AN EVALUATION OF THE IMPACT OF ACID MINE DRAINAGE ON WATER QUALITY OF THE LOWER OLIFANTS RIVER, SOUTH AFRICA

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T MOHALE

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AN EVALUATION OF THE IMPACT OF ACID MINE DRAINAGE ON WATER QUALITY OF THE LOWER OLIFANTS RIVER, SOUTH AFRICA

by

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DISSERTATION

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2021

DECLARATION

I declare that the dissertation hereby submitted to the University of Limpopo, for the degree of Master of Science in Geography has not previously been submitted by me for a degree at this or any other university; that it is my work in design and in execution, and that all material contained herein has been duly acknowledged.

30 May 2021

Mohale, T (Mr) Date

DEDICATION

The work is dedicated to my parents (Maleho and Max Mohale), my fiancée (Precia Makgoga), and our son (Nalamotse Max Mohale) with gracious love.

ACKNOWLEDGEMENTS

First and foremost, I would like to be thankful to God for granting me this opportunity, his continued protection and guidance enabled me to complete this milestone.

I would like to extend my sincere gratitude to my promoters and supervisory team, Dr Themba Lawrence Dube and Dr Munyaradzi Mujuru, for their willingness to impart valued knowledge and continuous encouragement in conducting this study. Their patience, constant encouragement, and constructive comments made me the better person I am today, without their dedicated guidance I would have not reached this stage, thank you.

I would like to thank the mining companies of the Phalaborwa area for providing access to the sampling sites and information on the management of mine wastewater at their operational site, with a special word of appreciation to Mr Joseph Muhlarhi. I am very grateful to Mr Phomelelo Mohale, who was with me at every site visit. Again, I would like to thank Lieutenant Colonel Solomon Lechoenyo of the South African National Defence Force (SANDF) for granting us access to collect water samples at the Ga-Selati River through their military base.

Lastly, my gratitude goes to my parents, Mr Max Mohale and Mrs Maleho Mohale, and my fiancée Ms Precia Makgoga for they constantly supported and checked on the progress of my research project.

ABSTRACT

Acid Mine Drainage (AMD) is the acidic water emanating from the mine tailing dams into the surrounding environment. AMD is regarded as a major environmental threat associated with mining. The lower Olifants River in the Kruger National Park (KNP) is considered an environmentally sensitive area, which exhibits high levels of aquatic ecosystems and supports a variety of terrestrial ecosystems within and around the KNP. The Phalaborwa mining industries have been discharging the acid mine drainage contaminated-water into the Ga-Selati River, a tributary to the Olifants River. Although the impacts in the upper Olifants River catchment have been well documented, it was the amount of AMD witnessed at KNP and the dying of fish within the lower Olifants River that raised issues of concerns. Hence, the study investigated the impact of acid mine drainage on water quality of the lower Olifants River, modelled the distribution of the dissolved heavy metals in the stream, and evaluated the applied mine wastewater management strategies at Phalaborwa mining industries.

In this study, water samples were collected seasonally (winter, spring, and summer) from 2019 to 2020, and the analytical methods and procedures were optimized for the determination of selected elements in the water samples. During the study, ion chromatography (IC) was used to detect chloride (Cl), sulphate (SO_4^-), nitrate (NO_3), and fluoride (F), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to detect pH, turbidity, electrical conductivity (EC), total dissolved solids (TDS), magnesium (Mg), manganese (Mn), sodium (Na), potassium (K), aluminium (Al) and calcium (Ca). Modelling of the distribution of dissolved heavy metals was performed using the inverse distance weighted (IDW) interpolation technique available in ArcGIS 10.8 software. The range of pH across four sampling sites was between 7.77 and 9.11, indicating an alkaline pH. The concentration of measured parameters elevated downstream points with some exceeding the target water quality range (TWQR) for aquatic ecosystems. The elevated concentration of SO_4^- at sites 3 and 4 (downstream points) showed that the acid mine drainage is still a matter of concern at the lower Olifants River catchment. However, the GIS models showed a decreasing trend of the concentration of heavy metal towards the KNP.

Key Concepts: Acid mine drainage; water quality; Olifants River; Ga-Selati River; Phalaborwa; mining; concentration; season variation

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LIST OF ABBREVIATIONS

AHP: Analytical Hierarchy Process

AMD: Acid Mine Drainage

ANOVA: Analysis of Variance

ATSDR: Agency for Toxic

AWARD: Association for Water and Rural Development

CCV: Continuous Calibration Verification

CR: Consistency Ratio

DFFE: Department of Forestry, Fisheries and the Environment

DMRE: Department of Mineral Resources and Energy

DWAF: Department of Water Affairs and Forestry

DWS: Department of Water and Sanitation

EA: Environmental Authorization

EIA: Environmental Impact Assessment

EMPr: Environmental Management Programme

EPA: Environmental Protection Agency

GIS: Geographical Information System

GPS: Global Positioning System

GS: Green Scorpion

IC: Ion Chromatography

ICP-OES: Inductively Coupled Plasma Optical Emission Spectroscopy

ICV: Initial Calibration Verification

IDW: Inverse Distance Weighted

LDEDET: Limpopo Department of Economic Development, Environmental, and Tourism

LOD: Limit of Detection

LOQ: Limit of Quantification

MEND: Mine Environment Neutral Drainage

MPRDA: Mineral and Petroleum Resource Development Act

NEMA: National Environmental Management Act

ND: Not Detected

NEM:WA: National Environmental Management: Waste Act

NWA: National Water Act

PMC: Phalaborwa Mining Company

PMI: Phalaborwa Mining Industries

PRC: Phalaborwa Regional Court

RSA: Republic of South Africa

SANPark: South African National Parks

SDS: Sodium Dodecyl Sulphate

SPSS: Statistical Package for Social Sciences

SRM: Standard Reference Materials

TWQR: Target Water Quality Range

WHO: World Health Organisation

WRC: Water Research Commission

WQI: Water Quality Index

XRF: X-ray Fluorescence

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

South Africa, as with other countries of the world, is endowed with different minerals resources, which may include among others gold, copper, platinum, coal, and diamond. The mining history has generated several economic benefits to the country, and it is still playing an important part in sustaining the position of the country in the global market (Inter-Ministerial Committee, 2010). However, some socialist, environmentalist, and mining critics argue that these benefits negatively affected the social and environmental aspects (Adler *et al.,* 2007). The extraction of mineral resources through mining has as serious environmental impact and the significant of this impact always depend on the mine status in terms of operational, decommissioned or abandoned (Bell *et al.,* 2001). The impact associated with mining activities can also depend on the geological settings of the area in which the mine exists. The acid mine drainage (AMD) is known to be the main environmental liability associated with the extraction industry (Mine Environment Neutral Drainage-program, 2001). It is generally characterised by elevated concentrations of dissolved metals, sulphate and low pH (Mine Environment Neutral Drainage-program, 2001). Other than mining activities, acidic drainage can also happen whenever the sulphate-bearing rocks are exposed to oxygen and water to produce acidic water with high concentration of sulphate. Such water poses additional risk to the aquatic and riverine organisms as well as the quality of the soil and water because of the contained elevated amounts of heavy metals (irons, manganese, aluminium, and other heavy metals) and metalloid such as arsenic (Magowo, 2014). In South Africa, AMD has been witnessed in various mining areas, which may include the Witwatersrand Gold fields, the KwaZulu-Natal, and the Mpumalanga Coalfields while those of mail concern were in Western, Eastern, and Central basins in Gauteng where the conditions were deemed critical (Ramla, 2012).

Freshwater is fundamental to life, yet the most limited natural resource worldwide. The earth's surface consists of 70 % of water, of which 3 % is made up of freshwater which deteriorates because of anthropogenic activities (Mahlatji, 2014; Davies and Day, 1998). Pollution puts many river systems including the Olifants River under great threat in South Africa (Heath *et al*., 2010). The Olifants River has been severely impaired because of the mushrooming numbers of the industrial development, agricultural, and mining activities that exist along the river. The river flows from Mpumalanga Highveld, passes through several economic hubs in Emalahleni, Middleburg, Steelpoort, and Phalaborwa on its way to the Kruger National Park, and ends in Limpopo River (Van Zyl *et al*., 2001). The Olifants River has been classified by the Department of Water and Sanitation as a stressed river with fair to poor overall ecological conditions (Department of Water Affairs and Forestry, 2000). The water quality in the lower Olifants River in the Kruger National Park is under great threat because of the number of anthropogenic activities upstream of the river (Roux *et al*., 2008). Threats that exist within the lower Olifants catchment include the treated and untreated sewage from the municipality, and discharges from the industrial and mining sites, which “have led to the deterioration of the water quality” at this sub-catchment (Heath *et al*., 2010). The state of the water quality can be determined by analysing the chemical, biological and physical characteristics of the given water, and its suitability depends on the intended use.

The Ga-Selati River is a tributary to the lower Olifants River, and it originates from the Drakensberg escarpment and flows through different economic activities before joining the lower Olifants River in Phalaborwa. The river was found to be feeding the Olifants River with AMD-contaminated water from the mining operations that exist adjacent to this river system in Phalaborwa (Myburgh and Botha, 2009). The study assessed the recent impact of the AMD in the lower Olifants River system, evaluated the applied mine wastewater management strategies in Phalaborwa, and modelled the transportation of dissolved heavy metals along both the Olifants and Ga-Selati Rivers.

1.2 Problem statement

The extractive industry has been playing and still plays a crucial part in the Phalaborwa economy, where the Palabora Mining Company operates one of the largest underground block cave copper mines in the world (Foskor, 2012). The operations of coal mines in the Olifants catchment area “started in the 1890s and by 2004 an estimated 50 000m^3 of mine wastewater was being discharged into the Olifants River daily, including the 64 000m^3 per day that was discharged from the closed and abandoned mines" (Mujuru and Mutanga, 2016). The unregulated release of acid mine drainage from the operating mines is considered to be a global problem. AMD can stay on the environment for a long time unless natural or artificial processes are introduced to counteract the acidity (Mulanga, 2016). The operations of copper and phosphate mines in Phalaborwa pose a great threat to water quality and aquatic ecosystems at the lower Olifants River including at the Kruger National Park (KNP), and thus as well affect the tourism sector. AMD has, if left untreated, the ability to pollute "ground and surface water sources, damaging the health of plants, humans, wildlife, and aquatic species" (Coetzee *et al.*, 2006). The unregulated release of the AMD has been labelled by the media houses as a ticking time bomb and may negatively affect the agricultural sector of the country (Mail & Guardian, 2019). The contamination of the freshwater by heavy metals from the mining operations is one of the serious environmental problems experienced worldwide.

The main area of concern regarding the AMD management is that some of the mining companies do not adhere to the authorised Environmental Management Programmes (EMPr) put in place to control the leachate of the AMD (Water Research Commission, 2009). This lack of adherence to the best management practices as stipulated in the EMPr may exacerbate the environmental consequences, which may cause deterioration of the water quality in the area around the operating mines.

Due to the deterioration of water quality caused by the persistent AMD, there is a need to study the management of the heavy metals in Phalaborwa to establish their levels of concentration, impacts, and dispersion in the area.

1.3 Research questions

The study answered the following research questions:

I. What are the long-term impacts of the AMD on water quality?
II. What are the seasonal variations in the water quality?

III. What are the applied AMD management strategies put in place by Phalaborwa mining companies to control AMD generation and its migration from the operational site?

IV. What is the efficacy of the applied policy and legal framework?

1.4 The motivation of the study

The mining industry is an important asset for the economy of many areas across South Africa, particularly with respect to exports and employment (Bussiere, 2009). Apart from the socio-economic benefits of mining, there are often significant threats associated with the activity on the natural resources and can also impact negatively on human livelihood (Simate and Ndlovu, 2014). Mining activities generate different types of wastes, which may also include AMD.

The Olifants River is from an ecological point of view, one of the most important rivers in South Africa that require maximum protection and continuous research. It is also one of the rivers in South Africa with the most biologically diverse systems with at least 49 fish species (Roux *et al*., 2008). Dabrowski *et al.* (2008) indicated that the Olifants River is one of the most contaminated rivers in Southern Africa because of the number of anthropogenic stressors that are existent due to different economic activities. The river serves as the main source of raw water to many purification plants of nearby communities including the Kruger National Park and also provides water for irrigation and other agricultural purposes in nearby agricultural land/farms. The mine industries such as the Palabora Mining Company and the Foskor mines have been responsible for serious salt enrichment primarily from sulphate and phosphate into the Ga-Selati River, a tributary of the Olifants River, and this was reported to be of great concern (South African National Parks, 2014; Riddell *et al.,* 2019; Association for Water and Rural Development, 2020).

Since the uncontrolled pouring of the AMD into the water resource can trigger poor water quality and also pose an immediate threat to the local communities as well as the nearby agricultural fields, it is important to continuously investigate the management of the AMD and the environmental implications associated with the pouring of the AMD in Phalaborwa area. Currently, there are more researches conducted at the upper Olifants and Ga-Selati River catchments while fewer researches exist at the lower sections of both Olifants and Ga-Selati River systems in Phalaborwa and this study will seek to close that gap.

1.5 Aim

The study aimed to investigate the impacts of mine wastewater from the mining activities at Phalaborwa on the water quality of lower Olifants River and evaluate management strategies.

1.6 Objectives

The aim was achieved through the following objectives:

I. Investigate the impacts of Phalaborwa mine wastewater on the water quality of the Olifants River.
II. Monitor the seasonal variation of water quality of the Olifants River for a period of one year.
III. Evaluate the existing AMD management strategies in Phalaborwa.
IV. Evaluate the effectiveness of the policy and legal framework in place on the management of AMD in Phalaborwa.

1.7 Hypotheses

The hypotheses of the study include the following:

I. AMD has led to negative environmental impacts in the lower Olifants River System. Heavy metals from the AMD are highly concentrated in the lower Olifants River and thus negatively influencing water quality at the Ga-Selati/Olifants confluence. These concentrations of the heavy metals are, therefore, transported into the Kruger National Park to cause further environmental damages.

   Alternative; AMD has no leads to environmental impact in the lower Olifants River system, as the mine wastewater is effectively controlled, and well treated at the source to avoid leachate into the Ga-Selati River system.
II. The policy and legal framework are not doing enough to control the migration of the heavy metals from the site. Noncompliance with the legal framework by the mining companies exhibits environmental consequences of the AMD. The poorly

enforced legal framework with small or no fine in case of any transgressions leads to noncompliance.

Alternatively, the policy and legal framework in place to control the migration of the heavy metals from mining sites are well enforced at the lower Olifants catchment. The effective control of the mine wastewater demonstrates levels of compliance with the policy and legal frameworks.

1.8 Structure of the research

The general layout of the dissertation

This dissertation is comprised of five chapters including this chapter (Chapter One) that provide the background and motivation for the study, problem statement, research questions, aim, and the overall objectives of the study. Figure 1.1 is the schematical representation of this layout.

Chapter Two of this study consists of the literature reviews, which include the general overview of the formation of AMD, its environmental impacts, and the prevention of AMD from the source.

Chapter Three describes the study area and presents the materials and methods used in the study.

Chapter Four presents and discusses the results of the laboratory tests. This chapter further outlines the statistical analysis of the results and the overall modelling of the distribution of the heavy metals along both the Olifants and Ga-Selati Rivers within the study area. The water quality index maps that show levels of seasonal pollutions are also presented in this chapter.

Chapter Five provides a synthesis that consolidates the findings of the research and the overall concluding remarks and recommendations for future studies.

A reference list is also provided at the end to acknowledge the author's work that was used in the dissertation. An Appendix section is the last part of this study and it provides the laboratory test results, some statistical analysis, and water quality modelling results.

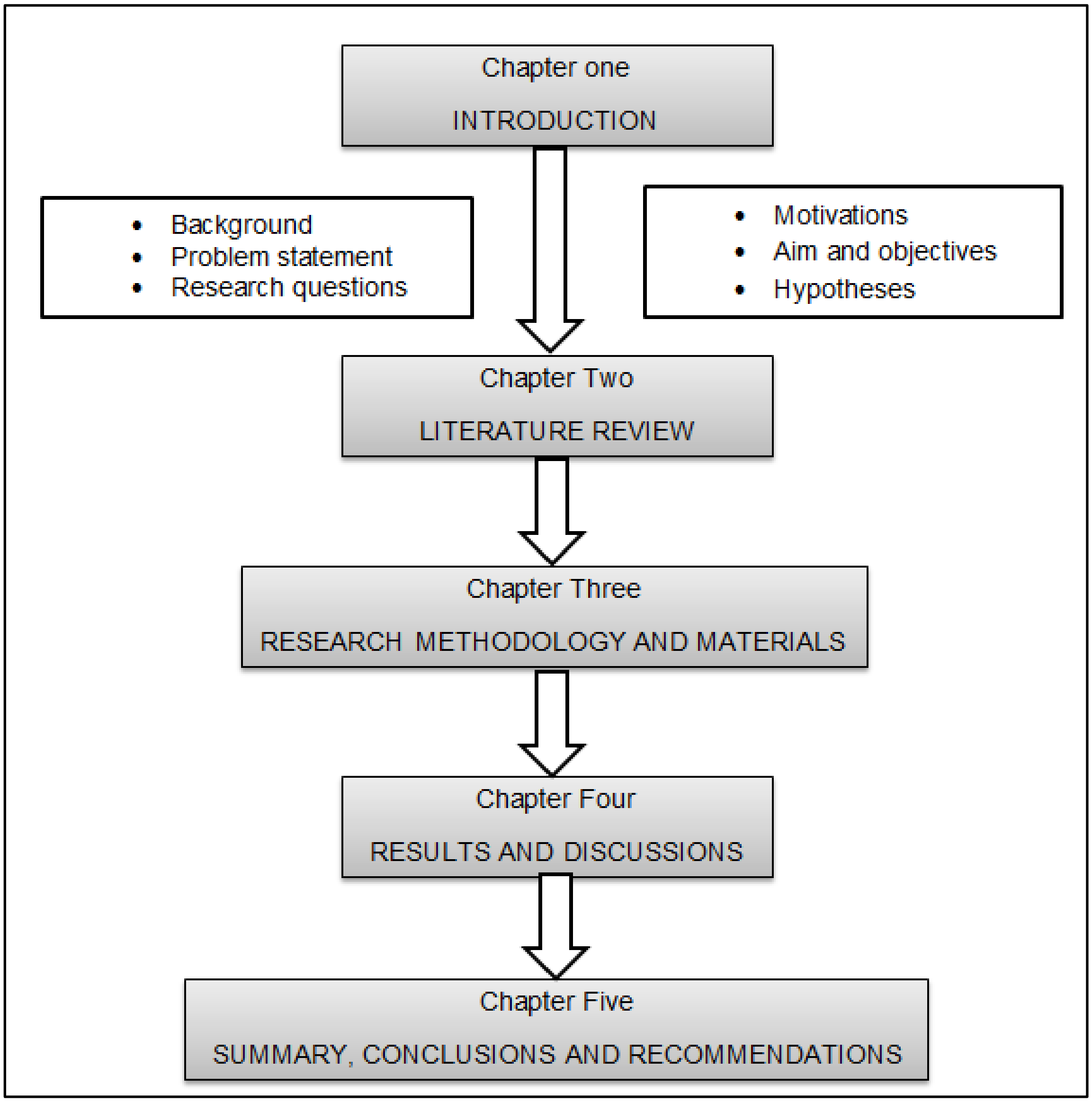

Figure 1.1: Layout of the dissertation.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

South Africa is confronted with water quality challenges, which are mainly caused by human activities (Department of Environmental Affairs, 2018). This chapter focuses on a literature review of the formation, impacts, and prevention measures of the AMD. The chapter reviews published and unpublished documents on the occurrence of the AMD in South Africa and other regions of the world. Furthermore, the chapter addresses the theoretical framework of the study at large.

2.2 Mining companies around the lower Olifants River

The lower Olifants River in Limpopo province is bordered by numerous human activities such as mining operations due to the occurrence of numerous minerals. Among others, some of the mined minerals around the lower Olifants River catchment include copper, phosphates, antimony, and gold production. Phalabora Mining Company (PMC) operates copper-bearing mineral ore with high commodity values in the metal industries (Ramahlo, 2013). Foskor Company also "operates one of the largest underground block-cave phosphate mines in the world" (Foskor, 2012). JCI Mining Company situated within the lower Olifants River catchment excavates "antimony and gold-bearing ores, with a long history in the operation of automobile industries" (Ramahlo, 2013). The mining sector has been identified as one of the key economic drivers Ba-Phalaborwa Local Municipality (Ba-Phalaborwa Local Municipality Final IDP document, 2020/21).

2.3 Formation of Acid Mine Drainage

The mining industry is considered one of the biggest waste producers in the world (Lebre and Corder, 2015). One of the waste aspects produced by mining activities is AMD and has received the attention of the world over the years. AMD is formed as result of the exposure of sulphate minerals (such as pyrite (FES_2)) to the oxygen (O_2) and water (H_2O) due to the mining activities (Akcil and Koldas, 2006). It is characterized by high concentrations of sulphate, elevated amounts of dissolved metals and a pH generally <4.5 (Demchak *et al.,* 2014). "Although this process can occur naturally, mining can promote AMD generation simply by increasing the number of" sulphates exposed (McCarthy, 2011). AMD occurs as a result of the "oxidation of sulphate minerals (Table 2.1) such as pyrite (FeS_2) as a result of exposure of these minerals to both oxygen and water" as indicated in the chemical reaction below (Simate and Ndlovu, 2014). The general conceptual model of the generation of the AMD from the source to the receiving environment is depicted in Figure 2.1.

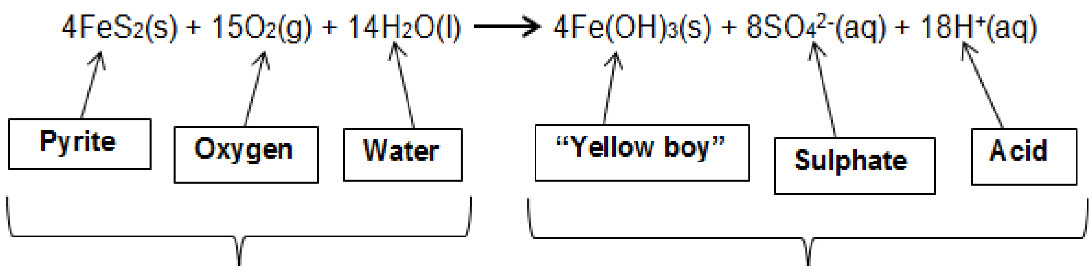

Table 2.1: Some important metal sulphates. Pyrite and marcasite are the predominant acid producers from mining activities (Simate and Ndlovu, 2014).

Metal sulphate	Chemical formula
Pyrite	FeS_2
Marcasite	FeS_2
Pyrrhotite	$Fe_{1-x}S$
Chalcocite	Cu_2S
Covellite	CuS
Chalcopyrite	$CuFeS_2$
Molybdenite	MoS_2
Millerite	NiS
Galena	PbS
Sphalerite	ZnS
Arsenopyrite	FeAsS

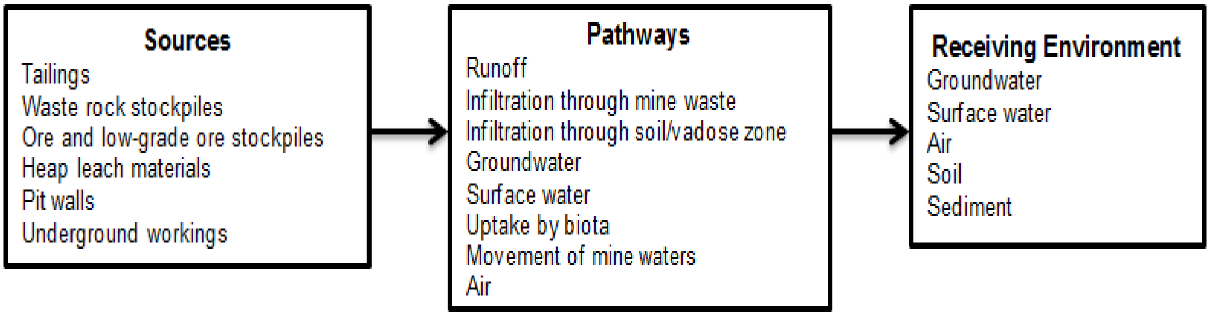

Figure 2.1: Generalized conceptual model of sources, pathways, and receiving environment at a mine or processing site (Ndlovu *et al.,* 2017).

The process of acidic mine wastewater formation is severely complex because it includes chemical, biological, electrochemical, and physical reaction processes that differ according to environmental and local geological structures (Mujuru and Mutanga, 2016). The oxidation of the pyrite-bearing rock, which is one of the most common sulphate minerals, "can follow several pathways involving surface interactions with dissolved O_2, Fe^{3+}, and other mineral catalysts such as MnO_2" as indicated in Figure 2.2 (Simate and Ndlovu, 2014).

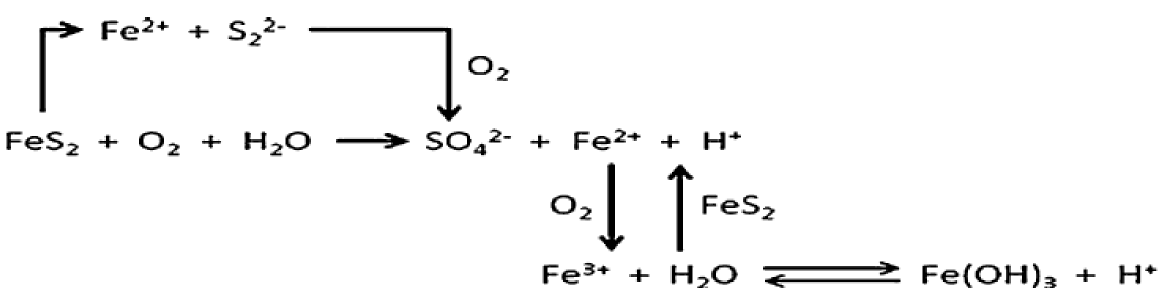

Figure 2.2: Model for the oxidation of pyrite (Buzzi *et al.,* 2013).

"Bacteria such as the *Thiobacillus ferroxidants* and *Thiobacillus thiooxidants* present in the sulphide-bearing deposits" can oxidise sulphur compounds to sulfuric acid (H_2SO_4) catalysing the production of the AMD (Kuyucak, 2002). Bio-oxidation of sulphide minerals can be clarified by direct and indirect mechanisms (Sangita *et al.*, 2010). The study done by Magowo (2014) indicated that the direct contact between the bacteria and the sulphide minerals is regarded as the direct mechanism and can be illustrated through the chemical reaction shown below:

$$FeS_2 + H_2O + 7/2O_2 \xrightarrow{\text{bacteria}} Fe^{2+} + 2SO_4^{2-} + 2H^+$$

The ferric iron produced by the bacteria can lead to the formation of sulfuric acids during the indirect mechanisms that can be illustrated by the following chemical reaction:

$$FeS_2 + 8H_2O + 14Fe^{3+} \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

$$14Fe^{2+} + 3.5\ O_2 + 14H^+ \xrightarrow{\text{bacteria}} 14Fe^{3+} + 7H_2O$$

The overall reaction can be presented as follows:

$$2FeS_2 + 15/2\ O_2 + H_2O \xrightarrow{\textit{T. ferroxidants}} Fe_2(SO_4)_3 + H_2SO_4$$

2.4 Impacts of Acid Mine Drainage on water resources

AMD is if left untreated, capable of contaminating both groundwater and surface water. The heap of waste rock dump forms AMD upon oxidation in the presence of rainwater that can either infiltrate to contaminate groundwater or flow on the earth's surface to contaminate surface water resources (Mujuru and Mutanga, 2016). Department of Water Affairs and Forestry (2014) indicates that over 70 % of the water used in both rural and urban areas is surface water, abstracted from various water bodies such as the rivers, lakes, streams, ponds, dams, and springs in South Africa which is severely threatened by the pouring of AMD from mining fields.

Mine wastewater is liable for transporting a very high load of acids into the streams and wetlands around the mining operational sites. Examples of heavy metals that can be leached into the waterbodies include among others copper, zinc, nickel, lead, magnesium, iron, aluminium mercury, cobalt, and arsenic. The high concentration of iron affects the turbidity of the streams resulting in a formation of the yellow or orange condition described as "yellow boy" responsible for interrupting the food chain. The presents of acids in the water resources can reduce the pH and degrade the quality of the water within water bodies. The water resources fail to support and maintain high numbers of ecosystem functioning due to the lowered pH. According to De Beer (2005), the lifespan of most of the concrete infrastructures such as culvert and bridge abutments are being reduced by the corrosive acid in the water bodies. Water containing high levels of sulphates is associated with the cause of catharsis, diarrhoea, and dehydration in human systems (Mujuru and Mutanga, 2016).

AMD-contaminated water can render water resources unfit for different water uses that may include domestic, agricultural, industrial, and recreational uses. Soil and mine waste particles carried in runoff from the mining site into the streams can destroy the lives of the tiny fly nymphs, insect larvae, and other organisms responsible for the basement of aquatic and riverine food chains (De beer, 2005).

In South Africa, one of the severe impacts of AMD was witnessed at the Western Basin where the mining shaft began decanting in August 2002, contaminating the Tweelopiespruit that drains into the Krugersdorp Game Reserve (Department of Water Affairs, 2013). The Tweelopiespruit consisted of several water quality parameters that went above the guidelines for stock watering, aquatic ecosystems, and the biological monitoring results demonstrated a shift from ecological category C (moderate modification and moderate levels of localised contamination) to category F (heavily modified and high levels of contamination that render the water unsustainable and unusable) between the year 2000 and 2004 (Department of Water Affairs, 2013). This condition has indicated a significant degradation of the water resources due to AMD decanting.

The severe contamination and acidification of the groundwater was observed in the Johannesburg mining district where mine tailings dumps have led to the increment of the concentration of heavy metals (Naicker *et al.,* 2003). In this area, polluted groundwater has been discharged into streams where they contribute up to 20 % of the streamflow, raising the levels of concentration of heavy metals in the stream water (Council for Scientific and Industrial Research, 2008). The effects of the AMD-contaminated water can spread for over 10 km from the source (Naicker *et al*., 2003). The evidence of the effect of AMD concentration was revealed in the Wonderfonteinspruit Catchment (Coetzee *et al.,* 2006).

The pollution of water resources by AMD-contaminated water significantly decreases the availability of the desired amount of water needed for economic development (Mujuru and Mutanga, 2016). In South Africa, basins that are already affected by the

AMD include the Olifants River, the Crocodile River (draining from the Western Basin through Tweelopiespruit into the Limpopo River) and the Vaal River which is draining from Eastern Basin, (through Blesbokspruit) and the Central Witwatersrand Basins, as well as the Komati River (Figure 2.3 and 2.4) (Mujuru and Mutanga, 2016). Globally, water quality guidelines exist for human use, maintenance of aquatic ecosystems, and other users such as agriculture, industrial, and recreation. The "South African water quality guidelines consist of" a series of seven volumes that were compiled by the Department of Water and Sanitation in line with the international standards (Department of Water Affairs and Forestry, 1996).

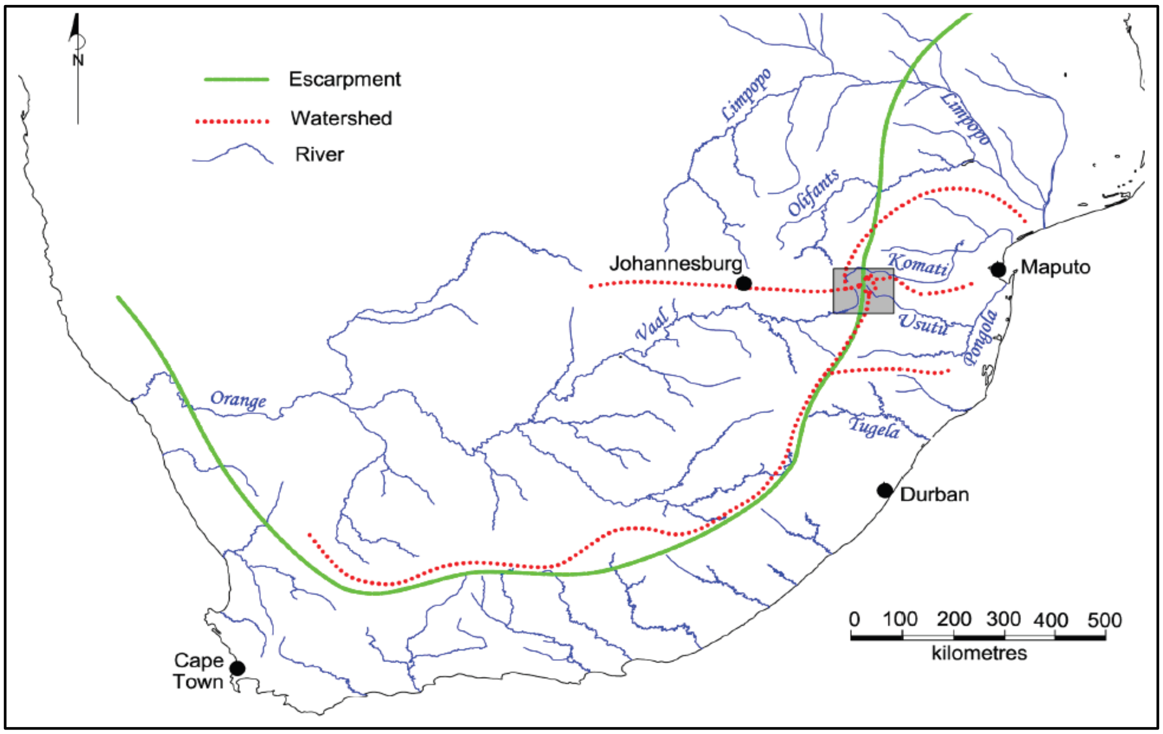

Figure 2.3: A map of AMD-contaminated river basins in South Africa (McCarthy, 2011; Mujuru and Mutanga, 2016).

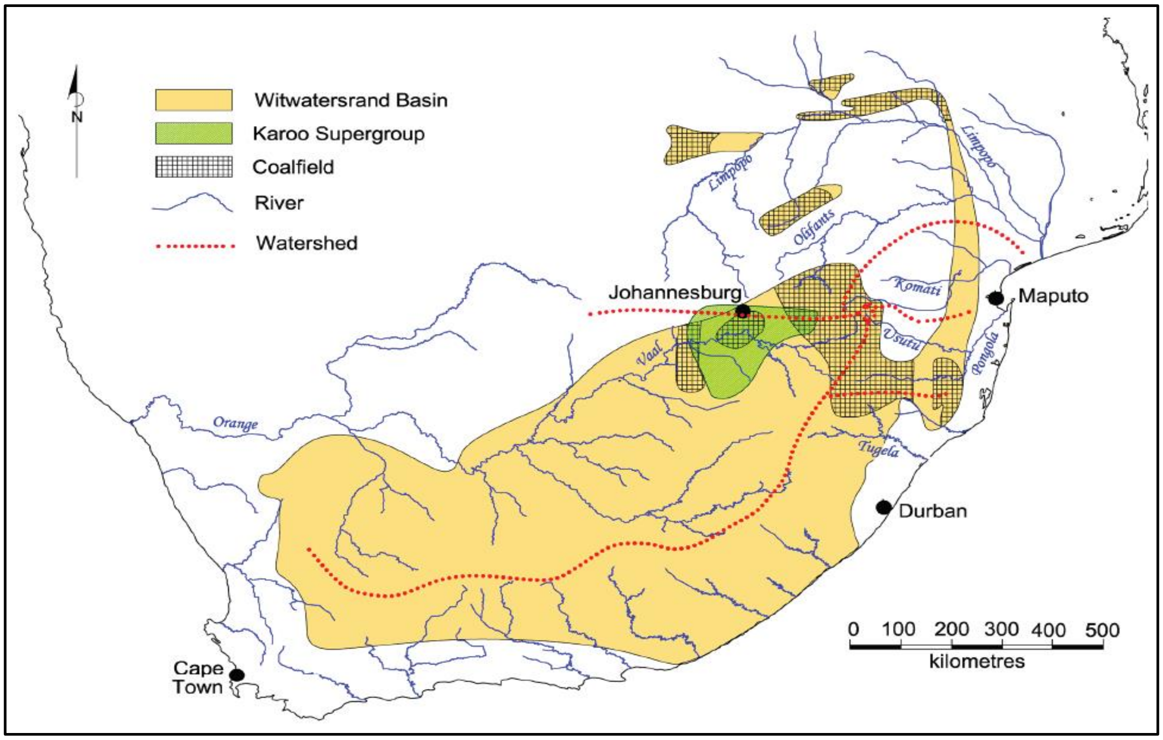

Figure 2.4: A map demonstrating the distribution of the coal and Witwatersrand gold basins that potentially affect the streams in South Africa (McCarthy, 2011; Mujuru and Mutanga, 2016).

2.5 Impacts of Acid Mine Drainage on biodiversity

The formation of the AMD due to the mining operations can release metals into the surrounding environment. The released metals can enter the biological systems and affect the food chain through aquatic ecosystems. Jennings *et al*. (2008) found that when fish are exposed directly to metals and hydrogen ions through their gills in water, the chronic and acute toxicity may cause respiratory problems and sudden death of the fish within water bodies. The presence of the heavy metals in water resources can serve as metabolic poisons that can result in the death of the aquatic ecosystems.

"Iron hydroxides and oxyhydroxides are capable of physically coating the surface of stream sediments and streambeds to destroy habitat, reducing the availability of clean gravels used for spawning, and" lowering the amount of food for fish that include the benthic macroinvertebrates (Jennings *et al.,* 2008). Metals in water bodies deplete oxygen, and therefore, subject marine life to difficult survival conditions. The general ecological effects of the AMD are the fragmentation of the habitat, introduction of harmful elements into the ecosystem as well as the destruction of the food chain which may also affect the terrestrial ecosystems that feed on marine life and drink water from the AMD-contaminated water bodies (Sangita *et al*., 2010). These effects all together can lead to reduced number of living organisms in streams (Burgers, 2002).

The death of the ecology resulting from the uncontrolled releasing of AMD into the nearby streams has been reported from worldwide areas. In Pennsylvania, the study that was conducted along the AMD-contaminated rivers noted that the fish were severely impacted at a pH ranging between 4.5 and 55 (Jennings *et al*., 2008). "Ten species showed some tolerance to the acid conditions of pH 5.5 and below; 38 species were found existing in waters with pH values ranging from 5.6 to 6.4; while 68 species were found at pH values higher than 6.4" (Jennings *et al*., 2008). Generally, streams impacted by AMD were found to be "dominated by fewer species and low to moderate numbers of only a few organisms" (Jennings *et al*., 2008). In the Boulder River watershed in Montana, a study conducted by Farag *et al*. (2003) found that the stream "impacted by approximately 300 abandoned metal mines were devoid of all fish" at close proximities of the mine sources. The populations of "cutthroat trout (O. clarki), brook trout (Salvelinus fontinalis), and rainbow trout (Oncorhynchus mykiss) were found further downstream and away from sources of" AMD (Farag *et al.*, 2003). In British Columbia, the abandoned Britannia copper mine was reported to have been releasing AMD into the local waters for a couple of years which resulted in the death of many species within the impacted streams (Jennings *et al.*, 2008).

In South Africa, AMD emanating from the East Rand, Central Rand, and West Rand have affected several streams which may include the Rietspruit, Blesbokspruit, and Natalspruit. Major rivers impacted by AMD "emanating from these mines include the Vaal River to the south and the Limpopo River to the North" where the ecological deteriorations resulting from AMD-contaminated water were recorded (Coetzee *et al.*, 2006). The upper Olifants River catchment in South Africa is among rivers in the Southern Africa that are highly polluted by the metals from mining operations where fish and crocodile mortalities were witnessed several times around Lake Loskop (Magowo, 2014). The mortality rate that was associated with the presence of metals was noted to have been increasing frequently in the past few years along the Olifants River (Figure 2.5) (Driescher, 2008). In 2008, a study done by Paton (2008) found that the population of crocodiles in the Loskop dam reduced from approximately 30 animals to 6 which was linked to the consumption of rancid fish fat after a fish die-off from sporadic incidents of the pouring of AMD into the lake. The Robinson Lake in Randfontein on the west rand was recorded to have plant species “around water bodies that contain high levels of sulphate” that destruct them around such water bodies (Magowo, 2014). Soils and plants along the riverbanks would often be encrusted with sulfate (Durand, 2012).

Figure 2.5: A) Demonstration of the dead fish at the Loskop Dam; B) Fish died in the lower Olifants River catchment close to the Phalaborwa Gate of the KNP; C) Crocodile died at the shore of Loskop Dam (Imaged adapted from Lebepe, 2018).

High levels of metal concentrations have been recorded in the Tweelopiespruit and Rietspruit where concentrations exceeded critical limits as suggested by the World Health Organisation (WHO) and were considered deadly to living organisms including humans if consumed (Durand, 2012; Nleya, 2016). Metals that were found to be highly concentrated in Tweelopiespruit and Rietspruit include aluminium, manganese, cobalt, zinc, and radium where almost all plant species have been killed (Figure 2.6) as a result of the release of heavy metal from the mining operation. The dissolved aluminium ions alone are the main cause of plant toxicity in acidic soils (Magowo, 2014). Plants require a proper balance of macro and micronutrients in the soil where soil pH plays a major role in the availability of nutrients and the development of a variety of plant species (Halcomb *et al*., 2009; Nleya, 2016). When the soil pH is below 5; nitrogen, phosphorus, and potassium are tied up in the soil and therefore not available to plants (Halcomb *et al.*, 2009). The study by Ochieng *et al*. (2010) revealed that the direct exposure to heavy metals from the AMD can also result in the disruption of metabolic functions of animal life (Nleya, 2016). The metabolic functions can be disrupted by heavy metals in two ways; (1) they become accumulated in most important organs and glands such as the heart, brain, kidneys, liver, and bone to disrupt their functions, and (2) they also inhibit the absorption, and interfere with important nutritional minerals from their original place and prevent their biological functions (Singh *et al.*, 2011; Nleya, 2016).

Figure 2.6: Absence of riparian plants around Robinson Lake in Randfontein, the source of the Tweelospruit (Image adapted from Durand, 2012.).

The study done by Bell *et al*. (2001) revealed that other than species of algae, no marine life appeared to have been existing in the seepage area, in and around “pollution control ponds, or in the streams around Middelburg colliery in” eMalahleni. Another cause for concern associated with the extraction and other industries in Phalaborwa and the Witbank-Middelburg complex (eMalahleni) areas was the decline in the number “of piscivorous bird, especially herons, which was more likely to be linked to the fading of the “health” of this river” because of the presence of heavy metals (Myburgh and Botha, 2009). The deaths of herons were observed in Loskop dam, Kruger National Park, and Massingir Dam where the post-mortems results showed excessive abdominal deposits of yellow fats such as pansteatitis (Myburgh and Botha, 2009).

Acid mine drainage can also pose an instant threat to the rural communities living close to mine tailing dumps if their water sources are contaminated with AMD. The Central, Eastern, and Western basin of the Witwatersrand mining area exist very close to the rural communities where most of their water resources are contaminated with AMD from mining dumps (Figure 2.7). The Princess Dumps “is an old and abandoned gold tailings dam” that exists very close to the community of Davidsonville, Roodepoort, west of Johannesburg (Figure 2.8), where AMD-contaminated water resources were witnessed. The uranium found in the AMD-contaminated water can be highly toxic to the health of human if consumed (Agency for Toxic Substances and Disease Registry, 2011).

