Cape Peninsula
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CONTAMINATION SOURCES AND CONCENTRATIONS OF METAL POLLUTANTS IN THE EERSTE RIVER, CAPE TOWN, SOUTH AFRICA

by

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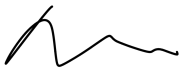
DECLARATION

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



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ABSTRACT

Rivers provide essential supporting, regulating, provisioning and cultural services to people. However, an 11% decline in South African river condition from 1999–2011 has been reported, largely attributed to increased water pollution. The decline in river condition is of great concern as it significantly undermines the ability of rivers to deliver valuable services to people. Anthropogenic activities generate large quantities of waste, such as heavy metals, which has the potential to cause long term effects on the ecosystem. Therefore, this study focused on the Eerste River and its associated estuary. The research objectives for this study were to determine whether various metals are present at environmentally significant levels along the length of the river in the water and sediment; and to determine whether there is a link between concentrations of various metals present at environmentally significant levels along the length of the river and the sources of contamination. To achieve the objectives, water and sediment samples were collected at different sites along the Eerste River in March 2021 (dry season) and August 2021 (wet season). The samples were prepared using an acid digestion procedure, and the water and sediment samples were analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Five metals are presented in the study, namely aluminium, manganese, iron, zinc and lead. Statistical analyses were conducted using the SigmaPlot 14 software. Statistically significant differences in metal concentrations between sampling sites were evaluated using a Kruskal–Wallis One-Way ANOVA on Ranks and Student Newman Kuels Method for post hoc tests. Statistically significant differences in metal concentrations between sampling seasons were evaluated using the Mann Whitney Rank Sum Test. In terms of the water sample results, the mean concentrations of the metals in the water are ordered from highest to lowest concentration in the dry season as follows: Fe>Al>Zn>Mn>Pb. The mean metal concentrations in the wet season in the water are ordered as follows: Al>Zn>Fe>Mn>Pb. In terms of the sediment sample results, the metal concentrations in the dry and wet season are ordered as follows: Fe>Al>Mn>Zn>Pb. The mean metal concentrations were generally higher in the wet season than in the dry season. The variations in the concentrations can be attributed to non-point source pollution, metal-containing road dust, wildfires and exhaust fumes, stormwater runoff and runoff from farms, and WWTW effluent discharges. Majority of the metals were significantly higher at site 4, which not only receives pollution from upstream sources, but also receives a vast amount of pollution from the Kuils River tributary. When comparing the metal concentrations against national and international water quality and sediment quality guidelines, it was observed that the mean aluminium concentrations in water exceeded the South African Water Quality Guidelines (SA WQG) and the Australia and New Zealand Guidelines for Fresh and Marine Water Quality. The mean manganese and iron concentrations in water did not exceed any guidelines. However, the iron concentration in the Eerste River estuary exceeded the South African Water Quality Guidelines for Coastal Marine Waters (SA WCG – CMW). No sediment quality guidelines have

been developed for aluminium, iron, and manganese nationally or internationally. The mean zinc concentrations in water exceeded the SA WQG, the Canadian Water Quality Guidelines for the Protection of Aquatic Life (CWQG) and the SA WQG – CMW. The mean zinc concentrations in sediment did not exceed any guidelines. The mean lead concentrations in water exceeded the SA WQG but the mean lead concentrations in sediment did not exceed any guidelines. It is concluded that the Eerste River is polluted, although there are significant differences in metal concentrations in both water and sediment along the length of the river. It is further concluded that WWTW effluent from the Macassar plant is not a main source of contamination, but it is contributing to some degree, along with several other sources such as stormwater runoff, natural occurrence, and non-point source pollution. It is recommended that further research be undertaken to better distinguish the sources of metal pollution in the Eerste River as well as to determine the impacts of metal contamination on river biodiversity. Further research should also be conducted to generate more data to develop South African sediment quality guidelines. Additional recommendations include continuous monitoring of metals in the river and in WWTW effluent to locate vulnerable areas and apply appropriate remediation/abatement measures.

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GLOSSARY

Acronyms/notations	Description
Al	Aluminium
CCT	City of Cape Town
DFFE	Department of Forestry, Fisheries and the Environment
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
EI	Ecological Infrastructure
Fe	Iron
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
Mn	Manganese
NEM: ICMA	National Environmental Management: Integrated Coastal Management Act (No. 24 of 2008) as amended
NEMP	National Estuarine Management Protocol
NWA	National Water Act (Act no 36 of 1998)
Pb	Lead
PES	Present Ecological State
SQG	Sediment Quality Guidelines
TWQR	Target Water Quality Range
WQG	Water Quality Guidelines
WWTW	Wastewater Treatment Works
Zn	Zinc
Km^2	Square kilometre
m^3	Cubic meter
µg/L	Microgram per litre
mg/L	Milligram per litre
mg/kg	Milligram per kilogram
mg/L	Parts per million

Terms:

"Adsorption" refers to the adhesion in an extremely thin layer of molecules (as of gases, solutes, or liquids) to the surfaces of solid bodies or liquids with which they are in contact (DEA, 2018).

"Biodiversity" refers to the variability among living organisms from all sources including, inter alia, terrestrial, marine and other aquatic ecosystems and the ecological complexes of which they are part. This includes diversity within species, between species and of ecosystems (Van Niekerk and Turpie, 2012).

"Bioremediation" refers to a method for removing/converting harmful contaminants like heavy metals into less harmful substances; and/or removing toxic elements from the contaminated environment; or degrading organic substances and ultimate mineralization of organic substances into carbon dioxide, water, nitrogen gas, etc., employing dead or alive biomass (Kapahi and Sachdeva, 2019).

"Carcinogenic" refers to a substance, organism, or environment that is known to be a causal factor in the production of a tumour (Martin, 2010).

"Catchment" refers the area from which a surface watercourse or a groundwater system derives its water. Catchments are separated by divides. A surface catchment area may overlie an aquifer system but may be unconnected with the aquifer rock itself if there are intervening impermeable aquicludes (Allaby, 2013).

"Contaminant" refers to any physical, biological, chemical, or radiological substance or matter in water (USEPA, 2016a).

"Ecotoxicity" refers to the potential for biological, chemical or physical stressors to affect ecosystems. Such stressors might occur in the natural environment at densities, concentrations or levels high enough to disrupt the natural biochemistry, physiology, behaviour and interactions of the living organisms that comprise the ecosystem (Truhaut, 1977).

"Effluent" refers to the liquid fraction after a treatment process (i.e., preliminary, primary, secondary or tertiary) in a wastewater treatment works (Van Niekerk and Turpie, 2012).

"Estuary" refers to a body of surface water that is permanently or periodically open to the sea; in which a rise and fall of the water level as a result of the tides is measurable at spring tides when the body of surface water is open to the sea; or in respect of which the salinity is higher than fresh water as a result of the influence of the sea, and where there is a salinity gradient between the tidal reach and the mouth of the body of surface water (Republic of South Africa, 2014).

“Eutrophication” refers to the process, usually anthropogenic, whereby nutrients accumulate in a body of water (Thomas *et al.*, 2010).

“Mutagenic” refers to the ability of an external agent to, when applied to cells or organisms, increase the rate of mutation (Martin, 2010).

“Non-point source pollution” refers to a pollution source that releases pollutants into the environment over a broad area, commonly consisting of multiple input sites (Reichard, 2011).

“Point source pollution” refers to a pollution source that releases pollutants into the environment at a physically discrete point (Reichard, 2011).

“Pollutant” refers to compounds introduced in the natural environment causing adverse changes, for example, adversely affecting health or causing other types of damage (Moldoveanu and David, 2015).

“Precipitation” (chemistry) refers to the chemical reaction that causes a solid to form from solution (DEA, 2018).

“Riparian habitat” refers to the physical structure and associated vegetation of the areas associated with a watercourse which are commonly characterised by alluvial soils, and which are inundated or flooded to an extent and with a frequency sufficient to support vegetation of species with a composition and physical structure distinct from those of adjacent land areas (Van Deventer *et al*., 2018).

“River” refers to a linear inland aquatic ecosystem with clearly discernible bed and banks, which permanently or periodically carries a concentrated flow of water. A river is taken to include both the active channel and the riparian zone as a unit (Van Deventer *et al.,* 2019).

“Sediment” refers to material derived from pre-existing rock, from biogenic sources, or precipitated by chemical processes, and deposited at, or near, the Earth’s surface (Allaby, 2013).

“Stormwater runoff” refers to stormwater run-off from paved areas, including parking lots, streets, residential subdivisions, of buildings, roofs, highways, etc. (Van Niekerk and Turpie, 2012).

“Teratogenic” refers to the ability of a substance, agent, or process to induce the formation of developmental abnormalities in a fetus (Martin, 2010).

“Wastewater” refers to water containing solid, suspended or dissolved material (including sediment) in such volumes, composition or manner that, if spilled or deposited in the natural environment, will cause, or is reasonably likely to cause, a negative impact (Van Niekerk and Turpie, 2012).

CHAPTER ONE

INTRODUCTION

1.1. Background

Ecological Infrastructure (EI), in the South African context, refers to ecosystems that are naturally functioning and provide ecosystem services to people, including healthy mountain catchments, rivers, wetlands, coastal dunes, and nodes and corridors of natural habitat (SANBI, 2014).

Ecological Infrastructure is like built infrastructure in that they both enable services to be provided as well as supporting socio-economic development. The natural environment can provide these ecosystem services either directly to society (such as by providing protection against sea surge on coastal roads), or natural catchment areas could be linked with built infrastructure as part of a more comprehensive infrastructure system, (like a dam and pipelines to provide water to nearby settlements). As with other types of infrastructure, EI already exists in the landscape, even if it has been degraded in some cases. However, just as with other forms of infrastructure, it should be maintained and managed, and in some cases, restored (SANBI, 2014).

Rivers represent irreplaceable freshwater resources that contribute to environmental conservation, recreation, and economic development (Feng, 2005). Rivers also provide vital ecosystem services such as clean water, energy, and transport (DEA&DP, 2005).

Water pollution is one of the biggest challenges modern societies face today. There are different types and levels of pollutants introduced into the environment by different activities and those pollutants impact river health differently (Street, 2008). Despite rivers being important habitats for various faunal and floral species, these systems have become severely contaminated with toxic substances. It is possible for the water quality of rivers to vary due to variations in geological morphology, vegetation, and land use (for example, agriculture, industrialization, and urbanization). Organic and inorganic pollutants, and other chemicals, including heavy metals, are produced by industries, agriculture, and urban settlements (Feng, 2005). Heavy metals are well-known environmental pollutants due to their toxicity, bioaccumulative nature, and persistence in the environment and can enter the environment through natural means as well as anthropogenic activities (Ali *et al*., 2019).

This present study was undertaken to determine the sources and concentrations of metal contaminants in the rivers in Cape Town, South Africa. A focus was put on the Eerste River as it has been one of the poorest rivers in Cape Town in terms of river health (Van Niekerk and Turpie, 2012; Van Niekerk *et al*., 2019). The Eerste River forms an estuary at Macassar which serves as an important habitat for fauna and flora. Estuaries are systems with high biodiversity and they provide many environmental and socio-economic benefits (Republic of South Africa,

2013). These benefits include protection from floods, providing raw building material, and being nurseries for juvenile fish. Estuaries also often serve as nodes for habitation and development (Republic of South Africa, 2013). However, the Eerste River has received chemical waste from a Munitions factory near the town of Macassar on its eastern bank, and wastewater effluent from the Macassar Wastewater Treatment Works on its western bank (Thomas *et al.,* 2010).

Furthermore, since the Eerste Rivers flows through highly urbanized areas (such as Stellenbosch and Macassar), it has been degraded to a great extent in terms of both water quality and aesthetic value. It can be assumed that the degradation is mainly due to polluted urban storm water runoff and the release of sewage effluent into these rivers. Although the Eerste River forms part of urban developments, significant portions of the river have agricultural lands. Therefore, the river has both urban and agricultural sources of non-point source pollution (Thomas *et al*., 2010).

1.2. Research problem

EI not only provides valuable services to people but also supports South Africa's economy by delivering valuable services and reducing risk. Therefore, when these systems are degraded, they must be restored (SANBI, 2014).

Rivers, as an example of EI provide essential supporting, regulating, provisioning and cultural services to people. However, Nel and Driver (2015) reported an 11% decline in South African river condition from 1999–2011, which is largely attributed to increased water pollution. The decline in river condition is of great concern as it significantly undermines the ability of rivers to deliver valuable services to people. Rapid urbanisation, industrialisation, agricultural activities and energy use are further contributing to the introduction of heavy metal pollutants into rivers (Shaeen & Pillay, 2019). These anthropogenic activities generate large quantities of waste which is ineffectively removed through Wastewater Treatment Works and has the potential to cause long term effects on the ecosystem (Olujimi *et al*., 2015).

This study focused on the Eerste River and its associated estuary, and the WWTW effluent which discharges into it. Despite the potential ecological and human risk posed by toxic substances such as heavy metals, very little information exists on the possible sources and occurrence of metals within the Eerste River. Therefore, this study aimed to fill this gap and the results from this study can open additional research areas, such as management interventions as it relates to metal pollution in rivers.

1.3. Research questions

1.3.1. Which metals are present at environmentally significant levels along the length of the Eerste River?

1.3.2. Is there a link between metal concentrations along the length of this river and the sources of contamination and land-use practices (such as the Wastewater Treatment Works in the lower reaches of the river)?

1.4. Research objectives

1.4.1. To determine if various metals are present at environmentally significant levels along the length of the river in the water and sediment.

1.4.2. To determine whether there is a link between concentrations of various metals present at environmentally significant levels along the length of this river and the sources of contamination (such as the Wastewater Treatment Works in the lower reaches of the river).

1.5. Limitations of the study

There were a few limitations experienced in the study and they are outlined below:

- Safety – A couple of the sampling sites were not safe as there were people undertaking suspicious/unlawful activities. Therefore, law enforcement presence was requested from the City of Cape Town and provided on both sampling occasions.
- Permissions to sample - Permission was sought from CapeNature to enter and sample within the Jonkershoek Nature Reserve as the site was the initial sampling site 1. While permission was granted in a timely manner, the mountain fires occurring in Stellenbosch in March 2021 prevented the sampling from occurring. Therefore, the sampling sites had to be changed. Furthermore, permission was sought and granted from the Spier Wine Farm to enter the premises and undertake water and sediment sampling.

CHAPTER TWO

LITERATURE REVIEW

2.1. Ecological infrastructure

According to SANBI (2014), the term ecological infrastructure (EI) in South Africa is defined as naturally functioning ecosystems providing ecosystem services to people. EI can be viewed as nature's equivalent to built infrastructure, and it underpins socio-economic development. It provides valuable services to people directly such as a river providing flood attenuation services or are included in a more comprehensive system that includes built infrastructure such as a natural catchment area that comprises a dam and pipes to distribute water to a community.

The Millennium Ecosystem Assessment (2005) defines ecosystem services as “benefits people obtain from ecosystems”, and goes on to distinguish between four categories of ecosystem services:

- Provisioning (such as food and water)
- Regulating (such as regulation of floods, drought, land degradation, and disease)
- Cultural (such as recreational, spiritual, and religious)
- Supporting services (such as soil formation and nutrient cycling)

Based on this definition, ecosystem services are provided by both naturally functioning, as well as highly modified ecosystems. However, within the South African context, EI underpins the delivery of a subset of ecosystem services i.e., those services delivered by naturally functioning ecosystems (Millennium Ecosystem Assessment, 2005). One element of ecological infrastructure (e.g., a river) can deliver more than one service, such as providing water for domestic use and irrigation, as well as food and recreation.

EI exists within the landscape, and in some cases, it may become degraded. It is therefore essential to maintain and/or restore ecological infrastructure, just as with all forms of infrastructure (SANBI, 2014). This can be done through the following approaches suggested by SANBI (2014):

- The integration of EI into land-use planning and decision-making
- Clearing invasive alien species from catchments and riparian areas
- Wetland rehabilitation
- Restoring and maintaining buffers of natural vegetation in riparian areas
- Improving rangeland management practices
- Maintaining protected/conservation areas

South Africa's economy relies, to some extent, on the services which are provided by EI such as clean water flowing from healthy catchments. Therefore, by ensuring that the EI is conserved and protected, the economy will benefit (SANBI, 2014).

2.2. Overview of rivers

The Western Cape Province also contains five Water Management Areas (WMA), namely: Berg, Breede, Gouritz, Olifants/Doorn and the western portion of Fish to Tsitsikamma (DEA&DP, 2005).

The City of Cape Town (CCT) is situated in the Berg-Olifants WMA, extending north to include both the Berg and the Olifants River catchments, as well as the smaller natural catchments within the CCT's boundaries (CCT, 2020). A vast network of rivers exists in Cape Town flowing under natural conditions which not only acts as a habitat for aquatic fauna and flora, but also act as an ecological infrastructure asset for the management, treatment and transport of storm water and treated wastewater effluent (CCT, 2018a). These rivers include: the Diep River, Eerste River, Salt River, Hout Bay (or Disa) River, Lourens River, Noordhoek Basin, Sand River, Silvermine River, Sir Lowrys Pass River, Sout River, and the South Peninsula Rivers (Bokramspruit, Schusters and Else Rivers) (CCT, 2020).

The main rivers and sub-catchments in the CCT are highlighted in Figure 2.1 below (CCT, 2020).

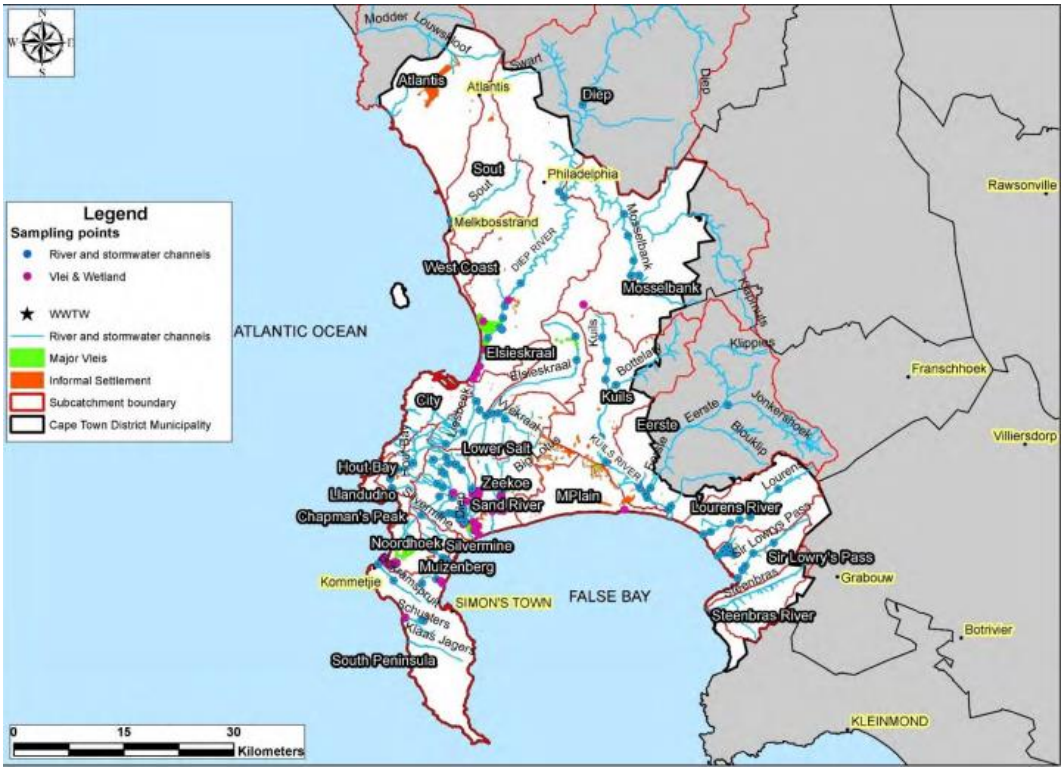


Figure 2.2.1: Main rivers and sub-catchments in the CCT (extracted from CCT, 2020)

2.3. State of rivers in Cape Town

The CCT implemented the Inland and Coastal Water Quality Improvement Strategy and Implementation Plan in 2012 to address the water quality in its watercourses. In the strategy, it was recognized that Cape Town's watercourses have ecological, aesthetic, recreational, and infrastructure functions that are vital to the city's functioning. The elements include beautification, sense of place, tourism, recreation, and health benefits for both residents and visitors. Cape Town's rivers, however, are constantly threatened by organic and inorganic pollution and litter, posing a threat to human health and biodiversity (CCT, 2018a).

According to CCT (2018a), urban water pollution is caused by a variety of factors, including:

- Water contamination caused by inadequate wastewater treatment and collection
- Direct discharge of sewage or greywater directly into storm water systems or the natural environment in informal areas
- Overflows of sewage due to accidental damage or aging infrastructure
- Industrial pollutants illegally disposed of in storm water systems or natural environments
- Animal waste and runoff from agricultural activities adjacent to and within the CCT
- Waterways polluted by litter and illegal dumping
- Degradation of wetlands and other natural systems that serve as filters

According to the CCT State of the Environment Report (2018a), in assessing Cape Town's freshwater ecosystems, the CCT examines water quality from two perspectives: public health (recreational contact) and ecosystem health (aware of people's dual importance and interdependence with freshwater environments). The indicators for both perspectives are derived from recommendations and guidelines of the national Department of Water and Sanitation

2.3.1. Public health and recreation evaluation

The suitability of inland waters for recreational purposes is determined using microbiological data, as described in the DWS guidelines for recreational intermediate contact. “Intermediate contact” refers to recreational activities such as water skiing and windsurfing, where full immersion in the water is likely to occur only occasionally, compared to full-contact activities, such as swimming (CCT, 2018a).

Furthermore, the CCT in 2009 set an internal target of achieving 80% adherence to the intermediate contact guideline by 2014 as part of the IMEP (Integrated Metropolitan Environmental Policy) Environmental Agenda for the CCT. According to 2016 water quality data, this target has generally not been met. Figure 2.3.1 shows that only four of the twenty rivers achieved 80% compliance with the IMEP target in 2016: Sir Lowry's Pass, Schusters, Lourens, and Silvermine rivers (CCT, 2018a).

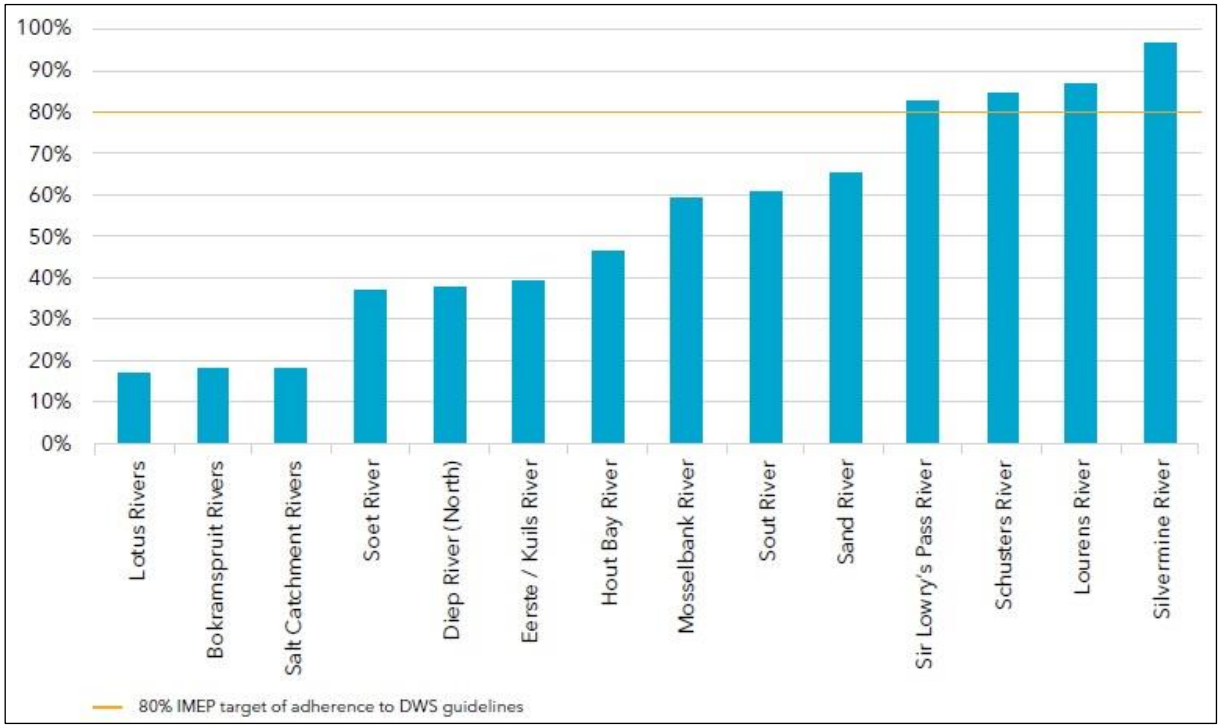


Figure 2.3.1: Specific rivers in Cape Town which met the DWS intermediate contact guideline during 2016 (extracted from the City of Cape Town State of the Environment Report, 2018).

2.3.2. Ecosystem health

To determine how healthy an ecosystem is, it is necessary to analyse its trophic state (the extent of nutrient enrichment) or its ecological condition. In these cases, phosphorus concentrations in the water bodies are used as indicators of the trophic state of the waterbodies, as phosphorus is commonly identified as a key nutrient pollutant in urban environments. In a freshwater system, an increase in phosphorus leads to eutrophication, where excess plant and algae growth leads to degrading water quality (CCT, 2016).

In 2016, 10 out of 14 river systems showed eutrophic or hypertrophic characteristics (Figure 2.3.2). Poor ecosystem health is indicated by these characteristics (CCT, 2018a). It should be acknowledged that the CCT does not primarily focus on metal contamination in urban rivers.

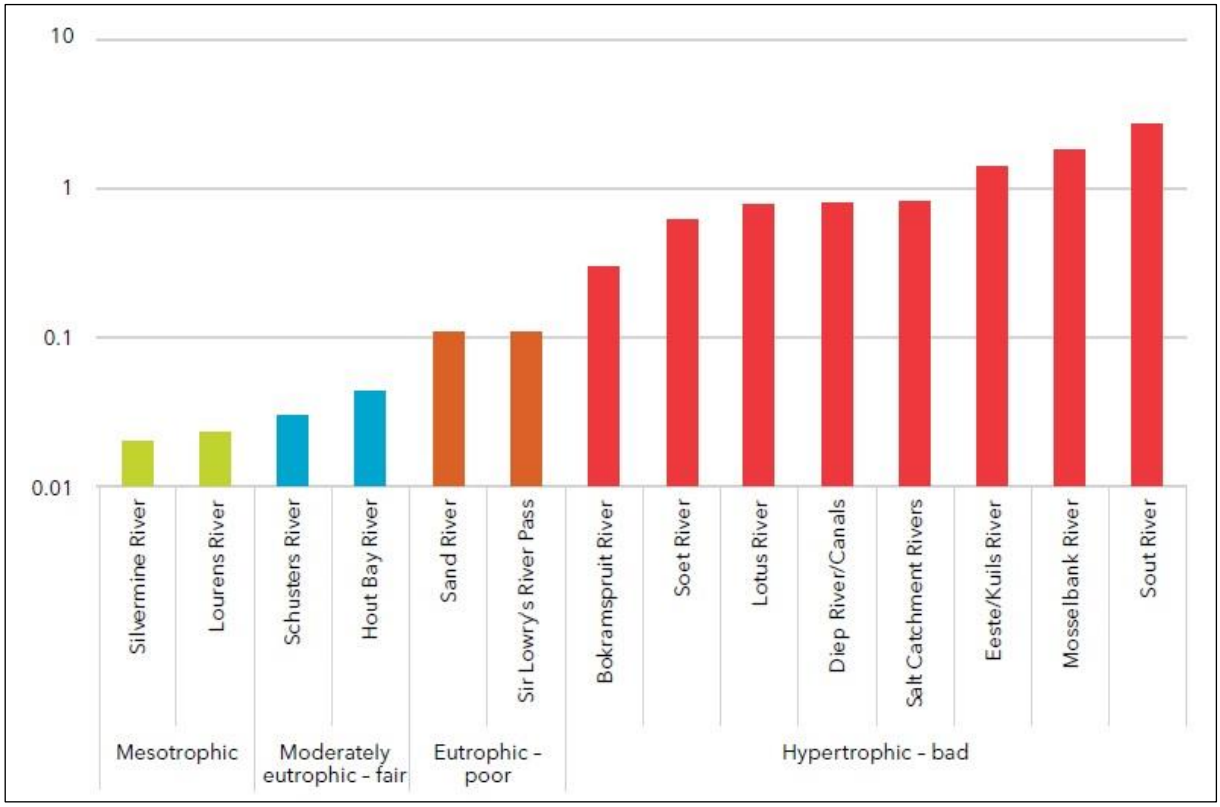


Figure 2.3.2: Trophic tendency in some Cape Town rivers during 2016 (extracted from the City of Cape Town State of the Environment Report, 2018).

Water quality data relating to main rivers and wetlands within Cape Town are collected through the implementation of the Inland Water Quality Monitoring Programme by the CCT. The data has been used to create a substantial database of sites that represents the water quality in Cape Town's main rivers and stormwater or effluent outflows into watercourses, with data for some watercourses going back to the late 1970's (CCT, 2020).

In watercourses where the water quality is a cause of concern, the data collected through the water quality monitoring programme provide important information related to the changes in the quality of watercourses. Therefore, according to CCT (2020), many of the monitoring points are located downstream of WWTW effluent discharge points, and in river reaches where contaminated runoff is likely to be encountered. Other sampling points are utilised to provide information related to the fitness for purpose of these watercourses and are in watercourses that are used for recreational purposes (CCT, 2020).

Based on the data collected from the CCT's Inland Water Quality Monitoring Programme, a marked increase in phosphorus enrichment is evident in all sub-catchments, except for the Lourens, Silvermine and Soet River sub-catchments (CCT, 2020). This means that most Cape Town's rivers are severely degraded.

2.4. The Eerste River

Approximately 60 kilometres east of Cape Town in the Western Cape lies the Jonkershoek Mountains, where the Eerste River originates. The river flows north-west from Jonkershoek to Stellenbosch before turning south and eventually discharges into the Atlantic Ocean at Macassar, in False Bay. With a catchment area of 420 km^2, the Eerste River measures approximately 40 km long. There are also several major tributaries that flow into it along its route to Macassar (Meek *et al*., 2009).

