HYDROCHEMICAL ASSESSMENT OF GROUNDWATER QUALITY AND ITS SUITABILITY FOR IRRIGATION AND DOMESTIC PURPOSES IN BREEDE WATER MANAGEMENT AREA, WESTERN CAPE

By

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Declaration

I, Matjiane Pontsho Makonko declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed **Date**

Abstract

Groundwater is an essential part of food and water security. This critical resource must be managed appropriately and used sustainably. The study was conducted in the Breede Water Management Area in the Western Cape province in South Africa. The aim was to assess the status of groundwater quality, the suitability of the water for domestic and irrigation purposes and factors contributing to the groundwater chemistry. Twelve (12) monitoring boreholes were selected for sample collection. The samples were analysed for major ions such as potassium (K^+), magnesium (Mg^{2+}), sodium (Na^+), calcium (Ca^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), nitrate (NO_3^-), fluoride (F^-) and physical variables like pH, electrical conductivity (EC), total dissolved solids (TDS) and temperature.

The suitability of groundwater for domestic use was assessed using the Water Quality Index (WQI) and Total Hardness (TH) in combination with the comparison of the major ion data with the South African Water Quality Guidelines (SAWQG) and the World Health Organisation (WHO) drinking water quality guidelines. The suitability of groundwater for irrigation was assessed using irrigation indices such as Permeability Index (PI), Magnesium Hazard (MH), Sodium Adsorption Ratio (SAR), Sodium Percentage (Na%) and graphical representation methods such as Wilcox Diagram and United States Salinity Laboratory (USSL) diagram. Multivariate statistical analysis and Piper diagrams were used to determine the geochemical processes influencing the groundwater quality in the Breede area.

The total hardness results showed that water from most boreholes is soft, with few boreholes with moderately hard and hard water. The WQI revealed that the overall groundwater in Breede is suitable for drinking. Most of the irrigation suitability indices showed that groundwater is suitable for irrigation, with a few sites that are doubtful for irrigation. The dominating water type in the area is Na-Cl, followed by mixed Ca-Mg-Cl, according to the Piper diagram. Multivariate statistical methods revealed that the groundwater in the study area is affected by the dissolution of rock salts, calcite dissolution, cation exchange and agricultural activities.

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Dedication

This thesis is dedicated to my family, to my husband Alucias Makonko and 3 children, Hlompho, Theto and Tshegofatso thank you for the unconditional love and happiness you bring to my life. To my brothers Thabo and Thato, I hope this inspires you to work hard on your dreams and be encouraged that you can achieve anything you want. To my parents Samuel and Julia Mohlatlole, thank you for always seeing me as a star, for your support, encouragement, and prayers.

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Abbreviations and Acronyms

CA	Correlation Analysis
DWAF	Department of Water Affairs and Forestry
DWS	Department of Water and Sanitation
EC	Electrical Conductivity
HCA	Hierarchical cluster analysis
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
Mbgl	Meters below ground level
MH	Magnesium hardness
meq/l	Milliequivalent per litre
Na%	Sodium Percentage
PCA	Principal Component Analysis
PI	Permeability Index
SAH	Salinity and Alkalinity Hazard
SAR	Sodium Adsorption Ratio
SAWQG	South African Water Quality Guidelines
TDS	Total Dissolved Solids
USSL	United States Salinity Laboratory
WHO	World Health Organisation
WMA	Water Management Area
WQI	Water Quality Index
WWTW	Wastewater Treatment Works

Glossary

Geochemical Assessment:	A technique used to evaluate processes affecting water quality
Hydro-chemical Facies (Water types):	Measured concentration of major ions in decreasing order
Major ions:	Positively and negatively charged ions that dissolve in natural waters
Multivariate Statistical Analysis:	Statistics method that analyses the relationship of different variables.
Over abstraction:	Unsustainable abstraction of water resources
Water quality:	The condition of the water based on its chemical, physical, and biological characteristics.
Water quality index:	An index used to determine suitability of water
Water Quality Suitability:	The ability of the water to be used for a different purpose

CHAPTER 1

INTRODUCTION

1.1 Background

Water is an essential need of life and is also of high importance in global socio-economic development. Water can come from surface or underground sources. South Africa is a water-scarce country; it is, therefore, essential to use water efficiently and sustainably.

The Western Cape province is a water-scarce area with economic activities that depend on water, thus putting pressure on the province's water resources (Western Cape Government, 2018). In addition, the agricultural sector is the most significant contributor to the economy of the Western Cape province and utilises about 40 % of the water resources (DEADP, 2011).

Cullis et al. (2018) highlighted that there is a direct link between economic growth and water quality. Economic growth results in a decline in water quality and threatens water-dependent industries. The Breede Water Management Area (WMA) has been experiencing significant urban and peri-urban growth, which has led to economic growth (Cullis et al., 2018). Several economic activities, such as agricultural, industrial, and mining, depend on water and, at the same time, contaminate water resources through wastewater discharge.

Water quality plays a vital role in these economic activities. Every water use requires a specific water quality criterion. If the water does not meet the given criteria, it is unsuitable for that particular economic activity. Water quality is as important as water availability because we will not get the correct results from economic activities without the required water quality. This implies that water quality must be part of water resource management and infrastructure development. There must be tied measures in place by decision-makers to manage water quality properly. This will assist municipalities and other authorities in the water sector to properly manage the challenges that are linked to economic development and social activities.

Proper management of water resources will require numerous water quality studies to better understand the quality state of the water, the major trends, and an evaluation to regulate the fitness of the water for its use.

The Breede WMA is one of the areas in the province with intensive agricultural activities. Good quality water is important in the agriculture sector to produce good quality food. Still, the same agricultural practices pollute the water resources by over-abstraction of the water resources and return flows from irrigation and agrochemicals (BGCMA, 2017). Poor surface water quality problems and water shortages in the province put significant strain on groundwater (Western Cape Government, 2018). There is a growing demand for groundwater in the province.

The estimated groundwater usage in the Breede WMA is 107 million m^3/a, where 103 million m^3/a is utilised solely for irrigation, with the remaining 4 million m^3/a used for domestic and stock-watering purposes (DEADP, 2011). Studies conducted in the Breede WMA identified the following water quality problems in the Breede River and its tributaries: salinity, nutrients enrichment, microbiological, agrochemicals from irrigation return flows, turbidity, impacts of sand mining, dissolved oxygen, and dairy industry (DEADP, 2011; BGCMA, 2017). There is, therefore, a possibility that groundwater can also be contaminated through surface and groundwater interaction and recharge from runoffs.

Dissolved salts and minerals in water serve as nutrients for plants and humans but are only required in small quantities (WHO, 2005). A higher concentration of chemical nutrients than required compromises the water quality, thus rendering it toxic to plants and humans (Molekoa et al., 2019). To gain a better understanding of the suitability of water used for different purposes, the chemical parameters must be analysed, focusing on the combined chemistry of all ions, not on individual ions (Belkhiri & Mouni, 2012).

There is, therefore, a need for a groundwater quality study in the Breede WMA. This study aims to assess the groundwater quality status, the suitability of the water to be used for irrigation and domestic purposes, and the potential polluting factors in Breede WMA. This will be achieved by collecting groundwater samples in the monitoring boreholes in the area and analysing them for major ions such as Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, F^- and physical properties like pH, EC, TDS, and temperature. Physical and chemical property results will be compared to international and local drinking water quality standards such as the World Health Organisation (WHO) drinking water standard and the South African Water Quality Guidelines (SAWQG) to determine the suitability of the water for drinking purposes. Other approaches will involve statistical analysis, geochemical assessment, and graphical methods to determine the suitability of the groundwater for drinking and irrigation purposes and the determination of potential polluting processes and factors.

1.2 Problem Statement

Cullis et al. (2018) mentioned that the Breede WMA has been experiencing rapid population growth in urban and peri-urban development. Population growth often leads to economic development which is mostly dependent on water and results in declining water quality. Most municipalities are not able to keep up with population growth in terms of providing basic services such as drinking water and proper sanitation, particularly in areas where informal settlements are growing rapidly. One of the leading man-made environmental pollution activities is discharging untreated or partially treated wastewater from domestic, industrial, mining and irrigation return flows into the water resources (DEADP, 2011).

The use of groundwater for irrigation and domestic purposes in the Breede WMA is growing rapidly because of surface water shortages and its deteriorating quality (BOCMA, 2015). A hydrochemical assessment of groundwater quality is crucial to ensure the suitability of the water for domestic and irrigation purposes. This will assist in searching for solutions for social and economic risks associated with declining water quality. Breede WMA is an agricultural area that contributes to the economy of the province and country through the export of agricultural products (BOCMA, 2015).

Some factors affecting groundwater quality negatively include irrigation return flows, ineffectively treated wastewater, and irrigation with untreated winery and other industrial effluents. The above factors contribute to salinity, nutrient enrichment, microbiological and agrochemical contaminations in the Breede River and its tributaries, causing the water to be less fit for its intended application (DEADP, 2011). The contaminated surface water can also reach groundwater resources through recharge systems and interaction between surface and groundwater (Singhal & Gupta, 2010). If the water quality problems are not dealt with, they will pose a threat or even destroy the most significant economic activity in the area, namely agriculture. Thus, leading to job losses and threatening food security.

Studies conducted in the Breede WMA (DEADP, 2011; BGCMA, 2017; Cullis et al., 2018) have focused primarily on surface water quality with minimal focus on a few aspects of groundwater. These studies focused on groundwater availability and allocation. The suitability of the groundwater quality for domestic and irrigation uses in the Breede WMA has not been adequately studied despite studies indicating that domestic consumption and irrigation account for 107 million m^3/a of groundwater supply (DEADP, 2011). This study will, however, endeavour to expand on this crucial aspect of groundwater. The computed research data obtained from this study will provide crucial information for authorities that will reveal water challenges in the Breede WMA. Furthermore, this will inform proper strategies for implementation concerning managing and developing groundwater resources.

1.3 Research objectives

- Assess the current groundwater quality status of the Breede Water Management Area by conducting chemical and physical analysis.

- Use of statistical and graphical presentation methods to analyse the major ion data to determine the suitability of the groundwater for drinking and irrigation purposes
- Compare the results with the requirements of WHO water quality standard and South African water quality standard for suitability of drinking purposes
- Develop a geochemical model fitted with data collected during the study to determine the processes which regulate hydrochemistry in this WMA.

1.4 Delineation of the research

The hydrochemical assessment of water quality can be categorised into physical, biological, chemical, organic, inorganic, and aesthetic (Babiker et al., 2007). This study will focus on the chemical and physical indicators only. Data analysis methods will also be limited to multivariate statistical analysis, graphical methods, index methods, and the use of water quality standards and guidelines.

CHAPTER 2

LITERATURE REVIEW

2.1 Groundwater

Groundwater is water found beneath the earth's surfaces in soil and rocks called aquifers. It is stored and moves through the pores and fractures of the aquifers. Groundwater can be found almost everywhere below the land and is less prone to pollution when compared to surface water resources (Jamuna, 2019). The quality of groundwater is different from one geological area to the other because of the different formations that are found underground (Shekhar, 2017).

Sources of groundwater pollution can be from both natural (geogenic) and human-induced sources (anthropogenic). Geogenic sources of pollution are the result of natural processes such as rock–water interaction, geological formations and aerobic or anaerobic conditions of the aquifers (Molekoa et al., 2019). Anthropogenic sources can be from agricultural return flow, over-exploitation of groundwater sources, sewage from poorly managed wastewater treatment works, chemical spillages from mines and industrial activities (Mallick et al., 2018). Water pollution is a state of water when it is no longer fit for its intended purpose.

Contaminants reach groundwater through surface and groundwater interaction, groundwater recharge systems, macro pores and abandoned wells. The contamination is spread in the aquifer by water movement and flow. Most contaminants move in the same direction as the groundwater flow (Singhal & Gupta, 2010).

Groundwater is an important source of water supply in South Africa and around the world. It is mostly used in the agricultural industry for irrigation and domestic purposes in rural areas with no municipal water supply (Shekhar, 2017). In South Africa, water used for domestic and irrigation purposes must meet the requirements stated in the water quality guidelines compiled by the Department of Water and Sanitation (DWS). The guidelines define the acceptable and unacceptable range values of constituents on different uses. If the water quality meets the requirements stated in the guidelines, then the water is considered suitable or fit for use. If the water does not meet the criteria, then the water is deemed unfit or unsuitable for that particular use.

Shekhar (2017) indicated that there are major ions of groundwater that may be assessed when conducting a groundwater quality study. These include both cations and anions. The major cations in water quality are sodium, potassium, calcium, magnesium, and the anions are bicarbonate, carbonate, chloride, fluoride, nitrate, and sulfate. These are the most important parameters to analyse when conducting a groundwater quality study.

2.2 Water quality description

Water quality defines the aesthetic, chemical, biological and physical properties of water. It is described as the fitness of water to meet the quality requirements of various water uses such as agricultural, domestic, industrial, and mining activities. The quality is influenced by constituents that dissolve in the water (DWAF, 1996a). Fitness for use is described as the judgment used to measure the suitability of the quality to meet the need of the water use.

2.3 Problems associated with water quality

If water is not of the right quality, it can affect water use in various ways. For example, soil can be damaged by irrigating with water with a sodium content higher than the accepted range according to water quality guidelines. Moreover, drinking water of poor quality can adversely affect the health of consumers. The impact of poor-quality water can be irreversible, depending on the extent of the damage and the duration of exposure. The effects can include health problems for human beings using the water for domestic purposes, productivity or yield problems on crops being irrigated, cost of treating the water and biodiversity of the aquatic ecosystem (DWAF, 1996b).

Water quality problems are linked to the constituents that affect them; not all constituents affect all water uses. When the concentration of the constituents exceeds the acceptable limits, they alter water quality and therefore cause water use problems. Other problems are caused by the interaction of two or more constituents or the presence or absence of certain constituents (DWAF, 1996a).

2.4 Determining groundwater quality status

Groundwater is one of the most important water supply sources in the Breede WMA. In some areas, it is the sole supply of drinking water. It is also used for socio-economic development, irrigation, and domestic uses. It is important that groundwater be properly used and managed to sustain it for future use. In the Breede WMA, several surface water resources are contaminated due to agricultural activities in the area. Proper management of the groundwater resources will require knowledge and information about the current water quality status of the aquifer system.

Researchers around the world adopted various methodologies for assessing groundwater quality. Many of these methods use a combination of major ion data and physical parameters to determine the suitability of the water for irrigation and domestic purposes and to assess the key factors that affect the water quality.

Major ions are ions that represent most of the dissolved substances in water; they consist of a combination of cations and anions (Hauser, 2018). Hydrogeologists use them to understand the general chemistry of aquifers. They can also be used to understand the water quality of surface sources. Their selection in water resource studies is based on their role in water quality, their impact on human health, their impact on plants and soil when used for irrigation and their pollution potential (Mohamed et al., 2018). Major cations are Na^+, Mg^{2+}, Ca^{2+} and K^+, while major anions are Cl^-, $SO_4{}^{2-}$, $CO_3{}^{2-}$, $NO_3{}^-$, HCO_3^- and F^-.

Chegbeleh et al. (2020) mentioned several methods used to study groundwater quality. Many of the methods depend on the data of major ions and physical parameters to reveal the chemistry of the water and its suitability for different uses. It is also able to determine the sources of pollution of that water resource. According to Belkhiri & Mouni (2012) classification of water obtain the best results when the concentration of all ions is considered rather than considering individual or paired ions.

Mokoena et al. (2020) used major ions to conduct a study in the Heuningnes catchment, which is in the Western Cape province of South Africa. They used major ions and physical variables to evaluate groundwater quality for domestic and irrigation purposes. Major ion concentrations were used to draw a Piper diagram which revealed that the dominating water type in the area is Na-Cl, and the groundwater quality in the area is affected by chemical weathering. The study used SAR, Na%, PI, MH, and salinity hazards to determine the fitness of the water for irrigation purposes. The irrigation suitability assessment revealed that the shallow boreholes in the area were not suitable for irrigation. The results revealed that 50 % of the samples collected were not suitable for drinking purposes by comparing the major ions to water quality standards WHO (2011) and SANS241.

Adelana et al. (2006) conducted a hydrochemical characterisation of groundwater study in the Cape flats in Cape Town, Western Cape, South Africa. With the use of the major ions the study was able to investigate sources and mechanisms of salinisation using geochemical techniques. The results revealed that sources of salinity in the Cape flats are anthropogenic sources.

Nolakana (2016) conducted a geochemical study for groundwater quality in Newcastle in the Kwazulu-Natal province, South Africa. The aim was to geochemically study the groundwater in the area and determine suitability for irrigation and domestic use. The concentration of the major ions was compared with the SAQWG and WHO water quality guidelines to determine suitability for domestic purposes. The major ions were also employed on the irrigation indices such as Na%, SAR, Residual Sodium Carbonate (RSC), Kelly's Ratio (KR), Magnesium Ratio (MR) and Permeability Index (PI) for irrigation assessment. A combination of hydro-chemical methods and multivariate statistical methods were used to understand the composition of controlling processes. All these methods use the concentration of the major ions to determine all the different aspects of groundwater quality. The results suggested that the groundwater in the area is alkaline. Most of the samples were found to comply with water quality guidelines and were suitable for drinking and irrigation. Major ion chemistry revealed that water in the area is influenced by rock-water interaction, Carbonate weathering, gypsum dissolution, cation exchange and rock salt dissolution.

Lalumbe & Kanyerere (2022) used major ions in a study in the Soutpansberg region in Limpopo Province, South Africa. They aimed to raise awareness on contamination of groundwater in rural areas and share knowledge on how water can be treated to protect food and water security and human health. This study found that some parts of the study were contaminated with F^-, NO_3^-, Cl^- and TDS when compared to water quality standards. SAR, Na%, MH, PI, and RSC were calculated using major ions and were able to determine that groundwater is suitable for irrigation purposes.

The major ions were also used by Bakari (2014) in a study in Chad Basin around Maiduguri, Nigeria. The aim of the study was to examine the impact of anthropogenic and natural sources of pollution on the aquifer system of the Chad Basin. The results show that Na^+, K^+, Mg^{2+}, Ca^{2-}, CO_3^{2-} and HCO_3^- are caused by geogenic sources such as calcium carbonate dissolution, ion-exchange processes, and silicate weathering, while Cl^-, NO_3^- and SO_4^{2-} are caused by anthropogenic activities.

Parimala Renganayaki & Elango (2014) studied the impact caused by recharge from a check dam on groundwater quality. The study was conducted near Chennai, Tamil Nadu, India. The major ions were used to assess how the surface water from the Dam impacts groundwater in the nearby area. The results showed that the water in the check dam and groundwater from boreholes around the dam were suitable for drinking and irrigation.

