLMWL (Figure 5.10). The groups reflect distinct isotopic categories corresponding to various meteoric and subsurface processes to which the waters have been subjected to.

The $\delta^{18}\text{O}$ values in group 1 are possibly indicative of secondary evaporation effects. In areas characterised by low humidity, the re-evaporation of precipitated water is assumed to give rise to vapour masses associated with an isotopic signature that plots above the LMWL (Clark and Fritz, 1997). The re-condensation of such vapour (in any substantial quantity) before mixing with the tropospheric reservoir can lead to water that also plots above the LMWL (Clark and Fritz, 1997). Thus, the observed isotopic labels of rainfall can be explained by the relatively low humidity in the study area during the dry season, resulting in depleted vapour (a more arid moisture source).

Dansgaard (1964) noted that intense and prolonged rainfall events tend to produce isotopically depleted precipitation as opposed to relatively small events, which is highlighted in this study by the content of RN1 ($\delta^2\text{H}$: -6.91‰ and $\delta^{18}\text{O}$: -3.39‰; heavier rainfall) in comparison to the composition of RN2 ($\delta^2\text{H}$: 10.72‰ and $\delta^{18}\text{O}$: -2.16‰; lighter rainfall). The phenomenon occurs as raindrops fall through dry air (low humidity), introducing re-evaporation and imparting kinetic fractionation, subsequently leading to more enriched isotope labels.

Group 2 may be representative of the isotopic composition related to present meteoric water. In other words, these waters likely reflect recent recharge and/or mixing, where the former indicates that water has spent an insignificant amount of time on the surface prior to infiltration (direct recharge).

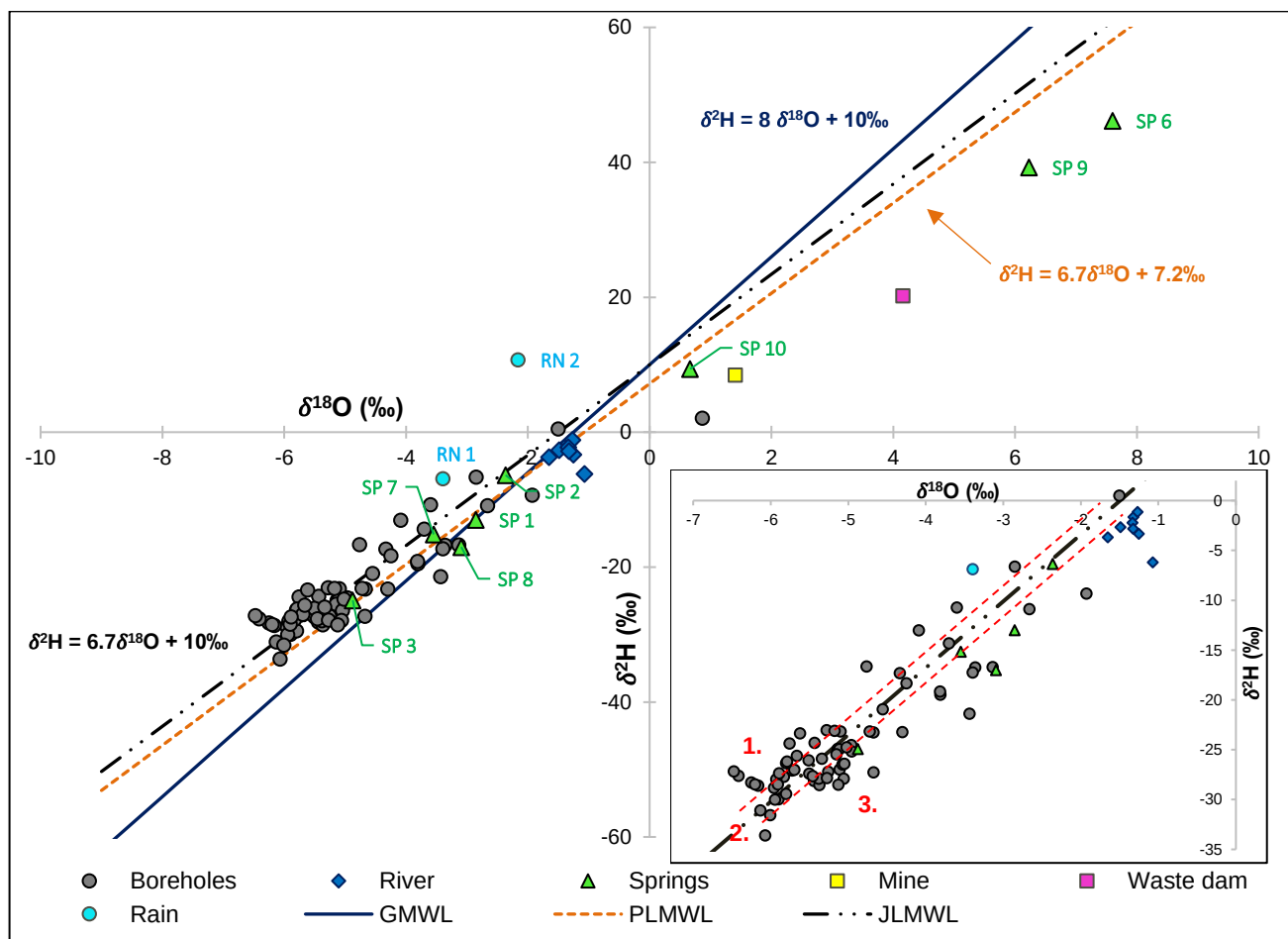


Figure 5.10. Stable isotopes of groundwater (boreholes), river, springs, mine, rain, and a waste dam plotted against the Johannesburg Local Meteoric Water Line, Pretoria LMWL, and Global MWL. The inset shows a zoomed-in view of the sites versus the JLMWL and delineation of the groups.

In arid and semi-arid environments, evaporation is seen as one of the predominant processes controlling the isotopic content of groundwater (Clark and Fritz, 1997). This influence was partially observed in group 3, which shows displacement of the data from the JLMWL. As evaporation proceeds from open water bodies, the heavier isotopes preferentially remain with the more condensed phase, resulting in enrichment (Gupta and Deshpande, 2005). As a result of the kinetic isotope fractionation, the river and spring sites have a higher relative enrichment of $\delta^{18}\text{O}$ than $\delta^2\text{H}$ and fall consistently below the JLMWL.

Worthy of note are sites SP 9 and SP 10, located in close proximity to one another (< 20 m). Despite both sites being open water bodies -and thus demonstrating significant enrichment of $\delta^{18}\text{O}$ - these sites were isotopically distinct. Similarly, the waste dam does not seem to influence SP 6 or BH 263. This is likely attributed to a geological barrier between the sites, indicating complex groundwater pathways.

5.4.1 Surface water-groundwater interaction

For the purpose of identifying potential SW-GW interaction, Figure 5.11 illustrates the isotopic compositions associated with sites at set distances from the river. Groundwater enrichment is often inferred as indirect recharge taking place from the surface or surface water, whereas depleted groundwater is commonly interpreted as recharge originating from precipitation (Sami, 1992) that can be identified as direct recharge. Data that are closely clustered, as represented by the zones, imply the possibility of similar sources of water and mixing trends (Abiye *et al.*, 2021).

There is a distinct difference between the river and groundwater sites located ≥ 1 km from the channel as shown by zones 1 and 3, respectively, with an intermediate composition represented by zone 2. Sites that characterise boreholes ≤ 500 m from the river contribute 88% to zone 2, inferred as a mixing zone between the Vaal River and groundwater. The deviation of isotopically enriched BH 193 and BH 52 belonging to zone 1 demonstrate their linkage with surface water (Figure 5.11).

The mixing line is slightly steeper ($s = 5.9$) than the evaporation line ($s = 5.7$), which eliminates evaporation as the sole cause for isotopic enrichment (Figure 5.11). This is consistent with the findings from Acheampong and Hess (2000), which found an evaporation slope of 5 ± 2 on a $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plot when evaporation takes place under humidity lower than 100%. The relatively enriched river isotopes plotted along the JLMWL demonstrate the connection with the meteoric water and shallow groundwater, which were exposed to a certain amount of evaporation prior to mixing.

SP 1 and SP 2 are groundwater-fed and most likely associated with SW-GW interaction, while SP 7 and 8 (located > 2 km from the river) demonstrate the effects of evapotranspiration and possible mixing with rainfall. The isotopic signal of SP 3 shows that depleted groundwater feeds this wetland system, which is unrelated to the SW-GW mixing process.

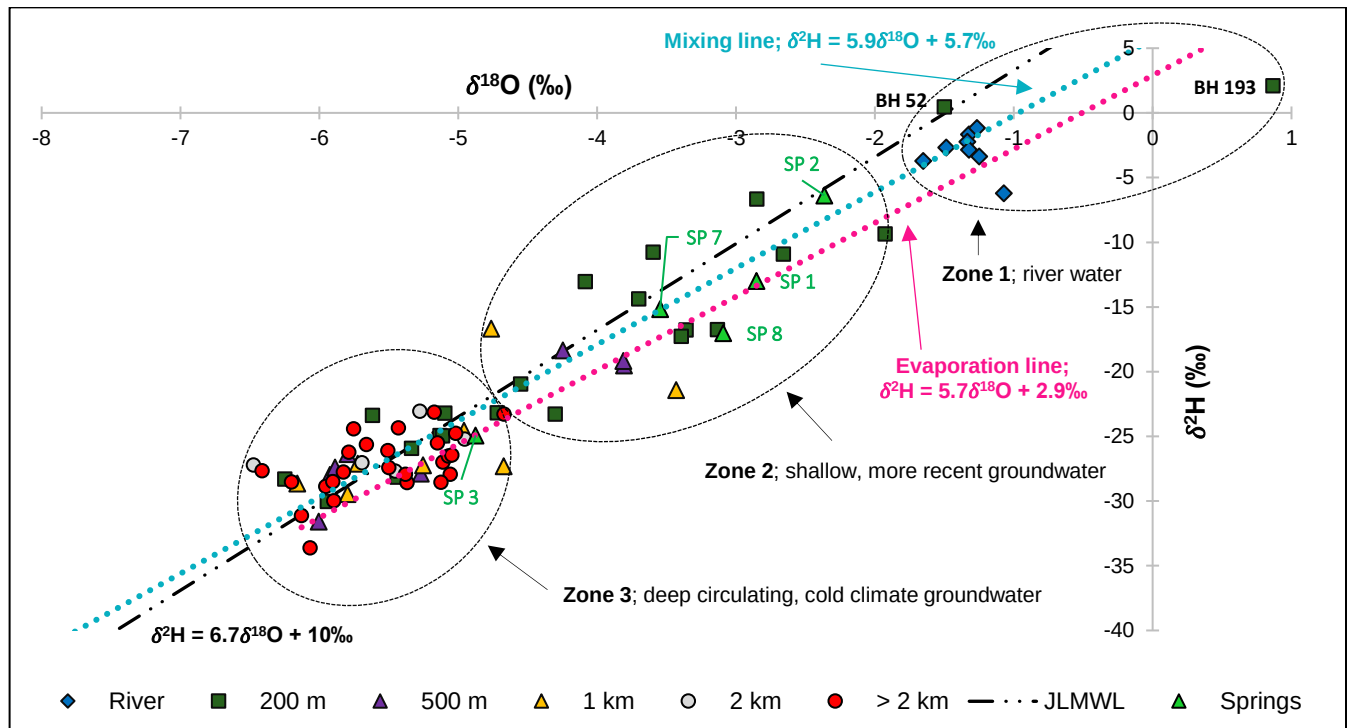


Figure 5.11. Stable isotopes of river, springs, and groundwater sites at set distances from the channel plotted against the Johannesburg Local Meteoric Water Line.

BH 193 and BH 52, together with the sites in zone 2, are hosted in both alluvial and fractured rock material, representing mostly shallow groundwaters (discussed below). In turn, these aquifer systems are expected to foster high hydraulic connectivity with surface water. Moreover, the location of these sites (predominantly down-gradient from the hills) suggests that depleted groundwater flows towards the enriched Vaal River, reflecting a degree of permeability between the aquifer systems. The isotopic similarity of sites at various distances from the river in zone 3 supports this observation.

The average percentage of the mixing proportions between the isotopically distinct river water (zone 1) and deep circulating groundwater (zone 3) are shown in Table 5.8. The sites located nearest to the channel (≤ 200 m) have the highest percentage of river water mixing with groundwater (55%), whereas the degree of mixing progressively decreases with distance from the river, representing 37% and 34% of river water mixing with groundwater at sites located 500 m and 1 km from the channel, respectively.

As such, the isotopic label changes in accordance with the distance from the river and, therefore, a wide range of isotope signals are associated with the mixing zone ($\delta^{18}\text{O}$: 0.87‰ to -1.93‰; $\delta^2\text{H}$: -23.26‰ to 2.10‰).

Table 5.8. The average percentage of river water mixing with groundwater at the set distances from the channel for zone 2 sites.

River distance	<i>n</i>	χ (%)	$\delta^{18}\text{O}$ ave. ($\pm \sigma$)
200 m	14	55	-3.07 (± 1.46)
500 m	3	37	-3.96 (± 0.25)
1 km	2	34	-4.1 (± 0.94)

ave. = average; *n* = sample size; σ = Standard Deviation

The groundwater levels (in metres below ground level; m.b.g.l) were plotted against the isotopes of the inferred zones (Figure 5.12 A) and distances from the river channel (Figure 5.12 B) to provide insight into the direction of SW-GW interaction. It was impractical to measure the Vaal River’s water depth due to its sheer size. Thus, the average depth of 4 m was used (Roos and Pieterse, 1993) to estimate the position of the river boundary below the surface. It should be noted that the depth was highly variable along the study reach; the south-eastern reaches were found to be shallower with riffles and visible bedrock while the northern and south-western reaches alternated with riffles and pools.