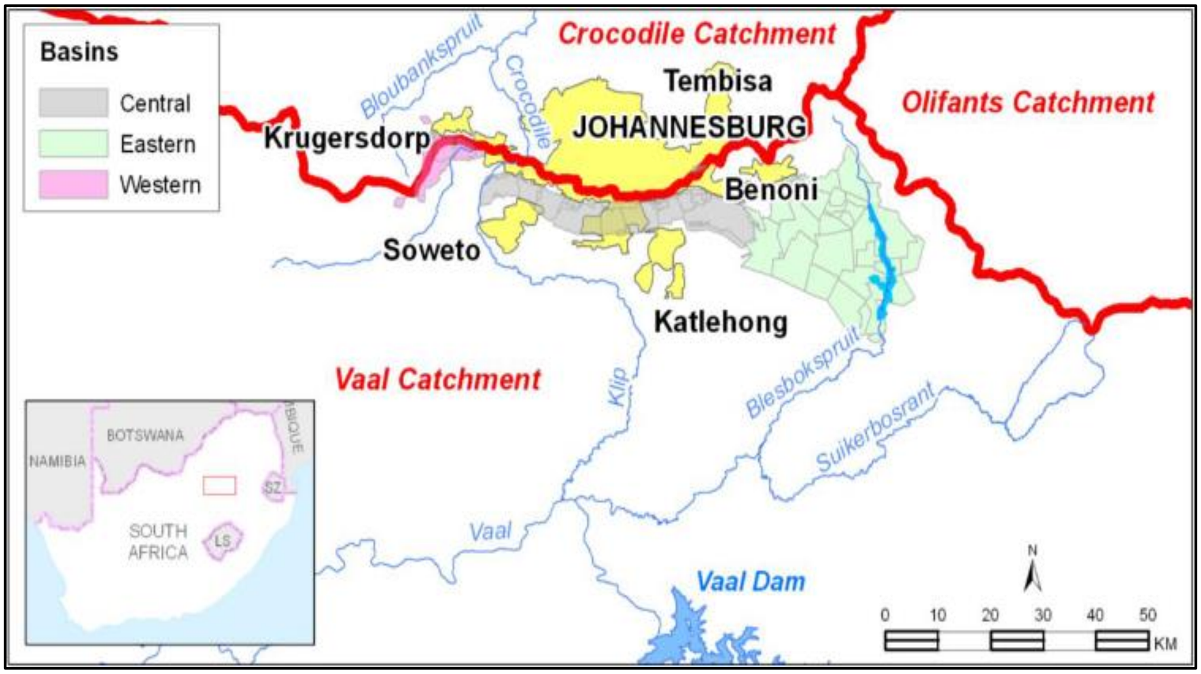

Figure 2.7: A map demonstrating the location of the Central, Eastern, and Western basins of the Witwatersrand mining area and surrounding communities (Department of Water and Sanitation, 2013).

Figure 2.8: Community of Davidsonville existing approximately 150 meters away from the AMD-contaminated man-made wetland where the ecological integrity of the watercourse has been severely compromised (Image adapted from Ngigi, 2009).

2.6 Acid Mine Drainage prevention

Prevention of the AMD formation involves protecting the sulphate-bearing minerals from interacting with air, water, and bacteria within the mining site to eliminate the process of sulphate oxidation (Kefeni *et al.,* 2017). The establishment of the source control methods can be considered important in new operating mines to prevent the generation of the acids (Greben *et al.,* 2009). The movement of clean and contaminated water should be taken seriously within the mining site and this movement can be controlled by the construction of ditches to divert water from interaction with sulfuric bearing ore deposits. In Sweden, the two most common methods used to prevent sulphate oxidation are the dry cover and water cover, wherein a dry cover, low-sulphate content tailings, clay sub-soils, oxide wastes, organic wastes, alkaline substrates, soils, and neutralising materials are commonly used to prevent AMD generation (Olds *et al*., 2012; Kefeni *et al*., 2017). Structures such as the grout curtains and slurry walls can also be used to control the groundwater migration (Kuyucak, 2012). Magowo (2014) suggested the blending of the "acid-generating and acid-neutralising material, producing benign composts" as another method to prevent AMD formation. The solid phase phosphates, which may include the apatite, can also be utilised to pyritic mine waste in order to precipitate ferric ion as ferric phosphate and this will reduce its potential as an oxidant to pyrite oxidation (Johnson and Hallsberg, 2005).

According to Magowo (2014), bacteria can also be utilised in the prevention of the formation of the AMD through the reduction of biological activities associated with the oxidation of sulphate. Biocides are poisonous substances that are capable of destructing the life of the bacteria such as *Thiobacillus ferroxidants* and *Thiobacillus thiooxidants* responsible for the formation of AMD (Motsi, 2010). The application of biocides can be used as a prevention method of AMD formation and is mostly applied to the running water since most biocides are water-soluble (Magowo, 2014).

Backfilling of open-pit mines is a common mining method, which eliminates the development of an open-pit lake, and eventually returns the groundwater to approximately pre-mining groundwater table (Lottermoser, 2007). The backfilling open-pit consists of a saturated anoxic zone below the groundwater table where mine waste with acid-generating capacity can be placed to prevent contact of sulphide minerals with oxygen (Lottermoser, 2007). The benefits of in-pit disposal compared to other tailings disposal methods (Lottermoser, 2007) may include:

- “Placement of tailings below the groundwater table, to ensure limited interaction with the hydrosphere and biosphere.
- No spillages, failures, or erosion of tailings dams can be associated with this method.
- Backfilling of a large open void with mine waste also improves the landscaping of the mining area and ensures the possibility of revegetation.
- And a greater depth of cover, ensuring suppression of oxidation of sulfidic wastes or radiological safety of uranium tailings.”

The following section discusses in detail, the above-mentioned source control measures that can be employed as an attempt to prevent or minimize the rate of AMD formation.

2.6.1 Flooding or sealing of underground mines

Flooding and sealing underground deep mines can be used to separate oxygen and water from interacting with the sulphate-bearing minerals (Johnson and Hallberg, 2005; Nleya, 2016). According to Johnson and Hallberg (2005), the dissolved oxygen (DO_2) which can be present in the flooding waters (ca. 8 to 9 mg/L) is used by mineral oxidizing micro-organisms present and replenishment of DO_2 by mass transfer and diffusion is impeded by sealing of the mine. The flooding and sealing of underground deep mines are only effective where all shafts and adits locations are known and where the inflow of water containing oxygen does not occur (Nleya, 2016).

2.6.2 Underground storage of mine tailings

The underground storage of mine tailing method “has been used for disposing and storing mine tailings that can potentially generate acid, with the main objective of preventing the contact between acid producing minerals and dissolved oxygen” (Nleya, 2016). The study done by Johnson and Hallberg (2005) indicated that during this method, “shallow water covers can be utilized, and their effectiveness can be enhanced by covering the tailings with a layer of sediments or organic” materials. Johnson and

Hallberg (2005) indicated that this prevention method has the dual benefit of limiting oxygen ingress and affording some protection against the re-suspension of the tailings due to the actions of wind and waves. The created organic layer can be incorporated in the dry covers used for surface storage of reactive minerals spoils, where the “sealed layer” that covers the spoil is normally created from clay (Nleya, 2016). This method was found to be effective in most of the gold mines in North America and Canada (Hilson and Murck, 2001). However, the method can be less effective in areas that experience acute wet and dry seasons that are likely to cause the drying and cracking of the cover than in temperate zones. Paste backfilling is more effective, and widely exercised as a procedure for mine recovery (Nleya, 2016; Benzaazoua and Bussiere, 2002). These backfilling mine workings by use of a mixture of mine tailings is done as an attempt to minimize the formation of acid, where “Portland cement and other binders can be added to mine tailings to form a waste disposal option that is both geotechnically stable and geochemically non-reactive” (Benzaazoua and Bussiere, 2002).

2.6.3 Desulfurization

Desulfurization of tailings as one of the techniques used to prevent AMD formation “involves the removal of sulphide minerals from mine tailings to create a benign sand fraction suitable to use as a general backfill and a companion low volume sulphide concentrate that requires careful disposal” (Nleya, 2016; Magowo, 2014). The study done by Benzaazoua *et al.* (2000) has shown that most of the “mine tailings contain small amounts of sulfide minerals that can be separated from non-acid forming silicate minerals using conventional mineral processing equipment to create a cleaned material with sufficient neutralizing potential to prevent any future acidity”. This method was proven to work at four different mines in Canada by Benzaazoua *et al*. (2000). Though this method is simple and cost-effective, it may not be readily applicable to counteract major AMD sources such as the underground mine workings (Nleya, 2016).

2.6.4 Mine capping and blending of mineral waste

This method (mine capping) is generally used for surface mines where, the capping can be applied to prevent rainfall from reaching acid-forming units in the backfilled mine (Fripp *et al*., 2000; Nleya, 2016). Typically, the cap is fly ash covered with topsoil and seeded, and this method can only be effective where the horizontal components of groundwater are negligible (Fripp *et al*., 2000; Nleya, 2016).

The blending of mineral wastes involves the mixing of acid generating and acid consuming materials to produce benign aggregates after the waste is disposed of in an open pit formed during backfilling mining (Jera, 2013). This method "is an appealing and possibly low-cost alternative for minimizing the formation of AMD in waste piles of some mines" (Johnson and Hallberg, 2005). The addition of the solid-phase phosphates such as apatite to pyritic mine waste for precipitation of iron as ferric phosphate is regarded the most effective alternative for this method as it reduces its potential to act as an oxidant of sulphate minerals (Nleya, 2016). The management of AMD through the use of high-carbonate mine waste (blending/covers) has been shown to effective at several mines such as Ok Tedi (Guinea), Grasberg (Indonesia), and Savage River (Australia) (Australian Government, 2016).

2.6.5 Anion surfactants application

Bacteria such as *Thiobacillus ferroxidants* and *Thiobacillus thiooxidants as stated in section 2.6* are well known to accelerate the rate of AMD formation and "therefore, the occurrence of the activity of lithotrophic (rock-eating) irons and sulphur-oxidizing bacteria found in mineral tailings is another technique employed" to counteract the formation of AMD from the source (Nleya, 2016). Generally, this method "involves the application of anionic surfactants such as sodium dodecyl sulphate (SDS), which are fatal to" the bacteria responsible for the formation of AMD (Johnson and Hallberg, 2005). The use of biocide is a short-term control measure and therefore requires repeated applications of the chemicals and the used bactericides can be toxic to the aquatic ecosystems (Sahoo *et al*., 2013; Nleya, 2016).

2.7 Conclusion

The aim of this chapter was to review the literature that already exists on the AMD in South Africa and globally, and develop the theoretical framework based on this literature that can be applied in this study. Literature survey shows that the impacts of AMD are well documented in the upper Olifants River catchment and other mining regions, but little exists on the lower Olifants River catchment. The literature further shows that more preventative measures are still required in various parts of mining regions in South Africa to control AMD from the source. Little research and publications on the AMD preventative measures by South African mining houses do exist. The literature reveals that there is a general decline in research within the area of new AMD prevention methods. AMD greatly influences the quality of the water and has huge ecological impacts. The unregulated release of AMD-contaminated severely degraded ecological habitat in most parts of the world.

CHAPTER THREE

RESEARCH METHODOLOGY AND MATERIALS

3.1 Introduction

This chapter aims to present all materials and general procedures used to obtain the required data to achieve the aim and objectives of the study. The chapter also details the description of the study area as well as the exact sampling points at the lower Olifants and Ga-Selati Rivers where surface water samples were collected in order to evaluate the impacts of AMD on water quality of the lower Olifants River. The permission to access the riparian zones for surface water sampling was granted by both the Department of Water Sanitation and the landowners/managers at the private properties.

The water quality of the water resources is commonly assessed by the use of water quality index (WQI). The parameters of the water quality were prepared from the analytical results of water samples and combined in a GIS environment so that the quality of water can be assessed. Numerous types of WQIs do exist for different uses. The most frequently used are Weighted Arithmetic Water Quality Index (Horton, 1965; Dojlido *et al*., 1994), National Sanitation Foundation Water Quality Index (Delphi method) (Dalkey, 1968), Oregon Water Quality Index (Deq, 2003), “and Canadian Council of Ministers of the Environment Water Quality Index” (Khan *et al*., 2003; Lumb *et al.,* 2006).

3.2 Description of the study area

The study was carried out at the lower Olifants and Ga-Selati Rivers (Figure 3.1) around the Phalaborwa mining industries which consist of two operating mining companies in Ba-Phalaborwa Local Municipality of Mopani District, Limpopo province of South Africa. The study site is situated approximately 7 km south of the town of Phalaborwa which is found between 23°54'15.42", S 31°2'32.10" E and 24°3'49.03" S, 31°10'27.67" E coordinates. The study area is also located near the confluence of the Ga-Selati and Olifants Rivers along the western border of the Kruger National Park (KNP) in the

Lowveld as depicted in Figures 3.1. Palabora Mining Copper (PMC) forms part of the Phalaborwa mining companies operating at the lower Olifants River catchment, where they mine and refine the copper as a product. Foskor is also found at the lower Olifants River catchment and it mines and refines the phosphate rocks into phosphoric acid and phosphate-based granular (Foskor, 2012). These two mines are located approximately 7 km (south) away from the confluence of Ga-Selati and Olifants Rivers. Mining and other industrial activities at Phalaborwa are major pollution sources at the lower catchment of the Olifants River with the Ga-Selati River being the main transporter of pollutants into the Olifants River. According to Gohell (2014) and Van Vuren *et al*., (1994), high salinity, pollution by metals, and high silt loads are the main conservation concerns, and they contribute to the decline of marine life such as fish species at the lower catchment of the Olifants River.

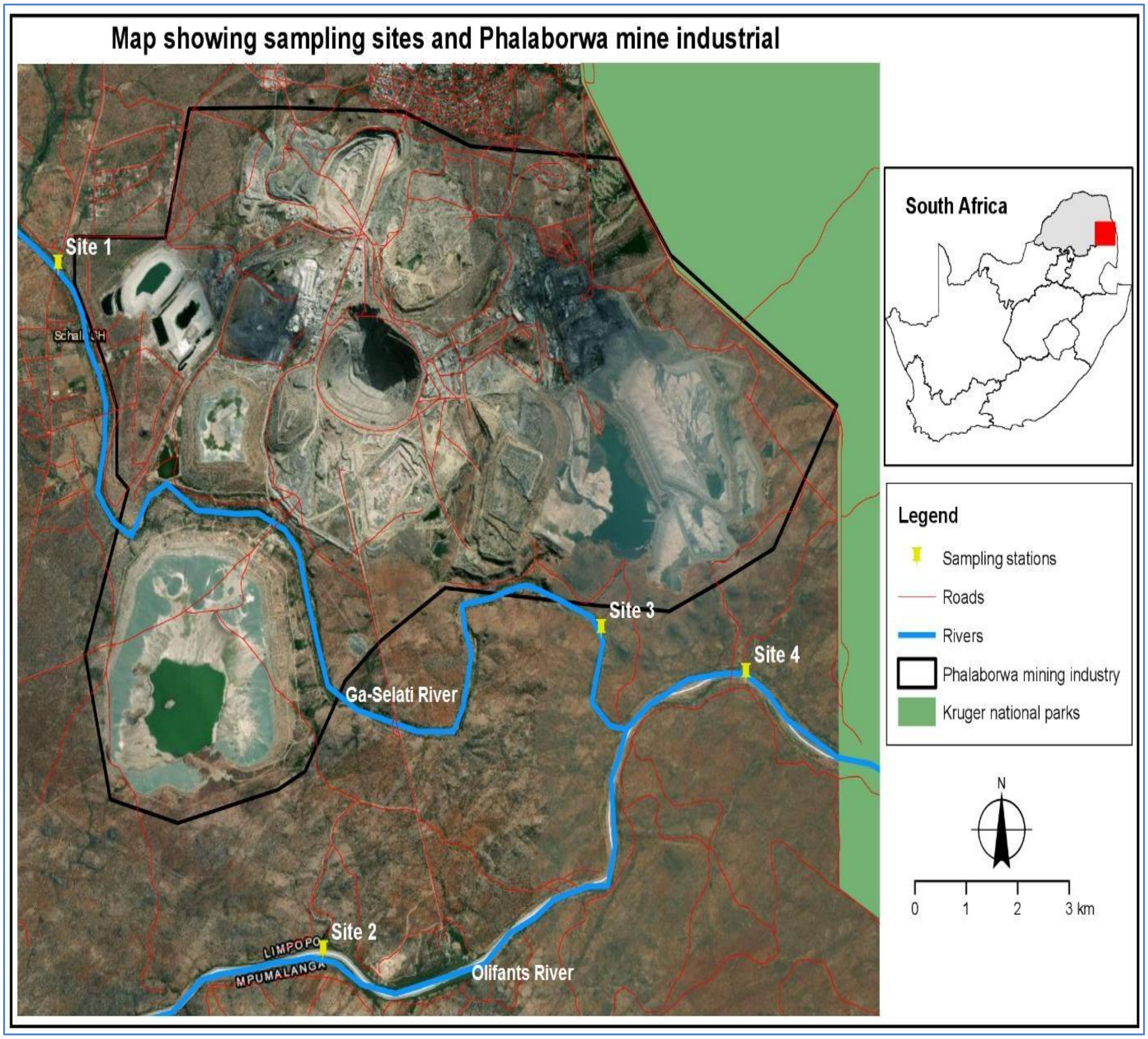

Figure 3.1: Perspective map of the study area showing lower Olifants and Ga-Selati Rivers, their confluence, sampling sites, and the Phalaborwa mining sites.

3.2.1 Land-use

The lower catchment of the Olifants River is comprised of small-scale subsistence farming with irrigation scheme, improved and unimproved grazing, water treatment works (Lepelle Northern Water Board), forestry, conservation areas i.e., Kruger National Park, industries and mining companies such as Foskor and Palabora Mining Company (Heath *et al*., 2010) (Figure 3.2 and 3.3). Minerals mined at the lower catchment of the Olifants River "include gold in the Blyde sub-catchment, antimony, clay minerals, copper, titanium, vermiculite, phosphate, zinc, silver, and zirconium at the Ga-Selati River sub-catchment" (Ramahlo, 2013). The area consists of some urban built-up (Phalaborwa area) and safari game lodges such as the Shona Langa Safari game lodge that exist at about 7 km away from the Ga-Selati/Olifants confluence. Table 3.1 presents a summary of the land-cover classes identified within the extent of the study.

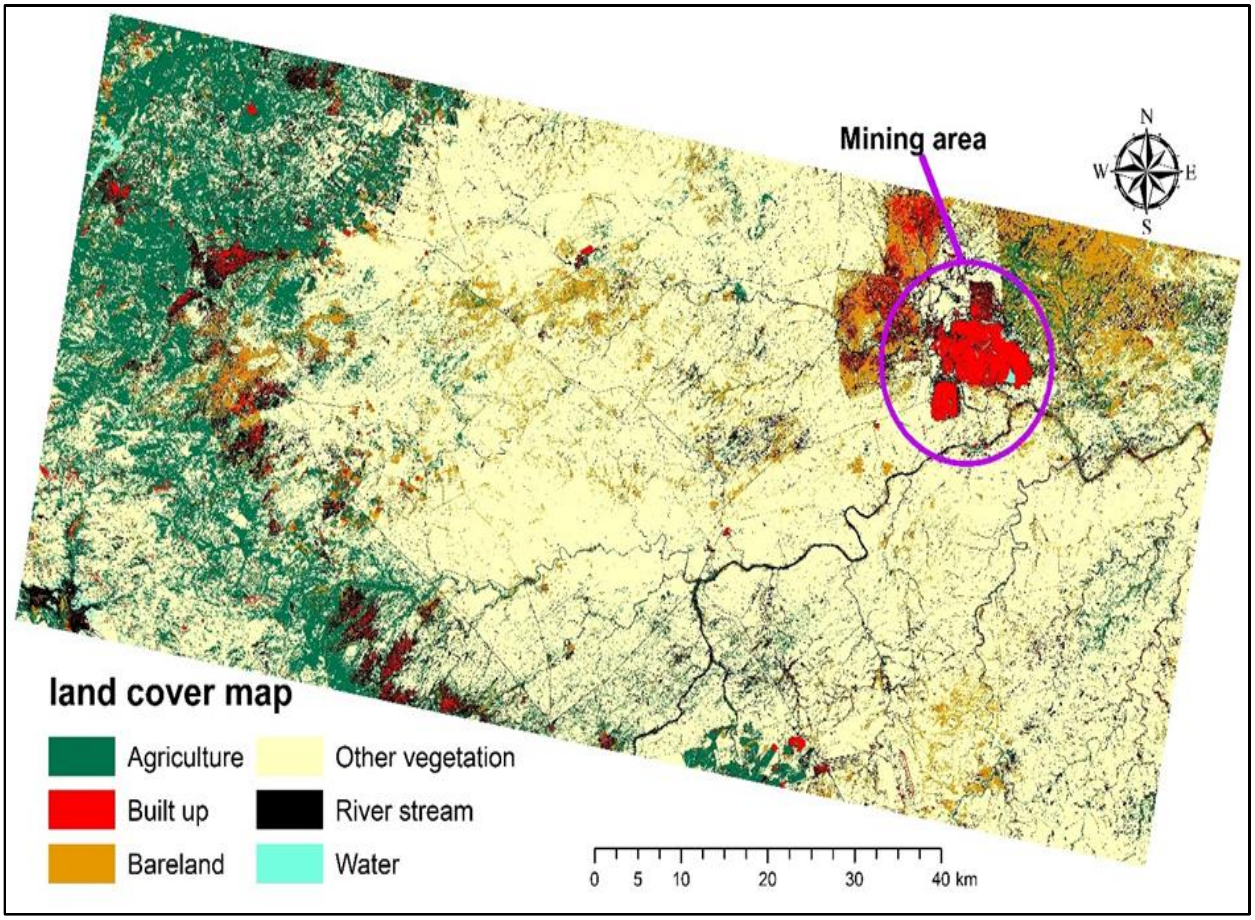

Figure 3.2: A map illustrating land-cover land-use activities around the lower Olifants River catchment.

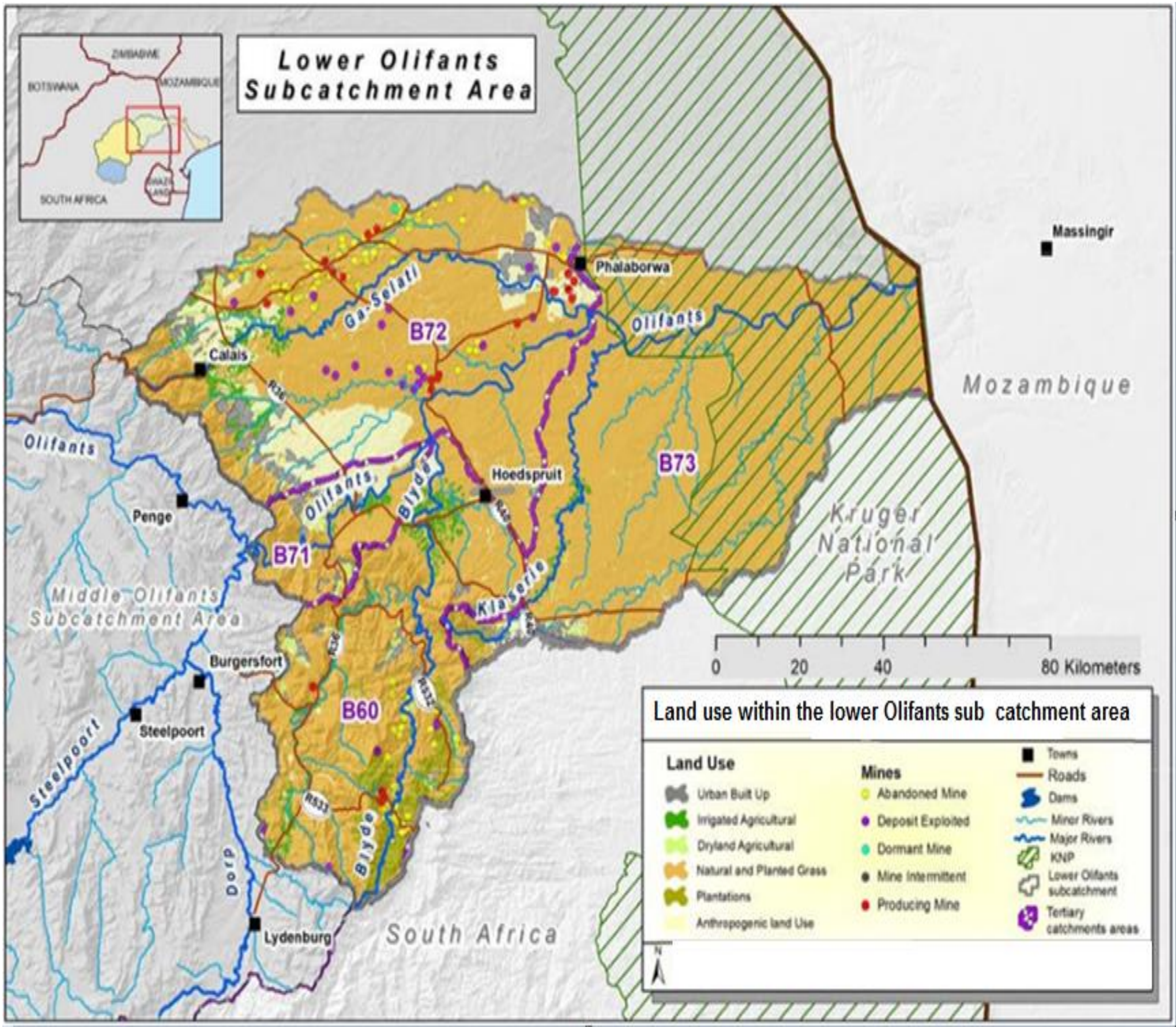

Figure 3.3: Land-use within the entire lower Olifants sub-catchment area (Map adapted from Association for Water and Rural Development, 2018).

Table 3.1: Description of land-cover classes identified within the extent of the study.

LULC classes	Description
Agriculture	Pasture, crop lands, fallow lands, groves.
Bare land	Beaches, sandy areas, mixed barren lands, transitional areas, dry salt areas, open areas, and empty riverbeds.
Built-up	Communication, commercial, utilities, Residential, industrial, transportation, and mixed areas, as well as mining area.
Other vegetation	Vegetation that was not presented in the above-existing classes.
River streams	River/streams.
Water	Ponds, lakes, estuaries, wetlands, and waterlogged areas.

Small-subsistence agricultural farms exist upstream of the sampling sites along both the Olifants and Ga-Selati Rivers. Agricultural land-use may potentially degrade streams by increasing non-point pollution sources, impacting the riparian and stream channel habitat, and altering flows (Allan, 2004). According to Quinn (2000), elevated concentrations of nutrients in streams can increase the development of algae, and lead to the altered composition of autotroph assemblage. The insecticide and herbicide runoff from the agricultural land is likely responsible for the disappearance of abundant invertebrate taxa and poor habitat quality (Allan, 2004). In areas where agricultural activities exist along stream margins and natural forest removed, streams experience raised temperatures and have less input of energy (Quinn, 2000). The expansion of human settlements that exist alongside of the Ga-Selati River, upstream of the sampling sites, may increase the rate and variety of pollutants generated from society. Streams that exist close to human settlement turn to receive a variety of pollutants which are likely to be associated with the degradation of the stream habitats. Sewage run-off and litter can be a visual nuisance. Sewage and other pollutants that humans discard into the streams may deplete oxygen because of eutrophication. As already stated in this study, mining land-use exists adjacent to the Ga-Selati River. AMD is one of the most recognised consequences of mining to freshwaters can be responsible for the elevation of the concentration of heavy metals in screams and the reduced abundances and diversity of aquatic ecosystems (Maret and Maccoy, 2002).

3.2.2 Surface hydrology

The hydrological structure of the study area includes the lower Olifants and Ga- Selati Rivers as the major perennial river systems flowing in the south-earthen directions of the study area. The Olifants River catchment covers portions of South Africa and Mozambique with approximately 85 % of the catchment found in the north-eastern part of South Africa (Ashton *et al.,* 2001; Lebepe, 2018). The Olifants River catchment extend to about 74 500 km^2 in South Africa with a large section found in Mpumalanga and Limpopo provinces and a small section in Gauteng province (Van Vuuren, 2010). The Olifants River has four catchment management areas namely: the upper; the middle; the Steelpoort; and the lower catchment (Claassen *et al.,* 2005; Lebepe, 2018).

It flows from the upper catchment in Highveld to the lower catchment passing through industrial, agricultural, and mining areas on its way towards the Kruger National Park (Van Zyl *et al*., 2001). Existence of anthropogenic activities along the Olifants River has rendered it the classification as stressed and the overall condition of the river ecosystems considered as *fair* to *poor* (Department of Water Affairs and Forestry, 2000; Water Research Commission, 2001). At the Kruger National Park, the lower Olifants River is regarded as environmentally sensitive with high levels of aquatic ecosystems (Roux *et al*., 2008; Aken, 2012). The cumulative impacts from the upstream put the biodiversity at this portion of the catchment at great threat (Rashleigh *et al*., 2009; Aken, 2012). The impacts associated with the anthropogenic activities at this portion include the siltation and reduced streamflow (Aken, 2012).

Ga-Selati River is a tributary of the Olifants River and it covers an area of about 2 340 mk^2 (Sally and Yawson, 2007). This river originates in the Drakensberg escarpment and flows through the Lowveld before its confluence with the lower Olifants River at about 148 km from its origin (Aken, 2012). As with the Olifants River, the Ga-Selati River is bordered by agricultural, mining, and industrial areas which are the reasons for concerns at the Kruger National Park as they can potentially affect the water quality. The study area falls within the three quaternary catchments that exist at the lower Olifants water management area. B72K quaternary catchment (outlet of the Ga-Selati/Olifants confluence) covers the sites 1 and 3 of the study. B72D quaternary catchment covers site 2 while B73C covers site 4 of the study.

3.2.3 Description of the sampling sites

The four sampling sites located in the lower Olifants and Ga-Selati Rivers were randomly selected using the Geographical Information System (GIS) toolset. GIS is "an organized collection of computer hardware, software, geographic data, and personnel designed to efficiently capture, store, update, manipulate, analyse, and display all forms of geographically referenced information" (Environmental Systems Research Institute, 1990). The adopted GIS approach in the selection of the sampling site was the Analytical Hierarchy Process (AHP) which was proposed by Saaty (1980). During this stage, two distinct procedures were followed to successfully select sampling sites.

Procedures followed include the development of a digital GIS database where the spatial information of the study area was formed, and the information layers were then analysed by the use of AHP to determine suitable sampling sites based on the distances from the potential AMD pollution sources along both Ga-Selati and Olifants Rivers. The selected sampling sites are shown in Figure 3.4. The potential AMD pollution sources (mining activities) do exist adjacent to the selected sampling sites. Table 3.2 describes the sampling sites in relation to the surrounding mining activities.

Table 3.2: Description of the sampling sites selected in the Olifants and Ga-Selati Rivers.

Site	Description
Site 1	Site 1 is located upstream of Phalaborwa mining companies and it is found along the Ga-Selati River under the R40 bridge. The site is dominated by slow-deep and slow-shallow habitats with sand and fine gravel. This site was used to determine possible pollutants and state of water quality before it could possibly mix with the wastewater from the Phalaborwa mining industries. The site is found on 23°58'38.47"S and 31° 4'26.05"E. The photograph of the site is shown in Figure 3.5(a).
Site 2	Site 2 is located at the Olifants River, close to the Shona Langa Safari Lodge at the lower Olifants River catchment. It is upstream of the Phalaborwa mining companies and is found at 240 4' 4.58"S "S and 310 7' 13.37"E. The site consists of a barrage located at approximately 260 m away towards the downstream directions of the sampling site. Water at this barrage is treated and purified by the Lepelle Northern Water Board (LNWB) and supplied to the town of Phalaborwa, industrial complex, as well as to the phosphates and copper mines (Lepelle Northern Water, 2010). Distribution of water from this barrage is mostly done as industrial and as portable water in numerous treatment plants. Generally, the site is characterised by moderately reduced river flow. The site was used to determine the state of water quality before possibly contaminated by mine wastewater from the Phalaborwa mining activities that seeps into the Ga-Selati River as the major tributary of the lower Olifants River. Three surface water samples were seasonally collected from this site. Figure 3.5(b) is a photograph of site 2.

Site 3	Site 3 is located downstream of all Phalaborwa mining companies along the Ga-Selati River, and it is at 24° 1'31.74"S and 31°10'8.37"E. This site is situated upstream of the Ga-Selati/Olifants confluence. It is characterised by reduced gradients of the river with the presence of large pools along the river. The substrate is rocky and covert in sediment. This site is located within the South African military base and consists of the chlorine dosing equipment before the Ga-Selati/Olifants confluence. Three surface water samples were also seasonally collected from this site. Figure 3.5(c) shows the photograph of site 3 with dominant bedrock along the Ga-Selati River.
Site 4	The site is located downstream of all Phalaborwa mining companies and Ga-Selati/Olifants confluence along the Olifants River. It is found between 2401' 52.57"S (latitude) and 31o 11' 38.74"E (longitude). The site is characterised by moderately decreased river flow because of the anthropogenic activities including the barrage that exists upstream of the Olifants River. The decreased water flow at this site exacerbates problems related to the water quality and causes some habitats to be destroyed. The site consists of mixed water from the Ga-Selati River, which flows adjacent to mining companies and Olifants Rivers that flow adjacent to agricultural fields towards the Kruger National Park. Three surface water samples were seasonally collected from this site. Figure 3.5(d) shows the photograph of site 2 with dominant bedrock along the river...

Figure 3.4.: Satellite photograph showing the water sampling sites in the Olifants and Ga-Selati Rivers (Google earth, 2010).

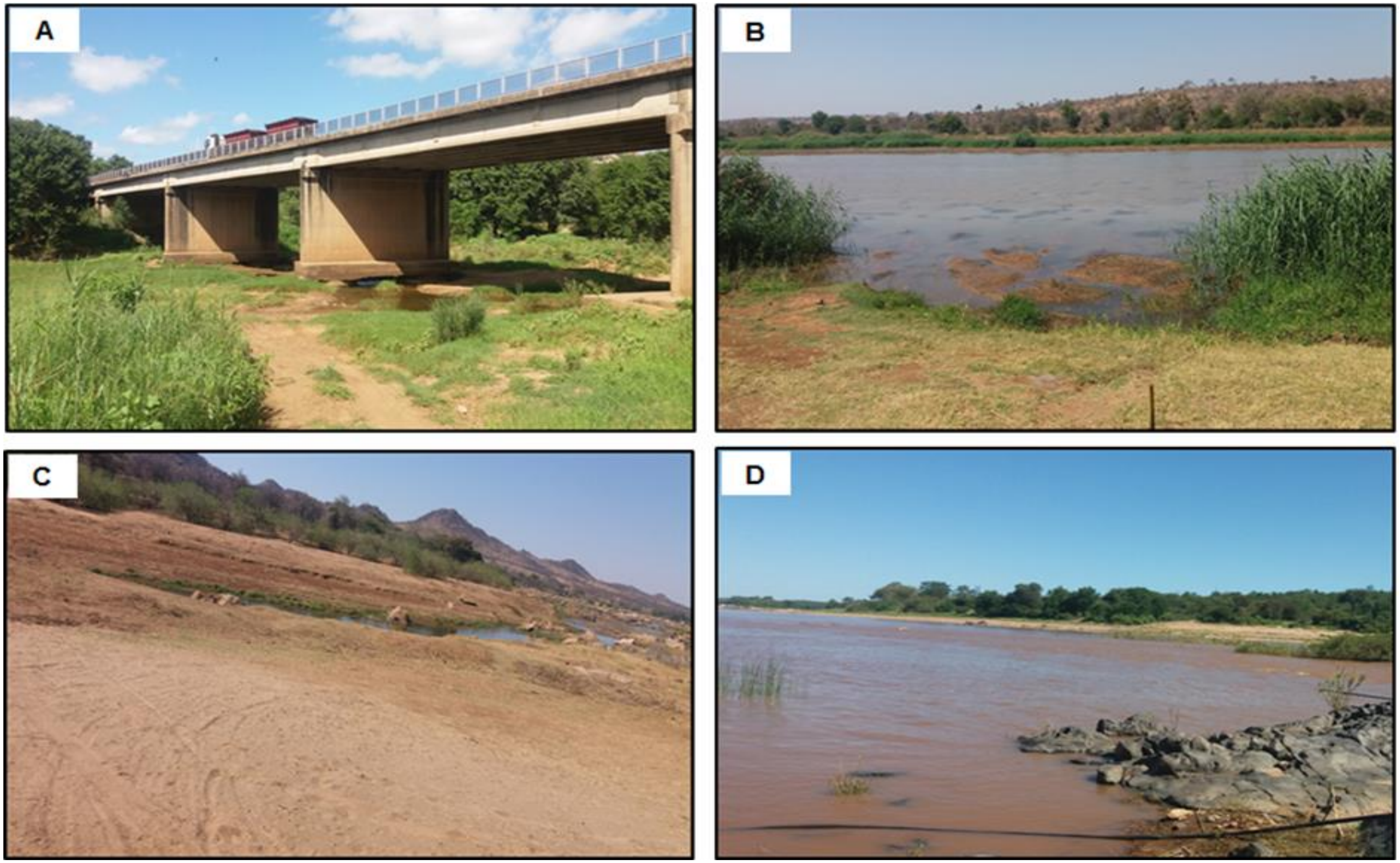

Figure 3.5: Site photographs: A) Site 1 - view upstream at Ga-Selati River showing the R40 Bridge; B) site 2 - view of the upstream at Olifants River; C) Site 3 – a view downstream at Ga-Selati River showing bedrocks; D) Site4 – a view downstream at Olifants River showing the dominant bedrock.

3.3 Data acquisition

This section focuses on the instruments and procedures optimized in the collection of surface water samples and further outlines the standard laboratory analysis procedures used to determine the physical and chemical parameters of the collected water samples.

3.3.1 Surface water sampling apparatus

For reliable results, the standard apparatus optimized in the collection of surface water samples included the new plastic bottles with caps, which were prewashed with distilled water to remove possible acids that might have existed in the bottles before sampling. Other instruments used included the cooler box with ice, a permanent marker for labelling, and the Global Positioning System (GPS) application which was used to record the coordinates where surface water samples were collected.

3.3.2 Surface water sampling procedure

The collection of the surface water samples were done according to the usually accepted sampling methods (United States Environmental Protection Agency, 2007; Quevauviller, 2001). Water samples were collected by the new prewashed bottles at about 100 centimetres underneath the surface of the lower Olifants and Ga-Selati Rivers. The bottle was opened and closed underwater to avoid mixing with the surface microlayer or oxidation of the sample (Stoichev *et al*., 2006). Prior to sampling, the sampling bottles were rinsed with the site water and the water used for rinsing was, thereafter, discarded away from the point of sampling. This procedure was used to equilibrate the sampling bottles to the same environment and to ensure complete removal of cleaning solution residues prior to sampling (Tutu, 2006; Stoichev *et al*., 2006; Lusilao-Makiese, 2012). The sampling bottles were filled with site water to their full capacity leaving no air space and tightly closed to avoid any leakages. The collected water samples were immediately labelled properly, stored in a cooler box which consisted of some ice, and taken to the laboratory. Three water samples were collected in every site which included the upstream and the downstream of the Phalaborwa mining activities along both Ga-Selati and lower Olifants River catchments, and that enabled the study to determine the impact of mining activities on water quality of the lower Olifants River in Phalaborwa area. The water samples were collected during the morning period before much of the evaporation could take place. GPS coordinates and photographs of each sampling sites were also recorded.

3.3.3 Sampling frequency

A total of thirty-six (36) Surface water samples were collected in three seasons of 2019/20 which included winter, spring, and summer from the four selected sampling sites and stored at a temperature of less than 4 ^{o}C. Twelve (12) surface water samples were collected seasonally, during high flows, which are the wet or rainy seasons, and during low flow, which are the dry seasons that have high rates of evaporation. The collection of water samples during the dry and wet seasons helped in determining the seasonal variations and significant impacts of weather patterns on water quality of the identified streams within the study area.

3.3.4 Laboratory determination procedures

Water samples were submitted to a SANAS accredited laboratory belonging to the City of Polokwane local municipality located at the University of Limpopo, Turfloop Campus. In order to determine the water quality profile at the lower Olifants and Ga-Selati Rivers, physical and chemical parameters (Table 3.3) were measured using the Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Spectro Instruments, Kleve, Germany) and ion chromatography (IC) (Metrohm, Switzerland) (Appendix 3 shows the laboratory results).

Table 3.3: Water quality parameters measured and incorporated in the study.

In-situ results	Laboratory results	
pH	pH	Sodium (Na)
Electrical conductivity	Electrical Conductivity (EC)	Aluminium (Al)
Turbidity	Turbidity	Fluoride (F)
	Total dissolved solids (TDS)	Chloride (Cl)
	Calcium (Ca)	Nitrogen (NO_3)
	Potassium (K)	Sulphate (SO_4^-)
	Manganese (Mn)	Vanadium (V)
	Magnesium (Mg)	

The division of the water samples into two parts was exercised upon arrival to the laboratory. The first part of the water sample was filtered under a vacuum with 0.45 μm filter paper (Merck Millipore, USA) and utilised in anions (F, Cl, NO_3 and SO_4^-) determination by ion chromatography (IC). The last part of the water sample was unfiltered and acidified with 1 % (v/v) (37 %, Sigma Aldrich, Germany) and analysed for cations which included, Ca, Mg, Mn, K, Al, and Na, other physical parameters (pH, turbidity, EC, and TDS) were analysed with appropriate meters.

3.3.4.1 Determination of cations concentrations

The "ICP-OES is one of the most powerful and well-known analytical tools for the determination of trace elements" (Murray *et al.,* 2001). As stated in the last section, the total analyses of measured cations were achieved using this spectrometric technique. The conditions of the instrument were optimized to achieve sufficient sensitivity and precision. The parameters for ICP-OES (Spectro Instruments, Kleve, Germany) that were used are indicated in Table 3.4 and each element was determined at various wavelengths.

Table 3.4: ICP-OES optimized conditions.

Parameters	Value settings
Plasma power	1700 W
Plasma gas flowrate	1500 L/min
Coolant flow	13 L/min
Auxiliary gas flowrate	2 L/min
Nebuliser gas flowrate	0.6 L/min
Sample uptake	2.0 ml/min
Measure time	60 s
Type of nebuliser	Burgener
Type of spray chamber	Cyclonic

All measurements were made against an external calibration curve and the samples were filtered with 45 µg L^{-1} syringe filters prior to analysis to prevent blockage of the instruments tubing and the nebulizers. A demountable quartz torch which consisted of an injector tube, a 1.8 mm internal diameter, a Burgener T2002 HP (Burgener Research, Mississauga, Canada) slurry nebuliser, and a cyclonic spray chamber (Glass Expansion, Hawthorn, Vic., Australia) formed part of the instruments that were used during the laboratory. The instruments were set up in a way that ensured triplicate ran measurements for each sample to ensure good quality control.

3.3.4.2. Determination of anion concentrations

The concentration of anions which included F, Cl, NO_3, and SO_4^- were measured using ion chromatography (IC). The technique used was a liquid chromatographic technique that uses ion exchange principles to isolate the different ionic species based on their affinity to the stationary phase. The column that was used for this analysis was a Metrosep A supp 5 with 150 mm length and 4.0 mm diameter. The IC was set at 13 minutes analysis time for each sample and the analysis was performed using the parameters in Table 3.5. The eluent solution was made up of 1.0 mM $NaHCO_3$ and 3.2 mM Na_2CO_3.

Table 3.5: IC parameters for anion determination.

Parameter	Value settings
Guard column	Metrosep A supp A/5 (Metrohm)
Analytical column	Metrosep A supp 5 (Metrohm)
Flow rate	0.7 ml/min
Temperature	25 ^{o}C
Injection volume	50 µl
Measure time	13 minutes

The 0.45 µm vacuum filter was used to filter the solution after the sonication. A 50 mM solution of H_2SO_4 was also used as a conductivity suppressor regenerant solution (Downing *et al*., 1998; Perkins *et al*., 1995; Lusilao-Makiese, 2012). A 1000 mg/L multi-standard stock solution of sulphate, nitrates, chloride, and fluoride was set by diluting an accurately weighed amount of their corresponding salts, namely and Na_2SO_4 (Merck), $NaNO_3$ (Merck) NaCl (Merck), and NaF (Merck) in one litre of deionized water (Millipore, USA). The sample was then filtered with a 0.45 µm filter and kept at 4 ^{0}C. The instrument was connected to the computer, to ensure accurate recording of the results.

3.3.4.3 Analytical method validation

To determine the limit of detection (LOD) and limit of quantification (LOQ) of the analytical procedure, reagent blanks were achieved by applying the sample preparation procedure. The calculations of the standard deviations were based on the concentration of reagent blanks. To ensure quality, precision, and accuracy of the results, analytical procedures were validated. The accuracy of the procedure for the total level determination of Al, Mn, Mg, Cl, F, Ca, SO_4^-, K, EC, TDS, and Na in water samples was verified by standard reference materials (SRM) 1643f where the recovery of the trace elements ranged between 84.0 – 95.6 % in water samples. Performance of analytical instruments and ICP-OES was observed by analysing the initial calibration verification (ICV) solution from the beginning to the end of every run. During this phase, the continuous calibration verification (CCV) solution was analysed after every 3 samples throughout the run.

3.4 Water quality parameters and preparation of thematic map layers

The selection of water quality parameters was guided by the number of analysed water quality parameters for individual seasons (winter 2019, spring 2019, and summer 2020). The thematic map layers of water quality parameters were, therefore, produced from the analytical results using the inverse distance weighted (IDW) interpolation technique available in ArcGIS 10.8 software. This technique is versatile, easy to use, and fairly accurate under numerous conditions, and captures the extent of local spatial variation (Signh *et al*., 2015). The resultant map layers were classified using manual breaks based on the recommended limits set by the South African water quality guidelines for the aquatic ecosystem (Department of Water Affairs and Forestry, 1996) and Environmental Protection Agency (2001). The classes created for all map layers were then reclassified and ranked on a scale of 1 to 5. Where, the value of 5 represents the most influential class with regard to water quality, while 1 corresponds to the least influential class.

