Assessment of water quality in the Groenwater Spruit, Postmasburg, Northern Cape

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Dissertation accepted in fulfilment of the requirements for the degree Master of Science in Environmental Sciences at the North West University

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Graduation: May 2023

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DECLARATION

I declare that *Assessment of water quality in the Groenwater Spruit, Postmasburg, Northern Cape* is my own work and it has not been submitted to any degree or for any examination in any university. I also declare to have abide by the NWU plagiarism code of conduct. Authors whose work has been used in this study are fully acknowledged.

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Date:	Signature:
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Supervisor: Prof. L.G Palamuleni	Signature:……………………………

ACKNOWLEDGEMENTS

A research of this nature needs determination, a resilient work ethic and keenness to be pushed to your limits emotionally, physically and mentally. I did not know if I could complete this research project since this past months were tough on me. However, my dedication to learning and expanding my horizons kept pushing. The completion of this research could not have been possible without the participation and assistance of so many people, whose names are not all mentioned. Their contributions are sincerely appreciated and gratefully acknowledged. However, I would like to express my deep indebtedness particularly to the following:

My supervisor Prof L.G Palamuleni, for going beyond the call of duty expected for a supervisor in providing support and advice through the entire journey.

This research would not be possible without the North-West University master's bursary financial assistance and the assistance from Prof H Drummond, the Dean of Faculty of Agriculture and Natural Sciences, who provided funds towards payment of registration in my final year. I am grateful.

To the Tsantsabane local municipality water department, I am beholden for the sampling permission and availing the department's technicians to assist with sampling. I would also like to acknowledge the Department of Geography and Environmental Sciences, the Department of Biological Sciences as well as the Centre for Applied Radiation and Technology (CARST) Mafikeng Campus. Special mention goes to Prof Ateba for permission to use his laboratory and other resources, Ms Mkiva for always doing her best to ensure that access to laboratory equipment was possible always and Ms Mokhine for assistance in the analysis of samples. For field assistance, I had support from the following people Mr Morapedi and Dr Bett, who drove me to my study area for the collection of my samples. I sincerely thank you for accompanying me on the long drives to Postmasburg.

To the foundation under my feet, my late grandmother Mrs Mahoko, thank you for teaching me about the importance of education and prayer. Your prayers are still following me. My late father Mr Tshipa, I thank you for always believing in me from such a tender age and for your eternal love. To my parents Mr and Mrs Ngwane as well as Mr and Mrs Maphasane, my siblings and cousins, thank you for the constant love, emotional and financial support. To my special friend Mr Medupe, thank you for all the unpaid therapy sessions and words of encouragement.

Lastly, I would like to thank God, my guardian angels and my ancestors. I owe it all to you.

DEDICATION

This one’s for me.

ABSTRACT

The Northern Cape province is known for its harsh climate with minimal rain and continued droughts, coupled with high evaporation. The province has two perennial rivers; the Orange river and the Vaal river systems supplying water for both economic and domestic needs of the province. The Lower Orange Water Management Area (WMA) is located in a way that the majority of its surface water is found in the main stem of the Orange river. Postmasburg connects both the Lower Orange WMA and the Lower Vaal WMA. The Groenwater Spruit is a south west flowing river that discharges into the Lower Orange WMA and directly intersects with the Orange river. The catchment area of the Lower Orange WMA is predominantly used for large-scale mining activities and agriculture with extensive irrigation schemes, producing large volumes of return flows. With all these anthropogenic stressors taking place within the catchment area, there is minimal water quality data available for the catchment area hence, the study was conducted to assess the water quality of the Groenwater Spruit.

To determine the water quality, this study collected seasonal measurements of 14 parameters (pH, temp, EC, TDS, DO, SO_4, NO_3, PO_4, Mn, Fe, As, Cr, *E. coli* and total coliform) from six sampling sites along the Groenwater Spruit during a one-year period. Physical parameters were measured *in-situ* using a hand-held instrument, chemical and microbiological parameters were analysed *ex-situ* using various laboratory methods. The obtained water quality results were assessed against the WHO, SANS (241) and DWAF for domestic water use standards and agricultural water use guidelines to give indication for the fitness for use. Furthermore, PCA was used to comprehensively evaluate all the selected water quality parameters across the Groenwater Spruit, to identify and analyse the sources of water pollution while ANOVA was used to compare seasonal variations at 95% confidence level.

Results for the physical parameters revealed that pH measured an average of 11 and 9.6 for the dry and wet periods, respectively. The measured pH values from both seasons were non-compliant to the set WHO (6.5 - 8.8) and DWAF (6.5 - 8.4) standards. The average TDS values for the dry and wet seasons (256.5 mg/L and 268.3 mg/L) were within the acceptable SANS set standard at $\leq$ 1200 mg/L but above the set DWAF guidelines of 0 - 0.02 mg/L. EC was only complaint to the DWAF guidelines of $\leq$ 540 mg/L, with an average measurement of 254 mg/L during the dry season and

517.1 mg/L for the wet season. Among all the selected chemical parameters for this study, DO, PO_4, Fe and Mn each measured values were above their specific set WHO, SANS and DWAF standards and guidelines. As and Cr were only compliant to their specific set SANS standards. SO_4 was compliant to SANS ($\leq$ 500 mg/L) and DWAF ($\leq$ 500 mg/L) standards with a mean of $<$ 90 mg/L for both seasons. NO_3 recorded a mean of 27.1 mg/L and 18.4 mg/L for the dry and wet seasons, respectively. These measured values were only within the acceptable WHO set standard ($\leq$ 50 mg/L) and the DWAF guidelines ($\leq$ 30 mg/L) but above the SANS standards. Total Coliform obtained from the study, for both seasons (67 cfu/100 mL and $\geq$ 685 cfu/100 mL for the dry and wet season) were higher than the WHO, SANS and DWAF set standard at $\leq$ 10 cfu/100 mL. The expected *E. coli* detection from WHO and SANS is 0 cfu/100 mL and so, the samples from the study area (39 cfu/100 mL and $\geq$ 837 cfu/100 mL for the dry and wet seasons) were non-compliant to this standard.

For the wet season sampling, PCA extracted three principal components that accounted for 91.9 % of the total variance. The strong positive loadings of F1 (temperature, Fe, As and Cr) were mainly influenced by variables related to natural and anthropogenic factors such as, rock weathering, dissolution, geomorphic variations, agriculture return flows, mining and industrial effluents. F2 with positive loadings of NO_3, PO_4, TDS and Mn signifies runoffs from chemical fertilizers, sewage and the disposal of manures and industrial activities prevalent in the catchment area. F3 had positive DO, which may be explained by the increased water volume in the Goenwater Spruit. Three components were retained for the dry season at 84.13% cumulative of the variance. The high positive loadings of F1 (temperature, EC, TDS, Fe, As, and Cr) were also influenced by natural factors and anthropogenic factors in the study area. The positive loadings of PO_4 and total coliform from F2 is mainly influenced by the direct pollution from manure, sewage and fertilizer, and from F3 (SO_4 and NO_3) is influenced by anthropogenic activities such as the discharge of untreated domestic, municipal waste waters. The findings from this study has highlighted the sources and types of pollution within the Groenwater Spruit. Therefore, it is recommended that long-term monitoring programmes be implemented focusing on the areas where increased anthropogenic activities have been observed.

Keywords: Groenwater Spruit, water quality, sources of water pollution, principal component analysis, natural factors, anthropogenic activities, domestic water use standards, agricultural water use guidelines

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LIST OF SYMBOLS

≤	less than or equal to
>	greater than
≥	greater than or equal to
±	plus-minus
mL	millilitre
cfu	colony forming units
L/min	litre per minute
km^3	cubic kilometre
m^3	cubic meter
mm	millimetre
m	metre
Mm	molar metre
mg/L	milligram per litre
mL/min	millilitre per minute
µL	microlitre
µm	micrometre
µS/cm	microSiemens per centimetre

LIST OF ACRONYMS

Al	Aluminium
AMDs	Acid Mine Drainages
CO_2	Carbon dioxide
Cd	Cadmium
Co	Cobalt
CSIR	Council for Scientific and Industrial Research
Cu	Copper
DEA	Department of Environmental Affairs
DEAP	Department of Environmental Affairs and Planning
DEAT	Department of Environment Affairs and Tourism
DO	Dissolved oxygen
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
DWS	Department of Water and Sanitation
EC	Electrical conductivity
Fe	Iron
H_2CO_3	Carbonic acid
Hg	Mercury
IDP	Integrated Development Plan
IPCC	Intergovernmental Panel on Climate Change
Mn	Manganese
NO_2	Nitrogen dioxide
NO_3^-	Nitrate

NCMP	National Chemical Monitoring Programme
NEMP	National Eutrophication Monitoring Programme
NEPAD	New Partnership for Africa's Development
NH_4^+	Ammonium
Ni	Nickel
NMMP	National Microbial Monitoring Programme
NTMP	National Toxicant Monitoring Programme
NPSP	Non-point source pollution
PO_4^{3-}	Phosphate
$POCl_3$	Phosphorus oxychloride
Pb	Lead
SO_4^{2-}	Sulphate
SAEO	State of the Environment Report
StatsSA	Statistics South Africa
TA	Total alkalinity
TDS	Total dissolved solids
UNEP	United Nations Environment Programme
USA	United States of America
WMA	Water Management Area
WRC	Water Resource Commission
WWTP	Waste water treatment plant
WSAs	Water Services Authorities
Zn	Zinc

CHAPTER ONE

1. INTRODUCTION

1.1. General background

Water scarcity and inadequate supply of fresh water resources are major concerns in arid regions around the world. Areas with moderate to severe water scarcity include the Middle East, India, northern China, Somalia, Mexico, north and southern Africa (Kummu *et al.*, 2010). Scarcity of water in the Arabian desert is severe compared to the other deserts, this is caused by the increase in population density as well as irrigation intensity. The availability of water and its consumption are observed to be countercyclical in certain regions, with water availability being low when water consumption is high. This countercyclical pattern is observed in several river basins for example, the Ganges basin situated in India and the Limpopo basin situated in Southern Africa (Mekonnen and Hoekstra, 2016).

The availability of fresh water is the highest limiting factor to South Africa's development (DEA, 2011). South Africa is classified as a water scarce country with an annual rainfall of about 492 millimeters distributed unevenly across all the nine provinces, driving the country repeatedly between floods and droughts (Colvin *et al.*, 2013). The country has built many dam systems to store water. Numerous water transfer schemes, moving water from one catchment to another through pipes, pumps and canals were also implemented to provide for the shortage (Coetzee *et al.*, 2010).

The Northern Cape province is known for its harsh climate with minimal rain and continued droughts, coupled with high evaporation caused by the intense summer months' heat. Annual rainfall ranges between 20 mm on the west coast to approximately 300 mm on the eastern side (Mukheibir, 2007). The province's supply vs. demand ratio in the year 2000 revealed water vulnerability to be real in the province by efficiently observing an undersupply of about 8 x 106 m^3 (DWAF, 2004). The high demand concerns for instance, elevated water usage rates, peak use, seasonal inconsistency, weak demand management, lack of water consumption planning, poor conservation and water losses from the past years are also contributing factors to the present water shortages faced by the Northern Cape province (Van Dyk, 2004).

Besides water scarcity, South Africa experiences water quality problems (Rand Water, 2020). The Department of Water and Sanitation (DWS) describes water quality as the chemical, physical, and biological properties of water determining its fitness for various uses and for the protection of the health and integrity of aquatic ecosystem (DWS, 2015). Various anthropogenic practices affects South Africa's water quality, these practices include deforestation, the destruction of river catchments and wetlands due to urbanization, damming of rivers, mining, industries, agriculture and energy use, the increase in human population (the activity serves as a long term problem since the increase in population is proportional to the increase in catchment destruction and pollution) (Rand Water, 2020).

The Northern Cape province has two perennial rivers; the Orange river and the Vaal river systems supplying water for both economic and domestic needs of the province (IDP, 2015/16). The Lower Orange Water Management Area (WMA) is located in a way that the majority of its surface water is found in the main stem of the Orange river (Volschenk *et al.,* 2005). In the Lower Orange WMA, irrigation is the dominant water use with 94% followed by 3% urban, 2% rural and 1% mining purposes (DWAF, 2004b). The Lower Vaal WMA is dependent on water discharges from the Upper and Middle Vaal WMA to cater for the urban, mining, agricultural and industrial sectors' water requirements within its area of jurisdiction (DWAF, 2004a). The water quality of these two perennial rivers has gradually been deteriorating as a result of the growing agricultural and industrial activities as well as the reduction of the inflow of high quality water from Lesotho (ORASECOM, 2007; IDP, 2015/16).

1.2 Problem statement

Postmasburg connects both the Lower Orange WMA and the Lower Vaal WMA (AURECON, 2014). The Groenwater Spruit is a south west flowing tributary of the Skeifontein river draining into the Orange river as the Soutloop river (Belcher and Grobler, 2015). The Soutloop river catchment discharges into the Lower Orange WMA and directly intersects with the Orange river (AURECON, 2014).

The land in the Lower Vaal WMA and the Lower Orange WMA is predominantly used for large-scale mining activities and agricultural purposes with extensive irrigation schemes, producing large volumes of return flows. These return flows impact the surface water's total dissolved solids (TDS) concentrations and contribute significantly to the nutrient loads relating to eutrophication (ORASECOM, 2007; Odume *et al.,* 2018). Algae caused by eutrophication has led to odour and colour complications in the intake water. This causes technical issues and high costs because some water treatment plants are not constructed to deal with treatment related to eutrophic waters (Nyenje *et al.,* 2010; Van Ginkel, 2011). Irrigation repercussions leads to the leaching of fertilizers, and more importantly, the leaching of salts deep in the soil, causing both the soil and the receiving rivers unsustainable (DWAF, 2004b). Effluents from the mines negatively impact the watercourses by enhancing the levels of suspended solids, leading to pH levels reduction and the transfer of heavy metals to receiving rivers also rendering them unfit for various intended purposes (Ochieng *et al.,* 2010; Opitz and Timms, 2016).

With all these anthropogenic stressors taking place within the catchment area, there is no available water quality data for the Groenwater Spruit (either no studies have been conducted or the data was not published). The only available water quality data is of groundwater, which is very minimal and old. It therefore, important that the raw water flowing from the Groenwater Spruit into the Orange river be monitored for physico-chemical and microbial quality to protect the surface water and the aquatic environment in general within the catchment area. Water quality monitoring would offer assistance to water authorities to identify and quantify pollution sources and impacts of pollution along the Groenwater Spruit. Monitoring would further assist with effective management strategies.

1.3 Objectives of the study

1.3.1. Main objective

The main objective of the study was to assess the water quality in Groenwater Spruit.

1.3.2 Specific objectives

The specific objectives of this research:

(i) To determine the current surface water quality of the Groenwater Spruit;

(ii) To determine if the current water quality complies with water quality standards for agricultural and domestic use;

(iii) To identify point and non-point sources of contaminants along Groenwater Spruit.

1.4 Research hypothesis

The research hypothesis for this study is outlined as follows:

H_1: The anthropogenic activities taking place within the Groenwater Spruit catchment area contributes to increased rates of contamination to the surface waters.

1.5 Rationale of the study

Streams and rivers are more prone to chemical and microbial pollution in comparison to groundwater. This results in elevated microbial and chemical loads within the flowing rivers (Mathebula, 2016). It is therefore important that the raw water flowing from the Groenwater Spruit into the Orange river is monitored for both chemical and microbial quality to prevent further degradation of the river's water quality and protect the aquatic environment in general. An assessment of water quality of the Groenwater Spruit would bring insights of its water quality status before discharging into the Orange river, its fitness for use for agricultural and domestic purposes and reduce potential water borne diseases.

1.6 Description of the study area

The Groenwater Spruit catchment area is a combination of two quaternary catchments D73A and D73, referred to as the Soutloop river catchment according to the referencing system of the South African Department of Water and Sanitation Affairs as depicted in Figure 1. Quaternary catchment D73A is drained by the Groenwater Spruit (Parsons and Rautenbach, 2011). Groenwater Spruit is a catchment with a geographic location of between longitude 24°11'59.3" and 23°06'11.5" and between latitude 28°19'55.0" and 28°07'51.5".