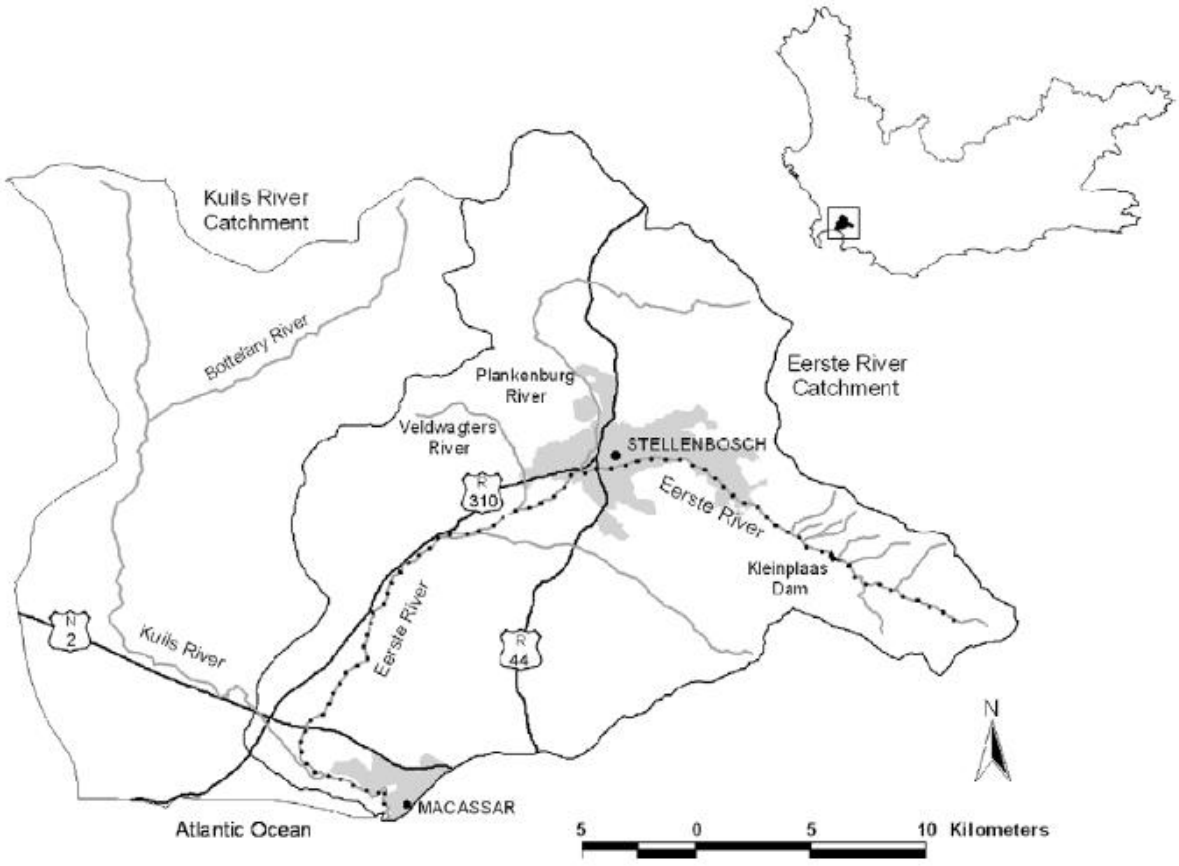


Figure 2.4.1: Eerste-Kuils catchment with its tributaries (extracted from Meek *et al.*, 2010)

In the landscape surrounding the Eerste River, one can find vineyards, orchards, crops, commercial forests, pastures, and habitations in highly urbanized areas. Stellenbosch, with a population of approximately 19 068 according to the 2011 census (StatsSA, 2020) is the main urban area along the river, with additional urban development present in Macassar (Meek *et al*., 2009). In the years since the European settlement, the Eerste River has experienced dramatic changes, similar to most rivers throughout highly developed areas. Humans have been using the river intensively since 1697, and over-abstraction became a problem as early as 1862 (Meek *et al*., 2013).

As the Eerste River flows through highly urbanized areas, it has been degraded to a great extent in terms of both water quality and aesthetic value. It can be assumed that the

degradation is mainly due to polluted urban storm water runoff and the release of sewage effluent into these rivers. Although the Eerste River forms part of urban developments, significant portions of the river are surrounded by agricultural lands. Therefore, the river has both urban and agricultural sources of non-point source pollution (Thomas *et al*., 2010).

The physical river system is in a poor state due to the discharge of influent into the river as multiple WWTW discharge effluent into tributaries which flows into the Eerste River, including the Macassar WWTW which discharges directly into the Eerste River estuary (Ngwenya, 2006). This leads to eutrophication caused by the extra nutrients entering the river systems from the WWTW. (Thomas *et al*., 2010).

Based on the data collected from the CCT's Inland Water Quality Monitoring Programme, the Eerste River's trophic state has significantly decreased over time and is currently among the worst-performing sub-catchments with respect to the trophic state. There has been a gradual increase of nitrogen enrichment over time in this sub-catchment. Furthermore, the sub-catchment consistently exhibits unacceptable toxicity levels, which have been associated with acute aquatic toxicity. A long-term trend has also been identified such as the increased proportion of measurements of Dissolved Oxygen that fall outside the acceptable range. Moreover, the majority of *Escherichia coli* (*E. coli*) measurements recorded at river sites in this sub-catchment from 2015 to 2020 fell within the poor to lower end categories of unacceptable levels for intermediate contact recreation in this sub-catchment (CCT, 2020).

Based on historical trends, Figure 2.4.2 below highlights the unacceptably poor trophic state of the Eerste River catchment in 2020.

Figure 2.4.2: Changes in the trophic state of the Eerste River catchment from 1985 to 2020 (extracted from CCT, 2020).

2.5. Overview of estuaries

Estuaries represent a transition zone between the freshwater and marine environments. The salinity in estuaries fluctuate often because of the state of the tide and the strength of river flow. Estuaries are frequently open to the sea year-round, but some are closed by sandbars during periods of low rainfall, when river flows are too weak to wash away accumulated sand (Breen and McKenzie, 2001; CCT, 2009).

Estuaries are systems with high biodiversity and they provide many environmental and socio-economic benefits. These benefits include protection from flood, providing raw building material, and being nurseries for juvenile fish. Estuaries also often serve as nodes for habitation and development (Republic of South Africa, 2013). Fauna and flora living in estuaries have adapted to survive the shifting conditions characteristic of estuaries. While evaporation from closed estuaries may result in extreme salinity, high freshwater input during floods can greatly reduce salinity. Estuarine fauna and flora can die in mass numbers when salinity levels exceed their tolerance range (Breen and McKenzie, 2001; CCT, 2009).

Although Cape Town's estuaries offer many benefits, intense development surrounds most of them, which has many negative effects. When the estuary closes, buildings located too close to the water's edge may be flooded. Also, stormwater runoff, industrial effluent and sewage effluent all contribute to nutrient overload and algae growth, along with toxic chemicals, heavy metals, and faecal matter pollution (CCT, 2009).

Furthermore, activities and development within the catchment area of estuaries may also have a negative effect (CCT, 2009). Runoff from farmlands may be polluted by nutrient-rich fertilisers and toxic pesticides (Pearce and Schuman, 1997; Mateo-Sagasta *et al*., 2017), while overgrazing and planting of crops too close to riverbanks may result in erosion which may increase the silt load in estuaries (Mateo-Sagasta *et al*., 2017). Large quantities of silt smother animals and inhibits plant growth by reducing light penetration in the water column (CCT, 2009). All of these, in conjunction with other impacts such as water abstraction (Pearce and Schuman, 1997) and alien plant invasion in the catchment area may result in the gradual shallowing of the estuary, or closure of the mouth (CCT, 2009). Thus, developing and utilizing natural resources within coastal zones needs to be economically, socially, and ecologically sustainable. Due to the impacts associated with development in the coastal zone, the National Environmental Management: Integrated Coastal Management Act (Act No. 24 of 2008) ("the NEM: ICMA") was established as a framework for integrated coastal and estuarine management.

South Africa has about 300 functional estuaries that are distributed throughout a ± 3200 km coastline of which 56 occurs along the Western Cape coastline (Van Niekerk *et al*., 2017). Of the 56 estuaries in the Western Cape, 16 occurs along the coastline of the City of Cape Town which stretches 307 km from near Silwerstroom on the west coast, around the Cape Peninsula and beyond False Bay to the Kogelberg coastal area in the east. With beaches that are world renowned for their beautiful landscapes and providing easy access to the outdoors, Cape Town's coastline is one of the CCT's most significant assets in terms of marine and coastal biodiversity. Therefore, to protect the city's coastline ecosystems and public health against coastal water pollution, effective monitoring of water quality is crucial (CCT, 2018a).

2.5.1. State of estuaries

In South Africa, 21% of estuaries are in a Natural state (A category), 40% in a Near Natural state (B category), 20% in a Moderately modified state (C category), 12% in a Heavily modified state (D category), and 7% in a Severely/Critically modified state. Based on the figures above, it appears as though more than half of South Africa's estuaries are in a relatively healthy state. However, this accounts for only 22% of total estuarine extent because the majority of these are small estuaries. More than 63% of the estuarine area has been significantly modified, putting important ecological processes under severe strain (Van Niekerk *et al*., 2019).

In the Western Cape, the predominantly closed estuaries along the West Coast were in a good state in 2017, while the larger permanently open estuaries were in a fair state. Contrastingly, the numerous small temporarily open/closed estuaries around Cape Town were generally in a poor condition. Estuaries along the south and south-east coast were in a better condition than those elsewhere in the country. Overall, only 5% of the estuaries in the Western Cape were in an excellent condition and an additional 26% in good condition. Unfortunately, due to the

majority of these estuaries being rather small systems surrounded in official protected areas, they only account for 4% of the estuary area in the province. Approximately 48% of all Western Cape estuaries were in a fair condition, representing more than 95% of the estuarine area in the province (Van Niekerk *et al*., 2017).

2.5.2. The Eerste River estuary

The Eerste River estuary characterises the point at which it flows into the ocean, and a Munitions factory and the Macassar Wastewater Treatment Works (WWTW) are located on the eastern and the western banks respectively. In addition, the Stellenbosch WWTW discharges effluent via the Veldwachters River, into the Eerste River (Thomas *et al*., 2010). As a result, this river receives treated effluent from various WWTW in its catchment as well as chemical waste from industrial drains. According to Van Niekerk *et al*. (2017), the approximate daily outflow of the Macassar WWTW is 26 400 m^3 per day. Historically, the Eerste Estuary was temporarily closed, and the inflow of seawater created estuarine conditions up to 2.5 km upstream from the mouth. However, discharge from municipal WWTWs along the Eerste River resulted in the mouth being permanently open, and since seawater penetrates only 500 m into the estuary under specific mouth and river flow conditions, there is limited tidal influence (Van Niekerk *et al*., 2019).

Based on the National Biodiversity Assessments (NBA) conducted in 2011 and 2018, the Eerste estuary Present Ecological State (PES) has not declined nor improved as the PES of the estuary has remained an “E” which means that the estuary has been Severely/Critically modified (Van Niekerk and Turpie, 2012; Van Niekerk *et al*., 2019). It should be noted that according to the NBA of 2011 and 2018, the recommended PES for the estuary is also an “E”. This is probably due to the following reasons:

- Flow modification due to multiple WWTW discharge (Van Niekerk and Turpie, 2012; Van Niekerk *et al*., 2019)
- Catchment hardening (Van Niekerk and Turpie, 2012; Van Niekerk *et al*., 2019)
- Water pollution due to malfunctioning WWTW (Van Niekerk and Turpie, 2012; Van Niekerk *et al*., 2019)
- Habitat loss (Van Niekerk and Turpie, 2012; Van Niekerk *et al*., 2019)
- Presence of invasive plants and fish (Van Niekerk *et al*., 2019)

2.6. Water quality guidelines

The DWS, then called the Department of Water Affairs and Forestry (DWAF) developed a set Water Quality Guidelines in 1992, which was thereafter updated in 1995. These were known as the South African Water Quality Guidelines (DWS WQG). These were used to inform water users about the physical, chemical, biological, and aesthetic properties of water. Therein, how to achieve the Target Water Quality Range (TWQR) is described along with additional information, such as what happens in the aquatic environment, and how these happenings affect the water quality (DWAF, 1996).

There were WQG developed for seven sectors, namely Domestic Water Use (Volume 1), Recreational Water Use (Volume 2), Industrial Water Use (Volume 3), Irrigation Water Use (Volume 4), Livestock Watering (Volume 5), Aquacultural Water Use (Volume 6), Aquatic Ecosystem (Volume 7). The TWQR for all these water-use sectors are summarised in Volume 8 (DWAF, 1996). For the present study, volume 7 was of importance. Within it, thresholds were provided for physico-chemical properties, nutrients, organic and inorganic substances, and metals. However, only ten metals were included, consequently there was little information available for some metals.

DWAF developed a set of four Water Quality Guidelines in 1992, which were thereafter updated in 1995, and were aimed at managing coastal and marine water quality for designated uses, namely Volume 1: Natural Environment, Volume 2: Recreational Use (updated and re-launched by the DEA in 2012), Volume 3: Industrial Use, and Volume 4: Mariculture. Volumes 1 and 4 have been updated and have culminated in the South African Water Quality Guidelines for Coastal Marine Waters - Volume 1: Natural Environment and Mariculture Use, 2018, (DEA WQG) with the objective of maintaining water bodies in a state that is fit for designated water uses. These guidelines identify various contaminants which are regulated (a threshold is set), and when complied with, should achieve optimal water quality (DEA, 2018).

The DEA WQG provides guidelines for physico-chemical properties, nutrients, organic and inorganic constituents, human pathogens, and metals. The DEA WQG boasts that it provides guidelines for 57 properties and constituents compared to the 1995 DWS WQG only providing guidelines for 29 properties. However, it should be noted that there is a vast array of metals that are environmentally hazardous, but the DEA WQG only provides guidelines on nine metals, namely arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver and lead (DEA, 2018).

2.7. Municipal jurisdiction

The Eerste River flows through two municipalities, namely the CCT Municipality in its lower reaches, and the Stellenbosch Municipality (SM) in its middle to upper reaches.

According to the Stellenbosch Municipal Spatial Development Framework (SM SDF), 2019, the Eerste River is one of two rivers that are important river systems in the municipality as it is a source of water, recreation, cultural experiences and assists with stormwater drainage. The upper section of the river is in a relatively pristine condition, while the middle reaches are surrounded by cultivated lands and urbanised areas. This has resulted in the middle reaches of the river being largely modified and degraded (SM SDF, 2019).

The 2019 SM SDF further highlights the need to clean polluted rivers. This not only applies to the Eerste River, but also to the polluted tributaries which flow into the Eerste River such as the Plankenburg River. However, the SM SDF does not indicate what measures will be

implemented to clean polluted rivers. In addition, the latest Stellenbosch Municipal Integrated Development Plan (SM IDP), 2021 highlights the poor state of rivers in the municipal area as a spatial challenge. The 2021 SM IDP reflects that majority of SM's infrastructure related expenditures went towards Wastewater Management; road transport; planning and development; and water, whereas environmental protection received the lowest allocation. The SM IDP (2021) further reflects that the SM has "undermined the value of biodiversity and its impact on valuable ecosystem services such as clean air, water and cultural benefits". Furthermore, SM has the Water Services By-Law, 2017, which regulates discharges into stormwater systems and rivers, among others.

As mentioned, the lower reaches of the Eerste River also flow through the CCT jurisdiction, and the status of the river and estuary has been highlighted in previous sections. The 2018 CCT SDF notes that the biophysical environment delivers important ecological services such as stormwater drainage and protection to people from coastal hazards. This is highlighted, as the CCT SDF contains a spatial strategy aimed at creating a balance between urban development and environmental protection.

The CCT also planned to enhance the wastewater treatment capacity at various WWTWs to ensure a healthy environment in downstream rivers in Cape Town and noted the need for investment in a regional facility for effective treatment of sludge (CCT SDF, 2018b). In addition, the CCT has the Wastewater and Industrial Effluent By-Law, 2013, which controls activities linked to the disposal of wastewater and industrial effluent in the CCT.

Since the Eerste River flows through two municipalities, a cooperative governance approach could be advantageous for managing the river. The term governance refers to the management of a society and its economy as well as how its institutions, organizations, and policies are managed. As understood in political science, the concept of governance refers to the shift from state government to multi-level government by civil society and private actors, as well as the creation of a division of authority and responsibility (Graversgaard *et al*., 2018). This concept can give rise to a cooperative governance model, in which society is directly involved in government decisions. Cooperative governance can therefore be viewed as multi-level and polycentric, with responsibilities assigned to whichever scale is most appropriate in light of existing responsibilities, local differences, and the size of the problem. A cooperative governance process is characterized by moving from hierarchical governance and the exercise of power by governments to more complex forms of relationship governance that occur within layered networked mechanisms that are collaborative in nature (Graversgaard *et al*., 2018).

In order for environmental governance to be effective, stakeholders need to interact within and across levels of government. Although departments and organizations are involved in the environmental governance process, inefficient cooperation has often been a problem due to the number of departments and organizations involved. The fragmentation of government has

additionally led to multifaceted solutions, including intergovernmental collaboration, interlocal consolidation, and interjurisdictional agreements. Network governance takes a holistic approach to implementing public policy through the development of relationships among governments, businesses, and civil society (Huang *et al*., 2017).

In light of the above, collaborative governance between these two municipalities would be beneficial to the management of this river. Although this is the case, no literature exists describing such collaborative governance.

2.8. Wastewater treatment works in Cape Town and related case studies

There are 26 wastewater treatment works (WWTWs) in Cape Town, but the CCT only reports on 17 WWTWs. The CCT uses the General Authorisations of the NWA, which are specifications established by the national Department of Water and Sanitation (DWS). These specifications are intended to safeguard the natural environment and health of anyone who may encounter the wastewater. At present, the CCT measures up to 32 parameters in treated effluent. In terms of monitoring, eight parameters are of primary importance to the CCT: namely pH, suspended solids, conductivity, ammonia, chemical oxygen demand, orthophosphates, nitrates, nitrites, and *E. coli* (CCT, 2018a).

As of 2016, the CCT had an 84.85% overall compliance rate. Since some WWTW had low compliance with standards, the CCT declared that in order to reach this level of overall compliance, certain WWTWs would have to achieve very high compliance results. Four sites showed overall compliance levels between 50% and 69%, three sites obtained between 80% and 89%, one site between 70% and 79%, and nine of the 17 treatment works achieved an overall compliance over 90% (CCT, 2018a).

A study conducted by Reinecke *et al*. (2003) reported the presence of lead and cadmium in the Eerste River and had suggested effluent discharges from sewage treatment plants and industries as possible routes of lead into river systems. In addition, a study undertaken by Olujimi *et al*. (2015) assessed the heavy metal variability in river water receiving effluents in Cape Town. Although the study did not specifically examine the Eerste River, it did study two of its tributaries, namely the Kuils River and the Veldwachters River. The results showed that cadmium and arsenic levels were higher than the water quality thresholds required to preserve aquatic life. Additionally, both the standards for human consumption and the preservation of aquatic life were breached by lead and mercury concentrations. The study also found that levels of metals in the river systems were higher upstream and downstream compared to the WWTP discharge points. The study concluded that the WWTPs might not be the sole pollution source of the river systems in the CCT as waste dumping along the river course, indiscriminate wastewater discharge from industries, storm water runoff from agricultural lands, and grey and domestic wastewater may also pollution sources.

Another study undertaken by Olujimi *et al*. (2016) compared the removal effectiveness of heavy and trace metals from wastewater treatment plant effluents in Cape Town and Stellenbosch, as well as the variation in metal levels. WWTWs included in the study were Athlone WWTW, Bellville old and new WWTWs, Kraaifontein WWTW, Potsdam WWTW, Stellenbosch WWTW, and Zandvliet WWTW. Water samples were collected from the WWTWs for a year in 2010 on a quarterly basis, and a total of 432 water samples which consisted of raw sewage, primary effluent, secondary effluent and final effluents were collected and analysed. The study found that final effluent concentrations for most of the metals were below the thresholds set by the South African water quality guidelines while As, Hg, Cd and Pb concentrations exceeded the maximum limits set by the Canadian Council of Ministers of the Environment. The WWTW which was most effective at removing heavy metals from the effluent was the Potsdam WWTW. Although the Macassar WWTW wasn't included in the study, the Stellenbosch WWTW discharges into the Eerste River tributary called the Veldwagters River, and the Bellville WWTW; Kraaifontein WWTW; and the Zandvliet WWTW discharges into the Eerste River tributary called the Kuils River.

It is the purpose of wastewater treatment systems to eliminate toxic pollutants and to maintain a clean environment to protect humans and other of organisms (Muga & Mihelcic, 2008). It is evident that industrialization has a negative impact on the environment, as demonstrated by the slow deterioration of the environment and the severe degradation of water quality (Chan *et al.*, 2009). Effluent discharges with relatively high quantities of trace metals are released into rivers and oceans as a result of WWTWs' incapacity to remove trace elements. As a result, it is critical to regularly monitor and remove trace metals from the environment, especially in WWTWs that discharge wastewater into various water bodies (Dimpe *et al.*, 2017).

Water quality is at risk not only from point sources of pollution, such as the return flows from WWTW, but also from non-point sources. Non-point sources are more difficult to identify and monitor than known point sources, which makes allocating costs to individual contributors for addressing these increasing water quality risks more challenging. The contamination of downstream water quality by greywater runoff from informal settlements is of growing concern. In South Africa, water quality risks are a growing concern, therefore, novel approaches are required to either treat the issue at its root or, alternatively, undertake physical and ecological interventions to lessen its effects (Cullis *et al*., 2018).

Trace metals can be removed using a number of technologies including ion-exchange, adsorption, membrane filtration, chemical precipitation, and chemical treatment. Among the above-mentioned techniques, adsorption tends to be preferred due to its flexibility and effectiveness. Scientists have extensively explored adsorbents such as carbon nanotubes and activated carbon for the removal of toxic contaminants from the environment (Al-Saadi *et al*.,

2013). These methods have many drawbacks, and environmentally friendly, cost-effective alternatives are needed.

Nyamukamba *et al*. (2019) conducted a study to evaluate physicochemical parameters, heavy metals, and antibiotics in the influents and final effluents of South African WWTWs. The study evaluated treated wastewater effluent quality of three wastewater treatment plants in South Africa's Vaal Triangle: Sebokeng, Rietspruit, and Leeuwkuil. Results showed that Leeuwkuil had an overall removal efficiency of 30%, while Rietspruit had a removal rate of 20.62% and Sebokeng had a removal rate of 17.32%. Individual metal removal efficiency was typically quite poor, most likely as a result of treatment plants operating under stress, poor design, and capacity overload. The treatment plants of Sebokeng and Leeuwkuil handle more water than they are designed to treat.

In light of the limitations imposed by most municipalities in terms of finances and technology, it is essential to consider alternative urban water systems that minimize wastewater generation or consider more effective, more appropriate treatment methods. To deter non-essential use of potable water, it would be wise to seek dry sanitation (or composting toilets), encourage greywater reuse by industry and agriculture, require the use of biodegradable detergents, or re-examine the water tariff structure. Investigating alternative treatment methods such as passive treatment, fresh methods for recovering energy, water, and nutrients, may also prove beneficial (Cullis *et al*., 2018).

2.8.1. Macassar WWTW

Originally, the Eerste River was a highly seasonal river, and the estuary was closed during summer months by a wind and wave-built sand bar which only opened with the first winter rains. The effluent discharged from the Macassar WWTW has contributed to the changed hydrological character of the river since it is now a perennial river and the estuary is open throughout the year (Thomas *et al*., 2010).

The State of Cape Town Report 2018 (CCT, 2018a) reported that the Macassar WWTW was one of 12 WWTWs that are equipped to produce treated effluent suitable for reuse. However, the same report identified the Macassar WWTW to be one of the lowest performing WWTW in terms of compliance with the NWA specifications since the plant scored of the lowest for Suspended Solids (44% compliance), Chemical Oxygen Demand (27% compliance), Ammonia (7% compliance), and *E. coli* (20% compliance).

2.9. Riverine pollution/contamination

Streams and rivers provide valuable freshwater resources, amenity, and economic development as well as important habitats for nature conservation and recreation (Feng, 2005). Riverine landscapes also provide vital ecosystem services such as clean water, energy, and transport (DEA&DP, 2005). A river (both the main course and its tributaries), is a

multifaceted ecological system carrying a significant load of matter, in various phases, from both natural and anthropogenic sources towards the sea. Rivers and their catchments play major roles in the social and economic development of their regions in which they are located and have been utilized by humans for many centuries (Feng, 2005). However, the majority of freshwater ecosystems around the world are experiencing some sort of change or decline. The majority of this tendency can be attributed to human activity. Few rivers in South Africa still serve their original purpose or maintain their ecological integrity, and the conservation status of freshwater ecosystems is low and rapidly diminishing (DEA&DP, 2005).

As the catchment's geological topography, vegetation, and land use (as modified by human endeavours like agriculture, industrialisation, and urbanization) change, so may the quality of the river. Nutrients, hazardous compounds including organic and inorganic pollutants, as well as other chemicals like heavy metals, are released by industries, agriculture, and urban areas (Feng, 2005). Water pollution in rivers occurs when these substances enter the waterways and alter their natural function thereby degrading the water quality of a river (Water and Rivers Commission, 1997). These pollutants can enter a riverine system from a range of land uses across its catchment. Some pollution comes from sources which can be identified such as a factory discharging its wastes into a drain and are called “point” source pollution. However, many pollutants can enter a water body from a wide area, such as fertilizers used throughout a farming area. These are called “non-point” or “diffuse” source pollution, and they are harder to manage (Water and Rivers Commission, 1997).

Numerous issues are brought on by the pollution and depletion of water resources, including a negative influence on aquatic life and the recreational value of inland water. In addition, it becomes very costly to treat such water for potable, irrigation, recreational or domestic use. Furthermore, metal pollution and manmade organic substances like pesticides and herbicides negatively affect both human and animal health (DEA&DP, 2005).

Freshwater systems in the CCT are mostly affected by improperly treated wastewater effluent, overflows from clogged or leaking sewer systems, broken pumps, and tainted stormwater (CCT, 2016). Major contributors to pollution and contamination include the rapid spread of informal settlements, the rate of urbanization, and the rise in backyard habitations. Inappropriate human waste discharge into rivers and drains as well as generally filthy runoff from informal settlements are the results of this (CCT, 2018a). Additionally, reckless, and illegal dumping of domestic waste and construction debris into open-space areas, rivers, wetlands, and the stormwater system results in additional issues. These types of riverine contamination can endanger aquatic life, freshwater ecosystems, as well as public health (CCT, 2016).

Furthermore, non-storm water discharged by stormwater drainage systems contributes significant pollution to urban waterways with adverse impacts on water quality and aquatic

ecosystems. As a result, eliminating these discharges has the potential to play an important role in improving water quality (Owusu-Asante, 2020).

In terms of estuaries, in the CCT more than 215 700 m^3 of wastewater is discharged into, or just above, estuaries daily from numerous municipal WWTWs. A comparison of data from 1991 and 2017 shows that WWTW discharge volumes to estuaries have more than doubled, indicating rapid population growth in coastal areas. Even though the majority of these discharges are treated, many of the WWTWs are malfunctioning, resulting in pollution in estuaries such as the Eerste estuary (Van Niekerk *et al*., 2017).

Coastal water that has been polluted may have detrimental effects on the health of humans in contact with the coastal waters and near-shore marine ecosystems. Other potentially dangerous pollutants that could have a negative impact on the delicate near-shore coastal ecosystems may also be present in these waters. In order to protect human health, the DWS has suggested coastal recreational standards, which have been enforced for a while. However, the Department of Forestry, Fisheries, and the Environment (DFFE) has been given the authority to manage coastal and marine waters and has proposed a new set of recreational guidelines, which coastal municipalities are gradually implementing (CCT, 2018a).

A study conducted by Wen *et al.* (2017) assessed organic pollutants of rivers around the globe. The study reviewed the current global trends resulting in river pollution and undertook horizon scanning to recommend solutions to the identified problems. The study findings highlight several threats, such as urbanization and intensification of livestock farming, as well as climate change and water extraction reducing river dilution capacity. If untreated wastewater is discharged into the environment, it releases pathogens which cause disease. Other organic pollutants found in treated effluent may accumulate and disturb entire river systems. Livestock farming also adds organic pollutant loads into rivers. The study also found that developing countries were disproportionately affected by these threats.

Kipyego and Ouma (2018) undertook an analysis of non-point source pollution loading on water quality in an urban-rural river catchment using GIS-based Pollutant Load (GIS-PLOAD Model) in the Sosiani River Watershed in Kenya. The area is characterised by four land uses and cover types such as agriculture, grassland, forest, and developed areas. The study showed that in the developed areas, 90% of rainfall ended up as runoff due to the paved surfaces, thereby carrying pollutant material into streams. There were also high levels of waste generation, gaseous automobile emissions, domestic detergents discharge, sewage and wastewater discharge from treatment works, and raw and septic leaks from poorly kept slums, further contributing to higher pollutant levels in the developed areas. Agricultural and forest land had low levels of pollution. Moreover, agricultural farms utilised fertilizers which also leaked into streams.

Cullis *et al*. (2018) investigated the economic risks caused by the decline in the water quality of the Breede River catchment. The study showed that there are many risks to the water quality such as intensive agriculture and urban development. These have resulted in many water quality problems such as increased salinity, nutrient enrichment, the presence of microorganisms, and agrochemicals. In addition, there are 18 WWTW in the Breede River Catchment. The Breede-Gouritz Catchment Management Agency (BGCMA), which has been monitoring water quality at several sampling points since 2010, provided water quality data. Electrical conductivity, pH, sodium, total suspended solids, ammonia, nitrate & nitrite, chemical oxygen demand (COD), ortho-phosphate, fecal coliforms, *E. coli*, fecal streptococci, turbidity, potassium, and total dissolved solids are all measured monthly in water samples. From the water quality data, the high levels of phosphorus along the full length of the river, and the high levels of COD was of concern. The study suggested that it may be due to WWTW effluent and non-point source pollution.

Verlicchi and Grillini (2020) collated water quality results from 44 peer reviewed papers published between 2001 and 2019 to review the surface and groundwater quality in South Africa and Mozambique, as well as the most critical pollutants for drinking purposes. Parameters monitored included macropollutants, inorganic chemicals such as heavy metals, microorganisms, micropollutants such as pharmaceuticals and pesticides, and polycyclic aromatic hydrocarbons (PAHs). For South Africa, the study found that nitrites and heavy metals such as Fe, Al, Zn, Cd, Cu, Ni, and As were found at high concentrations. The mining industry, stormwater runoff, and agricultural drains were highlighted as possible sources. Pathogenic bacteria such as *Vibrio cholerae, Aeromonas hydrophila, Shigella, Plesiomonas shigelloides*, and *Salmonella* were also found in high concentrations in the surface water. Land runoff from grazing animal areas where manure may be applied to the soil and untreated rural and zootechnical wastewater may be directly released into water bodies were identified as potential sources.

2.10. Metals

Pollution of the environment is one of the main issues facing contemporary society. Different activities introduce various types and concentrations of contaminants into the ecosystem, which have varying effects on river health (Street, 2008). In addition to their toxicity, heavy metals are bioaccumulative pollutants and persist in the environment for long periods of time. Heavy metals can enter the environment through natural means as well as anthropogenic activities. Weathering of metal-bearing rocks is one of their natural sources, whereas anthropogenic sources include mining and other industrial and agricultural activities (Ali *et al*., 2019). Since the 1940s, heavy metals have been mobilized and transported in the environment at an accelerated rate due to rapid industrialization and urbanization, according to these authors. In addition, urbanisation is one of the major factors relating to heavy metal

contamination in water bodies as it leads to an increase of impermeable surfaces associated with expansion of housing, roads, and business areas. As stormwater runoff collects pollutants from paved areas, it carries them to streams, rivers, wetlands, and other water bodies. These pollutants include metals, oils, grease, yard chemicals, dirt, bacteria, nutrients, and other pollutants. Stormwater runoff results from the replacement of forests and other natural areas with hard surfaces like roads, pavement, and roofs (Thomas *et al*., 2010).

Heavy metals are among the most common industrial pollutant by-products. The persistence of these chemicals in the environment, along with their potential toxicity and ecotoxicity, can have a significant impact on the environment (Table 2.10.1) (Street, 2008). Industrial processing and their ensuing use for commercial, agricultural, and economic growth have resulted in an increase of heavy metals in the environment, disturbing the biogeochemical cycles. Heavy metals, as persistent pollutants, can accumulate in the environment and have the potential to contaminate food chains, as the accumulation of potentially toxic heavy metals in biota poses a health risk to their consumers, including humans (Ali *et al*., 2019). A general pathway for the transport of metals can be summarized as shown in Figure 2.10.1.

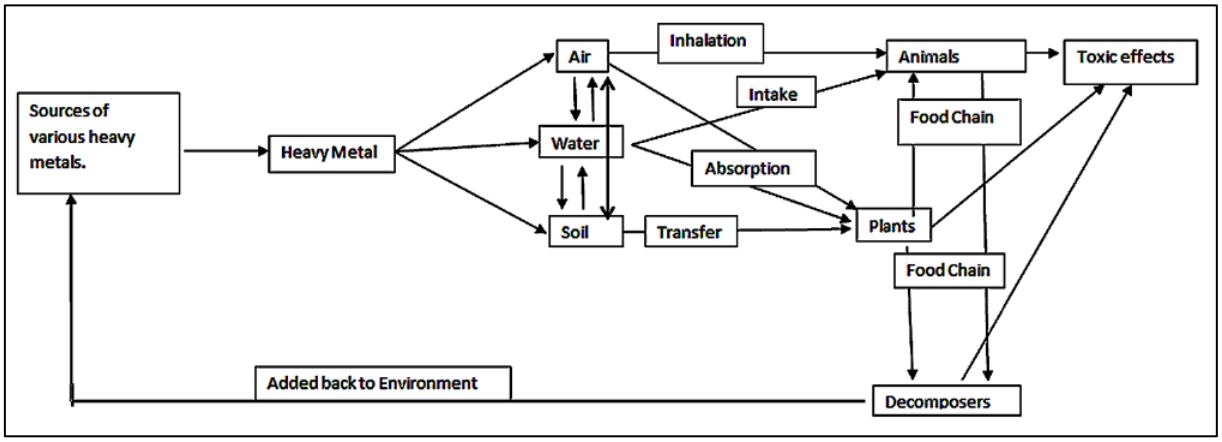


Figure 2.10.1: Pathway representing transport of metals through biotic and abiotic systems (extracted from Sharma *et al*., 2015).