3.5 Water quality assessment based on the Analytical Hierarchy Process (AHP)

Analytical Hierarchy Process (AHP) is a technique with multi-criteria for decision-making that allows the quantification and transformation of opinions to form a coherent decision-model. It is useful to decision-makers as it makes easier for them to draw best decisions, through reduction of the complex decisions into different hierarchical levels. After disaggregating complex decisions and building a hierarchy, it is essential to establish a pairwise comparative “analysis of the importance of various indicators in decision-making” (Saaty, 1980). The method of AHP was optimised to identify relative weights and priority of individual water quality parameters. The stepwise method suggested by Saaty (1980) was adopted for a successful plot. Figure 3.6 schematically presents the flow of the adopted methodology in the application of AHP. The scale of preference used in the assigning of numeric values is shown in Table 3.6.

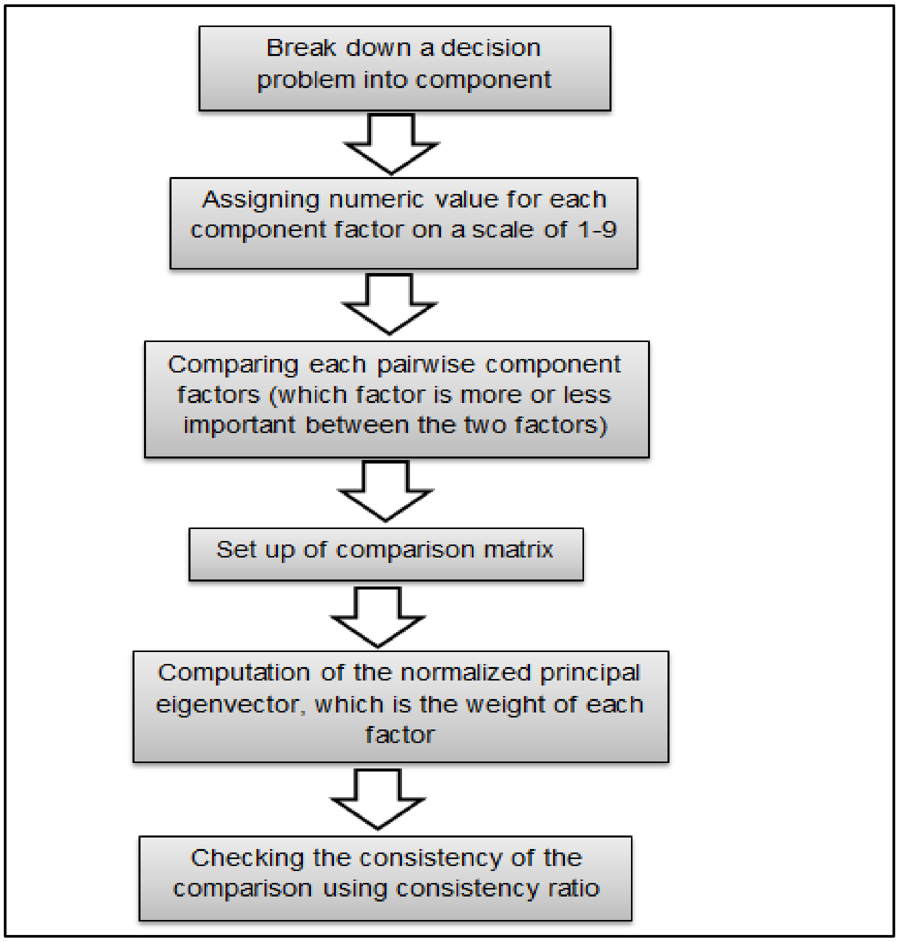

Figure 3.6: Stepwise approach in the application of AHP.

CR refers to the mathematical indicator used in the judgement regarding a decision that was randomly made. It constitutes an acceptance test of the weights of various component factors (Saaty, 1980). CR must be lower than 10 % to accept the computed weights, otherwise, the pair comparison matrix needs to be re-calculated (Saaty, 1980). CR was calculated using the following mathematical expression (Equation 1):

$$CI/RI = CR \quad (1)$$

where *RI* was the resulting consistency index average which relied on the order of the matrix and *CI* was the consistency index which was expressed as (Equation 2):

$$(\lambda_{max} - n)/(n-1) = CI \quad (2)$$

where λ_{max} was the largest or principal eigenvalue of the matrix and was easily calculated from the matrix and *n* was the order of the matrix.

Table 3.6: Preference scale between two factors in the AHP method.

Scale	Degree of preference	Explanation
1	Equal importance	Two elements contribute equally to the objective
3	Moderate importance	Experience and judgement slightly favour one element over another
5	Strong importance	Experience and judgement strongly favour one element over another
7	Very strong importance	One element is favoured very strongly over another
9	Extreme importance	The evidence favouring one element over another is of the highest possible order of affirmation
2, 4, 6, 8	Intermediate	Used to present compromises between the preference in weights 1, 3, 5, 7 and 9

3.5.1 GIS and inverse distance weighted (IDW)

The Survey of South Africa's toposheet was used for the digitalisation of boundaries of the study site with the help of ArcGIS software. Garmin 12-Channel GPS was used to record the precise locations of monitoring wells and the obtained data was later transferred into the GIS platform. The resultants WQIs attained from the water quality parameter were used in GIS and thematic maps were generated through spatial analyst module available in ArcGIS 10 software. IDW interpolation technique was also optimized for creating the WQIs thematic maps. Singh *et al*. (2015) showed that the IDW is a versatile, easy-to-use program, and fairly accurate under numerous range of conditions, and captures the extent of local spatial variation. Through the application of "IDW method, the property at each unknown location for which a solution is sought was expressed as mathematically by" the following equations (Singh *et al*., 2015):

$$z(\hat{s}_0) = \sum_{i=1}^{n} w_i(s_0) \cdot z(s_i)$$

Where $Z(\hat{S}_0)$ was the interpolated value estimated for the variable of interest at the station S_0, Z(Si) was the sample value at the station Si, $Wi(S_0)$ was the weight attached to the station Si and n was the stations' number. The main difference between all spatial interpolation methods relied on the computing of the weights Wi used in the interpolation. The simplest version of weights estimation used the inverse distances from all the points to the target one with the help of the following formula:

$$w_i(s_0) = \frac{1/d(s_0,\ s_i)^{\beta}}{\sum_{i=1}^{n}\left(1/d(s_0,\ s_i)^{\beta}\right)},\ \beta > 1,$$

Where $d(S_0, Si)$ was the distance from S_0 to Si and β was a parameter that must be determined. The weights decreased as the distance increases, especially when the value of β was large. The parameter β determined the degree of influence the neighbouring stations have on the estimates for a given station.

3.6 Legal framework and AMD management strategies assessment

The policy and legal assessment was achieved through cross-examining mine officials regarding cases of environmental noncompliance that might have been reported against the mining companies at the lower Olifants catchment. Literature was also reviewed for environmental transgressions that might have been published. The transgressions were checked against the National Water Act (Act No. 38 of 1998), the Mineral and Petroleum Resources Act (Act No. 28 of 2002), the National Environmental Management Act (Act 107 of 1998) and the National Environmental Management: Waste Act (Act No. 59 of 2008).

There are various techniques that can be used to counteract the acidic levels of the mine wastewater. Various techniques can also be applied by mining houses to avoid migration of AMD-contaminated water from their operational environment into the nearby streams. In order to identify the techniques that were put in place by the mining companies at the lower Olifants catchment, mining environmental officials were also cross-examined to get an overview of the applied AMD management strategies within their operations. The authorised Environmental Management Programme was also reviewed to obtain the approved AMD management strategies. The water quality results obtained through laboratory assessment during this study assisted to get an overview in terms of the effectiveness of the applied management strategies. The acquired information is presented under results section of this study.

3.7 Data analysis

The one-way analysis of variance (ANOVA) was used to determine the statistically significant differences between the generated data where the mean, median, standard deviation, and coefficient of variations were determined using the Microsoft Excel software. The statistical package for social sciences (SPSS) software was also used for one-way ANOVA, correlation (Appendix 1), and significant difference where the control values lower than 0.05 were considered to be significant. The one-way ANOVA in this regard refers to a statistical approach used to determine if there were any significant differences between the means of more than two independent sampling groups or set of data through the analysis of variance (Ostertagova and Ostertag, 2013). Each sampling site was therefore selected as group and its heavy metal concentration as the corresponding variables. The sample data was organised as indicated in Table 3.7.

Table 3.7: Sample Data.

	Site 1	Site 2	Site 3	Site 4
Sample Size	n_1	n_2	n_3	n_4
Sample Mean	$\overline{X}_1$	$\overline{X}_2$	$\overline{X}_3$	$\overline{X}_4$
Sample Standard Deviation	s_1	s_2	s_3	s_4

The null hypothesis was tested using the formula below:

$$H_0: \mu_1 = \mu_2 = \mu_3 = \cdots = \mu_k$$

where μ = sample sites mean, and k = number of sample sites. The alternative hypothesis (H_A) was accepted where the one-way ANOVA returned a statistically significant result which referred that there was at least two site means that were statistically significantly different from each other. One-way ANOVA is a numerical generalisation used in the two-sample t-test. The F statistic compared the variability between the sample sites to the variability within the sample sites and below is an indication (Table 3.8) of how it was worked out.

Table 3.8: One-way ANOVA table.

Source of Variation	Sum of Squares (SS)	Degree of Freedom (DoF)	Mean Square (MS)	F_0
Factor	$SSF=J\sum(\bar{y}i.-\bar{y}..)2$	I-1	$MST = SS_F/(I - 1)$	$F = MST/MSE$
Residual (Error)	$SSE=\sum\sum(yij-\bar{y}i.)2$	I(J-1)	$MSE = SS_E/(I(J - 1))$	
Corrected Total	$SST=\sum\sum(yij-\bar{y}..)2$	IJ-1		

$$F = \frac{MST}{MSE}$$

$$MST = \frac{\sum_{i=1}^{k}(T_i^2/n_i) - G^2/n}{k-1}$$

$$MSE = \frac{\sum_{i=1}^{k}\sum_{j=1}^{n_i} Y_{ij}^2 - \sum_{i=1}^{k}(T_i^2/n_i)}{n-k}$$

where F was the variance ratio for the overall test, MST was the mean square due to treatments (between sample sites), MSE was the mean square due to error (within sampling sites, residual mean square), Y_{ij} was an observation, T_i was a group total, G was the grand total of all observations, n_i was the number in group I, and n was the total number of observations.

3.8 Conclusion

The Olifants and Ga-Selati Rivers are perennial rivers that confluence in the Phalaborwa area. Numerous anthropogenic activities that may impact the streams do exist around the study area. Stream ecosystems are greatly affected by the anthropogenic across spatial scales. Four sampling sites were identified and visited during the sampling period of the study. Sampling procedures, samples conditioning, and storage conditions were considered and followed with care to avoid contamination of the collected water samples. The optimization of the analytical methodologies for the total concentration of pH, EC, TDS, Al, Mn, Mg, Na, K, F, SO_4^-, NO_3, and Cl was followed using an ICP-OES and IC. The analytical procedures were used for the purpose of ensuring accurate determination of the measured metal concentrations. The study has demonstrated the successful use of the IDW interpolation technique in the production of the thematic map layers. The AHP methodology was optimized to precisely identify the relative weight and priority of individual elements. The statistical analysis was also optimized to obtain statistical differences and correlations within the measured parameters.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presents and discusses the results that were obtained during the field and laboratory analysis. This was done in a way to achieve the objectives of the study. Four sites were explored to determine the status of the pollution of water resources by AMD from the mining industries in Phalaborwa. As part of the study, water samples were collected seasonally between 2019 and 2020. The analysis of heavy metals in the water samples from four sampling sites is presented in tables and graphs to illustrate the levels of water parameters and their dispersion. This chapter also outlines the reported cases of environmental noncompliance that were obtained by cross-examining mine officials within the lower Olifants River catchment, and further presents the seasonal variations of the heavy metals in the study area and predicts, through a Geographic Information System (GIS) application model, the dispersion of the dissolved heavy metals along both Ga-Selati and Olifants Rivers.

4.2 Water quality

Water is an essential natural resource because any living organisms require it for survival. The quality of the water can be assessed through the determination of the physical, biological, chemical, and aesthetic properties of water and this can also assist to conclude on its fitness for different uses and for the protection of the health and integrity of marine life (Department of Water Affairs and Forestry, 1996). Good water quality is vital to flourish health of aquatic ecosystems since most of their life processes occur in the watery environment. AMD generated as a result of mining operations can directly impact on the quality of the water along the nearby streams and major rivers. Water quality, under natural conditions, differs from river to river and can be influenced by several factors including the geomorphology, geology, and soils as well as the biotic composition (Dallas and Day, 2004). The quantity and quality of water in many rivers is affected by the human activities that exist along them and thus also affect the marine life they accommodate. Water quality variables include the anions, cations and *in-situ* attributes. In this regard, the *in-situ* parameters include pH, electrical conductivity and total dissolved solids. Table 4.1 presents the sampling events that were conducted for the study during the 2019/2020 seasons. The mean and standard deviation were determined using the Microsoft Excel software. In winter 2019, few water quality parameters were analysed as many were not detected (ND).

Table 4.1: Sampling events.

Year	Month	*In-situ* Parameters	Detailed Water Quality
2019	July	✓	✓
2019	October	✓	✓
2020	February	✓	✓

4.2.1 Water quality results

4.2.1.1 pH

The pH is mostly measured by the concentrated amount of hydrogen ions (H^+) and alkalinity by determining levels of hydroxyl (OH^-), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions in water (Lebepe, 2018; Davies and Day, 1998). Dallas and Day (2004) indicated that in an aquatic environment, pH measures serve as the main determinant of the chemical species as well as the presence and harmfulness of metals in water. Streams receiving the AMD emanating from the mining sites have a pH of less than 3 (Bartram and Ballance, 1996). According to the Department of Water Affairs and Forestry (1996), pH values are not supposed to vary from the range of historical data on the specific site and time of day by > 0.5 of pH unit, or by 5 %. The pH of natural waters is mostly determined by geological influences and biological activities (Aken, 2012). The seasonal pH mean values in summer of 2020 at Ga-Selati River upstream and downstream (sites 1 and 3) of Phalaborwa mining industries (PMI) ranged between 8.04 and 8.5, respectively, while at the Olifants River upstream and downstream (sites 2 and 4) ranged between 7.77 and 8.21, respectively (Figure 4.1). The highest pH was recorded at site 3 (downstream at Ga-Selati River) which could be associated with elevation of sulphates and total dissolved solids.

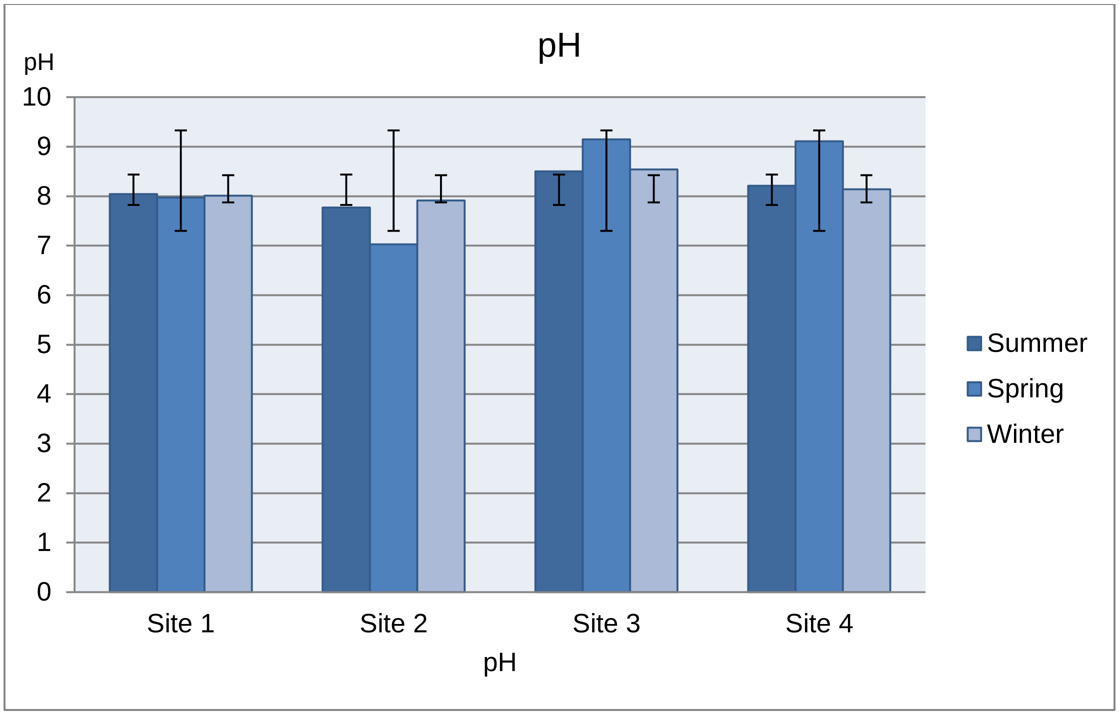

Figure 4.1: A graph showing pH mean values recorded in summer, spring and winter at the sampling sites.

According to the Target Water Quality Range (TWQR) set by the South Africa water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996), the pH concentrations at the two streams were therefore considered to be alkaline. The pH is an important element that has the ability to drive the corrosivity, solubility and speciation in the water bodies (Mulanga, 2016). These records support the findings from Heath *et al*. (2010) and Kekana (2013) where it is stated that the pH across Witbank to Phalaborwa in the Olifants River catchment is neutral to slightly alkaline.

The pH of the surface water at the downstream of both Olifants and Ga-Selati Rivers in spring of 2019 (Figure 4.1) were generally higher compared to summer. This could mean that more Cl was added into the surface water through the dosing equipment that exists along the Ga-Selati River. As in summer, the results of the study show that the surface water along both rivers in spring was alkaline. The pH mean values at the Olifants River upstream and downstream (sites 2 and 4) ranged between 7.03 and 9.11, respectively, while at Ga-Selati upstream and downstream (sites 1 and 3) the range was between 7.97 and 9.15, respectively. The variances of the pH values recorded from all sampling sites prove that there is a source of alkalinity at the downstream of these two streams.

The seasonal pH mean values for the surface water samples collected along Olifants River in winter of 2019 were 7.91 (upstream) and 8.14 (downstream) while Ga-Selati River recorded 8.01 (upstream) and 8.54 (downstream) (Figures 4.1). Higher values were generally observed in spring season because of more addition of either calcium hydroxide (Ca(OH)2) or dolomitic limestone (CaMgCO3) that is added into the Ga-Selati River to increase the pH of water before the Ga-Selati/Olifants confluence. As in spring and summer, the pH of the water along both streams in winter was alkaline.

4.2.1.2 Electrical conductivity

Electrical conductivity (EC) of water which refers to its ability to conduct an electrical current (Department of Water Affairs and Forestry, 1996) is considered a valuable indicator of the mineralization in water samples (Mulanga, 2016). The presence of ions such as HCO_3^-, $KHCO_3$, Mg, Ca, Cl and SO_4^-, that carry electrical charge in water, makes it more capable to conduct electrical current (Department of Water Affairs and Forestry, 1996). Electrical conductivity refers to a rapid and valuable surrogate means of the total dissolved solids (TDS) concentration of waters that have low organic content (Aken, 2012). EC and TDS are related and can be calculated by using the following generic equation (Department of Water Affairs and Forestry, 1996):

TDS (mg/l) = EC (mS/m at 250C) x 6.5

The rate at which the TDS change and the time of change is more vital as compared to the actual changes in the levels of the TDS in water (Department of Water Affairs and Forestry, 1996). The mean values of the electrical conductivity (mS/m) at the upstream and downstream along the Olifants River ranged between 52.67 mS/m and 56.4 mS/m, while upstream and downstream at Ga-Selati River, were between 147.33 mS/m and 203.33 mS/m (Figure 4.2), respectively, in summer. The one-way ANOVA indicated the significant difference between EC concentration values between the upstream and downstream at Ga-Selati River ($p>0.05$) (Table 4.2), and this could be associated with migration of wastewater from the industries operating at this section of the Ga-Selati River.

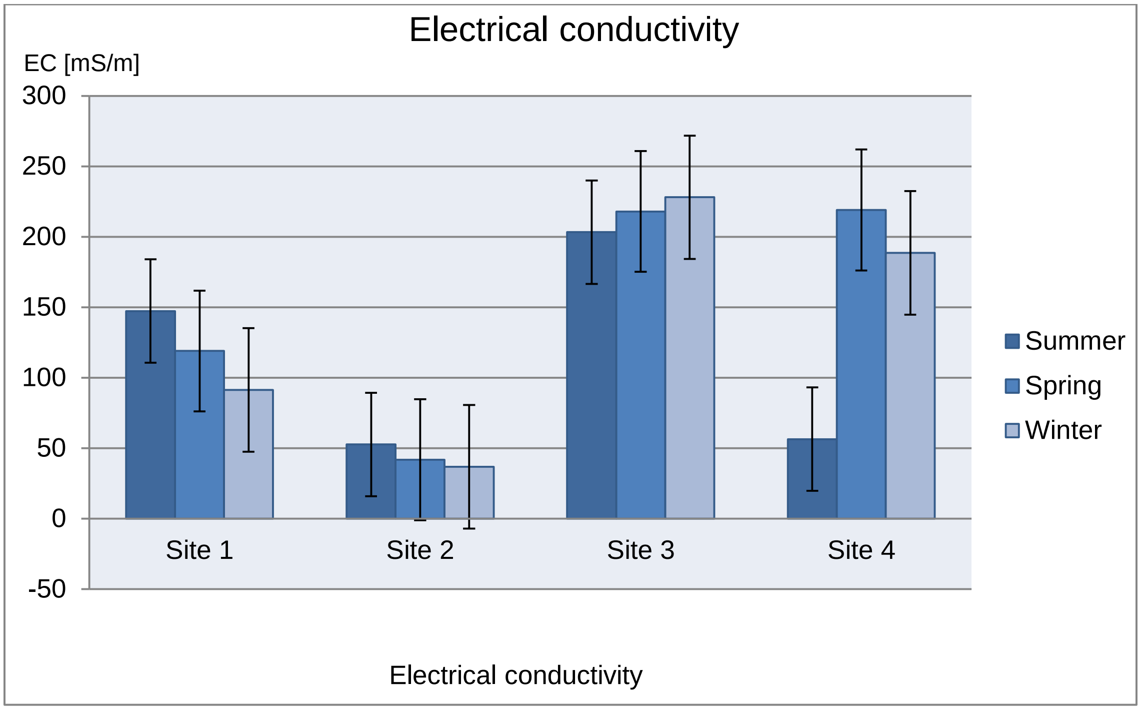

Figure 4.2: A graph showing electrical conductivity mean values (mS/m) recorded in summer, spring and winter at the sampling sites.

Table 4.2: Level of significant within the water parameters in summer (February 2020).

One-way ANOVA						
Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6914648	15	460976,5	23,81846	1,01E-34	1,723549
Within Groups	3406260	176	19353,75			

EC mean values at the upstream and downstream along the Olifants River ranged between 41.8 mS/m and 219 mS/m, while the upstream and downstream at Ga-Selati River recorded 119 mS/m and 218 mS/m (Figure 4.2), respectively, in spring. There was a notable increase on the EC concentration towards the downstream directions of both Olifants and Ga-Selati Rivers (sites 3 and 4). This increase could mean that the presents in water of ions such as Cl, SO_4^-, NO_3, K, Ca, and Mg were high at the downstream points of both Olifants and Ga-Selati Rivers in spring than in summer.

Apart from mine wastewater, the high concentration of these ions in spring could be as a result of limited dilutions due to low rainfalls during this season in 2019.

In winter, the Olifants River system recoded EC mean values of 36.8 mS/m (upstream) and 188.67 mS/m (downstream) while Ga-Selati River system recorded 91.45 mS/m (upstream) and 228 mS/m (downstream) (Figure 4.2). More ions were transported into the Olifants River system by the Ga-Selati River system in winter season of 2019 than any other season during the sampling period of the study.

4.2.1.3 Total dissolved solids

Total dissolved solids (TDS) are a measure of the total amount of elements dissolved in water. The dissolved elements can also be measured as salinity or as conductivity. Dallas and Day (2004) revealed that the elevated or decreased levels of TDS may delay the developmental progress and cause death of numerous freshwater organisms. Generally, the TDS ions found in the natural water resources is comprised of the cations such as calcium, sodium, magnesium and potassium, and the anions such as carbonate, bicarbonate, chloride and sulphate (Dallas and Day, 2004). According to the summer seasonal data collected in 2020, it is evident that there is an increase of TDS in the downstream directions of both two streams. The TDS mean values (Figure 4.3) at the Olifants River ranged between 342.33 mg/L upstream and 366.6 mg/L downstream, in summer, whereas along Ga-Selati River the range was between 957.67 mg/L upstream and 1321.67 mg/L downstream during the same season.

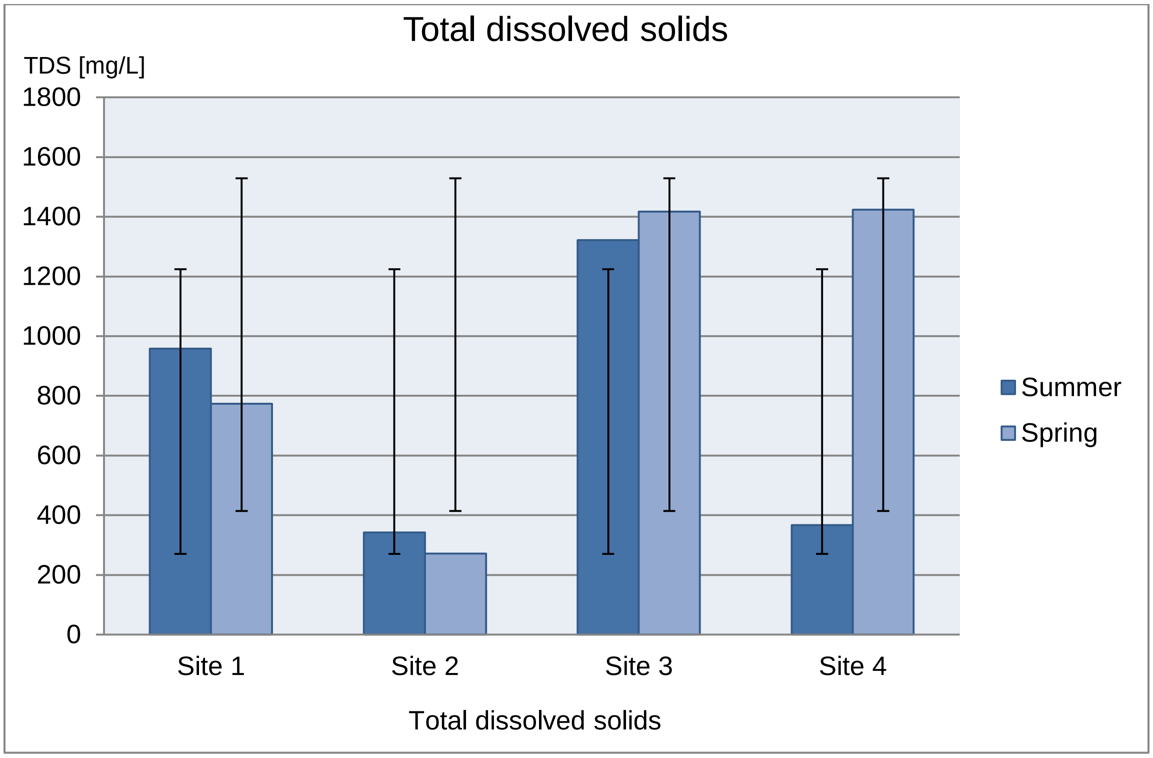

Figure 4.3: A graph showing total dissolved solids mean values (mg/L) recorded in summer and spring at the sampling sites.

These results point out to the existence of a source of salt at the downstream directions of both Olifants and Ga-Selati Rivers. The very high concentration of salt at the site 3 (downstream at Ga-Selati River) could mean that the source of salt is along this river. Site 4 (downstream at Olifants River) of the study recorded reduced concentration of salt and this could mean that the water gets diluted at the confluence of these two streams. The TDS concentrations are not allowed to change by more than 15 % from the normal cycles of the water resource at any time of the year (Department of Water Affairs and Forestry, 1996). This seasonal data was compared with the historical data that was collected between 2003 and 2010 by Golder Associates (2011) and the results showed more similarities.

In spring, the TDS mean values at the Olifants River upstream and downstream were 271.7 mg/L and 1423.5 mg/L while Ga-Selati upstream and downstream were 773.5 mg/L and 1417 mg/L (Figure 4.3), respectively. As with the EC, this increase could mean that the presents in water of ions such as Cl, SO_4^-, NO_3, K, Ca, and Mg were high at the downstream points of both Olifants and Ga-Selati Rivers in spring than in summer.

4.2.1.4. Fluoride

Fluoride (F) is a vastly reactive halogen gas. It occurs as the fluoride ion or in combination with calcium, potassium and phosphates (Department of Water Affairs and Forestry, 1996). In summer, the concentration of F at the downstream points along Ga-Selati River exceeded the critical level of 0.75 mg/L as set by South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996) by a mean value of 2.25 mg/L while the upstream recorded mean value of 0.53 mg/L (Figure 4.4). The Olifants River downstream points remained below the critical level of the dissolved F at a mean value of 0.5 mg/L, and 0.39 mg/L recorded at the upstream. F reacts rapidly at the alkaline pH values to develop complexes which cannot be easily absorbed by aquatic organisms. The study recorded alkaline pH values during the summer season and that could point out to the probable formation of complexes which could not be easily utilized by the aquatic organisms. The formation of these insoluble complexes is commonly exhibited by the rapid reaction between F, Ca, Mg and Al at alkaline pH values.

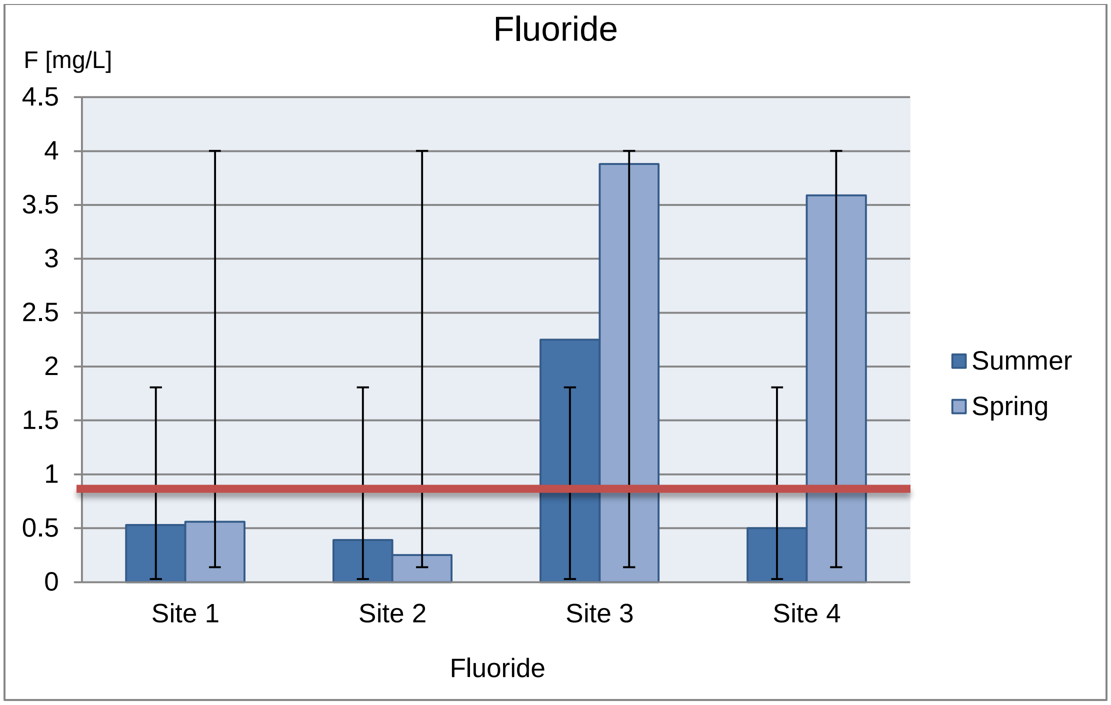

Figure 4.4: A graph showing fluoride mean values (mg/L) recorded in summer and spring at the sampling sites. Mean values at site 3 exceeded the TWQR of 0.75 mg/L.

As in summer, the concentration of F in spring exceeded the TWQR of 0.75 mg/L set by the South African water quality guidelines for aquatic ecosystems. The concentrations of F at the downstream points were significantly higher ($p>0.05$) (Table 4.3) than upstream points along both Olifants and Ga-Selati Rivers. Upstream and downstream (sites 2 and 4) at Olifants River recorded F mean values of 0.25 mg/L and 3.59 mg/L, respectively (Figure 4.4), with a low standard deviation of ± 1.85 (Table 4.4), while upstream and downstream (sites 1 and 3) at Ga-Selati River recorded F mean values of 0.56 mg/L and 3.88 mg/L, respectively (Figure 4.4), with a low standard deviation of ± 0.81 (Table 4.5).

These results could mean that the insoluble complexes which are formed by the reaction of F, Ca and Mg under alkaline pH conditions were formed in spring 2019 and persisted to summer 2020. According to Aken (2012), higher concentrations of F are primarily associated with its release from igneous rocks. The abundance of igneous rocks in the streams could also trigger the chemical composition of the fresh water in streams.

Table 4.3: Level of significant within the water parameters in spring, 2019.

One-way ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	12587172	15	839144,8	25,97182	6,8E-37	1,723549
Within Groups	5686527	176	32309,81			

Table 4.4: Standard deviation and variance of the concentrations of heavy metal in spring at the Olifants River.

Parameters	Unit	Min	Max	Variance	Standard Deviation
pH	-	4.4	9.16	3.37	± 1.84
EC	mS/m	41.1	231	9521.19	± 97.58
TDS	mg/L	267.15	1501.5	402270.2	± 634.25
F	mg/L	0.25	3.85	3.42	± 1.85
Cl	mg/L	24.8	193.4	8215.77	± 90.64
NO_3	mg/L	0.1	0.74	0.11	± 0.34
SO_4^-	mg/L	28.87	655.27	110060.1	± 331.75
K	mg/L	3.39	115.79	3301.34	± 57.46
Ca	mg/L	24.99	90.03	1199.47	± 34.63
Mg	mg/L	29.79	169.94	5356.85	± 73.19
Na	mg/L	32.15	215.47	9150.79	± 95.66
Mn	mg/L	0	0.11	0.00	± 0.05
V	mg/L	0.06	0.39	0.03	± 0.17

Table 4.5: Standard deviation and variance of the concentrations of heavy metal in spring water at Ga-Selati River.

Parameters	Unit	Min	Max	Variance	Standard Deviation
pH	-	7.93	9.18	0.42	± 0.64
EC	mS/m	116	229	2984.3	± 54.63
TDS	mg/L	754	1488.5	126086.7	± 355.09
F	mg/L	0.56	3.88	3.29	± 1.81
Cl	mg/L	117.43	195.06	1738.72	± 41.71
NO_3	mg/L	0.38	0.74	0.03	± 0.18
SO_4^-	mg/L	47.75	662.04	112265.3	± 335.06
K	mg/L	11.8	122.18	3586.68	± 59.89
Ca	mg/L	55.49	89.23	331.12	± 18.21
Mg	mg/L	55.45	173.92	4117.63	± 64.17
Na	mg/L	152.52	212.23	1019.58	± 31.93
Mn	mg/L	0.03	0.13	0.00	± 0.04
V	mg/L	0.12	0.39	0.02	± 0.14

4.2.1.5 Chloride

Dissolved chlorine is mostly found as chloride ion, which is known to be the major anion in seawater and in many South African inland water resources (Aken, 2012; Dallas and Day, 2004). These chloride ions are more important for aquatic systems and moderate the healthiness of the streams because of its capabilities of destroying harmful pollutants. However, the elevation of the levels of the chloride-containing compounds can be toxic to aquatic biota (Wepener *et al*., 2000). The summer seasonal chloride (Cl) concentration was lower at the upstream sampling points of both Olifants and Ga-Selati Rivers than the downstream points (Figure 4.5).

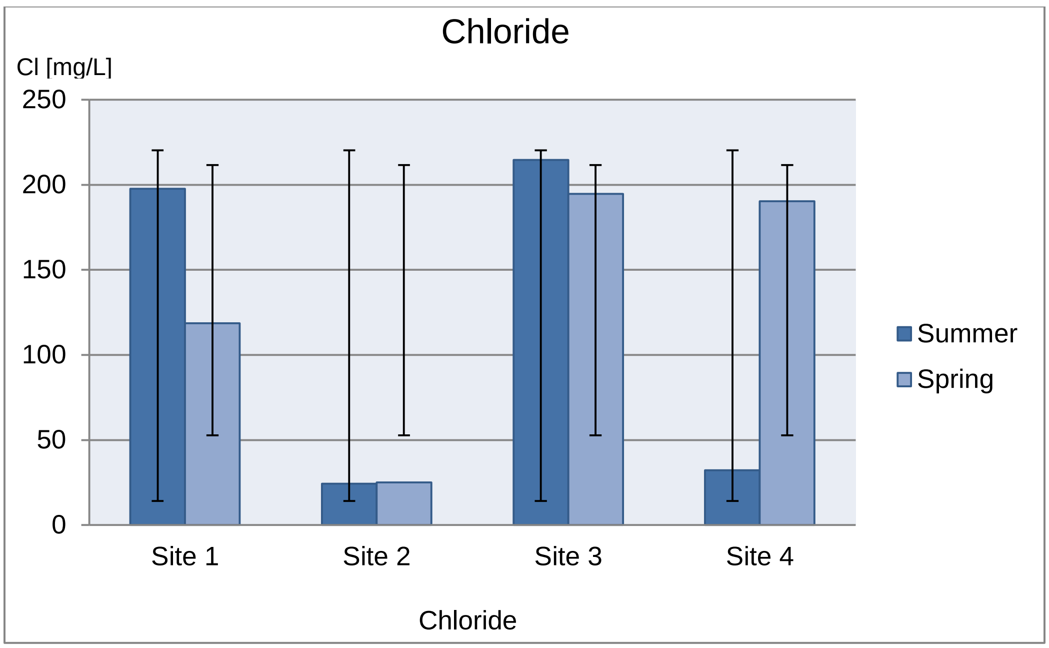

Figure 4.5: A graph showing chloride mean values (mg/L) recorded in summer and spring at the sampling sites.

Chloride is commonly used by wastewater treatment plants as a disinfectant and is generally introduced into streams through discharges from sewerage treatment plants. The Cl seasonal mean values upstream and downstream at the Olifants River ranged between 24.22 mg/L and 32.24 mg/L in summer, while the upstream and downstream at Ga-Selati River recorded mean values of 197.71 mg/L and 214.67 mg/L. As much as Cl is needed in freshwater, it is important that it remains within the tolerable levels. Currently, there are no Cl guidelines in place for protection of the fresh water in South African rivers. However, the Environmental Protection Agency (EPA) (2001) states that the dissolved Cl in both drinking and surface water must be less than 250 mg/L. The study recorded Cl concentration values of less than 250 mg/L across all the sampling points with the standard deviation of ± 4.38 (at Olifants River) and ± 9.3 (at Ga-Selati River) (Table 4.6 and 4.7) representing the change of concentration within the four sampling sites.

Table 4.6: Standard deviation and variance of the concentrations of heavy metal in summer at the Olifants River.

Parameters	Unit	Min	Max	Variance	Standard Deviation
pH	-	7.7	8.24	0.06	± 0.24
EC	mS/m	50.5	56.8	5.71	± 2.39
TDS	mg/L	328.25	369.2	240.77	± 15.52
F	mg/L	0.39	0.5	0.00	± 0.06
Cl	mg/L	24.21	32.38	19.21	± 4.38
NO_3	mg/L	0.91	1.27	0.03	± 0.16
SO_4^-	mg/L	127.6	152.8	167.96	± 12.96
K	mg/L	7.13	10.34	2.87	± 1.69
Ca	mg/L	32.45	36.3	2.52	± 1.59
Mg	mg/L	25.74	29.83	3.6	1.91
Na	mg/L	34.95	40.61	7.94	± 2.82
Mn	mg/L	0	0.01	0.00	± 0.00
V	mg/L	0.07	0.08	0.00	± 0.01

Table 4.7: Standard deviation and variance of the concentrations of heavy metal in summer at the Ga-Selati River.

Parameters	Unit	Min	Max	Variance	Standard Deviation
pH	-	8.02	8.68	0.07	± 0.25
EC	mS/m	143	205	948.27	± 30.79
TDS	mg/L	929	1332.5	40064.27	± 200.16
F	mg/L	0.53	2.9	1.38	± 1.17
Cl	mg/L	197.18	215.2	86.53	± 9.3
NO_3	mg/L	1.88	184	5420.76	± 73.63
SO_4^-	mg/L	103.93	557.41	61032.33	± 247.05
K	mg/L	11.14	81.68	1455.51	± 38.15
Ca	mg/L	56.11	75.06	71.32	± 8.44
Mg	mg/L	54.34	139.54	2069.14	± 45.49
Na	mg/L	185.78	195.81	14.33	± 3.79
Mn	mg/L	0	0.19	0.01	± 0.08
V	mg/L	0.15	0.37	0.01	± 0.12

The Cl seasonal mean values, upstream and downstream at Olifants River ranged between 25.02 mg/L and 190.43 mg/L while at Ga-Selati River the range was between 118.59 mg/L and 194.71 mg/L (Figure 4.5) in spring. This could mean that the Ga-Selati River was transporting high concentration of Cl into the Olifants River during this season. As stated earlier in this section, Cl is more important as they determine the healthiness of the streams and this could be benefiting the Olifants River. As in summer, the concentration of Cl in spring increased relatively at the downstream directions (sites 3 and 4) of the two rivers and that could also be one of the reasons led to an increased EC at this part of the streams. High concentration values of Cl were recorded in summer as compared to spring records. However, the mean values of Cl stayed below the 250 mg/L guidelines suggested by the EPA (2001). Currently, there are no Cl guidelines in place for the protection of the freshwater ecosystems in South African rivers.

4.2.1.6 Nitrate

Nitrates are the last product of the aerobic decomposition of organic nitrogen compounds and commonly occur in the form of combined nitrogen found in natural water (Dallas and Day, 2004). The main sources of nitrate are the municipal and industrial wastewaters and agricultural runoff (Department of Water Affairs and Forestry, 1996). The concentration of nitrate (NO_3) as one of the oxoanions (anions with oxygen content) was generally higher at the downstream than the upstream points along both Olifants and Ga-Selati Rivers. The high concentration of NO_3 at the lower Olifants catchment might be linked to the use of organic waste from domestic wastes, effluents, nitrogenous fertilisers, and herbicides in agricultural fields that exist within this catchment. The NO_3 mean values at site 1 (Ga-Selati upstream) were at 4.88 mg/L while at site 3 (Ga-Selati downstream) were at 1.88mg/L (Figure 4.6). This decrease in the concentration of NO_3 at downstream along Ga-Selati River is likely to be associated with the development of riparian vegetation that takes up NO_3 as nutrient. However, the concentration of NO_3 at the Olifants River elevated towards the downstream directions. The NO_3 mean values at the Olifants River ranged between 0.92 mg/L (upstream) and 1.21 mg/L (downstream) in summer (Figure 4.6). The NO_3 mean values generally exceeded the TWQR of 0.5 mg/L as suggested by the South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996) as marked in Figure 4.6 by a redline.

