

Hydrogeochemical evaluation and groundwater quality assessment for drinking and irrigation purposes in Bushbuckridge, South Africa.

By

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**A Masters Dissertation Submitted to the University of Venda, Faculty of Science
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Requirements for the Master of Earth Sciences in Mining and Environmental
Geology**

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DECLARATION

I, Singo Thivhilaheli, Student Number 15005554, declare that the dissertation titled - **Hydrogeochemical evaluation and groundwater quality assessment for drinking and irrigation purposes in Bushbuckridge, South Africa**- submitted for the Master of Earth Sciences in Mining and Environmental Geology, to the University of Venda is my own work and has not been previously submitted, in whole or in part, for any degree. All assistance and information from published and unpublished work have been fully acknowledged.

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Date

DEDICATION

This work is dedicated to my family and friends. To my late father, Melton Singo, you've taught me to stand out, be determined, be confident in myself, and never give up. I am especially appreciative of my mother Elisah Singo, my sisters Azwihangwisi and Rudzani Singo and my daughter Jessica Ramathieledza. You have served as my inspiration, my supporters, and my confidant.

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ABSTRACT

This study was conducted in Bushbuckridge, situated within the Sand River Catchment (SRC), Mpumalanga Province, South Africa, with the aim of evaluating the hydrochemistry and assessing the quality of groundwater for drinking and irrigation purposes. Groundwater samples ($n = 40$) were collected from different boreholes in different locations around the study area. Groundwater hydrochemical parameters including pH, total dissolved solids (TDS), electrical conductivity (EC), total hardness, major cations (Ca^{2+} , Na^+ , K^+ and Mg^{2+}) and major anions (F^- , Cl^- , NO_3^- , HCO_3^- and SO_4^{2-}) concentrations were assessed for the study area. Suitability for drinking was assessed based on comparison with selected standards and guidelines, such as the South African National Standard (SANS), Department of Water and Sanitation (DWS), World Health Organization (WHO) and by computation of Water Quality Index (WQI). Groundwater suitability for irrigation was assessed using eight irrigation indices: TDS, EC, Sodium Adsorption Rate (SAR), Sodium Percent (%Na), Kelly's Index (KI), Residual Sodium Carbonate (RSC), Permeability Index (PI) and Magnesium Hazard (MH). Groundwater type and facies characteristics was determined with the Piper diagram while geochemical controls were ascertained using Gibbs diagram. The results indicate cation and anion concentrations in the order; $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$, and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^- > \text{NO}_3^-$ respectively, while EC (14 – 551 mS/m), TDS (99 – 4411 mg/l), Cl (1.1 – 1290.6 mg/l), Na (16 – 758 mg/l), Mg (0.54 – 181 mg/l) and TH (15 – 1085) were variables with upper ranges significantly above SANS and WHO guidelines. According to the DWS guidelines the suitability of groundwater for drinking was classified as class – 0 (ideal; 10%), class – 1 (good; 24%), class – 2 (marginal; 40%), class – 3 (poor; 20%) and class – 4 (unsuitable; slightly over 7%). The WQI indicated that 40% of the analysed groundwater samples were of excellent quality, 56% good and 4% were found to be poor to unsuitable for drinking. Results for groundwater irrigation suitability potential for the analysed samples ($n = 40$) revealed four clusters; (a) most or all the samples are suitable based on TDS (65%), EC (75%) and SAR (100%), (b) just over half are suitable based on PI (59%) and %Na (55% permissible), (c) most of the samples are unsuitable based on RSC (77%), and (d) equal

distribution between suitable and unsuitable based on MH and KI (50%). According to the dominant cations and anions, the main water types were Na-HCO₃, Ca-HCO₃ and Mg-Ca-HCO₃ mixed type. Rock weathering was the dominant geochemical process, associated with evaporation. Water-rock interactions through silicate weathering and ion exchange reactions between Ca²⁺, Mg²⁺ and Na⁺ were determining factors influencing the hydrochemical evolution of groundwater in the study area. The findings of the study suggest that the groundwater quality in the Bushbuckridge area is under threat. There is need for prompt mitigation actions that seek to intensify water quality monitoring, more in-depth studies to characterize the source and fate of potential pollutants in the area.

Keywords: Groundwater quality, Hydrogeochemistry, Physicochemical parameters, irrigation, drinking water

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CHAPTER 1: INTRODUCTION

1.1 Background

Groundwater is one of the most essential renewable natural resources for fresh water globally (Molekoa et al, 2019) and its importance has increased as people depend on it for domestic, agriculture and industrial use (Aghazadeh et al, 2016). Nag and Das (2017) state that "it is believed that groundwater contains more necessary health nutrients in the right quantities when compared to surface water". Additionally, surface water is becoming insufficient to meet the demands of human activities; therefore, groundwater and waste water reuse are some of the alternatives for meeting the ever-increasing demand for water (Ako et al, 2011).

Different water quality standards are required for domestic, agricultural, and industrial uses of water (South African Water Quality Guidelines, 1996), Groundwater quality is described as the chemical, physical and biological characteristics of groundwater (Shekar, 2017). The chemical parameters are mostly reported from a laboratory in term of mg/litre and these may include PH, Nitrate, Chloride, Fluoride, Calcium, Sodium, Magnesium, Potassium, Iron, Manganese, Conductivity, Total dissolved solids, Sulphate. Physical parameters include colour, turbidity, odour etc. The bacteriological parameters include Total Coliform Bacteria, Faecal Coliform, Escherichia Coliform and Heterotrophic Plate Count (Shekar, 2017).

The quality of groundwater is dependent upon many factors such as the composition of recharge water, the interaction between the water and the soil, the rock with which it comes in contact in the unsaturated zone, and the residence time and reactions that occur within the aquifer (Batabyal and Chakraborty, 2015). The quality of ground water can also be altered by human activities such as use of fertilizer, waste from home, mining, and recreational activities.

In rural areas where the people rely heavily on groundwater for drinking and irrigation purposes, the quality of water has become a major concern. The use of contaminated water can have adverse effects on the economic and health status of rural people (Batabyal and Chakraborty, 2015). Therefore, it is emphasized that groundwater quality monitoring and hydro-geochemical processes evaluation of its usability are necessary for sustainable management of groundwater resources (Jousma, 2008).

1.2 Problem Statement

Some of our human rights includes access to safe drinking water and enough water (WHO, 2011); however, a study from DWAF (2008) indicated that 6.0 million people out of 49.4 million people in South Africa do not have access to safe drinking water, with rural areas accounting for 52 percent of the population.

The water supply systems of the Bushbuckridge local municipality comprise of both surface and groundwater schemes, with groundwater schemes mostly serving rural areas. When water is scarce in the Bushbuckridge Local Municipality, residents turn to other means of gathering and storing water, which can have serious health and hygiene consequences (Suzanna, 2009). Because the groundwater in the study area is being used at such a high risk to fulfil the needs of rural and urban users, any decline in groundwater quality might have disastrous consequences. As a result, characterizing geochemical elements and understanding the hydrogeochemical processes that persist in the area is critical.

The quality of groundwater is just as important as its quantity, so it is crucial to think about the whole picture when it comes to managing it (Neisi et al, 2018). The findings of this study can be used to determine the current state of groundwater quality, which can help decision-makers develop timely water resource management plans and thereby reduce any additional negative effects on human health.

1.3 Aim and objectives of the study

The aim of this study is to investigate hydro-geochemical evolution and groundwater suitability for drinking and irrigation purposes in Bushbuckridge (Mpumalanga Province), South Africa

The objectives are therefore:

- To determine the water quality status,
- To characterize the groundwater types, and
- To identify the hydrogeochemical mechanisms controlling the water chemistry.

1.4 Research questions

- Is the groundwater suitable for drinking purpose?
- Is the groundwater suitable for irrigation purpose?

- What are the hydrogeochemical mechanisms controlling the groundwater chemistry in the Bushbuckridge area?
- What are the hydrofacies in the Bushbuckridge area?

1.5 Justification

According to UN Committee on Economic, Social and Cultural Rights (2002), "water is necessary for life to exist, and everyone should have access to a sufficient (appropriate, safe, and accessible) supply".

Improving access to safe drinking water can have a direct impact on one's health (WHO, 2002); therefore, every effort should be made to achieve the safest possible drinking water quality. This study will examine the quality of water before the public uses it. Groundwater is used for household and irrigation purposes in the Bushbuckridge community; this study will classify the study area's groundwater quality based on the chemical elements present.

The findings of this study will be used to guide the Department of Water, researchers, and international organizations such as the World Health Organization in developing strategies, policies, and institutional infrastructures to provide communities with high quality, easily accessible water resources. This research will also be used to raise awareness in the Bushbuckridge Local Municipality about water scarcity and quality.

CHAPTER 2: LITERATURE REVIEW

2.0 Preamble

Hydrogeochemical investigation and groundwater quality assessment is important to the sustainability of groundwater resources. This chapter examines much relevant

research that has been conducted globally, in South Africa furthermore, in the Bushbuckridge area. Also, this chapter explains several approaches and analytical techniques for analysing groundwater quality. A literature review on hydrogeochemical processes and groundwater types and facies is explained in detail.

2.1 Groundwater quality

Groundwater is a valuable natural resource that plays a vital part in the economy. Groundwater accounts for over 30% of the world's fresh water. In most regions of the world, groundwater accounts for one-third of the freshwater utilized by people, but in some areas of the world, this ratio can exceed 100% (Clark and Biar, 2001). In South Africa, the total available renewable groundwater resource is estimated to be 10,343 mm³/a or 7,500 mm³/a under drought conditions (DWS, 2017).

Water quality refers to how suitable water is for its intended use, as determined by its physical, chemical, and biological characteristics. According to DWAF (1998), these characteristics are mainly influenced or controlled by substances that are dissolved or suspended in water. Moreover, Todd (1980) argues that subsurface geochemical reactions such as weathering, dissolution, precipitation, ion exchange, and numerous biological processes may have an impact on groundwater quality. All of these variables can have an impact on the type of water and the number of dissolved components in groundwater.

Groundwater quality is just as crucial as its quantity owing to the suitability of water for various purposes Belkhiri et al, (2010). Poor groundwater quality can reduce agricultural and horticultural productivity, resulting in severe economic losses. Polluted groundwater can harm the environment by contaminating streams and wetlands, as well as harming groundwater-dependent ecosystems. Human health might also be jeopardized by low-quality groundwater Xiaunjun et al, (2023).

Groundwater geochemical processes and reactions with aquifer minerals have a significant impact on water quality. The chemical and physical features of surrounding rocks, the quantitative and qualitative properties of through-flowing water bodies, and the products of human activity all influence the quality of water as it moves underground (Matthess, 1982).

2.1.1. Groundwater Quality: A brief overview from a global perspective

Several studies have been conducted globally, noticeably in India and China, where groundwater resources are under significant threat in terms of quality and quantity (Narsimha et al. 2018). A study was conducted by Narsimha et al (2018) in the central parts of Telangana, India. In the study, they collected a total of 105 samples and analyzed them for various chemical parameters. They used methods such as Water Quality Index and Gibbs diagram for evaluation. The results from Water Quality Index (WQI) revealed that from the groundwater samples, 60% and 36% fell under excellent and good water quality categories and are suitable for drinking purposes. It was also determined that 51% of fluoride (1.5 mg/L) and 71% nitrate concentrations (45 mg/L) of groundwater have concentrations that exceed the maximum acceptable limits, therefore making the groundwater unsuitable for drinking purposes. The results from the Gibbs Diagram revealed that groundwater chemistry is primarily controlled by rock-water interaction. It was also determined that most of the groundwater samples fall in deep meteoric percolation and $\text{Na}^+ - \text{SO}_4^{2-}$ types, but most belong to $\text{Ca}^{2+} - \text{Mg}^{2+} - \text{HCO}_3^-$, $\text{Na}^+ - \text{HCO}_3^-$ facies, and few are of $\text{Ca}^{2+} - \text{Mg}^{2+} - \text{Cl}^-$ and $\text{Na}^+ - \text{Cl}^-$ facies. For irrigation purposes, it was revealed that 90% of groundwater in the study area was said to be suitable.

Sakram and Adimalla (2018) conducted a study in the Mothkur region, Telangana State in India in the determination of chemical quality for both groundwater and surface water for drinking and irrigational purposes, the focus of the study was on groundwater since the majority of the population relies on groundwater for their everyday necessities, including drinking, housekeeping, and irrigation. Consequently, they collected 25 groundwater and 5 surface water samples, and the samples were analyzed for different chemical parameters. For drinking purposes, they assessed and compared their findings with WHO and BIS water quality standards. Their findings revealed that due to the concentrations of fluoride (32%), TDS (20%), TH (28%), and Cl^- (4%) of groundwater samples are not recommended for drinking.

For determining the water type, they used the Base-exchange indices and meteoric genesis indices and the results showed 67% as the $\text{Na}^+ - \text{HCO}_3^-$ type and 33% as the deep meteoric water percolation type of the water sources. Piper trilinear diagram was used for geochemical classification and the result indicated that 44% and 60% of

groundwater and surface water samples were $\text{Ca}^{2+}\text{--Na}^+ \text{--HCO}_3^-$ type and 29% of groundwater belong to $\text{Na}^+ \text{--HCO}_3^-$ types. Results from the Wilcox diagram, sodium adsorption ratio, percent sodium (%Na), residual sodium carbonate, and permeability index indicated that most of the groundwater samples are suitable for irrigation purposes.

Another study was conducted in the arid Yushenfu mining area, Shaanxi province in China. The study involved exploring and assessing the water quality for drinking and irrigation purposes (Liua et al,2019). For their study, they used Piper Trilinear and Gibbs diagram for a proper evaluation of the hydrochemical processes that are present in the area and to also understand the relationships between the hydrochemical composition in the groundwater. Ca^{2+} , Mg^{2+} , and HCO_3^- were revealed to be the main ions in the groundwater samples, and $\text{HCO}_3\text{--Ca}^+ (\text{Mg})$ is the principal hydrochemical type from the study. And also the groundwater quality in the study area was considered to be of good quality and appropriate for drinking and irrigation purposes currently good owing to the low concentrations of all the parameters that were tested for water quality. From the study, it was concluded that the groundwater chemistry was influenced by various processes, namely: Rock weathering, the dissolution of silicate minerals, and cation exchange. It was also discovered that in the neighbouring land used for agriculture, there was a high use of nitrogen fertilizer which resulted in a high concentration of NO_3 .

2.1.2 Groundwater Quality: A South African Perspective

According to Roselt and Mpofu (2021), South Africa is among the world's driest countries and has been described as a water-scarce country. Water scarcity in South Africa has been attributed in part to low rainfall and high rainfall variability associated with climate change. However, groundwater is an important natural resource for providing water to people in South Africa for domestic, industrial, and agricultural needs Monyatsi et al (2012).

Several studies have been conducted in South Africa with relation to geochemistry and water quality, for instance, a study conducted by Mulaudzi et al (2022) wherein they were investigating whether the groundwater in the Nwanedi agricultural community is suitable for use in domestic and agricultural purposes. They collected samples from different boreholes around the area and analyzed them for different

physiochemical parameters. From their results, it was concluded that the water was suitable for both agricultural and domestic use. Furthermore, it was also discovered that the hydrochemical composition is controlled by natural and anthropogenic processes such as on-sight sanitation, agricultural leachates, and domestic effluents.

Another study was conducted by Pamela Nolakana (2017) with the title “geochemical assessment of Groundwater and Suitability for Drinking and Irrigation Purposes in New Castle, KwaZulu-Natal, South Africa”. For their study, they collected 31 samples for analysis, and the samples were analyzed for various parameters. From the hydrochemical facies, it was discovered that rock-water interaction was the main process affecting the groundwater chemistry of the study area. For drinking purposes, they used the SAWQG water guidelines to evaluate its suitability. EC (salinity hazard), Sodium percent, Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC), Kelly's ratio (KR), Magnesium hazard, and Permeability index were used for analyzing irrigation water quality. The majority of the samples were found to be suitable for drinking purposes whereas it was also discovered that 12.90 % of the samples were said to be above the SAWQG based on their EC concentration and for TDS 16.13% of samples were also not suitable. From the results, it was concluded that the dominant ions were $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$. When using SAR and Permeability index all the samples were found suitable for irrigation whereas based on the Na%, RSC, Kelly's ratio, and Magnesium Ratio showed that the water from some of the boreholes and catchments was unsuitable for irrigation because of its potential to cause sodium hazard.

2.1.3 Groundwater Quality in Bushbuckridge Area

No studies have been conducted concerning the hydrogeochemistry of the Mpumalanga area or Bushbuckridge in particular. But studies around water quality have been done in previous years. According to Monyatsi et al, (2012), in most rural sections of Mpumalanga province, access to clean and portable water is a major concern. In a study that has been conducted by Monyatsi et al (2012), titled “Groundwater Quality in a South African rural community”, they concluded that the main source of drinking water in Mpumalanga province is not suitable for human consumption based on the detection of high levels of Magnesium, Calcium, Fluoride and nitrate which can pose a great threat to consumer's health.

The Bushbuckridge area relies mostly on groundwater resources for both domestic and agricultural needs (Mnisi (2011) and Mogakane (2018)). According to Mnisi (2011), the majority of people from the communities in Bushbuckridge Municipality rely on groundwater for their domestic and irrigation uses. However, the suitability of the water resources for these activities is not fully understood and out of 100% of the people, only 28% treat their water before use while the other 72% just use the water as it is. Consequently, there is a need to evaluate and assess the suitability of the water resources for the above-mentioned activities.

2.2 Groundwater Quality Parameters

2.2.1 Physical parameters

Physical properties of water refer to the appearance of water, which includes, color, temperature, turbidity, taste, and odor (DWAF, 1998). The water quality properties that may be determined by physical methods are properties such as conductivity and pH measurement.

❖ Electrical conductivity

Electrical conductivity (EC) is a good overall indicator of water quality and it measures the ease with which water conducts electricity. Pure water is a good insulator rather than a good conductor of electric current whereas seawater is a very good conductor of electric current due to its very high salt content. The electrical conductivity of water increases as ions concentration in the water rises. In general, the electrical conductivity of water is determined by the number of dissolved solids in it (Meride and Ayenew, 2016).

❖ pH

The pH of water is an important parameter in determining its acid-base balance. It can also be used to determine if water is acidic (pH less than 7) or alkaline (pH greater than 7 (Meride and Ayenew, 2016). Most unpolluted water sources have a pH between 6,5 and 8,5. Wherever acidification processes occur, pH levels below 6,5 can be discovered, the most severe example being acid mine drainage, where pH values as low as 3,0 can be found. Alkalinization procedures, such as exposing water to lime or other alkalis, can cause the pH to rise over 8.5 (DWAF, 1988).

2.2.2 Chemical parameters

Chemical Parameters Refer to the nature and concentration of dissolved substances such as salts, metals, and organic chemicals. Many chemical substances in water are essential as part of the daily intake required, but at high concentrations, they make water unpalatable and cause illnesses (DWAF, 1998).

❖ Calcium

Calcium is found naturally in groundwater. It can erode from limestone, marble, calcite, dolomite, gypsum, fluorite, and apatite, among other rocks. Calcium, which is found in water as Ca^{2+} ions, is a factor of water hardness (WHO, 2011, Lenntech). Calcium is necessary for the development and maintenance of a strong bone structure. Calcium in hard water might help you get the calcium you need daily. Calcium concentrations in hard groundwater can be in the hundreds of mg/l, higher than in soft groundwater (DWAF, 1998).

❖ Chloride

Chloride is negatively charged that is mostly found in the form of salts. Excess chloride gives water a saline taste and speeds up metal corrosion (DWAF, 1998). According to WHO (1996), even though chlorides have only little effect on living beings, their excessive consumption might cause considerable harm or poisoning. Chloride levels in water should not exceed 250 mg/L (WHO, 1996). Calcium concentration in rainwater and soft waters is often less than 10 mg/l. Chloride concentrations of up to 700 mg/l are frequent in arid places with saline soils, and high concentrations are found wherever salt contamination or marine incursion is encountered. (DWAF, 1998).

❖ Fluoride

Fluoride is a chemical element that is most commonly found in groundwater and has emerged as one of the most significant toxicological environmental threats worldwide. Weathering and leaching of fluoride-bearing minerals from rocks and sediments cause fluoride to arise in groundwater. Fluoride is good in supporting dental health by reducing dental caries when consumed in small amounts (0.5 mg/L), but greater doses (>1.5 mg/L) might induce fluorosis (Demelash et al, 2019).

❖ Iron

In its pure condition, the metallic iron is silvery-white, however, oxidation of the metal's surface causes it to appear brown or black (DWAF, 1998). Iron is found in groundwater as a result of its natural occurrence in subsurface rock formations and precipitation water that infiltrates via these formations (Ityel, 2011). Iron concentrations of more than 10 milligrams per liter (mg/l) are uncommon in groundwater (Ityel, 2011). A report from DWAF (1998) suggests that the concentration of iron in unpolluted freshwater ranges from 0,001 – 0,5 mg/l, however, if water is polluted by acid mine drainage, concentrations may be much higher.

❖ Total Hardness

Total hardness (TH) is the sum of calcium and magnesium concentrations expressed as mg/l calcium carbonate [CaCO_3] and is calculated as follows:

$$\text{TH} = [2,497 \times \text{Calcium (mg/l)}] + [4,118 \times \text{Magnesium (mg/l)}]$$

Water hardness is a common indicator of water's ability to react with soap, with hard water demanding significantly more soap to form a lather (WHO, 2011). Rainwater has a low total hardness and is very soft, with minimal calcium and magnesium. When soluble calcium and magnesium minerals are found in subsurface waters, overall hardness can be very high (DWAF, 1998).

❖ Magnesium

Magnesium is an alkaline earth metal that burns with brilliant light (thus its use in flares) to form magnesium oxide. Magnesium hydroxide is well known as a stomach antacid in the form of Milk of Magnesia and as magnesium sulfate as the well-known purgative, 'Epsom salts'. Magnesium is an essential nutritional element needed for the normal functioning of muscles.

The total dietary intake is about 250 mg/day in adults. In unpolluted fresh water, the magnesium concentration is usually less than 10 mg/l, except in some hard groundwater where the magnesium concentration may rise to several hundred mg/l (DWAF, 1998).

❖ Manganese

Manganese is a metal, common in soils and often associated with water, which is responsible for the dark tea-like color of some water sources. For example, the tea-colored water of the Western Cape is due to organic material present in the water together with manganese. The typical concentration of manganese in unpolluted water is 0,001 to 0,2 mg/l. In humic waters, the concentration may be naturally as high as 3 mg/l. Manganese concentrations above 5 mg/l may arise in cases of pollution, or from the bottom waters of dams (DWAF, 1998).

❖ Nitrate

Nitrate (NO_3) is a plant nutrient, being the end product of the oxidation of ammonia (NH_3) and nitrite (NO_2). Nitrate and nitrite can be readily converted from one to the other. In unpolluted water, the nitrate-nitrogen concentration is typically less than 2 mg/l as N. As nitrates are produced by the decay of plant, animal, and human wastes, pollution of water with nitrate is typically found wherever intensive land use activities take place, and nitrate-nitrogen concentrations exceeding 20 mg/l (as N) are a common occurrence in groundwater (DWAF, 1998).

❖ Potassium

Potassium is an alkali metal and is the main intracellular positive ion in living tissues. It is an essential dietary constituent. The concentration in unpolluted fresh water is typically 2-5 mg/l. High concentrations occur in runoff from irrigated lands, from fertilizer production, and in domestic wastes (DWAF, 1998).

❖ Sodium

Sodium is the alkali metal constituent of table salt or sodium chloride. Sodium is an essential dietary element needed to maintain electrolyte balance in the body. Sodium concentrations vary tremendously in water both over time and from place to place, being low in fresh waters (<50 mg/l) in regions of high rainfall, and high (as much as 500 mg/l) in areas with little rainfall. The concentration of sodium in seawater is 11000 mg/l. Sodium concentrations tend to be high in the ground and surface waters in the Western and Southern Cape and also in some mine wastes (DWAF, 1998).

❖ Sulfate

Sulfate can be found in a variety of minerals, such as barite (BaSO_4), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Greenwood & Earnshaw, 1984). The mineral composition of various drinking waters is influenced by these dissolved

minerals. Sulfate concentrations in unpolluted fresh water are typically less than 10 mg/l. Waters polluted by acid mine drainage and effluent return flows may contain as much as 500 mg/l sulfates or more (DWAF, 1998).

2.3 Drinking water quality

Safe drinking water is both a basic need for good health and a basic human right (WHO 2010). In most parts of the world, groundwater is the primary source of drinking water and is also commonly used for other domestic purposes such as cooking without any physical or chemical treatment. This is a bad habit that can lead to a variety of health problems. (Brindha and Elango, 2011). However, due to the lack of a treated piped water delivery infrastructure in certain sections of poor countries, this practice cannot be avoided. (Brindha and Elango, 2011). Some substances, such as iron, ammonia, nitrates, and arsenic, have negative health effects (WHO, 2011).

In many places of the world, fresh water is already in short supply (Jackson et al. 2001) and the level of access to safe drinking water varies across the country. However, four factors can be used to establish whether or not a user has access to this resource, namely, i) a sufficient quantity, ii) an acceptable quality, iii) local availability, and iv) affordable price (Jain et al., 2011). Due to the rising population, urbanization, and climate change, it will become much more limited in the next century (Jackson et al. 2001).

The availability of safe drinking water and sanitation is a global issue (Meride and Ayenew, 2016). Half of the population in underdeveloped countries suffers from health problems due to a lack of safe drinking water and pollution by bacteria. According to Napacho and Manyele (2010) the term "drinking water quality" refers to the relationship between the composition of water and the impact of natural and human processes. Chemical compounds are introduced into the water supply system through leaks and cross connections, resulting in the deterioration of drinking water quality.

According to the World Resource Centre, 41% of the world's population, or 2.3 billion people, are under "water stress," which implies their per capita water supply is less than 1.7m³/year. Fitzmaurice (2007). Furthermore, it is projected that 1.1 billion people lack access to safe drinking water and 2.6 billion people lack proper sanitation, all of which contribute to health issues. Every year, almost two million people die because

of a lack of adequate drinking water Hardberger (2005). According to statistics, about 6,000 children under the age of five die every day from water-related ailments around the world. Diarrhea, cholera, dysentery, typhoid, and polio can all be spread by contaminated water. Each year, 485 000 diarrhoeal fatalities are estimated to be caused by contaminated drinking water Heleba(2011).

