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# **BIOMONITORING OF HEAVY METALS IN THE EERSTE RIVER CATCHMENT AREA**

by

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*Thesis Submitted in Fulfilment of the Requirements for the Degree:*

**Doctor Philosophiae**

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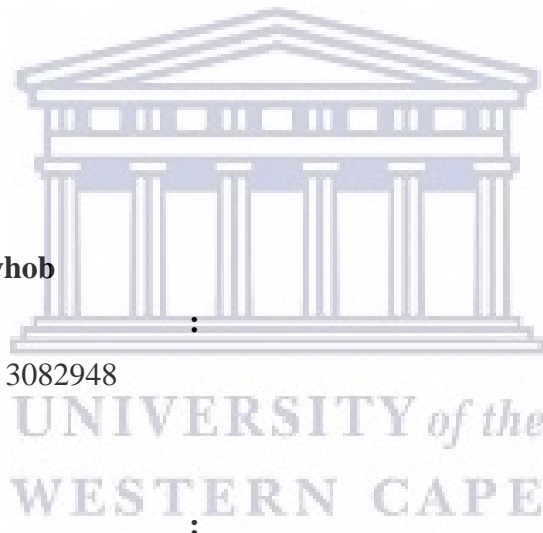
# DECLARATION

I, **Esam S. A. Elmayhob**, declare that the thesis entitled *Biomonitoring of Heavy Metals in the Eerste River Catchment Area, Cape Town*, submitted for the PhD degree at the University of the Western Cape is my own work. All the sources that I have used or cited have been indicated and acknowledged by means of complete references. This research project has never been submitted previously for any degree to any other institution.

**Esam S. A. Elmayhob**

**Student Number:** 3082948

**Date Signed**



# DEDICATION

*I dedicate this thesis to the spirit of my parents, to my family, my wife and my children, and everyone who has had merits over me from the beginning of my education.*



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# ABSTRACT

The risk of increasing global pollution dictates the need to understand environmental processes and develop innovative ways to monitor pollution levels and address associated problems. In order to address this need, this study used a selection of plants leaves (*Commelina benghalensis*, *Paspalum urvillei*, *Persicaria lapathifolia* and *Salix babylonica*) as biomonitors to assess the state of the environment, more specifically the concentration of certain heavy metal pollutants (Cu, Zn, Fe, Ni, Pb and Cd) of river water and soils in the Eerste River catchment, Western Cape, South Africa.

Every six weeks, from November 2011 to December 2012, water, soil and plant samples were collected from the twenty-two sites. Initiatory analyses on water (temperature, dissolved oxygen, pH, Electrical conductivity, nitrate nitrite and ammonia) were performed, as well as on the soil (pH and Electrical conductivity). Plant samples were prepared for digestion. Plant samples were digested with a sulphuric-peroxide mixture and digested with an Aqua Regia mixture of nitric acid and hydrochloric acid. The heavy metal content of water soil and plant, about 800 samples, was measured with an Agilent 710 Series ICP-OES.

The data obtained were divided according to river reaches and seasons. A set of statistical analyses were performed on the data using IBM SPSS version 22. All

statistical analyses were conducted at the 5% or 1% level of significance. We then developed a predictive statistical model using the plants in our study as biological monitors for heavy metal pollution in the water and soil.

The temperature of the river water ranged between 0.8 to 27.39°C and was significantly higher in summer and in the lower reach. The water pH ranged between 6.63 and 7.84 which was significantly higher in spring than in winter. The ammonium concentration in the river ranged from below the detection limit (ND) to 10.05 mg·l<sup>-1</sup> and was significantly lower in winter and in the upper reach. The concentrations of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> increased significantly in river water from the upper to the lower reaches, the nitrate concentrations were significantly higher in autumn. Thus, the water in the upper reaches was safe to drink according to World health organization recommendations for NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>. Soil pH ranged between 4.83 and 7.6—the middle reaches were significantly higher than the upper reaches. The electrical conductivity of the soil ranged between 43.5 and 1427 μS·cm<sup>-1</sup>. With regards to calcium, according to the Department of Water Affairs and Forestry (DWAF), the Eerste River catchment water is deemed soft, except the lower reaches.

The four studied plant species accumulate Fe and can be used as biomonitors of soil Fe levels. *Paspalum urvillei* S and *Persicaria lapathifolia* are good accumulators of Nickel and are useful biomonitors of soil Nickel concentrations. *Salix babylonica* L.

and *Persicaria lapathifolia* are good Zinc accumulators and can be used as biomonitors for water Zinc levels, and *Commelina benghalensis* L and *Paspalum urvillei* S Zinc and are useful for biomonitoring it in the soil. Similarly, *Paspalum*

*urvillei* and *Persicaria lapathifolia* can be used as biomonitors of copper in the soil. *Paspalum urvillei* can also be used as a biomonitor of Cadmium in the soil. *Salix babylonica babylonica* and *Paspalum urvillei* reflect the levels of lead in the water

The concentration of iron in the Eerste River water was within the normal range of Department of water affairs. Our values for Nickel in the soil were within the recommendations of the DoH, (1991). The concentration of Zinc in soil and water was within the recommendations. The copper concentration in water in this study was above the recommendations of DWAF, (1996) and Canadian Council of Ministers of the Environment (CCME) (2002). The concentrations of Cadmium in water was outside the recommended limits of DWAF (1996). The Pb concentration in water in this study was beyond the recommendations of DWAF (1996) and CCME (2002).

Simple linear regression analysis was used to estimate the correlation between the heavy metal concentrations in the plant, water, and soil. The leaves were the independent variable. To identify which plants were suitable as biological predictors for any of the heavy metals, whether in soil or water, we used only relationships that were significant at at least the 0.05 level. We extracted from our results the following: *Salix babylonica* can be used as a prospective biological monitor for cadmium in the water and as well as for copper, iron, lead and zinc in the soil. It is strongly recommended to use *C. benghalensis* as a biological monitor for Cu contamination in water. *P. urvillei* can be used as a prospective biological monitor for Cu and Ni in the water, in addition to that it can be used to monitor pollution of Cu, Fe, Ni, Pb and Zn in the soil. *P. lapathifolia* can be used as a prospective predictor for Cu and Ni in the water in the area. In addition to that it can be used to estimate

Cu, Fe, Pb and Zn contamination in the soil.

**Keywords:** Eerste River Catchment, biomonitoring, heavy metals, *Salix babylonica*, *Commelina benghalensis*, *Paspalum urvillei*, *Persicaria lapathifolia*



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# LIST OF ABBREVIATIONS

<b>CCME</b>	Canadian Council of Ministers Guidelines for Environmental Quality Concentration
<b>CMA</b>	Cape Metropolitan Area
<b>COD</b>	Chemical Oxygen Demand
<b>DEA</b>	Department of Environmental Affairs
<b>DO</b>	Dissolved Oxygen
<b>DoH</b>	Department of National Health and Population Development
<b>DWAF</b>	Department of Water Affairs and Forestry
<b>EC</b>	Electrical Conductivity
<b>EEA</b>	European Environment Agency
<b>EEC</b>	European Economic Community
<b>EU</b>	European Union
<b>r</b>	Correlation Coefficient
<b>UWQI</b>	Universal Water Quality Index ()
<b>WHO</b>	World Health Organization
<b>WRC</b>	Water Research Commission
<b>WWTW</b>	Wastewater Treatment Works

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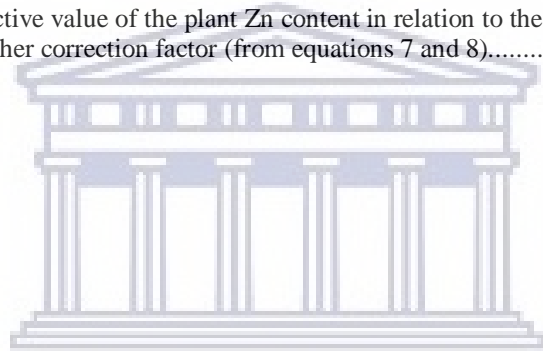
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# CHAPTER 1

## THEORETICAL FRAMEWORK

### 1.1 Background

The planet is facing rapid changes because of a variety of known and unknown pollutants in combination with climate change and loss of biodiversity, all of which threaten the ecosystem. Hence, the need for greater efforts to provide integrated information about the quality of the environment (Fränzle, 2003).

There are different sources of heavy metals in the environment, which may be of natural or anthropogenic origin. Anthropogenic sources stem from human activities such as industrial production, mining and agriculture. On the other hand, the weathering of magmatic, sedimentary and metamorphic rock and soil formation, as part of the rock cycle, are natural sources of heavy metals in surface and groundwater as well as in the atmosphere (Adriano, 2001; Bradl, 2005; Siegel, 2002).

Rocks and soils are the principal natural sources of heavy metals in the environment. The primary rocks, which are called magmatic or igneous rocks, crystallize from magma upon cooling down. Magma is defined as molten rock material originating from within the earth's mantle, which can be transported to the surface by several geological processes such as volcanism or plate tectonics (Bradl, 2005; Callender, 2003). Magma contains a large variety of different chemical elements.

Heavy metals may be incorporated as trace elements into the crystal lattice of the primary minerals, which form during the cooling of magma. This process is called isomorphic substitution, as the heavy metals substitute other atoms during the crystallization. The amount of isomorphic substitution is determined by the ion radius, the ion charge, and the electronegativity of the main element and the substituting element (Bradl, 2005).

Heavy metals in the environment may result from many different activities and sources, and may enter into the environment by a wide range of processes and pathways. Heavy metals are naturally found in the earth's crust and have been used in many different applications over decades. Generic sources of heavy metals include mining and industrial production such as foundries, smelters, oil refineries, petrochemical plants, chemical industry and untreated sewage sludge. Disperse sources include metal piping, traffic and combustion by-production from coal burning power plants (Botkin and Keller, 2003; Cunningham et al., 2001; Feng, 2005).

Atmospheric emissions are probably the most harmful to the environment and, consequently, to human health due to either the great quantity involved or their widespread dispersion which may result in many different exposure pathways. In particular, these three heavy metals—mercury (Hg), lead (Pb) and cadmium (Cd) are of great concern to human health and to the environment, mostly due to their ability to travel long distances in the atmosphere before deposition (Vosniakos et al., 2011). Industrialization and technological advancement have put an increasing burden on the environment by releasing large quantities of hazardous waste, heavy metals such

as Cd, chromium (Cr), and Pb as well as metalloids—elements with intermediate properties between those of typical metals and non-metals, such as arsenic (As) and antimony (*Latin: stibium, Sb*), and organic contaminants that have inflicted serious damage on the ecosystem. The build-up of heavy metals and metalloids in soil and water continues to create critical global health concerns, as these metals and metalloids cannot be degraded into non-toxic forms, but persist in the ecosystem. Contamination of the environment with heavy metals has increased beyond the recommended limit and is detrimental to all life forms (Ayangbenro and Babalola, 2017; Gaur et al., 2014; Tak et al., 2013).

Such releases have adversely affected human health and have produced toxic effects on plants and soil microorganisms associated with them. Toxic metal contaminants from wastes or other products may accumulate in the agricultural cycle (Tak et al., 2013). Furthermore, heavy metals can accumulate and migrate in soil environments. Due to their cumulative effects and long-term interactions, accumulation of heavy metals in soil negatively affects regional eco-safety and poses a threat to animals and plants. Additionally, heavy metals can also enter human bodies through the food chain, leading to an increased incidence like deformity and chronic diseases such as and cancer (Chang et al., 2014; Müller and Anke, 1994; Ramadan and Al-Ashkar, 2007; Tembo et al., 2006).

Heavy metals also play a role in the chemical pollution of surface water, which is considered a serious environmental issue in most countries and is caused by various pollutants. These include heavy metals, nitrogen, phosphorus, salts, pesticides, urban toxic chemicals, oil, certain radioactive isotopes, sediments and atmospheric

depositions, both from point and diffuse source discharges (Botkin and Keller, 2003; Cunningham et al., 2001; Feng, 2005). Globally, water pollution is steadily increasing. In order to circumvent a changeover from tolerable conditions to dangerous ones, efforts must be made to accumulate and collect records and obtain quantitative data about pollution processes and trends. To this end, controlling authorities should understand the local water quality processes and monitor the development of pollution trends in order to adequately prepare and address associated problems. Failure to check pollution trends may lead to loss of aquatic ecosystems and consequently, have a profound effect on downstream users, who may be primary users of water (Pearce et al., 1999).

## **1.2 Biotechnology in Environmental Monitoring**

Increasing public awareness has led to the need for reliable and comparable information on the state of the environment. In most European States specialised environmental agencies were established in the 1980s to collect this information. In the European Union (EU), the European Environment Agency (EEA) provides this information on a European level. Within the EU countries, free access to environmental information is guaranteed according to the European Economic Community (EEC) information directive 90/313/EEC (Directive, 1990).

The increasing scientific knowledge and public awareness led to stricter control of emissions into air and water as well as to the development of sometimes sophisticated programmes monitoring the environment. To determine chemicals in the environment, chemical analysis of the environmental compartments such as water, air and soil seems to be the first and most logical choice. But chemical analysis of those

media has its limits and shortcomings (Kienzl et al., 2003). An objective of preventative environmental protection must be to obtain and evaluate reliable information on the past, present and future situation of the environment. Besides the classic global observation systems such as satellites and instrumental measuring techniques like trace gas and online water monitoring, increasing use should be made of bioindicative systems that provide integrated information permitting preventative care of the environment and human health. In the last 20 years, bioindicators have shown themselves to be particularly interesting and intelligent measuring systems. As long ago as 1980, Müller considered the “bioindicative source of information” one of the pillars of modern environmental monitoring, since “bioindication is the breakdown of the information content of biosystems, making it possible to evaluate whole areas” (Markert et al., 2003; Müller, 1980).

Recently, the demand for the use of sustainable and eco-friendly environmental processes has rapidly grown and has been subjected to economic, public, and legislative pressure. In this regard, biotechnology provides a range of opportunities to effectively address issues pertaining to the monitoring, assessment, modelling, and treatment of contaminated water, air and solid waste streams. In this context, source tracking of environmental pollutants and process modelling using biologically-based methods are becoming increasingly important, mainly owing to the accuracy and robustness of such techniques (Pakshirajan et al., 2014).

### **1.3 Plant as Biomonitors**

A biomonitor refers to an organism that provides quantitative information on environmental quality (Aboal et al., 2006; Bargagli, 1998; Markert et al., 2003).

Mertens, Luysaert and Verheyen (2005) explored the use and abuse of trace metal concentrations in plant tissue for biomonitoring and pointed out practical constraints and limitations of plants as biomonitors for soil pollutions when compared to soil analyses. They maintained that biomonitors of soil quality were limited by factors such as metal bioavailability, variant responses of single plant species to different contaminants, the role of time, plant development and additional environmental factors on leaf metal concentrations, difficulty of leaf sampling due to tree height and, lastly, active aversion of roots to metal hotspots (Mertens et al., 2005).

### 1.3.1 Terms and Definitions

The terms “bioindication” and “biomonitoring” have a range of definitions. For ease of reference and to distinguish the quantitative and/or qualitative methodology, the definitions as provided by Markert et al. (1999, 1997, 2003) will be utilised and adopted throughout this study.

A *bioindicator* refers to “an organism (or part of an organism or a community of organisms) that contains information on the quality of the environment (or a part of the environment)”.

A *biomonitor* refers to “an organism (or a part of an organism or a community of organisms) that contains information on the quantitative aspects of the quality of the environment”. A biomonitor is always a bioindicator too, yet a bioindicator does not really meet the requirements for a biomonitor (Markert et al., 2003).

*Bioaccumulators* refer to organisms that accumulate one or more elements and/or

compounds from their environment” (Markert et al., 2003).

### **1.3.2 Advantages of Plants as Biomonitors**

Though there are some important limitations to the use of plants as biomonitors of soil pollution, their use has important advantages over soil analyses as indicators of soil quality, particularly when investigations are made on a large scale (Zhou et al., 2008; Madejón et al., 2006; Markert et al., 2003; Bargagli, 1998; Fränze, 2003). Both tools, i.e., bioindicators and biomonitors, can produce abundant information and data, and facilitate a deeper understanding of ecology. Subcellular compounds, cells and organisms are used as bioindicators to assess the quality of the ecosystem and the impact of environmental factors on the ecosystem. Furthermore, bioindicators can also be utilised to study environmental quality trends over longer periods of time whereas biomonitoring evaluates ecosystem management (Markert et al., 2003).

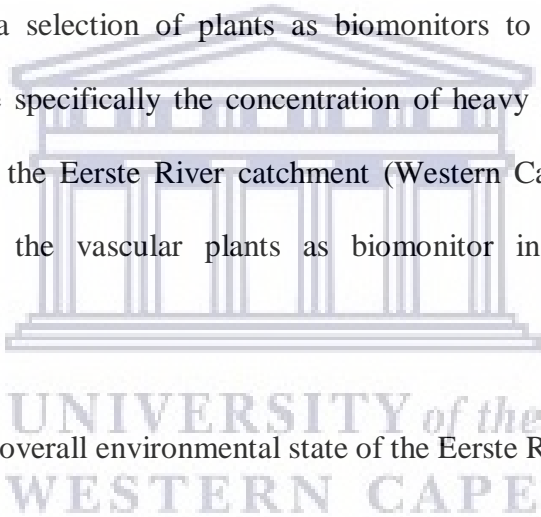
The use of living organisms as monitoring tools has many advantages. Organisms living in the environment are constantly exposed to the physical, biological and chemical influences of that particular environment. Organisms that have a tendency to accumulate chemical species can often accumulate significant quantities of material from very low concentrations in the environment (Abdel-Shafy & Mansour, 2016). Mosses, for example, have been used by many researchers to detect heavy metal concentrations due to their tendency to selectively adsorb heavy metals from their environment (Gerdol et al., 2000; Pott and Turpin, 1998).

Some plant species are particularly suitable candidates for biomonitoring metal concentrations in the soil by means of phytoextraction, this process happens because

these species accumulate trace metals from the soil in their above-ground biomass. Many research studies explored the capability of plants growing on polluted sites for uptake of soil metals (Ojekunle et al., 2014; Al-Khashman et al., 2011; Calzoni et al., 2007; Mertens et al., 2005).

## **1.4 Research Problem**

The risk of increasing global pollution dictates the need to understand environmental processes and develop innovative ways to monitor pollution levels and address associated problems that have become dire. In order to address this need, this study attempted to use a selection of plants as biomonitors to assess the state of the environment, more specifically the concentration of heavy metal pollution of river water and soils in the Eerste River catchment (Western Cape, South Africa). The study focuses on the vascular plants as biomonitors in the area, specifically questioning:

- 
- a. What is the overall environmental state of the Eerste River catchment?
  - b. What are the levels of heavy metals (Cu, Zn, Fe, Ni, Pb and Cd) in the Eerste River catchment and how do they compare with published acceptable standards?
  - c. What is the relationship between the quantity of heavy metals in plants and the external environment (water and soil)?

### **1.4.1 Aim**



The aim of this study was to obtain qualitative and quantitative data from vascular plants in the Eerste River catchment, in order to assess the overall state of the environment.

#### **1.4.2 Objectives**

The objectives to achieve the aim of the study were:

1. To assess the overall state of the environment by obtaining quantitative and qualitative data from vascular plant biomonitors in the Eerste River catchment;
2. To assess the current state of heavy metal pollution and changes that occur in the Eerste River catchment environment;
3. To determine the concentrations of heavy metals (Cu, Zn, Fe, Ni, Pb and Cd) pollutants in water, soil and plant leaf samples throughout the year in an aquatic ecosystem;
4. To create a statistical model from the plant samples used in this study for future research; and
5. To enhance current databases on pollution in the Western Cape region and facilitate ecosystem protection.

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# CHAPTER 2

## LITERATURE REVIEW: HEAVY METALS IN RIPARIAN ECOSYSTEMS

### 2.1 Introduction

The majority of society agree that rivers are wonderful places; providing habitat to fishes, birds and other forms of life and a place for recreation and relaxation. On the other hand, some people use rivers as a place for commerce and industry (Seelbach and Wiley, 1997). Freshwater in rivers and lakes reinforce ecosystems with diverse life forms that, at the same time with the water itself, provide services and goods of vital importance to human communities everywhere (Arthington et al., 2010; Carlisle et al., 2011). An important part of the planet's water cycle is the flow of its rivers (Karr and Chu, 2000).

Water is widely regarded as the most essential of natural resources; human activities directly threaten freshwater systems. Widespread land cover change, engineering schemes like irrigation, reservoirs and interbasin transfers, industrialization and urbanization, have all transformed water systems. They use water to provide economic benefits, but these are often accompanied by impairment of the ecosystems and a reduction in biodiversity (Rounsevell et al., 2018; Vörösmarty et al., 2010). The health of our rivers and wetlands is measured by the diversity and soundness of the relevant species.

The 'water asset' is a living asset, an asset means a resource, complete with organisms that associate with, and control, the water and cycles that determine how we can utilize this asset (Appendix 19: Stellenbosch Municipality Asset Management Policy, 2018). Streams are seen as the veins of our living scenes, and this is especially valid in semi-arid continental climates, for example, in South Africa. Water faces many threats on its journey from the headwaters of the river basin to water users and estuaries. Pollution from fertilisers, waste treatment plants and mining threaten to poison our rivers.

However, water is an irreplaceable resource. We cannot substitute water with anything else. Whilst coal as an energy source can be substituted by solar energy or biofuels, water cannot be replaced. As a water-scarce country, South Africa must act urgently to protect its water resources and ensure that we use what we have in the most efficient and effective ways possible (Colvin et al., 2013). “Water does not come from a tap, not even a dam; water is provided to us by healthy and functioning ecosystems” (Colvin et al., 2013).

## **2.2 Environmental Contamination with Heavy Metals**

Heavy metals are elements that occur naturally in the environment as a result of the natural weathering processes of bedrock. Heavy metals are generally found in the environment in low concentrations, and are usually contained in forms that are not easily accessible by plants (Nellessen and Fletcher, 1993; Prasad, 2004; Tyler et al., 1989). Unfortunately, due to the increase in anthropogenic activities that release heavy metals into the environment, the amounts of bioavailable heavy metals in the environment have drastically increased (Benavides et al., 2005; Islam et al., 2007;

Prasad, 2004).

Anthropogenic activities that contribute significantly to the release of biologically available heavy metals include urbanisation and the subsequent discharge of urban waste products, rapid industrialisation and the subsequent leakage of industrial wastes, mining and the leakage of mine waste, combustion of fossil fuels and the unsustainable increase in agricultural practices and the subsequent runoff of agricultural waste (Arora et al., 2008; Cai et al., 2007; Chen et al., 2008; Goi et al., 2006; Haroun et al., 2009; Malan et al., 2015; Mortvedt, 1996; Rodríguez Martín et al., 2006; Worthington, 2001).

**Table 2.1:** Activities that may introduce heavy metals into the environment

Activities	Heavy metals released	Reference
Urban waste products	Barium (Ba), Cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg), Selenium (Se), Silver (Ag), Nickel (Ni), Copper (Cu), and Zinc (Zn)	1
Combustion of fossil fuels	Arsenic (As), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Lead (Pb), Mercury (Hg), Selenium (Se), Nickel (Ni), Copper (Cu), Zinc (Zn), Iron (Fe) and Manganese (Mn)	2
Agricultural practices	Cadmium (Cd), Chromium (Cr), Cobalt (Co), Lead (Pb), Nickel (Ni), Copper (Cu), Zinc (Zn), Iron (Fe) and Manganese (Mn)	3
Mining and the leakage of mine waste	Arsenic (As), Bismuth (Bi), Cadmium (Cd), Copper (Cu), Iron (Fe), Manganese (Mn), Lead (Pb) and Zinc (Zn)	4
Industrialisation and the subsequent leakage of industrial wastes	Nickel (Ni), Cadmium (Cd), Silver (Ag), Copper (Cu), Tin (Sn), Gold (Au), Aluminium (Al), Zinc (Zn), Chromium (Cr), Lead (Pb) and Molybdenum (Mo)	5
1: (Aucott, 2006). 2. (Reddy et al., 2005). 3. (Micó et al., 2006). 4. (Benvenuti et al., 1997). 5. (Jadhav and Hocheng, 2012).		

Once released into the environment, heavy metals are generally retained in terrestrial and aquatic sinks. These sinks include major water bodies (rivers, springs, wetlands

and the ocean), soils and plants. In soils (soil is the result of subaerial exposure and the weathering of rock) and sediments (sediment is the result of erosional transport of material away from a weathering site and deposition in other location) (Hartemink, 2016). Heavy metals readily form stable complexes with organic acids, allowing them to persist for long periods of time in the environment. However, several factors can influence the mobility and therefore the persistence of heavy metals in soils and sediments. These factors include the pH, cation exchange capacity, and the amount of organic matter present in the soils and sediments (Benavides et al., 2005; Koeppe, 1977; Marschner, 2012; Mithöfer et al., 2004). Increased mobility of the heavy metals could, in turn, result in the heavy metals becoming more bioavailable to plants growing in the soils and sediments, and could also pose a great threat to water systems due to the leaching thereof into ground water sources, wetlands and river systems (Benavides et al., 2005; Islam et al., 2007; Prasad, 2004).

Even though the general knowledge of heavy metal bioaccumulation in freshwater systems has grown in recent years, there are still large gaps in our understanding. For example, most past studies of metals focus on a few taxa, single metals, or transfer mechanisms in a small portion of the food chain (Blum et al., 2010). Water contaminated with heavy metals would be unusable for human and domesticated animal consumption, irrigation, recreation, aquaculture and sustainable aquatic ecosystems.

Consequently, monitoring of trace metals in riparian ecosystems is fundamental to detection of contaminated areas and enabling the protection of the health of the water, aquatic biota and humans (Kibria, 2016; Madejón et al., 2018). Heavy metal



environmental contamination is a global issue. It significantly reduces the environmental quality and is a severe threat to living organisms. Some heavy metals are essential for the regulation of many processes in the body; they are also present in foodstuffs. However, any metal at elevated concentrations is problematic as they are toxic (cytogenetic) to living organisms (Iqbal, 2016; Matini et al., 2011; Tahir et al., 2017). Amongst the essential micronutrients, there are heavy metals such as Fe, Zn, Cu and Ni. Some heavy metals are potent cellular toxins, including Pb and Cd (Bilal et al., 2018; Schulze et al., 2005).

Humans are exposed to heavy metals through various routes. The major food chain path for human exposure is the consumption of food crops contaminated with heavy metals (Khan et al., 2008; Wilson and Pyatt, 2007). Accumulation of heavy metals in aquatic organisms, plants and soils is a growing concern because of the prospective risks to human health. This food chain pollution is one of the important ways for the entry of these toxic pollutants into the human body (Rattan et al., 2005).

**Table 2.2:** Heavy metals, natural concentrations, acceptable threshold levels and implications in disease (ppm).

Heavy metal	Concentrations under normal conditions	Environmentally acceptable threshold limits	Reference
Cadmium	0-5	5-10	1
Copper	0-1	1-30	1
Iron	0-1	1-10	1
Lead	0-10	10-50	1
Nickel	0.07	20	2
Zinc	0-5	5-10	1

1. (DWAF, 1993) (Holmes, 1996). 2. (WHO, 2005)

### 2.2.1 Cadmium Effects

**Aquatic systems:** Cd can harm the reproductive and nervous systems and it can decrease the ability of aquatic organisms to osmoregulate. Higher levels of Cd can have an impact on the growth and tissue structure of aquatic species; Arthropoda appear to be more sensitive to Cd than fish. Cd can bio-accumulate in shrimps, mussels, crawfish, oysters and fish (Kibria, 2016).

**Plants:** Cd is known to be toxic for plants at levels greater than 2.4 ppm (Nagajyoti et al., 2010). Cd toxicity in plants appears as Fe chlorosis accompanied by necrosis, wilting, red-orange leaf colouration, and general growth decline, which has been described for different species (Bradl, 2005). Iron chlorosis due to surplus cadmium appears to be due to an indirect or a direct interaction with iron in the leaf, the high cadmium content in the medium inhibits the uptake of iron by the plants (Das et al., 1997; Haghiri, 1973).

**Humans:** Cd is transferred to humans by food. If a cropland is irrigated with wastewater containing Cd, there is a chance of a transfer of Cd from crops to humans since crop plants have the ability to accumulate soil Cd in edible portions. Seafoods are also a source. Cd has been classified as a category one carcinogen. Consuming Cd contaminated foods can cause cancer, and diseases of the mammary glands, lungs, kidneys, bones and reproductive problems, including infertility (Kibria, 2016).

### 2.2.2 Copper Effects

**Aquatic systems:** Cu is extremely poisonous to invertebrates, fish and amphibians. Cu can damage the kidney, and diminish the growth of aquatic organisms such as fish. It is very toxic to amphibians; bio-accumulation of Cu occurs in fish and

molluscs with a high possibility of bioconcentrate in molluscs (Bicho et al., 2017; Kibria, 2016; Wagner et al., 2017; Wheeler et al., 2013).

**Plants:** Cu is one of the essential plant nutrients, although it is only needed in small amounts (<6 ppm) (Lohry, 2007). It is a constituent of a number of plant enzymes, in cytochrome oxidase, plastocyanin as well as in catalases and other oxidases. A high concentration of Cu causes physiological problems in plants; disruption of photosynthesis, respiration, cell wall metabolism, seed production, and other areas (Bradl, 2005; Schulze et al., 2005)

**Humans:** Cu is a vital trace element for humans, however, at high levels of Cu (>70 ppm), poisoning occurs and may result in cirrhosis of the liver and, in extreme cases, death (Kibria, 2016; Kibria et al., 2016).

### 2.2.3 Iron Effects

**Aquatic systems:** The abundance of freshwater organisms are greatly affected by the direct and indirect effects of Fe pollution (Vuori and Vuori, 1995; Zhang et al., 2017).

**Plants:** Fe is an essential element for many proteins and is required for cellular processes of higher plants such as cytochromes, but an excess of Fe (>100 ppm) (Lohry, 2007), leads to toxicity symptoms such as brown spots on the leaf. Photosynthesis is affected and oxidative stress occurs (Kampfenkel et al., 1995; Schulze et al., 2005). Excess Fe causes plant necrosis and colony disintegration, as well as root abscission. The synthesis of chlorophyll and protein, as well as

carbohydrate and the uptake of phosphate and nitrogen, are inhibited by excess iron (Xing et al., 2010).

**Humans:** At an extremely high level of Fe, it enters into the body crossing the level-limiting inhibition step and becomes saturated. Fe penetrates into cells of the heart, liver and brain. Due to the disruption of oxidative phosphorylation by ferrous iron ( $\text{Fe}^{2+}$ ), the toxicity of Fe on cells leads to iron-mediated tissue damage involving cellular oxidizing and reducing mechanisms. Intracellular organelles such as mitochondria and lysosomes are affected (Papanikolaou et al., 2005 and Markowitz, 2000).

A wide range of free radicals that are believed to cause cellular damage are produced by excess intake of Fe. The excess Fe results in hydrogen free radicals which attack DNA, resulting in cellular damage, mutation and malignant transformations which, in turn, cause an array of diseases (Grazuleviciene et al., 2009; Jaishankar et al., 2014).

#### 2.2.4 Lead Effects

**Aquatic systems:** Certain communities of aquatic invertebrates are more sensitive than others (0.2 to .007 ppm) (Department of Environmental Affairs (DEA), 2018). The oxygen supply can be reduced by high Pb concentrations because the Pb in the water reacts with oxygen to produce lead hydroxide. Larval fish are more susceptible than adults or eggs. Symptoms of lead toxicity in fish include spinal deformity and blackening in the tail region (Singh et al., 2012).

**Plants:** Pb is not an essential element for plants, even though it gets easily absorbed

and accumulated in plant parts. Excess Pb leads to various morphological and physiological problems in plants: chlorosis, stunted growth and blackening of the root system. Lead inhibits photosynthesis, disturbs water and mineral balance, changes hormonal status and affects membrane formation and permeability (Sharma and Dubey, 2005).

**Humans:** Pb is considered to be a carcinogen. It has significant effects on various parts of the body. Lead distribution in the body initially depends on the blood flow into various tissues and almost 95% of Pb is placed in the form of lead phosphate in the skeletal system (Papanikolaou et al., 2005). Lead toxicity was considered to be a classic disease and the signs that were seen in children and adults were largely pertaining to the central nervous system and the gastrointestinal expense (Markowitz, 2000).

Lead contamination causes loss of appetite, hypertension, headache, stomach ache, kidney failure, weakness, sleeplessness, arthritis, hallucinations and vertigo. Chronic exposure of Pb can result in mental retardation, birth defects, autism, psychosis, sensitivities, weight loss, hyperactivity, insensibility, muscular weakness, brain damage and may even cause death (Jaishankar et al., 2014; Martin and Griswold, 2009).

### **2.2.5 Nickel Effects**

**Aquatic systems:** A long time of exposure to a low concentration of Ni may result in reduced skeletal calcification and asphyxiation of fish (Bradl, 2005). Signs of Ni poisoning in fish include floating on the surface, rapid mouth and opercular

movements and, prior to death, convulsions and loss of equilibrium. Destruction of the gill lamellae by ionic Ni is also deadly to sensitive species as it decreases the ventilation rate and may cause blood hypoxia (Eisler, 1998).