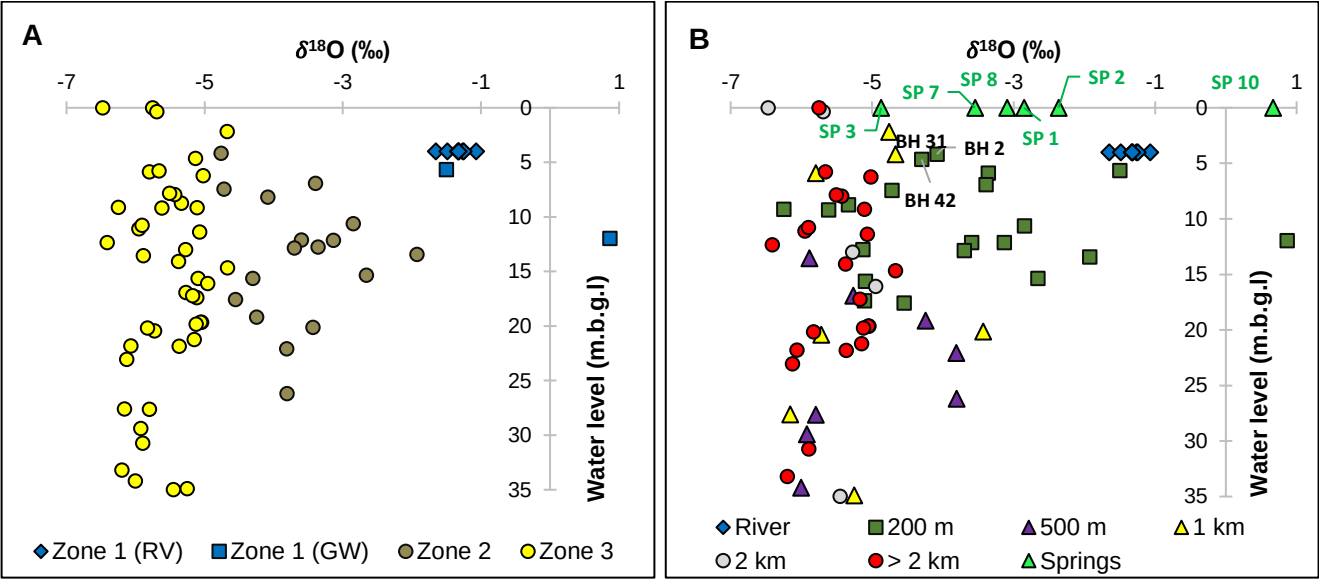


Figure 5.12. Groundwater level below the ground surface plotted against the stable isotopes of the (A) zones (RV = river; GW = groundwater) and (B) sites at set distances from the river channel.

The strongly depleted isotope signals ($\delta^{18}\text{O} < -5\text{‰}$), assigned to zone 3 at varying distances from the river channel, display variable groundwater levels below the surface. Zone 2 consists of sites ≤ 1 km from the river and reveals shallower groundwater levels, particularly the areas nearest to the river (≤ 200 m). In circumstances where the phreatic surface lies well below the river channel, subsurface discharge is not expected. Instead, groundwater recharge from streamflow may be a significant process (Smakhtin and Watkins, 1997). These observations could be interpreted as a *losing* surface water regime, whereby the water table in the vicinity of the channel is largely below the riverbed.

Considering the close association of shallow water levels (2.17 – 4.65 m.b.g.l) from sites BH 2, BH 31, and BH 42 with the river water (which are equal to or above the approximated riverbed boundary): this may be suggestive of potential near-surface baseflow contribution. These sites occur in the crystalline basement, which is characterised by the shallowest water table (discussed below), classifying this part of the river as a *gaining* reach.

5.4.2 Hydrochemistry and stable water isotopes

Hydrochemical properties can be used in conjunction with isotopic signatures to distinguish groundwater mixing, and assess the hydrological status between water resources (Geyh, 2000). The isotopic signatures identified by the three zones (Figure 5.11) are distinctly linked to the clusters defined by the hydrochemical HCA (Figure 5.13). Zone 1 is equivalent to cluster A and one site from cluster E1; zone 2 corresponds to clusters A, B, and E1, while zone 3 constitutes clusters C, D, and E2. Therefore, the isotopic compositions of these clusters are consistent with previous interpretations, indicating that a certain degree of mixing exists. Chemical and isotopic enrichment of the Vaal River relative to groundwater can be attributed to the higher evaporation rates associated with the dry season.

The classification of zone 2 consists of the clusters that recorded the highest groundwater salinity (EC 550 – 1600 $\mu\text{S}/\text{cm}$), in addition to relatively enriched isotopic content ($\delta^{18}\text{O} > -4.3 \text{‰}$), largely derived from sites within the Vaal River drainage system (≤ 200 m). These waters are likely sourced from an exchange with the river water and precipitation, as indicated by their similarity to the rainfall composition (RN 1). The mixing factor may be more prevalent in certain areas, accounting for relatively lower EC associated with cluster E1. Alternatively, the natural attenuation and filtering capacity of the media through which groundwater infiltrates could improve water quality. Note that the possibility of diffuse recharge, as a consequence of irrigation practices on the Vaal River floodplains, cannot be ignored. This is due to the disturbance of natural soil properties, creating more favourable pathways for infiltration across a larger area. As such, land-use activities may impact the isotopic composition under conditions of evaporative enrichment (Abiye *et al.*, 2021).

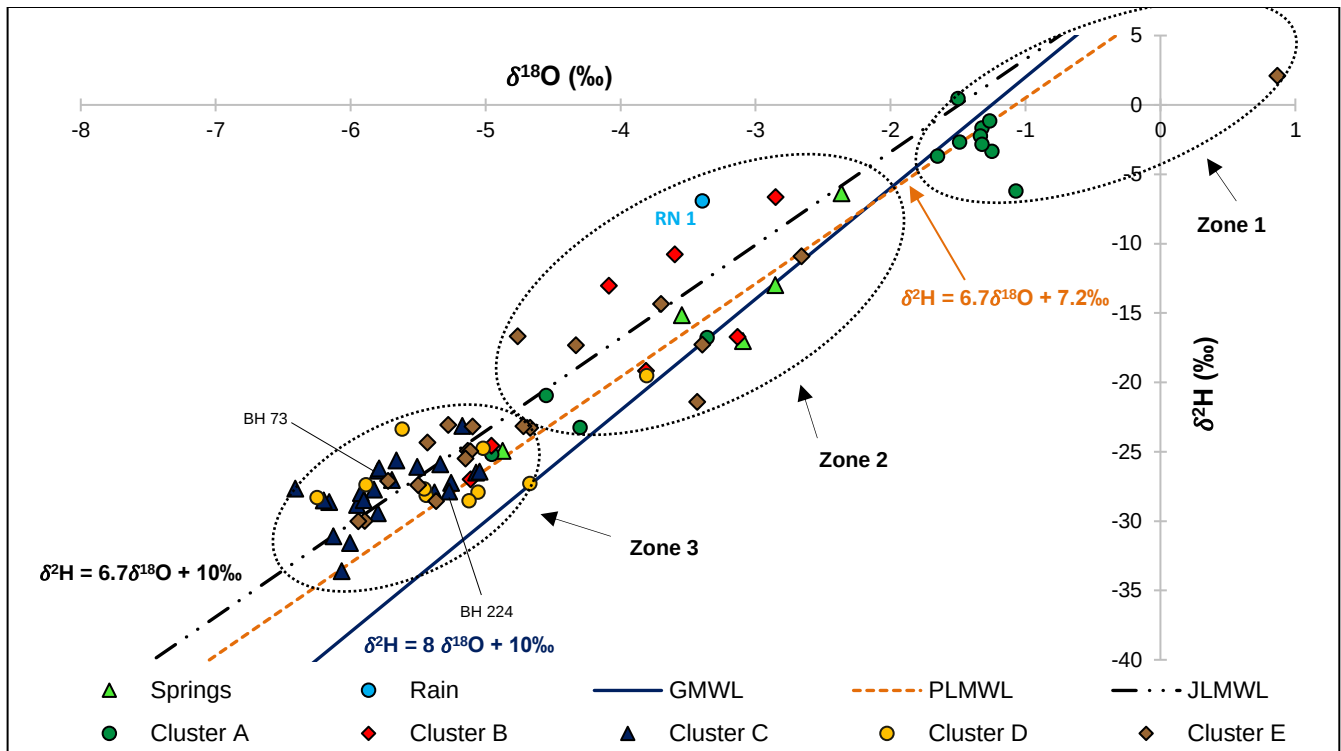


Figure 5.13. Stable isotopes of hydrochemical clusters and springs versus the Johannesburg Local Meteoric Water Line, Pretoria LMWL, and Global MWL.

On average, clusters C and D belonging to zone 3 typically recorded low salinity ($EC < 370 \mu S/cm$) whilst cluster E2 had slightly elevated concentrations ($EC < 530 \mu S/cm$). The mineralisation associated with cluster E2 is clearly a result of localised land-use activities. The general lack of clusters C and D in zone 2 indicates that recharge in these areas originates mostly from precipitation. The sites comprising the lowest major solutes, however, were relatively depleted ($\delta^{18}O < -5 \text{‰}$). This may be an indicator of recharge from a series of depleted rainfall events originating from high latitude and/or altitude moisture sources, possibly under cooler conditions. The slight variation in isotopic composition might be due to natural differences in the local and regional climate regimes. Evaporation is deemed a minor process during recharge in zone 3. The relatively resistant quartzite successions may serve as an explanation for the lower mineralisation observed at these sites.

The isotopic compositions associated with the outliers BH 73 and BH 224 as identified by the HCA (cluster C; $\leq 500 \text{ m}$ from the river) confirm their deviation from the general locations of sites assigned to cluster C ($> 2 \text{ km}$) (Figure 5.13). This is likely attributed to the influence of major structural deformations, geological contacts, and intrusions, or clogged riverbed conditions, restricting interaction with the river water.

5.4.3 Geological structure and stable water isotopes

The mixing evidence suggests that SW-GW interaction primarily occurs in the underlying Jeppestown Subgroup strata (Figure 5.14). These bedrock groundwaters consist of weathered metamorphosed sedimentary and lava units that host a multitude of structural features, potentially acting as pathways for hydrological connectivity. In particular, the lineations trending perpendicular to the strike of the units (Figure 5.15 A), the south to southeast-dipping fractures in bedding planes in the northwest of the study area (Figure 5.15 B), and various northwest-southeast trending faults may play a significant role for directing flow towards the river. They may also serve as point recharge zones (on the surface and from the river). Furthermore, porous Quaternary sediments are associated with the river system.

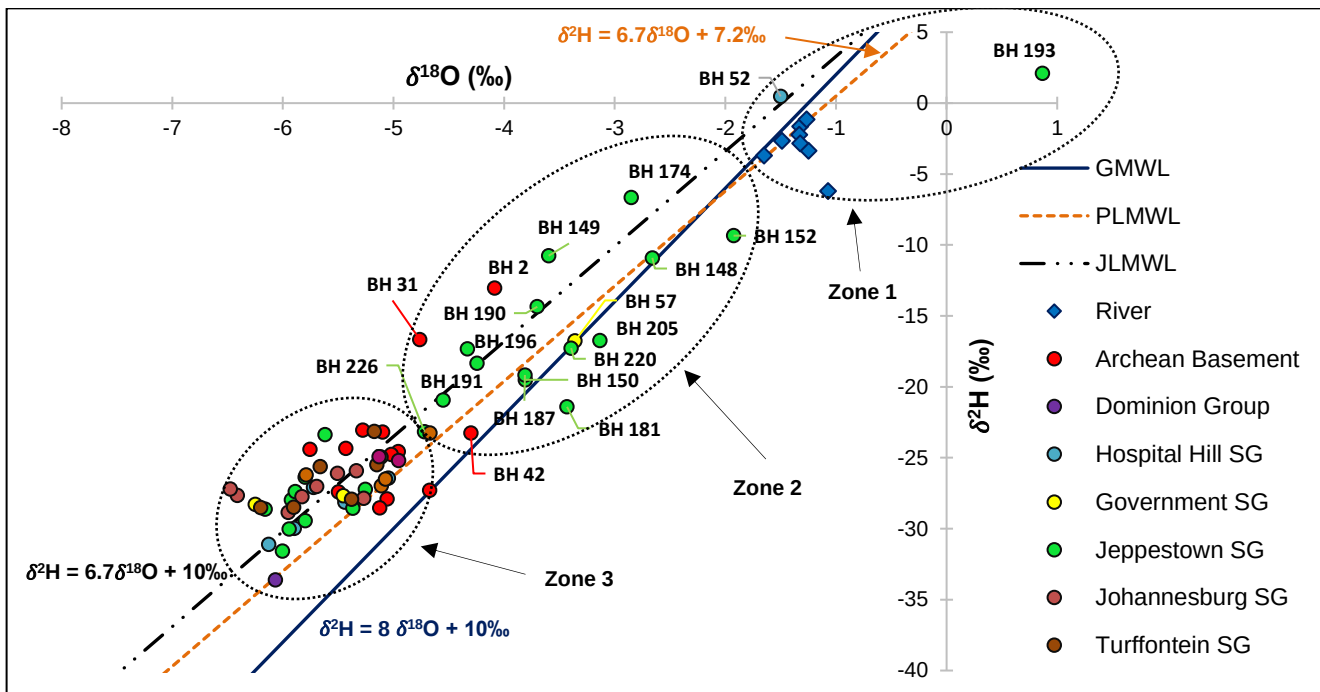


Figure 5.14. Groundwater isotopes of different underlying lithological units plotted against the Johannesburg Local Meteoric Water Line, Pretoria LMWL, and Global MWL (SG = Subgroup).

The intermediate isotopic composition of BH 2, BH 31, and BH 42, coupled with the shallow groundwater levels and springs present in the vicinity of the river channel (SP 1 and SP 2) point to baseflow contribution to streamflow in discrete zones of the basement complex. These areas are possibly characterised by deeply incised fractures, joints, and faults.