2.3.1 Drinking Water Quality Classification

Depending on the specific standards, the quality of groundwater influence how suitable it is for various purposes. Drinking water should be soft, free of harmful substances, and low in dissolved salts chemically (DWAF, 2005).

Water Quality Index, Department of Water and Sanitation (DWS), and South African National Standard (SANS) drinking water standards are discussed in this chapter.

2.3.1.1 Water Quality Index

The Water Quality Index is an effective monitoring instrument that provides useful information about water from different sources, it often integrates several water quality parameters to describe the state of the water resources and their suitability for drinking purposes (Olasoji, 2019). WQI is based on a scale of 0–300 whereby lower values indicate good water quality, whereas higher values are an indication of contaminated water Molekoa et al, (2019). Table 1 indicates the water quality clarification and ratings (Singh et al, 2016). According to Olasoji et al, (2019), the stages involved in Water Quality Index calculations include:

- (i) Assignment of weights (w_i) to each water quality parameter involved.
- (ii) Calculation of relative weights (W_i)

$$W_i = \frac{w_i}{\sum_i^n w_i} \quad \text{Equation (1)}$$

where W_i represents the relative weight of each parameter sampled, w_i represents the weight of each parameter, and n represents the total number of parameters.

- (iii) Quality rating scale calculation (Q_i)

$$Q_i = \frac{Ci \times 100}{Si} \quad \text{Equation (2)}$$

where Q_i is the quality rating, C_i is the concentration of each parameter (mg/l), and S_i is derived from the WHO water quality standard.

(iv) Calculation of Sub index (SI_i)

$$SI_i = Wi \times Qi \text{ Equation (3)}$$

(v) Finally, calculate Water Quality Index using the equation

$$WQI = \sum SI_i \text{ Equation (4)}$$

2.3.1.2. Department of Water and Sanitation (DWS)

This classification system describes the effects of increasing concentrations of each of the chemical parameters deemed important for domestic use. The technique uses a clear color and number code that ranges from idea to totally unacceptable water quality (DWAf, 1998). Water is classified to determine how suitable it is for various domestic uses, including drinking, food preparation, bathing, and washing clothes.

This classification also makes it simple to share information about water quality with the public and other stakeholders and helps with decision-making regarding the management of domestic water supply quality.

In collaboration with the Department of Health, the Department of Water Affairs and Forestry, currently known as the Department of Water and Sanitation, created this method for classifying water quality in 1996. This classification was revised in 1998, as detailed in the following document (DWAf, 1998).

The assessment guide classifies water quality into five classes (Class 0 to Class 4). The table below summarizes the various water classes and the possible effects to adverse water quality may have on consumers.

Table 1 DWAf, Classification of Water for Domestic Utilisation

Class / Colour	Description	Effects
		Drinking Health: No effects, suitable for many generations.

Class 0	Ideal water quality	Drinking Aesthetic: Water is pleasing. Food preparation: No effects. Bathing: No effects. Laundry: No effects.
Class 1	Good water quality	Drinking Health: Suitable for lifetime use. Rare instances of sub-clinical effects. Drinking Aesthetic: Some aesthetic effects may be apparent. Food preparation: Suitable for lifetime use. Bathing: Minor effects on bathing or on bath fixtures. Laundry: Minor effects on laundry or fixtures.
Class 2	Marginal water quality	Drinking Health: May be used without health effects by the majority of individuals of all ages, but may cause effects in some individuals in sensitive groups. Some effects possible after lifetime use. Drinking Aesthetic: Poor taste and appearance are noticeable. Food preparation: May be used without health or aesthetic effects by the majority of individuals. Bathing: Slight effects on bathing or on bath fixtures. Laundry: Slight effects on laundry or on fixtures.
Class 3	Poor water quality	Drinking Health: Poses a risk of chronic health effects, especially in babies, children and the elderly. Drinking Aesthetic: Bad taste and appearance may lead to rejection of the water. Food preparation: Poses a risk of chronic health effects, especially in children and elderly. Bathing: Significant effects on bathing or on bath fixtures. Laundry: Significant effects on laundry or on fixtures.
Class 4	Unacceptable water quality	Drinking Health: Severe acute health effects, even with short-term use. Drinking Aesthetic: Taste and appearance will lead to rejection of the water. Food preparation: Severe acute health effects, even with short term use. Bathing: Serious effects on bathing or on fixtures. Laundry: Serious effects on laundry or on fixtures.

2.3.1.3 South African National Standard (SANS) 241: 2015

The South African National Standard (SANS) 241: 2015 is a drinking water standard that specifies the minimum requirements for safe drinking water (Carter, 2017). The SANS classified water into two categories, a determinant that falls within the standard limits and a determinant that falls above the standard limits.

Table 2 SANS, Physical, Aesthetic and Chemical Allowable limits

DRINKING WATER

	<u>Risk</u>	<u>STANDARD LIMITS</u>
Physical and Aesthetic Determinands		
Colour (mg/l as Pt-Co)	Aesthetic	≤15
Conductivity (at 25 °C)	Aesthetic	≤170
Total Dissolved Solids (mg/l)	Aesthetic	≤1200
Turbidity (NTU)	Operational ^a	≤1
	Aesthetic	≤5
pH (at 25 °C) ^b	Operational	≥5 to ≤9.7
Chemical Determinands – Macro Determinands		
Free Chlorine (mg/l as Cl ₂) ^d	Chronic Health	≤5
Monochloromine (mg/l) ^{cd}	Chronic Health	≤3
Nitrate (mg/l as N) ^{ef}	Acute Health	≤11
Nitrite (mg/l as N) ^{efg}	Acute Health	≤0.9
Combined Nitrate plus Nitrite (mg/l) ^{efg}	Acute Health	≤1
Sulphate (mg/l as SO ₄ ²⁻)	Acute Health	≤500
	Aesthetic	≤250
Fluoride (mg/l as F)	Chronic Health	≤1.5
Ammonia (mg/l as N)	Aesthetic	≤1.5
Chloride (mg/l as Cl)	Aesthetic	≤300
Sodium (mg/l as Na)	Aesthetic	≤200
Zinc (mg/l as Zn)	Aesthetic	≤5
Chemical Determinands – Micro Determinands		
Antimony (µg/l as Sb)	Chronic Health	≤20
Arsenic (µg/l as As)	Chronic Health	≤10
Barium (µg/l as Ba)	Chronic Health	≤700
Boron (µg/l as B)	Chronic Health	≤2400
Cadmium (µg/l as Cd)	Chronic Health	≤3
Total Chromium (µg/l as Cr)	Chronic Health	≤50
Copper (µg/l as Cu)	Chronic Health	≤2000
Cyanide (recoverable) (µg/l as CN ⁻)	Acute Health	≤200
Iron (µg/l as Fe)	Chronic Health	≤2000
	Aesthetic	≤300
Lead (µg/l as Pb)	Chronic Health	≤10

The limits associated with risks for domestic water as determined by the South African National Standard (SANS) 241:2015 are as follows:

- Health risks: Parameters that exceed these limits can lead to acute or chronic health issues in people.
- Aesthetic risks: parameters that exceed these limits can lead to the water being deemed visually, aromatically, or palatably undesirable.
- Operational risks: parameters that exceed these limits may indicate that operational methods for ensuring compliance with water quality requirements have failed.

The water shall comply with the physical, aesthetic, and chemical numerical limits for lifetime consumption specified in Table 2.

2.3.2 Improving Drinking Water Quality

Water that is regarded as unsuitable for drinking purposes can be treated (at a cost) to remove any substance which may make it unsuitable, however, some substances are easier to remove from water than others. As a result, some treatments are less expensive to implement, while others are more expensive DWAF(1998).

There are several ways to improve water quality before using it for drinking purposes. The most commonly used practices are described below.

❖ *Boiling of water*

Boiling water is the most effective purification method when safe, treated water is not available (UMPC,2022). This method is also considered cheap and easy to implement (Assessment guide,). Boiling is the safest method to kill disease-causing germs including viruses, bacteria, and parasites. The boiling of water method can also be used to soften hard water, which is water with high concentrations of calcium and magnesium ions (Sengupta, 2013)

Advantages

- Cheap and easy to implement.
- Rapid results.

Disadvantages

- Cannot be used to treat more harmful substances such as lead and chloride

❖ ***Ion Exchange***

Ion exchange in water treatment removes unwanted ionic contaminants from water by exchanging them with another ionic substance. This treatment can be achieved through four methods namely, water softening, deionization, demineralization, and dealkalization.

❖ ***Water Softening***

Ion exchange in water softening is the process by which hardness minerals in the water, primarily calcium, and magnesium, are exchanged for sodium minerals. Since minerals are ionic, an exchange is possible. That is, it has an electric charge. The ion exchange process is based on the repulsion of like charges and the attraction of opposite charges.

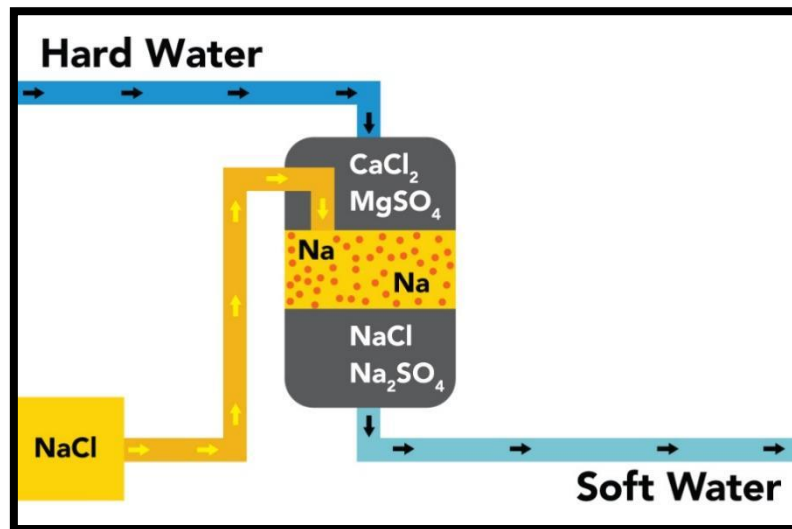


Figure 1 Water softening (Atlas scientific, 2022)

❖ ***Deionization***

In deionization treatment, the water is passed through a resin bed (either a pressure tank or a drop-in cartridge attached to the tank) where appropriately charged mineral particles attach to the resin beads. Non-water ions remain trapped in the resin while pure water continues to flow (Woodard, 2021).

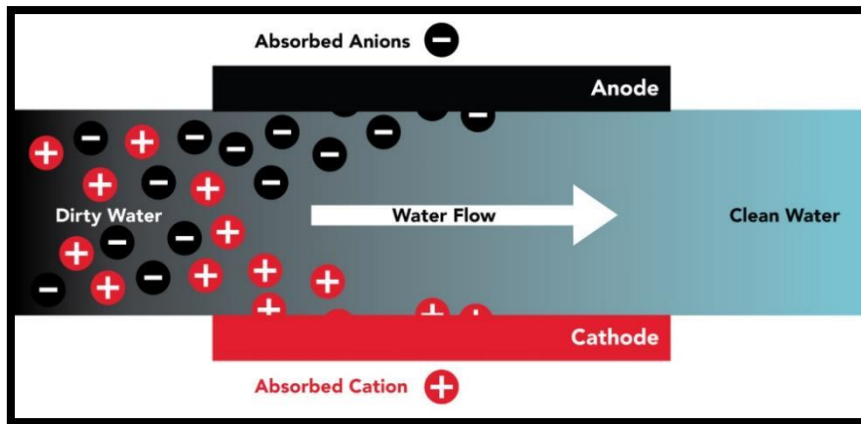


Figure 2 Deionization (Atlas scientific,2022)

❖ **Demineralization**

Demineralization of water is the removal of essentially all inorganic salts by ion exchange. In this process, strongly acidic cation resins in hydrogen form convert dissolved salts to their corresponding acids, and strongly basic anion resins in hydroxide form remove these acids.

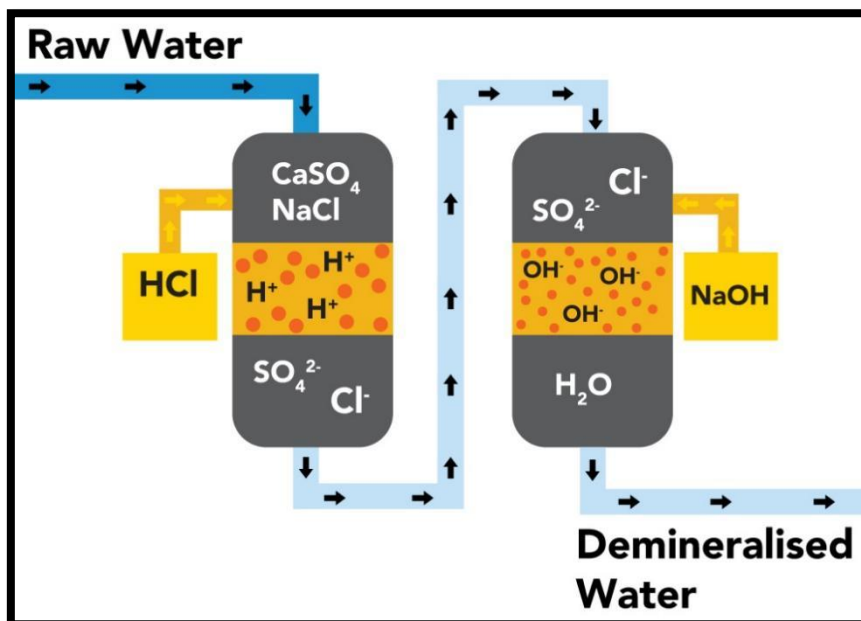


Figure 3 Demineralization (Atlas Scientific, 2022)

❖ **Dealkalization**

A dealkalizer functions similarly to a water softener in that it uses ion exchange to eliminate undesirable ions from a water source. Dealkalization, however, eliminates carbonate ions in favor of chloride ions rather than eliminating calcium and magnesium ions (Worch, 2019).

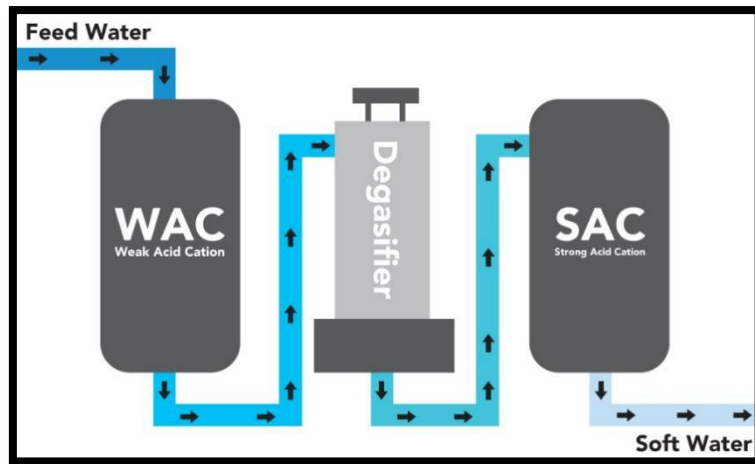


Figure 4 Dealkalization (Atlas Scientific, 2022)

Advantages of Ion Exchange

- Rapid results
- They can be used for short and long-term applications.

Disadvantages of Ion Exchange

- Long-term costs are expensive.
- When ion exchange beds are regenerated, salt water is dumped into the environment.

❖ Reverse Osmosis

Reverse Osmosis is a process that removes most of the dissolved solids and other contaminants from water by forcing it through a semi-permeable reverse osmosis membrane (. Reverse osmosis uses a high-pressure pump to increase the pressure on the salt side of reverse osmosis by forcing water through a semi-permeable reverse osmosis membrane, leaving almost all of the dissolved salts in the waste stream. works. The required pressure depends on the salinity of the feed water. The more concentrated the water supply, the higher the pressure required to overcome the osmotic pressure.

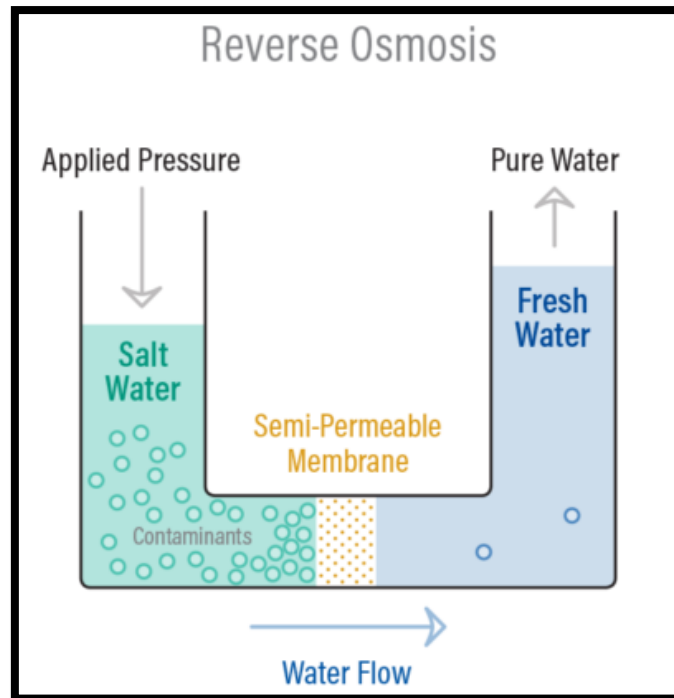


Figure 5 Reverse Osmosis

Advantages of Reverse Osmosis

- Eliminates or greatly reduces many harmful contaminants in water.
- It is more compact and requires less space than other desalting systems.

Disadvantages of Reverse Osmosis

- The installation cost of a reverse osmosis system is high.
- Pre-treatment is always required before reverse osmosis.

❖ Chemical Precipitation

Chemical Precipitation is a pH adjustment procedure that is mostly employed to remove dissolved metals from aqueous wastes. In this procedure, an acid or base is added to a solution to change the pH until the components that need to be removed have the lowest solubility (Rao and Kota, 2017). As pH rises, metal ions become less soluble and precipitate as hydroxide, decreasing the solubility of the metals. By raising pH with alkaline substances like lime or caustic soda, metals can be precipitated (Rao and Kota, 2017).

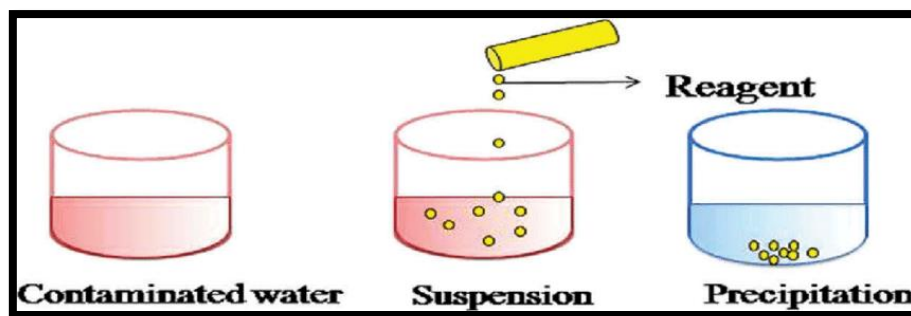


Figure 6 Chemical Precipitation (Chakraborty et al, 2020)

Advantages of chemical precipitation

- Effective for treating huge volumes of liquid waste.
- The procedure is affordable and make use of easily accessible chemical reagents.

Disadvantages of chemical precipitation

- Produces a significant amount of sludge, which adds to the operational costs associated with disposal.
- ineffective for treating heavy metal ions with low concentrations.

2.4 Irrigation water quality

The quality of irrigation water varies in different parts of the country (Zaman et al, 2018). The type of salts and their dissolved quantity has an impact on irrigation water quality. As the overall salt concentration in various soils rises, crop development difficulties emerge, resulting in lower crop yields (Muhammad and Aamir, 2016).

2.4.1 Irrigation water quality characterization

For irrigation purposes, there are four main criteria for evaluating water quality namely; salinity hazard, bicarbonate and carbonate concentrations, sodium hazard, and ionic imbalance (Zaman et al, 2018).

2.4.1.1 Salinity hazard

Salinity is the concentration of all soluble salts in water or soil (Imad and Ahmad, 2016). This has several negative effects on plants. The most crucial of these is that it reduces plants' ability to absorb water. As a result, even if the soil in the field looks to be moist, the plants will be withered (Brunton, 2011). Because of the high osmotic

potential of soil water, plant roots are unable to absorb it. As a result, water lost from the plant shoot through transpiration cannot be replaced, causing wilting (Zaman et al, 2018). If the salt concentration in the soil water is too high, the plant will be unable to absorb water and wilt, eventually dying. The exact point at which this occurs varies by plant type; some crops are more salt tolerant than others. Tolerance varies by stage of development, particularly during germination and seedling development when plants are most vulnerable.

2.4.1.2 Sodium hazard

The sodium adsorption ratio (SAR) is used to express the sodium hazard of irrigation water (Zaman et al, 2018). High SAR values indicate a risk of sodium replacing adsorbed calcium and magnesium ions, causing soil structure and plant root damage due to the permeability of soil being affected by high sodium ions in water, which causes infiltration issues. This is because sodium, when present in an exchangeable form in the soil, replaces calcium and magnesium adsorbed on the soil clays, causing soil particle dispersion. Water having a SAR less than or equal to 10 is of excellent quality (Kadyampakeni et al, 2018). However, if the water would be the primary source of irrigation for lengthy periods, it is thus recommended to avoid utilizing water with a SAR value larger than 10 (Zaman et al, 2018).

2.4.1.3 Bicarbonate and carbonate concentrations

When the soil solution becomes concentrated by evapotranspiration, carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-) will tend to precipitate calcium carbonate (CaCO_3) and magnesium carbonate (MgCO_3). As a result, the SAR value will rise, and the relative proportion of sodium ions will rise as well. As a result, the sodium hazard of the soil water will rise to a level higher than suggested by the SAR value. (Zaman et al, 2018).

2.4.1.4 Ionic imbalance

According to Wali et al (2021) when specific elements (ions) such as chloride, sodium, and boron in the soil or water are taken up by the plant and accumulate to concentrations high enough to cause crop damage or lower yields, toxicity issues arise. The extent of the damage is determined by the rate of uptake and the crop's sensitivity. Permanent, perennial crops (tree crops) are the most vulnerable ones. For

susceptible crops, damage often occurs at low ion concentrations Tuomisto et al (2017). Marginal leaf burn and interveinal chlorosis are frequently the first signs. Reduced yields result if the accumulation is large enough. Annual crops that are more tolerant are unaffected at low doses, but practically all crops will be damaged or killed if concentrations are high enough (Ayers and Westcot, 1985).

2.4.2 Improving Irrigation Water Quality

Before using water for irrigation purposes, several approaches can be used to improve its quality in terms of salinity and sodicity risks. The most common methods are discussed below

2.4.2.1 Water Amelioration using Gypsum

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which is high in calcium, can be added to water that is high in sodium (SAR above 6.0), either through irrigation water or by directly applying it to the land. This procedure is used to reduce the sodicity of water. The quantity of gypsum that must be added to irrigation water is determined based on the quality of the water (RSC and SAR levels) and how much water is required to irrigate the crop during the growing season Zhao (2006).

Advantages of using Gypsum

- simple to use
- the most effective amendment for reducing irrigation water sodicity.

Disadvantages of using Gypsum

- Gypsum added in excess can make the soil less capable to retain water, which can put plants under drought stress.

2.4.2.2 Water Amelioration using Sulphuric Acid

Arid areas tend to have salty soils and irrigation water, therefore frequent irrigation can lead to harmful sodium and bicarbonate ion build-up in the soil (Birhane and Hagos, 2021). sulfuric acid can be used to slow and reverse the increase in sodium and bicarbonate ions. Sulfuric acid,

when added in the right amounts to irrigation water or soil, has the potential to reduce residual carbonate content by eliminating bicarbonate ions, and lower salt concentrations in the water and soil (Eaton, 1950).

Advantages of using Sulphuric acid

- It is available at an affordable cost.

Disadvantages of using Sulphuric Acid

- High sulfur levels from the use of too much sulfuric acid cause calcium to get clogged in the soil and prevents its uptake by the plants.

2.4.2.3 Blending Water to a desired salinity

The quality of the salty/brackish water can be improved using available good water quality. This can be achieved by a standard calculation procedure. The crop to be irrigated determines the desired water salinity level.

An example was created by Zamen et al (2018) where a blend was made with 50% fresh water (EC 0.25 dS m⁻¹) with 50% brackish water (EC 3.9 dS m⁻¹). The resulting EC of the blended water would be:

EC (blended water) = (EC of freshwater × mixing ratio) + (EC of brackish water × mixing ratio)

$$= (0.25 \times 0.50) + (3.90 \times 0.50)$$

$$= 0.125 \times 1.95$$

$$= 2.075 \text{ dS/m}^1 \text{ which is equivalent to } 207.5 \text{ Ms/m}$$

2.5 Groundwater Geochemistry

Water traveling through the earth reacts to varying degrees with the minerals (and other substances) it encounters, and it is these rock-water interactions that give water its distinct chemistry (Akram et al, 2011). Groundwater geochemistry is a critical instrument for determining the quality of water in a given area and determining its use for domestic, irrigation, and industrial purposes (Wahed and Mahmoud, 2015).

Hydrogeochemical processes that are responsible for altering the chemical composition of groundwater vary concerning space and time. In any area, groundwater has unique chemistry due to several processes like soil/rock–water interaction during recharge and groundwater flow, prolonged storage in the aquifer, dissolution of mineral species, etc. (Subramani et al, 2010).

2.5.1 Geochemical Processes Responsible for groundwater chemistry

The chemistry of groundwater changes throughout time depending on the minerals present and the equilibrium circumstances. The chemistry of groundwater does not change drastically until it comes into contact with rocks that have a completely different composition. The total chemistry of groundwater at a given location and time is the consequence of dissolution, ion exchange, and precipitation processes continuing to operate as shown in Figure 7. Total salinity rises with time as groundwater moves, but one or more ions may depart from the solution due to ion exchange or precipitation when saturation conditions are met for that particular ion. (Freeze and Cherry 1979, Berner et al, 1987 and Edmunds and Carrilo-Rivera, 2002).