According to Ali *et al*. (2019), environmentally relevant and hazardous heavy metals and metalloids include chromium, nickel, copper, zinc, cadmium, lead, mercury, and arsenic. However, all heavy metals have the potential to be hazardous to biota, which includes humans, animals, plants, and microorganisms, if present in high amounts (Weber and Karczewska, 2004). Heavy metals that enter a waterbody, such as a river, can harm aquatic organisms, and accumulate in the waterbody's sediments through chemical adsorption and physical precipitation processes. When environmental conditions in the water or sediments change, such as pH, electrical conductivity (EC), oxidation reduction potential (ORP), and chemical oxygen demand (COD), these metal compounds can be released from the sediments and cause harm to the water environment (Zhang *et al*., 2015). Furthermore, according to Zhang *et al*. (2015), it is crucial to look at the heavy metal contents of both the sediments and the

waterbody since heavy metal contents in sediments are typically substantially higher than those in water.

The study conducted by Zhang *et al*. (2015) aimed to identify sources of metal contamination in the Bortala River, Northwest China by sampling surface sediments. Results of the study showed that certain metals (Cu, Ni, As, and Zn) originated from natural geological environment, and other metals (Cd, Pb, Hg and Cr) originated from anthropogenic activities, albeit at lower concentrations. However, another study by Liao *et al*. (2016) investigated metal contamination in the Maba River, South China and discovered that human activities like smelting and mining are the primary sources of the heavy metals detected in the sediments of the Maba River. In addition, Xu *et al*. (2018) conducted a study to reassess sources and risks of metal pollution in riverine sediments of Hainan Island in China. Heavy metals that accumulate in sediments can be used as an indicator for assessing pollution. In this study, Cr, Ni, Cu, Zn, As, Cd and Pb was measured. According to the study's findings, heavy metals have impacted the sediment quality of Hainan Island, which is likely to have a negative biological impact on local ecosystems. The most severe pollution occurred on northern and eastern Hainan Island, and it was primarily caused by anthropogenic sources as a result of social and economic development.

Metals found in agricultural soils as a result of anthropogenic activities such as mining have been identified as a potential threat to human health via the food chain in a study conducted by Marrugo-Negrete *et al*. (2017). The concentration of heavy metals in 83 agricultural soils irrigated by the Sin River in Northern Colombia was investigated in this study, and results identified mining areas upstream of the river to be the source of metal contamination. It is evident that metal contamination in rivers can have various sources. Hence identifying the main sources of contamination can aid in identifying proper management interventions for rivers.

Duncan *et al*. (2018) assessed heavy metal pollution in the Pra River and its tributaries in Ghana. The Pra River is used by villages along its route for domestic purposes, however, it has been impacted on by illegal mining activities. In this study, 216 water samples were collected from the Pra River and its two tributaries in the dry and wet season in 2017. Nine heavy metals were assessed with five of those exceeding safe drinking water guidelines making it unsafe for domestic purposes. Six metals (Pb, Cd, Cr, Ni, Fe, and Zn) were the principal metal pollutants in both the dry and wet seasons. However, Mn, As, and Cu were found in the rivers, but did not to contribute to the pollution effect.

In South Africa, specifically the Western Cape, a few studies have been carried out to investigate metal contaminants in water bodies. Sparks *et al*. (2017) published a study in which metal concentrations in intertidal water and surface sediment along the west coast Cape Peninsula in Cape Town. It was found that the source of the metal contaminants was because

of localized anthropogenic and natural rock weathering. Furthermore, it was found that the metal concentrations at the sites investigated in the study were like those reported in 1985 for the same sites. The study suggested that the intertidal environment in Cape Town has not been progressively contaminated with metals.

Moloi *et al*. (2019) assessed the potential health risks for humans exposed to river systems that receive effluent from WWTW. Treated and untreated effluent was collected from Maluti-a-Phofung municipality. The results showed that there were no significant differences between treated and untreated effluent, indicating the inability of the WWTW to adequately remove heavy metals.

Another study conducted by Sparks and Mullins (2016) investigated metal concentrations in the Helderberg Marine Protected Area (MPA) in False Bay, Cape Town. Certain areas are declared protected areas to protect it from anthropogenic impacts, and thus it is assumed that protected areas are free from these anthropogenic impacts. The Helderberg MPA is surrounded by urbanisation, as such, this study tried to ascertain whether metals from surrounding areas impact on protected areas. This was done through sampling and analysis of water, sediment, and mussels from the Helderberg MPA. Results showed that metal concentrations were higher than sediments for As, Mo, Cd, Cu and Fe which were like those found in areas adjacent to the MPA. Metal concentrations were also higher than in coastal waters. The study suggested that the MPA was exposed to contaminants from areas outside of the MPA. The study further suggested that coastal dynamics and longshore movements may be responsible for this. In addition, metal concentrations in sediments may be caused by sediments settling from the surrounding industrial area and domestic effluent release into False Bay.

A further study was conducted by Zhou *et al*. (2020) in which concentrations and sources of heavy metals in global river and lake bodies from 1927 to 2017 were investigated. Twelve heavy metals were investigated from 168 rivers and 71 lakes. Results showed that heavy metal with concentrations above threshold limits for World Health Organisation (WHO) and United States Environmental Protection Agency (USEPA) have generally increased over the span of the five decades. Additionally, the findings indicated that heavy metal concentrations above WHO and USEPA threshold levels were lower in industrialized nations and greater in poor nations. Rock weathering and waste discharge have replaced mining and manufacture as the primary sources of metal pollution.

The toxicity of heavy metals in water resources is a serious environmental concern that adversely affects plants, animals, and humans. Overly high levels of metals in soil can disrupt the microbiological balance and reduce the soil fertility. There may be adverse effects on animals and humans due to bioaccumulation of heavy metals in riverine ecosystems. Increased levels of heavy metals in biota can adversely affect the ecological health of aquatic

animal species and contribute to their population declines (Ali *et al*., 2018). More details on the impacts of metals on human and environmental health are provided in Table 2.10.1.

Table 2.10.1: The uses and impacts of metals on human and environmental health

Name	Use/s	Effects / impacts on Human health	Effects / impacts Environmental health	Reference/s
Chromium	Medical and dental implants Appliances and tools Natural human lipid and protein metabolism Common alloying component Leather and dye industry	Genotoxic Carcinogenic Acute respiratory challenges Acute dermatitis	For aquatic flora: Uptake in plants can result in decreased germination, growth reduction, photosynthesis impairment and oxidative imbalances. For aquatic fauna: Fish are most resistant to chromium toxicity, while daphniids and green algae are more sensitive than fish.	Achmad *et al.* (2017) Ertani *et al*. (2017) DWAF (1996)
Copper	Fungicides and pesticides Iron and steel industry	Induction of non-oxidative stress, DNA damage and reduced cell proliferation. Neurogenerative disorders	For aquatic fauna: Can cause brain damage in animals. Can damage DNA plasmids and affect embryo hatching of aquatic organisms.	DWAF (1996) Keller *et al*. (2017) Pohanka (2019) Royer *et al.* (2020)
Zinc	Metal galvanising Dye and pigment industry Pharmaceuticals Fertilizer and insecticide	Possible cytotoxic and genotoxic characteristics to certain types of cells (such as neuronal and epithelial)	Aquatic fauna may have oedema and liver necrosis as well as depressed white blood cell-thrombocyte counts. Invertebrates can have reduced shell growth rates, oxygen uptake and larval development. Inhibition of algal photosynthesis.	DWAF (1996) Król *et al*. (2017) Ng *et al*. (2017)
Cadmium	Manufacturing industry	Cancer Organ system toxicity Genotoxicity Interference with mitochondrial electron transport chain	For aquatic fauna: Teratogenic Mutagenic Carcinogenic	DWAF (1996) Rahimzadeh *et al.* (2017) Zwolak (2020)

Table 2.10.1 (continued)

Lead	Food canning industry Agrochemicals Metal industry Petro-chemical industry	Carcinogenic Genotoxic Affects cognitive performance in infants and children In adults, it causes cardiovascular, central nervous system, kidney, and fertility problems	For aquatic fauna: Interference with haemoglobin synthesis Interference with energy metabolism	DWAF (1996) Engwa *et al.* (2019) Kumar *et al.* (2020)
Cobalt	Alloys, especially superalloys Chemicals and ceramic production Cemented carbides and steels	DNA damage Carcinogenic Respiratory, cardiac, haematological, dermal, and neurological effects	Inhibition of transport in plants Can disturb photosynthesis in plants Reduced fish growth	Javed (2013) Ma & Hooda (2010) Mahey *et al*. (2020) Uddin and Rumman (2020)
Nickel	Alloy production Electroplating Production of nickel-cadmium batteries Catalyst in chemical and food industry	Carcinogenic Epigenic alterations Lung fibrosis Kidney and cardiovascular disease Teratogenic	Alteration of soil properties and disturbance of soil microflora For aquatic fauna: Impaired respiration Cytotoxicity and tumour formation Potential reductions in growth and reproduction Alterations in energy metabolism	Brix *et al.* (2017) Engwa *et al*. (2019) Genchi *et al.* (2020)
Iron	Chlor-alkali industry Household chemical industry Fungicide and petro-chemical industry	Hepatic fibrosis Cirrhosis Hepatocellular cancer Cardiac disease Diabetes	Iron can induce oxidative stress on a cellular level in aquatic fauna Iron can disrupt cell membranes, proteins, pigments and even damage DNA, eventually leading to death of the organism Inhibit nutrient uptake in plants and affect their productivity	Bakker *et al.* (2016) Britton *et al.* (1994) DWAF (1996)

Table 2.10.1 (continued)

Aluminium	Paper, metal construction, leather, and textile industry Pesticides Pharmaceuticals	Oxidative stress Immunologic alterations Genotoxicity Peptide denaturation Enzymatic dysfunction Metabolic derangement	Interference with ionic and osmotic balance Respiratory problems in aquatic organisms Interference with calcium metabolism in aquatic organisms	DWAF (1996) Igbokwe *et al.* (2019)
Manganese	Steel industry Fertilizer industry Chemical industry	Neurological disease Disrupts ATP synthesis	Disturbance in various metabolic pathways e.g., central nervous system	DWAF (1996) Engwa *et al.* (2019) Pfalzer & Bowman (2017)
Boron	Fibreglass, porcelain, detergents, enamels, herbicides and fertilizers, metallurgy.	Headache, hypothermia, restlessness, weariness, renal injury, dermatitis, alopecia, anorexia, and indigestion	Cell wall alteration, gene expression and cell division alteration, metabolism alteration	ANZG (2021) Brdar-Jokanovic (2020) NIH (2021)
Vanadium	Steel alloy, ceramics, dyes and printing fabrics, superconducting magnets, medical industry	Gastrointestinal symptoms, hepatotoxic, nephrotoxic, can affect male fertility.	Nephrotoxicity Reproductive alterations Alterations in tissues and organs	Australian Vanadium, Ltd. (2021) Wilk *et al*. (2017)
Arsenic	Mining industry, pesticide and fertiliser production, metal processing, chemical industry	Cancer of the skin, bladder, and lungs Development effects Pulmonary and cardiovascular disease	Impaired sexual reproduction Metabolism disturbances Growth reduction	DWAF (1996) Lander (1998) WHO (2018)
Selenium	Paint, food processing, steel industry Pesticide, glass and ceramics, and dye manufacturing industry	Hypotension, tachycardia Nausea, vomiting, diarrhea, fatigue, and skin lesions Decreased cognitive function, weakness, paralysis, and death	Reproductive impairment (larval deformity or mortality) Adverse impact on growth	DWAF (1996) Nuttall (2006) USEPA (2016b)

Table 2.10.1 (continued)

Strontium	Fireworks and flares, magnets, glow-in-the-dark paints and plastics, toothpaste	Carcinogenic Bone marrow damage, anaemia Impaired growth in children	Birth defects Growth inhibition of algae Reproductive impairment in invertebrates	ATSDR (2004) Pacholski (2014) Royal Society of Chemistry (2021)
Molybdenum	Steel and alloy industry Lubricant, catalyst, pigment Animal husbandry and agriculture	Gout-like symptoms Poor bone health Decreased fertility	Adverse growth and survival Abnormal development	Advanced Refractory Metals (2019) Eisler (1989) Rowles (2017)
Mercury	Paint industry, the fungicide industry, the paper and pulp industry, medical and dental industries, and the electrical equipment industry.	Adverse development of child in utero and early in life Toxic effects on the nervous, digestive, and immune systems, and on lungs, kidneys, skin and eyes	Immune system alterations in fish Disruption of gill epithelium Reproduction inhibition Neurotoxic	DWAF (1996) Morcillo *et al*. 2017 WHO (2017)
Barium	Drilling muds in oil and gas industry, ceramics, paints, bricks, tiles. Glass, rubber.	Heart rate disorder, hyper or hypotension, muscle weakness, paralysis.	Insufficient data. Barium is relatively non-toxic to aquatic life due as its readily excreted.	Donald (2017) Verbruggen *et al*. (2020)
Tin	Iron plating Stabilisers in certain plastics and as wood preservatives Food industry as food packaging and utensils	Renal necrosis Skin and eye irritation Cholangitis of the lower biliary tract Hepatotoxicity and neurotoxicity	Mitochondrial inhibition Growth inhibition	Britannica (2021) Cooney (1988) WHO (2005) Winship (1988)
Antimony	Alloys, automotive clutch, and brake parts Production of flame retardant chemicals semi-conductor industry for certain silicon wafer and infrared detector productions	Respiratory irritation Pneumoconiosis Antimony spots on the skin Gastrointestinal symptoms Cardiotoxicity Pancreatitis	Insufficient information available	PS Analytical (2018) Sundar and Chakravarty (2010)

With the impacts of heavy metals present in the environment noted above, and the increasing awareness of the persistence and nature of heavy metals, there has been a growing interest in the development of measures to remediate the contamination. Conventional methods such as adsorption, electro-dialysis, precipitation, ion exchange and reverse osmosis have been widely used but have drawbacks. These drawbacks include slow and inefficient removal of metals, generation of contaminated sludge which require careful disposal, high energy involved in the processes, blockage of membranes (Kapahi and Sachdeva, 2019), heavy costs, changing of soil characteristics, disruption of soil flora, and development of secondary pollution issues (Genchi *et al*., 2020). As such, there has been a need to develop effective and cheaper technology to remove heavy metals with an eco-friendly approach. One such approach is bioremediation (Kapahi and Sachdeva, 2019).

Bioremediation transforms contaminants like heavy metals into less hazardous/non-toxic substances and/or removes toxic elements from contaminated environments using dead or living biomass (Kapahi and Sachveda, 2019; Wang *et al*., 2012). Due to the presence of highly toxic metals that can cause cell death when accumulating in cells, using living biomass for metal remediation may not be a viable solution. Contrary to living biomass, dead biomass (biosorption) is not affected by toxicity and does not require any growth medium or nutrition. In the presence of heavy metals on the surface, a passive process occurs without involving energy expenditure, independent of metabolic activity, until equilibrium is reached (Kapahi and Sachveda, 2019). The presence of these characteristics makes dead biomass suitable for *in-situ* bioremediation; this is because it is an effective method of removing metals from river water, has high economic and ecological benefits, and is free from secondary pollution (Anawar and Chowdhury, 2020).

Different types of bioremediation media also exist such as bacterial bioremediation (using bacteria such as *Pseudomonas, Desulfovibrio, Bacillus*, and *Geobacter*), phycoremediation (algal bioremediation), and mycoremediation (fungal bioremediation) (Kapahi and Sachveda, 2019). Aside from the use of microorganisms for remediation, plants can also be used (Wang *et al.*, 2012). This process is called phytoremediation and makes use of plants to purify contaminated soil, air, and water (Genchi *et al*., 2020). Phytoremediation is a better approach owing to its low costs and widespread acceptance, regardless of the location (Anawar and Chowdhury, 2020). It is an economical plant-based solution utilizing plants' natural capabilities of concentrating elements from the environment and metabolizing dangerous compounds (Genchi *et al.*, 2020).

CHAPTER THREE

MATERIALS AND METHODS

3.1. Site description

The Eerste River is located within Cape Town's Eerste River catchment which covers an area of 420 km^2. The Eerste River is a short river with an approximate length of 40 km and originates in the Jonkershoek Mountains. The source of the river lies 60 km east of Cape Town at an altitude of 530 m, from where it flows in a north-westerly direction towards the town of Stellenbosch. The river abruptly turns south at Stellenbosch, eventually discharging in the Atlantic Ocean in False Bay near Macassar (Meek *et al*., 2013). This can be seen in Figure 3.2.1.

The river is influenced by flows from several tributaries along its route such as the Plankenburg River in its middle reaches, and the Veldwachters, Blouklip, and Kuils Rivers in its lower reaches (Ngwenya, 2006). In addition, the Eerste River supports land uses such as agricultural areas with intensive irrigation and forestry, communal grazing, nature conservation, and is surrounded by industrial and highly urbanised residential areas (Meek *et al*., 2013).

3.2. Sampling

Sampling took place at five sites. The coordinates of these sites were determined with the aid of a Geographical Positioning System (GPS) device (Figure 3.2.1):

- Site 1 - Upstream of Stellenbosch area
- Site 2 - Downstream of the Blouklip and Plankenburg confluence areas
- Site 3 - Upstream of the Kuils-Eerste confluence area
- Site 4 - Downstream of the Kuils-Eerste confluence area
- Site 5 - The Eerste River estuarine mouth

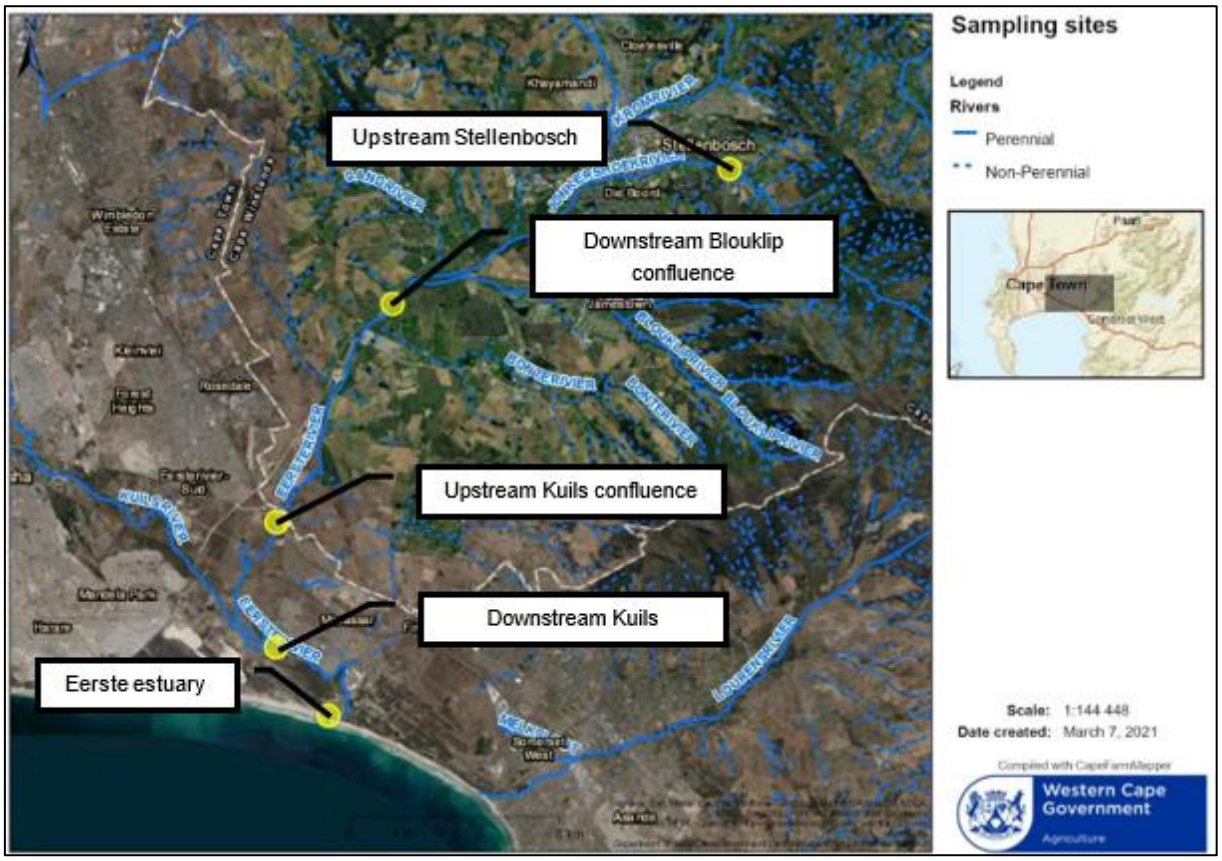


Figure 3.2.1: Sampling locations along the Eerste River (Cape Farm Mapper, 2021).

Five replicate samples of water and sediment were taken at each sampling site a few meters apart. Seasonal sampling took place once in the dry season (March 2021) and once in the wet season (August 2021).

Water samples were collected in polypropylene bottles and stored in a fridge at 4°C before analysis. Surface sediment samples up to a depth of 5 cm were collected using a sediment sampler and transferred to polypropylene bottles and stored at an appropriate temperature before analysis.

The mean monthly rainfall data for the study area during the study period (2021) were obtained from the South African Weather Services (SAWS) website.

In situ physico-chemical parameters were measured at each sampling site during these sampling occasions. These included pH, temperature, salinity, conductivity, dissolved oxygen, and total dissolved solids using the YSI Professional Plus multiparameter water quality meter shown in Figure 3.2.2.

Figure 3.2.2. YSI Professional Plus multiparameter water quality meter (taken from Van Walt, 2019)

3.3. Water and sediment analysis

Samples were prepared with an acid digestion procedure. The digested samples were taken to Stellenbosch University where metal analysis was undertaken, using an Inductively Coupled Plasma Mass Spectrometer.

3.3.1. Water digestion

Using a syringe, 10 ml of water from each of the collected replicates from each sampling site were placed in labelled test tubes. Heating blocks were pre-heated at 40°C. With a syringe, 5ml of nitric acid (65%) was added to the water samples as well as to the “blank” (test tube with only the 5 ml nitric acid and no water sample, to control for possible contamination). The test tubes were then placed into the heating block, which was at 40°C for 1 hour. After one hour at 40°C, the temperature of the heating blocks was increased to 120°C and the samples kept in the blocks for a further 3 hours. Labels were placed on volumetric flasks, pill vials and centrifuge tubes for each sample as well as the “blank”. A glass funnel with a Whatman No. 6 (90 mm) filter paper was placed into each volumetric flask. After the 3 hours at 120°C, the test tubes were removed from the blocks and the samples could cool. Once cooled, the samples were filtered through the filter paper into the respective labelled volumetric flasks. Distilled water was added to dilute the samples to 20ml. The liquid was then poured into a syringe and slowly squeezed through the filter nozzles containing 0.45 micrometer (µm) cellulose nitrate membrane filter paper into the correctly labelled pill vials. A 2 ml subsample was transferred into a labelled centrifuge tube with the use of a pre-set micropipette. The samples were diluted to 10 ml each using distilled water and stored in a refrigerator ready to be transported for analysis.

3.3.2. Sediment digestion

The replicate sediment samples from each of the sampling sites were dried in an oven for 48 hours at 60°C. The dried samples were then sieved prior to being weighed. Using a balance,

0.2-0.3 g subsamples were taken from the dried sediment. The weighed sediment subsamples were placed into labelled test tubes. A “blank”, which did not contain sediment, was also prepared. The heating blocks were pre-heated to 40°C and then 10 ml of nitric acid (65%) was added with the use of a syringe to each of the subsamples and the blank. The samples were then heated at 40°C in the heating block for one hour, thereafter to 120°C for three hours. Labels were placed on volumetric flasks, pill vials and centrifuge tubes. A glass funnel with Whatman No. 6 (90 mm) filter paper was placed into each of the volumetric flasks. After 3 hours, the test tubes were removed from the blocks and allowed to cool, then filtered through the Whatman No. 6 filter paper into the labelled volumetric flasks. The samples were then diluted to 20 ml with distilled water. Thereafter, the samples were poured into a syringe and slowly squeezed through the filter nozzles containing 0.45 µm cellulose nitrate membrane filter paper into the correctly labelled pill vials. A pre-set micropipette was used to draw up 1 ml subsamples that was transferred into labelled centrifuge tubes. Each of these subsamples were then diluted to 10 ml using distilled water and stored in a refrigerator ready for analysis.

3.3.3. Metal analysis

The water and sediment samples were analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The following metals were measured: aluminium, antimony, arsenic, boron, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, mercury, nickel, selenium, strontium, tin, vanadium, and zinc (appendices A and B). However, after initial analysis, the following metals are presented in this study based on the concentrations measured: aluminium, manganese, iron, lead, and zinc.

Metal concentrations in water samples were calculated using the formula:

$$Conc\ (mg/l) = [ICP - blank] \times 10$$

Metal concentrations in sediment samples were calculated using the formula:

$$Conc\ (mg/kg) = \left[\frac{ICP - blank}{sample\ mass\ (g)}\right] X\ 200$$

3.4. Quality control

The analytical data quality was ensured by implementing laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards, analysis of reagent blanks, recovery of known additions and analysis of replicates.

The limit of detection (LOD) and percentage accuracy on internal quality control (QC) for the samples were as follows:

- Aluminium (LOD = 0.0009 mg/L, QC = 113%)
- Manganese (LOD = 0.0002 mg/L, QC = 104%)
- Iron (LOD = 0.000194 mg/L, QC = 108%)

- Lead (LOD = 0.000019 mg/L, QC = 106%)
- Zinc (LOD = 0.000155 mg/L, QC = 109%)

3.5. Sediment grain size analysis

Grain size analysis define the sedimentary environment and give an understanding into physical regime. The purpose of grain size analysis is to characterise the sediment as a frequency distribution of grain size (Poppe *et al*., 2000). In this study, sediment grain size was analysed by Labco. Only sieve sizes ranging from 0.075 – 100 mm were utilised in the sediment analysis. Thereafter, sediments were categorized using ISO 14688-1 (2017) which is the international standard most commonly used for soils for engineering purposes but are applicable to natural soils *in situ*, those laid by man or comprised of synthetic material (Table 3.5.1).

Table 3.5.1: Range of particle sizes (extracted from ISO 14688-1, 2017)

Soil group	Particle size fractions (symbol)	Range of particle sizes mm
Very coarse soil	Large boulder (lBo)	>630
	Boulder (Bo)	>200 to ≤630
	Cobble (Co)	>63 to ≤200
Coarse soil	Gravel (Gr)	>2,0 to ≤63
	Coarse gravel (cGr)	>20 to ≤63
	Medium gravel (mGr)	>6,3 to ≤20
	Fine gravel (fGr)	>2,0 to ≤6,3
	Sand (Sa)	>0,063 to ≤2,0
	Coarse sand (cSa)	>0,63 to ≤2,0
	Medium sand (mSa)	>0,20 to ≤0,63
	Fine sand (fSa)	>0,063 to ≤0,20
Fine soil	Silt (Si)	>0,002 to ≤0,063
	Coarse silt (cSi)	>0,02 to ≤0,063
	Medium silt (mSi)	>0,006 3 to ≤0,02
	Fine silt (fSi)	>0,002 to ≤0,006 3
	Clay (Cl)	≤0,002

3.6. Statistical analysis

The statistical software package, SigmaPlot 14 was used to compare metal concentrations measured in water and sediment samples. The descriptive statistics are presented as means and standard deviations (±SD). Analysis of variance was used to determine statistical differences between sampling sites (spatial comparisons) and sampling seasons (temporal comparisons).

Kruskal–Wallis One-Way ANOVA on Ranks and Student Newman Kuels Method were used for post hoc tests. Temporal comparisons between dry and wet seasons for each sampling site were evaluated using the Mann Whitney Rank Sum Test. For all statistical analyses, the confidence interval was set at 95% ($p < 0.05$).

CHAPTER FOUR

RESULTS

This chapter presents the results of the analysis of the water and sediment samples collected from distinct points along the Eerste River during the study period. The results include *in situ* physico-chemical parameters monitored during the field work at each site, sediment characterisation, rainfall data and the statistical analysis of the metal concentrations of the samples taken during the field work in March 2021 (dry season) and August 2021 (wet season).

4.1. Physico-chemical parameters

Water and sediment samples were collected in the dry and wet season, and physico-chemical parameters were measured at each sampling site using a multiparameter water quality meter. Tables 4.1.1 and 4.1.2 presents the parameters for both sampling seasons.

Table 4.1.1: Dry season *in situ* physico-chemical parameters of the Eerste River (March 2021)

Date	GPS Coordinates	pH	Temperature (˚C)	Salinity (ppt)	Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Total Dissolved Solids (mg/L)
19/03/21	Site 1: Stellenbosch S 33˚ 56' 21.1" E 18˚ 53' 13.3"	8.07	21.9	0.04	92.5	12.34	53.30
19/03/21	Site 2: Spier S 33˚ 58' 28.0" E 18˚ 47' 01.9"	7.76	21.6	0.18	338	12.25	247
19/03/21	Site 3: Blouklip S 34˚ 01' 49.5" E 18˚ 44' 52.6"	7.84	20.2	0.2	384.4	8.59	274.3
19/03/21	Site 4: Macassar S 34˚ 03' 45" E 18˚ 44' 52.6"	7.82	21.5	0.41	941.4	3.56	533
19/03/21	Site 5: Estuary S 34˚ 04' 47.7" E 18˚ 45' 40.4"	8.19	20.5	1.67	3007	1.8	2067

Table 4.1.2: Wet season *in situ* physico-chemical parameters of the Eerste River (August 2021)

Date	GPS Coordinates	pH	Temperature (˚C)	Salinity (ppt)	Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Total Dissolved Solids (mg/L)
21/08/21	Site 1: Stellenbosch S 33˚ 56' 21.1" E 18˚ 53' 13.3"	7.8	12.8	0.04	65.8	21.56	55.9
21/08/21	Site 2: Spier S 33˚ 58' 28.0" E 18˚ 47' 01.9"	7.67	12.3	0.18	280.8	31.74	241.15
21/08/21	Site 3: Blouklip S 34˚ 01' 49.5" E 18˚ 44' 52.6"	7.22	12.5	0.21	309.4	34.7	279.5
21/08/21	Site 4: Macassar S 34˚ 03' 45" E 18˚ 44' 52.6"	7.27	13.5	0.37	588	28.62	494
21/08/21	Site 5: Estuary S 34˚ 04' 47.7" E 18˚ 45' 40.4"	7.39	12.9	0.45	703	14.5	585

4.2. Sediment characterisation

The predominant grain sizes at the five sampling sites were sand and gravel. Fine sand was predominant at sites 3 and 4, medium sand was predominant at site 2, course sand was predominant at site 5, and fine gravel was predominant at site 1. Silt and/or clay was present in small amounts at sites 2 and 3, with site 4 having the highest proportion of silt and/or clay compared to the other sites (Table 4.2.1). Differentiation between silt and clay could not be made as the grain size analysis only utilised sieve sizes ranging from 0.075 – 100 mm. As per ISO 14688-1, silt and clay have grain sizes smaller than 0.063 mm (ISO14688-1, 2017).

