

**UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA**

Denkleiers • Leading Minds • Dikgopolo tša Dihlalefi

Mini Dissertation

Submitted in partial fulfilment of the requirements for the degree

MSc Water Resource Management

In the Faculty of Natural & Agricultural Sciences

University of Pretoria

**Assessment of groundwater quality for irrigation and drinking
purposes in the Limpopo Granulite-Gneiss region, Limpopo
Province, South Africa**

Name: Nothando Mirrande Ndhlovu

Student number: U19315083

Supervisor: Dr Marius Claassen

Declaration

I, Nothando Mirrander Ndhlovu declare that the mini thesis/dissertation, which I hereby submit for the degree MSc in Water Resource Management at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Signature:



Date: 20 September 2024

Acknowledgments

I would like to thank God for giving me the mental ability to study further. I would like to thank my employer, the Department of Water and Sanitation, for the tuition funding and for giving me the time to do my research. I am thankful to Professor Fanus Venter who helped me restart my research and gave me the courage to complete my Master's degree studies. I am grateful to my supervisor, Dr. Marius Claassen for choosing to be my supervisor and for his guidance, diligence, patience, and constructive criticism. I would also like to thank my colleagues, Dr. Portia Fuku and Dr. Lindelani Lalumbe, who were instrumental in the conceptualisation of my research.

I would like to thank my classmate Promise Dlamini, without her support I would have given up when I lost all hope.

I would like to dedicate my research to my children, Wakwetsima Mangaliso Mapanzene and Siphephelo Amukelo Mapanzene. If mommy can do it at 40 years old, you can do so much more even sooner, before marriage and children.

Abstract

The global freshwater availability studies have classified South Africa as water stressed in 1999 and approaching water scarcity by the year 2025. While groundwater is available everywhere, it is not always in suitable quality meaning some groundwater dependent rural communities lack adequate information about the water quality status of their groundwater supplies. While there may be significant groundwater research studies done, the outputs never reach the impacted communities.

Groundwater accounts for nearly 70% of rural domestic water supply in Limpopo Province. Furthermore, rapid population growth and more frequent drought events have led to reduced surface water supply and increased in groundwater abstraction, putting groundwater resources under enormous pressure. As communities grow, more groundwater is abstracted, and land use changes to more paved roads, houses, shopping centres, and parking lots, decreasing groundwater recharge.

A total of 319 groundwater samples, from 17 monitoring sites located within Limpopo granulite-gneiss region, collected between 2000 and 2017, were analysed in order to evaluate its suitability for drinking and irrigation purposes. The abundance of cations and anions are showing $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- + \text{NO}_2^- > \text{F}^-$, respectively. The weighted average values show major anions are dominant over the major cations. Na^+ accounts for 48% of the cations and HCO_3^- accounts for 41% of the anions.

The pH of groundwater in the study area ranges from 6,9 to 9,2; with over 83,7% of the samples falling within the pH 7,5 to 8,5 range; while 5,0% of the samples are within the pH 6,5 to <7,5 range; and 11,3% samples are within the pH >8,5 to 9,2 range. TDS values range from 107 to 2426 mg/L with a weighted average of 1122 mg/L. At least 57% of the samples are categorically brackish and 43% are fresh.

On the Piper diagramme, the water samples are mainly plotting on Ca-Mg- HCO_3 type (zone 5) and mixed (Ca-Mg-Cl- SO_4 and Ca-Mg- HCO_3) type (zone 9), Ca-Mg- HCO_3 type indicating carbonate (temporary) hardness. The Gibbs diagramme indicates that groundwater chemistry is controlled mainly by evaporation dominance mechanisms, while high $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations relative to HCO_3^- concentrations, indicate silicate weathering involving reverse ion exchange. Pearson correlation analysis shows a very strong positive correlation of Na^+ with Cl^- (0,80), SO_4^{2-} (0,81), and F^- (0,78).

Suitability for irrigation assessment results show that all the groundwater samples were suitable for irrigation purposes based on sodium adsorption ratio, residual sodium carbonate, and permeability index. However, for the Kelly ratio index, seven monitoring sites are unsuitable for irrigation purposes.

Over 71% of the water samples have concentrations of nitrate higher than the WHO and SANS241 recommended guideline value of ≤ 11 mg/L, making 15 out of 17 monitoring sites unsuitable for drinking. However, the remaining two sites failed drinking water suitability in TDS, Na, Cl, SO₄, and F based on SANS241 and WHO, guidelines. To mitigate methemoglobinemia, a simpler, cheaper, and more immediate approach that is within the capabilities of communities is recommended.

Keywords: Groundwater quality, nitrate pollution, human health, agriculture

Table of Contents

Declaration	i
Acknowledgments	ii
Abstract	iii
Table of Contents	v
List of figures	vii
List of tables.....	viii
List of acronyms and abbreviations.....	ix
Chapter 1: Introduction	1
1.1. Introduction	1
1.2. Problem statement	5
1.3. Aim and objectives of the project.....	7
Chapter 2: Literature review	8
2.1. Introduction	8
2.2. Groundwater quality assessment using hydrochemical analysis.....	8
2.2.1. Data accuracy checking	9
2.2.2. Evaluation of the hydrogeochemical characteristics	9
2.2.3. Irrigation water quality assessment	10
2.2.4. Drinking water quality assessment	16
Chapter 3: Research method	20
3.1. Introduction	20
3.2. Assessment of the study area.....	20
3.2.1. Location.....	20
3.2.2. Regional geology	23
3.2.3. Drainage and climate	24
3.2.4. Role of groundwater in region 3	25
3.2.5. Soil.....	25
3.3. Chemical data acquisition and screening	25
3.3.1. Sample collection	26
3.3.2. Analytical methods applied	26
3.3.3. Analytical data accuracy determination	27
3.4. Groundwater quality assessment using Hydrochemical analysis	27
3.4.1. Evaluation of the hydrogeochemical characteristics.....	29
3.4.2. Suitability for irrigation assessment methods	31
3.4.3. Suitability for drinking assessment methods.....	32

3.5.	Programmes/ Application.....	32
3.6.	Ethical standards research protocol	33
3.7.	Discussion on expected results and impact of research.....	33
3.8.	Limitations of the study	33
Chapter 4:	Results	34
4.1.	Introduction	34
4.2.	Analytical data accuracy determination	34
4.3.	Chemical composition of groundwater.....	35
4.4.	Hydrogeochemical characteristics.....	50
4.5.	Suitability for irrigation	61
4.6.	Suitability for drinking.....	64
4.7.	Summary of results per borehole	73
Chapter 5:	Conclusions	90
5.1.	Introduction	90
5.2.	Hydrogeochemical characteristics	90
5.3.	Suitability for irrigation	91
5.4.	Suitability for drinking.....	92
5.5.	Protection and remediation recommendations	93
References	94

List of figures

Figure 1: The global projected ratio of water withdrawals to water supply in 2040 (Economist Intelligence Unit, 2021).....	4
Figure 2: Spatial distribution of nitrate concentrations, in South Africa, from the National Groundwater Quality Monitoring Programme.	6
Figure 3: Location of Limpopo Granulite Gneiss Groundwater Region, showing groundwater monitoring sites and rivers.....	21
Figure 4: Groundwater annual volume allocation splits for the Limpopo Granulite Gneiss Region.....	22
Figure 5: Location map of the Beit Bridge Complex within the Limpopo Complex showing adjacent cratons, and complexes modified from Basupi et al., 2022 after Watkeys, 1983.	24
Figure 6: Spatial distribution of Na ⁺ based on average concentration per monitoring site, 2000-2017.....	37
Figure 7: Spatial distribution of dominant cation (2000-2017).....	38
Figure 8: Spatial distribution of Ca ²⁺ based on average concentration per monitoring site (2000-2017).	38
Figure 9: Spatial distribution of Mg ²⁺ based on average concentration per monitoring site (2000-2017).....	39
Figure 10: Spatial distribution of K ⁺ based on average concentration per monitoring site (2000-2017)	39
Figure 11: Spatial distribution of HCO ₃ ⁻ based on average concentration per monitoring site (2000-2017).	40
Figure 12: Spatial distribution of SO ₄ ⁻ based on average concentration per monitoring site (2000-2017). ...	40
Figure 13: Spatial distribution of Cl ⁻ based on average concentration per monitoring site (2000-2017).....	41
Figure 14: Spatial distribution of NO ₃ ⁻ +NO ₂ ⁻ based on average concentration per monitoring site (2000-2017).....	42
Figure 15: Spatial distribution of pH based on average pH per monitoring site (2000-2017).	44
Figure 16: ZQMTUG2 and ZQMTUG4 pH trends over time.....	45
Figure 17: pH trends for 15 monitoring sites over time.	46
Figure 18: TDS spatial distribution according to Freeze and Cherry (1979) TDS classification.	48
Figure 19: ZQMALL2, ZQMBLT3, ZQMMES1, and ZQMSWW2 TDS trends (mg/L).....	48
Figure 20: TDS (mg/L) vs Cl ⁻ (mg/L) trend comparison for ZQMBLT2 and ZQMSWW2.....	49
Figure 21: Classification results of the groundwater using Piper diagramme (Group2 n>10).....	51
Figure 22: Classification results of the groundwater using Piper diagramme (Group1 n<10).....	52
Figure 23: i) Modified Piper (1944) diagramme explanation by (after Rao, 1998). ii) Hamilton et al., (1991) classification of water types (after Rao, 1998).....	52
Figure 24: Gibbs diagramme of the study area showing all samples.	53
Figure 25: Gibbs diagrams for monitoring sites: i) ZQMALL2, ii) ZQMBGG1, iii) ZQMBLT2, iv) ZQMBLT3, v) ZQMGS1, vi) ZQMGS1, vii) ZQMCHK2, viii) ZQMLGN1.....	54
Figure 26: Gibbs diagrams for monitoring sites: i) ZQMMES1, ii) ZQMMPE1, iii) ZQMSSN1, iv) ZQMWW1, v) ZQMSWW2, vi) ZQMTBK1, vii) ZQMTBK2.	55
Figure 27: Gibbs diagrams for bore hole sites i) ZQMTUG2, ii) ZQMTUG4.	56
Figure 28: The relationship between sodium and chloride.....	56
Figure 29: The relationship between the Na/Cl ratio and Ca+Mg (2000-2017).....	57
Figure 30: Scatter plots of Ca ²⁺ +Mg ²⁺ vs HCO ₃ ⁻ (2000-2017).....	58
Figure 31: CAI-I and CAI-II plots for all water samples (2000-2017).	58
Figure 32: %Na trend for ZQMTUG2 and ZQMTUG4.	62
Figure 33: Spatial distribution of KR.	63
Figure 34: ZQMALL2, ZQMLGN, ZQMTUG2 and ZQMTUG4 Kelly's Ratio trend.....	63
Figure 35: NO ₃ +NO ₂ as in N (mg/L) trend for borehole sites: ZQMALL2, ZQMBGG1, ZQMBLT, ZQMBLT3, ZQMGS1, ZQMGT1, ZQMCHK2 and ZQMLGN1.....	67
Figure 36: NO ₃ +NO ₂ as in N (mg/L) trend for borehole sites: ZQMMES1, ZQMMPE1, ZQMSSN, ZQMSWW1, ZQMSWW2, ZQMTBK1 and ZQMTBK2.....	68

Figure 37: Historical percentage of normal rainfall for the season map.....	69
Figure 38: Spatial distribution of NO ₃ +NO ₂ and percentage splits.	70
Figure 39: TDS, Na ⁺ , SO ₄ ²⁻ and F ⁻ trends for borehole ZQMTUG2 and ZQMTUG4.....	71
Figure 40: Spatial distribution of F ⁻	72

List of tables

Table 1: Irrigation water problems (Ayers and Westcot, 1985).....	11
Table 2: Irrigation water suitability research methods.....	15
Table 3: Limpopo household agricultural activity breakdown.....	23
Table 4: Summary of available data for groundwater region 3.	29
Table 5: Summary of water quality indices to be calculated for irrigation suitability assessment.....	32
Table 6: Summary of averages per monitoring site for various major ions.	35
Table 7: Statistical analysis of physicochemical parameters.....	36
Table 8: Summary of pH for samples per monitoring site (2000-2017).....	43
Table 9: Summary of TDS values for samples per monitoring site.....	47
Table 10: CAI-I and CAI-II results for all monitoring sites.	59
Table 11: Correlation coefficients of major physicochemical parameters in the study area	60
Table 12: Pearson's correlation coefficient classification (Ahemaitihali and Dong, 2022).....	60
Table 13: Summary of water quality indices classification for irrigation suitability assessment.....	62
Table 14: Summary of drinking water suitability assessment per borehole.....	64
Table 15: Summary of drinking water suitability assessment per borehole.....	65

List of acronyms and abbreviations

APHA	American Public Health Association
CI	Chloride Index
CSIR	Council for Scientific and Industrial Research
DMS	Dissolved Major Salts
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
DWS	Department of Water and Sanitation
EC	Electrical conductivity
ESP	Exchangeable Sodium Percentage
FAO	Food and Agriculture Organization
GIS	Geographic Information System
GRID	Global Resource Information Database
IBE	Ion Balance Error
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
KR	Kelly's ratio
L	Litre
MAR	Magnesium Adsorption Ratio
mbgl	metres below ground level
mEq	milli-equivalent
mEq/L	milli-equivalent per litre
mg/L	milli-grams per litre
MH	Magnesium Hazard
Mm ³	Million Cubic Metre
mS/m	milli-Siemen per metre
PI	Permeability Index
PS	Potential Salinity
RSC	Residual Sodium Carbonate
SA	South Africa
SABS	South African Bureau of Standards
SANS	South African National Standards
SAR	Sodium Adsorption Ratio
SAWQG	South African Water Quality Guidelines
SDG-6	Sustainable Development Goal Number 6
SDGs	Sustainable Development Goals
StatsSA	Statistics South Africa
TDS	Total Dissolved Solids
TH	Total Hardness
UN	United Nations
UNEP	United Nations Environment Programme
USCB	United States Census Bureau
USSL	United States Salinity Laboratory
WARMS	Water Use Authorisation and Registration Management System
WHO	World Health Organization
WMS	Water Management System
WRC	Water Research Commission
WRG	Water Resources Group

Chapter 1: Introduction

1.1. Introduction

According to Shiklomanov (1993) only 2,5% of the global surface and subsurface water is freshwater, but over 68% of it is frozen and unavailable, while over 30% is found below the earth's surface and known as groundwater (Freeze and Cherry 1979). Groundwater accounts for nearly 99% of readily available freshwater (Shiklomanov and Rodda, 2003). Two decades later, UN-Water (2022) acknowledges that this is still the case and this means groundwater has the capacity to provide societies across the globe with necessary social, economic, and environmental services, benefits, and opportunities. It is widely accepted that water is key to sustainable development and that water serves as a foundation for the achievement of many of the Sustainable Development Goals (SDGs) (Guppy et al. 2018), particularly SDG-6, the goal solely dedicated to water: 'To ensure availability and sustainable management of water and sanitation for all' (UN, 2015).

Over 2,5 billion people around the world depend exclusively on groundwater for their basic water needs (Grönwall and Danert, 2020). While, according to Margat and Van der Gun (2013), as much as 50% of the global population depends on groundwater for their drinking water supplies. FAO (2017) estimated as much as 40% of irrigated areas in the world get water from groundwater sources. Foster et al., 2013 argue that despite the reality of groundwater's significance, it remains poorly understood, resulting in inadequate management and protection. Freeze and Cherry (1979) suggested that for groundwater to continue to play a significant role in the development of water security, more effort will have to be made to protect it from the increasing threat of subsurface contamination, such as municipal and industrial waste disposal, agricultural activities, petroleum spills, mining activities, and radioactive waste. Furthermore, there are two disposal techniques that are being used and considered for the future, the deep-well injection of liquid and gas wastes and sanitary landfill for solid wastes (Freeze and Cherry, 1979).

Grönwall and Danert (2020) concur that the limited understanding of the groundwater quantity and quality is a consequence of a lack of data, which means critical information on groundwater remains as hidden as the resource itself. However, the lives of billions of people globally depend on the scientific research community to manage and protect this complex and hidden water resource (UN-Water, 2015). The growing water scarcity in many parts of

the world and the potential of groundwater means the need to manage it carefully can no longer be ignored (UN-Water, 2022). FAO (2017) found that groundwater use has increased significantly since the middle of the twentieth century, in such a way that annual groundwater withdrawals outstrip the rate of natural recharge in most areas. Scientific research and innovation for groundwater resource management such as Managed Aquifer Recharge adopted by some Arab countries requires a significant investment (UN-Water, 2022). In South Africa, the Groundwater Strategy 2010 addresses strategies for meeting climate change including artificial recharge, groundwater data collection, and increased groundwater research (DWA, 2010). Groundwater monitoring is a wise investment, since early detection of problems is cost-effective, allowing mitigation measures to be introduced before irreversible damage takes place (UN-Water, 2022). Groundwater monitoring plays a significant role in meeting growing water needs with respect to water availability and water quality, and it must be implemented (Adimalla et al., 2020). Investments should focus on strengthening traditional monitoring networks (i.e. in situ, low-cost, easy-to-maintain technology) because of their proven track record of generating data and information to support scientific knowledge generation (UN-Water, 2015). Grönwall and Danert (2020) recommend increased political will as one of the key drivers of adequate allocation of financial resources towards groundwater monitoring programmes.

Another global threat to groundwater management is the effect of climate change as intense climate extremes such as floods and droughts become more frequent (Grönwall and Danert 2020). Drought-induced water cuts can alter sanitation practices as observed by McGill et al., (2019), in Ramotswa, Botswana, where a switch back to forsaken groundwater-polluting pit latrines from flush toilets was inevitable. Rainfall is the main source of groundwater recharge (Mambo and Faccer, 2017); hence climate change also threatens groundwater quantity, because of the low recharge rate during droughts (UN-Water 2022). Furthermore, even when there is adequate rain, higher average annual temperatures will result in increased evapotranspiration, which reduces recharge (Mambo and Faccer, 2017). Moreover, changes in groundwater levels may also lead to changes in groundwater quality as (1) abstraction moves to deeper aquifers which may have high levels of specific constituents of concern for health (WHO, 2017), and (2) less dilution (Mambo and Faccer, 2017). Reduced groundwater recharge associated with climate change drought events in the Mediterranean region (Stigter et al., 2014) has resulted in amplified concentrations of solutes (chloride, nitrate, etc) in groundwater associated with lack of dilution from

precipitation and warmer temperatures, which increase evaporation (Mas-Pla and Menció, 2019). Severe flooding can damage wastewater infrastructure, and other poorly contained waste and stored chemicals, consequently mobilising contaminants such as chloride and nitrate (Gurdak et al., 2007). This kind of catastrophic flooding was observed recently in KwaZulu Natal, where 200-400mm rainfall poured within 24 hours (South African Government, 2022; Pinto et al., 2022). In addition, more intense storms may also destroy small alluvial aquifers (DWA, 2010).

The world's population is currently at 8,2 billion and is projected to continue rising over the coming 50-60 years, reaching a peak of around 10.3 billion people in the mid-2080s (UN-DESA, 2024). According to the 2009 population growth trajectory, the global demand for water in 2030, will be 40% more than available (2030 WRG, 2009). South Africa's population is over 60,6 million (StatsSA, 2022), with an average annual growth rate of 1,6% (StatsSA, 2019). By 2030, South Africa is projected to face a 17% water deficit under the current water supply and demand trajectory (2030 WRG, 2014). South Africa's water resources are relatively limited and drought-prone, with a low average rainfall of 450 mm per annum, 47% lower than the world's average of around 860 mm per annum (Basson, 2011). South Africa is also adversely affected by comparatively high evaporation, lacks a large unshared river system, and is poorly endowed with groundwater (Basson, 2011). The global freshwater availability studies (UNEP/GRID-Arendal, 2002) have classified South Africa as water stressed in 1999 and approaching water scarcity by the year 2025 based on severe combined impacts of global climate change-induced drought and growing food demands for a rapidly growing population living in predominantly arid to semi-arid regions.

The Economist Intelligence Unit (2021) paints yet another gloomy picture of South Africa's 2040 water stress projection as high with 40-80% withdrawal to supply ratio (Figure 1). DWAF (2000) reported that eight million South Africans were without water and predicted groundwater to be the most cost-effective solution. Fast forward, authors (du Toit et al., 2012; Grönwall and Danert, 2020) can confirm groundwater has been used to develop a bulk-water supply quickly and cost-effectively, to meet short- to medium-term water demands in South Africa and globally.

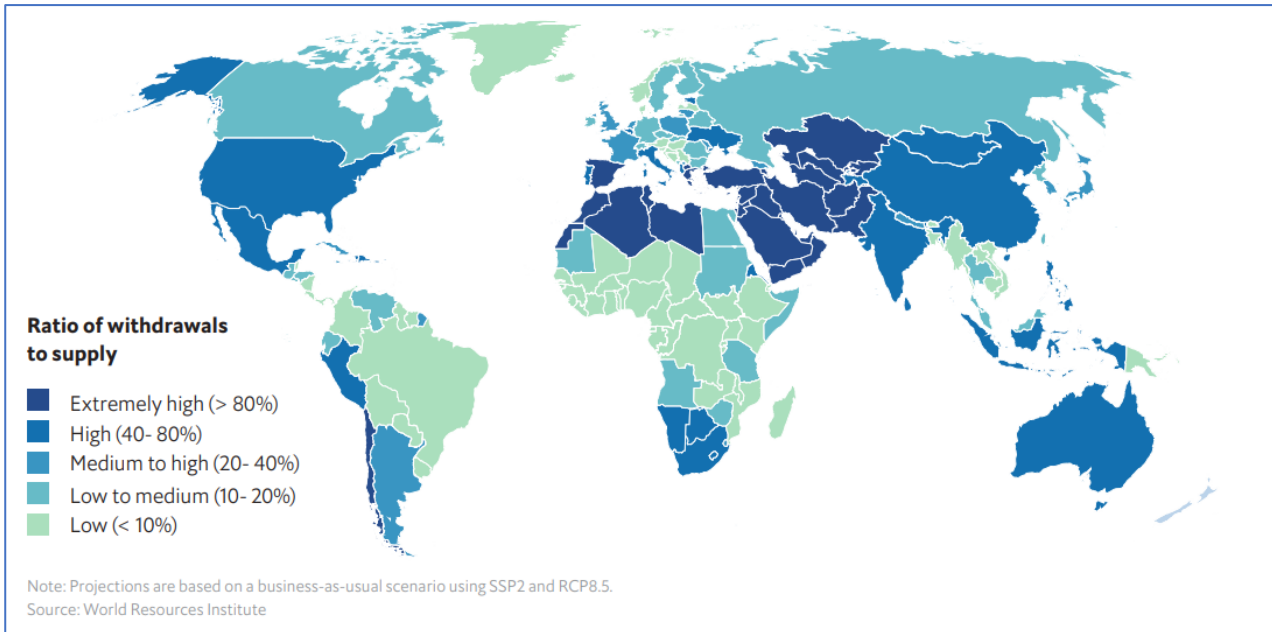


Figure 1: The global projected ratio of water withdrawals to water supply in 2040 (Economist Intelligence Unit, 2021).

Groundwater infrastructure is relatively cheap and can be made available faster than surface water infrastructure (Nel, 2017). While groundwater is available everywhere, it is not always of suitable quality meaning some groundwater-dependent rural communities lack adequate information about the water quality status of their groundwater supplies (Nel, 2017). While there may be significant groundwater research studies done, the outputs never reach the impacted communities (Lalumbe and Kanyerere, 2022a). Authors Lalumbe and Kanyerere (2022a) demonstrated the shortfall of scientific research, where scientific knowledge generated on groundwater quality is not targeted at raising community awareness around human health instead of academic awards and record keeping.

Groundwater is a recognised significant and strategic resource in many parts of South Africa (DWAF, 2000). According to WRC (2014), groundwater has been nurturing South African communities long before the promulgation of the National Water Act in 1998, which recognised its value as a public resource. Groundwater plays critical role in our water-scarce country through the storage of some rain and surface water (Mambo and Faccer, 2017). Groundwater is the main source of water and often the only source in most of the smaller towns in the arid areas of the republic (Mambo and Faccer, 2017).

In Limpopo Province, groundwater accounts for nearly 70% of the rural domestic water supply (du Toit et al., 2012). Furthermore, rapid population growth and more frequent

drought events have led to reduced surface water supply and increased groundwater abstraction, putting groundwater resources under enormous pressure (Nel, 2017; Gad and El Osta, 2020). As communities grow, more groundwater is abstracted, and land use changes to more paved roads, houses, shopping centres, and parking lots, decreasing groundwater recharge (Nel, 2017).

Groundwater, though hidden, is too precious to be ignored (Mambo and Faccer, 2017). The hidden nature of groundwater below the surface complicates the unseen quality required for human and agricultural consumption (de Lange et al., 2019). However, a significant proportion of groundwater is of good potable quality, requiring almost no treatment before distribution and use (de Lange et al., 2019). Once this hidden precious resource gets polluted, remediation is often very long, complex, and expensive (DWA, 2000). In some cases, the groundwater resource may be significantly polluted and abandoned indefinitely like the Ramotswa groundwater supply in Botswana was abandoned in the 1990s when the nitrate concentrations were found to be higher than the 50mg/L NO_3^- global drinking standards (Walmsley and Patel, 2011).

In South Africa, sustainable groundwater use, and management are critical for maintaining groundwater quantity and quality (DWA, 2010). Groundwater monitoring programmes are designed to acquire and interpret data that would indicate changes or trends in the groundwater quantity and quality so that conservation and protection measures are modified (Nel, 2017). Improved groundwater resource management is also necessary for sustainable development, and the broader SDGs (Guppy et al., 2018). Good quality of water, according to World Health Organization Guidelines (WHO, 2011a) and South African National Standards (SANS 241, 2011) is essential for food security and human health, which are part of Sustainable Development Goals 2 and 6, respectively (UN, 2015). SANS 241 describes the minimum requirements for potable water to be considered safe for human consumption. The quality of groundwater is equally important to its quantity because poor quality groundwater reduces the quantity of suitable groundwater for various purposes (Hussain and Rao, 2013). Groundwater also broadly supports economic development and social prosperity (Hussain and Rao, 2013).

1.2. Problem statement

There are hundreds of borehole water supplies in Limpopo province, a province known to have elevated nitrate concentrations exceeding 11 mg/L as nitrogen (Maherry et al., 2010).

Various studies have pointed to Limpopo province as a priority area for further groundwater nitrate research and remediation (Maherry et al., 2010). Vegter (2001) did a potability assessment on 750 water samples from Groundwater Region 3 and found over 50% of the samples had harmful concentrations of nitrate and fluoride and were deemed unsuitable for drinking. A brief nitrate screening of the 2000-2017 national groundwater quality data, shows that Limpopo nitrate pollution problems persist (Figure 2). Tredoux (2004) identified, fertilisers and on-site sanitation as the sources of groundwater nitrate pollution in rural communities. In a recent study of the Soutpansberg groundwater region, which is located south of the study area, Lalumbe and Kanyerere (2022a) concluded that high nitrate concentration levels in the area were associated with pit-latrines and the agricultural use of fertilisers. In South Africa, nitrate pollution has been identified by Marais (1999) as the single most significant reason for groundwater sources to be declared unfit for drinking.

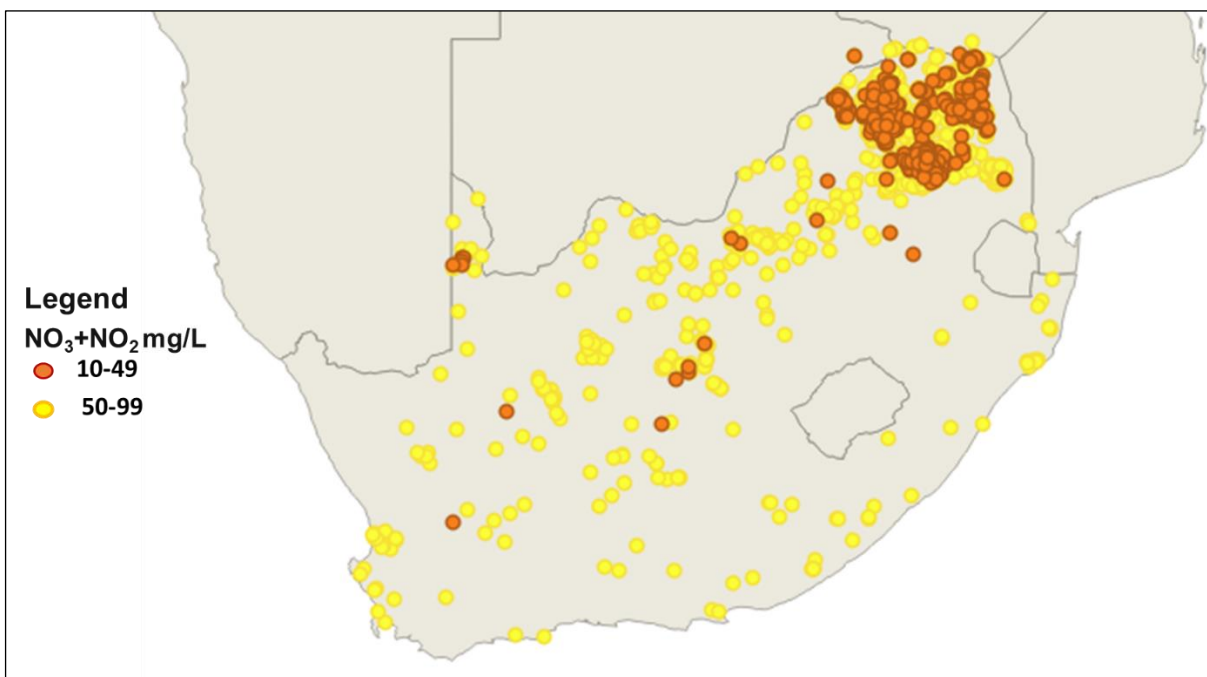


Figure 2: Spatial distribution of nitrate concentrations, in South Africa, from the National Groundwater Quality Monitoring Programme.

Limpopo's population is estimated to be over 5,9 million (StatsSA, 2022), showing a 1,3% average annual growth (StatsSA, 2019). Limpopo province at 37,9%, has the highest percentage of households involved in agricultural activities, while South Africa is at 17.2% (StatsSA, 2021).

Nell and van Huyssteen (2014) identified salination and sodification as major factors contributing to the degradation of agricultural land. Lack of dissemination of research data and groundwater hazard awareness leaves communities vulnerable to contaminated groundwater hazards (Lalumbe and Kanyerere, 2022a). A significant portion of the Groundwater Region 3, to the east, falls under the Musina Local municipality. As recently reported on SAnews (2022) the municipality has recently experienced public unrest due to lack of water supply to the communities, prompting urgent discussions by the Water and Sanitation Minister on plans to augment the water supply to the area.

1.3. Aim and objectives of the project

The main aim of the study is to assess the hydrogeochemical characteristics and the suitability of groundwater for irrigation and drinking purposes, in Limpopo Granite Gneiss region. The following objectives will assist in achieving this aim:

- To determine the hydrogeochemical characteristics of the groundwater based on physicochemical data from 2000 to 2017.
- To assess the suitability of the groundwater quality for irrigation based on physicochemical data from 2000 to 2017.
- To assess the suitability of the groundwater quality for drinking based on physicochemical data from 2000 to 2017.

The Research questions this project aims to answer the following questions:

- What is the hydrogeochemical nature of the groundwater and possible processes that influenced it?
- Is groundwater quality, in the Limpopo Granite Gneiss Region, suitable for irrigation and drinking purposes?

Chapter 2: Literature review

2.1. Introduction

In rural communities, groundwater is widely assumed to be safe for consumption because of its location below surface, hence communities readily use groundwater unaware of potential contaminants and safety hazards (Lalumbe and Kanyerere, 2022a). The major natural factors that affect groundwater quality are the chemical composition of recharge water, geohydrology of the host rock, geochemical processes occurring within the host rock, and the groundwater residence time (Bartos and Ogle, 2002). All water sources, including groundwater, contain contaminants and dissolved mineral salts with unpredictable concentrations, which vary with the mineralogical composition of the geological unit (Kirda, 1997; Nell and van Huyssteen, 2014). According to Mokoena et al., (2020), the type and concentration of dissolved minerals determine the suitability of water for different uses. Most of these mineral salts are harmless to humans and often beneficial to crops (Silva, 2004). However, Silva (2004) warns that the enrichment of certain minerals and salts reduces the quality of the water and ultimately, its suitability for use, consequently poor-quality water when used for irrigation over time, may result in the retention of the minerals salts after the water has been used by the crops. This in turn, over time, reduces soil quality and crop yield (Kirda, 1997; Silva, 2004).

Progress on SDG-6 indicates that the water quality data for over 3 billion people globally is unknown, putting many lives at risk (UN-Water, 2021). The main challenge is the scarcity of reliable data for area-specific groundwater assessments (UN-Water, 2022).

2.2. Groundwater quality assessment using hydrochemical analysis

Major ions can be used to determine the overall character of the water (Weaver et al., 2007). Weaver et al., (2007) also warns excessive ions in water can be harmful for human and crops. Groundwater monitoring programmes are designed to prioritise the routine collection of chemical laboratory analysis for major and minor ions (Weight, 2008). Field measurements (pH, temperature, and EC) are necessary for the interpretation of chemical data (Weaver et al., 2007). The Department of Water and Sanitation (DWS) groundwater quality monitoring programme collects groundwater samples, analyses its geochemical composition (Parson and Tredoux 1995), and makes data available (Lalumbe and Kanyerere 2022a). Mokoena et al., (2020) used major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), and anions (HCO_3^- , Cl^- , SO_4^{2-}), to assess the suitability of groundwater for drinking purposes.

2.2.1. Data accuracy checking

Various groundwater studies have been done throughout the world, including in South Africa, to determine the suitability of the water for irrigation and domestic purposes (Asante-Annor et al., 2018; Mukonazwothe et al., 2022). Most authors (Asante-Annor et al., 2018; Lalumbe and Kanyerere 2022a; Fadili et al., 2022; Hagan et al., 2022) began their hydrochemical assessment studies by checking the accuracy of the laboratory data, using percentage Ion Balance Error (%IBE) calculations Equation (1).

$$\text{Ion Balance Error (\%)} = \frac{\sum \text{cations} \frac{\text{meq}}{\text{L}} - \sum \text{anions} \frac{\text{meq}}{\text{L}}}{\sum \text{cations} \frac{\text{meq}}{\text{L}} + \sum \text{anions} \frac{\text{meq}}{\text{L}}} \times 100\% \quad (1)$$

Note: mEq/L = mg/L divided by atomic weight of ion divided by ionic charge (Bauder et al., 2003).

2.2.2. Evaluation of the hydrogeochemical characteristics

According to Yousef et al., (2009), the hydrogeochemical characteristics of the groundwater are determined by the geological formations, water-rock interaction, and relative mobility of ions.

2.2.2.1 Chemical composition of groundwater

The chemical composition of groundwater is a natural consequence of weathering and circulation of water in rocks and soils where ions leach out and dissolve in groundwater (Naseem et al., 2010). However, anthropological sources influence groundwater's chemical composition such as domestic and industrial discharges (Simsek and Gunduz, 2007).

A general description of pH, TDS and EC is usually presented to introduce groundwater physicochemistry, including the ranges of these parameters and the number of monitoring sites showing concerns (Asante-Annor et al., 2018; Lalumbe and Kanyerere, 2022a). Weaver et al., (2007) describe how major ions can be used to determine the overall character of the water. Major ions and their ratios can be used to understand the impact of rock chemistry on the composition of groundwater (Naseem et al., 2010). The description of major cations and anions distribution and relative abundance (Singh and Kumar, 2015). Description of minimum, maximum, and average values of physical and chemical parameters of groundwater samples were commonly featured (Aghazadeh and Mogaddam, 2010; Mokoena et al., 2020; Iqbal et al., 2021).

2.2.2.2. Hydrogeochemical characteristics

Understanding the hydrogeochemical characteristics of water is key for groundwater management since groundwater chemistry can reveal important information on the geological history of the aquifers and their suitability for various uses (Aghazadeh and Mogaddam, 2010). Lalumbe and Kanyerere (2022b) used chemical data from DWS to evaluate hydrogeochemical processes influencing groundwater quality in the Soutpansberg region. The authors were able to use the Piper trilinear (Piper, 1944) diagramme to understand the water type and hydrogeochemical facies; and they also applied Gibbs (Gibbs, 1970) diagrammes using Equations (2) and (3) all in mEq/L. The Piper trilinear diagramme uses the concentrations of major cations and anions to predict the geochemical evolution of groundwater (Singh and Kumar, 2015). The position of the cluster position of the site analyses on a Piper diagramme can be used to make a predictive conclusion as to the origin of the groundwater represented by the study (Singh and Kumar, 2015).