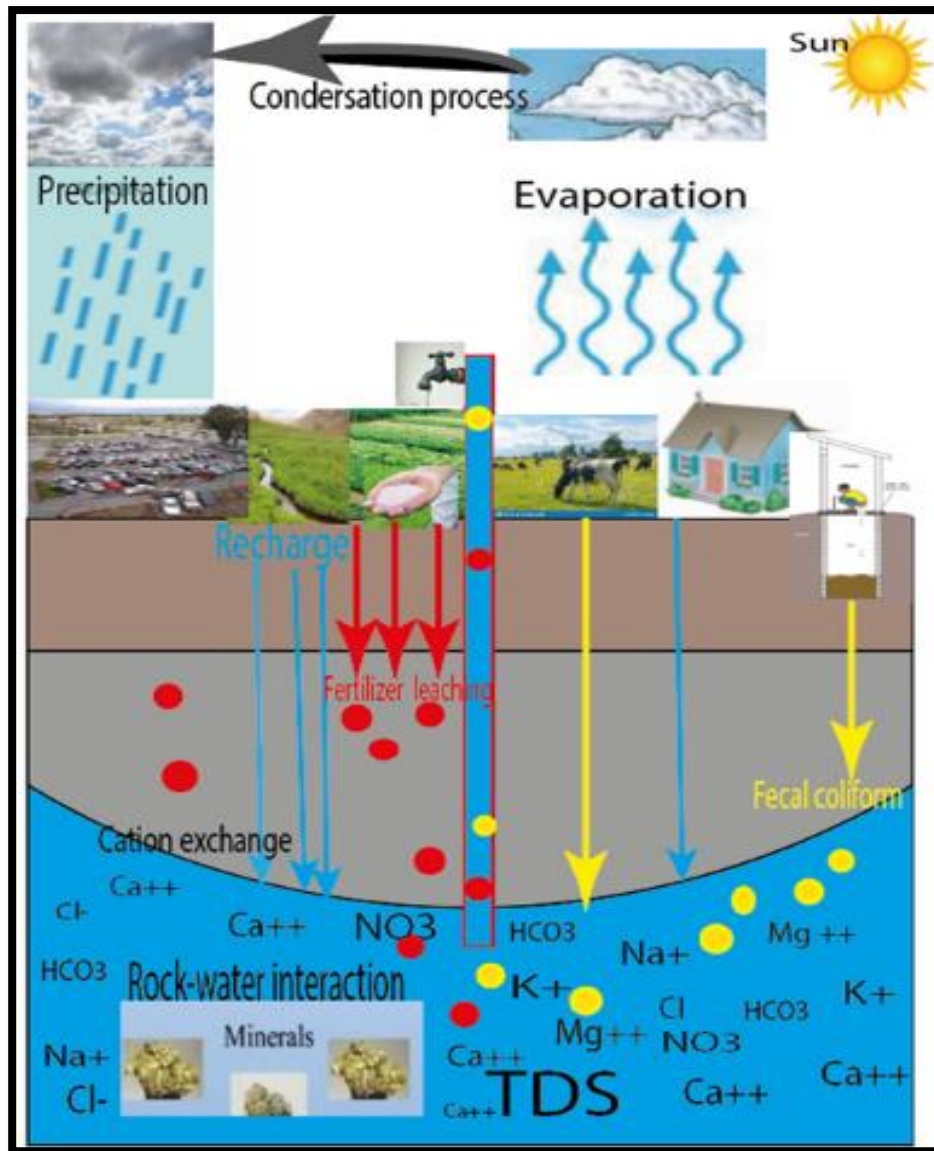


Figure 7 Summary of Process Influencing Geochemical Evolution of Water (Malugu, 2022).

The Gibbs diagram is a popular tool for determining the link between water composition and the lithological properties of aquifers. The Gibbs diagram depicts three separate fields: precipitation dominance, evaporation dominance, and rock–water interaction dominance (Gibbs, 1970). It is a plot of $\text{Na}^+ + \text{K}^+ / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ Vs TDS and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ as shown in Figure 8.

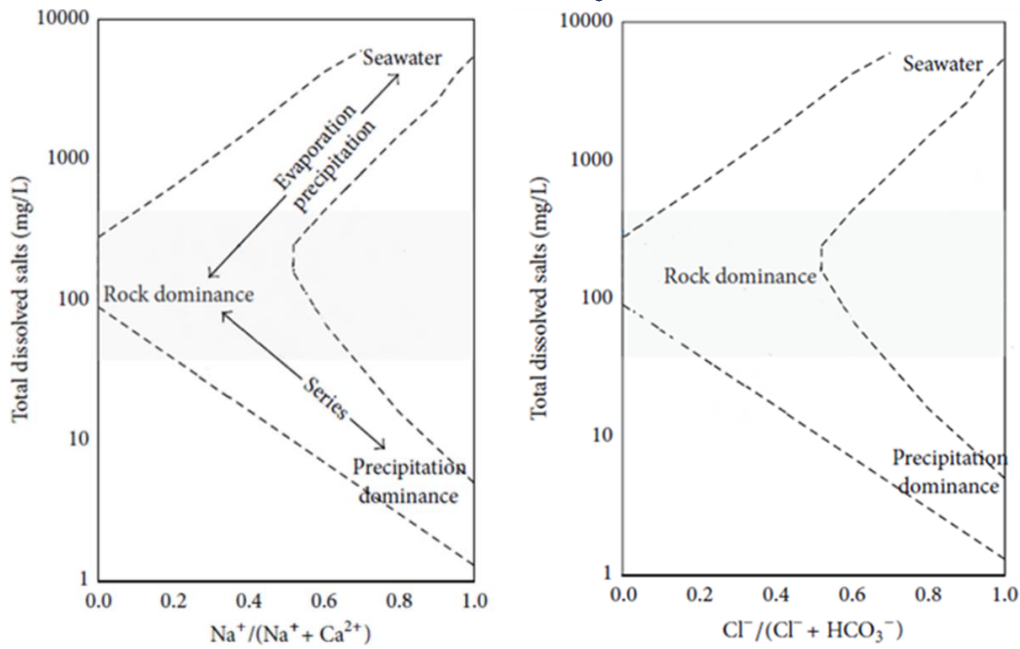


Figure 8 Gibbs Diagram (Gibbs, 1970)

2.2.1.1 Rock-Water Interaction

Various chemical interactions with solid phases occur as groundwater moves along its course from recharge to discharge locations. These chemical reactions vary in both space and time, and these can be influenced by the initial water's chemical composition, geological formations, and residence period. The degree of rock-water interaction and chemical reactions can be determined using the groundwater's principal ion concentrations (Elango and Kannan, 2007).

Various chemical processes, including weathering, ion exchange processes, oxidation, and reduction take place when rock and water contact.

Chemical Weathering

Chemical weathering is the partial or total dissolving of a rock (Diepetro, 2013). To change the composition of rocks, chemical weathering requires the interaction of rock with mineral solutions (chemicals) (Machayeki and Yuan, 2020).

Oxidation, hydrolysis, and carbonation are the primary chemical reactions involved in chemical weathering. Hydrolysis is a reaction with water, carbonation is a reaction with CO_2 to generate a carbonate, and oxidation is a reaction with oxygen to form an oxide.

As a result of these processes, a rock disintegrates because chemical weathering is more efficient on grain surfaces (Cheremisinoff, 1997).

Oxidation-reduction reactions

Oxidation-reduction processes (or redox reactions) are chemical reactions that include the transfer of electrons from one ion to another.

For example: $\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$

This depicts ferric iron being “reduced” to ferrous iron. The oxidation state of the surrounding environment—for example, water—controls redox reaction speeds and directions. Many elements can exist in multiple oxidation states, and the solubilities of the various oxidation states are expected to differ under natural settings. Iron is the most well-known example. Ferrous iron (Fe^{2+}) dissolves quickly in water, whereas ferric iron (Fe^{3+}) does not. When ferrous iron dissolves in suitably reducing groundwater, it oxidizes to the ferrous state and precipitates as an iron mineral, such as ferric hydroxide ($\text{Fe}(\text{OH})_3$) when the water reaches the surface (at a spring or a well).

Ion exchange processes

Ions in water tend to be drawn to solid surfaces due to their electrical charge. Ordinary mineral grains (e.g., feldspar or quartz) are one type of such surface Kim et al (2007), but they are far less efficient than the surfaces of minerals like iron oxides and clay minerals. Ion exchange mechanisms involve both anions and cations. Because their surfaces are continuously negatively charged, clays are very good at adsorbing cations.

Varied elements' ions have different tendencies for being adsorbed or desorbed. The following is the adsorption propensity of the principal cations in natural waters:

(Strongly adsorbed) $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ (weakly adsorbed) which means that calcium ions are much more likely to be adsorbed onto surfaces than sodium ions.

❖ *Precipitation*

Two different processes dominate how precipitation affects the hydrochemistry in regional groundwater. Firstly, the amount of groundwater recharge increases with rainfall. The enhanced precipitation recharge with low ion concentration will result in a

decrease in the groundwater's ion concentration. Secondly, the rain will carry the surface soil's soluble salt components into the aquifer, changing the groundwater's chemical composition (Zhongpei et al, 2022).

❖ **Evaporation**

There are many ways that evaporation can impact the quality of groundwater. One method is to make the groundwater more brackish by making it saltier. This is achieved during evaporation when some dissolved salts are left behind, increasing the salinity of the water (Elhoucine and Mohamed, 2021).

Furthermore, evaporation can layer or stratify the aquifer, causing some levels to have higher amounts of solids in them than others. The dissolved particles will obstruct water movement and reduce the availability of oxygen and other nutrients, which may result in a decline in the aquifer's overall water quality.

2.5.2 Groundwater types and hydrogeochemical facies

Hydrogeochemical facies can be used to determine correlations and similarities between the chemistry of waters in an aquifer (Ossa-Valencia and Betancur-Vargas, 2018). Facies are measured concentrations of main ions in decreasing order of magnitude.

Hydrogeochemical interpretation is done using a variety of ways based on data from geographical representations, as well as graphical and statistical methods. Stiff and Piper diagrams stand out among the graphical methods. It is feasible to conclude the primary processes that lead to the chemical composition of groundwater (Vinuta and Rahul, 2020).

2.5.2.1 Trilinear Piper Plot

For years, hydrochemical facies have been used in the chemical assessment of groundwater. The hydrochemical facies provide information on the source of groundwater's chemical quality because when an aquifer system contains a mix of rock types, the geochemical process becomes more complicated (Vinuta and Rahul 2020).

Piper (1994) proposed a trilinear diagram to classify groundwater facies. Cations are arranged on the tip of the right-hand triangle, whereas anions are arranged on the tip

of the left-hand triangle, and combinations of both cations and anions are depicted on the diamond shape block as shown in Figure 9. The Piper plot can generally be used to depict the geochemical evolution.

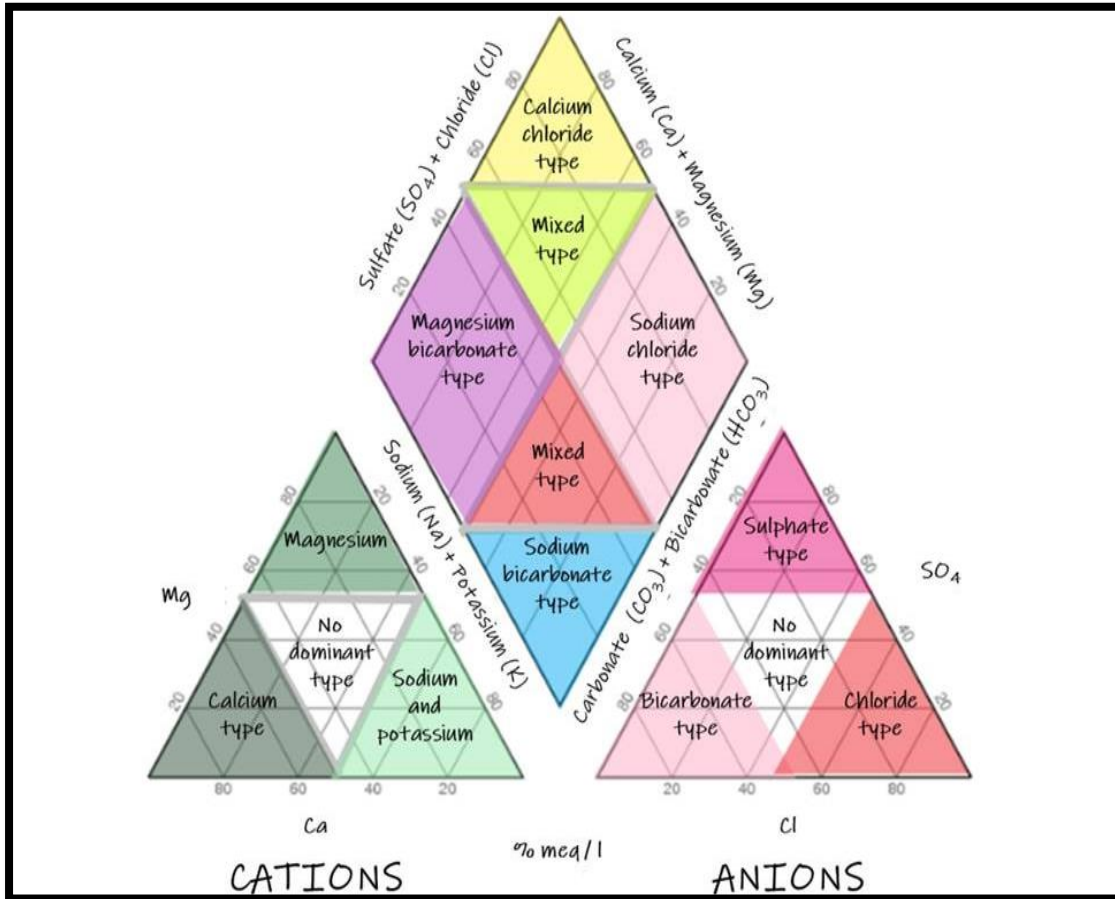


Figure 9 Piper Diagram showing groundwater types.

The piper diagram can be divided into the following categories:

❖ Ca-Cl Water Type

SO_4^- and Cl^- are dominant anions and Ca^{2+} and Mg^{2+} are dominant cations. This type of water is permanently hard. Combined concentrations of sulphate, chloride, magnesium, and calcium exceed 50 % of total meq/L.

❖ Mg-Ca- HCO_3 Water Type

This is magnesium bicarbonate. This groundwater has a temporary hardness. Ca^{2+} and Mg^{2+} are the predominate cations, while HCO_3^- and CO_3^{2-} are the predominate

anions. According to Hounslow (1995), groundwater with a magnesium carbonate water type comes from limestone and dolomite formations or active recharge zones with short residence times. Calcium, magnesium, and bicarbonate concentrations collectively exceed 50% of the total dissolved constituent load in meq/L.

❖ Na-Cl Water Type

According to Davis and Dewiest (1966), the water type may have resulted from inverse ion exchange or halite dissolution. Na^+ and Cl^- are the predominant cations and anions, respectively. Alkali metals, sulfate, and chloride concentrations when combined collectively make up over 50 % of the total meq/L. These hydrochemical facies' highly concentrated waters are regarded as brackish or, in rare instances, saline.

❖ Ca-Mg-Cl-SO₄ and Ca-Mg-HCO₃ Water Type

No cation-anion pair exceeds 50% of the total load of dissolved constituents in this type of groundwater. Such water type may be the consequence of several mineral dissolutions or the mixing of two groundwater sources with different chemical compositions.

❖ Na-HCO₃ Water Type

Na^+ and HCO_3^- and CO_3^{2-} are the two most prevalent anions and cations, respectively. The combined value of the concentrations of sodium, potassium, and bicarbonate exceeds 50% of the total meq/L. This water type is alkali carbonate in nature and according to their concentration of dissolved solids, these liquids usually have low hardness (Walton, 1970).

2.5.2.2 Stiff Diagram

Stiff diagrams are usually applied to show the major-ion concentrations of groundwater. The diagram's shape shows a relative proportion of various ions, while its size shows overall concentrations (Singh and Gewali, 2010). Anion concentrations are often shown on the right side of the picture, and cation concentrations are typically shown on the left. The ionic concentration increases with distance from the graph's centre as shown in Figure 10.

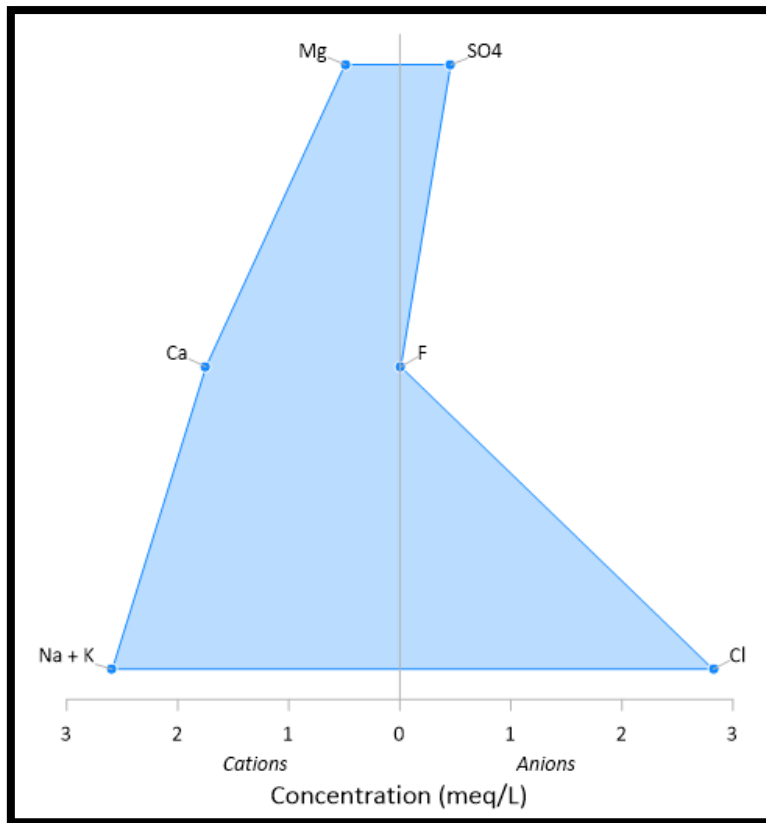


Figure 10 Example of Stiff Diagram

CHAPTER 3: RESEARCH METHODOLOGY

3.0 Preamble

This chapter presents the description of the study area, methodology and procedures that were used during the present study. The methodology consists of three phases: preliminary studies, field work, and office work. The fieldwork comprised mainly of hydrocensus and groundwater sampling while office work was made up of data analyses and interpretations. Methods for hydrochemical investigation as well as the analysis of the groundwater quality in the study area was also covered in this chapter.

3.1 Description of the study area

3.1.1 Location and Background information

The focus of this study is on the villages under the Bushbuckridge Municipality which falls between $31^{\circ} 0'E - 31^{\circ} 35'E$ and $24^{\circ} 30'S - 25^{\circ} 0'S$ under the Sand River Catchment in the Mpumalanga province, South Africa. The sub-system forms boundary with Limpopo province to the north, Kruger national park and Mozambique to the East. The area can be accessed via the R40 road from White River to Limpopo province (Google Earth, 2022). The study area is shown in Figure 11.

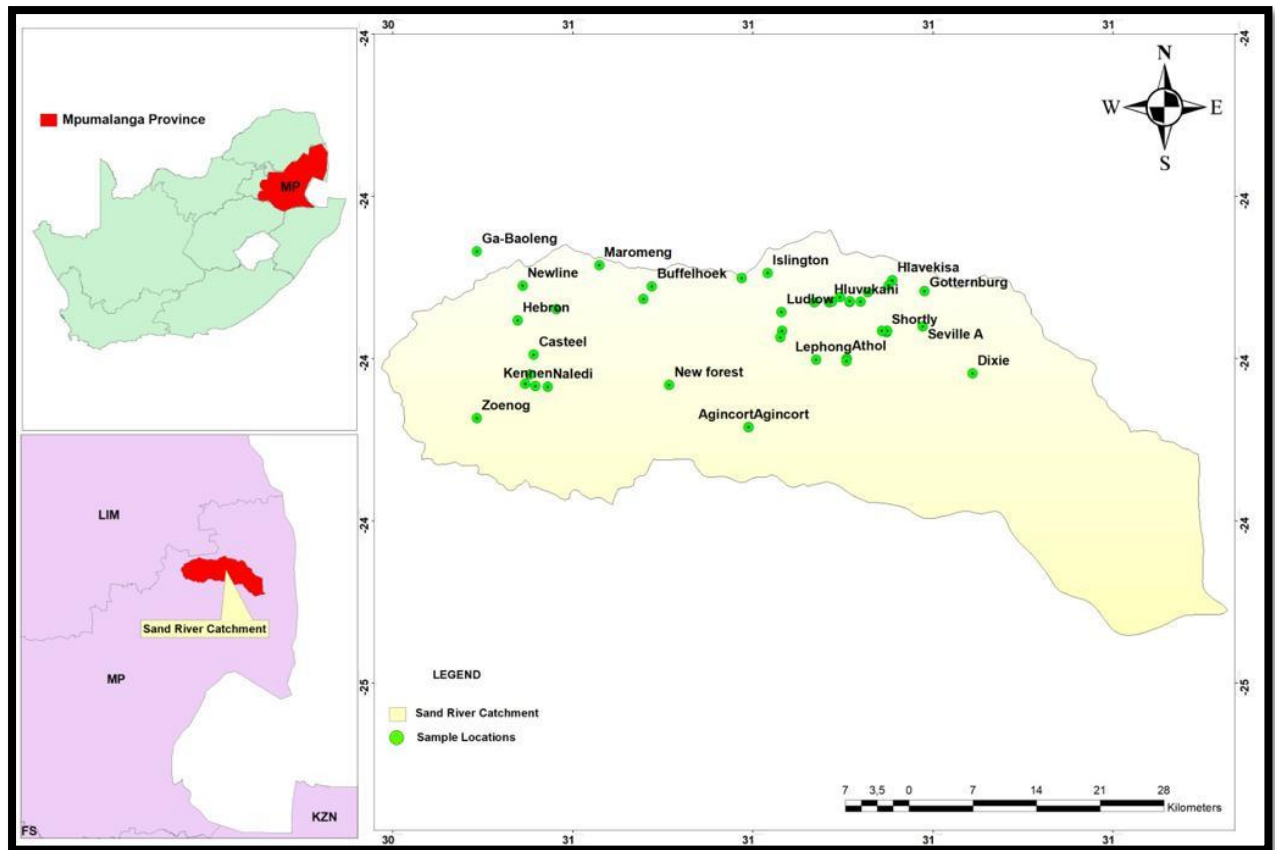


Figure 11 Location of the Study Area (ArcGIS,2022).

3.1.2 Topography

The study area is situated at an average elevation of 400 m to 800 m above the mean sea level (AMSL). The site is located on a smoothly rising and falling topography; whilst general the area drainage appears to be in a west to east direction (Google Earth, 2022).

3.1.3 Climate and rainfall

Bushbuckridge area falls within the Eastern Transvaal Middleveld and Lowveld climatic region with warm to hot sub-tropical climate (Mendiguren and Mabelane, 2001). There is much less rainfall in winter than in summer. The average annual temperature is 21.5 °C in this area. The average annual rainfall is 185 mm. The driest month is July. There is 6 mm of precipitation in July. Most precipitation falls in February, with 363 mm of precipitation being the highest during this month (World Weather Online, 2021).

3.1.4 Geological Setting

The geology of the study area is covered on the 1: 500 000 Scale, 2330 Phalaborwa map produced by the Geological Survey of South Africa, now the Council for Geoscience. The geology of the investigated area comprises mainly of the Nelspruit suit, Cuning Moor Tonalite, Makhutswi Gneiss and the Timbavati Gabbro. The Geology of the study area is shown in Figure 12.

3.1.4.1 Nelspruit suite

The Nelspruit suite is 80km long, stretched to the north of Barberton Greenstone Belt (Robb et al, 1983). The Nelspruit Suite is covered by Transvaal Supergroup rocks in the west and Karoo Supergroup rocks in the east (Jonson et al, 2006).

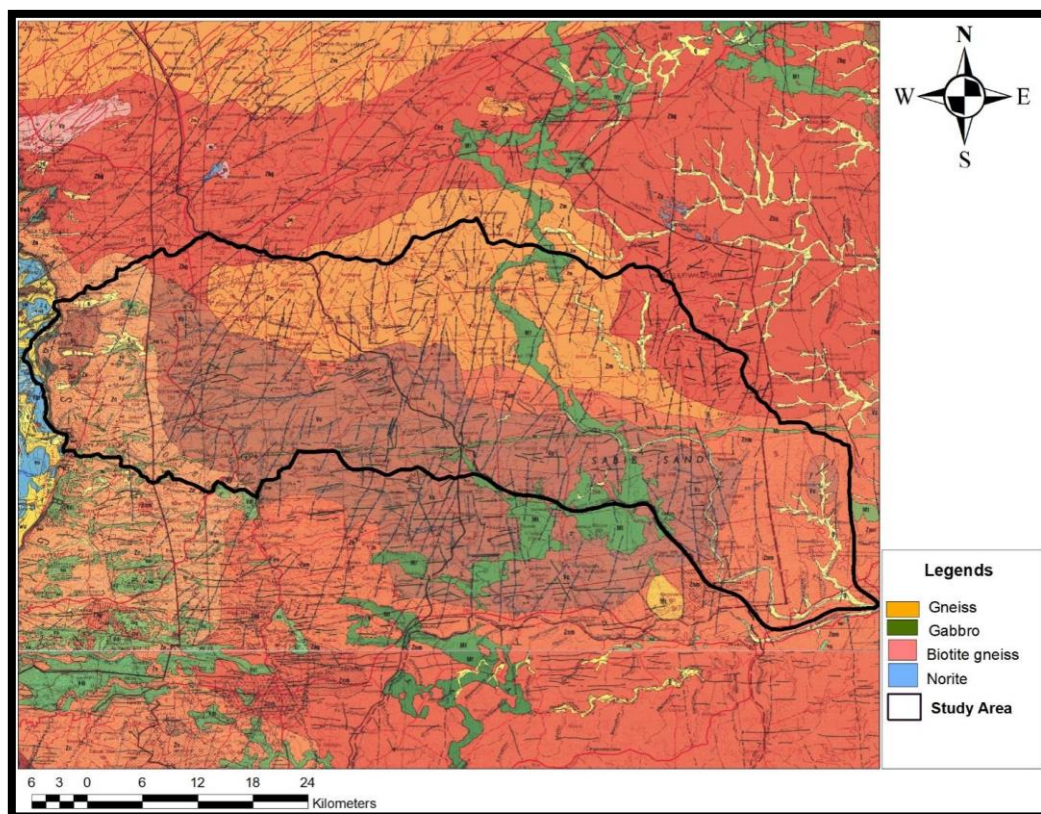


Figure 12 Geological setting of the study area

According to Robb et al (1978, 1979) the Nelspruit Suite is composed of different kinds of textures such as gneiss, poryphitic, granite and two small plutons. The most dominant texture is the course-grained, strongly poryphiritic granitoid which is composed of granodiorite or quartz monzonite. These granites are generally greyish

to pinkish in colour and comprise quartz, plagioclase, microcline perthite and biotite where the K-feldspar forms phenocrysts.