Table 4.2.1: Sediment characteristics at the five sampling sites based on ISO14688-1 (2017)

Sampling sites	Medium Gravel %	Fine gravel %	Course sand %	Medium sand %	Fine sand %	Silt and/or clay %
Site 1	30.0	45.9	23.3	<1	<1	0.0
Site 2	0.0	0.0	18.5	59.8	21.7	<1
Site 3	0.0	0.0	3.3	27.7	67.4	1.6
Site 4	2.0	5.8	17.3	22.3	43.4	9.3
Site 5	0.0	15.0	76.7	8.0	<1	0.0

4.3. Rainfall data

Table 4.3.1 shows that the highest rainfall occurred in the months of May, June and August, and the lowest rainfall occurred in January, February and April.

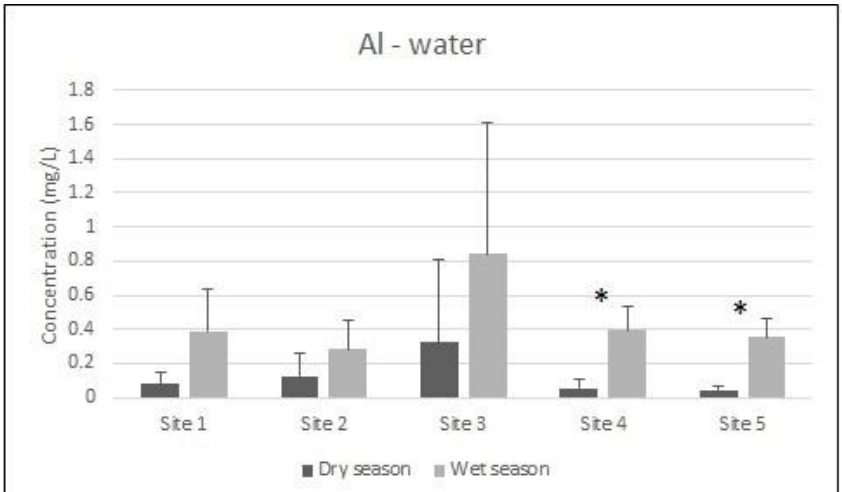
Table 4.3.1: Monthly rainfall data for the study area during the study period (obtained from SAWS)

Months	Rainfall (mm)
January 2021	0-10
February 2021	0-10
March 2021	25-50
April 2021	0-10
May 2021	100-200
June 2021	100-200
July 2021	50-100
August 2021	100-200
September 2021	10-25
October 2021	50-100
November 2021	50-100
December 2021	10-25

4.4. Metal concentrations

4.4.1. Aluminium

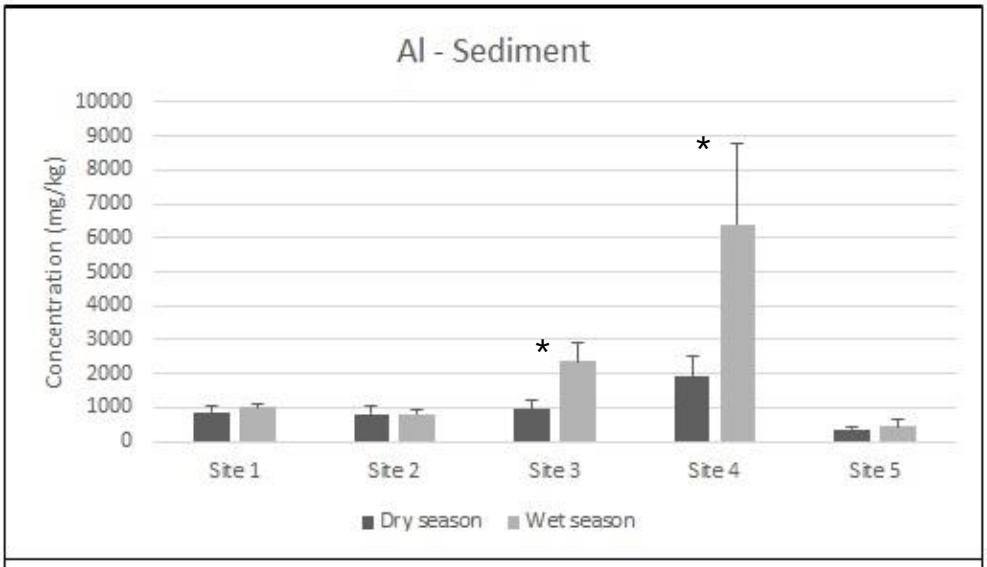
The mean aluminium concentrations (±SD) measured in the river water and sediment samples from the five sites are presented in Figures 4.4.1 and 4.4.2 respectively.



Aluminium – Water (mg/L)

		Dry season	Wet season
Site 1	Mean	0.0799[a]	0.3902[a]
	±SD	±0.0646	±0.2459
Site 2	Mean	0.1253[a]	0.2821[a]
	±SD	±0.1312	±0.1716
Site 3	Mean	0.3234[a]	0.8431[a]
	±SD	±0.4874	±0.7704
Site 4	Mean	0.0537[a]	0.3963[a]
	±SD	±0.0554	±0.1423
Site 5	Mean	0.0432[a]	0.3552[a]
	±SD	±0.0282	±0.1078

Figure 4.4.1: Mean and standard deviation of aluminium concentrations (mg/L) measured in the Eerste River water samples from the five sites for the wet and dry seasons. An asterisk (*) indicates a statistically significant difference between the dry and wet seasons at a particular site. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.



Aluminium – Sediment (mg/Kg)

		Dry season	Wet season
Site 1	Mean	#861.6[a]	#1016.9[a]
	±SD	±170.2	±110.5
Site 2	Mean	811.3[a]	807.4[b]
	±SD	±233.7	±100.9
Site 3	Mean	962.1[a]	2357.9[c]
	±SD	±244.8	±532.7
Site 4	Mean	1922.6[b]	6409.9[d]
	±SD	±579.8	±2392.0
Site 5	Mean	#357.8[c]	#452.5[e]
	±SD	±65.0	±180.7

Figure 4.4.2: Mean and standard deviation of aluminium concentrations (mg/kg) measured in the Eerste River sediment samples from the five sites for the wet and dry seasons. An asterisk (*) indicates a statistically significant difference between the dry and wet seasons at a particular site. The hash symbol (#) indicates a statistically significant difference between site 1 and site 5 within a particular season. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.

4.4.1.1. Spatial comparison of aluminium concentrations in river water samples between the five sampling sites for the dry and wet seasons

a) Dry season

The Kruskal Wallis One Way ANOVA on ranks analysis of aluminium concentrations in the water during the dry season indicated that there were no statistically significant differences (P = 0.554) between the five sampling sites.

b) Wet season

The statistical analysis of aluminium concentrations in the water during the wet season indicated that there were no statistically significant differences (P = 0.302) between the five sampling sites.

4.4.1.2. Spatial comparison of aluminium concentrations in river sediment samples between the five sampling sites for the dry and wet seasons

a) Dry season

The statistical analysis of aluminium concentrations in the sediment during the dry season indicated that there were statistically significant differences (P <0.001) between some of the sampling sites. Multiple pairwise comparisons revealed that there were significant differences between sites 3 and 4, sites 4 and 5, as well as sites 1 and 5 (P<0.05).

b) Wet season

The statistical analysis of aluminium concentrations in the sediment during the wet season indicated that there were statistically significant differences (P <0.001) between the five sampling sites. Significant differences between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5, and between sites 1 and 5 (P<0.05) were revealed through all pairwise multiple comparisons. The highest mean aluminium concentration (6409.9 ±2392 mg/kg) in sediment samples was found at site 4 in the wet season.

4.4.1.3. Temporal comparison of aluminium concentrations in river water samples between dry and wet seasons for the five sampling sites

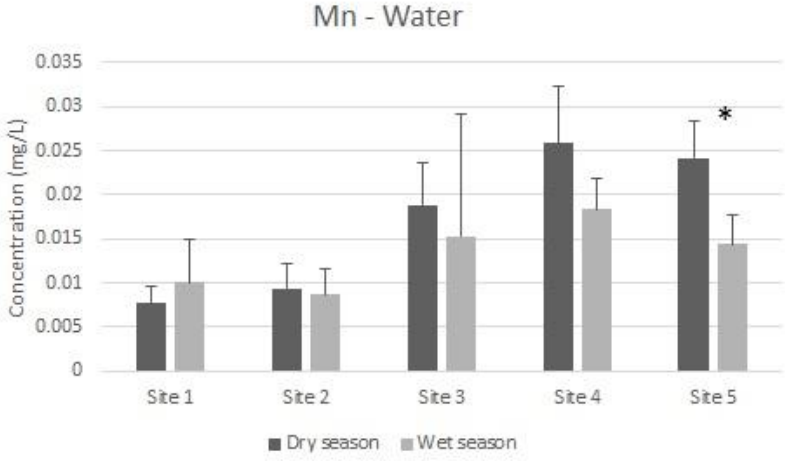
There were no statistically significant differences found between the dry and wet seasons for site 1 (P = 0.151), site 2 (P = 0.151) and site 3 (P = 0.095). Significant differences were found between the dry and wet seasons for site 4 (P = 0.008) and site 5 (P = 0.008).

4.4.1.4. Temporal comparison of aluminium concentrations in river sediment samples between dry and wet seasons for the five sampling sites

No statistically significant differences were found between the dry and wet seasons for site 1 (P = 0.222), site 2 (P = 0.841) and site 5 (P = 0.421). Significant differences were found between the dry and wet seasons for site 3 (P = 0.008) and site 4 (P = 0.008).

4.4.2. Manganese

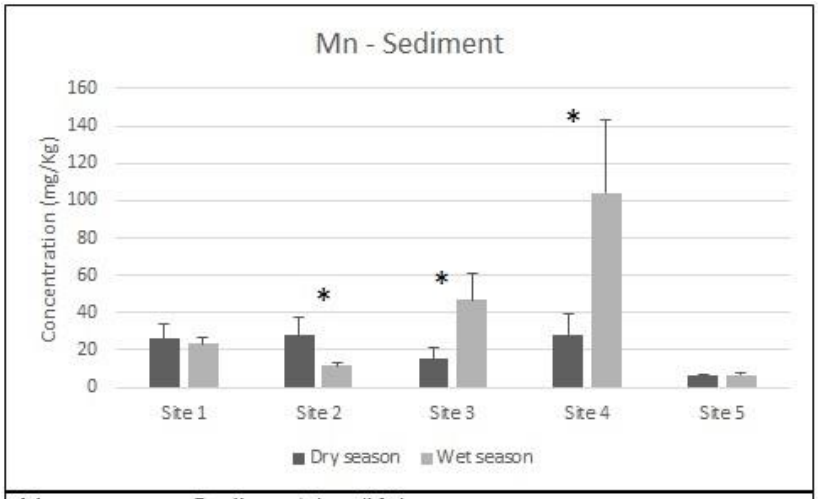
The mean manganese concentrations (±SD) measured in the river water and sediment samples from the five sites are presented in Figures 4.4.3 and 4.4.4 respectively.



Manganese – Water (mg/L)

		Dry season	Wet season
Site 1	Mean	#0.0076[a]	0.0100[a]
	±SD	±0.0020	±0.0048
Site 2	Mean	0.0094[a]	0.0087[a]
	±SD	±0.0028	±0.0028
Site 3	Mean	0.0189[b]	0.0153[a]
	±SD	±0.0048	±0.0138
Site 4	Mean	0.0259[b]	0.0183[b]
	±SD	±0.0064	±0.0036
Site 5	Mean	#0.0241[b]	0.0144[c]
	±SD	±0.0042	±0.0032

Figure 4.4.3: Mean and standard deviation of manganese concentrations (mg/L) measured in the Eerste River water samples from the five sites for the wet and dry seasons. An asterisk (*) indicates a statistically significant difference between the dry and wet seasons at a particular site. The hash symbol (#) indicates a statistically significant difference between site 1 and site 5 within a particular season. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.



Manganese – Sediment (mg/Kg)			
		Dry season	Wet season
Site 1	Mean	#26.0[a]	#23.2[a]
	±SD	±7.8	±3.3
Site 2	Mean	27.9[a]	11.6[b]
	±SD	±9.3	±1.1
Site 3	Mean	15.4[a]	46.9[c]
	±SD	±6.4	±14.3
Site 4	Mean	28.2[a]	104.2[d]
	±SD	±11.5	±39.1
Site 5	Mean	#6.2[b]	#6.6[e]
	±SD	±0.8	±1.1

Figure 4.4.4: Mean and standard deviation of manganese concentrations (mg/kg) measured in the Eerste River sediment samples from the five sites for the wet and dry seasons. An asterisk (*) indicates a statistically significant difference between the dry and wet seasons at a particular site. The hash symbol (#) indicates a statistically significant difference between site 1 and site 5 within a particular season. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.

4.4.2.1. Spatial comparison of manganese concentrations in river water samples between the five sampling sites for the dry and wet seasons

a) Dry season

The statistical analysis of manganese concentrations in the water during the dry season indicated that there were statistically significant differences (P = 0.001) between some of the sampling sites. All pairwise analysis of the groups revealed that there were significant differences between sites 2 and 3, as well as between sites 1 and 5 (P<0.05).

b) Wet season

The statistical analysis of manganese concentrations in the water during the wet season indicated that there were statistically significant differences (P = 0.035) between the five sampling sites. Significant differences were observed between sites 3 and 4, as well as between sites 4 and 5 (P<0.05).

4.4.2.2. Spatial comparison of manganese concentrations in river sediment samples between the five sampling sites for the dry and wet seasons

a) Dry season

The statistical analysis of manganese concentrations in the sediment during the dry season indicated that there were statistically significant differences (P 0.004) between the sampling sites. There were significant differences found between sites 4 and 5, as well as between sites 1 and 5 ($P<0.05$).

b) Wet season

The statistical analysis of manganese concentrations in the sediment during the wet season indicated that there were statistically significant differences ($P <0.001$) between the sampling sites. Multiple pairwise comparisons revealed significant differences between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5, and sites 1 and 5 ($P <0.05$). The highest mean manganese concentration (104.2 ±39.1 mg/kg) in sediment samples was found at site 4 in the wet season.

4.4.2.3. Temporal comparison of manganese concentrations in river water samples between dry and wet seasons for the five sampling sites

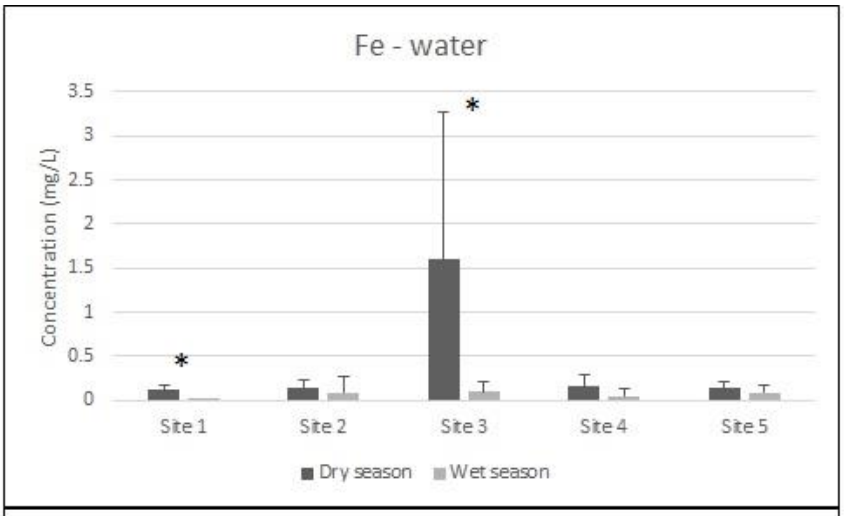
No statistically significant differences were found between the dry and wet seasons for site 1 ($P = 0.151$), site 2 ($P = 0.841$), site 3 ($P = 0.310$) and site 4 ($P = 0.095$). A significant difference was found between the dry and wet seasons for site 5 ($P = 0.008$).

4.4.2.4. Temporal comparison of manganese concentrations in river sediment samples between dry and wet seasons for the five sampling sites

No statistically significant differences were found between the dry and wet seasons for site 1 ($P = 0.690$) and site 5 ($P = 1.000$). Significant differences were found between the dry and wet seasons for site 2 ($P = 0.008$), site 3 ($P = 0.008$) and site 4 ($P = 0.008$).

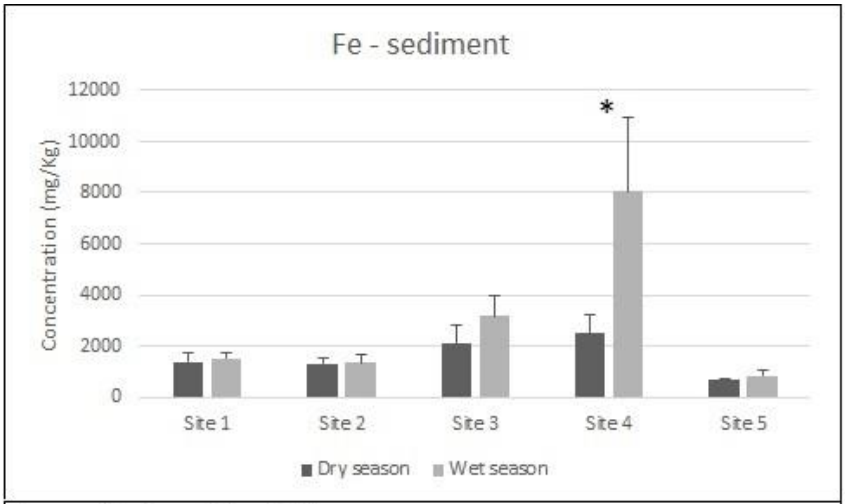
4.4.3. Iron

The mean iron concentrations (±SD) measured in the river water and sediment samples from the five sites are presented in Figures 4.4.5 and 4.4.6 respectively.



Iron – Water (mg/L)			
		Dry season	Wet season
Site 1	Mean	0.1148[a]	0.0001[a]
	±SD	±0.0510	±0.0002
Site 2	Mean	0.1390[a]	0.0856[a]
	±SD	±0.0885	±0.1914
Site 3	Mean	1.5981[a]	0.0952[a]
	±SD	±1.6760	±0.1154
Site 4	Mean	0.1572[a]	0.0503[a]
	±SD	±0.1373	±0.0786
Site 5	Mean	0.1370[a]	0.0855[a]
	±SD	±0.0658	±0.0928

Figure 4.4.5: Mean and standard deviation of iron concentrations (mg/L) measured in the Eerste River water samples from the five sites for the wet and dry seasons. An asterisk (*) indicates a statistically significant difference between the dry and wet seasons at a particular site. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.



Iron – Sediment (mg/Kg)			
		Dry season	Wet season
Site 1	Mean	#1391.6[a]	#1522.0[a]
	±SD	±349.7	±199.4
Site 2	Mean	1314.5[a]	1354.5[a]
	±SD	±185.2	±298.9
Site 3	Mean	2105.8[b]	3176.5[b]
	±SD	±677.5	±778.5
Site 4	Mean	2498.6[b]	8048.9[c]
	±SD	±727.2	±2904.8
Site 5	Mean	#668.1[c]	#837.8[d]
	±SD	±61.2	±194.1

Figure 4.4.6: Mean and standard deviation of iron concentrations (mg/kg) measured in the Eerste River sediment samples from the five sites for the wet and dry seasons. An asterisk (*) indicates a statistically significant difference between the dry and wet seasons at a particular site. The hash symbol (#) indicates a statistically significant difference between site 1 and site 5 within a particular season. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.

4.4.3.1. Spatial comparison of iron concentrations in river water samples between the five sampling sites for the dry and wet seasons

a) Dry season

All pairwise analysis revealed no significant differences between the sites (P>0.05).

b) Wet season

The statistical analysis of iron concentrations in the water during the wet season indicated that there were no statistically significant differences (P = 0.254) between the five sampling sites.

4.4.3.2. Spatial comparison of iron concentrations in river sediment samples between the five sampling sites for the dry and wet seasons

a) Dry season

The statistical analysis of iron concentrations in the sediment during the dry season indicated that there were statistically significant differences (P <0.001) between the sampling sites.

Significant differences were found between sites 2 and 3, sites 4 and 5, as well as between sites 1 and 5 (P<0.05).

b) Wet season

The statistical analysis of iron concentrations in the sediment during the wet season indicated that there were statistically significant differences (P <0.001) between the sampling sites. Significant differences were found between sites 2 and 3, sites 3 and 4, sites 4 and 5, as well as between sites 1 and 5 (P<0.05). The highest mean iron concentration (8048.9 ±2904.8 mg/kg) in sediment samples was found at site 4 in the wet season.

4.4.3.3. Temporal comparison of iron concentrations in river water samples between dry and wet seasons for the five sampling sites

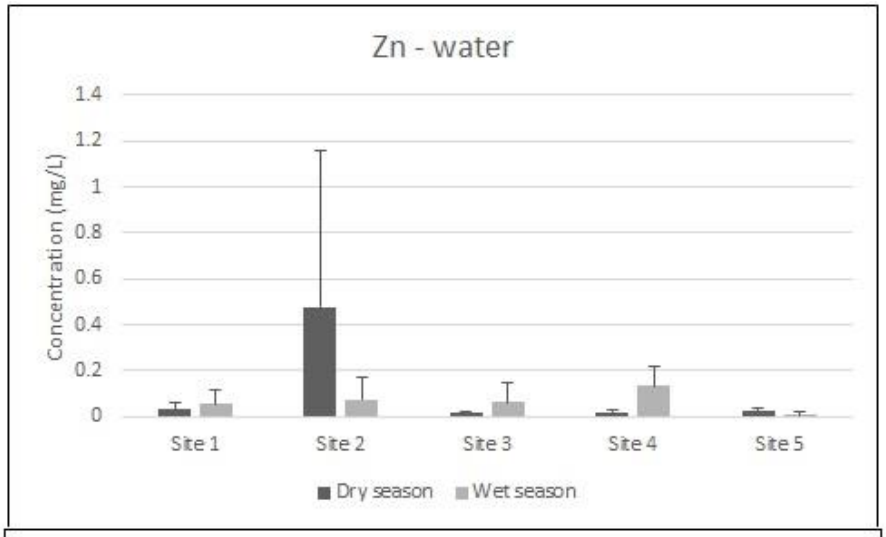
Statistical differences were found between the dry and wet seasons for site 1 (P = 0.008) and site 3 (P = 0.016). No statistically significant differences were found between the dry and wet seasons for site 2 (P = 0.151), site 4 (P = 0.095) and site 5 (P = 0.421).

4.4.3.4. Temporal comparison of iron concentrations in river sediment samples between dry and wet seasons for the five sampling sites

No statistically significant differences were found between the dry and wet seasons for site 1 (P = 0.690), site 2 (P = 1.000), site 3 (P = 0.056) and site 5 (P = 0.095). The dry and wet seasons were found to be statistically different (P = 0.008) for site 4.

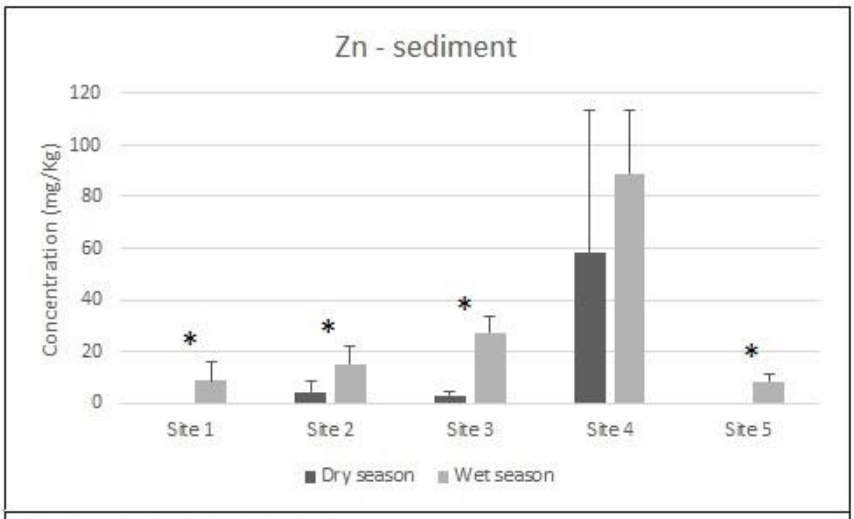
4.4.4. Zinc

The mean zinc concentrations (±SD) measured in the river water and sediment samples from the five sites are presented in Figures 4.4.7. and 4.4.8. respectively.



Zinc – Water (mg/L)			
		Dry season	Wet season
Site 1	Mean	0.0303[a]	0.0537[a]
	±SD	±0.0296	±0.0599
Site 2	Mean	0.4753[a]	0.0728[a]
	±SD	±0.6805	±0.1013
Site 3	Mean	0.0132[a]	0.0619[a]
	±SD	±0.0075	±0.0849
Site 4	Mean	0.0173[a]	0.1322[a]
	±SD	±0.0130	±0.0868
Site 5	Mean	0.0235[a]	0.0072[a]
	±SD	±0.0116	±0.0099

Figure 4.4.7: Mean and standard deviation of zinc concentrations (mg/L) measured in the Eerste River water samples from the five sites for the wet and dry seasons. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.



Zinc – sediment (mg/Kg)

		Dry season	Wet season
Site 1	Mean	0.0[a]	8.8[a]
	±SD	±0.0	±7.3
Site 2	Mean	4.4[b]	15.2[a]
	±SD	±3.9	±6.6
Site 3	Mean	2.8[b]	27.4[b]
	±SD	±1.7	±6.5
Site 4	Mean	58.3[c]	88.9[c]
	±SD	±54.9	±24.8
Site 5	Mean	0.0[d]	8.2[d]
	±SD	±0.0	±3.0

Figure 4.4.8: Mean and standard deviation of zinc concentrations (mg/kg) measured in the Eerste River water samples from the five sites for the wet and dry seasons. An asterisk (*) indicates a statistically significant difference between the dry and wet seasons at a particular site. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.

4.4.4.1. Spatial comparison of zinc concentrations in river water samples between the five sampling sites for the dry and wet seasons

a) Dry season

The statistical analysis of zinc concentrations in the water during the dry season indicated that there were no statistically significant differences (P = 0.093) between the five sampling sites.

b) Wet season

The statistical analysis of zinc concentrations in the water during the wet season indicated that there were no statistically significant differences (P = 0.286) between the five sampling sites.

4.4.4.2. Spatial comparison of zinc concentrations in river sediment samples between the five sampling sites for the dry and wet seasons

a) Dry season

The statistical analysis of zinc concentrations in the sediment during the dry season indicated that there were statistically significant differences ($P < 0.001$) between the five sampling sites. Significant differences were found between sites 1 and 2, sites 3 and 4, as well as between sites 4 and 5 ($P<0.05$).

b) Wet season

The statistical analysis of zinc concentrations in the sediment during the wet season indicated that there were statistically significant differences ($P < 0.001$) between the sampling sites. All pairwise analysis of the groups revealed significant differences between sites 2 and 3, sites 3 and 4, as well as between sites 4 and 5 ($P<0.05$). The highest mean zinc concentration (88.9 ±24.8 mg/kg) in sediment samples was found at site 4 in the wet season.

4.4.4.3. Temporal comparison of zinc concentrations in river water samples between dry and wet seasons for the five sampling sites

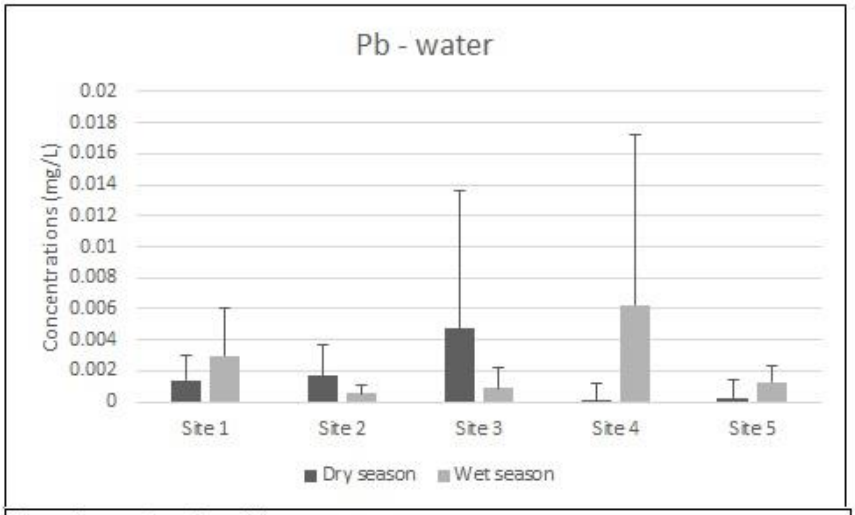
No statistically significant differences were found between the dry and wet seasons for site 1 ($P = 0.690$), site 2 ($P = 0.548$), site 3 ($P = 0.841$), site 4 ($P = 0.151$), and site 5 ($P = 0.056$).

4.4.4.4. Temporal comparison of zinc concentrations in river sediment samples between dry and wet seasons for the five sampling sites

Statistical differences were found between the dry and wet seasons for site 1 ($P = 0.032$), site 2 ($P = 0.032$), site 3 ($P = 0.008$), and 5 ($P = 0.008$). No statistically significant differences were found between the dry and wet seasons for site 4 ($P = 0.151$).

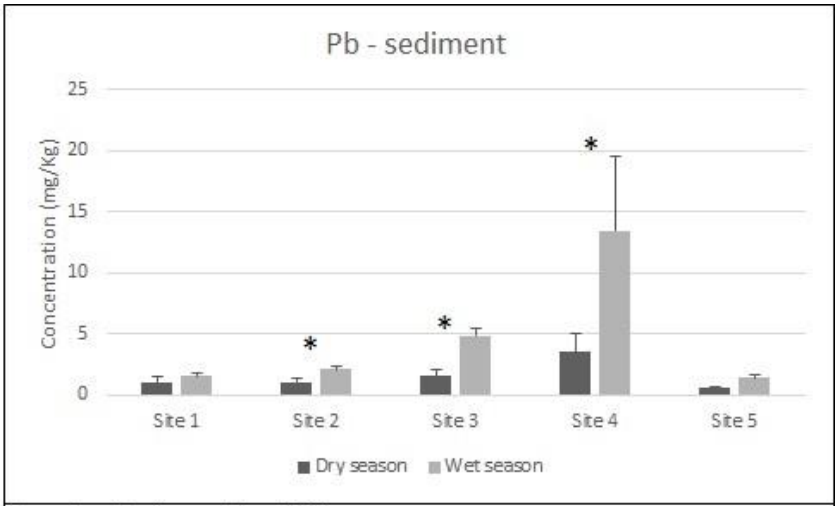
4.4.5. Lead

The mean lead concentrations (±SD) measured in the river water and sediment samples from the five sites are presented in Figures 4.4.9. and 4.4.10. respectively.



Lead – water (mg/L)			
		Dry season	Wet season
Site 1	Mean	0.0014[a]	0.0030[a]
	±SD	±0.0016	±0.0030
Site 2	Mean	0.0017[a]	0.0005[a]
	±SD	±0.0020	±0.0005
Site 3	Mean	0.0047[a]	0.0009[a]
	±SD	±0.0089	±0.0014
Site 4	Mean	0.0001[a]	0.0063[a]
	±SD	±0.0011	±0.0109
Site 5	Mean	0.0002[a]	0.0013[a]
	±SD	±0.0012	±0.0010

Figure 4.4.9: Mean and standard deviation of lead concentrations (mg/L) measured in the Eerste River water samples from the five sites for the wet and dry seasons. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.



Lead – Sediment (mg/Kg)			
		Dry season	Wet season
Site 1	Mean	#1.1[a]	1.5[a]
	±SD	±0.4	±0.2
Site 2	Mean	1.0[a]	2.1[b]
	±SD	±0.4	±0.3
Site 3	Mean	1.5[a]	4.8[c]
	±SD	±0.5	±0.6
Site 4	Mean	3.5[b]	13.4[d]
	±SD	±1.5	±6.2
Site 5	Mean	#0.5[c]	1.4[e]
	±SD	±0.2	±0.2

Figure 4.4.10: Mean and standard deviation of lead concentrations (mg/kg) measured in the Eerste River sediment samples from the five sites for the wet and dry seasons. An asterisk (*) indicates a statistically significant difference between the dry and wet seasons at a particular site. The hash symbol (#) indicates a statistically significant difference between site 1 and site 5 within a particular season. Different superscripted letters (a, b, c, etc.) indicate statistically significant differences between consecutive sampling sites per sampling season.