The Gibbs diagramme is commonly used in groundwater studies to understand water-rock interaction (Gibbs, 1970). There are three distinct fields in the Gibbs diagramme: precipitation dominance, evaporation dominance, and rock dominance.

$$\text{Anions: Gibbs ratio I} = \text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-) \quad (2)$$

$$\text{Cations: Gibbs ratio II} = (\text{Na}^+ + \text{K}^+) / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}) \quad (3)$$

2.2.3. Irrigation water quality assessment

Crop growth depends on irrigation water quality and soil drainage characteristics (Asante-Annor et al., 2018). The quality of irrigation water varies based on the type and the quantity of the ions dissolved in it (Simsek and Gunduz, 2007). The irrigated soils and crops grown using bad-quality water, are considered to be the eventual destination for these excessive ions as a result of evaporation and crop consumption, respectively (Simsek and Gunduz, 2007). Ultimately, the continuous use of high salt content irrigation water then leads to an increase in salt content in the soil (Simsek and Gunduz, 2007).

Ayers and Westcot (1985) describe four distinct water quality-related problems in agriculture (Table 1).

Table 1: Irrigation water problems (Ayers and Westcot, 1985)

Category	Description	Parameter
Salinity	Affects crop water availability	EC TDS
Infiltration rate	Affects infiltration rate of water into the soil.	SAR and EC
Specific Ion Toxicity	Affects sensitive crops	Sodium Chloride Boron Trace elements
Miscellaneous	Affects susceptible crops	Nitrogen Bicarbonate pH

Sodium Adsorption Ratio (SAR) as sodicity hazard index

The sodicity hazard of irrigation water is determined using the Sodium Adsorption Ratio (SAR) as described by Richards (1954) in Equation (4) (all in mEq/L). The SAR is an index of the potential of water to bring about sodic soil conditions (DWAF, 1996a). The SAR can also be defined as an index of the potential of a given irrigation water to induce sodic soil conditions (DWAF, 1999). Irrigation water containing high concentrations of Na⁺ relative to Ca²⁺ and Mg²⁺ degrades soil structure, causing excessive soil accumulation of sodium, which is known as soil sodicity (Bauder et al., 2003). This type of soil degradation hinders infiltration and may increase runoff, which in turn deprives crops of water nutrition (Bauder et al., 2003). The very high sodium concentration in groundwater is a result of natural and anthropogenic activities, and soil sodicity is a major concern, especially in semi-arid and arid regions (Levy and Nachshon, 2022). During the literature review, the SAR index was found to be the most common index used to assess groundwater suitability for irrigation (Naseem et al., 2010; Aghazadeh and Mogaddam, 2010; Etteieb et al., 2017; Fadili et al., 2022; Mukonazwothe et al., 2022; Asante-Annor et al., 2018).

$$SAR = Na^+ / \sqrt{(Ca^{2+} + Mg^{2+}) / 2} \quad (4)$$

SAR (sodium hazard) and EC (salinity hazard) values can be used to evaluate the quality of groundwater for irrigation using the United States Salinity Laboratory (USSL) diagramme (Richards, 1954). Salinity hazards adversely affect crop growth and yields, where salts accumulate in the crop root zone, depriving the roots of adequate water (Ayers and

Westcot,1985). Fipps (2003) concluded that the amount of water available to the crop is reduced when the electrical conductivity is higher, exhibiting poor crop yield.

Bauder et al., (2003) explain that the potential soil infiltration and permeability problems, caused by high sodicity irrigation water, cannot be adequately understood using SAR alone because the swelling potential of low salinity/EC water is greater than high salinity/EC water at the same sodium content.

Residual sodium carbonate

Residual Sodium Carbonate (RSC), expressed in Equation (5), is another important indicator of the hazardous effects of carbonate and bicarbonate if the water is used for irrigation (Richards, 1954; Raju, 2007). The RSC values for irrigation are classified by Richards, 1954 as follows: >1,25 mEq/L is suitable; 1,25 – 2,5 mEq/L are marginally suitable, and > 2,5 mEq/L is unsuitable. The continuous use of unsuitable water (RSC>2,5 mEq/L) increases salt build-up, which hinders air and water movement by clogging the soil pores (Nishanthiny et al., 2010). During the literature review, the RSC index was found to be the second common index used to assess groundwater suitability for irrigation, contributing valuable insight into irrigation groundwater studies (Naseem et al., 2010; Aghazadeh and Mogaddam, 2010; Mukonazwothe et al., 2022; Asante-Annor et al., 2018).

$$\text{RSC} = (\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{2+} + \text{Mg}^{2+}) \quad (5)$$

Percentage sodium

The percentage sodium (%Na), expressed in Equation (6) Wilcox (1948), is another important and widely used index in the suitability assessment of groundwater for irrigation (Hagan et al., 2022). A higher %Na reduces soil permeability, which reduces water flow, making the soil hard to plough and unsuitable for seeding development (Sujatha and Reddy, 2003). %Na and EC plots can be used to evaluate and classify groundwater suitability for irrigation (Khodapanah et al., 2009).

$$\%Na = (\text{Na}^+ + \text{K}^+) / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+) \quad (6)$$

Permeability index

The infiltration of water into the soil depends on the soil condition, such as the compaction, organic content, permeability, and the quality of the irrigation water (Asante-Annor et al.,

2018). Reduced permeability and infiltration rates lead to inadequate water supply to the crop roots (Asante-Annor et al., 2018).

The Permeability Index (PI), as described by Doneen (1964) and expressed by Equation (7), is a widely used index for assessing water's suitability for irrigation. There are three classifications for PI: Class I (>75%, suitable), class II (25–75%, good), and class III (<25%, unsuitable) (Doneen, 1964).

$$PI = \left[\frac{(\text{Na}^+ + \sqrt{\text{HCO}_3^-})}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+)} \right] \times 100\% \quad (7)$$

Magnesium hazard

Magnesium Hazard (MH) is also known as Magnesium Adsorption Ratio (MAR) and is expressed by Equation (8) (Reeve et al., 1954). The negative impact of magnesium on crop yield is significant when its concentration exceeds that of calcium (Richards, 1954). In natural waters like groundwater, the concentrations of calcium and magnesium ions maintain a state of equilibrium (Adimalla and Venkatayogi, 2018). However, Adimalla and Venkatayogi (2018) also note that calcium and magnesium do not behave similarly in the soil system when water is sodium-dominated and highly saline, magnesium tends to deteriorate soil structure. Sundaray et al., (2009) add that a shift in equilibrium caused by excess magnesium harms crop yield. The MAR values exceeding 50 are considered harmful and unsuitable for irrigation use.

$$MH = \left[\frac{(\text{Mg}^{2+})}{(\text{Ca}^{2+} + \text{Mg}^{2+})} \right] \times 100 \quad (8)$$

Kelly's Ratio

Kelly's ratio (KR) also known as Kelly's Index, is expressed by Equation (9) (Kelly, 1940). $KR > 1$ implies a surplus sodium ratio, which is unsuitable for irrigation, while $KR < 1$ implies a good sodium ratio, which is suitable for irrigation (Sundaray et al., 2009).

$$KR = (\text{Na}^+) / (\text{Ca}^{2+} + \text{Mg}^{2+}) \quad (9)$$

The assessment will concentrate mainly on groundwater characteristics, assuming that suitable soils will be irrigated (SAWQG, 1996a).

Table 2 summarises the following points on irrigation suitability research methods:

- Naseem et al., (2010) investigated irrigation water quality in Pakistan using SAR, RSC, PI, KR, MAR, and Na%.
- Dinka (2016) investigated the irrigation suitability of various surface water and groundwater sources at Matahara Plain, using cations, anions, pH, and EC to calculate the following chemical indices: Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC), Total Hardness (TH), PI, %Na, MH, TDS.
- In groundwater suitability for irrigation study, Lambussie-Karni District of Ghana, Asante-Annor et al., (2018) used physicochemical parameters to compare with FAO standards, where mathematical calculations were performed to determine sodium percentage (Na%), SAR, Residual Sodium Carbonate (RSC) and Permeability Index (PI).
- Mokoena et al., (2020) used (Na%), (SAR), Kelly's ratio (KR), (MH), and (PI) in an investigation of groundwater salinity using geophysical and geochemical approaches.
- Lalumbe and Kanyerere (2022a) evaluated the suitability of groundwater for irrigation in the Soutpansberg Region, using sodium SAR, Na%, PI, RSC, and MH.
- Mukonazwothe et al., (2022) used SAR, MAR, PI, RSC, Na%, KR and Chloride Index (CI).

Table 2: Irrigation water suitability research methods

Authors, type of study	SAR	RSC	TH	PI	Na%	MH	TDS	MAR	KR	CI	Soil type	Crop type
Naseem et al., 2010 <i>Irrigation only</i>	✓	✓		✓	✓			✓	✓		n/a	n/a
Aghazadeh and Mogaddam, 2010 <i>Irrigation and domestic purposes</i>	✓	✓	✓	✓	✓		✓				n/a	n/a
Lalumbe and Kanyerere, 2022a <i>Irrigation and domestic purposes</i>	✓	✓		✓	✓	✓	✓				n/a	n/a
Dinka, 2016 <i>Irrigation only</i>	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	PARTLY	PARTLY
Asante-Annor et al., 2018 <i>Irrigation only</i>	✓	✓		✓	✓						n/a	n/a
Talib et al., 2019 <i>Hydrogeochemical Characterisation, irrigation</i>	✓	✓		✓	✓	✓			✓		n/a	n/a
Mokoena et al., 2020 <i>Irrigation and domestic purposes</i>	✓			✓	✓	✓			✓		n/a	n/a
Mukonazwothe et al., 2022 <i>Irrigation and domestic purposes</i>	✓	✓		✓	✓		✓	✓	✓	✓	n/a	n/a
Etteieb et al., 2017 <i>Irrigation only</i>	✓				✓						n/a	n/a
Raihan and Alam, 2008 <i>Irrigation and domestic purposes</i>	✓		✓	✓	✓			✓	✓		n/a	n/a

2.2.4. Drinking water quality assessment

The consumption of bad quality drinking water can lead to a variety of short to long-term impacts such as health, aesthetics, and economics (SAWQG, 1996b). Common drinking water problems in groundwater are high concentrations of nitrate/nitrite and fluoride (Swartz, 2007). Nitrate, from chemical and organic fertilisers, is the most prevalent anthropogenic contaminant in groundwater globally (UN-Water, 2022). WHO (2017) describes excess natural fluoride, nitrate/nitrite, and arsenic as chemicals of significant health concern in some natural waters. Fluoride and nitrate, when present in excessive quantities, are two of ten key chemicals responsible for large-scale health effects through drinking water exposure (WHO, 2011a). However, only three (fluoride, nitrate, and arsenic) chemicals have been proven to cause significant health effects in humans through drinking water when they are present in excessive quantities (WHO, 2011a). Vegter (2001) found that over 50% of the samples in the current study area had harmful concentrations of nitrate and fluoride and were deemed unsuitable for drinking purposes.

Nitrate and nitrite

According to WHO (2003), nitrate and nitrite ($\text{NO}_3^- + \text{NO}_2^-$) are naturally occurring inorganic ions in the nitrogen cycle. Nitrate is the most stable and dominant of the two ions and is an important plant nutrient. In the plants, NO_3^- is present at varying concentrations (WHO, 2003). Unstable NO_2^- can easily be reduced by either chemical or biological processes to form the stable NO_3^- (WHO, 2003).

High concentrations of nitrate (NO_3^-) in drinking water are very toxic, can cause methemoglobinemia in bottle-fed babies, and are thus responsible for some deaths across the globe (U.S. Department of Health and Human Services, 1991; Fewtrell, 2004). The levels of nitrate in groundwater globally were found to be considerably higher than a few decades before 1984 and on a continuous rise (WHO, 1985). A gradual increase in nitrate concentrations has been observed in many European countries in the past decades; and in some parts, a double increase was observed over 2 decades (WHO, 2011b). The three key contributors to the progressive surge in nitrate levels in groundwater supplies globally over the last couple of decades are: (1) The increasing application of nitrogen-rich fertilisers in agriculture associated with growing food demands for a rapidly growing population; (2) poorly managed disposal

of wastes (animal and human excreta) and (3) changes in land base activity (Swartz, 2007; WHO, 2011b). Compounding the problem of nitrate groundwater pollution is the long retention time in the unsaturated zones of aquifers, making it inevitable for concentrations to continue growing for several decades, even if stringent preventative controls are placed (WHO, 1985). The impact of on-site sanitation on groundwater often varies from site to site and is influenced by hydrogeology, vegetation, rainfall, and other factors (Tredoux, 2004).

In a study of the impacts of unlined pit latrine sanitation on groundwater quality, Graham and Polizzotto (2013) found nitrate to be the most frequently detected pollutant and, hence, the most widely studied groundwater chemical pollutant. This is because there are high nitrogen concentrations in human excreta, making it the ideal indicator of pit latrine contamination (Graham and Polizzotto, 2013). The nitrate concentration in a particular aquifer fluctuates over time due to various factors like precipitation patterns, increased agricultural activities, deforestation, and poorly managed use of septic tanks and pit latrines (WA-DOH, 2018). WHO (2016) also notes that as a result of the delayed response of groundwater to changes in soil, some exposed groundwater resources have not yet shown the increase expected from the increased use of nitrogen fertiliser and unlined pit latrines. However, once the nitrate reaches an aquifer, the aquifer will remain contaminated for decades, even if substantial pollution reduction and/or protection measures are in place (WHO, 2016). Jensen et al., (2014) describe nitrate as a significant water quality concern in the United States and across the globe. When pollution is due to human activities on the surface, nitrate concentration typically decreases with depth from the surface (Nolan et al., 2002).

The World Health Organization (WHO, 2011b) guideline value for nitrate in drinking water is 50 mg/L as nitrate ion, which is adequate to protect bottle-fed infants, and hence, adequate for other population groups including pregnant women (WHO, 2016). The best method to manage nitrates/nitrites is by protecting the water source from contamination (WHO, 2011a). While the disinfection method will oxidise nitrite, the more toxic form, to nitrate, which will then sanitise the water and reduce the risk of gastrointestinal infection, which is a risk factor for methemoglobinemia (WHO, 2011a). Furthermore, because nitrate is a stable and highly soluble ion with a low potential for precipitation or adsorption, it is more challenging to remove it from water using

conventional treatment processes such as filtration or activated carbon adsorption (WA-DOH, 2018). It must be noted that unlike microbial pollution, nitrate-polluted water cannot be treated via boiling or chemical treatment, or even gamma radiation (Swartz, 2007; Swistock, 2022). Any boiling of nitrate-polluted water will most likely increase nitrate concentrations as water is lost during evaporation (Swistock, 2022). Additionally, in an effort to fight the AIDS epidemic, HIV-positive mothers are discouraged from breastfeeding, which may expose their infants to baby formulas prepared with nitrate-contaminated water (Tredoux et al., 2000). The reduction of nitrate ions in groundwater to acceptable levels is easily accomplished by blending it with nitrate-contamination-free surface water, which is not always available (Bohdziewicz et al., 1999). Other reduction methods, such as electrodialysis, ion exchange or biological processes, are costly but not always efficient (Bohdziewicz et al., 1999).

Fluoride hazard

The element fluorine is common and widely distributed in Earth's crust and occurs in the form of fluorides in minerals, such as fluorspar, rock phosphate, cryolite, apatite, and others (Fawell et al., 2006). Higher concentrations of fluorides are often associated with groundwater and vary with the type of rock through which the water flows, up to 10 mg/L (Fawell et al., 2006). High groundwater fluoride concentrations associated with granites and gneisses have been reported in India, Pakistan, West Africa, Thailand, China, Sri Lanka, and Southern Africa (Fawell et al., 2006). The World Health Organization (WHO, 2011a) guideline value for fluoride in drinking water is 1,5 mg/L. Epidemiological evidence shows that concentrations above 1,5 mg/L carry an increasing risk of dental fluorosis and that progressively higher concentrations intake leads to increasing risks of skeletal fluorosis (WHO, 2011a). Odiyo and Makungo (2012) found Limpopo Province to be one of the three provinces showing very high unsafe (for human consumption) fluoride levels in groundwater, often as high as 30 mg/L.

Sodium

High levels of sodium affect the palatability of drinking water; the average taste threshold for sodium is about 200 mg/L (WHO, 2017; SANS, 2015).

Sulphates

Sulphates in drinking water are derived naturally from numerous minerals, and sulphates are used commercially in the chemical industry and are discharged as industrial waste (WHO, 2011a). The highest levels of sulphates are commonly and naturally found in groundwater (WHO, 2011a). At levels greater than 1000 mg/L in drinking water, sulphates have a laxative effect; however, no increase in diarrhoea, dehydration, or weight loss has been observed (WHO, 2011a). Taste impairment thresholds are 250 mg/L and 500 mg/L for sodium sulphate and calcium sulphates, respectively (WHO, 2011a). SANS241 (2015) recommends 250 mg/L taste impairment threshold.

TDS

Total dissolved solids (TDS) are inorganic salts such as bicarbonates, chlorides calcium, magnesium, potassium, sodium, and sulphates, and small amounts of organic matter (WHO, 2017). TDS found in drinking water is derived from mainly natural sources and some anthropological sources such as sewage and industrial wastewater (WHO, 2017). While the concentration levels of TDS in drinking water are not a health concern, the palatability of water with TDS level below 600 mg/L is largely considered to be good; while levels above 1000 mg/L gives water a rather unpalatable taste, which is unsuitable for human consumption (WHO, 2011a).

Chapter 3: Research method

3.1. Introduction

The research approach is based on available historically collected data. Data processing and comparison will be undertaken based on previous similar studies.

3.2. Assessment of the study area

The name of the study area is Limpopo Granulite-Gneiss Belt, groundwater region 3 of 65, described by Vegter (1995).

3.2.1. Location

The Limpopo Granulite-Gneiss Belt (Groundwater Region 3) is located in the northernmost part of the Limpopo Province, South Africa. Towns included in the area are Musina and Alldays. This study focuses on the monitoring sites, which are spatially distributed in the Groundwater Region 3. Vegter (1995) divided South Africa into 65 different groundwater regions, in the Limpopo Province; the division was mainly based on rock type, geological age, and lithostratigraphy (Holland, 2012). The Region's northern border is mainly along the Limpopo River, the international boundary between South Africa and Botswana on the north-west side, South Africa and Zimbabwe on the north-east side (Figure 3). The study area is a lenticular shape, north-easterly trending belt, approximately 375 km in length and about 50 km average width, and covers 13 910 km² (Vegter, 2001). The monitoring sites are also shown in Figure 3, i.e. 15 boreholes and two geothermal springs.

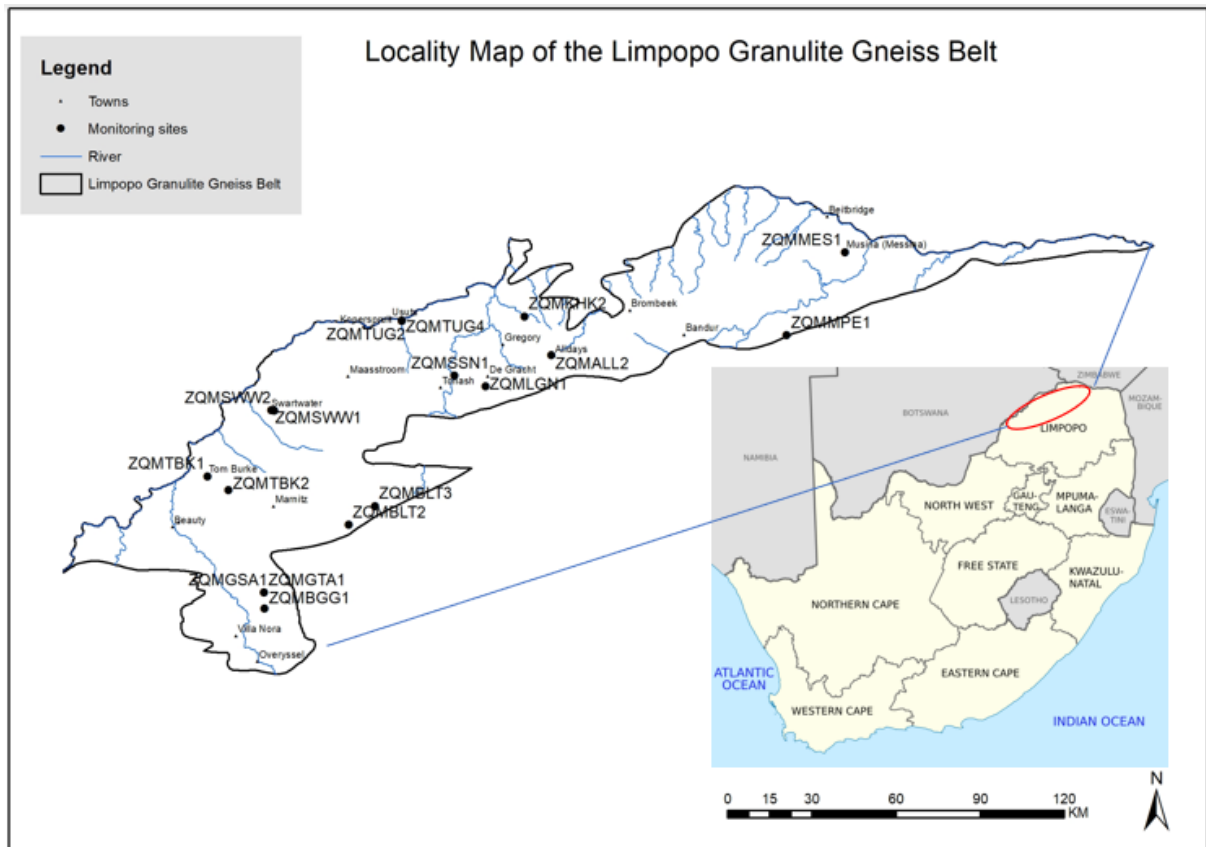


Figure 3: Location of Limpopo Granulite Gneiss Groundwater Region, showing groundwater monitoring sites and rivers.

The area consists of mainly villages, small communities, and informal settlements (Vegter, 2001). The economic activities are cattle and game ranching, irrigation along the major rivers, copper, and diamond mining (Vegter, 2001). Data acquired and received from the Water Use Authorisation and Registration Management System (WARMS, 2023) show that there are 466 registered active groundwater users (government, companies, and individuals), with a total allocation of over 46,9 Mm³ per annum, with 89,73% allocated for irrigation (Figure 4). While irrigation is generally the highest volume user, groundwater's most widespread role is that of a reliable source of supply for potable water (Braune et al., 2008). The study area spans three local municipalities, from east to west in this order: Lephalale, Blouberg, and Musina. Each local municipality falls under three different district municipalities.

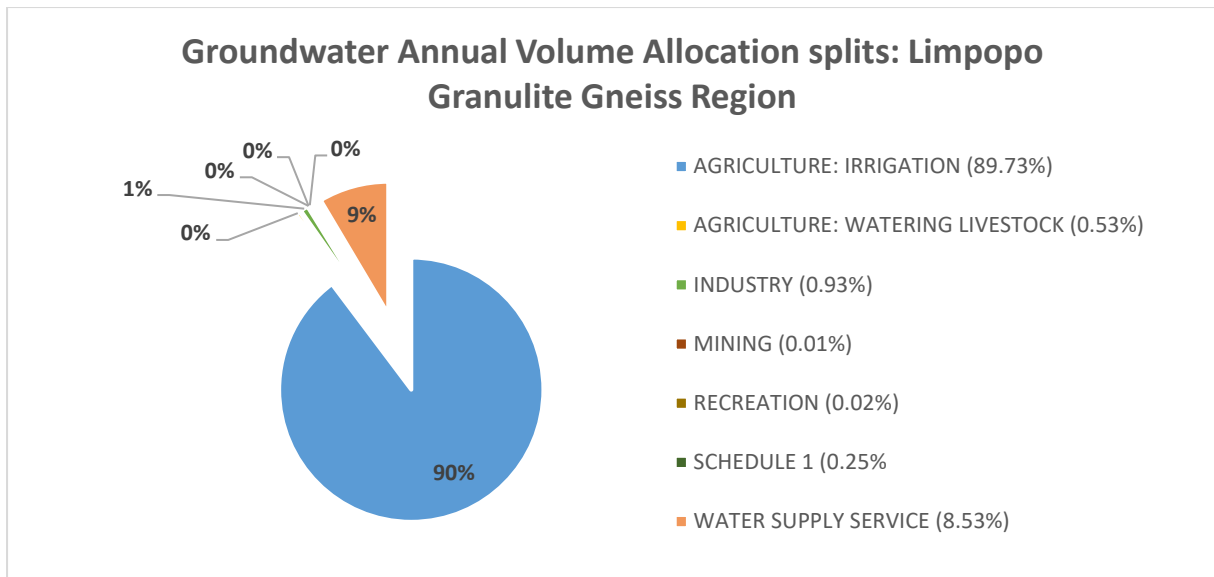


Figure 4: Groundwater annual volume allocation splits for the Limpopo Granulite Gneiss Region (WARMS, 2023).

Limpopo is one of the poorest provinces, where 65,1% of households are grant beneficiaries and over 90,3% of learners attending public schools are beneficiaries of school nutrition programmes (StatsSA, 2021). This poorest, grant-dependant province has the highest percentage of households (94,5%) who have adequate access to food, and it is also the leading province in the percentage of households (38,2%) involved in agricultural activities. Ninety-two percent of households in Limpopo are engaged in agriculture as an additional source of food dominated by grains (72,4%), and fruits and vegetables (55,7%) (Table 3). Access to suitable water for productive uses such as agriculture is vital to realise livelihood opportunities, generate income, and contribute to economic productivity (UN-Water, 2015). Investing in research and improved water management can help reduce poverty and sustain economic growth (UN-Water, 2015).

Table 3: Limpopo household agricultural activity breakdown(StatsSA, 2021).

Agricultural Activity	Limpopo Number of households	Limpopo household Percentage*	South Africa household Percentage
Livestock production	223 000	36,1	50,0
Poultry production	143 000	23,0	37,3
Grains and food crops	448 000	72,4	50,3
Industrial crops	6 000	0,9	0,5
Fruits and vegetables	345 000	55,7	53,3
Fodder grazing/ pasture grass of animals	4 000	0,6	0,5

* A particular household can be involved in more than one activity and percentages therefore do not add up to 100%.

While the proportion of South African households with access to an improved source of water increased from 84,4% to 88,7% between 2002 and 2021, Limpopo province experienced the highest decline of -4,4% over the same period, from 73,8% to 69,4%, (StatsSA, 2021). However, it is also reported that many more households were provided with water in 2021 than two decades earlier (StatsSA, 2021). Over 56,0% of households in Limpopo experience water interruptions, compared to 30,8% nationally (StatsSA, 2021). During water interruptions of at least two days, 10,9% of households turn to groundwater (boreholes, springs, and wells) as an alternative source of drinking water (StatsSA, 2019). It must also be noted that Limpopo, at 70,2% (5,5 million), has the highest percentage of households that use pit latrines for sanitation (StatsSA, 2019).

3.2.2. Regional geology

The study area is within the Limpopo Complex, a high-grade metamorphic terrane formed between the Zimbabwe (north) and Kaapvaal (south) cratons, comprising mainly gneisses (Johnson et al., 2006). The Limpopo Complex is subdivided into three zones: the Northern Marginal Zone, the Central Zone, and the Southern Marginal Zone. The Limpopo Granulite-Gneiss Belt area is dominated by polymetamorphosed and highly deformed supracrustal and intrusive rocks of the Beit Bridge Complex found within the Central Zone of the Limpopo Mobile Belt (Vegter, 2001; Vorster, 2003), as depicted in Figure 5. Vegter (2001) noted that little is known about the water-bearing properties of the aquifers in this groundwater region.

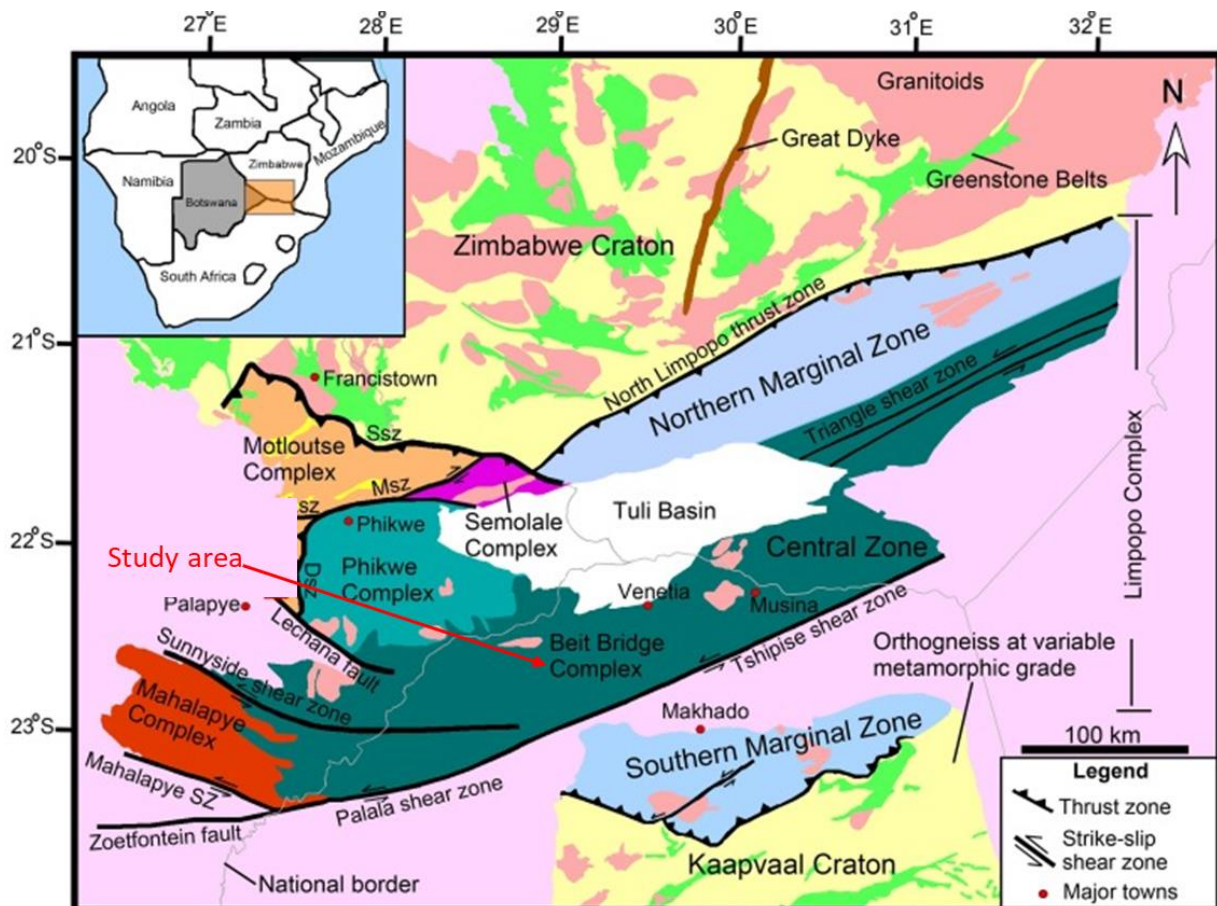


Figure 5: Location map of the Beit Bridge Complex within the Limpopo Complex showing adjacent cratons, and complexes modified from Basupi et al., 2022 after Watkeys, 1983.

3.2.3. Drainage and climate

The study area falls within the Limpopo basin, which is shared between South Africa, Botswana, Zimbabwe, and Mozambique. It has the following south-to-north major tributaries of the Limpopo River: Mokolo, Lephhalala, Mogalakwena, Kolope, and Sand, east to west, respectively (Vegter, 2001). Vegter 2001, describes these tributaries as part of the drainage regions A4, A5, A6, and A7, plus the narrow strip along Limpopo River far east of the study area. The most part of the study area lies between 850 and 600 meters above mean sea level (m.a.m.s.l), with the Limpopo River flowing as high as 800 m.a.m.s.l and dropping down to 300 m.a.m.s.l (Vegter, 2001). Although there are large rivers in the area, they do not necessarily have year-round flows (Vegter, 2001).

The climate in Region 3 is semi-arid subtropical (Vegter, 2001), with very hot summers (highs average: 33°C Musina), mild Winters (highs average: 25°C Musina), and summer rainfall. The hot and dry areas of the Limpopo River Basin, receiving about 200–400 mm annual rainfall, are located mainly within the Limpopo River Valley (FAO,

2004). The mean annual rainfall in the study area varies along the east-west direction, between 300 and 425 mm, respectively (Vegter, 2001).

3.2.4. Role of groundwater in region 3

Vegter, 2001 described the study area to be solely dependent on groundwater, all the water for household use, cattle and game ranching, and irrigation come from groundwater through boreholes and wellpoints. The water supply boreholes are mostly located along the sand of the Limpopo River, exception for the town Alldays, which draws its water from the Karoo lava and sedimentary rocks along the south most parts of the study area (Vegter, 2001).

3.2.5. Soil

Nell and Huyssteen (2014) mapped the median EC of the soil of the Limpopo granulite region in the range 0 - 40 mS/m, with median exchangeable sodium percentage (ESP) in the range 1,6 – 3,0. The soils in this region were found to be predominately alkaline with median soil pH_{water} of 6,6-7,3 (Nell and Huyssteen, 2014).

3.2. National groundwater quality monitoring

Parson and Tredoux (1993) using a literature study, developed a strategy to monitor groundwater quality on a national scale, for the then Department of Water Affairs and Forestry (DWAF). Following the recommendations from the study, pilot-scale monitoring network was established, between four and six stations per region across the 65 groundwater regions (Parson and Tredoux, 1995). Parson and Tredoux (1993) proposed strategies that were adopted, and a National Groundwater Quality Monitoring (ZQM) programme was then established in 1995 (Parson and Tredoux, 1995). The parameters chosen for the programme were a strategic trade-off between groundwater quality information needs and available financial resources (Parson and Tredoux, 1993). Parson and Tredoux (1993) also recommended monitoring frequency of six months, for the first five years.

3.3. Chemical data acquisition and screening

The Department of Water and Sanitation provides groundwater data to the public on request. National groundwater nitrate data was requested from DWS through the email address georequests@dws.gov.za. Upon screening of the national data, a study area was then chosen based on anomalous high nitrate values occurring in Limpopo

Province, from which groundwater region 3 was selected to be the preferred area of study. A second data request was made from DWS using the same email address, this time the whole hydrochemical dataset for Region 3, from 2000-2017, was requested and a CSV file named “zqm chem list” was received. The CSV file was then converted to xls. The Excel file had 469 data points from 17 monitoring stations, 15 boreholes, and two geothermal springs. After all the screening, 352 sample data points containing all the major anions and cations for each sampling event were selected for the hydrochemistry charge balance calculations. These 352 samples have analytical results for the following elements/compounds calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), bicarbonate (HCO_3^-), chloride (Cl^-), nitrate and nitrite ($\text{NO}_3^- + \text{NO}_2^-$), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), fluoride (F^-), silicon (Si) and total alkalinity as calcium carbonate. Other included parameters are Electrical Conductivity (EC), temperature, and pH, which were field-measured.

3.3.1. Sample collection

The frequency of monitoring is twice a year (end of wet season March/April and end of dry season September/October), this frequency is considered adequate since groundwater is relatively stable (Lalumbe and Kanyerere, 2022a). The ZQM programme was designed to monitor changes in groundwater quality in South Africa, and to identify possible influences (Lalumbe and Kanyerere, 2022a). Standard sampling procedure after Weaver et al., (2007) guidelines were reported to have been followed during the collection of groundwater samples (Lalumbe and Kanyerere, 2022a). These include purging of the borehole before sampling to ensure sample representativity while the geothermal spring samples were collected directly from the eye of the spring (Lalumbe and Kanyerere, 2022a). 500 mL polyethylene sampling bottles were used to collect groundwater (Lalumbe and Kanyerere, 2022a).

3.3.2. Analytical methods applied

In a recent paper where data from the same DWS groundwater quality programme was used, concerning the analytical methods authors Lalumbe and Kanyerere (2022a) describe cations and anions analysis using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Ion Chromatography (IC) respectively, which was done by DWS' SANS accredited laboratory in Roodeplaat, Pretoria (Lalumbe and Kanyerere, 2022a). They also described field measurements of EC, temperature, and

pH by handheld multi-parameter probe, at each sampling point (Lalumbe and Kanyerere, 2022a). All laboratory results are stored in DWS' Water Management System (WMS) database and made available on request.

3.3.3. Analytical data accuracy determination

Before the chemical analysis data is used for interpretation, its reliability has to be verified in a scientific manner (Mageshkumar and Vennila, 2018). This research study began with the ultimate accuracy test, percent Ion Balance Error (%IBE) using Equation 1, as also applied by Talib et al., (2019); Lalumbe and Kanyerere, (2022a); Mukonazwothe et al., (2022); Asante-Annor et al., (2018) and others. %IBE is a credible method used to evaluate analytical technique that was applied to groups of samples (Fritz, 1994).

$$\text{Ion Balance Error (\%)} = \frac{\sum \text{cations} \frac{\text{meq}}{\text{L}} - \sum \text{anions} \frac{\text{meq}}{\text{L}}}{\sum \text{cations} \frac{\text{meq}}{\text{L}} + \sum \text{anions} \frac{\text{meq}}{\text{L}}} \times 100\% \quad (1)$$

Note: mEq/L = mg/L divided by atomic weight of ion divided by ionic charge (Bauder et al., 2003).