3.1.4.2 Cuning Moor Tonalite

The Cuning Moor Tonalite intrudes the gneisses and the migmatites of the Nelspruit suite and it is a poorly exposed 50km long oval shaped body. It consists predominately of grey, medium grained equi-granular tonalite(Johnson et al, 2006).

3.1.4.3 Makhutswi Gneiss

The Makhutswi Gneiss is covered by the Transvaal Supergroup rocks in the west and the Karoo Supergroup in the east. It stretches in the southern direction for 60 km from the Murchison Greenstone Belt. It consists of a medium-grained light grey gneiss and some migmatite, with 15 cm leucocratic bands (Walraven, 1989). The Makhutswi Gneiss is complex in appearance, and it is intruded locally by small unmigmatized biotite gneiss composed of tonalite.

3.1.4.4 Timbavati Gabbro

The Timbavati Gabbro is composed of intrusions of mafic to ultramafic into granite. They consist of three rock types, these include Gabbro, Quartz-gabbro, and Olivine-gabbro (Johnson et al, 2006). According to Schutter (1986), all these rocks are blue, and they are composed of ludradorite, hypersthenaugine, and olivine.

3.1.5 Geohydrology

According to the Hydrogeological Map 2330 sheet, the granite is a somewhat lesser extent and seemed to be prone to weathering and jointing. The presence of numerous migmatites and dolerite dyke which appear at different levels relative to great depth contribute to groundwater potential. The aquifer is indicated as an intergranular and fractured aquifer with a median borehole yield of 0.5 – 2 l/s. Groundwater in the study area occurs in a fractured transitional zone between weathered and unweathered bedrock (Hydrogeological Map 2330 sheet).

3.2 Preliminary Studies

3.2.1. Desktop Studies

Desktop studies were conducted before the actual fieldwork or site visit to acquire first-hand information about the study area. This involved the gathering of information such as geology, hydrology, and geohydrology through the use of Arc-GIS, published geohydrological maps, satellite images, published geohydrology books, and published journals in hydrogeology.

3.2.2 Hydrocensus

Hydrocensus was conducted to collect information about the water status of the study area, this information includes water features (borehole yields, borehole depth, water levels), water supply sources, and sources of potential water pollution. This provided background information about the hydrological status of the study area.

3.3 Sample Collection

40 groundwater samples were collected from the study area. Sample collection, transportation, and analysis were done according to the methods and procedures published in the DWAF (1997). The samples were collected after 10 minutes of pumping and were transferred to pre-cleaned plastic bottles. A few parameters like EC and pH were measured in the field using a portable water analysis kit. The bottles caring samples were labelled and stored in a cooler box with ice cubes underneath. The samples were then transported to Labserve Analytical Services for analysis of other parameters. Carbonates (CO_3^{2-}), bicarbonate (HCO_3^-), and sulfate (SO_4) were analyzed by volumetric methods. All the concentrations are expressed in mg/l except for pH which is expressed in dimensionless numbers.

3.4 Groundwater Quality Analysis

3.4.1 Drinking water analysis

Results from the laboratory were organized in a data recording sheet and compared to the drinking water standards specified by SANS 241 (2015), DWS Guidelines (1998) quality of domestic water supply.

Table 3 DWS Drinking Water Quality Guideline

Classification	DWS GUIDELINE							
	Constituent (mg/l)	Detection	Class	Class 0	Class 1	Class 2	Class 3	Class 4
Physical and Aggregate Properties	TDS		-	450	1000	2400	3400	>3400
	pH		-	5-9.5	4.5-5 or 9.5-10	4-4.5 or 10-10.5	3-4 or 10.5-11	>11
	EC (mS/m)		-	70	150	370	520	>520
Hardness	Total hardness (T.H.)		-	200	300	600	600	>600
Metals	Calcium (Ca)		-	80	150	300	300	>300
	Magnesium (Mg)		-	70	100	200	400	>400
	Sodium (Na)		-	100	200	400	1000	>1000
	Iron (Fe)		0	0.50	1.00	5.00	10.00	>10
	Manganese (Mn)		-	0.10	0.40	4.00	10.00	>10
Nitrogen	Nitrate (as N)		-	6	10	20	40	>40
Inorganic Non-Metallic Constituents	Chloride (Cl)		-	100	200	600	1200	>1200
	Fluoride (F)		-	0.70	1.00	1.50	3.50	>3.5
	WATER QUALITY CLASS	0						
	Class 0	Ideal water quality-suitable for lifetime use						
	Class 1	Good water quality-suitable for use						
	Class 2	Marginal water quality-conditionally acceptable.						
	Class 3	Poor water quality-unsuitable for use without treatment.						
	Class 4	Dangerous water quality-totally unsuitable for use.						

The water quality index (WQI) method was also used for assessing the acceptable limit of groundwater for drinking. The WQI is a scale that assesses how several elements affect the general quality of water. WQI's value was determined using physical parameters (such as PH, EC, TDS, Cl, F, NO₃, Mg, Fe, and Na).

The water quality index is calculated to simplify a huge quantity of water quality data into a single numerical number. The steps involved in calculating WQI are as follows:

(i) Assignment of weights (w_i) to each water quality parameter involved.

(ii) Calculation of relative weights (W_i)

$$W_i = \frac{w_i}{\sum_i^n w_i} \quad (\text{Eq. 1})$$

(iii) Quality rating scale calculation (Q_i)

$$Q_i = \frac{C_i \times 100}{S_i} \quad (\text{Eq. 2})$$

(iv) Calculation of Sub index (SI_i)

$$SI_i = W_i \times Q_i \quad (\text{Eq. 3})$$

(v) Finally, calculate Water Quality Index using the equation

$$WQI = \sum SI_i \quad (\text{Eq. 4})$$

The calculated WQI values are then classified into five categories: excellent, good, poor, very poor, and unsuitable for drinking as indicated in Table 4 (Yadav et al., 2010; Tyagi et al., 2013). The WHO: 2004-2005 drinking standards have also been considered when calculating the WQI for the Bushbuckridge area.

Table 4 Water Quality Index Classification and Ratings

WQI range	Water quality class
0 - 25	Excellent water
26 - 50	Good water
51 - 75	Poor water
76 - 100	Very poor water
>100	Unfit for drinking

3.4.2 Irrigation Water Analysis

The agricultural suitability of groundwater samples was evaluated based on the following: Sodium Adsorption Ratio, Percentage Sodium, Kelly's Index, Residual Sodium Carbonate, Permeability Index, Magnesium Hazard, and Soluble Sodium Percentage.

3.4.2.1 Sodium Adsorption Ratio (SAR)

The sodium Adsorption Ratio assesses the sodium content of groundwater, and it is the most useful tool for determining groundwater suitability for irrigation (Masoud, 2013). The ratio of sodium to calcium and magnesium in irrigation water determines the rate of water infiltration into the root zone of crops (Zaman et al, 2018).

If irrigation water has a high Na content but a low Ca content, the ion exchange complex may become saturated with Na which destroys the soil structure, due to the spreading of clay particles and decreases the rate of plant development (Todd 1980). The SAR is calculated using the following formula (Ayers & Westcot 1985):

$$SAR = \frac{Na}{\sqrt{\frac{Ca+Mg}{2}}} \text{ -----Equation (1)}$$

Table 5 Classification of Groundwater samples based on SAR (USSD, 1954)

SAR	Water class
≤ 10	Fit
10-18	Marginal
18-26	Poor
>26	Unfit

3.4.2.2 % Na (Percentage Sodium)

Irrigation water that has high levels of sodium is of particular concern because sodium is known to have an impact on soil and constitutes a sodium hazard (Salifu et al, 2015). The presence of too much sodium in water has the unfavorable impact of altering soil characteristics and lowering soil permeability (Rao, 2008). Hence, the assessment of sodium percentage is necessary while considering the suitability for irrigation, which is computed by the following equation.

$$\%Na = \frac{(Na+K) \times 100}{(Ca+Mg+K)} \text{ ----- Equation (2)}$$

Table 6 Classification of Groundwater samples based on % Na (Wilcox 1955)

% Na	Water class
0-20	Excellent
20-40	Good
40-60	Permissible
60-80	Doubtful
>80	Unsuitable

3.4.2.3 Kelly's Index

Kelly's index method is calculated based on the Na^+ concentration measured against those of Ca^{2+} and Mg^{2+} (Kelley 1957). Groundwater with Kelley's index of less than 1 is considered suitable for irrigation and those with Kelley's index greater than 1 indicate the dominance of Na^+ in groundwater and therefore unsuitable for irrigation. Kelly's index is calculated by the following equation:

$$KI = \frac{Na}{Ca+Mg} \text{ ----- Equation (3)}$$

Table 7 Classification of Groundwater samples based on Kelly's Index (Kelly, 1957)

Kelly's Index	Water class
< 1	Suitable
> 1	Unsuitable

3.4.2.4 Residual Sodium Carbonate

(RSC) is a standard method of determining the risk of sodium permeability in irrigation water, and it takes into consideration bicarbonate/carbonate and calcium/magnesium concentrations (Rawat et al, 2018). Higher RSC values suggest that a significant amount of calcium and some magnesium ions precipitate from the solution, increasing the percentage of sodium in water and soil particles and thus increasing the risk of sodium hazard (Kshitindra et al, 2020). The Residual Sodium Carbonate is calculated by the following equation:

$$RSC = (CO_3^{2-} + HCO_3^-) + (Ca^{2+} + Mg^{2+}) \text{ ----- Equation (4)}$$

Table 8 Classification of Groundwater samples based on RSC

RSC value	Water Class
≤ 1.25	Safe
1.25 -2.5	Marginal
> 2.5	Unsafe

3.4.2.5 Permeability Index

The ability of water to move through the soil (permeability) is influenced by the long-term usage of irrigation water with a high salt concentration, as it is affected by the ions Na^+ , Ca^{2+} , Mg^{2+} , and HCO_3^- in the soil (Rawat et al, 2018). As a result, these cations and anions are utilized to determine the PI values of water to assess its quality. The Permeability index is calculated by the following equation:

$$PI = \frac{Na+K+\sqrt{HCO_3}}{Ca+Mg+Na+K} \times 100 \text{ -----Equation (5)}$$

Table 9 Classification of Groundwater samples based on PI

Permeability index	Water Class
> 75 %	Suitable
25-75 %	Good
<25 %	Unsuitable

3.4.2.6 Magnesium Hazard

Magnesium Hazard describes the extent to which magnesium in irrigation water damages the soil structure (Tahmabebi et al, 2018). Alkaline earth (Ca^{2+} and Mg^{2+}) is normally in a state of equilibrium in groundwater. Both Ca^{2+} and Mg^{2+} ions are associated with soil friability and aggregation, and both are important nutrients for crop growth (Rawat et al, 2018).

The presence of huge levels of Ca^{2+} and Mg^{2+} in groundwater can raise soil pH; also, a substantial amount of water is adsorbed between magnesium and clay particles, reducing soil infiltration capacity, which has negative effects on crops (Tahmabebi et al, 2018). The Magnesium Hazard is calculated by the following equation:

$$MH = \frac{Mg}{Ca+Mg} \times 100 \text{-----Equation (6)}$$

Table 10 Classification of Groundwater samples based on Magnesium Hazard

Magnesium Hazard	Water Class
< 50 %	Suitable
> 50%	Unsuitable

3.4.2.7 Soluble Sodium Percentage

The soluble sodium percentage is an important parameter in classifying irrigation water in terms of soil permeability (Nagarju et al, 2006). Mg^{2+} and Ca^{2+} ions found in clay particles tend to interchange with sodium ions present in irrigation water.

The exchange process lowers soil permeability, produces poor internal drainage, and hardens the soil, all of which negatively impact soil quality and seedling emergence. Furthermore, high sodium levels induce the interaction of sodium with chloride and

carbonates in soils, resulting in salinity and alkalinity. Plant growth and crop productivity are harmed by excessive soil salinity and alkalinity (singh et al, 2020).

$$SSP = \frac{Na}{Ca+Mg+Na} \times 100 \text{----- Equation (7)}$$

Table 11 Classification of Groundwater samples based on Sodium Soluble Percentage

Sodium Soluble Percentage	Water Class
<50	Good
>50	Poor

3.5 Groundwater Geochemistry characterization

3.5.1 Determination of Hydro-Geochemical Processes Influencing Groundwater Quality

The chemistry of water in the recharge area, as well as various geochemical processes occurring in the subsurface, influence the geochemical properties of groundwater (Sarikhani et al, 2015).

3.5.1.1 Gibbs diagrams

The Gibbs diagrams were used to determine groundwater chemistry between groundwater and aquifer minerals and to understand groundwater origin. (Subramani et al. 2009). Gibbs diagram (Gibbs 1970) represents the ratio of $(Na^+ / (Na^+ + Ca^+))$ and $Cl^- / (Cl^- + HCO_3^-)$ as a function of total dissolved solids (TDS), which is commonly used to assess the origin of dissolved chemical constituents such as precipitation, rock-weathering, and evaporation.

3.5.2 Determination of Groundwater types or groundwater facies

3.5.2.1 Piper Diagram

To determine the hydrochemical facies of groundwater the major cations and anions such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , CO_3^{2-} , HCO_3^- , SO_4^{2-} and Cl^- (in me/l) were plotted on Piper's trilinear diagram (Piper 1944, 1953). The Piper diagram method proposed by Piper (1994) is the appropriate method used for the classification and comparison of water types and ionic composition (Srinivasamoorthy et al, 2013).

CHAPTER 4: RESULTS AND DISCUSSION

4.0 Preamble

This chapter contains the results and discussions of experimental work done in Bushbuckridge, Sand River Catchment. The static summary of the physiochemical results is presented in this chapter. The suitability of the groundwater for drinking and

irrigational purposes in the study area were discussed in this chapter. This chapter also encompasses the evaluation of the hydrochemistry and the chemical signature of the boreholes in the study area.

4.1 Groundwater suitability for drinking

4.1.1 Groundwater physicochemical characteristics and spatial distribution

The statistical results showing concentrations of various physicochemical parameters of groundwater quality, such as pH, electrical conductivity (EC); total dissolved salts (TDS); total hardness (TH); and major anions and cations are presented in Appendix A. Table 12 shows the statistical summary of some of the selected physiochemical parameters. The summary included minimum, maximum, mean standard deviation and variance values.

Table 12 Statistical summary of groundwater physicochemical parameters and selected guideline values

Parameters	Unit	Min	Max	Mean	SD	SANS241 Limits	WHO Desirable
pH		6.5	8.08	7.49	0.35	5 – 9.7	7 – 8.5
EC	mS/m	14	551	125.28	101.43	≤ 170	–
TDS	mg/l	99	4411	941.8	801.84	≤ 1200	500
TH	mg/l	15	1085	360.8	285.48	–	100
NO ₃ ⁻	mg/l	0.01	118.23	4.65	27.78	≤ 12	50
SO ₄ ²⁻	mg/l	0.15	77.9	17.43	17.93	≤ 12	200
HCO ₃ ⁻	mg/l	56.12	847.9	406.37	269.55	–	300
F ⁻	Mg/l	0.12	1.37	0.63	0.36	≤ 12	–
Cl ⁻	mg/l	1.1	1290.6	162.08	136.46	≤ 12	250
Na ⁺	mg/l	16	738	149.8	139.99	≤ 12	50
K ⁺	mg/l	0.72	8.7	4.34	3.57	50	12
Ca ²⁺	mg/l	5.3	156	56.28	37.98	150	75
Mg ²⁺	mg/l	0.54	181	52.06	51.07	70	50

4.1.1.1 pH

At all phases of water treatment, careful pH management is required to achieve effective water clarity and disinfection. Although pH typically has little direct effect on consumers, it is one of the most significant operational water quality indicators because more corrosion risk exists in water with a lower pH (about pH 7 or less)

(WHO,2011). Failure to reduce corrosion can lead to the pollution of drinking water as well as negative impacts on its taste and appearance.

The pH values of groundwater in the study area range from 6.5 in Gotternburg village (Sample 35) to 8.08 in Shortly village (Sample 15) with a mean value of 7.49 pH value (Table 12). Evidently from Table 12, all the values of pH were found to be within the permissible range of 5-9.7 prescribed for drinking water according to SANS 241 (2015).

According to WHO (2011), pH values less than 7 indicate acidity, while pH values greater than 7 indicate alkalinity. Majority of the groundwater samples of about 85 % in the study area has a groundwater that is alkaline in nature, whereas the other 15 % of the groundwater samples in the west and south part of the study area indicated that their groundwater is acidic (See Figure 13).

The pH of groundwater is influenced by the type of rocks and sediments surrounding the area where recharge water infiltrates into the ground and it also depends on how long the groundwater has been in touch with a specific rock (Kumari and Rai, 2020). High alkalinity of the groundwater in the study area may be due to the interaction of groundwater with chemicals such as hydroxides, bicarbonates and carbonates.

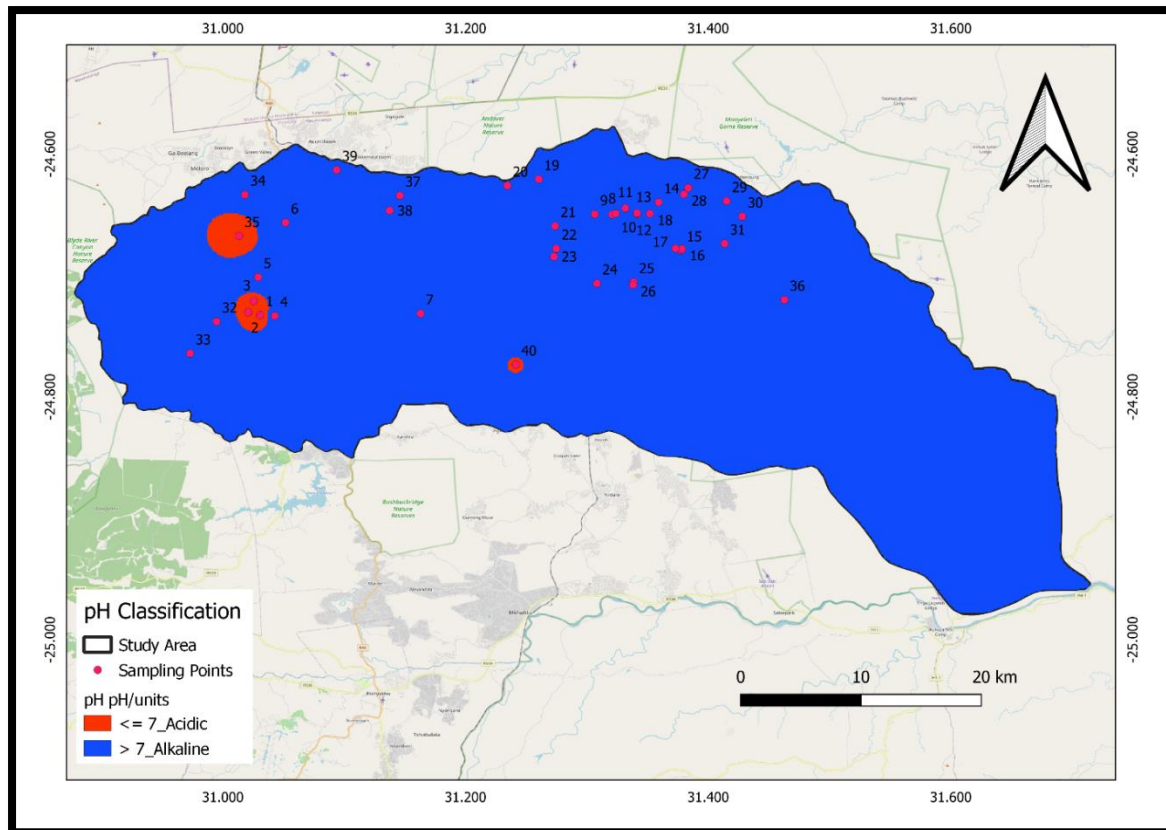


Figure 13 Spatial distribution map of Ph

4.1.1.2 Total Dissolved Solids

Total Dissolved Solids is a measurement of all dissolved compounds present in water. Groundwater with high TDS values should not be used for drinking purposes because excessive TDS concentrations may indicate the presence of contaminants that could be detrimental to human health (Oram, 2007).

The total dissolved solids (TDS) concentration in the groundwater varied from 99 mg/l in Gottenburg village (Sample 35) to 4411 mg/l in Hlvukani village (Sample 18) with an average of 941.8 mg/l (Table 12). Based on the results, 66 % of the groundwater samples were within the SANS 241(2015) acceptable limit of 1200 mg/l as indicated in Table 12 and were effectively suitable for drinking purposes.

However, 34 % of the groundwater samples, which were mostly concentrated on the East and North parts of the study area, exceeded the permissible limit and are not suitable for drinking, as shown on the spatial distribution map (See Figure 14). The high TDS values in this area may be due to some elevated concentration of minerals

such as Magnesium with a range of 52-169 mg/l and Calcium with a range of 45-117 mg/l.

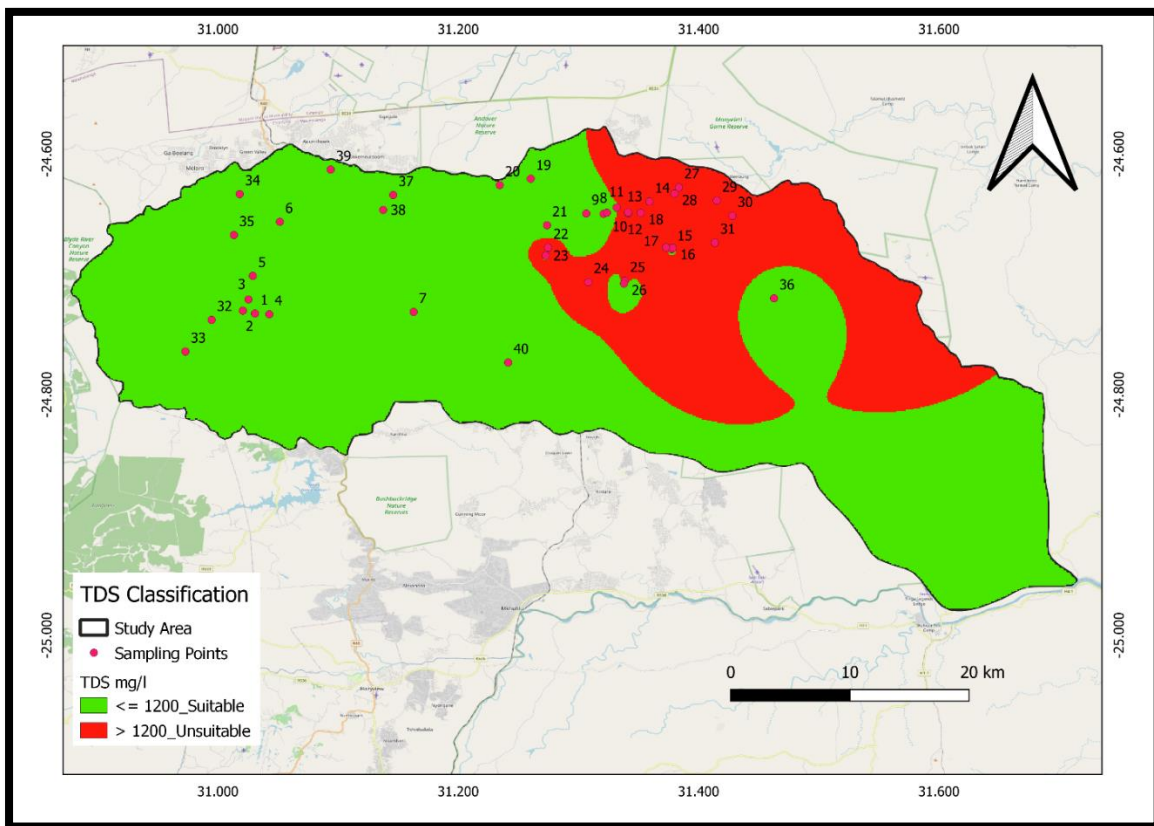


Figure 14 Spatial distribution map for Total Dissolved Solids

Furthermore, TDS values were classified according to Freeze and Cherry (1979) and it is clear from Table 13 that 23 samples (59%) contain fresh water which can be used for drinking. The remaining 17 samples (41%) contain brackish water that can only be used for irrigation.