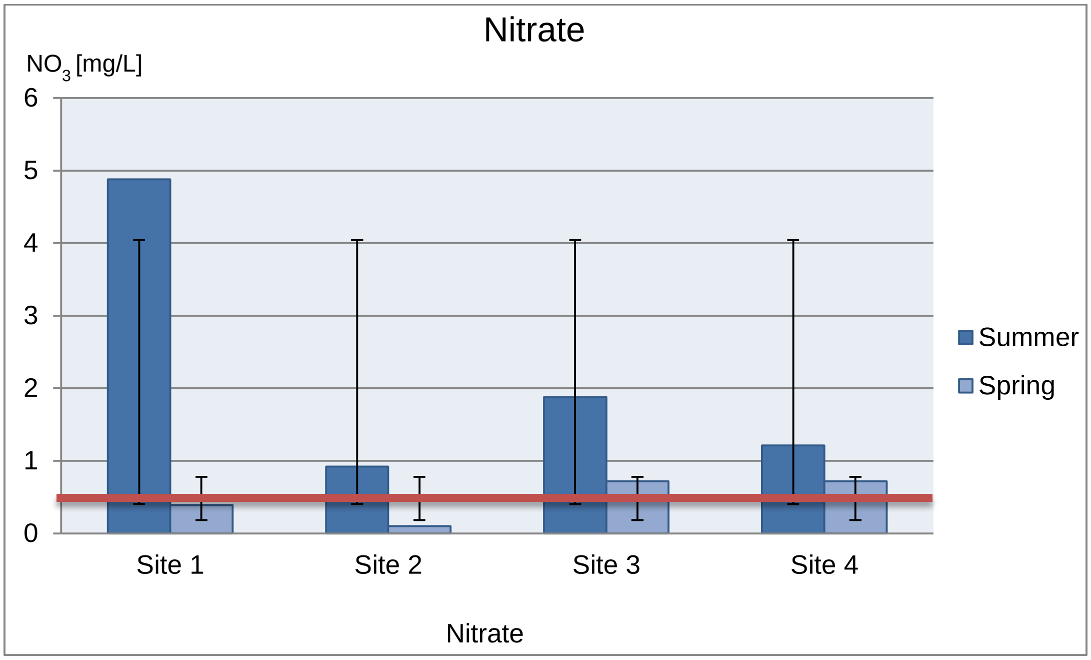

Figure 4.6: A graph showing nitrate mean values (mg/L) recorded in summer and spring at the sampling sites. Mean values at downstream and some of upstream exceeded the TWQR of 0.5 mg/L.

According to the Department of Water Affairs and Forestry (1996), the concentration of NO_3 at both Olifants and Ga-Selati Rivers points out to the conditions of mesotrophic which consists of an increased amount of biodiversity with unpleasant development of aquatic plants and blooms of blue-green algae.

As in summer, concentrations of measured oxoanions (anions with oxygen content (NO_3 and SO_4^-)), were generally high at the downstream points (sites 3 and 4) (Figure 4.6) along both Olifants and Ga-Selati Rivers. NO_3 occurs as a result of nitrogen cycles, where nitrogen can be converted into nitrates through both biological and non-biological processes (Carroll and Salt, 2004; Aken, 2012). The NO_3 mean values exceeded the TWQR of 0.5 as suggested by the South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996). The NO_3 seasonal mean values upstream and downstream in the Olifants River (sites 2 and 4) were 0.1 mg/L and 0.72 mg/L while Ga-Selati River recorded mean values of 0.39 mg/L and 0.72 mg/L, respectively (Figure 4.6). The concentrations of NO_3 along both the Olifants and Ga-

Selati Rivers were low in spring as compared to records in summer because of less erosion of NO_3 from agricultural fields. However, mesotrophic conditions at both Olifants and Ga-Selati Rivers persisted from spring 2019 to summer 2020 with the development of unpleasant blue-green algae and other aquatic plants.

4.2.1.7 Sulphate

Sulphate (SO_4^-) is also one of the oxoanions that were analysed during the summer season of 2020. It is normally formed from the dissolution of mineral sulphates in the soil and rock, where the mineral content may include calcium sulphate (gypsum) and other partially soluble sulphate minerals (Department of Water Affairs and Forestry, 1996; Karen, 2012). Currently, there are no guidelines (TWQR) for SO_4^- concentration in freshwater ecosystems. However, the South African water quality guidelines for domestic use of water (Department of Water Affairs and Forestry, 1996) states that the dissolved SO_4^- has to be less than 200 mg/L.

The upstream and downstream points at the Olifants River recorded SO_4^- mean values of 128.69 mg/L and 152.32 mg/L, respectively. Ga-Selati River upstream and downstream points recorded SO_4^- mean values of 104.21 mg/L and 555.25 mg/L, respectively (Figure 4.7).

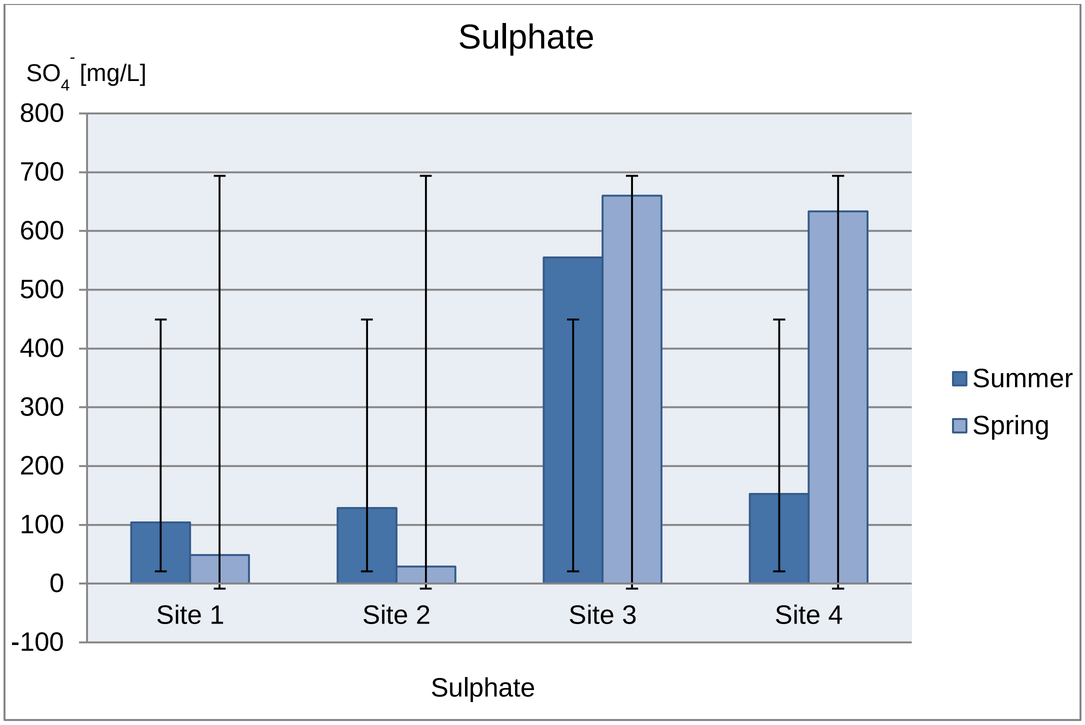

Figure 4.7: A graph showing sulphate mean values (mg/L) recorded in summer and spring at the sampling sites.

The concentration of SO_4^- at the downstream points along Ga-Selati River were relatively high and exceeded the critical levels of 200 mg/L set by the South African water quality guidelines for domestic use (Department of Water Affairs and Forestry, 1996). During this season, the lowest SO_4^- concentration was recorded at site 1 while the highest concentration was recorded at site 3. The sites 1 and 3 exist along the Ga-Selati River and the elevated levels of SO_4^- at site 3 can be associated with the mining of copper (with Sulphur dioxide as a by-product) (Chapman, 1996) along this stream. Sulphates play an important role as one of the main ions responsible for the elevation of levels of the TDS in marine environment (Dallas and Day, 2004).

The SO_4^- concentration elevated at the downstream points of both streams (sites 3 and 4) of the study area, in spring as in summer. The concentrations of SO_4^- at the downstream points of both Ga-Selati and Olifants Rivers in spring were above the critical levels of 200 mg/L set by the South African water quality guidelines for domestic water use (Department of Water Affairs and Forestry, 1996) (Figure 4.7). The downstream point of the Ga-Selati River (site 3) in spring recorded SO_4^- mean values of 660.16 mg/L while the upstream (site 1) recorded mean values of 48.43 mg/L (Figure

4.17). The downstream points of the Olifants River (site 4) recorded SO_4^- mean values of 633.28 mg/L while the upstream point (site 2) recorded mean values of 29.03 mg/L in spring. The concentration of SO_4^- elevated at the downstream points of both streams in spring. As in summer, the elevation SO_4^- at the downstream points can be associated with the mining of copper.

4.2.1.8 Calcium

The simple cations analysed the during summer season include the Ca, K, Mg, Na, Mn, and V. The concentrations of all these simple cations increased towards the downstream directions along both the Olifants and Ga-Selati Rivers with some exceeding the critical levels set by both the EPA (2001) and South African water quality guidelines for aquatic ecosystems and domestic use (Department of Water Affairs and Forestry, 1996).

Concentrations of Ca indicated that the water along both rivers was soft (<100 mg/L) with mean values ranging between 56.95 mg/L and 71.95 mg/L upstream and downstream, respectively along the Ga-Selati River, while at the Olifants River mean values ranged between 35.96 mg/L and 33.22 mg/L (Figure 4.8) upstream and downstream, respectively.

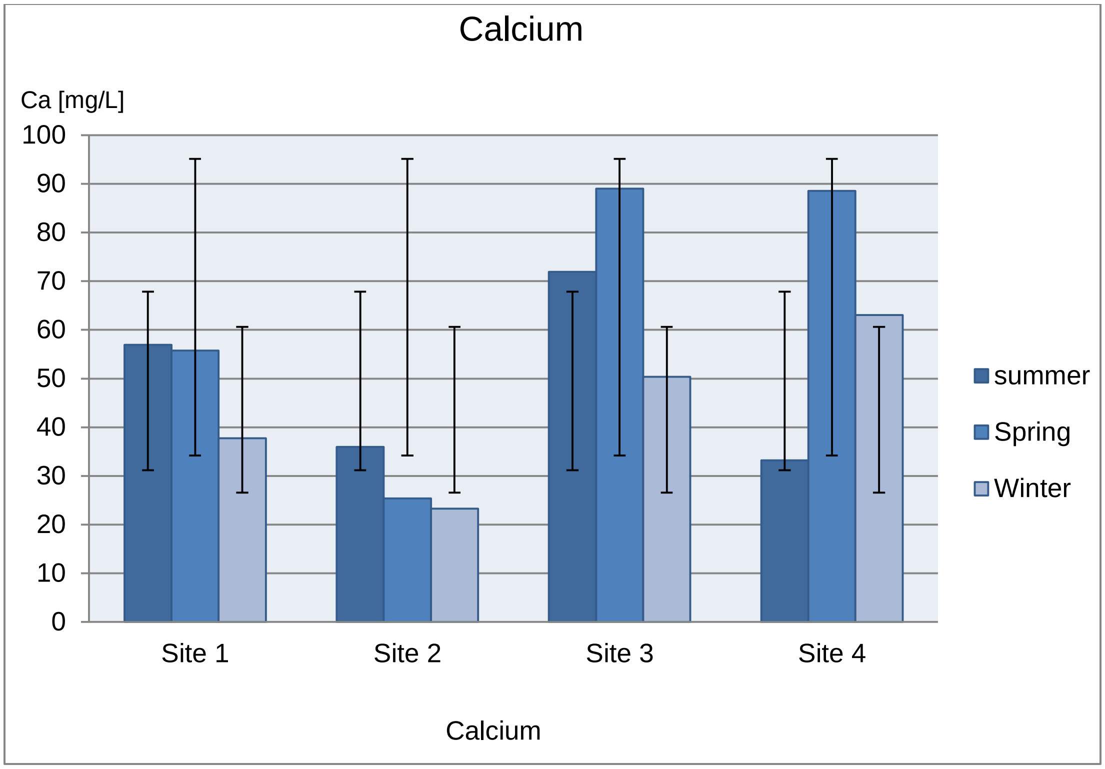

Figure 4.8: A graph showing calcium mean values (mg/L) recorded in summer, spring and winter at the sampling sites.

The high Ca concentrations were recorded at sites 1 and 3 which exist along the Ga-Selati River. These high concentrations along the Ga-Selati River could be associated with the effluent from mine wastewater systems since Ca can be present in high concentrations in tailings water (Ramollo, 2008). According to the Department of Water Affairs and Forestry (1996), Ca is an alkaline earth metal that mostly occurs as phosphate, sulphate or carbonate. Ca is an important element for living organisms and can be found in structural elements such as bone, teeth and exoskeletons (Aken, 2012). However, the obtained Ca results together with the pH levels at the Ga-Selati River could also mean that either calcium hydroxide (Ca(OH)2) or dolomitic limestone (CaMgCO3) might be used at the lower Olifants River catchment. The dosing infrastructure does exit along the downstream of Ga-Selati River just before the confluence of these two rivers at the study area. It uses the neutralizing agents for lowering the acidic levels at the Ga-Selati River. This is done to protect the lower Olifants River against the acidic mine water.

As in summer, the concentration of cations elevated at the downstream points of both Olifants and Ga-Selati Rivers with some exceeding the critical levels set by both the EPA (2001) and South Africa water quality guidelines for aquatic ecosystems and domestic use (Department of Water Affairs and Forestry, 1996) in spring. Ca concentration in spring 2019 indicated that the water was soft with mean values ranging between 25.4 mg/L and 88.58 mg/L upstream and downstream of Olifants River, and 55.78 mg/L and 89 mg/L upstream and downstream of Ga-Selati River (Figure 4.8) The concentration of Ca in spring were high compared to summer concentrations and that could mean that the water was more polluted in spring during reduced river flow than in summer during increased river flow.

In winter, the Ca concentrations at sites 3 and 4 were significantly higher ($p>0.05$) (Table 4.8) than at sites 1 and 2, with a 95 % confidence level (in winter). The Ca mean values ranged between 37.74 mg/L (upstream) and 50.34 mg/L (downstream) at Ga-Selati River (Figure 4.8), in winter. At the Olifants River in the same season, the seasonal Ca mean values ranged between 23.26 mg/L (upstream) and 63.06 mg/L (downstream). As in spring and summer, the water in winter along both streams was soft with mean values below 100 mg/L.

Table 4.8: Level of significant within the water parameters in winter, 2019.

One-way ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	341894,1	10	34189,41	11,38551	1,46E-13	1,909792
Within Groups	363349,5	121	3002,888			

4.2.1.9 Potassium

High potassium (K) concentrations can be associated with runoff in irrigated lands and from fertilizer production facilities. There are no guidelines for K in the freshwater ecosystem, however, the South African water quality guidelines for domestic use of water states that the concentration of K has to be less than 50 mg/L. Concentrations of K at the downstream points along Ga-Selati River in summer exceeded the limit of 50 mg/L with a mean concentration of 80 mg/L while the upstream points of this river recorded K mean values of 11.29 mg/L (Figure 4.9).

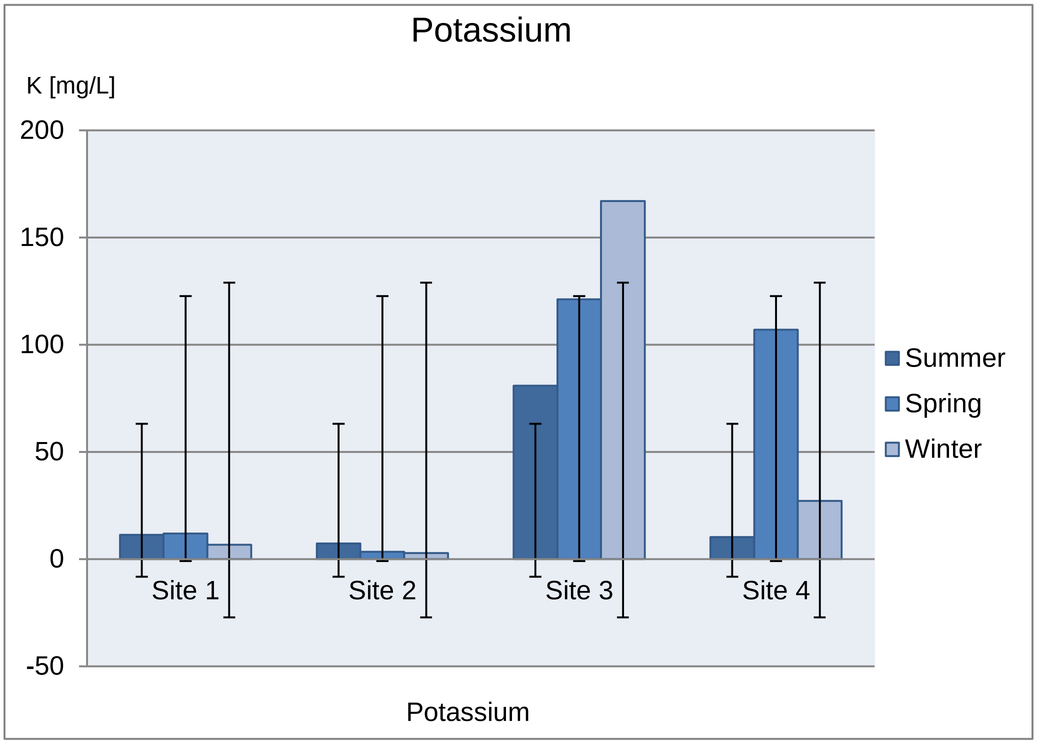

Figure 4.9: A graph showing potassium mean values (mg/L) recorded in summer, spring and winter at the sampling sites.

The concentrations of K along the Olifants River stayed below the critical levels, though the mean values progressively increased towards the downstream points. K mean values at Olifants River were 7.23 mg/L and 10.32 mg/L upstream and downstream (sites 2 and 4), respectively. According to the Phalaborwa Trade and Tourism Council (2011), potassium is among the fertilizer products produced by one of the industries located at the Phalaborwa industrial complex. This could mean that the increase of the K concentrations at the downstream points of these two rivers is as a result of the K production processes from the Phalaborwa industrial complex. However, it is recommended that the actual source of this be investigated further.

As in summer, the K concentrations progressively increased at the downstream points of Ga-Selati River in spring. The observations in this season (spring) showed a progressive increase in the concentration of K along Olifants River which is a totally different case as in summer. Currently, there are no TWQR in place for freshwater ecosystems in South Africa, however, the concentration of K downstream of both streams (sites 3 and 4) (Figure 4.9) exceeded the 200 mg/L suggested for domestic use the South African water quality guidelines, in spring. Upstream and downstream (sites 1 and 3) at Ga-Selati River recorded K mean values of 11.89 mg/L and 121.23 while Olifants River recorded K mean values of 3.44 mg/L and 107 mg/L, respectively. The concentrations of K in spring were high compared to summer records. The high concentrations of Ca, K and F led to the increase of EC in the water resources in spring and this could mean that the water consisted of more insoluble complexes during this season. The industry that produces K as fertilizers at the Phalaborwa industrial complex could be releasing more K into the Ga-Selati River.

K mean values at Ga-Selati River ranged between 6.68 mg/L (upstream) and 166.99 mg/L (downstream), while at Olifants River the range was between 2.76 mg/L (upstream) and 27.21 mg/L (downstream) (Figure 4.9) in winter. Although there are no water quality guidelines for K in South African rivers, it is important to consider the increase of the concentrations of K at the downstream directions of both Ga-Selati and the Olifants Rivers. The K concentration was notably high during the winter season than any other season during the sampling period (2019 – 2020). A notable increase of the concentration of Ca at the downstream directions along both Ga-Selati and Olifants Rivers was also observed in the winter season.

4.2.1.10 Magnesium

The pattern of magnesium (Mg) concentration distribution in summer was similar to that of K and Ca, i.e., progressively high concentration values at the downstream points along the Ga-Selati and Olifants Rivers (Figure 4.10). Mg is a common constituent of water that consists of common minerals such as magnesium carbonate and various magnesium silicates (Department of Water Affairs and Forestry, 1996). It is mostly found in high concentration and believed not to act as a limited toxin (Dallas and Day, 2004).

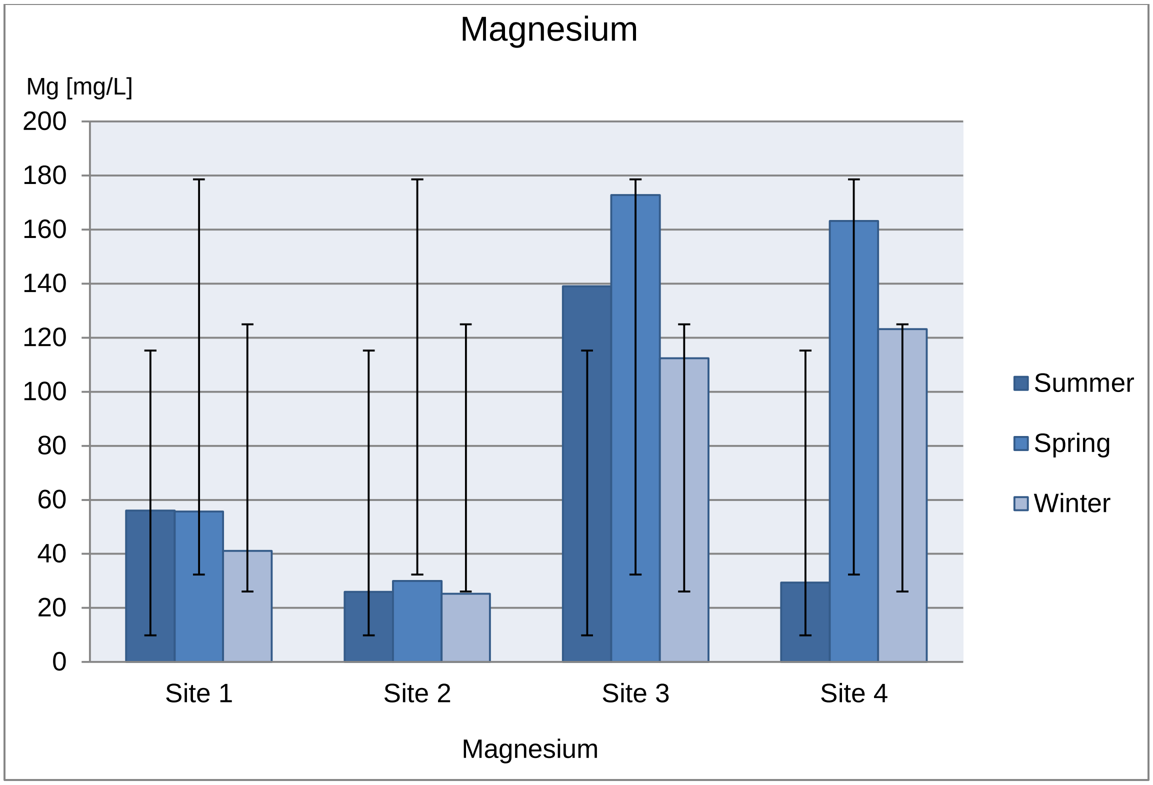

Figure 4.10: A graph showing magnesium mean values (mg/L) recorded in summer, spring and winter at the sampling sites.

Mg mean values at Ga-Selati River (sites 1 and 3) were 56.02 mg/L and 139.04 mg/L upstream and downstream respectively, while the Olifants River (sites 2 and 4) recorded mean values of 25.95 mg/L and 29.37 mg/L upstream and downstream, respectively, in summer. It is important to consider this change at the downstream points since there are no existing guidelines for Mg levels in the freshwater ecosystem in South Africa. These concentrations of Mg, Ca, K and F at alkaline pH water can interfere with the nutrient availability and create some insoluble complexes which disrupt the ecological functioning within the water bodies.

As with Ca, K, F, Cl, NO_3 and SO_4^-, concentration of Mg in spring elevated at the downstream points of both Ga-Selati and Olifants Rivers at an alkaline pH and increased EC conditions. Currently, Mg has no guidelines (TWQR) for South African freshwater ecosystems. However, it is also important to consider the change of concentration of these cations at the downstream points of both streams during this season. Mg mean values at the upstream and downstream of the Olifants River ranged between 30.02 mg/L and 163.24 mg/L while at Ga-Selati River the range was between

55.7 mg/L and 172.85 mg/L (Figure 4.10). The increase of the levels of Mg at the downstream points proves that there might be a source of magnesium between site 1 and 3, and site 2 and 4. The concentration of Mg was relatively high in spring than in summer. As in summer, the high concentration of F, Ca, Cl, K and Mg under the alkaline pH conditions lead to the formation of insoluble complexes that interfere with the availability of nutrients.

In winter, Mg seasonal mean values at the Olifants River were 25.27 mg/L (upstream) and 123.18 mg/L (downstream) while at Ga-Selati River were 41.11 (upstream) and 112.43 mg/L (downstream) (Figure 4.28a). Significant differences ($p>0.05$) (Table 4.8) were recorded between the upstream and downstream Mg, Na and V concentrations along the Olifants River, with high standard deviation (Table 4.9 and 4.10) indicating high concentrations of these ions at the downstream points, during this season.

Table 4.9: Standard deviation and variance of the concentrations of heavy metal in winter at the Olifants River.

Parameters	Unit	Min	Max	Variance	Standard Deviation
pH	-	7.7	8.2	0.03	0.18
EC	mS/m	35.4	194	6932.44	83.26
K	mg/L	2.38	65.35	615.86	24.82
Ca	mg/L	21.94	65.62	480.01	21.91
Mg	mg/L	24.95	123.74	2876.13	53.63
Na	mg/L	27.93	201.25	8874.65	94.21
Mn	mg/L	0	0.04	0.00	0.02
V	mg/L	0.04	0.28	0.02	0.13
Al	mg/L	0.08	0.08	0	0

Table 4.10: Standard deviation and variance of the concentrations of heavy metal in winter at the Ga-Selati River.

Parameters	Unit	Min	Max	Variance	Standard Deviation
pH	-	7.91	8.55	0.09	0.3
EC	mS/m	49.4	230	6127.39	78.28
K	mg/L	2.79	169.12	7715.71	87.84
Ca	mg/L	26.36	53.08	90.79	9.53
Mg	mg/L	18.76	113.75	1676.67	40.95
Na	mg/L	56.39	248.4	5817.5	76.27
Mn	mg/L	0	0.03	0.00	0.01
V	mg/L	0.03	0.24	0.01	0.11
Al	mg/L	0.08	0.09	0.01	0.01

4.2.1.11 Vanadium

As with K, Ca, Mg and other anions, V and Na mean values increased progressively towards the downstream directions of both rivers. The V mean values at the Olifants River (sites 2 and 4) ranged between 0.07 mg/L and 0.08 mg/L upstream and downstream, respectively (Figure 4.11) in summer.

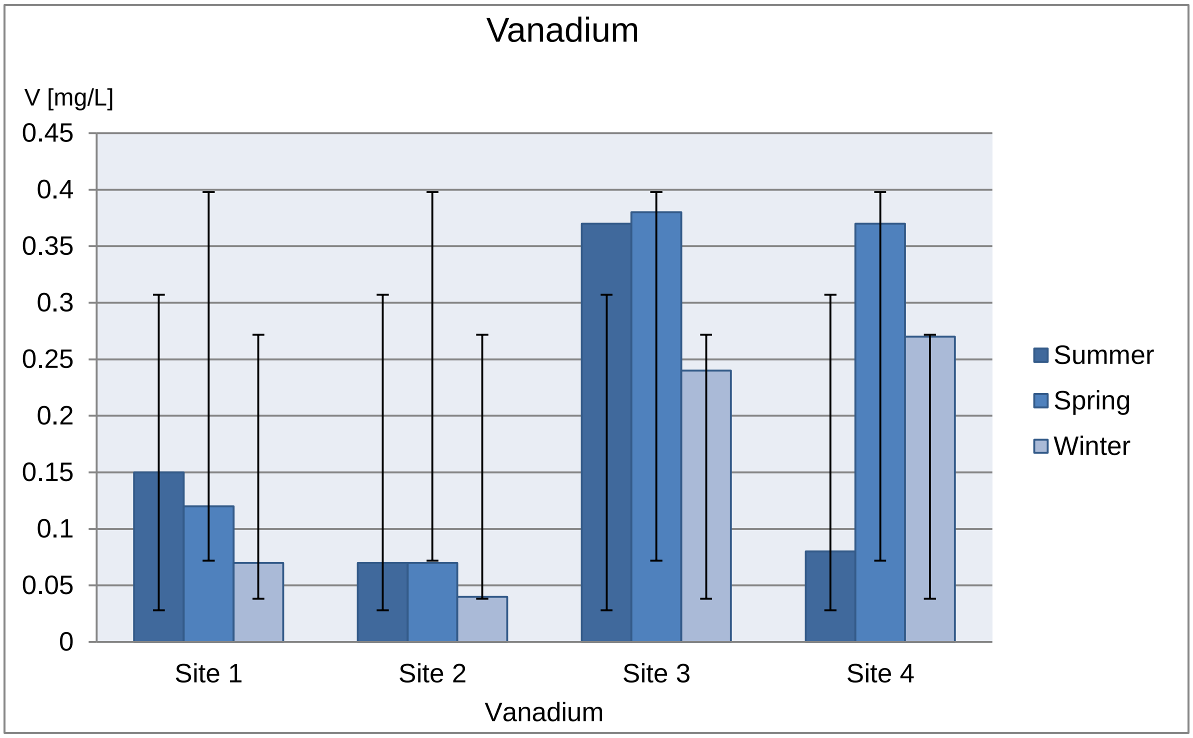

Figure 4.11: A graph showing vanadium mean values (mg/L) recorded in summer, spring and winter at the sampling sites.

High V concentrations were recorded along Ga-Selati River at site 3 with a mean value of 0.37 mg/L while the site 1 recorded mean value of 0.15 mg/L. Currently, there are no guidelines for V concentration in freshwater ecosystems. However, the TWQR for domestic use suggests that the V concentrations have to be less than 0.01 mg/L (Department of Water Affairs and Forestry, 1996). The study recorded V concentration values that were higher than the TWQR for domestic use. The study recorded some perfect correlation (Appendix 1a) between the concentrations of Mg and V in summer.

V mean concentration values at the upstream and downstream along the Olifants River ranged between 0.07 mg/L and 0.37 mg/L while Ga-Selati River recorded mean values of 0.12 mg/L and 0.38 mg/L (Figure 4.11) in spring, respectively. No TWQR in place for V in South African freshwater ecosystems. The concentration of V across all sampling sites exceeded the TWQR of 0.01 suggested for domestic use (Department of Water Affairs and Forestry, 1996).

The patterns of V concentration in winter were similar to the cations i.e., increasing at the downstream points. V seasonal mean values at the upstream and downstream of Olifants River ranged between 0.04 mg/L and 0.27 mg/L while at Ga-Selati River the range was between 0.07 mg/L and 0.24 mg/L upstream and downstream, respectively, in winter (Figure 4.11). The concentrations of V were generally high in spring while than any other seasons during the sampling period.

4.2.1.12 Sodium

Sodium (Na) as an alkali metal which reacts with water to form highly soluble, positively charged sodium ions which can be found in plant and animal matter (Department of Water Affairs and Forestry, 1996). Elevated concentrations of sodium are found in the industrial wastes with processes that give rise to brines (Department of Water Affairs and Forestry, 1996). Ga-Selati River (sites 1 and 2) recorded high concentrations of sodium (Figure 4.12) as compared to the sites 2 and 4 which exist along the Olifants River. As with V, Ca, K and Mg, no water quality guidelines for Na in South African rivers exist. However, the South African water quality guidelines for domestic use suggest that the Na concentration should be between 0 and 100 mg/L.

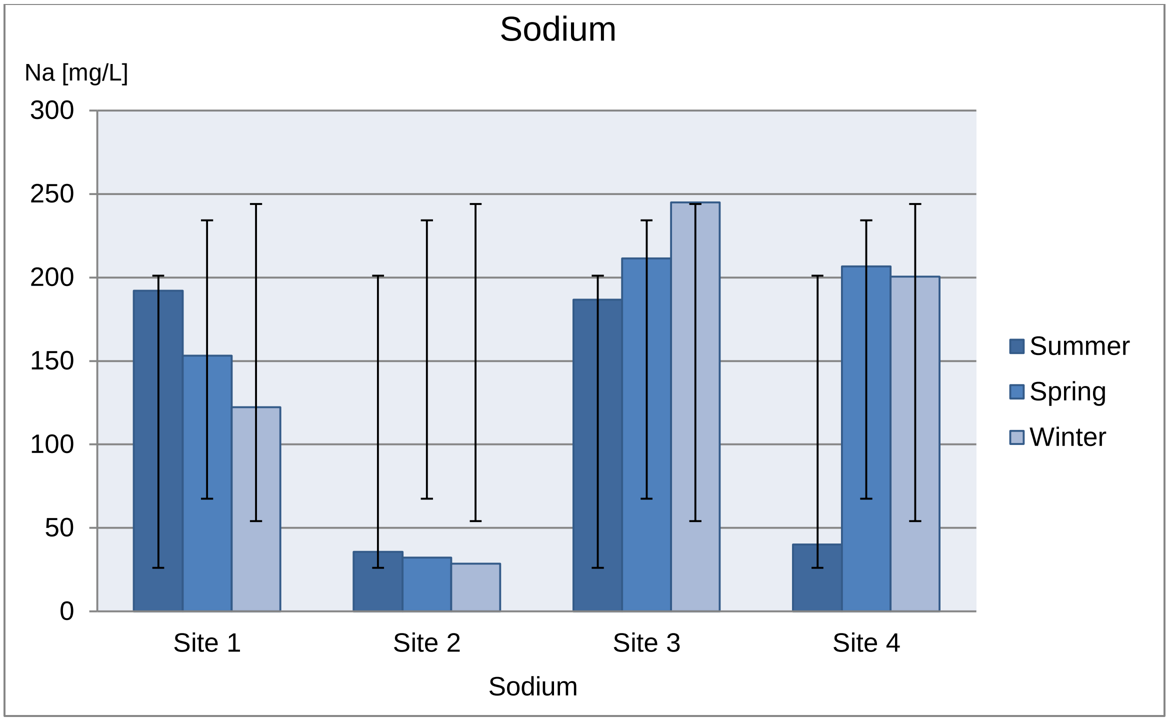

Figure 4.12: A graph showing sodium mean values (mg/L) recorded in summer, spring and winter at the sampling sites.

The highest concentration of Na was 192.04 mg/L recorded at site 1 and 186.65 mg/L recorded at site 3 existing along the Ga-Selati River in summer. The Olifants River recorded the lowest concentrations of Na with 35.6 mg/L at site 2 and 40.19 mg/L at site 4. The elevated Na levels at site 1 and 3 can be associated with geological and mining activities along these sites.

In spring, Na mean values at the upstream and downstream of Olifants River ranged between 32.26 mg/L and 206.66 mg/L while at Ga-Selati the range was between 153.21 mg/L and 211.49 mg/L (Figure 4.12). Na usually occurs as sodium chloride, sodium sulphate, bicarbonate or as nitrate (Department of Water Affairs and Forestry, 1996). Areas with high rainfall generally experience low levels of sodium while areas with low rainfall generally have high concentrations of sodium (Aken, 2012). The impact of sodium concentration in water is more associated with the impacts of TDS concentration because of its ability to act as cation exchanger (Kumar, 2003; Aken, 2012). The concentration of Na at site 2 were below the TWQR while site 1, 3 and 4 recorded concentrations that were higher than the suggested range for domestic use. The Ga-Selati River is shown to be the carrier of Na into the Olifants River.

In winter, Na seasonal mean values at Olifants River were 28.55 mg/L (upstream) and 200.54 mg/L (downstream) while Ga-Selati River recorded 122.38 mg/L (upstream) and 244.91 mg/L (downstream) (Figure 4.12). The concentrations of Na were generally high in winter than any other seasons during the sampling period.

4.2.1.13 Manganese

Manganese (Mn) is an important micronutrient (Dallas and Day, 2004). The observed concentrations of NO_3, SO_4^- and Cl are the salts that form part of Mn which can be associated with the pouring of AMD and are fairly soluble in water (Department of Water Affairs and Forestry, 1996). Elevated levels of Mn are harmful and can result in the disruption of several metabolic pathways (Department of Water Affairs and Forestry, 1996). The harmfulness of Mn rises as the pH levels of water decreases (Wang, 1987; Ramollo, 2008). The concentration of Mn in summer (Figure 4.13) were below the target water quality range of 0.18 mg /L set by the South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996).

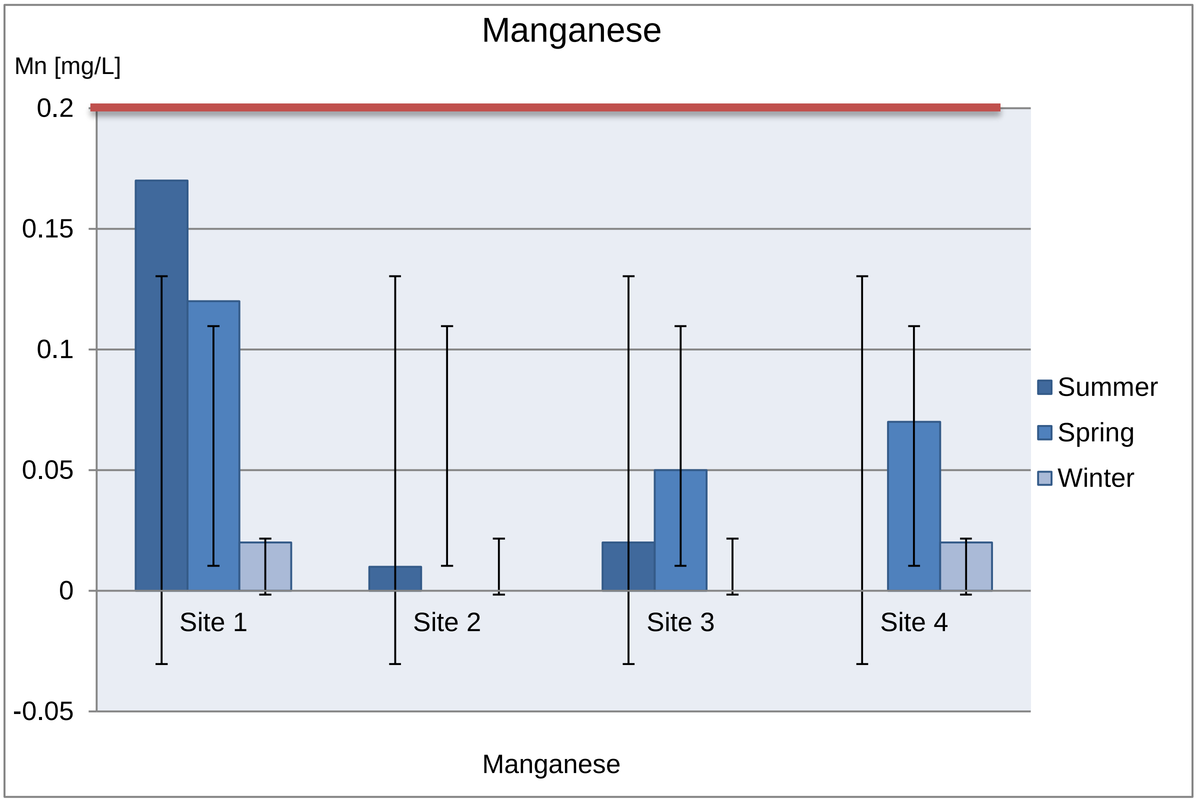

Figure 4.13: A graph showing manganese mean values (mg/L) recorded in summer, spring and winter at the sampling sites. Mean values were below TWQR of 0.18 mg/L.

High concentration of Mn was 0.17 mg/L recorded at site 1 and 0.02 mg/L recorded at site 3 which are the upstream and downstream (respectively) in the Ga-Selati River. In the Olifants River catchment, high Mn concentration was 0.01 mg/L recorded at site 2 (upstream) and 0 mg/L recorded at site 4 (downstream) in summer. The Mn concentrations in the Olifants River had no variance and standard deviation (Table 4.6) while in the Ga-Selati River the variance was 0.01 with the standard deviation of ± 0.08 (Table 4.7). The concentrations of Mn recorded at all sites were below the TWQR of 0.18 mg/L suggested for aquatic ecosystems by the Department of Water Affairs and Forestry (1996). As in the finding from Ramollo (2008), the results of this study showed that the mining operations did not contribute to Mn concentrations in the streams. The very low concentrations of Mn observed in this season can possibly be natural at the study area.

The concentrations of Mn in spring were below the critical levels of 0.18 mg/L set by the South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996) along both the Olifants and Ga-Selati Rivers in spring (Figure 4.13). Manganese is known to be related to acidic metalliferous discharge water and phosphate deposits from precious metal mines, municipal sewage and sludge and landfills (Nagpal, 2004). It has the ability to occur in two main forms in the water resources. It can either occur as soluble manganese (II) or as insoluble manganese (IV). The behaviour of Mn in the water resources is mostly controlled by the reduction and oxidation reactions which favour the formation of manganese (II) (Lebepe, 2018). Mn mean values at upstream and downstream of Olifants River (sites 2 and 4) stayed at 0 mg/L and 0.07 mg/L while at Ga-Selati River (sites 1 and 3) mean values were 0.12 mg/L and 0.05 mg/L, respectively (Figure 4.13) in spring. According to the study conducted by Aken (2012), the levels of Mn have been decreasing since 2005 at Ga-Selati River and are considered negligible.

Manganese was the only cation with concentrations that decreased at the downstream points of Ga-Selati River (site 3) with mean values of 0 mg/L while the upstream (site 1) recorded 0.02 mg/L in winter. However, the values of Mn stayed below TWQR of 0.18 mg/L set by the South African water quality guidelines for aquatic ecosystems

(Department of Water Affairs and Forestry, 1996) across the stream including at the Olifants River where Mn mean values were 0 mg/L recorded at site 2 and 0.02 mg/L recorded at site 4 in winter (Figure 4.13). The low concentration of Mn along both streams could mean that there is control and well-managed discharge of acidic metalliferous water and phosphate deposits from the mining complex and wastewater treatment works around the lower Olifants River catchment.

4.2.1.14 Aluminium

In alkaline pH waters, the Al precipitates as hydroxide, which would flocculate in water and tends to sink down and adsorb to sediment (Lebepe, 2018). The Al concentration at both Ga-Selati and Olifants Rivers was constantly high in every site of the sampling (Figure 4.14). At all sampling sites, the concentrations Al exceeded the TWQR of 0.01 mg/L (under pH of more than 6.5) set by the South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996).

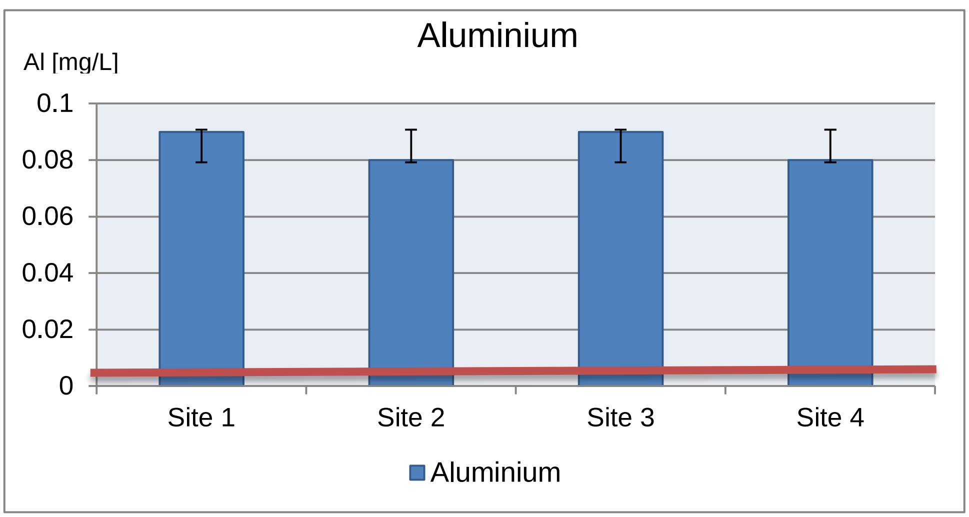

Figure 4.14: Aluminium mean values (mg/L) recorded in winter at the sampling sites. Mean values exceeded the TWQR of 0.01 mg/L at all sampling sites.

During this period (winter season of 2019), the Al mean values were relatively stable at 0.09 mg/L at both upstream and downstream along Ga-Selati River (sites 1 and 3), while at the Olifants River stayed at 0.08 mg/L at both upstream and downstream (sites 2 and 4) (Figure 4.26). These results could mean that the source of Al exist at the upstream of both Ga-Selati and Olifants Rivers. Further investigations can be required to identify the source of Al around Phalaborwa area.

4.3 Modelling of water quality using GIS

Modelling can be considered as a fundamental engineering method of solving problems (Barbour and Krahn, 2004). Modelling can be explained in different forms depending on the application. Their basic concept, however, remains the same i.e., the process of bringing solutions to physical problems by appropriate simplification of reality (Pakdaman *et al*., 2013; Mujuru and Mutanga, 2016). Surface water quality models can be effective tools to simulate and predict the levels, distributions, and impact of the heavy metal pollutants in a given water body (Qinggai *et al.,* 2013).

The simulation of the transport of heavy metals and accumulation in a river depends on instream processes that need to be integrated in a modelling strategy. The mass conservation equation is also an effective tool in modelling of the transportation of dissolved heavy metals (Trento and Alvarez, 2011; Wu, 2008). Figure 4.15 is a complete schematic illustration of the physical processes involved in the transportation of heavy metals in the surface water bodies. It highlights the general environmental pathways of heavy metals (Ji, 2008).