The 352 sample results with complete major and minor ion analysis, were tested for accuracy and reliability using the %IBE calculations described in Equation (1) (Weight, 2008). APHA (1999) describes the rationale behind this cation-anion balance is that all water samples are electrically neutral, meaning each water sample has the same total number of anions to cations, such that when they are added they equal zero.

Since IC cannot quantify bicarbonate ions, HCO_3^- was estimated using total alkalinity concentration expressed as CaCO_3 (Newcomer, 2019). For most groundwaters with pH between 6 and 8, the total alkalinity essentially represents the bicarbonate concentration (Weight, 2008). Total alkalinity concentration expressed as CaCO_3 was used to estimate bicarbonate (HCO_3^-). CaCO_3 was multiplied by 1,22 to estimate HCO_3^- concentration (Newcomer, 2019). However, the 1,22 multiplier only provides a good estimate for the HCO_3^- concentration at pH values ranging from 4 to 9 (Deutsch, 1997). According to Deutsch (1997) and Weight (2008) the %IBE should generally not exceed $\pm 5\%$; while $\pm 10\%$ is acceptable for research purposes Hamilton et al., (1991).

3.4. Groundwater quality assessment using Hydrochemical analysis

To assess the hydrogeochemical characteristics and suitability of groundwater from the study area, the geochemical compositions of 319 samples out of 409 received from the Department of Water and Sanitation from 2000 up to 2017 will be statistically

analysed (Table 4). This data includes the following hydrochemical parameters: Ca^{2+} , Cl^- , DMS, EC, F^- , K^+ , Mg^{2+} , NH_4 , $\text{NO}_2^- + \text{NO}_3^-$, Na^+ , PO_4 , SO_4^{2-} , Si, TAL, and pH. Total Dissolved Solids (TDS) will be calculated using in situ EC using Equation (2) (Weaver et al., 2007).

Water quality data will be interpreted on the basis of both individual analyses and sets of analyses (Hounslow, 1995). According to Ayers and Westcot (1985), laboratory determinants list for irrigation suitability assessments, this data is only short of Boron. No microbiological groundwater monitoring was done, hence no microbiological data is available. Suitability for drinking will be determined based on the available hydrochemical data.

$$\text{TDS} = 6,3 \times \text{EC (mS/m)} \quad (2)$$

A general description of pH, TDS, and EC will be done (Asante-Annor et al., 2018; Lalumbe and Kanyerere, 2022a). Major ions will be used to determine the overall character of the water (Weaver et al., 2007). The description of major cations and anion distribution will be done (Iqbal et al., 2021). Minimum, maximum, and average values (where applicable) of the physical and the chemical parameters of groundwater samples, will be presented (Aghazadeh and Mogaddam, 2010).

Table 4: Summary of available data for groundwater region 3.

	Monitoring Site	Date From	Date To	Number of years since 1st Sample date	Total Available Monitoring seasons for the period (years*2 frequency)	No. of samples taken
1	ZQMSWW1	2000/04/13	2017/09/19	17,5	35	29
2	ZQMTBK1	2000/04/13	2017/09/20	17,5	35	34
3	ZQMTBK2	2000/04/13	2017/09/20	17,5	35	35
4	ZQMTUG2 (spring)	2000/04/13	2017/09/19	17,5	35	35
5	ZQMTUG4 (spring)	2000/04/13	2017/09/19	17,5	35	35
6	ZQMALL2	2000/04/13	2017/09/12	17,5	35	35
7	ZQMBLT2	2000/04/17	2017/09/20	17,5	35	32
8	ZQMBLT3	2000/04/17	2017/09/20	17,5	35	32
9	ZQMKHK2	2000/04/12	2017/04/10	17,5	35	31
10	ZQMMES1	2000/05/04	2017/10/12	17,5	35	36
11	ZQMBGG1	2014/06/23	2017/05/17	3,0	6	5
12	ZQMSSN1	2014/01/08	2017/09/13	3,5	7	7
13	ZQMSWW2	2001/05/10	2017/09/19	16,5	33	31
14	ZQMGSA1	2002/08/28	2017/10/31	15,0	30	10
15	ZQMGT A1	2002/10/03	2017/10/30	15,0	30	8
16	ZQMLGN1	2015/05/15	2017/09/13	2,5	5	6
17	ZQMMPE1	2014/01/30	2017/10/12	3,5	7	8
						409

3.4.1. Evaluation of the hydrogeochemical characteristics

Groundwater quality provides ideas about the aquifer hydrological and geochemical conditions and the influential geochemical processes (Gad and El Osta, 2020). The hydrogeochemical characteristics of groundwater depend primarily on recharge, aquifer material, residence time, transport, and geochemical reactions (Gad and El Osta, 2020). The quality of water is a function of its physicochemical parameters that reflect groundwater characteristics and factors controlling the quality of water. The physicochemical parameters of groundwater reflect groundwater characteristics and factors controlling the quality of water (Gad and El Osta, 2020). Historical studies by Vegter (2001) found the hydrochemical types in this area to be $(Ca,Mg)(HCO_3)_2$ and $(Ca,Mg)Cl_2$.

3.3.1.1. *Chemical composition of groundwater*

The description of the general pH, TDS and EC will be done (Asante-Annor et al., 2018; Lalumbe and Kanyerere, 2022a). Major ions can be used to determine the overall character of the water (Weaver et al., 2007). The description of major cations and anion distribution will be done (Iqbal et al., 2021). Minimum, maximum, and average values (where applicable) of physical and chemical parameters of groundwater samples will be presented (Aghazadeh and Mogaddam, 2010).

3.3.1.2. *Hydrogeochemical characteristics*

The hydrochemical analysis will be done using Piper trilinear diagramme, Gibbs diagramme, and Schoeller's ChloroAlkaline Indices. Furthermore, water type will be identified using major ion geochemistry, and major processes responsible for hydrogeochemistry will be determined using literature. These methods will jointly be used to determine the hydrogeochemical characteristics and dominating factors controlling the chemical compositions.

Piper trilinear diagrammes will be drawn to understand the dominant water types. Gibbs diagramme will be used to understand hydrogeochemical processes such as precipitation, water–rock interaction mechanism and evaporation on groundwater geochemistry (Hwang et al., 2017) using Equations (3) and (4) in mEq/L (Gibbs, 1970).

$$\text{Anions: Gibbs ratio I} = \text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-) \quad (3)$$

$$\text{Cations: Gibbs ratio II} = (\text{Na}^+ + \text{K}^+) / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}) \quad (4)$$

Schoeller (1965) ChloroAlkaline Indices (CAIs) method using Equations (5) and (6) in mEq/L will be used to understand interactions between groundwater and host rocks.

$$\text{CAI- I} = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)] / \text{Cl}^- \quad (5)$$

$$\text{CAI- II} = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)] / (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{NO}_3^{2-}) \quad (6)$$

Pearson correlation coefficients of major physicochemical parameters will be calculated to determine whether irrigation, animal and human waste are influencing the groundwater in the study area (Sigter et al., 1998; Kumar et al., 2014).

3.4.2. Suitability for irrigation assessment methods

In this project a quantitative research study design was chosen to achieve the objectives of assessing the suitability of groundwater quality for irrigation and drinking purposes in Limpopo Granulite Gneiss Region. Using section 2.2.2 the author has opted to use some commonly used indices like SAR, RSC, Na%, PI, MH, and KR (Talib et al., 2019; Mokoena et al. 2020; Lalumbe and Kanyerere 2022a; Asante-Annor et al., 2018; Mukonazwothe et al., 2022). SAWQG (1996a)'s SAR classes will be used to categorise the samples (Table 5). Formulae summary of the six indices chosen is presented in Table 5. All mathematical calculations will be done on Excel for each sample, and summary tables of all major statistics like: minimum, maximum, mean, and standard deviation will be provided (Lalumbe and Kanyerere, 2022a). Minimum, maximum, and average values of physical and chemical parameters of groundwater samples. The assessment will concentrate mainly on groundwater characteristics, assuming that suitable soils will be irrigated (SAWQG, 1996a). The results will be compared to SAWQG and FAO standard guidelines. Spatial distribution maps of irrigation quality based on the indices will be done (Asante-Annor et al., 2018).

The irrigation suitability of groundwater in the study area will be assessed by calculating the following parameters: SAR, RSC, %Na, PI, MH, and KR. The major ions used are expressed in milliequivalents per litre (mEq/L).

Table 5: Summary of water quality indices to be calculated for irrigation suitability assessment

Equation number	Formula	Range mEq/L	Class
(7)	$SAR = Na^+ / \sqrt{(Ca^{2+} + Mg^{2+}) / 2}$ Richards (1954)	<10 10-18 18-26 >26	Excellent Good Fair Unsuitable
(8)	$RSC = (HCO_3^- + CO_2^{-3}) - (Ca^{2+} + Mg^{2+})$ Eaton (1950)	<1.25 1.25-2.5 >2.5	Suitable Fair Unsuitable
(9)	$\%Na = (Na^+ + K^+) / (Ca^{2+} + Mg^{2+} + Na^+)$ Wilcox (1948, 1955)	<20 20-40 40-60 60-80 >80	Excellent Good Permissible Doubtful Unsuitable
(10)	$PI = [(Na^+ + \sqrt{HCO_3^-}) / (Ca^{2+} + Mg^{2+} + Na^+)] \times 100$ Doneen (1964)	>75 75-25 <25	Safe Moderate Unsafe
(11)	$MH = [(Mg^{2+}) / (Ca^{2+} + Mg^{2+})] \times 100$ Reeve et al., (1954)	<50 >50	Suitable Unsuitable
(12)	$KR = (Na^+) / (Ca^{2+} + Mg^{2+})$ Kelly, (1940)	<1 >1	Safe Unsafe

3.4.3. Suitability for drinking assessment methods

The suitability of the groundwater for drinking will be assessed using $NO_3^- + NO_2^-$, TDS, Na^+ , SO_4^{2-} , and F (WHO, 2011a, SANS 241 2015). Drinking water quality compliance of these ions will be conducted against WHO (2011a) global guidelines and SANS 241 (2015) local standards. Comprehensive statistics will be calculated and presented in a summarised table, with mean, minimum, maximum, and standard deviation where applicable (Mokoena et al., 2020). Where there are unsuitability alarms, trend graphs will be used to see if any significant changes are occurring over time.

3.5. Programmes/ Application

- Statistical analysis using Microsoft Excel.

- Spatial distribution map of borehole sites showing identified higher than recommended parameters will be created using ArcGIS and Microsoft PowerPoint.

3.6. Ethical standards research protocol

Ethical Application NAS031/2021 was approved on 20 July 2023.

3.7. Discussion on expected results and impact of research

This project hopes to highlight the extent of groundwater quality contamination that may exist in the study area. This will contribute to the advancement of SDG-2 and SDG-6. The suitability of the groundwater for irrigation will advance SDG-2 which addresses food security and improved nutrition, promoting sustainable agriculture and ensuring an end to hunger, while the drinking water suitability will advance SDG-6's clean water for all, by promoting water resource management (UN, 2015). Access to household water supplies is critical for a family's health and social dignity (UN-Water, 2015). The UN Summary Progress Update 2021 on SDG-6 raises the issue of the lack of groundwater data and groundwater monitoring initiatives, emphasising that groundwater monitoring is a 'neglected area' (UN-Water, 2022).

The recommendation made herein will assist in pollution mitigation and management of the groundwater resource through a groundwater quality monitoring programme. And will promote the protection of human health and hopefully public awareness can be improved through the sharing of the outcomes of this study.

This study would like to raise awareness of groundwater quality through the identified pollution trends observed in the assessment. Rising nitrate in groundwater meant for human consumption is a serious health hazard (WHO, 1985). Therefore, the groundwater users especially mothers to infants need to be aware that boiling water only is not enough to protect babies from nitrate contaminated water (Swistock, 2022). Nitrate is a pollutant requiring a significant water treatment investment to save babies from methemoglobinemia.

3.8. Limitations of the study

Due to the nature of the study mini-dissertation and the strict timeframe only secondary data collected by the Department of Water and Sanitation will be considered; no primary sampling will be done for the duration of this project. The data received does not have water levels, temperature, and microbiological data.

Chapter 4: Results

4.1. Introduction

This chapter covers the analysis of water chemistry data acquired from the Department of Water and Sanitation. The data set contained analytical results of 409 samples which were collected from 2000 to 2017.

4.2. Analytical data accuracy determination

Only 352 sample data points containing all the major anions and cations were selected for ionic charge-balance calculations, to assess the general accuracy and usefulness of the water quality analyses. The ionic charge-balance calculations are used to assess the accuracy and usefulness of water quality analyses for major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (Cl^- , HCO_3^- , SO_4^{2-} , $\text{NO}_2^- + \text{NO}_3^-$, F^-) (Hamilton et al., 1991). Using the Excel spreadsheet, mEq/L for each ion was calculated using their respective molecular mass, and from these values, the IBE% was calculated using Equation (1). All samples (**33/352**) with values outside the +/-10% were deleted, and only 319 sample analyses were within the +/-10% acceptable accuracy range (Hamilton et al., 1991). All assessments henceforth were conducted on 319 sample analyses.

$$\text{Ion Balance Error (\%)} = \frac{\sum \text{cations} \frac{\text{meq}}{\text{L}} - \sum \text{anions} \frac{\text{meq}}{\text{L}}}{\sum \text{cations} \frac{\text{meq}}{\text{L}} + \sum \text{anions} \frac{\text{meq}}{\text{L}}} \times 100\% \quad (1)$$

4.3. Chemical composition of groundwater

The analysis of concentrations of various ions, present in groundwater, is used to describe the chemical characteristics of groundwater and in the identification of geochemical processes. The concentrations of major ions in the groundwater vary spatially and temporally, with some similarities observed within the same drainage system (Table 6). The abundance of cations and anions are showing $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- + \text{NO}_2^- > \text{F}^-$, respectively. The anion abundance pattern is similar to those found in the Soutpansberg region, south of the study area (Lalumbe and Kanyerere, 2022a). The weighted average values show major anions are dominant over the major cations. Na^+ accounts for 48% of the cations and HCO_3^- accounts for 41% of the anions.

Table 6: Summary of averages per monitoring site for various major ions.

Monitoring site	n	Cations				Anions					Drainage
		Ca^{2+} Ave	K^+ Ave	Mg^{2+} Ave	Na^+ Ave	$\text{NO}_3^- + \text{NO}_2^-$ Ave	Cl^- Ave	F^- Ave	SO_4^{2-} Ave	HCO_3^- Ave	
ZQMALL2	29	108,25	10,85	107,06	302,57	37,62	493,80	1,28	83,18	444,91	A63D
ZQMBGG1	4	75,90	0,84	76,10	98,43	52,79	121,00	0,70	60,98	318,98	A50G
ZQMBLT2	25	54,28	2,72	29,88	65,05	20,36	78,20	0,40	8,33	211,56	A63A
ZQMBLT3	27	119,02	6,58	114,14	71,83	65,34	216,77	0,77	30,38	351,25	A63A
ZQMGSA1	6	57,02	6,31	49,00	128,94	36,56	58,97	1,37	44,13	359,26	A50H
ZQMGTA1	4	41,15	3,50	40,41	114,45	20,39	104,44	0,57	29,23	287,01	A50G
ZQMKHK2	15	97,94	2,94	88,12	49,65	68,18	86,46	0,53	34,05	334,94	A63D
ZQMLGN1	6	57,14	11,04	88,85	196,72	12,83	354,59	0,47	77,48	318,62	A63D
ZQMMES1	29	121,08	5,14	100,63	83,01	11,82	239,42	0,57	155,13	316,01	A71K
ZQMMPE1	5	31,81	11,46	93,00	181,90	13,55	210,09	1,16	91,36	437,75	A71K
ZQMSSN1	4	71,85	1,90	82,33	149,95	34,51	202,50	2,67	47,10	400,05	A63B
ZQMSWW1	27	82,41	14,40	70,89	76,91	25,83	154,71	0,69	42,50	339,32	A50J
ZQMSWW2	23	120,90	16,77	128,38	147,53	35,79	351,38	0,78	100,88	407,00	A50J
ZQMTBK1	29	64,09	8,15	59,26	80,53	12,38	87,54	0,52	29,39	381,15	A50H
ZQMTBK2	30	94,58	10,18	96,39	130,70	23,60	266,27	0,49	77,21	384,33	A50H
ZQMTUG2	27	121,65	9,53	0,97	373,22	0,14	397,68	4,90	490,98	31,30	A63C
ZQMTUG4 (spring)	29	136,07	10,19	1,46	382,12	0,09	432,03	4,99	525,46	37,05	A63C
Weighted average		97,87	8,81	71,49	165,18	25,45	256,00	1,47	142,06	298,34	
Ranking		2	4	3	1	5	2	4	3	1	
Dominance		$\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$				$\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- + \text{NO}_2^- > \text{F}^-$					

Minimum, maximum, and average values of physical and chemical parameters of groundwater samples per monitoring site are presented in Table 7. The available temperature data was only for the geothermal sites ZQMTUG2 and ZQMTUG4, which were recorded as 44 and 33 degrees Celsius, respectively. The average Na⁺ concentration across all samples is 165 mg/L, which makes it the most dominant cation, followed by Ca²⁺ and Mg²⁺ concentrations at 98 mg/L and 71 mg/L, respectively. The average HCO₃⁻ concentration across all samples is 298 mg/L, which makes it the most dominant anion, followed by Cl⁻ and SO₄²⁻ concentrations at 256 mg/L and 142 mg/L, respectively. The fourth dominant anion is NO₃⁻+NO₂⁻ with an average concentration of 25 mg/L.

Table 7: Statistical analysis of physicochemical parameters

	ZQM_ID	pH	EC (mS/m)	TDS (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	K ⁺ (mg/L)	Na ⁺ (mg/L)	Cl ⁻ (mg/L)	F ⁻ (mg/L)	NO ₃ ⁻ +NO ₂ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	HCO ₃ ⁻ (mg/L)
1	ZQMALL2 (Av)	8,19	272	1711	108	107	11	303	494	1,28	38	83	445
	Min	7,89	58	362	45	45	1	9	4	0,17	0	14	306
	Max	8,69	338	2129	156	143	16	515	762	1,66	71	125	671
2	ZQMBGG1 (Av)	8,63	134	845	76	76	1	98	121	0,70	53	61	319
	Min	8,50	119	752	53	66	1	92	109	0,39	44	52	277
	Max	8,70	146	919	96	86	1	106	135	0,90	62	83	349
3	ZQMBLT2 (Av)	8,14	81	509	54	30	3	65	78	0,40	20	8	212
	Min	7,43	51	319	34	17	1	31	27	0,13	6	2	126
	Max	8,70	184	1157	90	67	9	188	319	1,50	30	26	376
4	ZQMBLT3 (Av)	8,09	177	1113	119	114	7	72	217	0,77	65	30	351
	Min	7,77	55	349	46	95	5	61	164	0,05	36	13	169
	Max	8,60	201	1266	180	181	7	88	273	1,08	109	40	435
5	ZQMGS1 (Av)	8,52	119	747	57	49	6	129	59	1,37	37	44	359
	Min	8,01	111	698	54	46	4	110	48	1,16	22	37	351
	Max	8,70	141	888	65	60	13	135	74	1,52	53	57	368
6	ZQMGT1 (Av)	8,73	103	649	41	40	3	114	104	0,57	20	29	287
	Min	8,46	88	551	16	37	3	108	68	0,16	17	26	251
	Max	8,80	147	926	105	48	4	131	162	0,86	26	37	379
7	ZQMKHK2 (Av)	8,18	140	881	98	88	3	50	86	0,53	68	34	335
	Min	7,52	83	525	47	35	1	36	58	0,16	13	20	202
	Max	8,70	176	1109	129	109	14	124	156	0,99	104	50	456
8	ZQMLGN1 (Av)	8,52	186	1175	57	89	11	197	355	0,47	13	77	376
	Min	7,90	81	508	13	9	2	64	60	0,22	2	26	0
	Max	8,82	279	1757	131	129	19	283	599	0,69	19	128	0
9	ZQMMES1 (Av)	8,20	169	1067	121	101	5	83	239	0,57	12	155	316
	Min	7,64	46	287	14	11	1	31	58	0,25	0	3	117
	Max	8,70	229	1441	173	161	7	105	380	0,91	51	400	386
10	ZQMMPE1 (Av)	8,52	147	929	32	93	11	182	210	1,16	14	91	438
	Min	8,20	17	107	9	7	1	9	18	0,07	1	2	49
	Max	9,10	247	1558	66	154	19	305	355	2,03	23	161	764
11	ZQMSSN1 (Av)	8,50	160	1010	72	82	2	150	203	2,67	35	47	400
	Min	8,30	152	956	51	75	1	135	166	2,08	33	43	350
	Max	8,80	171	1075	86	89	3	159	228	3,40	36	52	457
12	ZQMSWW1 (Av)	8,27	132	832	82	71	14	77	155	0,69	26	42	339
	Min	7,91	111	700	49	58	13	66	112	0,47	20	32	252
	Max	8,70	164	1033	112	83	16	90	214	0,97	33	74	365
13	ZQMSWW2 (Av)	8,14	226	1425	121	128	17	148	351	0,78	36	101	407
	Min	7,69	139	875	79	60	13	81	143	0,32	8	40	351
	Max	8,57	385	2426	211	234	21	264	792	1,09	71	213	589
14	ZQMTBK1 (Av)	8,24	110	693	64	59	8	81	88	0,52	12	29	381
	Min	7,87	89	563	23	52	3	63	63	0,31	4	20	281
	Max	8,70	154	970	91	73	10	109	175	1,03	23	49	432
15	ZQMTBK2 (Av)	8,18	178	1120	95	96	10	131	266	0,49	24	77	384
	Min	7,71	108	680	40	58	8	75	73	0,05	4	29	232
	Max	9,19	346	2182	201	202	14	250	763	0,93	65	195	476
16	ZQMTUG2 (Av)	7,58	239	1507	122	1	10	373	398	4,90	0,1	491	31
	Min	6,96	229	1440	108	1	9	324	298	0,44	0,0	447	17
	Max	8,07	251	1581	144	4	11	492	452	6,35	2,0	571	41
17	ZQMTUG4 (Av)	7,48	248	1565	136	1	10	382	432	4,99	0,1	525	37
	Min	6,91	227	1428	109	1	4	272	378	0,05	0,0	443	22
	Max	7,80	286	1802	203	7	12	444	527	9,94	0,9	784	51
	Weighted average		178	1122	98	71	9	165	256	1,47	25	142	298

Average pH calculator: <https://www.wolkersdorfer.info/en/average-ph-value.html>

The highest Na⁺ concentrations are found at borehole sites ZQMALL2, ZQMTUG2 and ZQMTUG4 (Figure 6). The Na⁺ anion dominance is, rather absent in the following borehole sites: ZQMBLT3, ZQMKHK2, ZQMMES1, and ZQMSWW1 (Figure 7), where the dominating anion is Ca²⁺, followed by Mg²⁺.

The spatial distribution of Ca²⁺ and Mg²⁺ average concentrations are presented in Figure 8 and Figure 9, respectively. The monitoring sites ZQMMES1, ZQMALL2, ZQMSWW2, and ZQMBLT3 are showing strong correlation between high Ca²⁺ and high Mg²⁺. However, the high average Ca²⁺ concentration at ZQMTUG2 and ZQMTUG4 is associated with low average Mg²⁺ concentration. The spatial distribution of average K⁺ concentration is presented in Figure 10.

The study area is mainly HCO₃⁻ anion dominant, except for the geothermal sites ZQMTUG2 and ZQMTUG4 where the average HCO₃⁻ is 31 mg/L and 37 mg/L, respectively (Figure 11). The average HCO₃⁻ concentration at ZQMBLT2 and ZQMGT A1, is 211 mg/L and 287 mg/L, respectively. Low average HCO₃⁻ concentration at ZQMTUG2 and ZQMTUG4 is strongly associated with high SO₄²⁻ and high Cl⁻ concentrations (Figure 12 and Figure 13, respectively).

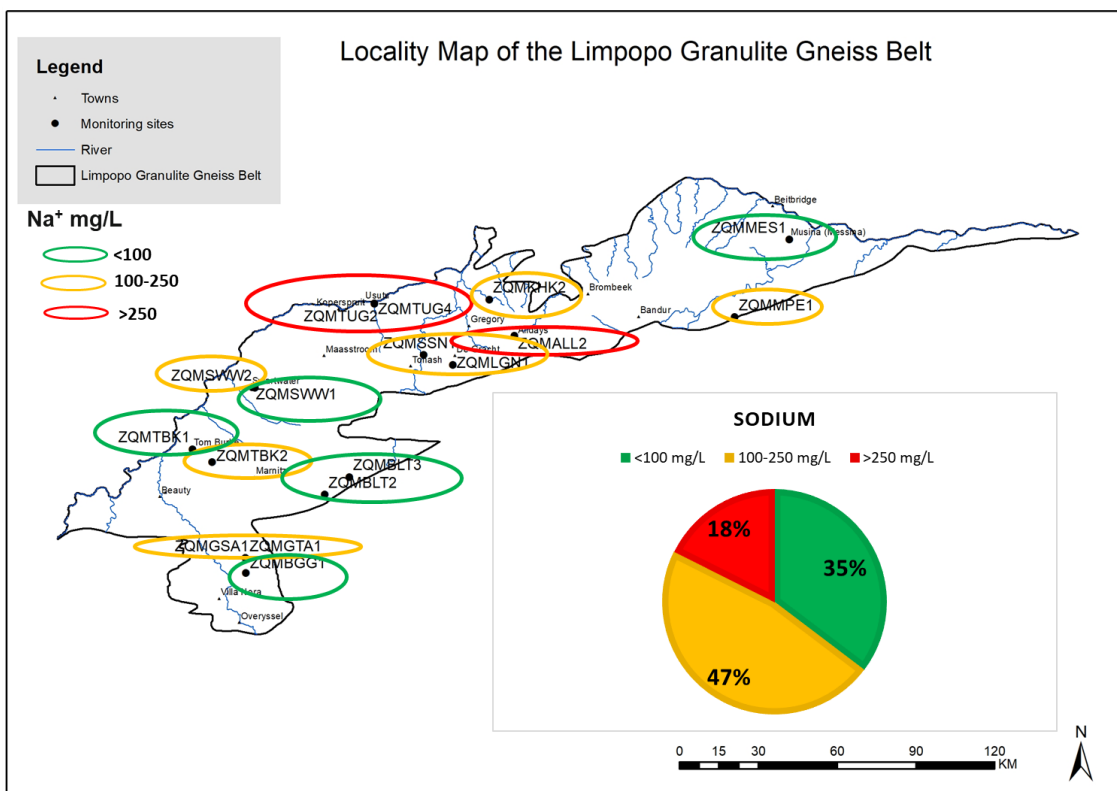


Figure 6: Spatial distribution of Na⁺ based on average concentration per monitoring site, 2000-2017.

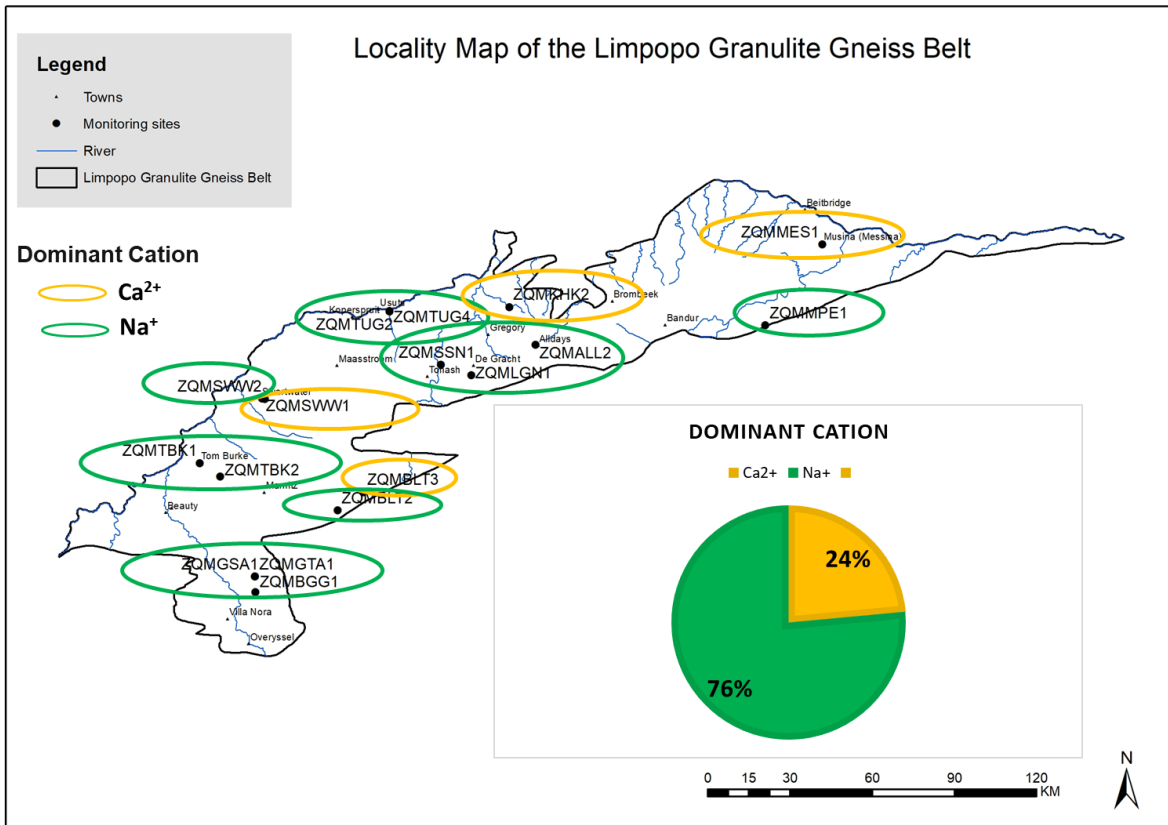


Figure 7: Spatial distribution of dominant cation (2000-2017).

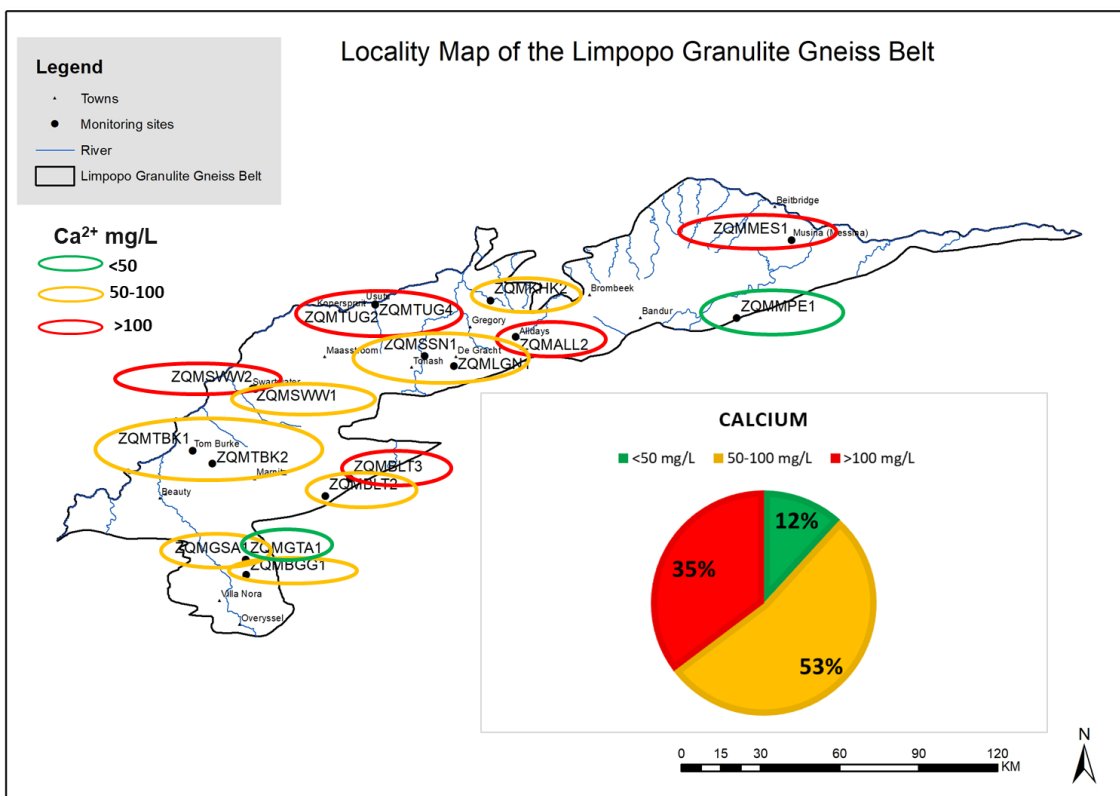


Figure 8: Spatial distribution of Ca²⁺ based on average concentration per monitoring site (2000-2017).

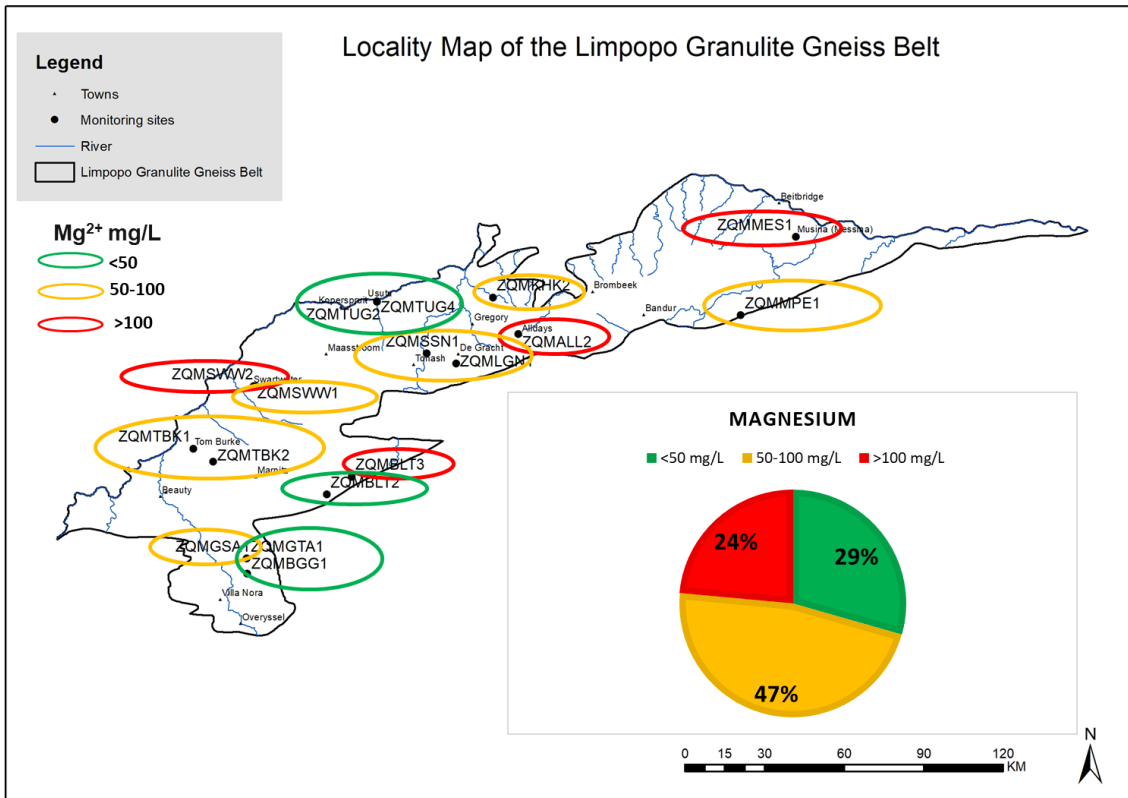


Figure 9: Spatial distribution of Mg²⁺ based on average concentration per monitoring site (2000-2017).