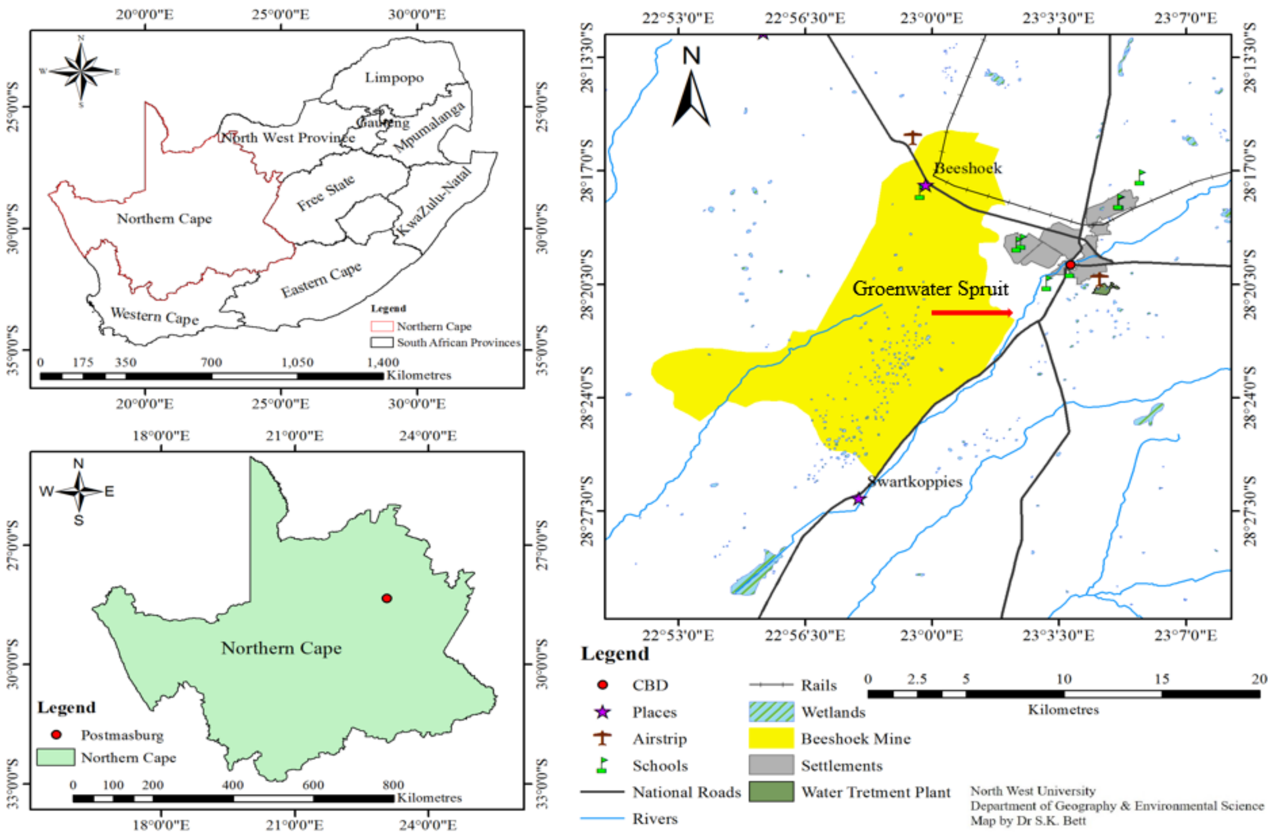

Figure 1: Map of the study area

1.7 Research ethics

To maintain the various ethics codes such as confidentiality, integrity, respect and honesty governing research, ethical clearance certificate was submitted and obtained from the North-West University ethical clearance committee. This certificate was a prerequisite in the completion of a Master’s degree with the North-West University. Consent to collect water samples from the Groenwater Spruit was approved and the outcomes from the study are projected for research purposes only.

1.8. Outline of dissertation chapters

This research project is sectioned into five chapters;

Chapter One gives a general overview of the research project, objectives of the study and the depiction of the study area.

Chapter Two outlines the overview of the factors affecting water quality, followed by a synopsis of the water quality problems predominant in South Africa.

Chapter Three provides a description of the various laboratory methods and statistical tools carried out to complete the prominent aim of this study.

Chapter Four provides a presentation of the results obtained from the study's analysis, compares and discusses the obtained results based on prior literature outcomes.

The study conclusions and recommendations are discussed in Chapter Five.

CHAPTER TWO

2. LITERATURE REVIEW

This chapter mainly focuses on the natural and anthropogenic factors affecting water quality, the different sources of pollution and their impact on aquatic systems, followed by a brief overview of the water quality problems predominant in South Africa. It concludes with the national water quality monitoring programmes implemented to solve the persistent and emerging water quality challenges being faced by the country.

2.1. Global water distribution

Water resources are a necessity for societal activities and economic developments. The overall rise in global water usage is influenced by the rapid economic and population growth, exacerbated by the fluctuating consumption patterns experienced in developing countries (Hanasaki *et al.,* 2013). Furthermore, climate change has caused water availability to become constrained in many parts of the world (Moss *et al.,* 2010). According to speculations made by United Nations Environment Programme (UNEP), it is estimated that within the next two decades, the global demand for water may possibly outstrip supply (UNEP, 2011).

The surface of the earth is covered nearly by 75% water. It is further estimated that the earth's hydrosphere contains about 1.4 billion km^3 of water. This is adequate to cover the whole globe with a layer of water which is 2,718 m deep. Yet, not all of these resources are made accessible for human necessities (Cassardo and Jones, 2011). Research compiled by Sophocleous (2004) and Lui *et al.* (2011), illustrates as shown in Figure 2, that majority of the Earth's water, over 96% is recovered from saline ocean waters. The remaining 3% makes up the Earth's fresh water with various physical states from a liquid state, to gas and solid. About 69% of the fresh water occurs as permanent snow cover and ice caps in polar and mountainous regions like Antarctica and Greenland, and is not readily available for consumption. Groundwater takes up 30% of the global freshwater and the remaining 0.3% of all freshwater is recovered from reservoirs, rivers and lakes (Cassardo and Jones, 2011).

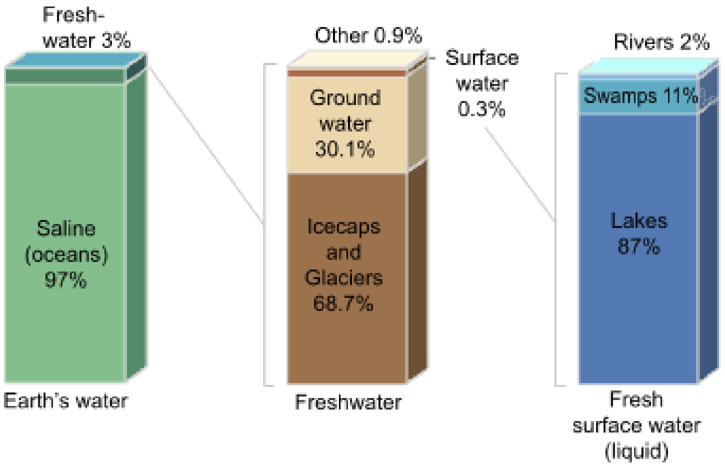

Figure 2: Distribution of Earth's water

Source: (Lui *et al.*, 2011)

2.2. Contextualizing South Africa's water resources

South Africa does not have adequate water, it is rated as the 30th arid country in the world with a mean annual rainfall of 450 mm per annum, lower than the world average of 860 mm (Basson, 2011). The mean annual evaporation ranges between 800 mm and 2000 mm, higher than the annual precipitation in certain parts of the country (Kohler, 2016). The highly variable and spatial distribution of rainfall across the nine provinces in the country contributes to the scarcity of fresh water resources (Adewumi *et al.*, 2010). In large parts of the country such as in the western part, including where the study was conducted (Northern Cape province), much of the rain reaching the ground evaporates rapidly and re-enters the atmospheric phase of the hydrological cycle (Mengistu *et al.*, 2021). The hydrological cycle is defined as a process of continuous water exchange or circulation within the hydrosphere, i.e. the atmosphere, the Earth's surface and the lithosphere (**Shiklomanov, 2009).**

The country's groundwater resources are scarce because South Africa mostly consists of hard rock formations with no major ground aquifers to be used on a national scale (Kohler, 2016). DWA (2013a), estimated that only about 20% of South Africa's groundwater is available for human needs. Groundwater is extensively used in rural and arid regions of the country. It was further discovered that approximately one-third of the population are dependent on groundwater for domestic necessities (DWA, 2013a).

Above 70% of the water consumed in both rural and urban regions of South Africa is surface water transferred from rivers, streams, lakes, ponds and springs (Ochieng *et al.*, 2010). Seven of the country's nine provinces rely profoundly on inter-basin transfers, catering for more than half of their water needs (Van der Merwe-Botha, 2009). Despite significant water transfers into the country from other systems to meet the country's demands, water requirements still exceed availability (DWAF, 2004a; DWA, 2010a). Drastic changes in rainfall are as a result of climate change, which severely impact South Africa's available water resources (Van der Merwe-Botha, 2009).

2.3 South Africa's water use

South Africa's water shortage affects different sectors of the economy dependent on water resources for production. Some economic sectors are more dependent on water resources compared to others. The severity of water shortage impact differs on different economic sectors (DWA, 2013b). Statistics on water use per sector of the country has not had major adjustments since the 2006 State of the Environment Report (SAEO), though the demand in the domestic and industrial sectors has expanded but the agricultural sector demand remain the largest (Boretti and Rosa, 2019; StatsSA, 2010). The summary of water use per sector in South Africa is presented below.

2.3.1 Agricultural water usage

With 60% of total water consumption, agriculture is the major water user in South Africa. This is followed by municipal with 29% consumption, which includes industrial and commercial users provided by municipal systems. Other sectors such as power generation, mining, industrial usage, afforestation, livestock and conservation equally make up the outstanding 11% as shown in Figure 3 (Viljoen and Van der Walt, 2018).

The continuous population growth has placed strain on the farming sector into yielding more crops than usual to ensure food security. Intensification of commercial cultivation activities have caused an increase in water extraction over the years, causing a rise in environmental concerns. Such concerns include; reduced groundwater and river flows, oxygen insufficiencies in aquatic environments, leading to possible extinction of species and the deterioration of water quality (CSIR, 2010; UNEP, 2016; Du Plessis, 2017).

2.3.2. Mining and Industrial water usage

Mining and industrial sectors are estimated to utilize 6% water while the energy sector accounts for about 2% of the country's water use (CSIR, 2010). Diverse mining sectors and industries make use of highly varied water amounts obtained either from municipalities or bulk schemes (UNEP, 2016). The industrial sector water usage ranges from manufacturing steel and iron, processing of agricultural products and forestry products, food processing, textiles, commercial industries to construction. Water is supplied to both these sectors by means of abstracting it from a water resource regulated in terms of the National Water Act or those serviced by water providers (water supply and wastewater treatment) (McCarthy, 2011; NEPAD, 2013). Power generation requires 2% of the country's water supply. The power generation water requirement may appear as a low water usage sector however, it is moderately higher because the South Africa has a numerous power stations and majority of these power stations were built to have an elevated water usage (Oberholster and Botha, 2014).

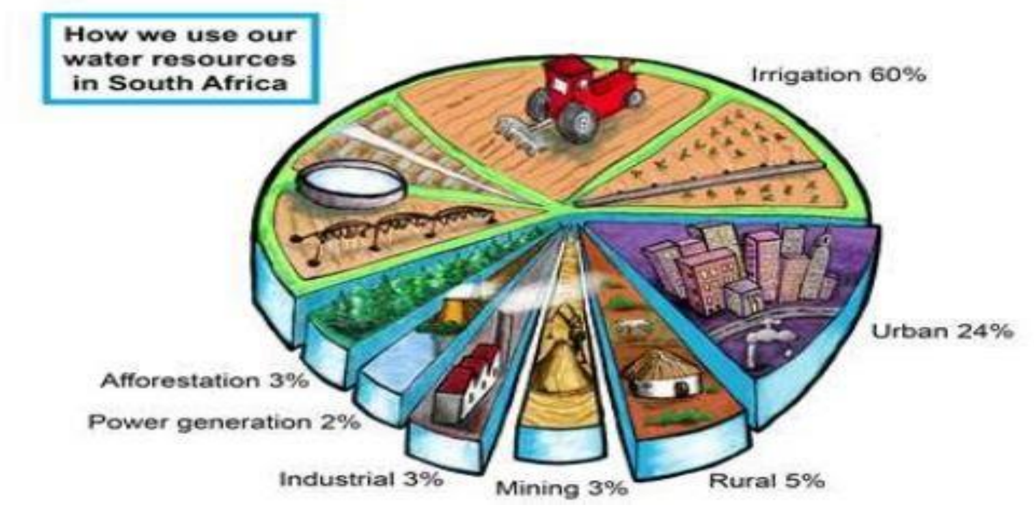

Figure 3: South African Water Sector Demand

Source: (DWA, 2013b)

2.3.2. Domestic water usage

Water is transferred into residential houses or properties through metered supply lines. Consumers use the supplied water for several desired needs to meet both their indoor and outdoor demands (Jacobs *et al.*, 2006). The total indoor water expenditure in a typical domestic household is approximately 80% water usage, which is mainly used for bathing, showering, toilet and laundry (Adewumi *et al.*, 2010). The average domestic water consumption in South Africa is around 237 litres per person per day, which is 64 litres per person per day more compared to the world average of 173 litres per person per day. The high water use is somewhat caused by the municipal non-revenue water, which is currently too high (Kohler, 2016).

The domestic water usage requirement of the country accounts for 29% (urban areas with 24% and rural areas with 5% water usage) (Du Plessis, 2017). Water consumption varies between the upper middle and lower income households. Water demands are expected to increase for domestic usage due to elevated population growth percentages with access to water services and also the expected development in the degree of living, leading to an increased per person water usage (Du Plessis, 2017). Water consumption in the urban regions is distributed into the following: domestic 50%; 26% unaccounted water; industries 12%; farming 10%; and municipalities 2%. The highest source of water usage in higher income areas is swimming pools and garden irrigation (CSIR, 2010; Hay *et al.*, 2012).

2.4. Factors affecting water quality

Water quality is affected by both anthropogenic and natural factors with geological, hydrological and climatic influences being the most crucial natural factors (Mathebula, 2016). The effects of human activities on water quality are of a wide range and differ in the extent to which they interrupt the ecosystem and restrict water usage. Several anthropogenic activities with the ability to impact surface water quality include agriculture, mining, population growth and waste disposal methods (Yadav and Kumar, 2011).

2.4.1 Anthropogenic activities

Agricultural activities

These activities contribute significantly to water pollutant loads across the world. Agricultural activities are among the regularly mentioned sources of pollution and are responsible for the degradation of water resources (Mustapha *et al.,* 2013; Adamu *et al.,* 2014). The most common agricultural water pollution is loss of top soil that is carried from agricultural lands. Rain water carries soil residues (fertilizers, pesticides as well as heavy metals) into nearby surface water bodies, thus affecting water quality (Khatri and Tyagi, 2015).

Agricultural runoff causes eutrophication in fresh water bodies. The main contributor to eutrophication is phosphate (PO_4^{3-}) and its high concentration stimulates cyanobacteria and algae growth, which reduces dissolved oxygen in water, threatening the aquatic life (Schmidt *et al.*, 2013; Chaudhry and Malik, 2017). Nitrogen rich fertilizers also cause dissolved oxygen deficiency in rivers, lakes and coastal zones. Fertilizers have high water solubility, increased runoff and leaching, resulting in groundwater pollution (non-point pollution) (Rosen and Horgan, 2009).

Mining activities

Water quality is also affected by past and current mining practices. Surface waters adjacent to mining areas are at a greater risk of pollution of waste drainage from mining activities (UNEP, 2010). Mining activities have increased the production of acid mine drainages (AMDs), which are major environmental problems related to mining not only in South Africa but across the world as well (Tutu, 2012). AMDs cause extremely acidic water (Mathebula, 2016).

Population growth

The world is being urbanized at a rapid rate concurrently with the increasing population rate. Majority of the population live in urban areas, leading to more constructional developments to satisfy the needs of the growing population (Leeson, 2018). Population growth generates more domestic and industrial waste contaminating fresh water systems (Gomes and Ebrary, 2009). Activities associated with urbanization were found to elevate levels of nitrogen, phosphorus, alkalinity, and the total dissolved solids (TDS) in surface waters (Allan and Castillo, 2007). Degraded streams and rivers discharging into urbanized landscapes recorded higher nutrient loads and contaminant concentrations altering the stream morphology and reducing the biodiversity (Hamid *et al.*, 2020).

Waste disposal methods

Municipal waste water treatment plants (WWTP) are direct sources of nutrient and feacal pollution. The impact of increased nutrient input causes a rise in sediment de-oxygenation downstream. The stream nutrient load will be negatively impacted and the effects persist several kilometers further downstream with long term effect on the stream's composition (Mathebula, 2017).

2.4.2 Natural factors

Geological factors

Geological factors result due to the influence of the geosphere on groundwater composition, predominantly through the effect of chemical water rock links in aquifers (Khatri and Tyagi, 2015). Different types of rocks are composed of different chemical determinants (Singh and Schulze, 2015). During chemical weathering, minerals are converted into new minerals and other by-products. Minerals such as halite (rock salt) and calcite (carbonate minerals) dissolve completely while others, particularly silicate minerals (silicon-oxygen compounds), are altered by a chemical process called hydrolysis. Hydrolysis is the reaction of minerals, taking place in weakly acidic waters. A number of natural surface waters are slightly acidic due to carbon dioxide (CO_2) from the air that dissolves in the water. Some of the dissolved CO_2 reacts with the surface water forming the chemical compound, carbonic acid (H_2CO_3) (White and Brantley, 2018; Nelson and Stephen, 2014). The dissolved solutes enter the upper layers of the rocks during the hydrological processes such as irrigation, flooding and rising groundwater levels or capillary rise. Once the solutes spread to the upper rock layer, they then alter the water quality in that area (Figure 4) (Singh and Schulze, 2015; Mathebula, 2016).