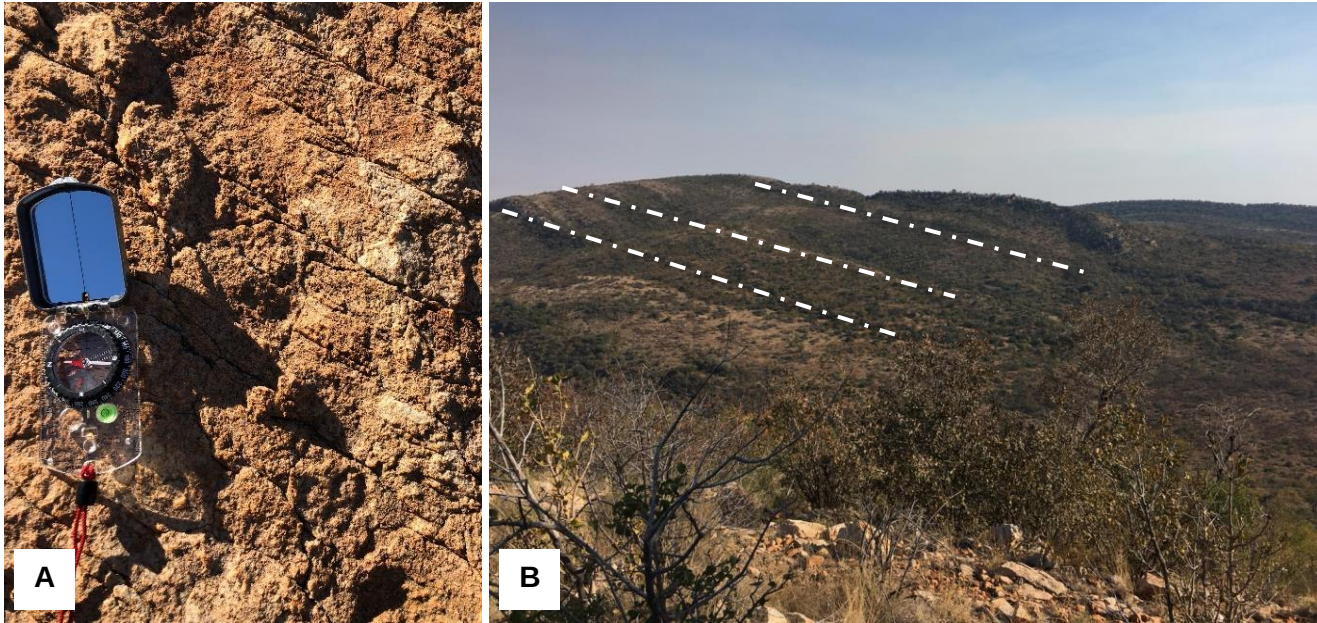


Figure 5.15. Images illustrating some of the **(A)** subparallel lineations in quartzite ($137^{\circ}/50^{\circ}$ NW) and **(B)** south to southeast-dipping bedding planes of the quartzite-dominated successions (northwest of the Vaal River).

Figure 5.16 shows the spatial location of zones 1 and 2 spring and groundwater sites, with reference to the river, alluvium, lithological units, and geological features. Notably, the geological lines representing structural features in the Jeppestown Subgroup largely trend across the channel approximately perpendicular to the flow direction of the Vaal River. Some of these perpendicular features appear to be promoting interaction between the water resources, whereas others do not (Figure 5.16). This provides evidence for areas of concentrated interaction controlled by variable fracture permeability. The presence of some sites belonging to the Government and Hospital Hill Subgroups in zone 2 points to water exchange that is rather limited in these areas and occurs in discrete zones.

Four possible scenarios are hypothesised to exist in the VDHS: (1) the weathered and/or structural zone is directly connected to the river system through vertical and/or horizontal fractures; (2) the weathered and/or structural zone is indirectly connected with the river system via the overlying alluvial media; (3) the weathered and/or structural zone is hydrologically disconnected and only the surface alluvium is directly connected with the river system; or (4) no-flow boundaries are present, isolating the underlying aquifers from the riverbed (e.g., impermeable bedrock).

The subdivision of the *losing* and *gaining* river reaches in the VDHS is presented in Figure 5.17. The *losing* river along the northern and south-western reaches is likely dictated by all four scenarios, where the water table in the fractured network is below the riverbed or the alluvial media facilitates connection; the systems may instead be completely underflowing the riverbed due to impermeable boundaries. The lack of alluvium in the crystalline basement suggests conditions associated with scenarios (1) and (4) in the *gaining* river reach. The former scenario describes the assumption that the river has eroded into the fractured bedrock, incising vertical and/or horizontal structural features (subject to small spacing distances between fracture networks), subsequently increasing the area for hydrological exchange.

In the case of the poor structural zone associated with the crystalline basement rocks, subsurface discharge is discrete with varying degrees of interaction- this is supported by the irregular electrical conductivity in this region. In a fractured aquifer setting under low flow conditions, Oxtobee and Novakowski (2002) found a relatively small proportion of baseflow forming part of total stream discharge in the Twenty Mile Creek, Smithville, Canada, despite the hydraulic head being equal to or above the river stage in certain areas. Accordingly, significant surface water loss to the underlying aquifers was not observed. The authors postulate that the fracture network was characterised by extremely poor vertical connection, which could also apply to the case of the basement complex.

Diffuse or continuous water exchange areas often occur in porous media settings (Oxtobee and Novakowski, 2002). The general lack of this trend observed in the isotopic labels, supported by the EC data, suggests that scenario (3) does not significantly contribute to hydrological connectivity. Instead, SW-GW interaction appears to be predominantly occurring in discrete point zones related to fracture permeability. However, given the proximity of some discrete sites, it may well be that the structural features and/or alluvial properties facilitate local diffuse recharge in certain areas (e.g., BH 148, 149, 150 and BH 190, 191; Figure 5.16).

The presence of sites underlain by the Jeppestown Subgroup, located ≤ 500 m in zone 3 (Figure 5.14), suggest the possibility of compartmentalised hydrogeological units through geological structures (scenario 4). Younger *et al.* (1993) highlight the significance of riverbed sediments, characterised by poor hydraulic properties, as a barrier to SW-GW connectivity and thus potential contamination from river water under *losing* stream conditions. Additionally, the presence of organic matter influence sorption processes and promote biodegradation, further attenuating pollutants. For these reasons, the transport of solutes into the aquifer may be affected by clogged preferential pathways and thus decrease the infiltration of river water. This potentially results in areas that are less impacted by river water, and therefore differ with respect to isotopic compositions and EC values.

Isotope depletion related to groundwater sites situated furthest from the river channel (> 1 km) in zone 3 may be sourced from deep fracture zones, and thus might signify deep circulating groundwater. Overall, the isotope data fails to reveal distinct contrasts between the lithological units, confirming aquifer connectivity across the geological contacts under the control of the heterogeneous structures. Moreover, it is evident that the various hydraulic characteristics associated with the diverse geology and riverbed sediments control the rate of recharge and mixing proportions.

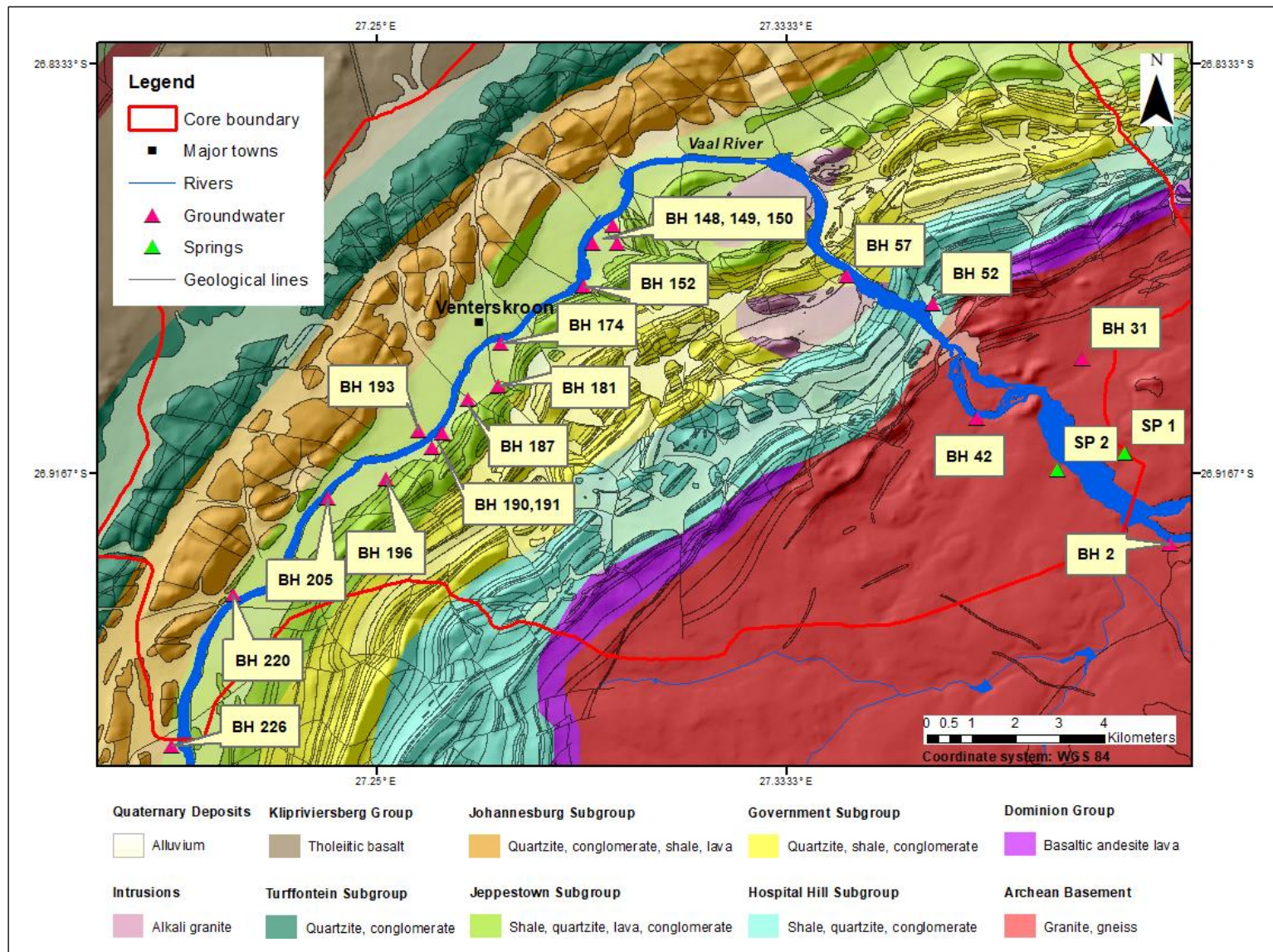


Figure 5.16. The spatial distribution of zones 1 and 2 groundwater and spring stable isotopes within 1 km distance from the river in relation to the underlying lithological units and Quaternary deposits. Geological lines represent lithological contacts and structural features.

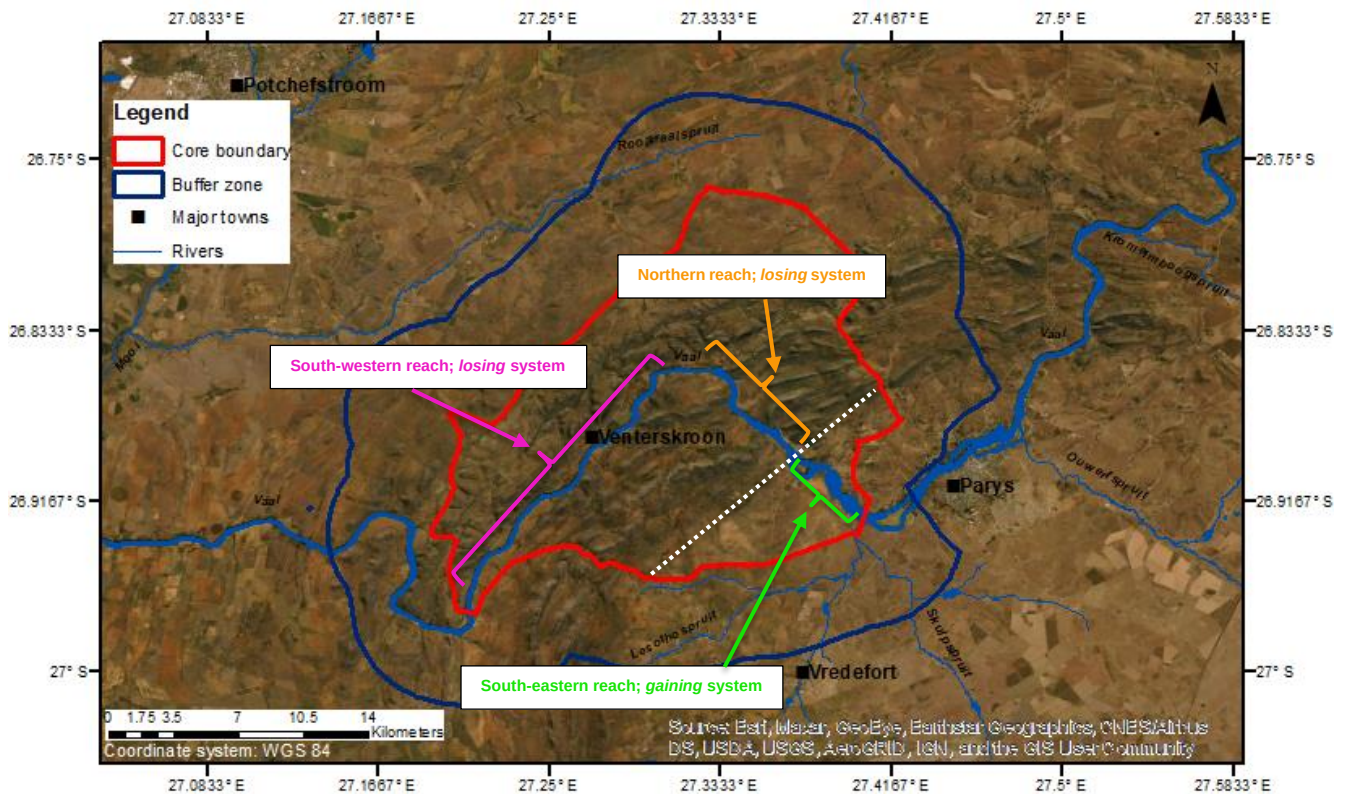


Figure 5.17. Location of the different river reaches in the core boundary of the Vredefort Dome Heritage Site.

5.4.4 Deuterium excess

The variability of deuterium excess (d -excess) may stem from different precipitation events developed under various vapour humidity and temperature conditions, as well as air masses of different moisture sources (Clark and Fritz, 1997). With the intention of evaluating the influence of moisture source conditions on isotopic compositions, d -excess was plotted against $\delta^{18}\text{O}$ for groundwater, river, and spring sites according to the identified zones (Figure 5.18). D -excess values ranged between -4.78 to +25.2‰, highlighting the diversity amongst sites.