**Plants:** Nickel is a necessary element in plants and many other biota. However, there has been much more anxiety about the toxicity of Ni than about its deficiency. Field observations have indicated a significant increase in Ni levels in forest and agricultural soils as well as in aquatic sediments during the last century (Pacyna and Pacyna, 2001). There are toxic effects at high concentrations; excess Ni reduces the growth and development of plants, induces leaf chlorosis and drooping, and decreases total plant production. Nickel toxicity also disrupts photosynthesis and alters related enzyme activities (Antonkiewicz et al., 2016; Chen et al., 2009).

**Humans:** The exposure of the general population to Ni is mainly via oral intake, primarily through water and food contamination (Haber et al., 2000). Many harmful effects of Ni are due to the interference with the metabolism of essential metals. The carcinogenic effects of Ni lead to enzyme inhibition and nucleic acid disruption, seemingly resulting primarily from its ability to replace other metal ions (Harasim and Filipek, 2015).

There are several types of Ni poisoning in humans: it may lead to pulmonary oedema, pneumonitis with adrenal cortical insufficiency, and hepatic degeneration, cancer of the respiratory tract, pulmonary eosinophilia and asthma. The most familiar effect of longtime exposure to Ni skin contact in humans is contact dermatitis (Bradl, 2005).

### 2.2.6 Zinc Effects

**Aquatic systems:** Zinc affects survival, growth and reproduction of animals. Aquatic plants can be negatively affected by elevated Zn levels. Zinc can cause gill damage, reduced growth and kidney impairment to aquatic organisms such as fish (Kibria et al., 2016)

**Plants:** Zinc is an essential component of many proteins in plants, e.g., it is often a component of dehydrogenases, certain species of carboanhydrase and of nucleic acid binding proteins zinc finger (Schulze et al., 2005). Zn toxicity symptoms include reduced yields and stunted growth, Fe-deficiency-induced chlorosis through decreases in chlorophyll synthesis and chloroplast degradation. Crops differ markedly in their susceptibility to Zn toxicity. In acid soils, graminaceous species are usually more sensitive to Zn toxicity than most dicots (Broadley et al., 2007; Liu et al., 2016).

**Humans:** Although zinc is an essential element for humans, an excessive concentration in food is of great concern because of its toxicity to humans. It can cause respiratory disorders, stomach cramps and skin problems (Kibria, 2016; Pandita et al., 2016).

### **2.3 The Use of Bio-Indicators and Bio-Monitors to Monitor Environmental Health**

As a result of the increase in bioavailable heavy metals in the environment, a significant interest exists in the development of cheaper and more effective methodologies to monitor environmental pollution and specifically heavy metals. Monitoring refers to the direct evaluation of specific components of the ecosystem repeated over time. This could, however, become a very expensive and time-

consuming practice. Therefore, interest in biological materials such as plants and animals that are known to accumulate heavy metals in their tissues has been suggested as a possible alternative to the direct monitoring methods.

Biomonitoring refers to the use of living organisms to obtain quantitative information regarding environmental quality (Madejón et al., 2006; Markert et al., 2003). Biomonitoring is based on the correlation between the pollutant concentration in the living organism and the concentrations in the environment (Gadzała-Kopciuch et al., 2004). In order for a biomonitoring system to be most effective, various bioindicator species need to be identified within an ecosystem. Bioindicator species can provide qualitative information on the state of the environment that they reside in (Mertens et al., 2005). Bioindicators have been used for many years to detect the deposition, accumulation and distribution of heavy metals in the environment (Asif et al., 2018; Ojekunle et al., 2014).

In freshwater and marine environments, macro-algae have been used extensively to measure heavy metal pollution (Alkhalifa et al., 2012; Conti and Cecchetti, 2003; Haritonidis and Malea, 1999; Kamala-Kannan et al., 2008; Maeda and Sakaguchi, 1990; Whitton and Kelly, 1995). Recently, however, there has been an increase in interest to use the bark and leaves of higher plants to monitor heavy metal concentrations in terrestrial environments (Aksoy et al., 2000; Aksoy and Öztürk, 1996; Aksoy and Şahin, 1999; Al-Khashman et al., 2011; Al-Shayeb et al., 1995; Calzoni et al., 2007; De Luccia, 2012; Djingova et al., 1993; Zurayk et al., 2001).

Quick urbanization and industrial expansion during the last few decades have



aggravated some serious concerns for the environment. Heavy metal pollution in rivers is one of the most important quality problems in several rapidly growing cities. This is a result of the lack of maintenance of water quality and sanitation infrastructure which failed to increase in conjunction with population and urbanization growth, particularly in developing countries (Ahmad et al., 2010; Akoto et al., 2008; Karbassi et al., 2008; Reza and Singh, 2010).

## **2.4 Heavy Metal Pollution and Monitoring of Rivers**

Plants that are used as bioindicators of ecosystem health can be defined as ‘sentinel’ organisms. Sentinel organisms accumulate and concentrate pollutants from their surroundings into their tissues so that an analysis of their tissues can provide a time-integrated estimate of the available pollutants. Plants work well as bioindicators because they are sedentary and therefore the results can be linked to local areas and long-lived plants allow for long-term monitoring studies along with the relatively easy means of collecting the plant tissues and finally analysing the tissues for the pollutant. The use of these biological materials along with the analytical techniques, allows for the improvement of the sensitivity and accuracy of traditional direct monitoring systems (Gadzała-Kopciuch et al., 2004).

The following are case studies collected from the literature that aim to provide a baseline of what can be expected in this study. Trace metals enter in the river from a range of sources; either natural or industrialist as stated in Table 2.1 (Cravotta III, 2008; Mohanty et al., 2001; Shahtaheri et al., 2008).

The waterways assume a marked role in transporting sewage and industrial

wastewater and runoff from agricultural and mining land. There are many studies that establish the water quality status in rivers (Department of Water and Sanitation, 2017; Reza and Singh, 2010; Singh et al., 2004). In a study by Adekola and Eletta along Asa River in Ilorin, Nigeria; Mn, Cr, Fe, Zn and Cu concentrations were measured in the sediment. The study concludes that Asa river sediments are contaminated on account of industrial discharges, domestic waste disposal and application of agrochemicals on farmlands as sources for heavy metals.

It has hence been suggested that this river ought to be put under observation since it is the main wellspring of fresh water in this area (Adekola and Eletta, 2007). The concentration of comprehensively the most detrimental (Cr, Ni, Cu, As, Cd and Pb) were estimated in surface water and sediment of Korotoa River, an urban stream in Bangladesh.

The concentration of Cr, As, Cd and Pb, were higher than the prescribed safety level quantity, which showed that the waterway Korotoa is contaminated by heavy metals coming from decades of domestic raw sewage, household and industrial wastes from surrounding areas and may have an adverse impact on this riverine biological ecosystem. (“The general contamination load was essentially higher in winter than the lower water flow in summer”) (Islam et al., 2015).

Water samples were collected in summer and winter at twelve different locations along the Brahmani River, and its tributaries, in Angul- Talcher Region of India. Analyses of Cd, Cr, Cu, Co, Fe, Mn, Ni, Pb, Hg and Zn were carried out. The data produced were utilized to compute the heavy metal contamination index of river

water. This study determined the heavy metal contamination profile and concluded that the river system was less polluted than other rivers in the area but showed a trend in seasonal variation. Significantly higher, metal concentration was measured in water during the summer season, due to higher flow rate of freshwater which dilutes the concentration of the heavy metals coming from the mining and associated industrial activities of pollutants to the river (Reza and Singh, 2010).

In 1975, a study published on pine trees growing on the bank of the Spokane River, Idaho, were used to monitor the river's former concentrations of Hg, Cr, Ag, Rb, Zn, Co and Fe reached because they correspond to the basic data of the sediment. Trees can be taken into account as sensors that record the environmental disturbances (Sheppard and Funk, 1975).

The use of periphyton and phytoplankton samples as monitors was undertaken in three midcontinent (USA) senior rivers the Ohio, Upper Mississippi and Missouri from 393 sites—researches concluded that the use of phytoplankton as indicators is useful for large river monitoring, especially downriver of pollution point-sources or close urban areas (Reavie et al., 2010).

## **2.5 Heavy Metal Pollution of South African River Systems and Monitoring the Health of These River Systems**

South African river systems provide water for various uses, including agricultural, industrial, recreational and domestic uses. Approximately 85% of all water being used for these activities is sourced from our river systems with approximately 15% sourced from groundwater (Department of Water and Sanitation, 2017). Almost all South African rivers are, however, under threat from agricultural runoff, industrial

and domestic effluents discharged from areas surrounding the rivers.

High concentrations of heavy metals are usually deposited on, and then integrated into, river sediments from where they are transported by fluid flow to different locations along the river. As a result, the quality of South African river systems are in a continuous form of deterioration, compromising the health of the aquatic ecosystems, as well as the well-being and livelihoods of those using these resources (Department of Water Affairs and Forestry, 1996; O’Keeffe, 2013; Okonkwo and Mothiba, 2005; Snyman et al., 2002).

Introduction of chemical pollutants into river systems can originate from point and/or non-point sources. Point source pollution originates from a known source such as effluent discharged from pipes and storm water drains. These point source pollutants are usually easy to monitor and because they are fixed sources, they usually show little variation over time and is usually easy to monitor (Camargo and Alonso, 2006; Davies and Day, 1998). On the other hand, non-point source pollutants have no fixed point of origin. These pollutants include agricultural runoff, sewage runoff and construction runoff. This makes their monitoring extremely difficult and the level of contamination could vary widely over space and time (Carpenter et al., 1998; Davies and Day, 1998).

The concern over the deterioration of the South African river systems and water quality has led to an increasing demand for water quality monitoring programs (Antonopoulos et al., 2001; van der Laan et al., 2012). As a result, various studies have been conducted on the quality of various South African river systems. Wade et

al., (2000) reported increased levels of heavy metals in the water and sediment of the Mooi River and argued that this was a result of the release of mine water from a nearby gold mine into one of the tributaries of the Mooi River.

Binning and Baird (2001) evaluated the heavy metal concentrations in the sediments of the Swartkops River in Port Elizabeth, South Africa. They found that chromium (Cr), lead (Pb), zinc (Zn), titanium (Ti), manganese (Mn), strontium (Sr), copper (Cu) and tin (Sn) concentrations in the river system were significantly higher than the concentrations found in a similar survey 20 years before. These authors also found that these heavy metal concentrations were significantly higher at points along the river where runoff from informal settlements and industry entered the river system.

Okonkwo and Mothiba (2005) evaluated the heavy metal concentrations in the surface waters from the Dzindi, Madanzhe and Mvudi rivers in Thohoyandou, South Africa. These authors analysed the water samples for Cd, Cu, Pb and Zn, and found that in all three river systems, Cd and Pb concentrations exceeded international standards for drinking water (World Health Organization/WHO, 1998).

Jackson et al (2007) investigated the degree of metal (Al, Cu, Fe, Mn, Ni, Pb and Zn) pollution at four different sampling sites along the Berg River and found that the high concentrations of these metals were due to leaching of metals into the river from waste and household products from the informal settlement close to the river. Jackson et al (2009) evaluated the heavy metal (Al, Cu, Fe, Pb, Mn, Ni and Zn) concentrations in the Plankenburg and Diep Rivers in the Western Cape, South Africa. These authors found that for most of the heavy metals evaluated, the

concentrations were higher than the recommended levels for drinking water.

The concentration of Cd, Cu, Fe, Pb, Mn, Ni, Zn, Al, Cr and Co concentrations in the soils collected along the bank of the lower Diep River in Cape Town, South Africa were determined. They indicated that most of the sampling sites along the river were contaminated with heavy metals with Al and Fe concentrations consistently higher than the other metal concentrations (Ayeni et al., 2010).

Songca et al. (2013) evaluated the heavy metal concentrations in the water and sediments of the Mzimvubu River in the Eastern Cape. These authors found that Pb concentrations within the river system were significantly higher than the recommended concentrations. Edokpayi et al. (2014) evaluated the Al, Cr, Cu, Fe, Mn, Pb and Zn concentrations in the Dzindi River in the Limpopo Province of South Africa and found that the concentrations of all the metals assessed exceeded the recommended levels in SA.

In Ma's study on the Bottelary River, nine metal elements were determined (Cd, Cr, Cu, Fe, Pb, Mn, Ni, vanadium/V and Zn), she found that most of element concentrations in plants were higher than those in the sediments, and were much greater than those in the water. However, for Fe, Pb, Mn and V, the greatest concentration levels were found in the sediments. She also found that, the rooted accumulator *Typha capensis* (Rohrb.), was a better candidate than *Phragmites australis* (Cav.) (which were the main plants of that study) for heavy metal uptake in the river. Her results were regarded as too high, as determined by the South African Water Quality Guidelines for Ecosystems (DWAF, 1996).

Another noticeable result was the significant increases in heavy metals specifically Ni concentrations in both plants and water were observed. The comparatively high value of Ni in water was noted from April to July, which coincided with the high rainfall season. This may be due to a number of reasons, such as runoff from the farms entering the river and increasing the Ni concentration in the river and/or Ni from the river sediment may have dissolved into the river water due to a decrease in the water pH over the rainy season (Ma, 2005).

From March to September in 2004, Feng (2005) determined inorganic chemicals pollution in the Bottelary River. Cape Town, South Africa. Water samples were collected six times at 13 different sites along the Bottelary River. The results showed that the water quality in the Bottelary River has been contaminated by nutrients and heavy metals. High concentrations of nitrogen (N), phosphorus (P), Zn, Cu and Cd were found in the water samples from the river.

Eutrophication problems could be caused by the excessive nitrogen and phosphorus levels. The Pb levels fell within the South African Water Quality Guidelines for aquatic ecosystems. The level of nutrients, Cd, Fe and Zn increased over the study period as a consequence of human activity inputs, particularly urban and agricultural runoff during the rainy season. The main sources of pollutants in the Bottelary River were a farm runoff, municipal runoff from Scottsdene Town and treated sewage effluent from the Scottsdene Wastewater Treatment Works (WWTW) (Feng, 2005).

Between 1990 and 2005 temporal and spatial trends were determined the water quality of the Eerste River. The following parameters were key indicators of water

quality: pH, electrical conductivity (EC), nitrogen, phosphorus and chemical oxygen demand (COD) were determined. The study concluded the spatial trends are greater than temporal trends in the water quality of the Eerste River where it is deteriorating significantly with distance to lowerstream, because of the human activity including fish farming in the dam upstream, farming, non-point sources of pollution and the poor water quality of the Kuils River. However. It was concluded that greater attention ought to be paid to these activities to ameliorate their impact on the Eerste River (Ngwenya, 2006). Previous research of water quality trends in the Eerste River was carried out by the DWAF in 1993.

This particular study was based on the assessment of time series plots of 12 year data for electrical conductivity, pH, chloride, nitrate, ammonia, and phosphate, at four stations located on the river during the period 1977 to 1989. On the basis of the time series assessment, it was concluded that no long-term trends were evident in the river system. In the assessment for spatial trend, the upper reaches were compared to the lower reaches of the river, and reported a steady decline in water quality downstream. This decline was ascribed to point and non-point sources of pollution in the catchment. Throughout this literature review however, no information regarding potential heavy metal contamination of the Eerste River could be obtained (DWAF, 1993).

Therefore, the aims of the current study was to determine the concentrations of heavy metals (Cu, Zn, Fe, Ni, Pb, Cd) in water, soil and plant leaves along the Eerste River, throughout the year and to determine whether higher plants can be used as biomonitors to assess the overall state of the Eerste River catchment.



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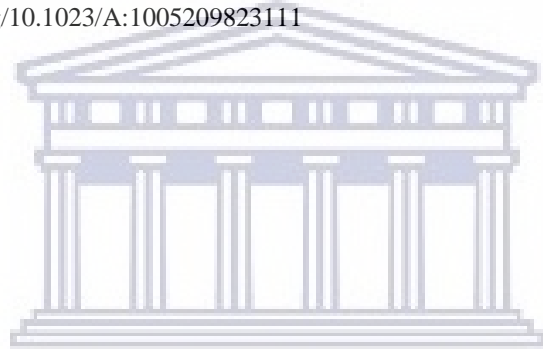
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# CHAPTER 3

## STUDY AREA: THE EERSTE KUILS RIVER CATCHMENT

### 3.1 Location

In the Cape Metropolitan Area (CMA) there are two important rivers, the Eerste and the Kuils Rivers (Figure 3.1). The smaller Kuils joins the larger Eerste near Macassar before ending in False Bay as one of the eleven estuaries. It is located 36 km south-east of Cape Town. The Eerste River catchment is the biggest at 660 km<sup>2</sup>. A large section of this catchment is divided between two municipalities, Stellenbosch and the CMA.

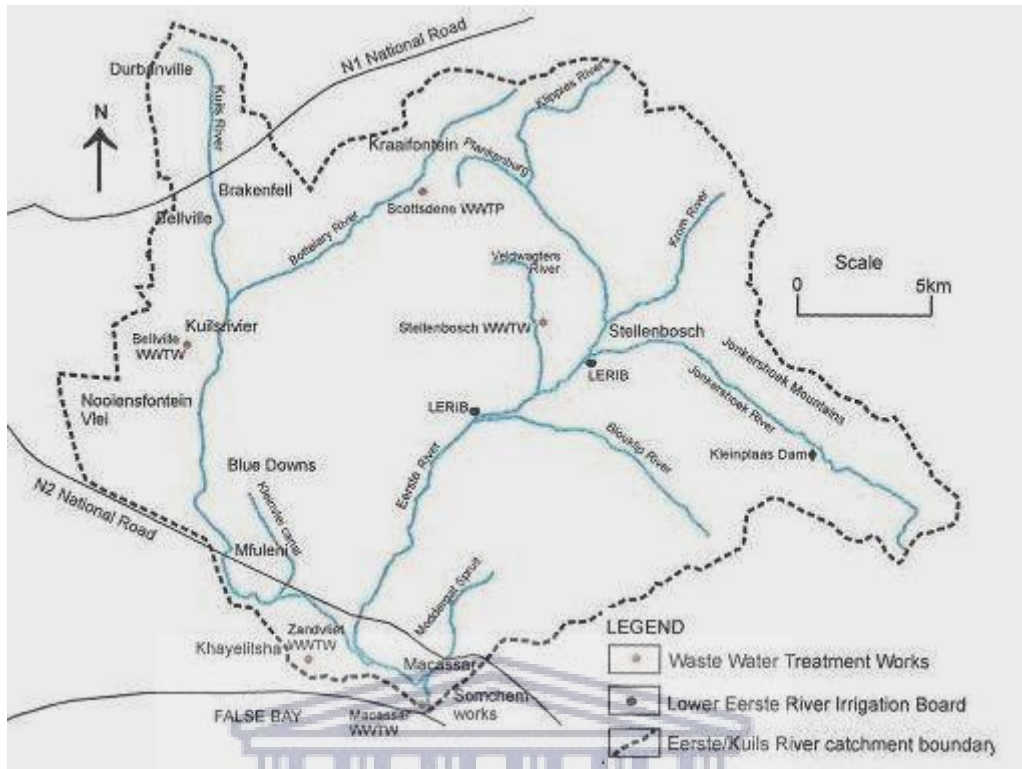
It is widely known that the estuary is only breached by the winter rains, and is closed during hot months of summer by prevailing wind and wave built sandbar. The hydrological character of the river has been changed by the discharge of the effluent of the sewage works, including those located in Macassar (Petersen, 2002). This has affected the water quality, health and aesthetic value of the river as it flows through urban areas (Petersen, 2002; Thomas et al., 2010).

The catchment is located in the South-Western Cape coastal area of South Africa between the Cape Fold Hottentots-Holland Mountains and the Cape Flats. The Kuils River originates from Durbanville's highland near the hills of Kanonkop in the Tygerberg, and it flows to the south where it passes through areas of both Bellville

and Kuils River. It then runs through the Cape Flats sandy plains, along the N2 highway through the Driftsands Nature Reserve curving east of the residential area of Khayelitsha to Macassar. The wetlands located in the lower part are very important for the biodiversity of the ecosystem. The Scottsville, Bellville and Zandvliet Waste Water Treatment Works (WWTW) discharge large amounts of treated sewage effluent which make the river perennial (Thomas et al., 2010).

The Eerste River initiates in the Jonkershoek Forest Reserve, in its midstream it flows through mainly agricultural land and the town of Stellenbosch towards the confluence with the Kuils River (Wiseman and Simpson, 1989). After the union with the Kuils River tributary in the Cape Flats area, the catchment has mainly unused and uncontrolled open land where the Moddergat Spruit joins the river. Two manufacturing plants, the Somchem factory and the Macassar WWTW are situated on the eastern and the western banks respectively (Petersen, 2002; Shand and Nicks, 1999; Wiseman and Simpson, 1989).

Consequently, alongside surface runoffs, this river also collects chemical wastes from industrial drains and treated sewage effluent from a number of WWTW situated in its catchment. In addition to the Macassar WWTW, the Stellenbosch WWTW releases effluent via the Veldwagter River, into the Eerste River. Petersen (2002) defined an approximate flow rate in terms of discharge contributed by both the Stellenbosch and Macassar WWTW plants as  $13.5 \text{ MI}\cdot\text{day}^{-1}$  and  $14 \text{ MI}\cdot\text{day}^{-1}$ , respectively. The total catchment area for both rivers is  $660 \text{ km}^2$  of which approximately 45% belongs to the Kuils River (Morant, 1991; Harrison, 1998; Petersen, 2002). This leaves an approximately  $360 \text{ km}^2$  as the entire catchment area of the Eerste River.



Source: (DWAF, 1993; Harrison, 1998; Petersen, 2002)

**Figure 3.1:** Location and distribution of the stream network in the Kuils-Eerste River urban catchment area

### 3.2 Landscape

Riparian areas are considered as the most dynamic of all landscape configurations, river movement and natural unrests are continually working together in these areas to generate characteristic dynamic environmental systems of importance to the diversity of biological habitats (Banner and MacKenzie, 1998; Kenwick, Shammin and Sullivan, 2009; Meek, Richardson and Mucina, 2010). In the South-Western Cape, until the end of the 19th century, there were no developments in the Blue Downs/Eerste River area. Some of the crown lands near the Eerste River station were reserved and subdivided between 1899 and 1906. The land between the Eerste River and Kuils River was sold toward 1899.

There were numerous changes from the 1890s for lots of land in the area. There were complaints about water shortage in 1907 and shifting dunes between 1890 and 1897. The aerial maps in 1926 showed numerous plots of arable land in the area, thus correspondence between 1921 and 1933 is concerned with the proposal that certain portions of the Eerste River Forest as Reserve area (Baumann, Webley and Avery, 2011).

The work compiled in this thesis was completed on the Eerste River catchment (Figure 3.1). As with most rivers in areas of development, the Eerste River has undergone dramatic changes due to intensive human use of the river resulting in over-abstraction and pollution. Currently, the landscape surrounding the Eerste River supports a number of land uses, including nature conservation, commercial forestry, residential use, various forms of agriculture and communal grazing.

Approximately, the first 6 km of the upper river reaches are bordered by natural vegetation within the Hottentots Holland and Jonkershoek Nature Reserves, and is relatively unaffected by human influence (Meek, Richardson and Mucina, 2010). Land-cover coverage for Kuils- Eerste River catchment residential areas is 12.8%, with commercial areas taking up 0.4%, agricultural land occupies 40.6%, Fynbos has 12.5% and the forests both riparian, mountain and shrubs occupy 14.6%. Grasslands only 10.8 %, while the road network covers 3.4% of the catchment (Chingombe, 2012).

Since 1981, the upper reach of the river has been regulated by the Kleinplaas Dam, above which the Eerste River is perennial (DWAF, 2004). During summer months, a



municipal weir above the dam diverts the rivers flow to the Idas Valley Dam, which supplies drinking water and water for domestic use to the town of Stellenbosch (Brown and Dallas, 1995). In order to provide compensation for downstream users, this flow is replaced with water from the Theewaterskloof Dam through an interbasin transfer scheme. Water from the Theewaterskloof Dam contains high sediment loads, significantly reducing the water quality and negatively affecting downstream biotas in the Eerste River (Brown and Magoba, 2009).

Stellenbosch is the main urban area along the river, with additional urban development present in Macassar (Meek, Richardson and Mucina, 2010). Just south of Stellenbosch, the Eerste River is joined by the Plankenburg River. Water is abstracted at this point, near the confluence with the Blouklip River, and along most of its length. Treated municipal effluent enters the river through the Veldwagters tributary. Below the confluence of the Veldwagters and Eerste Rivers, treated effluent is an important component of river flow in summer. This makes the river largely perennial in downstream areas (Meek, Richardson and Mucina, 2010).

### **3.3 Climate**

The climate range of the Kuils-Eerste River catchment range is average for the South-Western Cape which falls in the winter precipitation locale of the country with a trademark Mediterranean system. The climate is for the most part affected by the South Atlantic (Schulze, 1997; Petersen, 2002). The summers are dry, warm to sweltering with solid south-easterly breezes. Temperatures may reach 40°C. Winters are wet and chilly, with powerful north-westerly breezes that bring temperatures to as low as 0°C frequently leaving the peaks immersed in snow (Hendricks, 2003).

Orographic precipitation is the dominating types of precipitation because of the rugged geography influencing the territory. The peak rainfalls are the highest in entire Southern Africa. Around 85% of the precipitation happens inside a half year of the winter time frame, this is from April to September (Van Wyk, 1987). The highest mean monthly precipitation happens in June as a result of cold fronts which reach the Cape from the Atlantic Ocean. The zone is associated with high wind speeds in summer, especially the "South-Easters" that blow from the south-east. Berg winds with hot and dry land breezes additionally happen in winter. The highest wind speeds are recorded at Cape Point and the bordering mountains on the eastern side of False Bay making a wind shadow over the Eerste River territory (Petersen, 2002; Hendricks, 2003).

For example, the normal precipitation over the territory of the Cape Flats is around 600 mm per annum. This is considerably less than in the encompassing mountains, however, the mean yearly precipitation increases to around 800 mm in the eastern slopes due to the orographic impact, The mean yearly rainfall in the Jonkershoek area of the catchment ranges from 1100 to 1400 mm, of which for the most part happens during the winter months (Bennett and Kruger, 2015; Wicht et al., 1969). Annual total rainfall during the study period in 2011 and 2012, respectively, was 348.4 mm and 466.2 mm (South African Weather Service, Annual Report 2011/12. Pretoria).

### **3.4 Vegetation**

The catchment of the Kuils-Eerste River has been severely transformed into urban and agricultural areas (private homes and businesses can be found) alongside diverse farming interests. Vineyards, deciduous fruits, lucerne, pastures and forest plantations

are a common land cover. Most of the developed land is used for wine production. The rest of the developed land is used for developing natural products, lucerne and meadow. The other land covers are fynbos vegetation in the upper reaches, wetland vegetation and surface water bodies, for example, wetlands, marshes (vleis), lakes, ponds, reserves or dams (Thomas et al., 2010). In the Eerste River catchment, Western Cape, plant communities along the river include, vineyard occupying 20.4%, Fallow/Open Vineyard 14.4 % and Fynbos 12.5 % (Chingombe, 2012).

A sum of 246 plant species was identified along the stream, of which 131 were alien and 115 were indigenous. Of the foreign species, 21 are recorded as Category 1 intruders in South Africa (Republic of South Africa, 1983), furthermore, 12 have been proposed as emerging invaders as per Nel et al (2004). Alien species represented 62% of the general vegetation cover along the Eerste River riparian corridor (Nel et al., 2004).

Invading vegetation (wattle, poplars, spanish reed, kikuyu, and nasturtiums) has supplanted a significant part of the indigenous riparian vegetation throughout the Eerste River catchment. The trees have changed the physical nature the banks, where they have an effect on the formation of the river canal (River Health Programme, 2005; Dallas, 2007).

### **3.5 Geology**

The geology of the Cape Floristic Region comprises to a great extent of sandstones and shales of the Cape Supergroup and Malmesbury Group, Cape Granites, and more plentiful sand and alluvial stores of Tertiary and Quaternary Formations (Bioregion,

2002). The geology of the Eerste River catchment is formed out of Table Mountain Sandstone in the upper slopes and Malmesbury Shale and Cape Granite of the Bokkeveld Group in the lower area. The low-lying beach front plains are formed out of aeolian sands limestones (Brown and Dallas, 1995). The geological formations underlining a catchment are known to influence water quality, chemical and physical parameters. Rock properties can affect water electrical conductivity, pH, magnesium (Mg), Ca, and sulphate (So<sub>4</sub>) concentrations, among other parameters (Olson, 2012). The Table Mountain sandstone of the upper reaches yields very pure water. The granite and shales of the middle and limestone of the lower reaches have more marked effects (Kotze, 2001; Paxton, 2018).



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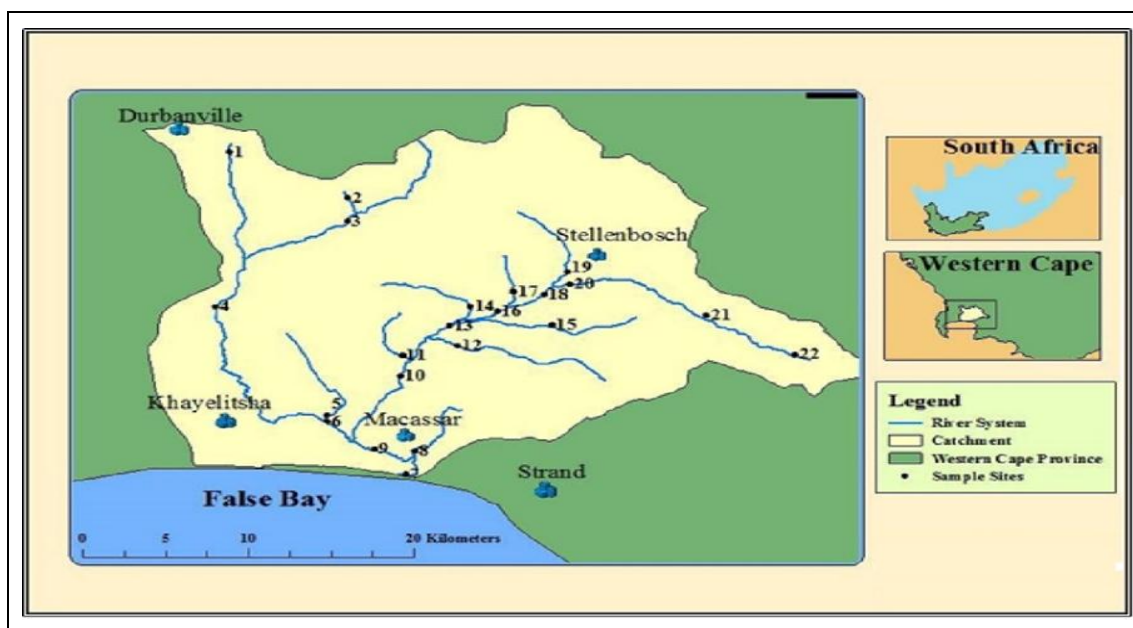
# CHAPTER 4

## MATERIALS AND METHODS

### 4.1 Location of Sampling Sites: Selection and Collection of Plant Species

In the Eerste River Catchment forty-two sites were examined for the presence of seven of the most common plant species. From these, twenty-two sites were chosen, including each principal tributary and the river after its confluence. The most common plants were *Commelina benghalensis* L, *Paspalum urvillei* S, *Persicaria lapathifolia* L and *Salix babylonica* L. The map and table show the location of the various sampling sites (Figure 4.1; Table 4.1).





**Figure 4.1:** The location of sampling sites, in the Kuilsriver-Eersteriver Catchment

**Table 4.1:** Locations and description of sites selected in the Eerste River catchment

Reaches	Sites	Acronym	Site Name	Coordinates	
				E	S
Middle reaches	1	Km	Kuils River in Durbanville	18°40'5.54"	33°50'44.44"
	2	Km	Scottsdene Tributary	18°43'57.88"	33°52'44.81"
	3	Km	Bottelary Groenland	18°43'57.19"	33°53'46.40"
	10	Em	Kompanies Drift	18°45'41.55"	34° 0'31.84"
	11	Em	Aspidispar Nursery Vlaeberg Road	18°45'43.94"	33°59'36.77"
	12	Em	Bonte River	18°47'32.40"	33°59'11.90"
	13	Em	Spier	18°47'12.62"	33°58'21.61"
	14	Em	Vlottenberg Digtebij, Sanddrif River	18°47'56.07"	33°57'28.37"
	15	Em	BlouklipRiver	18°50'32.89"	33°58'20.18"
	16	Em	Verdenheim	18°48'51.28"	33°57'40.87"
	17	Em	Veldwachers River	18°49'22.48"	33°56'51.88"
	18	Em	PPRI=Distell	18°50'20.86"	33°56'58.42"
	19	Em	Plankenbrug River	18°51'6.50"	33°55'57.75"
	20	Em	Old Strand Road	18°51'11.95"	33°56'28.70"

Lower reaches	4	Kl	Wesbank	18°39'40.21"	33°57'28.55"
	5	Kl	EersteRiver Canal	18°43'17.13"	34° 2'13.84"
	6	Kl	Kuils River Marshes	18°43'17.72"	34° 2'29.34"
	7	Jl	Estuary	18°45'46.09"	34° 4'46.64"
	8	Jl	Schoongesight Macassar	18°46'7.13"	34° 3'47.66"
	9	Jl	Macassar Road	18°44'50.49"	34° 3'43.32"
Upper reaches	21	Eu	Cape Nature	18°55'32.47"	33°57'57.20"
	22	Eu	Jonkershoek	18°58'31.00"	33°59'38.00"

\* E=Eerste River, K=Kuils River

## 4.2 Collection and Preparation Samples

Every six weeks, from 29/11/2011 till 18/12/2012, water and soil samples were collected from the twenty-two sites. Plant samples were collected at the same time from the sites where they occurred (Table 4.2).