4.4.5.1. Spatial comparison of lead concentrations in river water samples between the five sampling sites for the dry and wet seasons

a) Dry season

The statistical analysis of lead concentrations in the water during the dry season indicated that there were no statistically significant differences (P = 0.517) between the sampling sites.

b) Wet season

The statistical analysis of lead concentrations in the water during the dry season indicated that there were no statistically significant differences (P = 0.237) between the five sampling sites.

4.4.5.2. Spatial comparison of lead concentrations in river sediment samples between the five sampling sites for the dry and wet seasons

a) Dry season

The statistical analysis of lead concentrations in the sediment during the dry season indicated that there were statistically significant differences (P 0.001) between the sampling sites. All pairwise analysis of the groups revealed that there were significant differences between sites 3 and 4, sites 4 and 5, as well as between sites 1 and 5 ($P<0.05$).

b) Wet season

The statistical analysis of lead concentrations in the sediment during the wet season indicated that there were statistically significant differences ($P <0.001$) between the five sampling sites. There were significant differences found between sites 1 and 2, sites 2 and 3, sites 3 and 4, as well as between sites 4 and 5 ($P<0.05$). The highest mean lead concentration (13.4 ±6.2 mg/kg) in sediment samples was found at site 4 in the wet season.

4.4.5.3. Temporal comparison of lead concentrations in river water samples between dry and wet seasons for the five sampling sites

No statistically significant differences were found between the dry and wet seasons for site 1 ($P = 0.222$), site 2 ($P = 0.222$), site 3 ($P = 1.000$), site 4 ($P = 0.095$), and site 5 ($P = 0.056$).

4.4.5.4. Temporal comparison of lead concentrations in river sediment samples between dry and wet seasons for the five sampling sites

No statistically significant differences ($P = 0.056$) were found between the dry and wet seasons for site 1. Statistical differences were found between the dry and wet seasons for site 2 ($P = 0.008$), site 3 ($P = 0.008$), site 4 ($P = 0.008$), and site 5 ($P = 0.008$).

CHAPTER 5

DISCUSSION

5.1. Metal concentrations in river water

5.1.1. Aluminium

5.1.1.1. Spatial comparisons between sampling sites for the dry season

Aluminium is a naturally occurring element found in the earth's crust as well as many soils and rocks. Natural sources of aluminium, such as weathering of rocks, can release the metal into the environment, but anthropogenic sources of the metal, such as mining, aluminium-using industry, and alum, an aluminium compound, used in wastewater treatment, can release it, too (USEPA, 2021). Seawater generally contains between approximately 0.013 µg/L ($1.3x10^{-4}$ mg/L) and 5 µg/L (0.005 mg/L) of aluminium, and river water generally contains about 400 µg/L (0.4 mg/L) of aluminium (Lenntech, 2021a). The solubility of aluminium in water is strongly pH-dependent and is relatively insoluble at neutral pH levels. The presence of alkaline (pH > 8.0) or acidic (pH > 6.0) environmental conditions, or complexing ligands, may elevate aluminium concentrations in aquatic environments (DWAF, 1996).

The mean aluminium concentrations within the five sampling sites in the dry season for the present study ranged from 0.0432 mg/L (±0.0282) to 0.3236 mg/L (±0.4874) (Figure 4.4.1). In South Africa, a study undertaken by Shuping *et al.* (2011) investigated the accumulation and distribution of metals in *Bolboschoenus maritimus* (Cyperaceae) from the lower Diep River. That study reported a mean aluminium concentration in the water of 1.16 mg/L (±0.44) over four seasons. That study further noted that aluminium concentrations were almost always higher than the Target Water Quality Range (TWQR) set by DWAF in the 1996 South African Water Quality Guidelines for aquatic ecosystems (SA WQG) (DWAF, 1996). Additionally, a study undertaken by Olaniran *et al*. (2013) assessed physico-chemical qualities and heavy metal concentrations of the Umgeni and Umdloti Rivers in Durban, South Africa. That study reported a mean aluminium concentration range of 0.049 to 0.912 mg/L for the Umgeni River, and 0.037 to 1.875 mg/L for the Umdloti River. That study reported that in both cases, the mean aluminium concentrations exceeded the national water quality threshold. In the present study, the mean aluminium concentrations in water for the dry season were less than the concentrations reported in the above-mentioned studies. However, the mean aluminium concentrations for all sites in the present study exceeded the TWQR set by the SA WQG (0.01 mg/L) (DWAF, 1996). Sites 1 to 4 also exceed the Default Guideline Value (DGV) of 0.055 mg/L (for water with a pH more than 6.5 – table 4.1.1.) set by the Australia and New Zealand Guidelines for Fresh and Marine Water Quality (AGI, 2000). No water quality guidelines have been set for estuaries and/or coastal marine waters for aluminium in South Africa. However,

the aluminium concentrations measured near the estuary of the Eerste River in the present study might indicate an urgent need for such guidelines locally.

The results showed that there were no significant differences between the five sampling sites for both the wet and the dry season (Figure 4.4.1). However, despite the statistical insignificance, explanations for the general tendencies are outlined below.

The mean concentrations of aluminum were highest at site 3, followed closely by site 2. The lowest mean aluminium concentration was recorded at site 5, although sites 1 and 4 had relatively similar aluminium concentrations to site 5. Specifically for sampling site 3, the site is located in the Croyden area, running underneath a road bridge characterised by heavy vehicular traffic. Observations made during the site visits includes the site being adjacent to a small cluster of low-income houses, as well as two large factories to the left and right of the river. The aluminium concentrations at site 3 may have exceeded the TWQR set by DWAF and the DGV set by the AGI because of the heavy vehicular traffic crossing the road bridge each day. According to Hovorun *et al.* (2017), only 9% of the total volume in the production of a modern car consists of aluminium alloys, while 55% consists of cast iron and steel parts, 11% consist of plastics, rubber and glass makes up 7 and 3 % respectively, and non-ferrous alloys (magnesium, titanium, copper and zinc) is less than 1%. Other materials such as varnishes, paints, electric wires, facing materials, etc. make 13.5%. In addition, car exhaust fumes contain certain chemicals, including carbon monoxide, sulfur dioxide, nitrogen oxides, formaldehyde, benzene and soot; but it does not contain aluminium (Ulfvarson *et al.* 1988). Furthermore, a study undertaken by Fiala *et al.* (2021) investigated metals in road dust. That study reported that aluminium occurred naturally in the environment at concentrations 10 000 - 100 000 times higher than other heavy metals measured in that study. Therefore, it resulted in relatively insignificant anthropogenic contamination compared to the other measured metals such as lead, vanadium, or cobalt (Fiala *et al*., 2021).

When observing the concentrations in the lower reaches of the river, sites 4 and 5 still exceeded the TWQR set by DWAF and the DGV set by the AGI but had lower aluminium concentrations than site 3. Given that site 4 receives polluted water from the Kuils River (CCT, 2019) and site 5 receives effluent from the Macassar WWTW (Thomas *et al.*, 2010; Melato, 2011; CCT, 2019) and Rheinmetall Denel Munition (Thomas *et al.*, 2010), the decrease in aluminium concentrations at sites 4 and 5 may be due to the abundance of plants along the length of the river absorbing some metals (Shuping *et al.*, 2011; Genchi *et al*., 2020). *Salix mucronata* and *Phragmites australis* is abundant between sites 4 and 5 (Meek *et al*., 2009; Meek *et al*., 2013) and have been shown to effectively remove metal contaminants from riverine environments (El-Mahrouk *et al*., 2019; Prica *et al*., 2019). The reduction may also be due to wetlands along the length of the river filtering out pollutants (Sahu, 2014; Rebelo *et al*., 2018). Sites 2 and 3 are located downstream of the Blouklip and Veldwagters confluence

areas, where the Stellenbosch WWTW discharges effluent into the Veldwagters River, and the Blouklip River flows through residential and farm areas (Thomas *et al*., 2010) which have the potential to pollute the river through stormwater outflows. However, the WWTWs as the source of the aluminium is unlikely since the Kuils River receives effluent from various WWTWs (Olujimi *et al*., 2016), and the Macassar WWTW discharges effluent into the Eerste Estuary (Thomas *et al*., 2010), yet sites 4 and 5 contained less aluminium than sites 2 and 3. Therefore, while the reasons are largely unknown, it is deduced that the aluminium concentration at each site is not as a result of contaminated road dust or WWTW effluent. Rather, it is possible that either non-point source pollution, natural occurrence, or a combination thereof contributed to the aluminium concentrations exceeding water quality guidelines.

5.1.1.2. Spatial comparisons between sampling sites for the wet season

The mean aluminium concentrations within the five sampling sites in the wet season in the present study ranged from 0.2821 mg/L (±0.1716) to 0.8431 mg/L (±0.7704) (Figure 4.4.1.) and were similar to aluminium concentrations in water as reported by Olaniran *et al*. (2013) and relatively lower than the concentrations reported by Shuping *et al*. (2011) as noted in heading 5.1.1.1. In the present study, the mean aluminium concentrations for sites 1 to 5 exceeded the TWQR set by the SA WQG (0.01 mg/L) (DWAF, 1996). Sites 1 to 4 also exceeds the Australia and New Zealand Guidelines for Fresh and Marine Water Quality DGV of 0.055 mg/L (for water with a pH more than 6.5 – table 4.1.1.) (AGI, 2000). No water quality guidelines have been set for estuaries and/or coastal marine waters for aluminium in order to compare with concentrations at site 5.

As noted in heading 5.1.1.1, despite the statistical insignificance, explanations for the general tendencies are outlined below.

The results showed that the mean concentration of aluminium was highest at site 3 and lowest at site 2. As noted in heading 5.1.1.1, site 3 observations include heavy vehicular traffic on the road bridge passing over the Eerste River, low-income houses and two factories adjacent to the river. Contaminated road dust and WWTW discharge was ruled out as possible sources of the elevated aluminium concentrations in 5.1.1.1. Therefore, a combination of non-point source pollution and natural occurrence may have contributed to the aluminium concentrations exceeding water guidelines. Sites 4 and 5, located downstream of site 3 contained less aluminium . A possible reason for this is that the plants (Shuping *et al.*, 2011; Genchi *et al*., 2020) and wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river filtered out aluminium, and increased rainfall in the wet season (table 3.2.1) diluted the contaminants.

5.1.1.3. Temporal comparisons of water for the dry and wet seasons

When comparing the mean aluminium concentrations in river water from the five sampling sites between the two seasons, the results indicated that there were significant seasonal differences

for sites 4 and 5, and insignificant differences for sites 1 to 3. Whether the seasonal differences were significant or not, the general seasonal trend observed indicated the mean aluminium concentrations for all the sampling sites were higher in the wet season than the dry season. During organic and inorganic particle movement by water, more particles will flow when there is a greater water velocity (Skinner *et al.*, 2013; Earle, 2015). Naturally, this generally occurs during periods of high rainfall events (Fondriest Environment, Inc. 2021). When observing the differences in rainfall between the dry and wet season (table 4.3.1.), it becomes evident that the water velocity had increased due to the increase in rainfall in the wet season. As noted, site 4 receives polluted water from upstream sources as well as from the Kuils River (Melato, 2011; CCT, 2019). Aluminium contamination from upstream sources could have been bedded particles which moved downstream with the increase in water velocity or became suspended in the water as a result of the increase in water velocity, thereby also moving downstream (Earle, 2015; McGoldrick, 2020; Fondriest Environment, Inc. 2021). Site 5 is located adjacent to and receives effluent from the Rheinmetall Denel Munition factory (Thomas *et al*., 2010) which specialises in the development, design, and production of artillery, mortar, and infantry systems as well as large- and medium-calibre ammunition families (Rheinmetall, 2022). Bullets are made of lead alloys, often containing tin and antimony. Copper is sometimes coated over the outside of some bullets for improved performance. The most common type of casing is made of brass, but steel and aluminium are also used (Barnes, 2000). Site 5 receiving effluent from the Macassar WWTW and Rheinmetall Denel Munition (Thomas *et al.,* 2010), as well as potentially suspended pollutants washing downstream with the increase in rainfall could be a reason for the elevated aluminium concentration at site 5.

5.1.2. Manganese

5.1.2.1. Spatial comparisons between sampling sites for the dry season

Manganese is found naturally in soils, sediments, and metamorphic and sedimentary rocks. Similarly, industrial discharges can also lead to high manganese concentrations in receiving waters. A variety of industries use manganese, including steel, fertilizer, and chemical manufacturing (DWAF, 1996). In seawater, it was reported that manganese concentrations range from 0.4 to 10 µg/L ($4x10^{-4}$ to 0.01 mg/L), with an average of about 2 µg/L (0.002 mg/L). Fresh water concentrations generally range from 1 to 200 µg/L (0.001 to 0.2 mg/L) (WHO, 2011).

The mean manganese concentrations within the five sampling sites in the dry season in the present study ranged from 0.0076 mg/L (±0.0020) to 0.0259 mg/L (±0.0064) (Figure 4.4.3). A study by Duncan *et al*. (2018) assessed the Pra Basin, Ghana which has been subjected to many illegal mining activities. That study reported a mean manganese concentration of 0.129 mg/L during the dry season. Sparks *et al.* (2017) reported a mean concentration of 0.06 mg/L of manganese in intertidal waters from the west coast of the Cape Peninsula. Fatoki *et al.*

(2002) investigated trace metal pollution in the Umtata River, where a mean manganese level between 0.16 to 2.04 mg/L was reported in the river, which exceeded the SA WQG (DWAF, 1996). A further study undertaken by Edokpayi *et al*. (2014) assessed the heavy metal contamination of the Dzindi River in Limpopo. That study reported a mean manganese concentration of 0.15 mg/L in the river. The manganese concentration in water in the present study is considerably less than those reported in the above-mentioned studies. The mean manganese concentrations for all the sites in the present study also did not exceed the TWQR as set out in the SA WQG (0.18 mg/L) (DWAF, 1996), nor the Canadian Water Quality Guidelines for the Protection of Aquatic Life (CWQG) threshold set at 3.6 mg/L for acute exposure and 0.43 mg/L for chronic exposure (CCME, 2019). No water quality guidelines have been set for estuaries and/or coastal marine waters for manganese in order to compare with concentrations at site 5.

Statistical analysis of the samples indicated that there were significant differences between the upstream (sites 1 and 2) and downstream sites (sites 3 to 5). There were also significant differences between site 1 and site 5. The results show that the mean manganese concentrations were lowest at site 1 which is the upper most sampling site along the river. Site 1 is located relatively near the Jonkershoek Nature Reserve where the Eerste River originates, and it is also upstream of the town of Stellenbosch. Therefore, site 1 can be assumed to be the least polluted site along the length of the Eerste River. The highest mean manganese concentration was found further downstream at site 4, which is located downstream of the Eerste-Kuils confluence area and thus not only receives potentially polluted water from the Eerste River and its associated tributaries, but also from the Kuils River and its associated tributaries (Melato, 2011; CCT, 2019). Site 4 is located at the Macassar Kramat, running underneath a road bridge. Observations made during the site visits include visible warning signs erected by the CCT, indicating the water is not suitable for human contact and/or consumption. The water smelled of sewage and was dark and cloudy in colour. The sediment had a sludge-like consistency and had a strong sewage odour. This was not surprising as site 4 has been subjected to severe pollution in recent years. In 2018, much media scrutiny had been directed at the CCT and the Zandvliet WWTW after raw sewage from the Zandvliet WWTW was discharged into the lower Kuils River, eventually flowing into the lower Eerste River. Water samples from the Kuils River was sent to the South African Bureau of Standards for testing and revealed *E.coli* levels of between 200 and 36,000 per 100ml. Acceptable levels are around 80 per 100ml (capeetc, 2018; Green *et al*., 2018; Isaacs and Wolf, 2018). In addition to the raw sewage discharge, the Kuils River also receives WWTW effluent from at least 3 WWTW on its path and via tributaries (Thomas *et al*., 2010). Besides WWTW effluent, site 4 is located adjacent to the town of Macassar, as well as smaller farming areas. Therefore, storm water runoff from these areas can carry manganese into the river as it is present in everyday items that gets readily discarded such as matches, glass, perfume, bricks, paint,

fertilizer and animal food (CCME, 2019). The significant increase in WWTW effluent flowing through site 4 may also be the source of increased manganese levels. However, without testing effluent discharges from the WWTWs for metal contamination, the source cannot be conclusively identified. Further studies are needed in this regard. In addition, according to the 2017/18 Western Cape commodity census, there are many livestock farms along the Eerste River between site 2 and 3. Manganese has been found in livestock feed as well as manure (Hejna *et al.*, 2018). It is possible that manganese gets washed into watercourses as runoff and flows downstream. The differences between upstream and downstream sampling sites can also be attributed to the vast amount of pollution entering the lower reaches of the river (Thomas *et al*., 2010; Olujimi *et al*., 2016; Green *et al*., 2018; CCT, 2019). Although the concentration at site 5 was less than site 4, it was still significantly higher than at site 1. This difference can be attributed to the contamination from upstream sources flowing downstream. Nevertheless, the mean manganese concentrations from the five sampling sites were below national and international water quality guideline thresholds but should still be monitored.

5.1.2.2. Spatial comparisons between sampling sites for the wet season

In the present study, the mean manganese concentrations within the five sampling sites in the wet season ranged from 0.0087 mg/L (±0.0028) to 0.0183 mg/L (±0.0036) (Figure 4.4.3). It is considerably less than those reported in the studies by Sparks *et al.* (2017), Fatoki *et al.* (2002), and Edokpayi *et al*. (2014) as noted in heading 5.1.2.1, but slightly higher than the manganese concentration of 0.007 mg/L during the wet season as reported in a study by Duncan *et al*. (2018) in the Pra Basin, Ghana. Furthermore, Zhou *et al*. (2020) reported a global mean manganese concentration of 0.518 mg/L in rivers and lakes between 2010 to 2017. In the present study, the mean manganese concentrations for all the sites did not exceed the TWQR as set out in the SA WQG (0.18 mg/L) (DWAF, 1996), nor the CWQG threshold set at 3.6 mg/L for acute exposure and 0.43 mg/L for chronic exposure (CCME, 2019). No water quality guidelines have been set for estuaries and/or coastal marine waters for manganese in order to compare with concentrations at site 5.

Statistical analysis of the samples indicated that there were significant differences between upstream (sites 1 to 3) and downstream (sites 4 and 5) sampling sites. The highest mean manganese concentration was found at site 4, which is located downstream of the Eerste-Kuils confluence area and thus receives polluted water from the Kuils River and its associated tributaries (Thomas *et al*., 2010; Melato, 2011; Olujimi *et al*., 2016; CCT, 2019). As noted in heading 5.1.2.1., site 4 has been subjected to severe pollution in recent years from the discharge of raw sewage into the Kuils River (capeetc, 2018; Green *et al*., 2018; Isaacs and Wolf, 2018). Also noted in heading 5.1.2.1. is that the site is located adjacent to the town of Macassar, as well as smaller farming areas, and as such, stormwater runoff from these areas can carry discarded manganese containing materials (bricks, matches, paint, perfume,

fertilizer) into the river (CCME, 2019). Non-point source pollution from upstream sites can also be identified as a potential source since high rainfall events can carry contaminated material from upstream sources (Fondriest Environmental, Inc., 2014). The differences between the upper and lower sites can be attributed to the vast amount of pollution entering the lower reaches of the river (Thomas *et al*., 2010; Olujimi *et al*., 2016; Green *et al*., 2018; CCT, 2019). Interestingly, site 5 was statistically lower than sites 3 and 4. The reduction in the manganese concentration could be as a result of the plants (Shuping *et al*., 2011; Genchi *et al*., 2020) and wetlands (Sahu, 2014; Rebelo *et al*., 2018) located adjacent to site 5 filtering out manganese, and/or due to the increase in water velocity in the wet season, leading to contaminants being either diluted or discharged into the sea, thereby decreasing its concentration at site 5.

However, as with the dry season, the mean manganese concentrations from the five sampling sites in the wet season were below national and international water quality guideline thresholds but should still be monitored.

5.1.2.3. Temporal comparisons of water for the dry and wet seasons

When comparing the mean manganese concentrations in river water from the five sampling sites between the two seasons, the results indicated that there was no significant seasonal variation for all sites except for site 5. For site 5, the variation between seasons may also be attributed to a reduction in the water velocity associated with less rainfall in the dry season. During the wet season, the increased rainfall not only allows more pollutants to discharge into the sea, but it may also cause the estuary water level to rise, thereby diluting the mixture of pollutants in the water (Anawar and Chowdhury, 2020). As noted, there were no significant differences for sites 1 to 4, and whether these differences were significant or not, the general seasonal trend observed indicated that the mean manganese concentrations were higher in the dry season than the wet season for all sites except site 1. This could be as a result of non-point source pollution in and around the sites that did not readily flow downstream due to a reduced river water velocity in the dry season.

5.1.3. Iron

5.1.3.1. Spatial comparisons between sampling sites for the dry season

In natural waters, iron is often present in varying concentrations depending on the geology of the area and other chemical properties of the water body. Natural processes such as weathering of sulphide ores and igneous, sedimentary and metamorphic rocks, as well as sandstone leaching, can release iron into the environment. Mineral processing, sewage, landfill leachates, and corrosion of iron and steel, can also release iron into the environment. Iron is also used in several industries, such as fungicides and petrochemicals, in their processes and products (DWAF, 1996). In seawater, iron concentrations range from 1-3 µg/L (0.001 to 0.003

mg/L). Rivers contain approximately 0.5-1 mg/L of iron, and groundwater contains approximately 100 mg/L (Lenntech, 2021b).

The present study found that the mean iron concentrations within the five sampling sites in the dry season ranged from 0.1148 mg/L (±0.0510) to 1.5981 mg/L (±1.6760) (Figure 4.4.5). Sparks *et al.* (2017) reported a mean concentration of 3.28 mg/L of iron in intertidal waters from the west coast of the Cape Peninsula. A study by Fatoki *et al.* (2002) reported a mean iron concentration range between 0.10 to 4.47 mg/L in the Umtata River. Duncan *et al.* (2018) reported a mean iron concentration of 4.784 mg/L during the dry season in the Pra Basin, Ghana. Zhou *et al*. (2020) further reported a global iron concentration of 1.48 mg/L in global rivers and lakes from 2010 to 2017. The iron concentrations in water in the present study was less than the concentrations reported by Sparks *et al.* (2017), Zhou *et al.* (2020), and Duncan *et al*. (2018) but is relatively similar to the concentrations reported by Fatoki *et al.* (2002). In addition, at the time, the SA WQG noted that there was insufficient data to determine a threshold but indicated that the iron concentration should not be allowed to vary by more than 10 % of the background dissolved iron concentration for a particular site or case, at a specific time (DWAF, 1996). The mean iron concentration in the present study did not exceed the Canadian Federal Environmental Quality Guidelines which set a guideline value for freshwater at 0.6 mg/L (Government of Canada, 2019). The mean iron concentration at site 5, the Eerste Estuary, did however, exceed the threshold set (0.002 mg/L) by the South African Water Quality Guidelines for Coastal Marine Waters (SA WQG – CMW) (DEA, 2018).

Statistical analysis of the samples indicated that there were insignificant differences in the iron concentrations between the five sampling sites. The results show that the mean iron concentration was lowest at site 1, which, as noted above, is assumed to be the least polluted site along the length of the Eerste River. The mean iron concentration was higher at site 3. As noted in heading 5.1.1.1. site 3 runs underneath a road bridge and is in close proximity to a cluster of low-income houses and two factories. The road bridge experiences high vehicular traffic volumes each day and as noted, cast iron and steel parts make up 55% of the total volume in the production of modern cars (Hovorun *et al*., 2017), which could be deposited in road dust, making its way into the river through runoff. Many studies investigating the composition of road dust have revealed it being rich in iron (Sanderson *et al*., 2016; Čabanová *et al*., 2019; Wong *et al*., 2020). The most common sources of iron in road dust come from exhaust and non-exhaust sources, with brake wear predominantly producing iron (Čabanová *et al*., 2019). All the other sampling sites contained similar iron concentrations, therefore WWTW effluent discharging into rivers is ruled out as a possible source of iron contamination. Road dust containing iron settling in the river during the dry season with reduced water velocity being unable to move the metal downstream is a potential source of the iron contamination at site 3. Furthermore, as noted in heading 5.1.2.1, the area between sites 2 and 3 are

characterised by livestock farming. Iron, manganese and zinc are commonly included in feed since they are essential nutrients, and they are excreted in animal feces (Hejna *et al.*, 2018). It is possible that these metals accumulate in the ground and enter watercourses through runoff. However, since there were insignificant differences between the sites, the aforementioned factors may explain the patterns observed and why the iron concentrations at site 5 exceeded the SA WQG – CMW.

5.1.3.2. Spatial comparisons between sampling sites for the wet season

The mean iron concentrations within the five sampling sites in the wet season in the present study ranged from 0.001 mg/L (±0.0002) to 0.0952 mg/L (±0.1154) (Figure 4.4.5.) and is less than the iron concentrations reported in studies by Zhou *et al*. (2020), Fatoki *et al.* (2002) and Sparks *et al.* (2017) as noted in heading 5.1.3.1, as well as the mean iron concentration during the wet season of 2.493 mg/L in the Pra Basin, Ghana, as reported by Duncan *et al*. (2018). In addition, as noted above, the SA WQG did not determine a threshold due to insufficient data but indicated that the iron concentration should not be allowed to vary by more than 10 % of the background dissolved iron concentration for a particular site or case, at a specific time (DWAF, 1996). In the present study, the mean iron concentration in water in the wet season did not exceed the Canadian Federal Environmental Quality Guidelines which set a guideline value for freshwater at 0.6 mg/L (Government of Canada, 2019). The mean iron concentration at site 5, the Eerste Estuary, did however, exceed the threshold set (0.002 mg/L) by the SA WQG – CMW (DEA, 2018).

Statistical analysis of the samples indicated that there were no significant statistical differences between upstream and downstream sampling sites and the iron concentrations were relatively similar at each site. The results show that the mean iron concentration was lowest at site 1 which, as noted above, is assumed to be the least polluted site along the length of the Eerste River. The highest mean iron concentration was found at site 3. Nevertheless, as noted in heading 5.1.3.1., WWTW discharge was ruled out as potential sources of iron contamination. Since there were higher rainfall patterns for the wet season (table 4.3.1.), it is possible that the road dust containing iron and natural occurrences of iron flowed downstream with the increase in water velocity (Fondriest Environmental, Inc., 2014). As noted in heading 5.1.3.1, since there were insignificant differences between sampling sites, the aforementioned may explain the general tendencies observed and why the iron concentrations at site 5 exceeded the SA WQG – CMW.

5.1.3.3. Temporal comparisons of water for the dry and wet seasons

When comparing the mean iron concentrations in river water from the five sampling sites between the two seasons, the results indicated that there was significant seasonal variation at sites 1 and 3, and insignificant seasonal differences for sites 2, 4 and 5. The general seasonal

trend observed indicated that mean iron concentrations were relatively higher in the dry season at site 1, with the mean iron concentration being significantly higher in the dry season at site 3. As noted, site 1 was assumed to be the least contaminated site due to its distance away from urban areas, as well as the lack of effluent discharge from WWTW and other industries. Therefore, the statistical difference between seasons is unusual. A probable reason for this could be that although site 1 is the upper most site, it still is relatively close to urban areas, iron contaminants could have settled at the site during the dry season. Another reason could be natural weathering of iron-bearing rocks. The iron concentration at site 1 was the lowest in the wet season, and this may be due to the high rainfall in the wet season causing the river velocity to increase (Fondriest Environment, Inc. 2021). This increase would then result in bedded particles becoming suspended in the river water, and being washed downstream (McGoldrick, 2020). At site 3, the iron concentration was significantly higher in the dry season. This could be as a result of road dust containing iron as well as the natural occurrence of iron that did not readily flow downstream due to a reduced river water velocity in the dry season. Then, during the wet season, the contaminants washed downstream (Skinner *et al.,* 2013) and/or plants along the river contributed by filtering some metals out of the water (Shuping *et al*., 2011; Genchi *et al*., 2020).

5.1.4. Zinc

5.1.4.1. Spatial comparisons between sampling sites for the dry season

Zinc is found in rocks and ores, and is easily refined into pure, stable forms. Besides entering aquatic ecosystems naturally through weathering and erosion, it can also enter them through industrial processes. Zinc can be toxic to some fish and mammals at relatively low concentrations (DWAF, 1996). Zinc concentrations in natural surface waters are usually below 10 g/L (WHO, 2003). Zinc concentrations in seawater range from 0.6-5 µg/L ($6x10^{-4}$ to 0.005 mg/L) (Lenntech, 2021d).

In the present study, the mean zinc concentrations within the five sampling sites in the dry season ranged from 0.0132 mg/L (±0.0075) to 0.4753 mg/L (±0.6805) (Figure 4.4.7.). Duncan *et al*. (2018) reported a mean zinc concentration of 3.703 mg/L during the dry season in the Pra Basin, Ghana. Sparks *et al.* (2017) reported a mean concentration of 0.13 mg/L of zinc in intertidal waters from the west coast of the Cape Peninsula. Additionally, a study by Shuping *et al.* (2011) reported a mean zinc concentration of 0.398 mg/L in the lower Diep River over four seasons. The study by Jackson *et al.* (2007) further reported a zinc concentration range of 0.1 to 2.1 mg/L in the Berg River. The zinc concentrations in water in the present study is relatively similar to those outlined above with the exception of those reported in the study by Duncan *et al*. (2018). However, the mean zinc concentrations for sites 1 to 4 in the present study exceeded the TWQR set by the SA WQG (0.002 mg/L) for freshwater (DWAF, 1996) and site 5 exceeded the threshold set (0.02 mg/L) by the SA WQG – CMW (DEA, 2018). The

mean zinc concentration at sites 1 to 4 also exceeded the CWQG threshold set at 0.037 mg/L for acute exposure and 0.007 mg/L for chronic exposure in freshwater (CCME, 2018).

Statistical analysis of the samples showed that there were no significant differences between the zinc concentrations between the five sampling sites. Therefore, despite the insignificant differences, the following tries to explain why the zinc concentrations at each site exceeded water quality guidelines as well as the general tendencies observed on site. The results show that the mean zinc concentration was highest at site 2 and lowest at site 3. Site 2 is located at the Spier Wine Farm in Stellenbosch. Although the site is downstream of the Blouklip and Veldwagters confluence areas, it was evident that the river was relatively in pristine condition through site visit observations. At site 2, the river is bound by gabion walls to prevent the rock wall from collapsing. These gabion walls are made of a hexagonal mesh of galvanized steel wire (Gabion Supply, 2021) which is coated with a zinc-iron alloy and zinc metal to prevent corrosion of the metal (American Galvanizers Association, 2021). This is a possible source of the elevated zinc concentration at the site. Zinc generally enters aquatic environments through industrial activity or through natural weathering of zinc containing rocks (DWAF, 1996). Since all the sites contained zinc concentrations which exceeded water quality guidelines, including site 1 which receives no input from any industrial activity or WWTW effluent discharge, natural weathering of rocks is a plausible source of zinc at these sites.

5.1.4.2. Spatial comparisons between sampling sites for the wet season

The mean zinc concentrations within the five sampling sites in the wet season for the present study ranged from 0.0072 mg/L (±0.0099) to 0.1322 mg/L (±0.0868) (Figure 4.4.7) and is relatively similar to those reported in studies by Sparks *et al*. (2017), Shuping *et al.* (2011), and Jackson *et al.* (2007) as noted in heading 5.1.4.1, as well as the zinc concentration of 0.027 mg/L during the wet season in the Pra Basin, Ghana as reported by Duncan *et al.* (2018). In the present study, the mean zinc concentrations for sites 1 to 4 exceeded the TWQR set by the SA WQG (0.002 mg/L) for freshwater (DWAF, 1996), but site 5 did not exceed the threshold set (0.02 mg/L) by the SA WQG – CMW (DEA, 2018). The mean zinc concentration at sites 1 to 4 also exceeded the CWQG threshold set at 0.037 mg/L for acute exposure and 0.007 mg/L for chronic exposure in freshwater (CCME, 2018).