The lower d -excess ($< 10\text{‰}$) and more enriched values ($\delta^{18}\text{O} > -5\text{‰}$) associated with the river, groundwater, and springs in zones 1 and 2 were established to be mostly as a result of evaporation from an open water body (springs) and on the ground surface prior to infiltration, or from surface water before river seepage into the underlying aquifer followed by mixing with groundwater, of which some sites were subjected to secondary evaporation effects that are known to reduce d -excess and enrich isotopes (Clark and Fritz, 1997). Therefore, these sites are not useful in constraining the moisture source conditions. The considerable variation of d -excess values in the shallow zone 2 samples is suggestive of significant fractionation sourced from river water and exposure to evaporation.

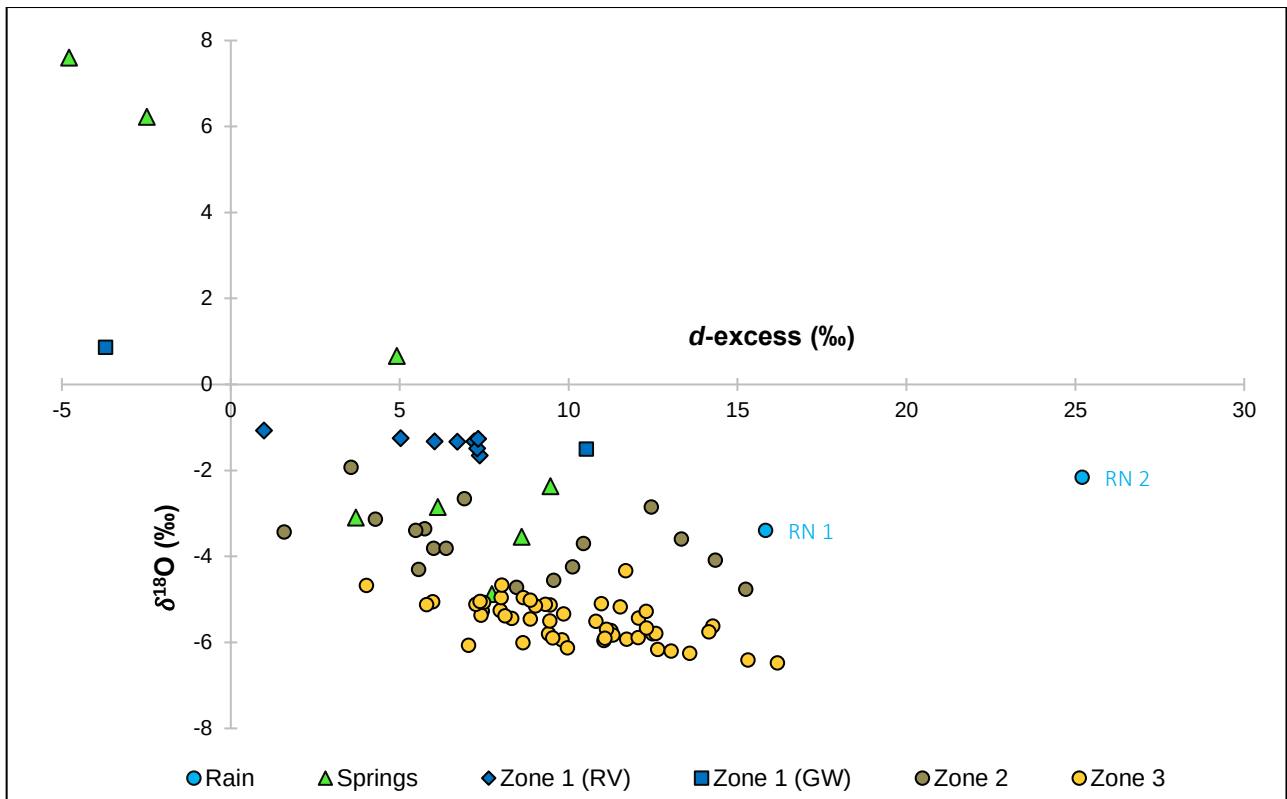


Figure 5.18. Deuterium excess plotted against $\delta^{18}\text{O}$ for river, springs, and groundwater in different zones (RV = river; GW = groundwater).

Dynamic d -excess values, linked to the zone 3 groundwater sites, demonstrate the effect from both local and regional moisture circulations. The dissimilarity of some of these values may indicate that groundwater was recharged from different recharge episodes. Low d -excess groundwaters suggest vapour related to evaporation under higher humidity and temperature conditions, generating more enriched moisture, while high d -excess groundwaters imply vapour that originated from evaporation under lower humidity and temperature conditions, producing depleted moisture (Clark and Fritz, 1997). Leketa *et al.* (2018) inferred low d -excess to be derived from the warmer Indian Ocean, while high d -excess is associated with the colder Atlantic Ocean and higher latitude regions. These observations could potentially indicate different moisture sources of recharge and mixing thereof.

The two rainfall events that occurred during field surveys show a local source of moisture (d -excess $> 10\text{‰}$), which was expected due to the affiliation of lower humidity with the dry season in the VDHS. However, there is a wide gap in d -excess values between RN 1 (15.83‰) and RN 2 (25.2‰). This is possibly attributed to different moisture sources or the amount effect of light rain showers in which RN 2 lasted approximately only 15 minutes under lower intensity.

5.5 Groundwater Levels

5.5.1 Depth to water level

The depth to water level is shown in Figure 5.19, reflecting water levels with an average of 15.07 m, minimum 0 m, and maximum 51.28 m below surface (Appendix A). The water levels display a broad northeast – southwest trend, corresponding largely to the geological formations; deep water levels are associated with topographic highs dominated by quartzite hills, whereas shallow water levels correlate to topographic lows dominated by the incised metamorphosed sedimentary strata, crystalline basement, and lava units. Walt *et al.* (2010) reported no effect of the Vaal River system on the water table level pattern, but this study shows that the groundwater level becomes variable and tends to become shallower in the vicinity of the Vaal River, indicating the thinning of the overburden/unsaturated zone moving towards the river.

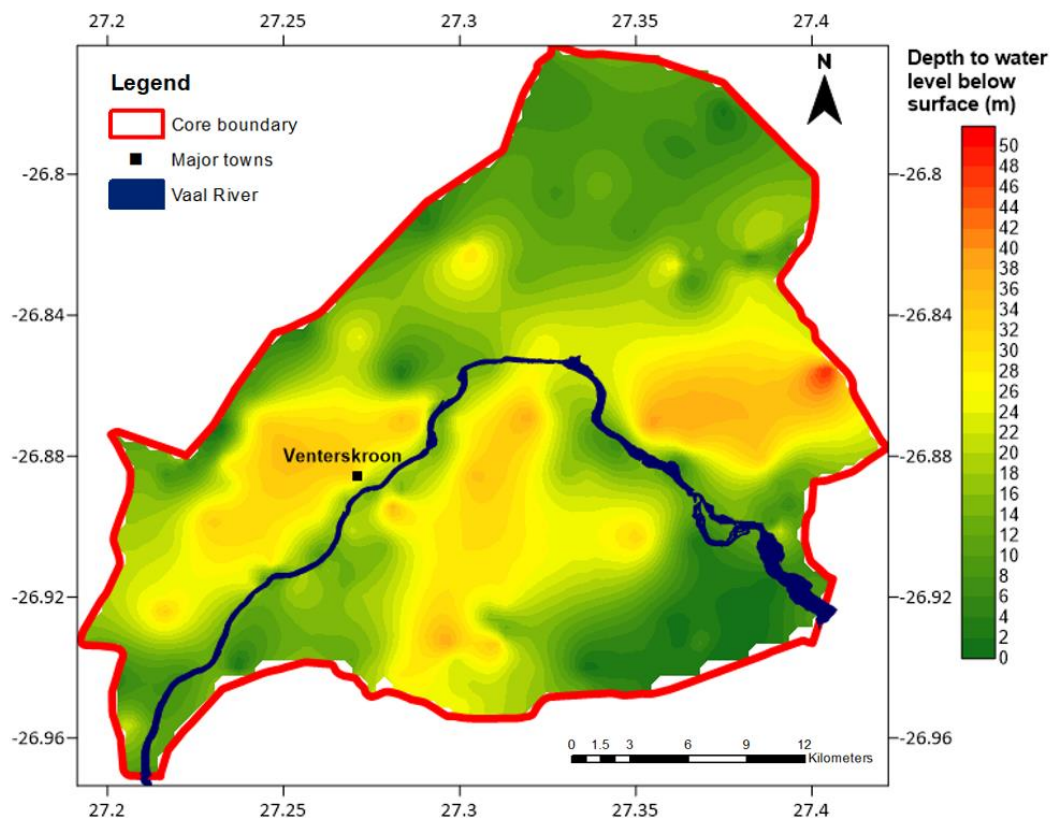


Figure 5.19. Interpolated map of the water table depth in the Vredefort Dome Heritage Site.

The simple regression analysis between the water table distribution and topography is shown in Figure 5.20, which indicates that 97% of the variance in the response variable (hydraulic head) can be explained by the explanatory variable (surface elevation). Thus, in general, the distribution of the hydraulic head is consistent with the landscape morphology, which subsequently controls groundwater flow direction. This suggests that the recharge rate is governed by topography (Mencio and Mas-Pla, 2008).

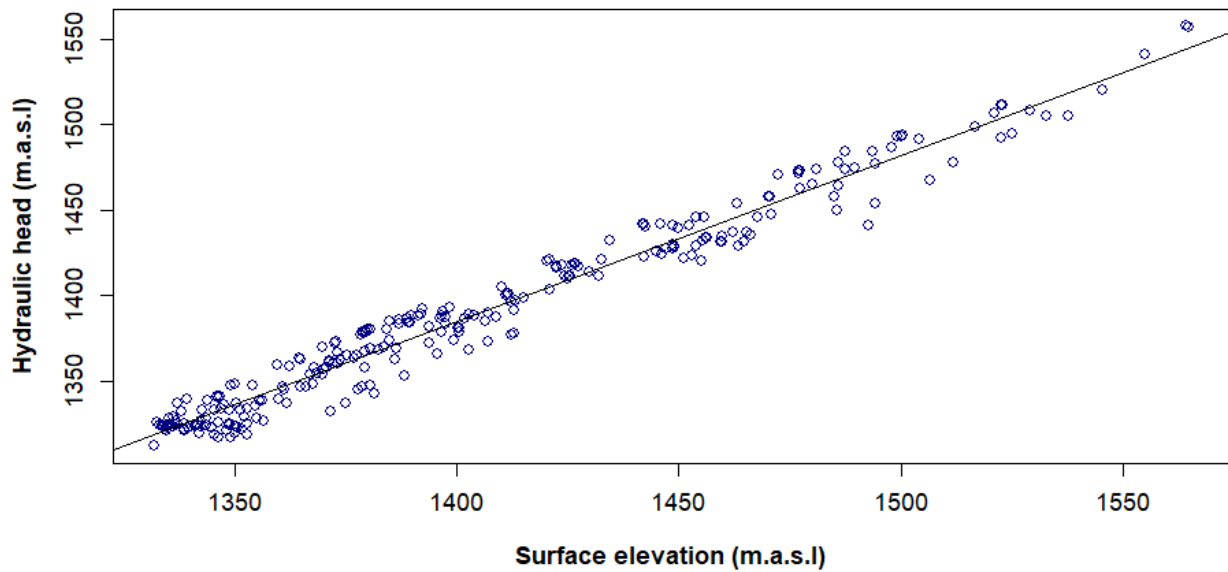


Figure 5.20. Simple regression analysis between hydraulic head and surface elevation ($R^2 = 0.97$).

5.5.2 Electrical conductivity and hydraulic head

Figure 5.21 shows that a similar hydraulic gradient is closely linked to sites located ≤ 1 km from the river; groundwater EC tends to be highest at shallower depths in relation to the surface elevation. In general, sites located > 1 km from the Vaal River have a higher hydraulic head with lower EC values and are clearly distinguished from the other sites. The less mineralised groundwater at topographic highs (hills) may reflect the resistance associated with hard rocks and may be related to variable residence time. In contrast, the shallow groundwater at topographic lows (valleys) displays the possibility of various near-surface sources that are responsible for the observed mineralisation.

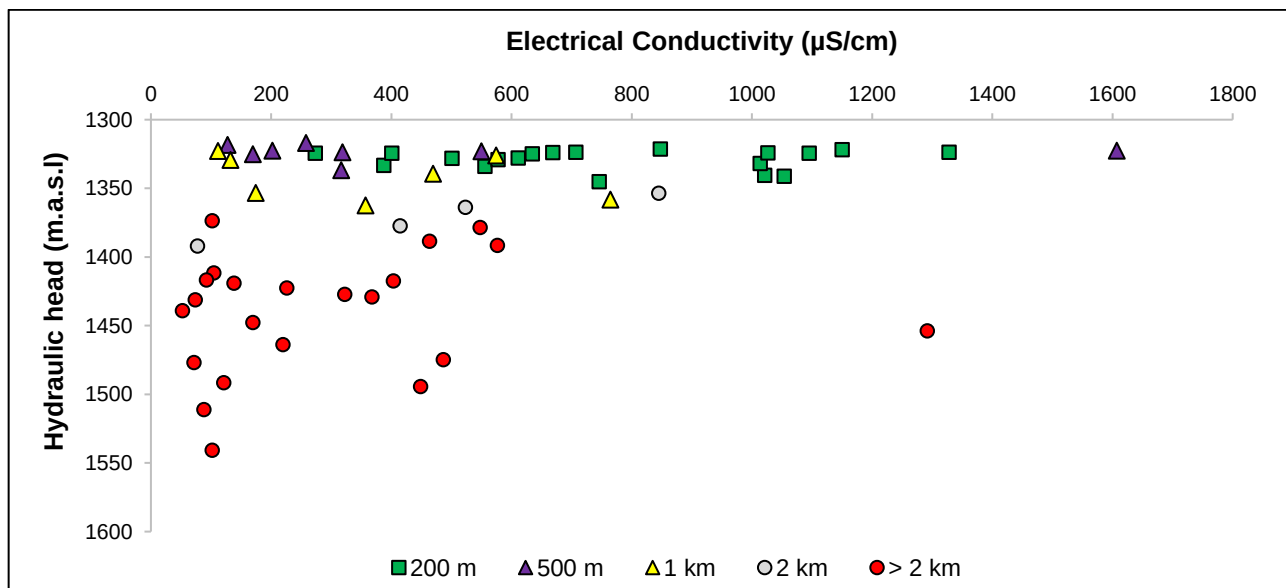


Figure 5.21. Hydraulic head measurements with electrical conductivity values for sites at specific distances from the river channel.