2.4.1 Major ion chemistry

2.4.1.1 Sodium

Bhunia et al. (2018) state that sodium is an abundant substance that is usually found in higher concentration in natural water. According to Golchin & Moghaddam (2016) excess sodium in groundwater used for irrigation destroys the soil structure of the area and affects soil drainage. It causes soil hardness which results in a reduction in permeability. In humans, excess sodium causes high blood pressure, hyperosmolarity, kidney stones and a salty taste (Sridharan & Senthil Nathan, 2017). Anthropogenic sources of sodium in water resources are domestic waste, industrial waste, and irrigated land (DWAF, 1996a).

2.4.1.2 Magnesium

According to Bhunia et al. (2018) there is ample magnesium in groundwater and other natural water sources. Singh et al. (2020) state that an excess concentration of magnesium leads to an unpleasant taste in drinking water. Magnesium and calcium are a measure of magnesium hardness. If the reaction between magnesium and calcium is not balanced, the soil's pH will increase, resulting in reduced infiltration capacity. This, in turn, reduces crop yield due to a lack of enough water (Singh et al., 2020). Magnesium activates enzymes in the human body (Bhunia et al., 2018).

2.4.1.3 Potassium

Potassium is also abundant and occurs naturally in the atmosphere. However, it occurs less than sodium, calcium, and magnesium. Potassium is also found in fertilisers (Bhunia et al., 2018). Other anthropogenic sources are effluents from wastewater treatment and run-offs from irrigated land. Excess potassium in water causes a bitter taste, nausea, and vomiting. It interacts with sodium in water and causes the water to be saline (DWAF, 1996a).

2.4.1.4 Calcium

Calcium is an alkaline earth metal that occurs naturally in water. When combined with magnesium, they are the main components of water hardness. It is vital in living organisms; it is known for strengthening bones in human beings. Its solubility in water is influenced by temperature and pH. In the metabolic system, calcium interacts with cations such as magnesium and anions such as bicarbonate, sulphate, and phosphate. In the domestic environment, calcium can cause scaling in water-heating appliances such as kettles, geysers, and urns (DWAF, 1996a).

2.4.1.5 Chloride

Chloride is an anion that occurs in natural waters. It can also be present in groundwater due to the leaching, weathering, agricultural return flow and domestic waste. Chloride also indicates that water pollution may be from high organic wastes of animals or industrial effluent. If drinking water has a chloride concentration above permissible limits in terms of drinking water quality standards, it can cause indigestion problems, heart and kidney damage, taste and palatability (Bhunia et al., 2018). In plants, chloride affects crop yields and causes leaf burn. It also increases the rate of corrosion in metals (DWAF, 1996b).

2.4.1.6 Sulfate

Sulfate is common in water; it can occur when rocks and mineral sulfate dissolve in water. Sulfate in drinking water causes diarrhea and a salty taste because it forms salts with most cations in the water. Anthropogenic causes of sulfate in water resources are acid mine waste and industrial effluent. Treatment processes for sulfate include ion exchange, microbiological reduction, and desalination processes such as demineralisation and distillation (DWAF, 1996a).

2.4.1.7 Bicarbonate

Carbonate is a concern in irrigation water since it affects the soil's physical structure. Excess bicarbonate in the water interacts with Na^+ to form $NaHCO_3$. This is called the residual sodium bicarbonate and is a measure used to determine the alkaline hazard of irrigation water (Bian et al., 2018). Natural sources of HCO_3^- in groundwater can be atmospheric CO_2, soil, and the dissolution of carbonate rocks (Al-Katheeri et al., 2009). Sridharan & Senthil Nathan (2017) state that the presence of bicarbonate in groundwater indicates that there was a mineral dissolution process.

2.4.1.8 Nitrate

According to Agyemang (2020), sources of nitrate in water are runoff from agricultural activities, fertilisers and animal excrement. In drinking water, it may lead to methemoglobinemia in infants. NO_3^- can also be converted to NO_2^- which can react with organic compounds to produce possible carcinogenic nitroso compounds in the stomach after ingestion. Water quality problems associated with nitrogen in irrigation water are its stimulating effect on plant growth and accelerating algae growth. Nitrogen has the potential to accelerate the growth of unwanted vegetation, leading to a delay in crop growth (DWAF, 1996b).

2.4.1.9 Fluoride

Agyemang (2020) states that fluoride concentration must be below 1.5 mg/L for water used for drinking. Fluoride causes dental fluorosis and skeletal fluorosis. The appropriate fluoride concentration for children is 0.6 mg/L. A higher concentration can lead to tooth decay. When it reacts with water, it forms hydrofluoric acid. Plants have a high tolerance for fluoride in the soil, but elevated levels in the soil in a short space of time may result in reduced crop yield (DWAF, 1996b).

2.4.2 Physical Parameters

Physical parameters alone are not linked to water quality problems, but they mostly influence the ions' toxicity. This makes them essential variables in water quality studies.

2.4.2.1 TDS and EC

TDS measures the total dissolved inorganic salts that have dissolved in the water. The concentration of TDS and EC are directly proportional to each other (Dhanasekarapandian et al., 2016). The concentration of EC indicates the presence of the major cations and anions. Geological characteristics influence the concentration of TDS, resulting from natural processes that happen when minerals in rocks dissolve in the water. Anthropogenic activities contributing to TDS are effluents from domestic and industrial activities, urban and cultivated land runoffs. TDS is linked with water quality problems like corrosion, scaling, and hardness due to the various inorganic salts that dissolve in the water (DWAF, 1996b).

2.4.2.2 pH

Water has a pH that ranges from 6.5 – 8.5. The pH has effects on the treatment processes. There are biological and anthropogenic activities that increase the pH levels, such as nutrient cycling, industrial effluent, acid mine drainage and acid-forming substances released into the atmosphere. When the pH is low below 7 the water tastes sour because it is acidic and when the pH is higher above 7 the water tastes bitter and soapy because of alkalinity. pH alone cannot be linked with health effects on humans, but it increases the toxicity of metal ions by increasing their solubility in water. In irrigation water, pH affects crop yield as affected by foliar damage (DWAF, 1996a).

2.5 Groundwater suitability for drinking purposes

Intake of polluted water leads to various illnesses, diseases, and death in many countries. Water used for drinking should be clean and have a low concentration of ions (Elumalai et al., 2020). Groundwater suitability for drinking purposes can be evaluated using the physical parameter and concentration of major ions compared to acceptable drinking water quality standards like SAWQG and WHO water quality guidelines. The standards and guidelines give value ranges for each chemical variable to comply with. They indicate that the concentrations of the chemical variables are at an acceptable or toxic level. Other methods that can be used for groundwater suitability for drinking include the Water quality index and total hardness.

2.5.1 Water Quality Guidelines

2.5.1.1 South African Water Quality Guideline (SAWQG)

The guidelines were developed by the Department of Water and Sanitation, as the custodians of water resources in South Africa. The guidelines are a decision support tool used for water quality judgements and are used by role players involved in the concept of water quality. This ensures that water quality in South Africa is judged in the same manner (DWAF, 1996a; DWAF, 1996b). The guidelines were developed in line with international standards and literature, but they are specific to the South African systems and situations. They are updated periodically to add new constituents and revise existing ones when new international and local information becomes available (DWAF, 1996a; DWAF, 1996b).

According to the guidelines, the concentration of the constituents must be maintained at a no-effect range. The no-effect range is the range where the concentrations of the constituents do not cause any harm to water use, even when the water is used for an extended period. This represents the ideal range (DWAF, 1996a; DWAF, 1996b).

2.5.1.2 World Health Organisation guidelines for drinking water quality

The purpose of WHO guidelines is to protect the health of the public. The guidelines provide important recommendations to manage the risk of drinking water quality. The guidelines serve as a supporting tool for the development of strategies that will ensure water used for drinking purposes is safe for consumers. Different countries use the WHO guidelines to develop their own drinking water standards specific to their system (WHO, 2017).

2.5.2 Water quality index (WQI)

WQI is a technique used in water quality studies for analysing the data. It is used for determining the state of water quality and its suitability for drinking and irrigation purposes in both surface and groundwater. Researchers use WQI for translating complex data with different variables into a single number that can reveal the status of water quality (El-Aziz, 2018). WQI classifies the water quality results into specific categories. The WQI value of between 0 – 50 is considered excellent, 50 – 100 is good, 100 – 200 is poor, 200 – 300 is very poor and above 300 indicates unsuitable water for drinking (Molekoa et al., 2019; Shaikh et al., 2020).

2.5.3 Total hardness

Total hardness is a result of the calcium and magnesium concentration in water. Water can have a temporary or permanent hardness. Temporary hardness results from calcium and magnesium bicarbonates, while permanent hardness is a result of salts like sulfate and chlorides.TH causes scaling in plumbing and household heating appliances, preventing the lathering with soap and increasing the boiling point (Singh et al., 2020). Water hardness can cause kidney failure in human beings (Nolakana, 2016). The presence of soluble calcium and magnesium in the geology causes natural water hardness (DWAF, 1996a).

Verlicchi & Grillini (2020) assessed critical pollutants in drinking water in Mozambique and South Africa. The study used water quality guidelines available in each country to compare the major ion data to determine the water's suitability for drinking purposes.

Ntanganedzeni et al. (2018) conducted a study in the Tugela Catchment in South Africa, which aimed to assess the groundwater quality and potential polluting sources in the Tugela Catchment. The study used geochemical and statistical methods and revealed that 80 % to 90 % of boreholes exceeded limits in terms of WHO and SAWQG water quality guidelines.

According to El-Aziz (2018), using water quality standards and guidelines are traditional methods that effectively evaluate groundwater's suitability for drinking purposes. El-Aziz (2018) conducted a study in the south-western region of Libya using traditional methods and WQI. Parameters such as EC, SSP, SAR, PI, and KR were compared to WHO water quality guidelines and used to calculate WQI for irrigation suitability. WQI can be used for evaluating groundwater suitability for both irrigation and drinking purposes.

Ranganai et al. (2001) conducted a groundwater study in Ramotswa Wellfied in Botswana. They used the Botswana drinking water standards and WHO drinking water quality guidelines to assess if the groundwater in Ramotswa can be used for drinking purposes. The results showed that nitrate values were above the WHO desirable level of 45 mg/l. Concentrations of iron, manganese, chloride, and sulphate were also occasionally found to be above the Botswana drinking water standards. Still, it was at a range that is considered not to cause any harm to human health.

Bhunia et al. (2018) used GIS and geo-statistic techniques to evaluate if the water in semi-arid region of Neyshabur can be used in agriculture for irrigation and homes for domestic. GIS was used to draw a map for spatial variation of the data to see how different sub-areas are from one another. The fitness of the water for drinking purposes was achieved by comparing the concentration of major ions and physical parameters with WHO (2011) recommended water quality standard.

Dhanasekarapandian et al. (2016) used WQI to assess groundwater quality in the Gridhumal river sub-basin, India. The results revealed that the water was not suitable for drinking.

2.6 Groundwater suitability for irrigation purposes

Irrigation water refers to water used to meet crops and plants' water requirements to help them grow. Irrigation refers to the application of water to the soil through various systems of tubes, pumps, and sprays. Irrigation water can be used for commercial crops, home gardening, potted plants, and the production of commercial floricultural crops. The type of soil, climate conditions, irrigation system and crop type have an influence on the plants towards the water quality. When determining the suitability of water for irrigation, both its effects on soil and plant must be considered. Water which is unsuitable for irrigation results in a reduced crop, impaired crop quality, impairment of soil suitability, and damage to the irrigation system (DWAF, 1996b).

The biggest challenge with irrigation water is the salinity and alkalinity hazard (SAH) of the water. Salinity measures the amount of salt present in the water. Alkalinity is the buffering capacity of the water, which is the measure of the water body to maintain a stable pH level. Evaluating the salinity and alkalinity hazard in water used for irrigation is essential. Salts pile up in the soil during irrigation, causing the soil to become saline. This will prevent the penetration of water to the roots of plants. The water requirements of the plants will not be met, resulting in reduced crop production and impaired crop quality. Excess salts in the soil also damage the physical structure of the soil, causing it to be less suitable for agricultural activities (Singh et al., 2020).

SAH can be determined by plotting the USSL diagram using the EC, which represents the salinity hazard parameter and the SAR which is the alkalinity or sodium hazard parameter. A Wilcox diagram is also an effective graphical presentation method used for evaluating the irrigation suitability of groundwater. It is a plot of the percentage sodium versus electrical conductivity (Bhunia et al., 2018; Singh et al., 2020).

Many local and international reports (Bhunia et al., 2018; El-Aziz, 2018; Ntanganedzeni et al., 2018; Srivastava, 2019; Singh et al., 2020) have also declared the following parameters as important and effective when determining the fitness of water for irrigation purposes; EC, SAR, Na%, PI.

Ntanganedzeni et al. (2018) used Na%, SAR, KR, MH, RSC, salinity hazard and PI to determine the fitness of groundwater in the Tugela Catchment in South Africa for irrigation purposes. The results from PI, SAR, MH, and RSC revealed that most of the boreholes in the area are suitable for irrigation, while results from KR, Na% and salinity hazard revealed that the water is permissible to unsuitable. The USSL suggested that water in the area is only suitable for irrigation on coarse-textured soil and only on crops that have a high tolerance for salt.

Sithole (2018) revealed the significance of using a combination of irrigation index methods (SAR, RSC, EC, PI, MR, and Na%) and graphical presentation methods such as (USS and Wilcox) to understand the groundwater quality for irrigation purposes. USSL results revealed that the water in the study area has high salinity and alkalinity, therefore, cannot be used for irrigation. The concentration of the major ions was found to exceed WHO limits. Both the graphical methods and irrigation indices revealed that groundwater in the area is polluted and unsuitable for irrigation.

Nyirenda et al. (2015) also conducted a study on the groundwater quality of Salima and Nkhotakota in Malawi. The results from irrigation indices showed that groundwater is suitable for irrigation in the area.

A study in North-eastern Tunisia conducted by Houatmia et al. (2016) also used the WQI and irrigation indices such as SAR, Na%, RSC, MH, and PI to determine irrigation suitability. The results suggested that the groundwater in the area is not suitable for irrigation.

These irrigation suitability methods are not only reliable for groundwater but can also be used to assess surface water suitability. Bhat et al. (2016) assessed surface suitability for drinking and Irrigation purposes on surface water resources of South-West Kashmir, India. The results from this study suggested that the surface water resources of South-West Kashmir were suitable for irrigation.

In Patuakhali District, a Southern Coastal region of Bangladesh, a hydrogeochemical and quality assessment of groundwater was conducted by Islam et al. (2017). The hydrogeochemical assessment used different indices such as Na%, SAR, RSC, KR, Wilcox diagram and USSL diagram for assessing its suitability for irrigation. The results showed that the water in the area is not suitable for irrigation.

2.6.1 Sodium Adsorption Ratio (SAR)

Dhanasekarapandian et al. (2016) reported that SAR is one of the major factors considered in determining the suitability of water for irrigation. Constituents that influence the concentration of SAR are sodium, magnesium, and calcium; their concentrations are directly proportional to the concentration of SAR. Excess sodium in irrigation water alters the physical structure of the soil and lowers its permeability. Salt in the soil prevents water from penetrating through the soil, which makes it difficult for water to reach the roots of plants; hence there will be reduced crop yield. The plant can also experience leaf burn, scorching, and dead tissue due to high sodium concentration (Dhanasekarapandian et al., 2016).

2.6.2 Sodium Percentage (Na%)

Sodium is the main contributor to the Sodium Adsorption Hazard. When Na^+ interacts with HCO_3^- and CO_3^{-}, it forms alkaline soil. When it reacts with Cl^- it forms saline soil. Excess sodium affects soil permeability; it changes the texture of the soil, making it hard to plough. The maximum allowed Na% for irrigation water is 60 %. The combined effect of Na% and EC results in a decrease in the osmotic activity in plants; this limits absorption of water and nutrients from the soil. Wilcox diagram is a plot of Na% and EC; it is often used to show this effect through a graphical presentation (Sharma et al., 2017).

2.6.3 Magnesium Hardness (MH)

Magnesium damages the structure of the soil. Magnesium and sodium make the soil alkaline. This alkalinity affects crop yield. When magnesium has a ratio of more than 50 %, the water becomes harmful and unsuitable for irrigation (Dhanasekarapandian et al., 2016). When magnesium and calcium are not in equilibrium, the pH increases and the infiltration capacity of the soil decreases. The lack of water on the plant decreases crop yield (Singh et al., 2020).

2.6.4 Permeability Index (PI)

Reduction in soil permeability results from long-term irrigation with poor quality water with high salt concentrations (Srivastava, 2019). PI is affected by calcium, magnesium, and bicarbonate (Elumalai et al., 2020). Sharma et al. (2017) indicated that PI has three classes to describe the quality of water. Class I shows 100 % permeability, and the water is suitable for irrigation. Class II shows a 75 % permeability, meaning it is slightly suitable. Class III shows 25 % permeability and is unsuitable for irrigation.

2.6.5 United States Salinity Laboratory (USSL) diagram

USSL is a graphical presentation method used for water quality data analysis. It is used as a data analysis method that reveals if water can be used for irrigation. It is plotted using sodium absorption ratio and electrical conductivity (Dhanasekarapandian et al., 2016). The *C* stands for conductivity which represents the salinity hazard. The *S* stands for SAR, which represents the sodium or alkali hazard. At *C1* the salinity is less than 250 µS/cm, which means the water can be used for irrigation and there won’t be any accumulation of salt on the soil. At *C2* the salinity ranges from 250–750 µS/cm. This water will start to affect sensitive plants and accumulate salt. At *C3* the salinity ranges from 750–2250 µS/cm; most plants will be affected by salinity. At *C4* the salinity is above 2250 µS/cm, and the water is unsuitable for irrigation. Only plants with high salt resistance can be irrigated with this water. The soil must also have good drainage (Singh et al., 2020).