Statistical analysis of the samples indicated that there were no significant statistical differences between the sites and the zinc concentrations were relatively similar at each site. The results show that the mean zinc concentration was highest at site 4 and lowest at site 5. Site 4 is located downstream of the Kuils-Eerste confluence area. The Kuils River is significantly polluted by WWTW effluent discharges, invasive alien vegetation, stormwater discharges, and urban and/or agricultural runoff (Thomas *et al*., 2010). In addition, close to 60% of the river is canalised (Asset Research, 2021). Furthermore, major unlawful occupation of land has occurred at the Driftsands Nature Reserve in Blue Downs (Jordan and Nombembe, 2021), and

Khayamandi in Stellenbosch (Booysen, 2021). These unlawful occupations are located adjacent to the Kuils River and Plankenburg River respectively, both flowing into the Eerste River. According to Dalu *et al*. (2017), land use changes associated with informal settlements and the increasing dependence on natural resources by vulnerable communities, results in a decrease in the ability of vegetation cover to mitigate disasters such as floods and/or extreme rainfall events leading to floods. In some instances, floods are generally rapid, carrying debris in the runoff. The main issue with informal settlements is the lack of waste management and sewage systems. Therefore, solid waste is scattered around the settlement, and liquid waste including laundry washing, baths, kitchens and other domestic uses are discharged on the premises. The waste eventually flows into rivers during rainy seasons (Mbonambi, 2016). As such, the Eerste River not only receives potentially zinc contaminated WWTW effluent from its tributaries such as the Kuils River and the Plankenburg River, but also from informal settlements along the river's edge, and non-point source pollution from upstream sources. These factors may explain why sites 1 to 4 exceeded the WQG set by DWAF and CWQG set by the CCME. Since the zinc concentration at site 5 was lower than its upstream counterparts and did not exceed the SAWQG-CMW, it is possible that the plants (Shuping *et al*., 2011; Genchi *et al*., 2020) and wetlands (Sahu, 2014; Rebelo *et al*., 2018) between the two sites filtered out zinc, or due to the increase in water velocity in the wet season, that some of the zinc was discharged into the sea, thereby decreasing its concentration at site 5.

5.1.4.3. Temporal comparisons of water for the dry and wet seasons

When comparing the mean zinc concentrations in river water from the five sampling sites between the two seasons, the results indicated that there was no significant seasonal variation for all of the sites. However, whether the seasonal differences were significant or not the general seasonal tendencies observed indicated that the mean zinc concentrations were higher in the wet season for sites 1, 3 and 4, and higher in the dry seasons for sites 2 and 5. The zinc concentration was highest at site 2 in the dry season which could be attributed to the gabion baskets present on site. However, the changes between the sites can be attributed to the increased rainfall in the wet season (table 4.3.1.), which increases water velocity, thereby allowing bedded particles to be suspended in the water, moving them downstream (Earle, 2015; McGoldrick, 2020; Fondriest Environment, Inc. 2021).

5.1.5. Lead

5.1.5.1. Spatial comparisons between sampling sites for the dry season

In aquatic environments, lead primarily comes from weathering of sulphide ores, particularly galena. In general, aquatic ecosystems do not have high amounts of dissolved lead (acetates and chloride salts), due to the insoluble nature of metallic lead and most common lead minerals such as sulfides, sulfates, oxides, carbonates, and hydroxides. Lead in aquatic ecosystems is

normally associated with suspended sediment and is typically complexed with organic compounds in the dissolved phase. Anthropogenic sources of lead in the aquatic environment include (DWAF, 1996):

- Runoff from precipitation, lead dust, and road runoff
- industrial and municipal wastewater discharge;
- mining, milling and smelting of lead and metals associated with lead; and
- the burning of fossil fuels.

Lead is present in seawater in trace amounts, usually between 2-30 ng/L (2×10^{-6} to 3×10^{-5} mg/L. The average concentration of lead in rivers is between 3 and 30 µg/L (0.003 to 0.03 mg/L). In 1995, the World Health Organization (WHO) set a lead limit of 50 µg/L (0.05 mg/L) which was lowered to 10 µg/L (0.01 mg/L) in 2010 (Lenntech, 2021c).

In the present study, the mean lead concentrations within the five sampling sites in the dry season ranged from 0.0001 mg/L (±0.0011) to 0.0047 mg/L (±0.0089) (Figure 4.4.9.). Lead was investigated in the study undertaken by Sparks *et al.* (2017). The results of that study, however, show that the concentration of lead was below the level of detection. Duncan *et al*. (2018) reported a mean lead concentration of 0.175 mg/L in the Pra Basin, Ghana during the dry season. A study undertaken by Olaniran *et al*. (2013) reported a mean lead concentration range of 0.023 to 0.082 mg/L for the Umgeni River, and 0.039 to 0.135 mg/L for the Umdloti River. In both those rivers, the mean lead concentrations exceeded the SA WQG threshold (DWAF, 1996). Additionally, Zhou *et al*. (2020) reported a global mean lead concentration of 0.116 mg/L in global lakes and rivers from 2010 to 2017. Furthermore, the study conducted by Reinecke *et al*. (2007) reported 0.03 to 0.04 mg/L of lead in the Eerste River. The lead concentrations in water in the present study was less than all the above-mentioned studies, with the exception of the Sparks *et al*. (2017) study.

In addition, the SA WQG set a TWQR of 0.0002 mg/L for soft water (<60 hardness), 0.0005 mg/L for medium water (60-119 hardness), 0.001 mg/L for hard water (120-180 hardness), and 0.0012 for very hard water (>180 hardness) (DWAF, 1996). It is difficult to accurately determine which threshold to use for comparison as water hardness was not measured in the present study. However, according to YSI Inc. (2021), water hardness can be approximated using Total Dissolved Solids (TDS) measurements, which were measured in the present study (table 4.3.1.). This hardness approximation gives an error similar to the TDS measurement of 20-30 mg/L of hardness. For site 1, the TDS measurement was 53.30 mg/L, which categorises it as soft water. Sites 2 and 3 had TDS measurements of 247 and 274.3 mg/L respectively, which categorises them as medium water. Sites 4 and 5 had TDS measurements of 533 and 2067 mg/L respectively, which categorises them as very hard water. As such, the mean lead concentrations for sites 1 to 3 in the present study exceeded the threshold at all hardness

levels, and the mean lead concentration at site 4 did not exceed any threshold. The mean lead concentration at site 5 also did not exceed the threshold set (0.002 mg/L) by the SA WQG – CMW (DEA, 2018).

Statistical analysis of the samples showed insignificant differences between lead concentration for all five sites. Despite being insignificant, the below explanations may address the general tendencies.

The results show that the mean lead concentration was highest at site 3 and lowest at site 4. The main anthropogenic sources of lead in aquatic systems includes lead dust and street runoff, industrial and municipal wastewater discharge, mining and combustion of fossil fuels (DWAF, 1996). Specifically at site 3, lead dust and street runoff could account for the elevated lead levels resulting in the lead concentration exceeding water quality guidelines. It is also possible that industrial and WWTWs effluent from upstream sources added to the lead concentration in the river. However, effluent discharge could not be conclusively identified as a source without analysis of the effluent. While there were no significant statistical differences between the lead concentrations at each site, it is alarming that the lead concentrations upstream of site 3 exceeds water quality guidelines, whereas the lead concentrations downstream of site 3 did not. An analysis of the 2018 California wildfire smoke was undertaken which revealed spikes of metal contaminants such as lead in the thick smoke which blanketed Northern California for two weeks (CARB, 2021; The Guardian, 2021). The wildfires which occurred near the Hottentots Holland Nature Reserve and raged through a portion of the Jonkershoek Nature Reserve in February 2021 (CapeNature, 2021), prior to dry season sampling undertaken for this study, could have been a source of lead contamination in the upper portions of the river. Due to the dry season having less rainfall than the wet season (table 4.3.1.), the river water velocity decreases, thereby reducing the ability of the river to carry mineral matter, chemicals, organic material, or metals further downstream (Fondriest Environmental, Inc., 2014; Earle, 2015; McGoldrick, 2020). This could explain why the lead concentrations were lower at the downstream sites. However, it should be noted that it is also possible that the lead concentrations did not exceed the water quality guidelines since the water hardness was approximated using TDS and may thus not be accurate.

5.1.5.2. Spatial comparisons between sampling sites for the wet season

The mean lead concentrations within the five sampling sites in the wet season for the present study ranged from 0.0005 mg/L (±0.0005) to 0.0063 mg/L (±0.0109) (Figure 4.4.9) and were less than the concentrations reported in the studies by Reinecke *et al*. (2007), Olaniran *et al*. (2013), and Zhou *et al*. (2020) as noted in heading 5.1.5.1, as well as the lead concentration of 1.025 mg/L reported by Duncan *et al*. (2018) during the wet season in the Pra Basin, Ghana.

Using the TDS measurements to approximate water hardness, for site 1, the TDS measurement was 55.9 mg/L, which categorises it as soft water. Sites 2 and 3 had TDS measurements of 241.15 and 279.5 mg/L respectively, which categorises them as medium water. Sites 4 and 5 had TDS measurements of 494 and 585 mg/L respectively, which categorises them as very hard water (YSI Inc., 2021). As such, the mean lead concentrations for sites 1 to 3 exceeded the threshold for the respective hardness levels, and the mean lead concentration at site 4 also exceeded the threshold. The mean lead concentration at site 5 did not exceed the threshold set (0.002 mg/L) by the SA WQG – CMW (DEA, 2018).

Statistical analysis of the samples showed insignificant differences between lead concentration for all five sites. Thus, the below explanation may address the general tendencies. The results show that the mean lead concentration was highest at site 4 and lowest at site 2. As noted, site 4 is extremely polluted from WWTW discharge to raw sewage and litter, carrying vast amounts of pollution into the Eerste River (Thomas *et al*., 2010; Olujimi *et al*., 2016; Green *et al*., 2018; CCT, 2019). There does not appear to be a direct source of lead contamination in the river. If the lead in the dry season was as a result on the wildfires occurring in February 2021, then it stands to reason that the increased rainfall associated with the wet season (table 4.3.1.) has increased river water velocity (Fondriest Environmental, Inc., 2014), thereby allowing upstream materials to flow downstream (Earle, 2015; McGoldrick, 2020). Other non-point source pollution from upstream locations and its tributaries such as the Kuils, Blouklip and Plankenburg rivers could also contribute to the lead concentration in the river, especially at site 4. It should be noted that it is also possible that the lead concentrations did not exceed the water quality guidelines since the water hardness was approximated using TDS and may thus not be accurate. Furthermore, the decrease in lead concentration at site 5 could be attributed to the increase in water velocity in the wet season, causing some of the lead to be discharged into the sea.

5.1.5.3. Temporal comparisons of water for the dry and wet seasons

When comparing the mean lead concentrations in river water from the five sampling sites between the two seasons, the results indicated that there was no significant seasonal variation for all the sites. Whether the seasonal differences were significant or not, the general seasonal trend observed indicated that the mean lead concentrations were higher in the wet season for sites 1, 4 and 5, and higher in the dry seasons for sites 2 and 3. The variation in seasonal patterns may be attributed to the movement of the metals during the wet season, and the increased water velocity associated with the increased rainfall (table 4.3.1.). Site 5 also receives effluent from the Macassar WWTW and a Munitions factory (Thomas *et al.,* 2010), as well as potentially suspended pollutants washing downstream with the increase in rainfall. The lead concentrations being higher in the dry season for sites 2 and 3, could also be attributed

to the water velocity as particles may have settled after the February 2021 fires due to a reduction in water velocity associated with lower rainfall in the dry season.

5.2. Metal concentrations in river sediments

5.2.1. Aluminium

5.2.1.1. Spatial comparisons between sampling sites for the dry season

For aluminium, the mean concentrations within the five sampling sites in the dry season ranged from 357.80 mg/kg (±65.0) to 1922.6 mg/kg (±579.8) (Figure 4.4.2). Shuping *et al.* (2011) reported an aluminium concentration range from 2756.9 to 13702.36 mg/kg over four seasons in the sediments of the lower Diep River. Sparks *et al*. (2016) reported a mean sediment aluminium concentration of 256.12 mg/kg in the Helderberg Marine Protected Area (HMPA) and 287.77 mg/kg in the Lourens River estuary. Nkqenkqa (2017) reported an aluminium concentration range from 711.74 to 5075.68 mg/kg in the Veldwachters River. Jackson *et al*. (2009) reported an aluminium concentration range from 1609 to 15018 mg/kg in the Plankenburg River and 175.5 to 14363.8 mg/kg in the Diep River. The mean aluminium concentrations in sediments in this study was much less than in the Diep River, Veldwachters River and Plankenburg River but more than the HMPA and the Lourens River estuary. No Sediment Quality Guidelines (SQG) could be found for aluminium.

Statistical analysis of the samples indicates that there were significant differences between the upper and lower reaches of the river. The sampling sites in the upper reaches recorded relatively similar aluminium concentrations to each other and the reason for this is largely unknown. It is plausible that natural occurrence or contaminated stormwater runoff resulted in the aluminium concentrations recorded. In the lower reaches of the river, the results showed that the mean concentrations of aluminum were highest at site 4 and lowest at site 5. There was also a significant difference between sites 1 and 5, with site 1 having a higher aluminium concentration than site 5. The elevated concentrations at site 4 can be attributed to the vast amount of pollution entering the lower reaches of the river via the Kuils River (Thomas *et al*., 2010; Melato, 2011; Olujimi *et al*., 2016; CCT, 2019). Studies have shown that smaller sediment grain sizes are linked to increased metal concentrations, due to the potential to be mobilized and accumulate, as well as the larger surface-to-volume ratio of finer sediments (Maslennikova *et al.*, 2012; Tansel and Rafiuddin, 2016). Site 4 had the greatest proportion of fine sand and silt and/or clay (table 4.2.1.). Thus, the accumulation potential of the finer sands predominant at site 4 could account for the increased aluminium concentration. In addition, aluminium makes up part of the clay particle, thus the aluminium concentration is naturally higher at site 4 (Skinner *et al*., 2013). Furthermore, possible reasons for the reduction of aluminium concentration at site 5 are three-fold. Firstly, the river meanders between sites 4 and 5, which slows down the river velocity, thereby depositing material at the loops (Skinner *et al.,* 2013; Earle, 2015). Secondly, the plants located between sites 4 and 5 such *Phragmites*

australis, *Salix mucranata* and *Cyperus textilis* (Meek *et al.*, 2009; Meek *et al*., 2013; Jacklin, 2022), and wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river may be filtering out some metal contaminants, thereby reducing the bedded load (Shuping *et al.*, 2011; El-Mahrouk *et al.*, 2019; Prica *et al.*, 2019; Genchi *et al*., 2020). Thirdly, the low metal contaminants can be attributed to the strong tidal currents associated with estuaries, removing contaminants from the estuary (Izegaegbe *et al*., 2020). These reasons for the reduction in aluminium concentrations at site 5 could also explain the difference in concentration compared to site 1.

5.2.1.2. Spatial comparisons between sampling sites for the wet season

For aluminium, the mean concentrations within the five sampling sites in the wet season ranged from 452.5 mg/kg (±180.7) to 6409.9 mg/kg (±2392.0) (Figure 4.4.2). No sediment quality guidelines have been developed for aluminium nationally (Gordon & Muller, 2010) or internationally due to the absence of adequate datasets for the metal (AGI, 2019; Government of Alberta, 2018). However, as noted in heading 5.2.1.1., a mean aluminium concentration of 2756.9 to 13702.36 mg/kg was recorded over four seasons in the sediments of the lower Diep River (Shuping *et al.,* 2011), 256.12 mg/kg in the Helderberg Marine Protected Area (HMPA), 287.77 mg/kg in the Lourens River estuary (Sparks *et al*., 2016), 711.74 to 5075.68 mg/kg in the Veldwachters River (Nkqenkqa, 2017), 1609 to 15018 mg/kg in the Plankenburg River, and 175.5 to 14363.8 mg/kg in the Diep River (Jackson *et al*., 2009). The mean aluminium concentrations in sediments in this study were similar to the studies noted above.

Statistical analysis of the sediment samples indicated that there were significant differences between all sampling sites. The results showed that the mean concentrations of aluminium were highest at site 4 and lowest at site 5. Since site 1 is relatively upstream of most anthropogenic activity, it is plausible that potentially contaminated stormwater runoff and natural occurrence contributed to the aluminium content. The concentration at site 2 was lower than site 1, and while the reason for this is largely unknown, it could be attributed to the large number of rocks, pebbles and boulders present between sites 1 and 2 which slows down the water velocity, allowing contaminants to settle and not flow downstream (Earle, 2015). The wet season received higher rainfall (table 4.3.1), therefore aluminium contamination from upstream sources could have flowed to downstream sites such as sites 3 and 4 which recorded significantly higher aluminium concentrations than the other sites. In addition, as noted in heading 5.2.1.1, elevated concentrations at site 4 can be attributed to the vast amount of pollution entering the lower reaches of the river via the Kuils River (Thomas *et al*., 2010; Melato, 2011; Olujimi *et al*., 2016; CCT, 2019), the higher proportion of fine sand, silt and/or clay potentially mobilizing and accumulating aluminium (Maslennikova *et al.*, 2012; Tansel and Rafiuddin, 2016), and the fact that aluminium is naturally found in clay minerals thereby naturally increasing the aluminium concentration at site 4 (Skinner *et al*. 2013). In addition, site 4 is located downstream of the Kuils-Eerste confluence area, and the high aluminium

concentration could be attributed to the site receiving vast amounts of polluted water from the Kuils River (Melato, 2011; Olujimi *et al*., 2016; CCT, 2019), as well as from non-point source pollution from upstream sources. For site 5, much like the other metals, reasons for the reduction in aluminium concentration at site 5 could be attributed to the meandering nature of the river depositing material at the loops when the velocity decreases (Skinner *et al.*, 2013), the abundance of plants (Shuping *et al.*, 2011; Genchi *et al*., 2020) and wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river between sites 4 and 5 filtering out some metal contaminants, strong tidal currents associated with estuaries, removing contaminants from the estuary (Izegaegbe *et al*., 2020), as well as the increased rainfall in the wet season, which can cause the estuary water level to rise, thereby diluting the mixture of pollutants in the water (Anawar and Chowdhury, 2020). The aluminum concentration at site 5 was also significantly different from site 1, and the aforementioned factors could be the reason for the difference as well.

5.2.1.3. Temporal comparisons of sediments for the dry and wet seasons

When comparing the mean aluminium concentrations in river sediments from the five sampling sites between the two seasons, the results indicated that there were significant seasonal differences for sites 3 and 4, and no significant differences for sites 1, 2 and 5. Whether the seasonal differences were significant or not, the general seasonal trend observed indicated the mean aluminium concentrations for all the sampling sites were higher in the wet season than the dry season except for site 2 which had relatively similar aluminium concentrations for both seasons. As noted in heading 5.1.1.3, generally, during periods of high rainfall, river flow is greater (Fondriest Environment, Inc. 2021), thereby moving particles within the water downstream (Skinner *et al.,* 2013; Earle, 2015; McGoldrick, 2020). This is a plausible reason for the variations at site 3 when observing rainfall patterns (table 4.3.1). As noted in many sections above, the Kuils River runs through many urban areas and unlawful settlements (Asset Research, 2021; Booysen, 2021; Jordan and Nombembe, 2021) which causes the introduction of an array of pollutants into the river (Mbonambi, 2016), including effluent from various WWTWs (Thomas *et al.*, 2010). Therefore, the aforementioned factors could also explain the significant increase in aluminium concentration at site 4 in the wet season since the site not only receives potentially contaminated water from upstream sources, but also from the Kuils River. Furthermore, sites 3 and 4 contained the highest proportions of fine sand, silt and/or clay. This could be attributed to sediment being washed down from upstream sites and/or runoff from surrounding areas with the increase of rainfall during the wet season. The high proportion of sand, silt and/or clay could also increase the aluminium concentration at sites 3 and 4 as explained in headings 5.2.1.1 and 5.2.1.2.

5.2.2. Manganese

5.2.2.1. Spatial comparisons between sampling sites for the dry season

The mean manganese concentrations within the five sampling sites in the dry season ranged from 6.2 mg/kg (±0.8) to 28.2 mg/kg (±11.5) (Figure 4.4.4). No SQG have been developed for manganese nationally (Gordon & Muller, 2010) or internationally due to the absence of adequate datasets for the metal (AGI, 2019; Government of Alberta, 2018). However, Sparks *et al*. (2017) reported a mean manganese concentration of 9.25 mg/kg in surface sediments along the west coast of the Cape Peninsula, Cape Town, South Africa. Nkqenkqa (2017) reported a mean manganese concentration range of 3.78 to 378.57 mg/kg in the Veldwachters River, Stellenbosch, South Africa. Jackson *et al*. (2009) reported a mean manganese concentration range of 15.93 to 225 mg/kg in the Plankenburg River, and the highest mean manganese concentration of 1353.5 mg/kg in the Diep River. Furthermore, a study conducted by Ibrahim and Omar (2013) reported a mean manganese concentration range from 68.9 to 176.5 mg/kg in the River Nile. The mean manganese concentrations in sediments in this study was relatively lower than those recorded in the studies noted above.

Statistical analysis of the samples indicated that there were no significant differences between sites 1 to 4 with the manganese concentration at site 5 being significantly less to the former sites. There was also a significant difference between sites 1 and 5, with site 1 having a higher manganese concentration that site 5. The results showed that the mean concentrations of manganese were highest at site 4 and lowest at site 5. Much like for aluminium, finer sediment was predominant at site 4, and due to the potential for mobilization and accumulation, could have contributed to the increased manganese concentration at site 4. Furthermore, clay minerals are generally aluminium rich, but magnesium is often present. Thus, the magnesium concentration may naturally be higher at site 4 (Kodama and Grim, 2014). Additionally, like aluminium, reasons for the reduction in manganese concentration at site 5 could be attributed to the meandering nature of the river depositing material at the loops (Skinner *et al.,* 2013), the abundance of plants (Shuping *et al*., 2011; Genchi *et al*., 2020) and wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river between sites 4 and 5 filtering out some metal contaminants, and the strong tidal currents associated with estuaries, removing contaminants from the estuary (Izegaegbe *et al*., 2020). The aforementioned factors can also explain the difference between site 1 and site 5.

5.2.2.2. Spatial comparisons between sampling sites for the wet season

The mean manganese concentrations within the five sampling sites in the wet season ranged from 6.6 mg/kg (±1.1) to 104.2 mg/kg (±39.1) (Figure 4.4.4). As mentioned in heading 5.2.2.1. above, a mean manganese concentration of 9.25 mg/kg was recorded in surface sediments along the west coast of the Cape Peninsula of South Africa (Sparks *et al*., 2017), 3.78 to 378.57

mg/kg in the Veldwachters River in Stellenbosch, South Africa (Nkqenkqa, 2017), 15.93 to 225 mg/kg in the Plankenburg River, 1353.5 mg/kg in the Diep River (Jackson *et al*., 2009) and 68.9 to 176.5 mg/kg in the River Nile (Ibrahim and Omar, 2013). The mean manganese concentrations in sediments in this study were relatively lower than those recorded in the studies noted above.

Statistical analysis of the sediment samples indicated that there were significant differences between all sampling sites, and between sites 1 and 5. The results showed that the mean concentrations of manganese were highest at site 4 and lowest at site 5. Since site 1 is relatively upstream of most anthropogenic activity, it is plausible that potentially contaminated stormwater runoff and natural occurrence contributed to the manganese concentration. Interestingly, Site 2 had a lower concentration than sites 1, 3 and 4. Site 2 is located on a private wine farm and while the reason for the decrease in manganese concentration is largely unknown, it could be attributed to the large number of rocks, pebbles and boulders present between sites 1 and 2 which slows down the water velocity, allowing contaminants to settle and not flow downstream (Earle, 2015). In addition, as noted in heading 5.1.2.1, there are many livestock farms along the Eerste River between site 2 and 3. Manganese has been found in livestock feed as well as manure (Hejna et al., 2018). It is possible that manganese accumulated in soil on site and washed into watercourses as runoff and flowed downstream with the increased water velocity associated with increased rainfall in the wet season (table 4.3.1). Therefore, contamination from upstream sources could have flowed to downstream sites such as sites 3 and 4 which recorded significantly higher manganese concentrations. In addition, site 4 is located downstream of the Kuils-Eerste confluence area, and the high manganese concentration could be attributed to the site receiving vast amounts of polluted water from the Kuils River (Melato, 2011; Olujimi *et al*., 2016; Green *et al*., 2018; CCT, 2019), as well as from non-point source pollution from upstream sources. Site 4 is also located adjacent to the town of Macassar, as well as smaller farming areas, and as such, stormwater runoff from these areas can carry discarded manganese containing materials (bricks, matches, paint, perfume, fertilizer) into the river (CCME, 2019). During the dry season, the decreased water velocity associated with less rainfall would have allowed metals to settle on the riverbed. Since site 4 predominantly contained higher finer sediments, as noted earlier, more metals could have accumulated in the sediments (Maslennikova *et al.*, 2012; Tansel and Rafiuddin, 2016) and became suspended with increased river water velocity associated with increased rainfall (Fondriest Environment, Inc. 2021). Furthermore, clay minerals are generally aluminium rich, but magnesium is often present. Thus, the magnesium concentration may naturally be higher at site 4 (Kodama and Grim, 2014). For site 5, much like the other metals, reasons for the reduction in manganese concentration at site 5 could be attributed to the meandering nature of the river depositing material at the loops when the velocity decreases (Skinner *et al.,* 2013), the abundance of plants (Shuping *et al*., 2011; Genchi *et al*., 2020) and

wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river between sites 4 and 5 filtering out some metal contaminants, strong tidal currents associated with estuaries, removing contaminants from the estuary (Izegaegbe *et al*., 2020), as well as the increased rainfall in the wet season, which can cause the estuary water level to rise, thereby diluting the mixture of pollutants in the water (Anawar and Chowdhury, 2020). These can also explain the difference between concentrations at site 1 and 5.

5.2.2.3. Temporal comparisons of sediments for the dry and wet seasons

When comparing the mean manganese concentrations in river sediments from the five sampling sites between the two seasons, the results indicated that there was significant seasonal variation for sites 2 to 4 with no significant variation for sites 1 and 5. At site 2, the general seasonal trend showed that the manganese concentration was significantly higher in the dry season than the wet season. During the dry season, the decreased water velocity associated with less rainfall (Fondriest Environment, Inc. 2021) could have allowed metals to settle to the riverbed (Earle, 2015; McGoldrick, 2020), thereby increasing its metal load. This could also be the reason that sites 3 and 4 recorded less manganese in the dry season. The reason for the reduction in manganese concentration in the wet season may also be due to plants located between sites 1 and 2 such as *Prionium serratum*, filtering out some contaminants (Meek *et al.*, 2013; Jacklin, 2022) and/or the large number of rocks, pebbles and boulders present between sites 1 and 2 which slows down the water velocity, allowing contaminants to settle at site 1 and not flow downstream to site 2 (Earle, 2015). The reduction at site 2 may also have been due to the increased rainfall in the wet season (table 4.3.1) increasing the water velocity, allowing sediment to move downstream from site 2. Conversely, at sites 3 and 4, the seasonal pattern indicated that the manganese concentrations were significantly higher in the wet season. This could be as a result of non-point source pollution in the vicinity of the sites that were bedded in the dry season becoming suspended in the water as a result of the increase in water velocity in the wet season, thereby moving the contamination downstream from upstream sites such as site 2 (Fondriest Environment, Inc. 2021). In addition, as noted in many other sections, site 4 receives potentially contaminated water from the Kuils River as well. It stands to reason that during the wet season, the increased rainfall would result in contaminants washing downstream from the Kuils River, thus contributing to the significant increase in manganese concentration at site 4.

5.2.3. Iron

5.2.3.1. Spatial comparisons between sampling sites for the dry season

The mean iron concentrations within the five sampling sites in the dry season ranged from 668.1 mg/kg (±61.2) to 2498.6 mg/kg (±727.2) (Figure 4.4.6). According to Zhang *et al*. (2016) the iron concentrations ranged from 1556.38 to 2281.16 mg/kg in sediments of the Bortala

River, China. Sparks *et al*. (2017) reported a mean iron concentration range of 835.68 to 1249.36 mg/kg in surface sediment along the west coast of the Cape Peninsula, Cape Town, South Africa. Nkqenkqa (2017) reported a mean iron concentration range of 781.24 to 28540 mg/kg in the Veldwachters River, Stellenbosch, South Africa. Jackson *et al*. (2009) reported a mean iron concentration range of 3763 to 19179 mg/kg in the Plankenburg River, and of 299.3 to 106279.5 mg/kg in the Diep River. The mean iron concentrations in sediments in this study were relatively similar to those recorded in the studies noted above. No SQG have been developed for iron nationally (Gordon & Muller, 2010) or internationally due to the absence of adequate datasets for the metal (Government of Alberta, 2018; AGI, 2019).

Statistical analysis of the samples indicated that there were significant differences between the upper, middle and lower reaches of the river. There were also significant differences between sites 1 and 5. The results showed that the mean concentrations of iron were highest at site 4 and lowest at site 5. The sampling sites in the upper reaches recorded relatively similar iron concentrations to each other, which may be attributed to non-point source pollution, natural occurrence, or a combination thereof. Sites 3 and 4 recorded relatively higher iron concentrations which could be attributed to non-point source pollution (such as informal settlement waste dumping, WWTW and industrial effluent discharge, road dust, etc.) received from the Eerste River tributaries as well as a combination of natural occurrences and anthropogenic sources along the length of the Eerste River. Studies by Tansel and Rafiuddin (2016) and Maslennikova *et al.* (2012) reported that smaller sediment sizes were correlated with higher metal concentrations. The reasons for this correlation included the potential to be mobilized and accumulate, as well as the larger surface-to-volume ratio of finer sediments. Sites 3 and 4 had the greatest proportion of fine sand and silt and/or clay. Thus, the accumulation potential of the finer sands predominant at these sites could account for the increased iron concentration. In addition, while clay minerals are generally composed of silica, aluminium or magnesium, iron is often present. Thus, the iron concentration may naturally be higher at site 4 (Kodama and Grim, 2014). Like aluminium and manganese, reasons for the reduction in iron concentration at site 5 could be attributed to the meandering nature of the river depositing material at the loops (Skinner *et al.,* 2013), wetlands (Sahu, 2014; Rebelo *et al*., 2018) and the abundance of plants (Shuping *et al*., 2011; Genchi *et al*., 2020) along the river between sites 4 and 5 such *Phragmites australis*, *Salix mucranata* and *Cyperus textilis* (Meek *et al.*, 2009; Meek *et al*., 2013; Jacklin, 2022) filtering out some metal contaminants (El-Mahrouk *et al.*, 2019; Prica *et al.*, 2019), and the strong tidal currents associated with estuaries, removing contaminants from the estuary (Izegaegbe *et al*., 2020) . This may also explain the difference between site 1 and 5.

5.2.3.2. Spatial comparisons between sampling sites for the wet season

The mean iron concentrations within the five sampling sites in the wet season ranged from 837.8 mg/kg (±194.1) to 8048.9 mg/kg (±2904.8) (Figure 4.4.6). As noted in heading 5.2.3.1. above, a mean iron concentration of 835.68 to 1249.36 mg/kg was recorded in surface sediment along the west coast of the Cape Peninsula, Cape Town, South Africa (Sparks *et al*., 2017), 781.24 to 28540 mg/kg in the Veldwachters River, Stellenbosch, South Africa (Nkqenkqa, 2017), 1556.38 to 2281.16 mg/kg in sediments of the Bortala River, China (Zhang *et al.* 2016), 3763 to 19179 mg/kg in the Plankenburg River, and of 299.3 to 106279.5 mg/kg in the Diep River (Jackson *et al*., 2009). The mean iron concentrations in sediments in this study were similar to those recorded in the studies noted above.