5.5.3 Groundwater levels and geological units

The groundwater level data were segregated and grouped according to the underlying geological units belonging to broad stratigraphic categories (Figure 5.22). The statistical evaluation of the hydraulic head measurements represented as a box and whisker plot shows the significant difference between the stratigraphic units ($P < 0.001$). Each lithological unit is characterised by unique qualities which govern hydraulic properties of groundwater, hence statistical dissimilarity in water levels. This significant variability provides evidence for the linear aquifer systems described by Brink *et al.* (2005), highlighting the important role of heterogeneous geology in the occurrence of groundwater. Note, however, the inter-aquifer connections are shown by homogeneous isotope signals.

The basement complex located south-east in the study area is characterised by the shallowest water levels. This is attributed to the near-surface occurrence of the outcrop and thin soil cover, reflecting high vulnerability to pollution. In contrast, the aquifers hosted in metamorphosed sedimentary and volcanic rocks located in the centre and north of the study area have overall greater mean water depths. The deeper water levels are likely related to lower groundwater potential, coupled with the effects of localised groundwater exploitation.

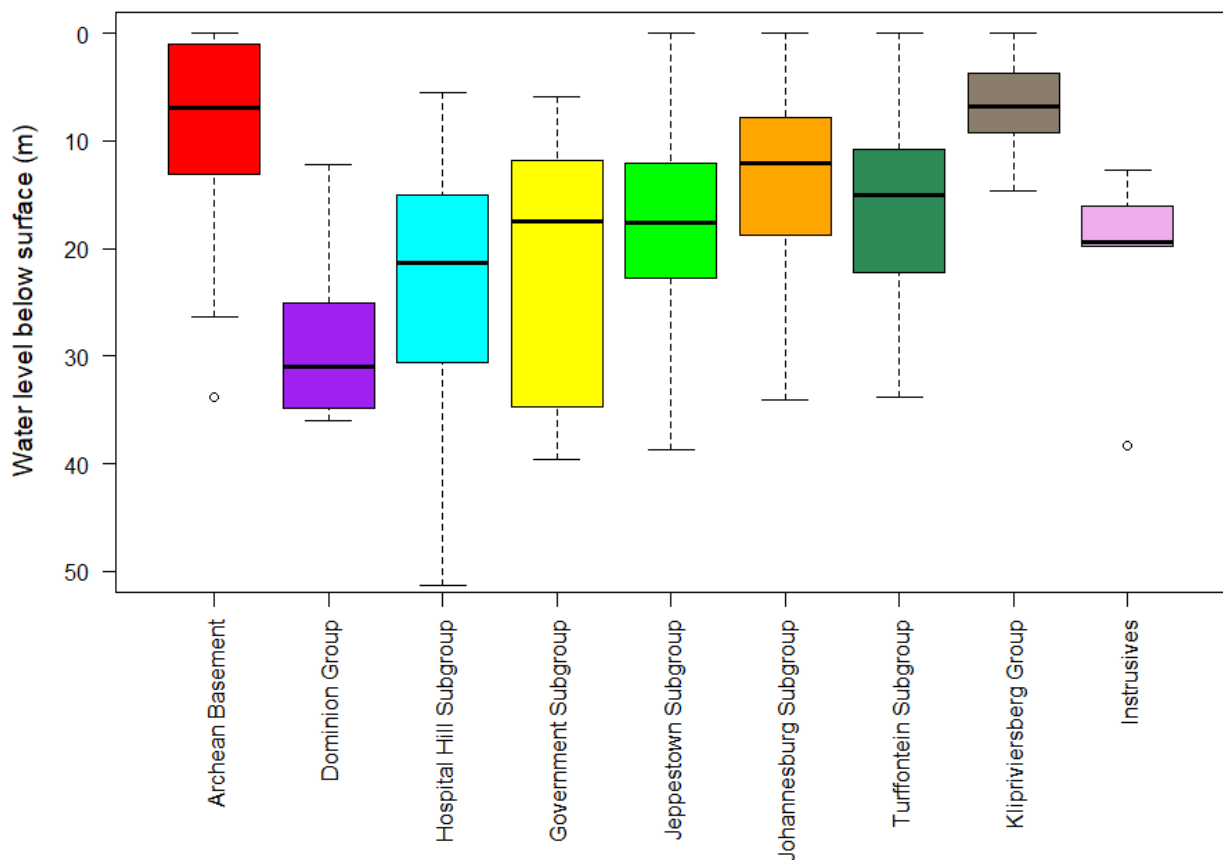


Figure 5.22. Box and whisker plot showing the water levels below surface per stratigraphic unit.

The south-western river reach is predominantly underlain by the Jeppetown Subgroup, which is characterised by a mean water level of 20.49 m below the surface. Walt *et al.* (2010) reported water depth ranging between 13 – 15 m for this subgroup, indicating that the lower groundwater levels are likely due to increased groundwater extraction. A similar trend of decreased water levels is observed for the Hospital Hill and Government Subgroups underlying the northern river reach. This demonstrates the sensitivity of surface water bodies to alterations in the water balance, subsequently inducing recharge conditions in these areas, as opposed to the natural baseflow contribution that was expected during the dry season. However, the basement complex maintains stability with shallow groundwater levels, confirming the possibility of subsurface contribution to streamflow.

Kilian *et al.* (2019) showed that an inversely proportional relationship exists between baseflow contribution to streamflow and the declining groundwater level (linked to anthropogenic withdrawals) in the Mississippi Delta (USA). Therefore, the lack of baseflow observed along the south-western reach may be a result of the evolving groundwater demand that gives rise to the likelihood of induced river infiltration as indicated by Walt *et al.* (2010), in line with the intermediate isotopic compositions of the sites in the vicinity of the Vaal River. Consequently, the flow direction of the contaminated groundwater may be redirected towards abstraction points -due to the reversal of the hydraulic gradient- and consequently, reduce the magnitude of water discharged into surface water. This can impose serious implications for the important and vulnerable biodiversity of the VDHS.

5.5.4 Groundwater flow direction

The heterogeneous topography controls the direction of groundwater movement, and thus exhibits significant influence on the hydraulic gradient towards the alluvial and bedrock aquifers associated with the Vaal River valley (Figure 5.23). The groundwater contour map displays spatial heterogeneity associated with discharge and recharge zones. Natural recharge processes were found to take place in the hilly regions, while discharge would occur into the river, wetlands and in the form of springs. Groundwater discharge into the river is limited to the crystalline basement due to increased groundwater abstraction. In the north- and south-western section of the study area (corresponding to the Johannesburg Subgroup), the equipotential lines (hydraulic gradient) are very dense, indicating higher groundwater velocity (Geyh, 2000) towards the river channel. This follows the steeper topography and stratigraphic dip direction. In contrast, the southern areas lack this trend, but it is assumed that the geological and topographic controls limit river-recharged groundwater movement to these areas. Instead, these surface water and groundwater associations are largely limited to the vicinity of the river channel (≤ 500 m) with a maximum distance of 1 km in some cases. This agrees with Hobbs *et al.* (2013) that postulated the restriction of compromised groundwater quality to the course of the Vaal River.

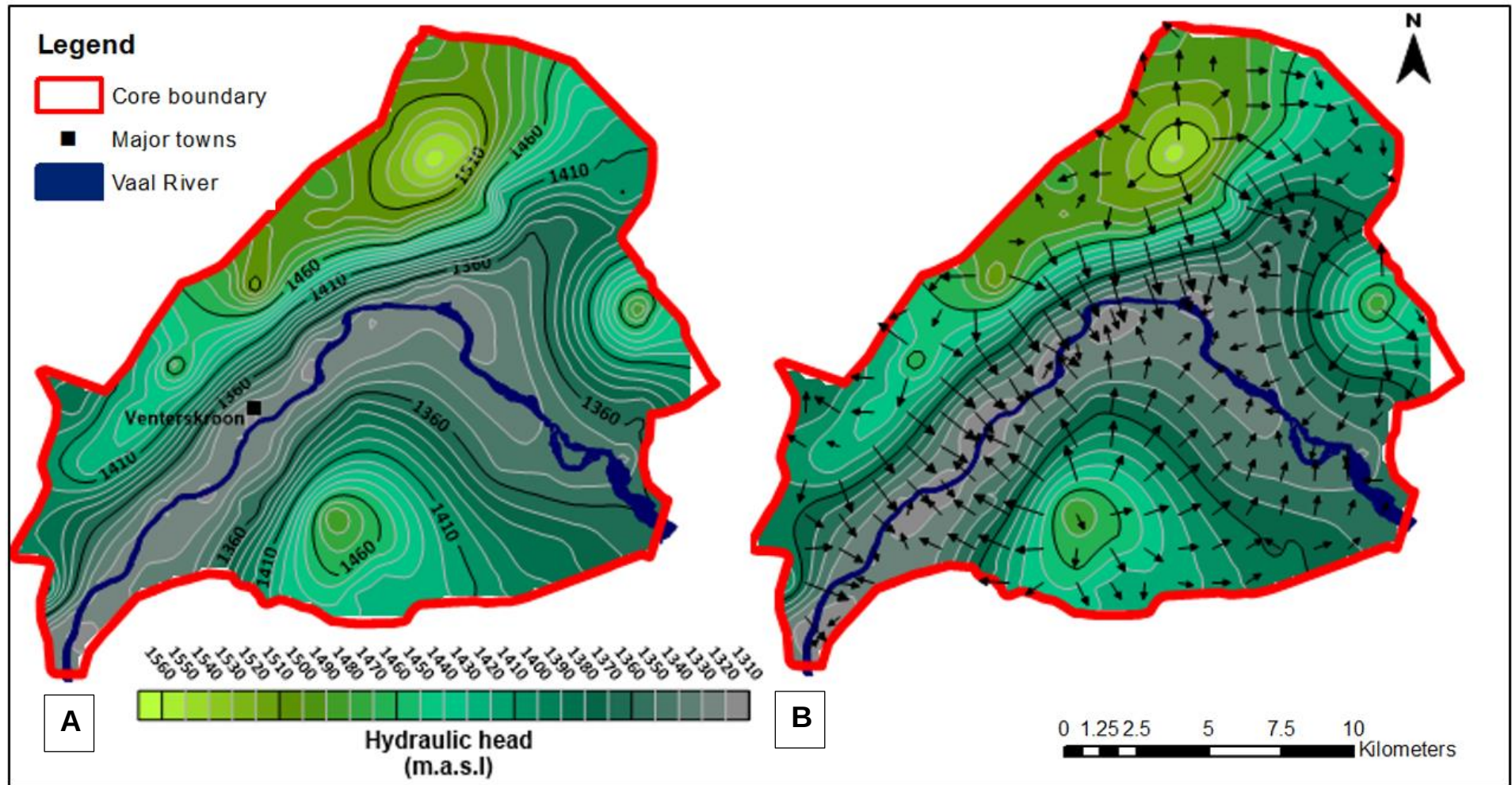


Figure 5.23. (A) Groundwater contour map in two-dimensions showing **(B)** the horizontal groundwater flow direction.

6. CONCLUSION

This study applied an integrated approach to identify the spatial heterogeneity and mechanisms controlling SW-GW connectivity in the VDHS. A combination of various data analyses has offered a unique multifaceted strategy to strengthen and justify the interpretations of the hydrological activity. The Vaal River was characterised as a *losing* system in the northern and south-western reaches, serving as a recharge zone, while the south-eastern reach was classified as a *gaining* system, providing baseflow to river discharge. This emphasises the inherent complexity of the intertwined processes controlling the hydrological connection, indicating the presence of various groundwater regimes.

Major ion analysis granted insight into the general water quality of the study area, however, provided inconclusive results on SW-GW interaction due to the low sample size and influence of local land-use activities. The PCA revealed a combination of hydrochemical controls, including mineralogical influences and the manifestation of negative impacts from anthropogenic activities. The former was delineated by the Ca-Mg-HCO₃⁻ water type, whereas the latter was associated with the Ca-Mg-Cl-SO₄²⁻ water type. The influence of human-induced pollution was highlighted by the microbiological quality of groundwater, which is of particular concern as all sites were found to have the presence of at least one bacterial species. Solutes associated with the bacterial dynamics were likely sourced from agricultural practices, septic tanks, or riverine inputs.

Cluster analysis identified five distinctive groups; cluster A comprising all river sites, and cluster B and E1 with groundwater sites in proximity to the river, representing pollution related to SW-GW interaction and anthropogenic activities; cluster C consists of sites predominantly at maximum distance from the river (> 1 km) and demonstrates the controls of natural hydrogeological processes; cluster D characterised by a mixture of natural and anthropogenic influences; and finally cluster E2, which appears to be dominated by localised human-induced contamination sources. The similarity between river water and groundwater assigned to the hydrochemical clusters A and B are consistent with the stable isotope data, EC values, and hydraulic head information pertaining to these sites. However, SW-GW interaction was not clearly defined by cluster E1, but the isotope results do provide evidence for some degree of hydrological connection.

Analysis of seasonal baseflow from 2013 to 2016 indicates that much of the subsurface contribution occurs during the dry season (BFI ~ 7%) as opposed to the wet season (BFI 1%). The Vaal River responds rapidly to precipitation events; delayed subsurface input does not significantly contribute to streamflow. Instead, artificial discharge predominantly maintains the perennial conditions. The limited baseflow observed to discharge into the river under low flow conditions has an isotopic composition consistent with springs and shallow groundwater in the crystalline basement.

The isotope results demonstrate the effect of various local hydrogeological, physiographic, and climatic conditions which gave rise to diverse isotopic compositions that were separated into distinct zones. The isotopic signatures indicate that mixing is taking place, producing a composition that reflects an integration of the isotopic variations of two end members. Groundwater is likely recharged through direct and indirect modes, where the latter constitutes evaporation prior to infiltration and mixing of water resources. Furthermore, the isotopic data suggest that physiography exerts more dominant control than lithology, and the strongly depleted rainfall can be attributed to the relatively low humidity.