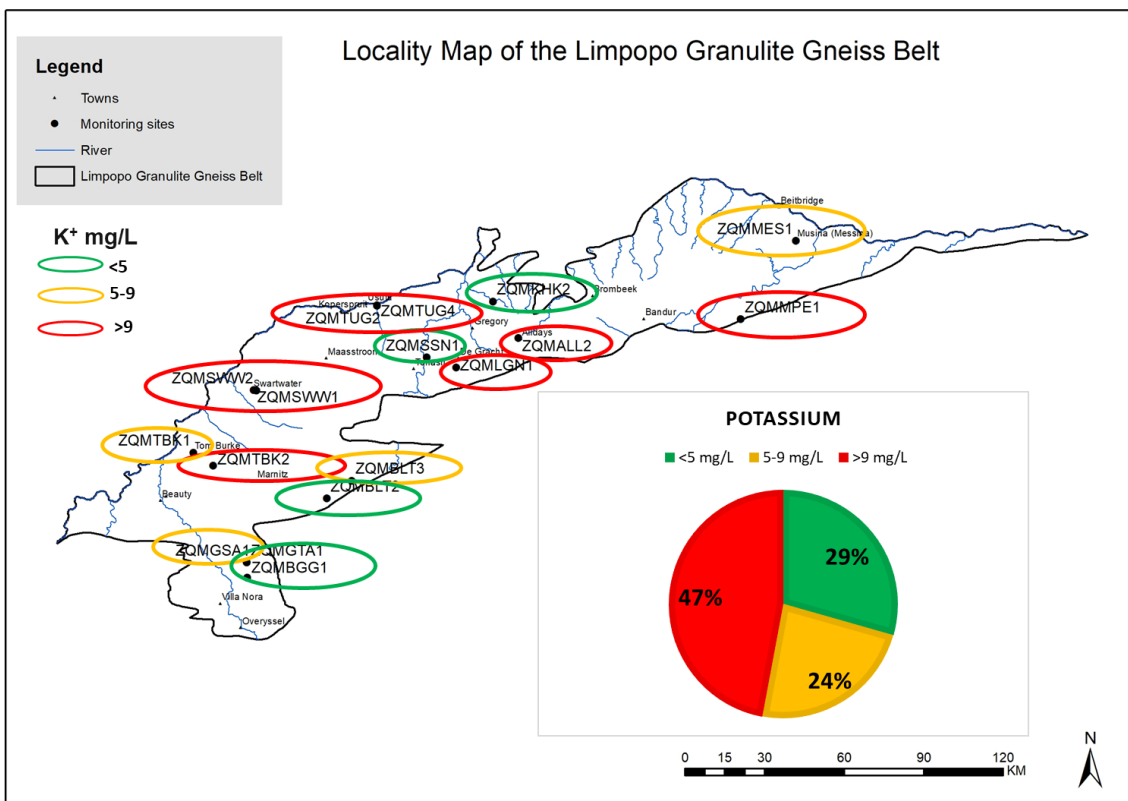


Figure 10: Spatial distribution of K⁺ based on average concentration per monitoring site (2000-2017)

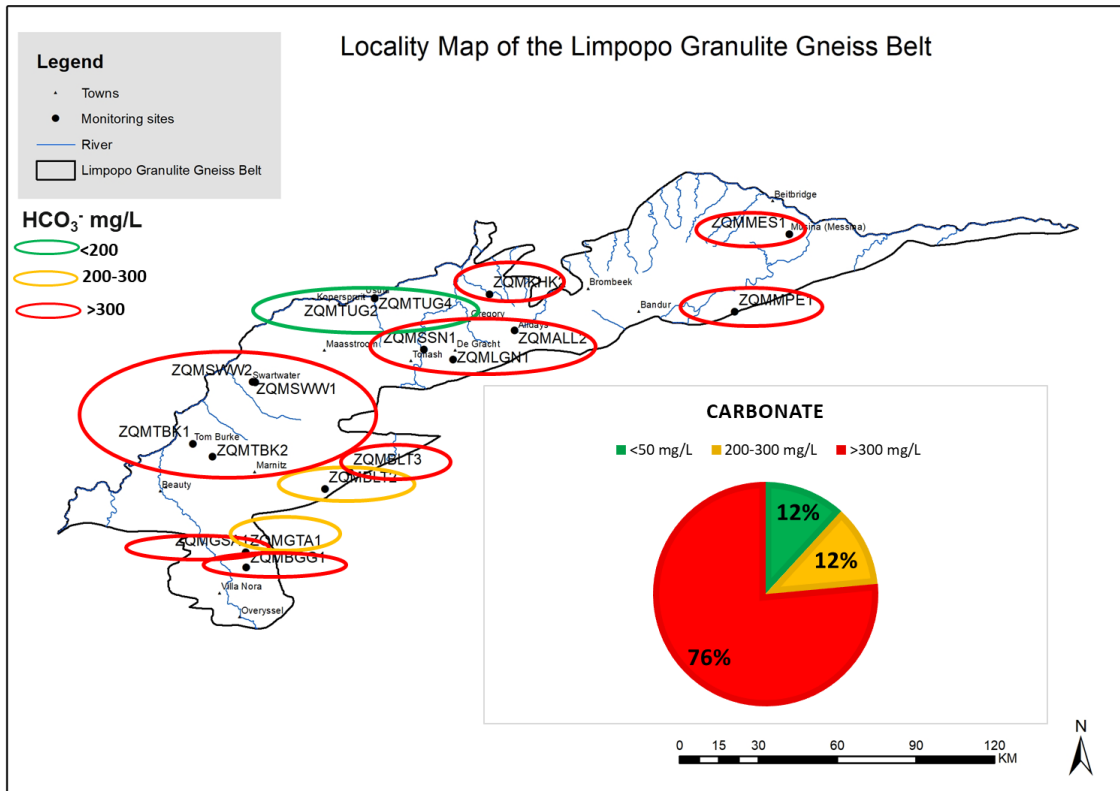


Figure 11: Spatial distribution of HCO₃⁻ based on average concentration per monitoring site (2000-2017).

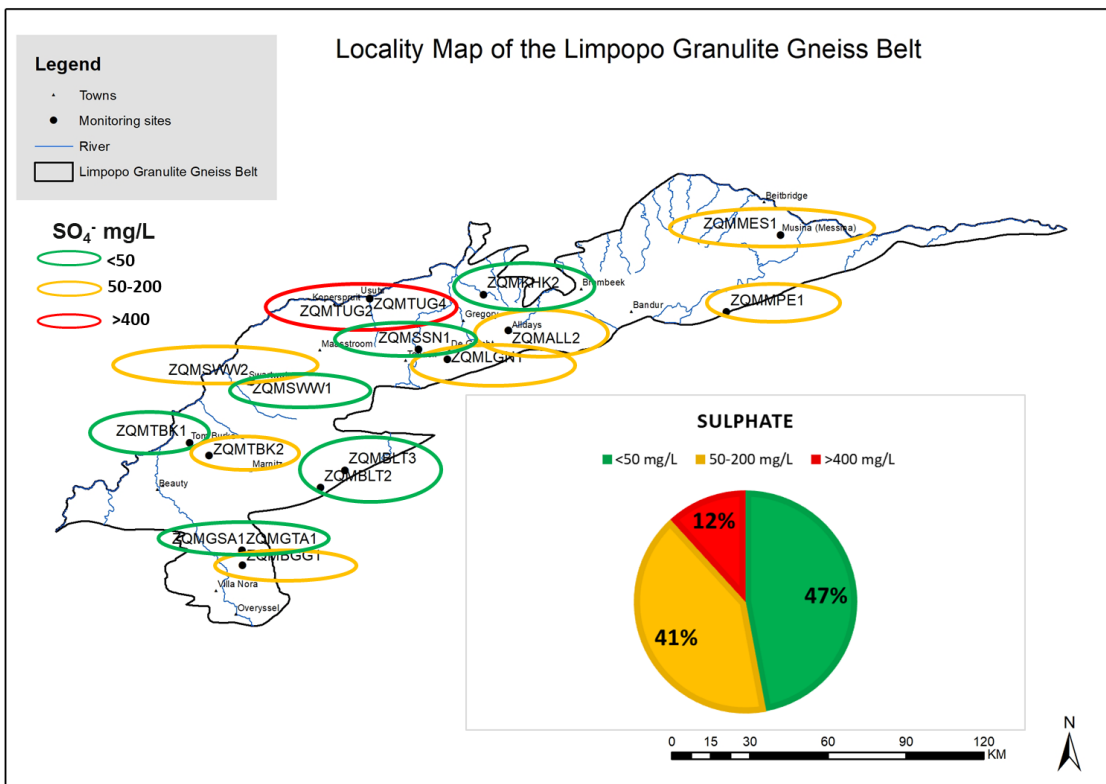


Figure 12: Spatial distribution of SO₄⁻ based on average concentration per monitoring site (2000-2017).

While the average Cl⁻ concentration in the study area is 256 mg/L, there are four sites with concentrations below 100 mg/L, ZQMKHK2, ZQMTBK1, ZQMBLT3, and ZQMGSA1 (Figure 13). The only sites with significantly low NO₃⁻+NO₂⁻ are ZQMTUG2 and ZQMTUG4, at 0,14 mg/L and 0,09 mg/L, respectively (Figure 14). The rest of the sites have elevated nitrate concentrations. The implications will be discussed in detail in the suitability for drinking assessment in Section 4.4.

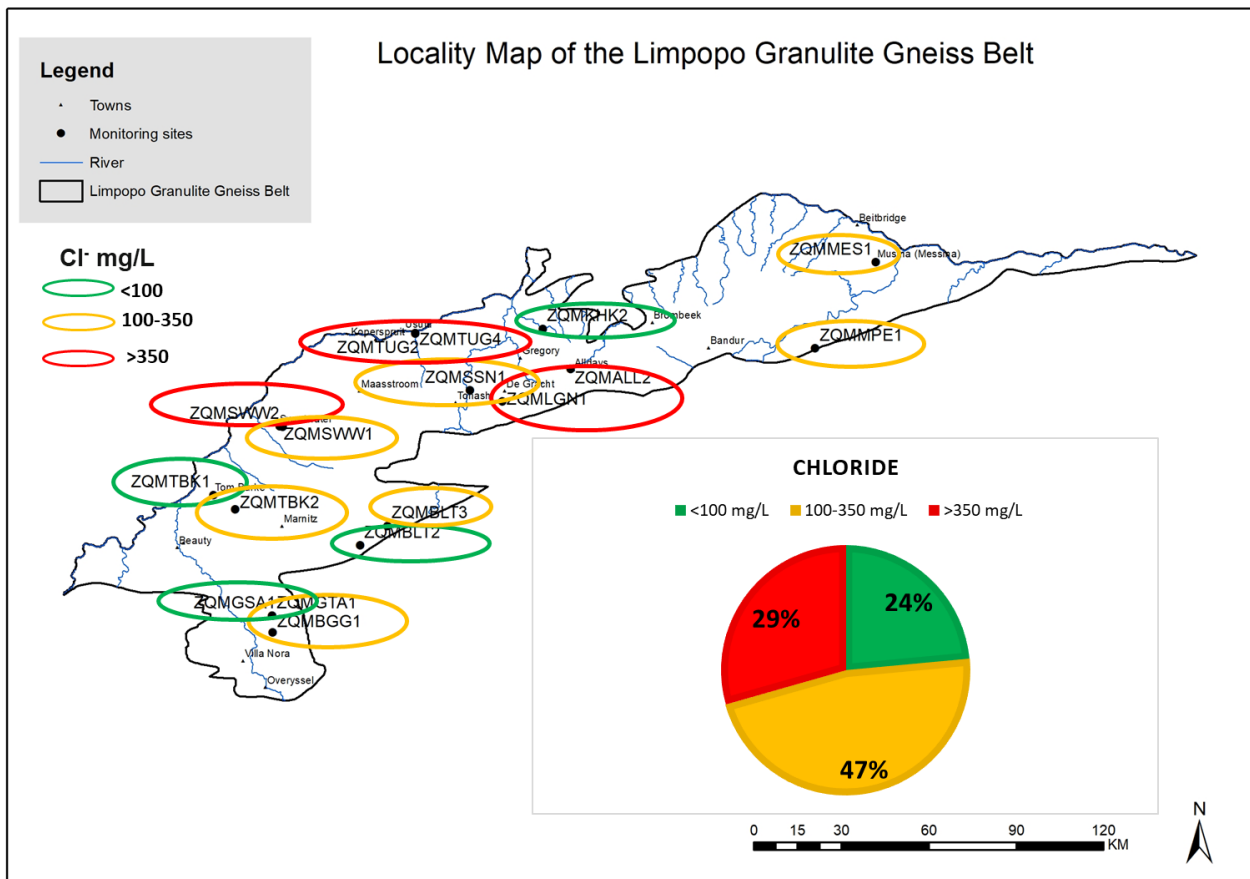


Figure 13: Spatial distribution of Cl⁻ based on average concentration per monitoring site (2000-2017).

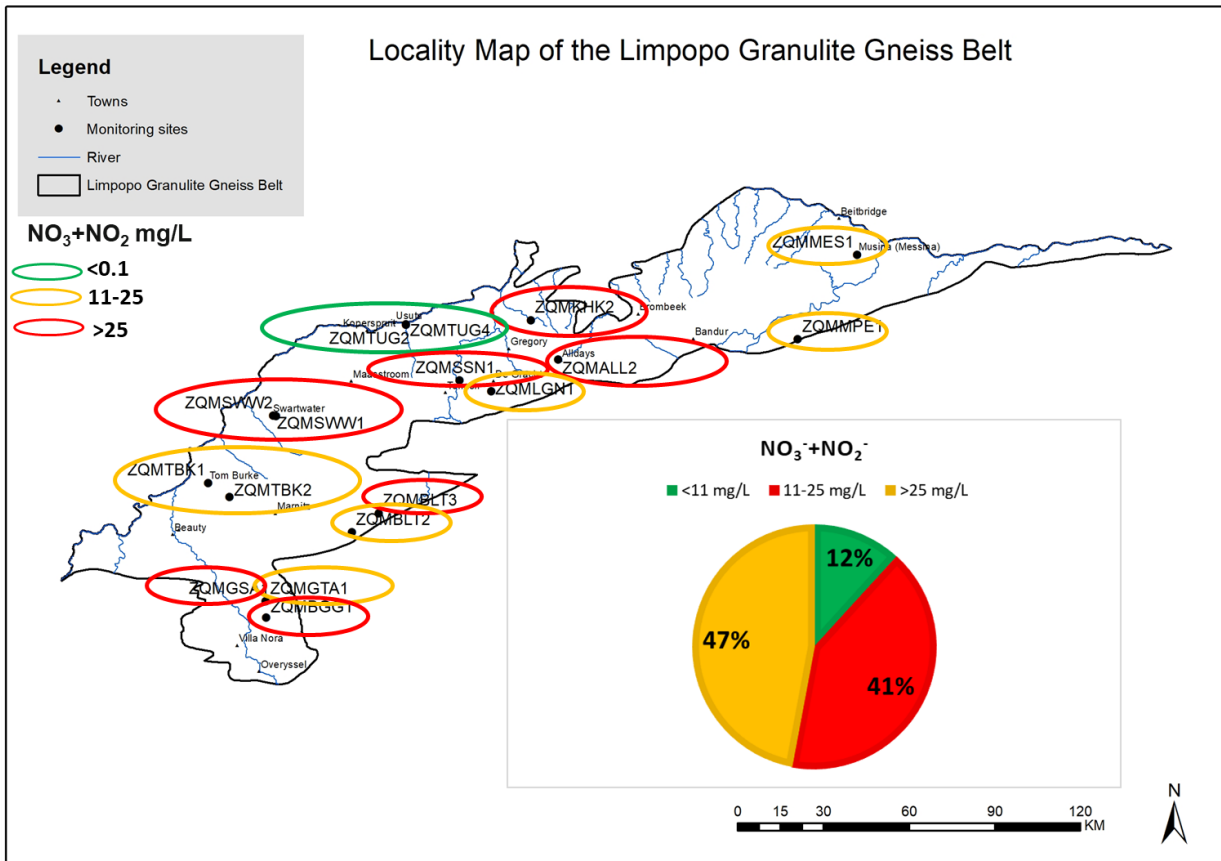


Figure 14: Spatial distribution of NO₃⁻+NO₂⁻ based on average concentration per monitoring site (2000-2017).

The pH of groundwater in the study area ranges from 6,9 to 9,2; with over 83,4% (266) of the samples falling within the pH 7,5 to 8,5 range; while 5,0% (16) of the samples are within the pH 6,5 to <7,5 range; and 11,6% (37) samples are within the pH >8,5-9,2 range (Table 8). The average pH for geothermal sites ZQMTUG2 and ZQMTUG4 is 7,58 and 7,48, respectively. The borehole sites ZQMALL2, ZQMBLT2, ZQMBLT3, ZQMGSA1, ZQMKHK2, ZQMMES1, ZQMSWW1, ZQMSWW2, ZQMTBK1 and ZQMTBK2 are within the pH 7,5 to 8,5 range. The borehole sites ZQMGG1, ZQMGT A1, ZQMLGN1, ZQMMPE1, and ZQMSSN1 are within the pH >8,5 to 9,2 range.

Table 8: Summary of pH for samples per monitoring site (2000-2017).

Monitoring site (n)	Average pH	pH 6,5-<7,5 (%)	pH 7,5-8,5 (%)	pH >8,5-9,5 (%)
ZQMALL2 (29)	8,19	0	79,3	20,7
ZQMBGG1 (4)	8,62	0	0,0	100,0
ZQMBLT2 (25)	8,14	0	84,0	16,0
ZQMBLT3 (27)	8,09	0	88,9	11,1
ZQMGSA1 (6)	8,52	0	66,7	33,3
ZQMGT A1 (4)	8,73	0	0,0	100,0
ZQMKHK2 (15)	8,18	0	80,0	20,0
ZQMLGN1 (6)	8,52	0	33,3	66,7
ZQMMES1 (29)	8,20	0	93,1	6,9
ZQMMPE1 (5)	8,52	0	40,0	60,0
ZQMSSN1 (4)	8,50	0	25,0	75,0
ZQMSWW1 (27)	8,27	0	77,8	22,2
ZQMSWW2 (23)	8,14	0	87,0	13,0
ZQMTBK1 (29)	8,24	0	79,3	20,7
ZQMTBK2 (30)	8,18	0	93,1	6,9
ZQMTUG2 (27)	7,58	25,9	74,1	0,0
ZQMTUG4 (29)	7,48	31,0	69,0	0,0

Average pH calculator: <https://www.wolkersdorfer.info/en/average-ph-value.html>

Figure 15 shows the spatial distribution of pH within the study area. The area is spatially dominated by the pH 7,5 to 8,5 range. It must be noted that groundwater pH changes as it moves from recharge areas to discharge areas (Hamilton et al., 1991). This will be discussed further in the next section under Piper diagramme. Furthermore, groundwater recharges from rainwater, and rainwater is weakly acidic, so it reacts with rock formations (Carroll, 1962), to form salts which are then discharged and transported into the sea (De Angelis, 2005). The dominating alkalinity in the study area is linked to high concentrations of sodium, magnesium, calcium, and bicarbonate ions, associated with mafic-ultramafic igneous rocks, similar to findings by Lalumbe and Kanyerere, (2022a) in Soutpansberg region south of the study area.

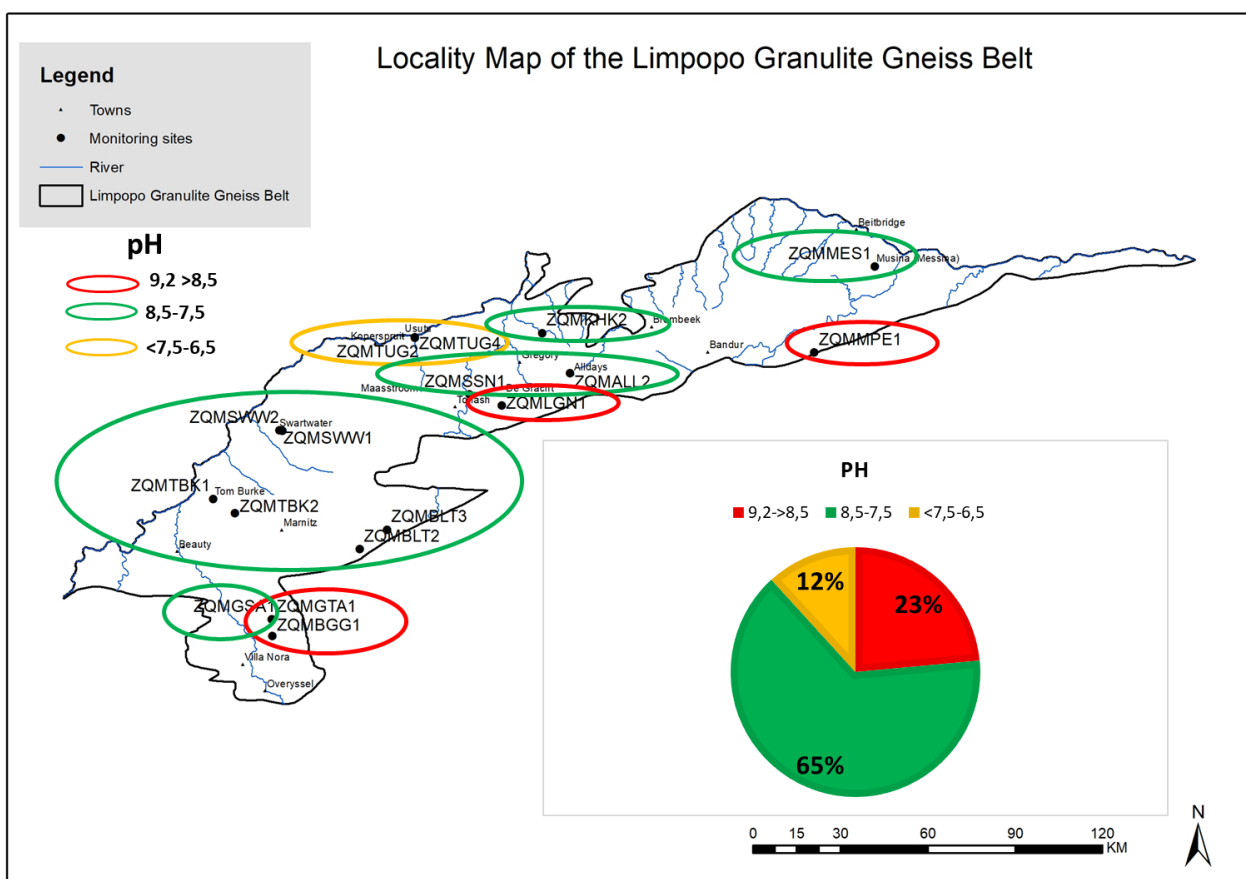


Figure 15: Spatial distribution of pH based on average pH per monitoring site (2000-2017).

Figure 16 shows the pH trends of the geothermal springs ZQMTUG2 and ZQMTUG4 from 2000 to 2017. There is a similar drop in pH observed in both boreholes in 2009, and again in 2016, which was followed by a rise in pH in 2017. Figure 17 show the pH trends of the other 15 borehole sites.

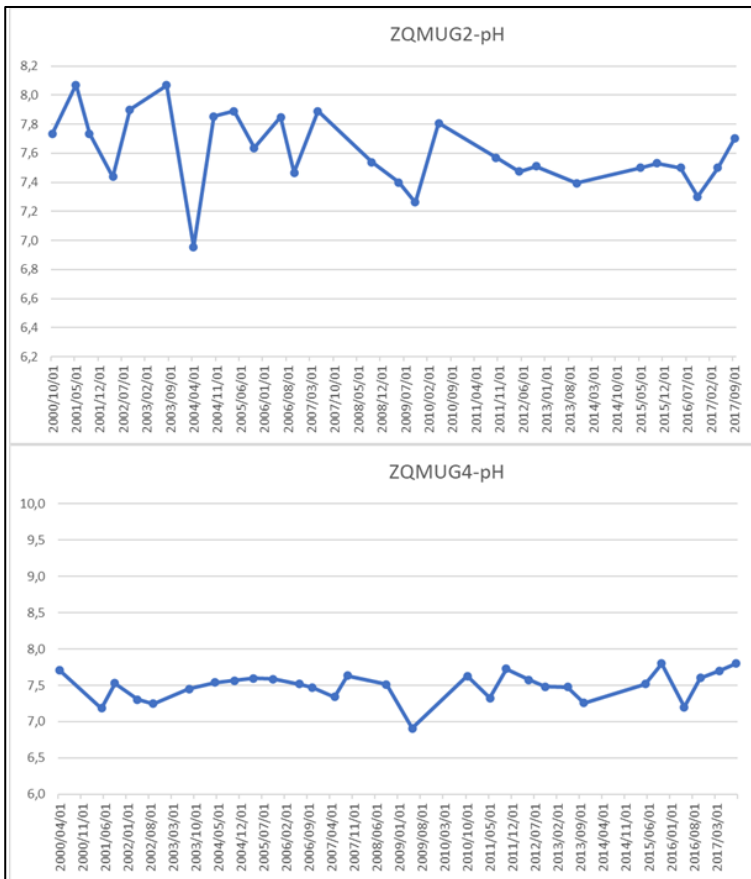


Figure 16: ZQMTUG2 and ZQMTUG4 pH trends over time.

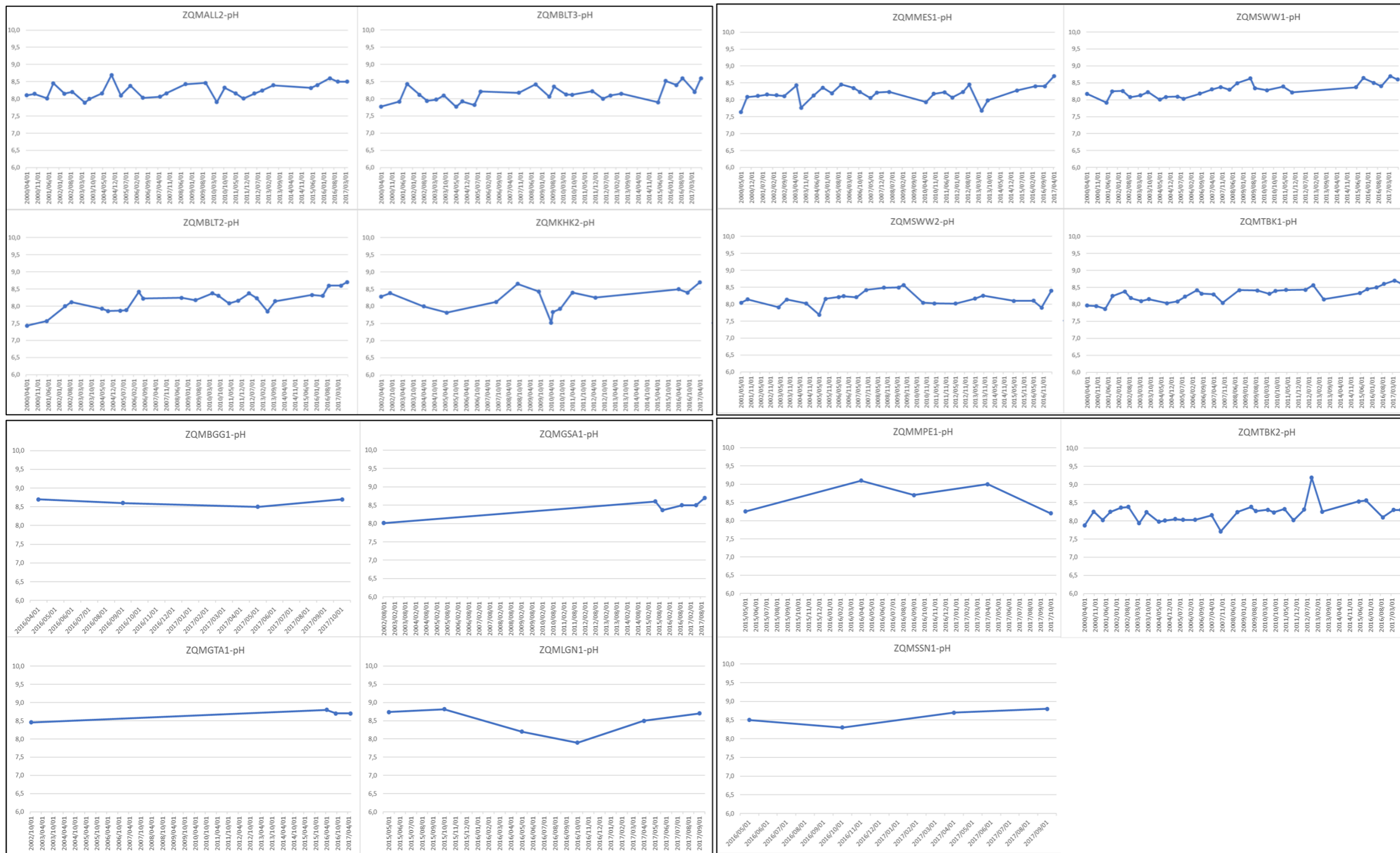


Figure 17: pH trends for 15 monitoring sites over time.

TDS values range from 107 to 2426 mg/L with a weighted average of 1122 mg/L (Table 9). According to Freeze and Cherry (1979), TDS classification, 43% of the water samples are freshwater type (<1000 mg/L) and the same samples are suitable for drinking purposes based on Davis and DeWiest (1966) classification. 57% of the samples are brackish (1000 - 10 000 mg/L). However, 41% of the sites can be classified as fresh and 57% as brackish based on the average TDS concentration the TDS concentrations are all below 3000 mg/L, hence all samples based on TDS alone are suitable for irrigation purposes (Davis and DeWiest, 1966). Ten out of seventeen sites are predominantly (>60% samples) brackish and the TDS spatial distribution is presented on Figure 18.

The historic trends of ZQMALL2, ZQMBLT3, ZQMMES1, and ZQMSWW2 are presented in Figure 19. For ZQMALL2 and ZQMBLT3 sites the trend is generally high with a few distinct low TDS anomalies over the period assessed.

Table 9: Summary of TDS values for samples per monitoring site.

Monitoring site	n	TDS (mg/L)			Fresh	Brackish	Saline	Brine
		Ave	Min	Max	% <1000	% 1000 - 10 000	% 10 000 - 100 000	% >100 000
ZQMALL2	29	1711	362	2129	3%	97%	0	0
ZQMBGG1	4	845	752	919	100%	0%	0	0
ZQMBLT2	25	509	319	1157	88%	12%	0	0
ZQMBLT3	27	1113	349	1266	15%	85%	0	0
ZQMGS1	6	747	698	888	100%	0%	0	0
ZQMGT1	4	649	551	926	100%	0%	0	0
ZQMKH2	15	881	525	1109	73%	27%	0	0
ZQMLGN1	6	1175	508	1757	33%	67%	0	0
ZQMMES1	29	1067	287	1441	31%	69%	0	0
ZQMMPE1	5	929	107	1558	40%	60%	0	0
ZQMSSN1	4	1010	956	1558	25%	75%	0	0
ZQMSWW1	27	832	700	1033	96%	4%	0	0
ZQMSWW2	23	1425	875	2426	17%	83%	0	0
ZQMTBK1	29	693	563	970	100%	0%	0	0
ZQMTBK2	30	1120	680	2182	40%	60%	0	0
ZQMTUG2	27	1507	1440	1581	0%	100%	0	0
ZQMTUG4	29	1565	1428	1802	0%	100%	0	0

Red fill indicates unsuitable water quality for drinking (SANS241, 2015)

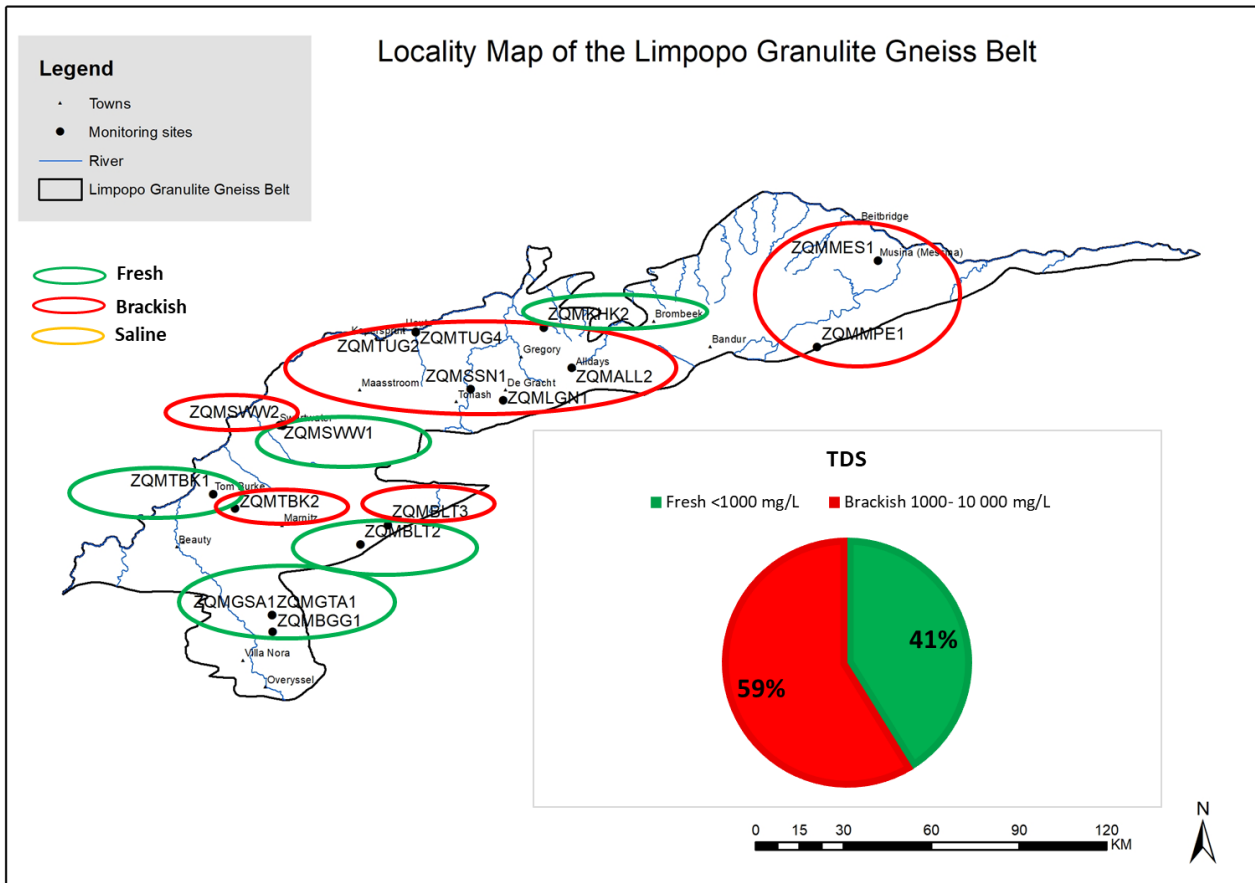


Figure 18: TDS spatial distribution according to Freeze and Cherry (1979) TDS classification.



Figure 19: ZQMALL2, ZQMBLT3, ZQMMES1, and ZQMSWW2 TDS trends (mg/L).

The TDS concentrations over time in ZQMBLT2 and ZQMSWW2, for example, are similar to the concentrations of Cl⁻ over the same period (Figure 20). In a study adjacent to the study area, Lalumbe and Kanyerere (2022a) also observed a strong association between the spatial distributions of Cl⁻ and TDS. In their study, the high salinity was found to be associated with fertilisers and pit latrines from the rural human settlements dominated by irrigation land use.

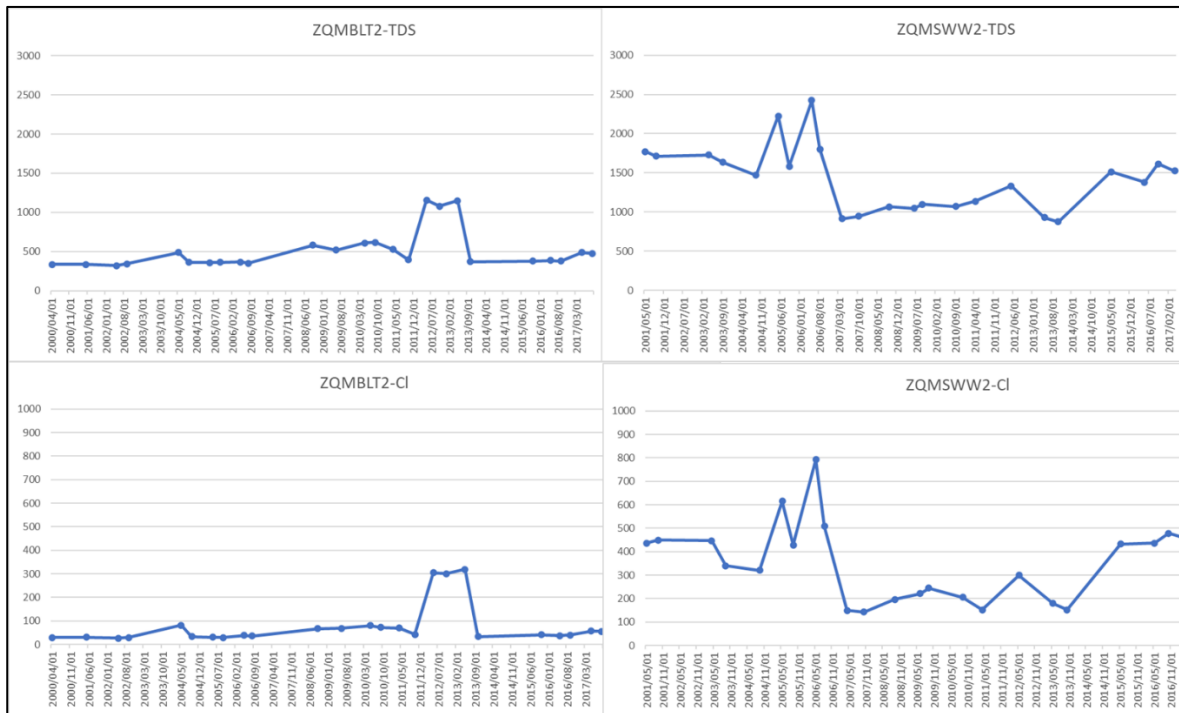


Figure 20: TDS (mg/L) vs Cl⁻ (mg/L) trend comparison for ZQMBLT2 and ZQMSWW2.