Table 13 Total Dissolved Solids based on Freeze and Cherry (1979)

Parameters	Range	Classification	Number of samples	Percentage %
TDS (mg/l) Freeze and Cherry (1979)	<1000	Fresh	23	59
	1000-10000	Brackish	17	41
	10000-1000000	Saline	0	-
	>1000000	Brine	0	-

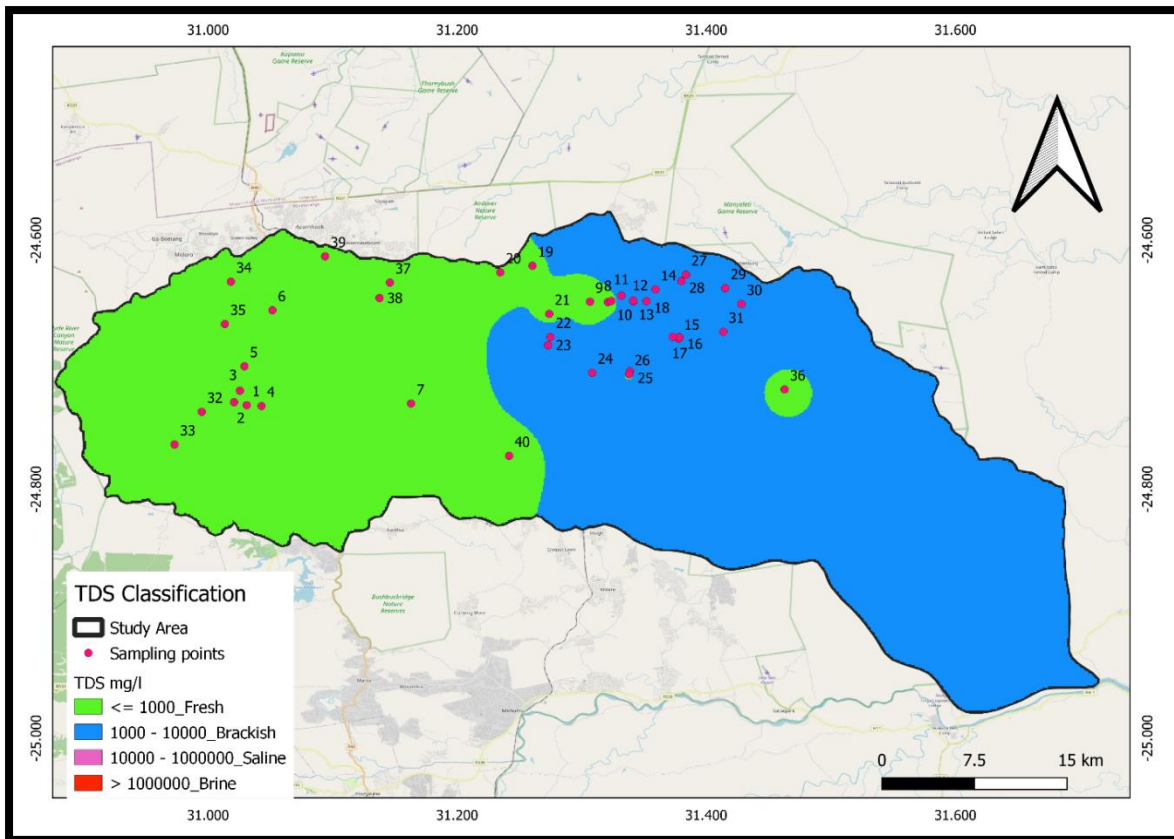


Figure 15 Spatial Distribution map of water type based on TDS (After Freeze and Cherry 1979)

4.1.1.3 *Electrical Conductivity*

Electrical conductivity, which varies with temperature, is a measure of the number of dissolved substances, chemicals, and minerals present in water samples. EC and TDS are directly proportional, when there is an increase in TDS there will automatically be an increase in EC value. Consequently, all the areas in the study area which recorded high TDS Values, are also high in EC values this is evident from the spatial distribution map (Figure 16).

The lowest EC value of 14 mS/m was recorded in Gottenburg village (Sample 35) while the highest EC value of 441 mS/m was recorded in Hluvukani village (Sample 18) with a mean value of 125.275 mS/m. The maximum permissible limit for EC indicated in Table 12 is 170 mS/m as set by SANS 241 (2015). In the study area about 71% of the groundwater were within the limit whereas 29% exceeded the permissible limit and regarded as unsuitable for drinking purpose.

The EC reveals whether the water is fresh or salty and the high salinity in groundwater in some part of the study area may be due to natural concentration of salts as evapo-transpiration exceeds precipitation in semi-arid climatic conditions prevailing in the area.

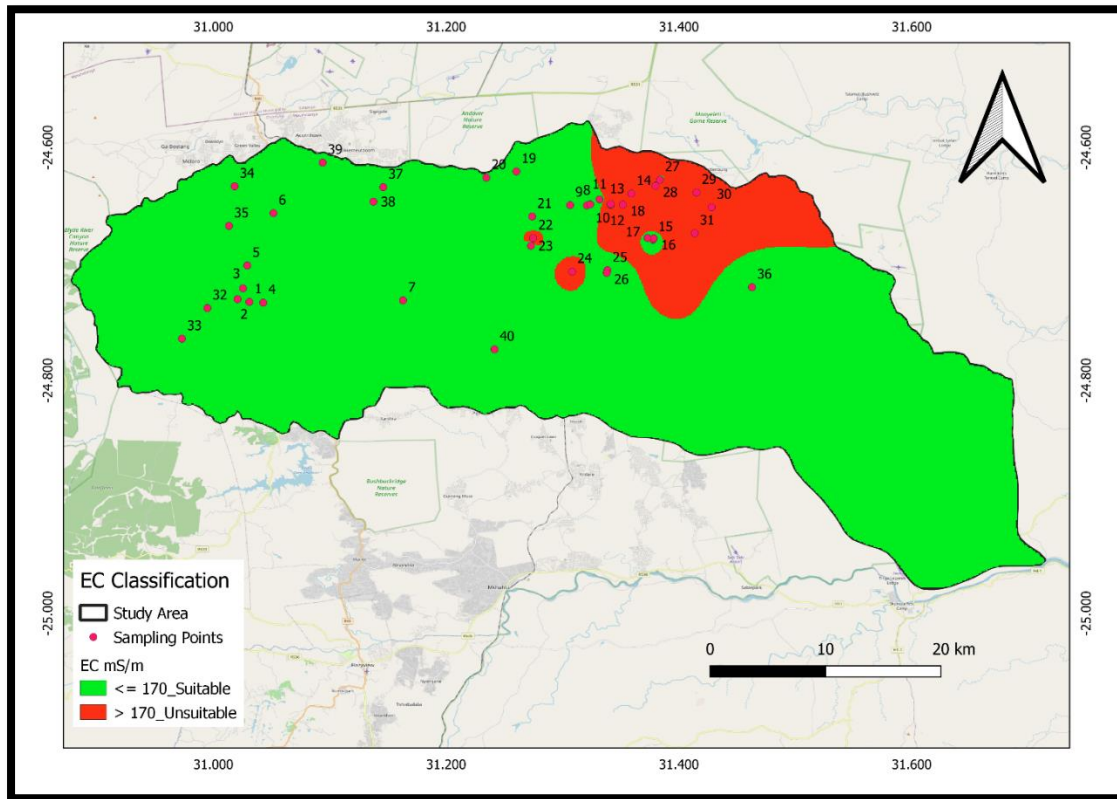


Figure 16 Spatial Distribution Map for EC

4.1.1.4 Total hardness

Total hardness (TH) measures the combination between calcium and magnesium concentrations expressed as mg/l calcium carbonate [CaCO₃]. For this study, the degree of hardness in water was classified based on the classification set by (Todd and Mays 2005): (0–75) soft, (75–150) moderately hard, (150–300) hard, (>300) very hard as shown in Table 14. Elevated Total hardness impacts water taste, especially when making tea or coffee, and hinders soap lathering (Todd, 2008). However, some Total hardness in water is advantageous to health since it helps to meet the needs for the key minerals calcium and magnesium.

Table 14 Total Hardness based on the classification set by Todd and Mays (2005)

Range	Classification	Number of samples	Percentage
0-75	Soft	9	22
75-150	Moderately hard	4	10
150-300	Hard	4	10
>300	Very hard	23	58

The Total Hardness values in the study area vary from 15 mg/l to 1085 mg/l with a mean of 360.8 mg/l. Accordingly, 9 samples had a soft degree, 4 samples had a moderate degree, 4 samples had a hard degree, and 23 samples had a very hard degree.

It is evident from the spatial distribution map (Figure 16) that the samples at the eastern part of the study area is dominated by hard to very hard water, whereas the western part of the study area has soft to moderately hard water. The reason for high Total hardness in the ground water may be due to high concentration of magnesium minerals and soluble calcium.

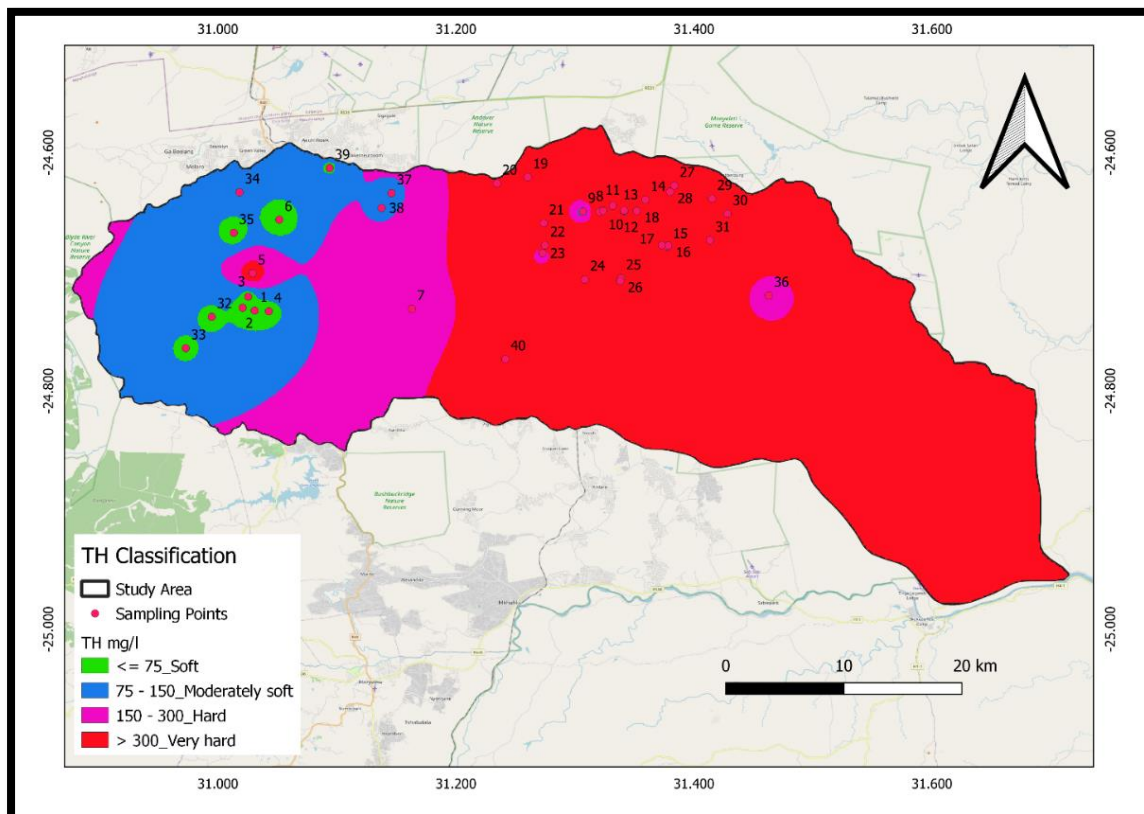


Figure 17 Spatial Distribution Map for Total Hardness

4.1.1.5 Nitrate

According to SANS 241(2015), the maximum permissible limit for nitrate in drinking water is 11 mg/l (Table 12). The nitrate values in the study area range from 0.01 mg/l in Hluvukani and Ludlow villages (Sample 8 and 23) to 118.23 mg/l in Lephong village (Sample 24) with an average of 4.65 mg/l

The study area has about 85% samples with nitrate within SANS 241 (2015) desirable limit for drinking waters and only 15% were found to be beyond the permissible limits of SANS standards. The excessive use of fertilizers, atmospheric rainfall and seepage from animal and human waste are the likely main causes of nitrate content in groundwater (Kumari and Rai, 2020).

Nitrate does not change the taste, colour or smell of water and also it does not impact the appearance of the water. However, too much intake of nitrate may affect how blood transfer oxygen in the human body and this may result into a condition known as methemoglobinemia (also known as blue baby syndrome) (DWAF, 1998).

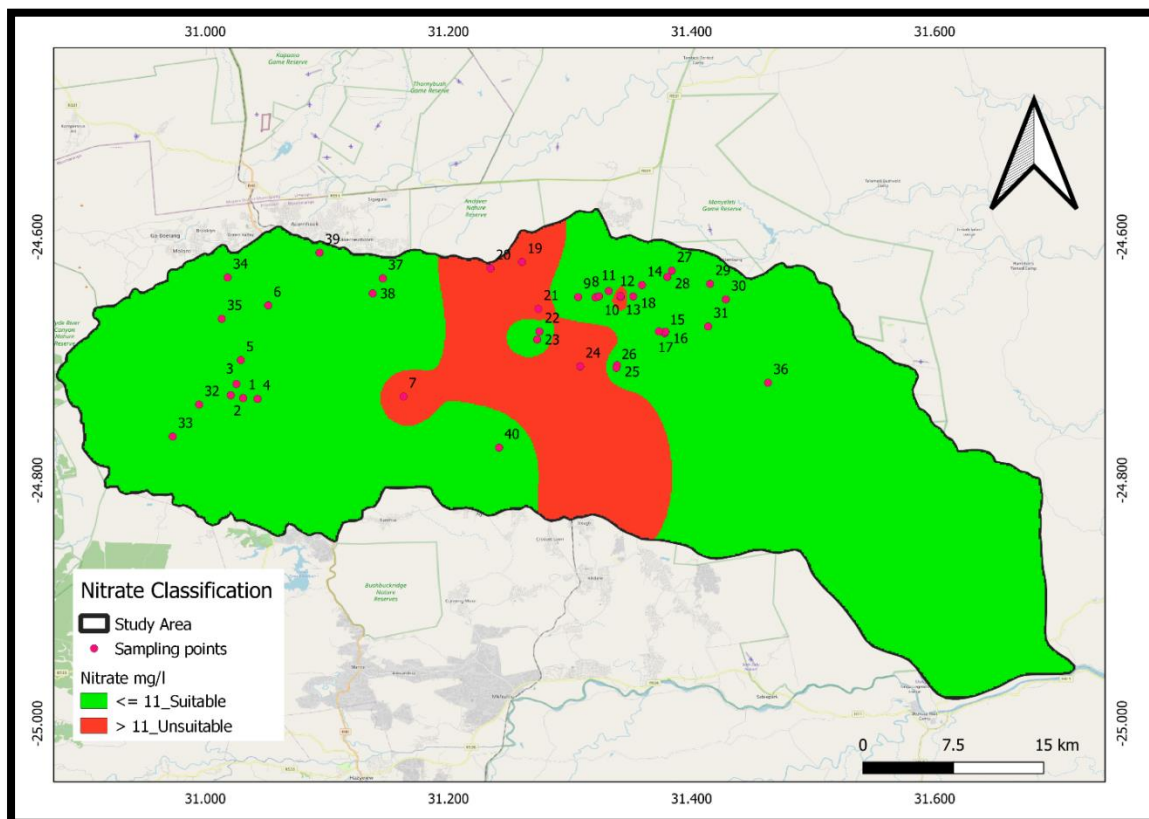


Figure 18 Spatial Distribution of Nitrate

4.1.1.6 Sulphate

The sulphate values in the study area range from 0.15 mg/l in Hluvukani and Ludlow villages (Sample 9 and 23) to 77.9 mg/l in Lephong village (Sample 24) with a mean value of 17.43 mg/l. The maximum permissible limit according to SANS 241 (2015) is 250 mg/l and all the groundwater samples fell within this limit. Figure 19 shows the spatial distribution of sulphate in the study area.

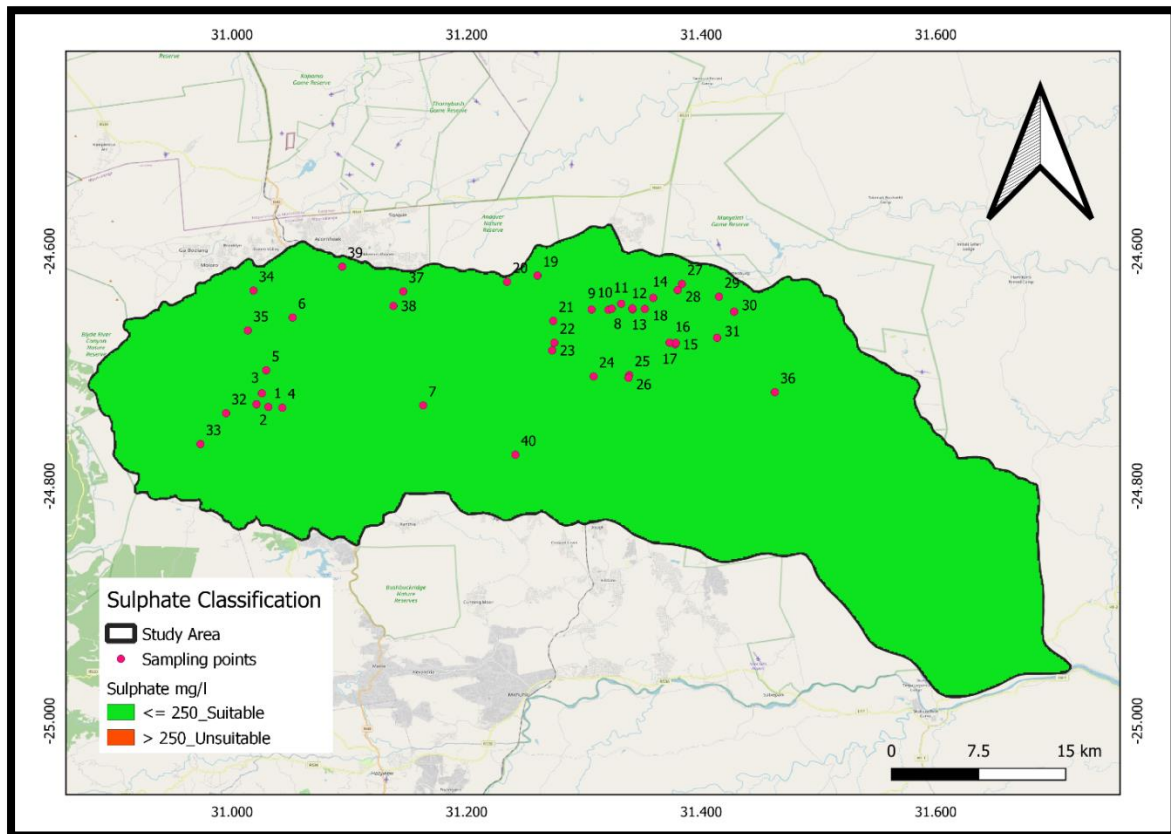


Figure 19 Spatial Distribution of Sulphate

4.1.1.7 Fluoride

Given the fact that fluoride is predominantly derived from the geology, fluoride concentrations are frequently inversely related to the degree of water-rock reaction. The presence of Fluoride may be due to the interaction of water with fluoride rich minerals like biotite, Microline perthite, and granodiorite rocks.

Fluoride was less dominant in the study area because all the groundwater samples fell within the permissible limit of 1.5 mg/L as set by SANS 241 (2015) for drinking purposes as shown in Figure 20. The concentrations of fluoride in the study area ranges from <0.12 to 1.37 mg/l with a mean value of 0.28 mg/l.

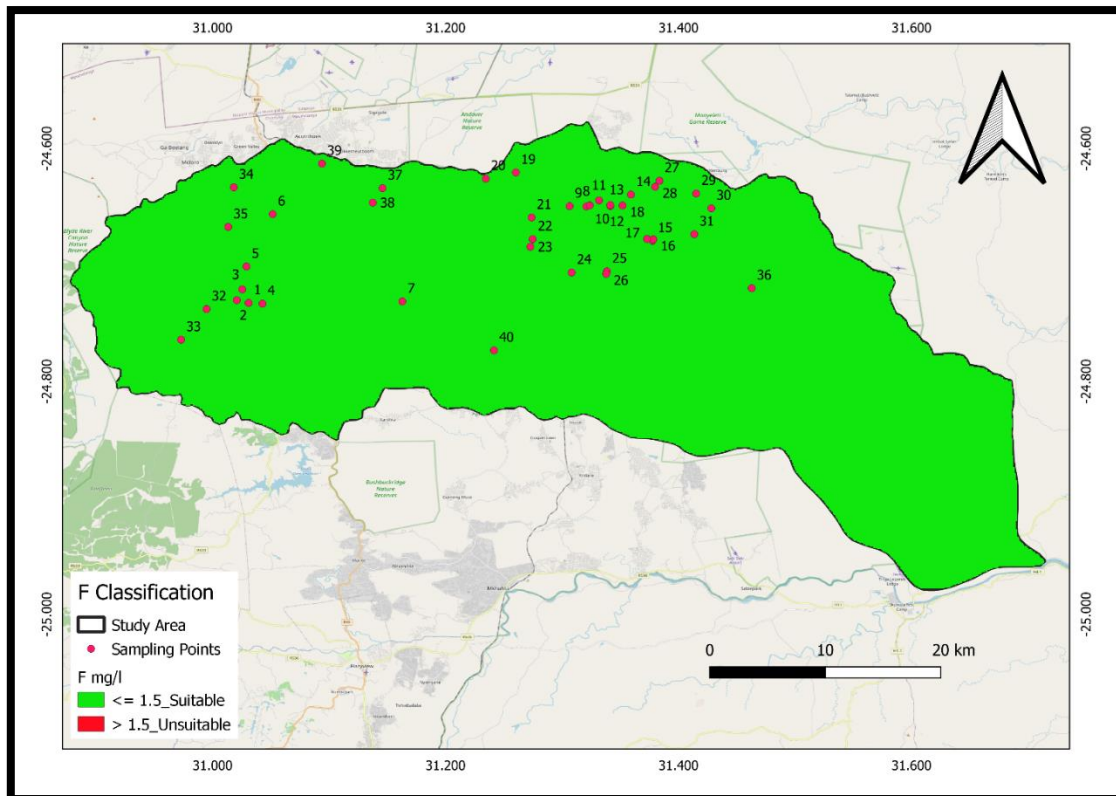


Figure 20 Spatial Distribution Map for Fluoride

4.1.1.8 Chloride

Chloride and/or sodium alone in water are usually not hazardous to your health but their presence can be an indicative that your water may also contain other toxins like germs, nitrates, or lead. With time, these elements can corrode or harm pipelines and water heaters, giving water a salty taste. People on low-sodium diets may find high salt levels in drinking water to be concerning.

The chloride concentrations in the groundwater ranges between 1.1 and 1290.6 mg/l with an average of 162.08 mg/l and the Sodium concentration of groundwater in the study ranges from 16 to 738 mg/l with an average of 149.8 mg/l (See Table 13). The highest value for both Cl and Na were recorded at Hlavekisa village (Sample 33) and the lowest value for Cl and Na were recorded at Hluvukani village (Sample 18).

The desirable and maximum permissible limit of Cl for potable water is 300 mg/L as set by SANS 241 (2015). The results from the groundwater samples of the study area revealed that 80% of the Cl values were within the safe limits, indicating suitability for drinking purposes whereas only 20 % of the groundwater samples located in Hluvukani (Sample 12, 13, 14 and 18), Ludlow (Sample 22 and 23), Maromeng

(Sample 30) and Newline (Sample 31) village were above the acceptable limit (See Figure 21).

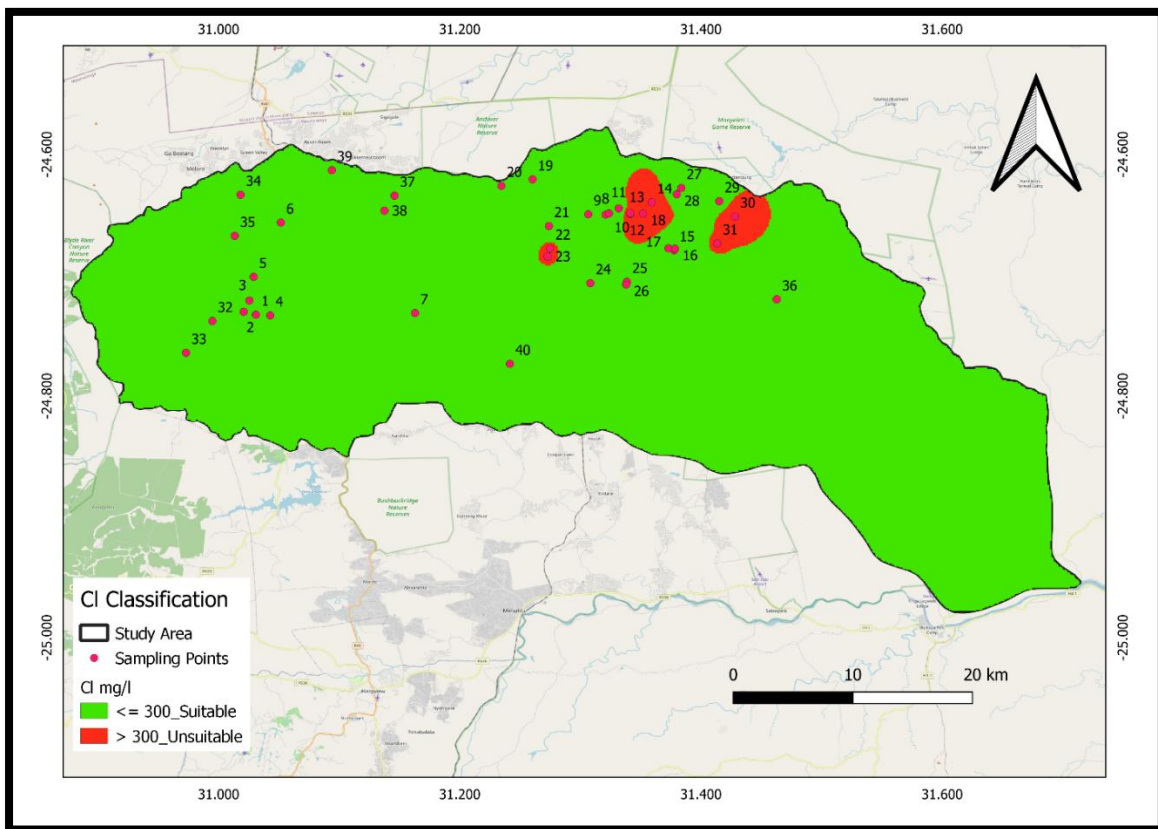


Figure 21 Spatial Distribution of Chloride

4.1.1.9 Sodium

Evident from the spatial distribution map (Figure 22), the results for Sodium revealed that only 11 (27.5%) of the groundwater samples in this area exceed the permissible limit of 200 mg/l as set by SANS 241 (2015), and the remaining 29 samples (72.5%) fell within the acceptable limit and are suitable to use for drinking purpose without any treatment.