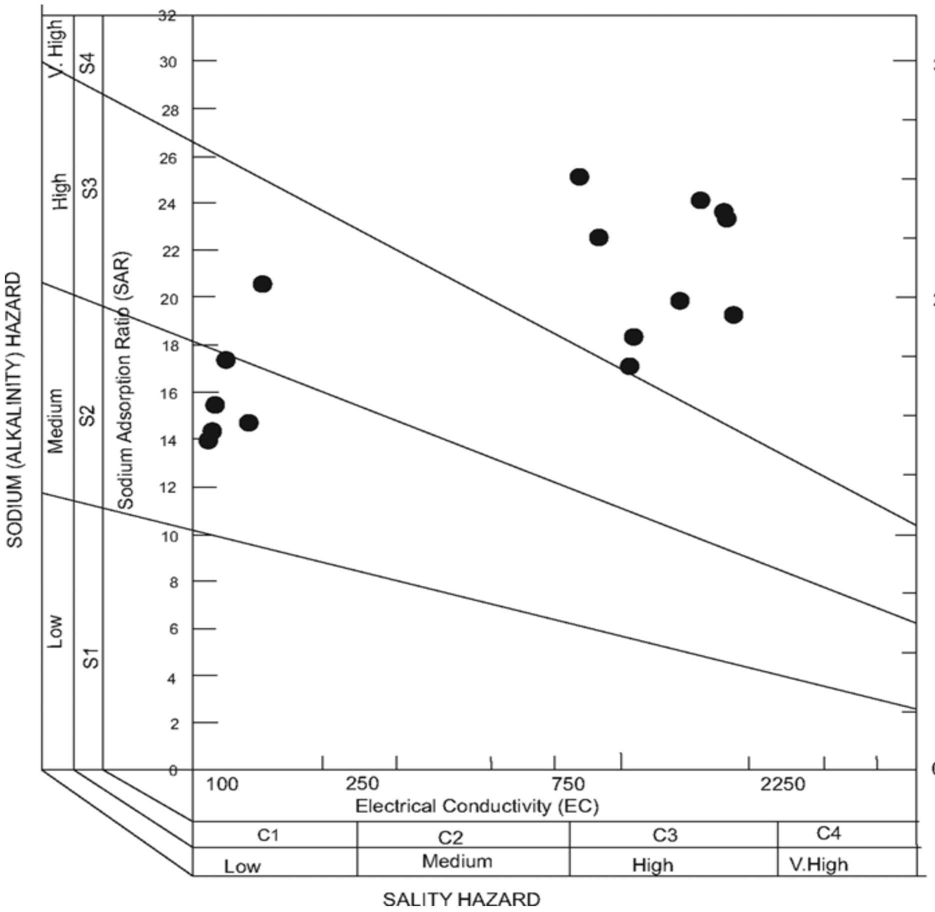

Figure 2.1: USSL diagram for groundwater suitability for irrigation (Malaza, 2017)

2.6.6 Wilcox Diagram

A Wilcox diagram is a plot of electrical conductivity against the percentage sodium. The diagram is used to determine the fitness of groundwater to be used for the irrigation of crops. The diagram is categorised into different categories, explaining the water quality and its capability to be used for irrigation. The categories are excellent to good, good to permissible, doubtful to unsuitable and unsuitable (Singh et al., 2020).

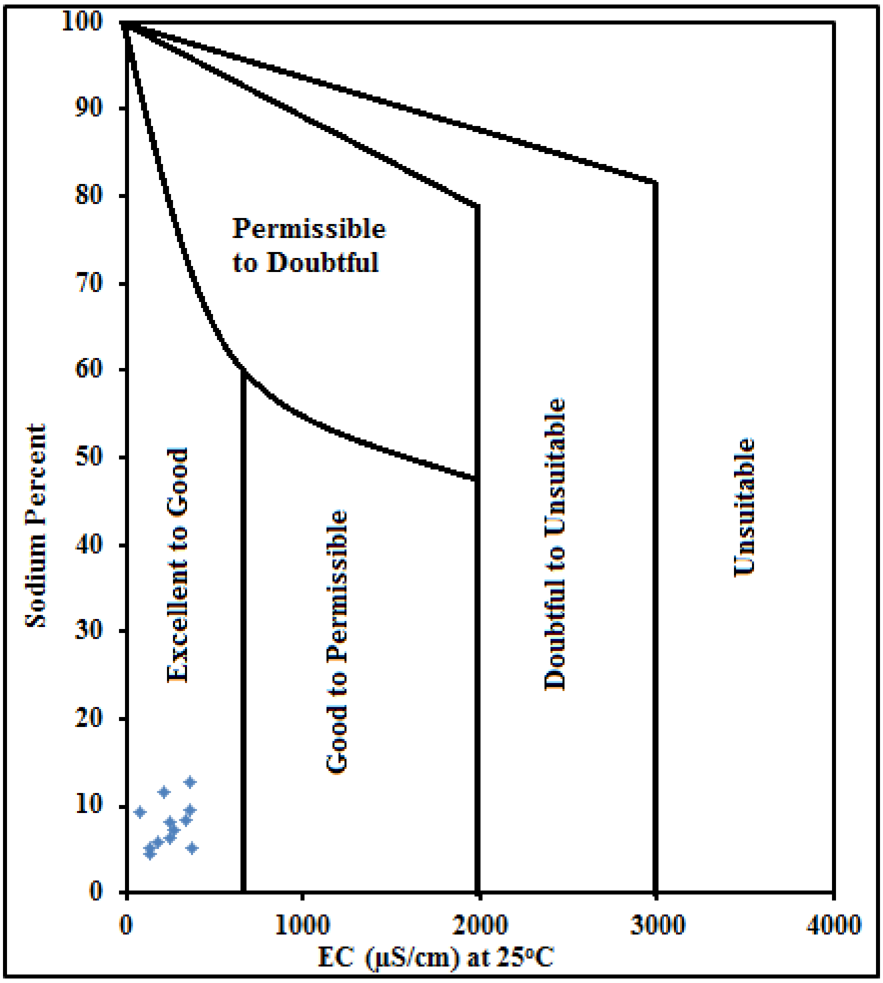

Figure 2.2: Wilcox diagram for groundwater suitability for irrigation (Bhat et al., 2016)

2.7 Geochemical Assessment of groundwater

Geochemical assessment refers to the evaluation of possible causes of groundwater quality evolution in the aquifer. The assessment includes both the natural and anthropogenic processes that affect groundwater quality. Various factors influence the groundwater chemistry, such as the geology of the area, degree of chemical weathering of various rock types, the quality of water recharging the aquifer, land use activities (Marghade et al., 2015), flow conditions such as water velocity and environmental conditions such as the temperature and pressure (Mohammadi, 2009).

Geochemical assessment is used as a tool to acquire information that helps in the effective management of groundwater quality. In an area like the Breede WMA where most economic activities depend on groundwater, it is important to understand the key controlling factors. This will help the authorities to put proper measures in place for using and developing groundwater.

Knowing key factors would help to protect the quality of groundwater (Yu et al., 2014). The advantage of geochemical assessment is that it gives important historical information about the geology of the area, sources of groundwater recharge, velocity, and direction of groundwater flow (Al-Katheeri et al., 2009).

2.7.1 Piper diagram

A Piper diagram is one of the methods used by researchers for geochemical assessment. The trilinear diagram is used to interpret the major ion data by showing the dominating water types, also known as water facies of the water body. Ravikumar et al. (2011) describe the facies as recognisable parts of different characters belonging to any genetically related system. Hydrochemical facies are distinct zones that possess cation and anion concentration categories. According to Sharma et al. (2017) and Ravikumar et al. (2011) the trilinear diagram consists of two triangles and a diamond shape in the middle. The cations are in the left triangle, while the anions are in the right triangle. The overall analysis of the sample takes place in the diamond shape. Piper simplifies large data, reveals the ions that dominate in the water sample and determines the similarities and differences in the water composition (Al-Katheeri et al., 2009).

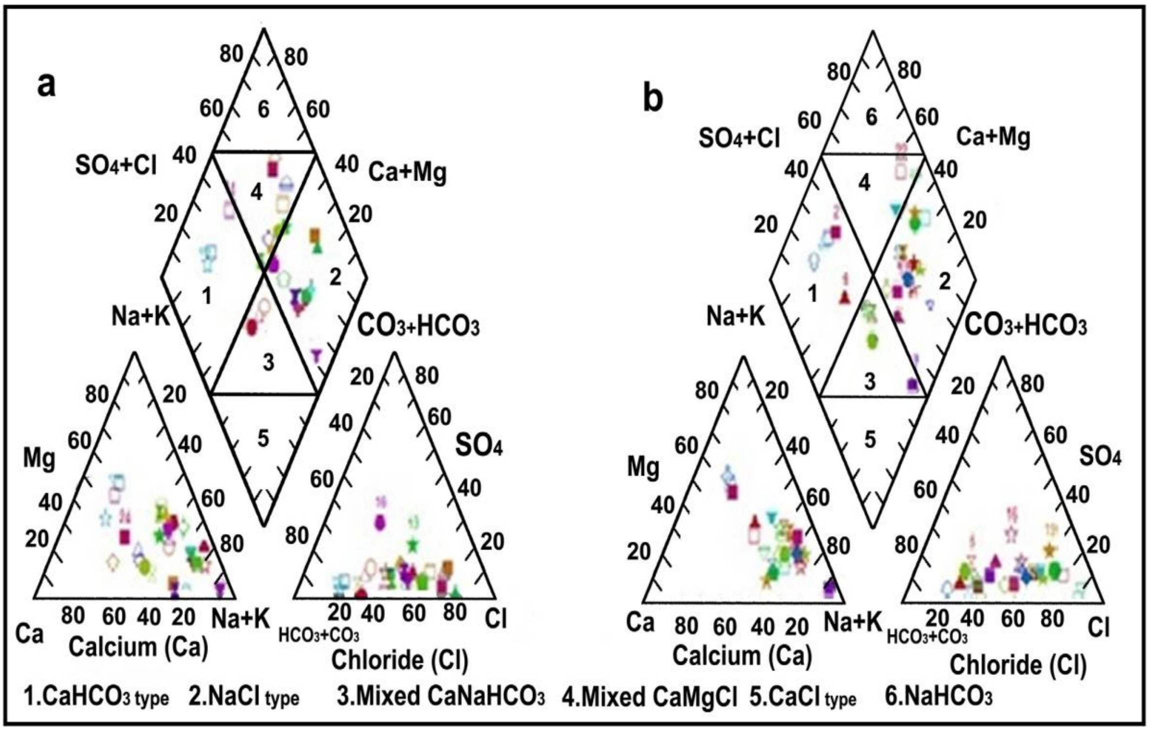

Figure 2.3: Piper diagram for geochemical facies (Dhanasekarapandian et al., 2016)

2.7.2 Geochemical Assessments using Multivariate Statistical Methods

Multivariate statistical analysis is another method used for geochemical assessment. It is used to understand the relationship between the variables (Elumalai et al., 2020). The method includes Correlation Analysis (CA) and Principal Component Analysis (PCA). These methods have confirmed their effectiveness in extracting critical information for geochemical assessment. It evaluates the spatial distribution of the pollutant (Dhanasekarapandian et al., 2016). Statistical analysis is different from graphical presentation methods because it provides information on the number of variables and can deduce relationships among variables (Srivastava, 2019). Using both graphical and statistical analysis will yield better results than using one method.

2.7.2.1 Correlation Analysis (CA)

Correlation analysis determines the relationship that the variables in a study have with one another. In terms of groundwater quality studies, CA can reveal the relationship between the major ions and the physical variables. This will reveal the sources of origin of the ions, which will then reveal the processes that influence the chemistry of a groundwater resource (Elumalai et al., 2020).

2.7.2.2 Principal Component Analysis (PCA)

PCA can be used to identify the relationship and origin of ions (Elumalai et al., 2020). It takes the large raw data and simplifies it into principal components (PC) arranged in decreasing order of importance. The PCs can be used to understand the processes that influence the chemistry of the aquifer. PCA is determined using three steps. The first step is to determine the correlation coefficient, the second step is to estimate factor loadings, and the third step is factor rotation and interpretation (Dhanasekarapandian et al., 2016). PCs with eigenvalues greater than 1 are used to further process the data. Varimax rotation is then applied to the PCs for further analysis of the data. Factor loadings with loading values of > 0.75 are considered strong, between 0.50 – 0.75 are considered moderate and between 0.30 – 0.50, are considered weak (Bouteraa et al., 2019).

Elumalai et al. (2020) applied multivariate statistical analysis in a study conducted in the Luvuvhu sub-catchment in Limpopo, South Africa. The study used PCA and CA to understand the potential pollution sources of the groundwater in the area. The results revealed that the water is fresh and acidic to alkaline. The Piper diagram showed that Ca-Mg-Cl and Ca-HCO_3 are the dominating water types of the area. PCA and Pearson correlation analysis revealed that groundwater in the area is affected by geogenic and anthropogenic activities.

Malaza (2017) used a Piper diagram to determine the dominating water type in a Soutpansberg around Tshikondeni, Limpopo Province, South Africa. The study focused on the type of natural and anthropogenic activities contaminating groundwater. The dominating water type was found to be Na^+-Cl^- followed by mixed Mg^{2+}-Ca^{2+}- SO_2^- using the Piper diagram. Leaching of ions and weathering are the two geogenic processes found to affect groundwater in the area. The anthropogenic sources of pollution were found to be from mining and agriculture.

Marghade et al. (2015) combined multivariate statistics method and the Piper diagram in a study in Nagpur in central India. The study aimed to identify the processes that influence groundwater chemistry in the area. The Piper diagram revealed that the dominating water types in the area are Ca–HCO_3, mixed Ca– Na–HCO_3 and mixed Ca–Mg–Cl types. PCA results showed high loadings of EC, TDS, TH, Cl^-, NO_3^-, Ca^{2+} and Mg^{2+} compared to other variables. This suggests that sources of contamination in the area are from anthropogenic activities. The second principal component (PC2) shows high loading of Na^+ and HCO_3^- which suggests that sources of contamination can also be from geogenic sources.

CHAPTER 3

METHODOLOGY

3.1 Study Area

3.1.1 Location

The Breede WMA is situated in the Western Cape Province in South Africa. It covers an area of 19 668 km^2 (DWAF, 2002). It is bounded in the west by the Berg Water Management Area, the Olifants/Doorn and Gouritz Water Management Areas in the north and east, respectively, and the Indian Ocean in the south (DWAF, 2002). Breede WMA consists of several municipalities, which are Breede valley, Theewaterskloof, Langerberg, Overstrand and Witzenberg (BOCMA, 2015). The main river is the Breede river and the largest dam is Theewaterskloof (Cullis et al., 2018).

3.1.2 Climate

Breede WMA experiences winter rainfall. April to September is the wet winter season and the dry hot season is from October to March. Rainfall is higher in the mountainous area, which is the southern part of the WMA, except for the mountainous area in the northern part of the valley which experiences less rainfall. The topography of the area is responsible for the different rainfall patterns of the area. The highest rainfall experienced in the mountains is 2 300 mm per annum, while the low-lying areas experience about 4 00 mm per annum. During the summer months, the weather is dry and hot, with significant evaporation. Temperatures vary between -1 °C in winter and 30 °C in the summer months (DWAF, 2008).

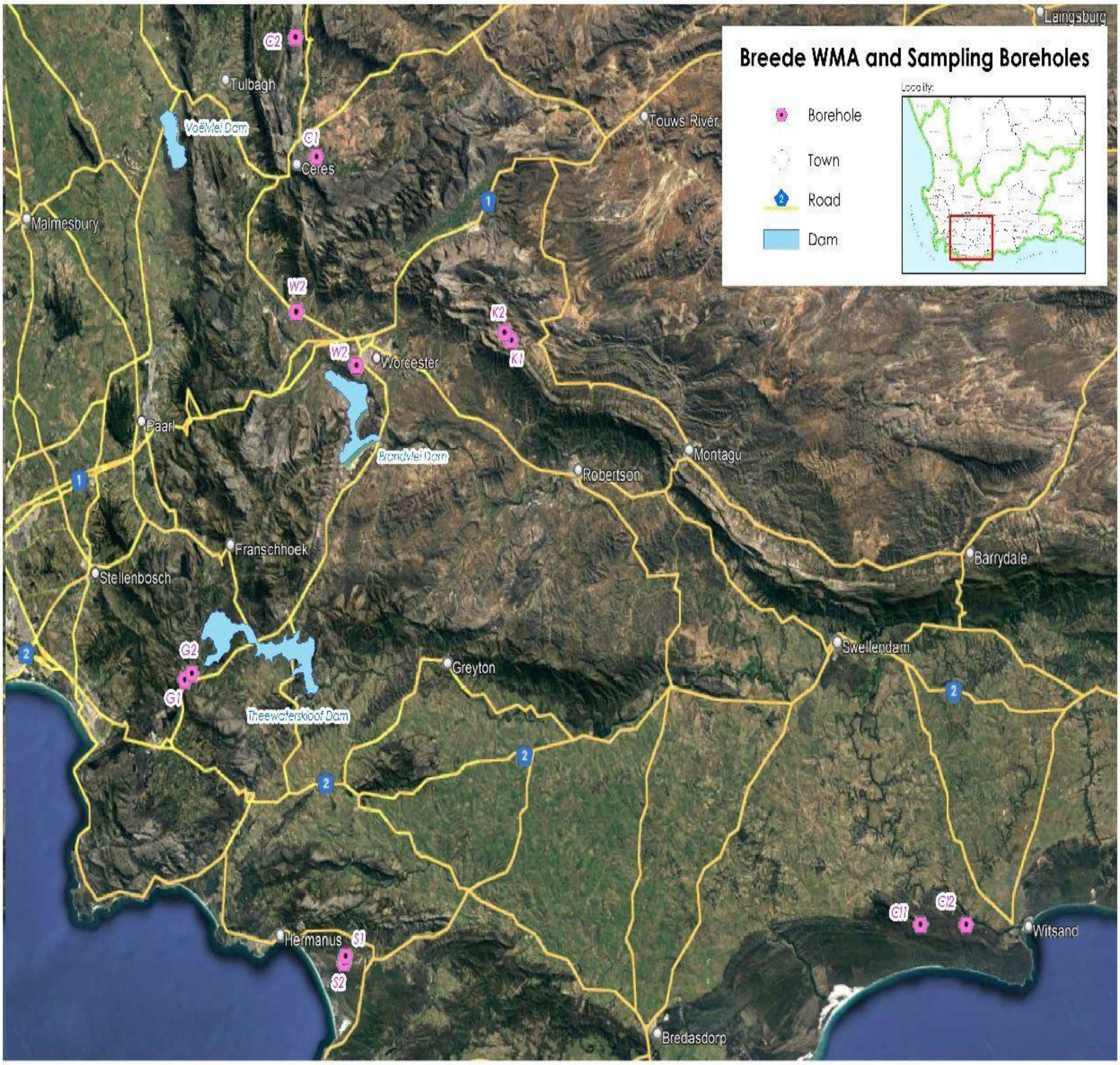

Figure 3.1: Breede Water Management Area and the selected boreholes

3.1.3 Geology

According to DWAF (2002), the dominating geology in the Breede WMA is the strata of the Cape Supergroup, with the mountain ranges comprising mainly Table Mountain sandstone. The Supergroup constitutes the largely arenaceous Table Mountain Group which unconformably overlies the Malmesbury and Cape Granite rocks and underlies the Bokkeveld Group. The Bokkeveld group predominantly comprises argillaceous beds and the uppermost

Witteberg Group consists of alternating shales and sandstones. The coastline consists of extensive limestones (DWAF, 2002).