4.4. Hydrogeochemical characteristics

The common hydrogeochemical processes associated with semi-arid regions are precipitation, evaporation, and rock–water interaction (Kumar and James, 2016). To be able to understand these complex hydrogeochemical processes, major ion chemistry, Piper and Gibbs diagrammes; Schoeller's chloroalkaline indices (CAIs) method, and Pearson correlation coefficients were considered

4.4.1. Piper

Figure 21 shows Piper diagramme for 11 sites ($n > 10$) while Figure 22 shows Piper diagramme for 6 sites ($n < 10$). Figures 23(i) and 23(ii) show the Modified Piper diagramme explanation and Hamilton et al., (1991) classification of water types, respectively. In Figure 21, the water samples are mainly plotted on Ca-Mg-HCO₃ type (zone 5) and mixed (Ca-Mg-Cl-SO₄ and Ca-Mg-HCO₃) type (zone 9) (Rao, 1998). Ca-Mg-HCO₃ type is carbonate (temporary) hardness (Rao, 1998). The distinct Ca-HCO₃ water types found in borehole sites ZQMALL2, ZQMBLT3, ZQMMES1, and ZQMSWW2 indicate shallow, recently recharged groundwater (Lalumbe and Kanyerere, 2022b). These observations are consistent with the findings by Vegter 2001, where the hydrochemical facies of this study area were found to be mainly Ca-Mg-HCO₃ and Ca-Mg-Cl. The mixed zone 9 type of water indicate the types of groundwater that cannot be identified as neither anion nor cation dominant (Todd and Mays 2005).

The least dominant water types are Na-Cl (zone 7) which came from mainly ZQMTUG2 and ZQMTUG4 and some samples from ZQMALL2; and Ca-Mg-Cl which came from a minority of the samples from ZQMMES1 and ZQMTBK2. The two geothermal sites ZQMTUG2 and ZQMTUG4 are identical and distinctively Na-Cl type (zone 7), a signature dominated by Na-SO₄-Cl ion water facies, suggesting recently recharged groundwater undergoing mineralisation. Zone 7 is also known to indicate halite dissolution (Ravikumar and Somashekar, 2015). These geothermal springs are, according to the Bond (1946) classification system, highly mineralised (TDS >1500 mg/L) sodium-chloride-sulphate water type, consistent with findings by Olivier and Jonker (2013), who found spring waters from Limpopo to be highly mineralised chloride-sulphate water type. According to Hamilton et al., (1991) groundwater type changes as it moves from recharge areas to discharge areas (Figure 23). This is because the ionic composition of water changes as water travels from

the atmosphere through precipitation, into and through sediments where mineral interaction begins (Hamilton et al., 1991).

The analytical values obtained from the groundwater samples when plotted on Piper diagramme show that the alkaline earth metals are significantly dominant (77%) over the alkalis $(Ca+Mg) > (Na+K)$, and strong acidic anions (56%) are slightly more than weak acidic anions $(SO_4+Cl+F) > (CO_3+HCO_3)$. Within the alkaline earth metals, a significant number of samples (42%) fall within the MIXED type facies, which is between the $Ca+Mg+HCO_3$ type (55%) and the $Ca+Mg+Cl+SO_4$ type (3%). No cation facies type (71%) dominance is observed over patches of Mg-type (7%) and Na+K type (22%), while on the anions we see carbonate type (55%) dominance over chloride type (28%) and mixed type (17%). The study area is hence described as mainly dominated by alkaline earth metals facies, which are associated with silicate minerals and occur naturally in secondary environments such as evaporites and brines (Hounslow, 1995). The study area is known to have marbles and calc-silicates rock formations found in the Gumbu Group of the Beit Bridge Complex (Vegter, 2001).

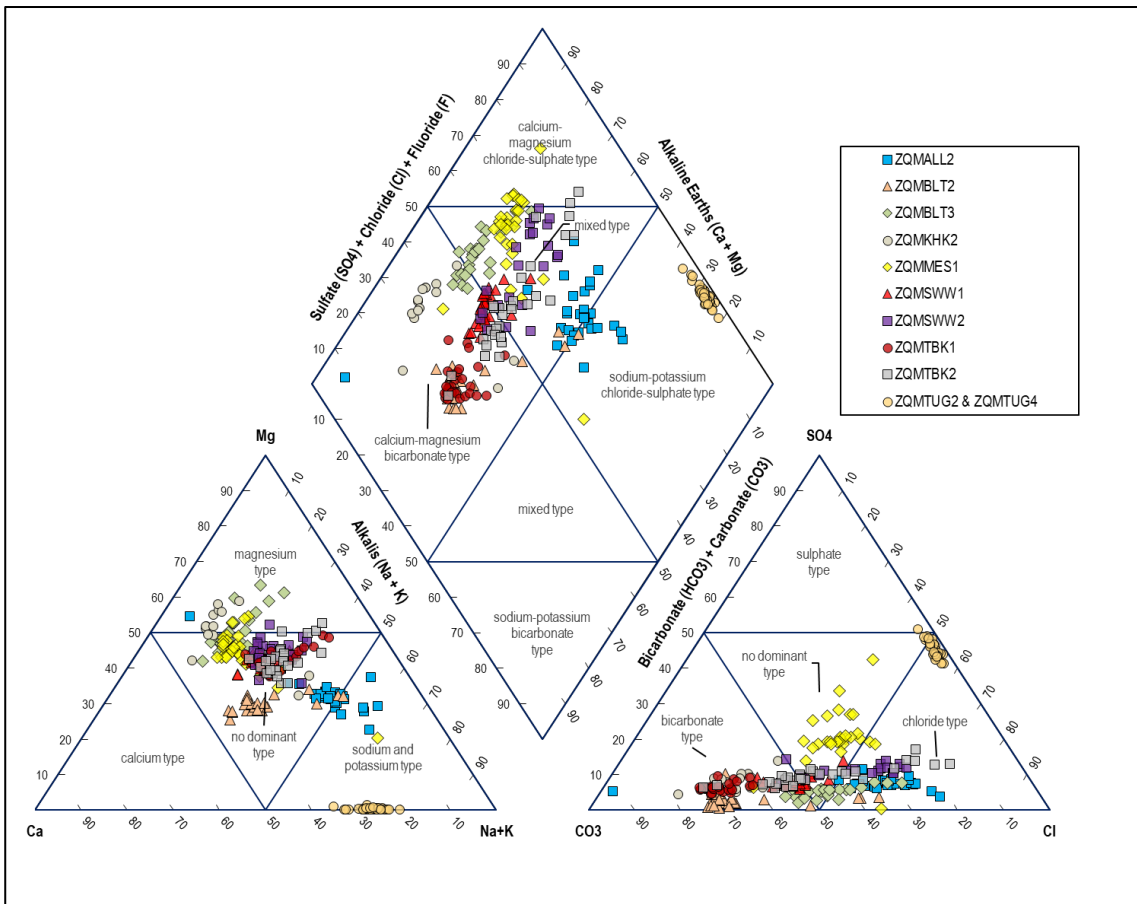


Figure 21: Classification results of the groundwater using Piper diagramme (Group2 n>10).

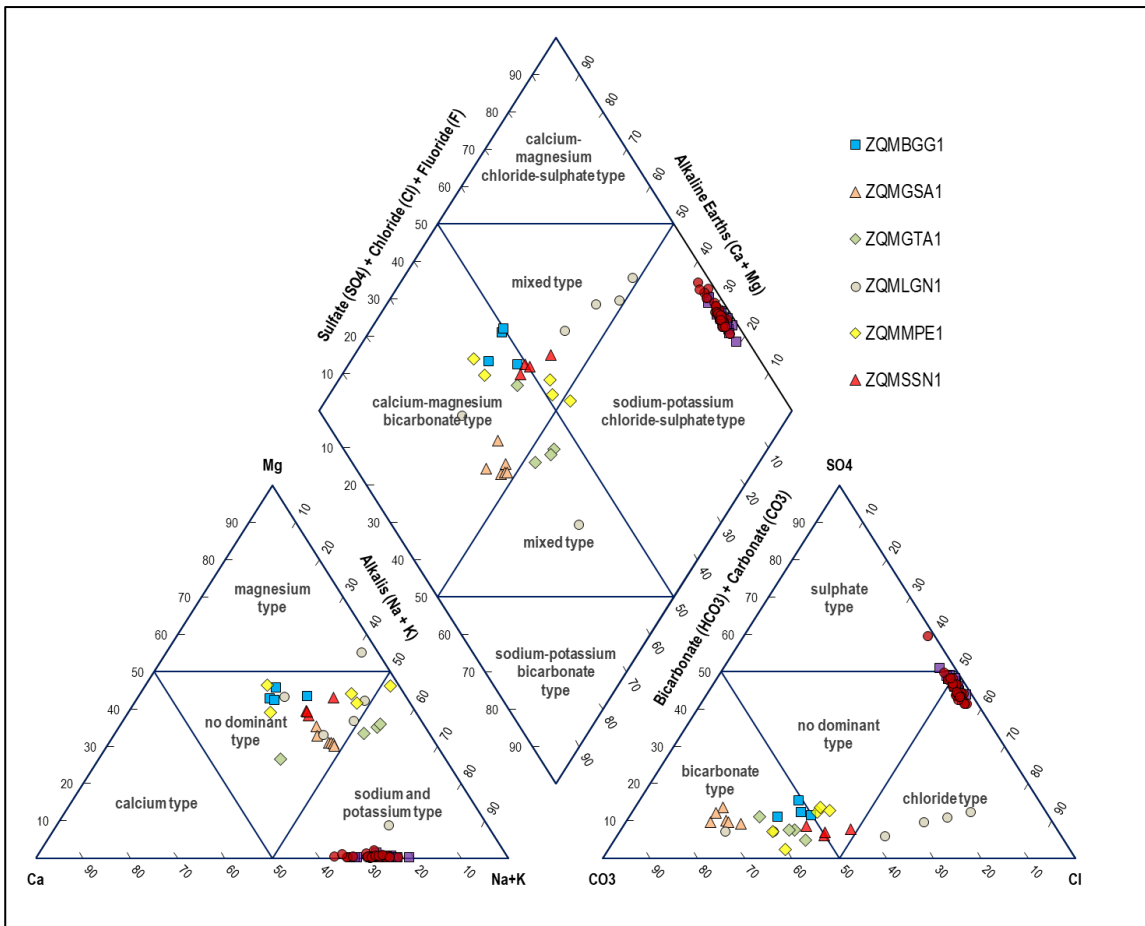


Figure 22: Classification results of the groundwater using Piper diagramme (Group1 n<10).

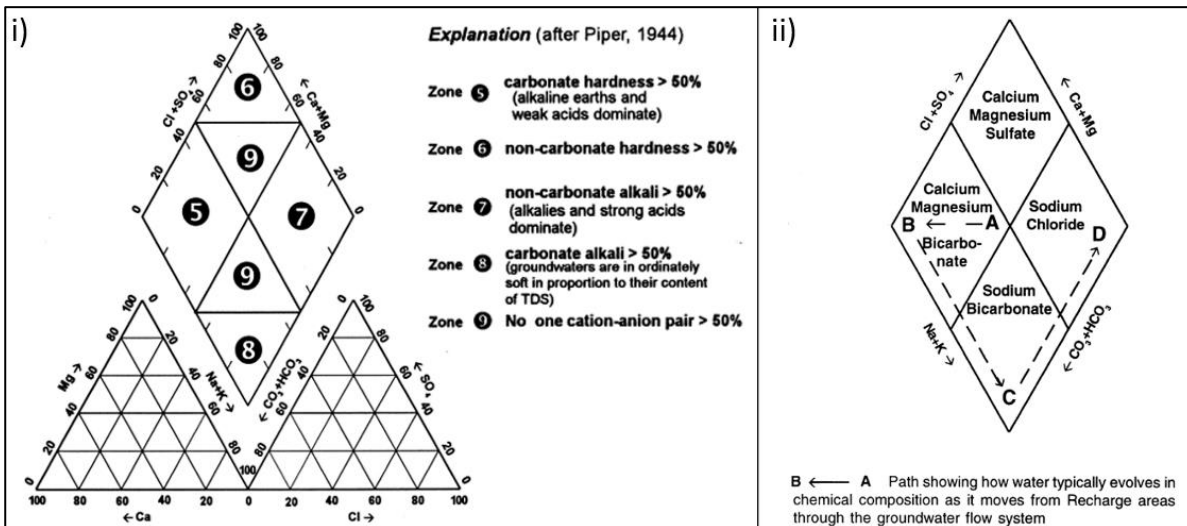


Figure 23: i) Modified Piper (1944) diagramme explanation by (after Rao, 1998). ii) Hamilton et al., (1991) classification of water types (after Rao, 1998).

4.4.2. Gibbs

All samples were plotted on the Gibbs diagramme (Figure 24). The study area data plots on Gibbs diagrammes indicate that evaporation dominance mechanisms are controlling groundwater chemistry. The chemical data of the study area are dominating the evaporation zone. This supports findings observed in the Piper diagramme being alkaline earth metal type facies, mainly occurring as evaporites and brines (Hounslow, 1995). Individual monitoring site Gibbs diagrammes are shown in Figures 25, 26, and 27.

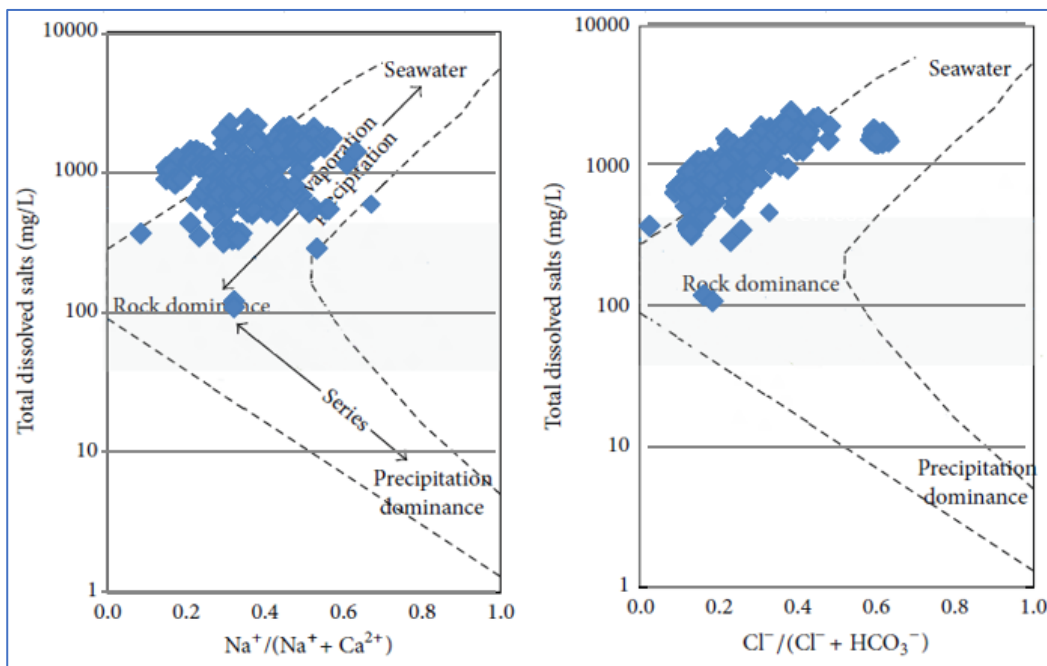


Figure 24: Gibbs diagramme of the study area showing all samples.

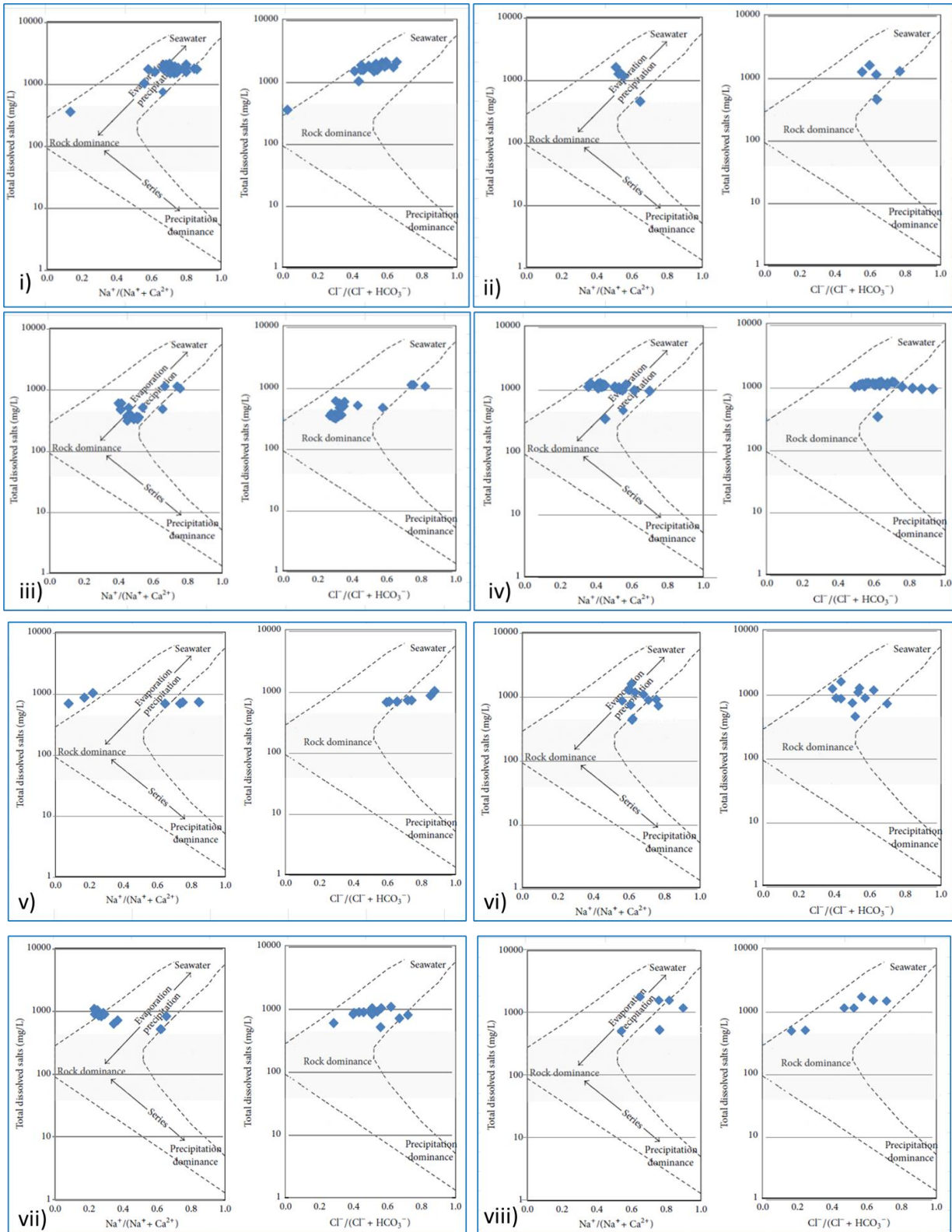


Figure 25: Gibbs diagrams for monitoring sites: i) ZQMALL2, ii) ZQMBGG1, iii) ZQMBLT2, iv) ZQMBLT3, v) ZQMGA1, vi) ZQMGA1, vii) ZQMCHK2, viii) ZQMLGN1

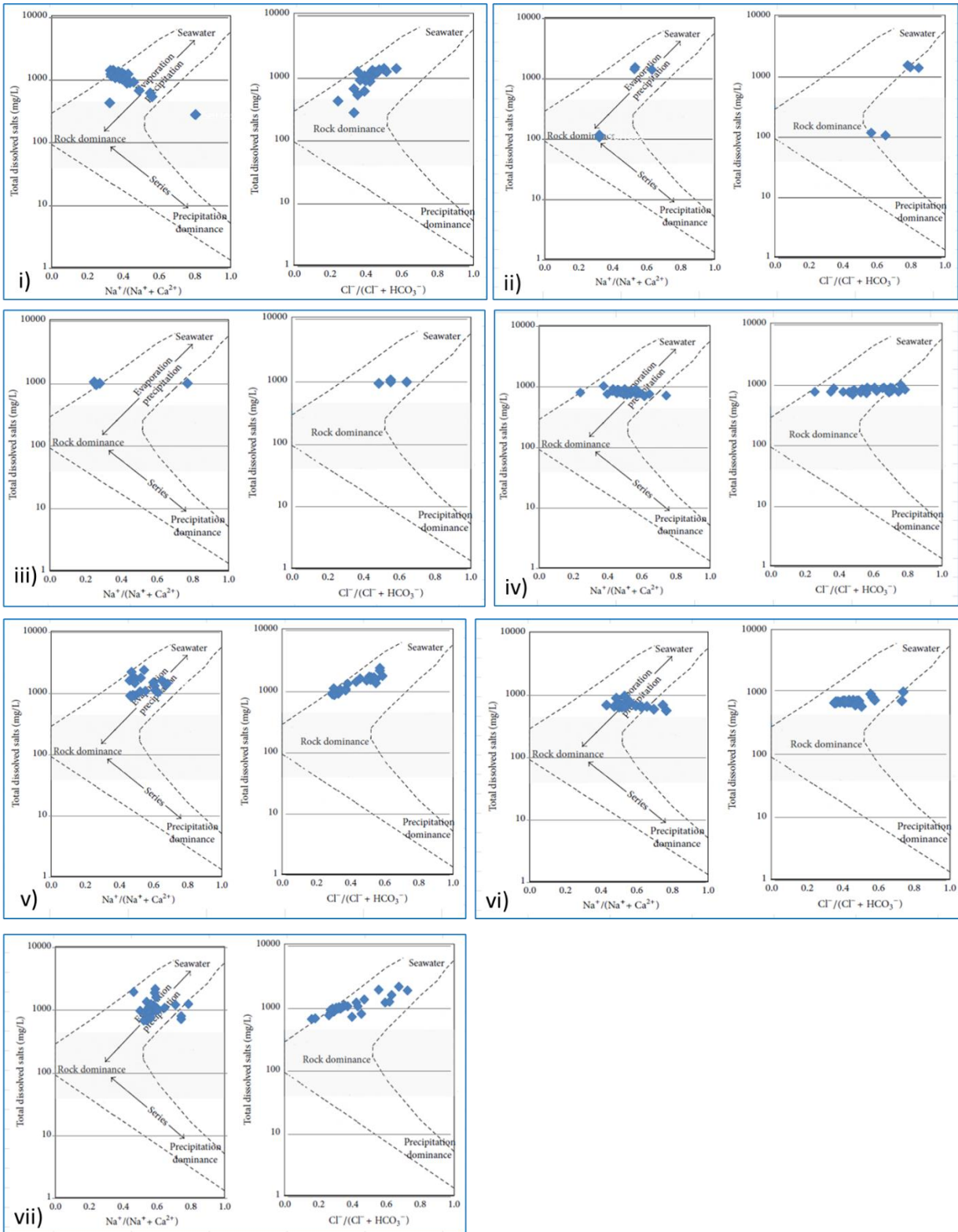


Figure 26: Gibbs diagrams for monitoring sites: i) ZQMME1, ii) ZQMMPE1, iii) ZQMSSN1, iv) ZQMWW1, v) ZQMSWW2, vi) ZQMTBK1, vii) ZQMTBK2.

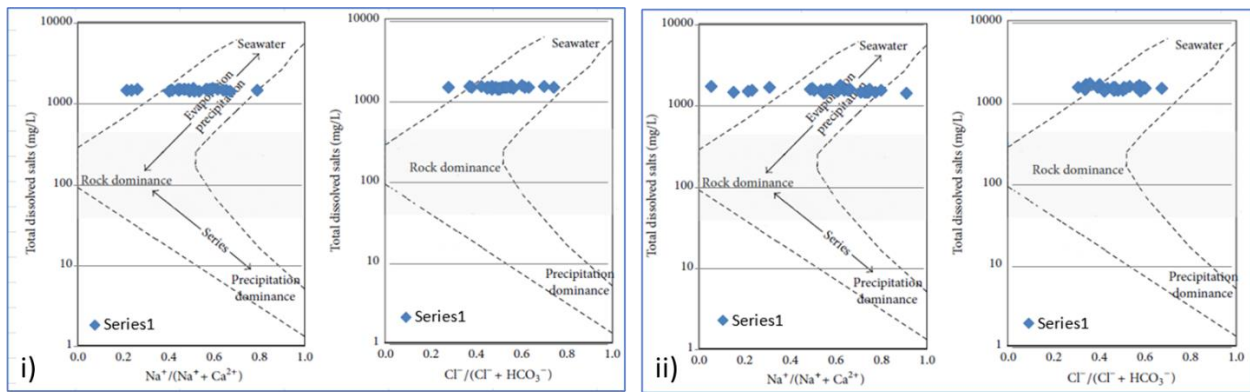


Figure 27: Gibbs diagrams for bore hole sites i) ZQMTUG2, ii) ZQMTUG4.

4.4.3 Geochemical scatter plots

The source of sodium was investigated using the Na/Cl ratio (Figure 28). If halite dissolution was the main source of Na^+ then the samples should plot in a 1:1 equiline (Na^+ vs. Cl^-), showing equal amounts of Na and Cl in groundwater and any deviation from this equiline suggests that other processes like ion exchange or weathering may have influenced the hydrogeochemistry of these samples (Kumar and James, 2016). To test ion exchange between Na and Ca, Na/Cl was plotted against Ca+Mg (Figure 29) and a negative relationship is observed, similar to studies by Kumar and James (2016) which show the possibility of ion exchange processes.

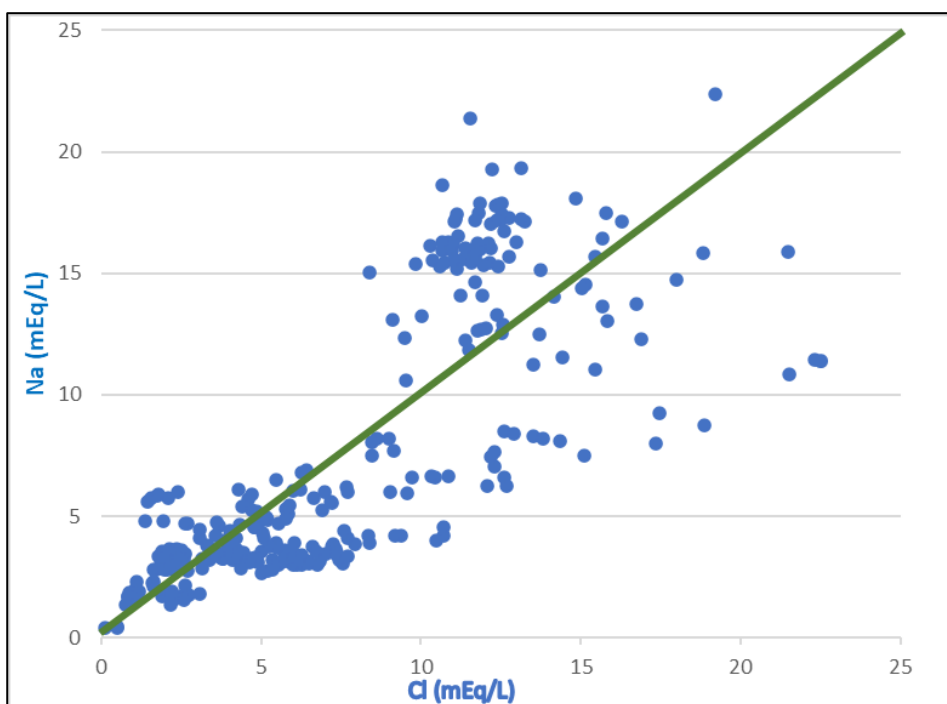


Figure 28: The relationship between sodium and chloride.

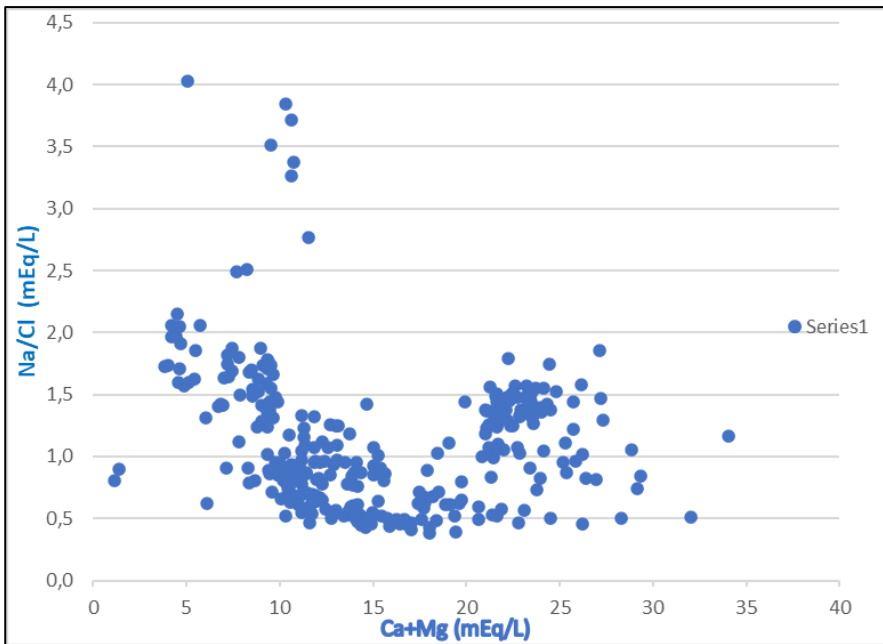


Figure 29: The relationship between the Na/Cl ratio and Ca+Mg (2000-2017).

In terrains which are predominately hard rock, silicate weathering is a common and significant geochemical process controlling the major ion chemistry of groundwater (Garrels and Mackenzie 1967). To test silicate weathering and cation exchange as the dominant controlling process of groundwater quality in the study area, the diagram $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs HCO_3^- was plotted on Figure 30 (Vinnarasi et al., 2021). All samples plotted above the 1:1 equiline indicating the dominance of Ca^{2+} and Mg^{2+} ions over the HCO_3^- ion (Figure 30), which is caused by rock weathering similar to observations by Gugulothu et al., (2022) in another study area. High $\text{Ca}^{2+} + \text{Mg}^{2+}$ relative to HCO_3^- is due to silicate weathering involving reverse ion exchange (Vinnarasi et al., 2021; Gugulothu et al., 2022).

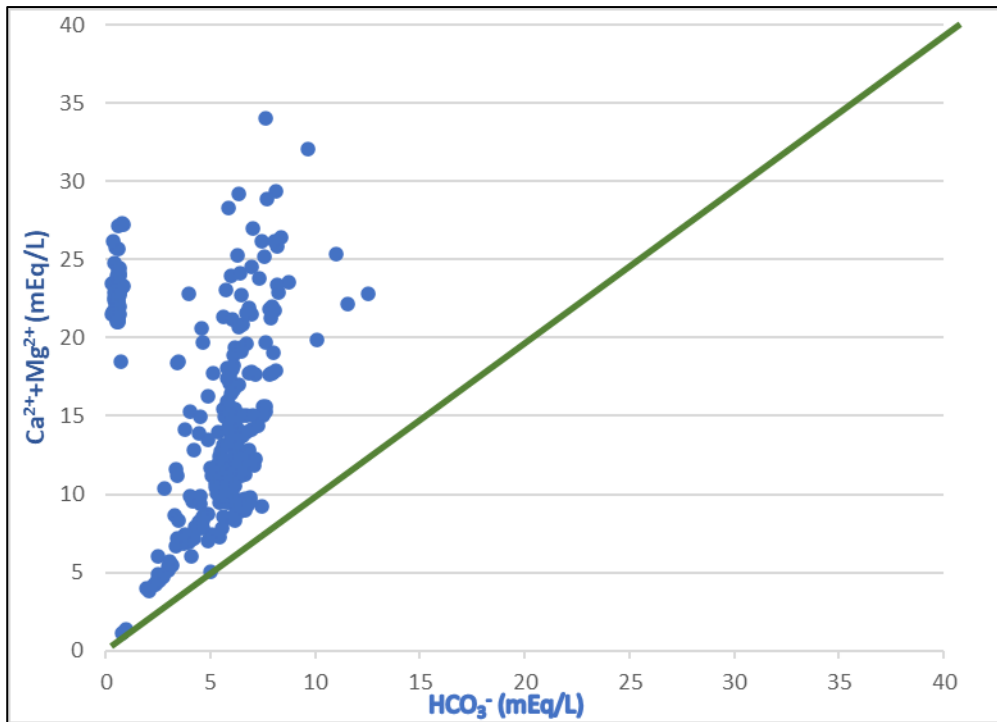


Figure 30: Scatter plots of $Ca^{2+}+Mg^{2+}$ vs HCO_3^- (2000-2017).

4.3.4. Schoeller (1965) ChloroAlkaline Indices (CAIs)

For CAI-I and CAI-II, 166 samples show forward ion exchange, 10 monitoring sites (>50%) dominate this ion exchange (Figure 31, Table 10). These findings suggest that both reverse and forward ion exchange processes have played a significant role in influencing the groundwater, similar to findings by Lalumbe and Kanyerere, (2022b) in Soutpansberg region south of the study area.

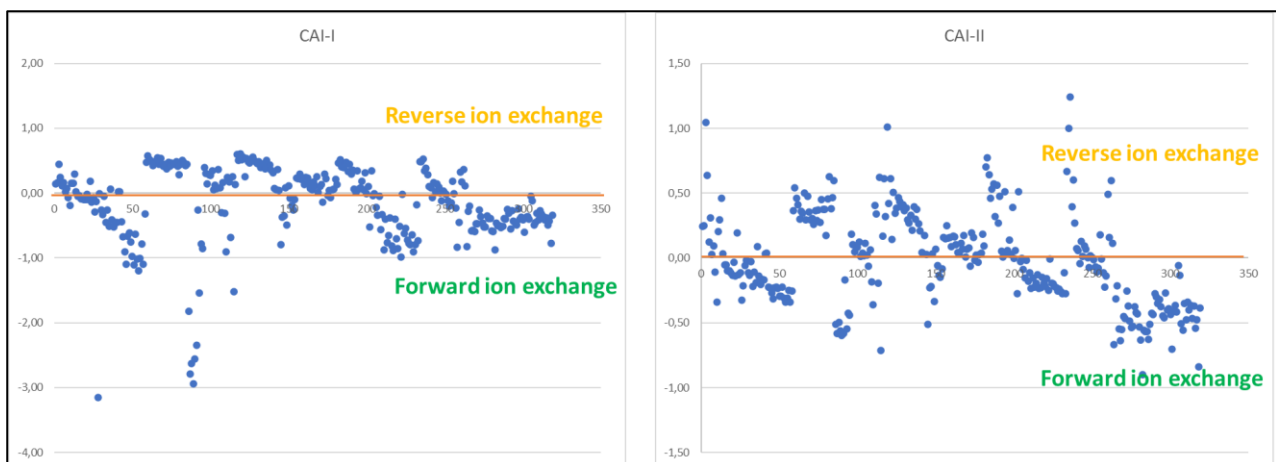


Figure 31: CAI-I and CAI-II plots for all water samples (2000-2017).

Table 10: CAI-I and CAI-II results for all monitoring sites.

Monitoring site (n)	Forward ion exchange (n)	% Forward	% Reverse
ZQMALL2 (29)	16	55%	45%
ZQMBGG1 (4)	4	100%	0%
ZQMBLT2 (25)	22	88%	12%
ZQMBLT3 (27)	0	0%	100%
ZQMGS1 (6)	6	100%	0%
ZQMGT1 (4)	4	100%	0%
ZQMKHK2 (15)	3	20%	80%
ZQMLGN1 (6)	2	33%	67%
ZQMMES1 (29)	1	3%	97%
ZQMMPE1 (5)	3	60%	40%
ZQMSS1 (4)	4	100%	0%
ZQMSWW1 (27)	3	11%	89%
ZQMSWW2 (23)	3	13%	87%
ZQMTBK1 (29)	29	100%	0%
ZQMTBK2 (30)	10	33%	67%
ZQMTUG2 (27)	27	100%	0%
ZQMTUG4 (29)	29	100%	0%

4.3.5. Pearson correlation analysis

Correlation coefficient analysis is commonly used to describe the relationship between two hydrochemical parameters found in groundwater, in terms of similarity and heterogeneity in their origins (Talib et al., 2019, Hagan et al., 2022; Lalumbe et al., 2022b; Gad and El Osta, 2020). However, Hem (1984) warns that it may be unrealistic to expect that any correlation system can be achieved without considering the wide differences in weathering products and weathering rates that characterise similar rock terranes exposed in different climatic environments.

Pearson's correlation coefficient was computed to investigate significant relationships between the hydrochemical parameters (Table 11). Table 12 presents the classification criteria used to describe the relationship between the parameters x and y based on correlation coefficient R. The correlation matrix revealed significant correlations between several parameters, most of which are very strong to strong, and positive.