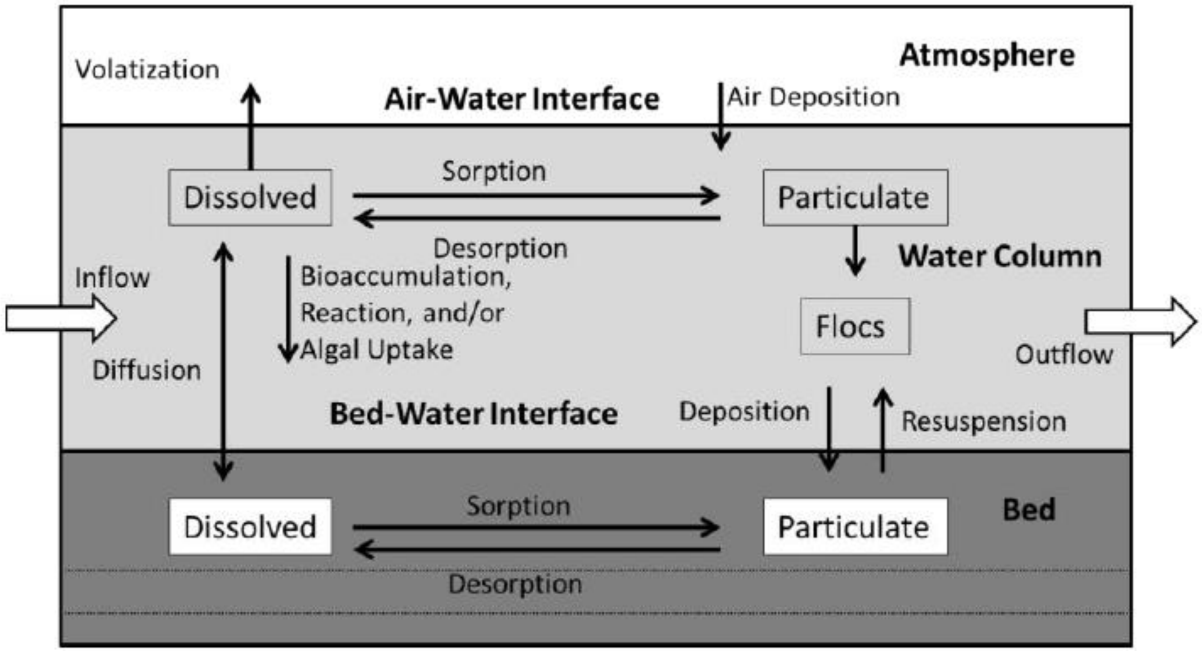

Figure 4.15: Fate and transport processes of heavy metals (Ji, 2008).

4.3.1 Thematic maps

For this study, a GIS application was employed to predict the distribution of dissolve heavy metals at both lower Olifants and Ga-Selati River. The thematic map layers (Appendix 2) of water quality parameters were therefore, produced from the analytical results using inverse distance weighted (IDW) interpolation technique available in ArcGIS 10.3 software. The resultant map layers were grouped into five classes based on limits set by the South African water quality guidelines for aquatic systems (Department of Water Affairs and Forestry, 1996) and the Environmental Protection Agency (2001) as already stated in the methodology section in chapter four. The classes created for all map layers are reclassified and ranked in a scale of 1 to 5 (Tables 4.11, 4.12 and 4.13), where the value of 5 represents the most influential class with regard to water quality, while 1 corresponds to the least influential class.

4.3.1.1 Thematic maps for summer of 2020

Table 4.11 presents the classes created for all thematic map layers during summer.

Table 4.11: Reclassified ranks of classes of water quality parameters (summer, 2020).

Parameter	Class	Rank	Parameter	Class	Rank
pH	7.70-7.89	5	Manganese	0.00-0.02	1
	7.89-8.09	5		0.02-0.06	1
	8.09-8.25	5		0.06-0.11	3
	8.25-8.42	5		0.11-0.16	3
	8.42-8.59	5		0.16-0.18	5
Turbidity	7.09-15.54	1	Nitrate	0.91-1.73	5
	15.54-24.01	1		1.73-2.56	5
	24.01-32.48	2		2.56-3.38	5
	32.48-40.95	2		3.38-4.21	5
	40.95-49.43	2		4.21-5.03	5
Electrical conductivity	50.70-81.56	1	Fluoride	0.39-0.80	5
	81.56-112.42	2		0.80-1.15	4
	112.42-143.28	3		1.15-1.50	3
	143.28-170.00	4		1.50-2.12	1
	170.00-204.99	5		2.12-2.89	1
Total dissolved solids	329.59-530.17	4	Chloride	24.21-62.27	5
	530.17-730.75	4		62.27-100.33	5
	730.75-931.33	4		100.33-138.39	5
	931.33-1200.00	5		138.39-176.45	5
	1200.00-1332.49	5		176.45-214.51	5
Magnesium	25.74-43.97	5	Sulphate	103.94-194.63	1
	43.97-67.09	5		194.63-285.32	2
	67.09-93.33	5		285.32-376.02	3
	93.33-118.23	5		376.02-500.00	4
	118.23-138.68	5		500.00-557.40	5
Calcium	32.45-41.31	1	Potassium	7.13-21.98	2
	41.31-50.49	2		21.98-36.84	2
	50.49-60.52	2		36.84-51.69	5
	60.52-68.54	3		51.69-66.55	5
	68.54-75.05	3		66.55-81.41	5
Sodium	34.95-67.12	3	Vanadium	0.07-0.13	5
	67.12-99.29	4		0.13-0.18	5
	99.29-131.46	5		0.18-0.24	5
	131.46-163.63	5		0.24-0.30	5
	163.63-195.80	5		0.30-0.36	5

The thematic map layers of the distribution of the dissolved heavy metals revealed a high concentration of ions such Mg, Ca, Cl, Na, V and K (rank 5) with an alkaline pH at the downstream points of the Olifants River towards the Kruger National Park (Figure

4.16, and Appendix 2a). The concentration of ions at the downstream points of Olifants River, therefore, showed a homogenous trend of being highly concentrated at the downstream along the Olifants River. As a result, the thematic maps revealed that the EC and TDS concentrations could also be highly influential hence ranked 5 at the downstream points of Olifants River. This part of the river is subjected to various pollutants from the Phalaborwa mining and industrial complex that gets carried away through the Ga-Selati River. The distribution of heavy metal maps revealed a common source of pollution along the Ga-Selati River which is predicted to be discharging heavy metals into the Ga-Selati River. Heavy metals could also be washed into to the Olifants River from the agricultural fields around Mica area along the R40 Klaserie road towards the Town of Hoedspruit as the maps revealed high concentrations of NO_3, SO_4^-, Na, and EC with an alkaline pH of water.

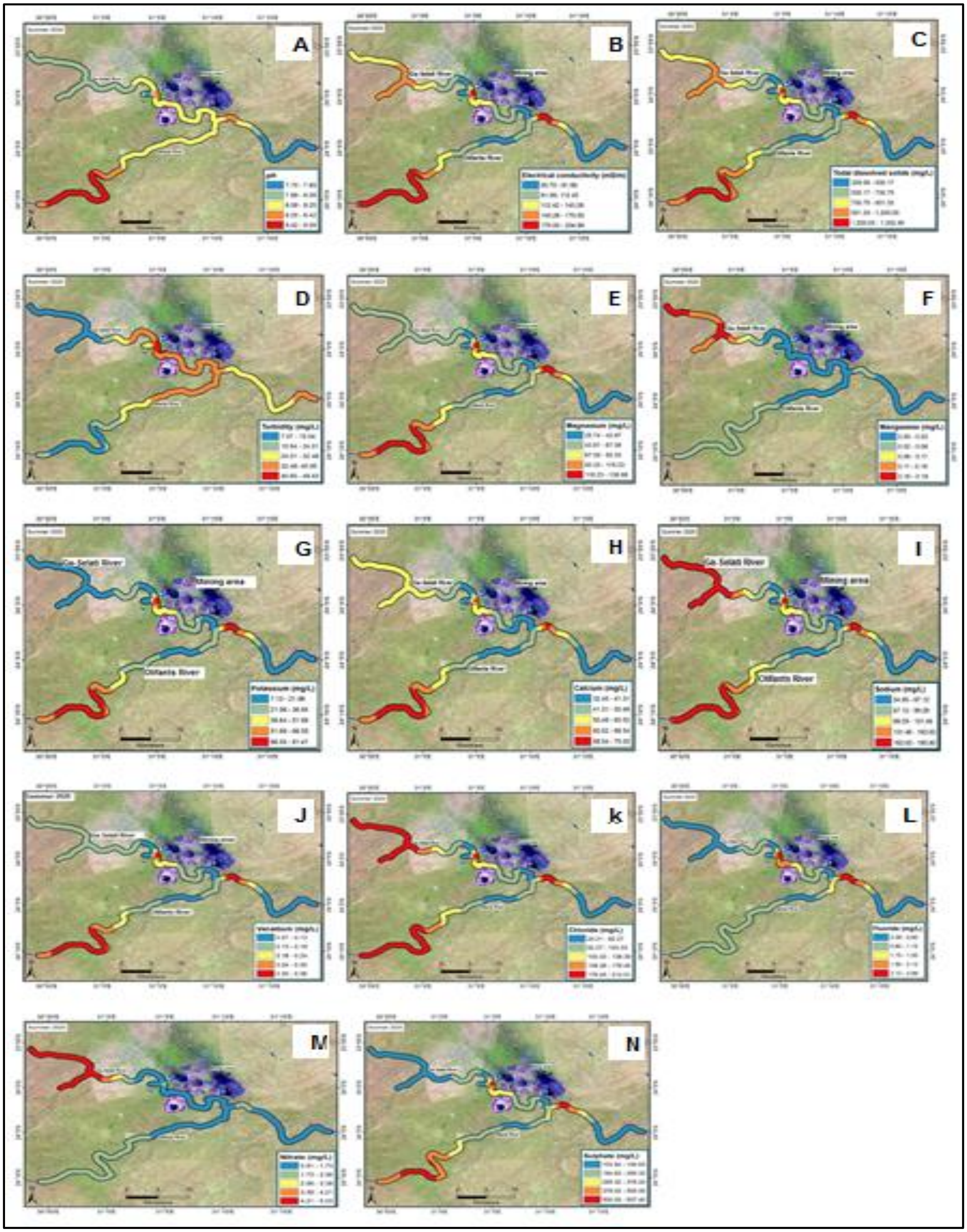

Figure 4.16: Spatial distribution of water quality parameters for summer of 2020, a) pH; b) EC; c) TDS; d) Turbidity; e) Mg; f) Mn; g) K; h) Ca; i) Na; j) V; k) Cl; l) F; m) NO_3 and n) SO_4^-.

According to the thematic maps, the concentrations of these heavy metals reduce as the water flows further away from the pollution sources. This could be as a consequence of dilutions during rainy days, settling of metals to sediments and/ uptake of ions such as NO_3 as nutrients. As stated, the thematic maps revealed reduced concentrations of the heavy metals to lower ranks with the least influential impacts as the water progressed towards the Kruger National Park. The concentrations of heavy metals at the Kruger National Park in summer were therefore revealed to be moderately influential. This reduction of the concentration of dissolved heavy metals at this part of the Olifants River could also be as a result of complete mixing of water from both Ga-Selati and Olifants Rivers due to increased levels of dilutions in the stream.

The turbidity water of along both Olifants and Ga-Selati Rivers was predicted to be less influential with rank 2 around the Phalaborwa mining industries including after the Ga-Selati/Olifants confluence. The water of the Olifants River at the downstream sampling points appeared dirty, however, the turbidity along the Olifants River improved further away from the Ga-Selati/Olifants confluence towards the Kruger National Park to a rank of 1. This improvement of the turbidity further away from the Ga-Selati/Olifants confluence could be as results of settling of suspended particles due to the reduced river flows and dilutions that could be taking place at this section of the Olifants River system.

The thematic maps of the concentrations of Mn and NO_3 revealed similarities at the downstream of Olifants River where concentrations remained constant from some other sections of the upstream. However, the NO_3 concentration map showed that the concentration of $N0_3$ was high at the upstream directions of Ga-Selati River and decreased towards the downstream directions of the same river. As indicated earlier, this decrease could be as a result of the use of NO_3 as nutrient by plant species. The concentration of N03 was also revealed to have increased at the western border of the Kruger National Park and later decreased to a condition of mesotrophic within the Kruger National Park. On the map, the distribution patterns of Mn showed similarities with those of other ions such as SO_4^-, Mg, Na, Cl, V and K, and reduced to least influential rank (rank 1) towards the Kruger National Park and stayed at least influential ranks throughout the Park. In summer, the concentration heavy metals were high at the downstream points of the Olifants River system than at the upstream points. Ga-Selati River showed to have been the carrier of ions in summer with the pollution sources revealed to be located around the Foskor mine operational fields.

4.3.1.2 Thematic maps for spring of 2019

Table 4.12 shows the classes created for all map layers during spring.

Table 4.12: Reclassified ranks of classes of water quality parameters for spring of 2019).

Parameter	Class	Rank	Parameter	Class	Rank
pH	4.40-5.00	1	Manganese	0.00-0.01	1
	5.00-6.35	5		0.01-0.04	1
	6.35-7.49	5		0.04-0.07	1
	7.49-8.45	5		0.07-0.11	1
	8.45-9.09	5		0.11-0.12	2
Turbidity	2.72-11.34	2	Nitrate	0.10-14.87	5
	11.34-19.96	2		14.87-27.28	5
	19.96-28.58	2		27.28-39.29	5
	28.58-37.20	1		39.29-50.00	4
	37.20-45.82	1		50.00-73.97	1
Electrical conductivity	41.10-78.98	5	Fluoride	0.25-0.97	5
	78.98-124.79	4		0.97-1.50	4
	124.79-170.00	3		1.50-2.42	2
	170.00-201.16	2		2.42-3.15	1
	201.16-230.49	1		3.15-3.87	1
Total dissolved solids	267.15-513.37	5	Chloride	24.80-58.82	5
	513.37-759.59	4		58.82-92.84	5
	759.59-1005.80	3		92.84-126.87	5
	1005.80-1200.00	3		126.87-160.89	5
	1200.00-1498.23	1		160.89-194-91	5
Mg	29.32-48.60	3	Sulphate	28.92-155.43	5
	48.60-82.62	5		155.43-281.94	5
	82.62-120.60	5		281.94-408.45	4
	120.60-149.52	5		408.45-500.00	2
	149.52-173.90	5		500.00-661.48	1
Calcium	25.11-35.29	2	Vanadium	0.06-0.12	5
	35.29-50.31	2		0.12-0.19	5
	50.31-66.35	3		0.19-0.25	5
	66.35-79.84	3		0.25-0.32	5
	79.84-90.02	4		0.32-0.38	5
Potassium	3.39-27.05	1	Sodium	32.15-77.55	3

	27.05-50.71	3		77.55-115.19	4
	50.71-74.37	5		115.19-162.57	5
	74.37-98.04	5		162.57-200.00	5
	98.04-121.70	5		200.00-215.45	5

In spring, the pH of water was alkaline with highly influential impacts (rank 5). The concentration maps of EC and TDS revealed high concentrations of EC and TDS with turbidity on rank 2 at the study area which then both decreased towards the western border of the Kruger National Park. The thematic map of the concentration of the dissolved heavy metal predicted a homogenous trend amongst the concentration levels ions i.e., highly concentrated towards the downstream directions of both Ga-Selati and Olifants Rivers. The concentration maps of Mg, Ca, K, Na, Cl, F and SO_4^- showed that the water at Ga-Selati River was highly polluted around the Phalaborwa mining industries towards the Ga-Selati/Olifants confluence (Figure 4.17, and Appendix 2b). The heavy metal concentration maps of these ions at the Olifants River showed a similar trend with the Ga-Selati River ion concentration pattern where the concentrations increased towards the downstream directions. As in summer, the heavy metal concentration maps showed a decrease in the concentration of Mg, Ca, K, Na, Cl F and SO_4^- towards the western border of the Kruger National Park. The concentration levels dropped from rank 5 to 1 within the Kruger National Nation Park during spring 2019 and this could be consequences of the fact that the complete mixing of water from Ga-Selati and Olifants Rivers brought some dilutions at this part of the Olifants River. Figure 4.17 shows the resultant maps of the concentrations of heavy metals in the water of Olifants and Ga-Selati Rivers in spring, 2019.

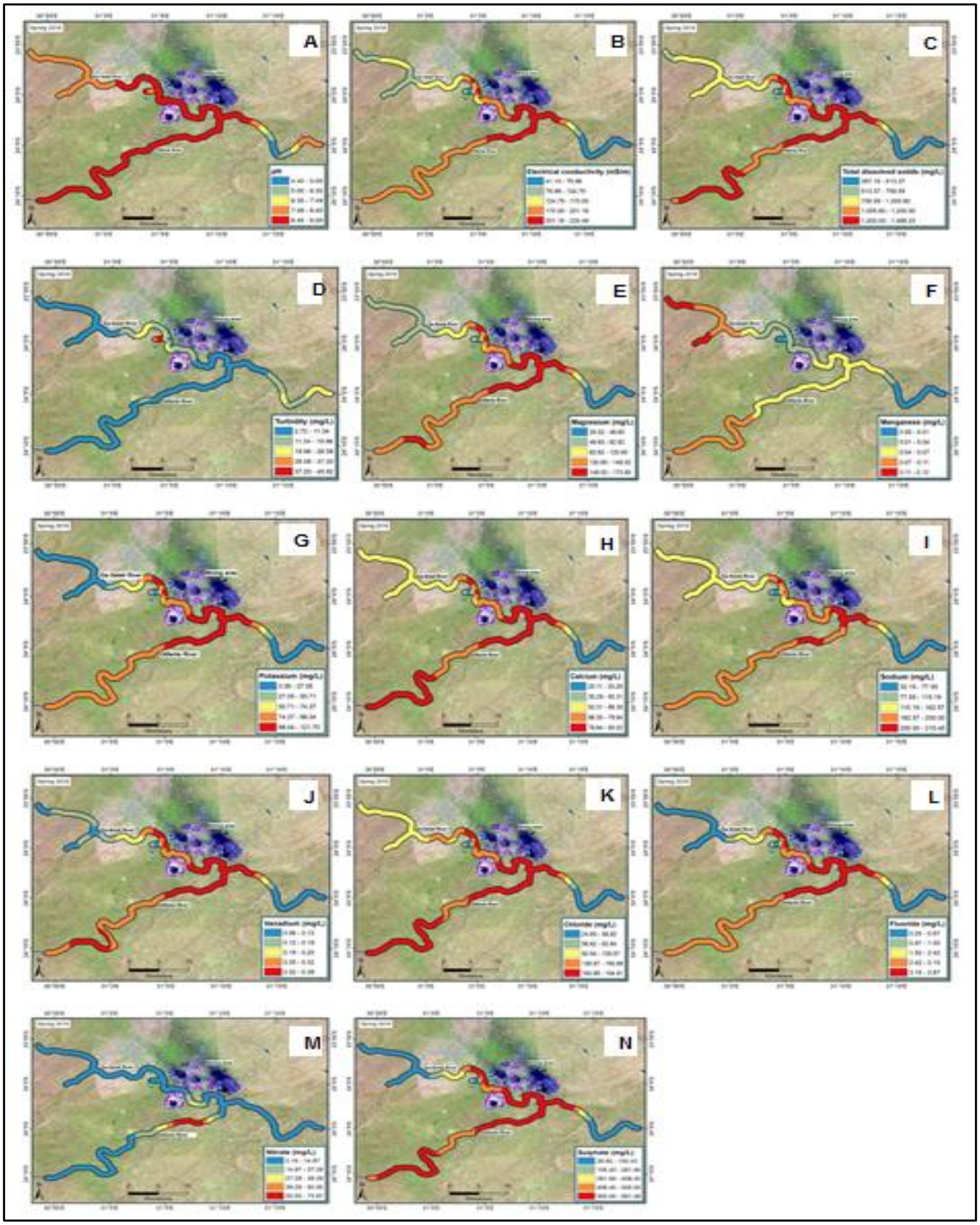

Figure 4.17: Spatial distribution of water quality parameters for spring 2019, a) pH; b) EC; c) TDS; d) Turbidity; e) Mg; f) Mn; g) K; h) Ca; i) Na; j) V; k) Cl; l) F; m) NO_3 and n) SO_4^-.

The NO_3 concentration map predicted the hypertrophic conditions at the Ga-Selati River under the bridge of the Lepelle Water Board road. The hypertrophic conditions refer to a condition where water bodies experience unpleasant development water plants and blooms of blue-green algae, including species which can be harmful to humans, livestock and wildlife (Department of Water Affairs and Forestry, 1996). The high concentration of NO_3 at this part of the Ga-Selati River could be as a result of the fertilizer plant (Sasol Nitro) which is located before the Foskor Mine, adjacent to the Ga-Selati River. Similar conditions of hypertrophic were also predicted by the thematic maps along the Olifants River at the Shona Langa Safari Lodge. This place is located approximately 600 meters away from the Lepelle Water Board Plant in the downstream directions along the Olifants River. The high concentration of NO_3 at this part of the Olifants River could be as a result of the use of fertilizers at the agricultural farms around the area of Mica. However, the NO_3 concentration map revealed a condition of mesotrophic towards the downstream points along both Ga-Selati and Olifants Rivers (Figure 4.17). As with other ions, the concentrations of NO_3 decreased towards the Kruger National Park directions and stayed low throughout the park.

The Mn concentration map showed trends that were below the critical levels of 0.18 mg/L set by the South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996), around both the Phalaborwa mining and industrial complex at Ga-Selati River. The trends remained similar at the Olifants River during this season. The concentration map of Mn demonstrated a decrease in the Mn content in the water of both Ga-Selati and Olifants Rivers at downstream directions. The concentration of Mn at the Kruger National Park along the Olifants River was predicted to be absent or very low with a range of 0.00 to 0.01 mg/L in spring.

4.3.1.3 Thematic maps for winter of 2019

Table 4.13 shows the classes created for all map layers during winter.

Table 4.13: Reclassified ranks of classes of water quality parameters (winter, 2019).

Parameter	Class	Rank	Parameter	Class	Rank
pH	7.70-7.96	5	Manganese	0.00-0.01	1
	7.96-8.04	5		0.01-0.02	1
	8.04-8.14	5		0.02-0.024	1
	8.14-8.33	5		0.024-0.03	1
	8.33-8.49	5		0.03-0.04	2
Electrical conductivity	35.40-70.15	5	Aluminium	0.080-0.082	5
	70.15-109.23	4		0.082-0.084	5
	109.23-140.77	4		0.084-0.085	5
	140.77-170.00	3		0.085-0.087	5
	170.00-229.99	1		0.087-0.089	5
Turbidity	7.46-42.50	2	K	2.38-35.53	2
	42.50-77.54	2		35.53-68.69	5
	77.54-112.58	2		68.69-101.85	5
	112.58-147.63	1		101.85-135.01	5
	147.63-182.67	1		135.01-168.17	5
Magnesium	18.76-39.34	3	Vanadium	0.03-0.07	5
	39.34-59.92	5		0.07-0.12	5
	59.92-82.56	5		0.12-0.17	5
	82.56-102.32	5		0.17-0.22	5
	102.32-123.73	5		0.22-0.26	5
Sodium	27.93-71.95	5			
	71.95-115.98	5			
	115.98-160.01	5			
	160.01-200.00	4			
	200.00-248.07	4			

As in spring and summer, the pH of the water at Ga-Selati and Olifants Rivers in winter was revealed by the thematic maps to be constantly alkaline from the upper sections of the streams before the upstream sampling points. The pH thematic map predicted increased pH levels on the water of the Olifants River at the Kruger National Park with rank 5. The high concentration of pH could be as a result of chemicals used to increase pH in the streams as a way of ensuring the protection of the stream within the Kruger National Park. The EC concentration map revealed that the Sasol Nitro dam located before the Foskor tailing dam could possibly be the main source of ions along the Ga-Selati River as the EC concentration was at rank 5 at this part of the Ga-Selati River. The turbidity of the water at this part was also higher than at the other parts of the Ga-Selati River. At the Olifants River, EC concentration map showed that more concentrations of ions were around the Mica agricultural farms. These concentrations, therefore, decreased towards the study area and increased again at the downstream points of the Olifants River. The concentration of EC along the Olifants River within the Kruger National Park reduced to a rank of 1. This could mean that the Olifants River at the Kruger National Park was less impacted by the concentration of heavy metals in winter, 2019.

As in spring and summer, the concentration maps of Mg, Ca, K, Na, and V in winter revealed high concentrations of these heavy metals at the Ga-Selati River adjacent to the Sasol Nitro dam and at the downstream points along the Olifants River. High concentrations of heavy metals were also revealed along the Olifants River at the Mica area, probably as a result of the extensive agricultural activities taking place at that part of the stream. The concentration patterns of Mg, Ca, K, Na and V were similar i.e., increased at the downstream directions, mainly as a result of mining and industrial activities taking place at this section of the lower Olifants River catchment. As observed in spring and summer, the heavy metal concentration levels dropped at the Kruger National Park along the Olifants River as predicted by the thematic maps. Figure 4.18 and Appendix 2c show the resultant maps of the levels of heavy metals in the water of Olifants and Ga-Selati Rivers in winter, 2019.

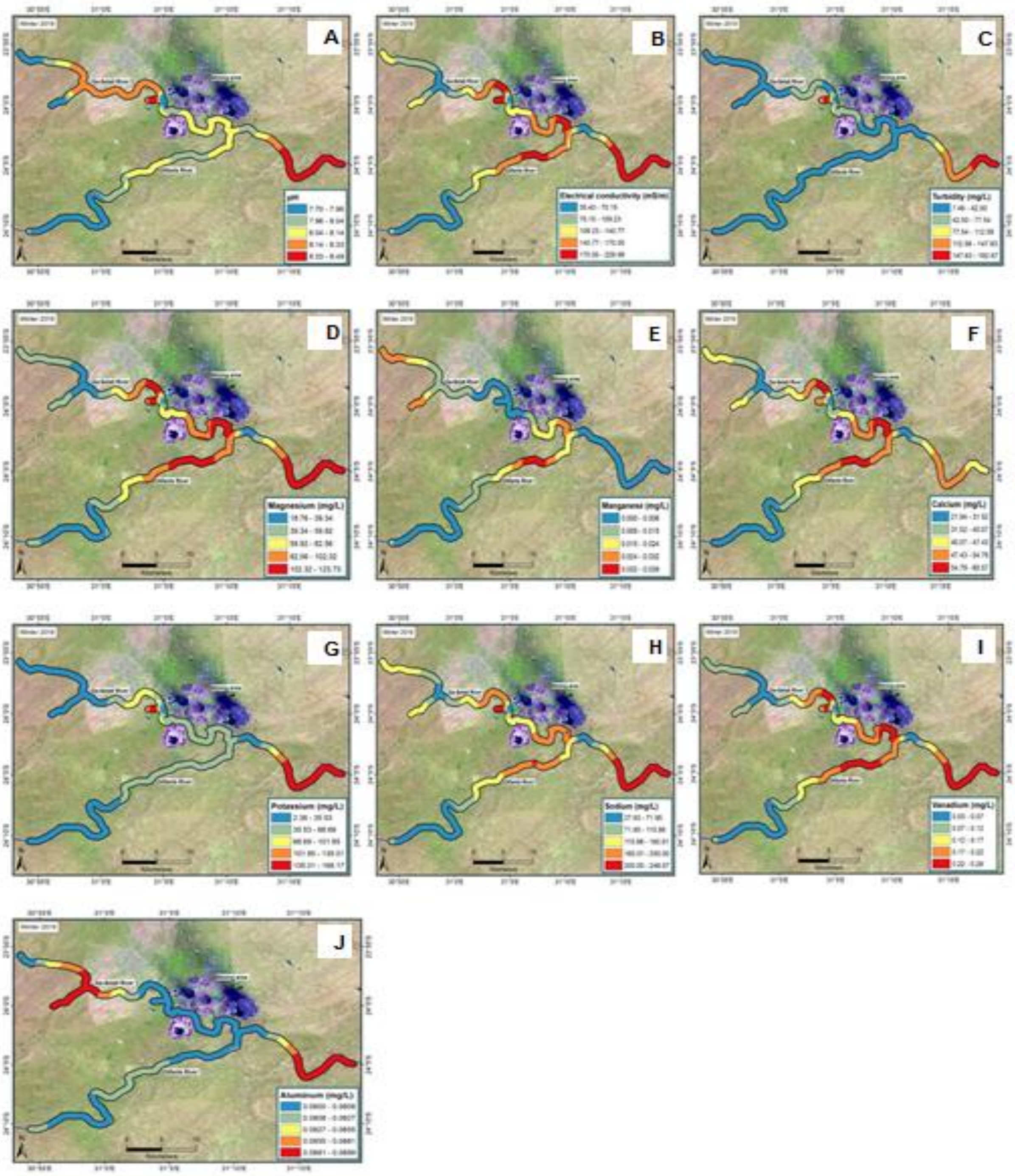

Figure 4.18: Spatial distribution of water quality parameters for winter of 2019, a) pH; b) EC; c) Turbidity; d) Mg; e) Mn; f) Ca; g) K; h) Na; i) V and j) Al.

The thematic map of the concentration Mn in winter revealed non-existence of Mn at the upper sections of both streams, few kilometres before the study area. This map showed that the Mn concentration at the study was below the TWQR of 0.18 set by the South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996). At the Kruger National Park, the thematic map showed the non-existence of Mn in winter (Figure 4.33). This was a complete difference case with Al concentrations. The thematic map of Al interestingly showed the consistent highest concentrations of Al with ranks exceeding the TWQR of 0.01 mg/L (under pH of more than 6.5) set by the South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996) at both Ga-Selati and Olifants Rivers. The thematic map predicted high concentration of Al around the Mica area, the study area as well as within the Kruger National Park towards the Limpopo River. The high concentration of Al could be associated with infrastructures such as bridges that exist within the two streams.

4.4 Water Quality Index results

In this study, AHP method was used to determine WQI based on the analytical results of water samples collected in the river system proximal to Phalaborwa mines. Water samples were collected in three different seasons (winter, summer and spring). As stated under the methodology, the water quality parameters considered for assessing water quality for spring and summer includes electrical conductivity, pH, hardness, colour, turbidity, fluoride, total dissolved solids, sulphate, chloride and sodium. For winter, a number of parameters were not detected (ND), hence few parameters were analysed and thus the parameters considered assessing water quality were relatively few and these include pH, electrical conductivity, turbidity, sulphate, sodium and aluminium.

The pairwise comparison analysis of the importance of various parameters, for individual seasons, with regard to water quality was based on literature and expert knowledge. Tables 4.14 and 4.15 show a pairwise comparison matrix and weights of individual parameters, which were used in preparing WQI maps for spring, summer, and winter (Figures 4.19, 4.20 and 4.21) using the weighted overlay method of ArcGIS. Consistency ratio (CR) of <2 % was achieved, for all maps, which means that the attributed weights were appropriate and reliable (Saaty, 1980). The WQI maps showed that the water was highly polluted (22.22 %) around the sampling sites in winter of 2019 than in spring of 2019 and summer of 2020, and this conditions may vary from year to year. The pollution levels decreased to 6.67 % in the Kruger National Park towards the Limpopo River. The spring WQI map showed that the pollution levels in the study area were moderate to low and increased towards the Limpopo River through the Kruger National. Pollution levels in summer ranged from moderate to high across all four sampling sites and increased towards the Limpopo River directions.

Table 4.14: Pairwise comparison and weightages of the Water Quality Index for summer and spring.

Matrix		pH 1	TDS 2	Turbidity 3	Colour 4	Electrical Conductivity 5	Chloride 6	Nitrate 7	Sulphate 8	Sodium 9	Fluoride 10	**normalized principal Eigenvector (Weight)**
pH	1	1	1	1	1	1	2	2	2	2	2	13,33%
TDS	2	1	1	1	1	1	2	2	2	2	2	13,33%
Turbidity	3	1	1	1	1	1	2	2	2	2	2	13,33%
Colour	4	1	1	1	1	1	2	2	2	2	2	13,33%
Electrical Conductivity	5	1	1	1	1	1	2	2	2	2	2	13,33%
Chloride	6	1/2	1/2	1/2	1/2	1/2	1	1	1	1	1	6,67%
Nitrate	7	1/2	1/2	1/2	1/2	1/2	1	1	1	1	1	6,67%
Sulphate	8	1/2	1/2	1/2	1/2	1/2	1	1	1	1	1	6,67%
Sodium	9	1/2	1/2	1/2	1/2	1/2	1	1	1	1	1	6,67%
Fluoride	10	1/2	1/2	1/2	1/2	1/2	1	1	1	1	1	6,67%

Table 4.15: Pairwise comparison and weightages of Water Quality Index for winter.

Matrix		pH	Turbidity	Electrical conductivity	Sulphate	Aluminium	Sodium	normalized principal Eigenvector (Weight)
		1	2	3	4	5	6	
pH	1	1	1	1	2	2	2	22,22%
Turbidity	2	1	1	1	2	2	2	22,22%
Electrical conductivity	3	1	1	1	2	2	2	22,22%
Sulphate	4	1/2	1/2	1/2	1	1	1	11,11%
Aluminium	5	1/2	1/2	1/2	1	1	1	11,11%
Sodium	6	1/2	1/2	1/2	1	1	1	11,11%

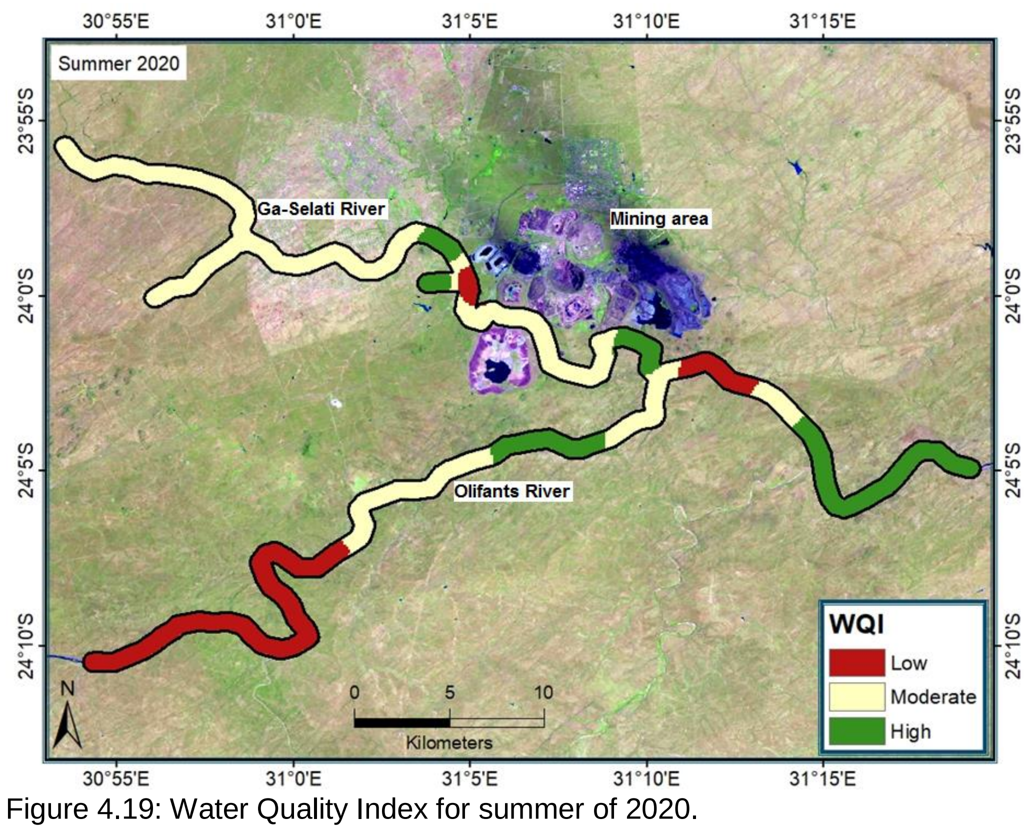

Figure 4.19: Water Quality Index for summer of 2020.

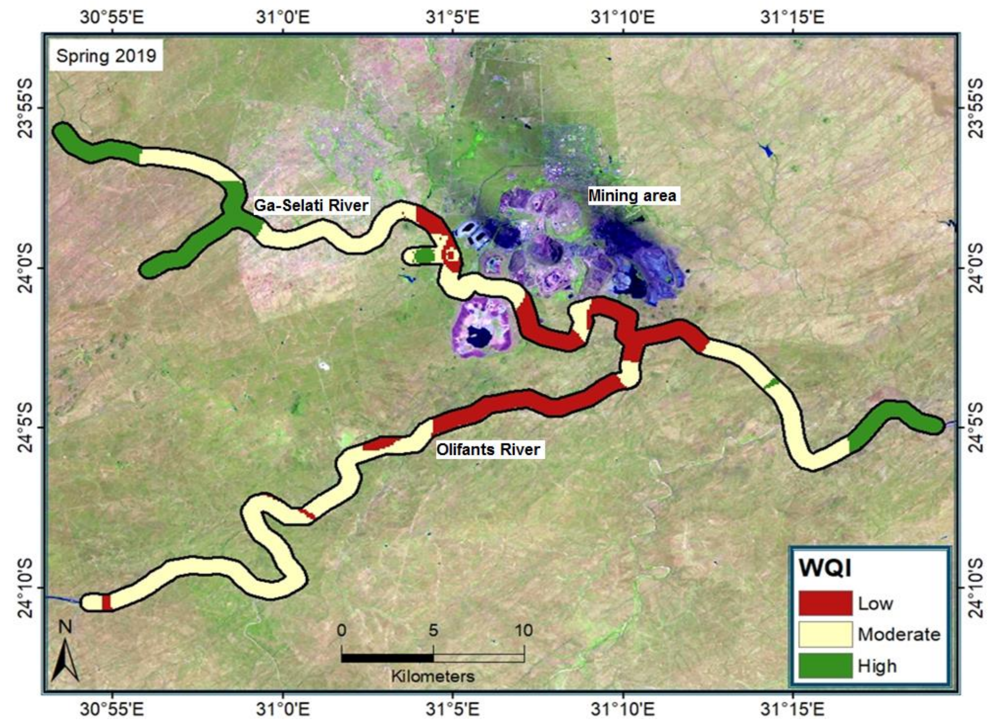

Figure 4.20: Water Quality Index for spring.

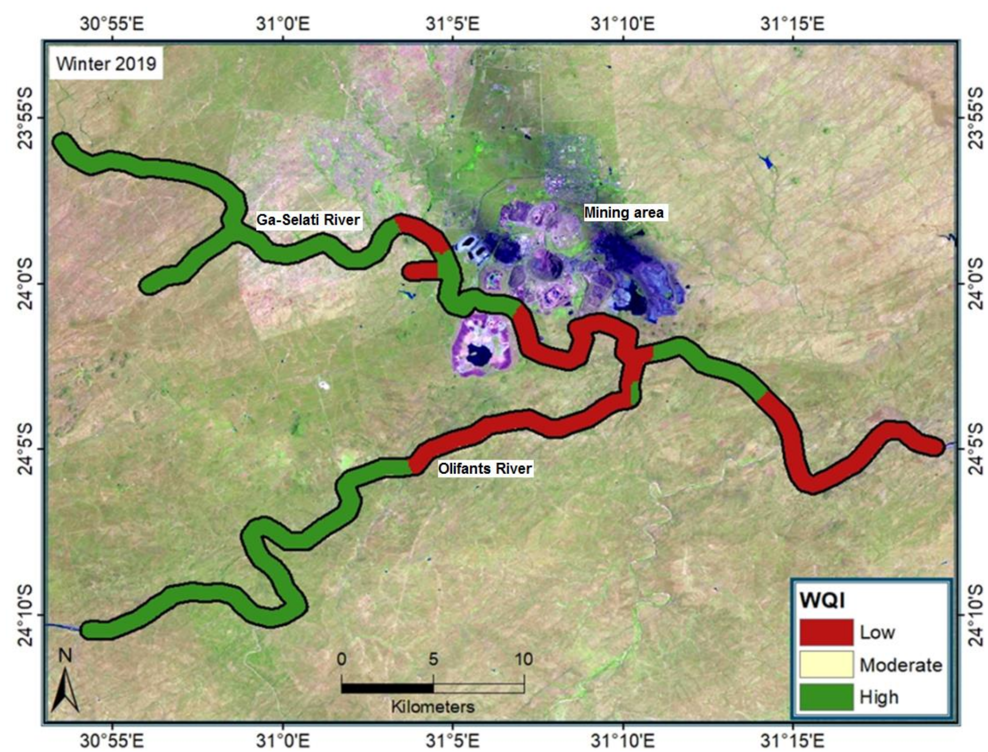

Figure 4.21: Water Quality Index for winter.

4.5 Application of the Acid Mine Drainage management strategies by Phalaborwa mining industries

AMD is a serious environmental problem because it has the ability to mix with natural water in the rivers and dams to cause severe degradation of the quality of natural water bodies. It is important to treat the mine wastewater to the permissible water standards before releasing the effluent into the natural water bodies. Various techniques can be used to counteract the acidic levels of the mine wastewater. The study has found that the Phalaborwa mining houses are all using the open limestone drains to introduce alkalinity treatment into the mine wastewater. These systems are specifically designed to treat the toxic mine wastewater where metals are removed through precipitation without clogging with particulates and metals hydroxide precipitates (Hedin *et al*., 2002). Large areas are always required for the effective operation of the open limestone drains. The AMD influent has to be allowed a sufficient time (several hours) to be in contact with limestone by increasing the length of the drain in the treatment system for effective neutralization to occur (Taylor *et al*., 2006).

According to the Draft consolidated Environmental Management Programme (EMPr) for Phalaborwa mining industries compiled by Golder Associates (2019), all decants water from the mining facilities, magnetite stockpiles and the effluent, as well as the runoff from various plants, is channelled into the return water tailing dams. These dams are monitored on a regular basis to maintain a check on slope stability. These tailing dams are equipped with draining pipes underneath to collect the infiltrated and treated water back into the operational systems. According to the consolidated EMPr for PMI, monitoring and modelling results have indicated that the return water tailing dams contribute less than 5 % of the contaminants at the Ga-Selati River.

Palabora Mining Company performs monitoring of the water quality on a monthly basis along both Ga-Selati and the lower Olifants Rivers. This monitoring is done at two sites along the Ga-Selati River: downstream of Foskor/upstream of Palabora Mining Company and upstream of the confluence with the Olifants River and downstream of Palabora Mining Company. At the lower Olifants River, three surface water samples, are taken on a monthly basis to compare upstream (Olifants River barrage) and downstream water qualities. The downstream monitoring point at the lower Olifants River is located approximately 300 m downstream of the Olifants/Ga-Selati Rivers confluence. According to the report compiled by Golder Associates (2019), it is, however, expected that the complete dilution of the water from both streams does not occur at this point. Therefore, another monitoring point was selected further downstream of the Palabora Mining Company, close to the Kruger National Park boundaries to monitor the water quality. At this monitoring point, it is assumed that the Ga-Selati and Olifants River waters have mixed completely (Golder Associates, 2019). This monitoring is done as an attempt to get an overview of the effectiveness of the applied wastewater management measures that are put on the operational site.

4.6 Effectiveness of the South African policy and legal framework on the management of AMD

There is a great threat facing the South African water and other environmental resources, and people as a result of pollution stemming from AMD that need strengthened and well-enforced legal frameworks. This section reviews the transgressions that were observed against the South African policy and legal framework that exist to control and manage the AMD around the mining areas. This section further reviews the delegation of power in advocating the regulatory framework to outline the levels at which AMD regulations are been handled. The transgressions were checked against the National Water Act (Act No. 38 of 1998), the Mineral and Petroleum Resources Act (Act No. 28 of 2002), the National Environmental Management Act (Act 107 of 1998) and the National Environmental Management: Waste Act (Act No. 59 of 2008).

South Africa is faced with an increased challenge of AMD including the one that occurs from the historical mines as a result of inadequate post-mining site management (Mujuru and Mutanga, 2016). Government initiatives to apportion responsibility for environmental rehabilitation have been met with denial and refusal by most of the mining companies (Van Eeden *et al.,* 2008). Several mines were abandoned before they can probably have some environmental and socio-economic impacts and therefore, it has remained quite difficult to legally hold mines accountable for such impacts (Mujuru and Mutanga, 2016). In instances where the owner of the abandoned mines cannot be traced and found, the state has to take responsibilities of remedying the impact using the taxpayer's money, who were never responsible for the problem, nor benefited from the profits while the mines were operational (Feris and Kotze, 2014). The country has 1200 kilolitres (Kl) of available freshwater (Durand *et al.,* 2010) which is unevenly distributed across the country and that could mean that South Africa is a water-stressed country, and thus effective protection of water resources is required (Durand *et al.,* 2010).