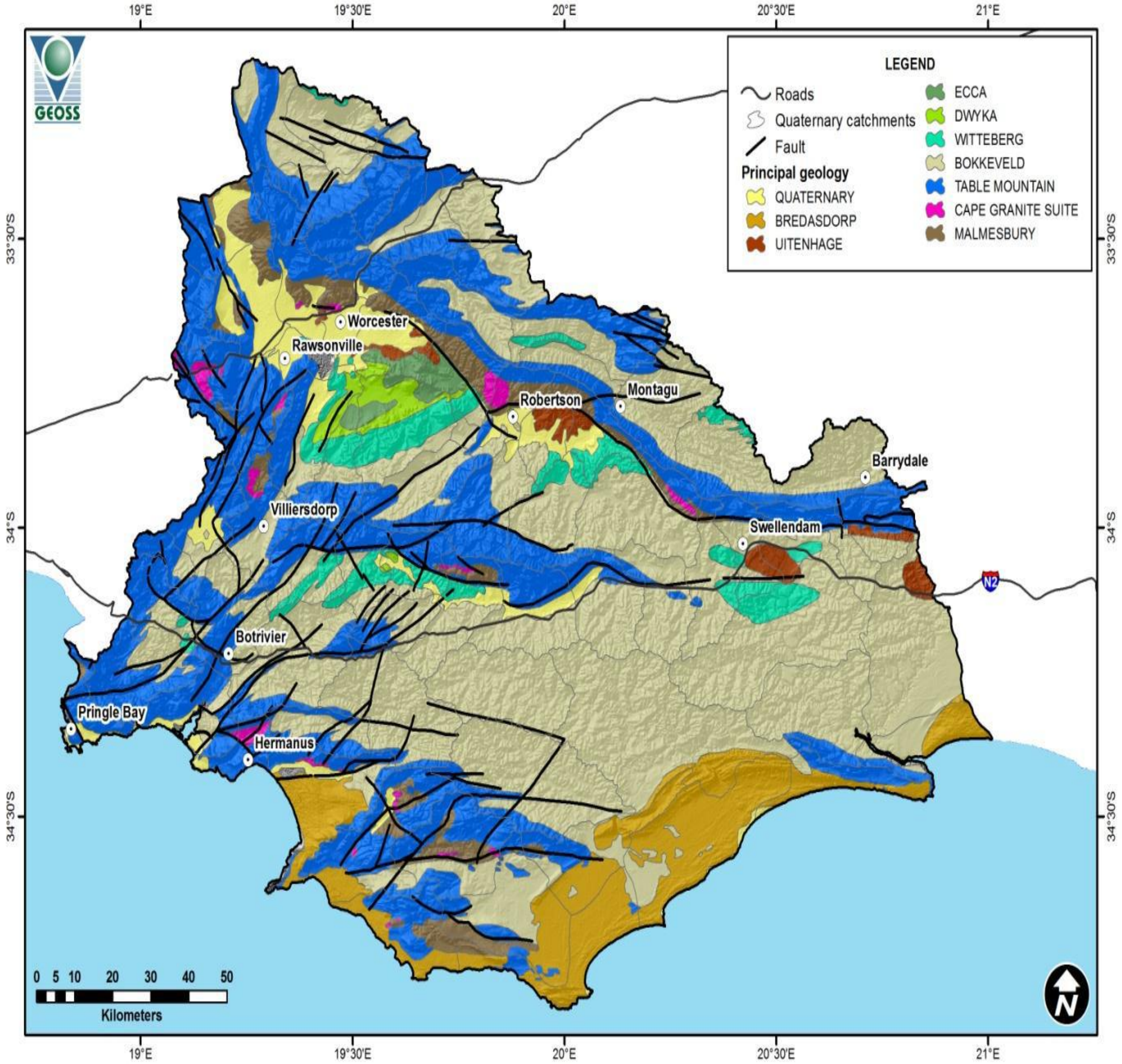

Figure 3.2: Geological setting of Breede Water Management Area (DEADP, 2011)

3.1.4 Economic activities

The dominant economic activity in Breede WMA is commercial agriculture. The area produces grapes, apples, pears, dairy and deciduous fruits. Livestock farming is also prevalent. Some areas in Breede are focused on dry land farming, which produces wheat and plant oils. Most of these products are exported (BOCMA, 2015).

3.2 Data Collection

Data for this study was acquired by collecting groundwater samples from 12 selected boreholes (Table 3.1). The Department of Water and Sanitation has 62 monitoring boreholes around the Breede WMA. For this study, 12 boreholes were selected based on several seasons. The boreholes were selected based on possible spatial distribution, allowing a reasonable representation of the study area. The second reason was the depth of the boreholes. Two boreholes were selected in every sub-area, one shallow borehole with a depth of less than 10 m and one deep borehole with a depth of 30 m. Some of the sub-areas did not have shallow boreholes; therefore, two deep boreholes were selected. Choosing boreholes with different depths allows for the collection of samples from multiple aquifers within the sub-area (Sundaram et al., 2009). The boreholes were also selected to represent various land activities, from domestic, agricultural, and industrial activities. Within the agricultural industry, various crop types and irrigation practices were considered which will address different contamination potentials with reference to pesticides and nutrients.

The samples were analysed for Mg^{2+}, Na^{+}, K^{+}, Ca^{2+}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-}, F^{-} and physical parameters such as pH, TDS, temperature, and EC. Samples were collected in the month of February which represents the summer season, May which represents autumn, and August which represents the winter season.

Table 3.1: Selected boreholes used for data collection

Borehole ID	Borehole No	Longitude	Latitude	Sampling depth (mbgl)	Area
BE00040	G1	19.06163	-34.07376	30	Grabouw
BE00045	G2	19.07631	-34.06578	30	Grabouw
BE00184	C1	19.34602	-33.39088	30	Ceres
G39936	C2	19.30362	-33.23544	16	Ceres
HG8	K1	19.75605	-33.63371	30	Koo Valley
ECK01	K2	19.74271	-33.62331	30	Koo valley
G30960	W1	19.42852	-33.66402	30	Worcester
G31010B	W2	19.30156	-33.59336	16	Worcester
BE00006	S1	19.39704	-34.44688	80	Stanford
BE00005	S2	19.40063	-34.43758	7	Stanford
BE00031	CI1	20.62863	-34.39495	30	Cape Infanta
BE00030	CI2	20.72643	-34.39495	30	Cape Infanta

mbgl = meters below ground level

3.2.1 Sampling Method and physical parameter analysis

The samples were collected using a bailer and applying the low flow method. The low-flow method allows for the collection of a good representative sample without purging the borehole. The sample is collected at a specific depth which is the flow zone of the borehole (Sundaram et al., 2009). The flow zone is at the depth where the screen of the borehole was inserted. Newell et al. (2000) mentioned that the low-flow method is suitable compared to the purging method because it eliminates variability introduced by purging. The advantage of the low-flow method is that it leaves the stagnant water within the borehole undisturbed. A representative sample is collected directly from the aquifer through the screened interval at the depth of the pump.

For sample collection, the bailer was slowly and gently lowered into the borehole until at a depth of the screen. The bailer was allowed to fill without disturbing the water column. The bailer was pulled up slowly and carefully without disturbing the stagnant water in the casing. The water was transferred into the sampling containers. The sample containers were rinsed three times with water from the borehole before collecetion of the sample.

The first sample was used to measure the EC, pH and temperature using the Extech digital multiparameter meter. From the bailer, the water was poured into a beaker. The first parameter to be analysed was temperature to avoid the influence of ambient temperature on the sample. The temperature and EC use the same electrode; therefore, they are measured simultaneously. The electrode was connected to the meter. The instrument was calibrated for all three parameters before coming to the site. The same procedure was followed using a pH electrode to measure the pH of the sample. The sample was discarded, and all electrodes were rinsed with deionised water, caps closed and stored.

The samples for the major ions and TDS were collected using the same procedure. High-density polyethylene (HDPE) (2 x 1.0 L) bottles were used for sampling. The bottles were thoroughly washed and rinsed with a solution of 1:1 nitric acid, followed by deionised water to remove any water-soluble compounds. At the sampling site, the bottles were rinsed three times with water from the borehole before taking water samples (Sundaram et al., 2009).

One bottle was for the anions and TDS and the other was for the cations. Samples collected for cations were preserved with nitric acid (Ravikumar et al., 2011). Concentrated nitric acid was transferred using a measuring cylinder while measuring the pH of the sample until the pH was less than 2.0. This minimised precipitation and adsorption to the container wall during transportation of the sample to the laboratory (Ravikumar et al., 2011; Molekoa et al., 2019). The samples for anions were kept in a cooler box with ice to keep them cool during transportation to avoid chemical changes (Weaver et al., 2007). All samples were labelled accurately with borehole number, sampling date, time, and borehole location.

3.2.2 Calibration of the Extech digital multiparameter meter

3.2.2.1 pH calibration

For pH, a 3-point calibration was conducted using the standard pH 4, 7 and 10 buffer solutions employing an Extech digital dissolved oxygen, conductivity, TDS, and pH multi-meter (Model DO700).

3.2.2.2 EC calibration

EC calibration was conducted using a reference solution of 1413 uS/cm employing an Extech digital dissolved oxygen, conductivity, TDS, and pH multi-meter (Model DO700).

3.3 Sample Analysis

The borehole samples were analysed using spectroscopic, spectrophotometric and titrimetric methods for the cations (Na^+, K^+, Ca^{2+} and Mg^{2+}), anions (NO_3^-, F^-, Cl^- and SO_4^{2-}) and physical parameters (EC, TDS and hardness), respectively.

3.3.1 Cation Analysis

The cations were analysed by Inductively Coupled Plasma-optical emission spectrometry (ICP-OES) using a Prodigy6 (Teledyne Leeman Labs) spectrometer. The samples were filtered using 0.45 µm filter paper prior to analysis to remove any suspended solids. Each sample was pipetted into a 100 ml volumetric flask and preserved with 1 ml of 65 % nitric acid. Sodium was analysed at a wavelength of 589.592 nm, calcium at 315.887 nm, magnesium at 285.213 nm and potassium at a wavelength of 285.213 nm.

3.3.2 Anion Analysis

Sulphate, chloride, fluoride, and nitrate were analysed using the Gallery Plus discrete analyser (Thermo Fischer Scientific). The fully automated analyser employs photometric measurement techniques for the quantification of the analytes. The samples were filtered through a 0.45 µm filter to obtain a clear sample. 2 ml of the sample was used for the analysis and determined at the anion-specific wavelengths. Sulphate was quantified at a wavelength of 420 nm, chloride at 480 nm, fluoride at 620 nm and nitrate at 540 nm.

3.3.3 Physical Parameter Analysis

The total dissolved solids and water alkalinity (via bicarbonate) were determined using a Titralab AT1000 Series (Hach) auto titrator. For the bicarbonate, a HACH-PHC805 electrode was used. 50 ml of the sample was used and titrated with 0.1*N* sulphuric acid.
TDS was calculated from the value of EC as analysed using the Titralab, employing an EC HACH-CDC401 electrode.

3.4 Data Analysis

3.4.1 Univariate Statistical Analysis

The physical and chemical results were analysed using Microsoft Excel (Microsoft Corporation, 2018). The software was used to plot line graphs of each physical and chemical variable to determine the trends of the variables through the different seasons and to check compliance of the variables against drinking water quality standards through the different seasons. The data was compared to SAWQG (DWAF, 1996a) and WHO drinking water quality guidelines (WHO, 2017). The data was used to evaluate if groundwater in the study area complies with the drinking water quality standards.

3.4.2 Water Quality Index analysis

Water quality index is an arithmetic-weighted method used in groundwater quality studies. It is used to determine the fitness of water for different uses (Loh et al., 2020). It is a very reliable, efficient, and useful method (Gibrilla et al., 2011; Bouteraa et al., 2019). In the current study, it was used to determine the suitability of groundwater in the Breede WMA for drinking purposes. The method takes water quality data and translates it into a value that describes the overall quality of water (Makokha, 2017).

The first step was to select water quality parameters of concern for the computation of the water quality index. Parameters were selected based on their importance or potential to contaminate the water sources (Makokha, 2017; Loh et al., 2020). The types of economic activities taking place in an area give an indication of the type of chemical constituents that can pollute water in the area. In the present study, the major cations (Na^+, Ca^{2+}, K^+, Mg^+), anions (Cl^-, SO_4^{2-}, NO_3^-, F^-) and physical parameters (pH, TDS, EC) were selected for the calculation of WQI in the study area.

Breede has multiple water quality polluters which include agriculture, wastewater treatment works and manufacturing factories (Cullis et al., 2018). According to Hauser (2018), major ions are a good representation of all potential polluters, representing most of the dissolved substances in water. They are used to understand the general chemistry of aquifers.

The second step was to assign weights to the water quality parameters. A weight of 1-5 was assigned to the parameters. In this study, WQI was determined to assess suitability for drinking purposes only. Therefore, the weights were assigned based on the impact the parameters have on drinking water and the health risk they can have on the human body. Another important factor used for assigning the weight was the probability of the parameter to exceed the water quality guidelines limits. F^-, SO_4^{2-} and Cl^- were assigned a weight of 5 based on their importance in drinking water and health implications if they are present in higher concentrations in drinking water (Makokha, 2017; Loh et al., 2020). TDS, pH, EC, Na^+, and Cl^- have been assigned a weight of 4 because the study area is an agricultural area. These parameters are likely to contaminate water resources in the area. Mg^{2+}, Ca^{2+}, and K^+ were assigned a weight of 2 because they are less harmful (Makokha, 2017).

The third step was to compute the WQI using the following 3 steps:

1. The relative weight of each parameter was computed using the following Equation 3.1 below.

$$RW_i = \frac{AW_i}{\sum_i^n AW_i} \tag{3.1}$$

RW$_i$ defines the relative weight of each parameter, *AW*$_i$ defines the assigned weight of each parameter, and *n* is the total number of parameters.

2. . The quality rating of each parameter was calculated using Equation 3.2 below.

$$Q_i = \frac{C_i}{Si}\, x100 \tag{3.2}$$

*Q*i represents the quality rating of each parameter in the sample, *C*i is the concentration of each parameter calculated in mg/l, and *S*i the permissible standard derived from the South African water quality guideline for drinking water.

3. The subindex of each parameter was calculated using Equation 3.3 below.

$$SI_i = Q_i\; x\; RW_i \tag{3.3}$$

*SI*i represents the subindex for each parameter, *Q*i represents the quality rating of the parameter based on the concentration of the parameter and *RW*i Defines the relative weight of each parameter.

The WQI of the water sample was computed using Equation 3.4 below.

$$WQI = \sum SIi \tag{3.4}$$

3.4.3 Total hardness

Total hardness was used to determine the suitability of water for human consumption. Water hardness can cause kidney failure in human beings (Dhanasekarapandian et al., 2016; Nolakana, 2016). According to Subramani et al. (2005); Parimala Renganayaki & Elango (2014); water with a hardness of less than 75 % is classified as soft, hardness of between 75 – 150 % is moderately hard, between 150 – 300 % is classified as hard, and anything above 300 % is classified as very hard. Total hardness was computed using Equation 3.5 below.

$$TH = 2.497Ca + 4.115\, Mg \tag{3.5}$$

The ionic concentrations were calculated in milligrams per litre (mg/l)

3.4.4 Irrigation suitability indicators

The suitability of the groundwater for irrigation purposes was assessed using the following indicators: Permeability Index, Sodium Adsorption Ratio, Magnesium Hazard, Sodium Percentage. All indicators were calculated using equations 3.6 - 3.9 below. Before calculating the indicators, the ion concentrations were converted to milliequivalent per litre (meq/L). The concentration in milligrams per litre was divided by atomic mass and multiplied by the charge to convert to milliequivalent per litre.

Sodium Adsorption Ratio

$$SAR = \frac{Na^{+}}{\frac{\sqrt{Ca^{2+} + Mg^{2+}}}{2}} \tag{3.6}$$

Magnesium Hazard

$$MH = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100 \tag{3.7}$$

Permeability Index

$$PI = \frac{Na^{+} + \sqrt{HCO_3^{-}}}{Ca^{2+} + Mg^{2+} + Na^{+}} \tag{3.8}$$

Sodium Percentage

$$Na\% = \frac{Na^{+} + K^{+}}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \times 100 \tag{3.9}$$

3.4.5 Graphical representation of groundwater suitability for irrigation

Graphical representation is a data analysis method that uses graphs and charts to analyse and interpret numerical data, functions, and other qualitative structures. It gives a visual display of the results. Wilcox and USSL diagrams were used in this study to evaluate whether groundwater is suitable for irrigation.

The Wilcox diagram was plotted using Sodium hazard (Na%) versus Salinity hazard (EC). The USSL diagram was plotted using SAR versus Conductivity with SAR. The diagrams were generated using Diagrammes v6.76 software (Simler, 2022).

3.4.6 Geochemical Assessment of groundwater

A geochemical assessment is a geological study that includes the change in chemistry. It is used in this study to reveal the processes that influence the chemistry of groundwater in Breede WMA. A geochemical process is important in groundwater studies because it gives an indication of sources of pollution in the area, especially in an area like Breede which has a variety of economic activities that can contaminate groundwater. It also reveals the type of natural processes that influence the chemistry of groundwater.

There are several methods that have been adopted for geochemical assessment which include multivariate statistical analysis, stable isotope method, geochemical modelling, structural equation modelling and redox indicator methods (Mallick et al., 2018). The current study used the conventional graphical method (Piper diagram) and statistical analysis (multivariate) to evaluate the geochemical processes that impact groundwater chemistry in the Breede WMA.

3.4.6.1 Piper diagram

In this study, a Piper diagram was used to assess the potential polluting processes in the study area. The diagram was plotted using the concentration of the major ions. The concentrations of the ions were converted into milliequivalent per litre before plotting the diagram using Diagrammes v6.76.

The diagram comprises two triangles on the left and right side and a diamond shape in the middle. The left triangle is where the cations are located, and the right triangle where the anions are indicated. The diamond shape represents where the overall analysis of the sample takes place. In the cation triangle, the base is the calcium axis, the right side is the sodium+potassium axis, and the left is the magnesium axis. In the anion triangle, the base is the chloride axis, the left is the carbonate plus bicarbonate axis, and the right is the sulfate axis.

In the Piper diagram, the sample points of the cations and anions are located in the triangles, with perpendicular lines drawn from the triangles to the diamond shape. The dominant water type for a given borehole is indicated at the intersection of the two lines (from the anion and cation) in the diamond shape (Nolakana, 2016).

3.4.6.2 Multivariate Statistical Analysis

PCA and Pearson correlation were computed using *R* v1.1 (R Core Team, 2019) The multivariate statistical methods were used to understand the relationship between the measured variables which will reveal the origin of the major ions.

Correlation Analysis was used to investigate the relationship between the constituents. The correlation coefficients of the constituents were calculated using the Pearson method. It is a technique used to determine if there is a relationship between two constituents and the strength of the relationship. Correlation also reveals if the relationship between the measured constituents is an increasing or decreasing relationship (Jamuna, 2019). The correlation matrix was computed between all measured constituents from all the groundwater samples in the Breede River area.

PCA was used to determine the factors that might affect the concentration of the measured variables (Marghade et al., 2015). The results showed thirteen Principal Components, of which only the first four PCs had eigenvalues > 1 as indicated in Table 3.2. The proportion of variation explained for each eigenvalue in the second column of Table 3.2. The cumulative percentage in the third column was computed by adding successive proportions of variation explained to obtain the running total. The selected principal components were those with corresponding eigenvalues > 1. The first four principal components explain over 77 % of the variance. Given the relatively high percentage of explained variance, only the first four PCs were retained for analysis. These principal components are assumed to adequately represent the overall variance. The variables were plotted on the PC1-PC2 plane to discriminate several groups of water samples. The PC1-PC2 plane allowed us to differentiate from relatively highly mineralized waters to alkaline waters.