The EC has a perfect relationship with TDS, which is trivial, since TDS is calculated from EC, and henceforth the correlation of any parameter against EC is the same as against TDS. There is a very strong positive correlation between TDS and Na⁺ (0.77) and Cl⁻ (0.95), and a strong positive correlation between TDS and Ca²⁺ (0.74) this is consistent with the observation made earlier in (Figure 20). There is also a very strong positive correlation of Na⁺ with Cl⁻ (0,80), SO₄²⁻ (0,81), and F⁻ (0,78). This very strong positive association of Na⁺

with Cl^- and SO_4^{2-} together with very strong positive association of TDS with Na^+ and Cl^- has been observed by Lalumbe and Kanyerere (2022b) and is known to indicate high levels of anthropogenic pollution in the groundwater with the elevated Na^+ coming from silicate weathering (Subba Rao et al., 2017; Marghade et al., 2021).

In ZQMTUG2 and ZQMTUG4 the high F^- is strongly associated with high SO_4^{2-} and high Na^+ . Both sites are geothermal springs. The northernmost parts of the Limpopo Province are known to consist of numerous springs, which contain high fluoride concentrations. The occurrence of high F^- , SO_4^{2-} , and Na^+ in groundwater is geogenic, the mineral Villiamite (NaF) may have contributed considerably to the enrichment of these ions (Chibi and Vinnicombe, 1999). Lalumbe and Kanyerere (2022b) also identified high F^- in the geothermal springs and concluded that high F^- is influenced by fluorite minerals associated with igneous and sedimentary rocks in the area.

Table 11: Correlation coefficients of major physicochemical parameters in the study area

	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	F^-	NO_3^-
pH	1											
EC	-0,39	1										
TDS	-0,39	1,00	1									
Ca^{2+}	-0,50	0,74	0,74	1								
Mg^{2+}	0,43	0,27	0,27	0,24	1							
Na^+	-0,53	0,77	0,77	0,42	-0,32	1						
K^+	-0,08	0,51	0,51	0,25	0,27	0,37	1					
Cl^-	-0,38	0,95	0,95	0,65	0,21	0,80	0,52	1				
SO_4^{2-}	-0,70	0,57	0,57	0,52	-0,51	0,81	0,18	0,57	1			
HCO_3^-	0,59	-0,04	-0,04	-0,08	0,78	-0,44	0,19	-0,11	-0,73	1		
F^-	-0,60	0,47	0,47	0,37	-0,57	0,78	0,13	0,46	0,85	-0,68	1	
NO_3^-	0,32	0,03	0,03	0,12	0,62	-0,37	-0,11	-0,10	-0,50	0,47	-0,42	1

*Note all ions are in mg/l

Table 12: Pearson's correlation coefficient classification (Ahemaitihali and Dong, 2022)

r_{xy} Value	Relevance
$r_{xy} = 0$	no association or no correlation
$0 < r_{xy} < 0.25$	very weak correlation
$0.25 < r_{xy} < 0.5$	weak correlation
$0.5 < r_{xy} < 0.75$	strong correlation
$0.75 < r_{xy} < 1$	very strong correlation
$ r_{xy} = 1$	perfect correlation

4.5. Suitability for irrigation

At least 57% of the samples are categorically brackish and 43% are fresh. Although brackish, the TDS values are all below 3000 mg/L and hence all borehole sites based on TDS alone were found to be suitable for irrigation purposes. The SAR, RSC, PI and MH indices calculations show all borehole sites are of moderate to suitable quality for irrigation purposes (Table 13). According to SAR index at least 97,8% of the samples are excellent quality for irrigation, with 2,2% being good quality for irrigation. No borehole site was found to be unsuitable for irrigation, based on SAR. The RSC index calculations are relatively consistent with the SAR, where 96,9% of the samples is suitable quality for irrigation and 2,5% is fair quality for irrigation.

The PI index identified 16% of the samples as suitable for irrigation and 84% moderately suitable for irrigation. The MH index identified 87% of the samples to be suitable for irrigation and 13% unsuitable for irrigation, the unsuitable samples were randomly distributed across all borehole sites except ZQMTUG2 and ZQMTUG4. The %Na assessment identified 21,6% of the water samples to be doubtful for irrigation, these samples come from mainly ZQMTUG2 and ZQMTUG4 sites, which are 100% doubtful for irrigation, and show a consistent trend of poor water quality (Figure 32). Continuous use of high %Na reduces soil permeability, which reduces water flow making the soil hard to plough and unsuitable for seeding development (Sujatha and Reddy, 2003). The KR calculations show 33% of the samples are unsuitable for irrigation. The 106 (33%) samples that are KR unsuitable belong to mainly monitoring sites ZQMGTA1 (75%), ZQMMPE1 (60%), ZQMLGN1 (83%) ZQMALL2 (86%), ZQMTUG2 (100%), and ZQMTUG4 (100%) (Figures 33 and 34).

Table 13: Summary of water quality indices classification for irrigation suitability assessment

Indices	Range (mEq/L)	Range (%)	Class	Reference	Number of Samples	Unsuitable groundwater Sites
SAR (Eq7)	<10 10-18 18-26 >26		Excellent Good Fair Unsuitable	Richards (1954)	308/319 (97,8%) 7/319 (2,2%) 0 0	N/A
RSC (Eq8)	<1.25 1.25-2.5 >2.5		Suitable Fair Unsuitable	Eaton (1950)	309/319 (97%) 8/319 (2,5%) 2/319 (0,6%)	N/A
%Na (Eq9)		<20 20-40 >40-60 >60-80 >80	Excellent Good Permissible Doubtful Unsuitable	Wilcox (1948, 1955)	15/319 (4,7%) 155/319 (48,6%) 80/319 (25,1%) 69/319 (21,6%) 0	Doubtful: ZQMTUG2 (100%) ZQMTUG4 (100%)
PI (Eq10)		>75 75-25 <25	Suitable Moderate Unsuitable	Doneen (1964)	50/319 (16%) 269/319 (84%) 0	N/A
MH (Eq11)		<50 >50	Suitable Unsuitable	Reeve et al., (1954)	277/319 (87%) 42/319 (13%)	ZQMGTA1 (75%) ZQMLGN1 (50%)
KR (Eq12)		<1* >1*	Suitable Unsuitable	Kelly, (1940)	213/319 (67%) 106/319 (33%)	ZQMALL2 (86%) ZQMGS1 (83%) ZQMGTA1 (75%) ZQMMPE1 (60%) ZQMLGN1 (83%) ZQMTUG2 (100%) ZQMTUG4 (100%)

*Not a percent, but a ratio

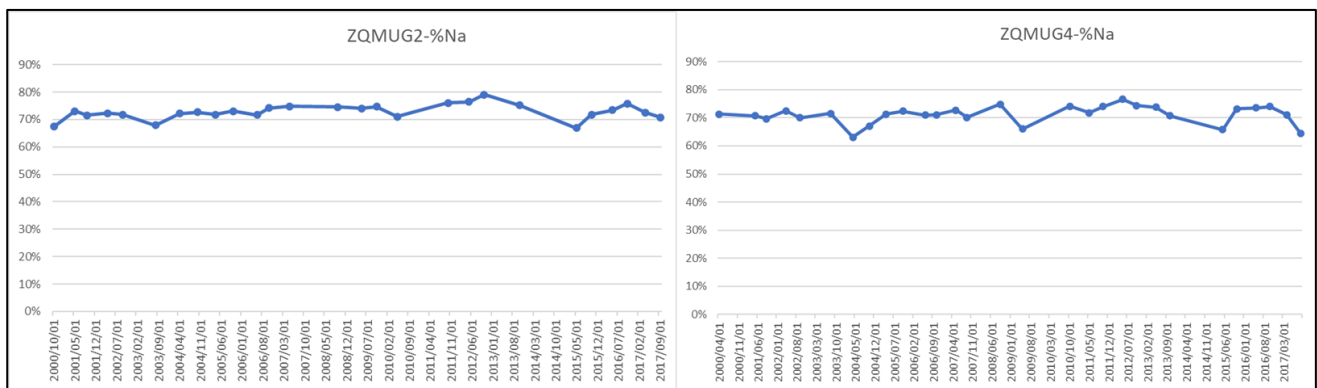


Figure 32: %Na trend for ZQMTUG2 and ZQMTUG4.

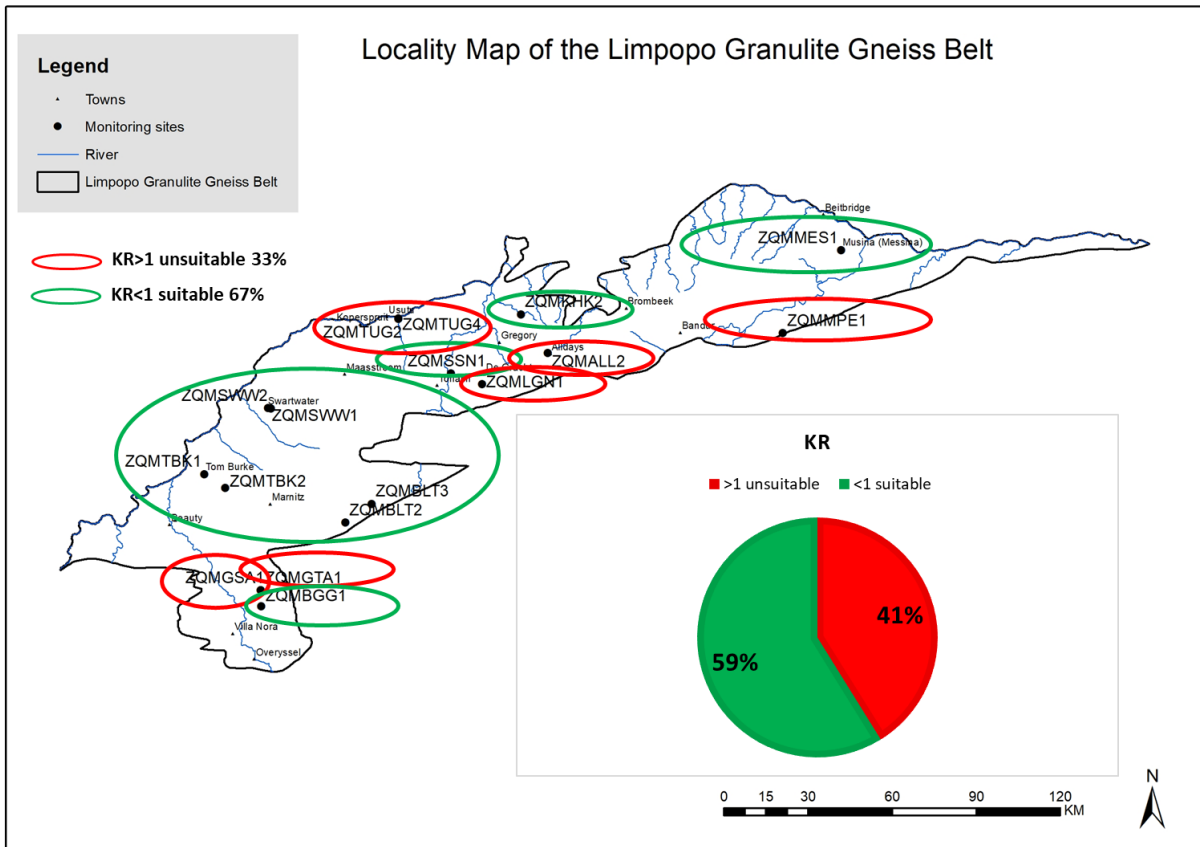


Figure 33: Spatial distribution of KR.

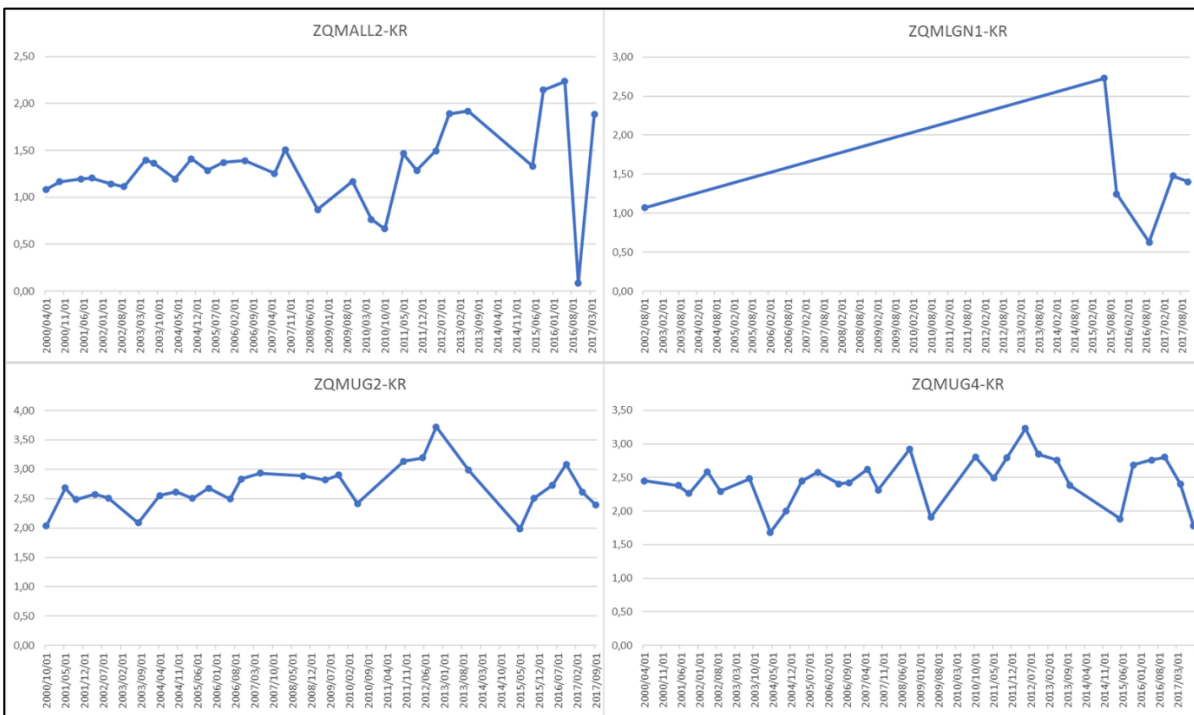


Figure 34: ZQMALL2, ZQMLGN, ZQMUG2 and ZQMUG4 Kelly's Ratio trend.

4.6. Suitability for drinking

Based on $\text{NO}_3^- + \text{NO}_2^-$ expressed as N concentrations, which is one of the essential priority chemicals to assess when investigating drinking water suitability (WHO, 2007). The World Health Organization (WHO, 2011b) guideline value for nitrate in drinking-water is ≤ 11 mg/L expressed as N, which is adequate to protect bottle-fed infants, and hence adequate for other population groups including pregnant women (WHO, 2016).

The fourth dominant anion was determined earlier in the chapter, to be $\text{NO}_3^- + \text{NO}_2^-$ with an average concentration of 25 mg/L. Over 71% of the samples has concentrations of $\text{NO}_3^- + \text{NO}_2^-$ higher than the WHO and SANS241 recommended guideline value of ≤ 11 mg/L (Tables 14 and 15).

Table 14: Summary of drinking water suitability assessment per borehole.

Monitoring site (n)	pH >8,5	$\text{NO}_3^- + \text{NO}_2^-$ (N) >11 mg/L	TDS >1000 mg/L	Na^+ >200 mg/L	Mg^{2+} >70 mg/L	Cl^- >300 mg/L	SO_4^{2-} >200 mg/L	F >1,5 mg/L	Ca >150 mg/L
ZQMALL2 (29)	8,2	38	1711	303	107	494	83	1,28	108
ZQMBGG1 (4)	8,6	53	845	98	76	121	61	0,70	76
ZQMBLT2 (25)	8,1	20	509	65	30	78	8	0,40	54
ZQMBLT3 (27)	8,1	65	1113	72	114	217	30	0,77	119
ZQMGS1 (6)	8,5	37	747	129	49	59	44	1,37	57
ZQMGT1 (4)	8,7	20	649	114	40	104	29	0,57	41
ZQMKHK2 (15)	8,2	68	881	50	88	86	34	0,53	98
ZQMLGN1 (6)	8,5	13	1175	197	89	355	77	0,47	57
ZQMMES1 (29)	8,2	12	1067	83	101	239	155	0,57	121
ZQMMPE1 (5)	8,5	14	929	182	93	210	91	1,16	32
ZQMSSN1 (4)	8,5	35	1010	150	82	203	47	2,67	72
ZQMSWW1 (27)	8,3	26	832	77	71	155	42	0,69	82
ZQMSWW2 (23)	8,1	36	1425	148	128	351	101	0,78	121
ZQMTBK1 (29)	8,2	12	693	81	59	88	29	0,52	64
ZQMTBK2 (30)	8,2	24	1120	131	96	266	77	0,49	95
ZQMTUG2 (spring) (27)	7,6	0,1	1507	373	1	398	491	4,90	122
ZQMTUG4 (spring) (29)	7,5	0,1	1565	382	1	432	525	4,99	136

Table 15: Summary of drinking water suitability assessment per borehole.

Parameter	Guideline value WHO, 2017	Guideline value SANS241, 2015	Unsuitable Samples	Unsuitable Sites
pH	6,5-8,5	5-9,7	11,6% based on WHO, 2017	ZQMGG1 (75%) ZQMGT1 (75%) ZQMLGN1 (50%)
NO ₃ ⁻ +NO ₂ ⁻ Expressed as N	≤11 mg/L NO ₃ -N	≤11 NO ₃ -N ≤0,9 NO ₂ -N	71,8% based on both guidelines	ZQMALL2 (96,5%) ZQMBGG1 (100%) ZQMBLT2 (92%) ZQMBLT3 (100%) ZQMGS1 (100%) ZQMGT1 (100%) ZQMKHK2 (100%) ZQMLGN1 (67%) ZQMMES1 (24%) ZQMMPE1 (60%) ZQMSSN1 (100%) ZQMSSW1 (100%) ZQMSSW2 (96%) ZQMTBK1 (90%) ZQMTBK2 (97%)
TDS	<1000	≤1200	40% based on SANS241, 2015	ZQMALL2 (93%) ZQMLGN1 (50%) ZQMMES1 (69%) ZQMMPE1 (60%) ZQMSSN1 (75%) ZQMSWW2 (61%) ZQMTBK2 (100%) ZQMTUG2 (100%) ZQMTUG4 (100%)
Na ⁺	<200	≤200	28,5% based on both guidelines	ZQMALL2 (90%) ZQMLGN1 (50%) ZQMMPE1 (60%) ZQMTUG2 (96%) ZQMTUG4 (100%)
SO ₄ ²⁻	<200	≤250	18% based on WHO, 2017	ZQMTUG2 (93%) ZQMTUG4 (90%)
F ⁻	<1,5	≤1,5	20% based on SANS241, 2015	ZQMSSN1 (100%) ZQMTUG2 (93%) ZQMTUG4 (90%)
Ca ²⁺	<200	≤150	8,5% based on SANS241, 2015	None
Mg ²⁺	<100	≤70	52% based on SANS241, 2015	ZQMALL2 (96%) ZQMBGG1 (75%) ZQMBLT3 (100%) ZQMKHK2 (80%) ZQMLGN1 (67%) ZQMMES1 (83%) ZQMMPE1 (60%) ZQMSSN1 (100%) ZQMSWW1 (52%) ZQMSWW2 (96%) ZQMTBK2 (70%)
Cl ⁻	250	≤300	37% based on SANS241, 2015	ZQMALL2 (93%) ZQMLGN1 (67%) ZQMMPE1 (50%) ZQMSWW2 (56,5%) ZQMTUG2 (92,6%) ZQMTUG4 (100%)

All units expressed in mg/L except pH.

The trends of the 15 borehole sites with significantly high $\text{NO}_3^- + \text{NO}_2^-$ concentrations are presented in Figures 35 and 36. There is no linear continuous increase observed for $\text{NO}_3^- + \text{NO}_2^-$ over the time presented. Starting northeast of the study area, we see ZQMMES1 located in Musina, showing major increase in $\text{NO}_3^- + \text{NO}_2^-$ from around 2012 rising as high as 51 mg/L before dropping significantly to levels below 11 mg/L. South of ZQMMES1 we have ZQMMPE1 which was monitored from 2015, a slight increase above 11 mg/L is observed for the wet and dry season of 2016 plus the end of wet season 2017, which was followed by a significant drop end of dry season 2017. A similar trend to ZQMMPE over 2015 and 2016 can be observed at ZQMBBG1, ZQMLGN1, ZQMGTA1, ZQMGS1, ZQMKHK2 and ZQMSSN1. This increase in $\text{NO}_3^- + \text{NO}_2^-$ levels correlate with the reduced percentage rainfall seasons of 2014, 2015 and 2016. However, ZQMALL2 which is seen to fluctuate significantly pre drought season, shows no fluctuation over this period, only an anomalous drop for August 2016 stands out. The lower percentage of normal rainfall for the 2016 season (Figure 37) didn't have effect on $\text{NO}_3^- + \text{NO}_2^-$ for monitoring sites ZQMBLT2 and ZQMBLT3, which fall within the same drainage area A63A. The levels of $\text{NO}_3^- + \text{NO}_2^-$ at ZQMBLT3 are so significantly high, they rose to 109 mg/L in August 2009, and have been consistently fluctuating between 60 and 80 mg/L between 2010 and 2017. ZQMSWW1 has been consistently fluctuating between 20 and 40 mg/L, while adjacently ZQMSWW2 has been on a decline from around 19 mg/L in 2010 to 8 mg/L in 2017.

Wetter seasons are more likely to recharge groundwater and improve the quality through dilution, while in some instances increased rainfall intensity could mean flooding of pit latrine and wastewater treatment plants overflow into the environment, contaminating rivers and boreholes (Howard et al., 2016). The spatial distribution of $\text{NO}_3^- + \text{NO}_2^-$ is presented in Figure 38. The source of high $\text{NO}_3^- + \text{NO}_2^-$ in this area and the greater Limpopo province is widely known to be associated with fertilisers and pit latrines from the rural human settlements dominated by irrigation land use. The strong positive association of nitrate+nitrite and magnesium, is observed in borehole sites ZQMALL2, ZQMBLT3, ZQMKHK2, ZQMLGN1, ZQMES1, ZQMSSN1, ZQMSWW1, ZQMSWW2, ZQMTBK1, and ZQMTBK2, which suggests water quality is influenced by magnesium nitrate fertilisers.

The study area covers several rural communities and irrigated lands. The groundwater use is associated with irrigation, livestock watering, and schedule1 uses. A number of communities, such as Alldays, Beauty, Maasstroom, Swartwater, Tom Burke, Marnitz, Musina and others, rely on groundwater as main source of water.



Figure 35: NO₃+NO₂ as in N (mg/L) trend for borehole sites: ZQMALL2, ZQMBGG1, ZQMBLT, ZQMBLT3, ZQMGA1, ZQMGA1, ZQMKHK2 and ZQMLGN1

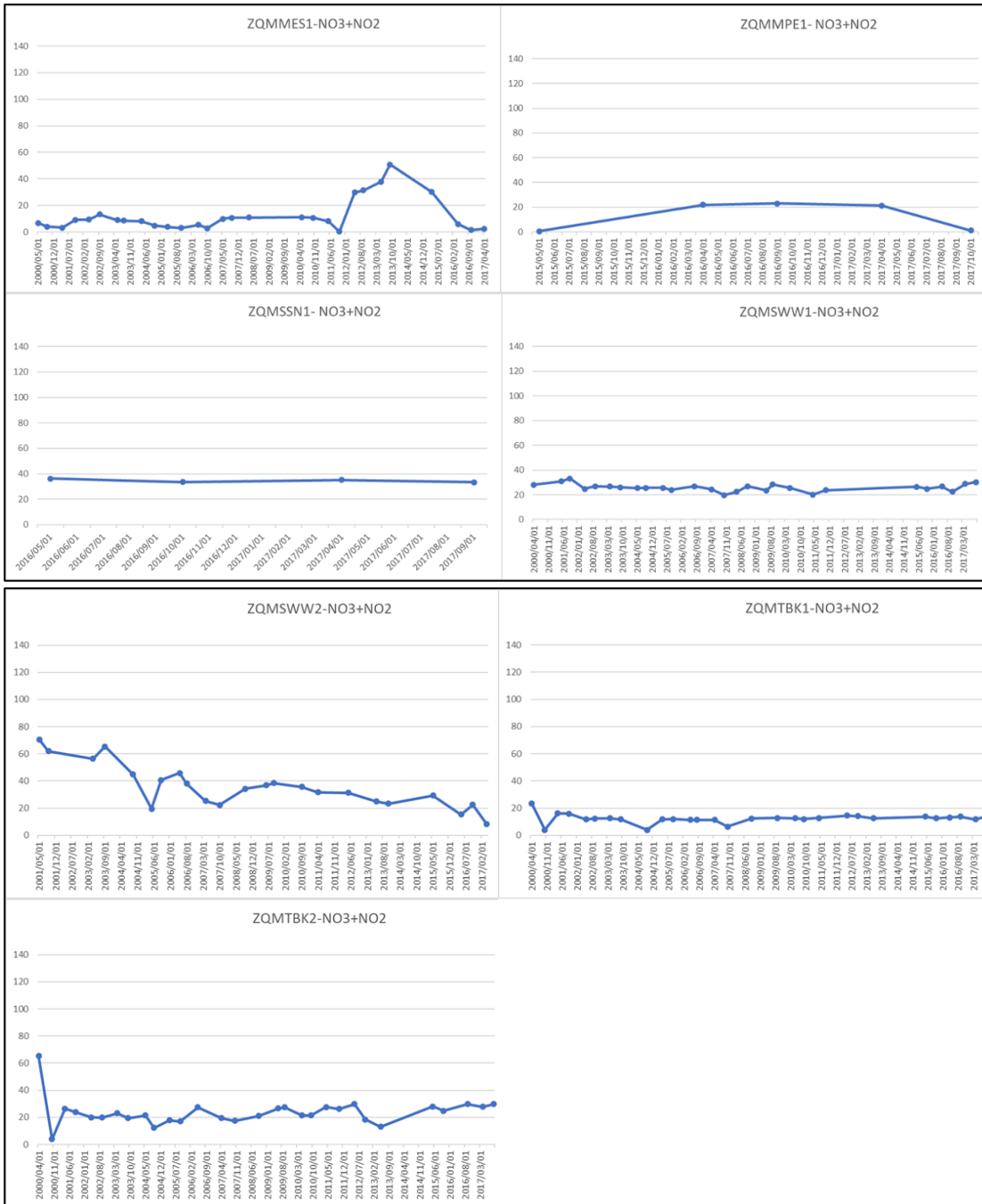


Figure 36: NO₃+NO₂ as in N (mg/L) trend for borehole sites: ZQMME1, ZQMMPE1, ZQMSSN, ZQMSWW1, ZQMSWW2, ZQMTBK1 and ZQMTBK2.

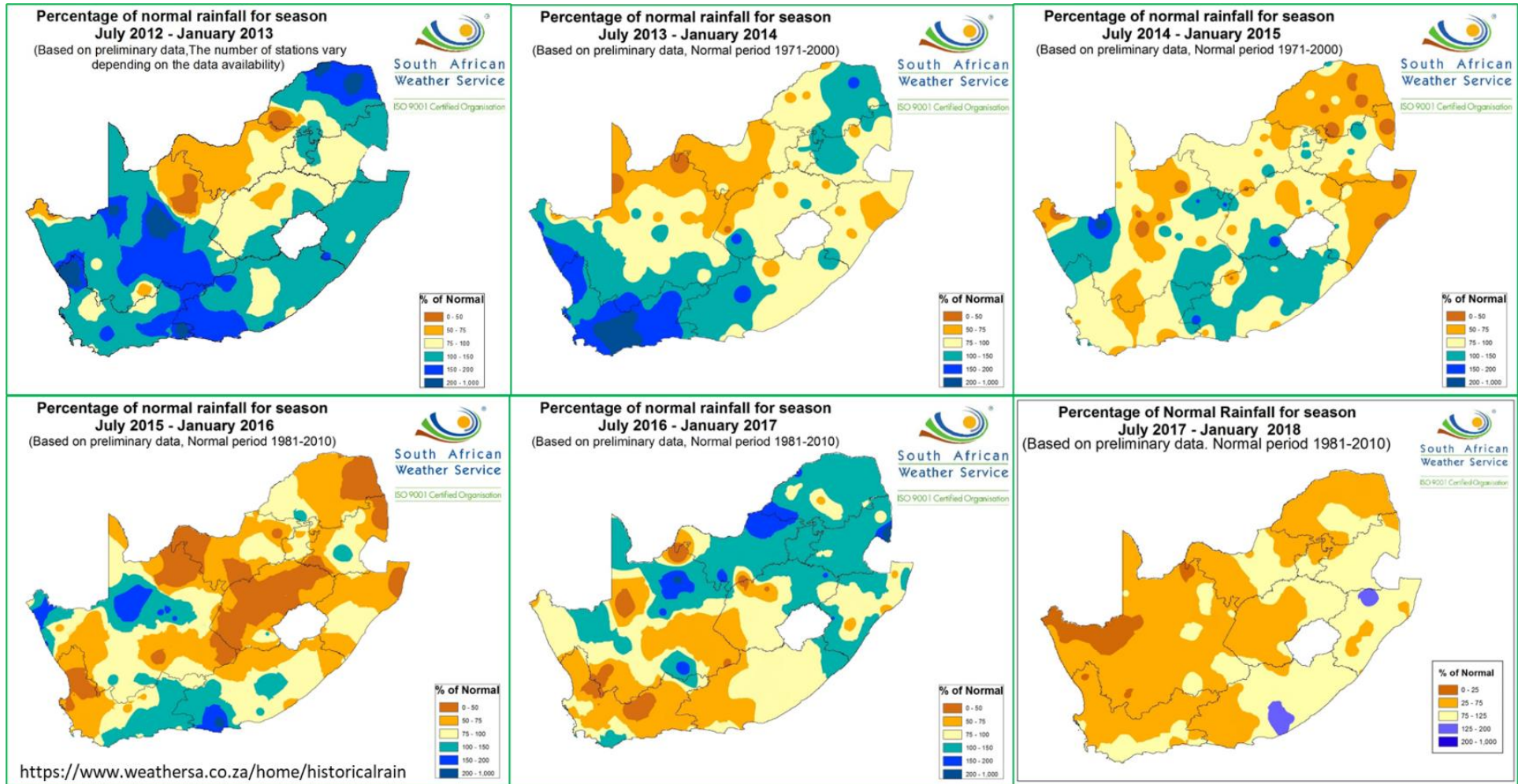


Figure 37: Historical percentage of normal rainfall for the season map.

(2015) and SAN241, (2015). Epidemiological evidence shows that concentrations above 1,5 mg/L carry an increasing risk of dental fluorosis and that progressively higher concentrations intake leads to increasing risks of skeletal fluorosis (WHO, 2011a).

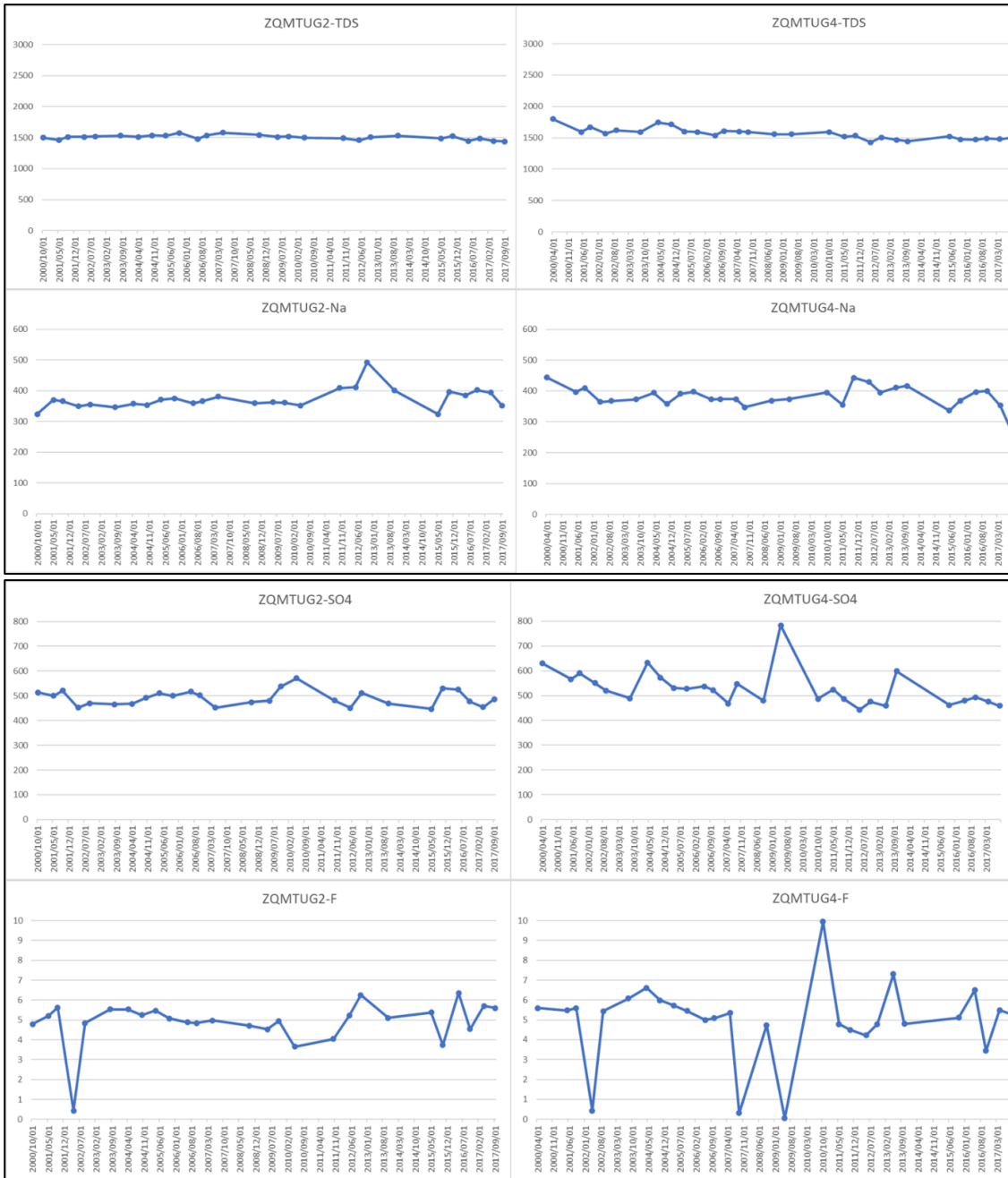


Figure 39: TDS, Na⁺, SO₄²⁻ and F trends for borehole ZQMTUG2 and ZQMTUG4.

The spatial distribution of F⁻ shows that 14 out of 17 sites have F⁻ concentrations that are suitable for drinking (Figure 40). The average fluoride concentrations for ZQMSS1, ZQMTUG2 and ZQMTUG4 are 2,7 mg/L; 4,9 mg/L and 5,0 mg/L, respectively.

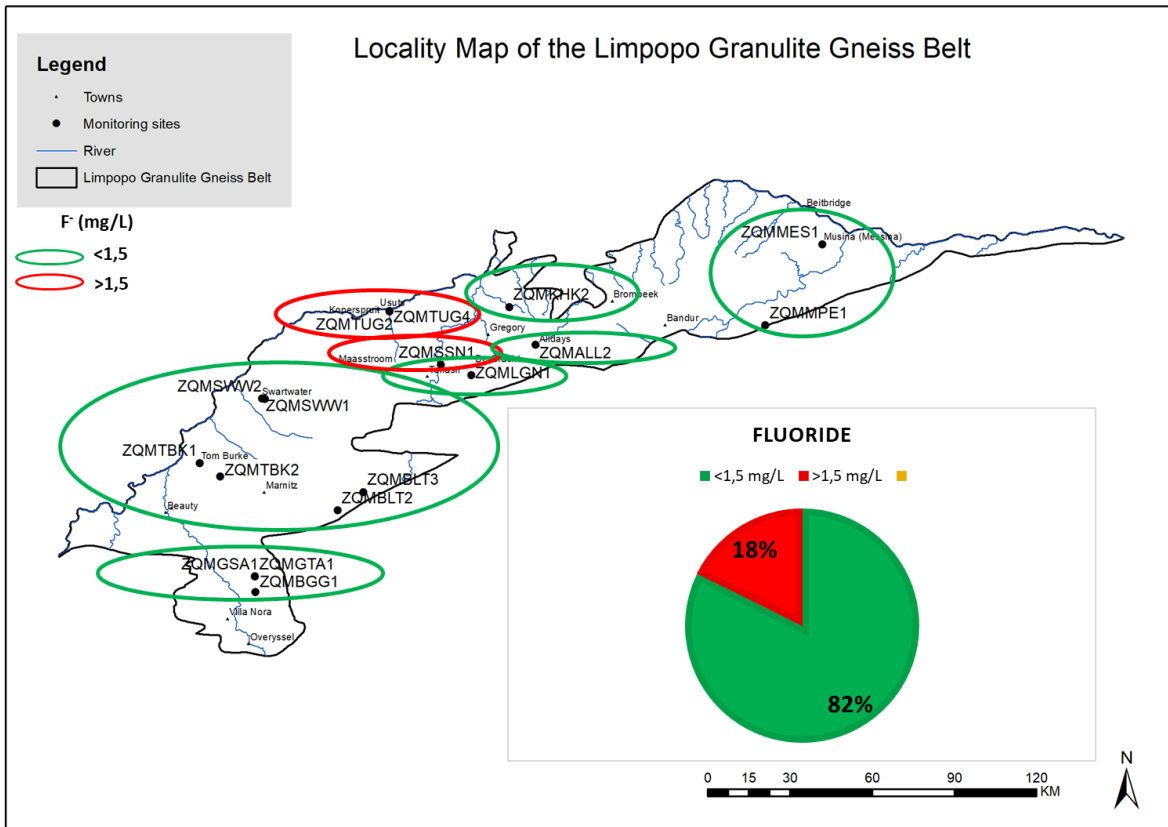


Figure 40: Spatial distribution of F⁻.