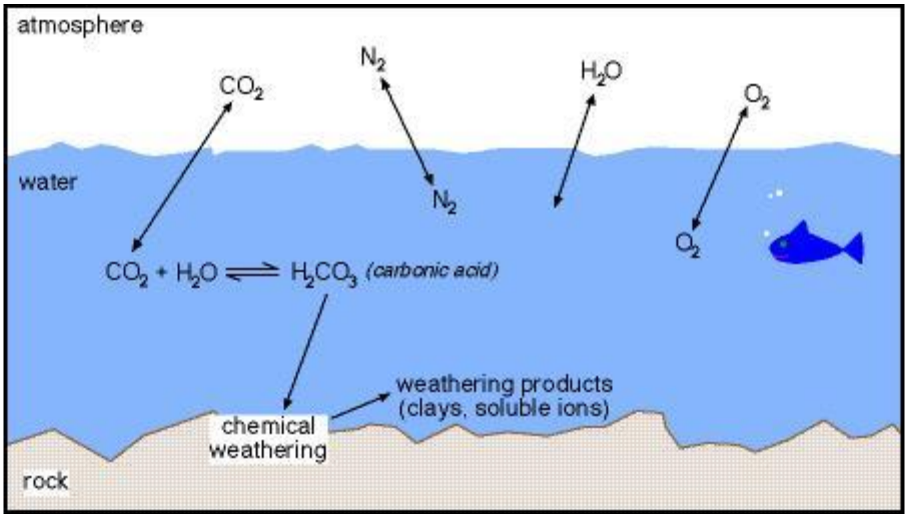

Figure 4: Chemical weathering process
Source: Columbia.edu, (2020)

Hydrological influences and climatic influences

The Intergovernmental Panel on Climate Change (IPCC), describes climate change as a large-scale and long-term shift in the global climatic conditions, which affects the physico-chemical water quality through direct and indirect processes. A direct process of climate change on chemical reactions is climate warming (global warming) (IPCC, 2015). Conversely, hydrological changes related to climate change are known to affect the physico-chemical water quality indirectly. Floods and droughts may possibly modify water quality through the dilution or concentration of dissolved substances (Khatri and Tyagi, 2015). Generally, temperature is regarded as the main factor affecting most physico-chemical equilibriums and biological reactions (Khatri and Tyagi, 2015).

Temperature affects surface water quality as it controls oxygen levels, influencing the rate of chemical and biological reactions within aquatic ecosystems. Increase in water temperature decreases the oxygen solubility as a result, decreasing the dissolved oxygen (DO) concentration. Reduced DO concentrations impacts on the duration and intensity of algal blooms (Whitehead *et al.*, 2009), while changes in air temperature affect the variability of rainfall in turn altering the levels of salinity in surface water (Yadav *et al.*, 2013).

Increased and more intense precipitation is known to increases nutrient runoff from agricultural lands to surface waters. Extreme rainfall leads to increased soil erosion and consequently the water becomes turbid and a number of pollutants are then introduced into the water bodies (Kundzewicz *et al.*, 2007). In instances of low river flow rates, the main effect on water quality is when there is a temperature increase (Khatri and Tyagi, 2015).

2.5 Different forms of Water pollution

Pollution of water is reckoned to be one of the main environmental problem across the world and is also associated with numerous environmental, social and economic concerns (Du Plessis, 2017). There are various definitions of pollution however, this study only cites two definitions. Chaudhry and Malik (2017), define a pollutant as a substance, which when introduced into an environment, causes detrimental effects. The pollutant is capable of causing both short and long term damage to the introduced environment (Chaudhry and Malik, 2017). Pollution is also described as the direct or indirect introduction of constituents into the environment by humans, resulting in lethal effects harmful to living organisms, and dangerous to the health of humans or interruption of aquatic ecosystems (Lui *et al.*, 2011). There are two main types of pollution namely; point and non-point water pollution sources. Figure 5 depicts some of the major direct/point and non-point source pollutants.

2.5.1 Point source pollution

When the source of water pollution is known or pollutants introduced into the water are from a distinguishable source such as, storm drain and sewage treatment plants, the pollution is identified as a point source pollution (Hogan, 2010; Copeland, 2016). Untreated and inefficiently treated sewage discharging schemes are the main point sources of pollution in freshwater bodies. Other point sources pollutants come from mining and industrial runoffs which includes, the chemical and electronics manufacturing factories, oil refineries, leather turning, breweries and municipal storm systems (Yang *et al.*, 2012; Yavini and Musa, 2013).

Rapid population growth in developing countries has led to high volumes of untreated or inadequately treated effluents from municipal treatment works being discharged into rivers or streams, polluting both surface water and groundwater and also disturbing the ecological balance of that river or stream (Somaya, 2011; Chaudhry and Malik, 2017). Studies conducted by Yuhong *et al*. (2009), and Nyamangara *et al*. (2013), revealed that point source pollution is easier to regulate compared to non-point source pollution and that most developed countries have managed to curb pollution from point sources pollutants.

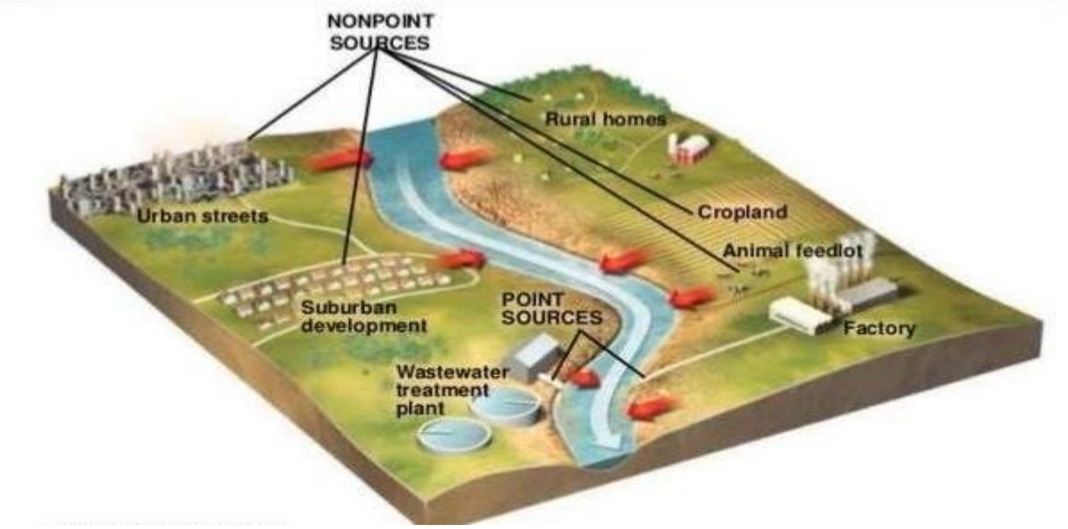

Figure 5: Sources of water pollution

Source: (Miller, 2005)

2.5.2. Non-point source pollution

When the source of water pollution is unknown or pollution does not come from a single distinct source, pollution is identified as non-point source pollution (NPSP). The pollution is often too challenging to control since it usually comes from various sources (Chaudhry and Malik, 2017). NPSP is considered to be the main contributor to water quality degradation and has become a global and regional environmental concern (Yang *et al.*, 2020). As per statistics compiled by Zhang *et al.* (2018), it was noted that about 30–50% of water sources on the surface of the earth have been affected by NPSP.

Agricultural runoff and urban storm runoff are anticipated as the leading contributors to NPSP (Islam *et al.*, 2018). This is due to the lack of absorption, inadequate use by plants and incorrect planting methods used in certain areas. During heavy rainfall seasons, runoff is easily produced and conveys these pollutants into water bodies thereby utterly affecting the water quality (Yang *et al.*, 2020). Increased concentration levels of nutrients such as nitrates, sulphates and phosphates are usually recovered in areas, where anthropological activities are largely practiced nearby water bodies. The enriched nutrients lead to the production of acids generated through the decomposition of fertilizers, leading to soil and rocks dissolution (Du Plessis, 2017).

Urban runoff that is not connected into a sewer could carry pollutants from industrial organic pollutants, combustion of fossil fuels, bacteria and metals into surface water (Landrigan *et al.*, 2020). Urban landscapes and gardens may also convey fertilizers and pesticides by runoffs into nearby water bodies. Industrial and municipal waste disposal sites adds to groundwater pollution (Islam *et al.,* 2018). These pollution sources can either be considered as point or non-point sources of pollution, based on the proportions of the disposal sites and the proportion of the receiving water body (Du Plessis, 2017). NPSP can be considered to be constant or seasonal. The effects differ based on the receiving water resource and its specific usage **(Poor *et al.,* 2006).**

2.6 South Africa’s water quality issues

South Africa faces a number of challenges with regard to water quality. Some of these are widely recognized, while less is known of the others (Griffin *et al.*, 2014). South Africa’s water quality is affected by natural processes such as seasonal trends, geology, climate and also anthropogenic activities (Abbaspour, 2011). The major threat to the country’s water supply is not the shortage of storage facilities but contamination by means of pollution of the available water resources (CSIR, 2010). The four major water quality concerns observed in South Africa are; sedimentation, salinity, microbial pollution (urban runoff) and eutrophication. Acidification has been included as well due to ages of unregulated operations from gold mines and sediments arising from mine tailings (DWS, 2015). A brief discussion of South Africa’s water quality concerns is provided in the preceding sections.

2.6.1 Salinization

Salinization is a persistent water quality concern throughout most of South Africa’s watercourses. Salinity is the total dissolved inorganic solids or salts in the water (not the individual ions) and is measured as total dissolved solids (TDS) (DEAT, 2006). High TDS levels are recorded during rainfall and wet seasons when there is an enhanced soil erosion. Other river systems are naturally saline due to their geological composition due to varying solubility of various minerals

(Mathebula, 2016). Furthermore, atmospheric deposits (e.g. sulphate salts) have also shown to increase salt loads in rivers (DWS, 2015). Natural salinization in most instances is observed in closed drainage basins of dry and semi-dry parts worldwide. The other regions are characterized through anthropogenic salinization (Rengasamy, 2006).

Anthropogenic activities contributing towards salinity includes: (i) municipal and industrial waste discharges; (ii) return irrigation flows hence; the Northern, Western and Eastern Cape river systems exhibit significant cumulative longitudinal salinity gradients because of industrial and irrigation return flows (Nordhaus *et al.*, 2009), (iii) urban runoff; (iv) surface mobilization of pollutants from mining, waste disposal sites and industrial operations (Volschenk *et al.,* 2005; Van Niekerk *et al.,* 2009). Enhanced salinity effects in watercourses roots salinization of irrigation soils leading to decreased crop productions, increased corrosion in domestic and industrial water delivery systems (pipes) and also causes alterations in freshwater biotic communities (DWS, 2015).

The Lower Vaal river, Olifants river, Breede and Crocodile river are considered as high risk salinization areas in South Africa. These salts arise from acid mine drainages (AMD) from the gold and coal-mining practices as well as runoffs from agricultural activities (CSIR, 2010). Similar to South Africa, Australia has a saline landscape, with agricultural domains encompassing large quantities of salt. The salts are locked deep within the soil profile, where they do not disturb plant development. The salt concentration within Australia's soil becomes a concern only when water is applied in large amounts. It was discovered that certain Australian land became salinized as a result of European cultivation methods practiced (Rahaman, 2013; Du Plessis, 2017).

2.6.2 Eutrophication

Eutrophication is the main and broadly known threat to the country's water quality. Eutrophication is the enrichment of nutrients such as nitrates and phosphates in excess of natural ratios (DWS, 2015). Eutrophication promotes the growth of microscopic green plants and algae, which stimulate the growth of cyanobacteria, posing harmful threats to the aquatic fauna and human users of the watercourse (DEAT, 2006; Griffin *et al.,* 2014). Nutrient enrichment leads to the depletion of oxygen in water bodies, resulting in mass mortalities of the aquatic organisms (Ramachandran, 2017). Eutrophication is instigated by the inflow of nutrients from the soil, rocks, and other natural features surrounding the surface water (Oberholster *et al.,* 2009). This process is uncontrollable and irreversible that is enhanced by the inputs of anthropogenic sourced nutrients predominantly through high organic matter contents, nitrogen dioxide (NO_2), nitrate (NO_3), phosphorus oxychloride ($POCl_3$), ammonium (NH_4) and high total alkalinity (TA). TDS enrichment and increased temperature have led to the overall deterioration of the water bodies (Van Ginkel, 2011; Panoramoi, 2015).

Eutrophication is a result of both indirect and direct causes:

- Indirect causes; includes the overcrowding of urban settlements and increased population growth, economic growth related to changes in catchment area, for instance, the construction of water storages in order to meet the requirements of the escalating population (DWS, 2002; Van Ginkel, 2011).

- Direct causes; consists of large amounts of discharge from WWTP, intensive farming practices, increased fertilizer usage to meet the demands of the steadily growing population, elevated nutrient polluted water discharge as well as weak agricultural applications (Van Ginkel, 2011).

A number of South African reservoirs exhibit signs of eutrophication and hypertrophic conditions (extreme nutrient concentrations) (DWAF, 2002; Thornton *et al.,* 2013; Matthews and Bernard, 2015). Eutrophication occurs across the globe in different parts of the world, for example, in North America, Jamaica and Eastern Europe rivers (Figure 6a) (Mendiondo, 2014). In South Africa, nutrient enrichment is linked with water bodies receiving large volumes of untreated waste water, agricultural runoff rich in fertilizer, industrial and mining pollutants (DWA, 2010b; CSIR, 2010). A number of South African reservoirs exhibit signs of eutrophication and hypertrophic conditions (extreme nutrient concentrations) (DWAF, 2002; Thornton *et al.,* 2013; Matthews and Bernard, 2015).

Eutrophication is evidently visible in the Blesbok Spruit, Hartebeespoort dam (Figure 6b) and the Barrage Reservoir. This issue is intensified as additional people migrate to urban areas, and their sewage systems discharging their wastes into watercourses (Van der Merwe-Botha, 2009). Since

South Africa has inadequate freshwater resources, it is urged that eutrophication of watercourses within the country to be taken seriously (Ginkel, 2011).

Figure 6: (a) Algal bloom in the North America's Lake Erie. (b) Blue-green algae forming a black crust on the Hartebeespoort dam in North-West province

Source: (Panoramoi, 2015 and Griffin *et al.,* 2014)

2.6.3 Urban runoff

The main sources of deteriorating microbiological water quality are urban runoffs from populated human settlements and overloaded sewage systems (DWS, 2015). Many waterborne pathogens are attributed to poor sanitation practices from poorly maintained or a lack of suitable sanitation infrastructure, which is a prevalent issue in South Africa (DEA, 2011). An example of this is observed in the Eastern Cape province in the Buffalo river, a highly populated area with no adequate sanitation infrastructure. The community consumes the water without any treatment, posing detrimental health risks. Surface water of the Buffalo river is of poor quality, with increased levels of bacterial quantities due to feacal pollution (Mathebula, 2017). The lack of sanitation infrastructure causes sewer overflows and forces the community to defecate in open spaces and during heavy rainfall events, the feaces are transported into the surrounding water bodies causing microbial contamination (Chigor *et al.,* 2013).

Microorganisms present in these contaminated water sources act as vectors for the spread of diseases such as gastroenteritis, cholera, hepatitis, typhoid fever, dysentery, salmonellosis, and infections (eye, skin and nose) (Musingafi, 2014). Majority of the waterborne disease causing pathogens are transmitted via the faecal-oral pathway, and the reservoirs for these microorganisms are normally animals, humans and sometimes the environment itself (Germs *et al.,* 2004). Urban runoff during rainy periods is also a major source of suspended sediment and heavy metals like; cadmium, chromium, manganese and iron (CSIR, 2010; DWA, 2010b; DWS, 2015).

2.6.4. Erosion and Sedimentation

Even though not documented as a worldwide water quality concern, soil erosion is a serious problem in South Africa. Soil erosion rates have increased significantly over the past decades due to human impacts (Van der Merwe-Botha, 2009). Majority of dams and rivers are affected by sedimentation and erosion. With regards to surface water, sedimentation is described as the movement and deposition of soil particles and other organic materials into the water courses (DWS, 2015). Large sediments recovered in surface water sources result from soil erosion processes. The presence of these sediments assists researchers to reflect on the natural geophysical and hydrological characteristics of catchments (Dallas and Day, 2004).

Sedimentation of surface water bodies modifies the chemistry water within water bodies, because these sediments transfer nutrients and lethal pollutants. In addition to sedimentation, the modification of the water chemistry is further intensified by eutrophication and pollution problems (Du Plessis, 2017). Sedimentation is an ongoing technical challenge still being faced by dam construction industries even after eras of research (Panoramoi,_2015)._Surface water degradation of the Yangtze river in China, is a perfect illustration of how unprecedented sedimentation and contamination of water has led to the eutrophication of Lake Udaisagar, India (Figure 7) (Panoramoi, 2015).