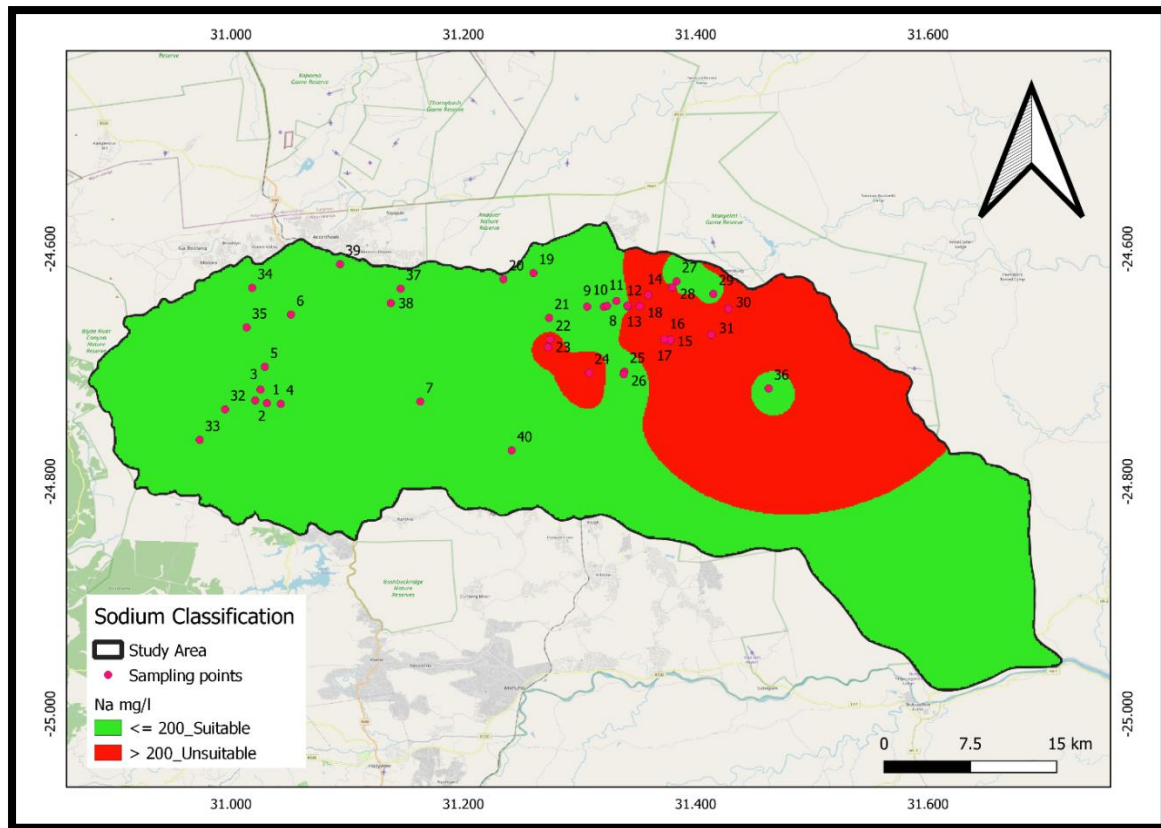


Figure 22 Spatial Distribution Map for Sodium

4.1.1.10 Potassium

The Potassium concentrations in the study area ranges from 0.72 to 8.7 mg/l with a mean value of 4.34 mg/l. According to SANS 241 (2015), the acceptable limit of Potassium in drinking water is 50 mg/l (Table 12), and all the samples fell within this limit and thus considered as suitable for drinking purposes as shown on the spatial distribution map (Figure 23).

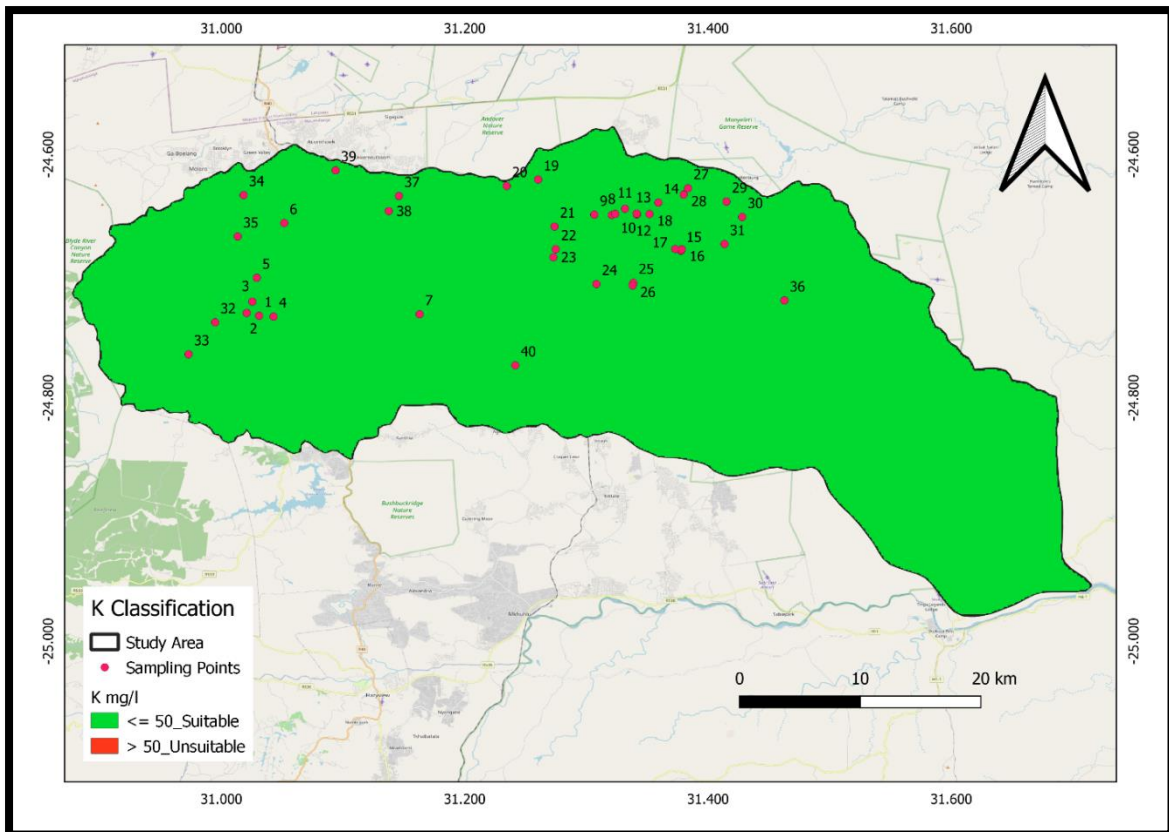


Figure 23 Spatial Distribution Map for Potassium

4.1.1.11 Calcium

The concentration of Calcium ranges from 5.3 to 156 mg/l with a mean value of 56.28 mg/l. The Ca limit desirable for drinking water is specified as 150 mg/l by SANS 241 (2015) (Table 12). Based on Calcium, all the groundwater samples (97.5 %) in the study were considered safe for drinking except for one sample (2.5 %) recorded at Hluvukani village (Sample 18) which had a value exceeding the permissible limit. Figure 24 shows the spatial distribution of Calcium in the study area.

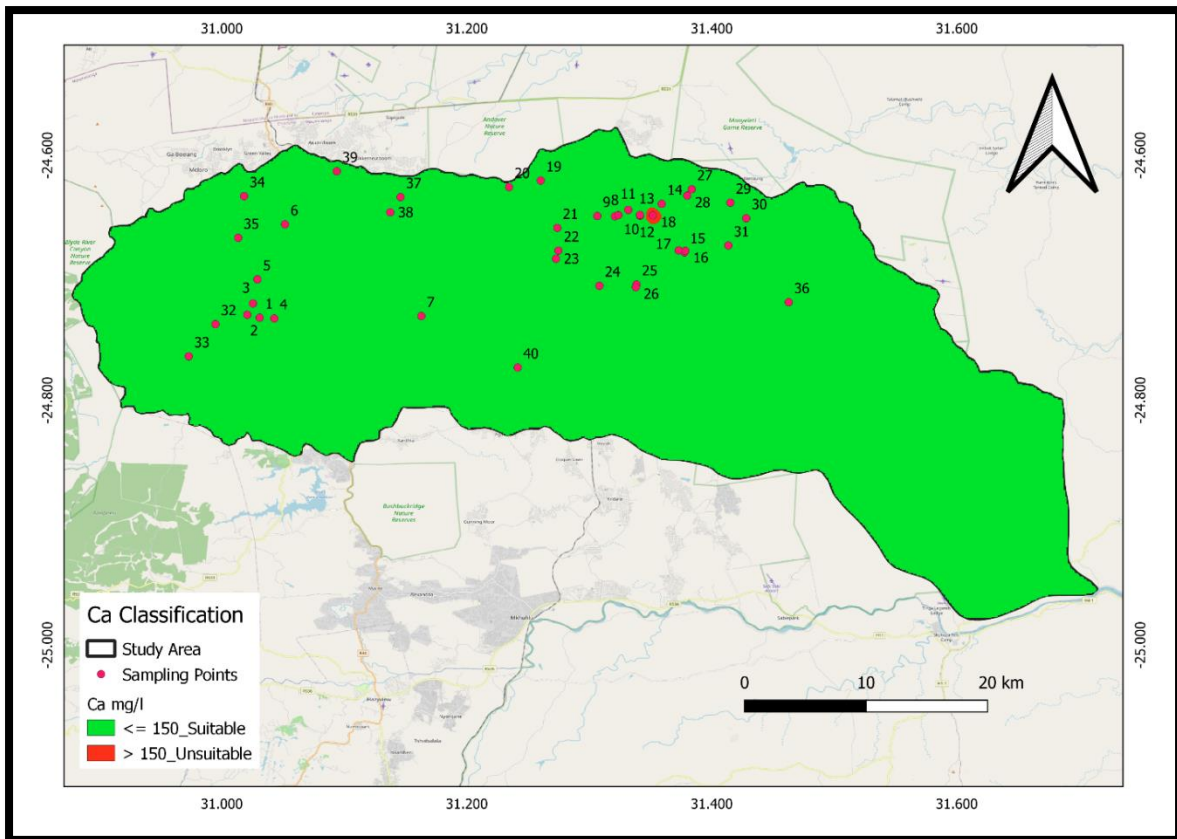


Figure 24 Spatial Distribution Map for Calcium

4.1.1.12 *Magnesium*

Magnesium concentration of groundwater in the study area ranged from 0.54 mg/l at Rooitablagte village (Sample 6) to 181 mg/l at Buffelshoek village (Sample 29) with a mean value of 52.06 mg/l. As it is clear from the spatial distribution map (Figure 25), the results revealed that 29 (72.5 %) of the groundwater samples fell within the acceptable limit of 70 mg/l for drinking water quality as set by SANS 241 (2015). And the remaining 11 (27.5) samples fell above the acceptable limit and are deemed unsuitable for drinking purposes.

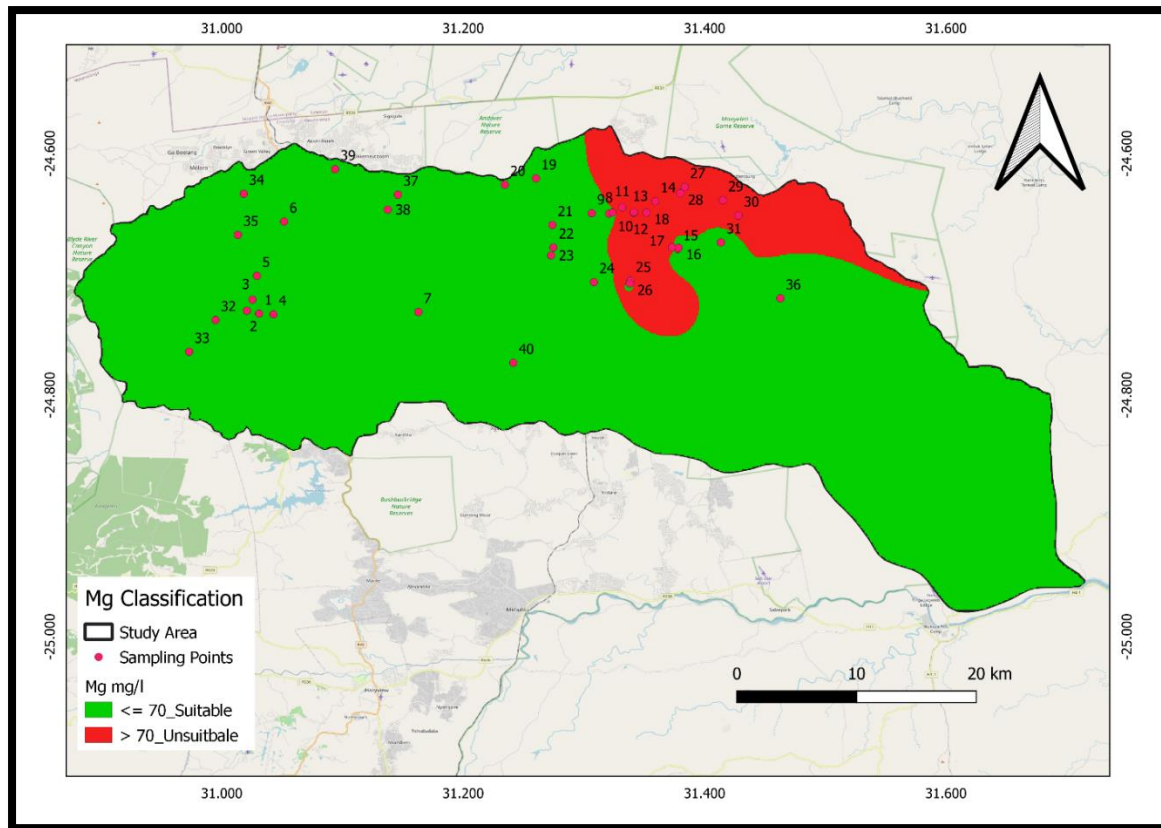


Figure 25 Spatial Distribution Map for Magnesium

4.1.2 Drinking water quality assessment based on DWS guidelines.

The results from the groundwater samples were compared to the DWS guideline indicated in Table 1 to determine their respective water classes. The groundwater quality status was therefore categorized into five classes (DWS,1998) namely: ideal water quality for lifetime use (Class 0), good water quality suitable for use (Class 1), marginal water quality-conditionally acceptable (class 2), poor water quality-unsuitable for use without treatment (class 3) and dangerous water quality-totally unsuitable for use (class 4).

Table 15 summarizes the DWS results for groundwater samples (n=40). As per the DWS classification, 10% of the total groundwater samples which were located in Rooiboklagte (Sample 6), Newline (Sample 34), Hebron (Sample 35) and Maromeng (Sample 39) village are classified as Class 0 and fell under the ideal water quality category. 24% of the groundwater samples belonged to Class 1 and has a good water quality category for drinking purposes. Majority of the groundwater samples of about 40 % possessed marginal water quality and were classified as Class 2 and are regarded as safe to use.

Table 15 Drinking water quality based on DWS Guideline

Water Class	Description of the water class	Number of samples	Percentage
Class 0	Ideal water quality-suitable for lifetime use	4	10%
Class 1	Good water quality-suitable for use	9	22.5%
Class 2	Marginal water quality-conditionally acceptable.	16	40%
Class 3	Poor water quality-unsuitable for use without treatment.	8	20%
Class 4	Dangerous water quality-totally unsuitable for use.	3	7.5%

About 20% of the groundwater samples belonged to Class 3 and had poor water quality due to elevated concentrations of Total Hardness (> 600), Nitrate (> 20 mg/l) and Sodium (> 400 mg/l). High values of Total hardness were recorded in Hluvukani (Sample 11,12 and 13), Athol village (sample 25), Hlavekisa (Sample 27 and 28) and Gotternburg village (Sample 29) and lastly high value of Nitrate was recorded at Islington village (Sample 19).

Of all the groundwater samples, the results revealed that only 7.5% of groundwater samples belonged to Class 4 and are considered to have dangerous water quality and therefore totally unsuitable to use. From this, a groundwater sample from a borehole in Hluvukani village (sample 18) was deemed unfit for use due to elevated concentrations of TDS (> 3400 mg/l), EC (> 520 mS/m), Na (> 1000 mg/l) and Cl (> 1200 mg/l), these high levels may be due to mineral dissolution. However, pollution derived from anthropogenic activities may also be a contributory factor. A pit latrine located in close proximity to the borehole may also contribute to the TDS. A sample in Seville C (Sample 30) had an elevated concentration of Na (> 1000 mg/l). Elevated concentration of Nitrate (> 40 mg/l) was recorded in Lephong (Sample 24) and deemed the water unsuitable for use. The possible source of the high nitrate level in this area may be due to runoff from animal waste since this borehole is located at a

proximity to a cattle dung. Figure 26 shows the spatial distribution of the water classes in the study area.

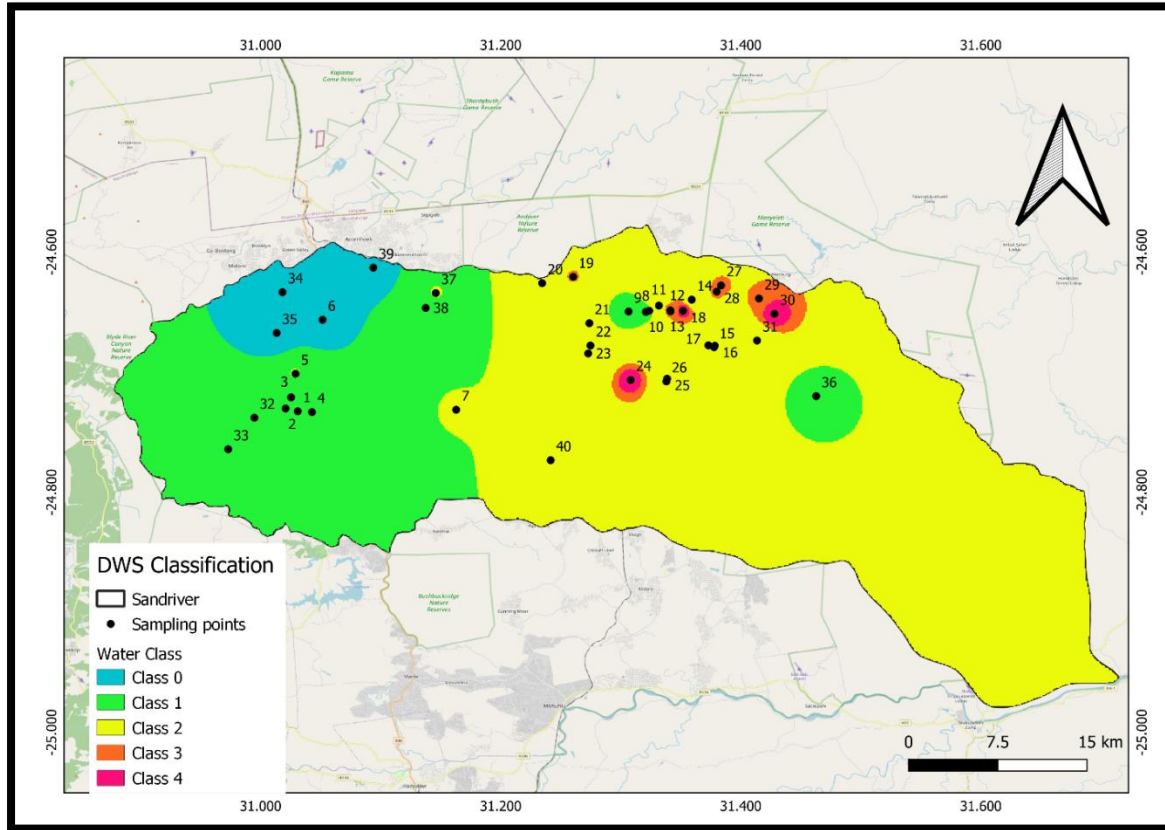


Figure 26 Classification of drinking water quality following DWS guidelines

4.1.3 Drinking water quality assessment based on Water Quality Index

To determine if groundwater is suitable for drinking, a water quality index was computed. WQI combines complicated data and creates a ranking that describes the current state of water quality which helps people understand water quality issues (Boyacioglu, 2007).

Table 16 summarizes the WQI values for groundwater samples (n=40). The calculated WQI values ranged from 7.42 to 350 meq/l with a mean value of 34.17 meq/l. The lowest WQI Value was recorded at Seville C village (Sample 36) and the highest value was recorded at Ludlow village (Sample 23). The groundwater quality status was therefore categorized into five types (Tiwari and Mishra, 1985) based on WQI values, namely excellent water (0-25), good water (26-50), poor water (51-75), very poor water (76-100) and water unsuitable for drinking (>100) (Tiwari and Mishra, 1985).

Table 16 Summary of the Water Quality Index Results

WQI	Minimum (meq/l)	Maximum (meq/l)	Mean meq/l)	Standard deviation	Variance
	7.42	350	34.17	51.94	2698.21

As per the WQI classification, 40% of the total groundwater samples fell under the excellent category, and 56% belong to the good water category for drinking purposes. About 2% for each category of groundwater samples were found to be of poor water quality and unfit for consumption. Figure 27 is showing the spatial distribution of WQI in the study area.

Table 17 Drinking Water Quality based on Water Quality Index Tiwari and Mishra (1985)

Water Quality Index	Classification	Number of samples	Percentage %
0-25	Excellent	16	40
26-50	Good	23	56
51-75	Poor	1	2
76-100	Very poor	0	-
>100	Unfit for consumption	1	2

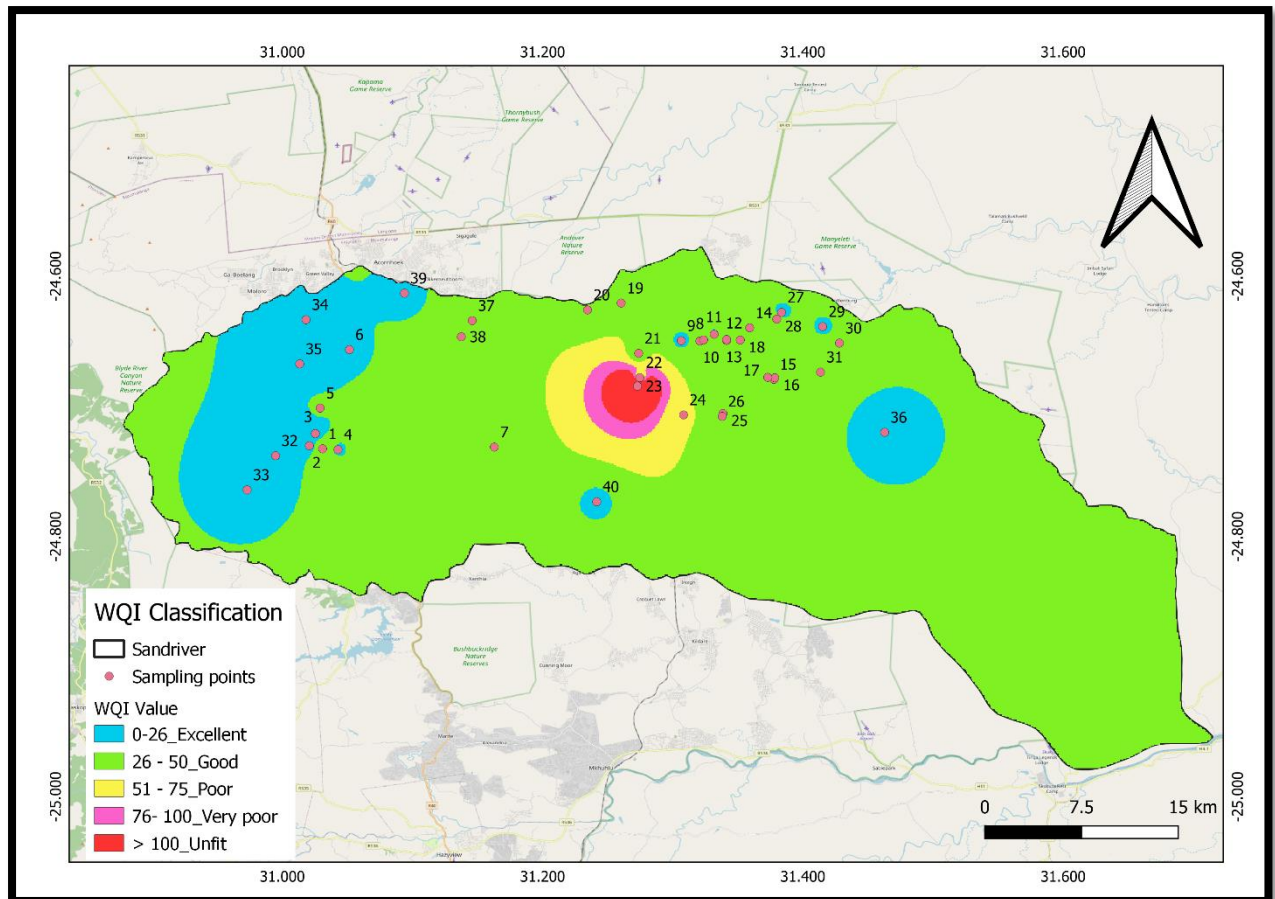


Figure 27 Spatial Distribution map of Water Quality Index

According to DWS Guideline standard only 4 samples belong to class 0 and has excellent water quality, however according to WQI 15 samples has excellent water quality. Among the samples that has excellent water quality from both Guidelines are sample 6, 34, 35, and 39. According to WQI 23 samples has good water quality, whereas 25 samples in DWS belonged to class 1 and 2 and has good and marginal water quality, respectively. According to DWS only 11 samples belong to class 3 and class 4 and has poor and dangerous water quality respectively, however according to WQI only 4 samples belong to poor and very poor water quality categories, respectively.

4.2 Groundwater suitability for irrigation

4.2.1 Irrigation water quality analysis

Table 18 shows the statistical summary of the results for all the indices computed for irrigational purposes.