Isotopically depleted groundwater sites (> 1 km) are assigned to clusters C and D, highlighting the significant hydrochemical differences between the water resources. This indicates that the influence of induced recharge or baseflow from the river is locally restricted to a maximum buffer distance of 1 km; sites located nearer to the channel are more prone to hydrological connection and contamination. These observations are supported by the regional groundwater flow paths towards the river that are governed by topography, as shown by the depleted groundwater isotope signals at various distances from the river. Thus, the elevated bacterial counts and major ion concentrations in areas outside of the 1 km buffer demonstrate the effects of localised human-induced pollution.

In the south-western and northern *losing* river reaches, the hydraulic head data shows that the water table was consistently below the riverbed in the vicinity of the Vaal River. Given the increased demand for groundwater and observed water-level declines in the region, abstraction is the probable cause for inducing recharge to underlying aquifers, deviating from the natural baseflow expected during the dry season. These interactions primarily occurred in the Jeppestown Subgroup, with minor exchange processes in the Hospital Hill and Government Subgroups. The fracture networks near the river exhibit both strong and poor vertical connections to the surface water that promote and limit groundwater exchange, respectively. In certain areas where the channel incises into the bedrock, the structural features may play an important role in facilitating the interaction process. Furthermore, the occurrence of riverbed sediments resulting in clogged pathways could restrict connectivity. This suggests compartmentalisation of the hydrogeological units, and SW-GW interaction is governed by site-specific hydraulic properties, thus restricted to discrete locations.

This study demonstrated the negative implications associated with poor water quality in the vicinity of the Vaal River because of increased groundwater exploitation. Considering the limited surface water supply, groundwater plays an important role in the future development of the VDHS. These dynamic hydrological exchanges have crucial functions in guiding the formulation of sound strategies to ensure the preservation of its world heritage reputation, through sustainable water use and land-use planning.

6.1 Recommendations

Based on the findings of this study, the following aspects are recommended for future investigations:

- Detailed spatio-temporal investigations are necessary to assess the effects of seasonality on SW-GW connection. Renewed monitoring of groundwater levels, microorganisms, standard chemical parameters, and stable water isotopes can be used to create a long-term database. This will improve the conceptualisation and understanding of the hydrological dynamics in the VDHS.
- The stream gauging stations in the vicinity of the VDHS need to be repaired to ensure the measurement of daily streamflow, to provide more reliable baseflow estimations.
- Important considerations are required to distinguish groundwater and interflow components, to discern subsurface discharge originating in surface water bodies.
- Research efforts should be directed towards identifying and differentiating pollution sources.
- The sample size of hydrochemical analyses should be increased to achieve a larger dataset for more reliable and detailed multivariate statistical analysis.
- Numerical models should be developed to evaluate the existence of interaction processes and associated quantity based on fracture properties.
- The riverbed sediments should be investigated and characterised to evaluate the effect on river-aquifer water quality interaction.
- Regular, long-term sampling of rainfall for stable isotope analysis is required, to increase understanding of precipitation origin related to seasonal influences.
- Tritium analysis should be included to help constrain the residence time of groundwater systems.
- Conduct geophysical surveys of the region to enhance understanding of structural characteristics and their associated linkage to hydrological connections.
- Include more detailed studies on the local biodiversity to improve understanding of the symbiosis between water resources and the ecosystem. Such investigations can address the influences of evapotranspiration on groundwater dynamics.
- Hydraulic tests should be conducted to investigate the hydrogeological properties of the aquifers and distinguish the depths between the fractured and alluvial aquifers. This can further confirm whether the river is *gaining* or *losing* water from the underlying aquifers across different reaches.
- The effect of borehole construction and design should be investigated to provide insight into the impact on hydrological exchanges in the vicinity of the Vaal River.

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8. APPENDICES

Appendix A. Details from the hydrocensus survey in the Vredefort Dome Heritage Site (August to September 2020). WD = well depth; WLBS = water level below surface.

Site	Longitude	Latitude	Use	*Sample type	WD (m)	WLBS (m)
RV 1	27.4359	-26.9069	Recreation	PHYC; WATC; ISO; BAC; BOD	-	-
RV 2	27.369	-26.9022	Recreation	PHYC; ISO	-	-
RV 3	27.338	-26.8566	Irrigation	PHYC; ISO	-	-
RV 4	27.2935	-26.8669	Recreation	PHYC; ISO	-	-
RV 5	27.2744	-26.8897	Recreation	PHYC; ISO	-	-
RV 6	27.2538	-26.9138	Recreation	PHYC; ISO	-	-
RV 7	27.2312	-26.937	Irrigation	PHYC; ISO	-	-
RV 8	27.2099	-26.9706	Recreation	PHYC; WATC; ISO; BAC; BOD	-	-
MN	27.2684	-26.9161	Abandoned	GLM; ISO	> 60	11.84
WD	27.337	-26.9426	Waste dam	ISO	-	-
SP 1	27.4021	-26.9127	Unutilised	GLM; ISO	-	0
SP 2	27.3884	-26.9161	Unutilised	GLM; ISO	-	0
SP 3	27.3805	-26.9271	Unutilised	GLM; ISO	-	0
SP 4	27.3745	-26.9358	Unutilised	GLM	-	0
SP 5	27.3595	-26.9279	Unutilised	GLM	-	0
SP 6	27.3358	-26.941	Unutilised	GLM; ISO	-	0
SP 7	27.3746	-26.7808	Unutilised	GLM; ISO	-	0
SP 8	27.233	-26.8724	Unutilised	GLM; ISO	-	0
SP 9	27.2369	-26.9399	Unutilised	GLM; ISO	-	0
SP 10	27.2365	-26.9397	Unutilised	GLM; ISO	-	0
BH 1	27.4187	-26.932	Domestic	GLM	56	13.47
BH 2	27.4112	-26.9312	Unutilised	GLM; PHYC; ISO	37	4.18
BH 3	27.4093	-26.9316	Unutilised	GLM	> 60	13.26
BH 4	27.404	-26.9312	Unutilised	GLM	> 60	7.45
BH 5	27.4004	-26.9264	Unutilised	GLM	> 60	9.6
BH 6	27.3854	-26.9191	Domestic and livestock	GLM	30	1.41
BH 7	27.3853	-26.9196	Domestic and livestock	GLM; PHYC; ISO	48	4.18
BH 8	27.3831	-26.9268	Unutilised	GLM	-	0
BH 9	27.376	-26.933	Livestock	GLM	24	0.93
BH 10	27.3762	-26.9342	Unutilised	GLM	52	0

BH 11	27.3758	-26.9343	Unutilised	GLM	56	0.04
BH 12	27.3765	-26.9346	Unutilised	GLM	53	0.03
BH 13	27.3763	-26.9353	Unutilised	GLM	6	0.73
BH 14	27.3708	-26.937	Unutilised	GLM	45	1.31
BH 15	27.3696	-26.94	Unutilised	GLM	48	1.8
BH 16	27.3698	-26.9402	Unutilised	GLM	43	2.4
BH 17	27.369	-26.9403	Unutilised	GLM	54	2.8
BH 18	27.3584	-26.9375	Unutilised	GLM	16	3.25
BH 19	27.3676	-26.9324	Domestic and livestock	GLM; PHYC; ISO; BAC	41	7.95
BH 20	27.3646	-26.9313	Unutilised	GLM	19	1.1
BH 21	27.3629	-26.9316	Unutilised	GLM; ISO	40	0
BH 22	27.3626	-26.9316	Unutilised	GLM	51	0
BH 23	27.3625	-26.9318	Unutilised	GLM	8	0
BH 24	27.3588	-26.9292	Unutilised	GLM	21	3.53
BH 25	27.4018	-26.9133	Domestic	GLM	30	9.81
BH 26	27.3956	-26.9037	Unutilised	GLM	22	12.69
BH 27	27.3964	-26.9004	Domestic	GLM	> 60	9.7
BH 28	27.3992	-26.8974	Domestic and livestock	GLM	> 60	11.64
BH 29	27.3896	-26.9001	Domestic	GLM	> 60	26.33
BH 30	27.3893	-26.8998	Livestock	GLM	> 60	6.39
BH 31	27.3934	-26.8934	Irrigation	GLM; PHYC; WATC; ISO; BAC; BOD	31	2.17
BH 32	27.3959	-26.8899	Domestic	GLM	26	12.52
BH 33	27.39	-26.8911	Domestic and livestock	GLM	25	12.76
BH 34	27.3892	-26.8878	Domestic and livestock	GLM; PHYC; ISO	33	13
BH 35	27.3904	-26.8877	Domestic and irrigation	GLM	> 60	11.12
BH 36	27.3839	-26.8914	Domestic	GLM	17	13.97
BH 37	27.3839	-26.8917	Livestock	GLM	50	13.33
BH 38	27.3797	-26.8972	Domestic	GLM; PHYC; WATC; ISO; BAC; BOD	18	15.62
BH 39	27.3923	-26.8855	Irrigation	GLM	> 60	12.63
BH 40	27.3969	-26.8828	Domestic and livestock	GLM	32	13.8
BH 41	27.3856	-26.8813	Unutilised	GLM	43	33.84
BH 42	27.372	-26.9055	Domestic	GLM; PHYC; ISO; BOD; BAC	33	4.65
BH 43	27.3676	-26.9043	Unutilised	GLM	> 60	1.86
BH 44	27.3671	-26.9038	Unutilised	GLM	55	1.65
BH 45	27.3614	-26.9008	Domestic and livestock	PHYC; WATC; ISO; BAC; BOD	-	-
BH 46	27.3512	-26.9035	Unutilised	GLM	44	32.01
BH 47	27.3509	-26.9036	Livestock	GLM	> 60	32.46
BH 48	27.3584	-26.8965	Game and livestock	GLM; PHYC; ISO	25	20.43
BH 49	27.3587	-26.8888	Unutilised	GLM	30	17.09

BH 50	27.3597	-26.8872	Unutilised	GLM	45	11.34
BH 51	27.3594	-26.8873	Domestic	PHYS; ISO	-	-
BH 52	27.3631	-26.8823	Domestic	GLM; PHYC; WATC; ISO; BAC; BOD	19	5.66
BH 53	27.3628	-26.8818	Domestic	GLM	24	5.61
BH 54	27.3618	-26.8815	Unutilised	GLM	> 60	5.56
BH 55	27.3648	-26.8765	Unutilised	GLM	> 60	33.38
BH 56	27.3494	-26.8821	Domestic and livestock	GLM; PHYC; ISO	21	12.77
BH 57	27.3456	-26.8766	Domestic and livestock	GLM; PHYC; ISO	17	5.88
BH 58	27.3534	-26.8716	Domestic	GLM	46	39.64
BH 59	27.3367	-26.8849	Domestic	GLM	26	19.82
BH 60	27.33	-26.8844	Domestic and livestock	GLM; PHYC; ISO	30	16.09
BH 61	27.3382	-26.8727	Domestic, livestock, and irrigation	GLM; PHYC; WATC; ISO; BOD; BAC	25	9.13
BH 62	27.4145	-26.8712	Domestic	PHYC; ISO	-	-
BH 63	27.3959	-26.8677	Game	GLM	48	35.02
BH 64	27.3955	-26.8672	Unutilised	GLM	> 60	34.56
BH 65	27.4114	-26.8608	Game	GLM	45	31.01
BH 66	27.4113	-26.86	Game	GLM	> 60	28.24
BH 67	27.4042	-26.8551	Domestic	GLM	40	51.28
BH 68	27.404	-26.8516	Domestic	GLM; PHYC; WATC; ISO; BAC	31	23.05
BH 69	27.3988	-26.8559	Unutilised	GLM	57	39.93
BH 70	27.3949	-26.8541	Game	GLM; PHYC; ISO	55	30.72
BH 71	27.3199	-26.8685	Domestic and livestock	GLM	45	38.33
BH 72	27.3265	-26.8632	Domestic and livestock	GLM	27	19.43
BH 73	27.32	-26.8564	Domestic	GLM; PHYC; ISO	36	27.62
BH 74	27.3235	-26.847	Irrigation	GLM	> 60	25.07
BH 75	27.3357	-26.8453	Domestic, livestock, and irrigation	GLM; PHYC; ISO	43	22.72
BH 76	27.3566	-26.8375	Domestic	GLM	40	19.39
BH 77	27.3566	-26.8371	Domestic	PHYC; WATC; BAC; BOD	-	-
BH 78	27.3598	-26.8294	Unutilised	GLM	> 60	21.51
BH 79	27.361	-26.8277	Unutilised	GLM	> 60	23.45
BH 80	27.3614	-26.8264	Domestic and livestock	GLM	> 60	29.5
BH 81	27.3639	-26.8292	Unutilised	GLM	> 60	10.36
BH 82	27.3657	-26.831	Domestic	GLM	27	6.63
BH 83	27.3645	-26.8239	Domestic and irrigation	GLM; PHYC; ISO	28	11.1
BH 84	27.3686	-26.8241	Unutilised	GLM	39	13.45
BH 85	27.3682	-26.8239	Domestic and irrigation	GLM	30	17.71
BH 86	27.371	-26.8237	Unutilised	GLM	23	11.47
BH 87	27.3778	-26.8291	Unutilised	GLM	30	21.5
BH 88	27.3816	-26.8223	Irrigation	GLM	28	11.53