Sediments arising from over-grazing, poor agriculture activities, destruction of the riparian vegetation and physical disturbance of land are caused by industrial and urban developments, mine tailings have polluted the local water resources (CSIR, 2010; DWA, 2010b). Certain parts of the

West Witwatersrand and the East Soweto situated within the Upper Vaal WMA, are perfect illustrations of this (Van der Merwe-Botha, 2009).

Figure 7: Eutrophication of Lake Udaisagar in Udaipur, India

Source: (Panoramoi, 2015)

2.6.5 Acidification and alkalinisation

The pH of natural water is mainly determined by its geological and atmospheric influences while, the aquatic ecosystems' pH is determined by the biological traits and health of that system (DWS, 2015; Du Plessis, 2017). In South Africa, freshwater resources are naturally well buffered however, human-induced acidification from industrial effluents and mine drainage causes the pH to decrease, resulting in the mobilization of elements such as iron (Fe), sulphate (SO_4), aluminium (Al), cadmium (Cd), mercury (Hg), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), cobalt (Co), as well as zinc (Zn) (CSIR, 2010). This will possibly impact the biota, domestic, industrial and agricultural users and is also capable of causing unnatural colours in surface water resources and corrosion of metal equipment and appliances (DWA, 2010b).

South Africa has been predominantly interested in the effects and management requirements for acid mine drainage (AMD) (DWA, 2010b). AMD is described as the discharge of acidic water produced during and after mining activities and it affects both surface water and groundwater in the areas that it occurs (DWS, 2015). The acidic water dissolves salts leading to increased salinity, lowers pH levels and also mobilizes metals from mine activities and residue deposits. AMD is not only associated with surface water and groundwater pollution, it is also responsible for the degradation of soil quality and aquatic habitats, this is because heavy metals seep into the environment (Opitz and Timms, 2016).

Extensive coal and gold mining activities in parts of the Gauteng and Mpumalanga provinces and extensive copper mining at certain parts of the Northern Cape province (Figure 8a) has led to serious water quality issues in rivers near mining areas (Heath *et al.,* 2010). In order to manage the elevated salinity levels in these rivers, water was released from upstream impoundments for dilution, which in turn stressed water availability upstream of the affected areas (Ashton and Dabrowski, 2011; Dabrowski and De Klerk, 2013; Griffin *et al.,* 2014). Depicted in Figure 8b is an additional example of the environmental detriments of mining in the USA. This environmental effects, only became visible few years later in the Sacramento river, when the number of fish die-off were documented. Operations were continued regardless of the concern and further caused AMDs and deposited polluted sediment deposits to the bottom of the river, which endangered aquatic organisms downstream (Du Plessis, 2017).

Figure 8(a): AMD contamination at O'Kiep, Northern Cape (b): AMD pollution produced by the Iron Mountain mining, United States of America

Source: (Griffin *et al.,* 2014 and Swenty, 2016)

Alkalinisation in South Africa is regarded as an emerging water quality challenge. Evaluations made by DWS points out that, general pH appears to be increasing, causing the river systems to be more alkaline (DWS, 2015). This might indicate the possible side effects from activities like the current brine management, where neutralization with lime is a common practice.

The impact to surface water resources of these particular activities are not taken into serious consideration. It was further recommended that this phenomenon be investigated in more detail (DWS, 2015).

2.7 National water quality monitoring programmes

The deterioration of South Africa's water quality is a major threat to the country's ability to provide sufficient water of fitting quality to meet developmental, economic and basic human needs while ensuring environmental sustainability (DEAP, 2011). To assure that the water quality meets the developmental and environmental needs, it is therefore, necessary to monitor the quality of the watercourses as they are under increasing stress from persistent and emerging challenges (Garizi *et al.,* 2011). Water quality monitoring is used to make water services authorities (WSAs) aware of the current and emerging water quality concerns to regulate compliance with drinking water standards and also, to protect other water uses. Assessments based on monitoring data assist law makers and water managers to measure the efficiency of water policies, determine if water quality is getting better or is deteriorating, and to develop new policies to best protect the environment and human health (Walakira and Okot-okumu, 2011). Currently, in South Africa, there are about 11 water quality monitoring programmes developed by the Department of Water Affairs (DWA) with the aim to assess the country's water resource status and to monitor its water quality trends (DEAP, 2011). Some of these monitoring programmes are summarized below.

2.7.1 The National Chemical Monitoring Programme (NCMP)

NCMP is well established in the country with hundreds of active monitoring sites, assessing both surface and groundwater. Adequate and valid data is present for certain water chemistry parameters of surface waters e.g. pH, major ions, salinity and major nutrients. However, data on oxygen levels, temperature and turbidity is limited while data for metals and organic pollutants is scanty (DWA, 2010c; DEAP, 2O11; DWA, 2011a,b; Griffin *et al.,* 2014; DWS, 2015).

2.7.2 The National Eutrophication Monitoring Programme (NEMP)

NEMP collects different water quality parameters including chlorophyll levels from approximately 80 reservoirs across the country. NEMP formulated guidelines for monitoring as well as management of urban impoundments focusing on local authorities and other local water managers (DWA, 2010c; DEAP, 2O11; DWA, 2011a,b; Griffin *et al.,* 2014; DWS, 2015).

2.7.3 The National Microbial Monitoring Programme (NMMP)

NMMP monitors the degree of faecal contamination of surface water in the country. The programme aims to identify and prioritize regions in the country, where health risks are elevated. The programme also aims to assess the status, trends and health risks of faecal pollution in these regions. Additionally, NMMP also assesses the effectiveness of measures taken to protect surface water resources against these threats. The DWA and the Water Resource Commission (WRC) have developed other monitoring initiatives for diseases caused by waterborne microorganisms. The initiatives cover a wider range of diseases and not limited to those associated with faecal pollution only (DWA, 2010c; DEAP, 2O11; DWA, 2011a, b; Griffin *et al.,* 2014; DWS, 2015).

2.7.4 The National Toxicant Monitoring Programme (NTMP)

NTMP aims to measure, assess and report on the status and trends in toxicants in surface and groundwater resources across the country. The programme was introduced to respond to the increasing distress about the presence and level of toxicants in water resources (DWA, 2010c; DEAP, 2O11; DWA, 2011a, b; Griffin *et al.,* 2014; DWS, 2015).

Research conducted for the WRC revealed that the geographical coverage of some aspects of water quality in the country is good while for others it is poor. Reporting is also limited excluding research for the NMMP, while the river reports only cover certain regions of the country (Griffin *et al.,* 2014). Access to these reports and monitoring data is relatively poor.

2.8 Chapter summary

Water resources are limited in South Africa, and thus constitute a major constraint to continued economic development and the sustainable livelihoods of people. An additional problem adding to this demand is water quality. The country's water quality is affected by both anthropogenic activities and natural influences, climate warming being the main driving natural activity. Anthropogenic activities responsible for polluting the scarce freshwater originates from agriculture, mining, industries and power generation evident in many areas. Water quality concerns that affect South African water bodies include; eutrophication, salinization, sedimentation, urban runoff, microbial contamination, and acid mine drainage (AMD). To assure that South Africa's water quality meets the developmental and environmental needs, the Department of Water Affairs (DWA) developed about 11 water quality monitoring programmes with the aim to monitor the quality status of the water resources and track water quality trends as they are under increasing stress from persistent and emerging challenges.

From the author's perspective, more preparations and monitoring sites are still required since the geographical coverage of some aspects of water quality in the country is good while for others it is poor. Also, reported data from these programmes is limited due to challenges like the; budget constraint of running the programmes, lack of personnel or samplers in some water management areas, and the persistent pressure to expand the networks due to increase in demand for more reliable data or information.

CHAPTER THREE

3. METHODOLOGY

In this section, the principles and applications of methods used to determine levels of selected physico-chemical and microbiological parameters are discussed as well as statistical approaches used to detect the sources of pollution along the Groenwater Spruit.

3.1 Data collection

3.1.1 Methods of water sampling and frequency

Sampling and analysis for the selected physico-chemical and the microbiological parameters was done during the wet and dry seasons of 2021. The sampling periods were strategically selected to observe the seasonal variations of water quality. Six sites were selected along the Groenwater Spruit (Figure 9) for water sampling. These precise sampling locations were selected based on the predominant land use and that they have the more representative sample, where the sampling site corresponds to a well-mixed area as per the ISO 5667-6:2014 water quality sampling guidelines.

Grab sampling method was used for the water sample collection. Water samples were collected using sterile one-litre plastic bottles, thoroughly pre-washed with distilled water and rinsed with the sample water to be collected to avoid any possible contamination. Water samples were collected in triplicate for precision purposes. The samples were labelled and transported in cooler boxes at 4 °C to the Centre of Applied Radiation Science and Technology (CARST) facilities, the accredited United States Environmental Protection Agency (USEAP) and National Institute of Standards and technology (NIST) laboratory at North-West University (NWU), Mafikeng campus for *ex-situ* analysis of water quality parameters.

3.2 Data analysis

3.2.1. Physico-chemical analysis

Various analytical procedures were used to collect data on physico-chemical determinants of the selected sampling points. Portable hand held apparatus and laboratory instruments were used to measure the selected surface water parameters. To obtain accurate and reliable test results, the equipment used were first calibrated following the manufacturers' guidelines before analysis took place.

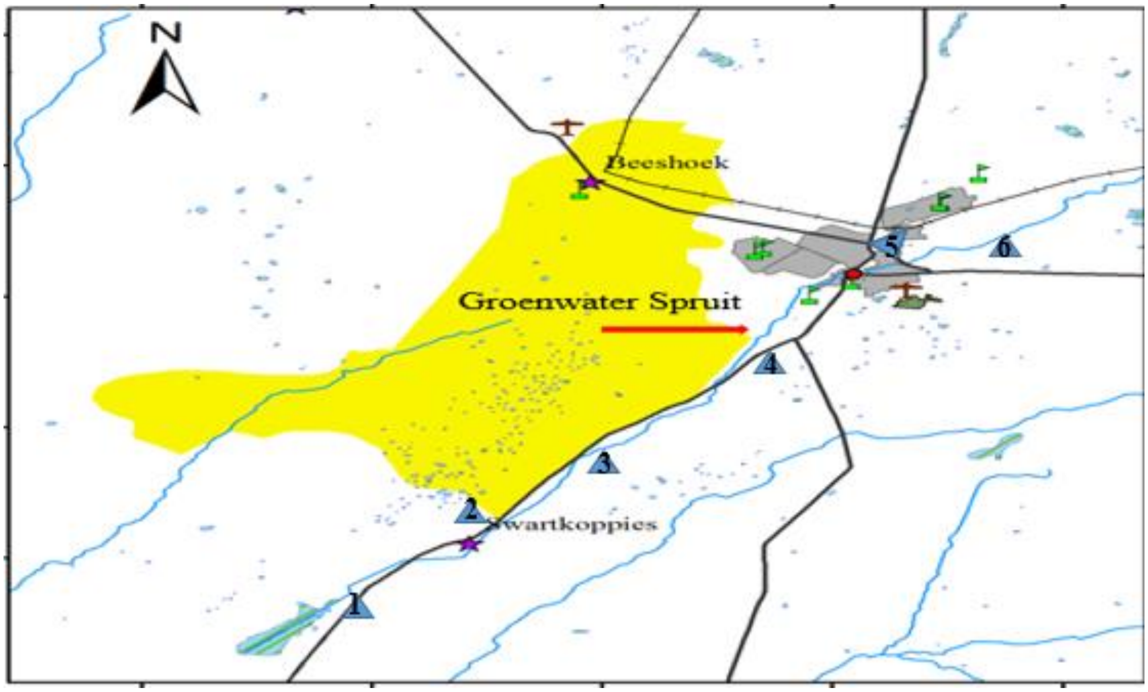

Figure 9: Map indicating sampling points of the Groenwater Spruit.

Sampling sites description

Sample site 1

Sample site 2 and site 3

Sample site 5 and site 6

(i*) In-situ* analysis

Some parameters were measured *in-situ* and they include temperature, TDS and electrical conductivity (EC) by way of YSI 650 water meter. YSI 650 water meter was used in the data for data collection because it is lightweight, compact, versatile, and easy to operate, and provides fast accurate measurements. Before each measurement was taken, the probe and measuring beaker were washed with distilled water and then rinsed with the specific water sample to be measured. The rest of the parameters were analysed in the laboratory.

(ii) *Ex-situ* analysis

The pH of the water samples and dissolved oxygen (DO) were measured at the NWU laboratories using a 2700 series benchtop meter. The probe was washed with distilled water before and after each measurement. Additional parameters selected for analysis are depicted in Table 1.

Table 1: Parameters and method used for laboratory analysis

Parameter	**Method and equipment**	**Units**
Sulphates	Ion chromatography- ISO 10304-2	mg/L
Nitrates	Ion chromatography- ISO 10304-2	mg/L
Phosphates	Ion chromatography- ISO 10304-2	mg/L
Manganese	ICP-MS NexION 2000	mg/L
Iron	ICP-MS NexION 2000	mg/L
Arsenic	ICP-MS NexION 2000	mg/L
Chromium	ICP-MS NexION 2000	mg/L

(1) Ion chromatography (IC) analysis

Ion chromatography (IC) is a subsection of liquid chromatography used to determine ionic solutes like, cations, inorganic anions, transition metals, bases as well as low molecular-weight organic acids (Jackson, 2000). As the composition of water samples can be altered during or after the sampling, this study selected ion chromatography for sample analysis since it offers certain advantageous features over the classic wet methods for determinations of organic and inorganic ions in water samples such as: high sensitivity, short analysis time and selectivity in samples with complex matrices and uses safe, cheap, and environmentally friendly chemicals to list a few traits (Weiss, 2016).

During the determination of anions (NO_3^-, NO_2^- PO_4^{3-}, SO_4) by IC, the following procedures were followed as per ISO - standards. The water samples were prepared by suspending the water samples in a chromatograms of anions standard solution to remove ionic species present. Water from the extraction of the sample was then injected into the carrier fluid. Ionic separation of the sample took place. The anions in a sample were moved through the system by an ionic solution (An eluent of 1.7 mM Na_2CO_3 + 1.6 mM $NaHCO_3$ at a flow rate of 0.85 mL/min. 20 µL), and then the various anions were further separated in a column (Metrohm Metrosep A Supp 3 (250 × 4.6 mm) column) with an ion-exchange resin (stationary phase). A suppressed conductivity detector at the end of the column was used to measure the quantity of the selected anions and from the process, a chromatogram was produced that represented the sample components (Michalski, 2018).

(2) Inductively coupled plasma mass spectrophotometry (ICP-MS) analysis

The determination for total concentrations of trace metals (As, Cr, Fe, and Mn) were measured using ICP-MS - NexION 2000. The NexION 2000's three gas channel flexibility offers the ability to target various interferences in order to get the best method detection limits. ICP-MS was also chosen for this study because it is more sensitive than other methods, fast, can run multiple elements at once Disadvantages is that it is expensive than other options (Pruszkowski *et al.*, 2017).

Before analysis, nitric acid was added to the water samples at a low concentration (0.4 mL) for sample preservation. A minimum of 5 mL of standard solution were used for each run. The water samples with a depth of 8 mm were introduced into an argon plasma (carrier gas running at 0.99 L/min) in a form of aerosol droplets. The plasma dried the aerosol, dissociated the molecules and then removed the electrons from the components, forming singly-charged ions. These ions were directed into a mass filtering device known as the mass spectrometer. The samples were running at a temperature of 2°C. Upon exiting the mass spectrometer, ions touched the electron multiplier serving as a detector. The impact of these ions released a cascade of electrons, which were amplified until they became a measureable pulse. The software ELAN was used to compare the intensities obtained from the measured pulses to those from obtained from the standards, which were used to produce the calibration curve to determine the concentration of the selected elements (Bazilio and Weinrich, 2012).

3.2.2 Microbiological analysis

The presence of total coliforms and *E. coli* (bacterial indicator for faecal contamination) were analysed using the membrane filtration method. Water samples were analysed within 24 hours after collection. Aliquots of 100 mL from each sample were filtered through a 0.45 µm filtering paper. The filters were then placed on mFC and mENDO agar plates respectively. The plates were incubated aerobically at 45 °C and 37 °C for 24 hours respectively. The presence of blue and metallic sheen colonies on mFC and mENDO agar plates were used to identify the presence of faecal contamination (USEPA, 2009).