Table 18 Groundwater quality indices for irrigation

Sample	TDS	EC	SAR	% Na	KI	RSC	PI	MH
S1	116	17	2.78	54.23	1.15	2.24	96.77	33.77
S2	181	26	3.25	58.65	1.39	3.25	99.00	29.19
S3	146	21	2.49	54.24	1.08	1.34	83.13	26.90
S4	134	19	2.52	51.24	1.03	1.82	85.50	35.82
S5	809	111	0.87	26.60	0.36	6.56	58.54	34.88
S6	111	16	9.71	82.55	4.51	2.60	123.81	14.39
S7	487	68	2.87	52.69	1.10	2.00	71.39	47.13
S8	489	68	2.75	49.58	0.97	9.67	90.42	58.68
S9	232	33	2.27	52.86	0.99	4.74	99.04	26.70
S10	924	127	1.60	36.41	0.56	10.17	69.38	59.33
S11	1142	152	0.33	9.82	0.10	4.55	38.48	79.97
S12	1565	203	1.76	39.19	0.64	0.81	55.42	55.37
S13	1388	185	1.38	33.46	0.49	-0.07	50.08	56.29
S14	1659	215	2.68	49.32	0.96	8.96	71.62	56.53
S15	1033	142	5.19	64.08	1.78	18.63	100.04	63.25
S16	1345	179	5.17	64.69	1.80	20.73	100.06	60.46
S17	1235	165	2.88	47.87	0.91	16.70	82.08	73.04
S18	4411	551	4.36	59.92	1.48	2.75	71.27	64.12
S19	982	135	3.32	56.22	1.26	6.85	78.68	47.60
S20	724	99	1.89	40.98	0.68	5.81	68.61	56.25
S21	770	105	1.63	37.29	0.58	4.79	63.03	57.73
S22	1545	201	2.55	49.64	0.98	2.17	64.95	47.17
S23	1171	156	8.13	72.94	2.57	6.00	90.48	73.71
S24	1423	190	4.02	60.80	1.54	7.80	80.44	47.21
S25	1458	194	1.66	36.49	0.57	7.53	61.20	62.93
S26	763	105	2.60	46.87	0.87	10.87	82.47	65.59
S27	1216	162	0.82	20.91	0.25	7.15	49.53	75.44
S28	1466	196	2.27	43.86	0.77	12.15	71.30	64.67
S29	1402	187	0.88	21.59	0.27	4.16	45.68	79.71
S30	2191	285	4.15	56.75	1.30	13.03	77.68	74.83
S31	1805	234	8.21	80.37	4.05	22.78	113.03	2.72
S32	160	23	2.61	54.61	1.13	2.39	89.67	26.41
S33	117	17	1.21	37.62	0.54	2.73	86.32	22.89
S34	171	24	1.64	40.28	0.66	1.97	73.27	39.45
S35	99	14	2.81	56.60	1.26	1.14	85.59	20.31
S36	746	102	6.55	69.89	2.29	13.71	107.93	60.43
S37	397	55	3.60	57.60	1.34	3.22	82.36	50.76
S38	603	84	6.14	68.34	2.13	6.18	94.56	61.10
S39	215	30	3.72	58.63	1.39	3.57	95.41	50.33
S40	841	115	1.52	37.28	0.59	2.33	58.01	44.58
Min	99	14	0.33	9.82	0.1	-0.1	38.48	2.72
Max	4411	551	9.71	82.55	4.51	22.8	123.8	80
mean	941.8	125.28	3.17	49.82	1.21	6.64	79.16	50.2
SD	801.84	101.43	2.12	15.65	0.9	5.66	19.08	18.9

Total Dissolved Solids, Electrical Conductivity, Sodium adsorption ratio (SAR), Sodium percentage (Na%), Kelly's Index (KI), Residual Sodium Carbonate (RSC), permeability index (PI) and Magnesium hazard were used to determine the suitability of groundwater for irrigation in this study (Table 19).

For plant growth apart from soil type and quality, water is also an essential component (Sridharan and Senthil, 2017). Thus, it is crucial to determine the suitability of groundwater for irrigation based on the effect of water's mineral constituents on both plants and soils.

Table 19 Classification of groundwater based on its suitability for irrigation usage

Parameter	Range	Classification	Number of samples	Percentage %
TDS	<450	Good	12	30
	450-2000	Marginal	26	65
	>2000	Unsuitable	2	5
EC	< 25	Suitable	9	24
	25- 300	Marginal	30	73
	> 300	Unsuitable	1	3
SAR	≤ 10	Suitable	40	100
	10-18	Marginal	0	0
	18-26	Unsuitable	0	0
	>26	Unfit	0	0
% Na	0-20	Excellent	1	2,5
	20-40	Good	10	25
	40-60	Permissible	22	55
	60-80	Doubtful	5	12.5
	>80	Unsuitable	2	5
KI	< 1	Suitable	20	50
	> 1	Unsuitable	20	50
RSC	≤ 1.25	Safe	3	7.5
	1.25 -2.5	Marginal	6	15
	> 2.5	Unsafe	31	77.5
PI	> 75 %	Suitable	23	59
	25-75 %	Good	17	41
	< 25 %	Unsuitable	0	0
MH	< 50 %	Suitable	16	49
	> 50%	Unsuitable	24	51

4.2.2 Classification and spatial distribution of irrigation potential

Knowledge of the quality of irrigation water is critical to understand what management is necessary for long-term agricultural productivity (Srinivasamoorthy et al. 2014). Irrigation suitability and risk assessment of groundwater are evaluated by measuring various irrigation indices. Spatial distribution of the selected irrigation indices is summarised below.

4.2.2.1 Total Dissolved Solids

For irrigation purposes, the quality of water depends on the number of dissolved salts. Too much salts in water reduces its uptake by the plant and if water uptake is appreciably reduced, the plant growth rate is also reduced. In the study area the TDS values varied from 99 mg/l in Hebron village (Sample 35) to 4411 mg/l in Hluvukani village (Sample 18) with a mean value of 941.8 mg/l.

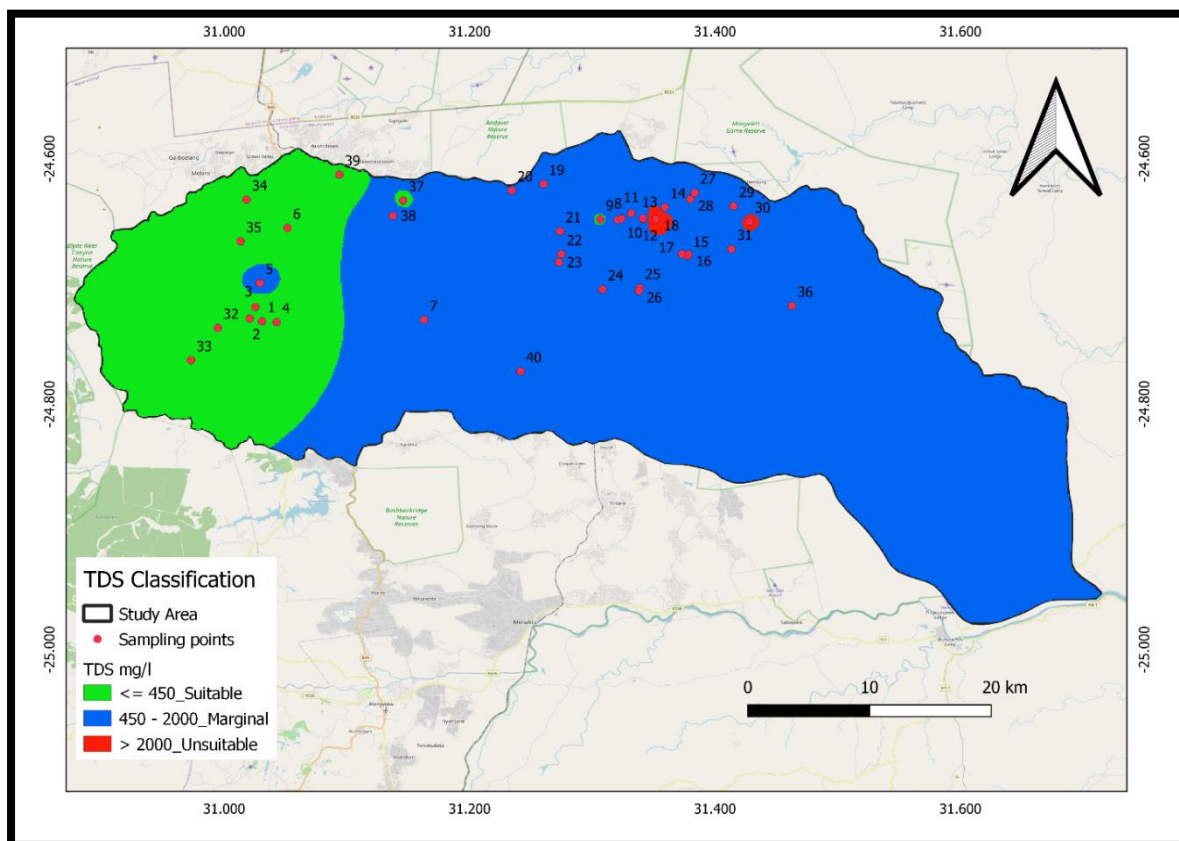


Figure 28 Spatial distribution of Total Dissolved Solids

The results revealed that about 30% of our groundwater samples were considered to be suitable for irrigation, majority of the groundwater samples of about 65% fell under

the marginal category and only 5% (2 samples) in Hluvukani village (Sample 18) and Seville C village (Sample 30) were regarded to be unsuitable for irrigation as shown in Table 19. Figure 28 shows the spatial distribution of TDS for irrigation water quality in the study area.

4.2.2.2 Electrical Conductivity

EC is used to assess the dangers of water salinity. Crop productivity suffers greatly if EC exceeds 300 mS/m, and it is preferred if EC is less than 25 mS/m (Westcott and Ayers 1984). The values of EC in the study area range from 14 mS/m in Hebron village (Sample 35) to 551 mS/m in Hluvukani village (Sample 18) with a mean value of 125.28 mS/m.

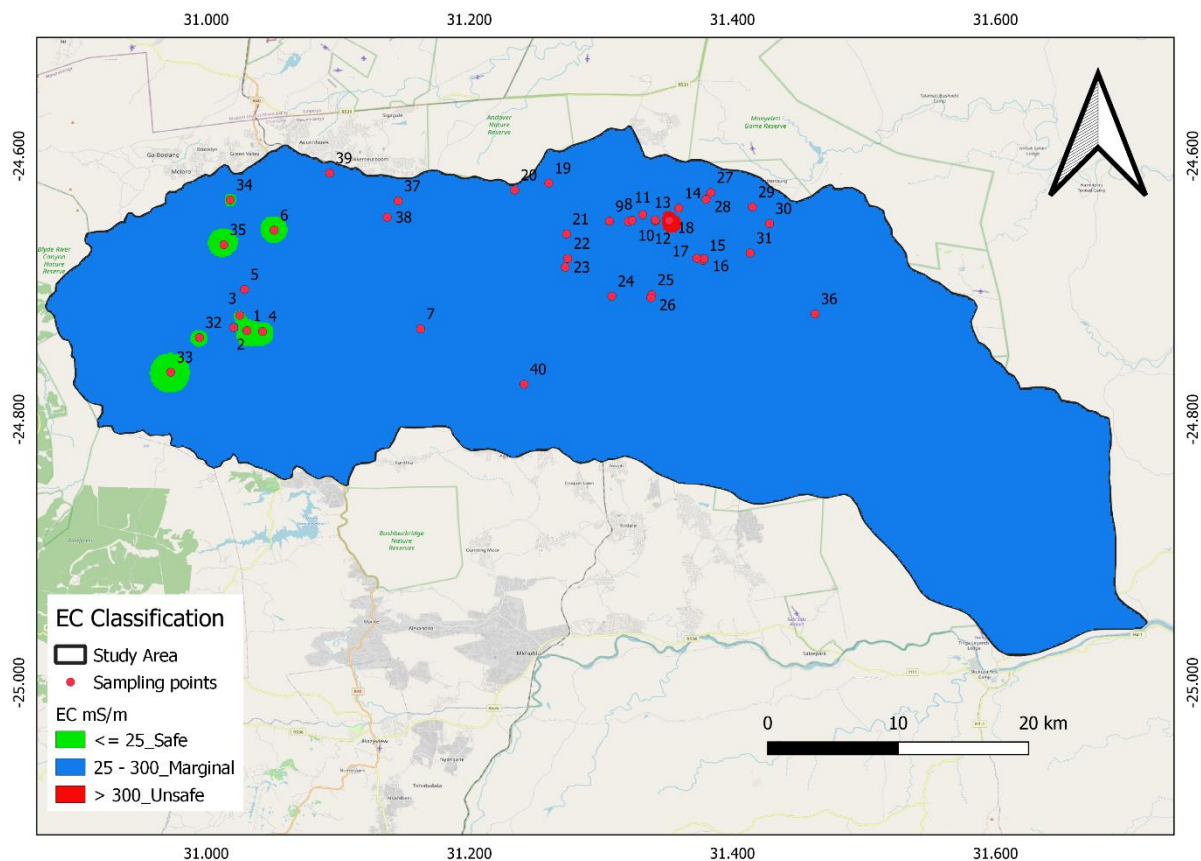


Figure 29 Spatial Distribution of Electrical Conductivity

The results revealed that majority of the groundwater samples of about 73% fell under the marginal category, 24% of the samples fall under the safe category and only 2 % in Hluvukani village (Sample 18) was deemed unsafe for use in irrigation. Figure 29 shows the spatial distribution of EC around the study area.

4.2.2.3 Sodium Adsorption Rate

The Sodium Adsorption Rate evaluates the sodicity hazard of water by assessing the effect of relative cation concentrations on Na^+ accumulation in the soil. Groundwater with higher SAR is normally not suitable for irrigation because higher sodium deposition may deteriorate soil characteristics by reducing soil permeability and thus inhibiting the supply of water required by crops (Ahamed et al, 2013).

The SAR calculated results ranged from 0.33 meq/l in Hluvukani village (sample 11) to 9.71 meq/l in Rooiboklaagte village (Sample 6) with an average of 3.17 meq/l. As shown in Table 24, all the groundwater samples in the study area based on SAR are regarded as suitable for irrigation since they all have SAR values which are less than 10. Figure 30 shows the spatial distribution of SAR in the study area.

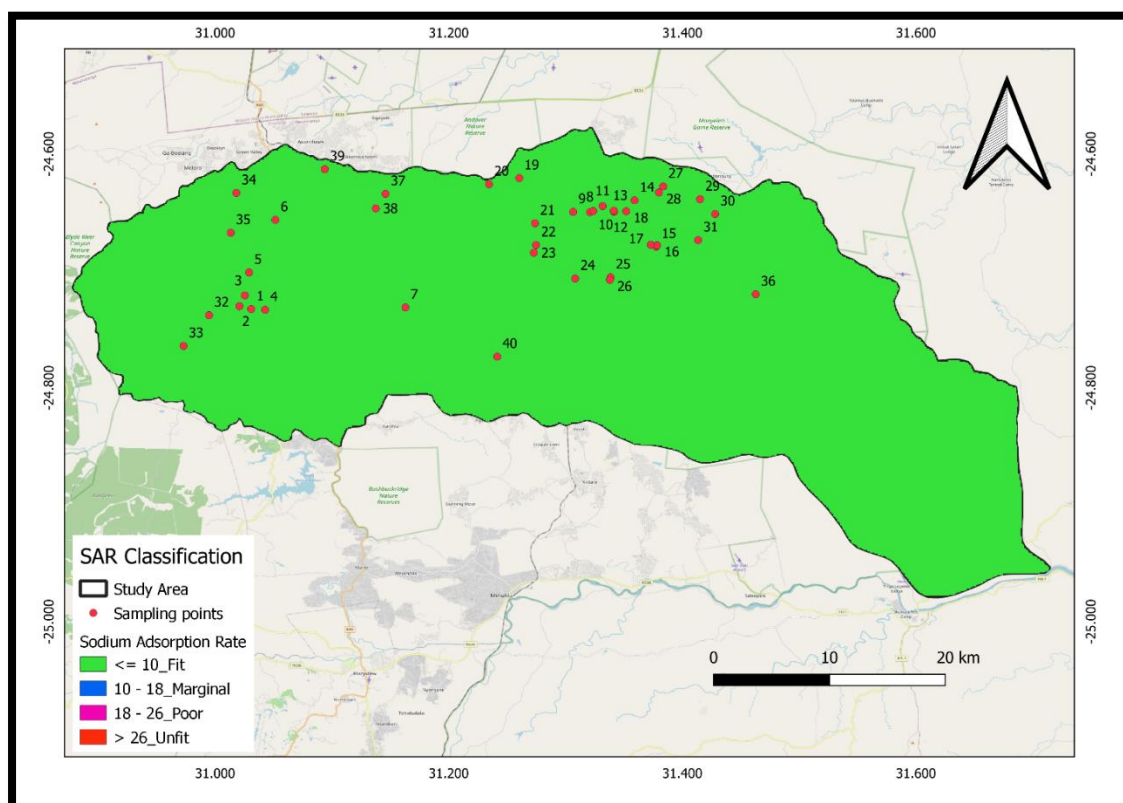


Figure 30 Spatial Distribution of Sodium Adsorption Rate

4.2.2.4 Percentage Sodium (% Na)

The percentage of sodium is important for determining suitability of water for irrigation purposes because the high level of sodium in irrigation water causes exchange interactions between the calcium and magnesium ions found in soil clay particles, which in turn reduces soil permeability, internal drainage, and air flow Subhasish and

Prolay (2021). The classification of groundwater samples from the study area with respect to %Na is represented in Figure 31.

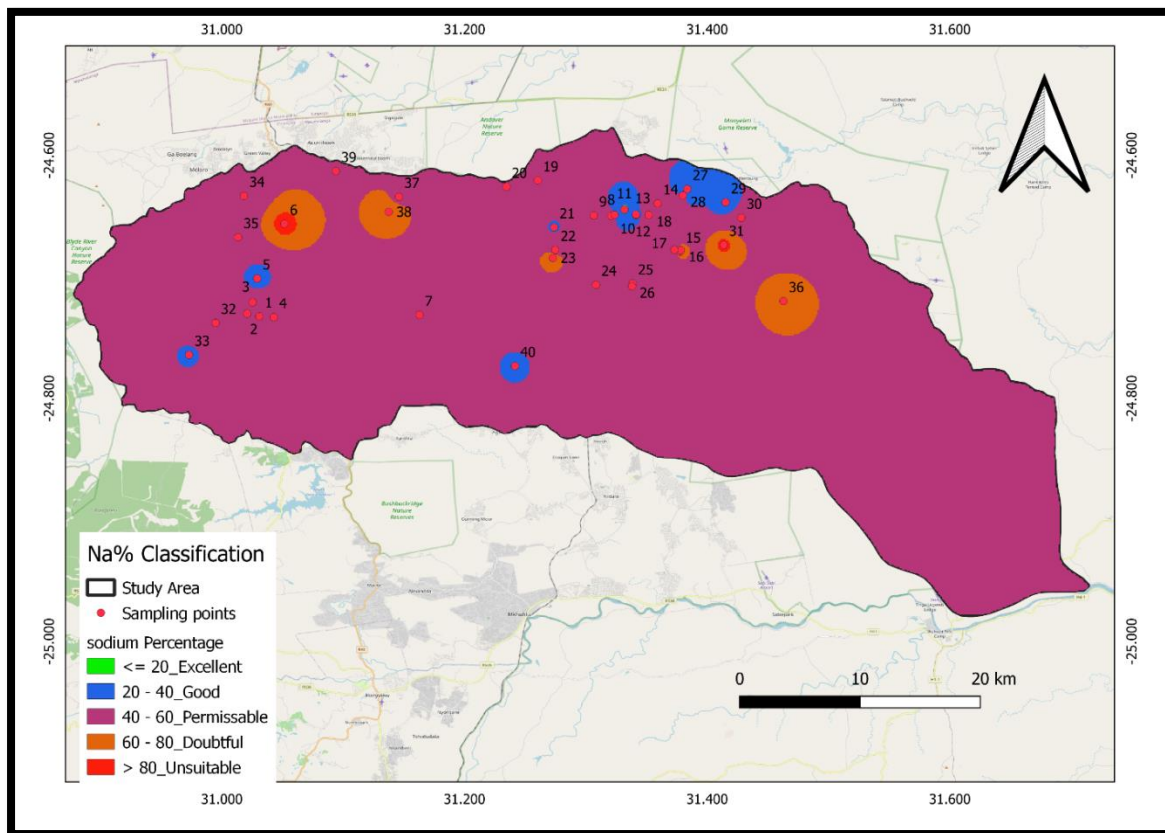


Figure 31 Spatial Distribution of Na%

The calculated Na% results range from 9.82 in Hluvukani village (Sample 11) to 82.55 in Rooiboklaagte village (sample 6) with a mean value of 49.82. Based on %Na results, only one sample (sample 11) in Hluvukani village fell under excellent water quality for irrigation purposes.

Most of the groundwater in the study area in most of the locations fell under permissible and good category with about 54 % (22 samples) and 24% (10 samples) under each category respectively. 15% and 5 % of the groundwater samples fell under doubtful and unsuitable categories respectively. The villages with groundwater regarded as either doubtful or unsuitable includes Rooiboklaagte (Sample 6), Shortly (Sample 15 and 16), Ludlow (Sample 23), Lephong (Sample 24), Newline (Sample 31), Seville C (Sample 36) and Agincort (Sample 38). Figure 31 shows the spatial distribution of % Na in the study area.

4.2.2.5 Kelly's Index

Kelly's index Kelly ratio compares sodium to calcium and magnesium and a Kelly's Index greater than one suggests that the water has too much salt. Water with a Kelly's ratio of less than one is therefore appropriate for irrigation (Kelly, 1963) (Table 19). Figure 32 shows the spatial distribution of Kelly's Index in the study area.

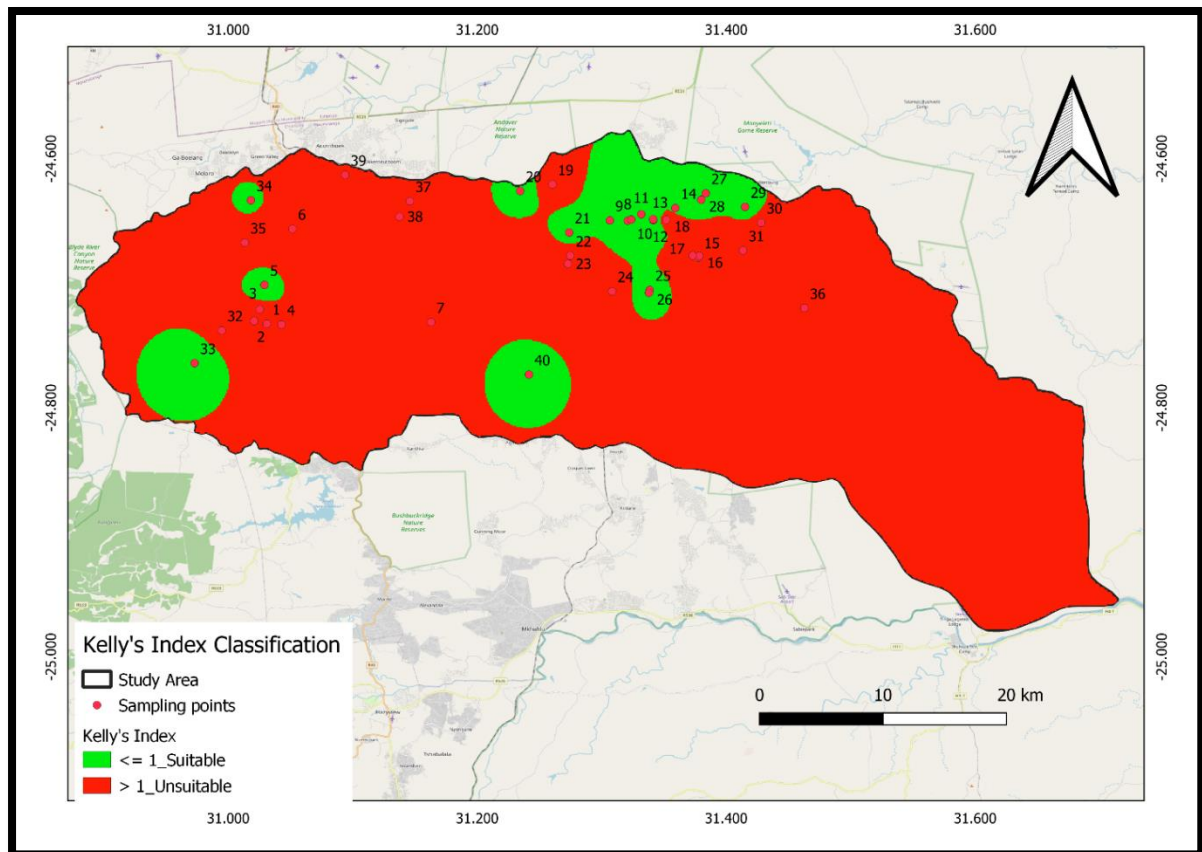


Figure 32 Spatial distribution of Kelly's Index

The calculated Kelly's Index in the study area range from 0.098 to 4.506 with a mean value of 1.21. According to Kelly's Index about 49% of the groundwater samples shows that the water is suitable to use for irrigational purposes, whereas 51% of our samples indicate that they are not suitable for use as irrigational water (Table 19).

4.2.2.6 Residual Sodium Carbonate

The evaluation of residual sodium carbonate is critical for determining the hazardous effect of carbonates and bicarbonates on the quality of water for agricultural purposes (Singh, 2014). A high amount of bicarbonates over carbonates poses danger on irrigation water because bicarbonates can cause damage to soil texture by dissolving

organic matter in the soil (Hannam et al, 2019). Figure 33 shows the spatial distribution of RSC in the study area.