Table 3.2: Eigenvalues and percentage variance of PCs

Principal Component	**Eigenvalue**	**Variance %**	**Cumulative Variance %**
PC 1	5.8	44.8	44.8
PC 2	2.0	15.7	60.5
PC 3	1.1	8.7	69.3
PC 4	1.0	7.8	77.0

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Drinking water suitability assessment

Water used for drinking should be free of toxic substances, have a low total dissolved solid and be soft (Salem et al., 2019). South African Water Quality Guidelines DWAF (1996) and World Health Organisation guidelines for drinking water quality WHO (2017) were used as the foundation to evaluate the capability of groundwater for domestic purposes. A descriptive statistical summary of the water quality data is presented in Table 4.1.

Table 4.1:Descriptive statistics of groundwater chemistry of Breede WMA

Variables	Min	Max	Std dev	Median	Mean	SAWQG DWAF (1996)	Number of samples exceeding SAWQG target	WHO (2017) Guidelines	Number of samples exceeding WHO guidelines target
pH	4.3	8.3	1.4	5.8	6.1	6.0-9.0	16	-	-
Temp (^{0}C)	15.8	25.5	2.1	19.7	19.6	-	-	-	-
EC (mS/m)	5.5	194.6	60.3	65.8	78.6	70	16	-	-
TDS (mg/l)	39.1	1383.1	390.0	170.9	373.5	450	12	600	9
Na^+ (mg/l)	7.0	280.0	81.1	24.0	68.9	100	9	200	3
Mg^{2+} (mg/l)	1.0	41.0	1.1	5.5	9.1	30	3	100	0
Ca^{2+} (mg/l)	0.4	92.0	21.6	8.5	17.5	32	6	200	0
K^+ (mg/l)	0.7	11.0	2.8	3.5	4.1	50	0	15	0
HCO_3^- (mg/l)	1.0	262.2	72.2	18.7	51.1	-	-	-	-
F^- (mg/l)	0.2	2.3	0.4	0.2	0.3	1	2	1.5	0
SO_4^{2-} (mg/l)	4.6	53.7	14.3	9.7	17.1	200	0	250	0
NO_3^- (mg/l)	0.5	4.0	0.7	1.0	1.1	6	0	50	0
Cl^- (mg/l)	10.7	599.2	151.3	44.5	121.2	100	15	250	6

pH: has no units, - : represents no standard value available, Max = maximum, Min = minimum, std dev = standard deviation.

According to DWAF (1996a), the required range for pH in drinking water is between 6.0 - 9.0. The pH in the study area ranges from 4.3 to 8.3, with an average of 6.1. Figure 4.1 indicates that boreholes G1, G2, C1 and C2, located in Grabouw and Ceres, respectively, had pH values out of the target range according to DWAF (1996) for all seasons. Borehole K1 had a pH below the minimum required limit in August, the winter season. Boreholes CI1 and CI2 only show lower pH values in August during the winter rainy season. The pH results reveal that the groundwater in the Breede WMA is acidic. Acidic groundwater in the study area may be due to anthropogenic activities, such as agriculture, from the use of fertilisers (Sarath Prasanth et al., 2012). Cullis et al. (2018) mentioned that the Breede WMA has about 18 Wastewater Treatment Works (WWTW) which service a large portion of the population. Due to the increase in population, many of these WWTW are unable to handle the increasing load. This may lead to an overflow of untreated domestic effluent which reaches the groundwater, causing it to become acidic. In May, the pH meter broke during the sampling period. Hence other boreholes were not measured for pH in May.

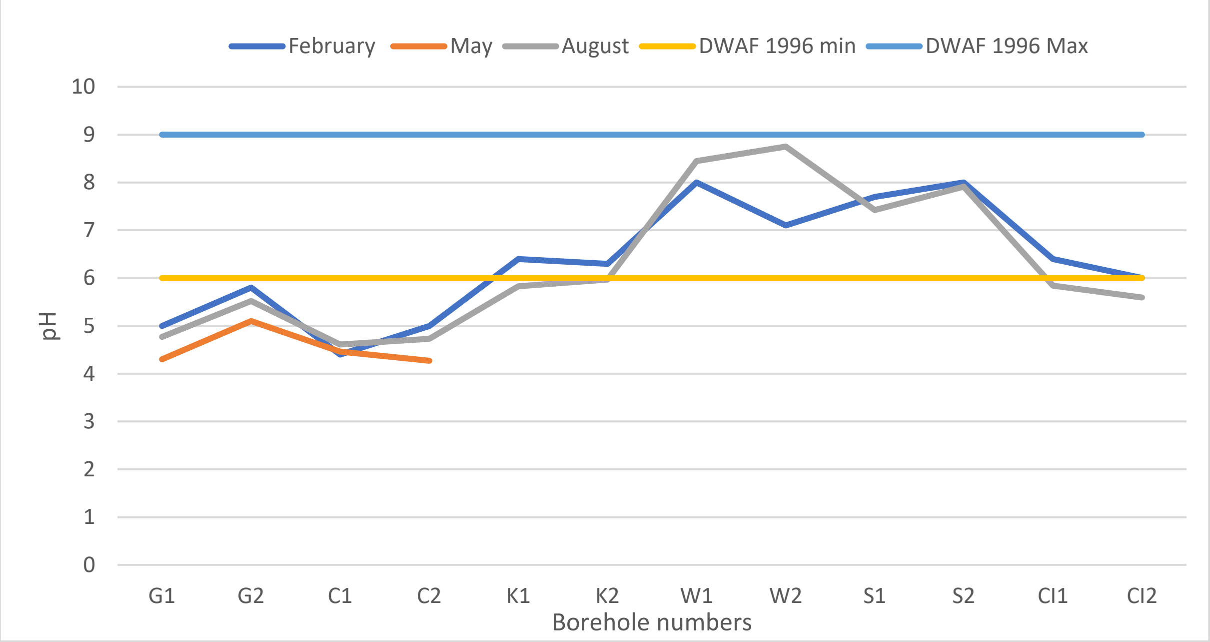

Figure 4.1: pH level of the groundwater samples in Breede WMA

The EC in the study area ranges from 5.5 to 194.6 mS/m with an average of 78.6 mS/m. According to DWAF (1996), the limit for EC in drinking water is 70 mS/m. Figure 4.2 indicates that during the dry summer season in February, boreholes G1, C1, K1, K2, W1, S1 CI1 and CI2 were higher than the 70 mS/m limit. In May, i.e. autumn, only boreholes W1, S1, CI1 and CI2 had an EC higher than the required limit. In August, representing the winter season, boreholes G1, W1, CI1 and CI2 were higher than the limit. Generally, the EC in the entire Breede WMA has elevated levels.

The rising levels of EC in the boreholes indicate a rise in ionic activity in the water. The value of EC appears to increase with an increase in temperature. In February, a hot summer month, 66.7 % of the samples showed a higher value for EC that exceeded the required SAWQG than the other seasons. Boreholes CI1 and CI2 in Cape Infanta indicate high EC that exceeds SAWQG in all three seasons. Cape Infanta is a coastal area. The high EC is presumably due to salt in the groundwater due to seawater intrusion.

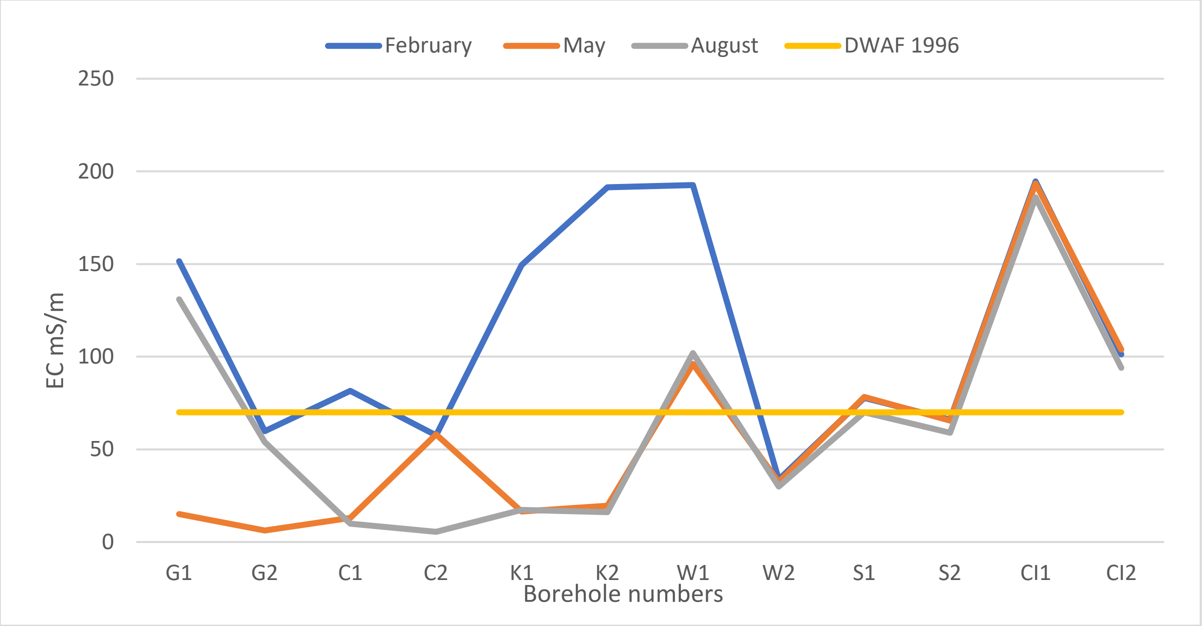

Figure 4.2: Electrical Conductivity of the groundwater samples in the Breede WMA

TDS has a minimum of 39.1 to a maximum of 1383.1 mg/L, with an average of 373.5 mg/L. Most boreholes have TDS values within the required limit according to DWAF (1996) and WHO (2017). Figure 4.3 indicates that borehole W1 in Worcester, CI1 and CI2 in Cape Infanta have TDS above the limit for both standards in all three seasons. Borehole S1 in Stanford has a TDS concentration that is acceptable according to WHO (2017), but it is above the limit in terms of DWAF (1996). According to Sarath Prasanth et al. (2012), TDS may result from domestic effluent and the leaching of salts from the soil.

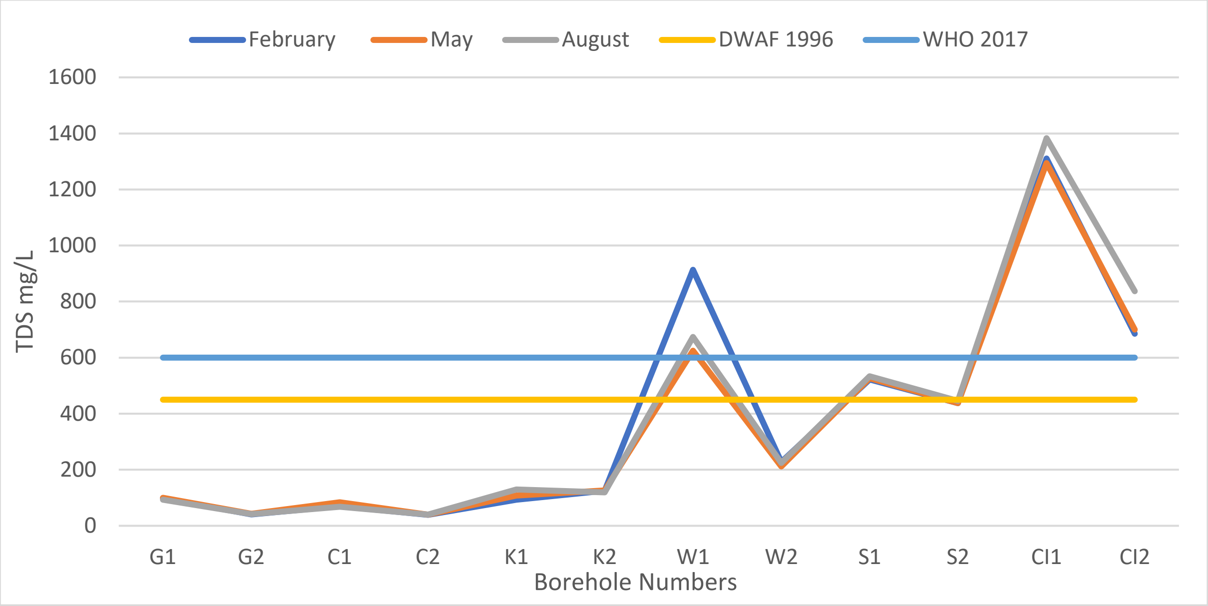

Figure 4.3: Total dissolved Solids for groundwater samples in Breede WMA

Sodium concentration in the area has the lowest concentration of 7 mg/L and a maximum of 280 mg/L, with an average of 68.9 mg/L. Most boreholes have concentrations which are within acceptable limits according to DWAF (1996) and WHO (2017). Figure 4.4 indicates that CI1 has a sodium concentration that is above the limit for both DWAF (1996) and WHO (2017), and CI2 complies with WHO (2017) and is above limits for DWAF (1996). Borehole K2 at Koo Valley has a sodium concentration above the recommended limit in May, while W1 in Worcester has sodium above the limit in February and August, which is summer and winter, respectively. The sodium concentration in Cape Infanta might be due to seawater intrusion since Cape Infanta is a coastal area.

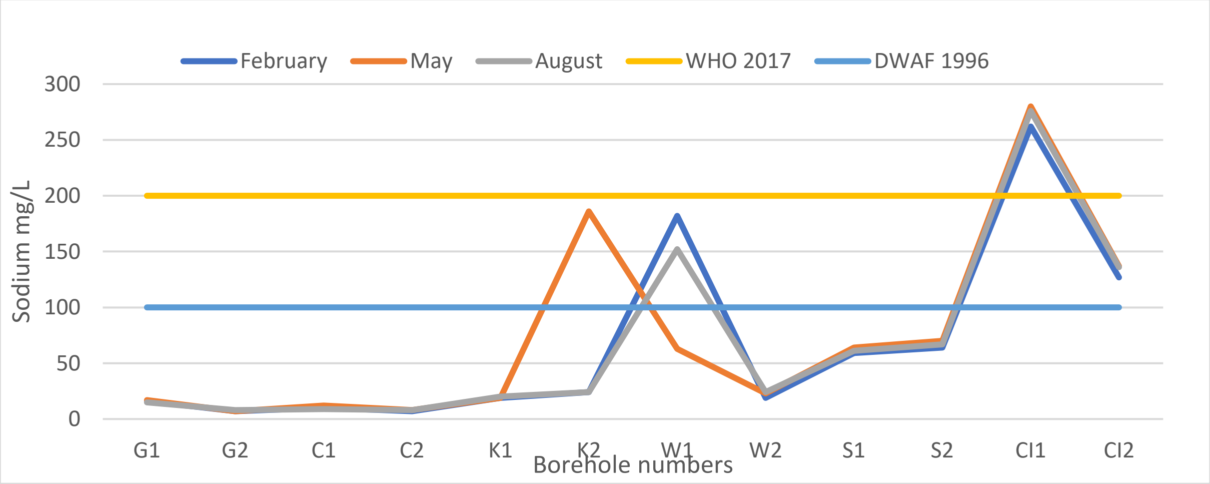

Figure 4.4: Sodium concentration of the groundwater samples in Breede WMA

Calcium has concentrations ranging from 0.4 mg/L to 92 mg/L and an average of 17.5 mg/L. All boreholes in the area have calcium concentrations within the acceptable drinking limit according to DWAF (1996) and WHO (2017), except boreholes S1 and S2 in Stanford. This is likely due to the geological formation in Stanford. The general lithology of the area is sandy and calcareous (Holm, 2011). Figure 4.5 reveals that the two boreholes in Stanford have a high concentration of calcium that exceed DWAF (1996) in all seasons. Elevated concentration of calcium in water used for domestic purposes can cause abdominal ailments, encrustation and scaling (Sarath Prasanth et al., 2012).

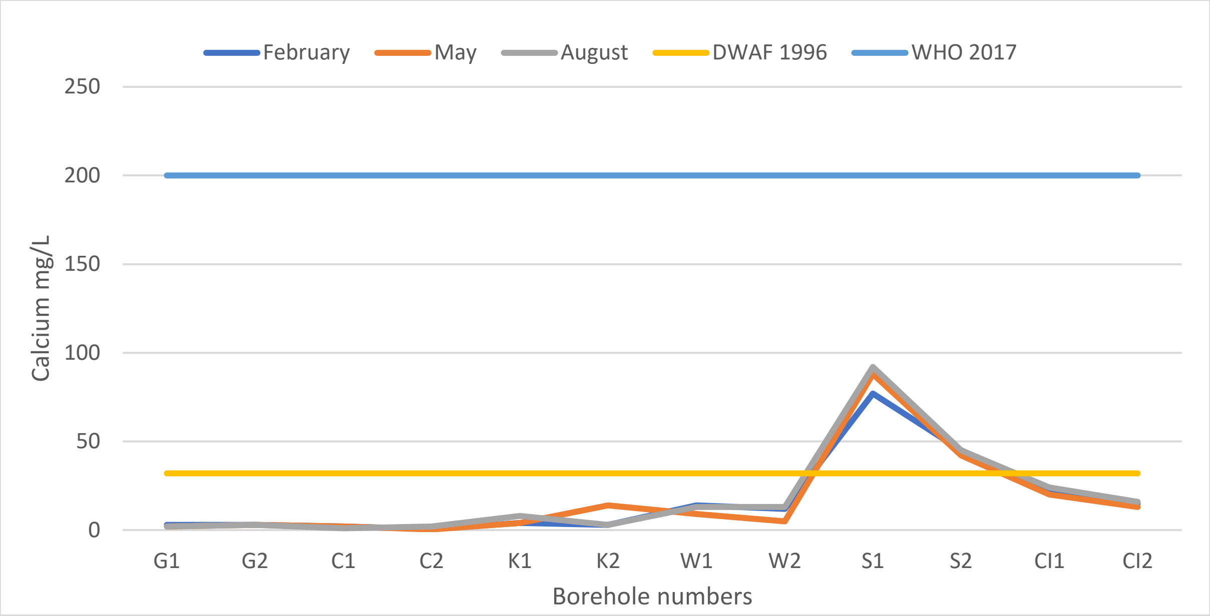

Figure 4.5: Calcium concentration of the groundwater samples in the Breede WMA.

Magnesium ranges from 1.0 mg/L to 41 mg/L, with an average of 9.1 mg/L. All boreholes in the area show a concentration of magnesium which comply with both DWAF (1996) and WHO (2017), except for borehole CI1 in Cape Infanta, which does not comply with DWAF (1996) but complies with WHO (2017) in all seasons as indicated in Figure 4.6. Magnesium, just like calcium, is abundant in groundwater. Magnesium in groundwater can be caused by the presence of dolomite in sedimentary rocks.