3.3 Statistical analysis

Multivariate analysis of the Groenwater Spruit water quality data set was performed through the principal component analysis (PCA) technique to determine the point and non-point sources of contamination (Liu *et al.*, 2003). PCA was performed using statistical package for social scientists (SPSS) v.29.0 software. Some studies (Najah and Khan, 2012; Elipek *et al.*, 2017) used PCA to summarize the statistical correlation among physico-chemical parameters within the water samples. However, in this study, PCA was applied to parameters (and not to sampling points) in order to determine the possible sources of contamination. The method is useful in the reduction of environmental data and the interpretation of physico-chemical and biological measurements (Razmkhah *et al.*, 2010; Kebede and Kebedee, 2012), to identify factors influencing water systems, to establish suitable water management strategies and they are also useful for the rapid solutions for pollution concerns (Akpan, 2013; Al-Badaii *et al.*, 2013). The fundamental concept of PCA is to lessen the dimensionality of multivariate data sets by obtaining new set of variables, while retaining much variation present in the datasets without any loss of the original information. This is accomplished by converting the original dataset into new set of variables called the principal components (PCs) (Wood, 2009; Mahmood, 2018). In addition, one-way analysis of variance (ANOVA) was applied to compare means of the sampling points and between the seasons and to test for the significance of each water quality parameter (Park, 2005). The statistics were performed at 95% confidence interval and at 0.05% alpha.

3.4. Evaluation of the water quality data against guidelines and standards

The results of the Groenwater Spruit water quality were assessed against both international and national guidelines and standards namely; the World Health Organization (WHO, 2011) drinking water guidelines, the South African National Standards SANS: 241(2015) domestic water use standards and the South African water quality guidelines for agricultural water use of the Department of Water Affairs and Forestry (DWAF, 1996). This was carried out to give indication for the fitness for use and potential impacts on the aquatic environment.

3.5 Chapter summary

This chapter outlined the methods and techniques used to assess the water quality of the Groenwater Spruit. Sampling of the selected physico-chemical and the microbiological parameters of the Groenwater Spruit was conducted during the dry and wet seasons of 2021 to observe the seasonal variations of water quality. The obtained results of the Groenwater Spruit water quality were assessed against the WHO (2011), SANS (2015) and DWAF (1996) for domestic water use standards and agricultural water use guidelines to give indication for the fitness for use and potential impacts on the aquatic environment. Furthermore, statistical analyses were applied to sampling points to determine the possible sources of contamination and compare seasonal variations. The next chapter deals with the results and discussion.

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

This chapter presents results obtained from the selected sampling sites along the Groenwater Spruit located within the Tsantsabane local municipality jurisdiction. The chapter begins with results of the physico-chemical analysis for the sampled seasons presented in section 4.1, followed by microbiological results in section 4.2. A discussion of the statistical analysis from SPSS of all the physico-chemical and microbiological data for the 2021 sampled seasons is presented in section 4.3, which is followed by a summary of the obtained results in section 4.4.

4.1. Physico-chemical concentration of the Groenwater Spruit surface water

The mean and standard deviation of the sampled physical parameters were calculated and the obtained results are presented in Tables 2 and 3. The results obtained depict the physical characteristics of the Groenwater Spruit water quality.

4.1.1. Temperature

Majority of surface water quality parameters are affected by environmental conditions such as solar radiation, precipitation, atmospheric pressure as well as temperature (Pompei *et al.*, 2020). Temperature affects surface water quality as it controls oxygen levels, influencing the rate of chemical and biological reactions within aquatic ecosystems (Whitehead *et al.*, 2009). Although temperature influences the overall physico-chemical and biological quality of water, there are no stipulated guideline values for agricultural and domestic water use. For this study, the temperature mean range was between 21 ℃ to 23 ℃ and 23 ℃ to 25.2 ℃ for dry and wet seasons respectively (Table 2).

The temperature of the water samples varied from season to season ($P = 0.04$). ANOVA results showed that there was significant difference ($P < 0.05$) in temperature at all sites except for sites 1 and 2 during the dry season and sites 4 and 6 during the wet season. This could be explained by inflow of water from tributaries with lower water temperatures along the quaternary catchments D73A and D73B stretch. In the study area, the dry season was associated with lower temperatures ranging between 20 °C and 23 °C (Li *et al.*, 2020).

Table 2: Temperature and pH analysis results

Sample site	**Temperature (°C)**				**pH**			
	Dry season	P-value	Wet season	P-value	Dry season	P-value	Wet season	P-value
1	20 ± 0.3	0.07	23 ± 1.7	0.01	10.9 ± 0	0	9.7 ± 0.1	0.01
2	22 ± 0.6	0.30	25 ± 0.1	0	11.6 ± 0.1	0.01	10 ± 0.1	0
3	23 ± 0.1	0	25 ± 0.2	0.04	11.6 ± 0	0	10 ± 0	0
4	22 ± 0.2	0.04	24 ± 1.5	0.06	10.3 ± 0	0	10 ± 0	1
5	21 ± 0.1	0	25 ± 0.3	0	11.1 ± 0	0	8.4 ± 0	0
6	21 ± 0.1	0.01	24 ± 0.4	0.12	10.6 ± 0	0	9.2 ± 0	-0.33
WHO (2011)	NS				6.5- 8.5			
SANS (2015)	NS				5.0-9.7			
DWAF (1996)	NS				6.5-8.4			

Note: NS = No standard

4.1.2. pH

The pH scale is used to explain how acidic or alkaline an aqueous solution is. Water ranges from a scale of 1 to 14, with the natural pH of water being approximately 7 (Dobrowksy *et al.*, 2014). Within aquatic ecosystems, pH is known to influence the solubility of lethal metals that might be harmful to human health and aquatic organisms (Nienie *et al.*, 2017). Table 2 shows that for both sampled seasons, all sites were within the upper threshold of pH 9 (alkaline) with an exception to site 5 only (weakly alkaline) during the wet season. This may be attributed to the fact that Postmasburg soil is very rich in manganese and iron ore hence the large scale mining activities contributes to higher pH levels. A study conducted by Pawar (2010), revealed that deposited minerals also increase the alkalinity levels of water resources. Furthermore, the photosynthesis of phytoplankton (aquatic plants) contributes to the increase of pH levels in aquatic ecosystems. The elimination of free carbon dioxide during photosynthesis, was discovered to increase pH levels (Masere *et al*., 2012; Sakai *et al*, 2013). This supports arguments by Kale (2014), which states that during photosynthesis, more carbon dioxide is absorbed, resulting in higher pH levels.

The measured pH values varied significantly according to the seasonal variation. Groenwater Spruit's pH was above the WHO (2011) water quality standards (6.5 - 8.5), SANS (2015), (5 - 9.7) domestic water quality use standards and DWAF (1996), (6.5 - 8.4) agricultural water quality use guidelines especially during the dry season. The sampling sites geology (Appendix 1) could perhaps be responsible for the high pH concentrations of the surface water (Nienie *et al*., 2017). The minimum pH average measured, ranged between 10.3 and 8.4 while the maximum average measured, ranged between 11.6 and 10 for the dry and wet seasons, respectively. Kapembo *et al*. (2016), carried out a study in a comparable environment, which revealed the same trend with the pH values during the dry and wet seasons as were the results obtained in this study. ANOVA further noted a significant difference ($P \leq 0.05$) in pH at all sites during the dry season and no significant difference was noted at site 4 ($P > 0.05$) during the wet season. This significant difference could be due to anthropogenic activities such as point source pollution derived from agricultural runoffs and waste water discharge (Purushothaman *et al.*, 2013; Utom *et al.*, 2013).

4.1.3. Total dissolved solids (TDS)

TDS consist of major inorganic salts; carbonates, potassium, bicarbonates, magnesium, chlorides, sulphates, iron, phosphates and nitrates of calcium, sodium etc. and minor amounts of organic matter (Ravikumar *et al*., 2013). Table 3 shows the mean concentration of TDS measured in this study, which ranged between 174 mg/L to 306 mg/L and 171 mg/L to 451 mg/L during the dry and wet seasons, respectively. The mean concentration of all sampled sites shows that the dry season (256.5 mg/L) has a lower TDS concentration compared to the wet season (268.3 mg/L) as large amounts of sediment loads are mobilized during the wet seasons. High TDS concentrations during the wet season are due to the influence of activities such as municipal and industrial effluents (Mahananda, 2010). Garg *et al*. (2010) and Kirubavathy *et al*. (2005) recorded results similar to this study with high TDS values during the wet season.

One-way ANOVA showed no significant variation ($P > 0.05$) among the values of TDS at all sites between the seasons and between all the sampled sites for the dry and wet seasons. All sampling sites during both seasons were within the SANS (2015), (≤ 1200 mg/L) domestic water use standards while, none of the sampled sites during both seasons complied with the DWAF (1996), (≤ 0.02 mg/L) agricultural water use guidelines. These results revealed that water from the Groenwater Spruit is suitable for human consumption but could pose potential negative effects for agriculture. Irrigation with water containing high TDS levels introduces salts into the soil profile. Water with high TDS levels when used for irrigation, it introduces salts into the soil horizons. When little or no salt leaching occurs, these salts accumulate resulting in saline soils. Crop production reduces when crops are grown on saline soils, this is because crops are sensitive to increased soil salinity (DWAF, 1996).

Table 3: Total dissolved solids and electric conductivity analysis results

Sample site	**TDS (mg/L)**				**EC (µS/cm)**			
	Dry season	P-value	Wet season	P-value	Dry season	P-value	Wet season	P-value
1	174 ± 1	1	171 ± 0	0.1	350.7 ± 2.5	6.3	341.3 ± 1.5	2.3
2	235.3 ± 61.9	0.3	253.7 ± 1.2	1.3	543.3 ± 0.6	0.3	520 ± 9.9	97
3	279.7 ± 0.6	38.2	223.3 ± 1.5	2.3	569.7 ± 15.9	252.3	451.7 ± 0.6	0.3
4	322.7 ± 5.8	33.3	271 ± 1.7	3	624.3 ± 2.5	6.3	541.3 ± 4	16.3
5	260.3 ± 1.5	0.2	451 ± 1.7	3	521.7 ± 1.5	2.3	224.3 ± 1.2	1.3
6	266.7 ± 0.6	0.3	239.7 ± 1.5	2.3	534 ± 1	1	482 ± 2.7	7
WHO (2011)	NS				≤ 200			
SANS (2014)	≤ 1200				≤ 170			
DWAF (1996)	0-0.02				≤ 540			

Note: NS = No standard

4.1.4. Electrical conductivity (EC)

The EC values give an estimation of ions present in water such as carbonate, magnesium and bicarbonate carrying electrical charge(s). When these chemical elements are present, water is provided with the ability to conduct electricity (DWAF, 1996). For this study, EC average values ranged from 350.7 µS/cm to 624.3 µS/cm and 224.3 µS/cm to 541.3 µS/cm during the dry and wet seasons respectively as depicted in Table 3. All sampled sites from both seasons were non-compliant to the set WHO (2011), (≤ 200 µS/cm) and SANS (2015), (≤ 170 µS/cm) domestic water quality use standards. Agricultural water quality use guidelines by DWAF (1996), (≤ 540 µS/cm) was met by sites 1, 5 and 6 during the dry season and all of the sampled sites during the wet season with the exception to site 4 (541.3 µS/cm).

High EC values were recorded during the dry season sampled water. Verma *et al.* (2013) and Anhwange *et al.* (2012) observed that moderately high to very high EC values are mostly recorded during dry seasons while low values are recorded in wet seasons. Increased EC values during dry seasons are normally caused by evaporation, leading to increased ions concentration. The reduced conductivity in the wet seasons might be because of the high rainfall, which lowers the level of dissolved solids by dilution of water (Menció *et al.*, 2017). One-way ANOVA showed no significant variation among the values of EC between all the sites and for both sampled seasons ($P > 0.05$).

High concentrations of TDS in domestic water cause an unpleasant taste to water and may also harmfully affect the kidneys function, have laxative effect and also have adverse effects of sodium on certain cardiac patients and hypertension sufferers (Mohsin *et al.*, 2013). With regards to agricultural water use, high concentrations of TDS similar to EC, reduces crop yields when grown on high salt affected soils (Bauder *et al.*, 2011).

4.2. Chemical properties

4.2.1. Dissolved oxygen (DO)

Dissolved oxygen is the maximum concentration of oxygen with the ability to dissolve in water (Rao and Rao, 2010). DO fluctuates daily, seasonally and with variation in water temperature. DO parameter is used to assess the waste assimilative capacity of the waters (Wavde and Arjun, 2010).

The wet sampled period seasonal DO mean concentration was found to be lesser compared to the dry sampled period concentration. DO seasonal mean values ranged from 90 mg/L to 96.9 mg/L and 87 mg/L to 96.9 mg/L for the dry and wet seasons, respectively (Table 4). The temperature mean range recorded in this study was between 21 ℃ to 23 ℃ and 23 ℃ to 25.2 ℃ for the dry and wet seasons respectively, with higher temperatures during the wet season. The findings of Ali *et al.* (2016), on the correlation between higher temperatures and low DO concentrations supports the results obtained from this study.

The low DO levels for the Groenwater Spruit water samples are possibly due to the result of nitrification activity along the catchment area (Strady *et al.*, 2017). Biological nitrification is a process mediated by microbes during the oxidation of ammonia to remove nitrogenous compounds from waste waters (Norton and Stark, 2011). Discharging effluents containing ammonia into receiving streams has a direct lethal effect on aquatic organisms, causing oxygen depletion (Ward, 2018). Hence, it is necessary that domestic and industrial wastewater treatment plants remove the ammonia before discharging the treated water.

No significant difference was noted between the two seasons as well as between the sampled sites during the dry sampling period ($P > 0.05$). A significant variation was noted at sites 2 ($P = 0.02$) and 6 ($P = 0$) during the wet period samplings, respectively. The variation could have been due to the input of sewage effluents from the Tsantsabane sewage treatment plant. . The effluents may have had lowered the concentration of DO recorded at sampling site 6 (87.4 mg/L), since the sewage effluent discharged undergoes biodegradation, depleting oxygen in water bodies (Masundire, 2013).

Table 4: Dissolved oxygen and sulphates analysis results

Sample site	**DO (mg/L)**				**Sulphates SO_4 (mg/L)**			
	Dry season	P-value	Wet season	P-value	Dry season	P-value	Wet season	P-value
1	93.1 ± 0.1	0	90.1 ± 0.3	0.01	84.7 ± 7.7	178.8	9.7 ± 0.1	0.13
2	90.2 ± 2.9	8.7	95.6 ± 0.2	0.02	<1	0	10 ± 0.1	0
3	95.8 ± 1.6	2.4	94.1 ± 0.3	0.07	63 ± 5.8	68.5	10 ± 0	0
4	95.3 ± 0.8	0.6	93.1 ± 0.6	1	<1	0	10 ± 0	0
5	96.9 ± 2.4	5.9	91.9 ± 2.4	0.1	<1	0	8.4 ± 0	0
6	94.1 ± 2.1	4.4	87.4 ± 0.1	0	<1	0	9.2 ± 0	0
WHO (2011)	NS				≤ 500			
SANS (2015)	NS				≤ 500			
DWAF (1996)	6.0-9.0				NS			

Note: NS = No standard

Although high DO concentrations show less water pollution as high DO means that less organic matter is decomposed in the water course (Masundire, 2013), the high DO concentrations obtained in this study during both seasons did not comply with the DWAF (1996), standard for the agricultural water use limit range of 6.0 - 9.0 mg/L. Although DO concentrations were above the agricultural guidelines, there has been no direct effects noted for agricultural use.

4.2.2. Sulphates

Sulphates occur naturally in the environment as a constituent of the sulphur cycle (WHO, 2011). During the sulphur cycle terrestrial process, sulphate (evaporites) and sulphide-containing rocks and minerals (barite, epsomite and gypsum) are first eroded, releasing the stored sulphur into the environment. When the sulphur is mixed with oxygen, it is then converted into sulphate (SO_4^{2-})

(WHO, 2004b; Bashir *et al.*, 2012). Besides the natural occurrence, sulphates are also introduced into the environment through various anthropogenic activities such as; the discharge from mines, agricultural, industrial and domestic waste water into surface water (Ukpong and Abaraogu, 2015).

Results of this study revealed that the majority of the sampling sites measured sulphate values < 1.0 mg/L as shown in Table 4. The undetectable sulphate values may be due analytical error based on the small sample used or sulphates are gradually absorbed by a large number of aquatic organisms since they are an essential mineral, providing good nutrients for both plants and aquatic organisms (Rückert, 2016). Water samples from both seasons were acceptable for domestic use as per the SANS (2015), (≤ 500 mg/L) and WHO (2011), (≤ 500 mg/L) standards. No agricultural water use standards were set by DWAF. Due to concentration fluctuations, ANOVA noted a significant variation (P = 0) between most sampled sites during both seasons, and there was no significant variation between the sampled seasons. The land uses prevalent in these sites such as the discharge from agricultural and domestic waste water into Groenwater Spruit could explain the variations along the Groenwater Spruit.

4.2.3. Nitrates

Nitrates are a form of nitrogen found in various forms in terrestrial and aquatic ecosystems. Nitrates are essential plant nutrients but, in excess levels, they are capable of causing significant water quality problems (Irenosen *et al.*, 2012). Naturally, nitrate concentrations in groundwater and surface water is normally low and elevated as a result of anthropogenic activities (Ravikumar *et al.*, 2013). Table 5 depict that the dry and wet period water sampled sites recorded nitrate concentrations above the set SANS (2015), (≤ 11 mg/L) standard with minimum concentrations of 19.3 mg/L and 13.2 mg/L for the dry and wet seasons, respectively.