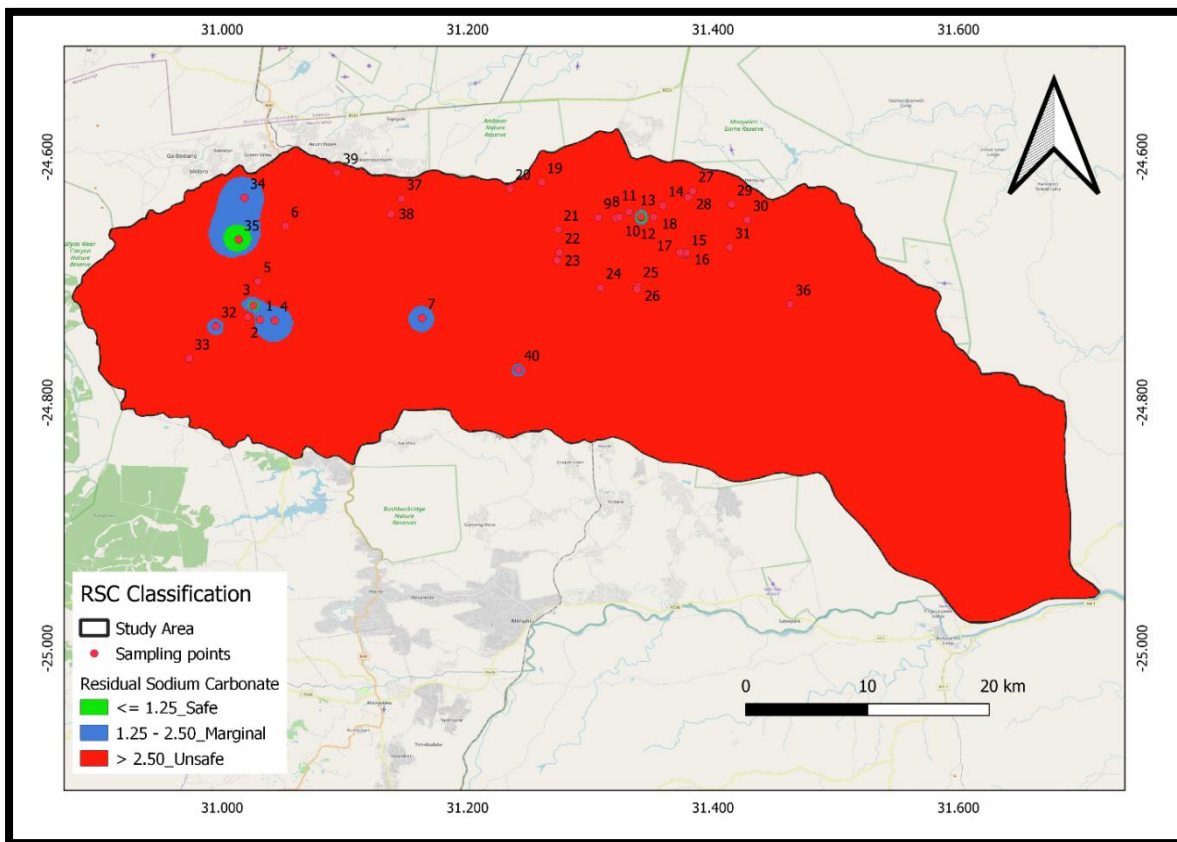


Figure 33 Spatial distribution of Residual Sodium Carbonate

The calculated RSC values in the study area range from -0.07 meq/l in Hluvukani to 22.78 meq/l in Newline village with an average of 6.64 meq/l. 10 % of the groundwater samples in the study area fell under the safe category having RSC below 1.25 meq/l, 15 % of samples have RSC values between 1.25 and 2.5 meq/l and are considered marginal, and the rest 75 % having RSC above 2.5 meq/l are unsuitable for irrigation.

4.2.2.7 Permeability Index

Permeability is the ability of soil to conduct water and air to the plant roots. When PI is greater than 75%, it indicates that the water is suitable for irrigational purposes. And when PI is less than 25% it suggests that the water is unsuitable to use for irrigation (Table 19). The PI values in the study area ranges from 24.84 to 101.44 with a mean value of 79.16. According to PI calculated values, the groundwater in the study area fell under suitable and good category with 59% and 41 % for each category, respectively. No groundwater samples were discovered to be below the unsuitable

range for irrigational purposes based on Permeability Index. Figure 34 shows the spatial distribution of PI in the study area.

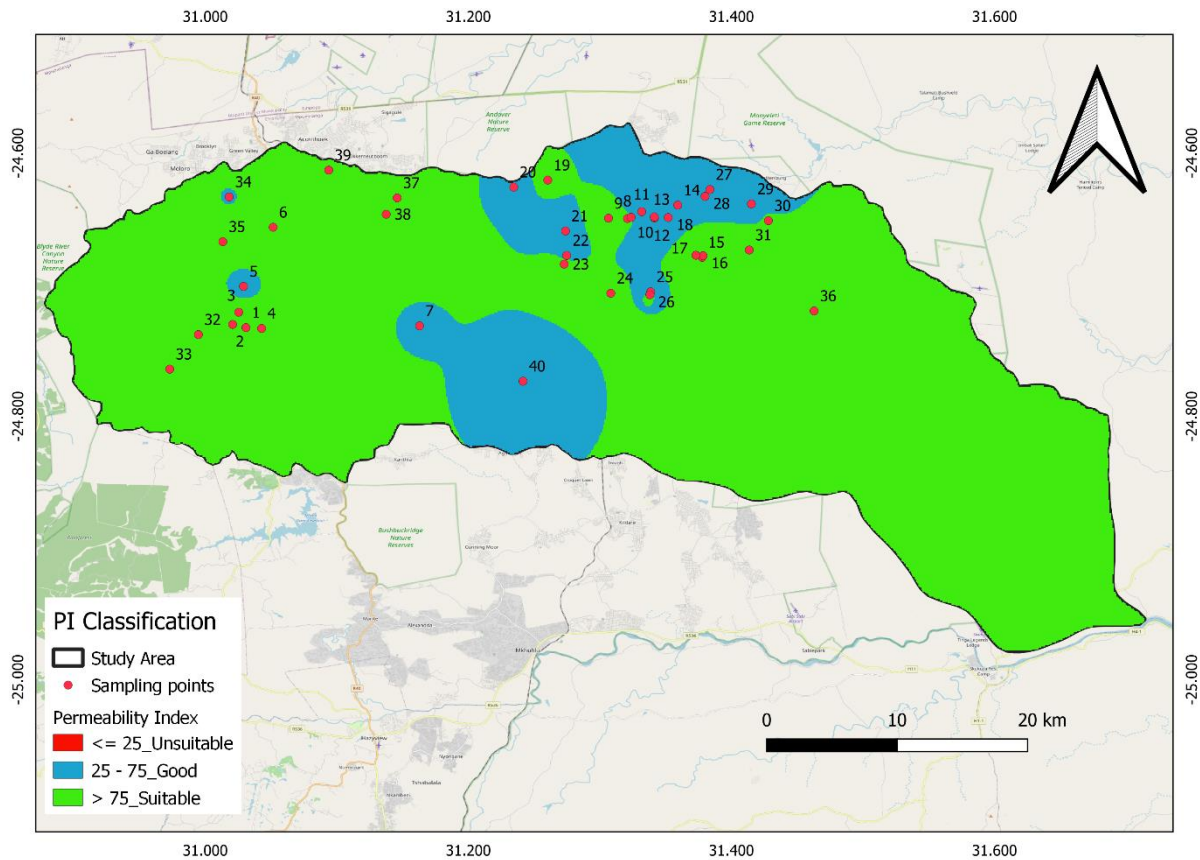


Figure 34 Spatial distribution of Permeability Index

4.2.2.8 Magnesium Hazard

Normally, Ca^+ and Mg^+ maintain a state of equilibrium in groundwater. However, large amounts of magnesium in the soil has a direct impact on crop yield because it tends to convert the soil quality into alkaline and this eventually decreases crop production (Kumari and Rai, 2020). From the study area, the calculated Magnesium Hazard values ranges from 2.72 at Maromeng village to 79.97 at Hluvukani village with a mean value of 50.19. It was revealed that based on Magnesium hazard that about 49% of the groundwater samples were suitable for irrigation, whereas 51% of the groundwater samples were considered to be unsuitable for irrigation purposes (Figure 35).

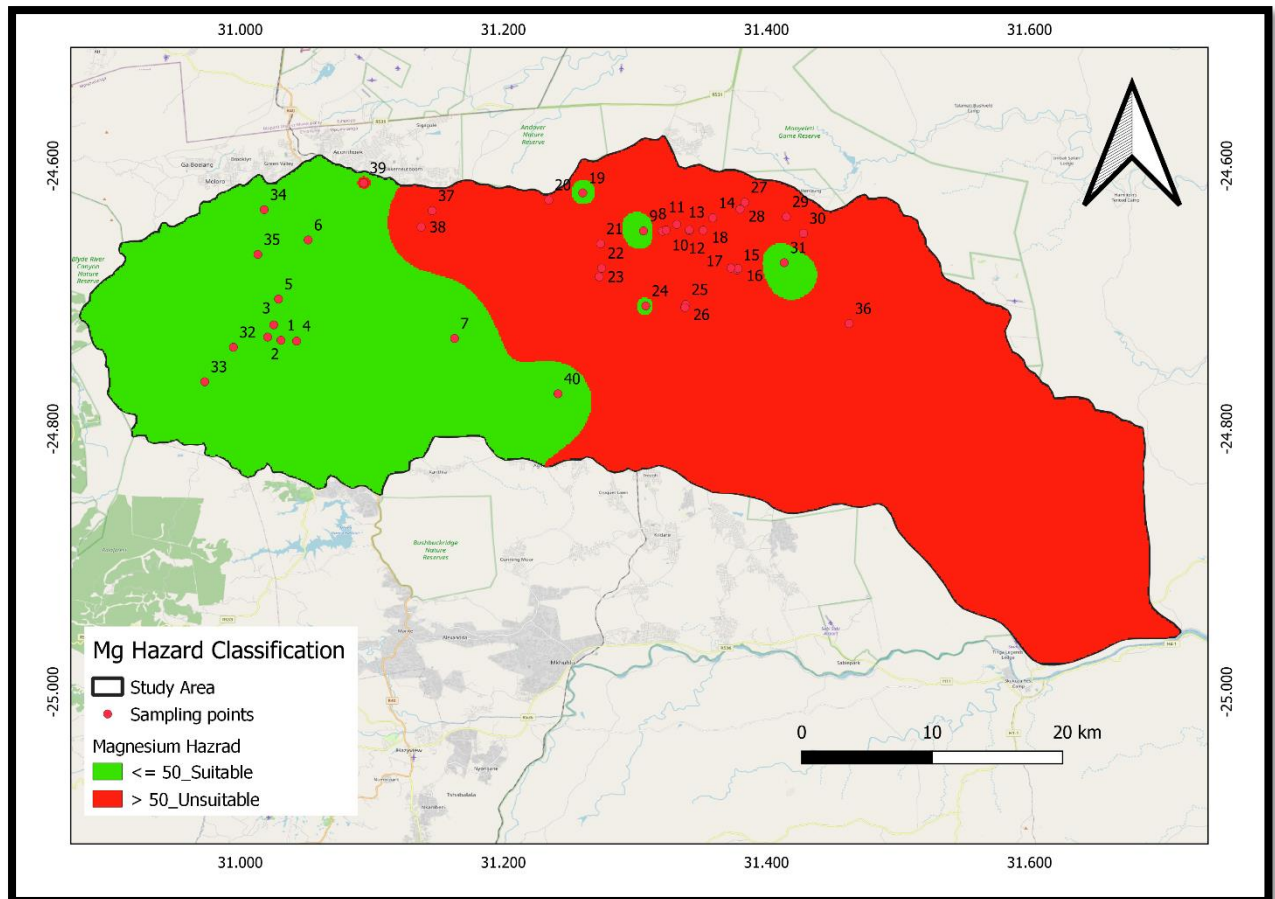


Figure 35 Spatial Distribution of Magnesium Hazard

4.3. Groundwater Dominant Types and Chemical Facies

A Piper diagram is a simple and widely used method for determining the type of groundwater. In this study, groundwater facies are mostly concentrated in field 5 ($\text{Mg}^+ - \text{Ca}^{2+} - \text{HCO}_3^-$) with 45% of the groundwater samples falling under this type. The remaining groundwater samples fell under field 7 ($\text{Na}^+ - \text{Cl}^-$), field 8 ($\text{Na}^+ - \text{HCO}_3^-$) and field 9 (Mixed type), with 2.5%, 7.5% and 35%, respectively as shown in Figure 36.

The cations plotted in the diagram are showing the dominance of Sodium type with 54% of the samples falling under this field and the remaining 39 % and 7 % falling under mixed type and Magnesium type respectively. In the anion plot, it is evident that Bicarbonate type is dominant with 98 % of the samples falling in this field while the remaining 2 % is under the Chloride type.

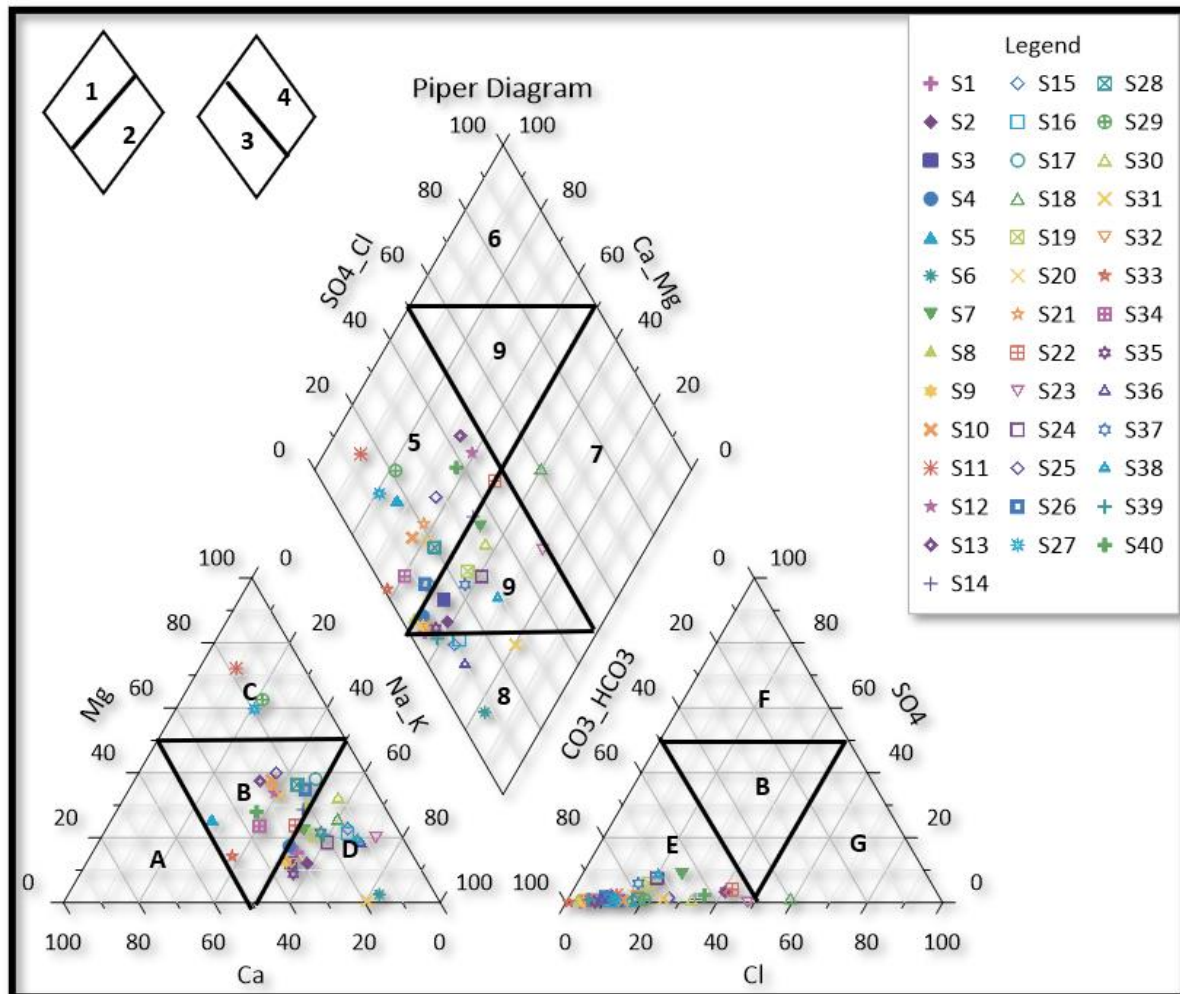


Figure 36 Piper diagram showing hydrochemistry of groundwater samples in the study area. (5 = Ca-HCO₃, 9 = mixed type (Ca-Na-HCO₃), 8 = Na-HCO₃ B = No dominant type, C = Magnesium type D = Sodium type, E = Bicarbonate type)

The plot of data on diamond shape field revealed that that the content of alkaline earth ($Mg^{+} - Ca^{2+}$) is higher than that of alkalis ($Na^{+}-k^{+}$), and the content of weak acid roots ($HCO_3^{-}—CO_3^{2-}$) is higher than that of strong acid roots ($Cl^{-} - SO_4^{-}$). Thus, the total hydrochemistry of the study area is dominated by alkaline earth and weak acids.

4.4 Processes Influencing Groundwater Chemistry

The Gibbs diagram was used to establish the processes responsible for the groundwater chemistry in the Sand River Catchment. The diagram consists of three distinct fields such as precipitation dominance, evaporation dominance, and rock interaction dominance areas and they are achieved by comparing the concentration of TDS versus the weight ratios of $Na^{+}/(Na^{+}+Ca^{2+})$ or TDS versus the weight ratios of $Cl^{-}/(Cl^{-}+HCO_3^{-})$ to identify the influencing factors of the groundwater hydrochemistry.

In the study area, the results shown in Figure 37 reveals that most of the samples are in the rock weathering dominant field, which indicates that chemical weathering of rock-forming minerals such as carbonates and bicarbonates are the prevailing natural mechanism in determining the groundwater chemistry. Additionally, the groundwater was also influenced by evaporation since about 10% of the samples in the study area fall in this zone. The study area is in the arid region and the evaporation would be due to climate conditions. Evaporation increases salinity through increasing Na^+ and Cl^- content and subsequently TDS.

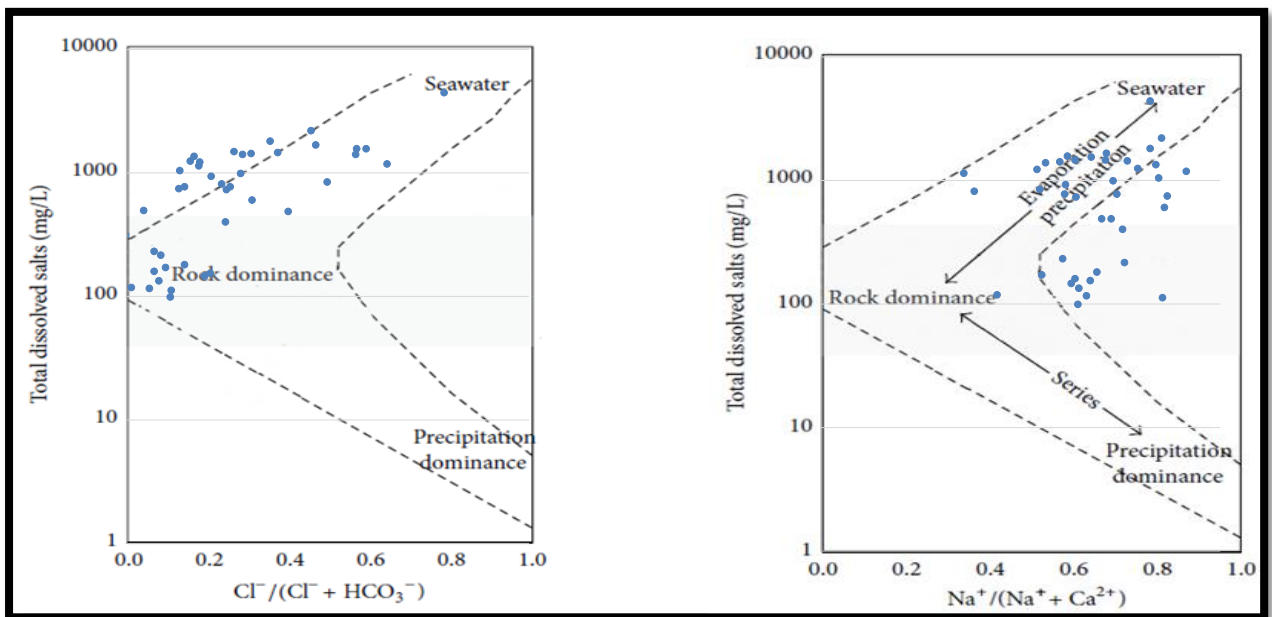


Figure 37 Gibbs diagram showing factors controlling groundwater chemistry

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.0 Preamble

The main aim of the research was to evaluate the hydrogeochemistry and assess groundwater quality for drinking and irrigation purposes in Bushbuckridge, Sand River Catchment, Mpumalanga province, South Africa. The research's conclusion, and recommendations are presented in this concluding chapter.

5.1 Summary of the research

In order to achieve the aim of this study 40 boreholes were identified and sampled from different locations in the study area. The groundwater samples were then sent to the laboratory for further analysis by measuring concentrations of hydrochemical parameters of groundwater such as pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), major cations (Ca^{2+} , K^+ , Mg^{2+} and Na^+ ,) and major anions (Cl^- , F^- , HCO_3^- , NO_3^- and SO_4^{2-}).

The following objectives were set to assist further in achieving the aim of this study namely, determining water quality status, identifying the hydrogeochemical mechanisms controlling the water chemistry and characterising the groundwater types and hydrochemical facies.

Suitability for drinking was assessed based on comparison with selected standards and guidelines, such as the South African National Standard (SANS), Department of Water and Sanitation (DWS), World Health Organization (WHO) and by computation of Water Quality Index (WQI). Groundwater suitability for irrigation was assessed using eight irrigation indices: TDS, EC, Sodium Adsorption Rate (SAR), Sodium Percent (%Na), Kelly's Index (KI), Residual Sodium Carbonate (RSC), Permeability Index (PI) and Magnesium Hazard (MH). Groundwater type and facies characteristics was determined with the Piper diagram while geochemical controls were ascertained using Gibbs diagram.

5.2 Conclusions

The results of the study indicate that the groundwater in the area has a pH range of 7.58 to 8.89, making it slightly alkaline. pH, Sulphate, Fluoride and Potassium all have concentrations that are within the SANS 241 standard limit for all the samples.

The SANS 241 Standard recommended limits are exceeded in about 29% and 34% of EC and TDS samples, respectively, rendering them unfit for drinking purposes. In terms of cation and anion concentration, SANS 241 standards were found to be exceeded in about 15% of nitrate water samples, 20% of chloride water samples, 27.5% of sodium water samples, 2.5% of calcium water samples, and 27.5% of magnesium water samples. In the eastern part of the study area, more than 58% of water samples fall into the "very hard" category when comparing the total hardness to the classification set by Todd and Mays (2005).

The results from DWS drinking standard shows that 20% and 7.5 % of the groundwater samples fell under poor water quality (class 3) and class 4 "dangerous water quality categories, respectively. This was due to elevated concentrations of TDS, EC, TH, CL, Na and Nitrate. Water quality index suggests that majority of the groundwater samples parts is suitable for drinking whereas only 4% of the groundwater samples fell under the poor and unfit categories with 2% each and is not suitable for drinking.

TDS, EC, SAR, %Na, RSC, KI, PI and MH were measured to evaluate suitability for irrigation and assess the risk of groundwater. According to TDS, EC, SAR, %Na and PI values, the majority of the groundwater samples in the study area fell into the "good" and "marginal" ranges, respectively. However, based on RSC and MH most of the groundwater samples fell under the "unsuitable" water quality for irrigation. The results from KI revealed that 50% of the groundwater samples fell under "suitable" water quality and 50% groundwater samples fell under "unsuitable" water quality for irrigation purpose.

The results from Gibbs Diagram showed that most of the samples (80%) fell under the rock dominant field, which indicates that chemical weathering of rock-forming minerals such as carbonates and bicarbonates are the prevailing natural mechanism in determining the groundwater chemistry. Some few samples (10%) fell under the evaporation dominant field due to that the study area is in the arid region and the evaporation would be due to climate conditions.

A Piper diagram was used to determine the groundwater types and hydrochemical facies that are dominating at the study area. The results revealed that the hydrochemical facies in the study area are $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$, $\text{Na}^+\text{-Cl}^-$, $\text{Na}^+\text{-HCO}_3^-$ and mixed type. The dominant groundwater types in the study area includes sodium type,

Magnesium type, Bicarbonate type, Chloride type and Mixed type. Additionally, the overall hydrochemistry of the study area is dominated by alkaline and weak acids.

Based on the results from both Gibbs and Piper Diagram, it is concluded that cation exchange is the most important factor in controlling the chemical characteristics of the Sandriver Catchment groundwater and also the dissolution of carbonate minerals and evaporative salts also plays a role. Based on the study area's overall assessment, 47% and 50.75% of the sampled boreholes revealed that the groundwater quality was appropriate for irrigation and drinking purposes without any treatment, respectively.

5.3 Recommendations

- The research's findings will be helpful in assessing the groundwater quality situation for appropriate groundwater resource management and consumption for drinking and irrigation use.
- It is recommended that areas with poor or undoubtedly suitable water quality be monitored on a small scale in order to properly detect them and implement appropriate management strategies.
- Remedial actions are required before using groundwater samples for drinking purposes if they have excessive TDS, electrical conductivity, calcium, magnesium, and total content. Among the effective methods in obtaining requirements for safe drinking water are boiling the water, ion exchange, precipitation with sodium carbonate, settling, and filtering,
- Reverse Osmosis, Electrolysis are some of the most effective methods that can be used for treatment of drinking water with high concentrations of Nitrate, Chloride and Sodium.
- Groundwater samples that are unsuitable for irrigation can be treated using gypsum water amelioration, sulfuric acid water amelioration, and blending water to the desired salinity.
- The spatial maps produced can be used by the general public to understand more about contamination in groundwater in the study area.
- Future aspects of the study must concentrate on the dangers to human health posed by groundwater contamination.
- For the most effective groundwater management and continual protection of water quality against future deterioration, frequent evaluation is recommended.

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