Statistical analysis of the samples indicated that there were significant statistical differences between the upper, middle and lower reaches of the river. There were also significant differences between sites 1 and 5. The results show that the mean iron concentrations were lowest at site 5 and highest at site 4. The sampling sites in the upper reaches (sites 1 and 2) recorded relatively similar iron concentrations to each other, which may be attributed to non-point source pollution, natural occurrence, or a combination thereof. Sites 3 and 4 recorded relatively higher iron concentrations which could be attributed to non-point source pollution (such as informal settlement waste dumping, WWTW and industrial effluent discharge, road dust, deposition from air, etc.) received from the Eerste River tributaries as well as a combination of natural occurrences and anthropogenic sources along the length of the Eerste River. Studies have shown that smaller sediment sizes were correlated with higher metal concentrations. The reasons for this correlation included the potential to be mobilized and accumulate, as well as the larger surface-to-volume ratio of finer sediments (Maslennikova *et al.* 2012; Tansel and Rafiuddin 2016). Sites 3 and 4 had the greatest proportion of fine sand and silt and/or clay. Thus, the accumulation potential of the finer sands predominant at these sites could account for the increased iron concentration. In addition, iron is often present in the composition of clay minerals. Thus, the iron concentration may naturally be higher at site 4 (Kodama and Grim, 2014). For sites 2 and 3, as noted in heading 5.1.3.1, the area between sites 2 and 3 are characterised by livestock farming. Iron is commonly included in feed since it is an essential nutrient, and they are excreted in animal feces (Hejna *et al.,* 2018). It is possible that these metals accumulate in the soil and enter watercourses through runoff, flowing downstream during periods of high rainfall. For site 5, much like the other metals, reasons for the reduction in iron concentration at site 5 could be attributed to the meandering nature of the river depositing material at the loops when the velocity decreases (Skinner *et al.,* 2013), the abundance of plants (Shuping *et al*., 2011; Genchi *et al*., 2020) and wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river between sites 4 and 5 filtering out some metal contaminants, strong tidal currents associated with estuaries, removing contaminants from the

estuary (Izegaegbe *et al*., 2020), as well as the increased rainfall in the wet season, which can cause the estuary water level to rise, thereby diluting the mixture of pollutants in the water (Anawar and Chowdhury, 2020). This may also explain the difference between site 1 and 5.

5.2.3.3. Temporal comparisons of sediments for the dry and wet seasons

When comparing the mean iron concentrations in river sediments from the five sampling sites between the two seasons, the results indicated that there was significant seasonal variation at site 4, and no significant seasonal differences for sites 1, 2, 3 and 5. The general seasonal trend observed indicated that the mean iron concentrations were relatively higher in the wet season, with the mean iron concentration being significantly higher in the wet season at site 4. The elevated concentrations at site 4 can be attributed to the vast amount of pollution entering the lower reaches of the river via the Kuils River (Thomas *et al*., 2010; Melato, 2011; Olujimi *et al*., 2016; CCT, 2019). Studies have shown that smaller sediment grain sizes are linked to increased metal concentrations, due to the potential to be mobilized and accumulate, as well as the larger surface-to-volume ratio of finer sediments (Maslennikova *et al.*, 2012; Tansel and Rafiuddin, 2016). Site 4 had the greatest proportion of fine sand and silt and/or clay (table 4.2.1.). Thus, the accumulation potential of the finer sands predominant at site 4 could account for the increased iron concentration. In addition, while clay minerals are generally aluminium rich, iron is often present. Thus, the iron concentration may naturally be higher at site 4 (Kodama and Grim*,* 2014).

5.2.4. Zinc

5.2.4.1. Spatial comparisons between sampling sites for the dry season

For zinc, the mean concentrations within the five sampling sites in the dry season ranged from 0.0 mg/kg (±0.0) to 58.3 mg/kg (±54.9) (Figure 4.4.8). The mean zinc concentrations for all five sites did not exceed the threshold set (123 mg/kg for freshwater and 124 mg/kg for marine/estuarine) by the Canadian Sediment Quality Guidelines (SQG) for the Protection of Aquatic Life (CCME, 1999).

While the zinc concentrations at each sampling site did not exceed the SQG set by the CCME, statistical analysis of the samples showed that there were significant differences between sediments in the middle reaches (sites 2 and 3) of the river compared to the upper (site 1) and lower reaches (sites 4 and 5) of the river. The results showed that the mean concentrations of zinc were highest at site 4 and lowest at sites 1 and 5, where zinc concentrations were below detection limits at sites 1 and 5. Site 1 is the upper most site and is least affected by anthropogenic activities. Since zinc is an essential nutrient for both plants and animals, it is possible that the abundance of plants and aquatic fauna present in the river at or above site 1 could have absorbed the zinc for their own use (Ruiters, 2012), thereby reducing the concentration to a point that it was not detectable. As noted, site 4 is located downstream of

the Kuils-Eerste confluence area, and the high zinc concentration could be attributed to the site receiving vast amounts of polluted water from the Kuils River (Thomas *et al*., 2010; Melato, 2011; Olujimi *et al*., 2016; CCT, 2019), as well as from non-point source pollution from upstream sources. Studies reported that smaller sediment sizes were correlated with higher metal concentrations. The reasons for this correlation included the potential to be mobilized and accumulate, as well as the larger surface-to-volume ratio of finer sediments (Maslennikova *et al.*, 2012; Tansel and Rafiuddin, 2016). Site 4 had the greatest proportion of fine sand and silt and/or clay. Thus, the accumulation potential of the finer sands predominant at these sites could account for the increased zinc concentration. For site 5, much like the other metals, reasons for the reduction in zinc concentration at site 5 could be attributed to the meandering nature of the river depositing material at the loops when the velocity decreases (Skinner *et al.,* 2013). Secondly, the abundance of plants located between sites 4 and 5 such *Phragmites australis*, *Salix mucranata* and *Cyperus textilis* (Meek *et al.*, 2009; Meek *et al*., 2013; Jacklin, 2022), and wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river between sites 4 and 5 filtering out some metal contaminants, thereby reducing the bedded load. Thirdly, the strong tidal currents associated with estuaries could be removing contaminants from the estuary (Izegaegbe *et al*., 2020).

5.2.4.2. Spatial comparisons between sampling sites for the wet season

For zinc, the mean concentrations within the five sampling sites in the wet season ranged from 8.2 mg/kg (±3.0) to 88.89 mg/kg (±24.8) (Figure 4.4.8). The mean zinc concentrations for all five sites did not exceed the threshold set (123 mg/kg for freshwater and 124 mg/kg for marine/estuarine) by the Canadian SQG for the Protection of Aquatic Life (CCME, 1999).

Although the zinc concentrations at each sampling site did not exceed the SQG set by the CCME, statistical analysis of the samples indicated that there were significant differences between the upper, middle and lower reaches of the river. The results show that the mean iron concentrations were lowest at site 5 and highest at site 4. Sites 1 and 2 recorded relatively similar zinc concentrations to each other which may be attributed to non-point source pollution and stormwater runoff, natural occurrence, or a combination thereof. Sites 3 and 4 recorded relatively higher zinc concentrations which could be attributed to the higher proportion of sand and silt/clay found at the two sites. Studies reported that smaller sediment sizes were correlated with higher metal concentrations. The reasons for this correlation included the potential to be mobilized and accumulate, as well as the larger surface-to-volume ratio of finer sediments (Maslennikova *et al.*, 2012; Tansel and Rafiuddin, 2016). Thus, the accumulation potential of the finer sands predominant at these sites could account for the increased zinc concentration. For site 5, much like the other metals, reasons for the reduction in zinc concentration at site 5 could be attributed to the meandering nature of the river depositing material at the loops when the velocity decreases (Skinner *et al.,* 2013), the abundance of

plants (Shuping *et al*., 2011; Genchi *et al*., 2020) and wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river between sites 4 and 5 filtering out some metal contaminants, strong tidal currents associated with estuaries, removing contaminants from the estuary (Izegaegbe *et al*., 2020), as well as the increased rainfall in the wet season, which can cause the estuary water level to rise, thereby diluting the mixture of pollutants in the water (Anawar and Chowdhury, 2020).

5.2.4.3. Temporal comparisons of sediments for the dry and wet seasons

When comparing the mean zinc concentrations in river sediments from the five sampling sites between the two seasons, the results indicated that there was significant seasonal variation for all of the sites except site 4. Whether the seasonal differences were significant or not, the general seasonal trend observed indicated that the zinc concentration for each site was higher in the wet season. For most of the metals discussed above, it is evident that site 4 is the most polluted site. Thus, the fact that there was no significant difference for the site is not that unusual. It shows that even with heavy rainfall washing particles downstream, the zinc concentration at site 4 remained higher than the other sampling sites. At site 1, the zinc concentration was undetectable in the dry season and the zinc concentration in the wet season may be due to stormwater runoff, but the definitive source at site 1 is largely unknown. As noted in heading 5.1.4.1, the river section at site 2 is bound by gabion walls which contains zinc (American Galvanizers Association, 2021). Sometimes, the zinc coating on the gabion walls become corroded in some places through contact with ions from dissolved soil particles and rain (Racin and Hoover, 2001). It is possible that the corrosion of the gabions could have been a route for zinc to enter the sediment load during the wet season, thereby increasing the zinc concentration. For the rest of the sites, the increased zinc concentration may be attributed to the increased rainfall in the wet season (table 4.3.1.), which increases water velocity, thereby allowing bedded particles to be suspended in the water, moving them downstream from sources of contamination (Earle, 2015; McGoldrick, 2020; Fondriest Environment, Inc. 2021).

5.2.5. Lead

5.2.5.1. Spatial comparisons between sampling sites for the dry season

For lead, the mean concentrations within the five sampling sites in the dry season ranged from 0.5 mg/kg (±0.2) to 3.5 mg/kg (±1.5) (Figure 4.4.10). The mean lead concentrations for all five sites did not exceed the threshold set (35 mg/kg for freshwater and 30 mg/kg for marine/estuarine) by the Canadian SQG for the Protection of Aquatic Life (CCME, 1998).

Although the lead concentrations at each sampling site did not exceed the SQG set by the CCME, statistical analysis of the samples indicated that there were significant differences between the upper, middle and lower reaches of the river with significant differences also observed between sites 1 and 5. The results showed that the mean concentrations of lead

were highest at site 4 and lowest at site 5. Sites 1 to 3 recorded relatively similar lead concentrations, which may be attributed to non-point source pollution. In addition, as noted in heading 5.1.5.1, an analysis of the 2018 California wildfire smoke revealed spikes of metal contaminants such as lead in the thick smoke which blanketed Northern California for two weeks (CARB, 2021; The Guardian, 2021). Therefore, the wildfires which occurred near the Hottentots Holland Nature Reserve and raged through a portion of the Jonkershoek Nature Reserve in February 2021 (CapeNature, 2021), prior to dry season sampling undertaken for this study, could have been a source of lead contamination in the upper portions of the river. Since there was less rainfall in the dry season (table 4.3.1), the particles present in the smoke could have settled and became bedded in the river sediment (Fondriest Environmental, Inc., 2014). As noted, site 4 is located downstream of the Kuils-Eerste confluence area, and the high lead concentration could be attributed to the site receiving vast amounts of polluted water from the Kuils River (Thomas *et al*., 2010; Melato, 2011; Olujimi *et al*., 2016; CCT, 2019), as well as from non-point source pollution from upstream sources. The Eerste River and the Kuils River flows through urbanised areas, where older houses could have lead pipes which can leach lead ions into rivers via stormwater outflows. Similar for all the other metals, site 4 had the greatest proportion of fine sand and silt and/or clay (table 4.2.1.). Thus, the accumulation potential of the finer sands predominant at site 4 could account for the increased lead concentration (Tansel and Rafiuddin, 2016). For site 5, much like the other metals, reasons for the reduction in lead concentration at site 5 could be attributed to the meandering nature of the river depositing material at the loops when the velocity decreases (Skinner *et al.,* 2013), the abundance of plants (Shuping *et al*., 2011; Genchi *et al*., 2020) and wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river between sites 4 and 5 filtering out some metal contaminants, and strong tidal currents associated with estuaries, removing contaminants from the estuary (Izegaegbe *et al*., 2020). This could also explain the difference between site 1 and 5.

5.2.5.2. Spatial comparisons between sampling sites for the wet season

For lead, the mean concentrations within the five sampling sites in the wet season ranged from 1.4 mg/kg (±0.2) to 13.4 mg/kg (±6.2) (Figure 4.4.10). The mean lead concentrations for all five sites did not exceed the threshold set (35 mg/kg for freshwater and 30 mg/kg for marine/estuarine) by the Canadian SQG for the Protection of Aquatic Life (CCME, 1998).

While the lead concentrations at each sampling site did not exceed the SQG set by the CCME, statistical analysis of the samples indicated that there were significant statistical differences between all sites. The results show that the mean lead concentrations were lowest at site 5 and highest at site 4. The lead concentration steadily increases from site 1 to 4 which may be attributed to non-point source pollution, stormwater runoff, lead pipes, and the February 2021 wildfires. As noted, site 4 is also located downstream of the Kuils-Eerste confluence area, and

the high lead concentration could be attributed to the site receiving vast amounts of polluted water from the Kuils River (Thomas *et al*., 2010; Melato, 2011; CCT, 2019), as well as from non-point source pollution from upstream sources. In addition, as noted in heading 5.2.5.1, site 4 had the greatest proportion of fine sand and silt and/or clay (table 4.2.1.). Thus, the accumulation potential of the finer sands predominant at site 4 could account for the increased lead concentration (Tansel and Rafiuddin, 2016). For site 5, much like the other metals, reasons for the reduction in lead concentration at site 5 could be attributed to the meandering nature of the river depositing material at the loops when the velocity decreases (Skinner *et al.,* 2013), the abundance of plants (Shuping *et al*., 2011; Genchi *et al*., 2020) and wetlands (Sahu, 2014; Rebelo *et al*., 2018) along the river between sites 4 and 5 filtering out some metal contaminants, and strong tidal currents associated with estuaries, removing contaminants from the estuary (Izegaegbe *et al*., 2020).

5.2.5.3. Temporal comparisons of sediments for the dry and wet seasons

When comparing the mean lead concentrations in river sediments from the five sampling sites between the two seasons, the results indicated that there was significant seasonal variation for sites 2 to 4. The general seasonal trend observed indicated that the mean lead concentrations were higher in the wet season for all the sites. This could be because of anthropogenic sources such as contaminated stormwater runoff, non-point source pollution from tributaries, WWTW effluent from tributaries, lead pipes, or deposition from air as a result of the February 2021 wildfires and/or exhaust fumes that were bedded in the dry season but moved downstream with the increased rainfall in the wet season. At site 2, there are no obvious sources of lead, thus the lead present at site 1 could have moved downstream. At sites 3 and 4, due to the increased rainfall in the wet season (table 4.3.1), runoff from roads as well as effluent from industries and WWTW could increase the lead concentration in the river sediment. Since fine sand, silt and clay are correlated with higher metal concentrations and sites 3 and 4 contained the highest proportion of fine sand, silt and/or clay (Tansel and Rafiuddin, 2016), it is plausible that this contributed to the increased lead concentrations at these two sites.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The research objectives for the study were to determine if metals are present at environmentally significant concentrations along the length of the river in the water and sediment, and to determine whether there is a link between concentrations of various metals present at environmentally significant levels along the length of this river and the sources of contamination. To achieve the objectives, this study analysed water and sediment samples from the Eerste River during the dry (April 2021) and wet (August 2021) seasons of the study period. Initial analysis measured 20 metals, but only five metals were presented in this study. These include aluminium, manganese, iron, zinc and lead.

The results showed that for aluminium, there were no significant differences in metal concentrations in water between the sampling sites for both the dry and wet season, whereas there were significant differences in the sediment between the sampling sites for the dry and wet seasons. The differences in the sediment may be due to non-point source pollution from the Eerste River tributaries, stormwater runoff, natural occurrence, or a combination thereof. Furthermore, there were significant differences in the water between the dry and wet seasons for sites 4 and 5 as the aluminium concentrations were higher in the wet season. This can be attributed to increased rainfall resulting in particle movement, as well as increased stormwater runoff and effluent from industries and WWTWs, in conjunction with non-point source pollution from the Eerste River tributaries. Significant differences in the sediment between the dry and wet seasons were also detected for sites 3 and 4 as the aluminium concentration was higher in the wet season. A reason for this may be the increased rainfall resulting in particle movement, non-point source pollution from activities along the length of the river, the high proportion of fine sand, silt and/or clay present at sites 3 and 4 which has been linked to higher metal concentrations in previous studies, as well as the natural occurrence of aluminium in clay. For both the dry and wet seasons, the mean concentrations in the water at all five sites exceeded the TWQR set by the South African Water Quality Guidelines of 1996, and sites 1 to 4 exceeded the DGV of 2000 set by the Australia and New Zealand Guidelines for Fresh and Marine Water Quality. However, no SQG could be found for aluminium for comparative purposes.

For manganese, the results showed that there were significant differences in the water and sediment between the sampling sites for the dry and wet seasons. These differences can be attributed to stormwater runoff from residential and farm areas, WWTW effluent discharge as well as pollution from the Eerste River tributaries. There were also significant differences in the water between the dry and wet seasons for site 5 as the manganese concentration was higher in the dry season. This difference can be attributed to a reduction in the water velocity

associated with less rainfall in the dry season. In the wet season, increased rainfall not only allows more pollutants to discharge into the sea, but it may also cause the estuary water level to rise, thereby diluting the mixture of pollutants in the water. Significant differences in sediment manganese concentrations between the dry and wet seasons were also detected for sites 2, 3 and 4 as site 2 recorded higher concentrations in the dry season and sites 3 and 4 recorded higher concentrations in the wet season. Site 2 could have recorded higher concentrations in the dry season due to decreased rainfall, allowing sediments to become bedded, as well as decreased concentrations in the wet season due to the abundance of plants and wetlands filtering out the contaminants. The increased manganese concentrations at sites 3 and 4 may be due to non-point source pollution in the vicinity of the sites, increased rainfall resulting in particle movement and stormwater runoff, and the high proportion of fine sand, silt and/or clay present at sites 3 and 4 which has been linked to higher metal concentrations in previous studies. For both dry and wet seasons, the mean manganese concentrations in the water for all the sites did not exceed the TWQR as set out in the South African Water Quality Guidelines of 1996, nor the 2019 Canadian Water Quality Guidelines for the Protection of Aquatic Life threshold for acute exposure and chronic exposure. No SQG were found for manganese.

For iron, there were significant differences in the water and sediment between the sampling sites for the dry and wet seasons. There were significant differences in the water between the dry and wet seasons for sites 1 and 3. Significant differences in the sediment between the dry and wet seasons were also detected for site 4. This could be as a result of road dust containing iron as well as the natural occurrence of iron that did not readily flow downstream due to a reduced river water velocity in the dry season. Furthermore, the results showed that there were significant differences in the water iron concentrations between the sampling sites in the dry season and no significant differences in the wet season. The differences can be attributed to iron-containing road dust flowing into the river, and the reduction in rainfall in the dry season causing pollutants to become stagnant. The mean iron concentration in the water did not exceed the Canadian Federal Environmental Quality Guidelines of 2019 which set a guideline value for freshwater, while the mean iron concentration at site 5, the estuary, exceeded the threshold set by the 2018 South African Water Quality Guidelines for Coastal Marine Waters. However, no SQG could be found for iron in order to compare to the measured concentrations in the present study.

For zinc, the results showed that there were no significant differences in water metal concentrations between the sampling sites for both the dry and wet seasons, whereas there were significant differences in the sediment between the sampling sites for the dry and wet seasons. This may be due to the dry season’s reduced water flow because of decreased rainfall, causing suspended contaminants to settle in the sediments, then becoming suspended again once the water flow increases due to increased rainfall in the wet season. In addition,

there were no significant differences in the water between the dry and wet seasons, but there were significant differences in the sediment between the dry and wet seasons for sites 1, 2, 3, and 5. This could be attributed to possible corrosion of the zinc-coated gabion baskets present at site 2. However, the changes between the sites can be attributed to the increased rainfall in the wet season, which increases water velocity, thereby allowing bedded particles to be suspended in the water, moving them to downstream sites. The mean zinc concentrations for sites 1 to 4 in the water exceeded the TWQR set by the South African Water Quality Guidelines of 1996 for freshwater and the 2018 Canadian Water Quality Guidelines for the Protection of Aquatic Life threshold for acute and chronic exposure in freshwater. Whereas in the dry season, concentrations at site 5 exceeded the threshold set by the South African Water Quality Guidelines for Coastal Marine Waters of 2018, but not in the wet season. The mean zinc concentrations in the sediments for all five sites did not exceed the threshold set by the Canadian SQG of 1999.

In terms of lead, the results showed that there were no significant differences in water metal concentration between the sampling sites for both the dry and wet seasons, whereas there were significant differences in the sediment between the sampling sites for the dry and wet seasons. This may be due to lead dust and street runoff, as well as WWTW and industrial effluent discharge. In addition, there were no significant differences in the water between the dry and wet seasons, but there were significant differences in the sediment between the dry and wet seasons for sites 2, 3, and 4. This increased concentration in the wet season may be due to the lead deposition from air pollution such as wildfires, fine sand, silt and/or clay increasing the metal load as well as contaminated water entering the Eerste River from its tributaries (for sites 3 and 4), as well as contaminated stormwater runoff. Comparisons against WQG were approximated, as water hardness was not measured in the study but rather estimated using TDS. In the dry season, lead concentrations in the water exceeded the South African Water Quality Guidelines of 1996 for sites 1 to 3 and concentrations at sites 1 to 4 exceeded the South African Water Quality Guidelines of 1996 in the wet season. The mean lead concentrations in the sediments for all five sites did not exceed the threshold set by the Canadian SQG of 1998 for both seasons.

It can therefore be concluded that there were significant differences in concentrations of the metals in the water and sediment along the length of the river. Some concentrations in the water and sediment exceeded available WQG, SQG and concentrations measured in additional studies. It is further concluded that non-point source pollution, metal-containing road dust, wildfires, stormwater runoff and runoff from farms, and natural occurrence contributed to the metal contamination. There is little evidence to prove that WWTW effluent is the main source of contamination, but it may be contributing to the metal contamination to some degree.

6.2. Recommendations

- Further research is required to better distinguish the sources of metal contamination in the river and its tributaries.
- Further research on the impacts of metal contamination on the Eerste River biodiversity is also required.
- This study has highlighted the lack of South African sediment quality guidelines as a gap in the scientific literature. Therefore, more research must be done on sediment contamination in South Africa in order to generate significantly more data.
- There is a need for continuous metal monitoring in the Eerste River to locate vulnerable areas and apply appropriate remediation measures. To this end a co-management approach should be investigated by the City of Cape Town and Stellenbosch Municipality.
- Wastewater treatment works should regularly be monitored for metal contaminants and abatement measures put in place if the metal concentrations exceed permissible levels.

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APPENDICES

Appendix A: Concentrations (mg/l) of water samples for all metals measured in this study in the dry and wet seasons

Sample ID - Dry season	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr
Blank water 13/4/2021	0.014390	0.010895	0.000000	0.000354	0.000519	0.007519	0.000007	0.000575	0.016965	0.007932	0.000041	0.000320	0.001187
D - S1 - W1	0.013258	0.151651	0.001000	0.002143	0.004844	0.056466	0.000034	0.000000	0.000000	0.000000	0.000075	0.000103	0.020673
D - S1 - W2	0.015360	0.060554	0.001000	0.000305	0.008275	0.112371	0.000038	0.000000	0.000000	0.033586	0.000226	0.000378	0.023767
D - S1 - W3	0.013824	0.015641	0.000000	0.000000	0.007955	0.080571	0.000035	0.000000	0.024454	0.061173	0.000000	0.000496	0.020964
D - S1 - W4	0.008769	0.026632	0.001000	0.000174	0.006856	0.136649	0.000051	0.000000	0.000000	0.056954	0.000063	0.000839	0.017469
D - S1 - W5	0.015621	0.144931	0.001000	0.004836	0.010294	0.187976	0.000066	0.000000	0.237856	0.000000	0.000214	0.000255	0.017120
D - S2 - W1	0.524904	0.194621	0.001000	0.000000	0.014093	0.251043	0.000107	0.000000	0.000000	1.583982	0.001193	0.000682	0.088599
D - S2 - W2	0.037886	0.004278	0.001000	0.000000	0.008343	0.041695	0.000064	0.000000	0.195738	0.684566	0.001004	0.001185	0.066043
D - S2 - W3	0.019046	0.009887	0.001000	0.000000	0.007578	0.075430	0.000047	0.000000	0.005767	0.052080	0.000478	0.000419	0.058248
D - S2 - W4	0.000000	0.103508	0.001000	0.000644	0.007186	0.118330	0.000084	0.000000	0.000000	0.020657	0.000815	0.000048	0.053791
D - S2 - W5	0.547198	0.314055	0.001000	0.002025	0.009747	0.208451	0.000130	0.000000	0.045251	0.035400	0.000844	0.000000	0.069094
D - S3 - W1	0.030747	0.080811	0.000000	0.000000	0.015170	1.111787	0.000165	0.000000	0.000000	0.017176	0.000446	0.000408	0.083204
D - S3 - W2	0.296326	0.263933	0.001000	0.000944	0.025894	4.434895	0.000199	0.000000	0.000000	0.015691	0.000731	0.000000	0.081256
D - S3 - W3	0.351302	0.094984	0.000000	0.000000	0.019012	0.667244	0.000119	0.000000	0.105998	0.000000	0.000352	0.000000	0.072786
D - S3 - W4	0.002911	0.000000	0.000000	0.000000	0.013669	0.154220	0.000078	0.000000	0.066544	0.018238	0.000106	0.000000	0.067008
D - S3 - W5	0.556804	1.178364	0.001000	0.001168	0.020546	1.622261	0.000218	0.000000	0.000000	0.015063	0.000431	0.000000	0.093232
D - S4 - W1	0.047932	0.023957	0.000000	0.000000	0.025686	0.104100	0.000081	0.000000	0.000000	0.032616	0.000435	0.000000	0.192946
D - S4 - W2	0.010807	0.049011	0.001000	0.000000	0.016857	0.070820	0.000096	0.000000	0.000000	0.024433	0.000596	0.000000	0.151513
D - S4 - W3	0.008449	0.145658	0.001000	0.000000	0.030775	0.068917	0.000096	0.000000	0.048277	0.004621	0.000542	0.000000	0.203052
D - S4 - W4	0.005755	0.050095	0.000000	0.000538	0.033107	0.396336	0.000163	0.000000	0.000000	0.022080	0.000791	0.000000	0.178145
D - S4 - W5	0.023894	0.000000	0.000000	0.000000	0.023033	0.145962	0.000072	0.000000	0.000000	0.002785	0.000515	0.000000	0.154151
D - S5 - W1	0.056241	0.051531	0.000000	0.000000	0.019931	0.243150	0.000165	0.000000	0.000000	0.031876	0.000467	0.000000	0.262248
D - S5 - W2	0.041666	0.074938	0.001000	0.001485	0.020541	0.071877	0.000082	0.000000	0.000000	0.007826	0.000511	0.000000	0.221405
D - S5 - W3	0.030909	0.055465	0.001000	0.000000	0.023309	0.139240	0.000140	0.000000	0.000000	0.037127	0.000409	0.000000	0.207072
D - S5 - W4	0.090933	0.033818	0.000000	0.000000	0.029585	0.094477	0.000075	0.000000	0.000000	0.023685	0.000463	0.000000	0.238182
D - S5 - W5	0.075760	0.000000	0.001000	0.000000	0.027369	0.136133	0.000118	0.006818	0.128224	0.017076	0.000944	0.000000	0.338164

Appendix A (continued)

Sample ID - Dry season	Mo	Cd	Sn	Sb	Ba	Hg	Pb
Blank water 13/4/2021	0.000040	0.000025	0.000086	0.000032	0.000872	0.000009	0.000365
D - S1 - W1	0.000049	0.000275	0.000000	0.000031	0.007304	BDL	0.001726
D - S1 - W2	0.000000	0.000052	0.000272	0.000062	0.009495	0.000030	0.001546
D - S1 - W3	0.000000	0.000000	0.000000	0.000130	0.008629	0.000035	0.000513
D - S1 - W4	0.000000	0.000000	0.000000	0.000092	0.010491	0.000007	0.003734
D - S1 - W5	0.000015	0.000000	0.000261	0.000142	0.012976	0.000022	0.000000
D - S2 - W1	0.000076	0.000074	0.000299	0.000280	0.019650	0.000022	0.004619
D - S2 - W2	0.000000	0.000000	0.000000	0.000087	0.014338	BDL	0.000000
D - S2 - W3	0.000000	0.000006	0.001199	0.000097	0.056533	0.000017	0.001053
D - S2 - W4	0.000091	0.000000	0.000000	0.000123	0.013038	0.000000	0.000920
D - S2 - W5	0.000155	0.000000	0.000253	0.000186	0.013836	0.000000	0.002410
D - S3 - W1	0.000228	0.000000	0.000204	0.000033	0.015911	0.000000	0.000371
D - S3 - W2	0.000405	0.000000	0.000000	0.000123	0.020004	BDL	0.000000
D - S3 - W3	0.000181	0.000000	0.000000	0.000009	0.016497	BDL	0.000000
D - S3 - W4	0.000002	0.001786	BDL	0.000031	0.012580	BDL	0.020519
D - S3 - W5	0.000224	0.000000	0.000432	0.000153	0.043976	0.000000	0.003150
D - S4 - W1	0.000000	0.000000	0.000000	0.000037	0.018668	BDL	0.000467
D - S4 - W2	0.000000	0.000000	0.000000	0.000075	0.015609	0.000000	0.000000
D - S4 - W3	0.000041	0.000000	0.000000	0.000000	0.017248	0.000013	0.000403
D - S4 - W4	0.000273	0.000000	0.000147	0.000282	0.015125	BDL	0.001532
D - S4 - W5	0.000000	0.000000	0.000000	0.000000	0.016165	BDL	0.000000
D - S5 - W1	0.000014	0.000000	0.000000	0.000113	0.014025	BDL	0.002285
D - S5 - W2	0.000103	0.000000	0.000000	0.000000	0.013912	BDL	0.000000
D - S5 - W3	0.000000	0.000000	0.000006	0.000007	0.013662	0.000000	0.000026
D - S5 - W4	0.000000	0.000000	0.000000	0.000003	0.015964	0.000000	0.000000
D - S5 - W5	0.000101	0.000000	0.000000	0.000071	0.016996	BDL	0.000000

***BDL - Below Detection Limits**

Appendix A (continued)