BH 89	27.3829	-26.8218	Domestic	GLM	35	21.46
BH 90	27.3829	-26.8219	Unutilised	GLM	29	21.55
BH 91	27.3833	-26.8229	Irrigation	GLM	42	5.14
BH 92	27.3835	-26.8229	Irrigation	GLM	12	5.22
BH 93	27.3828	-26.8233	Irrigation	GLM	16	3.46
BH 94	27.3846	-26.8287	Domestic and livestock	GLM; PHYC; WATC; ISO; BAC; BOD	> 60	21.84
BH 95	27.386	-26.8282	Unutilised	GLM	28	18.04
BH 96	27.3884	-26.8288	Domestic	GLM	32	19.06
BH 97	27.3885	-26.8289	Domestic	GLM	> 60	19.66
BH 98	27.3886	-26.8289	Unutilised	GLM	45	19.51
BH 99	27.3909	-26.828	Domestic and livestock	GLM	25	13.7
BH 100	27.3923	-26.8254	Unutilised	GLM	28	9.92
BH 101	27.394	-26.8248	Unutilised	GLM	38	17.25
BH 102	27.3938	-26.8204	Unutilised	GLM	25	5.72
BH 103	27.3942	-26.824	Domestic and livestock	GLM	30	16.06
BH 104	27.3933	-26.8237	Unutilised	GLM	32	9.62
BH 105	27.39	-26.8172	Domestic and irrigation	GLM; PHYC; ISO	26	20.18
BH 106	27.3953	-26.8105	Domestic	GLM	23	17.33
BH 107	27.4	-26.8025	Domestic	GLM	47	15.29
BH 108	27.3999	-26.801	Irrigation	GLM	20	13.81
BH 109	27.3997	-26.8009	Irrigation	GLM	38	12.67
BH 110	27.4002	-26.8001	Domestic	GLM	30	13.71
BH 111	27.3877	-26.7934	Domestic and livestock	GLM	20	10.04
BH 112	27.3597	-26.794	Livestock	GLM	20	6.73
BH 113	27.36	-26.7934	Livestock	GLM	11	4.01
BH 114	27.3667	-26.7852	Domestic	GLM; PHYC; WATC; ISO; BOD; BAC	> 60	9.15
BH 115	27.3764	-26.7856	Domestic	GLM	11	2.62
BH 116	27.3852	-26.7829	Unutilised	GLM	> 60	7.67
BH 117	27.3746	-26.7806	Domestic and livestock	GLM	20	0.66
BH 118	27.3738	-26.7798	Domestic and livestock	GLM	12	4.3
BH 119	27.3614	-26.7932	Unutilised	GLM	29	4.06
BH 120	27.375	-26.7799	Domestic and livestock	GLM	30	2.51
BH 121	27.3773	-26.7785	Unutilised	GLM	22	9.63
BH 122	27.3419	-26.7638	Unutilised	GLM	40	14.37
BH 123	27.3334	-26.7766	Domestic and livestock	GLM	28	6.12
BH 124	27.3337	-26.7766	Unutilised	GLM	11	6.77
BH 125	27.3339	-26.7767	Unutilised	GLM	8	6.85
BH 126	27.3285	-26.767	Unutilised	GLM	13	9.27
BH 127	27.328	-26.7661	Domestic	GLM; PHYC; ISO	> 60	14.67

BH 128	27.3266	-26.7657	Domestic	GLM	> 60	7.75
BH 129	27.3159	-26.798	Domestic and livestock	GLM; PHYC; WATC; ISO; BAC; BOD	30	11.37
BH 130	27.316	-26.7983	Unutilised	GLM	40	11.49
BH 131	27.3392	-26.8034	Livestock	GLM; PHYC; ISO	26	14.07
BH 132	27.3282	-26.8062	Unutilised	GLM	> 60	6.69
BH 133	27.3283	-26.8063	Unutilised	GLM	33	7.7
BH 134	27.3502	-26.8163	Domestic	GLM; PHYC; ISO	> 60	7.83
BH 135	27.3497	-26.8168	Unutilised	GLM	> 60	7.85
BH 136	27.3472	-26.822	Livestock	GLM	22	12.04
BH 137	27.3345	-26.8241	Livestock	GLM	44	13.26
BH 138	27.3168	-26.8286	Domestic and livestock	GLM; PHYC; WATC; ISO; BAC; BOD	42	12.34
BH 139	27.3027	-26.8213	Irrigation	GLM	46	32.44
BH 140	27.3024	-26.8208	Unutilised	GLM	> 60	27.62
BH 141	27.3017	-26.8189	Unutilised	GLM	> 60	18.21
BH 142	27.2937	-26.8247	Domestic	GLM	48	20.65
BH 143	27.2955	-26.8166	Livestock and game	GLM	45	11.47
BH 144	27.293	-26.8152	Domestic and livestock	PHYC; ISO	20	-
BH 145	27.2918	-26.8151	Domestic and livestock	GLM	20	3.52
BH 146	27.3083	-26.8545	Domestic	GLM; PHYC; ISO	> 60	13.12
BH 147	27.3035	-26.8594	Domestic and game	GLM; PHYC; WATC; ISO; BOD; BAC	> 60	17.38
BH 148	27.2981	-26.8662	Domestic and game	GLM; PHYC; ISO	21	15.35
BH 149	27.2939	-26.87	Domestic and game	GLM; PHYC; ISO; BAC	> 60	12.12
BH 150	27.2989	-26.8699	Domestic, livestock, and game	GLM; PHYC; ISO	40	26.18
BH 151	27.2937	-26.8743	Domestic and livestock	GLM	45	12.37
BH 152	27.2922	-26.8786	Domestic	GLM; ISO	24	13.43
BH 153	27.3035	-26.8851	Domestic	GLM; PHYC; ISO	41	34.98
BH 154	27.3038	-26.8851	Unutilised	GLM	45	34.71
BH 155	27.2927	-26.8669	Unutilised	GLM	11	9.87
BH 156	27.2922	-26.8662	Domestic	PHYC; ISO	> 60	-
BH 157	27.2915	-26.8658	Domestic	GLM; PHYC; ISO	56	29.39
BH 158	27.2884	-26.871	Domestic	GLM	> 60	32.29
BH 159	27.2829	-26.8693	Domestic	GLM; PHYC; WATC; ISO; BAC; BOD	> 60	34.9
BH 160	27.2859	-26.874	Domestic	GLM	39	30.49
BH 161	27.2833	-26.8568	Domestic	GLM; PHYC; ISO	15	0.35
BH 162	27.2714	-26.8466	Unutilised	GLM	> 60	25.2
BH 163	27.2633	-26.8434	Domestic and game	GLM; PHYC; ISO	28	17.22
BH 164	27.2557	-26.8442	Domestic	GLM	30	1.94
BH 165	27.2552	-26.8434	Unutilised	GLM	15	5.19
BH 166	27.2425	-26.8534	Domestic	GLM	12	7.86

BH 167	27.2424	-26.8615	Domestic	GLM; PHYC; ISO	39	10.78
BH 168	27.2427	-26.8614	Unutilised	GLM	20	11.14
BH 169	27.2433	-26.8665	Livestock	GLM	32	24.85
BH 170	27.2451	-26.8715	Unutilised	GLM	55	33.77
BH 171	27.239	-26.8687	Livestock	GLM	38	22.18
BH 172	27.2681	-26.8869	Domestic	GLM	> 60	30.06
BH 173	27.2689	-26.8864	Domestic	GLM; PHYC; ISO	49	34.19
BH 174	27.2752	-26.8902	Domestic and game	GLM; PHYC; ISO; BAC	30	10.63
BH 175	27.2753	-26.8902	Unutilised	GLM	17	10.73
BH 176	27.28	-26.8896	Unutilised	GLM	45	23.49
BH 177	27.2805	-26.8889	Unutilised	GLM	30	19.59
BH 178	27.2827	-26.8897	Domestic and livestock	GLM; PHYC; ISO	58	13.54
BH 179	27.281	-26.8947	Unutilised	GLM	> 60	38.72
BH 180	27.2785	-26.9051	Livestock	GLM	16	14.24
BH 181	27.2749	-26.8988	Domestic	GLM; PHYC; ISO	30	20.13
BH 182	27.2671	-26.8921	Domestic	GLM	37	17.64
BH 183	27.263	-26.8906	Domestic and livestock	GLM	38	27.11
BH 184	27.2622	-26.8913	Domestic	GLM; PHYC; ISO; BAC	32	27.59
BH 185	27.261	-26.8972	Unutilised	GLM	> 60	26.73
BH 186	27.2643	-26.8985	Unutilised	GLM	> 60	16.35
BH 187	27.2685	-26.9016	Domestic	GLM; PHYC; ISO	25	22.08
BH 188	27.2675	-26.9023	Unutilised	GLM	30	16.43
BH 189	27.27	-26.9178	Unutilised	GLM	18	17.89
BH 190	27.2633	-26.9086	Domestic	GLM; PHYC; ISO; BAC	46	12.85
BH 191	27.2614	-26.9114	Unutilised	GLM; PHYC; ISO	> 60	17.58
BH 192	27.2593	-26.9085	Unutilised	GLM	10	6.77
BH 193	27.2585	-26.9081	Domestic	GLM; PHYC; WATC; ISO; BAC; BOD	28	11.97
BH 194	27.2587	-26.9121	Domestic	GLM	14	10.28
BH 195	27.2575	-26.9125	Domestic and game	GLM	> 60	19.9
BH 196	27.2519	-26.9178	Domestic	GLM; PHYC; ISO	35	19.17
BH 197	27.2495	-26.9129	Unutilised	GLM	13	11
BH 198	27.2486	-26.9127	Domestic	GLM	25	11.15
BH 199	27.2464	-26.9132	Domestic	GLM	40	12.36
BH 200	27.2474	-26.9114	Domestic	GLM	40	29.6
BH 201	27.2432	-26.9146	Domestic	GLM	28	12.62
BH 202	27.2426	-26.9168	Domestic	GLM	44	16.66
BH 203	27.242	-26.9168	Domestic	GLM	38	22.86
BH 204	27.2417	-26.9166	Unutilised	GLM	51	26.52
BH 205	27.2402	-26.9217	Domestic and irrigation	GLM; PHYC; WATC; ISO; BAC	> 60	12.13

BH 206	27.2286	-26.8972	Domestic and livestock	GLM; PHYC; ISO	43	33.2
BH 207	27.234	-26.8878	Unutilised	GLM	53	21.53
BH 208	27.2335	-26.8818	Unutilised	GLM	39	28.8
BH 209	27.2337	-26.8818	Domestic and livestock	GLM	50	29.43
BH 210	27.2299	-26.8791	Livestock	GLM; PHYC; ISO	15	5.77
BH 211	27.2297	-26.8794	Domestic and livestock	GLM	46	6.39
BH 212	27.222	-26.8817	Unutilised	GLM	> 60	4.88
BH 213	27.2214	-26.881	Domestic	GLM; PHYC; WATC; ISO; BAC; BOD	35	21.23
BH 214	27.2161	-26.8855	Domestic and livestock	GLM	39	6.27
BH 215	27.2134	-26.8865	Domestic and livestock	GLM	42	15.06
BH 216	27.218	-26.9049	Game	GLM	43	21.13
BH 217	27.2156	-26.9199	Game	GLM	36	25.47
BH 218	27.216	-26.924	Game	GLM	> 60	34.09
BH 219	27.2302	-26.9309	Domestic	GLM	27	15.26
BH 220	27.2208	-26.9414	Domestic	GLM; PHYC; ISO; BOD	52	6.91
BH 221	27.2127	-26.9524	Domestic and livestock	GLM; PHYC; ISO	33	8.73
BH 222	27.1995	-26.9437	Unutilised	GLM; ISO	-	0
BH 223	27.1914	-26.9345	Domestic and livestock	GLM	26	13.82
BH 224	27.2076	-26.9585	Livestock and irrigation	GLM; PHYC; ISO	29	16.91
BH 225	27.2064	-26.9572	Domestic	GLM	29	24.31
BH 226	27.2084	-26.9722	Domestic	GLM; PHYC; WATC; ISO; BAC; BOD	> 60	7.45
BH 227	27.2383	-26.9439	Unutilised	GLM	> 60	18.42
BH 228	27.2141	-26.9699	Domestic	GLM; PHYC; ISO	25	9.18
BH 229	27.2342	-26.944	Livestock	GLM	29	19.08
BH 230	27.2326	-26.9383	Unutilised	GLM	20	11.49
BH 231	27.2328	-26.9437	Unutilised	GLM	> 60	15.95
BH 232	27.2513	-26.9418	Domestic	GLM	28	16.95
BH 233	27.2689	-26.9417	Domestic and livestock	GLM	27	15.95
BH 234	27.2696	-26.9418	Unutilised	GLM	20	15.79
BH 235	27.2707	-26.9391	Unutilised	GLM; PHYC; WATC; ISO; BAC; BOD	14	10.45
BH 236	27.2704	-26.9392	Unutilised	GLM	> 60	10.81
BH 237	27.2699	-26.9394	Domestic and livestock	GLM	24	11.2
BH 238	27.2716	-26.939	Domestic	GLM	28	16.62
BH 239	27.2754	-26.9363	Unutilised	GLM	> 60	15.8
BH 240	27.2794	-26.9316	Domestic and livestock	GLM	33	19.64
BH 241	27.2964	-26.9199	Domestic and livestock	GLM	40	30.65
BH 242	27.2965	-26.9331	Unutilised	GLM	> 60	39.17
BH 243	27.3079	-26.9259	Unutilised	GLM	20	15.54
BH 244	27.3124	-26.9215	Unutilised	GLM	34	27.34

BH 245	27.3095	-26.9264	Livestock and game	GLM	38	14.98
BH 246	27.2813	-26.9429	Domestic	GLM	45	28.12
BH 247	27.2812	-26.9424	Livestock	GLM	> 60	27.98
BH 248	27.2802	-26.9434	Domestic	GLM	> 60	23
BH 249	27.2801	-26.9435	Domestic	GLM	> 60	22.26
BH 250	27.28	-26.9436	Unutilised	GLM	> 60	22.39
BH 251	27.2987	-26.938	Game	GLM; PHYC; ISO	56	21.82
BH 252	27.304	-26.9452	Unutilised	GLM	> 60	21.02
BH 253	27.3016	-26.9508	Domestic, livestock, and game	GLM	34	25.03
BH 254	27.31	-26.933	Domestic and livestock	GLM	45	35.96
BH 255	27.3128	-26.93	Unutilised	GLM	16	12.24
BH 256	27.3124	-26.9394	Domestic, livestock, and game	GLM	30	24.8
BH 257	27.3146	-26.9412	Domestic, livestock, and game	GLM; PHYC; ISO	42	19.66
BH 258	27.3149	-26.9422	Irrigation	GLM	25	19.11
BH 259	27.3162	-26.94	Game, domestic, and irrigation	GLM; PHYC; ISO	> 60	19.82
BH 260	27.3208	-26.9403	Game, domestic, and irrigation	GLM	34	19.02
BH 261	27.3342	-26.9453	Unutilised	GLM	53	11.82
BH 262	27.3349	-26.9432	Unutilised	GLM	30	8.18
BH 263	27.3361	-26.9429	Domestic and livestock	GLM; PHYC; ISO; BOD; BAC	25	6.22

*GLM = groundwater level mapping; PHYC = *in situ* physico-chemical parameters; WATC = major ion water chemistry; ISO = stable water isotopes;

BAC = bacteria; BOD = biological oxygen demand.