**Table 4.2:** The collection dates and their allocation to seasons and to wet & dry periods

Visit No	Visit Date	Seasons	Dry & Wet Period	
1	2011-2011	Spring	Dry	
2	10-01-2012	Summer		
3	21-02-2012			
4	11-04-2012	Autumn	Wet	
5	16-05-2012			
6	28-06-2012	Winter		
7	07-08-2012			
8	19-09-2012	Spring		
9	15-11-2012			
10	18-12-2012	Summer		

Water samples were collected in 300-ml plastic bottles, filtered in the laboratory and

frozen after initial analyses (Afolayan, 2018). Approximately 1 kg of soil was collected in a plastic bag from the river sediment at each site. In the laboratory stones and plant debris were removed. The samples were dried, sieved (2 mm) and stored in a plastic bag (Markert, 2007; Tribes, 2010; U.S. Natural Resources Conservation Service Soil Survey Staff, 2014). Leaf samples were collected in brown paper bags. In the laboratory, they were washed with deionized water to remove dust (Kos et al., 1996; Steinnes, 2000) and then dried at 70°C, milled and stored in plastic containers (Ghani et al., 2012; Markert, 2007).

### **4.3 Field Tests**

Water temperature (°C) and dissolved oxygen (% ,  $\text{mg}\cdot\text{l}^{-1}$ ) were directly recorded in the river with YSI 55 (Kentucky Division of Water (KDOW), 2009; Tahoe, 2010).

### **4.4 Laboratory Tests**

In the laboratory, initial determinations were conducted within 24 hours of collection: electrical conductivity (EC), hydrogen ion concentration (pH), Ammonium ( $\text{HN}_4^+$ ), nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ) tests were carried out (Water Research Commission, 2000). Determinations of ammonium, nitrite and nitrate were achieved with a reflectometer using Aquamerck ®11 117 Ammonium Tests, the Aquamerck ® 8032 Nitrate and the Aquamerck ® 8025 Nitrate Merck test strips (Adams, 2011). The electrical conductivity was measured in the water with a YSI model 35-EC meter, and the hydrogen ion concentration by a Thermo Scientific Orion Star A111 pH meter (Rowell, 2014). Soil pH was measured in damp soil samples using the sticky point method (Jackson, 1959). Soil electrical conductivity was determined with the same sample by filling a conductivity cup and measuring with an EC meter ( $\mu\text{S cm}^{-1}$ )

(Jackson, 1959; Malan et al., 2015).

## **4.5 Digestion**

### **4.5.1 Plant Samples**

A sulphuric-peroxide mixture was used (Allen et al., 1986) to digest 0.4 g plant material, at low heat until the H<sub>2</sub>SO<sub>4</sub> fumes, then at 350°C in a heating block until a clear and almost colourless solution was obtained. The digest was diluted to 100 ml with 0.1% HCl.

### **4.5.2 Soil Samples**

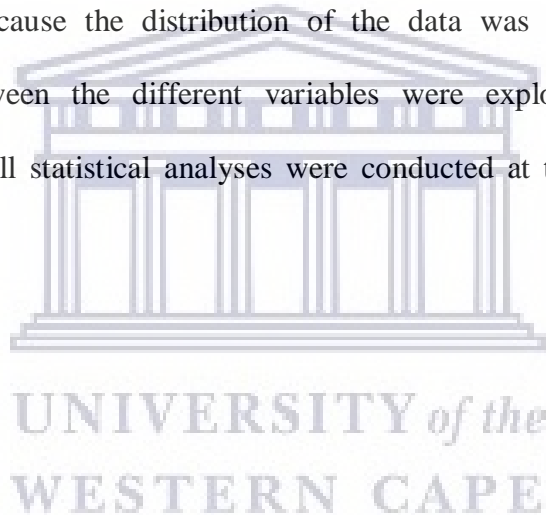
Soil samples were digested with Aqua Regia mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3 (HNO<sub>3</sub>:HCl). A 0.5 g sample was placed in a digestion tube with 12 ml Aqua Regia solution and heated for 3 hours at 110°C in a heating block or till dry, taken up in 2% nitric acid, filtered and diluted to 100 ml with 2% nitric acid. A blank sample was prepared following the same procedures with plant and soil samples, respectively, without the soil or plant material (Radojevic and Bashkin, 2007). This was done for every set of 19 digestion samples in the heating block.

## **4.6 ICP Determination of Metal Concentration**

About 800 digested samples (soil and plant) were measured for certain heavy metals concentrations (Cu, Zn, Fe, Ni, Pb and Cd) with an Agilent 710 Series ICP-OES.

## **4.7 Data Analysis**

First, all data were verified and tabulated according to the different sites along the different sections of the river (up-, mid- and low-stream), and through the different seasons, and then entered into a Microsoft Office Excel© spreadsheet, forming a matrix of sampling sites versus all the examined variables for water, soil and various plant species. The data were subjected to various statistical and classification analyses using IBM SPSS version 22. Initially, the data sets were inspected using descriptive statistical analysis, then they were checked for normal distribution using Shapiro-Wilk test. Significant differences between the soil, water, and plants in the different seasons and various sections were explored using Kruskal-Wallis one-way ANOVA tests because the distribution of the data was not normal. The inter-relationships between the different variables were explored using a bivariate correlation test. All statistical analyses were conducted at the 5%- or 1%-level of significance.



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# CHAPTER 5

## RESULTS OF THE ANALYSIS OF WATER, SOIL AND PLANTS FOR SELECTED PHYSICAL AND CHEMICAL PARAMETERS

### 5.1 Spatiotemporal Characteristics

#### 5.1.1 Water Temperature and Dissolved Oxygen

Along the river, the temperature of the water showed an increasing trend from the upper to the lower reach, with highly significant differences ( $p < 0.01$ ) between various river reaches. The lowest mean temperature value was ( $10.60 \pm 0.80^\circ\text{C}$ ) in winter, and the highest mean temperature value was ( $27.39 \pm 1.07^\circ\text{C}$ ) in summer, with a significant difference between seasons ( $p < 0.01$ ) (Table 5.1). The increase in temperature downstream paralleled a significant decrease in DO ( $p < 0.01$ ) along the river. Autumn and winter showed the maximum mean values for dissolved oxygen (DO), while spring and summer showed the lowest mean values, with a significant difference among seasons ( $p < 0.01$ ). The highest DO mean value was ( $11.30 \pm 0.49 \text{ mg.l}^{-1}$ ) in winter, and the lowest was ( $3.56 \pm 0.64 \text{ mg.l}^{-1}$ ) in autumn (Table 5.1).

#### 5.1.2 Water pH and Electrical Conductivity

The pH of the river water showed a significant increasing trend along the river ( $p < 0.01$ ), the upper reach had the lowest values ( $6.63 \pm 0.22 \text{ pH}$ ), and the lower reach had the highest values ( $7.84 \pm 0.18 \text{ pH}$ ).

The spring and summer samples showed the peak values while winter and autumn showed the lowest (Table 5.1). The pH showed a significant difference between the seasons ( $p=0.02$ ). As expected, the EC showed a significant increasing trend from the upper- to the lower reaches as well ( $p<0.01$ ). The lowest mean value was in upper reach during winter ( $38.25\pm 3.77 \mu\text{S cm}^{-1}$ ), and the highest mean value was in the lower reach during spring ( $734.06\pm 1058.51 \mu\text{S cm}^{-1}$ ) (Table 5.1). There was no significant difference between seasons in EC values.

### 5.1.3 Water Ammonium, Nitrite and Nitrate

The chemical analysis of all water samples showed spatiotemporal variation through the different river reaches and various seasons. The ammonium ( $\text{NH}_4^+$ ) showed a significant increase in the trend along the river from upper to lower reach ( $p<0.01$ ).

During winter it showed the least values and was close to zero in the upper reach, and the peak values were measured during summer, in the lower reach it was ( $10.05\pm 2.08 \text{ mg.l}^{-1}$ ) (Table 5.1), with a significant difference among seasons ( $p<0.01$ ).

The nitrite ( $\text{NO}_2^-$ ) values increased significantly from the upper to lower reaches ( $p<0.01$ ); in the upper reach they were very close to zero during all seasons. However, they peaked in spring in the lower reach ( $0.10\pm 0.06 \text{ mg.l}^{-1}$ ) (Table 5.1), with significant differences among seasons ( $p<0.01$ ) and along the river reaches.

Similarly, the concentrations of nitrate ( $\text{NO}_3^-$ ) differed significantly ( $p<0.01$ ) along the river reach, they were close to zero in upper reach, and the peak values were in the middle reach for all seasons. The highest mean value was during autumn ( $15.18\pm 3.94 \text{ mg.l}^{-1}$ ) (Table 5.1).



**Table 5.1:** The mean ( $\pm$ SE) for temperature ( $^{\circ}$ C), dissolved oxygen ( $\text{mg.l}^{-1}$ ), pH, electrical conductivity ( $\mu\text{S cm}^{-1}$ ), and nitrogen species ( $\text{mg.l}^{-1}$ ) in water samples collected in the Eerste-Kuils River as affected by seasons (winter, spring, summer, and autumn) and reach (upper, middle, and lower reach) ND=refers to samples where the parameter was not detected.

Parameter	Reach	Winter	Spring	Summer	Autumn
Temperature $^{\circ}\text{C}$	Upper reach	10.60 ( $\pm 0.80$ )	16.07 ( $\pm 1.33$ )	19.77 ( $\pm 0.76$ )	14.35 ( $\pm 0.39$ )
	Middle reach	12.71 ( $\pm 0.28$ )	19.20 ( $\pm 0.48$ )	24.60 ( $\pm 0.61$ )	16.04 ( $\pm 0.39$ )
	Lower reach	13.39 ( $\pm 0.40$ )	21.57 ( $\pm 0.98$ )	27.39 ( $\pm 1.07$ )	18.08 ( $\pm 0.74$ )
Dissolved Oxygen $\text{mg.l}^{-1}$	Upper reach	11.30 ( $\pm 0.49$ )	9.30 ( $\pm 0.65$ )	8.38 ( $\pm 0.56$ )	10.86 ( $\pm 0.22$ )
	Middle reach	8.29 ( $\pm 0.44$ )	5.68 ( $\pm 0.35$ )	4.00 ( $\pm 0.34$ )	6.07 ( $\pm 0.52$ )
	Lower reach	5.89 ( $\pm 0.78$ )	4.68 ( $\pm 0.98$ )	3.95 ( $\pm 1.03$ )	3.56 ( $\pm 0.64$ )
pH	Upper reach	6.63 ( $\pm 0.22$ )	7.33 ( $\pm 0.33$ )	7.1 ( $\pm 0.29$ )	6.71 ( $\pm 0.41$ )
	Middle reach	7.23 ( $\pm 0.04$ )	7.33 ( $\pm 0.04$ )	7.35 ( $\pm 0.036$ )	7.16 ( $\pm 0.07$ )
	Lower reach	7.55 ( $\pm 0.06$ )	7.84 ( $\pm 0.18$ )	7.83 ( $\pm 0.18$ )	7.47 ( $\pm 0.08$ )
EC $\mu\text{S cm}^{-1}$	Upper reach	38.25 ( $\pm 3.77$ )	63.08 ( $\pm 8.04$ )	62.08 ( $\pm 7.63$ )	67.45 ( $\pm 9.84$ )
	Middle reach	628.68 ( $\pm 82.51$ )	698.64 ( $\pm 54.39$ )	637.82 ( $\pm 46.22$ )	660.89 ( $\pm 70.92$ )
	Lower reach	1 986.17 ( $\pm 640.8$ )	2 734.06 ( $\pm 1058.5$ )	2 538.24 ( $\pm 894.5$ )	2 629.58 ( $\pm 1463.2$ )

*/Continued*

**Table 5.1:** The mean ( $\pm$ SE) for temperature ( $^{\circ}$ C), dissolved oxygen ( $\text{mg.l}^{-1}$ ), pH, electrical conductivity ( $\mu\text{S cm}^{-1}$ ), and nitrogen species ( $\text{mg.l}^{-1}$ ) in water samples collected in the Eerste River -Kuils River as affected by seasons (winter, spring, summer, and autumn) and reach (upper, middle, and lower reach) ND=refers to samples where the parameter was not detected (*continued*)

Parameter	Reach	Winter	Spring	Summer	Autumn
$\text{NO}_2^-$ $\text{Mg.l}^{-1}$	Upper reach	ND	ND	ND	ND
	Middle reach	0.09 ( $\pm$ 0.05)	2.89 ( $\pm$ 0.89)	0.79 ( $\pm$ 0.22)	1.18 ( $\pm$ 0.58)
	Lower reach	0.10 ( $\pm$ 0.06)	3.21 ( $\pm$ 1.74)	0.25 ( $\pm$ 0.09)	0.49 ( $\pm$ 0.18)
$\text{NO}_3^-$ $\text{Mg.l}^{-1}$	Upper reach	ND	0.33 ( $\pm$ 0.33)	ND	ND
	Middle reach	10.54 ( $\pm$ 3.21)	12.60 ( $\pm$ 2.26)	11.02 ( $\pm$ 2.58)	15.18 ( $\pm$ 3.94)
	Lower reach	10.08 ( $\pm$ 1.82)	7.17 ( $\pm$ 1.46)	4.65 ( $\pm$ 1.40)	8.25 ( $\pm$ 2.26)
$\text{NH}_4^+$ $\text{Mg.l}^{-1}$	Upper reach	ND	0.08 ( $\pm$ 0.08)	0.1 ( $\pm$ 0.07)	0.2 ( $\pm$ 0.11)
	Middle reach	0.93 ( $\pm$ 0.28)	3.31 ( $\pm$ 1.10)	7.58 ( $\pm$ 1.54)	2.64 ( $\pm$ 0.71)
	Lower reach	1.93 ( $\pm$ 0.73)	3.91 ( $\pm$ 1.47)	10.05 ( $\pm$ 2.08)	5.38 ( $\pm$ 2.15)

#### 5.1.4 Soil pH and Electrical Conductivity

In all seasons, the soil pH values tend to be acidic in the upper and lower reaches ( $\text{pH}<7$ ), however the lowest values were noticed in the upper reach. The highest values ( $\text{pH}>7$ ) were recorded in the middle reach (Table 5.2). Overall, the middle reach was significantly higher ( $p<0.001$ ), but no significant difference was detected amongst the seasons ( $p=0.234$ ). The same trend was recorded for the soil electrical conductivity (EC). The lowest values were in the upper reach and the middle reach was significantly higher compared to the upper and lower reaches ( $p<0.001$ ) (Table 5.2). There was no significant difference detected amongst the seasons ( $p=0.107$ ).

#### 5.1.5 Calcium

The calcium (Ca) concentrations in water increased significantly ( $p<0.01$ ) from upper reach ( $1.71\pm 0.44 \text{ mg.l}^{-1}$ ) to lower reach ( $26.88\pm 1.29 \text{ mg.l}^{-1}$ ). Vice versa for soil which decline significantly ( $p<0.02$ ) from upper reach ( $60.62\pm 14.75 \text{ mg.kg}^{-1}$ ) to lower reach ( $17.77\pm 4.06 \text{ mg.l}^{-1}$ ) (Table 5.3). The *S. babylonica* and *P. urvillei* showed a significant increase in concentration ( $p<0.01$  and  $p<0.09$ ) from upper to lower reach, respectively the *C. benghalensis* showed significant decline in concentrations ( $p<0.01$ ) while no significant differences were found for *P. lapathifolia* (Table 5.3).

The highest mean value in water ( $19.19\pm 2.03 \text{ mg.l}^{-1}$ ) and *C. benghalensis* ( $70.76\pm 5.74 \text{ mg.kg}^{-1}$ ) were recorded in samples collected in winter (Table 5.4). The highest mean value in soil ( $63.73\pm 16.33 \text{ mg.kg}^{-1}$ ) and *S. babylonica* ( $82.24\pm 7.15 \text{ mg.kg}^{-1}$ ) were recorded in samples collected in summer (Table 5.4).

**Table 5.2:** The mean ( $\pm$ SE) for pH and electrical conductivity ( $\mu\text{S cm}^{-1}$ ) in soil samples as affected by seasons (winter, spring, summer, and autumn) and reach (upper, middle, and lower reaches).

Parameter	Reach	Winter	Spring	Summer	Autumn
pH	Upper reach	5.43 ( $\pm$ 0.130)	5.45 ( $\pm$ 0.153)	5.44 ( $\pm$ 0.173)	4.83 ( $\pm$ 0.078)
	Middle reach	7.56 ( $\pm$ 0.101)	7.60 ( $\pm$ 0.091)	7.44 ( $\pm$ 0.045)	7.41 ( $\pm$ 0.072)
	Lower reach	6.25 ( $\pm$ 0.173)	6.45 ( $\pm$ 0.102)	6.09 ( $\pm$ 0.127)	5.91 ( $\pm$ 0.172)
EC $\mu\text{S cm}^{-1}$	Upper reach	43.50 ( $\pm$ 9.500)	54.67 ( $\pm$ 5.795)	57.33 ( $\pm$ 21.464)	64.50 ( $\pm$ 20.819)
	Middle reach	539.58 ( $\pm$ 106.874)	859.94 ( $\pm$ 122.109)	1 427.00 ( $\pm$ 303.595)	1 080.58 ( $\pm$ 320.254)
	Lower reach	328.46 ( $\pm$ 51.683)	499.12 ( $\pm$ 89.944)	531.79 ( $\pm$ 116.433)	571.21 ( $\pm$ 109.511)

**Table 5.3:** The mean ( $\pm$ SE) for the measured metal ( $\text{mg}\cdot\text{l}^{-1}$ ) in water and soil and plants ( $\text{mg}\cdot\text{kg}^{-1}$ ) along the different reaches of the river. ND refers to samples where the metal was not detected.

Parameter	Reach	Water	Soil	<i>S. babylonica</i>	<i>C. benghalensis</i>	<i>P. urvillei</i>	<i>P. lapathifolia</i>
Ca	Upper reach	1.71 ( $\pm$ 0.44)	60.62 ( $\pm$ 14.75)	19.67 ( $\pm$ 12.04)	64.08 ( $\pm$ 7.09)	15.11 ( $\pm$ 3.64)	69.43 ( $\pm$ 7.57)
	Middle reach	17.56 ( $\pm$ 0.76)	51.91 ( $\pm$ 8.45)	25.60 ( $\pm$ 5.19)	66.97 ( $\pm$ 3.30)	34.71 ( $\pm$ 3.58)	52.33 ( $\pm$ 4.22)
	Lower reach	26.88 ( $\pm$ 1.29)	17.77 ( $\pm$ 4.06)	80.29 ( $\pm$ 5.79)	39.14 ( $\pm$ 3.71)	42.55 ( $\pm$ 4.52)	43.54 ( $\pm$ 3.54)
Fe	Upper reach	1.04 ( $\pm$ 0.61)	27.65 ( $\pm$ 14.89)	1.94 ( $\pm$ 1.35)	0.97 ( $\pm$ 0.10)	0.37 ( $\pm$ 0.11)	4.20 ( $\pm$ 0.78)
	Middle reach	0.78 ( $\pm$ 0.19)	17.97 ( $\pm$ 1.98)	1.21 ( $\pm$ 0.09)	1.39 ( $\pm$ 0.06)	1.22 ( $\pm$ 0.10)	1.92 ( $\pm$ 0.10)
	Lower reach	0.81 ( $\pm$ 0.26)	21.69 ( $\pm$ 4.29)	1.28 ( $\pm$ 0.13)	0.78 ( $\pm$ 0.10)	1.07 ( $\pm$ 0.08)	2.45 ( $\pm$ 0.30)
Ni	Upper reach	0.73 ( $\pm$ 0.38)	1.86 ( $\pm$ 0.65)	0.86 ( $\pm$ 0.50)	0.02 ( $\pm$ 0.02)	0.001 ( $\pm$ 0.001)	4.79 ( $\pm$ 1.13)
	Middle reach	1.92 ( $\pm$ 0.25)	1.54 ( $\pm$ 0.20)	1.19 ( $\pm$ 0.26)	0.02 ( $\pm$ 0.01)	0.05 ( $\pm$ 0.01)	1.30 ( $\pm$ 0.27)
	Lower reach	1.15 ( $\pm$ 0.28)	1.86 ( $\pm$ 0.34)	0.35 ( $\pm$ 0.14)	0.01 ( $\pm$ 0.01)	0.06 ( $\pm$ 0.01)	1.90 ( $\pm$ 0.47)
Zn	Upper reach	1.33 ( $\pm$ 0.54)	4.02 ( $\pm$ 0.90)	0.79 ( $\pm$ 0.23)	0.56 ( $\pm$ 0.10)	0.11 ( $\pm$ 0.06)	1.40 ( $\pm$ 0.22)
	Middle reach	0.89 ( $\pm$ 0.17)	2.35 ( $\pm$ 0.25)	0.75 ( $\pm$ 0.07)	0.75 ( $\pm$ 0.05)	0.50 ( $\pm$ 0.04)	1.08 ( $\pm$ 0.08)
	Lower reach	0.25 ( $\pm$ 0.13)	2.87 ( $\pm$ 0.41)	0.86 ( $\pm$ 0.11)	0.59 ( $\pm$ 0.10)	0.56 ( $\pm$ 0.05)	1.15 ( $\pm$ 0.17)
Cu	Upper reach	0.65 ( $\pm$ 0.37)	2.93 ( $\pm$ 0.56)	3.75 ( $\pm$ 1.70)	0.33 ( $\pm$ 0.03)	0.04 ( $\pm$ 0.03)	0.31 ( $\pm$ 0.04)
	Middle reach	2.09 ( $\pm$ 0.25)	3.30 ( $\pm$ 0.25)	1.39 ( $\pm$ 0.30)	0.24 ( $\pm$ 0.01)	0.15 ( $\pm$ 0.01)	0.20 ( $\pm$ 0.01)
	Lower reach	1.36 ( $\pm$ 0.31)	3.22 ( $\pm$ 0.43)	2.99 ( $\pm$ 0.65)	0.22 ( $\pm$ 0.02)	0.14 ( $\pm$ 0.02)	0.24 ( $\pm$ 0.02)
Cd	Upper reach	0.27 ( $\pm$ 0.21)	1.13 ( $\pm$ 0.41)	ND	ND	0.19 ( $\pm$ 0.19)	0.91 ( $\pm$ 0.73)
	Middle reach	0.81 ( $\pm$ 0.16)	2.02 ( $\pm$ 0.22)	0.84 ( $\pm$ 0.23)	0.22 ( $\pm$ 0.09)	0.74 ( $\pm$ 0.23)	0.71 ( $\pm$ 0.17)
	Lower reach	0.95 ( $\pm$ 0.31)	2.66 ( $\pm$ 0.37)	0.27 ( $\pm$ 0.13)	ND	2.80 ( $\pm$ 0.47)	1.36 ( $\pm$ 0.32)
Pb	Upper reach	2.04 ( $\pm$ 0.61)	3.04 ( $\pm$ 0.65)	ND	0.01 ( $\pm$ 0.01)	0.004 ( $\pm$ 0.002)	0.03 ( $\pm$ 0.01)
	Middle reach	1.62 ( $\pm$ 0.19)	2.57 ( $\pm$ 0.22)	1.14 ( $\pm$ 0.27)	0.01 ( $\pm$ 0.003)	0.01 ( $\pm$ 0.001)	0.01 ( $\pm$ 0.001)
	Lower reach	1.56 ( $\pm$ 0.29)	3.24 ( $\pm$ 0.39)	2.42 ( $\pm$ 0.54)	0.01 ( $\pm$ 0.002)	0.01 ( $\pm$ 0.002)	0.01 ( $\pm$ 0.003)

**Table 5.4:** The mean ( $\pm$ SE) for the measured metal ( $\text{mg.l}^{-1}$ ) in water and in soil and plants ( $\text{mg.kg}^{-1}$ ) during the different seasons. ND refers to samples where the metal was not detected.

Parameter	Season	Water	Soil	<i>S. babylonica</i>	<i>C. benghalensis</i>	<i>P. urvillei</i>	<i>P. lapathifolia</i>
Ca	Winter	19.19 ( $\pm$ 2.03)	42.03 ( $\pm$ 7.80)	28.32 ( $\pm$ 9.17)	70.76 ( $\pm$ 5.74)	19.49 ( $\pm$ 3.26)	61.07 ( $\pm$ 6.45)
	Spring	19.05 ( $\pm$ 1.38)	39.79 ( $\pm$ 7.18)	32.89 ( $\pm$ 5.55)	64.56 ( $\pm$ 5.062)	41.63 ( $\pm$ 5.57)	63.58 ( $\pm$ 6.85)
	Summer	18.32 ( $\pm$ 1.47)	63.73 ( $\pm$ 16.33)	82.24 ( $\pm$ 7.15)	61.48 ( $\pm$ 3.99)	26.21 ( $\pm$ 4.57)	40.59 ( $\pm$ 4.85)
	Autumn	16.10 ( $\pm$ 1.23)	19.22 ( $\pm$ 5.12)	78.49 ( $\pm$ 5.93)	36.35 ( $\pm$ 3.39)	51.65 ( $\pm$ 4.74)	44.76 ( $\pm$ 3.24)
Fe	Winter	0.82 ( $\pm$ 0.27)	17.88 ( $\pm$ 6.88)	1.16 ( $\pm$ 0.69)	1.20 ( $\pm$ 0.10)	0.47 ( $\pm$ 0.1)	3.43 ( $\pm$ 0.51)
	Spring	0.58 ( $\pm$ 0.31)	24.83 ( $\pm$ 3.60)	1.34 ( $\pm$ 0.12)	1.29 ( $\pm$ 0.07)	1.07 ( $\pm$ 0.14)	2.13 ( $\pm$ 0.16)
	Summer	0.60 ( $\pm$ 0.20)	13.25 ( $\pm$ 1.81)	1.25 ( $\pm$ 0.11)	1.51 ( $\pm$ 0.09)	1.57 ( $\pm$ 0.10)	1.63 ( $\pm$ 0.12)
	Autumn	1.45 ( $\pm$ 0.43)	23.87 ( $\pm$ 5.60)	1.28 ( $\pm$ 0.16)	0.53 ( $\pm$ 0.09)	1.00 ( $\pm$ 0.09)	2.62 ( $\pm$ 0.35)
Ni	Winter	1.03 ( $\pm$ 0.39)	1.69 ( $\pm$ 0.40)	0.83 ( $\pm$ 0.35)	0.04 ( $\pm$ 0.02)	0.005 ( $\pm$ 0.003)	3.89 ( $\pm$ 0.80)
	Spring	0.97 ( $\pm$ 0.23)	1.97 ( $\pm$ 0.31)	1.20 ( $\pm$ 0.34)	0.02 ( $\pm$ 0.01)	0.04 ( $\pm$ 0.006)	1.89 ( $\pm$ 0.50)
	Summer	1.70 ( $\pm$ 0.32)	1.35 ( $\pm$ 0.31)	1.04 ( $\pm$ 0.36)	0.01 ( $\pm$ 0.005)	0.07 ( $\pm$ 0.01)	0.55 ( $\pm$ 0.24)
	Autumn	2.99 ( $\pm$ 0.51)	1.61 ( $\pm$ 0.34)	0.35 ( $\pm$ 0.17)	0.007 ( $\pm$ 0.007)	0.06 ( $\pm$ 0.01)	2.17 ( $\pm$ 0.53)
Zn	Winter	0.74 ( $\pm$ 0.30)	3.45 ( $\pm$ 0.52)	0.71 ( $\pm$ 0.16)	0.57 ( $\pm$ 0.05)	0.08 ( $\pm$ 0.03)	1.13 ( $\pm$ 0.15)
	Spring	0.24 ( $\pm$ 0.12)	2.49 ( $\pm$ 0.35)	0.82 ( $\pm$ 0.07)	0.77 ( $\pm$ 0.06)	0.55 ( $\pm$ 0.07)	1.14 ( $\pm$ 0.10)
	Summer	0.69 ( $\pm$ 0.24)	2.31 ( $\pm$ 0.40)	0.61 ( $\pm$ 0.11)	0.75 ( $\pm$ 0.09)	0.59 ( $\pm$ 0.04)	1.21 ( $\pm$ 0.16)
	Autumn	1.63 ( $\pm$ 0.37)	2.59 ( $\pm$ 0.45)	1.03 ( $\pm$ 0.11)	0.61 ( $\pm$ 0.15)	0.57 ( $\pm$ 0.06)	0.98 ( $\pm$ 0.13)
Cu	Winter	2.32 ( $\pm$ 0.45)	3.64 ( $\pm$ 0.47)	3.93 ( $\pm$ 1.08)	0.23 ( $\pm$ 0.03)	0.03 ( $\pm$ 0.02)	0.29 ( $\pm$ 0.04)
	Spring	1.37 ( $\pm$ 0.33)	3.50 ( $\pm$ 0.38)	0.30 ( $\pm$ 0.05)	0.26 ( $\pm$ 0.02)	0.16 ( $\pm$ 0.01)	0.21 ( $\pm$ 0.01)
	Summer	1.84 ( $\pm$ 0.36)	2.65 ( $\pm$ 0.33)	2.71 ( $\pm$ 0.57)	0.22 ( $\pm$ 0.02)	0.17 ( $\pm$ 0.02)	0.16 ( $\pm$ 0.007)
	Autumn	1.69 ( $\pm$ 0.40)	3.81 ( $\pm$ 0.51)	2.49 ( $\pm$ 0.71)	0.23 ( $\pm$ 0.02)	0.13 ( $\pm$ 0.02)	0.26 ( $\pm$ 0.03)
Cd	Winter	0.25 ( $\pm$ 0.11)	0.95 ( $\pm$ 0.26)	ND	0.18 ( $\pm$ 0.18)	0.72 ( $\pm$ 0.39)	1.05 ( $\pm$ 0.50)
	Spring	0.92 ( $\pm$ 0.27)	2.03 ( $\pm$ 0.33)	0.96 ( $\pm$ 0.31)	0.12 ( $\pm$ 0.12)	0.31 ( $\pm$ 0.21)	0.73 ( $\pm$ 0.26)
	Summer	0.91 ( $\pm$ 0.26)	2.38 ( $\pm$ 0.34)	0.72 ( $\pm$ 0.31)	0.24 ( $\pm$ 0.12)	1.24 ( $\pm$ 0.38)	0.98 ( $\pm$ 0.29)
	Autumn	0.99 ( $\pm$ 0.33)	2.98 ( $\pm$ 0.44)	0.29 ( $\pm$ 0.16)	ND	3.15 ( $\pm$ 0.58)	0.97 ( $\pm$ 0.28)
Pb	Winter	1.07 ( $\pm$ 0.31)	2.64 ( $\pm$ 0.43)	0.28 ( $\pm$ 0.28)	0.01 ( $\pm$ 0.01)	0.005 ( $\pm$ 0.001)	0.02 ( $\pm$ 0.007)
	Spring	1.17 ( $\pm$ 0.25)	2.94 ( $\pm$ 0.32)	0.57 ( $\pm$ 0.30)	0.003 ( $\pm$ 0.001)	0.01 ( $\pm$ 0.001)	0.007 ( $\pm$ 0.002)
	Summer	2.49 ( $\pm$ 0.34)	2.60 ( $\pm$ 0.38)	1.94 ( $\pm$ 0.42)	0.004 ( $\pm$ 0.001)	0.006 ( $\pm$ 0.001)	0.004 ( $\pm$ 0.001)
	Autumn	1.68 ( $\pm$ 0.28)	3.02 ( $\pm$ 0.44)	2.67 ( $\pm$ 0.70)	0.01 ( $\pm$ 0.003)	0.01 ( $\pm$ 0.002)	0.008 ( $\pm$ 0.003)

**Table 5.5:** The mean ( $\pm$ SE) for the accumulation of heavy metals and Ca ( $\text{mg}\cdot\text{kg}^{-1}$ ) in the various plant species (*Salix babylonica*, *Commelina benghalensis*, *Paspalum urvillei* and *Persicaria lapathifolia*).