Sample ID - Wet season	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr
Blank Water 31/08/2021	0.013596	0.011233	0.000000	0.000300	0.000330	0.023274	0.000008	0.000000	0.000000	0.009234	0.000047	0.000344	0.002742
W - S1 - W1	0.000000	0.010666	0.000000	BDL	0.001830	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.003058
W - S1 - W2	0.014867	0.516843	0.001000	0.000000	0.010974	0.000000	0.000022	0.000000	0.020275	0.017728	0.000057	0.000000	0.001208
W - S1 - W3	0.015525	0.646307	0.000000	0.000000	0.014734	0.000000	0.000039	0.008323	0.304244	0.134369	0.000000	0.000000	0.005367
W - S1 - W4	0.323176	0.298876	0.001000	0.002597	0.011348	0.000419	0.000329	0.000000	0.000000	0.100794	0.000033	0.000000	0.008303
W - S1 - W5	0.209342	0.478495	0.000000	0.000000	0.011235	0.000000	0.000000	0.000000	0.000000	0.015779	0.000000	0.000000	0.000000
W - S2 - W1	0.000000	0.146943	0.001000	0.000000	0.009880	0.000000	0.000146	0.000000	0.000000	0.064865	0.001323	0.000000	0.127030
W - S2 - W2	0.022411	0.388919	0.001000	0.000000	0.008717	0.000000	0.000226	0.000000	0.000000	0.000000	0.001055	0.000000	0.111381
W - S2 - W3	0.027639	0.207655	0.001000	0.000762	0.006683	0.000000	0.000069	0.000000	0.000000	0.000000	0.000754	0.000000	0.088520
W - S2 - W4	0.014870	0.530107	0.001000	0.000000	0.012698	0.428028	0.000123	0.000000	0.000000	0.245946	0.001702	0.000000	0.123560
W - S2 - W5	0.002790	0.137004	0.001000	0.000000	0.005554	0.000000	0.000061	0.004877	0.128199	0.053394	0.000932	0.000000	0.098883
W - S3 - W1	0.009957	0.773314	0.001000	0.012405	0.017463	0.291728	0.000311	0.000000	0.000000	0.150726	0.000730	0.000000	0.086048
W - S3 - W2	0.200550	2.185631	0.001000	0.000000	0.038623	0.076016	0.000106	0.000000	0.000000	0.000000	0.000890	0.000000	0.094845
W - S3 - W3	0.000000	0.286804	0.001000	0.000000	0.007491	0.000000	0.000060	0.000000	0.010618	0.159021	0.000757	0.000000	0.080106
W - S3 - W4	0.000000	0.506484	0.001000	0.000000	0.006032	0.084614	0.000020	0.000000	0.008008	0.000000	0.000663	0.000000	0.066480
W - S3 - W5	0.003186	0.463472	0.001000	0.000000	0.006961	0.023699	0.000031	0.000000	0.000000	0.000000	0.000736	0.000000	0.087278
W - S4 - W1	0.220045	0.271250	0.001000	0.000000	0.018165	0.021157	0.000235	0.000000	0.000000	0.203702	0.001845	0.000000	0.441858
W - S4 - W2	0.049038	0.641497	0.001000	0.000000	0.021972	0.000000	0.000223	0.000000	0.000000	0.089845	0.002115	0.000000	0.518537
W - S4 - W3	0.048469	0.355893	0.001000	BDL	0.012750	0.000000	0.000113	0.000000	0.003774	0.000000	0.001086	0.000000	0.273325
W - S4 - W4	0.025606	0.371707	0.001000	0.000003	0.020783	0.187240	0.000309	0.000000	0.198902	0.198885	0.002357	0.000000	0.431213
W - S4 - W5	0.027634	0.341220	0.001000	0.000000	0.017959	0.043023	0.000217	0.000000	0.000000	0.168639	0.001942	0.000000	0.360072
W - S5 - W1	0.056334	0.259796	0.001000	0.000000	0.013707	0.000000	0.000096	0.000000	0.011553	0.000000	0.001285	0.000000	0.347086
W - S5 - W2	0.038137	0.451764	0.001000	0.000204	0.013676	0.143056	0.000131	0.000000	0.000000	0.000000	0.001089	0.000000	0.293316
W - S5 - W3	0.021752	0.248588	0.001000	0.000000	0.009912	0.070915	0.000063	0.000000	0.158998	0.015999	0.000660	0.000000	0.217558
W - S5 - W4	0.071747	0.333081	0.001546	0.001744	0.018646	0.213310	0.000208	0.000000	0.000000	0.019795	0.002135	0.000000	0.447024
W - S5 - W5	0.043686	0.482594	0.001000	0.000744	0.015961	0.000000	0.000121	0.003299	0.128224	0.000000	0.001560	0.000000	0.360309

***BDL - Below Detection Limits**

Appendix A (continued)

Sample ID - Wet season	Mo	Cd	Sn	Sb	Ba	Hg	Pb
Blank Water 31/08/2021	0.000044	0.000016	0.000122	0.000039	0.000916	0.000012	0.000195
W - S1 - W1	BDL	0.000000	BDL	0.000000	0.000000	BDL	0.000000
W - S1 - W2	0.000000	0.000000	0.000278	0.000000	0.002964	BDL	0.005004
W - S1 - W3	0.000000	0.000000	0.000000	0.000000	0.002820	BDL	0.002380
W - S1 - W4	0.000075	0.000047	0.000000	0.000000	0.003586	0.000000	0.006705
W - S1 - W5	0.000000	0.000000	0.000000	0.000000	0.000187	BDL	0.002045
W - S2 - W1	0.000090	0.000000	0.000030	0.000040	0.015254	BDL	0.000896
W - S2 - W2	0.000390	0.000000	0.000000	0.000058	0.011169	BDL	0.000189
W - S2 - W3	0.000146	BDL	0.000000	0.000000	0.009303	BDL	0.000000
W - S2 - W4	0.000094	0.000007	0.000001	0.000014	0.017695	BDL	0.001155
W - S2 - W5	0.000248	0.000000	0.000000	0.000000	0.008749	BDL	0.000618
W - S3 - W1	0.000305	0.000043	0.000000	0.000000	0.008444	0.000163	0.003240
W - S3 - W2	0.000118	BDL	0.000000	0.000000	0.009464	BDL	0.000467
W - S3 - W3	0.000107	BDL	0.000000	0.000000	0.004826	BDL	0.000000
W - S3 - W4	0.000000	BDL	0.000000	0.000000	0.005437	BDL	0.000746
W - S3 - W5	0.000282	BDL	0.000000	0.000000	0.009012	BDL	0.000044
W - S4 - W1	0.000889	0.001159	0.000000	0.000113	0.007897	BDL	0.025763
W - S4 - W2	0.000643	0.000000	0.000000	0.000255	0.010551	BDL	0.001061
W - S4 - W3	0.000326	BDL	0.000000	0.000035	0.003408	BDL	0.000405
W - S4 - W4	0.000909	BDL	0.000000	0.000298	0.009181	BDL	0.001410
W - S4 - W5	0.000535	BDL	0.000000	0.000334	0.006489	BDL	0.002697
W - S5 - W1	0.000311	BDL	0.000175	0.000182	0.010742	BDL	0.001226
W - S5 - W2	0.000442	0.000000	0.000071	0.000103	0.008088	BDL	0.002301
W - S5 - W3	0.000111	0.000000	0.002494	0.000509	0.007522	BDL	0.000468
W - S5 - W4	0.000640	0.000000	0.000813	0.000193	0.016425	BDL	0.002372
W - S5 - W5	0.000646	BDL	0.000000	0.000039	0.011519	BDL	0.000136

***BDL - Below Detection Limits**

Appendix B: Concentrations (mg/kg) of sediment samples for all metals measured in this study in the dry and wet season

Sample ID - Dry season	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se
Blank Sediment 14/4/2021	0.006114	0.016996	0.000494	0.000390	0.000960	0.029085	0.000019	0.273120	0.000000	0.015651	0.000031	0.000494
D - S1 -S1	5.809986	1105.822214	2.077356	1.013174	32.584262	1530.255798	0.355570	0.238954	0.000000	0.000000	0.373549	0.000000
D - S1 -S2	2.390712	879.212230	1.736708	0.562160	31.412879	1474.307892	0.342414	0.344916	0.000000	0.000000	0.319497	0.000000
D - S1 -S3	0.000000	843.264232	1.627072	0.686511	31.122714	1859.150138	0.334292	0.087260	0.000000	0.000000	0.307799	0.000000
D - S1 -S4	0.000000	625.917617	1.710898	0.469340	16.833983	987.097217	0.191412	0.571381	0.000000	0.000000	0.324390	0.000000
D - S1 -S5	0.260787	853.604534	1.632336	0.598705	18.196303	1107.138539	0.489966	0.418444	0.000000	0.000000	0.247439	0.000000
D - S2 -S1	1.715846	938.046149	2.136773	1.432909	33.552391	1475.831382	0.506467	0.467841	0.000000	6.346147	0.432534	0.000000
D - S2 -S2	0.278754	1159.974041	2.228827	1.156512	40.872975	1530.586857	0.444849	0.130837	0.000000	10.246113	0.444955	0.000000
D - S2 -S3	0.000000	602.201558	2.951946	0.686976	18.010901	1263.840896	0.325297	0.404186	0.000000	1.495652	0.519307	0.000000
D - S2 -S4	0.000000	706.814658	1.558520	1.016389	25.729299	1085.915328	0.393582	0.250307	0.000000	2.412771	0.428375	0.000000
D - S2 -S5	0.000000	649.216904	2.352763	1.403774	21.572630	1216.498341	0.313639	0.382037	0.000000	1.336781	0.363074	0.000000
D - S3 -S1	0.000000	672.954819	1.147181	1.023460	8.736370	1195.134444	0.301391	0.259778	0.000000	0.874836	0.580787	0.000000
D - S3 -S2	1.302566	764.700641	2.526918	1.431753	10.528825	1824.713046	0.260159	0.608875	0.000000	3.395254	0.537681	0.000000
D - S3 -S3	0.895097	1015.119167	2.855114	1.829957	20.623999	2309.978437	0.405939	0.643363	0.000000	4.873768	0.876998	0.000000
D - S3 -S4	0.080143	1077.791193	2.524771	1.888861	13.616759	2153.189444	0.474282	0.659416	0.000000	1.205560	0.982671	0.000000
D - S3 -S5	8.943174	1279.966015	4.375409	3.218334	23.356013	3045.973236	0.491582	1.073947	0.000000	3.593833	1.488783	0.000000
D - S4 -S1	1.678868	1672.826281	2.507267	4.144234	28.778032	2431.414437	0.518050	5.087896	0.000000	32.403658	0.932142	0.000000
D - S4 -S2	7.443267	2946.477081	4.086821	11.207707	47.961905	3748.753673	0.943255	0.997456	0.000000	154.161389	2.411233	0.208660
D - S4 -S3	2.523949	1518.552280	2.152626	3.570524	23.395192	1874.183960	0.492193	1.376579	0.000000	17.602448	0.839834	0.000000
D - S4 -S4	6.387655	1704.302463	2.324383	4.412367	20.248199	2253.278924	0.506487	1.711440	0.000000	35.838156	0.999682	0.000000
D - S4 -S5	5.143058	1770.979690	2.347442	5.161654	20.706659	2185.436217	0.577389	0.278533	0.000000	51.698030	0.949683	0.000000
D - S5 -S1	15.533407	454.271726	0.444180	3.214235	7.179588	724.002336	0.113453	0.506240	0.000000	0.000000	0.443382	0.000000
D - S5 -S2	27.366393	305.437206	0.391488	2.860676	6.226412	682.340172	0.139604	0.301870	0.000000	0.000000	0.390260	0.000000
D - S5 -S3	12.381046	290.624073	0.304140	2.321327	4.895926	565.973175	0.087773	0.372379	0.000000	0.000000	0.299291	0.000000
D - S5 -S4	20.007863	375.420324	0.443822	2.726156	6.098309	702.776355	0.124315	0.280772	0.000000	0.000000	0.391674	0.000000
D - S5 -S5	14.218022	363.254589	0.480554	2.794313	6.563870	665.356597	0.103786	0.280772	0.000000	0.000000	0.442829	0.000000

Appendix B (continued)

Sample ID - Dry season	Sr	Mo	Cd	Sn	Sb	Ba	Hg	Pb
Blank Sediment 14/4/2021	0.001187	0.000243	0.000011	0.000171	0.000166	0.001141	0.000016	0.001502
D - S1 -S1	0.020673	0.000000	0.000005	0.010868	0.000000	4.433261	0.000000	1.081054
D - S1 -S2	0.023767	0.000000	0.000000	0.000000	0.000000	3.930590	0.000000	1.290947
D - S1 -S3	0.020964	0.000000	BDL	0.000000	0.000000	3.805044	0.001446	0.828017
D - S1 -S4	0.017469	0.000000	BDL	0.000000	0.000000	2.833595	0.000000	0.548845
D - S1 -S5	0.017120	0.000000	0.000000	0.000000	0.000000	5.733086	0.000000	1.563782
D - S2 -S1	0.088599	0.000000	0.001502	0.000000	0.000000	10.340886	0.000000	1.366986
D - S2 -S2	0.066043	0.000000	0.008722	0.000000	0.000000	9.121753	0.000000	1.430430
D - S2 -S3	0.058248	0.000000	BDL	0.000000	0.000000	3.154875	0.000000	0.654956
D - S2 -S4	0.053791	0.000000	0.001943	0.065915	0.000000	3.707123	0.000000	0.750610
D - S2 -S5	0.069094	0.000000	0.000000	0.207143	0.000000	4.012652	0.000000	0.829389
D - S3 -S1	0.083204	0.000000	0.001461	0.000000	0.000000	3.978925	0.000000	0.796372
D - S3 -S2	0.081256	0.000000	0.000000	0.025907	0.000000	4.479868	0.000693	1.117630
D - S3 -S3	0.072786	0.000000	0.007933	0.017684	0.000000	6.982141	0.000000	1.909105
D - S3 -S4	0.067008	0.000000	0.005729	0.000000	0.000000	6.596963	0.000813	1.667166
D - S3 -S5	0.093232	0.000000	0.000000	0.210628	0.000000	7.973933	0.000000	2.049533
D - S4 -S1	0.192946	0.020685	0.032447	0.000000	0.000000	14.879138	0.001278	3.104676
D - S4 -S2	0.151513	0.447841	0.133037	0.026093	0.000000	32.106439	0.018560	6.200981
D - S4 -S3	0.203052	0.000000	0.017246	0.000000	0.000000	12.702977	0.000000	2.616408
D - S4 -S4	0.178145	0.000000	0.028994	0.003542	0.000000	15.314779	0.000000	2.602787
D - S4 -S5	0.154151	0.055211	0.047694	0.000000	0.000000	15.363311	0.002104	2.967888
D - S5 -S1	0.262248	0.000000	0.062899	0.000000	0.000000	8.942880	0.000000	0.613060
D - S5 -S2	0.221405	0.000000	0.062990	0.000000	0.000000	8.550923	0.000080	0.454719
D - S5 -S3	0.207072	0.000000	0.053924	0.000000	0.000000	7.013030	0.000000	0.330605
D - S5 -S4	0.238182	0.000000	0.053216	0.074345	0.000000	8.789476	0.000000	0.578041
D - S5 -S5	0.338164	0.000000	0.057348	0.000000	0.000000	9.566425	0.000000	0.760759

***BDL - Below Detection Limits**

Appendix B (continued)

Sample ID - Wet season	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se
Blank Sediment 1/09/2021	0.004216	0.016848	0.000100	0.000624	0.000563	0.013526	0.000026	0.000000	0.894286	0.006902	0.000025	0.000337
W - S1 -S1	0.560126	1071.757769	2.094987	1.427461	20.262139	1496.155662	0.269250	0.000000	0.381854	12.357273	0.319472	0.000000
W - S1 -S2	3.764075	1030.004271	2.087145	1.161496	25.912326	1450.089346	0.311655	0.000000	0.000000	0.000000	0.261933	0.000000
W - S1 -S3	2.520930	845.203692	1.904857	0.339352	20.612476	1289.904676	0.297354	0.000000	0.000000	18.967725	0.253808	0.000000
W - S1 -S4	3.593609	995.083977	2.257187	0.814999	21.813831	1836.925577	0.327893	0.000000	0.000000	8.340311	0.357905	0.000000
W - S1 -S5	1.318743	1142.357038	2.285225	0.666139	27.473230	1537.048571	0.369225	0.000000	2.733820	4.558004	0.328379	0.000000
W - S2 -S1	2.031301	927.915898	3.410467	1.316714	11.416258	1743.948043	0.265928	0.000000	10.988204	16.344762	0.963011	0.000000
W - S2 -S2	5.315207	674.493226	2.468832	1.508230	12.855044	1521.545523	0.290871	0.000000	2.054637	8.231732	1.321281	0.000000
W - S2 -S3	0.596573	740.252795	1.793116	0.805922	11.436903	992.754701	0.260425	61.157747	8.335370	24.706947	0.560729	0.000000
W - S2 -S4	9.083213	867.864030	2.096848	1.059781	12.537477	1138.618802	0.379386	0.916666	0.669466	17.099784	0.598367	0.000000
W - S2 -S5	2.488799	826.274800	2.624289	0.771283	10.003367	1375.577572	0.254849	0.516578	7.677628	9.546477	0.487704	0.000000
W - S3 -S1	9.919552	2662.591473	4.934900	3.900737	58.464166	3677.145416	0.897819	0.335243	4.557847	33.969824	1.820296	0.000000
W - S3 -S2	2.097880	2667.723430	4.631816	3.718066	63.823418	3480.493220	0.818603	0.378553	2.351936	21.307108	1.813260	0.000000
W - S3 -S3	2.726602	1901.056575	3.546865	3.084600	36.432613	2544.359365	0.580105	0.712568	4.820482	19.824625	1.214223	0.000000
W - S3 -S4	3.277037	2881.280209	4.947934	4.189518	45.732681	4003.115043	0.839103	0.519498	1.587392	28.615929	1.879509	0.021647
W - S3 -S5	3.160047	1676.889773	2.955130	3.416587	29.926004	2177.319851	0.485694	3.114891	12.839064	33.084411	1.112494	0.000000
W - S4 -S1	3.822147	8139.456023	13.433547	11.373115	140.134027	9555.447381	2.422459	1.960643	6.843069	94.424675	4.996707	0.332262
W - S4 -S2	4.809374	4184.818820	7.435074	7.972994	73.321308	5463.158301	1.240450	2.205759	9.140094	58.182004	3.239880	0.064398
W - S4 -S3	6.209087	4471.522589	7.850508	8.685536	73.140852	5641.241236	1.286077	3.044700	14.211362	74.803450	3.477646	0.249877
W - S4 -S4	2.186811	5598.996067	10.194143	11.406088	81.456546	7250.719247	1.688623	4.755870	18.268667	92.408490	4.618380	0.234871
W - S4 -S5	4.750553	9654.764053	16.981090	18.179902	152.931381	12333.915324	2.909990	0.417012	2.052072	124.552349	6.861000	0.257726
W - S5 -S1	17.380137	422.585789	0.878234	4.040502	6.902671	792.539168	0.135046	0.521489	0.097590	7.847176	0.582274	0.000000
W - S5 -S2	23.188728	724.397175	1.244424	5.871048	8.039120	1112.532831	0.173428	0.447843	0.769562	11.387968	0.661734	0.000000
W - S5 -S3	17.949874	506.763810	0.957399	3.905488	6.686777	916.504850	0.144081	0.012950	8.521098	6.368768	0.564850	0.000000
W - S5 -S4	14.848025	371.146118	0.908269	3.502529	6.337679	782.545355	0.110196	0.000000	0.000000	11.022751	0.657374	0.000000
W - S5 -S5	15.236328	237.633342	0.574886	2.653008	5.092615	584.867436	0.070034	0.000000	0.000000	4.562538	0.445304	0.000000

Appendix B (continued)

Sample ID - Wet season	Sr	Mo	Cd	Sn	Sb	Ba	Hg	Pb
Blank Sediment 1/09/2021	0.001089	0.000172	BDL	0.000097	0.000129	0.000747	0.000010	0.000198
W - S1 -S1	0.853706	0.000000	BDL	0.000000	0.000000	3.108865	BDL	1.433806
W - S1 -S2	0.751754	0.000000	BDL	0.000000	0.000000	3.314961	0.000000	1.642031
W - S1 -S3	0.745992	0.000000	BDL	0.000000	0.000000	2.713378	0.000000	1.255063
W - S1 -S4	1.029273	0.000054	BDL	0.000000	0.000000	4.615168	BDL	1.765115
W - S1 -S5	1.639230	0.000000	BDL	0.000000	0.000000	3.924608	BDL	1.587272
W - S2 -S1	6.941508	0.000000	BDL	0.000000	0.000000	7.389619	0.002533	1.867284
W - S2 -S2	1.865440	0.000000	BDL	0.010086	0.000000	2.987450	0.003311	1.822094
W - S2 -S3	1.391933	0.000000	BDL	0.000000	0.000000	4.590663	0.001136	1.953336
W - S2 -S4	1.503635	0.000000	BDL	0.000000	0.000000	4.344080	0.004198	2.377409
W - S2 -S5	0.914511	0.000000	BDL	0.000000	0.000000	3.485096	0.000000	2.386940
W - S3 -S1	9.577717	0.000000	BDL	0.000000	0.000000	15.358034	0.001386	5.119039
W - S3 -S2	7.120883	0.000000	BDL	0.000000	0.000000	14.662501	0.004634	4.860225
W - S3 -S3	4.860467	0.000000	BDL	0.000000	0.000000	10.358248	0.000647	3.793019
W - S3 -S4	7.257575	0.000000	BDL	0.000000	0.000000	18.129049	0.004040	5.485214
W - S3 -S5	8.586908	0.000000	BDL	0.000000	0.000000	10.425943	0.007157	4.943030
W - S4 -S1	75.546296	0.000000	BDL	0.000000	0.000000	39.395599	0.023019	17.598866
W - S4 -S2	126.299624	0.000000	BDL	0.000000	0.000000	26.351802	0.014118	8.695657
W - S4 -S3	168.714473	0.000000	BDL	0.000000	0.000000	32.987978	0.012919	8.331096
W - S4 -S4	170.504435	0.008036	BDL	0.004573	0.000000	36.960168	0.031122	10.417626
W - S4 -S5	106.186103	0.000000	BDL	0.026404	0.000000	55.023944	0.042671	22.198113
W - S5 -S1	1315.113149	0.000000	BDL	0.000000	0.000000	10.168312	0.009118	1.372797
W - S5 -S2	1390.104250	0.000000	BDL	0.000000	0.000000	10.322537	0.007065	1.613055
W - S5 -S3	1143.458598	0.000000	BDL	0.000000	0.000000	8.475121	0.004340	1.287780
W - S5 -S4	1296.627089	0.000000	BDL	0.000000	0.000000	8.652878	0.006400	1.572229
W - S5 -S5	1056.747873	0.000000	BDL	BDL	0.000000	6.875835	0.002616	1.023082

***BDL - Below Detection Limits**

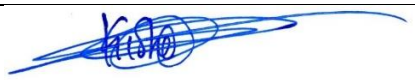
Appendix C: Permits

- Ethics exemption letter
- CapeNature permit
- Spier permission letter

Cape Peninsula University of Technology

Statement of Permission

A Data/Site permit is required for this study.

Reference no.	209052988/04/2021
Surname & name	Jacobs, L.
Student Number	209052988
Degree	Master of Environmental Management
Title	Contamination sources and concentrations of metal pollutants in the Eerste River, Cape Town, South Africa
Supervisor(s)	Prof JAMES PHILANDER ODENDAAL
FRC Signature	
Date	2021 April 22

P.O. Box 1906 · Bellville 7535 South Africa ·Tel: +27 21 953 8677 (Bellville), +27 21 460 4213 (Cape Town)

Ethics Exemption Letter **Reference no: 209052988/04/2021**

Office of the Chairperson **Research Ethics Committee**	**Faculty of Applied Sciences**

On 21 April 2021, the Faculty Research Ethics Committee of the Faculty of Applied Sciences determined that the research activities related to a project to be undertaken by Jacobs, L. for a degree (Master of Environmental Management) at the Cape Peninsula University of Technology do not require ethics clearance. The ethics exemption for the project is approved.

Title of project:	Contamination sources and concentrations of metal pollutants in the Eerste River, Cape Town, South Africa

Comments (Add any further comments deemed necessary, e.g. permission required)

1. Human subjects are not included in the proposed study.
2. This permission is granted for the duration of the study.
3. Research activities are restricted to those detailed in the research proposal.
4. The research team must comply with conditions outlined in AppSci/ASFREC/2015/1.1 v1, CODE OF ETHICS, ETHICAL VALUES AND GUIDELINES FOR RESEARCHERS.

	21/04/2021
Signed: Chairperson: Faculty Research Ethics Committee	**Date**

CapeNature

VROLIJKHEID NATURE RESERVE

postal	P O Box 57, Robertson, 6705
physical	Vrolijkheid Nature Reserve, Robertson – McGregor Road
website	www.capenature.co.za
enquiries	**Carlo Arendorf**
telephone	+27 72 506 9580
fax	+27 86 556 7734
email	**caarendorf@capenature.co.za**
reference	1/2/2/1/2/J
date	**29 October 2020**

Ms. L Jacobs
Cape Peninsula University of Technology
Private Bag 652
CAPE TOWN
8000

Dear Ms. Jacobs

APPLICATION TO ENTER IN A NATURE RESERVE FOR SCIENTIFIC PURPOSES

I refer to your application to enter in a nature reserve for scientificresearch purposes in the Western Cape Province.

Attached is permit No. **CN32-28-15078** dated **29 October 2020** to collect specimens in the Western Cape Province. Please take special note of the standard conditions attached to the permits. I specifically draw your attention to permit condition (i). **It is imperative that you make contact with the Reserve Manager BEFORE you intend collecting on any nature reserve, conservation area, wilderness area and / or state forest**. No deviation is allowed from the fore-mentioned conditions without the prior written approval of the Chief Executive Officer: Western Cape Nature Conservation Board.

Also take note of the *pro forma* (copy attached), which must please be used when submitting your collection / distribution records to CapeNature as per the conditions to your permit. Please feel free to add columns for extra data to the *pro forma* but no columns should be deleted. This pro forma is also available electronically from CapeNature.

Should you have any queries please do not hesitate to contact this office.

Yours faithfully,

CHIEF EXECUTIVE OFFICER

Western Cape Province

Telephone No: (027) 021 483 0000
E-mail: permits.fax@capenature.co.za
PGWC Shared Services Centre
cnr Bosduif and Volstruis Streets
Bridgetown
7764

CapeNature

Facsimile No: (027) 0865567734
Internet: www.capenature.co.za
Private Bag X29
Gatesville
7766

PERMIT TO
ENTER IN A NATURE RESERVE FOR SCIENTIFIC PURPOSES

Issued in terms of the provisions of the Nature Conservation Regulations no. 955 of 1975

Not Transferable

HOLDER

Full Name:	Miss Lynn Jacobs	**Identity No:**	9101130030080
Trade Name:	Cape Peninsula University of Technolog	**Registration No:**	
Postal Address	P O Box 352	**Physical Address:**	
City / Town:	Cape Town	**City / Town:**	
Province / State:	Western Cape	**Province / State:**	
Country:	South Africa	**Country:**	
Postal / Zip Code:	8000	**Longitude:**	
		Latitude:	

In terms of and to the provisions of the abovementioned Regulations framed thereunder, the holder of this permit and persons specified on the attached addendum is authorised to enter or to enter and remain in a nature reserve or any portion thereof for scientific purposes. See conditions on last page.

DETAILS

Permit / License No:	CN32-28-15078
Expiry Date:	31/12/2021
Date Issued:	29/10/2020
Amount Paid:	R 0.00
Reference:	
File Code:	1/2/2/1/2/J

Stamp: CapeNature FAUNA • FLORA • HUNTING • CITES

DESCRIPTION — PROPERTY

Organization	Cape Peninsula University of Te
Full Name:	Miss Lynn Jacobs
Identity Number:	9101130030080
Postal Address	Eerste River
City / Town:	Cape Town
Province / State:	Western Cape
Country:	South Africa
Postal / Zip Code:	NA
Longitude:	
Latitude:	

SPECIES (SCIENTIFIC NAME)		QTY	NOTE
A) None	(A) None)	0	See special conditions: Special conditions apply.
A) None	(A) None)	0	Sediment and water samples may be collected. No fauna and flora may be collected.

C. Arendorf 29/10/2020

Issued By:	Approved on Behalf CEO	Effective Date:	Signature of Holder:
Carlo Arendorf	Western CapeNature Conservation Board		I acknowledge, accept and understand fully the permit conditions as described.

STANDARD CONDITIONS

1. The holder of this permit shall return it together with a full report of all activities, findings and observations made while on the nature reserve to the Chief Executive Officer, Western Cape Nature Conservation Board, Private Bag X29, Gatesville, 7766, within fourteen days from the date of expiry thereof.
2. THIS PERMIT IS SUBJECT TO SPECIAL CONDITIONS.

SPECIAL CONDITIONS

CONDITIONS APPLICABLE TO RESEARCHERS UNDERTAKING RESEARCH OR OTHER COLLECTING WORKS ON PROVINCIAL CONSERVATION AREAS AND / OR PRIVATELY OWNED LAND IN THE PROVINCE OF WESTERN CAPE:

1. THE MANAGER OF THE RELEVANT CONSERVATION AREA(S) (IF ANY) MUST BE INFORMED TIMEOUSLY BEFORE ANY CONSERVATION AREA IS ENTERED FOR COLLECTING OR RESEARCH PURPOSES AND THE MANAGER'S WRITTEN PERMISSION TO ENTER SUCH RESERVE MUST BE ACQUIRED BEFOREHAND. THIS PERMIT DOES NOT GRANT THE PERMIT HOLDER AUTOMATIC ACCESS TO ANY NATURE RESERVE, CONSERVATION AREA, WILDERNESS AREA AND / OR STATE FOREST. ANY OTHER / FURTHER CONDITIONS OR RESTRICTIONS THAT THE MANAGER MAY STIPULATE AT HIS / HER DISCRETION MUST ALSO BE ADHERED TO. THIS PERMIT MUST BE AVAILABLE TO BE SHOWN ON DEMAND.
2. For projects of more than one year's duration a progress report must be submitted to The Chief Executive Officer: Western Cape Nature Conservation Board before 31 December of each year.
3. One copy of all completed reports, publications, or articles (including books, videos, CDs, DVDs etc.) resulting from the project/collection must be submitted to The Chief Executive Officer: Western Cape Nature Conservation Board free of charge.
4. Should a report, publication, article or thesis arise from this project/collection, an acknowledgement to Western Cape Nature Conservation Board must be included.
5. The Forest Act 1984 (Act 122 of 1984) and regulations, the Nature Conservation Ordinance, 1974 (Ordinance 19 of 1974) and all regulations in terms of the Ordinance must be adhered to.
6. No material (fauna or flora) may be collected, disturbed or removed without the express WRITTEN permission from CapeNature.
7. Representatives of all species collected should be deposited in a curated collection in a recognized institution in South Africa such as a museum collection or herbarium that allows access to future researchers. Proof of in-principle acceptance of material must be supplied up front with the permit application.

NUMBER OF PERSONS ENGAGED IN THIS PROJECT:
Ms. Lynn Jacobs - ID No: 9101130030080
Prof. James Odendaal - ID No: 7208085274082

TITLE OF PROJECT:
Sources and concentrations of metal pollutants in the Eerste River, Cape Town, South Africa.

This permit is subject to the following special conditions:
1. Copies of all reports or publications resulting from this research must be forwarded to CapeNature for internal dissemination to relevant staff.
2. The permit holder must contact the Conservation manager of Jonkershoek (now part of Hottentots Holland WHS) at least 2 weeks in advance to discuss and agree on logistic arrangements for the field work.
3. The permit holder must have an appropriate vehicle for the field work.
4. Standard conditions must apply.

Import format for SOB data

The data should be saved in a Microsoft Excel spreadsheet. The later the version the better.

The spreadsheet should contain the following columns with the column headings in row 1:

Column	Description
Date	Enter full date e.g. 25/9/1994
LocalityName	Name of locality e.g. town name, reserve name, farm name etc.
DegreesSouth	Number of Degrees South of 0 degrees South
MinutesSouth	Number of minutes South
SecondsSouth	Number of seconds South
DegreesEast	Number of Degrees East of 0 degrees East
MinutesEast	Number of minutes East
SecondsEast	Number of seconds East
QuarterDegree	Enter if degrees, minutes, seconds are unknown
Species	Full scientific name eg. Panthera pardus or Cacosternum nanum parvum
Record Type	Type of record: Specimen, Observation, Photograph, Audio, Literature, Scat
Collector	Name of the person that collected the record
LodgingCode	The unique number that each institution assigns each record eg. PEM-00348 (must have a dash before the number)
Contact	The name of the contact person at the Institution
Institution	The Institution where the record is lodged
Remarks	Any associated remarks or notes that you wish to include with the record

Date	LocalityName	DegreesSouth	MinutesSouth	SecondsSouth	DegreesEast	MinutesEast	SecondsEast	QuarterDe	Species	Record Type	Collector	LodgingCode	Contact	Institution	Remarks
1-Jan-1995	Clanwilliam	32	35	10	18	52	3		Naja nigricollis woodi	Specimen	A Turner	PEM-00325	W Branch	Port Elizabeth Museum	Dead on road
25-Jul-1998	Sandputs							2822CA	Tomopterna cryptotis	Audio	L Minter	TM-64002	M Whiting	National Museum	

Date	LocalityName	DegreesSouth	MinutesSouth	SecondsSouth	DegreesEast	MinutesEast	SecondsEast	QuarterDegree	Species

RecordType	Collector	LodgingCode	Contact	Institution	Remarks

22 February 2021

To whom it may concern:

Letter of Permission | Water Quality of the Eerste River Research

This letter hereby confirms that permission has been granted for Lynn Jacobs to enter the Spier premises on agreed dates and times to sample the Eerste River's water quality as part of her thesis, which forms part of her Masters degree in Environmental Management.

If you have any questions or concerns, please feel free to contact me directly.

Yours sincerely,

Orlando Filander
Farm Manager
Tel : +2783 235 2255
Email : orlandof@spier.co.za