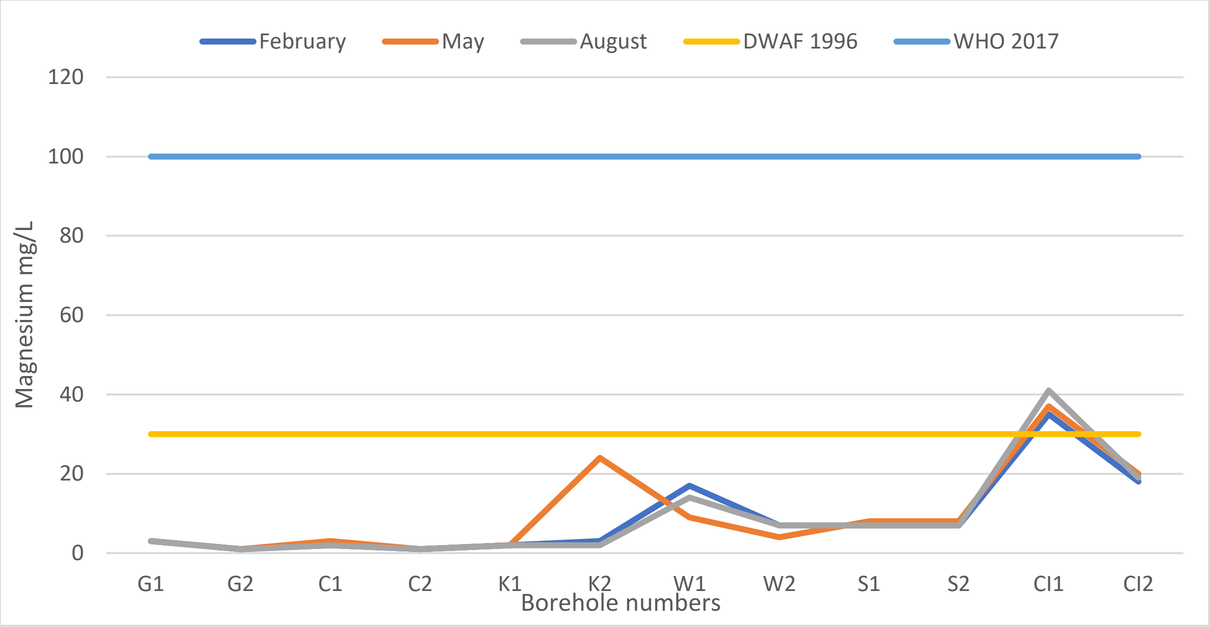

Figure 4.6: Magnesium concentration of the groundwater samples in the Breede WMA

The concentration of potassium in the study area ranges from 0.7 mg/L to 11 mg/L, with an average of 4.1 mg/L. Figure 4.7 indicate that magnesium has concentrations which comply with the acceptable limit for drinking purposes according to DWAF (1996) and WHO (2017) in all seasons. Sarath Prasanth et al. (2012) mentioned that potassium naturally has a low concentration than calcium, magnesium, and sodium; its concentration in water rarely reaches 20 mg/l.

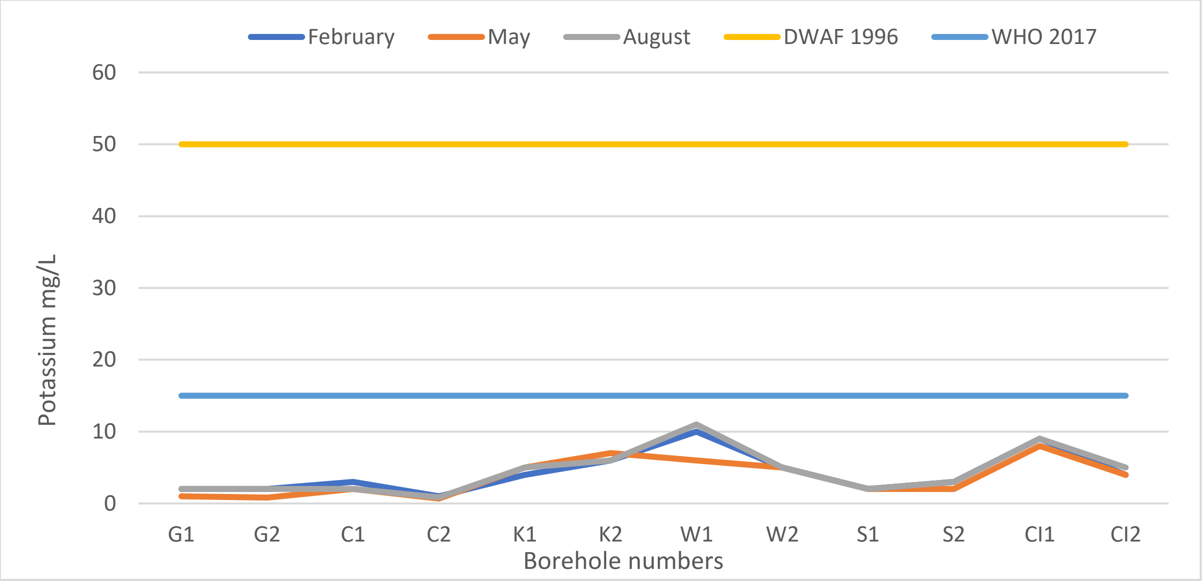

Figure 4.7: Potassium concentration of the groundwater samples in Breede WMA

Nitrate ranges from 0.5 mg/L to 4.0 mg/L, with an average of 1.1 mg/L. Figure 4.8 shows that the nitrate concentration in the whole area complies with DWAF (1996) and WHO (2017) for drinking purposes. Nitrate in groundwater can come from both geogenic and anthropogenic activities. Geogenic activities can be due to the oxidation of ammonia-nitrogen to nitrite. Anthropogenic activities could be attributed to the use of fertilisers and precipitation from septic tanks. A high nitrate concentration that exceeds drinking water quality standards can result in serious health problems (Enitan-Folami et al., 2020).

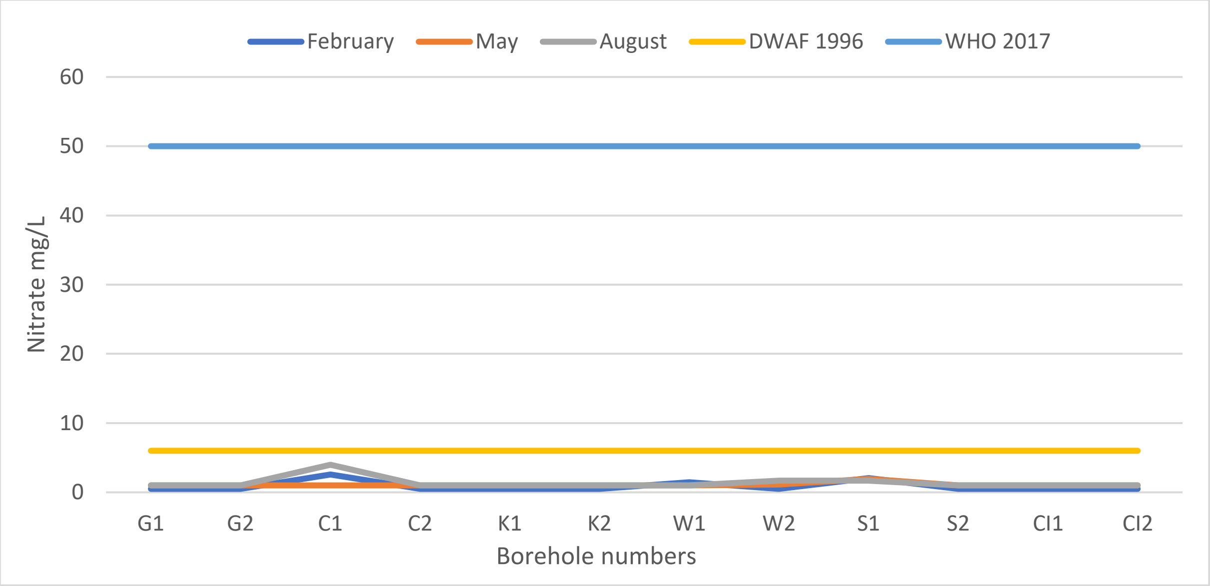

Figure 4.8: Nitrate concentration of the groundwater samples in the Breede WMA.

The chloride concentration ranges from 10.7 mg/L to 599.2 mg/L, averaging 121.2 mg/L. The two boreholes in Cape Infanta don't comply with DWAF (1996) and WHO (2017) in all the seasons for chloride. This may be caused by seawater intrusion. Boreholes S1 and S2 in Stanford and W1 in Worcester only comply with WHO (2017) in all seasons, according to Figure 4.9 and do not comply with standards set out in DWAF (1996). Since Cape Infanta and Stanford are coastal areas, the chloride levels might be elevated due to seawater intrusion. Sarath Prasanth et al. (2012) mentioned that other sources of chloride in groundwater are weathering, effluents from both domestic and industrial activities, and leaching of sedimentary rocks. Borehole W1 is located near an animal farm. The high chloride levels that exceed water quality guidelines might be due to stormwater that contains animal waste recharging the aquifer.

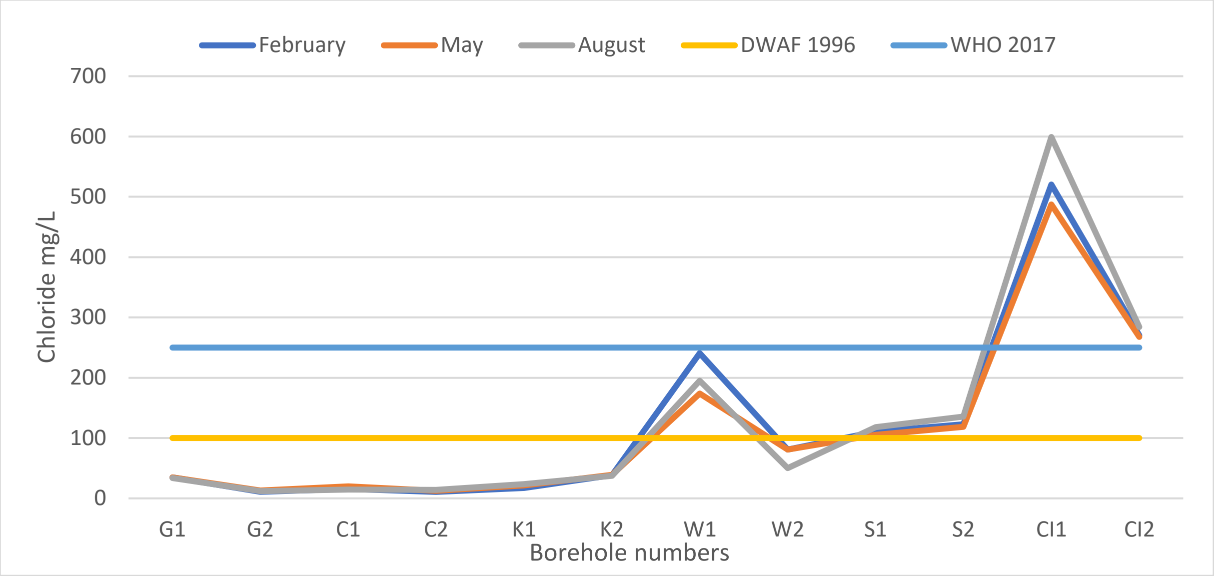

Figure 4.9: Chloride concentration of the groundwater samples in Breede WMA

Figure 4.10 shows the trend for bicarbonate concentration. Only three boreholes have a bicarbonate concentration that exceeds 100 mg/L, which are borehole W1 in Worcester, S1 and S2 in Stanford. Bicarbonate does not have a target limit value from DWAF (1996) and WHO (2017). Nolakana (2016) indicated that bicarbonate reveals the alkalinity of the water. Elevated concentrations of bicarbonate suggest that the water is alkaline.

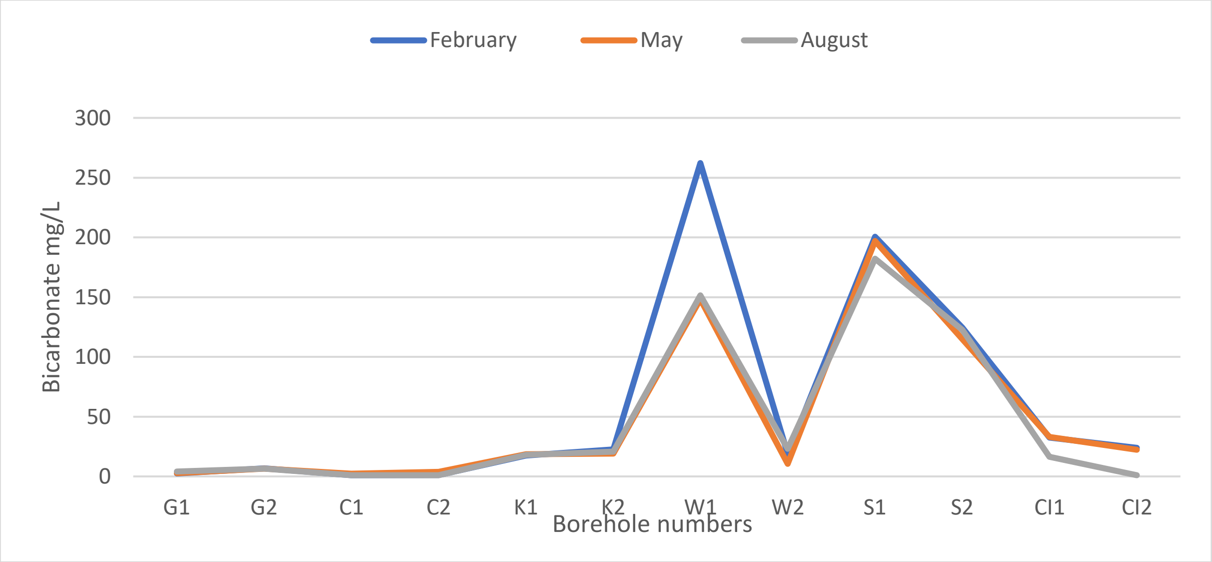

Figure 4.10: Bicarbonate concentration of the samples in the Breede WMA

Sulfate concentrations range from a minimum of 4.5 mg/L to a maximum of 53.7 mg/L, with an average of 17.1 mg/L. All the samples in the study area comply with the guidelines of DWAF (1996) and WHO (2017). Figure 4.11 below shows that the water is suitable for drinking in terms of sulfate.

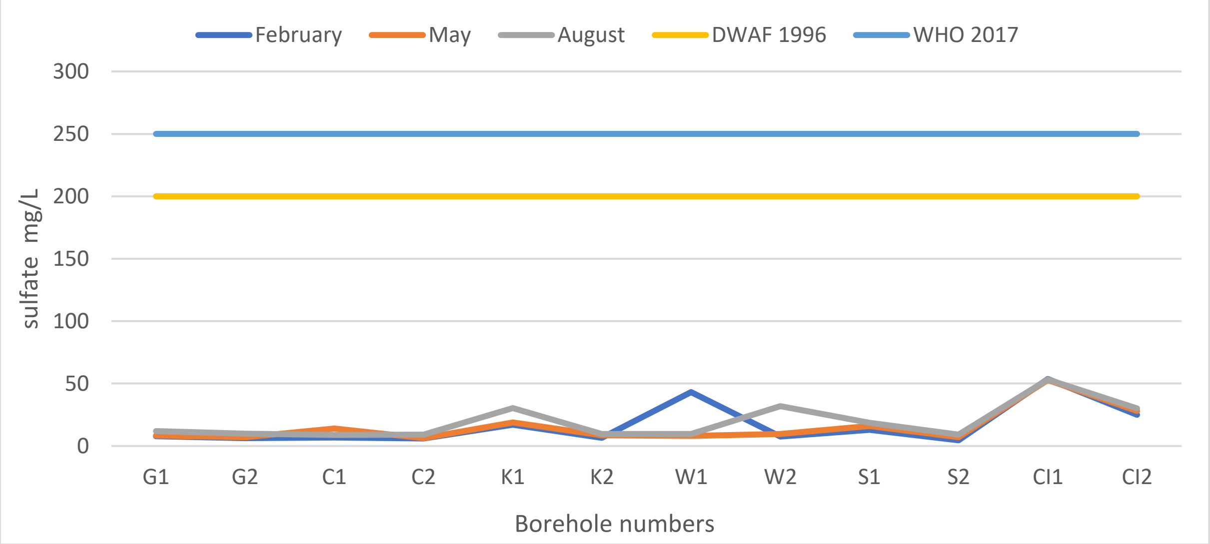

Figure 4.11: Sulfate concentration of the groundwater samples in Breede WMA

Fluoride ranges from 0.2 mg/L to 2.3 mg/L, with an average of 0.3 mg/L. Most samples have concentrations that comply with both DWAF (1996) and WHO (2017), except for two boreholes. Figure 4.12 reveal that borehole K1 in Koo Valley did not comply in August and CI1 did not comply in February. This might be due to natural processes in the aquifers such as leaching and weathering of fluoride from rocks. Borehole K1 is situated in a mountainous area and CI1 by the side of the road with no noteworthy impacting factors. Fluoride in drinking water causes fluorosis, a condition where the teeth get stained. Fluoride can also affect skeletal bones (Nolakana, 2016).

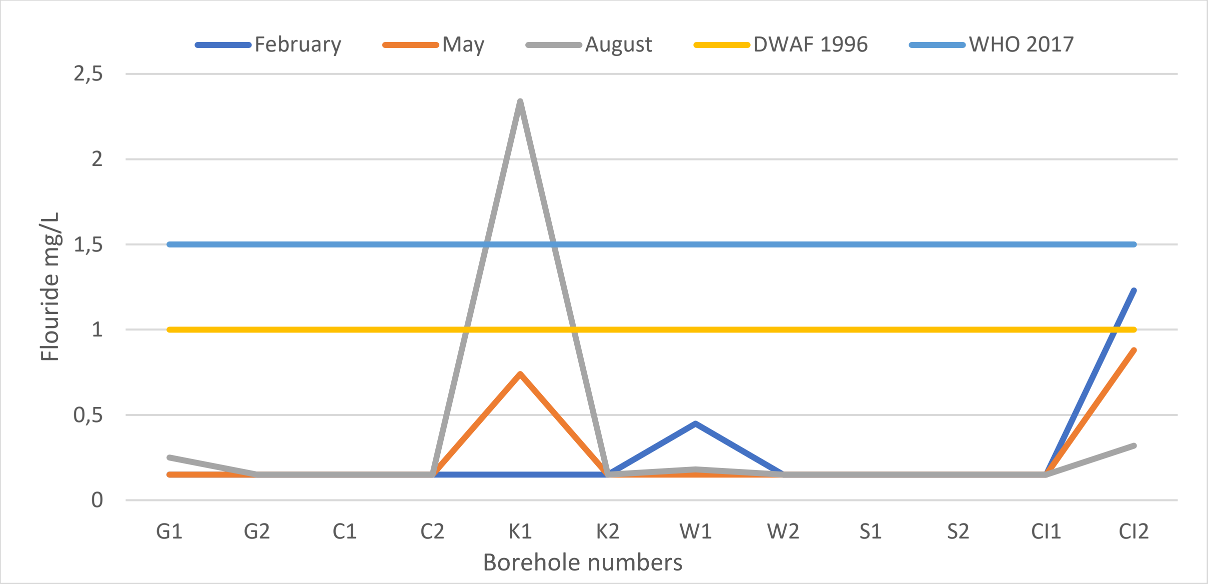

Figure 4.12: Fluoride concentration of the groundwater samples in Breede WMA

4.2 Water Quality Index

WQI was used to assess the fitness of groundwater quality for drinking purposes in the study area (Gibrilla et al., 2011; Molekoa et al., 2019). WQI simplifies large data sets to reveal the character of the water quality of the area. It classifies the water into categories that reveal the contamination levels of the water. WQI uses the major ion data to give a one-value answer that has useful meaning in terms of water quality (El-Aziz, 2018). The values range from 0 – 300, i.e., 0 - 50 (water quality is excellent for drinking), 50 – 100 (water quality is good), 100 – 200 (water quality is poor), 200 – 300 (water quality is very poor) and values above 300 (unsuitable water for drinking and irrigation) (Molekoa et al., 2019).