Contrary to this, all sampled sites during both seasons had nitrate concentrations within WHO (2011), (≤50) limits with maximum concentrations of 33.9 mg/L and 28 mg/L for the dry and wet seasons; respectively. The elevated Groenwater Spruit nitrate concentrations during the dry season are caused by less dilution of effluents from waste water treatment plants (Van Vliet and Zwolsman, 2008) and animal waste (droppings) since animals were present in most parts of the river during sampling.

The lower concentrations of nitrate along the Groenwater Spruit is explained by the increased water supply from soil leaching and overland flow during wet periods (Van Vliet and Zwolsman, 2008). However, the results showed higher nitrate concentrations during the wet season for sites 5 and 6 (downstream) possibly as a result of the increased mixing of stream flow or the rise of concentrations originating from waste water discharges since these two sites are located near the Tsantsabane waste water treatment plant (Strady *et al.*, 2017). There was no significant variance (P > 0.05) between all sites during both the wet and dry sampled seasons. However, ANOVA noted a significant variation of the total nitrate concentration between the wet and dry sampled seasons. The high nitrate concentrations obtained during the wet season was not expected. Normally, the increased river volume during the wet season is known to have a dilution effect on pollutant levels (Emeka *et al.*, 2009).

Table 5: Nitrates and phosphate analysis results

Sample site	**Nitrates (mg/L)**				**Phosphate (mg/L)**			
	Dry season	P-value	Wet season	P-value	Dry season	P-value	Wet season	P-value
1	25.3 ± 2.4	5.8	14.6 ± 0.9	0.7	104.5 ± 13.6	18.6	8.4 ± 0.9	0.9
2	21.6 ± 7.1	50	14 ± 0.3	0.1	8.55 ± 7.8	6.7	77.2 ± 19.9	39.7
3	33.9 ± 22.8	52.1	13.7 ± 0.1	0.2	12.4 ± 1.9	3.6	12 ± 11.5	13.2
4	31.6 ± 23.1	53.4	13.2 ± 0.4	0.2	6.8 ± 1.4	2.1	2.6 ± 0.1	0.01
5	30.8 ± 21.7	47.1	26.6 ± 18.9	35.6	580.6 ± 37.8	21.5	234 ± 17.9	32.2
6	19.3 ± 6.2	37.9	28 ± 20.9	43.8	5.7 ± 0.1	0.01	119.2 ± 15.7	24.8
WHO (2011)	≤50				NS			
SANS (2015)	≤ 11				NS			
DWAF (1996)	≤30				≤0.5			

Note: NS = No standard

In this study, the high nitrate concentrations in the Groenwater Spruit could be attributed to accumulation of sewage sludge from the WWTP during the dry season and are then leached into the river during the wet season through runoff.

Overall, the quality of Groenwater Spruit water with respect to the South African standards (2015), (SANS ≤ 11 mg/L) was found to be unfit for domestic use, which could possibly cause methaemoglobinaemia (Chan, 2011). When water with high nitrate concentration is consumed, nitrite reacts with haemoglobin (the oxygen carrying red blood pigment) forming methaemoglobin, which is incapable of carrying oxygen. This reaction can be hazardous in infants (Johnson, 2019). All of the sites were within the set agricultural water use standard with the exception to 3 sites due to less dilution. Nonetheless, high concentration in agriculture may motivate extreme vegetative development and cause lodging, slower crop ripeness and poor crop quality (Laurent and Ruelland, 2011).

4.2.4. Phosphorus

Phosphorus is usually present in natural water as phosphates. Phosphorus is an essential element for plant life hence it is commonly used as a fertilizer (Fadiran *et al.*, 2008). Soil erosion is known to be a major contributor of phosphorus to watercourses (Berhe *et al.*, 2018). The total phosphate concentrations of the Groenwater Spruit depicted much variation across the river profile for both seasons (Table 5). The lowest mean concentration was found at site 6 (5.7 mg/L) and site 4 (2.6 mg/L) for dry and wet sampled periods, while the highest mean total phosphate concentration was recorded at site 5 (580 mg/L and 234 mg/L) for both seasons.

The relatively high levels of phosphate observed at sites 2, 5 and 6 during the wet season could be due to animal and human waste discharges as well as surface runoffs. The decreased concentrations noted at sites 1, 3 and 4 during the wet season may possibly be explained by increased inflow of water from the tributaries along the quaternary catchments D73A and D73B stretch. The low water circulation during the dry season could explain the high content of phosphate as noted at sites 1 and 5. Furthermore, site 1 was mostly used by livestock for drinking water, resulting in animal waste pollution. Site 5 was polluted by human waste since it is in close proximity to the WWTP.

It is evident from Table 5 that the total phosphate mean concentrations recorded for all the sampled sites in both seasons were above the recommended DWAF (1996), concentration guidelines of 0.5 mg/l. Thus, the water from Groenwater Spruit may not be suitable for irrigation. High phosphate in the irrigation water inhibits root development, leading to reduced and delayed crop production (Benzioni and Ventura, 1998).

No significant difference was noted between the seasons. Statistics noted a significant difference at sites 6 and 4 ($P = 0.01$) during the dry and wet seasons respectively. The significant difference could be explained by the anthropogenic activities and natural influences (e.g. erosion, manure and sewage) along the river, which could contribute to the high levels of phosphate (Drolc and Vrtovšek, 2010).

4.2.5. Manganese (Mn)

Manganese is an abundant element found in the Earth's crust. In groundwater, manganese is widespread. Numerous countries worldwide have areas with unacceptably high manganese concentrations (WHO, 2004). In this study, Mn mean concentration were lower during the dry period, ranging between 1.2 mg/L to 3.5 mg/L while high Mn values were recorded during the wet season ranging between 15.6 mg/L to 88.1 mg/L. Similar results were obtained by Musa *et al*. (2008), where they interpreted that the high Mn concentrations during wet periods are likely to be caused by leaching of Mn from the soil and municipal discharge by rain water into the river. However, the high levels of manganese in the water samples across all the sampling points of this study could be due to a number of manganese mining activities taking place within the Postmasburg town (AURECON, 2014). During the wet season, excessive surface run-offs from these mining activities deposit manganese elements in the surface water with higher levels accumulating at the downstream (site 4, 5 and 6) (Kaonga *et al.* 2010). Factors influencing the downstream Mn accumulation in the Groenwater Spruit include the occurrence of hydraulic disturbances (flow reversals) and rapidly varying flow velocities that could transport and suspend Mn particles (Brandhuber, 2015). During the dry season, water levels in most parts of the Groenwater Spruit dry up with little or no washing of municipal discharge into this river and its tributaries. Hence, the study recorded lower Mn levels during the dry season and higher levels during the wet season.

ANOVA showed no significant variation ($P > 0.05$) between the Mn values for both seasons at all the sampling sites (Table 6). The wet season samples were non-compliant to the SANS (2015), (≤ 0.5 mg/L) and DWAF (1996), (0.02 mg/L - 10 mg/L) standards. The dry season samples were also non-compliant to the SANS (2015), limits but acceptable for the DWAF (1996), agricultural water use guidelines (0.02mg/L - 10mg/L). The obtained non-compliant SANS (2015), domestic water use limits may cause deficiencies resulting in anemia, growth impairment and skeletal abnormalities (Ghosh *et al.*, 2020; Rahman *et al.*, 2019). In agriculture, plants differ in their sensitivity nature to Mn. Extreme Mn concentrations affect crop yield due to various plants' sensitivity to its uptake through plant roots (DWAF, 1996; Chen *et al.*, 2018).

Table 6: Manganese and iron analysis results

Sample site	**Manganese (Mn) (mg/L)**				**Iron (Fe) (mg/L)**			
	Dry season	P-value	Wet season	P-value	Dry season	P-value	Wet season	P-value
1	3.5 ± 4.9	24.2	15.6 ± 17	29.4	138.1 ± 133.7	17.9	251.7 ± 157.7	24.9
2	2.2 ± 3.1	9.3	26.7 ± 31.2	97.9	691.7 ± 67.4	45.4	785.3 ± 173.4	30.1
3	1.2 ± 1.7	2.8	31.7 ± 15.7	24.9	499.8 ± 115.5	13.4	796.9 ± 241.4	58.3
4	1.3 ± 1.7	3	53.7 ± 12.5	15.7	792.4 ± 98	96.6	708.3 ± 43.6	18.9
5	3.4 ± 3.1	9.3	88.1 ± 56.9	32.4	531.2 ± 9.4	88.3	647.2 ± 188.9	35.7
6	1.7 ± 1.3	1.7	46.7± 63.6	40.50	597.1 ± 2.5	6.1	592.1 ± 146.3	21.4
WHO (2011)	NS				NS			
SANS (2015)	≤ 0.5				≤ 2			
DWAF (1996)	0.02-10				5-20			

Note: NS = No standard

4.2.6. Iron (Fe)

Iron is the fourth abundant element in the Earth's crust and the most abundant heavy metal. Fe is found in surface waters as salts containing Fe (III) when the water pH is above 7 (Li *et al.*, 2016). Similar to manganese, iron ore is also found in excess in Postmasburg, due to the number of mining activities taking place within the Tsantsabane local municipality (AURECON, 2014). For the past three thousand years, iron ore has been extracted from immense reserves in chemical and classic rocks i.e. sedimentary, igneous and metamorphic. Iron ore is usually found as hematite (Fe_2O_3), magnetite ($Fe^{3+}{}_2O_4$) and goethite Fe (OH) (Morris, 2012).

Fe concentrations were relatively high during the dry season (138.1 mg/L - 792.4 mg/L) and the wet season (251.7 mg/L - 796.9 mg/L) as presented in Table 6. Samples from both seasons were not within the acceptable SANS (2015) and DWAF (1996) standard range 0 - 2 mg/L and 5 - 20 mg\L, respectively. ANOVA noted no significant variation ($P > 0.05$) among all the sampled sites for both sampling periods. A significant variation was noted between the seasons. Apart from the fact that iron occurs naturally in water through the weathering of rocks (White and Brantley, 2018) and that Postmasburg's soil has a high iron content, other contributing factors for the high recorded results are acidic mine water drainage, landfill leachates and sewage effluents (WHO, 2003). Iron-rich agricultural water interferes with photosynthesis, transpiration and respiration, leading to plant damage and eventual plant death (Kresović *et al.*, 2017). In terms of domestic water use, health effects may occur at extremely high Fe concentrations. Excessive consumption of Fe water may result in hemochromatosis, a tissue damage condition occurring as a consequence of Fe accumulation (Torres-Agustín *et al.*, 2013; Rahman *et al.*, 2021). In addition, high iron in water content leads to an overload, which can cause diabetes, kidney, liver, pancreas and heart damage, and cardiovascular diseases among others (Powers, *et al.*, 2003; Kell, 2010).

4.2.7. Arsenic (As)

Heavy metal are metals and metalloids with a high density that is harmful at low concentrations, and includes cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and arsenic (As) to mention few (Sharma *et al.*, 2014). Although some of these heavy metals are vital for the health of humans at low concentrations due to their co-enzymatic role, others are harmful at any concentration level

(MacFarlane *et al.*, 2003). Rapid urbanization and industrialization caused an increased mobilization rate of these metals into watercourses (Tue *et al.*, 2012).

Arsenic is naturally recovered on the earth's crust and is distributed throughout the environment in the land, air and water. It is very toxic in its inorganic form (Flanagan *et al.*, 2012). Societies are exposed to increased levels of inorganic arsenic by drinking contaminated water, using contaminated water for cooking and irrigation of food crops, eating contaminated food and through smoking tobacco and industrial processes (Quansah *et al.*, 2015).

The levels of As in the surface water detected in the current study are presented in Table 7. The average concentrations of As detected in surface water collected during the dry and wet seasons ranged between 0.7-2.2 mg/L and 0.9-2.9 mg/L, respectively. The recorded As concentration from both the sampled seasons complied to the SANS (2015) domestic water use standard (≤ 10 mg/L). Contrary to this, there was no compliance from both sampled seasons for the set WHO (2011), limit of 0.01 mg\L. Concerning DWAF (1996) agricultural guidelines, sites 2 (2.1 mg/L) and 4 (2.2 mg/L) during the dry period as well as site 2 (2.9 mg/L) and 5 (2.1 mg/L) during the wet period were non-compliant to the set standard of 0.1 - 2 mg/L. ANOVA noted no significant variation ($P > 0.05$) for all sites during the dry season. Sites from the wet season noted a significant difference ($P = 0.01$) for the sampled sites 1 - 4.

According to DWAF (1996), crop yields are depressed at high As concentrations. Since arsenic is toxic to humans, consumption of edible plant parts containing accumulated arsenic is dangerous. Primary symptom of arsenic poisoning includes nerve damage, characterized by sensory loss in the peripheral nervous system (Flora, 2011). Arsenic poisoning can be both chronic and acute. Chronic poisoning is characterized by skin lesions, hyperpigmentation and cancer, while acute poisoning may lead to death from upper respiratory, pulmonary, gastrointestinal and cardiovascular failure (Jomova *et al.*, 2011; Engwa *et al.*, 2019). Thus, it is important to conduct assessments of heavy metal contamination of the environment and to develop new strategies and /or to improve existing strategies to remediate the contamination to protect human (Harmanescu *et al.*, 2011).

Table 7: Arsenic and chromium analysis results

Sample site	Arsenic (As) (mg\L)				Chromium (Cr)(mg\L)			
	Dry season	P-value	Wet season	P-value	Dry season	P-value	Wet season	P-value
1	0.7 ± 0.4	0.2	0.9 ± 0	0	1.4 ± 1.5	2.4	1.3 ± 0.6	0.4
2	2.1 ± 0.4	0.1	2.9 ± 0	0	3.3 ± 1.1	1.2	3.7 ± 0.7	0.5
3	1.8 ± 0.3	0.1	1.8 ± 0	0	3.2 ± 2.3	5.5	3.2 ± 0.2	0.03
4	2.2 ± 0.3	0.1	1.9 ± 0	0	4.7 ± 2	4.2	3.4 ± 0.4	0.2
5	1.9 ± 0.2	0.1	2.1 ± 0.3	0.1	2.7 ± 1.2	1.3	2.8 ± 0.8	0.1
6	1.5 ± 0	0.2	1.9 ± 0.3	0.1	3.2 ± 0.6	0.4	2.8 ± 1.3	1.7
WHO (2011)	0.01				0.05			
SANS (2015)	≤ 10				≤ 50			
DWAF (1996)	0.1-2.0				0.1-1.0			

Apart from natural occurrence, As enters surface water through anthropogenic activities such the overuse of chemical fertilizers or herbicides and petroleum production. Sampling site 2 along the Groenwater Spruit is located within the Postmasburg town, where land use is prevalent to the above mentioned anthropogenic activities, which provides an explanation as to why the site had higher recorded concentrations of As during both seasons (Flora, 2015).

4.2.8. Chromium (Cr)

Cr is among the most abundant elements found in the Earth’s crust. Cr has numerous oxidation states, from Cr (0) (elemental chromium) to Cr (VI) (hexavalent chromium). The most common as well as stable Cr form is the trivalent form Cr (III), naturally recovered in chromite ore and is used for the manufacturing chromium metals (Sun *et al.*, 2015). The Cr concentration ranged between and 1.4 - 4.7 mg/L and 1.3 - 3.7 mg/L during dry and wet seasons, respectively.

The average concentrations of Cr detected in surface water collected during the dry season and wet seasons ranged between 1.4 - 4.7 mg/L and 1.3 - 3.7 mg/L, respectively. It is assumed that increased concentrations of heavy metals during dry seasons could be explained by a reduced dilution of the chemical input (Van Vliet and Zwolsman, 2008; Van Vliet *et al.*, 2011). ANOVA recorded no significant difference during the dry period and the wet season, excluding site 3 (P = 0.03) during the wet season. Statistics noted no significant variation among the sampled seasons. The variation at site 3 could be due to metal runoffs from mines located near the sampling site.

The recorded Cr concentration from both sampled seasons complied to the SANS (2015), domestic water use standard (≤ 50 mg/L). Contrary to this, there was no compliance from both sampled seasons for the set WHO (2011), (≤ 0.05 mg/L) and DWAF (1996), (0.1 - 1.0 mg/L) limits (Table 7). When Cr is consumed at greater concentration, it causes taste effects and nausea. It is also assumed to have carcinogenic effects via the oral route and to cause gastrointestinal cancer as well (WHO, 2011; Mohammadi *et al.*, 2019). Numerous researchers have reported about the toxicity of Cr in different agricultural plants (Dasaram *et al.*, 2011; Ozdener *et al.*, 2011; Kumar *et al.*, 2013; Rakesh and Raju, 2013). At high concentrations, Cr was observed to be toxic at several levels from reduced crop yield through effects on leaf and root growth, to inhibition on enzymatic activities and mutagenesis (alteration on the plant's DNA, resulting in gene mutations).

4.3. Microbial properties of the Groenwater Spruit

The obtained results of the microbial analysis are presented in Table 8.