Parameter	<i>S. babylonica</i>	<i>C. benghalensis</i>	<i>P. urvillei</i>	<i>P. lapathifolia</i>	p-value
<b>Ca</b> $\text{mg}\cdot\text{kg}^{-1}$	59.17 ( $\pm$ 4.05)	59.04 ( $\pm$ 2.61)	34.71 ( $\pm$ 2.640)	51.04 ( $\pm$ 2.95)	<0.01
<b>Fe</b> $\text{mg}\cdot\text{kg}^{-1}$	1.28 ( $\pm$ 0.10)	1.186 ( $\pm$ 0.052)	1.086 ( $\pm$ 0.068)	2.241 ( $\pm$ 0.130)	<0.01
<b>Ni</b> $\text{mg}\cdot\text{kg}^{-1}$	0.91 ( $\pm$ 0.17)	0.017 ( $\pm$ 0.005)	0.047 ( $\pm$ 0.005)	1.730 ( $\pm$ 0.244)	<0.01
<b>Zn</b> $\text{mg}\cdot\text{kg}^{-1}$	0.79 ( $\pm$ 0.05)	0.699 ( $\pm$ 0.044)	0.475 ( $\pm$ 0.033)	1.125 ( $\pm$ 0.071)	<0.01
<b>Cu</b> $\text{mg}\cdot\text{kg}^{-1}$	2.0 ( $\pm$ 0.30)	0.237 ( $\pm$ 0.011)	0.133 ( $\pm$ 0.009)	0.218 ( $\pm$ 0.010)	<0.01
<b>Cd</b> $\text{mg}\cdot\text{kg}^{-1}$	0.61 ( $\pm$ 0.15)	0.144 ( $\pm$ 0.061)	1.240 ( $\pm$ 0.210)	0.914 ( $\pm$ 0.154)	<0.01
<b>Pb</b> $\text{mg}\cdot\text{kg}^{-1}$	1.45 ( $\pm$ 0.24)	0.008 ( $\pm$ 0.002)	0.009 ( $\pm$ 0.001)	0.008 ( $\pm$ 0.001)	<0.01

Highest values were recorded in spring for *P. urvillei* ( $19.49 \pm 3.26 \text{ mg} \cdot \text{kg}^{-1}$ ) and *P. lapathifolia* ( $61.07 \pm 6.45 \text{ mg} \cdot \text{kg}^{-1}$ ) (Table 5.4). Water samples showed no significant difference among seasons; while soil samples showed a significant difference ( $p < 0.05$ ). In a similar way plant samples showed significant differences among seasons, with  $p < 0.01$  for *S. babylonica*, *C. benghalensis* and *P. urvillei*, and it was  $p = 0.011$  for *P. lapathifolia*. *S. babylonica* showed the highest accumulation for Ca, then *C. benghalensis* and the least was for *P. urvillei* (Table 5.4).

### 5.1.6 Iron

The iron (Fe) values were higher in the upper reach for water ( $1.04 \pm 0.61 \text{ mg} \cdot \text{l}^{-1}$ ) and soil ( $27.65 \pm 14.89 \text{ kg}^{-1}$ ) than in the middle reach, and showed a slight increase again in lower reach ( $0.81 \pm 0.26 \text{ mg} \cdot \text{l}^{-1}$ ) and ( $21.69 \pm 4.29 \text{ kg}^{-1}$ ), respectively, with no significant differences in water and soil along the river (Table 5.3). The Fe in water showed significant difference among seasons ( $p = 0.06$ ) as well as in soil ( $p < 0.01$ ).

The highest mean values for Fe for *S. babylonica* and *P. lapathifolia* were in upper reach ( $1.94 \pm 1.35 \text{ mg} \cdot \text{kg}^{-1}$ , and  $4.20 \pm 0.78 \text{ mg} \cdot \text{kg}^{-1}$ ), respectively, with no significant differences for *S. babylonica* along the river. The highest mean values for Fe for *C. benghalensis* and *P. urvillei* were in middle reach ( $1.39 \pm 0.06 \text{ mg} \cdot \text{kg}^{-1}$ , and  $1.22 \pm 0.10 \text{ mg} \cdot \text{kg}^{-1}$ ), respectively (Table 5.3), with significant differences for *C. benghalensis* ( $p < 0.01$ ), *P. urvillei* ( $p < 0.01$ ) and *P. lapathifolia* ( $p = 0.02$ ).

The highest mean value for water was in autumn ( $1.45 \pm 0.43 \text{ mg} \cdot \text{l}^{-1}$ ), for soil was in spring ( $24.83 \pm 3.60 \text{ mg} \cdot \text{kg}^{-1}$ ), for *S. babylonica* in spring ( $1.34 \pm 0.12 \text{ mg} \cdot \text{kg}^{-1}$ ), for *C. benghalensis* ( $1.51 \pm 0.09 \text{ mg} \cdot \text{kg}^{-1}$ ) and *P. urvillei* ( $1.57 \pm 0.10 \text{ mg} \cdot \text{kg}^{-1}$ ) in summer, and for *P. lapathifolia*



( $3.43 \pm 0.51 \text{ mg} \cdot \text{kg}^{-1}$ ) in winter (Table 5.4). The differences in Fe concentration among seasons were significant ( $p < 0.01$ ) for soil and all plant species.

### 5.1.7 Nickel

For nickel (Ni), the highest mean value in water was in in the middle reach ( $1.92 \pm 0.25 \text{ mg} \cdot \text{l}^{-1}$ ), and the lowest was in upper reach ( $0.73 \pm 0.38 \text{ mg} \cdot \text{l}^{-1}$ ) (Table 5.3), with no significant differences along the river but a significant difference ( $p < 0.01$ ) among seasons. In soil, the lowest mean value was in middle reaches ( $1.54 \pm 0.20 \text{ mg} \cdot \text{kg}^{-1}$ ), and the highest mean value was similar in both upper and lower reaches ( $1.86 \pm 0.34 \text{ mg} \cdot \text{kg}^{-1}$ ) with no significant differences along the river, and no significant difference ( $p = 0.09$ ) occurred among seasons.

The highest mean value in water was in autumn, for soil, *S. babylonica* and *C. benghalensis* in spring, for *P. urvillei* ( $0.07 \pm 0.01 \text{ mg} \cdot \text{kg}^{-1}$ ) in summer, and for *P. lapathifolia* ( $3.89 \pm 0.80 \text{ mg} \cdot \text{kg}^{-1}$ ) in winter (Table 5.4). There were significant differences among seasons ( $p < 0.01$ ) for *P. urvillei* and *P. lapathifolia*, and no significant differences for *S. babylonica* and *C. benghalensis* (Table 5.4).

In all reaches along the river, the highest Ni concentrations were in *P. lapathifolia* then *S. babylonica*, and the lowest concentrations were in *C. benghalensis* (Table 5.5), with no significant differences for *S. babylonica* but significant for *C. benghalensis* ( $p = 0.04$ ), *P. urvillei* ( $p < 0.01$ ), and *P. lapathifolia* ( $p < 0.01$ ) along the river.

### 5.1.8 Zinc

The zinc (Zn) concentrations showed significant decline from upper to lower reaches in both water and soil ( $p = 0.16$  and  $0.43$ ) respectively. The highest mean values for water and soil

were in the upper reach ( $1.33\pm 0.54 \text{ mg}\cdot\text{l}^{-1}$ ) and ( $4.02\pm 0.90 \text{ mg}\cdot\text{kg}^{-1}$ ) respectively, and the lowest mean value for water was in lower reach ( $0.25\pm 0.13 \text{ mg}\cdot\text{l}^{-1}$ ) and for soil was in the middle reach ( $2.35\pm 0.25 \text{ mg}\cdot\text{kg}^{-1}$ ). The *P. lapathifolia* showed the highest concentration of Zn in all reaches along the river then the *S. babylonica*, and the least were in *P. urvillei* (Table 5.3), with no significant differences for *S. babylonica* and *P. lapathifolia*, and significant differences for *C. benghalensis* ( $p=0.02$ ) and *P. urvillei* ( $p<0.01$ ) along the river.

The highest mean value for water ( $1.63\pm 0.37 \text{ mg}\cdot\text{l}^{-1}$ ) was during autumn, for soil ( $3.45\pm 0.52 \text{ mg}\cdot\text{kg}^{-1}$ ) during winter, for *S. babylonica* ( $1.03\pm 0.11 \text{ mg}\cdot\text{kg}^{-1}$ ) during autumn, for *C. benghalensis* ( $0.77\pm 0.06 \text{ mg}\cdot\text{kg}^{-1}$ ) during spring, for *P. urvillei* ( $0.59\pm 0.04 \text{ mg}\cdot\text{kg}^{-1}$ ) and *P. lapathifolia* ( $1.21\pm 0.16 \text{ mg}\cdot\text{kg}^{-1}$ ) during summer (Table 5.4). Among seasons, there were significant differences for water samples ( $p<0.01$ ), soil ( $p<0.31$ ), *S. babylonica* ( $p<0.05$ ), *C. benghalensis* ( $p<0.07$ ), *P. urvillei* and *P. lapathifolia* ( $p<0.01$ ). In terms of zinc accumulation in plants *P. lapathifolia*>*S. babylonica*> *P. urvillei* (Table 5.5).

### 5.1.9 Copper

The copper (Cu) concentration in water showed significant differences ( $p<0.05$ ) along the river and no significant differences were detected in soil samples, the highest values were in the middle reach for both water ( $2.09\pm 0.25 \text{ mg}\cdot\text{l}^{-1}$ ) and soil ( $3.30\pm 0.25 \text{ mg}\cdot\text{kg}^{-1}$ ), and the lowest were in the upper reach ( $0.65\pm 0.37 \text{ mg}\cdot\text{l}^{-1}$ ) and ( $2.93\pm 0.56 \text{ mg}\cdot\text{kg}^{-1}$ ), respectively (Table 5.3). The highest mean value for water samples ( $2.32\pm 0.45 \text{ mg}\cdot\text{kg}^{-1}$ ) was in winter, for soil ( $3.81\pm 0.51 \text{ mg}\cdot\text{kg}^{-1}$ ) in autumn, for *S. babylonica* ( $3.93\pm 1.08 \text{ mg}\cdot\text{kg}^{-1}$ ) in winter, for *C. benghalensis* ( $0.26\pm 0.02 \text{ mg}\cdot\text{kg}^{-1}$ ) in spring, for *P. urvillei* ( $0.17\pm 0.02 \text{ mg}\cdot\text{kg}^{-1}$ ) in summer, and for *P. lapathifolia* ( $0.29\pm 0.04 \text{ mg}\cdot\text{kg}^{-1}$ ) in winter (Table 5.4). The water samples ( $p<0.25$ ) and *P. urvillei* and *P. lapathifolia* ( $p<0.01$ ) showed significant difference among seasons, but

no significant differences for soil, *S. babylonica*, and *C. benghalensis*. The highest concentration of Cu along all river reaches was in *S. babylonica* while similar amounts were recorded in *C. benghalensis* and *P. urvillei*. The lowest values were measured in *P. lapathifolia* which had about ten times less than *S. babylonica*. There were no significant differences for *S. babylonica* and *C. benghalensis* and significant for *P. urvillei* ( $p < 0.01$ ) and *P. lapathifolia* ( $p < 0.01$ ) along the river (Table 5.5).

### 5.1.10 Cadmium

The cadmium (Cd) showed an increasing concentration along the river from upper to lower reaches for both water and soil (Tables 5.3 and 5.5). However, there was no significant difference for water and with a significant difference for soil ( $p = 0.01$ ) along the river. Remarkably, the mean values of Cd in the soil were more than two-times higher than water in all reaches along the river. The *S. babylonica* showed highest mean values in middle reach ( $0.84 \pm 0.23 \text{ mg.kg}^{-1}$ ) with no significant differences for *S. babylonica*, *C. benghalensis*, and *P. lapathifolia* along the river. *P. urvillei* had the highest mean values in lower reach ( $2.80 \pm 0.47 \text{ mg.kg}^{-1}$ ) (Table 5.3), with significant differences for *P. urvillei* ( $p < 0.01$ ) (Table 5.5).

The highest mean value for water ( $0.99 \pm 0.33 \text{ mg.l}^{-1}$ ) and soil ( $2.98 \pm 0.44 \text{ mg.kg}^{-1}$ ) was in autumn, for *S. babylonica* ( $0.96 \pm 0.31 \text{ mg.kg}^{-1}$ ) in spring, for *C. benghalensis* ( $0.24 \pm 0.12 \text{ mg.kg}^{-1}$ ) in summer, for *P. urvillei* ( $3.15 \pm 0.58 \text{ mg.kg}^{-1}$ ) in autumn, and for *P. lapathifolia* ( $1.05 \pm 0.50 \text{ mg.kg}^{-1}$ ) in winter (Table 5.4). The soil and *P. urvillei* samples showed significant difference among seasons ( $p < 0.01$ ) for both, *S. babylonica* ( $p = 0.29$ ), and no significant differences for water, *C. benghalensis*, and *P. lapathifolia*. The highest accumulation for Cd was in *P. urvillei*; then *P. lapathifolia*, and the lowest was in *C. benghalensis* (Table 5.4).

### 5.1.11 Lead

The mean value for lead (Pb) in water was higher in upper reach ( $2.04 \pm 0.61 \text{ mg.l}^{-1}$ ), and the lowest was in lower reach ( $1.56 \pm 0.29 \text{ mg.l}^{-1}$ ). While, in soil it was higher in lower reach ( $3.24 \pm 0.39 \text{ mg.kg}^{-1}$ ) and lowest in middle reach ( $2.57 \pm 0.22 \text{ mg.kg}^{-1}$ ) with no significant differences in both water and soil along the river (Table 5.3).

The highest mean value for water ( $2.49 \pm 0.34 \text{ mg.l}^{-1}$ ) samples was in summer, for soil ( $3.02 \pm 0.44 \text{ mg.kg}^{-1}$ ) and *S. babylonica* ( $2.67 \pm 0.70 \text{ mg.kg}^{-1}$ ) in autumn, for *C. benghalensis* ( $0.01 \pm 0.003 \text{ mg.kg}^{-1}$ ) in both autumn and winter, for *P. urvillei* ( $0.01 \pm 0.002 \text{ mg.kg}^{-1}$ ) in autumn, and for *P. lapathifolia* ( $0.02 \pm 0.007 \text{ mg.kg}^{-1}$ ) in winter (Table 5.4). The water samples showed significant differences among seasons ( $p=0.02$ ), *S. babylonica* ( $p=0.01$ ), *C. benghalensis* ( $p<0.01$ ), *P. urvillei* ( $p=0.002$ ), and no significant differences for soil and *P. lapathifolia* (Table 5.4). *S. babylonica* and *C. benghalensis* samples showed significant differences ( $p<0.01$ ), and *P. urvillei* and *P. lapathifolia* showed no significant differences along the river. The highest accumulation of Pb was in *S. babylonica* > *P. urvillei* > *C. benghalensis* (Table 5.5).

## 5.2 The Relationship Between the Measured Parameters and the Various River Reaches and Seasons

### 5.2.1 Nitrite, Nitrate and Ammonium

In water samples, the  $\text{NO}_2^-$  and  $\text{NH}_4^+$  had significant positive relationship ( $p<0.01$ ) versus temperature, EC, Ca and significant negative relationship ( $p<0.01$ ) versus DO. The relationship was also significantly positive ( $p<0.05$ ) versus season change. The  $\text{NH}_4^+$  had extra significant positive ( $p<0.01$ ) relationship versus change in reaches along the river. The

$\text{NO}_3^-$  has fewer significant relationships, it was significantly positive ( $p < 0.01$ ) versus EC and Ca and to less extent ( $p < 0.05$ ) versus change in reach along the river (Table 5.6).

### 5.2.2 Calcium

The Ca had significant positive relationship versus Fe and Ni in the soil, and significant positive relationship versus Fe and Pb and significant negative relationship versus Zn in *S. babylonica*. *C. benghalensis* had only significant positive relationship versus Fe and Zn, and *P. urvillei* and *P. lapathifolia* had significant positive relationship versus Fe, Ni, Zn, Cu, Cd, and Pb (Table 5.7).

### 5.2.3 Iron

Remarkably, the Fe in water samples had no significant relationship versus all of the measured parameters (Table 5.6). However, Fe concentrations in *C. benghalensis* and *P. urvillei* samples had a significant relationship versus the change in season and also reach along the river (Table 5.7).

### 5.2.4 Nickel

The Ni in water samples had a significant positive relationship ( $p < 0.01$ ) versus change in season, and significant negative relationship ( $p < 0.05$ ) versus DO (Table 5.6). It had significant positive relationship versus change in season and reach along the river for *P. urvillei*, and significant negative relationship versus change in season and reach along the river for *C. benghalensis*. For *S. babylonica*, there was only a significant negative relationship versus change in reach, and for *P. lapathifolia* there was only a significant negative relationship versus change in seasons (Table 5.7).

**Table 5.6:** Correlation matrix depicting Spearman's simple linear correlation coefficient (r) amongst all the investigated parameters in water samples. The asterisks illustrate the significant correlation (2-tailed) between the various parameters, where \*\*= $p < 0.01$ ; and \*= $p < 0.05$ .

Parameter	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Fe	Ni	Zn	Cu	Cd	Pb
Season	0.145*	-0.047	0.238**	0.094	0.321**	0.177**	0.010	0.126	0.234**
Reach	0.100	0.157*	0.296**	-0.044	-0.007	-0.193**	-0.038	-0.019	-0.037
Temperature °C	0.398**	0.081	0.347**	-0.082	0.064	-0.202**	-0.082	0.125	0.135
DO	-0.278**	-0.116	-0.425**	0.028	-0.153*	0.080	-0.008	0.011	-0.033
pH	0.105	0.043	-0.014	-0.102	-0.048	-0.227**	-0.049	-0.067	0.041
EC	0.235**	0.318**	0.309**	-0.017	0.037	-0.101	0.184**	-0.019	-0.107
Ca	0.197**	0.366**	0.250**	-0.020	0.021	-0.078	0.157*	-0.054	-0.041

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**Table 5.7:** Correlation matrix depicting Spearman's simple linear correlation coefficient ( $r$ ) amongst all the investigated parameters in the soil, *S. babylonica*, *C. benghalensis*, and *P. lapathifolia* samples. The asterisks illustrate the significant correlation (2-tailed) between the various parameters, where \*\*= $p < 0.01$ ; and \*= $p < 0.05$ .

Sample	Parameter	Fe	Ni	Zn	Cu	Cd	Pb
Soil	Season	-0.090	-0.048	-0.099	-0.027	0.350**	0.000
	Reach	-0.067	0.054	0.015	0.032	0.248**	0.060
	Ca	0.294**	0.223**	-0.100	-0.009	0.128	0.050
<i>S. babylonica</i>	Season	0.135	-0.168	0.080	-0.027	-0.066	0.344**
	Reach	0.100	-0.192*	0.062	0.046	-0.104	0.327**
	Ca	0.211*	0.008	-0.188*	-0.151	-0.065o	0.289**
<i>C. benghalensis</i>	Season	-0.253**	-0.0232*	-0.041	-0.095	0.010	0.305**
	Reach	-0.278**	-0.252*	-0.147	-0.097	-0.098	0.231**
	Ca	0.259**	0.115	0.245**	0.021	0.017	-0.132
<i>P. urvillei</i>	Season	0.378**	0.475**	0.468**	0.255**	0.402**	0.144
	Reach	0.205*	0.322**	0.297**	0.149	0.450**	0.161
	Ca	0.459**	0.355**	0.473**	0.206*	0.203*	0.366**
<i>P. lapathifolia</i>	Season	-0.160	-0.203*	-0.152	-0.141	0.101	-0.028
	Reach	-0.067	-0.089	-0.109	-0.052	0.166*	-0.101
	Ca	0.571**	0.173*	0.216**	0.407**	0.265**	0.207*

### 5.2.5 Zinc

The Zn in water samples had a significant positive relationship ( $p < 0.01$ ) versus change in season, and significant negative relationship ( $p < 0.01$ ) versus temperature, pH, and change in reach along the river (Table d). The Zn accumulation had a significant positive relationship ( $p < 0.01$ ) only for *P. urvillei* samples (Table 5.6).

### 5.2.6 Copper

The Cu in water samples had significant positive relationship versus EC ( $p < 0.01$ ) and versus Ca ( $p < 0.05$ ) (Table 5.6). The Cu in *P. urvillei* samples had a significant positive relationship ( $p < 0.01$ ) versus change in season (Table 5.7).

### 5.2.7 Cadmium

In water samples, the Cd had no significant relationship versus all examined parameters (Table 5.6). The Cd in soil and *P. urvillei* samples had a significant positive relationship ( $p < 0.01$ ) versus change in both seasons and reach along the river, and in *P. lapathifolia* samples it was significantly positive ( $p < 0.05$ ) (Table 5.7).

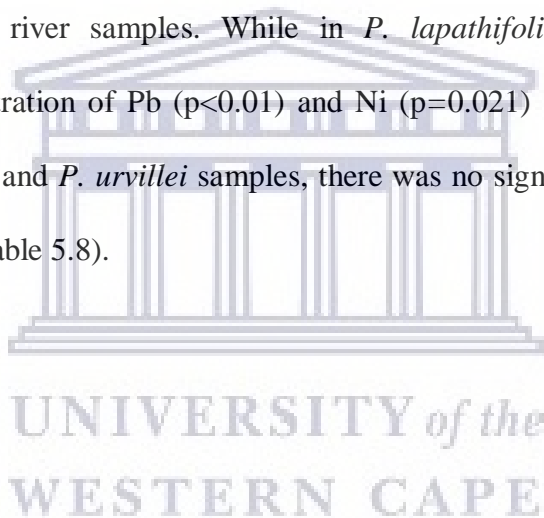
### 5.2.8 Lead

In water samples, the only significant relationship was positive between Pb versus change of seasons (Table 5.6). The *S. babylonica* and *C. benghalensis* samples had a significant positive relationship ( $p < 0.01$ ) versus change in both seasons and reach along the river (Table 5.7).



### 5.3 Comparison Between the Two Main Tributaries of the River

When we compare the results of the two-main tributaries of the river, the Kuils river and Eerste river, for water samples, the Kuils tributary had a significantly higher concentration of Ca ( $p < 0.01$ ), EC ( $p < 0.01$ ), and pH measurement ( $p < 0.01$ ), while Eerste river tributary had a significantly higher concentration of DO ( $p < 0.01$ ),  $\text{NO}_3^-$  ( $p < 0.01$ ), and  $\text{NH}_4^+$  ( $p = 0.33$ ). In soil samples, the Ca concentration was significantly higher in Eerste river samples ( $p < 0.01$ ). In *C. benghalensis* samples, there were significant higher concentrations of Cu ( $p = 0.009$ ) and Zn ( $p = 0.042$ ) in Eerste river samples. While in *P. lapathifolia* samples, there were significant higher concentration of Pb ( $p < 0.01$ ) and Ni ( $p = 0.021$ ) in Eerste river tributary samples. In *S. babylonica* and *P. urvillei* samples, there was no significant differences in all the measured elements (Table 5.8).



**Table 5.8:** The mean for the measured parameters in the various samples (water, soil, *S. babylonica*, *C. benghalensis*, *P. urvillei*, and *P. lapathifolia*).

Samples	Tributary	Pb	Ni	Zn	Ca	Cu	Fe	Cd	DO	Temp	EC	pH	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>
Water	Kuils River	1.51	1.23	0.40	28.00	2.11	0.40	1.00	4.70	19.85	1100.6	7.61	1.16	15.31	3.87
	Eerste River	1.74	1.84	1.05	13.02	1.72	0.90	0.76	6.32	19.94	482.64	7.23	1.24	7.62	3.89
Soil	Kuils River	2.22	2.03	2.27	79.17	3.26	24.08	2.32	-	-	-	-	-	-	-
	Eerste River	3.06	1.70	2.74	16.19	3.48	18.39	2.09	-	-	-	-	-	-	-
<i>S. babylonica</i>	Kuils River	1.26	1.25	0.77	56.99	1.35	1.45	0.44	-	-	-	-	-	-	-
	Eerste River	1.60	0.82	0.77	60.89	2.19	1.18	0.62	-	-	-	-	-	-	-
<i>C. benghalensis</i>	Kuils River	0.01	0.02	0.82	57.21	0.29	1.10	0.06	-	-	-	-	-	-	-
	Eerste River	0.01	0.02	0.62	61.28	0.22	1.25	0.18	-	-	-	-	-	-	-
<i>P. urvillei</i>	Kuils River	0.01	0.05	0.44	34.89	0.15	0.93	0.58	-	-	-	-	-	-	-
	Eerste River	0.01	0.04	0.47	35.50	0.13	1.19	1.47	-	-	-	-	-	-	-
<i>P. lapathifolia</i>	Kuils River	0.02	2.63	1.00	52.34	0.22	2.24	0.51	-	-	-	-	-	-	-
	Eerste River	0.01	1.43	1.18	48.76	0.21	2.23	1.07	-	-	-	-	-	-	-

# CHAPTER 6

## STATISTICAL MODELLING

### 6.1 Introduction

The study measured the concentration of seven heavy metals in the plant, soil, and water sampled from the Eerste River catchment area in the Western Cape during twelve months (2011-2012). A multi-linear regression method was used to build models based on two independent variables which were soil and water, and the dependent variable which is the plant. The model aims to estimate a specific parameter (Statistical indicators) of the soil and water and to predict the concentration of the heavy metals in the plant using the concentration of heavy metals in soil and water for each of the heavy metals. The general equation was as follows (equation 1):

$$y = \beta_1 x_1 + \beta_2 x_2 + \varepsilon \quad (1)$$

(Bremer, 2013). Where  $x_1$

and  $x_2$  refer to the soil and water, respectively, and  $y$  referred to the plant (equation

2).

$$p = \beta_1 \bar{s}_1 + \beta_2 \bar{w} + \varepsilon \quad (2)$$

If we know the concentration of the heavy metals in the plant ( $p$ ), we can use the same model to predict the concentration of heavy metals in the soil ( $s$ ) and

water ( $w$ ). When  $\varepsilon = \text{zero}$  (perfect fit).

❖ **Where:**

$p$ : Refers to the heavy metal concentration in the plant.

$\bar{w}$ : Refers to the mean of heavy metal concentration in the water.

$\bar{s}$ : Refers to the mean of heavy metal concentration in the soil.

$\beta_2$ : The coefficient of the heavy metal concentration in the water.

$\beta_1$ : The coefficient of the heavy metal concentration in the soil.

❖ **Coefficient:**

The regression coefficient is a statistical measure of the average functional relationship between two or more variables. In regression analysis, one variable is considered as dependent and other(s) as an independent. Thus, it measures the degree of dependence of one variable on the other(s) (Seltman, 2015). The regression coefficient was first used for estimating the relationship between the concentration of the heavy metals in plant leaves and water and soil.

The coefficients are estimated by the multi-linear regression method mentioned above. The coefficient indicates the concentration of the water or soil to the plant content of an element.

The concepts of simple-linear regression and multi-linear regression are similar, the simple-linear regression has one independent factor while the multi-linear regression has two or more factors (Myers and Myers, 1990).

## 6.2 The Two Possible Assumptions

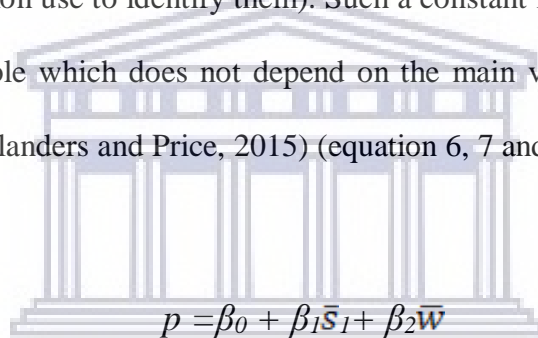
1. The heavy metals in the plant leaves come from the soil and water through the plant roots (as vascular plants). Then the multi-linear regression in this case may be presented without the coefficient of the third source of the heavy metals ( $\beta_0$ ) (equations 3, 4 and 5).

$$p = \beta_1 \bar{s}_1 + \beta_2 \bar{w} \quad (3)$$

$$\beta_0 = 0$$

$$s = \frac{p - \beta_2 \bar{w}}{\beta_1} \text{ and } w = \frac{p - \beta_1 \bar{s}}{\beta_2} \quad (4 + 5)$$

2. The heavy metals in the plant leaf come from the soil, water and a third source—the atmosphere. Then the multi-linear regression will include third source ( $\beta_0$ ) which is a constant. It may refer to a constant function or its value (it is common use to identify them). Such a constant is commonly represented by a variable which does not depend on the main variable(s) of the studied problem (Flanders and Price, 2015) (equation 6, 7 and 8).



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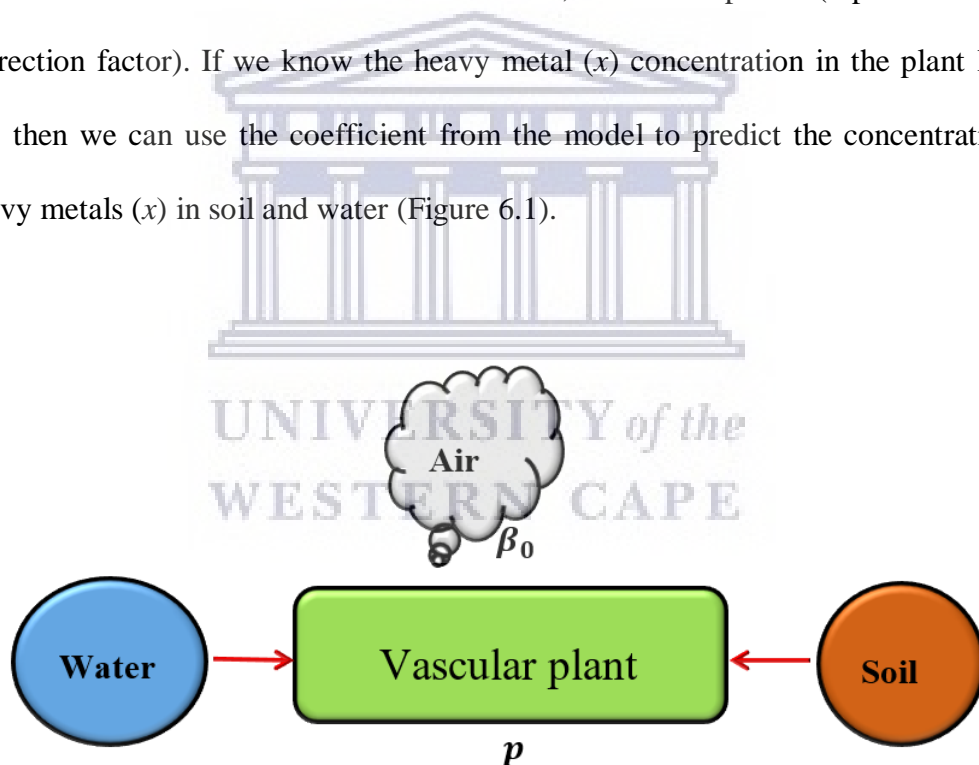
$$s = \frac{p - (\beta_0 + \beta_2 \bar{w})}{\beta_1} \text{ and } w = \frac{p - (\beta_0 + \beta_1 \bar{s})}{\beta_2} \quad (7 + 8)$$

The plants studied on the river banks had access to soil and water via their roots. The species *Commelina* and *Persicaria* tended to be at the water edge: absorption may not have been limited to the root

. (plant nutrient absorption can be by plant root and plant tissue) (Fageria, 2001; Solanki et al., 2015).

The concentration of heavy metal in water and soil causes the accumulation of the heavy metals in the plants and different levels of the food chain (Chang et al., 2014; Shakhila and Mohan, 2013).

**This study assumes.** The concentration of any heavy metal ( $x$ ) in the plant leaves is related to the concentration of same heavy metal ( $x$ ) in soil and water. This is examined with and without a third source, the atmosphere (represented as a correction factor). If we know the heavy metal ( $x$ ) concentration in the plant leaves ( $p$ ), then we can use the coefficient from the model to predict the concentration of heavy metals ( $x$ ) in soil and water (Figure 6.1).



**Figure 6.1:** The perceived element in the plant is dependent on its presence in the water, soil and air where the plant accrues.

In the subsequent analysis, using the collected data of the concentrations of selected heavy metals from water, soil and plant samples, a simple linear regression analysis was used to estimate the correlations between plant leaves and water and soil as independent variables, both of them affect the heavy metals concentration in plant leaves.

## 6.3 Correlations

### 6.3.1 Cadmium

From Tables 6.1 and 6.2 it is clear that the Cd contents of *Salix babylonica* and *Commelina benghalensis* were good predictors of the water concentration of Cd. The results were not significant for *Paspalum urvillei* and *Persicaria lapathifolia*. None of the plants gave a good indication of the Cd level in the soil.

**Table 6. 1:** The predictive value of the plant Cd content in relation to the Cd content of water and soil (from equations 4 and 5).

Cd	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
Water	1.868	0.001	0.100	<0.001	-0.038	0.956	0.063	0.454
Soil	0.035	0.798	-0.005	0.672	0.082	0.679	0.033	0.225

**Table 6.2:** The predictive value of the plant Cd content in relation to the Cd content of water, soil and third source (from equations 7 and 8).

Cd	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
Other factors	0.001	0.024	0.000	0.219	0.001	0.053	0.000	<0.001



<b>Water</b>	1.462	0.008	0.093	0.001	-0.366	0.597	-0.045	0.567
<b>Soil</b>	-0.135	0.374	-0.014	0.313	-0.128	0.563	-0.039	0.184

### 6.3.1.1 *Salix*

Without the third source, there was a positive coefficient from the soil and water, but it was statistically significant in water (Table 6.1). The concentration of the Cd showed a slight positive, but significant coefficient with the third source. The water gave a higher positive coefficient, greater than those found in the plants which was statistical significance (Table 6.2).

### 6.3.1.2 *Commelina*

Without the third source, in water showed positive coefficient and was statistically significant (Table 6.1). The level approximation of the Cd concentration in the water gave a positive  $\beta$  value with and without the third source but was negative with the soil. The coefficient for water was statistically significant with and without third source.

### 6.3.2 Copper

Table 6.3 shows that the Cu contents of all plant species were good predictors of the soil concentrations of Cu. *Commelina benghalensis*, *Paspalum urvillei* and *Persicaria lapathifolia* species were used to predict the Cu content in the water with *Commelina* performing the best. The Cu content of *Salix* was the best predictor of the concentration of Cu in the soil and gave significant correlation for both water and soil with the third source (Table 6.4) none of the other plants gave a good indication of the Cu level in the water or in the soil.

**Table 6.3:** The predictive value of the plant Cu content in relation to the Cu content of water and soil (from equations 4 and 5).