The WQI values in the study area range from 21.4, which indicates excellent water quality for drinking, to 198.8, indicating poor water quality for drinking, with an average of 70.5, as shown in Table 4.2. The WQI measure for the overall Breede WMA was 64.5; the value falls in the good water quality category, implying that most of the groundwater in the area is suitable for drinking without any treatment. There are a few areas which show poor water quality for drinking purposes, while there are those that show excellent water quality for drinking purposes.

The two boreholes in Grabouw, G1 and G2, are in the excellent category. Both boreholes comply with the WHO (2017) and DWAF (1996) standards for most measured variables. Boreholes in Ceres (C1 and C2) and Koo Valley (K1 and K2) are also within the excellent category. Most of their variables complied with the standards. Borehole W1 in Worcester has a WQI value of 111.4, which falls in the poor water quality category. This borehole had a high concentration of sodium, chloride, EC, bicarbonate, and TDS compared to WHO (2017) and DWAF (1996). This might be due to the intense farming around the area and the animal waste from a horse farm near the borehole. Borehole W2 is within the excellent water quality category, and most variables were within the limit of the WHO standard and DWAF guidelines.

Boreholes S1 and S2 in Stanford are categorised as poor and good water quality, respectively. Borehole S1 showed a high concentration of calcium, bicarbonate, EC, chloride, and TDS complied with WHO (2017) and did not comply with DWAF (1996). Borehole S2 also showed a high concentration of TDS and EC when compared to WHO (2017) and DWAF (1996) standards. Borehole CI1 and CI2 in Cape Infanta had WQI of 198.8 and 117.5, respectively; they are both within the poor water quality for drinking purposes. Most of the measured variables were not meeting the acceptable value range according to DWAF (1996) and WHO (2017). Cape Infanta is a coastal area with the possibility of groundwater in this area experiencing seawater intrusion.

Table 4.2: Water Quality Index for the classification of drinking water

Borehole Number	**WQI value**	**Description**
G1	40.3	Excellent
G2	22.7	Excellent
C1	24.9	Excellent
C2	21.4	Excellent
K1	42.6	Excellent
K2	47.0	Excellent
W1	111.4	Poor
W2	40.5	Excellent
S1	100.1	Poor
S2	78.9	Good
CI1	198.8	Poor
CI2	117.5	Poor
Overall WQI	64.5	Good

4.3 Total hardness Results

The total hardness ranges from 6.6 mg/l to 244.1 mg/l, averaging 81 mg/l. Table 4.3 indicates that 58.3 % of the samples, i.e. boreholes G1, G2, C1, C2, K1, K2, and W2, fall in the soft category, where the TH is less than 75 mg/l. 25 % of the samples fall in the moderately hard category, which is the category where TH is between 75 to 150 mg/l, which are samples from boreholes W1, S2 and CI2. S1 and CI1 fall in the hard category, which is the category where the TH is between 150 to 300 mg/l, accounting for the remaining 16.7 % of the samples. Water samples that have TH above 300 mg/l are very hard. Magnesium and calcium contribute to water hardness (El-Aziz, 2018).

Table 4.3: Total Hardness concentration of the groundwater in Breede WMA

Borehole Numbers	Total Hardness (mg/l)	Classification
G1	18.2	Soft
G2	11.6	Soft
C1	13.8	Soft
C2	6.6	Soft
K1	21.6	Soft
K2	56.4	Soft
W1	84.8	Moderately hard
W2	49.7	Soft
S1	244.1	Hard
S2	140.0	Moderately hard
CI1	209.9	Hard
CI2	114.8	Moderately hard

4.4 Irrigation water suitability assessment

The groundwater quality used for irrigation in agricultural areas is important because it affects food productivity. Groundwater can become contaminated by pesticides, fertilisers, domestic waste, and other chemicals from various activities such as domestic, industrial, mining and agriculture (Singh et al., 2020). Hence it is crucial to assess the suitability of the water used for irrigation purposes. Various indices were used in this study to assess the suitability of the water for irrigation purposes, such as percentage sodium, electrical conductivity, permeability index, magnesium hardness, Sodium adsorption ratio and graphical methods such as the Wilcox diagram and the United States Salinity laboratory diagram.

4.5 Electrical Conductivity

According to El-Aziz (2018), EC is used to evaluate how salinity hazard affects the soil. Salinity hazard indicates the presence of salt in the water (Singh et al., 2020). The EC results in the Breede WMA ranged from 320.0 uS/cm to 1913,7 uS/cm with an average of 749,7 uS/cm.

Table 4.4 below indicates that 50 % of the boreholes fall within the good water category (boreholes G2, C1, C2, K1, W2, and S2). Boreholes G1, K2, W1, S1, CI1 and CI2 are within the doubtful category. There are no boreholes that fall in the unsuitable category.

Table 4.4: Electrical Conductivity concentration for the classification of irrigation water

Electrical Conductivity (uS/cm)	Description	Number of boreholes	Percentage (%)	Boreholes
0 - 250	Excellent	0	0	-
250 - 750	Good	6	50	G2, C1, C2, K1, W2, S2
750 - 2250	Doubtful	6	50	G1, K2, W1, S1, CI1, CI2
> 2250	Unsuitable	0	0	-
Total		12	100 %	

4.6 Sodium Adsorption Ratio (SAR)

SAR, also known as sodicity, means the water will induce sodic soil conditions (DWAF, 1996b). It is influenced by the concentration of the major ions sodium, magnesium and calcium (Sridharan & Senthil Nathan, 2017). A high SAR in water samples indicates that there are more sodium ions compared to magnesium and calcium (Nolakana, 2016). According to Sharma et al. (2017) and El-Aziz (2018), water used for irrigation is classified according to categories in terms of SAR. SAR values of 0 - 10 are classified as excellent for irrigation, SAR values of 10 - 18 are good, 18 - 26 are doubtful and values above 26 are unsuitable for irrigation.

SAR ranges from 0.3 to 2.9, with an average of 1.1. Table 4.5 indicates that the water in the study is fit for irrigation in terms of SAR. 100 % of the boreholes are in the excellent category for irrigation purposes. The presence of calcium and other lime sources decreases the sodium adsorption ratio (DWAF, 1996b). Therefore, the low SAR in the area might be due to the presence of calcium and other lime sources.

Table 4.5: Sodium Adsorption Ratio classification of the study area

Sodium Adsorption Ratio	Description	Number of boreholes	Percentage (%)
0 - 10	Excellent	12	100
10 - 18	Good	0	0
18 - 26	Doubtful	0	0
> 26	Unsuitable	0	0
Total		12	100 %

4.7 Sodium percentage

High sodium concentration that exceeds acceptable irrigation water quality guidelines destroys the soil's physical structure and lowers drainage. This will affect crop yield (Sridharan & Senthil Nathan, 2017). When Na^+ combines with CO_3^{2-}, the soil structure becomes alkaline and subsequently saline when combined with Cl^-. These two conditions result in reduced crop yield (Dhanasekarapandian et al., 2016).

The sodium percentage shows a minimum of 35.8 % and a maximum of 77.9 %, with an average of 64.6 %. Table 4.6 shows that 8.3 % of boreholes in the area fall in the good class for irrigation, while 16.67 % fall within the permissible class and 75% are in the doubtful class.

Table 4.6: Sodium percentage classification of the Breede WMA

Sodium Percentage (Na%)	Class	Number of boreholes	Percentage (%)	Boreholes
0 - 20	Excellent	0	0	-
20 - 40	Good	1	8.3	S1
40 - 60	Permissible	2	16.7	S2, W2
60 - 80	Doubtful	9	75	G1, G2, C1, C2, K1, K2, W1, Cl1 and Cl2
> 80	Unsuitable	-	-	-
Total		12	100	

4.8 Permeability Index (PI)

Poor permeability is caused by irrigating crops with water that has poor quality. The salts in the water accumulate in the soil and prevent water from penetrating to reach the roots of the plants (Srivastava, 2019). The PI is influenced by the concentration of calcium, magnesium, sodium and bicarbonate (Sridharan & Senthil Nathan, 2017). Sharma et al. (2017) stated that PI is categorised into classes. Class I water has 100 % permeability which means the water is suitable for irrigation, Class II has a permeability of 75 % which is slightly suitable, and Class III has a permeability of 25 %, which means the water is unsuitable for irrigation.

According to El-Aziz (2018), a PI value less than 25 % is safe for irrigation, values between 25-75 % are moderately safe and values above 75 % are unsafe. The values of PI in the study area range from 12.1 % to 60.1 %, with an average of 28.5 %. Table 4.7 shows that 41.7 % of the boreholes were safe for irrigation, 58.3 % were moderate, and no unsafe samples.

Table 4.7: Permeability Index classification of the study area

Permeability Index Percentage	Description	Number of boreholes	Percentage (%)	Boreholes
< 25	Safe	5	41.7	G1, C1, K2, CI1, CI2
25 - 75	Moderate	7	58.3	G2, C2, K1, W1, W2, S1, S2
> 75	Unsafe	0	0	-
Total		12	100	

4.9 Magnesium Hazard (MH)

Magnesium damages soil structure and makes the soil alkaline. This results in reduced crop yield (Ravikumar et al., 2011). When water has a magnesium hardness of more than 50 %, the water is considered unsuitable for irrigation and suitable for irrigation when MH < 50 % (Ismail & El-Rawy, 2018). Magnesium hazard in Breede ranges from 12.4 % to 73.8 %, with an average of 52.9 %. Table 4.8 shows that 41.7 % of the boreholes were suitable for irrigation and 58.3 % were unsuitable for irrigation.

Table 4.8: Magnesium Hardness classification of the study area

Magnesium Hazard (%)	Description	Number of boreholes	Percentage (%)	Boreholes
< 50	Suitable	5	41.7	G2, K1, W2, S1, S2
> 50	Unsuitable	7	58.3	G1, C1, C2, K2, W1, CI1, CI2
Total		12	100	

4.10 Wilcox Diagram

Figure 4.13 illustrates a Wilcox diagram, which is a plot of Na% with respect to EC. The diagram indicates that 75 % of the samples fall in the excellent to good category and 25 % fall in the good to doubtful category. Boreholes W1, CI1 and CI2 are in the good to doubtful category. The remaining boreholes indicate that groundwater in the study area is suitable for irrigation in terms of the Wilcox diagram.

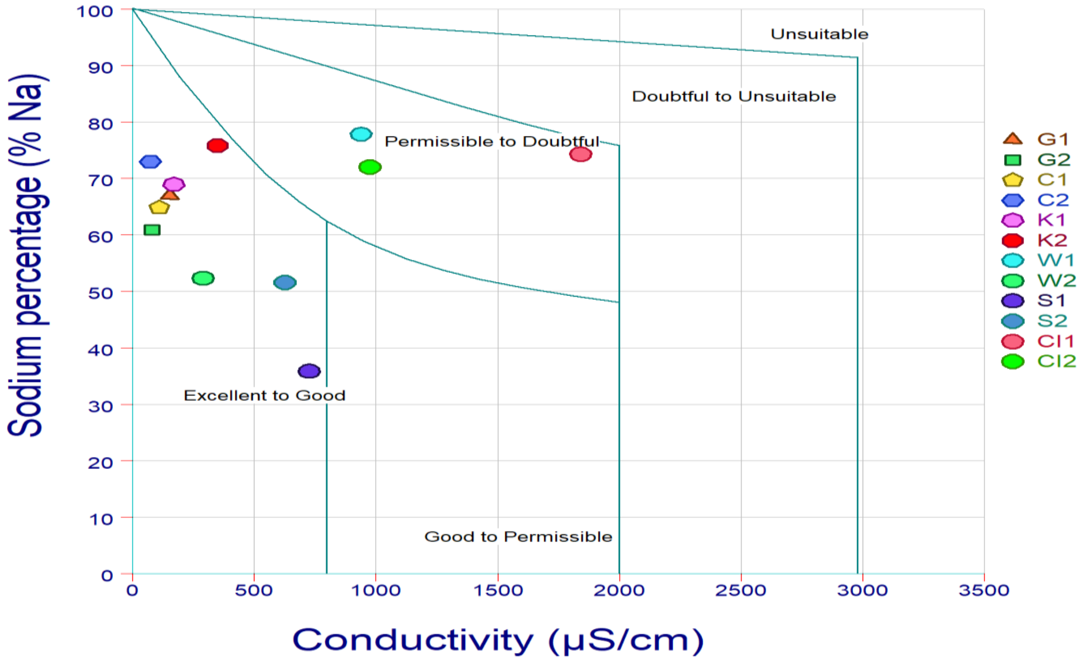

Figure 4.13: Wilcox diagram for the Breede Water Management Area

4.11 USSL Diagram

A USSL diagram was used to categorise groundwater quality in the Breede WMA and its suitability for irrigation. The diagram is a plot of SAR against EC. Figure 4.14 shows that 41.7% of boreholes belonged to the low salinity (EC < 250) and low sodium content (SAR < 10) C1S1 category. Water in this category is very good for irrigation. It can be used in all types of soil and all types of plants. 33.3 % of boreholes fall in the C2S1 area which is the medium salinity (250 < EC < 750) and low sodium hazard category (SAR < 10). 8.3 % of boreholes fall in the C3S1, the high salinity (750 < EC < 2250) and low sodium content area, the water is partially suitable for irrigation. 16.67 % of boreholes fall in the C3S2, which is the high salinity (750<EC<2250) and medium sodium content (10 < SAR < 18) area. The water in this area is not recommended for irrigation and should not be used on soils with poor permeability (Alavi et al., 2010). Groundwater from both the C3S1 and C3S2 category should not be used on soils with poor permeability (Singh et al., 2020). The results from the USSL diagram reveal that water in Borehole W1 in Worcester and boreholes CI1 and CI2 in Cape Infanta must only be used on crops with a high salt tolerance and soil with high permeability.

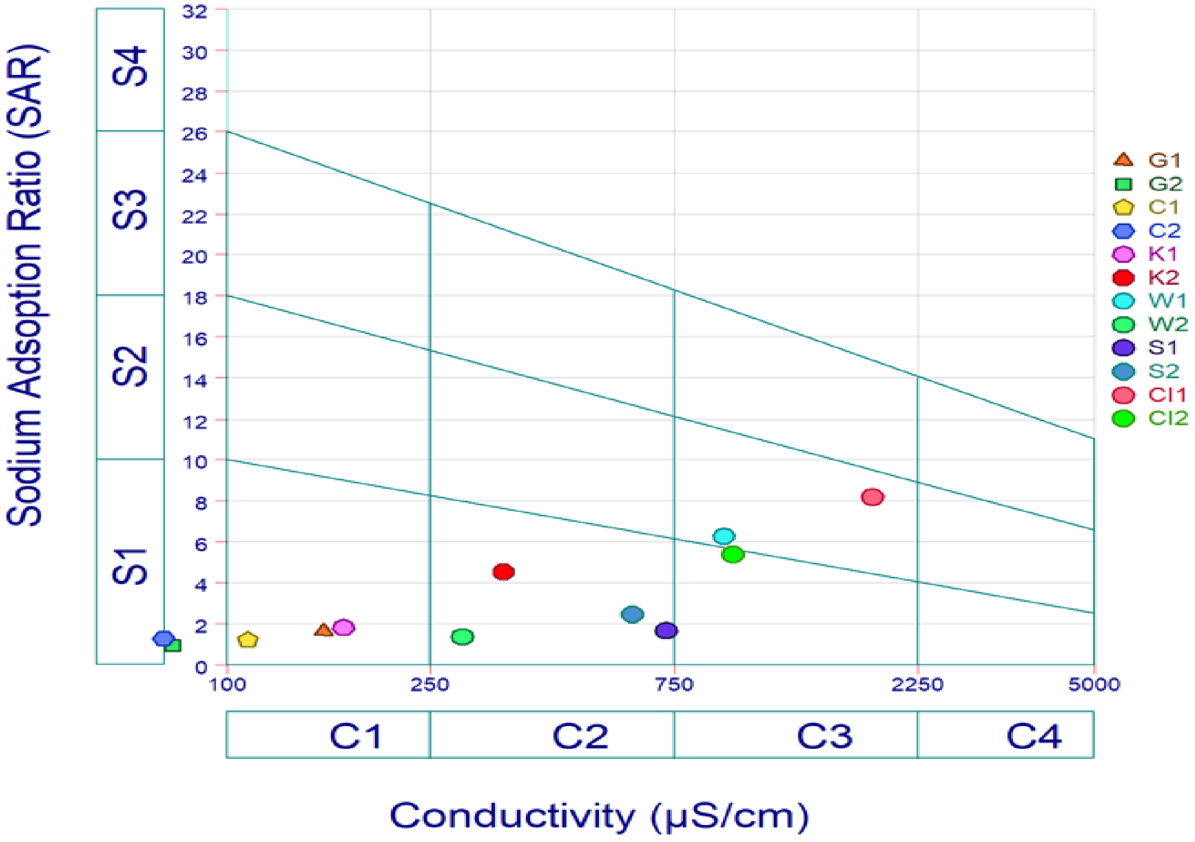

Figure 4.14: United States Salinity Laboratory diagram for the Breede WMA

4.12 Piper Diagram

A Piper diagram was used to evaluate the hydrochemistry of the Breede WMA and determine the possible sources of groundwater pollution in the area. Furthermore, to classify groundwater into hydrochemical facies, also known as water types. The hydrochemical facies reveal the history of the groundwater by giving out information about the common composition and origin of the ions (Mokoena et al., 2021). The diagram was plotted using major cations and anions. The cations were plotted on the left triangle and the anions on the right triangle. The results are revealed in the diamond shape (Sharma et al., 2017)**.** The diamond field is further divided into six fields. Each field describes a hydrochemical water type which are NaCl, $CaHCO_3$, $NaHCO_3$, CaCl, mixed CaMgCl and mixed $CaNaHCO_3$ (Ismail & El-Rawy, 2018).