Appendix B. Major ion concentrations for all sites expressed in mg/L. TAL is expressed as mg/L as CaCO₃.

Site	TDS	TAL	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
RV 1	486	140	171	62	132	5.6	55	9.6	51	21
RV 8	484	132	157	58	130	4.4	56	9.9	52	21
BH 31	500	300	366	34	72	1.7	58	1.6	48	38
BH 38	472	252	307	51	63	3.2	37	2.7	61	31
BH 45	1264	140	171	242	123	72	51	3.1	136	73
BH 52	670	240	293	53	202	0.1	61	2	62	60
BH 61	332	204	249	27	25	2.1	19	0.7	28	35
BH 68	126	56	68	8	2	5.7	8	1.4	8	10
BH 77	448	292	356	23	45	4.6	47	0.9	42	38
BH 94	350	216	263	21	19	8.6	27	2	37	28
BH 114	1022	216	263	191	161	37	20	0.5	163	56
BH 129	72	32	39	6	6	1.2	6	0.6	6	5
BH 138	104	80	98	3	2	0.1	6	0.5	13	8
BH 147	436	208	254	38	84	9.3	21	1.4	46	47
BH 159	146	8	10	38	14	11	20	8.9	5	7
BH 193	558	260	317	63	117	0.1	13	1.8	58	70
BH 205	1176	236	288	150	530	16	56	2.6	181	87
BH 213	454	272	332	62	38	4.6	35	0.5	65	34
BH 226	540	140	171	111	88	11	24	1.2	60	48
BH 240	204	124	151	10	16	4.7	19	0.7	12	21

Appendix C. Mean (ave.) and standard deviation (σ) of the *in situ* physico-chemical parameters at set distances from the river for groundwater sites. EC = electrical conductivity ($\mu\text{S}/\text{cm}$); Temp = Temperature ($^{\circ}\text{C}$); pH (standard units); Riv. dist. = river distance.

Site	EC ave.	$\pm$ EC σ	pH ave	$\pm$ pH σ	Temp ave	$\pm$ Temp σ	Riv. dist.
RV 1	963.2	2.04	8.28	0.04	19.57	0.05	-
RV 2	975.33	2.61	9.1	0.02	19.96	0.58	-
RV 3	987.93	5.89	7.78	0.14	18.42	0.05	-
RV 4	921.6	6.32	8.83	0.01	22.14	0.1	-
RV 5	978.2	2.11	9.16	0.07	33.31	0.15	-
RV 6	991.13	3.34	9.03	0.04	19.93	0.18	-
RV 7	1029.2	1.78	8.48	0.05	18.81	0.19	-
RV 8	982.47	1.06	8.97	0.05	20.3	0.07	-
BH 2	1544.47	2.83	8.16	0.01	19.87	0.05	200 m
BH 38	746.07	6.27	8.35	0.03	18.8	0	200 m
BH 42	1053.87	0.52	6.73	0	17.9	0	200 m
BH 51	388.87	6.92	7.89	0.04	19.63	0.05	200 m
BH 52	1021.33	7.86	8.5	0.06	17.9	0	200 m
BH 56	555.6	2.97	7.21	0.01	23.4	0	200 m
BH 57	1013.67	1.35	7.84	0.03	19.34	0.2	200 m
BH 61	387.6	8.19	6.63	0.01	19.17	0.05	200 m
BH 146	847.73	0.46	7.53	0.01	19.9	0	200 m
BH 147	707.13	1.13	7.81	0.01	21.4	0	200 m
BH 148	500.67	4.03	7.7	0.05	20.46	0.2	200 m
BH 149	1328.07	1.1	7.5	0.05	20.71	0.5	200 m
BH 156	530.27	2.02	8.01	0.01	21.03	0.1	200 m
BH 174	1095.47	1.06	7.6	0.01	20.77	0.05	200 m
BH 190	668.87	1.19	7.67	0.01	19.77	0.05	200 m
BH 191	1026.53	4.34	7.37	0.09	20.91	0.2	200 m
BH 193	634.6	2.77	8.51	0.01	18.28	0.04	200 m
BH 205	1150.2	6.39	6.69	0.02	18.7	0.04	200 m
BH 220	577.53	0.64	6.69	0.02	19.23	0.05	200 m
BH 221	273.27	1.22	6.7	0.04	21.67	0.15	200 m
BH 226	611	8.14	8.8	0.03	20.53	0.14	200 m
BH 228	400.67	1.76	5.62	0	18.65	0.11	200 m
BH 73	169.53	4.09	6.48	0.22	21.06	0.05	500 m
BH 150	319	2.27	7.27	0.01	21.35	0.05	500 m
BH 157	257.8	0.56	8.01	0.02	20.88	0.04	500 m
BH 173	127.35	1.03	7.58	0.01	21.87	0.06	500 m
BH 178	316.67	1.45	6.68	0.21	21.42	0.14	500 m
BH 187	1607.07	1.58	8	0.02	22.48	0.07	500 m
BH 196	550.13	1.25	5.91	0.08	19.34	0.41	500 m

BH 224	202	0	7.02	0.03	20.99	0.04	500 m
BH 7	356.87	2.85	7.64	0.02	15.19	0.1	1 km
BH 31	764.4	2.5	9.02	0.15	19.48	0.28	1 km
BH 45	1182.07	1.22	7.62	0.01	21.78	0.04	1 km
BH 48	469.73	0.7	7.72	0.03	21.08	0.07	1 km
BH 75	132.48	1.28	8.21	0	21.67	0.05	1 km
BH 159	174.59	0.68	6.29	0.01	21.17	0.05	1 km
BH 181	574.47	1.06	7.92	0.06	23.99	0.18	1 km
BH 184	111.62	0.65	8.06	0.01	21.26	0.29	1 km
BH 34	523.27	0.8	8.14	0.02	20.75	0.08	2 km
BH 60	844.73	1.16	7.98	0.07	19.77	0.52	2 km
BH 153	414.6	1.5	7.82	0.01	21.2	0	2 km
BH 161	77.65	0.36	7.9	0.29	17.5	0	2 km
BH 19	463.53	2.03	8.24	0.01	20.81	0.16	> 2 km
BH 62	481.53	2.5	8.13	0.01	21.32	0.26	> 2 km
BH 68	169.67	0.99	7.12	0.02	19.57	0.24	> 2 km
BH 70	448.73	0.59	8.02	0.04	21.28	0.25	> 2 km
BH 77	680.07	3.86	8.36	0.77	21.39	0.17	> 2 km
BH 83	101.98	0.98	8.36	0.04	20.27	0.36	> 2 km
BH 94	547.73	3.95	8.63	0.09	22.1	0.17	> 2 km
BH 105	104.81	0.58	7.13	0.08	20.16	0.05	> 2 km
BH 114	1291.6	6.87	7.67	0.04	20.17	0.05	> 2 km
BH 127	486.73	5.7	7.13	0.03	21.35	0.18	> 2 km
BH 129	88.37	2.11	8.53	0.25	18.75	0.21	> 2 km
BH 131	101.88	0.13	7.43	0.08	19.8	0	> 2 km
BH 134	138.25	1.05	8.06	0.01	20.99	0.21	> 2 km
BH 138	120.99	1.14	8.39	0.05	19.43	0.13	> 2 km
BH 144	163.87	1.74	6.69	0.05	20.58	0.09	> 2 km
BH 163	71.74	1.1	7.65	0.07	20.54	0.25	> 2 km
BH 167	52.62	2.17	7.42	0.02	20	0	> 2 km
BH 206	73.62	0.42	4.83	0.01	19.34	0.05	> 2 km
BH 210	92.41	1.95	6.54	0.15	18.6	0	> 2 km
BH 213	576.47	6.67	8.38	0.04	20.61	0.39	> 2 km
BH 240	226.07	0.26	8.47	0.08	21.2	0.34	> 2 km
BH 251	219.73	1.75	8.03	0.02	22.21	0.03	> 2 km
BH 257	322.4	0.51	8.33	0.02	19.78	0.15	> 2 km
BH 259	367.93	2.58	8.06	0.02	20.76	0.2	> 2 km
BH 263	403.4	2.41	8.2	0	19.95	0.09	> 2 km

Appendix D. Stable isotopes of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) and associated standard deviations (σ) and deuterium excess (d -excess) for all sites.

Site	$\delta^2\text{H}$ (‰)	$\pm \text{}^2\text{H } \sigma$ (‰)	$\delta^{18}\text{O}$ (‰)	$\pm \text{}^{18}\text{O } \sigma$ (‰)	d -excess (‰)
RN 1	-6.91	0.64	-3.39	0.15	15.83
RN 2	10.72	0.89	-2.16	0.11	25.20
MN 1	8.45	4.08	1.41	0.60	-0.97
WD 1	20.21	0.36	4.16	0.13	-7.65
RV 1	-3.70	0.32	-1.65	0.15	7.37
RV 2	-1.65	3.28	-1.32	0.33	7.21
RV 3	-2.67	0.34	-1.49	0.05	7.30
RV 4	-6.19	0.36	-1.07	0.17	0.98
RV 5	-1.16	5.33	-1.27	0.43	7.32
RV 6	-2.23	1.11	-1.33	0.18	6.70
RV 7	-3.35	3.29	-1.25	0.28	5.03
RV 8	-2.83	0.37	-1.32	0.07	6.04
SP 1	-12.99	0.24	-2.85	0.09	6.13
SP 2	-6.37	0.48	-2.36	0.30	9.47
SP 3	-24.93	0.36	-4.87	0.12	7.73
SP 6	46.16	0.30	7.60	0.13	-4.78
SP 7	-15.15	0.42	-3.55	0.23	8.61
SP 8	-17.02	0.26	-3.09	0.19	3.70
SP 9	39.24	2.89	6.23	0.29	-2.48
SP 10	9.37	1.20	0.66	0.12	4.91
BH 2	-13.04	7.58	-4.09	0.72	14.34
BH 7	-27.29	0.43	-4.67	0.20	4.02
BH 19	-24.33	0.37	-5.43	0.14	12.06
BH 21	-24.40	0.60	-5.75	0.05	14.15
BH 31	-16.67	2.43	-4.76	0.38	15.24
BH 34	-23.06	1.90	-5.28	0.22	12.30
BH 38	-23.18	2.52	-5.10	0.22	10.97
BH 42	-23.26	0.24	-4.30	0.15	5.56
BH 45	-24.56	0.23	-4.96	0.20	8.66
BH 48	-27.09	2.57	-5.72	0.23	11.25
BH 51	-28.14	0.42	-5.44	0.11	8.32
BH 52	0.47	0.67	-1.50	0.06	9.46
BH 56	-24.93	1.10	-5.13	0.19	5.74
BH 57	-16.77	0.96	-3.36	0.20	8.00
BH 60	-25.20	0.37	-4.95	0.21	13.58
BH 61	-28.29	0.61	-6.25	0.12	9.45
BH 62	-27.40	0.35	-5.50	0.06	9.97
BH 68	-31.10	0.95	-6.13	0.14	9.53
BH 70	-29.98	0.39	-5.90	0.11	12.49
BH 73	-26.36	0.00	-5.80	0.00	9.41
BH 75	-29.44	0.46	-5.80	0.22	11.69
BH 83	-28.84	0.28	-5.95	0.11	7.41
BH 94	-28.56	0.69	-5.37	0.25	11.31

BH 105	-27.74	1.88	-5.83	0.38	7.25
BH 114	-26.99	0.25	-5.11	0.13	8.03
BH 127	-23.26	2.99	-4.67	0.42	7.48
BH 129	-26.50	0.32	-5.07	0.05	8.12
BH 131	-27.92	0.58	-5.38	0.10	10.81
BH 134	-26.09	0.38	-5.51	0.13	15.31
BH 138	-27.65	0.24	-6.41	0.10	12.59
BH 144	-26.20	3.28	-5.79	0.46	10.52
BH 147	-24.95	1.22	-5.11	0.22	9.31
BH 148	-10.91	0.22	-2.66	0.07	6.91
BH 149	-10.76	7.91	-3.60	0.71	13.34
BH 150	-19.50	0.32	-3.81	0.21	6.01
BH 153	-27.67	2.39	-5.45	0.43	8.87
BH 152	-9.34	0.51	-1.93	0.16	3.56
BH 156	-30.02	1.46	-5.94	0.23	9.80
BH 157	-27.97	2.22	-5.92	0.29	11.72
BH 159	-27.23	0.24	-5.25	0.17	7.97
BH 161	-27.03	0.46	-5.69	0.07	11.12
BH 163	-23.13	0.33	-5.17	0.06	11.53
BH 167	-28.48	0.51	-5.90	0.04	11.08
BH 173	-31.58	0.81	-6.00	0.24	8.65
BH 174	-6.65	5.90	-2.85	0.48	12.45
BH 178	-27.39	0.42	-5.89	0.10	12.06
BH 181	-21.41	0.35	-3.43	0.13	1.58
BH 184	-28.63	0.67	-6.16	0.01	12.64
BH 187	-19.17	0.45	-3.81	0.16	6.37
BH 190	-14.35	2.75	-3.70	0.20	10.44
BH 191	-20.94	0.39	-4.55	0.11	9.56
BH 193	2.10	0.46	0.87	0.22	-3.70
BH 196	-18.33	6.14	-4.25	0.44	10.12
BH 205	-16.73	0.41	-3.13	0.07	4.28
BH 206	-28.50	0.36	-6.20	0.09	13.04
BH 210	-25.63	0.27	-5.66	0.19	12.31
BH 213	-25.48	0.47	-5.15	0.24	9.02
BH 222	-27.20	1.28	-6.47	0.56	16.18
BH 220	-17.27	0.34	-3.39	0.15	5.47
BH 221	-25.91	0.49	-5.34	0.11	9.85
BH 224	-27.87	0.49	-5.27	0.15	7.44
BH 226	-23.17	0.54	-4.72	0.13	8.46
BH 228	-23.38	3.36	-5.62	0.29	14.26
BH 240	-26.43	0.35	-5.05	0.11	7.37
BH 251	-33.61	0.31	-6.07	0.22	7.03
BH 257	-27.91	0.27	-5.06	0.08	5.97
BH 259	-28.54	0.28	-5.12	0.13	5.79
BH 263	-24.76	0.70	-5.02	0.10	8.87