Cu	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
Water	12.189	0.168	49.140	<0.001	24.798	<0.001	35.999	<0.001
Soil	2.852	<0.001	1.225	<0.001	0.756	<0.001	1.373	<0.001

**Table 6.4:** The predictive value of the plant Cu content in relation to the Cu content of water, soil and other correction factor (from equations 7 and 8).

Cu	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
Other factors	0.191	<0.001	0.202	<0.001	0.099	<0.001	0.175	<0.001
Water	-9.672	0.248	8.116	0.225	4.812	0.337	7.976	0.085
Soil	0.553	0.293	0.021	0.901	-0.025	0.884	0.264	0.088

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### 6.3.2.1 *Salix*

The concentration of Cu had a positive coefficient without the third source for the soil- this was higher than in the concentration of the other plants, and a highly statistically significant prediction (Table 6.3).

### 6.3.2.2 *Commelina*

The concentration of the Cu, without the third source, in water was positively coefficient and the highest correlated among the plants in the water, also statistically significant. In the soil it was positively coefficient and of high statistical significance

(Table 6.3).

### 6.3.2.3 *Paspalum*

The concentration of the Cu in water and soil were positive coefficient and statistically significant (Table 6.3). The approximation for water was higher than the soil for the  $\beta$  value. The correlation for water and soil were statistically significant.

### 6.3.2.4 *Persicaria*

The concentration of the Cu in water and soil were positively coefficient and statistically significant (Table 6.3). The approximation for water was higher than the soil for the  $\beta$  value. The correlation for water and soil were statistically significant.

### 6.3.3 Iron

Table 6.5 shows that the Fe content of the plant species were in the water higher than the soil, while it was statistically significant with the soil. *Salix babylonica*, *Commelina benghalensis*, *Paspalum urvillei* and *Persicaria lapathifolia* were used to predict the soil Fe content. The Fe content of *Persicaria* was the best predictor of the soil concentration of Fe. When the third source was taken into account (Table 6.6), none of the plants were a good indication of the Fe level in the water or in the soil.

**Table 6.5:** The predictive value of the plant Fe content in relation to the Fe content of water and soil (from equations 4 and 5).

Fe	<i>Salix</i>	<i>Commelina</i>	<i>Paspalum</i>	<i>Persicaria</i>
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	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
<b>Water</b>	0.049	0.518	0.100	0.116	0.039	0.555	0.125	0.307
<b>Soil</b>	0.013	<0.001	0.018	<0.001	0.010	<0.001	0.034	<0.001

**Table 6.6:** The predictive value of the plant Fe content in relation to the Fe content of water, soil and other correction factor (from equations 7 and 8).

Fe	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
<b>Other factors</b>	1.295	<0.001	1.291	<0.001	1.185	<0.001	2.043	<0.001
<b>Water</b>	0.002	0.963	0.043	0.192	-0.022	0.572	0.020	0.811
<b>Soil</b>	-0.004	0.083	-0.006	0.005	-0.004	0.035	0.009	0.020

### 6.3.3.1 *Salix*

The concentration of the Fe had a positive coefficient without third source It gave a highly statistically significant prediction to the soil Fe concentration (Table 6.5). With the third source, the coefficient for the third source was positive and statistically significant (Table 6.6). The approximation for water and soil Fe content gave a low and positive  $\beta$  value. The correlation for soil was only statistically significant without third source.

### 6.3.3.2 *Commelina*

The concentration of the Fe was positive coefficient without the third source in the water and soil, it was statistically significant with the soil (Table 6.5). With the third

source, the coefficient for the other factor was positive and statistically significant (Table 6.6). The approximation for soil gave a low positive  $\beta$  value but higher than the water. The correlation for the water was statistically significant.

### **6.3.3.3 *Paspalum***

The concentration of the Fe had a positive coefficient without the third source in the water and soil and was statistically significant (Table 6.5). With the third source, the coefficient for the third source was positive and statistically significant (Table 6.6).

The approximation for water gave a positive  $\beta$  value higher than the soil. The correlation for soil was statistically significant.

### **6.3.3.4 *Persicaria***

The concentration of Fe had a positive coefficient in the soil and was statistically significant (Table 6.5). With the third source, the coefficient for the third source was the highest positive  $\beta$  value and statistically significant (Table 6.6).

## **6.3.4 Nickel**

Tables 6.7 and 6.8 shows that the Ni content in the plant leaves was a more effective predictor in the *Paspalum* and *Persicaria* leaves with respect to the water, they gave a significant correlation. Thus, *Paspalum* and *Persicaria* were the good predictors of water concentration of Ni. The *Paspalum* also significantly predicted the soil Ni

content.

**Table 6.7:** The predictive value of the plant Ni content in relation to the Ni content of water and soil (from equations 4 and 5).

Ni	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
<b>Water</b>	1.118	0.134	1.141	0.064	6.455	<0.001	3.422	0.001
<b>Soil</b>	0.031	0.511	0.075	0.075	0.189	0.001	0.019	0.778



**Table 6.8:** The predictive value of the plant Ni content as to the Ni content of water, soil and other correction factor (from equations 7 and 8).

Ni	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
Other factors	0.007	0.258	0.019	<0.001	0.036	<0.001	0.029	<0.001
Water	0.585	0.506	-0.026	0.968	3.424	0.002	1.326	0.250
Soil	0.008	0.867	0.009	0.838	0.062	0.260	-0.079	0.255

#### 6.3.4.1 *Paspalum*

The concentration of the Ni gave the highest positive coefficient without the third source of all plant species, but was statistically insignificant for predicting both the water and the soil Ni content (Table 6.7). With the third source, the water coefficient of the Ni gave the highest positive coefficient content and statistically significant (Table 6.8).

#### 6.3.4.2 *Persicaria*

The concentration of the Ni in the water gave high positive coefficient with level Nickel content and statistically significant (Table 6.7). With the third source, the third source coefficient of the Ni was low and statistically significant (Table 6.8).

#### 6.3.5 Lead

From Table 6.9 it is clear that the Pb content in the plant leaves was more effective as a predictor in *Paspalum urvillei* for both water and soil. *Salix babylonica* and

*Persicaria lapathifolia* used also predict the soil Pb content.

**Table 6.9:** The predictive value of the plant Pb content in relation to the Pb content of water and soil (from equations 4 and 5).

Pb	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
Water	0.025	0.153	0.043	0.753	0.180	0.031	0.041	0.625
Soil	0.032	<0.001	0.052	0.059	0.062	<0.001	0.078	<0.001

**Table 6.10:** The predictive value of the plant Pb content in relation to the Pb content of water, soil and other correction factor (from equations 7 and 8).

Pb	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
Other factors	0.001	0.002	0.008	0.002	0.008	<0.001	0.006	0.001
Water	0.006	0.729	-0.102	0.472	0.016	0.828	-0.052	0.544
Soil	0.014	0.095	-0.001	0.965	0.015	0.301	0.039	0.084

### 6.3.5.1 *Salix*

The concentration of the lead Pb had a positive coefficient with the soil Pb content and was statistically significant (Table 6.9). With the third source, the effect for the other factor had a low positive coefficient and was statistically significant (Table 6.10).

### 6.3.5.2 *Commelina*

The Pb had a positive coefficient with the third source the coefficient was positive



and statistically significance (Table 6.10).

### **6.3.5.3 Paspalum**

The concentration of the lead Pb had the highest positive coefficient in *Paspalum* of all the species and significant for water and soil (Table 6.9). With the third source, the coefficient for the third source was just positive and statistically significant (Table 6.10). The level of approximation for the water gave highest positive  $\beta$  value, the correlations statistically significant for the water and the soil.

### **6.3.5.4 Persicaria**

The concentration of the lead Pb gave the highest coefficient with the soil, it was highly significant (Table 6.9). With the third source, the concentration of the Pb in the water was negative coefficient and the soil was positive coefficient but was statistically insignificant for both. The coefficient for the third source was positive and statistically significant (Table 6.10).

### **6.3.6 Zinc**

From Table 6.11 is clear that the f Zn concentration in the plant leaves gave a low positive contribution (low  $\beta$  value) for the soil in all species with water. Thus we can use all the plant species as predictors but the *Salix* gave the best result. None of the plants gave a good indication of the Zn level in the water.

**Table 6.11:** The predictive value of the plant Zn content in relation to the Zn content of water and soil (from equations 4 and 5).

Zn	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
<b>Water</b>	1.485	0.573	46.437	0.102	1.677	0.354	10.128	0.143
<b>Soil</b>	1.103	<0.001	0.537	<0.001	0.500	<0.001	0.910	<0.001



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**Table 6.12:** The predictive value of the plant Zn content in relation to the Zn content of water, soil and other correction factor (from equations 7 and 8).

Zn	<i>Salix</i>		<i>Commelina</i>		<i>Paspalum</i>		<i>Persicaria</i>	
	$\beta$	P value	$\beta$	P value	$\beta$	P value	$\beta$	P value
<b>Other factors</b>	0.833	<0.001	0.681	<0.001	0.452	<0.001	1.121	<0.001
<b>Water</b>	-0.634	0.710	-41.933	0.025	0.091	0.940	2.411	0.591
<b>Soil</b>	-0.260	0.225	-0.070	0.451	0.103	0.223	-0.098	0.553

### 6.3.6.1 *Salix*

The concentration of the Zn was a positive coefficient and statistically significant with the soil Zn content. *Salix* was the best species for predicting soil Zn content (Table 6.11). With the third source, the coefficient for the third source was positive and statistically significant (Table 6.12). The approximation for the soil gave the highest positive coefficient ( $\beta$  value), the correlations was high statistically significant.

### 6.3.6.2 *Commelina*

The concentration of the Zn in the soil was positive coefficient and was statistically significant (Table 6.11). With the third source, the coefficient for the third source was positive and high statistically significant (Table 6.12).

### 6.3.6.3 *Paspalum*

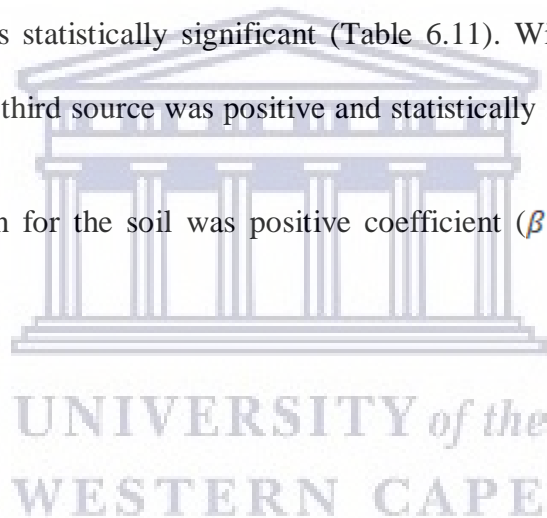
The concentration of the Zn had a positive coefficient without the third source in the water, and was statistically significant (Table 6.11). With the third source, the coefficient for the third source was positive and statistically significant (Table 6.12).

The approximation for the soil was positive contribution ( $\beta$  value) and statistically significant.

#### **6.3.6.4 *Persicaria***

The concentration of the Zn was the positive coefficient without the third source in the soil and it was statistically significant (Table 6.11). With the third source, the coefficient for the third source was positive and statistically significant (Table 6.12).

The approximation for the soil was positive coefficient ( $\beta$  value) and statistically significant.



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# CHAPTER 7

## DISCUSSION

### 7.1 Introduction

As mentioned elsewhere, rivers are considered as an essential place for the well-being of humankind (See Chapter 2, section 2.1 of this study). However, many rivers around the globe are mistreated by the inhabitants of the surrounding areas. These rivers are severely at risk, subsequently, the rivers cannot be utilized at their full potential for the benefit of the ecosystem. There is a lack of awareness by both the people and the decision-makers. Therefore, decision-makers need to be alerted and incorporated in the process of conservation efforts. Hence, there is an urgent need for additional knowledge to be added to the heavy metals environmental pollution database of the river ecosystems, which will be crucial for human society (Parker and Oates, 2016; Wong et al., 2007).

In this research, we studied some features of the ecosystem in the Eerste River catchment directly with the goal of creating a biomonitoring model. The model uses certain common plants species in the study area (See Chapter 4, Figure 4.1). Moreover, we determined a number of physical and chemical parameters in water, soil and plants samples, which were taken from 22 sites mentioned in the study, within twelve months (2011-2012).

Several indicators were used to verify the quality of the river water. The indicators used were measured to determine spatial and temporal changes. To classify the water features, we chose four indicators in the river water, the indicators are: water temperature, dissolved oxygen, hydrogen ion concentration (pH) and conductivity. (Diamantini et al., 2018; Kannel et al., 2007). Then, we examined other indicators based on the human effect on the river catchment. The indicators are as follows: ammonium (NH<sub>4</sub><sup>+</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) (Kononenko et al., 2018; Program, 2004; Vadde et al., 2018; Wall, 2013) and selected heavy metals in water, soil and plants.

## 7.2 Water Temperature and Dissolved Oxygen

The temperature of the water increased significantly from the upper reaches to the lower reaches. The average water temperature was the lowest in winter 10.6°C, and highest in summer 27.39°C (Table 5.1). The outcome of the water temperature found in this study gave a narrower range than the results published by the South African Department of Water Affairs (DWA) in 1996 for inland South African water bodies, which was between 5 to 30°C (Department of Water Affairs and Forestry, 1996) .

The water temperatures results are similar to those of Mwangi (2014), in which he studied the water quality in the upper reaches of Kuils River. He stated that the average water temperature was between 14.84 and 23.96°C (Mwangi, 2014). Furthermore, Feng (2005) concluded that the water temperatures found in the Bottelary River, was between 9.2-23.1°C. Noteworthy, the samples collection in the present study started in the early morning from the upper reaches (~06:00), then, to the middle reach and ended in the lower reaches around 16:00. Our results are in line



with Ficklin et al. (2013) and Post et al. (2018), where they state that the dissolved oxygen (DO) is inversely related to the water temperature. We recorded the highest DO value when the water temperature was the lowest, hence, the highest DO was recorded in winter in the upper reaches; and, the lowest DO was recorded in the summer in the lower reaches (Table 5.1). The same contrast was found by Huang et al. (2017). Increases in the consumption of dissolved oxygen in the water is linked to the increase of water temperature which leads to increasing rates of biochemical reactions and transformation processes occurring in water ecosystems (Ji, 2017).

DO ranged between  $3.56 \text{ mg}\cdot\text{l}^{-1}$  and  $1.3 \text{ mg}\cdot\text{l}^{-1}$ , which was to some extent similar to the study carried by Mwangi (2014) in the upper reaches of Kuils River. In that study the mean was between  $5.4$ - $2.47 \text{ mg}\cdot\text{l}^{-1}$  (Mwangi, 2014), Feng (2005) recorded higher values than this study, although, we were in the Feng's range, which was between  $0.97 \text{ mg}\cdot\text{l}^{-1}$  and  $7.9 \text{ mg}\cdot\text{l}^{-1}$  (Feng, 2005).

According to the Universal Water Quality Index (UWQI), if the DO of water is between  $6$  to  $8 \text{ mg}\cdot\text{l}^{-1}$ , the water quality is considered acceptable to excellent. On the other hand, if the DO is  $3 \text{ mg}\cdot\text{l}^{-1}$  or less, the water quality is considered unacceptable and classed as polluted water (Engineering and Buca, 2007). The recommended South African Water Quality Guidelines for Coastal Marine, the minimum of dissolved oxygen in marine and estuarine waters is  $8.0 \text{ mg}\cdot\text{l}^{-1}$  (Department of Environmental Affairs, 2014). Using the above-mentioned water standards, we found that the mean DO in the upper reaches in all seasons indicates that the water quality was in excellent condition.

As for the middle reaches, the quality of the water is found to be excellent only in the winter, and acceptable in the other seasons. Finally, in the lower reaches, we found it to be below the acceptable range in both winter and spring, and in the summer and autumn, the water was in the polluted range. The various readings may be due to the lack of rainfall and water temperature in both summer and autumn. Dissolved oxygen in river water is related to temperature and rainfall positively affects DO concentrations in the river water (Munoz et al., 2015).

### **7.3 Water pH and Electrical Conductivity**

The pH of the water is considered as one of the main factors of water quality. In freshwater, which supports aquatic life, the pH is between 5.0-9.0 (DWAf, 1996; Robertson, 2004). According to the South African standards, the pH of surface water should be between 6-8  $\text{mg}\cdot\text{l}^{-1}$  (Dallas, 2004; Department of Water Affairs and Forestry, 1996; Dzwauro and Mujuru, 2017).

Throughout the years, there were changes in the pH of the water found in Eerste River catchment. The lowest recorded value for pH was 4.5, it is rare to find alkaline water in South African rivers (Petersen and Buthelezi, 2005). The pH may affect the use of surface water in agricultural, industrial and urban situations (Maputo et al., 2008). The highest mean pH values were recorded in the lower reaches of Eerste River catchment in spring and summer, and the lowest was found in the upper reaches in autumn and winter (Table 5.1). That was in line with Ngwenya (2006), who reported values of 6.8 to 7.6 pH in Eerste River catchment (Ngwenya, 2006). There was a direct relation between pH and EC, as can be seen in (Table 5.1).

The same relation was found by Leveling (2002) in his study. The range of pH measured in this study was between 6.63-7.84 (Table 5.1), which was suitable for aquatic life according to (DWAF, 1996; Robertson, 2004), these readings showed a significant increase down the Eerste River. Feng (2005) found that the pH in the Bottelary River was between 6.73 and 8.02. Mwangi (2014), found in the upper reaches of Kuils River pH ranged between 7.61 and 8.22. Thus, our recordings were in a similar range to both the study of Feng and Mwangi.

The dissolved salts and ions in the water were estimated by the EC, which according to Pal et al. (2015), is considered as “the ability of current conduction”. Furthermore, Pal et al. (2015) recorded a direct relation between the temperature and EC in water. The value of electrical conductivity depends on the concentration of ions present in water, which is the ability of 1.0 cm<sup>3</sup> of water to conduct electricity at 25.0°C (Barron and Ashton, 2005). Similarly, we found a direct relation between the temperature and EC in water, and the same relation was found between the pH and EC.

The EC of water is affected by water flow (Chusov et al., 2014). That can be due to the gradual differences from upper reaches to lower reaches caused by water flow changing in the river, recorded a slight increase in values. EC values increased as the river descended through the plains; in our study, it was significant in the upper and lower reaches and that can be contrasted to Ngwenya (2006). In winter, we recorded the lowest means of EC at the upper reaches, while, the highest was recorded at the lower reaches in spring, it was insignificant with the seasons (Table 5.1). The conductivity and salinity varies in the case of estuaries because of the changes of water levels in the raise and fall of the tides (Pal, M., Samal, N.R., Roy, P.K. and

Roy, 2015; Qiu and Zhu, 2015). The increase of EC recorded in the lower reaches at the estuary of the Eerste and Kuils River catchment, can be due to the difference levels caused by the rise and fall of the ocean tides and the introduction of salty, marine water into the lower reaches.

#### **7.4 Water Ammonium, Nitrite and Nitrate**

Nitrogen is considered as an essential component for living organisms, it is further labelled as an important constituent of proteins and genetic material (Harper *et al.*, 2017). As part of the nitrogen cycle, it undergoes biological and non-biological transformations in the environment. To reach the organic form of nitrogen, plants and bacteria convert it from the inorganic one. In the environment, inorganic nitrogen occurs as nitrate ( $\text{NO}_3^-$ ) nitrite ( $\text{NO}_2^-$ ) and the ammonium ion ( $\text{NH}_4^+$ ). Of these forms, nitrate is usually the most stable and most common form found in aquatic environments (Burres, 2010).

In our study, ammonium concentration differs significantly with distance. The highest was recorded in summer in the lower reaches of the river (Table 5.1), which may be attributed to the waste water effluent in the river and the use of fertilizers, as well as the increase of temperature and the lack of rain. It can be noted that the lowest concentrations of ammonium in water were recorded in the upper reaches of the river during winter (below the detection levels). These results agrees with those of Lindenbaum (2012) and Meng *et al.* (2018).

The lowest temperature, pH and ammonium in water were recorded in winter in the upper reaches of the river this may be due to the lack of pollutants and the high flow

of the river. On the other hand, the highest values were recorded in the lower reaches in summer and autumn respectively it may be caused by the pollutants in the river and low river flow. With a direct relationship between temperature, pH and ammonium. These results are in line with (Department of Water Affairs and Forestry, 1996; Leoni et al., 2018; Ngwenya, 2006). The relationship between the ammonium and the dissolved oxygen was inverse, as also found by Quirós (2003).

In line with the recommendations of World Health Organization (WHO) with regards to drinking water, the water in the upper reaches of the river is the only water that is usable for drinking. That is determined by the concentration of the ammonium in the water, which must be less than  $0.2 \text{ mg.l}^{-1}$  (WHO, 2016).

In this study, nitrate showed significant differences, the highest concentration was recorded in the middle reaches in all seasons; the highest value was captured in autumn, which was  $15.18 \text{ mg.l}^{-1}$ . Similarly, Charkhabi and Sakizadeh (2006) captured the highest nitrate levels in autumn in the Siahroud River, Iran. These results were in line with Feng (2005), they also recorded the highest value in autumn. In our study, the Bottelary River was one of the sites we covered in the Eerste River catchments, especially the Bottelary Groenland site. The increase in the nitrate in this area may be attributed to agriculture activities, specifically from the vineyards, it may be due to an increase in the use of fertilizers, this leads to low quality of river water. The nitrate in the Bottelary River measured by Feng (2005), were more than 6 times higher than our study, this may be due to the uneven discharge of wastewater treatment works in this tributary. Mwangi (2014), recorded  $3.1 \text{ mg.l}^{-1}$  in the Kuils River, which was one of the sites we studied. Both studies differed from our

measurements, as the nitrate level in our study was  $4.65 \text{ mg.l}^{-1}$ ; higher than that recorded by Mwangi (2014).

In the upper reaches, the nitrate was below detection in the Eerste River catchments in all seasons, it may be due to a lack of human activities, especially agricultural and sewage. This is similar to Shinozuka et al. (2017), in which they covered three rivers in the Tatura River Basin in Japan. Furthermore, it corresponded with Nyamangara et al. (2013), where they searched the upper reaches of Manyame River, Zimbabwe.

All the above-mentioned studies, along with ours, found that the human activity such as agricultural and sewage is a major factor in increasing nitrate pollution in rivers, which results in a risk to low quality environments and for the life of organisms in the rivers.

The findings indicate that the nitrite levels differed significantly from the upper to the lower reaches. The highest was recorded in the lower reaches of the river, which was  $3.21 \text{ mg.l}^{-1}$  in autumn, and that decreased in summer and further declined in winter. In Feng (2005), the highest levels were recorded later in spring and in early winter in the middle reaches of Bottelary River, which partially aligns with our results.

According to the South African Water Quality Guidelines from the Department of Environmental Affairs (DEA) regulations in 2014, the river catchments must not contain more than  $1 \text{ mg.l}^{-1}$  of nitrite, and  $2.4 \text{ mg.l}^{-1}$  of nitrate will be acceptable in the estuaries; our research findings were within these limits (Department of Environmental Affairs, 2014). Our records of nitrite in the upper reaches of the river

were below detection, which might be caused by the lack of human activity such as agricultural and sewage in the upper reaches. The upper reaches water is potable as drinking water according to the WHO's (2016) guidelines for drinking-water quality, the nitrite level was lower than 0.3 mg.l<sup>-1</sup>.

## **7.5 Soil pH and Electrical Conductivity**

From the results collected in our study, the pH of the soil did not change very significantly with the seasons and that was similar to Zhao et al. (2018), in Mun River Basin, Thailand. However, our results differed from those of Salim et al. (2015), where soil pH differed significantly throughout the four seasons; with the highest in summer and the lowest in autumn in Uttrakhand, India. Moreover, our results differed from those of Conradie et al. (2002), where he found a significant difference in soil pH between the warm and cold seasons in the areas of Viticulture in Stellenbosch/Durbanville Districts of the Western Cape, South Africa.

When we measured the soil electrical conductivity (EC), which gives an indication of the soil salinity, in Eerste River catchment; there were no seasonal differences, but there were significant differences between the reaches. The highest value was recorded in the middle reaches in summer, which was 1427 mm cm<sup>-1</sup>, whereas, 43.5 mm cm<sup>-1</sup>, which was the lowest value recorded was in the upper reaches in winter.

In general, the highest values were recorded in the middle reaches in all seasons, and the lowest values were in the upper reaches in all seasons of the Eerste River catchment. These results may be caused by the changes in land use, and pollution (Bugan et al., 2015) there were numerous changes from the 1890s for most of the

land in the area of Eerste River catchment (see Chapter 2, 3.2. Landscape). According to Bagan et al. (2015), measuring soil salinity is considered crucial to primary producers in the environment, because it affects the plants' production process in the surrounding area, and it also affects the water salinity in the river's environment.

The Department of Water Affairs and Forestry (DWAF) have more than forty years of qualitative data of the South African rivers' environment. Moreover, the Water Research Commission (WRC) funded multiple projects with regards to the soil salinity across South Africa. The majority of research focussed was on the temporal/spatial trends of the soil salinity. Our study was an attempt to support the recent South African national database of rivers environment (Pal et al., 2015). Which targeted the Eerste River catchments. In which we noted that the soil salinity was high in the middle reaches, which previous studies indicated that it might be caused by the change of human activity and pollution (cf. Bagan et al., 2015; van Rensburg et al., 2011).

## **7.6 Calcium**

Calcium (Ca) is one of the main causes of the hardness of drinking water. Different studies have shown a direct relationship between cardiovascular disease and other health problems with the hardness of drinking water (Kidwai, 2018; Sengupta, 2013). The finding indicates that the Ca in the river water increases downstream. The highest value was recorded in the lower reaches, which was  $26.88 \text{ mg.l}^{-1}$ , and the lowest was recorded in the upper reaches, which was  $1.71 \text{ mg.l}^{-1}$  (Table 5.3). The concentrations of Ca in the river water can be the result of an increase of human



activity, pollutants, sewerage and agriculture nutrients (Potasznik and Szymczyk, 2015). The concentrations varied significantly with season. The highest Ca concentration in water was recorded in winter which was  $19.19 \text{ mg.l}^{-1}$ , the lowest was  $16.1 \text{ mg.l}^{-1}$  recorded in autumn (Table 5.4). In order to determine the water hardness, the DWAF (1996) states that if the Ca concentration in water was lower than  $60 \text{ mg.l}^{-1}$ , the water is then considered soft.

The Ca findings in our study were all lower than  $60 \text{ mg.l}^{-1}$ , therefore, the Eerste River water is deemed soft. Moreover, with regards to the limits of Ca in water, the DWAF states that it must not exceed  $15 \text{ mg.l}^{-1}$ , and our findings were in line with that through the river, except for the lower reaches, which was  $26.88 \text{ mg.l}^{-1}$  (Table 5.3).

Mathebula (2016) studied three dams in the Vaal River system from the Lesotho Highlands, in which they found that the concentration of Ca in Katse and Sterkfontein Dam was higher than our results. As for the Ca concentration in Vaal Dam's water, Mathebula found that it was higher than all of our records in Eerste River.

Potasznik and Szymczyk (2015) states that the Ca concentration in the Symsarna River's catchment in Poland was between  $11.04$  and  $55.45 \text{ mg.l}^{-1}$ . Our results were in range with lowest record of Potasznik and Szymczyk's study. Furthermore, they found seasonal differences in the Ca concentration, in which they found the lowest in spring and summer, however, in our study the lowest was recorded in autumn. In a study in Sagbama Creek, Niger Delta in Nigeria, Seiyaboh et al. (2017) found that the Ca concentration in the river water was between  $1.01$  and  $2.22 \text{ mg.l}^{-1}$ , and that is in

line with the Ca concentration in the upper reaches of the Eerste River.

The Ca concentration in river soil in the Eerste River increased significantly from the lower to the upper reaches. The highest Ca in soil was recorded in the upper reaches, which was 60.62 mg·kg<sup>-1</sup>; as for the lowest was recorded in the lower reaches, which was 17.77 mg·kg<sup>-1</sup> (Table 5.3). These results were different to Jeziorski's et al. (2008) study, in which they recorded positive relationship between the Ca concentration in the soil and the Ca in water; however, in our study, the relationship between the two was inverse. The abovementioned soil Ca concentrations might be due to the lack of plants cover around the river area, in the lower reaches, which is considered a crucial factor in determining the Ca concentration in soil. Another reason for the Ca concentration in soil is pollution, where the middle and lower reaches receives more pollutants than the upper reaches (King and Buckney, 2000; Potasznik and Szymczyk, 2015).

Throughout seasons, the measurements of Ca in soil gave significant differences, the highest was 63.73 mg·kg<sup>-1</sup>, in summer. The lowest was 19.22 mg·kg<sup>-1</sup>, recorded in autumn (Table 5.4). In line with our results, Duniway et al. (2010) also noted that the Ca in soil was at its highest in the season where rain is not common, it may be due to the increased concentration of ions in the soil and an increase in pH as well (Ghorpade et al., 2013).

The Ca concentration in the leaves of *Salix babylonica* and *Paspalum urvillei* varies significantly across the reaches increasing from the lower to the upper reaches. The highest Ca value in *S. babylonica* was 80.28 mg kg l<sup>-1</sup>; as for the *P. urvillei* it was

42.55 mg.l<sup>-1</sup>, which was half of the Ca concentration in the *S. babylonica* (Table 5.3). These results might be caused by the fact that both plants grow on the river banks and not in the water, which may result in higher Ca in the soil and as result available to the plant (Duniway et al., 2010).

In Table 5.3, it can be noticed that the concentration of Ca in water, *S. babylonica* and *P. urvillei*, was similar, and opposite (Negatively correlated ) to the trend in the soil; this might indicate that the Ca absorbed from the water by the plants is more than that from the soil. Duncan and Casler (2003) mentioned that certain species of *P. urvillei* have a high tolerance of the soil salinity, which is caused by the Ca salts and their accumulation in the plant. However, throughout the seasons both plants did not show any similarity to the Ca concentration in water and soil. The lowest concentrations levels in both plants were recorded in winter, which was 28.32 mg·kg<sup>-1</sup> in *S. babylonica*, and 19.49 mg·kg<sup>-1</sup> in *P. urvillei*.

The measurements of Ca concentration in *P. lapathifolia* gave the highest value of 69.43 mg·kg<sup>-1</sup> in the upper reaches; and the lowest was 43.45 mg·kg<sup>-1</sup>, which was captured in the lower reaches (Table 5.4). Thus, it has given a different direction to the *S. babylonica* and *P. urvillei* plants. This might be due to the dependence of *P. lapathifolia* in the supply of Ca on the soil more than water. There was no seasonal trend consistent with either water or soil. The highest was recorded in spring, which was 63.58 mg·kg<sup>-1</sup> and the lowest was in summer, which was 40.59 mg·kg<sup>-1</sup> (Table, 5.4).

*Commelina benghalensis* plant gave the highest Ca concentration in its leaves in the

middle reaches, which was  $66.97 \text{ mg}\cdot\text{kg}^{-1}$ , and the lowest value at the lower reaches was  $39.14 \text{ mg} / \text{kg}^{-1}$ , and was significantly different between river reaches (Table 5.3). The Ca concentrations in *C. benghalensis* throughout the seasons paralleled the concentration of Ca in water. The highest was recorded in winter, then spring, then summer and the lowest in autumn (Table 5.4). Due to the interference of Ca concentration with the movement and the availability of different heavy minerals in plants and their environment; the concentration of Ca in both soil, water and plants was widely explored in different studies (cf. Eller and Brix, 2016; Olaniran et al., 2013; Österås and Greger, 2006; Özkay et al., 2014).

## 7.7 Iron

The concentrations of iron (Fe) in soil and water were highest in the upper reaches of the river,  $1.04 \text{ mg}\cdot\text{l}^{-1}$  in water, and  $27.65 \text{ mg}\cdot\text{kg}^{-1}$  in soil. The lowest Fe concentrations in soil and water were recorded in the middle reaches, where in water the concentration was  $0.78 \text{ mg}\cdot\text{l}^{-1}$ , and in soil it was  $17.97 \text{ mg}\cdot\text{kg}^{-1}$ . In the lower reaches intermediate concentrations were found (Table 5.3).

In Jackson's et al. (2007) study of the Berg River, Western Cape, South Africa, the concentration of iron in the river water was between  $1.4$  and  $14.6 \text{ mg}\cdot\text{l}^{-1}$ . Their lowest recorded value was higher than the upper limit of our study. In the study of Jackson et al. (2009) in the Plankenburg and Diep Rivers, Western Cape, South Africa, the Fe concentration in the water of the Plankenburg River was  $0.5$ - $25.7 \text{ mg}\cdot\text{l}^{-1}$  and thus the lower limits in their study were comparable to our results. The higher limits were again much higher than in this study; as were well as the results in the Diep River. Where the concentration of Fe in the water was  $48 \text{ mg}\cdot\text{l}^{-1}$ . It may be due to

weathering processes that release iron in the water.

The major naturally occurring ferrous minerals from the constituent rocks of the upstream mountain regions (McKnight and Bencala, 1988). According to our study (Table 2.2), the concentration of Fe in the Eerste River water was within the normal range (DWAF, 1993). In the Edokpayi et al. (2014) study in the Dzindi River, in Limpopo Province, South Africa, the concentration of iron in the river water was between 0.79 and 1.72 mg·l<sup>-1</sup>, the minimum levels in their study were consistent with our results. The upper levels were slightly higher than our results. This might be due to organic matter in the upper reaches, where it gave a yellow color. The upper reaches of the Eerste River water were brown in colour and colourless in the lower and middle reaches; this might be due to leachate from the fynbos plant cover in the upper reach. This was in line with Moroi et al. (2012).