Figure 4.15 shows that the dominant water type is sodium and potassium (cation triangle), with 11 boreholes in this category. One borehole (S1) is dominated by the calcium water type. In the anion triangle, the dominant water type is the chloride type, 10 of the boreholes are in this category, while two (K1 and S1) are in the no-dominant type. The diamond shape area (where the overall analysis of the boreholes is done) reveals that Na-Cl is the dominant water type of the Breede WMA with 11 boreholes in this category, followed by the mixed Ca-Mg-Cl with one borehole (S1). The plot also reveals that the alkali metals (Na^+ and K^+) exceed alkaline-earth metals (Ca^{2+} and Mg^{2+}), and strong acids (Cl^- and SO_4^{2-}) exceed weak acids (HCO_3^- and CO_3^{2-}) (Marghade et al., 2015; Musaed et al., 2020).

The dominance of calcium in borehole S1 in Stanford can be attributed to the dissolution of carbonate minerals containing calcium (Mallick et al., 2018). The Na-Cl water type can be attributed to rock salt dissolution and ion exchange (Nolakana, 2016). The mixed Ca-Mg-Cl type shows that the water comes from mixed sources (Solomon, 2013). This water type is dominant in the Stanford area, a coastal area where the soil is rich with lime. The mixed Ca-Mg-Cl can be attributed to seawater intrusion and calcite dissolution.

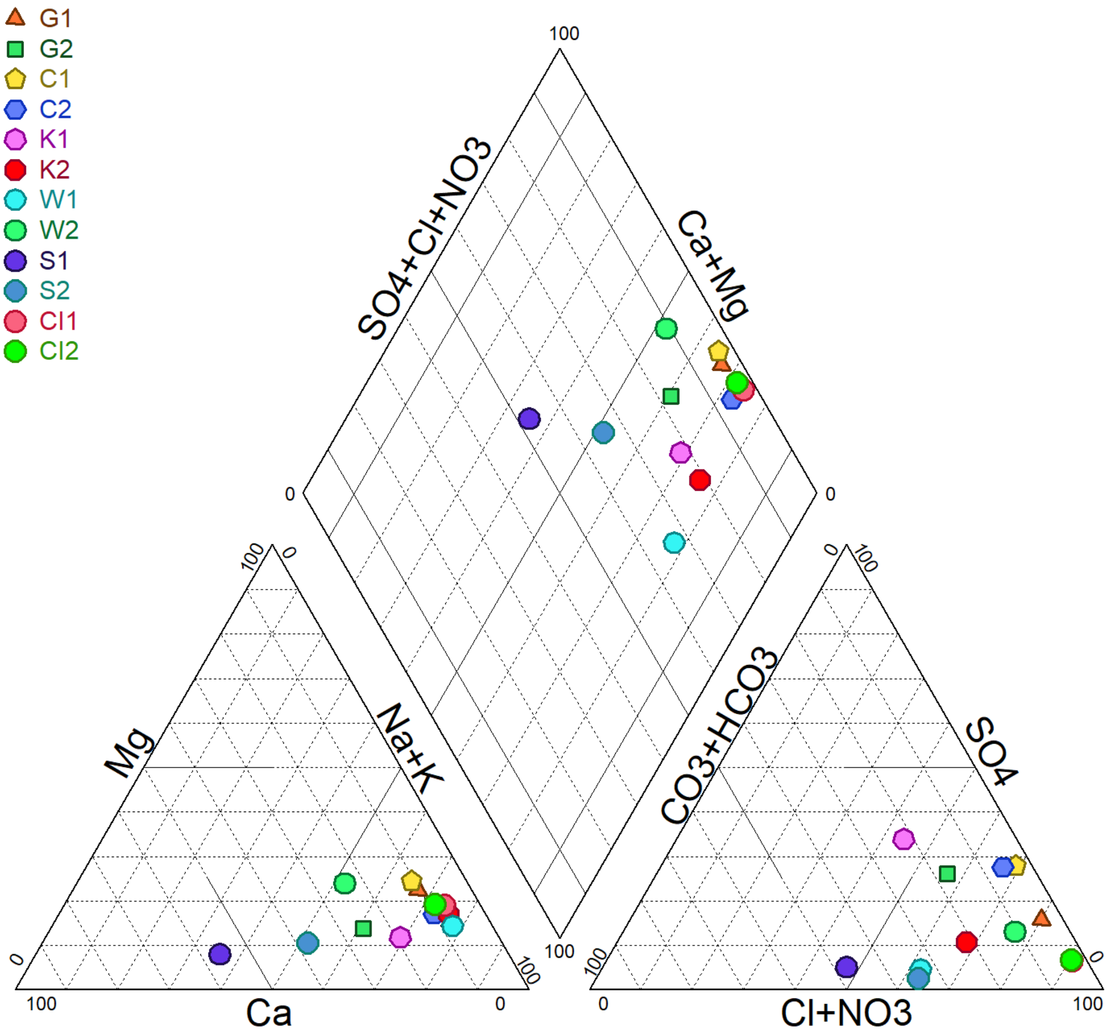

Figure 4.15: Piper diagram of Breede WMA

4.13 Multivariate Statistical Analysis Results

The Pearson correlation matrix was used to determine the relationship between the major ions and physical variables, as shown in Figure 4.16**.** The results show that TDS strongly correlates with Cl^-, Mg^{2+}, Na^+, Ca^{2+}, HCO_3^-, K^+ and SO_4^{2-}. This suggests that these ions are the main constituents contributing to groundwater salinity in the study area. Their relationship with salinity is directly proportional. Processes such as evaporation and seawater intrusion are known to contribute to the salinization of groundwater (World Water Quality Alliance, 2021). Strong correlations between cations and anions exist, for example, Cl^- and Na^+, Cl^- and Mg^{2+},

Cl^- and Ca^{2+}. The Na^+ and Cl^- relationship may be attributed to the dissolution of rock salt and or seawater intrusion. The strong relationships between Cl^- and Mg^{2+}, as well as Cl^- and Ca^{2+}, indicate that cation exchange may greatly influence groundwater composition.

Moreover, the positive relationship between sodium and sulfate may indicate contributions of evaporitic salts to the groundwater chemistry. Agricultural activity may influence and contribute to these chemical elements. For example, fertilizers produced from potassium sulfate components may contribute to the concentration of these variables and subsequently influence groundwater chemistry.

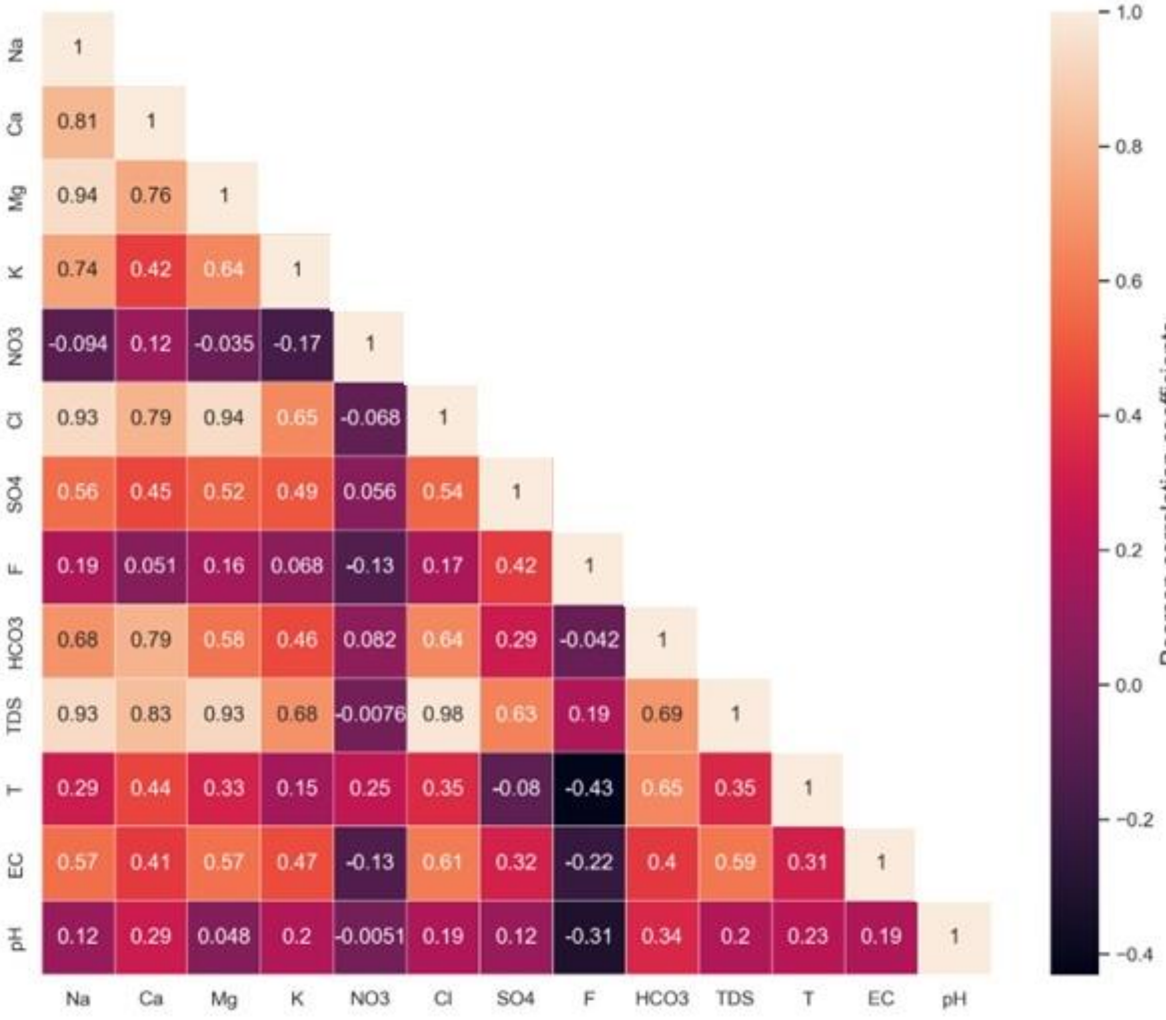

Figure 4.16: Pearson correlation matrix of groundwater chemistry in Breede WMA

PCA was conducted to identify the relationship and the origin of the ions. Four PCs with eigenvalues > 1 were selected. The first and second principal components, PC1 and PC2 account for 44.9% and 15.7% of the variance, respectively (Figure 4.17).

Table 4.9: Chemical variables loading on principal components 1 and 2

Variables	PC1	PC2
Na	0.4	-0.0
Ca	0.1	0.6
Mg	0.4	-0.1
K	0.3	-0.1
NO3	-0. 1	0.2
Cl	0.4	-0.0
SO4	0.4	-0.1
F	0.0	-0.3
HCO3	0.1	0.6
TDS	0.4	0.1
T	-0.1	0.4
EC	0.3	0.1
pH	-0.0	0.2

PC1 has shown to associate with Mg^{2+}, SO_4^{2-}, Na^+, K^+, Cl^-, and TDS. This suggests that the sources of these major ions are mineralisation. The loadings of these constituents are relatively high compared to the other constituents, as shown in Table 4.9. The correlation of Cl^- and SO_4^{2-} with major ions may also indicate the salinisation of the water due to agricultural activities (World Water Quality Alliance, 2021). The contribution of SO_4^{2-} may be caused by fertilisers (Marghade et al., 2015). It follows that PC1 describes highly mineralized water samples than PC2. PC2 accounts for only 15.7 % of the variance and is mainly associated with Ca^{2+}, HCO_3^-, NO_3^-, temperature and pH. PC2 is related to alkaline waters characterised by a relatively high concentration of bicarbonates compared to the concentration of other constituents.

The plane associated with PC1 and PC2 accounts for over 60 % of the total variance and adequately represents the initial data variability. The PC1-PC2 plane allowed the differentiation from relatively highly mineralized waters to alkaline waters. Importantly, the pH of most natural water systems is determined by chemical reactions involving the carbonate system. The relationship in PC2 between pH and carbonates indicates that the high pH groundwaters may be a result of calcite dissolution or rainfall input. It follows that the dissolution of a small amount of calcite may compromise fresh groundwater leading to its rising pH.

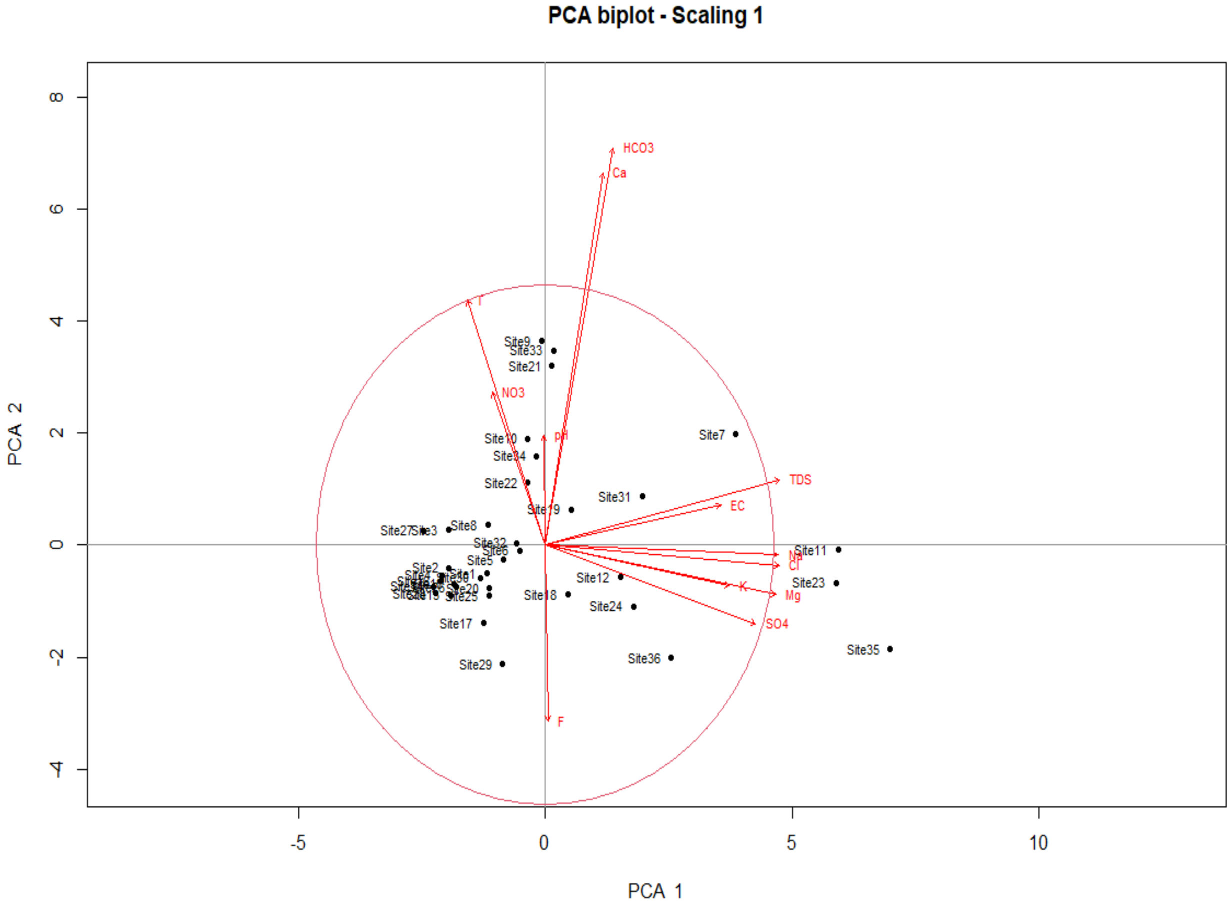

Figure 4.17: Principal Component analysis biplot of groundwater analysis in Breede WMA

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The study aimed to determine the status of groundwater quality and to evaluate if the water is suitable to be used in homes for domestic purposes and irrigation by the agricultural sector. Another important component of the study was determining possible sources of pollution and factors contributing to the groundwater chemistry in the Breede WMA. This was achieved by collecting groundwater samples from boreholes in the area and analysing them for selected physical parameters and major ions.

SAWQG and WHO drinking water quality guidelines were used to evaluate compliance of the variables, i.e. major ions and physical parameters, to acceptable concentrations. Results showed that the groundwater quality status in Breede WMA is good since most of the measured variables comply with the water quality guidelines.

WQI and total hardness were used to determine the water's suitability for domestic purposes. The results of the total hardness showed that water from most boreholes was soft, with a few being moderately hard and hard. The WQI revealed that the overall groundwater in Breede is suitable for drinking. Most boreholes showed excellent water quality. There are a few boreholes that showed poor water quality.

The suitability of the groundwater for irrigation was carried out using various irrigation indices such as the Permeability Index (PI), Electrical Conductivity (EC), Sodium Adsorption Ratio (SAR), Magnesium Hazard (MH), Sodium Percentage (Na%). The above were also used in combination with graphical representation methods such as the United States Salinity Laboratory (USSL) and Wilcox diagrams. The irrigation indices revealed that the majority of the groundwater in Breede is suitable for irrigation. Water from boreholes in the doubtful category should not be used for extended periods. Moreover, the water should preferably be used on crops with high salt tolerance and soil with high permeability.

The results from the USSL diagram reveal that water in Borehole W1 in Worcester and boreholes CI1 and CI2 in Cape Infanta must only be used on crops with high salt tolerance and soil with high permeability. The Wilcox diagram showed that boreholes W1, CI1 and CI2 are in the good to doubtful category while the other samples were in the excellent to good category for irrigation purposes.

A Piper diagram and Multivariate statistical analysis were applied to determine the geochemical processes that influence the groundwater quality in the Breede area. The Piper diagram showed that the dominating water in Breede is Na-Cl followed by mixed Ca-Mg-Cl. Na-Cl can be attributed to rock salt dissolution and ion exchange processes. Mixed Ca-Mg-Cl can be attributed to seawater intrusion and calcite dissolution. Pearson correlation data revealed that processes influencing the chemistry in the area could include the dissolution of rock salts and or seawater intrusion. The strong relationships between Cl^- and Mg^{2+}, as well Cl^- and Ca^{2+}, indicate that cation exchange may greatly influence groundwater composition. PCA results revealed that mineralisation of the groundwater and alkaline waters influence the groundwater chemistry of the area

5.2 Recommendations

This study recommends that water in the boreholes along the coastal area and borehole W1 in Worcester be treated before being used for domestic and irrigation purposes. There must be consistent groundwater quality monitoring in Breede Water Management Area to identify changes in groundwater quality. Future studies in groundwater quality must include heavy metals, biological parameters, and pesticides. The effects of pesticides from agricultural run-off, biological parameters from domestic waste and heavy metals from industrial waste must be monitored to properly manage the groundwater resources. Municipal authorities should develop initiatives to educate the surrounding communities, especially farmers, on water quality, its potential impact on their practices, and possible treatment methods to improve water quality.

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