4.3.1. Total coliform (TC)

Coliform bacteria are a large group of different species of bacteria that are interconnected. They include both faecal coliform bacteria, and bacteria naturally found in the intestines of warm-blooded animals, non-faecal coliforms and bacteria. Faecal coliforms comprise both pathogenic and non-pathogenic species (Feng *et al.*, 2012; Wahyuni, 2015). In aquatic ecosystems, coliforms are mainly caused by the contamination of human and animal wastes from leaching animal manure, improperly treated waste water and sewage discharge, storm water runoff or from domestic animals (Divya and Solomon, 2016). The presence of TC bacteria serves as an indicator that the water may be exposed to contamination by harmful microorganisms (An and Breindenbach, 2005).

The TC sampled during the dry period ranged from <1 cfu/100 mL - 39.7 cfu/100 mL. Higher counts were recorded during the wet periods (< 1 cfu/100 mL - 251.2 cfu/100 mL) (Table 8). Apart from surface run-offs during the wet seasons, the high TC count could be assumed to be caused by anthropogenic actions such as the discharge of untreated residential sewage (Pompei *et al.*, 2020). It can be noted that all the water sampled sites were within the permissible standards of WHO (2011), (≤ 10 cfu/100 mL), SANS (2015), (≤ 10 cfu/100 mL), and DWAF (1996), (≤ 10 cfu/100 mL) for domestic and agricultural water limits during the dry season with the exception to site 3 (11 cfu/100 mL) and site 5 (39.7 cfu/100 mL).

Table 8: Total coliform count and *E. coli* analysis results

Sample site	Total coliform (cfu/ 100 mL)				*E. coli* (cfu/ 100 mL)			
	Dry season	P-value	Wet season	P-value	Dry season	P-value	Wet season	P-value
1	<1 ± 0	0	7 ± 3	9	<1 ± 0	0	13.3 ± 0.6	0.3
2	7.7 ± 0.6	0.3	251.2 ± 1.5	2.2	23.3 ± 0.6	0.3	251.4 ± 1.5	2.3
3	11 ± 1	1	250.9 ± 2.1	4.4	<1 ± 0	0	11.7 ± 0.6	0.3
4	3.6 ± 2.1	4.3	119.7 ± 2.1	4.3	9 ± 1	1	50.3 ± 1.5	2.3
5	39.7 ± 2.1	4.3	<1 ± 0	0	7 ± 3	9	250.7 ± 2.1	4.3
6	3 ± 1	1	58 ± 3.6	13	<1 ± 0	0	249.7 ± 0.6	0.3
WHO (2011)	≤10				0			
SANS (2015)	≤ 10				0			
DWAF (1996)	≤10				1-1000			

Site 3 is located adjacent to a sewage pipe while site 6 is located near the treatment plant, making them more prone to faecal contamination. Results obtained from water samples collected during the wet period indicate that, only site 1 (7 cfu/100 mL) and 5 (<1 cfu/100 mL) submitted to the set guidelines for domestic and agricultural water use. This is because the other sites were adequately diluted and located far from the sewage systems making them less prone to contamination.

Total coliform bacteria can be transmitted by means of eating raw crops irrigated with contaminated water and may cause diseases like gastroenteritis, dysentery, cholera and typhoid fever (Blanton *et al.*, 2015; Haque *et al.*, 2010). The possibility of being infected by these microbial pathogens correlates with the level of pollution of the water and the amount of contaminated crops ingested (Shahid *et al.*, 2015). A significant difference was only noted (P = 0) at site 1 and site 5 for the dry season and wet season respectively. This is because no colony growth was observed during the assay, this could be explained by the seasonal dominance of growth or die-off of coliform bacteria in the stream (Cho *et al.*, 2016). Seasonal means were highly significant at 95% significance level. The variation could also be explained by the dilution process due to seasonal variations.

4.3.2. *Escherichia coli (E. coli)*

E. coli is the only member of the total coliform group of bacteria found in the intestines of mammals, including humans. Irrigation with water of poor microbiological quality is capable of increasing levels of bacteria on produce (Benjamin *et al.*, 2013). Results obtained from various studies (Rodgers *et al.*,2003; Soh *et al.*, 2008; Rochelle-Newall *et al.*, 2015) revealed that microbial contaminations are detected at higher concentrations during the wet seasons. During wet season, there is an increase in water temperature that occurs due to the depletion of the ozone layer, leading to a process that may possibly stimulate bacterial activity in aquatic ecosystems (Soh *et al.*, 2008). Correspondingly, the *E. coli* detected in this study (Table 8) was lower during the dry sampled period (<1 cfu/100 mL - 23.3 cfu/100 mL) compared to the wet sampled period (11.7 cfu/100 mL - > 251.4 cfu/100 mL). Similar to phosphate, high levels of *E. coli* were also observed at sites 2, 5 and 6 during the wet season, which could be attributed to animal and human waste discharges as well as surface runoffs. During the dry period, site 2 noted the highest *E. coli* count (23.3 cfu/100 mL); the site is also polluted by animal wastes since animals use it occasionally as a drinking source.

E. coli counts from both sampled seasons did not comply to the set WHO (2011) and SANS (2015) guidelines, this is because the set guidelines value for *E. coli* prescribed by WHO (2011) and SANS (2015) is none detectable colony forming unit (CFU) in any 100 mL sample of water. Conversely, all the sampled water from both seasons were within the permissible standards of

DWAF (1996) for agricultural water use limits. Since *E. coli* is a member of the total coliform, high concentrations in domestic water also cause diseases similar to those cause by TC, which are gastroenteritis, salmonellosis, dysentery, cholera and typhoid fever (Blanton *et al.*, 2015; Haque *et al.*, 2010).

AVONA noted no significant difference ($P > 0.05$) at all sites for the wet season. During the dry season, a significant difference ($P = 0$) was noted at sites 1, 3 and 6, which could be attributed to the fact that *E. coli* can enter a 'dormant' (viable but non-culturable) state (Van Elsas *et al.*, 2011). During this state, microbial cells cannot be easily recovered on standard laboratory media, but are still present as viable cells. This state can be caused by imposed stress conditions such as, toxic metals present in the water source (Semenov *et al.*, 2008; Van Elsas *et al.*, 2011). High concentrations of Fe and Cr recorded in this study are assumed to have restricted bacterial growth and modified their metabolic pattern as well (Kalantari and Ghaffari, 2008). This is because, high concentration of Fe is extremely toxic and may implicate to enhance bactericide effects of antimicrobial agents (Williams *et al.*, 2011). While, the hexavalent Cr has been recognized as one of the most dangerous environmental pollutants due to its ability to cause mutations in most microorganisms (Abskharon *et al.*, 2010). A significant difference was also noted in the measurements between the sampled seasons. The variations could possibly be due to runoff laden with effluents from the WWTP.

4.4. Principal component analysis (PCA)

The study's principal component analysis (PCA) results are summarized in Tables 9 and 10. The recorded PCA results are used to determine the possible sources of contamination along the Groenwater Spruit.

4.4.1 PCA for wet season

For the wet season sampling, three principal components were extracted and the resultant is the scree plot in Figure 10. The scree plot assists to choose the principal components as well as to understand the basic data structure. PCA results summarized in Table 9 include the eigenvalues, the percentage of variance explained by each component and the cumulative variance. The results are completed by examination of the loadings of the three extracted components. PCA groups the parameters in each cluster due to their influences to similar pollution characteristics. In this study, PCA indicated that the first three principal components, together, accounted for 91.9 % of the total variance in the dataset for the wet season sampling. As such, only three components were retained and results are presented in Table 9 Liu *et al.* (2013), divided the factor loadings as strong, moderate and weak, corresponding to absolute loading values. In this study, the factors have been segmented and explained as strong positive (≥ 0.75), moderate (0.60 – 0.50) and strong negative (≥ -0.75), respectively.

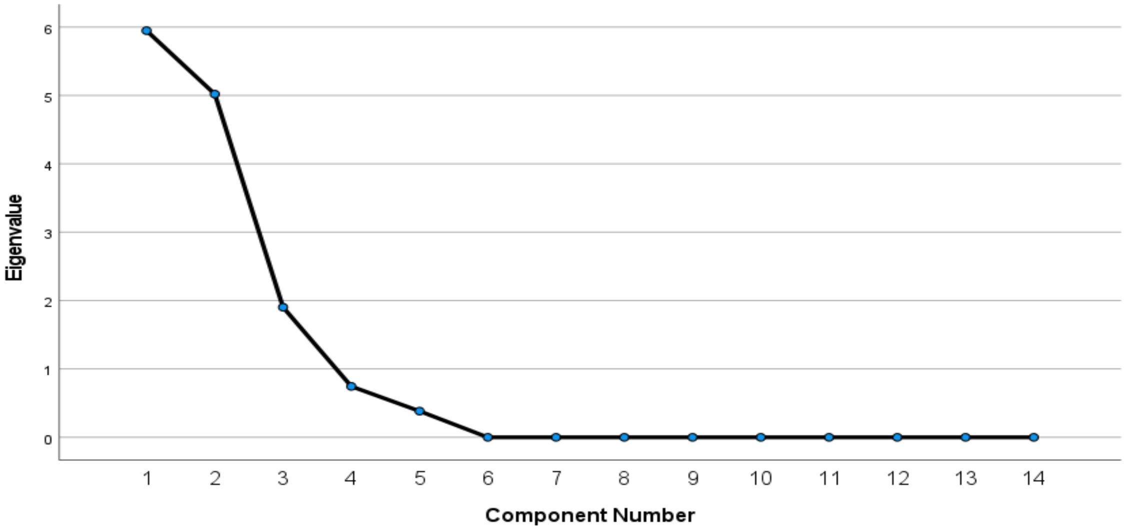

Figure 10: Wet season scree plot

The first principal component (F1) explained 39.7 % total variance (Table 9), with a strong and positive loading of temperature, Fe, As and Cr with a moderate loading of TFC. Most factors from this group were mainly influenced by variables related to natural factors. Cr enters into the environment by natural inputs and anthropogenic sources. Volcanic eruptions, geological weathering of rocks, soils and sediments are the natural sources of Cr (Ali *et al.*, 2019). Anthropogenic influences of Cr come from industrial effluents and waste dumps in the river and agricultural lands near Groenwater Spruit (Patel and Parihk, 2013).

Arsenic enters the environment through the natural weathering of rocks and anthropogenic activities such as mining, petroleum production, smelting processes and coal combustion (Tong *et* *al.*, 2014; Mudhoo *et al.*, 2011; Gautam *et al.*, 2014**)**. These activities are prevalent in the Groenwater Spruit catchment. The soil in Postmasburg is characterized by high Fe levels and as such, as water percolates through soil and rocks it dissolves this mineral and carry it into groundwater or surface water during the wet season. The corrosion of iron pipes can leach Fe into water bodies (WHO, 2003). Runoff from mining activities taking place within the catchment area could also be the possible Fe pollution sources.

Table 9: Wet season rotated component matrix

	Component		
	1	2	3
Temp	**.866**	.285	.305
pH	.139	**-.981**	.098
EC	.465	**-.753**	-.396
TDS	.339	**.883**	.249
DO	.251	.119	**.928**
SO_4	**-.918**	-.225	.127
NO_3	-.023	**.823**	-.516
PO_4	.203	**.952**	-.123
Mn	.269	**.858**	.082
Fe	**.974**	-.043	.130
As	**.916**	.129	-.093
Cr	**.980**	-.088	-.008
TC	.683	-.613	.240
E. coli	.467	.439	-.616
Eigenvalues	5.55	5.37	1.95
Total variance (%)	39.65	38.36	13.93
Cumulative variance (%)	42.49	78.35	91.94

The high positive temperature loading is attributed to natural influences such as hydrological, climatological, spatial and temporal scale, geomorphic variations as well as structural features of the region and the study catchment area (Dallas and Rivers-Moore, 2011). High water temperature is known to reduce levels of DO in aquatic ecosystems, negatively affecting the growth and productivity of aquatic life (Whitehead *et al.*, 2009).

Within the Greonwater Spruit, cattle farming is a dominant activity upstream hence, the moderate presence of TC possibly resulted from surface runoffs and channel runoffs. F1 also contained large negative loading on SO_4 (−0.918). The sulphate deficiency is attributed to low sulphate sorption along the study area (Till, 2010). Sulphate is naturally soluble in soil solutions and subject to loss through leaching in soils with low sorption capacities (Anderson, 2020). A study conducted by Wong and Wittwer in 2009 showed that the reduced sulphates sorption capacity combined with intense rainfall during the sowing season also leads to the transposition of sulphates from top soil layer, leading to a sulfur deficiency. F1 is mainly influenced by NPS pollution and the wet season sampling also plays a role in the mobilization of these contaminants.

The second principal component (F2) explained 38.4 % of the total variance. F2 had strong and positive loadings of nitrate, phosphate, TDS and Mn. This component reflected influences from both the natural and anthropogenic sources. Nitrate could be attributed to the regular use of chemical fertilizers, sewage and the disposal of manures prevalent in the catchment area. Phosphate contaminates the surface water through both point and non-point sources (NPS). Natural decomposition of rocks and minerals, agricultural runoff, erosion and sedimentation and direct input by animals are the NPS of phosphates, while point sources are sewage effluents and industrial discharges (Shrimali and Singh, 2001; Singh *et al.*, 2013).

TDS in surface water originates from natural sources, urban runoff, municipal and industrial waste and the actual plumbing infrastructure which is prevalent in the study area (Gupta *et al.*, 2019). Normally, Mn concentrations are higher in surface water than groundwater because large quantities of the Mn seeps into the water due to anthropogenic activities such as drilling from mining activities and industrial discharges (WHO, 2011; Caruso *et al.*, 2012). High Mn concentrations could also be attributed to high traffic density, which is highly prevalent at one of the sampling sites located within the Postmasburg town, the site is supposed to have contributed to the strong loadings. This is affirmed by Loranger *et al.* (1994), who noted that in Montreal, Canada, areas with intermediate and high traffic densities recorded high Mn concentrations. Strong negative loadings of pH (-981) and EC (-713) were recorded. The loadings are attributed to natural factors such as climate, bedrock and surficial geology of the study catchment (Dougall, 2007; Rothwell *et al.*, 2010). A moderate negative loading on TC (-0.613) was also noted.

The relationships between pH and occurrence of total coliforms values shown in Table 9 reveal that the decreasing of pH, decreased the appearance and growth of fecal coliforms. Results obtained in this study are consistent with results presented by other studies (Bach *et al.*, 2005; Wahyuni, 2015; Shamsudin *et al*., 2016). This is because different bacterial strains prefer different pH levels for optimal growth. F2 is affected by both point and NPS pollution however; point sources are the major contributing sources.

The third principal component (F3) only had a strong positive loading on DO and negative loadings on *E. coli* and nitrates, which explained 13.9% of the total variance. The higher DO value of this factor may be explained as a result of the increased water volume in the Goenwater Spruit during the wet season (Kamble and Vijay, 2011). The moderate negative loadings of nitrate and *E. coli* are both influenced by organic pollution such as municipal sewage treatment discharge, industrial wastes, runoffs from urban areas and farming effluents (Dallas and Day, 2004). Usually, organic pollution leads to decreases in DO concentrations due to the increased microbial activity occurring during the degradation of the organic matter but, in this study component, an inverse correlation is observed (Mwangi, 2014). F3 is mostly affected by non-point pollution sources.

4.4.2. PCA for dry season

During the dry season, four principal components were extracted and the resultant was the scree plot in Figure 11. These components explained 96.76% of the variance. However, for this study, only three components were retained (Table 10), which cumulatively explained 84.13% of the variance.

The first principal component (F1) explained 48.7% of the total variance, with a strong and positive loading on temperature, EC, TDS, Fe, As, and Cr as depicted in Table 10. The high positive temperature loadings are attributed to natural influences such as hydrological, climatological, spatial and temporal scale, geomorphic variations as well as structural features of the region and the study catchment area (Dallas and Rivers-Moore, 2011).