4.7. Summary of results per borehole

ZQMALL2 (n=29)

In ZQMALL2, 29 samples were analysed between April 2000 and March 2017. The water pH ranges from 7,89 to 8,69; with the pH average of 8,19, the water is hence, weakly alkaline. The TDS concentration of the water ranges from 362 mg/L to 2129 mg/L; with the TDS average concentration of 1711 mg/L, 97% of the water samples are brackish. The cation dominance in mg/L is in this order: $\text{Na}^+(303) > \text{Ca}^{2+}(108) \geq \text{Mg}^{2+}(107) > > \text{K}^+(11)$, while the anions dominance in mg/L is in this order: $\text{Cl}^-(494) > \text{HCO}_3^-(445) > \text{SO}_4^{2-}(83) > \text{NO}_2^- + \text{NO}_3^- (38) > \text{F}^-(1,28)$.

On the Piper diagram, the water is between Na-Cl type (zone 7) and mixed type (zone 9), dominated by Na-Cl- HCO_3 ion water facies. Zone 7 is known to indicate halite dissolution (Ravikumar and Somashekar, 2015). Mixed Zone 9 with Ca- HCO_3 water type, indicates shallow, recently recharged groundwater. Furthermore, the maximum nitrate+nitrite of 70,6 mg/L is observed alongside high magnesium at 134,8 mg/L. The strong positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 5,87 mEq/L, the water is excellent for irrigation. The site has average RSC index of -2,70 mEq/L, which is also suitable for irrigation. The average for Permeability index is 68%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 46% and hence suitable for irrigation. Moreover, the %Na index average of 56% gives the water a “permissible for irrigation” classification. The average Kelly’s Ratio is 1,32, indicating higher sodium relative to calcium plus magnesium in over 86% of the samples.

The brackish nature of this water emanating from 1711 mg/L average TDS, makes it unsuitable for drinking purposes. The chloride, sodium, magnesium and nitrate+nitrite concentrations are also too high and unsuitable for drinking purposes at 494 mg/L, 303 mg/L, 107 mg/L, and 38 mg/L, respectively. The nitrate+nitrite concentrations are ranging from 0,47 mg/L recorded in October 2016, to 70,6 mg/L recorded in May 2011. Except for the anomalous high and low, the nitrate+nitrite concentrations have been fluctuating between 20 mg/L and 40 mg/L, over the sampling period, and are extremely unsafe for human consumption.

ZQMBGG1 (n=4)

In ZQMBGG1, only four samples were analysed in 2016 (2) and 2017 (2). The water pH ranges from 8,50 to 8,70, with the pH average of 8,62 the water is hence, alkaline. The TDS concentration of the water ranges from 752 mg/L to 919 mg/L, with the TDS average concentration of 845 mg/L. 100% of the water samples are fresh. The cation dominance in mg/L is in this order: $\text{Na}^+(98) > \text{Mg}^{2+}(76) \geq \text{Ca}^{2+}(76) >> \text{K}^+(0,8)$, while the anions dominance in mg/L is in this order: $\text{HCO}_3^-(319) > \text{Cl}^-(121) > \text{SO}_4^{2-}(61) > \text{NO}_2^- + \text{NO}_3^-(53) > \text{F}^-(0,7)$.

On the Piper diagram, the water is predominately Ca-Mg- HCO_3 type (zone 5), a signature dominated by Ca-Mg-Cl- HCO_3 ion water facies, indicate shallow, recently recharged groundwater, recharging water with temporary hardness rainwater.

Based on the calculated SAR average value of 2,30 mEq/L, this water is excellent for irrigation. The site has average RSC index of -1,82 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 58%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 47% and hence suitable for irrigation. Moreover, the %Na index average of 38% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,62 which is suitable for irrigation purposes.

While the water is of freshwater quality based on the average TDS of 845 mg/L, for drinking water suitability assessment, this water fails the pH suitability which is $>8,50$. The magnesium and nitrate+nitrite concentrations are also unsuitable for drinking purposes at 76 mg/L, and 53 mg/L, respectively. The nitrate+nitrite concentrations are ranging from 44,4 mg/L recorded in September 2016, to 62,4 mg/L recorded in October 2017. All four water samples have significantly high nitrate+nitrite concentrations, more than four times the limit, which is a health hazard.

ZQMBLT2 (n=25)

In ZQMBLT2, 25 samples were analysed between April 2000 and March 2017. The water pH ranges from 7,43 to 8,70, with the pH average of 8,14 the water is weakly alkaline. The TDS concentration of the water ranges from 319 mg/L to 1157 mg/L, with the TDS average concentration of 509 mg/L, 88% of the water samples are fresh. The cation dominance in mg/L is in this order $\text{Na}^+(65) > \text{Ca}^{2+}(54) > \text{Mg}^{2+}(30) > \text{K}^+(2,7)$, while the anions dominance in mg/L is in this order $\text{HCO}_3^-(212) > \text{Cl}^-(78) > \text{NO}_2^- + \text{NO}_3^-(20) > \text{SO}_4^{2-}(8) > \text{F}^-(0,4)$.

On the Piper diagram, the water is predominately Ca-Mg- HCO_3 type (zone 5), a signature dominated by Ca-Mg-Cl- HCO_3 ion water facies, indicating shallow, recently recharged groundwater, recharging water with temporary hardness rainwater. There is no association observed between high nitrate+nitrite and magnesium.

Based on the calculated SAR average value of 1,93 mEq/L, this water is excellent for irrigation. The site has an average RSC index of -0,52 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 69%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 31% and hence suitable for irrigation. Furthermore, the %Na index average of 40% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,68 which is suitable for irrigation purposes.

While the water is of freshwater quality based on the average TDS of 509 mg/L, for drinking water suitability assessment, this water fails only the nitrate+nitrite concentrations, which are slightly high and unsuitable for drinking purposes at an average of 20 mg/L. The nitrate+nitrite concentrations are ranging from 5,6 mg/L recorded in February 2013, to 29,7 mg/L recorded in June 2009. The nitrate+nitrite concentrations have been stable in the 20 mg/L levels between September 2013 and March 2017.

ZQMBLT3 (n=27)

In ZQMBLT3, 27 samples were analysed between April 2000 and March 2017. The water pH ranges from 7,77 to 8,60, with the pH average of 8,09 the water is weakly alkaline. The TDS concentration of the water ranges from 349 mg/L to 1266 mg/L, with the TDS average concentration of 1113 mg/L, 85% of the water samples are brackish. The cation dominance in mg/L is in this order $\text{Ca}^{2+}(119) > \text{Mg}^{2+}(114) > \text{Na}^+(72) \gg \text{K}^+(6,6)$, while the anions dominance in mg/L is in this order $\text{HCO}_3^-(351) > \text{Cl}^-(217) > \text{NO}_2^- + \text{NO}_3^-(65) > \text{SO}_4^{2-}(30) > \text{F}^- (0,77)$.

On the Piper diagram, the water is mainly mixed type (zone 9) and with a few samples being Ca-Mg- HCO_3 type (zone 5). The Ca-Mg-Cl- HCO_3 ion water facies indicate shallow, recently recharged groundwater, recharging with temporary hardness rainwater. The maximum nitrate+nitrite of 109 mg/L is observed alongside high magnesium at 138 mg/L. The strong positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 1,36 mEq/L, this water is excellent for irrigation. The site has average RSC index of -5,08 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 40%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 46% and hence suitable for irrigation. Furthermore, the %Na index average of 24% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,30 which is suitable for irrigation purposes.

The brackish nature of this water emanating from 1113 mg/L average TDS, makes it unsuitable for drinking purposes. The magnesium and nitrate+nitrite concentrations are also too high and unsuitable for drinking purposes at 114 mg/L, and 65 mg/L, respectively. The nitrate+nitrite concentrations are significantly high, ranging from 36 mg/L recorded in April 2000; to 109 mg/L recorded September 2009. The nitrate+nitrite concentrations have been fluctuating between 20 mg/L and 40 mg/L since March 2010, soon after the highest concentration was recorded.

ZQMGS1 (n=6)

In ZQMGS1, only six samples were analysed in 2002 (1), 2015 (1), 2016 (2) and 2017 (2). The water pH ranges from 8,01 to 8,70, with the pH average of 8,52 the water is weakly alkaline. The TDS concentration of the water ranges from 698 mg/L to 888 mg/L, with the TDS average concentration of 747 mg/L, 100% of the water samples are fresh. Cation dominance in mg/L is in this order $\text{Na}^+(129) > \text{Ca}^{2+}(57) > \text{Mg}^{2+}(49) > \text{K}^+(6,3)$, while anions dominance in mg/L is in this order $\text{HCO}_3^-(359) > \text{Cl}^-(59) > \text{NO}_2^- + \text{NO}_3^-(37) > \text{SO}_4^{2-}(44) > \text{F}^-(1,37)$.

On the Piper diagram, the water is predominately Ca-Mg- HCO_3 type (zone 5), a signature dominated by Ca-Mg- HCO_3 ion water facies, indicating shallow, recently recharged groundwater, recharging water with temporary hardness rainwater.

Based on the calculated SAR average value of 3,57 mEq/L, this water is excellent for irrigation. The site has an average RSC index of 0,94 mEq/L, which is suitable for irrigation. The average for the Permeability Index (PI) is 76%, which is suitable for irrigation. The Magnesium Hazard (MH) index average is 42% and hence suitable for irrigation. Furthermore, the %Na index average of 54% gives the water a "permissible for irrigation" classification. The average Kelly's Ratio calculation is 1,41 which is unsuitable for irrigation purposes.

While the water is of freshwater quality based on the average TDS of 747 mg/L, for drinking water suitability assessment, this water fails the pH and nitrate+nitrite concentrations, which are high and unsuitable for drinking purposes at 8,52 and 37 mg/L, respectively. The water pH ranges from 8,01 recorded in August 2002; to 8,70 recorded in October 2017. The nitrate+nitrite concentrations are ranging from 22 mg/L recorded in October 2017, to 53 mg/L recorded August 2002. The nitrate+nitrite concentrations have been fluctuating between 20 mg/L and 40 mg/L between 2015 and 2017.

ZQMGTA1 (n=4)

In ZQMGTA1, only four samples were analysed in 2002 (1) 2016 (2), and 2017(1). The water pH ranges from 8,46 to 8,80; with a pH average of 8,73 the water is alkaline. The TDS concentration of the water ranges from 551 mg/L to 926 mg/L, with the TDS average concentration of 649 mg/L, 100% of the water samples are fresh. Cation dominance in mg/L is in this order $\text{Na}^+(114) > \text{Ca}^{2+}(41) > \text{Mg}^{2+}(40) > \text{K}^+(3,5)$, while anions dominance in mg/L is in this order $\text{HCO}_3^-(287) > \text{Cl}^-(104) > \text{NO}_2^- + \text{NO}_3^-(20) > \text{SO}_4^{2-}(29) > \text{F}^-(0,57)$.

On the Piper diagram, the water is mixed type (zone 9), dominated by Na-Cl-HCO₃ ion water facies.

Based on the calculated SAR average value of 3,86 mEq/L, this water is excellent for irrigation. The site has an average RSC index of 0,92 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 85%, which is suitable for irrigation. The Magnesium Hazard (MH) index average is 54% and hence unsuitable for irrigation. Furthermore, the %Na index average of 60% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 1,56 which is unsuitable for irrigation purposes.

While the water is of freshwater quality based on the average TDS of 649 mg/L, for drinking water suitability assessment, this water fails the pH and nitrate+nitrite concentrations, which are unsuitable for drinking purposes at 8,73 and 20 mg/L, respectively. The water pH ranges from 8,46 recorded in October 2002; to 8,80 recorded in April 2016. The nitrate+nitrite concentrations are ranging from 16,5 mg/L recorded in April 2016, to 26,3 mg/L recorded in October 2002. The limited data shows nitrate+nitrite concentrations have been stable at around 20 mg/L during the sampling period.

ZQMKHK2 (n=15)

In ZQMKHK2, 15 samples were analysed between April 2002 and April 2017. The water pH ranges from 7,52 to 8,70, with the pH average of 8,18 the water is weakly alkaline. The TDS concentration of the water ranges from 525 mg/L to 1108 mg/L, with the TDS average concentration of 880 mg/L, 73% of the water samples are fresh. Cation dominance in mg/L is in this order $\text{Ca}^{2+}(98) > \text{Mg}^{2+}(88) > \text{Na}^+(50) > \text{K}^+(2,9)$, while anions dominance in mg/L is in this order $\text{HCO}_3^-(335) > \text{Cl}^-(86) > \text{NO}_2^- + \text{NO}_3^-(68) > \text{SO}_4^{2-}(34) > \text{F}^-(0,53)$.

On the Piper diagram, the water is distinctively Ca-Mg- HCO_3 type (zone 5), dominated by Ca-Mg-Cl- HCO_3 ion water facies, indicate shallow, recently recharged groundwater, recharging water with temporary hardness rainwater. The maximum nitrate+nitrite of 104 mg/L is observed alongside high magnesium at 107 mg/L. The strong positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 1,11 mEq/L, this water is excellent for irrigation. The site has average RSC index of -3,18 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 42%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 44% and hence suitable for irrigation. Furthermore, the %Na index average of 21% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,29 which is suitable for irrigation purposes.

While the water is of freshwater quality based on the average TDS of 880 mg/L, for drinking water suitability assessment, this water fails the magnesium and nitrate+nitrite concentrations, which are unsuitable for drinking purposes at 88 mg/L, and 68 mg/L, respectively. The nitrate+nitrite concentrations, which are more than five times higher than WHO and SANS241 recommended guideline value, are the single most significant unsuitability for drinking purposes. The nitrate+nitrite concentrations range from 13,1 mg/L recorded in September 2010, to 104 mg/L recorded in September 2009. The nitrate+nitrite concentrations have been fluctuating around 80 mg/L levels between April 2011 and April 2017.

ZQMLGN1 (n=6)

In ZQMLGN1, only six samples were analysed in 2015 (2) 2016 (2) and 2017 (2). The water pH ranges from 7,90 to 8,82, with the pH average of 8,52 the water is alkaline. The TDS concentration of the water ranges from 508 mg/L to 1757 mg/L, with the TDS average concentration of 1175 mg/L, 67% of the water samples are brackish. Cation dominance in mg/L is in this order $\text{Na}^+(197) > \text{Mg}^{2+}(89) > \text{Ca}^{2+}(57) > \text{K}^+(11)$, while anions dominance in mg/L is in this order $\text{Cl}^-(355) > \text{HCO}_3^-(319) > \text{SO}_4^{2-}(77) > \text{NO}_2^- + \text{NO}_3^-(13) > \text{F}^-(0,47)$.

On the Piper diagram, the water is mixed type (zone 9), dominated by Na-Cl-HCO₃ ion water facies. The maximum nitrate+nitrite of 18,8 mg/L is observed alongside high magnesium at 110 mg/L. The strong positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 4,75 mEq/L, this water is excellent for irrigation. The site has average RSC index of -1,44 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 74%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 54% and hence unsuitable for irrigation. Furthermore, the %Na index average of 57% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 1,43 which is unsuitable for irrigation purposes.

For drinking water suitability assessment, the brackish nature of this water emanating from 1175 mg/L average TDS, makes it unsuitable for drinking purposes. The chloride, sodium, magnesium, and nitrate+nitrite concentrations are also too high and unsuitable for drinking purposes at 355 mg/L, 319 mg/L, 89 mg/L, and 13 mg/L, respectively. The nitrate+nitrite concentrations are ranging from 2,1 mg/L recorded in May 2015, to 18,8 mg/L recorded in May 2016. The nitrate+nitrite concentrations have been stable in the 18 mg/L levels between October 2015, and April 2017; which was then followed by a decline down to 6,6 mg/L in September 2017.

ZQMME1 (n=29)

In ZQMME1, 29 samples were analysed between May 2000 and October 2017. The water pH ranges from 7,64 to 8,70, with the pH average of 8,20 the water is weakly alkaline. The TDS concentration of the water ranges from 287 mg/L to 1441 mg/L, with the TDS average concentration of 1067 mg/L, 69% of the water samples are brackish. Cation dominance in mg/L is in this order Ca^{2+} (121)> Mg^{2+} (100) Na^+ (83)> K^+ (5), while anions dominance in mg/L is in this order HCO_3^- (316)> Cl^- (239)> SO_4^{2-} (155)> $\text{NO}_2^- + \text{NO}_3^-$ (12)> F^- (0,47).

On the Piper diagram, the water is mainly mixed type (zone 9) and with a few samples being Ca-Mg-Cl- SO_4^{2-} type (zone 6). The Ca-Mg-Cl- HCO_3^- ion water facies is dominating the mixed type which indicate shallow, recently recharged groundwater, recharging with temporary hardness rainwater. The maximum nitrate+nitrite of 50,9 mg/L is observed alongside high magnesium at 143 mg/L. The strong positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 1,67 mEq/L, this water is excellent for irrigation. The site has an average RSC index of -5,18 mEq/L, which is suitable for irrigation. The average for the Permeability Index (PI) is 45%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 41% and hence suitable for irrigation. Furthermore, the %Na index average of 28% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,43 which is suitable for irrigation purposes.

For drinking water suitability assessment, the brackish nature of this water emanating from 69% of the water samples with TDS >1000 mg/L, makes it unsuitable for drinking purposes. The magnesium and nitrate+nitrite average concentrations are also high and unsuitable for drinking purposes at 100 mg/L and 12 mg/L, respectively. Although the nitrate+nitrite average concentrations are slightly high, the highest concentration is 50,9 mg/L, recorded in September 2013. The nitrate+nitrite concentrations fell significantly since September 2013, down to 2,4 mg/L in October 2017.

ZQMMPE1 (n=5)

In ZQMMPE1, only five samples were analysed in 2015 (1) 2016 (2), and 2017 (2). The water pH ranges from 8,20 to 9,10, with a pH average of 8,52 the water is weakly alkaline. The TDS concentration of the water ranges from 107 mg/L to 1558 mg/L, with the TDS average concentration of 929 mg/L, 60% of the water samples are brackish. Cation dominance in mg/L is in this order $\text{Na}^+(182) > \text{Mg}^{2+}(93) > \text{Ca}^{2+}(32) > \text{K}^+(12)$, while anions dominance in mg/L is in this order $\text{HCO}_3^-(438) > \text{Cl}^-(210) > \text{SO}_4^{2-}(91) > \text{NO}_2^- + \text{NO}_3^-(13) > \text{F}^- (1,16)$.

On the Piper diagram, some of the samples are mixed type (zone 9) and others are Ca-Mg- HCO_3 type (zone 5). The Ca-Mg-Cl- HCO_3 ion water facies indicate shallow, recently recharged groundwater, recharging with temporary hardness rainwater.

Based on the calculated SAR average value of 4,01 mEq/L, this water is excellent for irrigation. The site has an average RSC index of 1,60 mEq/L, which is fair for irrigation. The average for Permeability Index (PI) is 89%, which is suitable for irrigation. The Magnesium Hazard (MH) index average is 62% and hence unsuitable for irrigation. Furthermore, the %Na index average of 50% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 1,12 which is unsuitable for irrigation purposes.

For drinking water suitability assessment, the brackish nature of this water emanating from 60% of the water samples with TDS > 1000 mg/L, makes it unsuitable for drinking purposes. The percentage samples with unsuitable concentrations, for drinking purposes, of chloride, sodium, magnesium, and nitrate+nitrite, are 50%, 60%, 60%, and 60%; respectively. The nitrate+nitrite concentrations range from 0,5 mg/L recorded in May 2015, to 22,5 mg/L recorded in September 2016. The nitrate+nitrite concentrations have been stable in the 20 mg/L levels between April 2016 and April 2017, which was then followed by a decline down to 1,1 mg/L in October 2017. It must be noted that the chemical analysis data from this borehole site displays rather erratic tendencies, the data from May 2015 and October 2017 show extremely low TDS concentrations of 107 mg/L and 119 mg/L, respectively. This anomalous TDS low also means other relevant parameters such as chloride, sodium, magnesium and nitrate+nitrite are also minimal on the same dates, which skews the average values and overall suitability of the water.

ZQMSSN1 (n=4)

In ZQMSSN1, only four samples were analysed in 2016 (2) and 2017 (2). The water pH ranges from 8,30 to 8,80, with the pH average of 8,50 the water is alkaline. The TDS concentration of the water ranges from 955 mg/L to 1075 mg/L, with the TDS average concentration of 1010 mg/L, 75% of the water samples are brackish. Cation dominance in mg/L is in this order $\text{Na}^+(150) > \text{Mg}^{2+}(82) > \text{Ca}^{2+}(72) > \text{K}^+(1,9)$, while anions dominance in mg/L is in this order $\text{HCO}_3^-(400) > \text{Cl}^-(203) > \text{SO}_4^{2-}(47) > \text{NO}_2^- + \text{NO}_3^-(35) > \text{F}^-(2,7)$.

On the Piper diagram, some of the samples are mixed type (zone 9) and others are Ca-Mg- HCO_3 type (zone 5). The Ca-Mg-Cl- HCO_3 ion water facies, indicate shallow, recently recharged groundwater, recharging with temporary hardness rainwater. The maximum nitrate+nitrite of 36,1 mg/L is observed alongside high magnesium at 89 mg/L. The strong positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 3,46 mEq/L, this water is excellent for irrigation. The site has an average RSC index of -0,56 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 67%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 50% and hence suitable for irrigation. Furthermore, the %Na index average of 48% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,92 which is suitable for irrigation purposes.

For drinking water suitability assessment, the brackish nature of this water emanating from 75% of the water samples with TDS >1000 mg/L, makes it unsuitable for drinking purposes. Moreover, the magnesium, nitrate+nitrite and fluoride average concentrations are high and unsuitable for drinking purposes at 82 mg/L, 35 mg/L, and 2,7 mg/L, respectively. The nitrate+nitrite concentrations are three times higher than the SANS241 (2015) limit, and the most problematic ranging from 33,3 mg/L recorded in September 2017; to 36,1 mg/L recorded in May 2016. The nitrate+nitrite concentrations were stable at around 33 mg/L during the sampling period. All samples from this site have fluoride concentrations above 1,5 mg/L a limit recommended by SAN241 (2015). This borehole site is closest to the geothermal sites ZQMTUG2 and ZQMTUG4 which also have significantly high fluoride at 4,90 mg/L and 4,99 mg/L, respectively.

ZQMSWW1 (n=27)

In ZQMSWW1, 27 samples were analysed between April 2000 and March 2017. The water pH ranges from 7,91 to 8,70, with the pH average of 8,27 the water is weakly alkaline. The TDS concentration of the water ranges from 700 mg/L to 1033 mg/L, with the TDS average concentration of 832 mg/L, 96% of the water samples are fresh. Cation dominance in mg/L is in this order $\text{Ca}^{2+}(82) > \text{Na}^{+}(77) > \text{Mg}^{2+}(71) > \text{K}^{+}(14)$, while anions dominance in mg/L is in this order $\text{HCO}_3^{-}(339) > \text{Cl}^{-}(155) > \text{SO}_4^{2-}(43) > \text{NO}_2^{-} + \text{NO}_3^{-}(25) > \text{F}^{-}(0,4)$.

The maximum nitrate+nitrite of 33,2 mg/L is observed alongside high magnesium at 77 mg/L. The strong positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 1,78 mEq/L, this water is excellent for irrigation. The site has an average RSC index of -1,59 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 55%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 43% and hence suitable for irrigation. Furthermore, the %Na index average of 34% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,47 which is suitable for irrigation purposes.

The water is of freshwater quality based on the average TDS of 832 mg/L. However, for drinking water suitability assessment, the magnesium and nitrate+nitrite average concentrations are high and unsuitable for drinking purposes at 71 mg/L, 25 mg/L, respectively. The nitrate+nitrite concentrations are high, ranging from 19,7 mg/L recorded in October 2007; to 33,2 mg/L recorded September 2001. The nitrate+nitrite concentrations have been fluctuating between 20 mg/L and 30 mg/L between 2002 and 2017.

ZQMSWW2 (n=23)

In ZQMSWW2, 23 samples were analysed between May 2001 and November 2016. The water pH ranges from 7,69 to 8,57; with a pH average of 8,14, the water is weakly alkaline. The TDS concentration of the water ranges from 875 mg/L to 2426 mg/L, with the TDS average concentration of 1425 mg/L, 83% of the water samples are brackish. Cation dominance in mg/L is in this order Na^+ (148)> Mg^{2+} (128)> Ca^{2+} (121)> K^+ (17), while anions dominance in mg/L is in this order HCO_3^- (407)> Cl^- (351)> SO_4^{2-} (101)> NO_2^- + NO_3^- (36)> F^- (0,78).

On the Piper diagram, the water is mainly mixed type (zone 9), with minor Ca-Mg- HCO_3 type (zone 5), the dominating Ca-Mg-Cl- HCO_3 ion water facies, indicate shallow, recently recharged groundwater, recharging water with temporary hardness rainwater. The maximum nitrate+nitrite of 70,6 mg/L is observed alongside high magnesium at 162 mg/L. The strong positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 2,68 mEq/L, this water is excellent for irrigation. The site has an average RSC index of -4,87 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 51%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 47% and hence suitable for irrigation. Furthermore, the %Na index average of 37% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,57 which is suitable for irrigation purposes.

The brackish nature of this water emanating from 2426 mg/L average TDS, makes it very unsuitable for drinking purposes. Furthermore, the chloride, magnesium and nitrate+nitrite concentrations are too high and unsuitable for drinking purposes at 351 mg/L, 128 mg/L, and 36 mg/L, respectively. The nitrate+nitrite concentrations are ranging from 8,1 mg/L recorded in April 2017, to 70,6 mg/L recorded May 2001. The nitrate+nitrite concentrations fell significantly since September 2009, from 38,4 mg/L down to 8,1 mg/L in April 2017.

ZQMTBK1 (n=29)

In ZQMTBK1, 29 samples were analysed between April 2000 and March 2017. The water pH ranges from 7,87 to 8,70, with the pH average of 8,24 the water is weakly alkaline. The TDS concentration of the water ranges from 563 mg/L to 970 mg/L, with the TDS average concentration of 693 mg/L, 100% of the water samples are fresh. Cation dominance in mg/L is in this order $\text{Na}^+(81) > \text{Ca}^{2+}(64) > \text{Mg}^{2+}(59) > \text{K}^+(8)$, while anions dominance in mg/L is in this order $\text{HCO}_3^-(381) > \text{Cl}^-(88) > \text{NO}_2^- + \text{NO}_3^-(12) > \text{SO}_4^{2-}(29) > \text{F}^-(0,52)$.

On the Piper diagram, the water is predominately Ca-Mg- HCO_3 type (zone 5), a signature dominated by Ca-Mg-Cl- HCO_3 ion water facies, indicate shallow, recently recharged groundwater, recharging water with temporary hardness rainwater. The maximum nitrate+nitrite of 23,2 mg/L is observed alongside high magnesium at 73 mg/L. The positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 2,09 mEq/L, this water is excellent for irrigation. The site has average RSC index of 0,51 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 65%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 45% and hence suitable for irrigation. Furthermore, the %Na index average of 40% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,63 which is suitable for irrigation purposes.

The water is of freshwater quality based on the average TDS of 693 mg/L. However, for drinking water suitability assessment, this water fails only the nitrate+nitrite concentrations, which are slightly high and unsuitable for drinking purposes, at an average of 12 mg/L. The nitrate+nitrite concentrations range from 4,0 mg/L recorded in October 2000, to 23,2 mg/L recorded in April 2000. The nitrate+nitrite concentrations have been stable below 20 mg/L between November 2000 and September 2017.

ZQMTBK2 (n=30)

In ZQMTBK2, 30 samples were analysed between April 2000 and March 2017 the water pH ranges from 7,71 to 9,19, with a pH average of 8,18, the water is weakly alkaline. The TDS concentration of the water ranges from 680 mg/L to 2182 mg/L, with the TDS average concentration of 1120 mg/L, 60% of the water samples are brackish. Cation dominance in mg/L is in this order Na^+ (131)> Mg^{2+} (96)> Ca^{2+} (95)> K^+ (10), while anions dominance in mg/L is in this order HCO_3^- (384)> Cl^- (266)> SO_4^{2-} (77)> $\text{NO}_2^- + \text{NO}_3^-$ (24)> F^- (0,49).

On the Piper diagram, the water is mainly mixed type (zone 9) and with a few samples being Ca-Mg- HCO_3 type (zone 5). The Ca-Mg-Cl- HCO_3 ion water facies, indicate shallow, recently recharged groundwater, recharging with temporary hardness rainwater. The maximum nitrate+nitrite of 65,3 mg/L is observed alongside high magnesium at 161 mg/L. The strong positive association of nitrate+nitrite and magnesium, suggests water quality is influenced by magnesium nitrate fertilisers.

Based on the calculated SAR average value of 2,70 mEq/L, this water is excellent for irrigation. The site has average RSC index of -2,55 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 58%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 47% and hence suitable for irrigation. Furthermore, the %Na index average of 41% gives the water a “good for irrigation” classification. The average Kelly’s Ratio calculation is 0,66 which is suitable for irrigation purposes.

For drinking water suitability assessment, the brackish nature of this water emanating from 60% of the water samples with TDS >1000 mg/L, makes it unsuitable for drinking purposes. Moreover, the magnesium and nitrate+nitrite average concentrations are also high and unsuitable for drinking purposes, at 96 mg/L, and 24 mg/L, respectively. The nitrate+nitrite concentrations are high, ranging from 4,0 mg/L recorded in October 2000; to 65,3 mg/L recorded in April 2000, a similar trend observed in ZQMTBK1. The nitrate+nitrite concentrations have been fluctuating around 20 mg/L between 2001 and 2017.

ZQMTUG2 (n=27)

In ZQMTUG2, 27 samples were analysed between January 2000 and September 2017. ZQMTUG2 is a geothermal spring, with 44 degrees Celsius temperature. The water pH ranges from 6,96 to 8,07, with a pH average of 7,58, the water is very weakly alkaline. The TDS concentration of the water ranges from 1440 mg/L to 1581 mg/L, with the TDS average concentration of 1506 mg/L, 100% of the water samples are brackish. Cation dominance in mg/L is in this order $\text{Na}^+(373) > \text{Ca}^{2+}(122) > \text{K}^+(10) > \text{Mg}^{2+}(0,97)$, while anions dominance in mg/L is in this order $\text{SO}_4^{2-}(491) > \text{Cl}^-(398) > \text{HCO}_3^-(31) > \text{F}^-(5) > \text{NO}_2^- + \text{NO}_3^-(0,1)$.

On the Piper diagram, the water is distinctively Na-K-Cl- SO_4 type (zone 7), and the signature is dominated by Na- SO_4 -Cl ion water facies, suggesting recently recharged groundwater undergoing mineralisation. The water is highly mineralised (TDS >1500 mg/L) sodium-chloride-sulphate water type.

Based on the calculated SAR average value of 9,32 mEq/L, this water is excellent for irrigation. The site has average RSC index of -5,60 mEq/L, which is suitable for irrigation. The average for Permeability Index (PI) is 76%, which is suitable for irrigation. The Magnesium Hazard (MH) index average is 0,68% and hence suitable for irrigation. Furthermore, the %Na index average of 73% gives the water a “doubtful for irrigation” classification. The average Kelly’s Ratio calculation is 2,68 which is unsuitable for irrigation purposes.

For drinking water suitability assessment, the brackish nature of this water emanating from TDS average concentration of 1506 mg/L, makes it very unsuitable for drinking purposes. Moreover, the magnesium and nitrate+nitrite average concentrations are also high and unsuitable for drinking purposes, at 96 mg/L, and 24 mg/L, respectively. The nitrate+nitrite concentrations are high, ranging from 4,0 mg/L recorded in October 2000; to 65,3 mg/L recorded April 2000, a similar trend observed in ZQMTBK1. The nitrate+nitrite concentrations have been fluctuating around 20 mg/L between 2001 and 2017.

The brackish nature of this water emanating from 1506 mg/L average TDS, makes it extremely unsuitable for drinking purposes. Furthermore, the sulphate, chloride, sodium, and fluoride concentrations are also too high at, 491 mg/L, 398 mg/L, 373 mg/L, and 5 mg/L, respectively. The fluoride concentrations are above 1,5 mg/L a limit set by both WHO, 2015 and SAN241, 2015.

ZQMTUG4 (n=29)

In ZQMTUG4, 29 samples were analysed between April 2000 and March 2017. ZQMTUG4 is a geothermal spring, with 33 degrees Celsius temperature. The water pH ranges from 6,91 to 7,80, with a pH average of 7,48, the water is very weakly alkaline. The TDS concentration of the water ranges from 1428 mg/L to 1565 mg/L, with the TDS average concentration of 1801 mg/L, 100% of the water samples are brackish. Cation dominance in mg/L is in this order $\text{Na}^+(382) > \text{Ca}^{2+}(136) > \text{K}^+(10) > \text{Mg}^{2+}(1,46)$, while anions dominance in mg/L is in this order $\text{SO}_4^{2-}(525) > \text{Cl}^-(432) > \text{HCO}_3^-(37) > \text{F}^-(5) > \text{NO}_2^- + \text{NO}_3^-(0,1) >$.

On the Piper diagram, the water is distinctively Na-K-Cl-SO₄ type (zone 7), a signature dominated by Na-SO₄-Cl ion water facies, suggesting recently recharged groundwater undergoing mineralisation. The water is highly mineralised (TDS >1500 mg/L) sodium-chloride-sulphate water type.

Based on the calculated SAR average value of 9,03 mEq/L, this water is excellent for irrigation. The site has an average RSC index of -6,25 mEq/L, which is suitable for irrigation. The average for the Permeability Index (PI) is 74%, which is moderately suitable for irrigation. The Magnesium Hazard (MH) index average is 0,90% and hence suitable for irrigation. Furthermore, the %Na index average of 71% gives the water a “doubtful for irrigation” classification. The average Kelly’s Ratio calculation is 2,46 which is unsuitable for irrigation purposes.

The brackish nature of this water emanating from 1801 mg/L average TDS, makes it very unsuitable for drinking purposes. Furthermore, the sulphate, chloride, sodium, and fluoride concentrations are also too high and unsuitable for drinking purposes, at 525 mg/L, 432 mg/L, 382 mg/L, and 5 mg/L, respectively. The fluoride concentrations are above 1,5 mg/L a limit set by both WHO, 2015 and SAN241, 2015.

Chapter 5: Conclusions

5.1. Introduction

The main aim of the study was to assess the hydrogeochemical characteristics and the suitability of groundwater for irrigation and drinking purposes, in the Limpopo Granite Gneiss region. The first part of the study was to determine the hydrogeochemical characteristics of the groundwater. The second and third parts of the study were to assess the suitability of the groundwater quality for irrigation and for drinking purposes, respectively.

5.2. Hydrogeochemical characteristics

The first objective of the study was to determine the hydrogeochemical characteristics of the groundwater based on physicochemical data from 2000 to 2017. The concentrations of major ions in the groundwater were found to vary spatially and temporally, with some similarities observed within the same drainage system. The abundance of cations and anions showed $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- + \text{NO}_2^- > \text{F}^-$, respectively. Na^+ accounts for 48% of the cations and HCO_3^- accounts for 41% of the anions. However, HCO_3^- anion dominance was found to be absent at the geothermal monitoring sites ZQMTUG2 and ZQMTUG4, where the average HCO_3^- concentrations were 31 mg/L and 37 mg/L, respectively. Low HCO_3^- concentrations at ZQMTUG2 and ZQMTUG4 were found to be strongly associated with high SO_4^{2-} and Cl^- concentrations.

The average Na^+ concentration across all samples was 165 mg/L, which made it the most dominant cation, followed by Ca^{2+} and Mg^{2+} concentrations at 98 mg/L and 71 mg/L, respectively. The average HCO_3^- concentration across all samples was 298 mg/L, which made it the most dominant anion, followed by Cl^- and SO_4^{2-} concentrations at 256 mg/L and 142 mg/L, respectively. The fourth dominant anion was $\text{NO}_3^- + \text{NO}_2^-$ with an average concentration of 25 mg/L. The highest Na^+ concentrations observed were at monitoring sites ZQMALL2, ZQMTUG2, and ZQMTUG4. The Na^+ anion dominance was found to be absent in ZQMBLT3, ZQMKHK2, ZQMMES1, and ZQMSWW1, where the dominating anion was Ca^{2+} , followed by Mg^{2+} . The monitoring sites ZQMMES1, ZQMALL2, ZQMSWW2, and ZQMBLT3 showed a strong correlation between high Ca^{2+} and high Mg^{2+} . However, the high Ca^{2+} concentrations at the geothermal sites ZQMTUG2 and ZQMTUG4 were associated with low Mg^{2+} concentrations. Furthermore, ZQMTUG2 and ZQMTUG4 were the only sites with significantly low $\text{NO}_3^- + \text{NO}_2^-$ concentrations at 0.14 mg/L and 0.09 mg/L, respectively.