Edokpayi et al. (2016) recorded the highest iron concentrations in Dzindi River, in the Limpopo Province, South Africa in winter and summer. However, in our study, significantly higher Fe concentrations were recorded in autumn and winter (Table 5.4). The highest Fe concentration in the soil of the Eerste River catchment occurred during the spring (2011 and 2012), which was 24.83 mg·kg<sup>-1</sup>, and significantly different to the lowest value in summer, which was 13.25 mg·kg<sup>-1</sup> (Table 5.4). The concentration of Fe in soil may vary due to the season depending on the amount of rain. In the wet season, the Fe concentration increases and it decreases in the dry seasons. This was found in our study and agreed with the Olatunji et al. (2016) results, from the soil around the perimeter of an iron factory in Fashina area, Ile-Ife in Nigeria.

In the study of Nde and Mathuthu (2018) in the upper Crocodile Catchment Area, in North-West Province, South Africa. The concentration of Fe was recorded in several different areas are, the Fe concentration in soil in agricultural areas was  $17.26 \text{ mg}\cdot\text{kg}^{-1}$ . As for the urban areas, the Fe concentration was  $20.25 \text{ mg}\cdot\text{kg}^{-1}$ . In industrial areas the Fe concentration was  $28.55 \text{ mg}\cdot\text{kg}^{-1}$ . Our results were similar to the areas of agricultural and urban activities only, which may be due to the similarity of activities in these areas with the study of Nde and Mathuthu (2018). A study on a rapidly urbanized area in the upper Yangtze Basin in China by Jia et al. (2018), found that the average Fe concentration in the soil of the studied area was  $37.3 \text{ mg}\cdot\text{kg}^{-1}$ , which was higher than our measurements and this may be due to the acceleration of urbanization and the increase of human activity in the area Jia et al. (2018) studied in China, which could become a reality for the Eerste River. Iron is the fourth most abundant mineral in the earth's crust and one of the important elements that is necessary for the plants. However, high levels within the plant tissue become toxic to the plant, which could lead to damage of lipids, proteins and the DNA (Connolly and Guerinot, 2002; Nikolic and Pavlovic, 2018). The iron content of *Salix babylonica* was in the range 1.21 to  $1.94 \text{ mg}\cdot\text{kg}^{-1}$  and that of *Persicaria lapathifolia* 1.92 to  $4.20 \text{ mg}\cdot\text{kg}^{-1}$  (Table 5.3).

In a study conducted by Lavin et al. (2015) in central Florida in America on the concentration of some elements in the leaves of *Salix* species they found the highest Fe concentrations in the spring. The reason may be due to the acidity of the soil, which leads to greater absorption of iron (Kuzovkina and Quigley, 2005). This is consistent with our study where significantly higher Fe concentrations occurred in the leaves of *S. babylonica* in the spring ( $1.34 \text{ mg}\cdot\text{kg}^{-1}$  Table 5.4). Various studies have

been interested in *Commelina spp* as a medicinal plant and an additional source of nutrients such as iron for human consumption (cf. Orni et al., 2018; Schwartz et al., 1988). The Fe concentration in *Commelina benghalensis* was significantly higher in the middle reaches at  $1.39 \text{ mg}\cdot\text{kg}^{-1}$  than in the lower reaches at  $0.78 \text{ mg}\cdot\text{kg}^{-1}$ .

In terms of seasons there was again a significant difference, the highest concentration was in the summer  $1.51 \text{ mg}\cdot\text{kg}^{-1}$  and the lowest in the autumn  $0.53 \text{ mg}\cdot\text{kg}^{-1}$  (Tables 5.3 and 5.4). It is noteworthy that in most studies the concentration of Fe in the *Commelina spp* gave higher values than what we recorded in our study. For instance, in the study done by Mahadkar et al. (2012) in the Kolhapur River in India they found that the Fe concentration in the *Commelina spp* was  $115.92 \text{ mg}\cdot\text{kg}^{-1}$ .

In the study of the Kalipur site, located in India by Kisku et al. (2000), Fe was found in *Commelina* at  $250 \text{ mg}\cdot\text{kg}^{-1}$ . Furthermore, in the studies of Umoh et al. (2014b), it was found that the concentration of Fe in the leaves of *Commelina* was  $2.08 \text{ mg}\cdot\text{kg}^{-1}$  in the Ibeno coastline, Akwa Ibom State in Nigeria.

The Fe concentration in *P. lapathifolia* leaves measured in this study ranged from  $1.63$  to  $3.43 \text{ mg}\cdot\text{kg}^{-1}$  (Table 5.4). In the Ibeno coastline, Akwa Ibom State in Nigeria. The concentration in *Paspalum vaginatum* (Umoh et al., 2014c) leaves was higher than the  $2.98 \text{ mg}\cdot\text{kg}^{-1}$ , which we found in *Paspalum urvillei* (Tables 5.3 and 5.4). The concentration of Fe in *Paspalum urvillei* leaves in our study differed significantly with reaches. It was highest in the middle reaches, at  $1.22 \text{ mg}\cdot\text{kg}^{-1}$  and the lowest at the upper reaches, at  $0.37 \text{ mg}\cdot\text{kg}^{-1}$ . During the seasons, the lowest concentration of Fe in *P. urvillei* leaves was in winter at  $0.47 \text{ mg}\cdot\text{kg}^{-1}$  and the highest concentration in

summer was  $1.57 \text{ mg}\cdot\text{kg}^{-1}$  with the differences being significant (Tables 5.3 and 5.4). The Fe concentration in *P. urvillei* was  $339.5 \text{ mg}\cdot\text{kg}^{-1}$  in a greenhouse study at the Universidade Federal de Viçosa, Brazil (Santana et al., 2014). They studied three plant species and their tolerance for high Fe concentrations and the possibility of using them as a phytoremediation.

## 7.8 Nickel

The nickel (Ni) concentration in the Eerste River water ranged from 0.73 to  $1.92 \text{ mg}\cdot\text{l}^{-1}$ . Olujimi et al. (2015) found that the concentration of Ni in Cape Town rivers that received industrial and sewage effluents ranged from  $0.027 \text{ mg}\cdot\text{l}^{-1}$  to  $0.106 \text{ mg}\cdot\text{l}^{-1}$ . Ni concentrations in the Vaal dam ranged from  $0.0028 \text{ mg}\cdot\text{l}^{-1}$  to  $0.027 \text{ mg}\cdot\text{l}^{-1}$  (Retief et al., 2009). Ni concentrations in the waters of the Eastern Cape Rivers ranged from  $0.201 \text{ mg}\cdot\text{l}^{-1}$  to  $1.7 \text{ mg}\cdot\text{l}^{-1}$  (Awofolu et al., 2005).

In a study on the Blyde River in Pilgrim's Rest and surrounding area in South Africa, the Ni concentration in the river water averaged  $0.09 \text{ mg}\cdot\text{l}^{-1}$  (Van Jaarsveldt, 1999). Our results found higher values than the abovementioned studies; this may be due to the discharge of industrial and sewage effluents into the river. South African Water Quality guidelines for different water uses for livestock  $1 \text{ mg}\cdot\text{l}^{-1}$ , thus just the upper reach water in the standards.

Singh et al (2008) found the Ni concentration in water in India was between 0.56 and  $1.82 \text{ mg}\cdot\text{l}^{-1}$  and recorded the highest values in the rainy seasons which increased river water flow. Furthermore, Awofolu et al. (2005) recorded the highest value of Ni in spring and that differs from our results, as we found the highest values in autumn and



summer, during periods of low flow, which were respectively 1.7 and 2.99 mg·l<sup>-1</sup> respectively with significant differences (Table 5.4) counter to we found in our study, Chiba et al. (2011) They found in a seasonal study of water pollution in sub-basin, Southeast of Brazil, that the water nickel concentration was higher in wet seasons and less in dry seasons.

The Ni concentration found in the soil of the Eerste River catchment ranged from 1.54 mg·kg<sup>-1</sup> to 1.86 mg·kg<sup>-1</sup> (Table 5.3). The concentration of Ni in the soil in both our study and in the Retief et al. (2009) study in the Vaal Dam in South Africa, and also in the Awofolu et al. (2005) study in Tyume River, South Africa were all below the maximum allowed in soil by the Department of National Health and Population Development (DoH). South African laws and guidelines instructs that the maximum permissible concentrations of Ni in soil should be 15 mg·kg<sup>-1</sup> (DoH, 1991; Steyn et al., 1996).

In a study on soil pollution of the hydroelectric dam on the Lancang River in China 2009, the highest Ni mean in soil was found at the lower reaches, which was 42.43 mg·kg<sup>-1</sup>. The lowest was found in the upper reaches 5.57 mg·kg<sup>-1</sup>. While in Ansari and Malik (2010), Ni concentrations were found in the industrially polluted city of Ghaziabad in Uttar Pradesh, India, to be between 24.7 and 31.8 mg·kg<sup>-1</sup>.

Nickel concentrations in the Vaal Dam soil in South Africa had the highest value in the summer at 2.54 mg·kg<sup>-1</sup> and the lowest value was in the autumn were 0.82 mg·kg<sup>-1</sup> (Retief et al., 2009). While in our study the highest values were in spring, they were 1.97 mg·kg<sup>-1</sup> and the lowest in summer were 1.35 mg·kg<sup>-1</sup> which differed

significantly (Table 5.4). May be caused by high nickel in the Vaal Dam to periods of stagnation water in the dam (Canada, 2009).

The concentration of Ni in the *Salix babylonica* leaves showed no significant differences with the reaches, and ranged between 0.35 mg·kg<sup>-1</sup> to 1.19 mg·kg<sup>-1</sup>. During the seasons, the Ni concentration values were given in *S. babylonica* leaves had significant differences, the highest was recorded in spring at 1.2 mg·kg<sup>-1</sup> and lowest was in autumn at 0.35 mg·kg<sup>-1</sup> (Table 5.3 and 5.4).

Kaplan et al. (2009) studied the concentration of trace metals in unwashed leaves of some trees in the city of Zonguldak in Turkey. It was found that the Ni concentration in *Salix babylonica* leaves was between 0.71 and 5.89 mg·kg<sup>-1</sup>. These results were generally higher than the results obtained in our study. That may be because the leaves used in Kaplan's study were unwashed and the sampling sites were in areas with high traffic density leading to increased contamination in those areas.

Ali et al. (2003) studied the garden of the National Botanical Research Institute, Lucknow, India. It was found that the Ni concentration in the *Salix acmophylla* leaves was 2.86 mg·kg<sup>-1</sup> and was higher than what was recorded in our study. In Watson et al. (2003), two species of willow plants (*S. burjatica* and *S. triandra*) were studied to evaluate their resistance to heavy metals, the Ni concentration in the leaves was found to be between 5.9 and 9.3 mg·kg<sup>-1</sup>.

Jama-Rodzeńska and Nowak (2012) studied the Wastewater Treatment Plant Janówek near Wrocław, Poland to assess the capacity of the *Salix viminalis* as a Ni

accumulator. The concentration found in the *Salix* leaves was between 3.41 and 7.83 mg·kg<sup>-1</sup>. The ability of the willow plant to concentrate a number of heavy metals in its tissue may be due to the synthesis of phytochelatins, which act as chelators and are important for heavy metal detoxification (Mehrandish et al., 2019). The Ni concentrations of both studies were greater than the levels recorded in our study.

The Ni concentration in *Commelina benghalensis* was generally very low compared to that of *Salix babylonica* and *Paspalum urvillei*. The concentration of Ni with reaches in *C. benghalensis* leaves varied 0.01 mg·kg<sup>-1</sup> to 0.02 mg·kg<sup>-1</sup>. With seasons in the leaves of *C. benghalensis* the lowest value recorded in the autumn at 0.007 mg·kg<sup>-1</sup> and a significantly higher value was found in winter at 0.04 mg·kg<sup>-1</sup> (Tables 5.3 and 5.4). In the Nabulo et al. (2008) study that assessed heavy metal contamination in wetlands in the Lake Victoria Basin in Uganda, the Ni concentration in the leaves of *Commelina benghalensis* was found to be 16.3 mg·kg<sup>-1</sup>. This is much higher than the values recorded in our study in the Eerste River (Table 5.4).

Umoh et al. (2014) examined heavy metal levels in *Commelina benghalensis* as an indicator of heavy metal contamination around the Mobil terminal operation base South Eastern Niger Delta, Nigeria. The Ni concentration in the leaves *C. benghalensis* in the dry season was 150 mg·kg<sup>-1</sup> and in the wet season 30 mg·kg<sup>-1</sup>. This was contrary to our study, where the highest concentrations were recorded in the wet season. Their values were also much higher.

Azam et al. (2014) have recorded *Commelina benghalensis* as one of the plants that

survives in water bodies that receive many pollutants from many human activities in Hazaribagh, Dhaka, Bangladesh. It was concluded that *C. benghalensis* can be used for phytoremediation.

The Ni concentration in *Paspalum urvillei* leaves recorded the lowest concentrations after *Commelina benghalensis*. In the Eerste river catchment, the Ni concentration in *P. urvillei* leaves was highest at the lower reaches at 0.06 mg·kg<sup>-1</sup> and the lowest was at the upper reaches 0.001 mg·kg<sup>-1</sup>, where the Ni concentration in the leaves of the studied plants was generally lower. During the seasons, the highest Ni concentration in *P. urvillei* leaves was in the summer at 0.07 mg·kg<sup>-1</sup> and the lowest concentration in winter at 0.005 mg·kg<sup>-1</sup> (Tables 5.3 and 5.4). There were significant differences with both season and river reach.

No study was found on the Ni concentration in *Paspalum urvillei* leaves, but with *Paspalum distichum*, Bhattacharya et al. (2010) at the Sultanpur National Park in India, found that the Ni concentration was between 7.44 and 13.7 mg·kg<sup>-1</sup>, which is higher than the measurements recorded in our research. The Ni concentrations in *Persicaria lapathifolia* were the highest among the plants in this study, ranging from 0.55 to 4.79 mg·kg<sup>-1</sup>. No specific study was found to record any Ni concentration in the leaves of *Persicaria lapathifolia*.

However, the nickel concentration in *Polygonum aviculare* (same family) was found to be between 6.7 and 17 mg·kg<sup>-1</sup> in the samples taken from the city of Kraljevo which is located in the central part of Serbia (Radulović et al., 2014). Also, Khankhane and Varshney (2008) found at various sites of contaminated drainage in

Jabalpur, India, that the concentration of Ni in *Polygonum persicaria* was  $19 \text{ mg}\cdot\text{kg}\cdot\text{l}^{-1}$  due to pollution.

## 7.9 Zinc

The zinc (Zn) concentration in the Eerste River catchments recorded the highest value at the upper reaches  $1.33 \text{ mg}\cdot\text{l}^{-1}$  and the lowest at the lower reaches  $0.25 \text{ mg}\cdot\text{l}^{-1}$ . The highest values were recorded in autumn  $1.63 \text{ mg}\cdot\text{l}^{-1}$  and the lowest value in spring  $0.24 \text{ mg}\cdot\text{l}^{-1}$ . There were no significant differences in Zn value in water between river reaches, while there were significant differences with the seasons in the waters of the Eerste river catchment. In Ma's (2005) study, the concentration of Zn in the water of the Bottelary River, Western Cape, South Africa ranged from  $0.016$  to  $0.036 \text{ mg}\cdot\text{l}^{-1}$ . These values were lower than our study values. Jackson et al. (2009) determined the concentration of heavy metals in the Plankenburg and Diep Rivers, Western Cape, South Africa. It was found that the concentration of Zn in the water was between  $0.1$  and  $4.4 \text{ mg}\cdot\text{l}^{-1}$ . As for the Plankenburg, it was between  $0$  to  $1.1 \text{ mg}\cdot\text{l}^{-1}$ . The Plankenburg River values were lower than what was recorded in our study. In the Diep River, the higher values were higher than ours. In their study of the concentration of trace metals in the Berg River, Western Cape, South Africa, Jackson et al. (2007) found that the Zn concentration in the river water was between  $0.01$  to  $2.1 \text{ mg}\cdot\text{l}^{-1}$ , with values higher than what we recorded.

Shozi (2015) studied the distribution of heavy metals in the Msunduzi River Catchment, Kwazulu-Natal, South Africa, the Zn concentration in the waters was found between  $0.33$  to  $4.52 \text{ mg}\cdot\text{l}^{-1}$ . Edokpayi et al. (2016) found that the concentration of Zn in the river water was between  $0.001$  and  $0.54 \text{ mg}\cdot\text{l}^{-1}$  in the

Mvudi River, Limpopo Province North-Eastern part of South Africa. Based on the recommendations from Department Of Water Affairs And Forestry, the recommended maximum safe of Zn concentration in water is  $0.036 \text{ mg}\cdot\text{l}^{-1}$  (DWAF, 1996). However, in the Canadian Council of Ministers of the Environment Quality Guidelines Environmental quality guidelines as stipulated by (CCME) the Zn in water must be between  $0.002$  and  $0.004 \text{ mg}\cdot\text{l}^{-1}$  (CCME, 2002). The measurements founded in our study do not meet these conditions as well as the other studies mentioned in South Africa where the results of Zn concentration in water were beyond the recommended limits.

The highest concentration of Zn in soil in the area of the Eerste River catchment was  $4.02 \text{ mg}\cdot\text{kg}^{-1}$  in the upper reaches, the lowest was  $2.35 \text{ mg}\cdot\text{kg}^{-1}$  in the middle reaches. Within the seasons, the highest concentration of Zn in the soil was  $3.45 \text{ mg}\cdot\text{kg}^{-1}$  in winter, while the lowest in summer was  $2.31 \text{ mg}\cdot\text{kg}^{-1}$  (Tables 5.3 and 5.4). Zn concentrations in soil with reaches and seasons gave significant differences. The higher Zn levels at the upper reaches is due to the lower soil pH of 6.63 (Table 5.1), an inverse correlation where the decrease in soil pH leads to an increase in Zn in the soil (Kabata-Pendias and Pendias, 2001; Mccauley et al., 2017). The reason for the increase of Zn during the winter may be due to agricultural activities in the region due to the use of aerosol fertilizers used for agricultural crops during the winter (Niyigaba et al., 2019).

In a study aimed at measuring a number of trace metals in South African soil, where Herselman (2007) reported that there is a lack of Zn in the soil in most samples where 91% of the samples taken in the study had a concentration of Zn less than 1.5

mg·kg<sup>-1</sup>. The Jackson et al. (2007) study of the Berg River Western Cape, South Africa found the Zn concentration in the soil of the river had a wide range of 3.8 to 395 mg·kg<sup>-1</sup>. Edokpayi et al. (2016) found the concentration of Zn in Mvudi River, South Africa was 24.01 mg·kg<sup>-1</sup> in the wet seasons, while during the dry seasons 29.11 mg·kg, which was contrary to our study in terms of Zn concentrations were larger than what we found and we recorded the highest value in wet seasons.

The largest sources of soil contamination with Zn are human activities, with the concentration of Zn in the soil at a mining site near Pretoria at 7,300 mg·kg<sup>-1</sup> (Oyourou et al., 2019). At the municipal sewage treatment plant in the village of Blowie, Poland, the highest concentration of Zn was found in treated sludge 293.3 mg·kg<sup>-1</sup> (Zubala et al., 2017). According to the guidelines of the Department of National Health and Population Development, Pretoria, South Africa (DoH, 1991), the Zn concentration in soil should not exceed 185 mg·kg<sup>-1</sup>. According to the Australian and New Zealand guidelines for the assessment and management of contaminated sites (1992), the soil Zn concentration should not exceed 200 mg·kg<sup>-1</sup>. Our values were well below these levels. The concentration of Zn in *Salix babylonica* in the area of the Eerste River catchment with river reaches recorded the highest values at the lower reaches 0.86 mg·kg<sup>-1</sup> and the lowest in the middle reaches 0.75 mg·kg<sup>-1</sup>. While within the seasons the highest values were in the autumn 1.03 mg·kg<sup>-1</sup> and the lowest in the summer 0.61 mg·kg<sup>-1</sup> (Tables 5.3 and 5.4). It gave significant differences with river reaches and no significant differences were recorded with the seasons.

Zn concentration in willow species measured by Dos Santos Utmazian and Wenzel

(2007) in a metal smelting area in Anoldstein (Carinthia, Austria) was found to be 240 mg·kg<sup>-1</sup> in the *Salix babylonica* when the Zn concentration in soil was 220 mg·kg<sup>-1</sup>. When the soil was 1710 mg·kg<sup>-1</sup> the Zn concentration in *S. babylonica* was 640 mg·kg<sup>-1</sup>. These measurements were higher than what we found in our study in the *S. babylonica* leaves and in the soil as well.

Keller et al. (2003) studied Zn concentration in the stem and root of *Salix viminalis* in India and found that the Zn concentration in the roots was below the detection limit. As for the stem, Zn concentration was between 240 to 294 mg·kg<sup>-1</sup>. According to Kuzovkina and Quigley (2005), *Salix* species are suitable as a bio-accumulator for heavy metals and Zn. The concentration of Zn in the leaves of *Commelina benghalensis* in the area of the Eerste River catchment with river reaches recorded the highest values in the middle reaches 0.75 mg·kg<sup>-1</sup> and the lowest at the upper reaches 0.56 mg·kg<sup>-1</sup>. While with the seasons the highest values in spring were 0.77 mg·kg<sup>-1</sup> and the lowest in summer 0.61 mg·kg<sup>-1</sup> (Tables 5.3 and 5.4). There were no significant differences with river levels and seasons.

In a study of invasive plant species in the Eastern Nile Delta in Ismailia Governorate in Egypt, *Commelina benghalensis* was examined by El-Hamid and El Bous (2019), they found that the Zn concentration in *C. benghalensis* was 46 mg·kg<sup>-1</sup>. Their measurements were much larger than ours. That may be due to the agricultural and industrial waste dumped in the Eastern Nile Delta.

Mahadkar et al. (2012) in Kolhapur, India, studied the nutritional evaluation of some edible wild plants as a source of minerals, including *Commelina benghalensis*, where



the Zn concentration was  $0.268 \text{ mg}\cdot\text{kg}^{-1}$  and was lower than our recorded values. In the study of *Commelina benghalensis* as an indicator of heavy metal contamination by Umoh et al. (2014) along Mobil Terminal Operational Base, Delta Niger in Nigeria, found the Zn concentration in the *Commelina benghalensis* leaves to be  $0.0019 \text{ mg}\cdot\text{kg}^{-1}$ , which is lower than our measurements. The concentration of Zn in *Paspalum urvillei* leaves yielded the highest values at lower reaches  $0.56 \text{ mg}\cdot\text{kg}^{-1}$ , and the lowest was at the upper reaches  $0.11 \text{ mg}\cdot\text{kg}^{-1}$ . Within the seasons, the highest values in spring were  $0.77 \text{ mg}\cdot\text{kg}^{-1}$  and the lowest was in winter  $0.57 \text{ mg}\cdot\text{kg}^{-1}$  (Tables 5.3 and 5.4), with significant differences with river reaches and seasons.

In a study to attempt to rehabilitate the New Union Gold Mine in Limpopo, South Africa, Mulugisi et al. (2009) found that the Zn concentration in *Paspalum dilatatum* was between  $17$  and  $47 \text{ mg}\cdot\text{kg}^{-1}$ , which was higher than our value. That may be due to the growth of *P. dilatatum* in mine contaminated grounds. Mulugisi et al. (2009), studied the accumulation of Zn for several plant species in the contaminated sites in Esteiro de Estarreja, in Portugal. They found that the concentration of Zn in the roots and stem *Paspalum urvillei* was  $199$ - $299 \text{ mg}\cdot\text{kg}^{-1}$  respectively.

The highest values of Zn concentration in *Persicaria lapathifolia* in the Eerste River catchments with river reaches gave the highest values among all the studied plant species. The highest values were  $1.4 \text{ mg}\cdot\text{kg}^{-1}$  at the upper reaches. The lowest was  $1.08 \text{ mg}\cdot\text{kg}^{-1}$  at the middle reaches. The values in summer were  $1.21 \text{ mg}\cdot\text{kg}^{-1}$  and the lowest in autumn was  $0.98 \text{ mg}\cdot\text{kg}^{-1}$  (Tables 5.3 and 5.4) and did not give any significant differences with river levels and seasons.

In a study of different sanitation sites in Jabalpur, India, Khankhane and Varshney (2008) found that Zn concentration in *Polygonum persicaria* was  $2.65 \text{ mg}\cdot\text{kg}^{-1}$  and was higher than our measurements due to plant growth in areas that were contaminated. Hao and Jiang (2015) also studied the concentration of heavy metals in soil and plants in the Mine of Chongqing, Southwest of China. It was found that the concentration of Zn in *Polygonum lapathifolium* root was  $46.94 \text{ mg}\cdot\text{kg}^{-1}$  and in the stem  $26.19 \text{ mg}\cdot\text{kg}^{-1}$ . These values were much bigger than our value. This might be due to the contaminated area of mining activities.

### 7.10 Copper

The copper (Cu) concentration in the water of the Eerste River was highest in the middle reaches at  $2.09 \text{ mg}\cdot\text{l}^{-1}$  and lowest in the upper reaches at  $0.65 \text{ mg}\cdot\text{l}^{-1}$ . For the seasons, the highest value was recorded in winter at  $2.32 \text{ mg}\cdot\text{l}^{-1}$  and the lowest value in spring was  $1.37 \text{ mg}\cdot\text{l}^{-1}$  (Tables 5.3 and 5.4), giving significant differences with both seasons and river reaches. The higher Cu concentration in the middle and lower reaches may be due to the increased use of fungicides, especially in viticulture, which is consistent and aligns with Kovačič et al. (2013). As for the Cu concentration in winter may be due to increased Cu runoff from the surrounding environment to the river water. In Ma's (2005) study on the Bottelary River in Cape Town, South Africa, the Cu concentration in the River water was between  $0.013$  and  $0.031 \text{ mg}\cdot\text{l}^{-1}$ . In Shoji. (2015) study to assess the distribution of heavy metals in the Msunduzi River Catchment in KwaZulu-Natal, South Africa the Cu concentration in the river water varied from below the detection limits to  $0.059 \text{ mg}\cdot\text{l}^{-1}$ . These results were much lower than the findings of our study.

Jackson et al. (2009) determined the concentration of heavy metals in the Plankenburg and Diep Rivers, Western Cape, South Africa. The Cu concentration in the Diep River water was between 0.1 and 0.6 mg·l<sup>-1</sup>, while in the Plankenburg River it was between 0.4 and 2.2 mg·l<sup>-1</sup>. These results are comparable to those obtained in our study. Jackson et al. (2007) also found in their study of the concentration of heavy metals in Berg River, Western Cape, South Africa, that the Cu concentration in the river water was between 0 to 2.2 mg·l<sup>-1</sup>. Again the results of our study were comparable to those of Jackson et al. (2007 and 2009).

Edokpayi et al. (2016) studied the Mvudi River Limpopo Province in the north-eastern part of South Africa. They found that the Cu concentration in the river water was between 0.024 and 0.185 mg·l<sup>-1</sup>. These results were below the thresholds in our study. Based on the recommendations of DWAF (1996), the recommended maximum Cu concentration in water is between 0.002 to 0.012 mg·l<sup>-1</sup>. As for the recommendations of the Environmental Quality Guidelines, the Canadian Council of Ministers Guidelines for Environmental Quality Concentration (CCME, 2002) Cu in water should be between 0.002 and 0.004 mg·l<sup>-1</sup>. The measurements found in our study do not meet these conditions as well as the studies mentioned in South Africa where the results of Cu concentration in water were beyond the recommended limits. The concentration of Cu in soil in the Eerste River catchment ranged from 2.93 to 3.3 mg·kg<sup>-1</sup> and with seasons ranged from 2.65 to 3.8 mg·kg<sup>-1</sup> (Table 5.3 and 5.4). In the Herselman. (2007) study of heavy metals concentration in soils in South Africa, the Cu concentration in South African soil was often between 0.44 and 20.4 mg·kg<sup>-1</sup>.

There were specific areas indicated in the study which lacked Cu in the soil, including the Western Cape area. Awofolu et al. (2005), found the Cu concentration in the Tyume River substrate, South Africa was between 0.082 and 0.49 mg·kg<sup>-1</sup> and these values were lower than the concentrations found in our study.

In the Olowoyo et al. (2012) study at the waste dumpsite of the University of Limpopo, Medunsa Campus, Pretoria, it was found that the concentration of Cu in the soil was between 17.25 and 18.57 mg·kg<sup>-1</sup>. These values are much higher than the concentrations obtained in our study because the samples in the Olowoyo et al. (2012) study were taken from a waste-contaminated site. In the soil of Vaal Dam in South Africa, Retief et al. (2009) found that Cu concentration was between 1.31 and 11.07 mg·kg<sup>-1</sup> and that the highest values were recorded in summer.

The allowable values for soil Cu concentrations in South Africa differed; According to the Ministry of National Health and Population Development (DoH, 1991), the highest Cu concentration in South African soil must be 100 mg·kg<sup>-1</sup>. According to the Water Research Commission in Pretoria, South Africa (WRC, 1997), the highest permissible concentration must be 6.6 mg·kg<sup>-1</sup>.

The concentration of Cu in the *Salix babylonica* leaves gave the highest concentrations among plant species in this study. With the seasons there is significant differences. The Cu concentration in the leaves were as follows: the highest was in winter at 3.93 mg·kg<sup>-1</sup> and the lowest in spring at 0.3 mg·kg<sup>-1</sup> (Tables 5.3 and 5.4).

Ali et al. (2003) examined the possibility of using *Salix acmophylla* as an

accumulator of heavy metals for phytoremediation. They found that the Cu concentration in *Salix acmophylla* leaves was between 0.002 and 0.126 mg·kg<sup>-1</sup>. Kuzovkina et al. (2004) selected five *Salix* species (*S. lucida* Muhl, *S. eriocephala* Michx., *S. nigra* Marsh., *S. exigua* Nutt and *S. discolor* Muhl) and used them for phytoremediation. The Cu concentration in the stem and roots of the *Salix* species was found to be between 2.5 and 25 mg·kg<sup>-1</sup>. Kuzovkina and Quigley (2005) also emphasized the importance of *Salix* species in previous studies to address degraded environments and especially wetlands. *Salix* species were considered to be a promising resource for alleviating the effects of environmental degradation and of use for remediation projects.

The concentration of Cu in the leaves of *Commelina benghalensis* ranged from 0.22 to 0.33 mg·kg<sup>-1</sup> (Table 5.3 and 5.4). Mahadkar et al. (2012) ran an evaluation study of some edible wild plants in India, including *Commelina benghalensis* and its potential to provide some minerals to humans. The Cu concentration in the leaves of *Commelina benghalensis* was 0.27 mg·kg<sup>-1</sup>. These measurements were within the scope of our study. A study of the biological Flora of Egypt by El-Hamid and El Bous (2019) including some invasive plants, found a Cu concentration of 4 mg·kg<sup>-1</sup> in *Commelina benghalensis*.

In a study of different contaminated drain sites of Jabalpur, India, Khankhane and Varshney (2008), found that the Cu concentration in *Commelina communis* was 30 mg·kg<sup>-1</sup>. The results of the previous two studies are greater than the values recorded in our study and that may be due to the large number of human activities in India and Egypt because of the high population density. The concentration of Cu in the

*Paspalum urvillei* was highest in the middle reaches at  $0.15 \text{ mg}\cdot\text{kg}^{-1}$  and the lowest at the upper reaches at  $0.04 \text{ mg}\cdot\text{kg}^{-1}$ . (Tables 5.3 and 5.4). There were significant differences between river reaches. The overall range was from  $0.17$  to  $0.03 \text{ mg}\cdot\text{kg}^{-1}$ .

A study of mine rehabilitation around the New Union Gold Mine in Limpopo, South Africa by Mulugisi et al. (2009), examined, the accumulation of heavy metals in five grass species. It was found that the Cu concentration in *Paspalum dilatatum* leaves was between  $17$  and  $47 \text{ mg}\cdot\text{kg}^{-1}$ . These values were significantly higher than our results. This may be due to the growth of *Paspalum dilatatum* in soil contaminated by mining activities. In the Shu et al. (2002) study in Guangdong Province China, in the Fankou and Lechang mines to verify heavy metals contamination in soil and dominant plants in the region, the Cu concentration in the shoots and roots of *Paspalum distichum* was between  $8.79$  and  $32.27 \text{ mg}\cdot\text{kg}^{-1}$ . These values are greater than what we found in *P. urvillei* leaves in this study.

Ying et al. (2008) studied grass tolerances of different concentrations of heavy metals in different mine locations in southern China. They found that the concentration of Cu in *Paspalum notatum* for all sites ranged from  $18.2$  to  $65.3 \text{ mg}\cdot\text{kg}^{-1}$ . The concentration of Cu in the leaves of *Persicaria lapathifolia* varied significantly with the seasons. The highest concentration was found in winter at  $0.29 \text{ mg}\cdot\text{kg}^{-1}$  and the lowest in summer  $0.16 \text{ mg}\cdot\text{kg}^{-1}$  (Tables 5.3 and 5.4), there were significant differences during the seasons. The overall range was from  $0.16$  to  $0.31 \text{ mg}\cdot\text{kg}^{-1}$ .