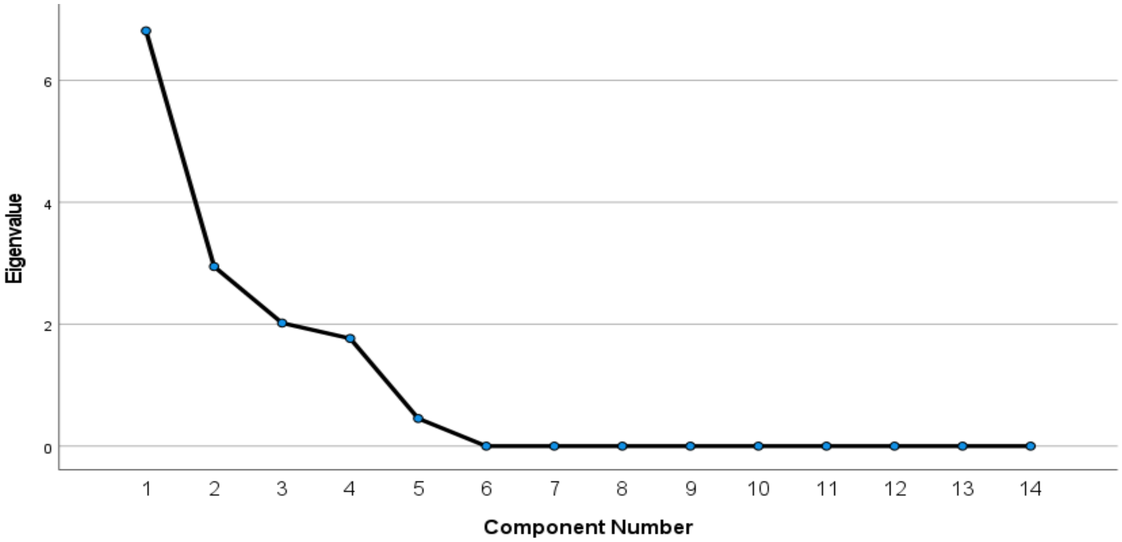

Figure 11: Dry season scree plot

TDS and EC are water quality parameters used to indicate the salinity level. The sources of TDS and EC can come from natural influences, i.e. geological condition and sea water, and from human activities, i.e. domestic and industrial waste and also agriculture (Rusydi, 2018). In this study, the strong EC and TDS loadings were attributed to wastewater discharges from sewage treatment plant.

Heavy metals, As and Cr pollution originated from industrial wastewater, mining and agricultural runoff near Groenwater Spruit. Fe is naturally found in the Earth's crust and the soil in Postmasburg is characterized by high Fe levels, hence it is assumed that its strong loadings are due to bedrock weathering since the samples were collected during the dry season when the water levels were relatively low (Herath *et al.*, 2022). Below the Earth's surface, there is a rigid and dense layer of bedrock; and cracks within bedrock provide pathways for air and water, which chemically react to break up rock, ultimately forming soil, in this case soil with high Fe content (Hancock *et al.*, 2011).Weathering is considered an important hydro-geologic process because it can occur at greater depths and enhances the permeability of bedrock aquifers (Worthington *et al.*, 2016).

Table 10: Dry season sampling rotated component matrix

	Component		
	1	2	3
Temp	**.758**	-.224	-.115
pH	-.113	.015	.370
EC	**.996**	-.017	-.042
TDS	**.943**	.079	-.303
DO	.557	.672	-.423
SO_4	-.696	-.221	-.489
NO_3	.314	.424	-.570
PO_4	-.147	**.980**	.133
Mn	**-.748**	.540	.324
Fe	**.950**	-.074	.256
As	**.939**	.134	.271
Cr	**.961**	-.174	-.052
TC	.157	**.946**	.173
E. coli	.371	-.098	**.859**
Eigenvalues	6.81	2.95	2.02
Total variance (%)	48.67	21.05	14.43
Cumulative variance (%)	48.67	69.71	84.14

On the other hand, Mn and SO_4 depicted strong negative loadings. SO_4 is abundant in watercourses, influenced by both natural and anthropogenic sources (Miao *et al.,* 2011). The low SO_4 loadings are most likely to be caused by the strong positive TC loadings of 0.970. When sulphate ions reach the anaerobic regions within the saturated soil or groundwater during microbial SO_4 reduction, the SO_4 reducing bacteria start producing sulfides (S^{2-}) thus, causing the concentration of dissolved SO_4^{2-} in water to decrease (Porowski *et al.*, 2017). Much of Postmasburg's soil, bedrock and groundwater contains Mn. Mn exist in several oxidation states but, the II and IV oxidation states are of paramount importance in natural waters (Tufekci and Celik, 2011). Mn concentrations in surface waters are generally low because surface water is more oxidized than groundwater therefore, the Groenwater Spruit's strong negative Mn loadings are attributed to Mn oxidation (McBeath *et al.*, 2020). Oxidation of Mn^{+2} to insoluble Mn^{+3}/Mn^{+4} results in the formation of manganese oxides and hydroxides. These particles drop out of suspension in surface waters, leaving the water depleted in Mn. Thus, dissolved Mn does not accumulate in surface water and oxygenated aquifer systems (Yu *et al*., 2015; Zhou and Fu, 2020). F1 components for the dry season were strongly influenced by natural factors, a similar trend was observed in component F1 during the wet period (Table 9), whereby the sources of pollution resulted from NPS.

The second principal component (F2) explained 21.1% of the total variance, with strong and positive loadings of PO_4, TFC and moderate loadings of DO and Mn (Table 10). Fecal coliform bacteria measured higher levels in the water due to the direct overflow of the untreated human sewage and waste from mammals and birds or NPS from agricultural (spreading manure and fertilizer) and storm runoff, and from sewage (Kim *et al.*, 2014; Kindiki *et al.*, 2018). Generally, organic matter has a dominant impact on total coliforms (Seo *et al.*, 2019), which is why PO_4 in this study was believed to contribute to the strong fecal coliforms loadings. With regards to this study, the source of pollution was observed to be point source pollution arising from sampling site 1. Sampling site 1 was located in an area, where livestock mainly use it for drinking water purposes, in turn resulting in high loads of animal wastes in that particular water body.

Mn (0.536) and DO (0.626) depicts moderate loadings. DO content in water is a significant indicator of the water quality and an important factor in water purification. A high DO content indicates that the water can be purified rapidly (favorable for the degradation of several pollutants). Conversely, a low DO content leads to the slow degradation of pollutants in water (Liu *et al.*, 2013). Reduced oxygen levels in the Groenwater Spruit is attributed to decomposition process, whereby DO in the water is consumed when excess organic materials such as large algal blooms are decomposed (Izdebska, 2016). Thus, moderate DO levels were noted in this study because other sampling sites were eutrophic during the dry sampling season due to lack of dilution. Mn is a ubiquitous component of soils, rocks and water. It can be leached from soil and rock into the underlying groundwater and surface water (Caruso *et al.*, 2012). Since the moderate Mn was noted during the dry season, Mn content in the water samples could probably be explained by the geology of the sampling sites and does not depend on anthropogenic activities due to little or no leaching (Nienie *et al.*, 2017).

The third principal component (F3) explained 14.4% of the total variance, with positive loadings of SO_4 and nitrate. Over the past decades, groundwater and surface water quality has deteriorated worldwide by nitrate pollution due to industrial waste water, intensive use of fertilizers in agriculture and the release of untreated urban sewage (Ren *et al.*, 2021). Similarly, groundwater and surface water is gradually polluted by SO_4 through the discharge of domestic, municipal and industrial waste waters (Torres-Martínez *et al.*, 2020). With regards to this study, the common influential factor from both SO_4 and nitrate was the discharge of untreated domestic, municipal waste waters. Sampling sites 5 and 6 were located near the Tsantsabane wastewater treatment plant (with persistent infrastructure malfunctioning), making them more prone to such pollution. The strong negative *E. coli* correlation was also influenced by organic pollution such as municipal sewage treatment discharge, industrial wastes, runoffs from urban areas and farming effluents. The loadings appeared to be very low due to little or no runoffs during the dry season (Dallas and Day, 2004). The F3 source of contamination was as a result of point source pollution arising from the untreated municipal waste water.

4.5. Chapter summary

Since water quality concerns can be prevented, it is therefore, necessary and imperative to protect water bodies from pollution using applicable legislation and guidelines. Water quality in Groenwater Spruit was found to be highly polluted and impacted by anthropogenic activities. Majority of the individual sites measured water quality parameters were found to be above the recommended WHO, SANS and DWAF standards, rendering it unsuitable for its domestic and agricultural purposes. According to the results of the principal component analysis, it was clear that NO_3, PO_4, TDS, EC, DO, SO_4 and heavy metals, were found to be the most abundant parameters responsible for water pollution in the Groenwater Spruit.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATIONS

In this section, the conclusions of the study are briefly discussed and recommendations based on the findings of the study are presented. Section 5.1 contains the conclusion and the recommendations appear in section 5.2.

5.1 Summary of findings and conclusion

The summary of the research findings with regards to the set main research objective which was: To determine the physico-chemical and microbiological water quality of the Groenwater Spruit and the three specific objectives. A brief discussion of each specific objective is described below.

(i) To determine the current surface water quality of the Groenwater Spruit

The selected physical parameters measured in this study are; pH, temp, TDS and EC. The pH values from both the wet and dry season were observed to be in the upper pH 9 threshold (alkaline) except site 5 (weakly alkaline) during the wet season sampling. The pH average of both seasons also fell within the upper pH 9 threshold indicating that Postmasburg water was naturally high in alkaline. The measured TDS levels did not raise any concern; the recorded average values were acceptable by the SANS set domestic water use standards. Conversely, TDS measured relatively high values to the set DWAF agricultural water use guidelines for both the individual sampled sites and the mean of all sites. The EC for both seasons recorded values, which were relatively above SANS, WHO and DWAF recommended standards. The high salt levels measured in this study impacted the environment by degrading crop productivity and soil quality since these salts reduced the ability of crops and plants to take up water; leading to lower yields, responsible for economic losses in agricultural production. The chemical properties (DO, nitrates, phosphates, manganese, iron, arsenic and chromium) measured in this study during both seasons were very concerning, with the exception of the measured sulphates concentrations. They were found to be higher than the set WHO, SANS and DWAF for domestic and agricultural standards.

The microbial properties of water samples i. e. total coliform and *E. coli* in the Groenwater Spruit were investigated. The average measurement of TC recorded 67 cfu/100 mL and ≥ 685 cfu/100 mL for dry and wet sampled seasons, respectively. The results indicated a significant differences of TC at sites 2 and 4 during the dry season. During the wet season, significant differences were noted only at site 6. The reasons for these significant variations are discussed in Section 4.2. Meanwhile, the total mean contamination of *E. coli* detected 39 cfu/100 mL and ≥ 837 cfu/100 mL for dry and wet seasons respectively. Similar to TC, the *E. coli* results levels of significant variations between all sampling points. The significant variations in *E. coli* were noted at all sites during the dry season. The wet season noted a significant difference at sites 2, 4 and 5. The detection of microbiological contamination of the Groenwater Spruit was of serious concern because during heavy flows, the pathogenic strain(s) were leached into the Orange river, increasing contamination levels of this perennial river, which may have had adverse health effects on humans consuming the water and on the aquatic life. With regards to agricultural use, agricultural productivity would decline due to reduction in soil fertility since these pathogenic microbes would have had altered the soil microbial community.

(ii) To determine if the current water quality complies with water quality standards for agricultural and domestic use

For the physical parameters, pH measured a mean of 11 and 9.6 for the dry and wet periods, respectively. The measured pH values from both seasons were non-compliant to the WHO (6.5 - 8.8) and DWAF (6.5 - 8.4) standards. The average pH during the wet season was within the SANS (5 - 9.7) acceptable standard. The TDS measured mean values for the dry and wet seasons (256.5 mg/L and 268.3 mg/L) were within the acceptable SANS set standard of ≤ 1200 mg/L but above the DWAF guidelines of 0 - 0.02 mg/L. EC was only within the acceptable DWAF guidelines of ≤ 540 mg/L, with an average of 254 mg/L during the dry season and 517.1 mg/L for the wet season.

Among all the selected chemical parameters for this study, DO, phosphate, Fe and Mn measured values were above the set WHO, SANS and DWAF standards and guidelines, while arsenic and chromium were only compliant to SANS standards. Sulphate is the only chemical parameter that was compliant to both SANS (≤ 500 mg/L) and DWAF (≤ 500 mg/L) standards with a mean of < 90 mg/L. Nitrate measured average values for the dry and wet seasons of 27.1 mg/L and 18.4 mg/L, respectively. These measured values were only within the acceptable WHO set standard ≤ 50 mg/L and the DWAF guidelines of ≤ 30 mg/L but above the SANS standards.

The average of TC counts recorded was 67 cfu/100 mL and ≥ 685 cfu/100 mL for the dry and wet seasons, respectively. TC counts obtained from the study for both seasons were higher than the WHO, SANS and DWAF set standard of ≤ 10 cfu/100 mL. The expected *E. coli* detection from WHO and SANS is 0 cfu/100 mL therefore, the samples from the study area did not comply with these limits. This is because, the detected mean contamination levels were 39 cfu/100 mL and ≥ 837 cfu/100 mL for the dry and wet seasons, respectively. The set DWAF guideline for *E. coli* is 1 - 1000 cfu/100 mL and from the obtained results, it was scientifically impossible to conclude if they were above or within the accepted set standard range because some plates showed too many colonies to count.

(iii) To identify point and non-point sources of contaminants along Groenwater Spruit

PCA grouped the parameters due to their influences to similar pollution characteristics. PCA results for the wet season revealed that both point and non-point sources of pollution were responsible for the water pollution within the Groenwater Spruit. Results from the dry season concluded that the pollution was due to point source contamination.

5.2. Recommendations

With reference to this study, the following recommendations were suggested:

- There is a need to properly manage wastes in the Tsantsabane local municipality and monitor human activities to ensure minimal negative effects on the surface water. To be able to control point source pollution, rain and sewage diversion measures are recommended in order to cut off the sewage outlet and decrease the load of pollution into the river.

- Strict enforcement of the national and international regulation agencies will help reduce the present levels of pollution introduced by uncontrolled effluent discharges and protect both the water bodies and the environment in general. These strict regulations must also be extended to domestic waste drainage for comparable reasons.

- In order for these recommendations to be effective and achieve persuasive results, those to be policed must be given sustainable environmental education. The Tsantsabane society at large must also be educated about the need for environmental protection. Community campaigns and mass education programs on environmental problems including water pollution and prevention is a must to make Postmasburg an environmentally literate society. More knowledge about the environment would ensure more effective environmentally responsible communities. It is a collective responsibility to keep the environment healthy and make it safe to live in. Taking these courageous steps locally, nationally and internationally would mean an improved water quality for the society, the country and future generations.

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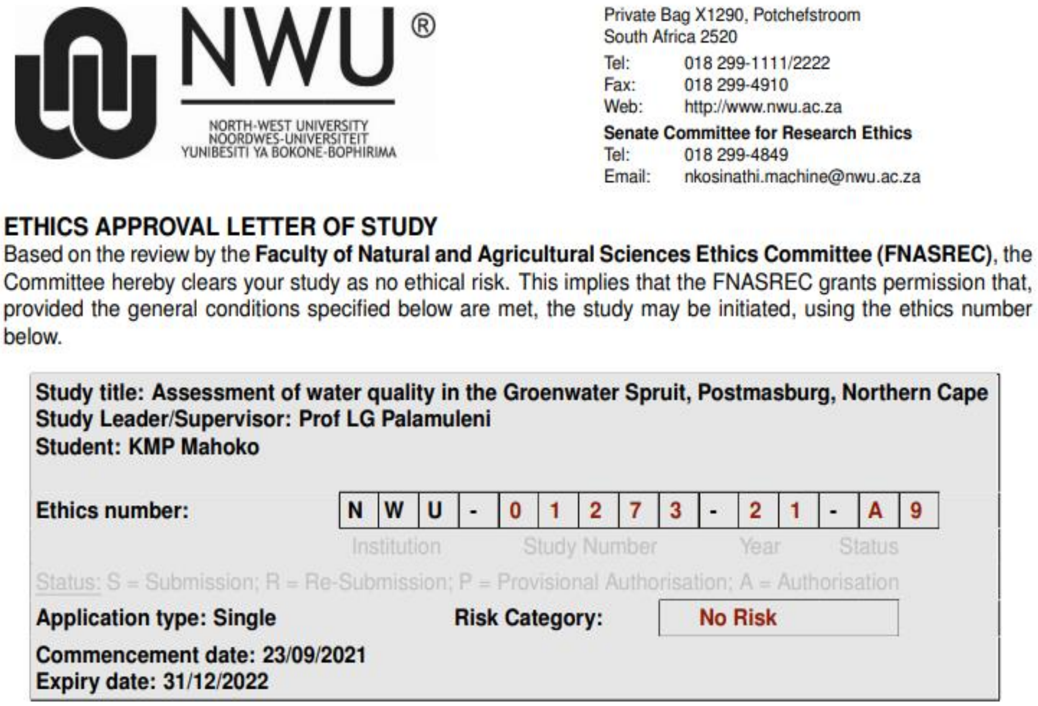
APPENDICES

Appendix 1: Ethical clearance



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ETHICS APPROVAL LETTER OF STUDY

Based on the review by the **Faculty of Natural and Agricultural Sciences Ethics Committee (FNASREC)**, the Committee hereby clears your study as no ethical risk. This implies that the FNASREC grants permission that, provided the general conditions specified below are met, the study may be initiated, using the ethics number below.

Study title: Assessment of water quality in the Groenwater Spruit, Postmasburg, Northern Cape
Study Leader/Supervisor: Prof LG Palamuleni
Student: KMP Mahoko

Ethics number: N W U - 0 1 2 7 3 - 2 1 - A 9
Institution / Study Number / Year / Status

Status: S = Submission; R = Re-Submission; P = Provisional Authorisation; A = Authorisation

Application type: Single **Risk Category:** No Risk

Commencement date: 23/09/2021
Expiry date: 31/12/2022