4.6.1 National Environmental Management Act

The Department of Forestry, Fisheries and the Environment (DFFE) is responsible for the enforcement of the NEMA (Act 107 of 1998). The Environmental Impact Assessment (EIA) Regulations (2014) (as amended in 2017), published in terms of the NEMA (as amended) requires that an EIA be conducted for any activities that affect the environment and is listed in terms of the EIA regulations. The EMPr together with some of the EIA reports need to be approved by the government officials where the Environmental Authorization (EA) will therefore be issued with some conditions that need to be fully adhered to. This Act requires prevention and mitigation of pollution where the cost of clean-up can be sourced from the polluter in case the owner fails to adhere to best practices measures as stipulated in the approved or authorized EMPr and EA conditions.

The study has recorded no transgression against this legislation during the 2019/2020 seasons of the year. However, it was reported on the media (Creamer Media, 2015) and by the Department of Environmental Affairs (2015) that during the summer of 2013/14, the Bosveld Phosphates Pty Ltd that operates within the lower Olifants River catchment, has been found guilty and sentenced in the Phalaborwa Regional Court (PRC) for unlawfully and/ negligently releasing the contaminated mine water into the Ga-Selati River which caused significant environmental pollution along the Ga-Selati River and Olifants River. According to the media report, the tailings dam owned by the Bosveld Phosphates, overflowed as a result of the heavy rainfall, releasing the highly acidic water into the nearby Ga-Selati River which then resulted in the death of fish over a distance of 15 km from the industry location. The Bosveld Phosphates pleaded guilty to contravening conditions stipulated conditions in both the National Environmental Management Act (Act No.107 of 1998) and the National Water Act (Act No.36 of 1996). The level of the contaminations at that stage prompted quick intervention by the relevant authorities.

The South African National Parks (SANParks) together with the Department of Water and Sanitation (DWS) made sure that the appropriate mitigation measures are implemented by Bosveld Phosphates. The successful prosecution of this mining company was led by the Green Scorpion (GS) of the DFFE. The Bosveld Phosphates company at that stage was fined an amount of R1.450 million with a suspended sentence of R1.1 million for contravening section 34(1) and (3) of the NEMA as well as the section 19(1) of the NWA. This means that the company paid a fine of R350 000.00 for such a huge environmental offence. The amount was too little for a mining company and the damage that the acid mine drainage has on water resources. In most cases, noncompliance is motivated by the light fines that come with an environmental offence. However, according to the media report, a total amount of R48 million was spent by Bosveld Phosphates in implementing the remedial measures (Creamer Media, 2015). During the time of spillage, several state organs such as the DWS, the Limpopo Department of Economic Development, Environment and Tourism (LDEDET) as well as the SANParks were the key players that ensured that the emergency actions were taken, and measures are put in place to rectify the environmental deviations that were caused the Bosveld Phosphates.

4.6.2 National Water Act

The Department of Water and Sanitation is responsible for the enforcement of the NWA (Act No. 36 of 1998). This Act regulates different water uses including for the mining water use and ensures protection of the water resources in South Africa. This Act, like NEMA, supports the polluter-pays principle in which mining companies responsible for the pollution on water resources would be held liable for cleaning-up costs (Munnik, 2010). Section 19 of the NWA, with the title “Prevention and remedying effects of pollution" is believed to be one of the most important sections of this Act. This section "states that:

1) An owner of land, a person in control of land or a person who occupies or uses the land on which-

(a) any activity or process is or was performed or undertaken; or

(b) any other situation exists, which causes, has caused or is likely to cause pollution of a water resource, must take all reasonable measures to prevent any such pollution from occurring, continuing or recurring."

According to this section (section 19), pollution can be "defined as the direct or indirect alteration of the physical, chemical or biological properties of a water resource" (Republic of South Africa, 1998). This water pollution definition is not limited to only damage and liability but also damage to property and this section is closely related to the section 28 of the NEMA where wide responsibilities of care and liability are imposed on the polluters' directive to take reasonable measures in counteracting against the acidity of AMD (Feris and Kotze, 2014). According to section 19(2) of NWA, such measures, as with NEMA section 8, may include but not limited to; the termination, modification "or control of any act or process responsible for the cause of the pollution; compliance with any prescribed waste standard or management practice; containment of prevention of the movement of pollutants from the operational site; elimination of any source of pollution; and remediation of the effects" caused by pollution (Republic of South Africa, 1998). Section 19 of the Act states that subject to sub-items (3)-(5) of NWA, an administrative directive can be issued to the mine that fail to apply sound measures to do so. The section further indicates that, if it happens that the mine "fails to comply with the directive, the government will, therefore, take measures" on the behalf of the mine to address the pollution caused and recover all costs from the mine (Republic of South Africa, 1998).

Some of the mining activities require authorization for water use as indicated in Chapter 4 of NWA titled 'Use of Water". New mines with the activities triggered in section 21 of this Act, need to apply for the water use license (WUL). The issued water use license comes with various conditions, which are legally binding, and any breach to those conditions can result in criminal or administrative sanctions (Section 29 of NWA, 1998). Section 22(2)(c) of the "NWA states that any person who uses water for the purposes of the discharge or disposal of waste or water containing waste must comply with any applicable waste standards or management practices prescribed in regulations made under sections 26"(1)(h) and (i), unless the conditions of the relevant water use authorization provide otherwise (Republic of South Africa, 1998). Practically, the enforcement of this legislation has consisted of some serious challenges, partially because of the capacity constraints at the Department of Water and Sanitation (Munnik, 2010).

According to the seasonal water quality results obtained from both Ga-Selati and Olifants Rivers during the 2019/2020 seasons, the levels of contaminants associated with the mining activities at the lower Olifants River catchment were generally high in summer and spring. However, most of the heavy metals stayed below the TWQR set by the South African water quality guidelines for aquatic ecosystems and EPA (2001). This includes the manganese which is known to be associated with acidic metalliferous discharge water and phosphate deposits from mining activities. The water quality results showed the controlled levels of contaminants throughout the seasons, hence no transgressions were recorded against this act particularly in the management of AMD at the lower Olifants River catchment.

4.6.3 Mineral and Petroleum Resource Development Act (MPRDA)

The Department of Mineral Resources and Energy (DMRE) governs the MPRDA (Act No. 28 of 2002). The Act aims to transform the minerals and the extractive sector and promote equitable access to mineral resources (Republic of South Africa, 2002). The MPRDA promotes the sustainable principles of the NEMA by monitoring the mining activities and socio-economic developments that honour ecological resources (Feris and Kotze, 2014). This Act integrates several other policy frameworks that may include the Mining Charter of 2002 (as amended), the codes of Good Practice for the Mineral Industry as well as the Housing and Living Condition Standards for the Mineral Industry (Mujuru and Mutanga, 2016).

As with NWA and NEMA, MPRDA has liability provisions that might be applied in the management of AMD. As indicated in section 38(1)(d) of the MPRDA, it is the responsibility of the mine to rehabilitate the environment to a reasonable or satisfying natural state or condition that would allow other land uses to take place. In terms of this Act, under section 38(1)(e), liabilities should be imposed to any mine responsible for any environmental damage, pollution or ecological degradation resulted from mining activities and all these liabilities should be valid until the closure certificate is issued. The study done by Feris (2012) states that these environmental liabilities will be active in terms of NWA and NEMA, despite been ceased under MPRDA by way of closure certificate.

Besides the MPRDA, mining regulatory frameworks have previously existed for quite long in South Africa with a wide range of responsibilities covering environmental and personnel protection as well as imposing liabilities to the mining companies. Like many of the mining legislation and regulations, section 68(2) of the Mineral Act of 1991 was against that the mine water should exit the mining premises containing, either insoluble and/ or suspended, any injurious matter. These mining legislations have been modified and improved over time. The capacity to enforce or implement them is, however, still a constraint. Practically, the “polluter pays” principle has remained quite difficult to implement since most of the defunct mines are ownerless and this principle becomes more effective when the mine is operational (Feris and Kotze, 2014). Mining houses at the lower Olifants River catchment are still in operational and to this stage environmental compliance is well enforced.

4.6.4 National Environmental Management: Waste Act (NEM:WA)

NEM:WA (Act No. 59 of 2008) is administered by DFFE and it regulates the management of waste, including the waste that can be generated as a result of the mining operations which have the potential to affect the water resources. AMD is not a residue deposit, however, the fact that it is produced due to the leachate from mining wastes, gives the Act power to hold the facilities at which the AMD was generated accountable (Kidd, 2009). Section 16 emphasizes that any operations that generate waste such mines, should take sound measures to prevent the dispersion of such waste

(Republic of South Africa, 2008). The section further indicates that where such generation cannot be avoided, the waste must be treated and disposed of in an environmentally friendly manner which will not pose danger to the health or the environment or cause an unpleasant noise, visual or odour impacts. Section 26 of NEM:WA is also against the disposal of waste on land or in water resources (Republic of South Africa, 2008). The NEM:WA integrates the MPRDA, NWA and NEMA in terms of its duties and liabilities. As with NEMA, NWA and MPRDA, the NEM:WA has modified the constitutional obligations into statutory provisions, reiterating the public trust doctrine with regard to the water law (Feris, 2012). However, these statutes such as NWA, NEMA, MPRDA as well as the NEM:WA have been reviewed through amendments and regulations to make them more functional and effective enough with regard to the environmental and AMD management. As with NWA, NEMA, MPRDA, the study has recorded no transgressions against the NEM:WA during the 2019/2020 seasons.

4.6.5 Statutory shortfalls

The main shortfall that has been identified by the study in most of the existing legislative frameworks used in the management of AMD is that there is total confusion in terms of the delegation of power amongst various government departments at the national provincial and municipal levels (Oelofse *et al*., 2007). The fragmentation and overlapping of the institutional roles and responsibilities have exacerbated the ineffectiveness of the statutory liability (Mujuru and Mutanga, 2016). There is a need to rationalize such confusing delegation of power and responsibilities starting at the national levels. With the existing statutory framework, the government can only be reactive to the mismanagement of the AMD rather than been proactive (Oelofse *et al*., 2007). The “polluter pays” principle is a clear example of the pricing structure and enforcement mechanism used to discourage pollution which is too reactive rather proactive.

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

This chapter presents the summary and conclusions emerging from the study, provides recommendations and areas requiring future research and further development. Untreated AMD presents long-term serious environmental challenges when released into the environment with the toxicity of its constituents. In South Africa, a paradigm case is presented whereby the AMD threat to the freshwater system has reached acute levels in recent years (Ewart, 2011; Rose, 2013). This could mean that the AMD management strategies which may include source prevention, treatment of mine wastewater as well as the financial provisions need to be prioritized before the commencement of the mining activities to ensure the protection of water resources. The contamination of the surface waters by acid mine drainage and other acidic effluents from industrial and mining activities remain a serious problem in South Africa. As seen in the study area, the contamination of the water sources by the AMD adversely affects the aesthetic appearance of the waters and damages the aquatic ecosystems that exist within the given water bodies. Such conditions can further make surface water resources more susceptible to organic contamination. In most cases, AMD polluted water overflows when the rain fills the tailing dams at the mining sites resulting in the contamination of the groundwater as well as the local rivers. In South Africa, AMD remains one of the major causes of concern since the country depends on the rivers as well as the rainwater to ensure sustainable supply of domestic water in several communities.

Currently, the Olifants River falls within the rivers that are severely threatened in South Africa because of the number of anthropogenic stressors such as extensive agriculture, industrial and mining pollution as well as the untreated or partially treated sewage (De Villiers and Mkwelo, 2009). Van Vuuren (2009) emphasised that there has been reports of mysterious deaths of fish and crocodiles in the Olifants River, including in the Kruger National Park, and these incidents attracted the media’s attention and resulted in the formation of the ‘Consortium for the Restoration of the Olifants River Catchment’ initiative. The lower Olifants River remains a major source of raw water at this section of this river in the sense that it supplies water to the commercial agriculture, domestic supply for Phalaborwa, Namakgale, Mica, Hoedspruit, and other surrounding areas including to the mines, industries, the Kruger National Park and Mozambique (Association for Water and Rural Development, 2018). Water quality at the lower Olifants catchment is mainly affected by the mining and industrial return flows from the Phalaborwa mining and industrial complex. The pouring of mine wastewater into the Ga-Selati River poses a great threat to the water quality downstream at the Kruger National Park (Department of Water and Sanitation, 2018).

5.2 Summary

The concentration of heavy metals from the AMD-contaminated water in the Olifants and Ga-Selati Rivers was determined using the ICP-OES and IC. There were elevated concentrations of metals such as magnesium, sodium, vanadium, sulphates, potassium, and calcium at sites 3 and 4 throughout the sampling period of the study which can be attributed to the mining activities and the geological formations of the area. Fluoride at site 3 exceeded the TWQR of 0.75 mg/L as set by South African water quality guidelines for aquatic ecosystems (Department of Water Affairs and Forestry, 1996) by a mean value of 2.25 mg/L while the upstream recorded mean value of 0.53 mg/L in summer. The Olifants River downstream points remained below the TWQR of the dissolved F at a mean value of 0.5 mg/L, and 0.39 mg/L recorded at the upstream. The water at both rivers was soft (<100 mg/L) with mean values ranging between 56.95 mg/L and 71.95 mg/L upstream and downstream, respectively along the Ga-Selati River, and 35.96 mg/L and 33.22 mg/L upstream and downstream at the Olifants River. The significant difference was indicated by the one-way ANOVA between the upstream and downstream values of EC at both Olifants and Ga-Selati Rivers ($p>0.05$). The concentrations of heavy metal were high at the downstream points than at the upstream points in summer at alkaline pH of water.

The pH remained alkaline with calcium indicating soft waters in spring. However, calcium concentration was higher in spring than in summer. The water in the streams was more polluted in spring during reduced river flow than in summer during increased river flow due to evapotranspiration in spring, and dilutions in summer. Fluoride in spring exceeded the TWQR of 0.75 mg/L suggested for aquatic ecosystems by the South African water quality guidelines. The concentrations of F at the downstream points were significantly higher ($p>0.05$) than upstream points along both Olifants and Ga-Selati Rivers. A notable increase in EC concentrations towards the downstream directions of both Olifants and Ga-Selati Rivers were observed in spring as in summer.

As in spring and summer, the pH of the water along both streams in winter was alkaline with Ca indicating the softness of the water through mean values ranging between 37.74 mg/L (upstream) and 50.34 mg/L (downstream) at Ga-Selati River, and 23.26 mg/L (upstream) and 63.06 mg/L (downstream) at the Olifants River. There was a notable increase in the concentration of EC at the downstream points of both streams in winter.

Thematic maps of the concentration of heavy metal revealed a potential pollution source at the Ga-Selati River. The maps showed more contaminations to be concentrated adjacent to the Sasol Nitro located within the Phalaborwa industrial complex. At the Olifants River, agricultural farms at the area of Mica are predicted to be the main sources of NO_3 along the lower Olifants River. The concentrations of heavy metals were revealed through thematic mapping that they decrease as they move further away from the pollution sources, mainly as a result of dilutions and up-taking of ions by aquatic biota as nutrients. The thematic maps showed a low concentration of heavy metals along the Olifants River in the Kruger National Park towards the Limpopo River. The rivers at the study were more polluted in winter 2019, followed by spring 2019 while summer 2020 recorded the least pollution.

The study has recorded no transgression against the NWA (Act No. 36 of 1996), MPRDA (Act No. 28 of 2002), NEMA (Act 107 of 1998) and/ NEM:WA (Act No. 59 of 2008) during the 2019/2020 seasons of the year. However, it was reported on the media that during the summer of 2013/14, the Bosveld Phosphates Pty Ltd that operates within the lower Olifants River catchment, was found guilty and sentenced in the Phalaborwa

Regional Court (PRC) for unlawfully and/ negligently releasing the contaminated mine water into the Ga-Selati River which caused significant environmental pollution along the Ga-Selati River and Olifants River. Most of the heavy metals during the 2019/2020 seasons stayed below the TWQR set by the South African water quality guidelines for aquatic ecosystems and EPA (2001). This includes the manganese which is known to be associated with acidic metalliferous discharge water and phosphate deposits from mining activities.

5.3 Conclusions

The study aimed to investigate the impacts of mine wastewater from the mining activities at Phalaborwa on water quality of the lower Olifants River and evaluate management strategies. This was achieved through: accessing the impacts of mine wastewater on water quality of the lower Olifants and Ga-Selati Rivers by determining the concentrations of the physical and chemical constituents in the water at four sampling sites; monitoring the seasonal variation of water quality of both Olifants and Ga-Selati Rivers; evaluating the existing AMD management strategies; and the effectiveness of policy and legal framework in place on the management of AMD in Phalaborwa. This was also done to provide answers to the research questions (section 1.3) of this study.

5.3.1 Impacts of mine wastewater on the water quality of Olifants and Ga-Selati River

The water quality in the Olifants River is influenced by the mining, industrial and agricultural activities that exist adjacent to this stream. Ga-Selati River is responsible for the transportations of pollutants into the lower Olifants River. Water quality at the Olifants River during the three sampling seasons was slightly polluted with high levels of turbidity, TDS, and EC. It was evident that the concentration levels of measured heavy metals observed at the downstream points of the Olifants River were generally higher than upstream. The pH at both Olifants and Ga-Selati rivers was mostly alkaline throughout the duration of the study. Based on the parameters assessed, it was evident that there was some liming taking place within the study area. This was supported by the increased concentrations of Ca, Na, Mg, and other associated alkalinity at sites 3 and 4 of the study. The concentration of these metals together with SO_4^- showed that the AMD is still a matter of concern at the lower Olifants River catchment. The assessed TDS concentrations proved that there is an existing source of salt along the Ga-Selati River. The downstream at the Olifants River recorded decreased concentrations of salt as compared to the downstream at the Ga-Selati River. The decrease of salt concentration at the downstream points of the Olifants River (after Ga-Selati/Olifants confluence) was mainly associated with the dilutions that were taking place at these points during the duration of the study.

The assessed K concentration showed that there might be a source of K along the Ga-Selati River, as the concentration of K stayed above TWQR throughout the duration of the study. The concentration of NO_3 at both Ga-Selati and Olifants Rivers were also high. The Al concentration stayed above the TWQR across all four sampling sites. Sources of Al might be existing upstream of the study area. The assessed Mn concentration showed that was a controlled discharge of metalliferous water from the mining sites during the duration of the study. The concentration of Mn stayed below the TWQR across the four sampling sites. Ga-Selati River was more polluted with the measured parameters than the Olifants River during the duration of the study. The Ga-Selati River, a tributary of the Olifants River, was therefore proven to be the carrier of pollutants. Based on investigations discussed in this study, the null hypothesis (section 1.7a) was rejected in favour of the alternative as per the analysis results showed.

5.3.2 Seasonal variation of water quality

The water quality from year to year may vary due to several other reasons such as mining activities or the amount of rain season received in summer. A decreasing trend in the concentration of heavy metal was observed from the dry- to the wet-seasons. The 2019 winter season recorded a high concentration of measured parameters with alkaline pH values. This high concentration of heavy metals in winter was associated with the solution of chemicals from the agriculture, mining and industrial complex within the lower Olifants catchment. The water quality in the spring season of 2019 was slightly polluted than in winter. The summer season of 2020 showed an improved water quality status at the study area. This improvement could be as a result of dilutions of streams by rainwater, proper management of tailing at mining sites to avoid excessive overflows and applied erosion control measures at the agricultural fields. Moreover, the GIS modelling results revealed an improved state of the water quality along the Olifants River at the Kruger National Park towards Limpopo River. The state of the water quality improved as the river flows further from the pollution sources (industrial, mining and agricultural areas).

5.3.3 AMD management strategies and compliance with legal framework

The acidic mine wastewater is counteracted by the use of open limestone drains to introduce alkalinity treatment into the wastewater. The monitoring of the pollution rate at the lower Olifants catchment by the mining houses plays a critical role in the determination of the effectiveness of the applied management strategies. The mining activities were found to have been contributing 5 % of the pollution of streams at the Ga-Selati River. The operation of the mining activities in the study area was evaluated to be, overall, in compliance with the regulatory framework and AMD management strategies applied fairly well. This conclusion also rejects the null hypothesis stipulated in section 1.7b in favour of the alternative.

5.4 Recommendations

The results obtained in the study, provide insight into the understanding of the current AMD status and its impact on the water quality of the lower Olifants River. The study has shown that the land-use activities within the lower Olifants catchment do affect the quality of the water of both Olifants and Ga-Selati Rivers. Further investigations would be required to determine the following:

- The source of aluminium within the lower Olifants catchment as the study recorded levels that are of concern at upstream and downstream sampling points along both Olifants and Ga-Selati Rives. The persistence of aluminium and other heavy metals may harm the aquatic ecosystem.
- The source of potassium along the Ga-Selati River as the downstream sampling points recorded elevated concentrations of the potassium. Potassium is associated with the production or use of fertilizers and could not be as a result of

the mining operations at the lower Olifants River. It is, therefore recommended that the actual source of this be investigated since the presence of potassium may harm the aquatic ecosystem.

- In addition to the water quality monitoring done by mining houses on a monthly basis, it would be important to have an investigative study on the large Ga-Selati River catchment to get a proper understanding of the state of water quality along this river and the land-use impact that could be influencing the water quality at Ga-Selati River. The results of these studies could be compared to the already available studies on the entire lower Olifants catchment to get an overview of the influence of seasons on the water quality of these streams.
- Given the seriousness and scale of AMD it remains vital to keep on work towards effective and affordable treatment options.

Overall, the findings of this work provide new insight into the status and impact of mine wastewater at the lower Olifants catchment. The study is a contribution to work on monitoring of the impact of mine wastewater whose findings can be key in decision-making and policy development, and development of remedial measures.

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APPENDIX 1

CORRELATION

a) Summer correlation.

Variables	pH	Electrical Conductivity	Total dissolved solids	Turbidity	Colour	Total Hardness	Fluoride as F	Chloride as Cl	Nitrate as NO3	Sulphate as SO4	Potassium as K	Calcium as Ca	Magnesium as Mg	Sodium as Na	Manganese as Mn	Vanadium as V
pH	**1**															
Electrical Conductivity	0,690	**1**														
Total dissolved solids	0,690	1,000	**1**													
Turbidity	0,093	-0,329	-0,329	**1**												
Colour	0,135	-0,221	-0,221	0,978	**1**											
Total Hardness	0,777	0,949	0,949	-0,097	-0,002	**1**										
Fluoride as F	0,585	0,710	0,710	0,358	0,435	0,825	**1**									
Chloride as Cl	0,575	0,968	0,968	-0,479	-0,367	0,842	0,575	**1**								
Nitrate as NO3	0,019	0,490	0,490	-0,746	-0,672	0,190	-0,067	0,690	**1**							
Sulphate as SO4	0,797	0,752	0,752	0,214	0,274	0,921	0,854	0,567	-0,201	**1**						
Potassium as K	0,802	0,822	0,822	0,133	0,204	0,959	0,864	0,657	-0,091	0,994	**1**					
Calcium as Ca	0,667	0,994	0,994	-0,354	-0,242	0,952	0,684	0,955	0,460	0,762	0,829	**1**				
Magnesium as Mg	0,791	0,927	0,927	-0,041	0,049	0,998	0,844	0,807	0,130	0,944	0,975	0,930	**1**			
Sodium as Na	0,517	0,942	0,942	-0,533	-0,421	0,788	0,514	0,995	0,753	0,489	0,584	0,927	0,749	**1**		
Manganese as Mn	-0,100	0,386	0,386	-0,814	-0,743	0,084	-0,185	0,598	0,970	-0,304	-0,197	0,368	0,023	0,667	**1**	
Vanadium as V	0,792	0,927	0,927	-0,041	0,047	0,998	0,843	0,807	0,131	0,944	0,975	0,930	1,000	0,749	0,022	**1**

b) Spring correlation.

Variables	pH	Electrical Conductivity	Total dissolved solids	Turbidity	Colour	Total Hardness	Fluoride as F	Chloride as Cl	Nitrate as NO3	Sulphate as SO4	Potassium as K	Calcium as Ca	Magnesium as Mg	Sodium as Na	Manganese as Mn	Vanadium as V
pH	**1**															
Electrical Conductivity	0,688	**1**														
Total dissolved solids	0,688	1,000	**1**													
Turbidity	-0,255	-0,631	-0,631	**1**												
Colour	-0,263	-0,610	-0,610	0,996	**1**											
Total Hardness	0,676	0,980	0,980	-0,521	-0,498	**1**										
Fluoride as F	0,650	0,949	0,949	-0,422	-0,394	0,989	**1**									
Chloride as Cl	0,682	0,988	0,988	-0,695	-0,679	0,954	0,904	**1**								
Nitrate as NO3	0,686	0,995	0,995	-0,656	-0,638	0,975	0,935	0,995	**1**							
Sulphate as SO4	0,642	0,935	0,935	-0,393	-0,369	0,984	0,997	0,888	0,923	**1**						
Potassium as K	0,647	0,942	0,942	-0,412	-0,383	0,986	0,999	0,897	0,928	0,996	**1**					
Calcium as Ca	0,685	0,991	0,991	-0,658	-0,645	0,973	0,929	0,995	0,997	0,919	0,923	**1**				
Magnesium as Mg	0,668	0,969	0,969	-0,481	-0,457	0,998	0,996	0,936	0,961	0,992	0,994	0,958	**1**			
Sodium as Na	0,666	0,963	0,963	-0,755	-0,741	0,907	0,841	0,991	0,974	0,819	0,834	0,975	0,882	**1**		
Manganese as Mn	0,197	0,265	0,265	-0,705	-0,737	0,125	-0,019	0,385	0,319	-0,035	-0,033	0,341	0,070	0,489	**1**	
Vanadium as V	0,676	0,969	0,969	-0,469	-0,444	0,996	0,997	0,931	0,957	0,993	0,994	0,953	0,999	0,875	0,052	**1**

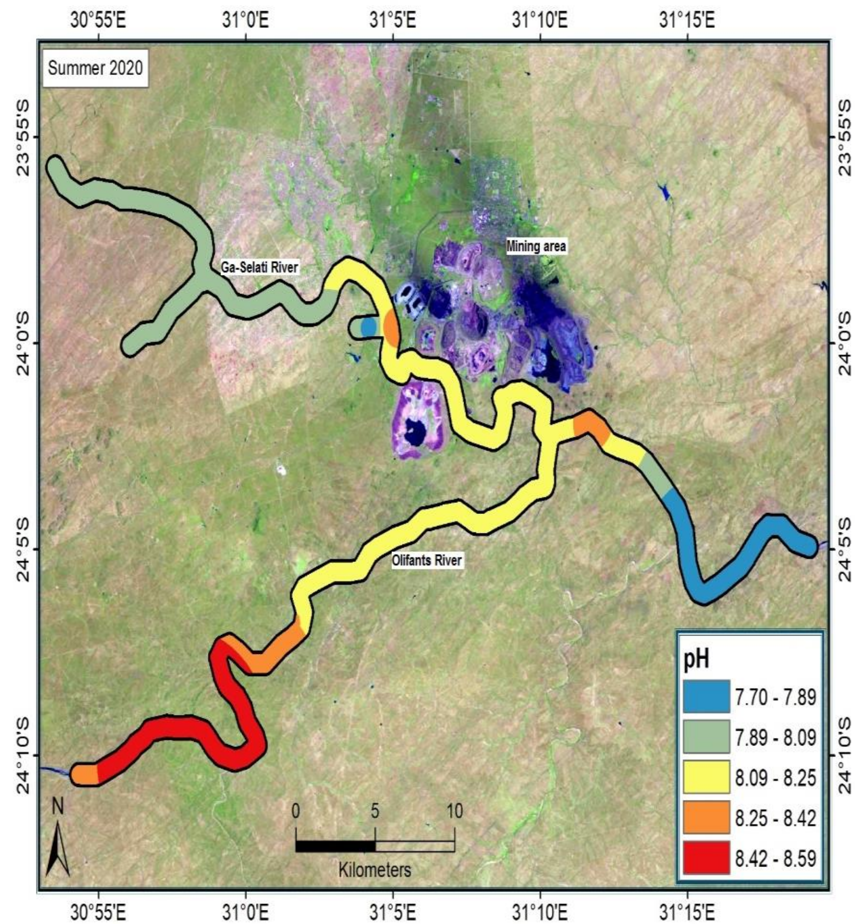
c) Winter correlation.

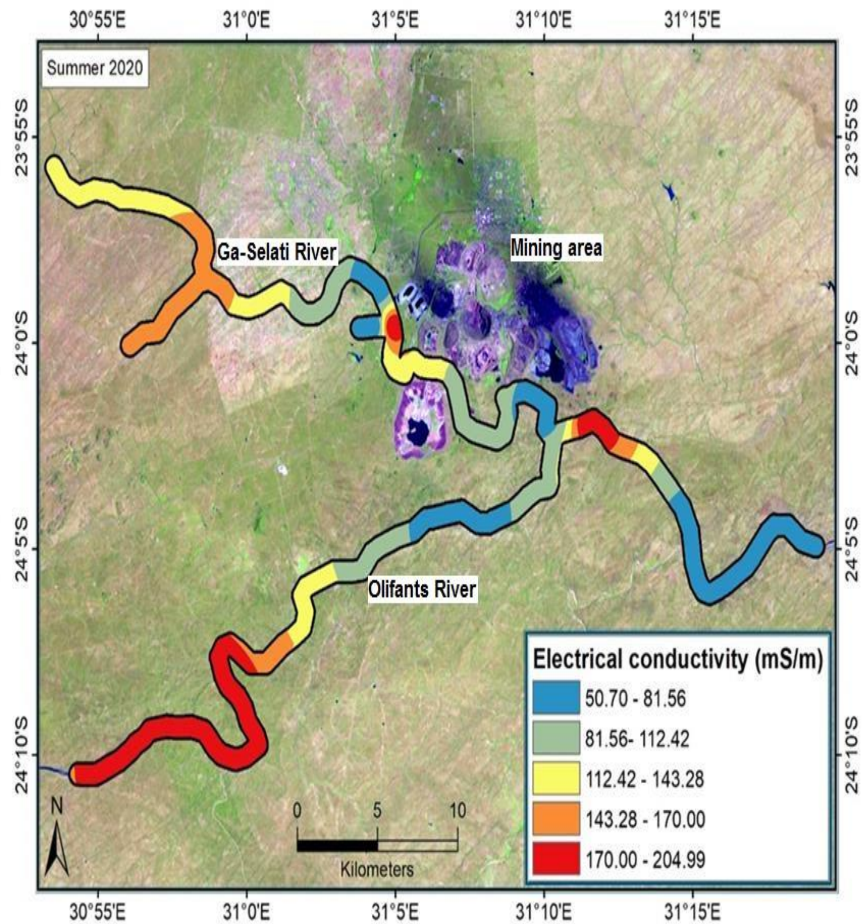
Variables	pH	Electrical Conductivity	Turbidity	Sulphate as SO4	Potassium as K	Calcium as Ca	Magnesium as Mg	Sodium as Na	Manganese as Mn	Vanadium as V	Aluminium as Al
pH	**1**										
Electrical Conductivity	0,699	**1**									
Turbidity	0,784	0,640	**1**								
Sulphate as SO4	0,725	0,955	0,658	**1**							
Potassium as K	0,843	0,887	0,907	0,909	**1**						
Calcium as Ca	0,388	0,873	0,196	0,808	0,565	**1**					
Magnesium as Mg	0,558	0,955	0,448	0,954	0,772	0,942	**1**				
Sodium as Na	0,649	0,984	0,597	0,889	0,835	0,879	0,919	**1**			
Manganese as Mn	-0,339	0,093	-0,483	-0,072	-0,279	0,379	0,172	0,198	**1**		
Vanadium as V	0,570	0,949	0,449	0,960	0,775	0,929	0,998	0,905	0,164	**1**	
Aluminium as Al	0,440	0,172	0,335	0,072	0,272	-0,055	-0,031	0,212	-0,078	-0,029	**1**

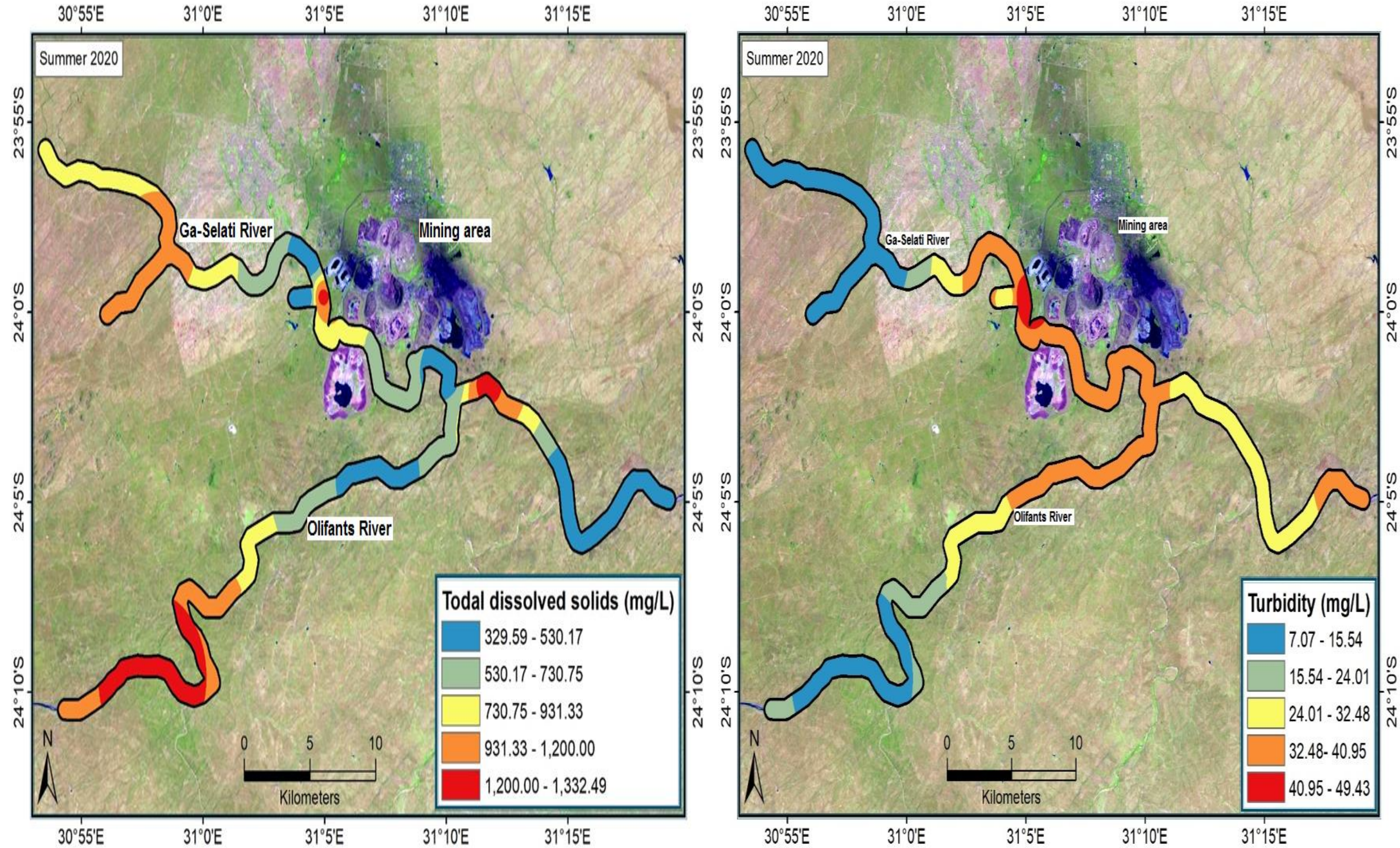
APPENDIX 2

THEMATIC MAP LAYERS

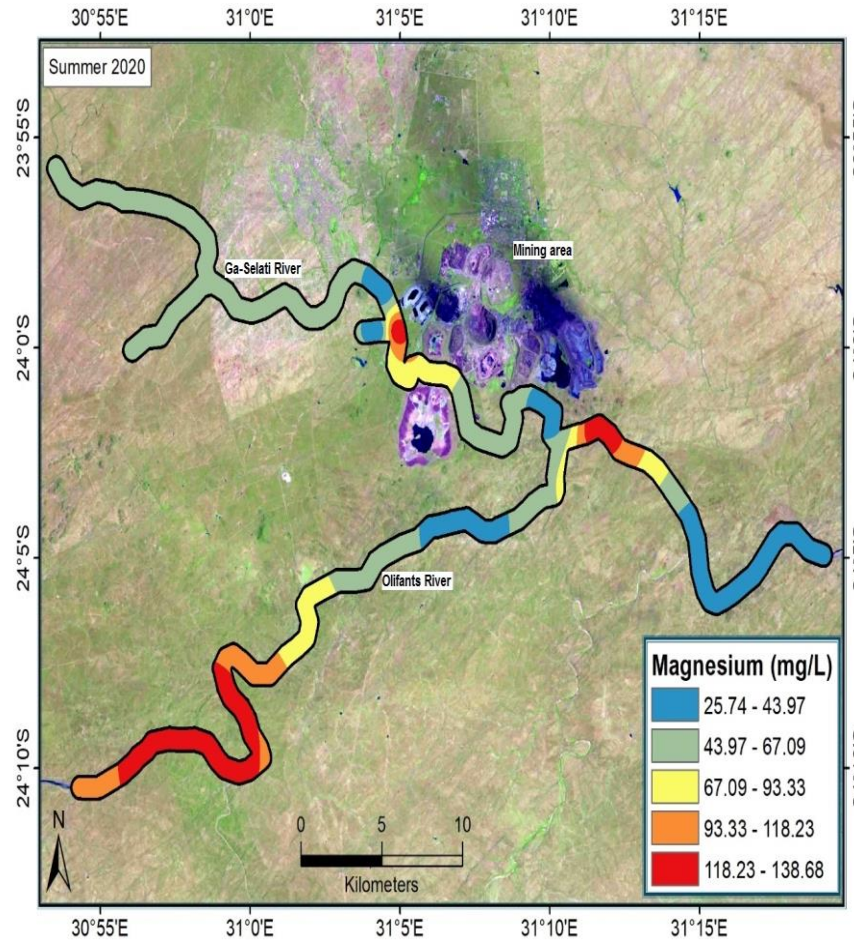
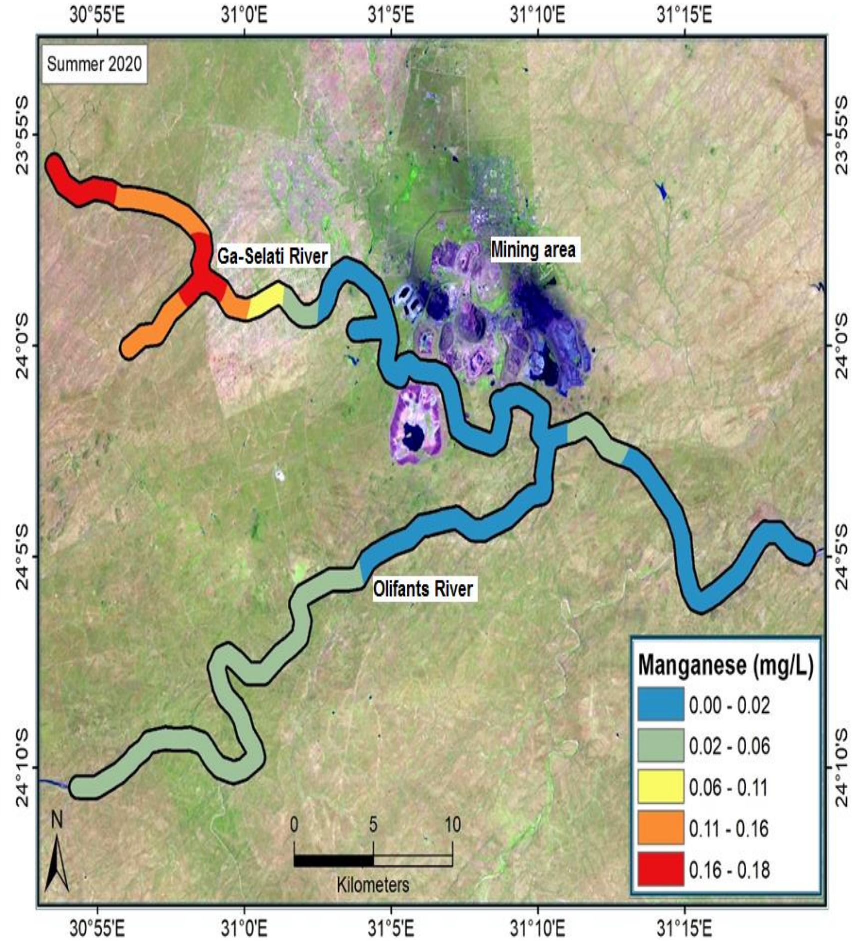
a. Summer thematic maps.