In a study of different contaminated drain sites of Jabalpur, India, Khankhane and

Varshney (2008) found that the Cu concentration in *Persicaria lapathifolia* was 37 mg·kg<sup>-1</sup>. The results of the previous study are greater than the values recorded in our study and may be due to the human activities in India because of the high population density. The concentration of Cu in *Polygonum aviculare* (family of *Polygonaceae*) was found to be 4.5 to 8.6 mg·kg<sup>-1</sup> in samples taken from the City of Kraljevo located in the central part of Serbia. That may be due to the traffic around the area, Cu is released from car tires and brakes (Kole et al., 2017). The results recorded in the two studies were larger than the results obtained in our study.

### 7.11 Cadmium

The concentration of cadmium (Cd) in the water of the Eerste River catchment ranged from 0.25 to 0.99 mg·l<sup>-1</sup> (Tables 5.3 and 5.4). In the Ma (2005) the study of the concentration of Cd in the waters of the Bottelary River in the Western Cape, South Africa, was between 0.0005 and 0.003 mg·l<sup>-1</sup>. These results are much lower than we found in our study.

Edokpayi et al. (2016) study in the Mvudi River Limpopo Province, north-eastern part of South Africa, found that the concentration of Cd in river water was between 0.0003 to 0.001 mg·l<sup>-1</sup>. Olujimi et al. (2015) studied the variation in levels of heavy metals in river water which receives wastewater in Cape Town, South Africa. It was found that the concentration of Cd in the water of the studied rivers was between 0.00009 to 0.014 mg·l<sup>-1</sup>. Fatoki et al. (2004) studied the concentration of Cd in the Umtata River which rises in the plateau region of the Eastern Cape and its impact on local rural communities. They found that the concentration of Cd in the water ranged between 0.002 and 0.007 mg·l<sup>-1</sup> these results were lower than what we found in our

study.

Based on recommendations from DWAF (1993), the recommended maximum safe Cd concentration in water is between 0 and 0.005 mg·l<sup>-1</sup>. The measurements in our study were much higher than the maximum and do not meet these conditions. As for the studies mentioned in South Africa, the results of the concentration of Cd in water were within the recommended limits.

In Eerste River, the highest Cd concentration was in the soil of the lower reaches at 2.66 mg·kg<sup>-1</sup>, while the lowest concentration was 1.13 mg·kg<sup>-1</sup> in the upper reaches. The highest Cd concentration in autumn was 2.98 mg·kg<sup>-1</sup>, while the lowest concentration in winter was 0.95 mg·kg<sup>-1</sup> (Tables 5.3 and 5.4). There were significant differences with river reaches and seasons. May be caused by the lack of rain, which causes low flow of water and the accumulation of pollutants.

In Herselman's (2007) study of heavy metals concentration in South Africa, the concentration of Cd in South African soil was often between 0.001 and 0.06 mg·kg<sup>-1</sup>. In Shamuyarira and Gumbo's (2018) study to assess trace minerals in wastewater and sludge in Limpopo Province, South Africa, the concentration of Cd in river soils receiving treated wastewater was found to be between 0.021 and 0.022 mg·kg<sup>-1</sup>. Awofolu et al. (2005) found that the concentration of Cd in the soil of the Tyume River, South Africa was between 0.002 and 0.007 mg·kg<sup>-1</sup>. The values of these studies were lower than the concentrations in our study. Retief et al. (2009) found in Vaal Dam substrate in South Africa to contain between 0 and 0.293 mg·kg<sup>-1</sup> of Cd. The values were lower than our study. On the other hand, the highest values were



recorded in autumn and winter, which is consistent with what we found in our research where the highest values were recorded in autumn and winter. The concentration of Cd in the leaves of *Salix babylonica* with the reaches was between below detection level (ND) and 0.84 mg·kg<sup>-1</sup>. During the seasons, it was between ND and 0.96 mg·kg<sup>-1</sup> (Tables 5.3 and 5.4).

Concentrations of Cd in the *Salix babylonica* leaves were found by Dos Santos Utmazian and Wenzel (2007) in the metal smelting area of Anoldstein, Carinthia, Austria, where the Cd concentration in the *S. babylonica* leaves was 83.8 mg·kg<sup>-1</sup> when the Cd concentration in the soil was 32.7 mg·kg<sup>-1</sup>, and the Cd concentration in the *S. babylonica* was 17.4 mg·kg<sup>-1</sup> when the Cd concentration in the soil was 4.34 mg·kg<sup>-1</sup>, these concentrations of Cd were greater than what we recorded in our study in the *S. babylonica* leaves and soil.

McBride et al. (2016) conducted a study on the accumulation of heavy metals in the leaves of 14 species of willow cultivated in a hydroponic manner, with the highest concentration of Cd in willow species 70 mg·kg<sup>-1</sup> with no toxic symptoms on plants, these measurements were higher than what we found in our study because they deliberately add a higher concentration of Cd to the water in their experiments.

Kuzovkina et al. (2004) selected five types of *Salix* and used it as phytoremediation. The concentration of Cd in the stem and roots of the *Salix* plant was between 18.3 and 181 mg·kg<sup>-1</sup>, higher than our findings. Kuzovkina and Quigley (2005) also emphasized the importance of *Salix* species in previous studies to address degraded environments and especially wetlands.

The concentrations of Cd in the leaves of *Commelina benghalensis* was the lowest in the studied plant species, between ND and  $0.24 \text{ mg}\cdot\text{kg}^{-1}$  (Tables 5.3 and 5.4). Sekabira et al. (2011) used *Commelina benghalensis* as a heavy-metals monitor for urban drainage in the Nakivubo channel, Kampala city in Uganda. The concentration of Cd in the leaves of *Commelina benghalensis* was between  $0.66$  and  $1.1 \text{ mg}\cdot\text{kg}^{-1}$ . These results were slightly higher than what we found in our study, which may be due to the fact that the Nakivubo channel is the main recipient of organic and liquid waste from the streets and suburbs of Kampala.

Jha et al. (2016) studied the accumulation of heavy metals in some wetland plants in the city of Kolkata in India. It was found that the concentration of Cd in the stem and root of *Commelina benghalensis* was  $17.74$  and  $60.16 \text{ mg}\cdot\text{kg}^{-1}$ , respectively. These results were higher than what we found in our study probably due to the increase of human activities in the city of Kolkata in India, and the not being the primary site of uptake.

Mganga et al. (2011) studied the plants growing around the North Mara Gold Mine, Tanzania. They classified them according to their heavy metals content and the possibility of using them for phytoremediation. It was found that the concentration of Cd in *Commelina benghalensis* shoots was  $30 \text{ mg}\cdot\text{kg}^{-1}$  and in the roots  $19 \text{ mg}\cdot\text{kg}^{-1}$  when it was  $19 \text{ mg}\cdot\text{kg}^{-1}$  in the soil. These measurements were higher than what we found in our study in the leaves of *C. benghalensis* and in soil. The reason may be that *C. benghalensis* in the study of Mganga is growing around the area of mining activities. The concentration of Cd in *Paspalum urvillei* leaves with river reaches recorded the highest concentration at the lower reaches  $2.8 \text{ mg}\cdot\text{kg}^{-1}$  while the lowest

concentration was at the upper reaches  $0.19 \text{ mg}\cdot\text{kg}^{-1}$ . With the seasons, the highest concentration in autumn was  $3.15 \text{ mg}\cdot\text{kg}^{-1}$ . The lowest concentration in spring was  $0.31 \text{ mg}\cdot\text{kg}^{-1}$  (Tables 5.3 and 5.4). There were significant differences with river reaches and seasons.

In a study of mine land rehabilitation around the New Union Gold Mine in Limpopo, South Africa by Mulugisi et al. (2009) and the accumulation of heavy metals in five grass species, it was found that the Cd concentration in *Paspalum dilatatum* leaves was  $1 \text{ mg}\cdot\text{kg}^{-1}$ . These results were in the range of our results.

Sa'idu et al. (2013) examined a heavy metal analysis in *Paspalum orbiculare* and soil along the major highways in Kano, Nigeria, where the concentration of Cd was between  $0.12$  and  $0.19 \text{ mg}\cdot\text{kg}^{-1}$  in leaves, and in the soil was between  $0.18$  and  $0.25 \text{ mg}\cdot\text{kg}^{-1}$ . These results were in the range of our results of the concentration of Cd in the *Paspalum urvillei* as well as in the soil. The concentration of Cd in the leaves of *Persicaria lapathifolia* was with river reaches between  $0.71$  and  $1.36 \text{ mg}\cdot\text{kg}^{-1}$ .

During the seasons, it was between  $0.37$  and  $1.05 \text{ mg}\cdot\text{kg}^{-1}$  (Tables 5.3 and 5.4). Hao and Jiang (2015) studied the concentration of heavy metals in soil and vegetation around the Mine of Chongqing, Southwest of China. It was found that the concentration of Cd in the roots of *Polygonum persicaria*  $0.42 \text{ mg}\cdot\text{kg}^{-1}$  in the shoot  $0.94 \text{ mg}\cdot\text{kg}^{-1}$ . These values were lower than the values recorded in our study in the leaves of *Persicaria lapathifolia*. In Malinowska and Jankowski (2016) study of the effect of agrochemicals on the accumulation of heavy metals in the grass that grow on the edges of crop fields in farms located in Siedlce County in the east-central part

of Poland, the concentration of Cd in *Polygonum persicaria* was 0.25 mg·kg<sup>-1</sup>. These measurements are less than what we got in our study. Vimala et al. (2011) studied the evaluation of antioxidant plants in traditional Malaysian medicine and they are free of heavy metals. The leaves of the *Persicaria minor* (Huds), which is from the same family of *Persicaria lapathifolia*, was found to be free of cadmium.

## 7.12 Lead

There were no differences in the lead (Pb) concentration in the water along the river. However, with seasons, the lowest concentration of Pb in the water was in winter at 1.07 mg·l<sup>-1</sup>. The highest concentration occurred in summer at 2.49 mg·l<sup>-1</sup> (Tables 5.3 and 5.4). These were significant. The Pb in water comes from natural and industrial sources, but the most important sources are usually industrial from leachates, roads, car exhausts and other activities (Garbarino et al., 1995; Varkouhi, 2009). Edokpayi et al. (2016) in the Mavudi River in North-Eastern Limpopo Province found that the concentration of Pb in river water was between 0.002 and 0.042 mg·l<sup>-1</sup>.

In Shози's (2015) study to assess the distribution of heavy metals in Msunduzi River Catchment in KwaZulu-Natal, South Africa, the highest Pb concentration in river water was found to be 0.0045 mg·l<sup>-1</sup>, and these results were significantly lower than in our study. In Ma (2005), study on the Bottelary River in Cape Town, South Africa, the concentration of Pb in river water was below detection limits.

Based on the recommendations from DWAF (1993), the maximum recommended safe Pb concentration in water is between 0.001 to 0.2 mg·l<sup>-1</sup>. Pb in water according to Environmental quality guidelines as stipulated by CCME (2002) should be

between 0.001 to 0.007 mg·l<sup>-1</sup> (CCME, 2002). The measurements in our study do not meet these conditions as Pb concentrations in the water of the Eerste River were outside the recommended limits. It may be due to the increase in human activities in the area from the acceleration of urbanization and the proximity of the river course often to the traffic area, thus being affected by car exhausts. This was in align with Mombeshora et al. (1983) studied on water bodies in Nigeria and along the Ona River, where he found an increase in lead concentration around heavy traffic areas.

The Pb concentration in soil in the Eerste River catchment ranged from 2.57 to 3.24 mg·kg<sup>-1</sup> (Table 5.3 and 5.4). In Herselman's (2007) study of the heavy metals concentration in South Africa soils, the Pb concentration in South African soil was often between 0.3 and 15.7 mg·kg<sup>-1</sup>. In the Shamuyarira and Gumbo (2018), study to assess trace metals in wastewater and sludge in Limpopo Province, South Africa, the Pb concentration in river soil receiving treated wastewater was found to be between 0.42 and 30.05 mg·kg<sup>-1</sup>. The results of our study were within the range of the previous two studies. Awofolu et al. (2005) found the Pb concentration in the soil of the Tyume River in South Africa was between 0.04 and 0.067 mg·kg<sup>-1</sup> and these values were lower than the concentrations found in our study.

Olowoyo et al. (2012) studied a dumpsite of the University of Limpopo, Medunsa Campus, Pretoria. It was found that the concentration of Pb in soil was between 9.92 and 11.62 mg·kg<sup>-1</sup>. These values are much higher than the concentrations obtained in our study because the samples in Olowoyo study were taken from a waste-contaminated site. In Vaal Dam soil in South Africa, Retief et al. (2009) found that Pb concentration was between 0.001 and 0.025 mg·kg<sup>-1</sup> and that the highest values

were recorded in summer. This is partly consistent with what we found in our research, where the highest values were recorded in autumn and summer (i.e. dry seasons). Maybe caused by the lack of rain, which causes semi-stagnation of water and the accumulation of pollutants in the soil.

The allowable values of Pb concentration in agricultural soil in South Africa differed; according to the guidelines of the DoH, the highest Pb concentration allowed in South African soil was 56 mg·kg<sup>-1</sup> (DoH, 1991). Whereas, according to the WRC, Pretoria, Pb concentration allowed in South African is 6.6 mg·kg<sup>-1</sup> (WRC, 1997). Overall, the results of our study were within the limits allowed in both cases.

The Pb concentrations in the leaves of *Salix babylonica* recorded the highest concentrations of the plant species studied in this study, with the highest concentration at the lower reaches 2.42 mg·kg<sup>-1</sup> and the lowest was below the detection limits at the upper reaches. During the seasons, the values of Pb concentration in the leaves of *Salix babylonica* gave the highest values in autumn at 2.67 mg·kg<sup>-1</sup> and the lowest in winter was 0.28 mg·kg<sup>-1</sup> (Table 5.3 and 5.4). The measurements were significant with both reaches and seasons.

In Kaplan et al. (2009) in Zonguldak, Turkey studied the concentration of trace metals in unwashed leaves of some trees. It was found that the Pb concentration in *Salix babylonica* leaves was between 4 and 5.65 mg·kg<sup>-1</sup>. These results were generally higher than the results obtained in our study. The leaves collected in Kaplan et al. (2009) were unwashed and the sampling sites were in areas with high traffic density leading to increased pollution of those areas.

Jama-Rodzeńska and Nowak (2012) studied the Wastewater Treatment Plant Janówek near Wrocław, Poland to assess the capacity of *Salix viminalis* as a bio-accumulator for Pb. The concentration of Pb in *Salix* leaves was between 7.8 and 12.6 mg·kg<sup>-1</sup>. In a sewage-contaminated area, Kuzovkina and Quigley (2005) found that the *Salix* species serve as bio-accumulators for heavy metals, including Pb.

Ali et al. (2003) examined the garden of the National Botanical Research Institute, Lucknow, India the lead concentration in the *Salix acmophylla* leaves was found to be between 0.001 and 0.18 mg·kg<sup>-1</sup>. Watson et al. (2003) studied two species of willow plant *Salix burjatica* and *S. triandra x viminalis*) to assess its resistance to heavy metals, the Pb concentration in leaves was found to be between 0.081 and 0.21 mg·kg<sup>-1</sup>. The results of the previous two studies were lower than those recorded in our study.

The concentration of Pb in the leaves of *Commelina benghalensis* at all river reaches equal to 0.01 mg·kg<sup>-1</sup>. During the seasons, the values of Pb concentration in the leaves *Commelina benghalensis* gave the lowest in summer, 0.004 mg·kg<sup>-1</sup> and the highest in winter and autumn was 0.01 mg·kg<sup>-1</sup> (Table 5.3 and 5.4). The measurements gave significant values with reaches and seasons. In the Kisku et al (2000) study at the Kalipur site in India, the concentration of Pb in *Commelina benghalensis* was 0.092 mg·kg<sup>-1</sup> when it was 0.11 mg·kg<sup>-1</sup> in the soil. These results were greater than we found in our study because water is contaminated with industrial wastewater in their region.

Sekabira et al. (2011) used *Commelina benghalensis* for phytoremediation of heavy

metals in urban sewage at the Nakivubo channel, Kampala city in Uganda. They found the concentration of Pb in *Commelina benghalensis* leaves was between 13.0 and 16.72 mg·kg<sup>-1</sup>. These results were higher than what we found in our study may be due to the reason that Nakivubo channel is the main receptance of organic waste and industrial liquid from the streets and suburbs of Kampala. In the Jha et al. (2016) study of the accumulation of heavy metals in some wetland plants in the city of Kolkata, India, the concentration of Pb in the stem and root of *Commelina benghalensis* was 17.74 and 60.16 mg·kg<sup>-1</sup>, respectively. These results were higher than we found in our study of human activities in the city of Kolkata in India, and the fact that Pb tends to accumulate in roots.

In study of heavy metals levels, *Commelina benghalensis* was used as an indicator of heavy metals pollution at the Mobil Oil Plant in the southeast of the Niger Delta, Nigeria. The concentration of Pb in leaves was 950 mg·kg<sup>-1</sup> in the dry season, 380 mg·kg<sup>-1</sup> in the wet seasons (Umoh et al., 2014). These values were high in the wet season which contradicts with our study, and concentrations were higher than we recorded. The concentration of Pb in *Paspalum urvillei* leaves ranged from 0.004 to 0.01 mg·kg<sup>-1</sup>. Throughout the seasons, the concentration values of Pb in the leaves of *Paspalum urvillei* varied significantly; the least was in winter (0.005 mg·kg<sup>-1</sup>) and the highest was in spring and autumn (0.01 mg·kg<sup>-1</sup>) (Table 5.3 and 5.4).

Sa'idu et al. (2013) examined heavy metals in *Paspalum urvillei* along major highways in Kano, Nigeria, where the Pb concentration was found to be between 9 and 12.2 mg·kg<sup>-1</sup>, when the concentration in the soil was between 7.8 and 13.8 mg·kg<sup>-1</sup>. These results were significantly higher than we found. In a study of mine



land rehabilitation around the New Union Gold Mine in Limpopo South Africa by Mulugisi et al. (2009) and the accumulation of heavy metals in five grass species, it was found that the Pb concentration in *Paspalum dilatatum* leaves was 4.2 mg·kg<sup>-1</sup>. These values were larger than the results obtained in our study for the Pb concentration in the *Paspalum urvillei*.

In the work of Shu et al. (2002) in Guangdong Province, China (Fankou and Lechang mines) on metal contamination in the soil and plants in the region, the Pb concentration in *Paspalum distichum* was between 15.24 and 705.5 mg·kg<sup>-1</sup> in the stem and was between 26.08 and 1899.07 mg·kg<sup>-1</sup> in the root. These values are much higher than what we found in the *Paspalum urvillei* leaves in this study because the study of Shu et al. (2002) was in areas of mining activities, and analysed stem and roots.

The concentration of Pb in the leaves of *Persicaria lapathifolia* was between 0.004 and 0.02 mg·kg<sup>-1</sup> (Tables 5.3 and 5.4). Vimala et al. (2011) studied the evaluation of antioxidant plants in traditional Malaysian medicine and if they were free of heavy metals. The leaves of *Persicaria minor* (Huds), one of the species of the same family of *Persicaria lapathifolia* were found to be relatively Pb free. In the Malinowska and Jankowski (2016) study of the effect of agrochemicals on the accumulation of heavy metals in weeds that grow on the edges of crop fields in farms located in Siedlce County in the central eastern part of Poland, the Pb concentration in *Polygonum persicaria* was found to be 2.05 mg·kg<sup>-1</sup>. These measurements are higher than what we found in our study and may be due to agricultural activities in the crop growing area. Hao and Jiang (2015) studied the concentration of heavy metals in the soil and

plants around the Chongqing Mine in southwest China.

It was found that the concentration of lead in the roots of *Polygonum lapathifolium* was  $4.01 \text{ mg}\cdot\text{kg}^{-1}$  and in the stem,  $3.9 \text{ mg}\cdot\text{kg}^{-1}$ . These values were higher than the values recorded in our study in the *Persicaria lapathifolia* leaves due to mining activity in Chongqing Mine. The Pb concentration in *Polygonum aviculare* was found to be between 0 and  $17.7 \text{ mg}\cdot\text{kg}^{-1}$  in the samples taken from Kraljevo in the central part of Serbia. This may be due to traffic density in this area because the highest values were recorded near the Ibar Highway (Radulović et al., 2014).

### **7.13 The Relationship Between the Various Measured Parameters and the Various River Reaches and Seasons**

#### **7.13.1 Nitrite, Nitrate and Ammonium**

The first part we applied the Correlation matrix depicting Spearman's simple linear correlation coefficient ( $r$ ) amongst all the investigated parameters in water samples, the levels of significance  $p < 0.01$  and  $p < 0.05$  (Table 5.6).

Nitrite ( $\text{NO}_2^-$ ) measurements in the water had a positive relationship with seasons ( $p < 0.05$ ) (Table 5.6). Rantanen et al (2018) also recorded in their study of seasonal concentrations of  $\text{NO}_2^-$  in the drinking water distribution system in the capital Helsinki, Finland, with a positive relationship between the seasons and the  $\text{NO}_2^-$  concentration.

There is also a strong positive relationship between  $\text{NO}_2^-$  concentration and temperature. In our study, the higher the temperature, the greater the concentration of

$\text{NO}_2^-$  in the water of the river, as well as the relationship with electrical conductivity EC (Table 5.1). The presence of ions in the water more, including  $\text{NO}_2^-$ , increases the EC in the water (Shabalala et al., 2013).

Thus, the relationship between  $\text{NO}_2^-$  and the temperature, conductivity, and Calcium concentration in the river water was positive and strong ( $p < 0.01$ ) (Table 5.6). Vadde et al. (2018) assessed water quality and determined the risks of pollution of the Tiaoxi River in China, they found a positive relationship between the concentration of  $\text{NO}_2^-$  in river water and the EC.

A strong negative relationship ( $p < 0.01$ ) was found between the concentration of  $\text{NO}_2^-$  and dissolved oxygen (DO) in river water (Table 5.6). The higher the  $\text{NO}_2^-$  values, the lower the DO concentration (Table 5.1). (Gómez et al., 2002) found a negative effect of dissolved oxygen increase when using water oxygen filters on  $\text{NO}_2^-$  concentration. Increasing the bioactivity in the water by living organism leads to an increase in  $\text{NO}_2^-$ , and DO consumption in the water (Larsen et al., 2010).

Nitrate ( $\text{NO}_3^-$ ) measurements in the water had a strong positive relationship with the river reaches ( $p < 0.01$ ) (Table 5.6). The  $\text{NO}_3^-$  concentration in the upper reaches was below the detection limit (ND) and increased in the middle and lower reaches of the river in the presence of human activities in general and agricultural in particular with the use of fertilizers. Neal et al. (2006) studied the Thames and its tributaries,  $\text{NO}_3^-$  concentrations were much lower at the upper reaches than at the lower reaches, and the reason was often due to Nitrate sources from agricultural activities were more at the upper reaches.

A strong positive relationship was between found nitrates and both the electrical conductivity (EC) and the concentration of Ca ( $p < 0.01$ ) (Table 5.6). Bhateria and Jain (2016) found a positive relationship between EC and  $\text{NO}_3^-$  in which the concentrations of EC increased with the high level of  $\text{NO}_3^-$  in the presence of human activities and the widespread use of agricultural fertilizers. Ammonium ( $\text{NH}_4^+$ ) measurements in the water had a strong positive relationship with reaches, seasons, water temperature, Electrical conductivity and calcium concentration ( $p < 0.01$ , Table 5.6). In the Meng et al. (2018) study of the Fenhe River in the Shanxi Province in China, they found a close correlation between concentrations of forms of nitrogen, including ammonium  $\text{NH}_4^+$ , with human activities in general, and in particular the use of fertilizers in agricultural activities, therefore, areas far from human activities have lower levels of nitrogen pollutants. In our study, the top of the river was less had limited activities,  $\text{NH}_4^+$  values were lower than in the middle and lower reaches of the river.

Leoni et al (2018) examined the distribution of  $\text{NH}_4^+$  in the water of the lakes of northern Italy. They found that ammonium was linked to the seasons it was higher in the warmer seasons than in the cold seasons thus correlating positively with the temperature, the higher the temperature, the higher the  $\text{NH}_4^+$  concentration in the river water. Gali et al. (2012) studied electrical conductivity in water as a proxy for estimating the chemical properties of sewage quality in the Des Moines Lobe area in Iowa State USA. They found negative relationship between EC and the concentration of ammonium in water. This, however, is contrary to what we found in our study where the relationship is positive and strong, and this may be due to the difference in the nature of the region and the geological structure.

There was a strong negative relationship between the concentration of ammonium in the water and the dissolved oxygen in the water ( $p < 0.01$ ) (Table 5.6). Sakalauskiene (2001) confirmed that where there is a lack of oxygen in the water, the values of ammonium begin to increase and this is paired with increased turbidity of the water as a result of impurities because of the bacteria's consumption of organic matter and nitrogen release.

### **7.13.2 Heavy Metals**

The concentrations of nickel in the water had a strong positive relationship with the seasons ( $p < 0.01$ ) (Table 5.6). Eliku and Leta (2018) found a strong positive relationship between the concentration of nickel in the water of the Awash River in Ethiopia within the dry seasons. In our study, the highest values of nickel concentration in river water were recorded in summer and autumn (Table 5.4) may be caused by the lack of rain, which causes semi-stagnation of water and the accumulation of pollutants in the soil. There was a negative relationship between the concentration of nickel in the water and the dissolved oxygen in the water ( $p < 0.05$ ) (Table 5.6), and this was contrary to what Zhang et al (2018) found in Zhanjiang Bay, China where there was a positive relationship between the concentrations of nickel in the water and the amount of dissolved oxygen in the water.

Zinc concentrations in the Eerste River catchment water had a strong positive relationship with seasons ( $p < 0.01$ , Table 5.6). Koffi et al. (2014) found a positive relationship between zinc concentration and change in seasons in The Estuary Bietri Bay, Ebrie Lagoon, Cote D'ivoire, where they found the highest levels of zinc in water in the dry season. We also found in our study that the highest concentrations of

zinc were recorded in the water in the autumn rather than in the winter (Table 5.4). There is a strong negative relationship between the concentration of Zn in the water and between river reaches, temperature and pH ( $p < 0.01$ , Table 5.6). In the Water Transfer Project from South to North of China 2019, Nong et al. (2019) found that the zinc concentration was positively associated with the spatial change from upper to the lower reaches of the water transfer channel. Zhang et al. (2018) found in Zhanjiang Bay, China that there was a negative relationship between zinc concentrations in water and pH, but he recorded a positive relationship between zinc concentration and temperature, and this was contrary to what was found in our study.

Copper concentrations in the Eerste River catchment water had a strong positive relationship with electrical conductivity ( $p < 0.01$ ) and there was a positive relationship with the concentration of calcium in the water ( $p < 0.05$ , Table 5.6). Gizaw et al. (2014) recorded in the Ethiopian Rift Valley a positive relationship between concentration of copper in water and electrical conductivity, and calcium concentration in water.

Lead concentrations in the Eerste River catchment water had a strong positive relationship with Electrical conductivity ( $p < 0.01$ ). Eliku and Leta (2018) found a strong positive correlation between lead concentration in the water of the Awash River in Ethiopia with dry seasons. In our study, the highest values of lead concentration in river water were recorded in summer and autumn (Table 5.4).

The second part we applied the Correlation matrix depicting Spearman's simple linear correlation coefficient ( $r$ ) amongst all the investigated parameters in the soil,  $S$ .

*babylonica*, *C. benghalensis*, *P. urvillei* and *P. lapathifolia* samples, the levels of significance  $p < 0.01$  and  $p < 0.05$  (Table 5.7).

For the seasons, Fe concentrations in the leaves of *Commelina benghalensis* had a strong negative relationship ( $p < 0.01$ ), and in *Paspalum urvillei* leaves a strong positive relationship ( $p < 0.01$ ). For the reaches, the iron concentrations in the leaves of *Commelina benghalensis* had a strong negative relationship ( $p < 0.01$ ), and in *Paspalum urvillei* leaves a positive relationship ( $p < 0.05$ ) (Table 5.7). For calcium, Fe concentrations had a strong positive relationship ( $p < 0.01$ ) in the soil and in the leaves of *Paspalum urvillei*, *Commelina benghalensis* and *Persicaria lapathifolia*. In *Salix babylonica* leaves, there was a positive relationship ( $p < 0.05$ ). Singh and Dahiya (1976) showed that calcium carbonate concentration has a direct and positive effect on Fe concentration in soil.

For the seasons, the leaf Ni concentrations had a negative relationship ( $p < 0.05$ ) with *Commelina benghalensis* and *Persicaria lapathifolia*. Whereas with *Paspalum urvillei* leaves there was a strong positive relationship ( $p < 0.01$ ) (Table 5.7). For the reaches, the leaf Ni concentrations had a negative relationship ( $p < 0.05$ ) with *Salix babylonica* and *Commelina benghalensis*, but with *Paspalum urvillei* there was a strong positive correlation ( $p < 0.01$ ) (Table 5.7). For calcium, the Ni concentrations had a strong positive relationship ( $p < 0.01$ ) with soil. The Ni in *Paspalum urvillei* leaves and *Persicaria lapathifolia* leaves also had a strong positive relationship ( $p < 0.01$ ) (Table 5.7). Arif et al. (2016) found a positive correlation with calcium concentration with Ni concentration in soil.

For seasons and reaches, the Zn concentrations in the leaves had a strong positive correlation ( $p < 0.01$ ) with *Paspalum urvillei* (Table 5.7). For calcium, the leaf Zn concentrations had a strong positive correlation ( $p < 0.01$ ) in the leaf of *Commelina benghalensis*, *Paspalum urvillei* and *Persicaria lapathifolia*. As for *Salix babylonica*, there was a negative relationship ( $p < 0.05$ ) (Table 5.7). For the seasons, leaf Cu concentrations had a strong positive correlation ( $p < 0.01$ ) with *Paspalum urvillei*. For Ca, Cu concentrations had a positive relationship in *Paspalum urvillei* leaves ( $p < 0.05$ ), and in *Persicaria lapathifolia* there was a strong positive relationship ( $p < 0.01$ ) (Table 5.7).

For seasons and reaches, the soil Cd concentration had a strong positive relationship ( $p < 0.01$ ) as did the *Paspalum urvillei* leaf Cd level. For the reaches, the leaf Cd concentrations had a positive relationship in the case of *Persicaria lapathifolia* ( $p < 0.05$ ) (Table 5.7). For calcium, leaf cadmium concentrations had a positive correlation ( $p < 0.05$ ) in *Paspalum urvillei* leaves, while in *Persicaria lapathifolia* leaves there was a strong positive correlation ( $p < 0.01$ ) (Table 5.7). For seasons and reaches, Pb concentrations had a strong positive correlation ( $p < 0.01$ ) with *Salix babylonica* leaves and *Commelina benghalensis* leaves (Table 5.7). For calcium, leaf lead concentrations had a strong positive relationship ( $p < 0.01$ ) in *Salix babylonica* and *Paspalum urvillei*, but with *Persicaria lapathifolia* just a positive relationship ( $p < 0.05$ ) (Table 5.7)

#### **7.14 Comparison Between the Two Main Tributaries of the River**

Watersheds often include both urban and agricultural land. The Eerste River catchment has two permanent rivers, the Kuils River and Eerste River. The Eerste



drains a larger surface area that extends through the Stellenbosch Municipal District before the Kuils River joins it near Macassar (Thomas et al., 2010). Table 5.8 shows no differences in the heavy metals studied in both the water and the soil of the rivers. The mean calcium concentration in the water and soil of the Kuils River was significantly higher than in the Eerste River. The increased Ca in the water may be due to the crossing of the Kuils River, cape flats area through the sandy soil.

When comparing the other measured parameters in the water of the Eerste River and the Kuils River the dissolved oxygen concentration in the Eerste River was significantly higher (Table 5.8). The water electrical conductivity (EC) and pH were significantly higher in the Kuils River. The  $\text{NO}_3^-$  levels were significantly lower in the Eerste River.

The Eerste River at the source the lack of human activities contributed with the decrease in temperature to increase the concentration of DO in the water, and the lack of sources of pollution with  $\text{NO}_3^-$  because there are no human activities except in the middle and bottom of the river (Fourie, 2005; Mwangi, 2014). No significant values were recorded for the mean concentrations of nitrite in the water of the two rivers, while the lowest values for nitrate concentrations in the water of the Eerste River were significant, and the mean concentrations of ammonium in the water of the Eerste River were slightly higher than the Kuils River and significant values were recorded (Table 5.8).

The Cu concentrations in the *Salix babylonica* leaves in the Eerste River were significantly higher (Table 5.8). Chen et al. (2012), when studying two types of

willow under different hydrological conditions in China, found that the biomass of *Salix babylonica* contained quantities of Cu of statistical significance and the possibility exists of using *Salix babylonica* to get rid of Cu contamination through phytoremediation. Wani et al. (2011) studied *Salix babylonica* as a viable heavy metal accumulation, They mentioned many previous studies that recommended it, and they further note that *Salix babylonica* has the ability to accumulate large quantities of heavy metals in tissues such as Cu and Zn. Yang et al. (2014) studied the variation in the absorption of copper and Zn in 12 kinds of willow, and concluded that *Salix babylonica* was good for Zn and Cu accumulation.

Ni was significantly lower in *Persicaria lapathifolia* leaves in the Eerste River (Table 5.8). Baldantoni and Alfani (2016) studied the benefit of using vascular plants for passive biomonitoring along the Irno River in Italy, and concluded that *Persicaria lapathifolia* had a high ability to concentrate lead in its tissues.