Thus, indicating that the geothermal water quality was not influenced by human activities. Regrettably, the other 15 sites had elevated nitrate concentrations. There was a strong positive correlation between nitrate+nitrite and magnesium concentrations in monitoring sites ZQMALL2, ZQMBLT3, ZQMKHK2, ZQMLGN1, ZQMES1, ZQMSSN1, ZQMSWW1, ZQMSWW2, ZQMTBK1, and ZQMTBK2, which suggests that water quality was influenced by magnesium nitrate fertilisers.

The pH of groundwater in the study area was found to range from 6,9 to 9,2; with 83,4% of the samples falling within the pH 7,5 to 8,5 range; while 5,0% of the samples were within the pH 6,5 to <7,5 range; and 11,6% samples are within the pH >8,5 to 9,2 range. The pH averages for geothermal sites ZQMTUG2 and ZQMTUG4 were 7,58 and 7,48, respectively. The monitoring sites ZQMGG1, ZQMGS1, ZQMGTA1, ZQMLGN1, and ZQMMPE1, were within the pH >8,5 to 9,2 range, which is alkaline.

Two water-type clusters were identified using the Piper diagramme method. 15 of the sites are within the Ca-Mg-HCO₃ type (zone 5) and mixed (Ca-Mg-Cl-SO₄ and Ca-Mg-HCO₃) type (zone 9), while ZQMTUG2 and ZQMTUG4 are within Na-K-Cl-SO₄ type (zone 7). The Gibbs diagramme indicates that evaporation dominance mechanisms are controlling groundwater chemistry. Schoeller's chloroalkaline indices (CAIs) method suggests both forward and reverse ion exchange influenced the water chemistry in the study area. The mechanism, controlling groundwater chemistry in the study area was found to be primarily geogenic processes such as silicate weathering, ion exchange, and evaporation. Additionally, significant evidence supported secondary anthropogenic influence from land use activities such as irrigation and onsite sanitation. Most villages in the study area do not have municipal sanitation systems, but pit latrines. The combination of pit latrines and unregulated agricultural activities have escalated negative impacts on groundwater quality in the study area.

5.3. Suitability for irrigation

The third objective of this study was to assess the suitability of the groundwater quality for irrigation purposes. The suitability of the groundwater for irrigation will advance SDG-2 which addresses food security and improved nutrition, promoting sustainable agriculture and ensuring an end to hunger. At least 57% of the samples were categorically brackish and 43% were fresh. lulu

However, for the PI index, 16% of the samples were suitable for irrigation purposes, while 84% were moderate quality for irrigation purposes. For the MH index, 87% of the samples were suitable for irrigation, while 13% were unsuitable for irrigation. The 13% unsuitable samples were randomly distributed across all borehole sites, except ZQMTUG2 and ZQMTUG4. The %Na assessment identified 21,6% of the water samples to be of doubtful quality for irrigation, these came from mainly ZQMTUG2 and ZQMTUG4 sites, which were 100% doubtful for %Na, presenting a consistent trend of poor water quality in these geothermal sites. The KR calculations showed that 33% of the samples were unsuitable for irrigation. The 106 samples which were KR unsuitable belong to mainly monitoring sites ZQMLGN1 (83%) ZQMALL2 (86%), ZQMTUG2 (100%), and ZQMTUG4 (100%).

5.4. Suitability for drinking

The third objective of this study was to assess the suitability of the groundwater quality for drinking purposes. The drinking water suitability will advance SGD-6's clean water for all, by promoting water resource management and water quality awareness (UN, 2015).

Nine (53% of the sites) borehole sites were found to have average TDS levels above 1000 mg/L which is unsuitable for drinking purposes. Over 56% (179) of the samples from the study area recorded TDS >1000 mg/L. The most noticeable elements of concern for drinking suitability are $\text{NO}_3^- + \text{NO}_2^-$ and some isolated exceedances of fluoride. The $\text{NO}_3^- + \text{NO}_2^-$ concentrations were found to be above the local and global guideline values in 15 monitoring sites. This placed nitrate pollution at the centre of the study area's groundwater problems, which concurs with Marais (1999) who identified nitrate as the single most significant reason for groundwater sources to be declared unsuitable for drinking. Nitrate is regarded as one of the essential priority chemicals (WHO, 2007).

The 15 out of 17 monitoring sites were found to have higher than recommended $\text{NO}_3^- + \text{NO}_2^-$ concentrations. The four sites ZQMLGN1, ZQMMES1, ZQMMPE1 and ZQMTBK1 had the least unsafe average $\text{NO}_3^- + \text{NO}_2^-$ concentrations of 13 mg/L, 12 mg/L, 14 mg/L and 12 mg/L, respectively. There was no linear continuous increase observed for $\text{NO}_3^- + \text{NO}_2^-$ over the time presented. While nitrate may be a naturally occurring compound, its enriched presence in groundwater in this area is often associated with land-based activities such as pit latrines and the agricultural use of fertilisers (Tredoux, 2004, Lalumbe and Kanyerere, 2022a). The impacts of pit latrines vary from place to place and from point to point (Tredoux, 2004). The study area covers several rural communities and irrigated lands. The groundwater use is

associated with irrigation, livestock watering, and schedule1 uses. A number of communities, such as Alldays, Beauty, Maasstroom, Swartwater, Tom Burke, Marnitz, Musina and others, rely on groundwater as main source of water.

The two geothermal springs ZQMTUG2 and ZQMTUG4 which do not have elevated nitrate, were found to have high TDS, Na⁺, Cl⁻, SO₄²⁻, and F⁻ based on SANS241:2015 guidelines, rendering them also unsuitable for drinking. The water from both sites contains average F⁻ concentration of 5 mg/L, which is significantly above the recommended drinking limit of 1,5 mg/L (SANS 241, 2015). The high levels of fluoride in these sites occur naturally. Epidemiological evidence shows that concentrations above 1,5 mg/L carry an increasing risk of dental fluorosis and that progressively higher concentrations intake increases risks of skeletal fluorosis (WHO, 2011a). All 17 monitoring sites water quality based on 2010 to 2017 chemical analysis were found to be unsuitable for drinking purposes.

5.5. Protection and remediation recommendations

Nitrate is a major health risk for bottle-fed infants, it causes methemoglobinaemia also known as “blue-baby syndrome” (WHO, 2011a). Methemoglobinemia is a serious health condition, which threatens the lives of bottle-fed infants significantly. A simpler, cheaper and more immediate approach that is within the capabilities of communities is recommended. To mitigate methemoglobinemia, authorities should adequately flag nitrate polluted groundwater and educate the community particularly mothers about this deadly non-microbial contaminant. The author suggests that at the clinics, during prenatal and postnatal consultations, mothers should be made aware that while boiling water works to kill microbial contaminants, extended boiling of water, which is contaminated by nitrate can increase the levels of nitrate in the water during evaporation (Swistock, 2022). Alternative safe water should be made available to mothers on a regular basis, and the blending of surface water and groundwater should be promoted. The author also recommends that sustainable and affordable groundwater remediation options should be considered and implemented urgently to further prevent bottle fed babies from drinking formula made from nitrate contaminated water. Magnesium nitrate should be flagged as unsuitable for use as a fertiliser in this area, to prevent future groundwater contamination this area. This will promote sustainable groundwater use for future generations.

References

- 2030 WRG, (2009). 2030 Water Resources Group. Annual report. Charting our water future: Economic frameworks to inform decision-making. 1-173. Washington, DC.
- 2030 WRG, (2014). 2030 Water Resources Group. Annual report. Building Partnerships for Water Security. 1-74. Washington, DC.
- Adimalla, N., and Venkatayogi, S., (2018). Geochemical characterization and evaluation of groundwater suitability for domestic and agricultural utility in semi-arid region of Basara, Telangna State, South India. *Applied Water Science*, 8:44, 1-14.
- Adimalla, N., Dhakate, R., Kasarla, A., and Taloor, A.K., (2020). Appraisal of groundwater quality for drinking and irrigation purposes in Central Telangana, India. *Groundwater for Sustainable Development*, 10, 100334.
- Aghazadeh, N., and Mogaddam, A.A., (2010). Assessment of Groundwater Quality and Its Suitability for Drinking and Agricultural Uses in the Oshnavieh Area, Northwest of Iran. *Journal of Environmental Protection*, 1(01), 30-40.
- Ahemaitihali, A., and Dong, Z., (2022). Spatiotemporal Characteristics Analysis and Driving Forces Assessment of Flash Floods in Altay. *Water*, 14, 331.
- APHA, (1999). American Public Health Association. Standard Methods for the Examination of Water and Wastewater. 1030 E. Checking Correctness of Analyses, 38-30. American Public Health Association, American Water Works Association and Water Environment Federation, 1-541. Washington D.C.
- Asante-Annor, A., Bewil, P.N., and Boateng, D., (2018). "Evaluation of Groundwater Suitability for Irrigation in the Lambussie-Karni District of Ghana", *Ghana Mining Journal*, 18 (1), 9-19.
- Ayers, R.S. and Westcot, D.W., (1985). Water quality for Agriculture. FAO Irrigation and Drainage Paper no. 29 (1), 1-174. Food and Agriculture Organization, Rome.
- Bartos, T.T., and Ogle, K.M., (2002). Water Quality and Environmental Isotopic Analyses of Ground-Water Samples Collected from the Wasatch and Fort Union Formations in Areas of Coalbed Methane Development—Implications to Recharge and Ground- Water Flow, Eastern Powder River Basin, Wyoming. U.S. Geological Survey Water-Resources Investigations Report 02-4045; 1-96.
- Basson, M.S., (2011). Water development in South Africa. UN-Water International Conference 3-5 October 2011. Zaragoza, Spain.
- Basupi, T.O., Tsunogae, T., Takahashi, K., Tsutsumi, Y., (2022). Neoproterozoic arc magmatism and Paleoproterozoic high-pressure granulite-facies metamorphism in the southern Motloutse Complex, eastern Botswana: Implications for the western extension of the Limpopo Complex. *Precambrian Research* 369, 106534
- Bauder, T.A.; Waskom, R.M.; Sutherland, P.L.; Davis, J.G., (2003). Irrigation Water Quality Criteria—0.506; Colorado State University: Fort Collins, CO, USA. Fact Sheet No. 0.506, 1-4.
- Bohdziewicz, J., Bodzek, M., Wąsik, E., (1999). The application of reverse osmosis and nanofiltration to the removal of nitrates from groundwater. *Desalination* 121, 139-147.

- Bond GW (1946) 'n Geochemiese opname van die grondwatervoorraade van die Unie van Suid-Afrika. Memoir Geological Survey of South Africa, 41, 90-94.
- Braune, E., Hollingworth, B., Xu, Y., Nel, M., Mahed, G. and Solomon, H., (2008). Protocol for the Assessment of the Status of Sustainable Utilization and Management of Groundwater Resources with Special Reference to Southern Africa. WRC report no. TT 318/08, 1-72. Water Research Commission, Pretoria.
- Carrol, D., (1962). Rainwater as a Chemical Agent of Geologic Processes A Review. The geochemistry of rainwater. United States Government Printing Office, Washington.
- Chibi, C., and Vinnicombe, D.A., (1999). Fluorides and Nitrates: Their occurrence in rural South Africa, current removal technologies and promising new approaches. WRC report no KV120/99.
- Davis, S.N.; DeWiest, R.J., (1966). Hydrogeology; 463, Wiley: New York, NY, USA.
- De Angelis, M., (2005). Major Ions in Seawater. Online abstract <https://doi.org/10.1002/047147844X.oc1707>
- de Lange, J., Molaolwa G., Kotzé Y.L., van der Merwe J, Esterhuizen L., Mantyeane A.M., (2019). Training Manual for Groundwater Resource Management and Groundwater Governance for Municipalities in South Africa. WRC Report No. TT 790/19.
- Deutsch, W.J., (1997). Groundwater Geochemistry: Fundamentals and Applications to Contamination, Lewis Publishers
- Dinka, M.O., (2016). Quality composition and irrigation suitability of various surface water and groundwater sources at Matahara Plain. Water Resources, 43 (4), 677–689.
- Doneen, L.D., (1964). Notes on Water Quality in Agriculture published as a Water Science and Engineering Paper 4001, Department of Water Science and Engineering, University of California.
- DWA, (2010). Department of Water Affairs. Groundwater strategy 2010. 1-78. Pretoria, South Africa.
- DWAF, (2000). Department of Water Affairs and Forestry. Policy and Strategy for Groundwater Quality Management in South Africa. First Edition 2000. 1-45. Pretoria, South Africa.
- du Toit, W., Holland, M., Weidemann R., Botha F., (2012). Can groundwater be successfully implemented as a bulk water resource within rural Limpopo Province? Analysis based on GRIP datasets. Water SA, 38 (3), International Conference on Groundwater Special Edition.
- Eaton, F.M., (1950). Significance of Carbonates in irrigation waters. Soil Science, 69, 123–134.
- Etteieb, S., Cherif, S. Tarhouni, J., (2017). Hydrochemical assessment of water quality for irrigation: a case study of the Medjerda River in Tunisia. Applied Water Science 7:469–480.
- Fadili, H.E., Ali, M.B., Mahi, M.E., Cooray, A.T., Lotfi, E.M., (2022). A comprehensive health risk assessment and groundwater quality for irrigation and drinking purposes around municipal solid waste sanitary landfill: A case study in Morocco. Environmental Nanotechnology, Monitoring and Management 18,100698; 1-18.

- FAO, (2004). Drought impact mitigation and prevention in the Limpopo River Basin A situation analysis. 1-178 Food and Agriculture Organization of the United Nations, Rome.
- FAO, (2017). Food and Agriculture Organization. Water for Sustainable Food and Agriculture. A report produced for the G20 Presidency of Germany, 1-33. Food and Agriculture Organization of the United Nations, Rome.
- Fawell, J., Bailey, K., Chilton, J., Dahi, E., Fewtrell, L. and Magara, Y., (2006). Fluoride in drinking-water. London, IWA Publishing on behalf of the World Health Organization (WHO Drinking-water Quality Series; 1-44.
- Fewtrell, L., (2004). Drinking-water nitrate, methemoglobinemia, and global burden of disease: A discussion. *Environmental Health Perspectives*, 112(14), 1371-1374.
- Fipps, G., (2003). Irrigation Water Quality Standards and Salinity Management Strategies, Texas Farmer Collection, 1-19.
- Foster S., Chilton J., Nijsten G., Richts A., (2013). Groundwater - A global focus on the 'local resource'. *Current Opinion in Environmental Sustainability*, 5(6), 685-695.
- Freeze, R.A.; Cherry, J.A., (1979). *Groundwater*; Prentice-Hall Inc.: Englewood Cliffs, NJ, USA, 1-624.
- Gad, M., and El Osta, M., (2020). Geochemical controlling mechanisms and quality of the groundwater resources in El Fayoum Depression, Egypt. *Arabian Journal of Geosciences* 13(861), 1-23.
- Garrels, R.M., and Mackenzie, F.T., (1967). Origin of the chemical compositions of some springs and lakes. In W. Stumm (Ed.), *Equilibrium concepts in natural water systems*. *Advances in Chemistry Series* 67, 222–242.
- Gibbs, R.J., (1970). Mechanisms Controlling World. *Water Chemistry*. *Science*, 170(3962), 1088–1090.
- Graham, J.P., and Polizzotto, M.L., (2013). Pit Latrines and Their Impacts on Groundwater Quality: A Systematic Review. *Environmental Health Perspectives*, 121(5), 521-530.
- Grönwall, J., and Danert, K., (2020). Regarding Groundwater and Drinking Water Access through A Human Rights Lens: Self-Supply as A Norm. *Water*, 12(419), 1-21.
- Gugulothu, S., Subba Rao, N., Das R., Dhakate, R., (2022). Geochemical evaluation of groundwater and suitability of groundwater quality for irrigation purpose in an agricultural region of South India. *Applied Water Science*, 12(142), 1-13.
- Guppy, L., Uyttendaele, P., Villholth, K.G., Smakhtin, V., (2018). *Groundwater and Sustainable Development Goals: Analysis of Interlinkages*. UNU-INWEH Report Series, Issue 04. United Nations University Institute for Water, Environment and Health, Hamilton, Canada.
- Gurdak, J.J., Hanson, R.T., McMahon, P.B., Bruce, B.W., McCray, J.E., Thyne, G. D. and Reedy, R. C., (2007). Climate variability controls on unsaturated water and chemical movement, High Plains aquifer, USA. *Vadose Zone Journal*, 6(3), 533–547.

- Hagan, G.B., Minkah R., Yiran, G.A.B., and Dankyi, E., (2022). Assessing groundwater quality in peri-urban Accra, Ghana: Implications for drinking and irrigation purposes. *Groundwater for Sustainable Development* 17; 100761.
- Hamilton, P. A., Shedlock, R. J. and Phillips, P. J.; (1991). Water quality assessment of the Delmarva Peninsula, Delaware, Maryland and Virginia: Analysis of available ground-water-quality data through 1987. U.S. Geological Survey Water Supply Paper 2355, B1-B65.
- Hem, J.D., (1984). Study and Interpretation of chemical characteristics of Natural Water. Third edition. US Geological Survey Water-Supply Paper 2254, 1-272.
- Holland, M., (2012). Evaluation of factors influencing transmissivity in fractured hard-rock aquifers of the Limpopo Province. *Water SA*, 38, 3.
- Hounslow, A.W., (1995). Water quality data: analysis and interpretation. CRC Lewis Publisher, New York, USA, 1-417.
- Howard, G., Calow, R., Macdonald, A., Bartram, J., (2016). Climate Change and Water and Sanitation: Likely Impacts and Emerging Trends for Action. In: *Annual Review of Environment and Resources*, 41, 253-276.
- Hussain, M., and Rao, T.V.D.P., (2013). Assessment of the ground water quality and its suitability for drinking and irrigation purposes: A case study of Patancheru, Andhra Pradesh, India. *Archives of Applied Science Research*, 5(6), 232-238
- Hwang, J.Y., Park, S., Kim, H.K., Kim, M.S., Jo, H.J., Kim, J.I., Lee, G. M., Shin, I.K. and Kim, T. S., (2017). Hydrochemistry for the Assessment of Groundwater Quality in Korea. *Journal of Agricultural Chemistry and Environment*, 6, 1-29.
- Iqbal, J., Su, C., Rashid, A., Yang, N., Baloch, M.Y.J., Talpur, S.A., Ullah, Z., Rahman, G., Rahman, N.U., Earjh, and Sajjad, M. M., (2021). Hydrogeochemical Assessment of Groundwater and Suitability Analysis for Domestic and Agricultural Utility in Southern Punjab, Pakistan. *Water*, 13(3589), 1-23.
- Jensen, V.B., Darby, J.L, Chad Seidel, and Gorman, C., (2014). Nitrate in Potable Water Supplies: Alternative Management Strategies, *Critical Reviews in Environmental Science and Technology*, 44:20, 2203-2286.
- Johnson, M. R., Anhaeusser, C.R. and Thomas, R.J., (editors) (2006). *The Geology of South Africa*. Geological Society of South Africa and the Council for Geoscience, 301-318.
- Kelly, W.P., (1940). Permissible composition and concentration of irrigated waters. *Proceedings of the American Society of Civil Engineers*, 66, 607-613.
- Khodapanah, L., Sulaiman, W.N.A., and Khodapanah, N., (2009). Groundwater Quality Assessment for Different Purposes in Eshtehard District, Tehran, Iran. *European Journal of Scientific Research*, 36 (4): 543-553.
- Kirda, C., (1997). Assessment of irrigation water quality, *CCI_HEAM–Options Mediterraneennes*, Series. A, no. 31, 367-377

- Kumar, P.J.S., Jegathambal, P., James, E.J., (2014). Chemometric evaluation of nitrate contamination in the groundwater of a hard rock area in Dharapuram. South India. *Applied Water Science*, 4, 397–405.
- Kumar, P.J.S., and James, E.J., (2016). Identification of hydrogeochemical processes in the Coimbatore district, Tamil Nadu, India, *Hydrological Sciences Journal*, 61(4), 719-731.
- Lalumbe, L., and Kanyerere, T., (2022a). Assessment of Concentration Levels of Contaminants in Groundwater of the Soutpansberg Region, Limpopo Province, South Africa. *Water*, 14, 1354; 1-16.
- Lalumbe, L., and Kanyerere, T., (2022b). Characterisation of Hydro-Geochemical Processes Influencing Groundwater Quality in Rural Areas: A Case Study of Soutpansberg Region, Limpopo Province, South Africa. *Water*, 14, 1972; 1-17
- Levy, G.J., and Nachshon, U., (2022). Sodic soils. Reference Module in Earth Systems and Environmental Sciences. Elsevier. Abstract.
- Mageshkumar, P., and Vennila, G., (2018). Assessment of errors in water quality data using ion balancing methods - A case study from Cauvery River, South India. *Indian Journal of Geo Marine Sciences*, 49 (1), 57-62.
- Maherry, A., Tredoux, G., Clarke S., Engelbrecht P., (2010). State of Nitrate Pollution in Groundwater in South Africa. CSIR 3rd Biennial Conference 2010. Science Real and Relevant. CSIR International Convention Centre, Pretoria, South Africa, 30 August – 01 September 2010.
- Mambo, J., and Faccar K., (Eds) (2017). Understanding the social and environmental Implications of Global Change. South African Risk and Vulnerability Atlas, 2nd edition. Pretoria, South Africa.
- Marais, S., (1999). Dependency of communities on groundwater for water supply and associated nitrate and fluoride problems. Paper presented at Water Research Commission Workshop on Fluorides and Nitrates in Rural Water Supplies, Mafikeng, South Africa, 9–10 March 1999.
- Margat, J., and Van der Gun, J., (2013). Groundwater around the World: A Geographical Synopsis. Boca Raton, Fla., CRC Press.
- Mas-Pla, J., and Menció, A., (2019). Groundwater nitrate pollution and climate change: Learnings from a water balance-based analysis of several aquifers in a western Mediterranean region (Catalonia). *Environmental Science and Pollution Research*, 26, 2184–2202.
- McGill, B.M.; Altchenko, Y.; Hamilton, S.K.; Kenabatho, P.K.; Sylvester, S.R.; Villholth, K.G., (2019). Complex interactions between climate change, sanitation, and groundwater quality: A case study from Ramotswa, Botswana. *Hydrogeology Journal*, 27 (3), 997-1015.

- Mokoena, P., Kanyerere, T., and van Bever Donker, J., (2020). Hydrogeochemical characteristics and evaluation of groundwater quality for domestic and irrigation purposes: a case study of the Heuningnes Catchment, Western Cape Province, South Africa. *Springer Nature Applied Sciences*, 2, 1548.
- Mukonazwothe, M., Munyai, L.F., Mutoti, M.I., (2022). Groundwater quality evaluation for domestic and irrigation purposes for the Nwanedi Agricultural Community, Limpopo Province, South Africa. *Heliyon* 8 (4), e09203; 1-13.
- Naseem, S., Hamza, S., and Bashir, E., (2010). Groundwater Geochemistry of Winder Agricultural Farms, Balochistan, Pakistan and Assessment for Irrigation Water Quality. *European Water* 31: 21-32.
- Nel, M., (2017). Groundwater. The Myths, the Truths, and the basics. Water Research Commission. 1-116. Pretoria, South Africa.
- Nell, J.P., and van Huyssteen C.W., (2014). Geology and groundwater regions to quantify primary salinity, sodicity and alkalinity in South African soils, *South African Journal of Plant and Soil*, 31:3, 127-135.
- Newcomer, D., (2019). Ion Balance Calculations for Groundwater at the 100-Hr-3 Operable Unit. ECF-100HR3-19-0105, REV. 0; 1-70. U.S. Department of Energy, Washington DC.
- Nishanthiny, S.C., Thushyanthy, M., Barathithasan, T. and Saravanan, S., (2010). Irrigation Water Quality Based on Hydro Chemical Analysis, Jaffna, Sri Lanka. *American-Eurasian Journal of Agriculture and Environmental Science*, 7 (1): 100-102.
- Nolan, B.T., Hitt, K.J., and Ruddy, B.C., (2002). Probability of nitrate contamination of recently recharged ground waters in the conterminous United States. *Environmental Science and Technology* 36, 2138–2145.
- Odiyo, J.O., and Makungo, R., (2012). Water quality problems and management in rural areas of Limpopo Province, South Africa. *Water SA*, 38(5), 731-736.
- Parson, R., and Tredoux, G., (1993). The development of a strategy to monitor groundwater quality on a national scale. WRC Report, no. 482/1/93. Water Research Commission, Pretoria.
- Parson, R., and Tredoux, G., (1995). Monitoring groundwater quality in South Africa: Development of national strategy. *Water SA* 21 (2) 113-116.
- Pinto, I., Zachariah, M., Wolski, P., Landman, S., Phakula, V., Maluleke, W., Bopape, M., Engelbrecht, C., Jack, C., McClure, A., Bonnet, R., Vautard, R., Philip, S., Kew, S., Heinrich, D., Vahlberg, M, Singh, R., Arrighi, J., Thalheimer, L., Aalst, M., Li, S., Sun, J., Vecchi, G., Yang, W., Tradowsky, J., Otto, F.E.L., and Dipura, R., (2022). Climate change exacerbated rainfall causing devastating flooding in Eastern South Africa. *World Weather Attribution. Scientific Report*, 1-31.
- Piper, A.M., (1944). A graphical procedure in the geochemical interpretation of water analysis. *Geophys. Union. Trans*, 25, 914–928.

- Raihan, F., and Alam, J. B., (2008). Assessment of Groundwater Quality in Sunamganj of Bangladesh. *Iranian Journal of Environmental Health Science and Engineering*, 5 (3), 155-166.
- Raju, N.J., (2007). Hydrogeochemical parameters for assessment of groundwater quality in the upper Gunjanaeru River basin, Cuddapah District, Andhra Pradesh, South India. *Environ. Geol.* 52 (6), 1067–1074.
- Rao, N.S., (1998). MHPT.BAS: A computer program for modified hill-piper diagram for classification of ground water. *Computers and Geosciences* 24(10), 991-1008.
- Ravikumar, P., and Somashekar, R.K., (2015). Principal component analysis and hydrochemical facies characterization to evaluate groundwater quality in Varahi river basin, Karnataka state, *Indian Applied Water Science*, (2017) 7,745–755.
- Reeve, R.C., Bower, C.A., Brooks, R.H., Gschwend, F.B., (1954). A comparison of the effects of exchangeable sodium and potassium upon the physical condition of soils. *Soil Science Society of America Journal*, 18, 130–132.
- Richards, L.A., (1954). *Diagnosis and Improvement of Saline and Alkali Soils*. United States Department of Agriculture (USDA). Handbook No. 60,160. Washington DC.
- SANews, (2022). South African Government News Agency. Plans to fix Musina water supply in the pipeline. <https://www.sanews.gov.za/south-africa/plans-fix-musina-water-supply-pipeline>
- SANS 241, (2015). South African National Standard 241-1; (2015). Drinking Water, Part 1: Microbiological, Physical, Aesthetic and Chemical Determinants. 241-2: 2015 Drinking Water, Part 2: Application of SANS 241-1. SABS (South African Bureau of Standards): Pretoria, South Africa.
- SAWQG, (1996a). *South African Water Quality Guidelines Volume 4: Agricultural Water Use: Irrigation Second Edition*, 1-195. Department of Water Affairs and Forestry, Pretoria.
- SAWQG, (1996b). *South African Water Quality Guidelines Volume 1: Domestic Water Use Second Edition*, 1-214. Department of Water Affairs and Forestry, Pretoria.
- Schoeller, H., (1965). *Qualitative Evaluation of Groundwater Resources*. In *Methods and Techniques of Groundwater Investigations and Development*; UNESCO: Paris, France.
- Shiklomanov, I., (1993). *World Water Resources*. In: Gleick, P., Ed., *Water in Crisis, Water in Crisis: A Guide to the World's Fresh Water Resources*. Oxford, New York.
- Shiklomanov, I.A., and Rodda, J., (2003). *World Water Resources at the Beginning of the Twenty-First Century*. Cambridge, UK, Cambridge University Press.
- Sigter, T.Y., van Ooijen, S.P.T., Post, V.E.A., Appelo, C.A.J., Carvalho, A.M.M.D., (1998). A hydrogeological and hydrochemical explanation of the groundwater composition under irrigated land in a Mediterranean environment, Algarve. *Port. J. Hydrol.*, 208, 262–279.
- Silva, E.L.L., (2004). Quality of irrigation water in Sri Lanka, Status and trends, *Asian Journal of Water and Environment Pollution*, 1(1–2), 5–12.

Simsek, C., and Gunduz, O., (2007). IWQ index: A GIS integrated technique to assess irrigation water quality", *Environmental Monitoring and Assessment*, 128, 277-300.

Singh, A.K., and Kumar, S.R., (2015). Quality assessment of groundwater for drinking and irrigation use in semi-urban area of Tripura, India. *Ecology, Environment and Conservation*, 21 (1),97-108.

South African Government, (2022). National State of Disaster-In-Numbers – 18 April 2022. Newsroom. <https://www.gov.za/speeches/national-state-disaster-numbers-%E2%80%93-18-april-2022-18-apr-2022-0000>

StatsSA, (2019). Statistics South Africa. General Household Survey. Statistical Release P0318, Pretoria.

StatsSA, (2021). Statistics South Africa. General Household Survey. Statistical Release P0318, Pretoria.

StatsSA, (2022). Statistics South Africa. Mid-year population estimates. Statistical Release P0302, Pretoria.

Stigter, T.Y., Nunes, J.P., Pisani, B., Fakir, Y., Hugman, R., Li, Y., Tomé, S., Ribeiro, L., Samper, J., Oliveira, R., Monteiro, J.P., Silva, A., Tavares, P. C. F., Shapouri, M., Cancela da Fonseca, L. and El Himer, H., (2014). Comparative assessment of climate change and its impacts on three coastal aquifers in the Mediterranean. *Regional Environmental Change*, 14(supplementary1), 41–56.

Subba Rao, N., Marghade, D., Dinakar, A., Chandana, I., Sunitha, B., Ravindra, B., and Balaji, T., (2017). Geochemical characteristics and controlling factors of chemical composition of groundwater in a part of Guntur district, Andhra Pradesh, India. *Environmental Earth Sciences*, 76: 747, 1-22.

Sujatha, D., and Reddy, R., (2003). Quality characterization of groundwater in the south-eastern part of the Ranga Reddy district, Andhra Pradesh, India. *Environmental Geology*, 44(5), 579- 586.

Sundaray, S.K., Nayak, B.B., and Bhatta, D., (2009). Environmental studies on river water quality with reference to suitability for agricultural purposes: mahanadi river estuarine system, India - a case study. *Environmental. Monitoring and Assessment*, 155, 227–243.

Swartz, C., (2007). Guidebook for the selection of small water treatment systems for potable water supply to small communities. WRC Report No TT 319/07

Swistock, B., (2022). Nitrates in Drinking Water. Penn State Extensions; 1-3. The Pennsylvania State University, Pennsylvania

Talib, M.A., Tang, Z., Shahab, A., Siddique, J., Faheem, M., and Fatima, M., (2019). Hydrogeochemical Characterization and Suitability Assessment of Groundwater: A Case Study in Central Sindh, Pakistan. *International Journal of Environmental Research and Public Health*.

The Economist Intelligence Unit, (2021). Reimagining urban water systems. The City Water Optimization Framework. The Economist Intelligence Unit Limited, London. International Journal of Environmental Research and Public Health. 16(886), 1-21.

Todd, D.K., and Mays, L.W., (2005). Groundwater hydrology. Wiley, New York, 636.

Tredoux, G., Talma A.S., and Engelbrecht, J.F.P., (2000). The Increasing Nitrate Hazard In Groundwater In The Rural Areas. WISA 2000 Biennial Conference, Sun City, South Africa, 2000.

UNEP/GRID-Arendal, (2002). Water Availability in Africa. Vital Climate Graphics Africa <https://www.grida.no/resources/7031>

UN, (2015). United Nations. Transforming Our World: The 2030 Agenda for Sustainable Development. A/RES/70/1. United Nations, New York.

UN-DESA (2024). United Nations Department of Economic and Social Affairs, Population Division (2024). World Population Prospects 2024: Summary of Results (UN DESA/POP/2024/TR/NO. 9).

UN-Water, (2015). United Nations Water. The United Nations World Water Development Report 2015: Water for A Sustainable World. United Nations Educational, Scientific and Cultural Organization, France.

UN-Water, (2021). United Nations Water. Summary Progress Update 2021 – SDG 6 – water and sanitation for all. Version: July 2021. Geneva, Switzerland.

UN-Water, (2022). The United Nations World Water Development Report. GROUNDWATER: Making the invisible visible. United Nations Educational, Scientific and Cultural Organization, France.

U.S. Department of Health and Human Services, (1991). [ATSDR] Agency for Toxic Substances and Disease Registry. Case Studies in Environmental Medicine: 16 Nitrate/Nitrite Toxicity. Environmental Alert.

Vegter, J. R., (1995). Groundwater resources of South Africa: An explanation of a set of national groundwater maps. WRC report (Water Research Commission), no. TT74/95.

Vegter, J. R., (2001). Hydrogeology of groundwater. Region 3: Limpopo granulite-gneiss belt. WRC report (Water Research Commission), no. TT 136/00.

Vinnarasi, F., Srinivasamoorthy, K., Saravanan, K., Gopinath, S., Prakash, R., Ponnumani, G., and Babu, C., (2021). Chemical weathering and atmospheric carbon dioxide consumption in Shanmuganadhi, South India: evidence from groundwater geochemistry. Environ Geochem Health 43:771–790.

Vorster, C.J., (2003). Map: Simplified Geology: South Africa; Lesotho and Swaziland. Council of Geoscience.

WA-DOH, (2018). Washington State Department of Health. Guidance Document Nitrate Treatment and Remediation for Small Water Systems, Publication Number 331-309 (Revised) Olympia, WA

Walmsley, B., and Patel, S. (2011). Botswana handbook on environmental assessment legislation in the SADC region, 3rd edition. Chapter 4: Botswana. Development Bank of Southern Africa (DBSA) in collaboration with the Southern African Institute for Environmental Assessment (SAIEA).

WARMS, (2023). Water Use Authorisation and Registration Management System. Raw data received via email communication from DWS personnel.

Watkeys, M.K., (1983). Brief explanatory notes on the provisional geological map of the Limpopo Belt and environs. Geological Society of South Africa Special Publication 8, 5–8.

Weaver, J.M.C., Cave, L., Talma, A.S., (2007). Groundwater Sampling, 2nd ed.; WRC Report No. TT303/07; Water Research Commission: Pretoria, South Africa.

Weight, W.D., (2008). Hydrogeology Field Manual, 2nd ed.; McGraw-Hill Companies Inc.: New York, NY, USA.

WHO, (1985). World Health Organization. Health Hazards from Nitrates in Drinking Water. Environmental Health. 203.385 HE. Copenhagen, Denmark.

WHO, (2003). World Health Organization. Nitrate and nitrite in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality. Guidelines for drinking-water quality, 2nd ed. Addendum to Vol. 2. Health criteria and other supporting information. World Health Organization, Geneva, Switzerland.

WHO, (2007). Chemical safety of drinking-water: Assessing priorities for risk management. World Health Organization, Geneva, Switzerland.

WHO, (2011a). World Health Organization. Guidelines on Drinking-Water Quality, 4th ed. World Health Organization: Geneva, Switzerland

WHO, (2011b). World Health Organization. Nitrate and nitrite in drinking-water Background document for development of WHO Guidelines for Drinking-water Quality. World Health Organization: Geneva, Switzerland.

WHO, (2016). World Health Organization. Nitrate and Nitrite in Drinking-water Background document for development of WHO Guidelines for Drinking-water Quality. World Health Organization: Geneva, Switzerland

WHO, (2017). World Health Organization. Guidelines for Drinking- Water Quality, fourth ed. World Health Organisation, Geneva, Switzerland.

Wilcox, L.V., (1948). The Quality of Water for Irrigation Use, US Department of Agriculture, Technical Bulletin No. 962, 1-40.

Wilcox, L.V., (1955). Classification and Use of Irrigation Waters. US Department of Agriculture, Washington, DC, Circular No. 969, 1-19.

WRC, (2014). Water Research Commission. 20 Years of Groundwater Research, Development, and Implementation in South Africa 1994-2014. SP 78/14. Water Research Commission, Pretoria, South Africa.

Yousef, A.F., Saleem, A.A., Baraka, A.M., and Aglan, O.S., (2009). The impact of geological setting on the groundwater occurrences in some Wadis in Shalatein-Abu Ramad area, SE desert, Egypt. *European Water* 25/26, 53-68.