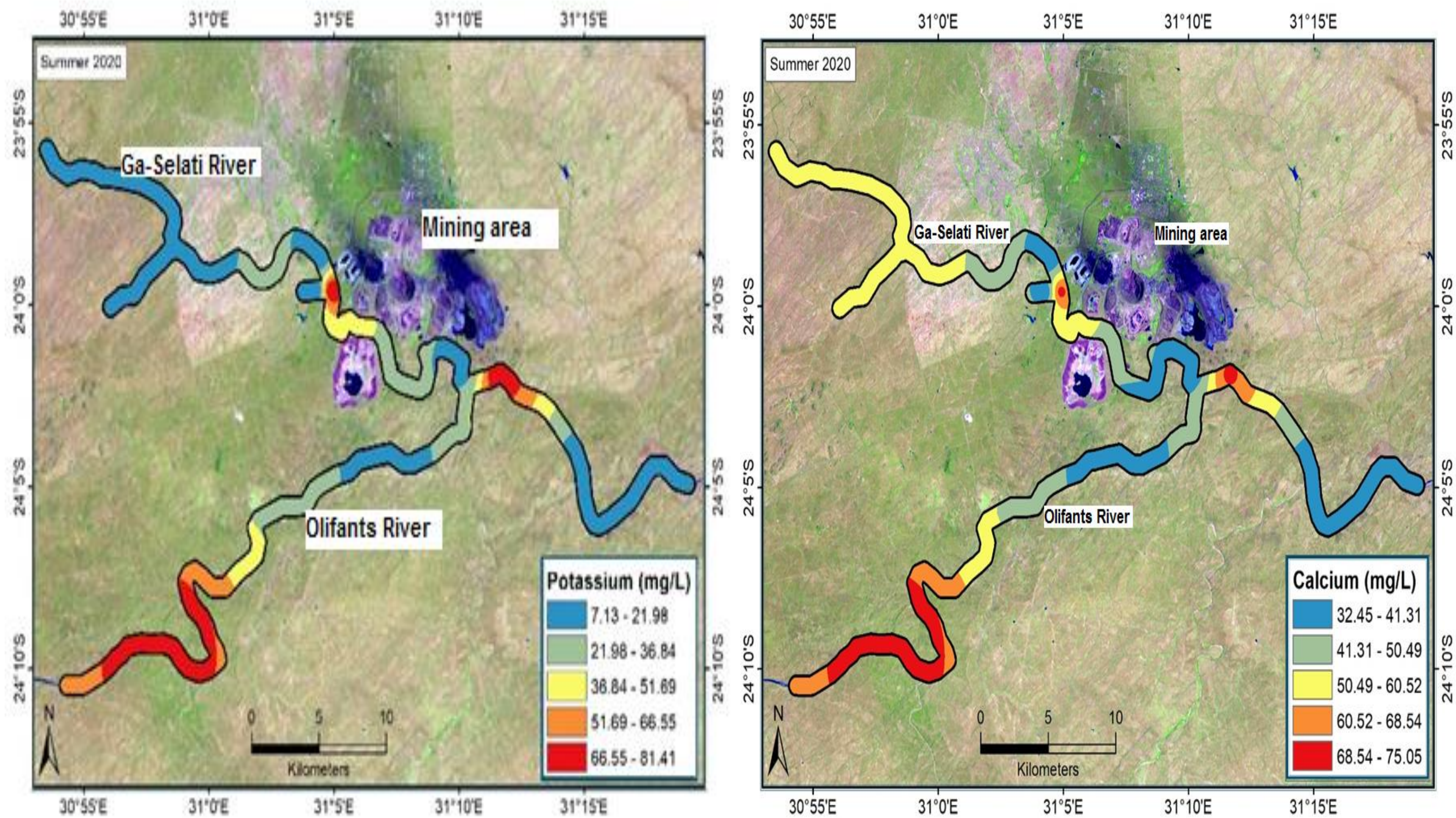




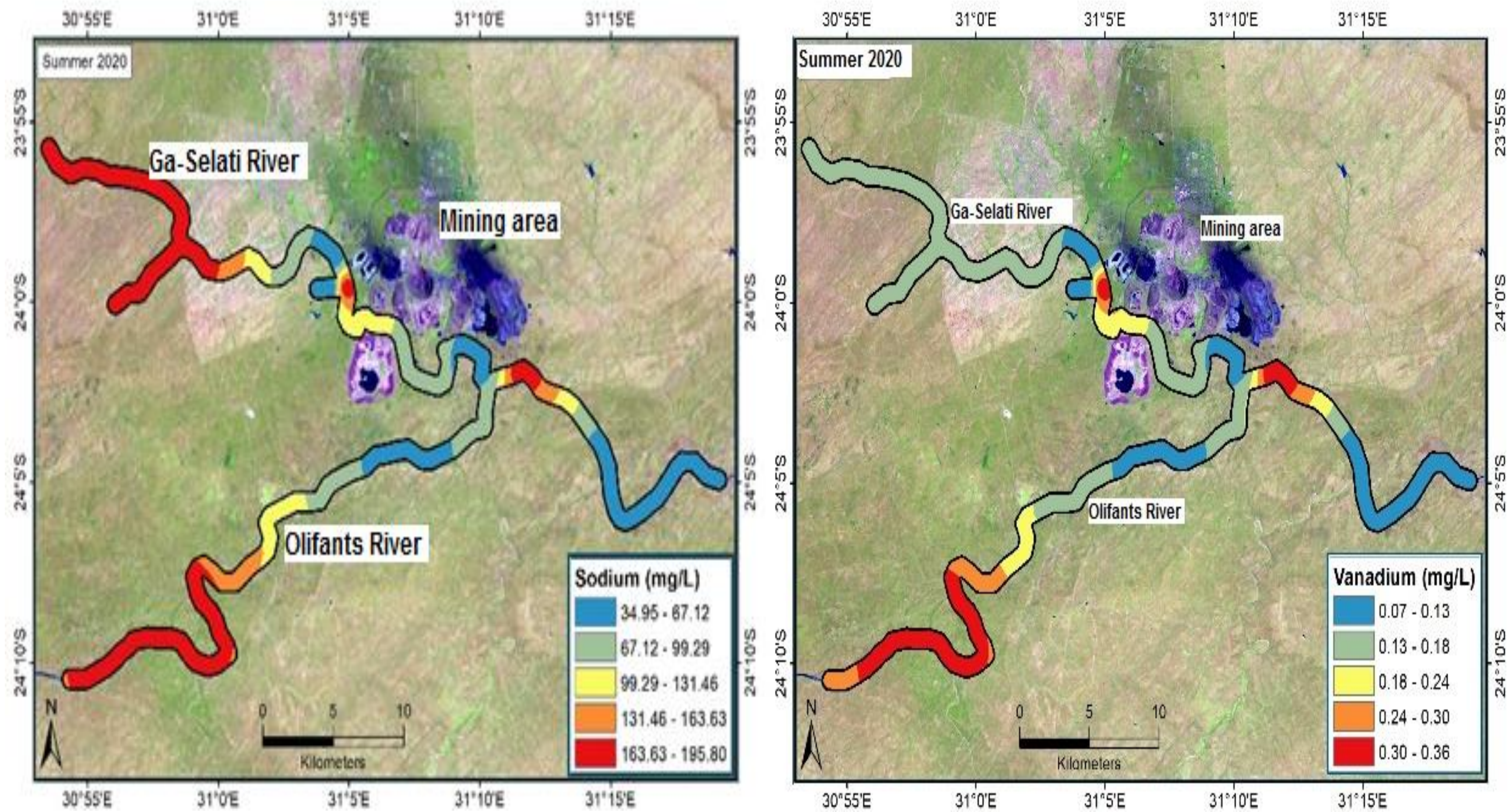


Summer 2020
Ga-Selati River
Mining area
Olifants River
Todal dissolved solids (mg/L)
329.59 - 530.17
530.17 - 730.75
730.75 - 931.33
931.33 - 1,200.00
1,200.00 - 1,332.49
Kilometers
Summer 2020
Ga-Selati River
Mining area
Olifants River
Turbidity (mg/L)
7.07 - 15.54
15.54 - 24.01
24.01 - 32.48
32.48- 40.95
40.95 - 49.43
Kilometers

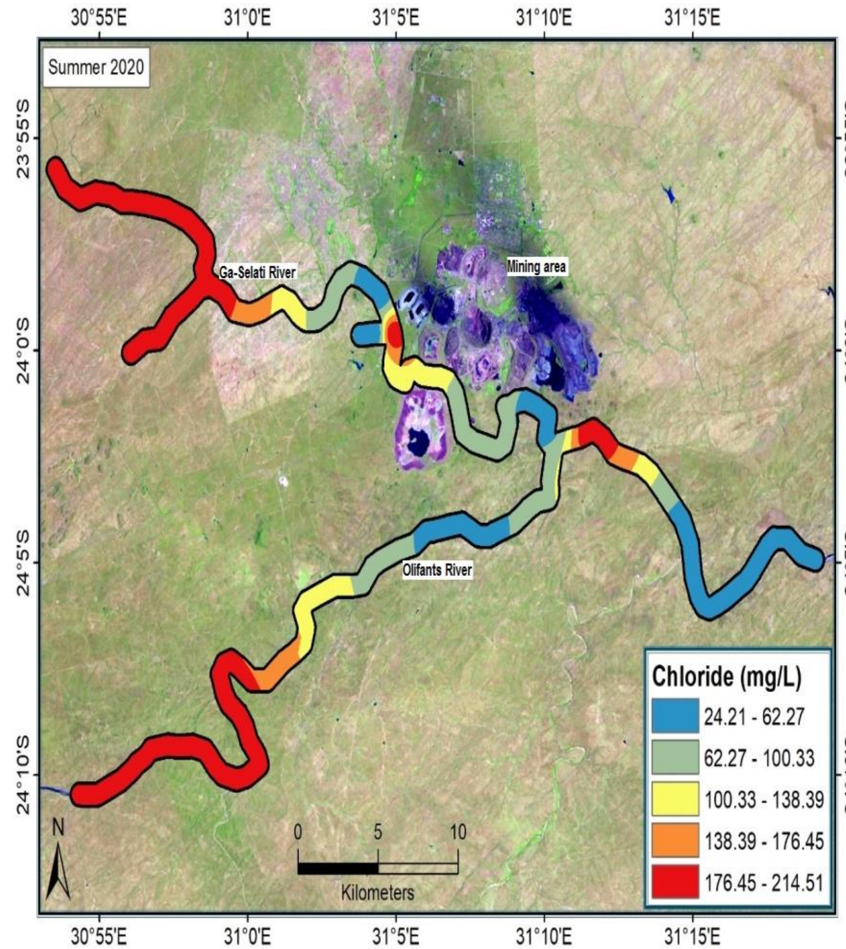

30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
Summer 2020
23°55'S
24°0'S
24°5'S
24°10'S
Ga-Selati River
Mining area
Olifants River
Magnesium (mg/L)
25.74 - 43.97
43.97 - 67.09
67.09 - 93.33
93.33 - 118.23
118.23 - 138.68
N
0
5
10
Kilometers

30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
Summer 2020
23°55'S
24°0'S
24°5'S
24°10'S
Ga-Selati River
Mining area
Olifants River
Manganese (mg/L)
0.00 - 0.02
0.02 - 0.06
0.06 - 0.11
0.11 - 0.16
0.16 - 0.18
N
0
5
10
Kilometers

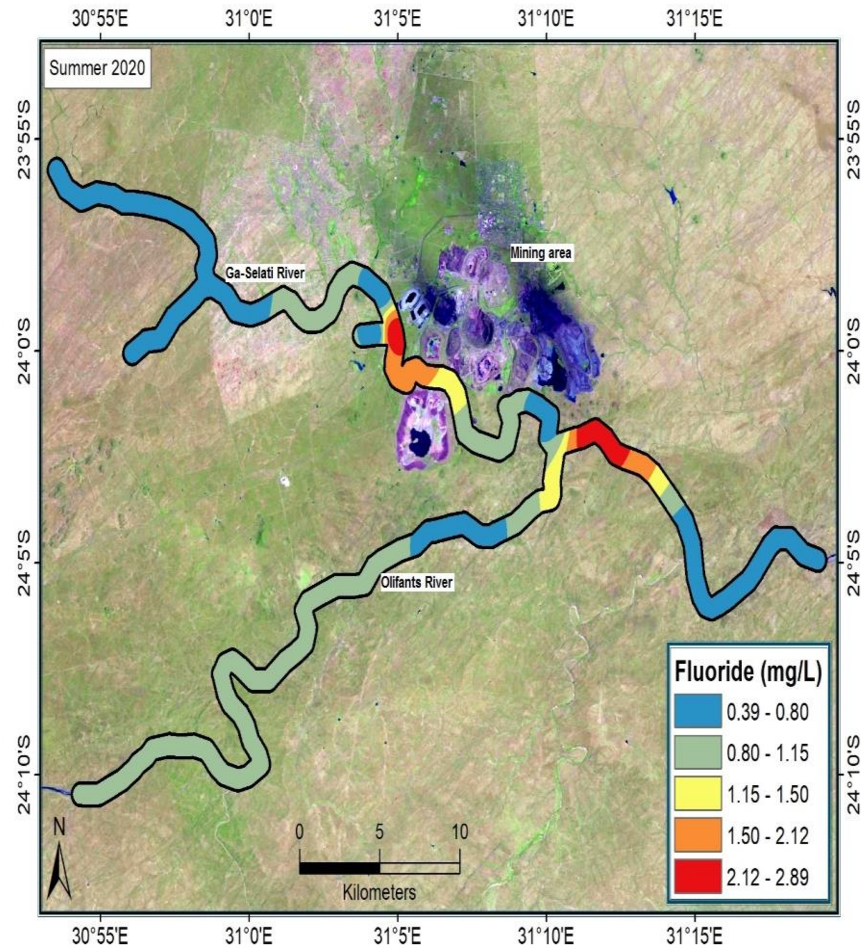


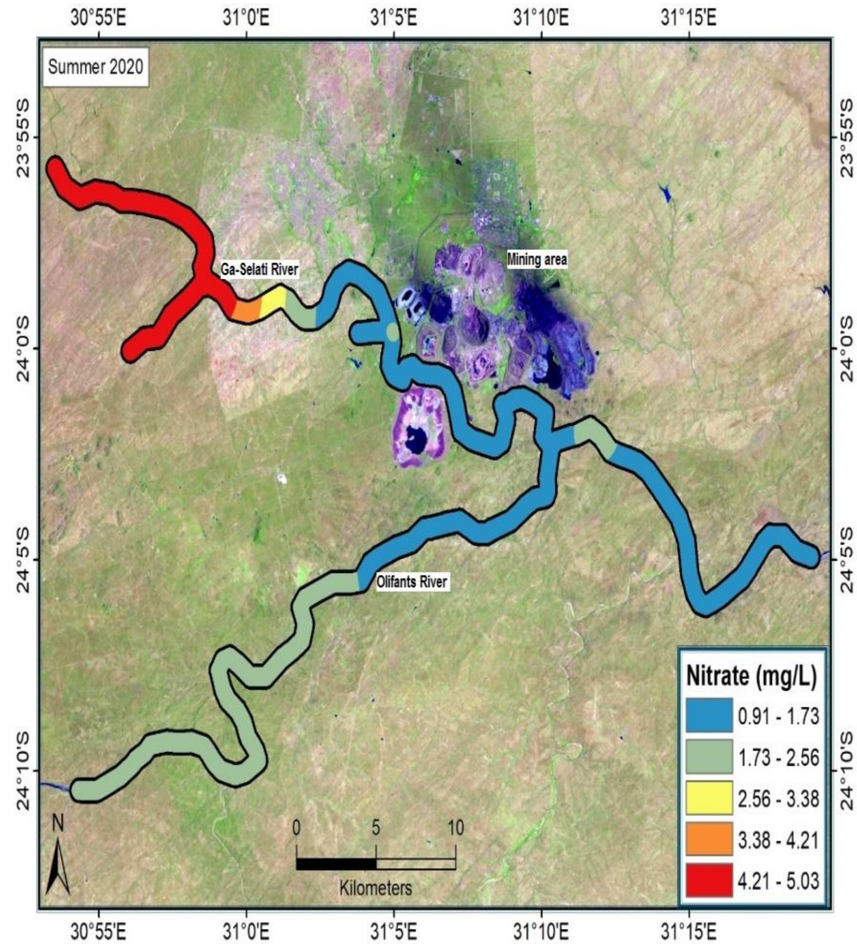
Summer 2020
Ga-Selati River
Mining area
Olifants River
Potassium (mg/L)
7.13 - 21.98
21.98 - 36.84
36.84 - 51.69
51.69 - 66.55
66.55 - 81.41
Kilometers
Summer 2020
Ga-Selati River
Mining area
Olifants River
Calcium (mg/L)
32.45 - 41.31
41.31 - 50.49
50.49 - 60.52
60.52 - 68.54
68.54 - 75.05
Kilometers



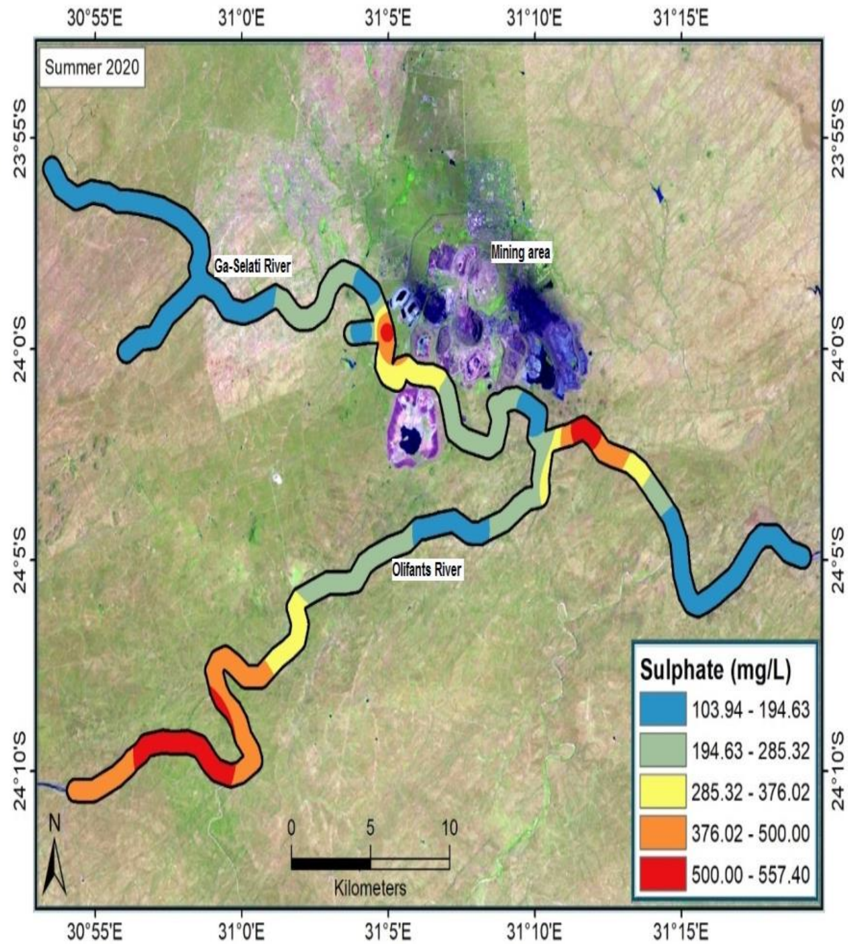
Summer 2020
Ga-Selati River
Mining area
Olifants River
Sodium (mg/L)
34.95 - 67.12
67.12 - 99.29
99.29 - 131.46
131.46 - 163.63
163.63 - 195.80
Kilometers
0 5 10
Summer 2020
Ga-Selati River
Mining area
Olifants River
Vanadium (mg/L)
0.07 - 0.13
0.13 - 0.18
0.18 - 0.24
0.24 - 0.30
0.30 - 0.36
30°55'E 31°0'E 31°5'E 31°10'E 31°15'E
23°55'S 24°0'S 24°5'S 24°10'S


Summer 2020
Ga-Selati River
Mining area
Olifants River
Chloride (mg/L)
24.21 - 62.27
62.27 - 100.33
100.33 - 138.39
138.39 - 176.45
176.45 - 214.51
N
0 5 10
Kilometers
30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S


Summer 2020
Ga-Selati River
Mining area
Olifants River
Fluoride (mg/L)
0.39 - 0.80
0.80 - 1.15
1.15 - 1.50
1.50 - 2.12
2.12 - 2.89
N
0 5 10
Kilometers
30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S

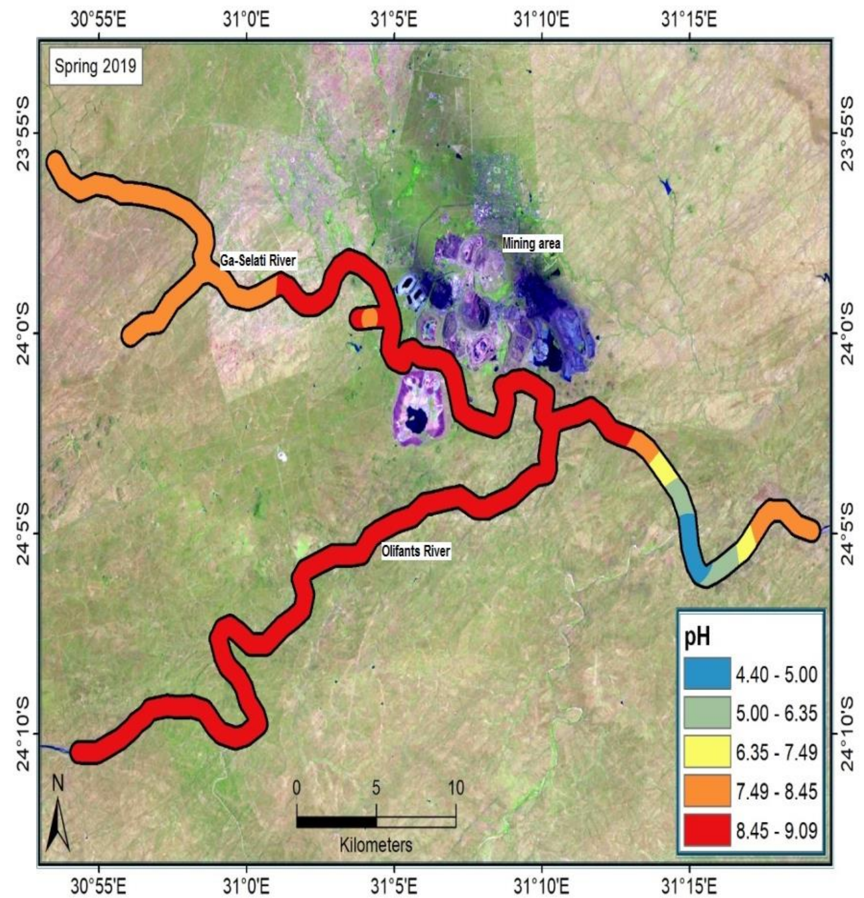


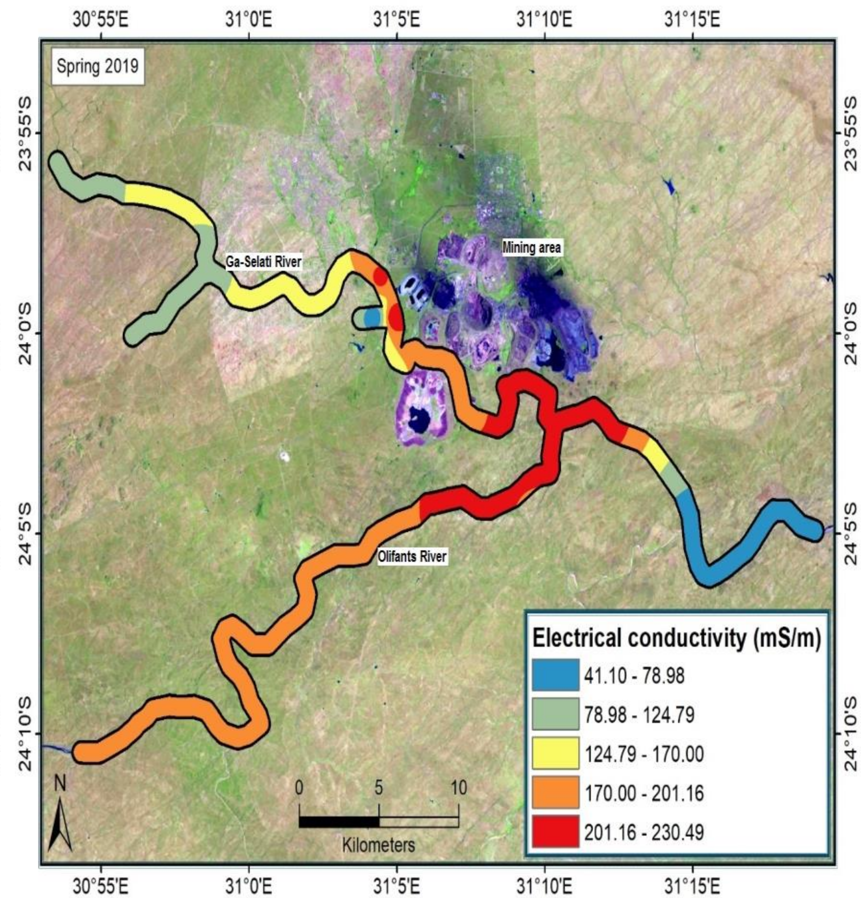
Summer 2020
Ga-Selati River
Mining area
Olifants River
Nitrate (mg/L)
0.91 - 1.73
1.73 - 2.56
2.56 - 3.38
3.38 - 4.21
4.21 - 5.03
Kilometers

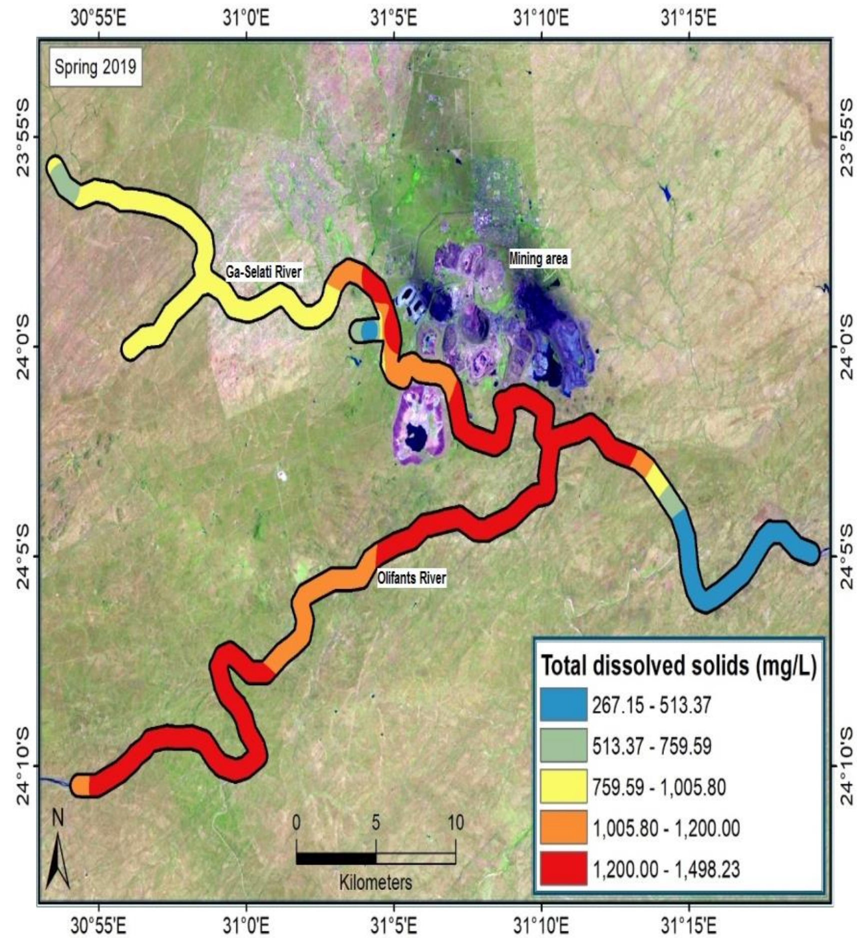


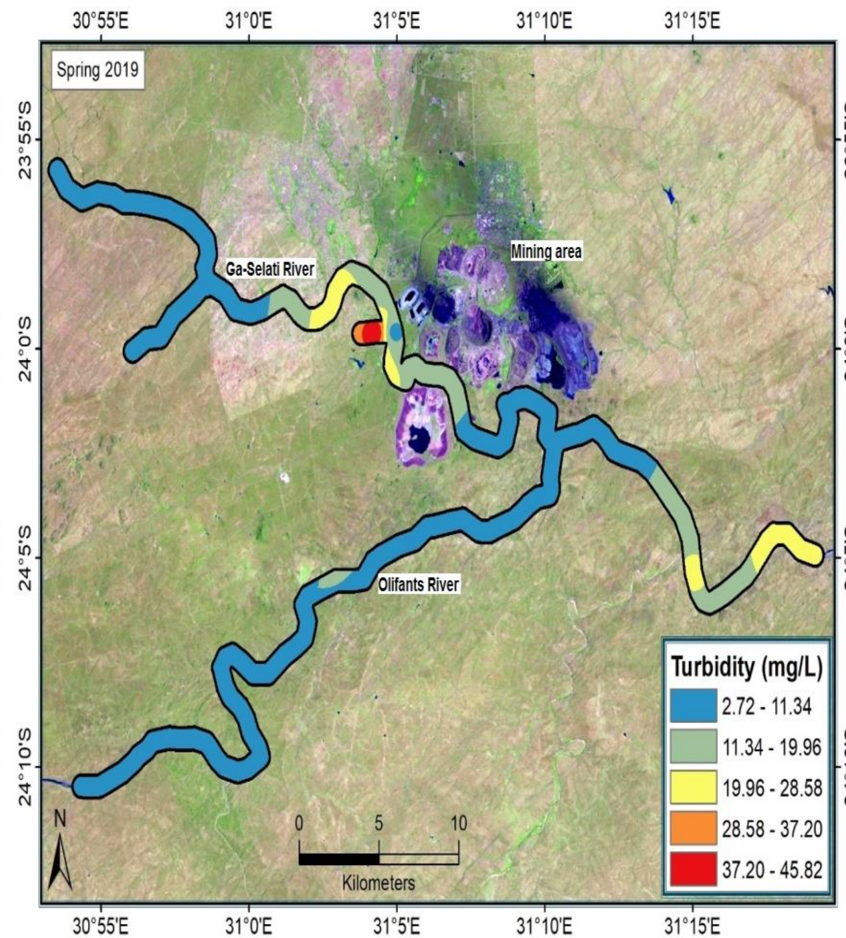
Summer 2020
Ga-Selati River
Mining area
Olifants River
Sulphate (mg/L)
103.94 - 194.63
194.63 - 285.32
285.32 - 376.02
376.02 - 500.00
500.00 - 557.40
Kilometers

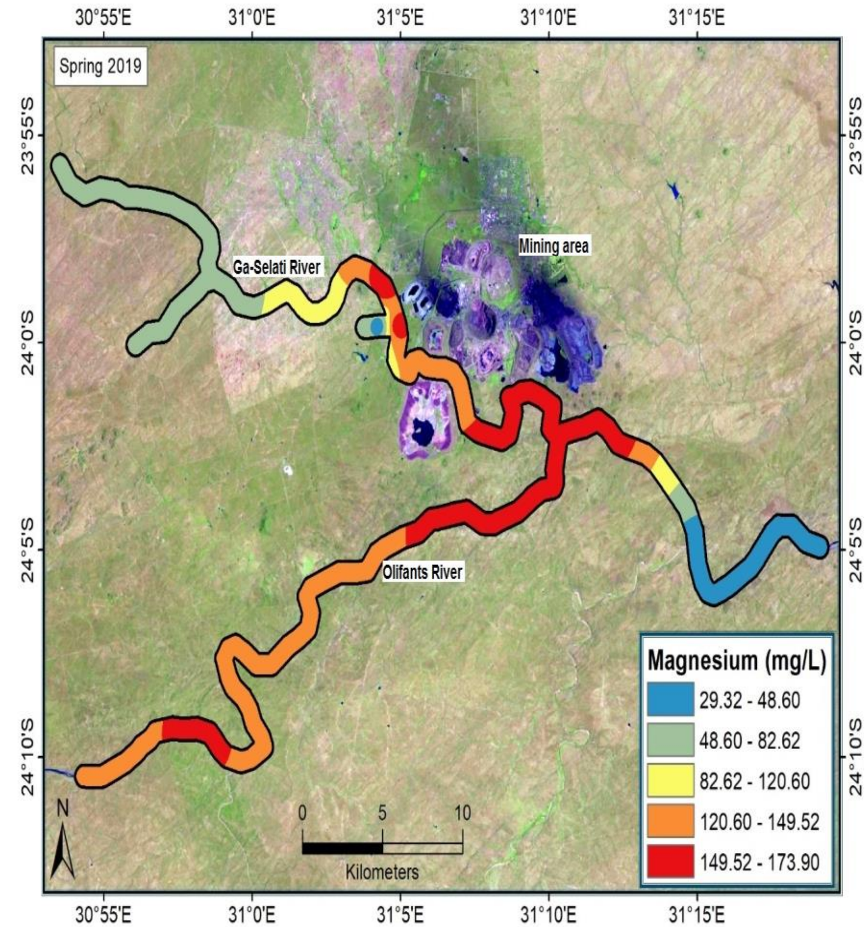
b. Spring thematic maps.

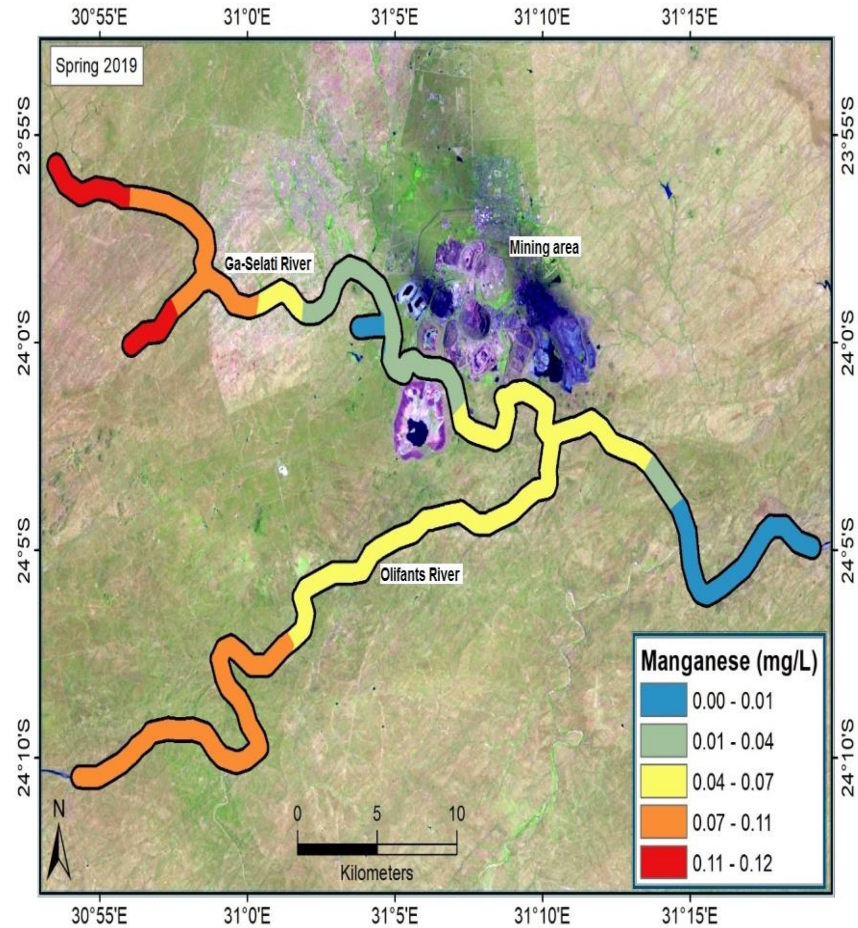


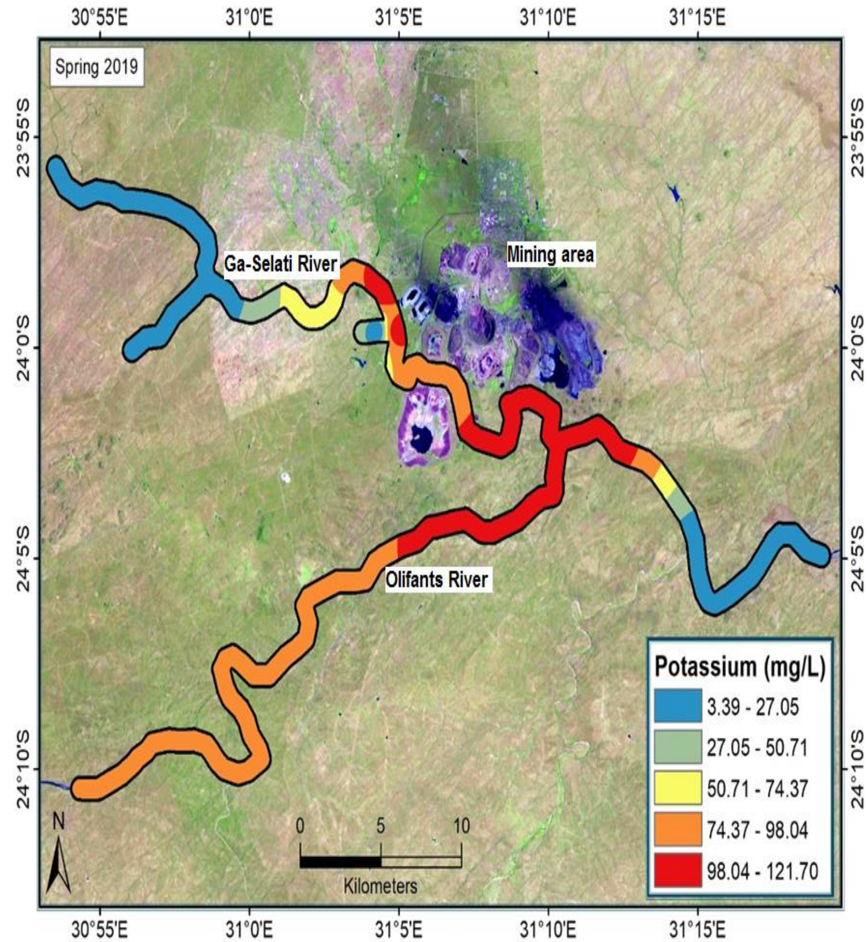



Spring 2019
Ga-Selati River
Mining area
Olifants River
Total dissolved solids (mg/L)
267.15 - 513.37
513.37 - 759.59
759.59 - 1,005.80
1,005.80 - 1,200.00
1,200.00 - 1,498.23
Kilometers
0
5
10
N
30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S

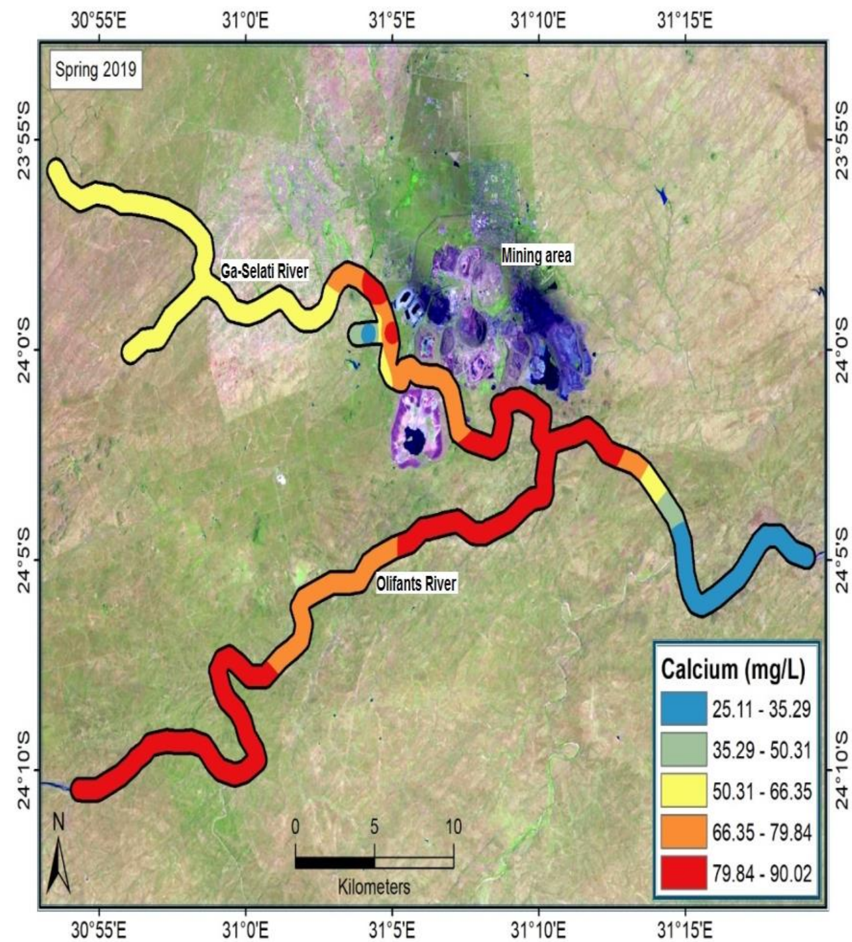

Spring 2019
Ga-Selati River
Mining area
Olifants River
Turbidity (mg/L)
2.72 - 11.34
11.34 - 19.96
19.96 - 28.58
28.58 - 37.20
37.20 - 45.82
Kilometers
0
5
10
N
30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S


Spring 2019
Ga-Selati River
Mining area
Olifants River
Magnesium (mg/L)
29.32 - 48.60
48.60 - 82.62
82.62 - 120.60
120.60 - 149.52
149.52 - 173.90
Kilometers
0
5
10
N
30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S

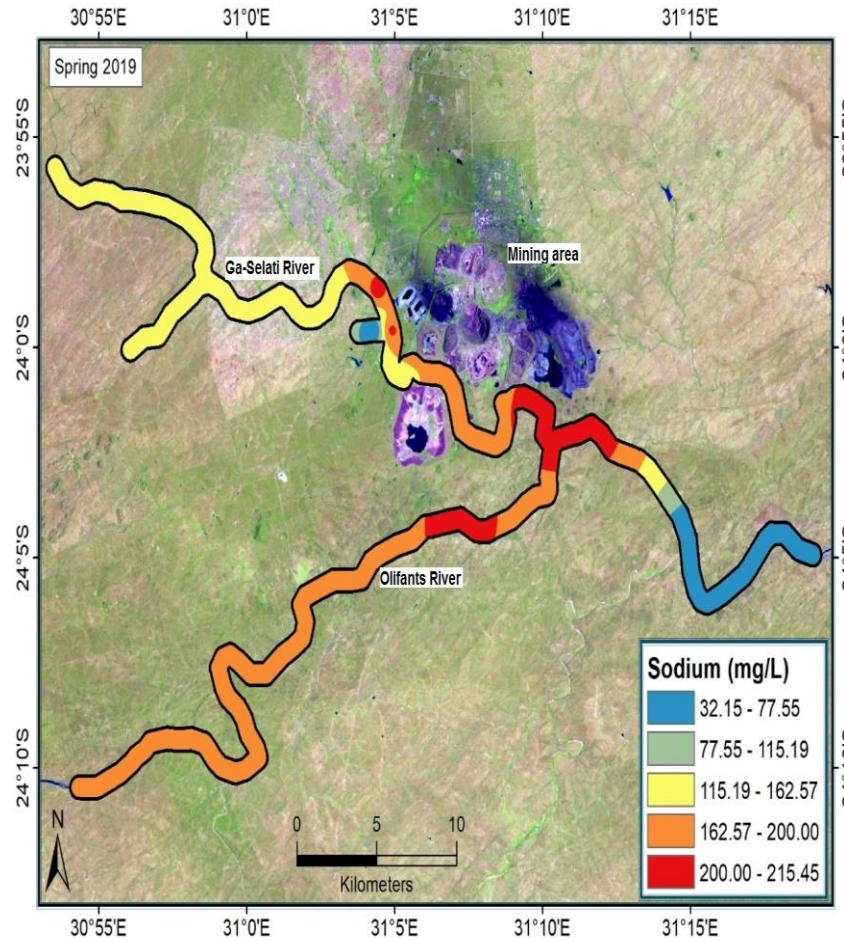

Spring 2019
Ga-Selati River
Mining area
Olifants River
Manganese (mg/L)
0.00 - 0.01
0.01 - 0.04
0.04 - 0.07
0.07 - 0.11
0.11 - 0.12
Kilometers
0
5
10
N
30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S

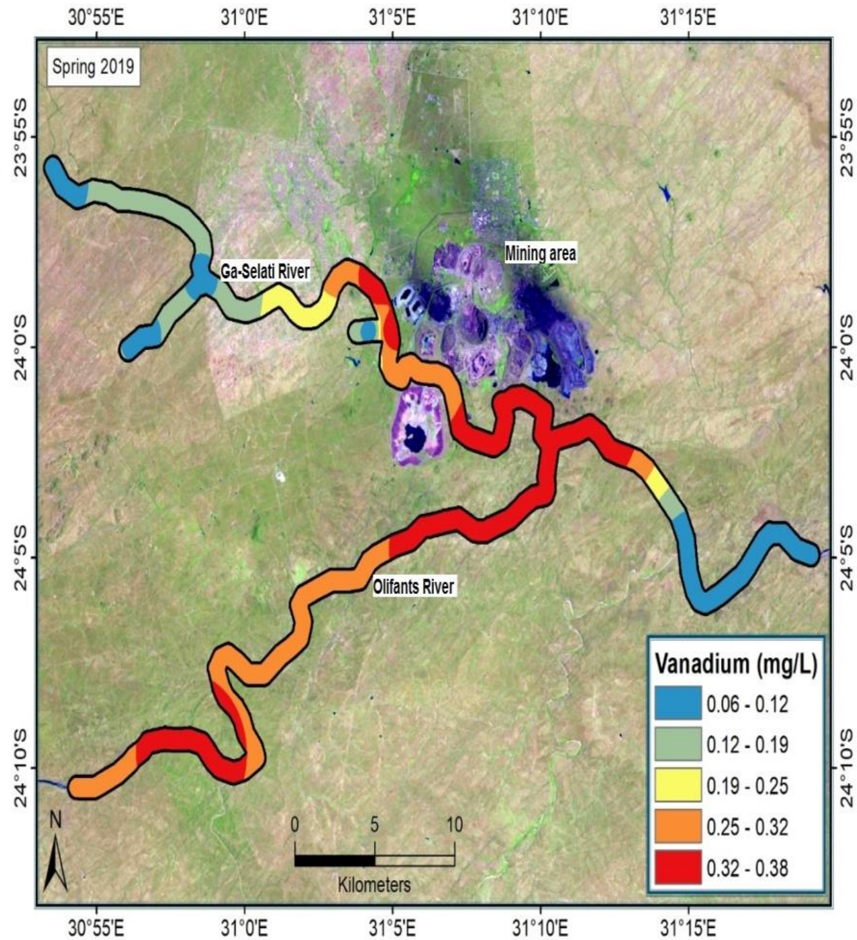


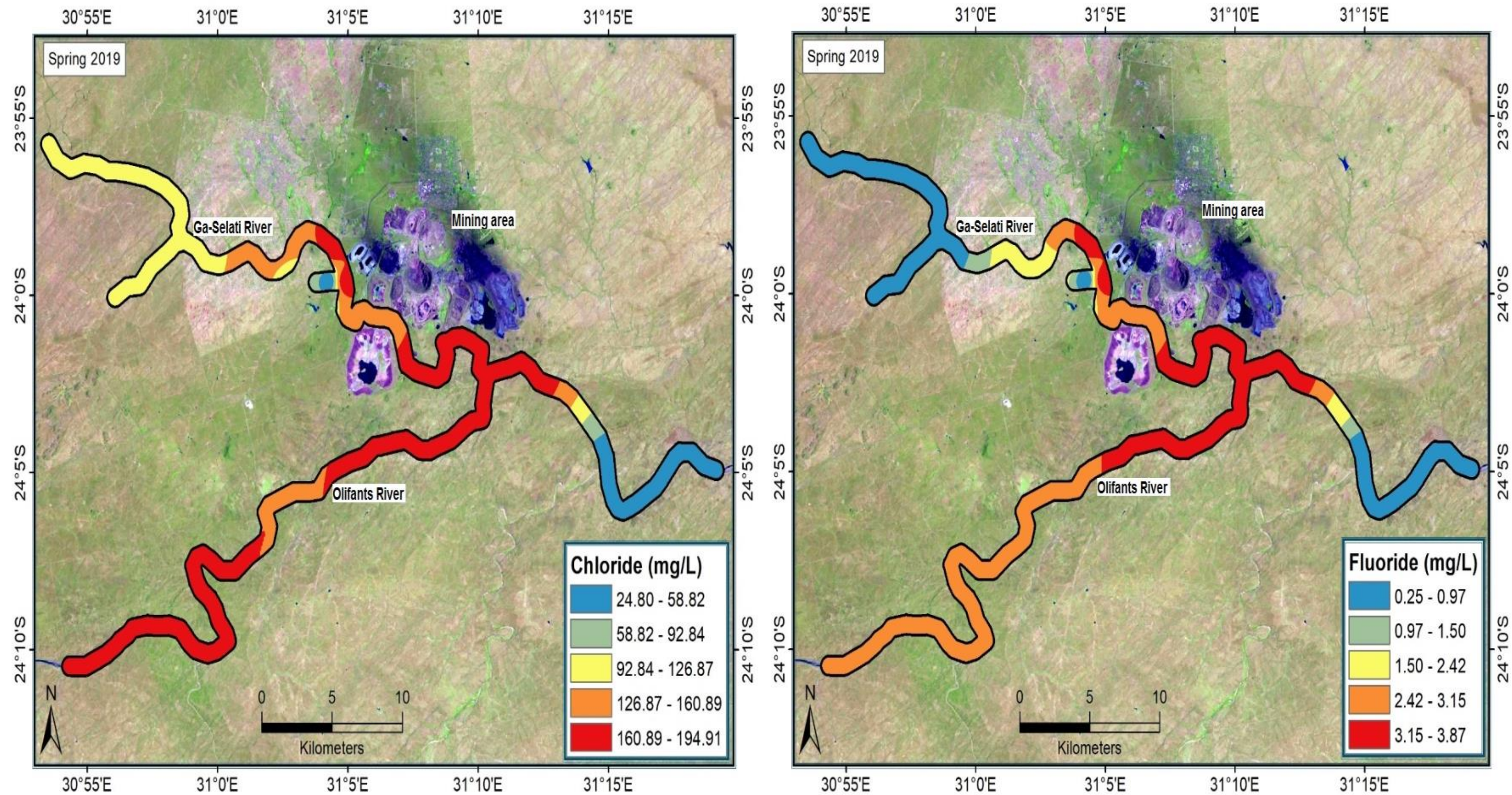
Spring 2019
Ga-Selati River
Mining area
Olifants River
Potassium (mg/L)
3.39 - 27.05
27.05 - 50.71
50.71 - 74.37
74.37 - 98.04
98.04 - 121.70
0 5 10
Kilometers
N
30°55'E 31°0'E 31°5'E 31°10'E 31°15'E
23°55'S 24°0'S 24°5'S 24°10'S

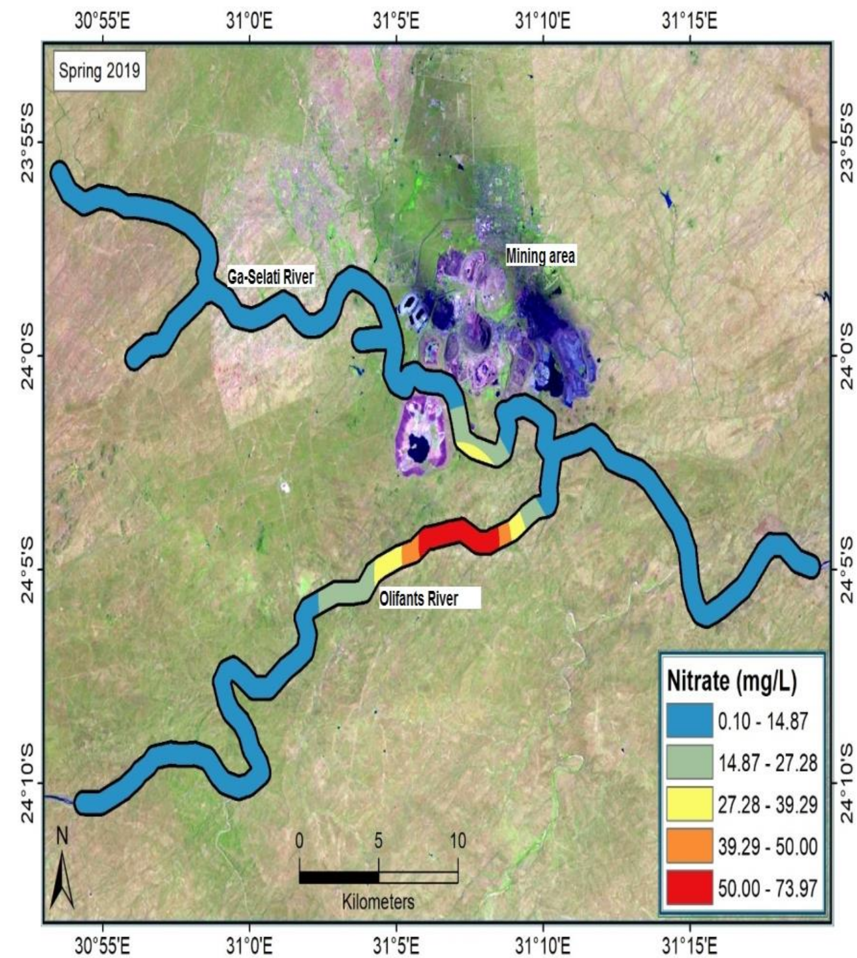


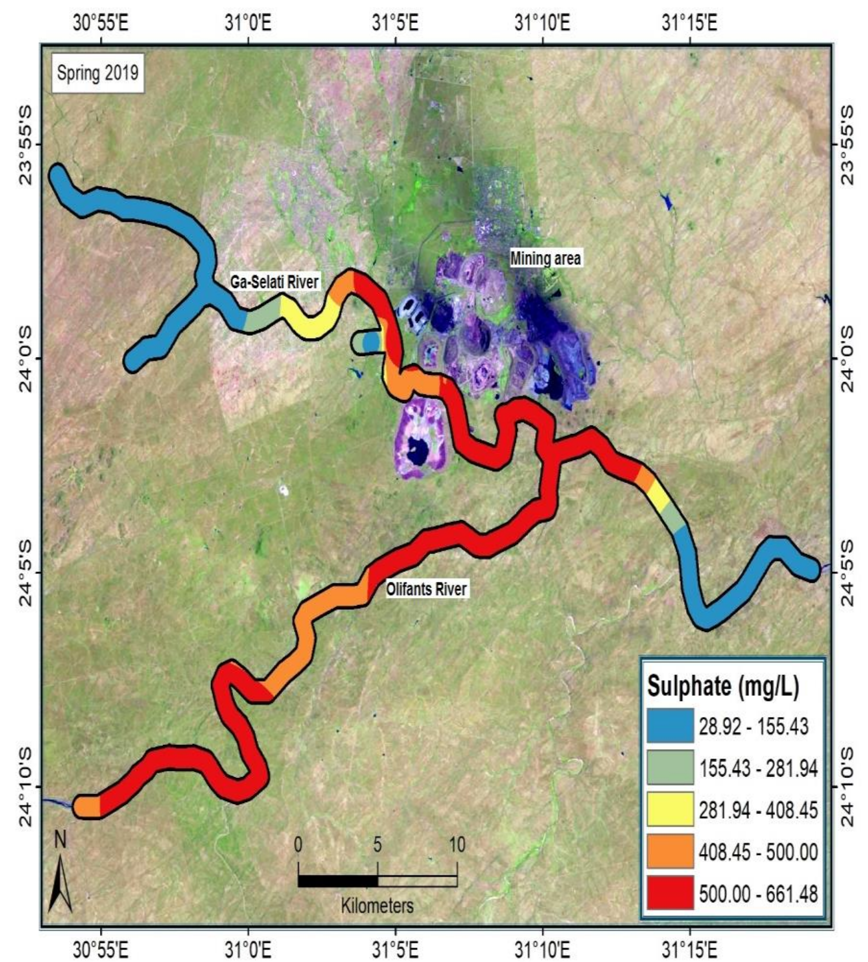
Spring 2019
Ga-Selati River
Mining area
Olifants River
Calcium (mg/L)
25.11 - 35.29
35.29 - 50.31
50.31 - 66.35
66.35 - 79.84
79.84 - 90.02
0 5 10
Kilometers
N
30°55'E 31°0'E 31°5'E 31°10'E 31°15'E
23°55'S 24°0'S 24°5'S 24°10'S


Spring 2019
Ga-Selati River
Mining area
Olifants River
Sodium (mg/L)
32.15 - 77.55
77.55 - 115.19
115.19 - 162.57
162.57 - 200.00
200.00 - 215.45
Kilometers

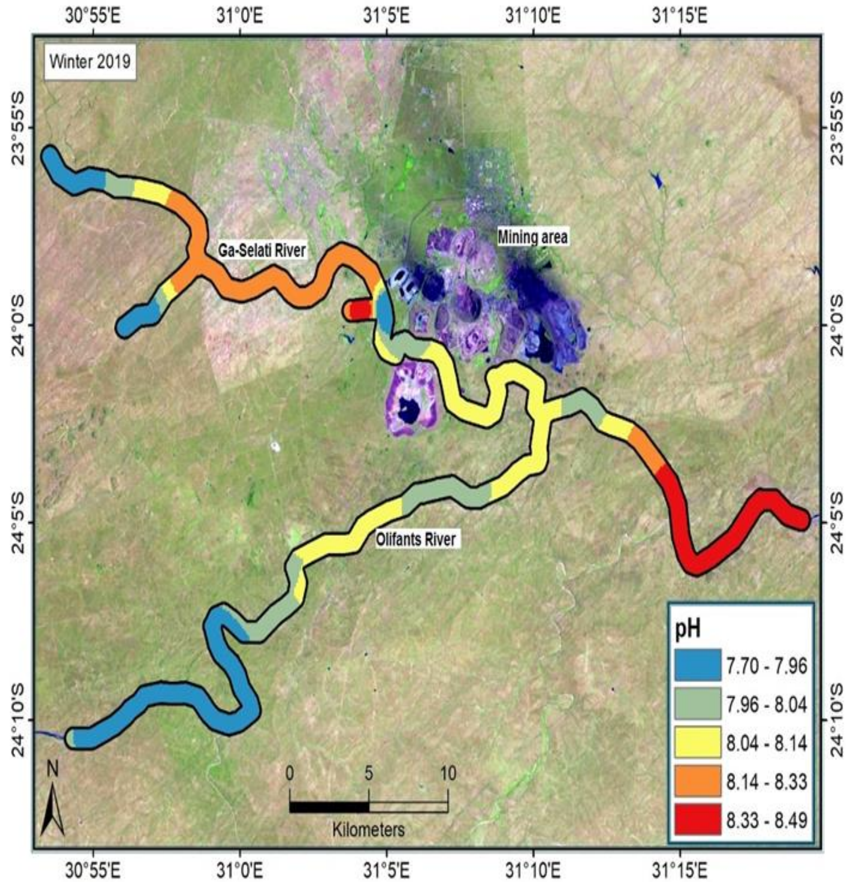

Spring 2019
Ga-Selati River
Mining area
Olifants River
Vanadium (mg/L)
0.06 - 0.12
0.12 - 0.19
0.19 - 0.25
0.25 - 0.32
0.32 - 0.38
Kilometers

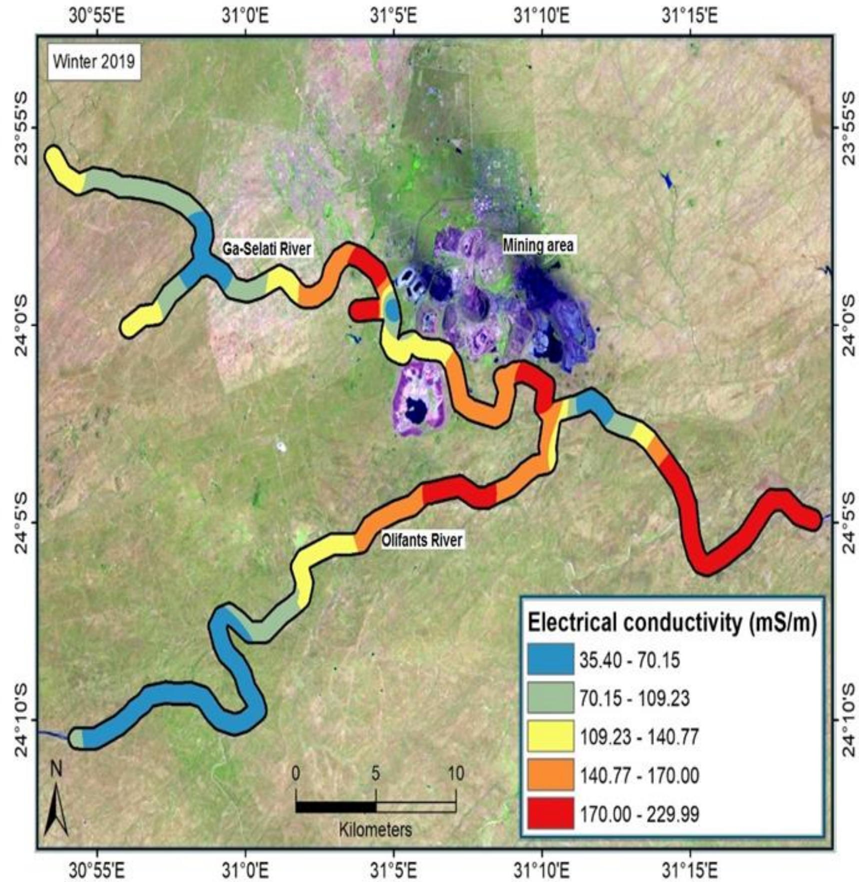

Spring 2019
Ga-Selati River
Mining area
Olifants River
Chloride (mg/L)
24.80 - 58.82
58.82 - 92.84
92.84 - 126.87
126.87 - 160.89
160.89 - 194.91
Kilometers
Fluoride (mg/L)
0.25 - 0.97
0.97 - 1.50
1.50 - 2.42
2.42 - 3.15
3.15 - 3.87
30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S

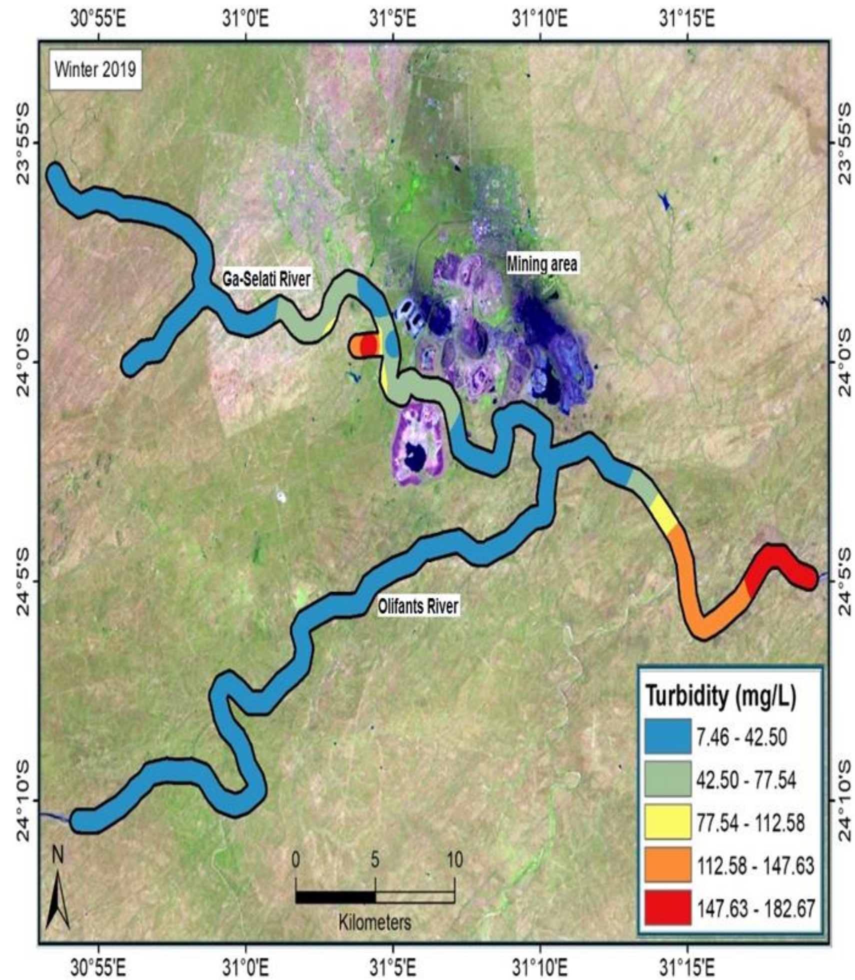

Spring 2019
Ga-Selati River
Mining area
Olifants River
Nitrate (mg/L)
0.10 - 14.87
14.87 - 27.28
27.28 - 39.29
39.29 - 50.00
50.00 - 73.97
0 5 10
Kilometers
N
30°55'E 31°0'E 31°5'E 31°10'E 31°15'E
23°55'S 24°0'S 24°5'S 24°10'S

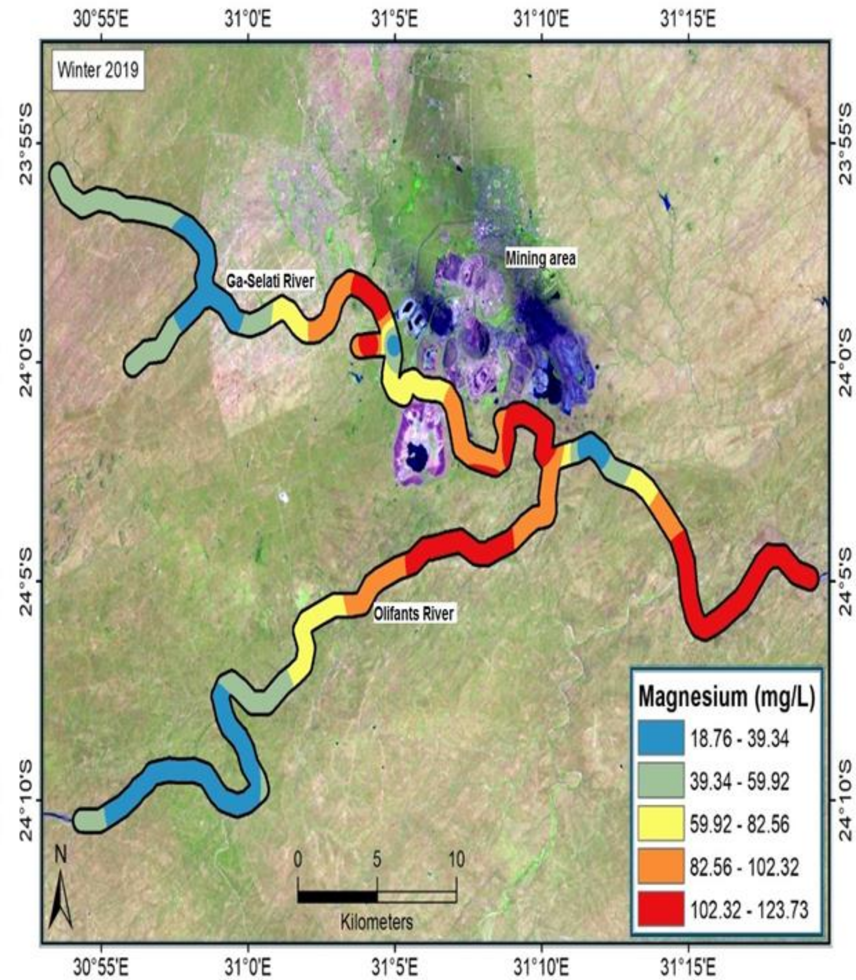

Spring 2019
Ga-Selati River
Mining area
Olifants River
Sulphate (mg/L)
28.92 - 155.43
155.43 - 281.94
281.94 - 408.45
408.45 - 500.00
500.00 - 661.48
0 5 10
Kilometers
N
30°55'E 31°0'E 31°5'E 31°10'E 31°15'E
23°55'S 24°0'S 24°5'S 24°10'S

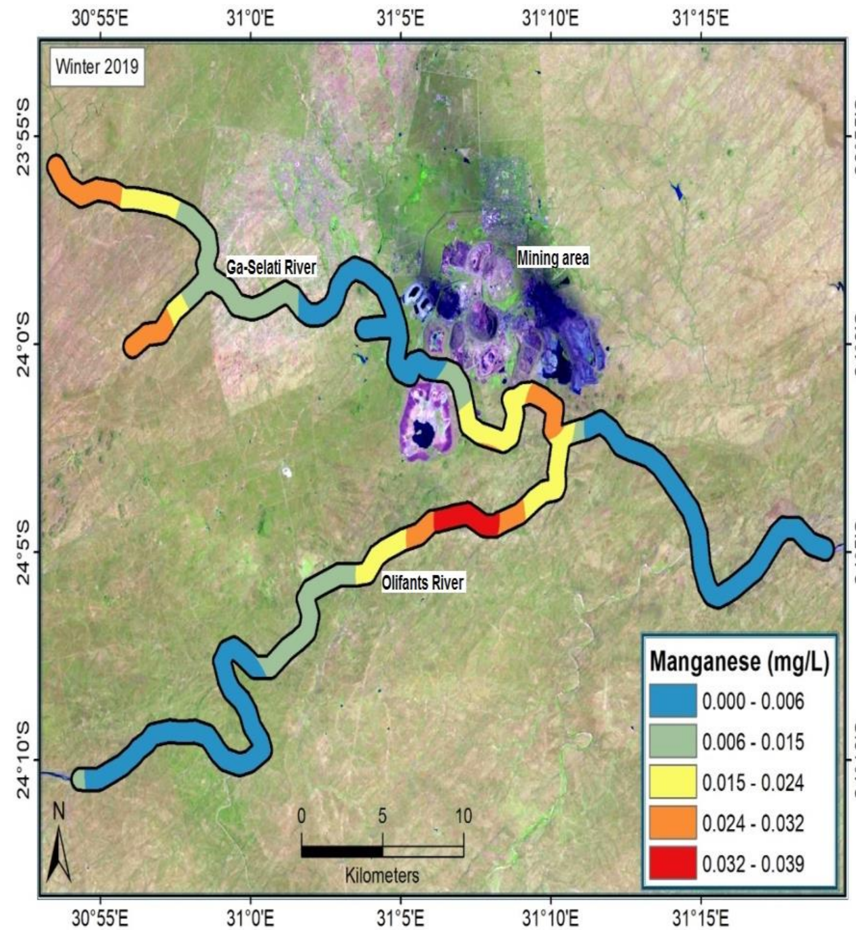
c. Winter thematic maps.

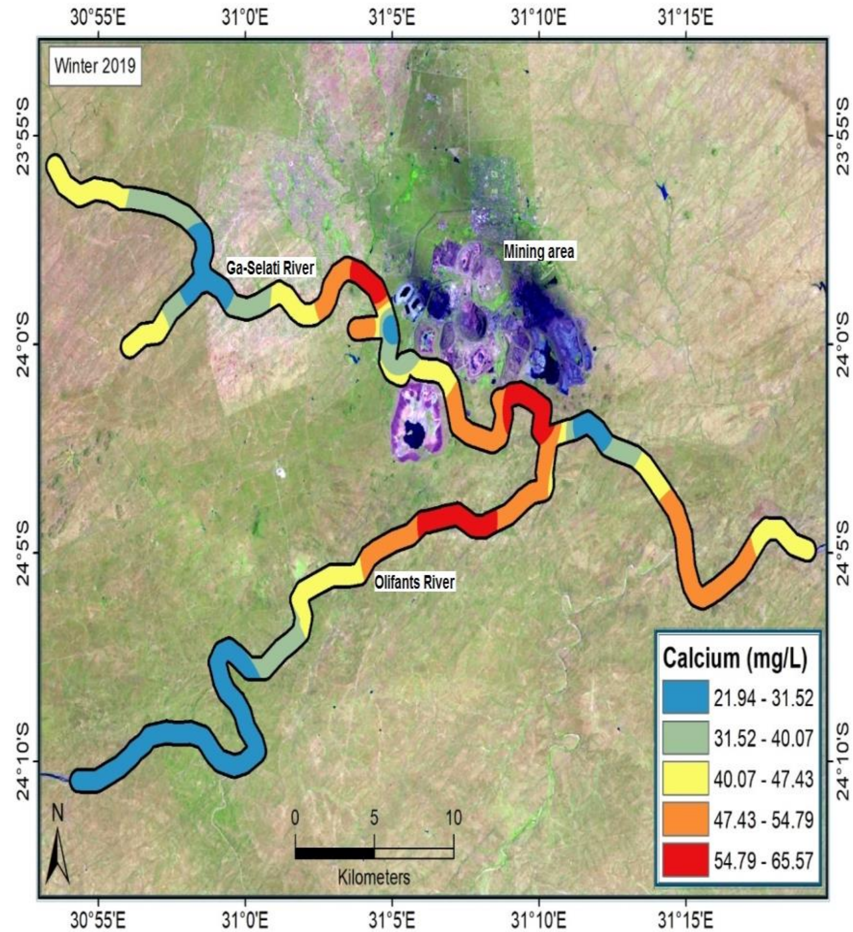


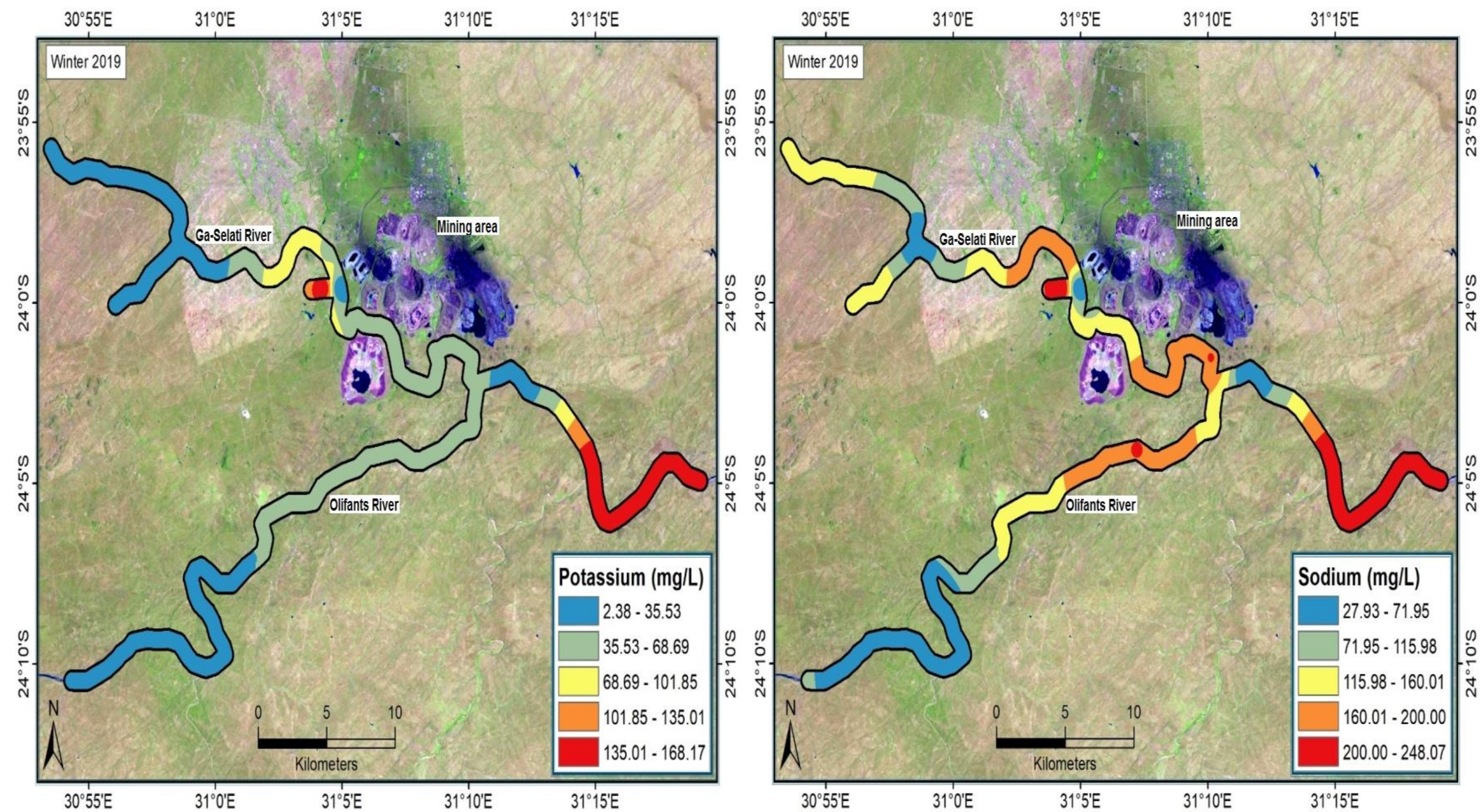


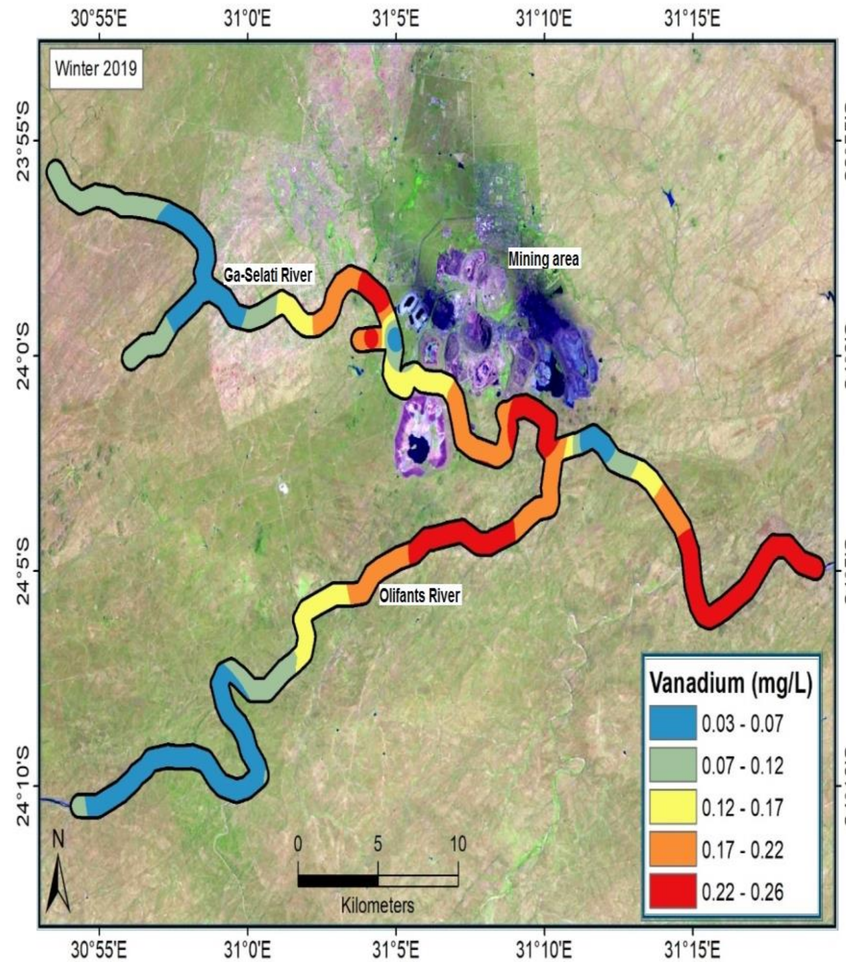

30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S
Winter 2019
Ga-Selati River
Mining area
Olifants River
Turbidity (mg/L)
7.46 - 42.50
42.50 - 77.54
77.54 - 112.58
112.58 - 147.63
147.63 - 182.67
N
0
5
10
Kilometers

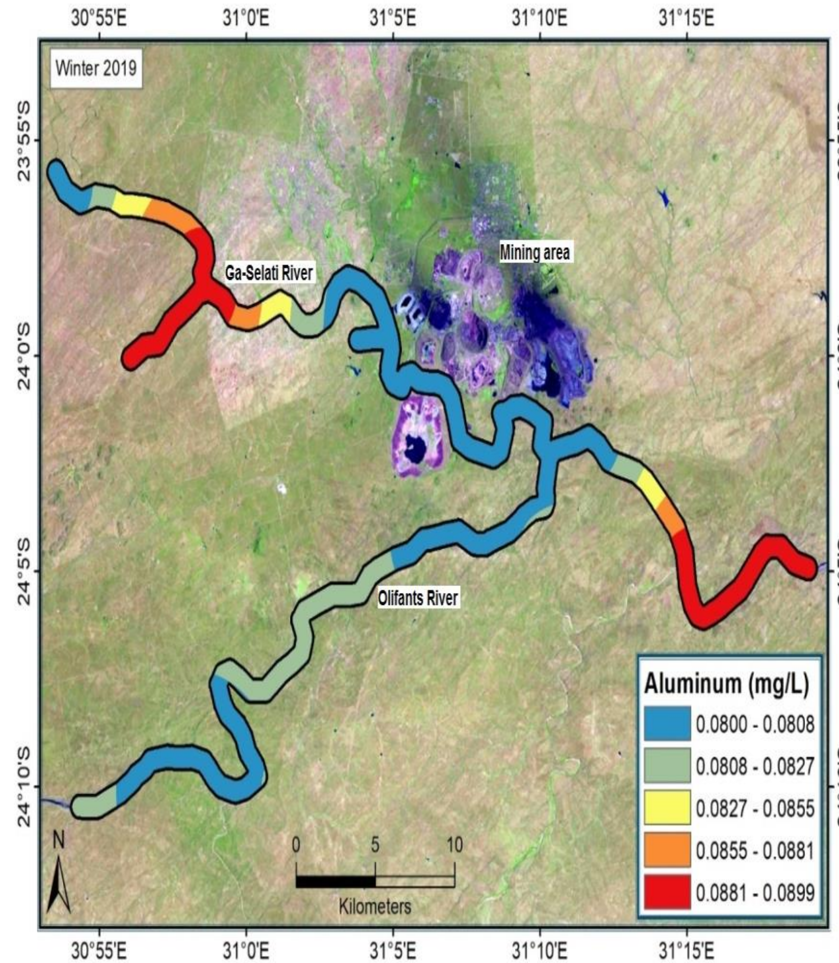

30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S
Winter 2019
Ga-Selati River
Mining area
Olifants River
Magnesium (mg/L)
18.76 - 39.34
39.34 - 59.92
59.92 - 82.56
82.56 - 102.32
102.32 - 123.73
N
0
5
10
Kilometers


Winter 2019
Ga-Selati River
Mining area
Olifants River
Manganese (mg/L)
0.000 - 0.006
0.006 - 0.015
0.015 - 0.024
0.024 - 0.032
0.032 - 0.039
0 5 10
Kilometers
N
30°55'E 31°0'E 31°5'E 31°10'E 31°15'E
23°55'S 24°0'S 24°5'S 24°10'S


Winter 2019
Ga-Selati River
Mining area
Olifants River
Calcium (mg/L)
21.94 - 31.52
31.52 - 40.07
40.07 - 47.43
47.43 - 54.79
54.79 - 65.57
0 5 10
Kilometers
N
30°55'E 31°0'E 31°5'E 31°10'E 31°15'E
23°55'S 24°0'S 24°5'S 24°10'S


Winter 2019
Ga-Selati River
Mining area
Olifants River
Potassium (mg/L)
2.38 - 35.53
35.53 - 68.69
68.69 - 101.85
101.85 - 135.01
135.01 - 168.17
Kilometers
Winter 2019
Ga-Selati River
Mining area
Olifants River
Sodium (mg/L)
27.93 - 71.95
71.95 - 115.98
115.98 - 160.01
160.01 - 200.00
200.00 - 248.07
Kilometers


30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S
Winter 2019
Ga-Selati River
Mining area
Olifants River
Vanadium (mg/L)
0.03 - 0.07
0.07 - 0.12
0.12 - 0.17
0.17 - 0.22
0.22 - 0.26
N
0 5 10
Kilometers


30°55'E
31°0'E
31°5'E
31°10'E
31°15'E
23°55'S
24°0'S
24°5'S
24°10'S
Winter 2019
Ga-Selati River
Mining area
Olifants River
Aluminum (mg/L)
0.0800 - 0.0808
0.0808 - 0.0827
0.0827 - 0.0855
0.0855 - 0.0881
0.0881 - 0.0899
N
0 5 10
Kilometers

APPENDIX 3

LAB RESULTS

a) Summer laboratory results.

Determinant	Method	Units	SANS 241 limits	Analysis Results					Analysis Results					Analysis Results	
				Sample ID/Code					Sample ID/Code					Sample ID/Code	
Physical and Aesthetic															
				Ga-Selati upstream 1	Ga-Selati upstream 2	Selati upstream 3	Ga-Selati downstream 1	Ga-Selati downstream 2	Ga-Selati downstream 3	Olifants upstream 1	Olifants upstream 2	Olifants upstream 3	Olifants downstream 1	Olifants downstream 2	Olifants downstream 3
pH	ME-003	@25º C	5.0 – 9.7	8.07	8.02	8.04	8.37	8.68	8.46	7.80	7.80	7.70	8.18	8.24	8.20
Electrical Conductivity	ME-004	mS/m	≤170	151	148	143	203	205	202	50.5	54.0	53.5	55.9	56.8	56.5
Total dissolved solids	ME-004	mg/L	≤1200	981.5	962	929.5	1319.5	1332.5	1313	328.25	351	347.75	363.35	369.2	367.25
Turbidity	ME-005	NTU	≤1	7.07	11.5	9.18	29.4	11.4	49.5	28.3	34.5	25.6	40.6	38.1	35.4
Inorganic															
Fluoride as F	ME-012	mg/L	≤1.5	0.53	0.53	0.53	2.88	0.97	2.90	0.39	0.39	0.39	0.50	0.50	0.50
Chloride as Cl	ME-012	mg/L	≤300	197.71	197.18	198.23	214.56	214.25	215.20	24.28	24.22	24.21	32.24	32.09	32.38
Nitrate as NO3	ME-012	mg/L	-	4.78	5.04	4.83	1.92	1.88	1.84	0.91	0.93	0.93	1.15	1.20	1.27
Sulphate as SO4	ME-012	mg/L	≤500	104.21	103.93	104.50	552.87	557.41	555.47	128.73	127.60	129.75	151.90	152.25	152.82
Metals															
Potassium as K	ME-011	mg/L	-	11.36	11.37	11.14	80.53	80.61	81.68	7.40	7.16	7.13	10.34	10.29	10.34
Calcium as Ca	ME-011	mg/L	-	58.61	56.13	56.11	70.00	75.06	70.80	35.96	36.30	35.62	33.26	33.96	32.45
Magnesium as Mg	ME-011	mg/L	-	57.54	54.34	56.17	138.88	138.71	139.54	26.19	25.74	25.92	29.30	29.83	28.98
Sodium as Na	ME-011	mg/L	≤200	195.81	191.77	188.53	187.54	185.78	186.64	35.13	34.95	35.11	40.13	40.61	39.82
Manganese as Mn	ME-011	mg/L	≤0.4	0.18	0.14	0.19	0.03	0.03	ND	ND	ND	0.01	ND	ND	ND
Vanadium as V	ME-011	mg/L	-	0.15	0.15	0.15	0.37	0.37	0.37	0.07	0.07	0.07	0.08	0.08	0.08
Aluminium as Al	ME-011	mg/L	≤0.3	ND	ND	ND	ND	ND	ND	ND	ND	0.01	ND	ND	ND

b) Spring laboratory results.

Determinant	Method	Units	SANS 241 limits	Analysis Results					Analysis Results					Analysis Results	
				Sample ID/Code					Sample ID/Code					Sample ID/Code	
Physical and Aesthetic															
				Ga-Selati Upstream 1	Ga-Selati Upstream 2	Ga-Selati Upstream 3	Olifants Downstream 1	Olifants Downstream 2	Olifants Downstream 3	Olifants Upstream 1	Olifants Upstream 2	Olifants Upstream 3	Ga-Selati Downstream 1	Ga-Selati Downstream 2	Ga-Selati Downstream3
pH	ME-003	@25º C	5.0 – 9.7	8.02	7.95	7.93	9.14	9.02	9.16	8.31	8.38	4.40	9.18	9.10	9.17
Electrical Conductivity	ME-004	mS/m	≤170	120	121	116	225	201	231	43.0	41.3	41.1	229	209	216
Total dissolved solids	ME-004	mg/L	≤1200	780	786.5	754	1462.5	1306.5	1501.5	279.5	268.45	267.15	1488.5	1358.5	1404
Turbidity	ME-005	mg/L	≤1	3.01	2.98	2.72	4.75	6.23	8.02	45.9	21.4	20.2	4.5	14.2	3.10
Inorganic															
Fluoride as F	ME-012	mg/L	≤1.5	0.56	0.56	0.57	3.83	3.09	3.85	0.25	0.25	0.25	3.87	3.88	3.88
Chloride as Cl	ME-012	mg/L	≤300	117.43	119.14	119.21	192.46	185.42	193.40	25.06	24.80	25.19	194.50	195.06	194.58
Nitrate as NO3	ME-012	mg/L	-	0.38	0.39	0.41	0.71	0.70	0.74	0.10	0.10	0.10	0.72	0.70	0.74
Sulphate as SO4	ME-012	mg/L	≤500	47.75	48.78	48.75	653.05	591.53	655.27	28.87	28.90	29.32	659.22	662.04	659.21
Metals															
Potassium as K	ME-011	mg/L	-	11.83	11.80	12.05	115.79	90.26	114.95	3.52	3.42	3.39	119.93	121.57	122.18
Calcium as Ca	ME-011	mg/L	-	55.49	55.79	56.07	89.46	90.03	86.26	24.99	25.71	25.49	88.86	88.92	89.23
Magnesium as Mg	ME-011	mg/L	-	55.45	55.51	56.14	169.94	152.98	166.79	30.32	29.94	29.79	173.06	171.56	173.92
Sodium as Na	ME-011	mg/L	≤200	152.52	153.57	153.53	215.47	198.99	205.49	32.45	32.19	32.15	211.81	210.43	212.23
Manganese as Mn	ME-011	mg/L	≤0.4	0.10	0.13	0.13	0.07	0.11	0.02	ND	ND	ND	0.05	0.03	0.06
Vanadium as V	ME-011	mg/L	-	0.12	0.12	0.12	0.39	0.34	0.39	0.07	0.07	0.06	0.39	0.38	0.38
Aluminium as Al	ME-011	mg/L	≤0.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

c) Winter laboratory results.

Determinant	Method	Units	SANS 241 limits	Analysis Results					Analysis Results					Analysis Results	
				Sample ID/Code					Sample ID/Code					Sample ID/Code	
Physical and Aesthetic															
				Ga-Selati Upstream 1	Ga-Selati Upstream 2	Ga-Selati Upstream 3	Olifants Upstream 1	Olifants Upstream 2	Olifants Upstream 3	Ga-Selati Downstream 1	Ga-Selati Downstream 2	Ga-Selati Downstream 3	Olifants Downstream 1	Olifants Downstream 2	Olifants Downstream 3
pH	ME-003	@25º C	5.0 – 9.7	8.34	7.91	7.95	8.07	7.96	7.70	8.55	8.55	8.51	8.14	8.20	8.08
Electrical Conductivity	ME-004	mS/m	≤170	49.4	115	110	38.8	35.4	36.2	228	230	226	194	189	183
Turbidity	ME-005	mg/L	≤1	7.46	10.9	8.23	18.2	21.8	23.2	183	166	145	7.72	9.57	10.5
Inorganic															
Sulphur as S	ME-011	mg/L	-	6.69	17.32	17.33	12.23	12.32	12.03	181.53	182.81	184.05	149.71	152.53	148.95
Metals															
Potassium as K	ME-011	mg/L	-	2.79	8.62	8.63	2.67	2.38	3.22	169.12	165.70	166.15	65.35	64.47	64.01
Calcium as Ca	ME-011	mg/L	-	26.36	43.40	43.46	24.14	21.94	23.69	51.23	46.72	53.08	64.13	65.62	59.43
Magnesium as Mg	ME-011	mg/L	-	18.76	52.16	52.42	25.08	24.95	25.77	113.75	110.58	112.95	123.74	123.25	122.54
Sodium as Na	ME-011	mg/L	≤200	56.39	156.40	154.35	28.34	27.93	29.37	248.40	240.57	245.77	201.25	199.66	200.70
Manganese as Mn	ME-011	mg/L	≤0.4	0.01	0.03	0.03	ND	ND	ND	ND	ND	ND	0.03	ND	0.04
Vanadium as V	ME-011	mg/L	-	0.03	0.09	0.09	0.04	0.04	0.04	0.24	0.24	0.24	0.27	0.26	0.27
Aluminium as Al	ME-011	mg/L	≤0.3	0.09	0.09	0.08	0.08	0.08	0.08	0.08	0.09	0.09	0.08	0.08	0.08