### **7.15 The Modelling**

A predictive model was developed based on basic data collected during our study, from the Eerste River catchment. This model uses data collected over six weeks of sampling for the 22 sites. A set of parameters was measured in water and soil samples, as well as the concentration of a group of heavy metals in water, soil, and plant leaves.

A predictive model was prepared using the multi-linear regression method based on two independent variables which were soil and water, and the dependent variable which was the plant. The model aims to estimate a specific parameter of the soil and

water, and to predict the concentration of the heavy metals in the plant using the concentration of heavy metals in soil and water. The general equation was as follows (equation 1):

$$p = \beta_1 \underline{s} + \beta_2 \underline{w} + \varepsilon \text{ (Bremer, 2013).}$$

Where the source of the accumulated heavy metals in the tissue of the plant comes first from the soil, then water and a small part of the air (Kabata-Pendias, 2000; Vongdala et al., 2019). The regression coefficient was first used for estimating the relationship between the concentration of the heavy metals in plant leaves and water and soil.

The atmosphere is a possible third source therefore the multi-linear regression will include a third source ( $\beta_0$ ) which is a constant. The aerosols particles of air pollution with heavy metals settle into the soil and water (Kacholi and Sahu, 2018). Such a constant is commonly represented by a variable which does not depend on the main variable(s) of the studied problem (Flanders and Price, 2015). Thus, we have two parts of the predictive model in our study.

❖ 1: Without the third source.

$$p = \beta_1 \underline{s} + \beta_2 \underline{w}$$

$$s = \frac{p - \beta_2 w}{\beta_1} \text{ and } w = \frac{p - \beta_1 s}{\beta_2}$$

❖ 2: With the third source.

$$p = \beta_0 + \beta_1 s + \beta_2 w$$

$$s = \frac{p - (\beta_0 + \beta_2 w)}{\beta_1} \text{ and } w = \frac{p - (\beta_0 + \beta_1 s)}{\beta_2}$$

The concentration of any heavy metal ( $x$ ) in the leaves of the plant is related to the concentration of same heavy metal ( $x$ ) in the soil and water. This is examined with and without a third source, the atmosphere (represented as a correction factor). If we know the heavy metal ( $x$ ) concentration in the plant leaves ( $p$ ), then we can use the coefficient from the model to predict the concentration of heavy metals ( $x$ ) in soil and water. From this we estimated the potential of the available species for use as bio-monitors for the heavy metals.

### 7.15.1 *Salix babylonica* (L.)

The results obtained from *S. babylonica* leaves were more promising than those of the other species in estimating the concentration of Cd in water ( $\beta$ ), showing significant correlation without extra source ( $\beta_0$ ) (Tables 6.1 and 6.2). Cu in general gave the highest correlation ( $\beta$ ) without the third source ( $\beta_0$ ) with water and soil

(Tables 6.3 and 6.4). The concentrations of Cu, Fe and Zn were only significant with soil without the third source (Tables 6.3, 6.5 and 6.11). As for Pb, it only provided significant values with the soil without the third source (Table 6.9).

In general, many studies focused on the use of *Salix* in the biological monitoring of air pollutants, such as in the studies of Chrabaszcz and Mróz (2017), Steyn and Chaumerliac (2014) and Wuytack et al. (2010). Investigated the build-up of heavy metals in *Salix babylonica*, they recommended it as a biomonitor for heavy metals, including Cd, Cu, Fe, Pb and Zn. Liu et al. (2017) also mentioned the possibility of heavy metals accumulation in the tissues of *S. babylonica* including Ni, but Ni did not give significant values with *S. babylonica* in our study.

Zeiner and Cindrić (2017) found that there are varying concentrations of heavy elements except Ni in the tissues of the *S. babylonica* when studying medicinal plants. Also, given the aforementioned studies of heavy mineral deposits in the tissue of *S. babylonica*, its use for biomonitoring of air was supported.

#### **7.15.2 *Commelina benghalensis* (L.)**

The Cd gave a positive correlation ( $\beta$ ) in the leaves of *C. benghalensis*, as only Cd, and not the other heavy metals, gave a significant value with water without the third source (Table 6.1). As for Cu, it gave the highest significant correlation between the heavy metals in the leaves of *C. benghalensis* and water (Table 6.3). Fe and Zn in the leaves of *C. benghalensis* gave significant results with soil without the third source (Tables 6.5 and 6.11). However, in the presence of the third source, the Cu, Fe, Ni, and Zn in the leaves of *C. benghalensis* gave significant values with the other factor

(Tables 6.3, 6.6 and 6.12). Concentrations of Pb in the leaves of *C. benghalensis* did not give any significant relationship with or without the third source.

In a study carried out by Adesuyi et al. (2018) on biomonitoring of the level of heavy minerals in wetland plants around Lake of Lagos in Nigeria, it was found that *C. benghalensis* had great potential to assess the environmental heavy metal pollution in the region.

Ge and Zhang (2015) studied the plants that grew around the Xinqiao Copper Mine, in China, after increased mining activities. It was found that *C. communis* has the ability to accumulate Cu, Pb and Zn in its tissues, thus reflecting the environmental situation in the polluted area.

### **7.15.3 *Paspalum urvillei* S**

The concentration of heavy metals was uneven in *Paspalum urvillei*, Cu and Ni leaves gave a positive correlation coefficient ( $\beta$ ) in *P. urvillei* leaves and gave significant values with water and soil without the third source (Tables 6.3 and 6.7), whereas Fe, Pb and Zn gave significant values with the soil without the third factor (Tables 6.5, 6.9 and 6.11). All studied heavy metals except Cd gave significant values for the other factor without the third source (Tables 6.4, 6.6, 6.8, 6.10 and 6.12).

We did not find studies looking at the possibility of using *P. urvillei* as a biological monitor, but some studies indicate the possibility of using other species of the same genus.

Ying et al. (2008) when studying plants around the Yangtze River in China, found that *Paspalum notatum* has the ability to withstand concentrations of heavy metals and has a promising future in treating soils contaminated with heavy metals.

Sa'idu et al. (2013) found in a study of heavy metal accumulation in *Paspalum orbiculare* on the highway in Kano Nigeria, where they found that the accumulation of heavy metals in *Paspalum orbiculare* was greater along the highway than in other places thus giving an indication of the places most polluted with heavy metals.

A study was carried out by Adesuyi et al. (2018) to biomonitor the level of heavy metals in wetland plants around Lagos Lagoon in Nigeria. They found that *Paspalum vaginatum* has great potential for assessing the Cu pollution, and this was consistent with our study as *Paspalum urvillei* gave the highest association with Cu.

#### **7.15.4 *Persicaria lapathifolia* (L.)**

Cu gave a large and positive correlation coefficient ( $\beta$ ) in the leaves of *P. lapathifolia* which was significant with water and soil without the third source (Tables 6.3). Ni gave a significant value with water without the third source (Table 6.7), whereas the iron, Pb, and Zn in the leaves of *P. lapathifolia* gave significant values with soil without the third source (Tables 6.5, 6.9 and 6.11). All heavy metals studied in *P. lapathifolia* except for Cd gave significant values to the other factor without the third source (Tables 6.4, 6.6, 6.8, 6.10 and 6.12).

Baldantoni and Alfani (2016), studied vascular plants along the Irno River in Italy. They found that the *Persicaria lapathifolia* had a promising future in the bio-

monitoring of heavy metals, especially with Pb. This was consistent with our study, whereby Pb correlated better with *Persicaria* leaves than in these of the other studied plants (Table 6.9). Salinitro et al. (2019), studied the increase of heavy minerals in soil and vegetation in Italy. *Polygonum aviculare* was examined as a possible monitor of soil contamination with heavy metals, but there was no linear relationship between the minerals in the soil and minerals in the plant. This differed from our study, as there are some minerals that had a strong association between plants, soil, and water, and gave significant values, especially with Cu and Ni (Tables 6.3 and 6.7).





## 7.16 References

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# CHAPTER 8

## CONCLUSION AND SYNTHESIS

### 8.1 Conclusion

At the end of our work, we would like to conclude by summarizing what we have found with respect to the heavy metal situation of the Eerste River catchment area in the Western Cape, Cape Town, South Africa. Also, the possible use of the four plant species selected (*Salix babylonica*, *Commelina benghalensis*, *Paspalum urvillei* and *Persicaria lapathifolia*) as biological monitors for contamination with heavy metals (copper, cadmium, iron, nickel, lead and zinc) in river water and soil.

Human interventions through various activities that produce known and unknown waste, climate changes and declining biodiversity are affecting the environment in all respects on the face of the globe. In our research, we used plant species to obtain quantitative information that would assist us in developing a predictive model that was prepared to obtain information about the state of water and soil, in particular, to identify the environmental situation in terms of heavy metal pollution in the study area.

A number of criticisms have been directed at the use of plants as biological monitors, and have been met with a set of responses (Chapter 1, 1.3). The plant as a biomonitor: after reviewing previous studies, it became apparent that the plant has an

advantage as a biomonitor, as the plant is fixed in its place and does not move. Accordingly, clear information can be obtained about the study area, unlike taking humans and animals such as fish and crustaceans to obtain data for the environmental impact assessment, as they are moving permanently and may move from one place to another in varying periods. Thus, the history of the movement of these organisms must be taken before using them as biomonitors.

Several previous studies on the environment of rivers, the environment surrounding them, and their biological diversity were listed, outlining the contribution of these environments to support biological diversity and its effects on human health in the event of its exposure to pollution. This is principally so with heavy metals resulting from various human activities for water and soil pollution, absorption and accumulation within living organisms, especially plants. Many studies that focus on biomonitoring have been published over the last few decades Madejón et al., 2006; Markert et al., 2003; Gadzała-Kopciuch et al., 2004; Aksoy et al., 2000; Aksoy and Öztürk, 1996; Aksoy and Şahin, 1999; Al-Khashman et al., 2011; Al-Shayeb et al., 1995; Calzoni et al., 2007; De Luccia, 2012; Djingova et al., 1993 and Zurayk et al., 2001.

The area studied in our research was in the Cape Metropolitan area (CME) and our focus was on the Eerste River catchment that contains two important rivers in the region, namely the smaller Kuils and the larger Eerste that meet in the Macassar area before the estuary in False Bay. This is one of the eleven estuaries in False Bay. The Eerste catchment area contains large parts of the Cape Town and Stellenbosch regions, with an area of 660 km<sup>2</sup>. Within these spaces, there are many factories and

sewage treatment plants that release waste and treated wastewater into the riverbed (Thomas et al., 2010). The area of the river catchment was surveyed along the two rivers, and we started with forty sites. The plant species were identified in these locations and we chose the sites where the most common plant species were found across the sites, including each main tributary. We selected 22 sites for sampling, along the Eerste and Kuils rivers, which were divided, according to topography, into three groups: upper, middle and lower reaches.

We collected samples from November 2011 to December 2012 at a visit rate of every six weeks with a total of ten field trips to collect samples from study sites. They were samples of river water, river bank soil and leaves of the selected plants in the study. Some measurements of water were taken directly in the river using portable instruments (temperature and dissolved oxygen). The other measurements were carried out within 24 hours after returning to the lab, namely, electrical conductivity (EC), pH, ammonium ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), and nitrate ( $\text{NO}_3^-$ ).

The soil was air-dried at room temperature until completely dry, then prepared and stored until digestion. Water samples were frozen until the date of measuring the heavy metals. Soil and plant samples were digested according to the methods used in most studies and approved by researchers. After obtaining the extract, the concentration of heavy metals in the plant and soil extract and in water samples was measured by the Agilent 710 Series ICP-OES. The data obtained were analysed after inclusion in an Excel Spread Sheet and divided into groups according to river levels (upper, middle and lower reaches), and also according to the seasons. A set of statistical analyses were performed on the data using IBM SPSS version 22.

Initially, the data sets were inspected using descriptive statistical analysis, then they were checked for normal distribution using Shapiro-Wilk W test. Significant differences between the soil, water, and plants in the different seasons and various sections were explored using Kruskal-Wallis one-way ANOVA tests because the distribution of the data was not normal. The inter-relationship between the different variables was explored using a bivariate correlation test. All statistical analyses were conducted at the 5% or 1%, levels of significance.

We took the data obtained from the plant, soil and water samples to develop a predictive statistical model intended to use the specified plants in our study as a biological monitor for heavy metals pollution.

**Our results obtained were as follows:**

The temperature of the river water ranged between 0.8 to 27.39°C, the lowest recorded in the upper reaches during winter. While the highest recorded in the lower reaches during the summer and gave significant differences with the seasons and reaches. Our results were consistent with most studies done on the South African rivers and inland waters in general. The dissolved oxygen (DO) in river water inversely related to the water temperature. The highest values were recorded in winter and autumn, in the upper reaches, and the lowest in summer and spring in the lower reaches. They generally ranged between 3.56 and 11.3 mg·l<sup>-1</sup>. This trend is in line with most previous studies. As for the conditions of South African water quality for coastal waters, our results were often in accordance with the conditions in the upper reaches, but the lower reaches were outside the specifications.

The pH of the river's water was recorded as the lowest at the top of the river in the winter and autumn. As for the highest, it was at the bottom of the river in the summer and spring seasons, it ranged in general between 6.63 and 7.84 pH and gave significant differences with the seasons, the lowest was in the upper reaches during winter and the highest was in lower reaches during spring. Our results were close to and within the range of most previous studies in the region and in South Africa. The pH of the water was in a direct relationship with the electrical conductivity (EC) in the water of the river, and thus it was in the same direction in the pH of the water. It ranged between 38.25 to 2734.06  $\mu\text{S}\cdot\text{cm}^{-1}$  the lowest was in winter and the highest was in spring, but it did not differ significantly with the seasons, and our results did not agree with most of the previous studies and the effect of the tide was marked in the lower reaches of the estuary where it significantly increases the EC, by entering the salty water from the ocean and mixing it with the river water.

The ammonia ( $\text{NH}_4^+$ ) concentration in the river water showed a temporal and spatial variation within the river reaches and seasons. The lowest concentration was below the detection limit (ND) at the upper reaches during the winter, and the highest was 10.05  $\text{mg}\cdot\text{l}^{-1}$  at the lower reaches during summer. The  $\text{NH}_4^+$  concentrations differed significantly with the seasons. Through our study, there was a direct relationship between the concentration of  $\text{NH}_4^+$  in water with the temperature and acidity of the water. On the other hand, the relationship was inverse between the concentration of  $\text{NH}_4^+$  and the DO in the water. When compared to the recommendations of the World Health Organization (WHO), only the upstream water had an  $\text{NH}_4^+$  concentration of less than 0.2  $\text{mg}\cdot\text{l}^{-1}$ .

The concentration of nitrite  $\text{NO}_2^-$  increased significantly in river water from the upper to the lower reaches. The lowest concentration was below the detection limits (ND) in the upper reaches in all seasons, while the highest was  $3.21 \text{ mg}\cdot\text{l}^{-1}$  in the lower reaches in spring. It gave significant differences with the seasons and reaches. Thus, water in the upper reaches was safe to drink according to WHO recommendations for  $\text{NO}_2^-$  concentration, less than  $0.3 \text{ mg}\cdot\text{l}^{-1}$ . Nitrates ( $\text{NO}_3^-$ ) were the lowest in the upper reaches where they were below the detection levels (ND) for all seasons, except for spring, which was  $0.33 \text{ mg}\cdot\text{l}^{-1}$  and the highest concentrations were in the middle reaches, in autumn, at  $15.18 \text{ mg}\cdot\text{l}^{-1}$ .

Regarding the results of soil analysis, the lowest pH values were recorded at the upper reaches, 4.83 pH, and the highest were at the middle reaches, 7.6 pH, in spring. Only the middle reaches differed significantly. The electrical conductivity of the soil have the same trend with acidity of the soil, where the lowest values were recorded in the upper reaches, the lowest of which was  $43.5 \mu\text{S}\cdot\text{cm}^{-1}$  during the winter and the highest values were in the middle reaches  $1427 \mu\text{S}\cdot\text{cm}^{-1}$  during the summer. There were no significant differences between the seasons. We further noted that the salinity of the soil was higher in the central regions, where previous studies indicated that it might be caused by a change in human activity and pollution, and this would affect agricultural activity in the region.

The concentration of calcium (Ca) increased significantly in both *Salix babylonica* and *Paspalum urvillei* from the upper to the lower reaches. The values were between  $19.67$  and  $80.29 \text{ mg}\cdot\text{kg}^{-1}$  in *Salix* and between  $15.11$  and  $42.55 \text{ mg}\cdot\text{kg}^{-1}$  in *Paspalum urvillei*. Soil samples showed a significant difference in Ca concentrations, ranging



between  $17.77 \text{ mg}\cdot\text{kg}^{-1}$  at lower reaches and  $63.73 \text{ mg}\cdot\text{kg}^{-1}$  during summer and gave significant differences. The *Salix babylonica* was highest in its accumulation of Ca in summer at  $82.24 \text{ mg}\cdot\text{kg}^{-1}$ , with significant differences. The Eerste River catchment water is deemed soft. Moreover, with regard to the limits of Ca in water, the DWAF (1996) states that it must not exceed  $15 \text{ mg}\cdot\text{l}^{-1}$ , and our findings were in line with that stipulation through the river, except for the lower reaches, which was  $26.88 \text{ mg}\cdot\text{l}^{-1}$ .

Iron (Fe) concentrations differed significantly between seasons in soil and water, and were between  $0.58 \text{ mg}\cdot\text{l}^{-1}$  during spring and  $1.45 \text{ mg}\cdot\text{l}^{-1}$  during autumn in water and between  $13.25 \text{ mg}\cdot\text{kg}^{-1}$  during summer and  $24.83 \text{ mg}\cdot\text{kg}^{-1}$  during spring in the soil. It also gave significant differences in the four studied plants with seasons, so the studied plant species are good accumulators of Fe in their leaves and can be used as biomonitors, especially when the samples are taken seasonally. The concentration of Fe in the Eerste River water was within the normal range (DWAF, 1993).

Concentrations of nickel (Ni) differed significantly between seasons in soil. The concentrations were  $1.35 \text{ mg}\cdot\text{kg}^{-1}$  during summer to  $1.97 \text{ mg}\cdot\text{kg}^{-1}$  during spring. For the plants, there were significant differences between the seasons in both *P. urvillei* and *P. lapathifolia*. So, they are accumulators of Ni, and can be used as biomonitors of Ni in the soil, especially when the samples are taken seasonally. Our values for Ni concentration in soil were within the recommendations of the DoH (1991). Regarding the South African Water Quality guidelines for different water uses for livestock, just the upper reach water was within the recommended standards.

Zinc (Zn) concentrations during the seasons gave significant differences in water. The concentrations were between 0.24 mg·kg<sup>-1</sup> during spring and 1.63 mg·l<sup>-1</sup> during autumn, as well as in *S. babylonica* between 0.61 mg·kg<sup>-1</sup> during summer and 1.03 mg·kg<sup>-1</sup> during autumn and *P. lapathifolia* between 0.98 mg·kg<sup>-1</sup> during autumn and 1.21 mg·kg<sup>-1</sup> during summer. As for the reaches, there were significant differences with *Commelina benghalensis* between 0.56 mg·kg<sup>-1</sup> at the upper reaches and 0.75 mg·kg<sup>-1</sup> at the middle reaches, and for the reaches, there were significant differences with *P. urvillei* between 0.11 mg·kg<sup>-1</sup> at the upper reaches and 0.53 mg·kg<sup>-1</sup> at the lower reaches.

Thus, *S. babylonica* and *P. lapathifolia* are accumulators of Zn and can be used as biomonitors of Zn in the water especially when the samples are taken seasonally. Both *C. benghalensis* and *P. urvillei* are accumulators of Zn in the water and can be used as biomonitors of Zn in the soil especially when the samples are taken with river reaches. Our values for Zn concentration in soil was within the recommendations of the DoH, (1991) and Australian and New Zealand guidelines for the assessment and management of contaminated sites (1992). Also, the Zn concentration in water in this study was above recommendations of DWAF (1996) and CCME (2002).

The concentration of copper (Cu) in water gave significant differences with reaches and seasons, and the concentrations were between 0.65 mg·l<sup>-1</sup> at the upper reaches and 2.32 mg·l<sup>-1</sup> during winter. In *P. urvillei* Cu ranged between 0.03 mg·kg<sup>-1</sup> during winter and 0.17 mg·kg<sup>-1</sup> during summer and in *P. lapathifolia* 0.16 mg·kg<sup>-1</sup> during summer and 0.31 mg·kg<sup>-1</sup> at the upper reaches—both gave significant differences with the seasons and reaches. Thus, *P. urvillei* and *P. lapathifolia* are accumulators of

Cu and can be used as biomonitors of Cu in the water, with seasons and reaches. In this study, the concentrations of Cu in soil and water were within the recommended limits of DoH (1991) and WRC (1997). The Cu concentration in water in this study was beyond the recommendations of DWAF (1996) and CCME (2002).

The cadmium (Cd) concentration gave significant differences with river reaches in the soil and the concentrations were between  $1.13 \text{ mg}\cdot\text{kg}^{-1}$  at the upper reaches and  $2.66 \text{ mg}\cdot\text{kg}^{-1}$  at the lower reaches. *P. urvillei* gave significant differences with the lower reaches at a concentration of  $2.8 \text{ mg}\cdot\text{kg}^{-1}$ . As for the seasons, it gave both soil between  $0.95 \text{ mg}\cdot\text{kg}^{-1}$  during winter and  $2.98 \text{ mg}\cdot\text{kg}^{-1}$  during autumn and *P. urvillei* between  $0.72 \text{ mg}\cdot\text{kg}^{-1}$  during winter and  $3.15 \text{ mg}\cdot\text{kg}^{-1}$  during autumn with significant differences. Thus, *P. urvillei* is an accumulator of Cd in soil and can be used as a biomonitor of Cd in the soil especially when the samples are taken with seasons and with lower reach. In this study, the concentrations of Cd in water were outside the recommended limits of DWAF (1996).

The lead (Pb) concentration gave significant differences with the seasons in the water, and the concentrations were between  $1.07 \text{ mg}\cdot\text{l}^{-1}$  during winter and  $2.49 \text{ mg}\cdot\text{l}^{-1}$  during summer. *S. babylonica* and *P. urvillei* have significant differences with the seasons and reaches, *S. babylonica* between ND at the upper reaches and  $2.67 \text{ mg}\cdot\text{kg}^{-1}$  during autumn and *P. urvillei* between  $0.004 \text{ mg}\cdot\text{l}^{-1}$  at the upper reaches and  $0.01 \text{ mg}\cdot\text{l}^{-1}$  at middle and lower reaches during spring and autumn. Thus, *S. babylonica* and *P. urvillei* are accumulators of Pb and can be used as biomonitors of Pb in the water when the samples are taken with seasons and reaches. In our study, the concentrations of Pb in water and soil were within the limits allowed. According to

the guidelines of the Department of National Health and Population Development (DoH), the highest Pb concentration allowed in South African soil was  $56 \text{ mg}\cdot\text{kg}^{-1}$  (DoH, 1991). And according to the Water Research Commission, Pretoria, Pb concentration allowed in South African is  $6.6 \text{ mg}\cdot\text{l}^{-1}$  (WRC, 1997). On the other hand, the water of the Eerste River catchment was outside the recommended limits of Pb concentration, regarding to DWAF (1996) and CCME (2002).

When studying the correlation (measure or degree of the relationship between the measured parameters and the various river reaches and seasons), we found a number in water parameters. The relationship between  $\text{NO}_2^-$  and the temperature, EC, and Ca concentration in the river water was strongly positive ( $p < 0.01$ ), this relation was aligned with the results the of Shabalala et al. (2013) and Vadde et al. (2018). On the other hand,  $\text{NO}_2^-$  had a strong, negative relationship ( $p < 0.01$ ) with DO, and this agrees with Gómez et al. (2002) and Larsen et al. (2010).

The relationship between  $\text{NO}_3^-$  and the Ca an EC in the river water was strongly positive ( $p < 0.01$ ).  $\text{NH}_4^+$  measurements in the water had a strong positive relationship with water temperature, EC and Ca concentration ( $p < 0.01$ ). For the seasons the concentrations of  $\text{NO}_2^-$  has positive relationship ( $p < 0.05$ ), and strong positive relationship with  $\text{NH}_4^+$ . For the reaches, the concentrations of  $\text{NO}_3^-$  has a positive relationship ( $p < 0.05$  and strong positive relationship with  $\text{NH}_4^+$ ).

With regard to the relationship between the heavy metals and the various river reaches and seasons, we found in water that the concentrations of Ni had a strong positive relationship with the seasons ( $p < 0.01$ ). As for the relationship between Ni

and DO, it was a negative relationship in the water ( $p < 0.05$ ). Zinc concentrations in the water had a strong positive relationship with seasons ( $p < 0.01$ ). A strong negative relationship ( $p < 0.01$ ) between the concentration of Zn in the water and between river reaches, temperature and pH. Cu concentrations in the water had a strong positive relationship with EC ( $p < 0.01$ ). And also had a positive relationship with the concentration of calcium in the water ( $p < 0.05$ ). Pb concentrations in the water had a strong positive relationship with seasons ( $p < 0.01$ ).

Therefore, when studying the parameters in Eerste River catchment water in the seasons and reaches, we must take into account the positive and negative relationships (correlations) that we found in our study.

The simple linear correlation coefficient is the strength of the relationship amongst all the four plant species samples with the investigated parameters in the soil and the season, reach and Ca: for the soil the concentration of Fe and Ni had a strong positive relationship with Ca ( $p < 0.01$ ). And the concentration of Cd had a strong positive relationship with seasons and reaches ( $p < 0.01$ ).

For *Salix babylonica*, the concentration of Fe had a positive relationship with Ca ( $p < 0.05$ ). The concentration of Zn had a negative relationship with Ca ( $p < 0.05$ ). The concentration of Pb had strong positive relationships with the season, reach and Ca ( $p < 0.01$ ). For *Commelina benghalensis*, the concentration of Fe had a strong negative relationship with the season and reach ( $p < 0.01$ ). The concentration of Ni had a negative relationship with the season and reach ( $p < 0.05$ ). The concentration of Zn

had a strong positive relationship with Ca ( $p < 0.01$ ). The concentration of Pb had a strong positive relationship with the season and reach ( $p < 0.01$ ).

For *Paspalum urvillei*, the concentration of Fe had a strong positive relationship with the season and Ca ( $p < 0.01$ ), it also had a positive relationship with reach ( $p < 0.05$ ). The concentration of Ni and Zn had a strong positive relationship with the season, reach and Ca ( $p < 0.01$ ). The concentration of Cu had a strong positive relationship with the season ( $p < 0.01$ ), as well as a positive relationship with Ca ( $p < 0.05$ ). The concentration of Cd had a strong positive relationship with the season and reach ( $p < 0.01$ ), as well as a positive relationship with Ca ( $p < 0.05$ ). The concentration of Pb had a strong positive relationship with Ca ( $p < 0.01$ ).

For *Persicaria lapathifolia*, the concentration of Fe had a strong positive relationship with Ca ( $p < 0.01$ ). The concentration of Ni had a negative relationship with the season and positive with Ca ( $p < 0.05$ ). The concentrations of Zn, Cu and Cd had a strong positive relationship with the Ca ( $p < 0.01$ ). The concentration of Cd had a positive relationship with the reach ( $p < 0.05$ ). The concentration of Pb had a positive relationship with Ca ( $p < 0.05$ ).

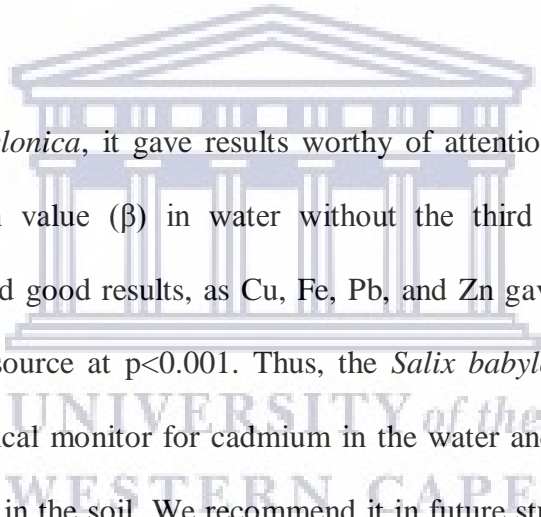
Therefore, when studying the parameters in Eerste River catchment soil and four plant species we studied in the season, reach and Ca must be taken into account the positive and negative relationships (correlations) that we got in our study. Noticeable there no relationships: for the soil, the concentration of Zn, Cu and Pb in all parameters. For *S. babylonica* and *C. benghalensis* the concentration of Cu and Cd.

The two main rivers in Eerste River catchment (Eerste and Kuils rivers), were compared. Regarding the measurements of the two rivers water, the values of dissolved oxygen were significantly higher in the Eerste River, at  $6.32 \text{ mg}\cdot\text{l}^{-1}$ . Regarding the temperature, it was similar between the two rivers, no significant differences were recorded, and the highest in the Eerste River was recorded at  $19.94^{\circ}\text{C}$ . This is inconsistent with what we recorded in the values of DO, as it was assumed that the values of DO decreased with increasing temperature (direct relationship). The EC and pH were significantly higher in the Kuils River at  $1100.6$  and  $7.61 \text{ }\mu\text{S}\cdot\text{cm}^{-1}$ , respectively.

Concentrations of nitrites were the highest in the Eerste River  $1.24 \text{ mg}\cdot\text{l}^{-1}$ . Ammonia levels were similar between the two rivers, but significantly higher in the Eerste River at  $3.89 \text{ mg}\cdot\text{l}^{-1}$ . As for nitrates, the highest recorded value was  $15.31 \text{ mg}\cdot\text{l}^{-1}$  in the Kuils River, which was significantly higher than the lowest value recorded in the Eerste River at  $7.62 \text{ mg}\cdot\text{l}^{-1}$ . Thus, both were polluted by human activities, the most important of which is sanitation, and this agreed with Green et al. (2018).

The Ca concentrations in the soil and water were significantly higher in the Kuils River, where they reached  $28 \text{ mg}\cdot\text{l}^{-1}$ . Was double value was recorded in the Eerste River  $13.02 \text{ mg}\cdot\text{l}^{-1}$ . This is due to the passage of the Kuils River through the sandy lands in the Cape Flats region. The Ca in the soil of the Kuils River was five times what we recorded in the soil of the Eerste River, and significantly higher than the minimum values in the Eerste River. The highest concentrations of Pb, Ni, Zn and Fe were recorded in the water of the Eerste River in the middle and lower reaches of the river. *S. babylonica* leaves from the Eerste River had significantly higher

concentrations of Zn and Cu levels than these from the Kuils River. *P. lapathifolia* had significantly higher concentrations of Pb and Ni in the Kuils River than in the Eerste River. Using data collected from concentrations of heavy metals selected from water, soil and plant samples. Simple linear regression analysis was used to estimate the correlation between the heavy metal concentrations in the plant, water, and soil leaves as independent variables, then the third source of heavy metals that may have been from the atmosphere was added. Both affect the concentration of heavy metals in plant leaves. To identify which plants are suitable to be a biological monitor and for any of the heavy metals, whether in soil or water. We extracted from our results the following:



For the *Salix babylonica*, it gave results worthy of attention, as Cd was given the highest correlation value ( $\beta$ ) in water without the third source at  $p < 0.001$ . *S. babylonica* also had good results, as Cu, Fe, Pb, and Zn gave the values in the soil without the third source at  $p < 0.001$ . Thus, the *Salix babylonica* can be used as a prospective biological monitor for cadmium in the water and as well as for copper, iron, lead and zinc in the soil. We recommend it in future studies and the possibility of it being used as a biological monitor with third source in Cu, Fe and Zn, especially in the area of the Eerste River catchment. A group of studies have examined the accumulation of a group of heavy metals within the tissues of *Salix babylonica* and the possibility of using it as a biological monitor for soil pollution with heavy metals such as Liu et al. (2017) and Zeiner and Cindrić (2017).

In *Commelina benghalensis*, Cu and Cd concentrations gave significant results in water with our study without the third source at  $P < 0.001$ , and Cu with C.



*benghalensis* compared to other plant species have the highest value of correlation ( $\beta$ ) in water without the third source. *C. benghalensis* also had good results, as Cu, Fe, and Zn gave correlation values ( $\beta$ ) in the soil without the third source at  $p < 0.001$ . Thus, according to our results, it is strongly recommended to use *C. benghalensis* as a biological monitor for Cu contamination in water in the area. In addition to that it can also be used to biological monitor for Cd contamination in water; also, as an indicator of Cu, Fe and Zn in the soil. We recommend it in future studies and the possibility of it being used as a biological monitor for third source in Cu, Fe, Ni and Zn in the area of the Eerste River catchment. Adesuyi et al. (2018) mentioned the possibility of using *Commelina benghalensis* to assess with heavy metal pollution. Moreover, Ge and Zhang (2015) mentioned the use of *C. communis* to assess the environmental situation after heavy metal pollution.

In *Paspalum urvillei*, Cu and Ni concentrations yielded significant results in water with our study without the third source at  $p < 0.001$ . *P. urvillei* also had good results with the soil, as Cu, Fe, Ni, Pb, and Zn were given correlation values ( $\beta$ ) in the soil without the third source at  $p < 0.001$ . Accordingly, *P. urvillei* can be used as a prospective biological monitor for Cu and Ni in the water in the area, in addition to that it can be used to monitor pollution of Cu, Fe, Ni, Pb and Zn in the soil. We recommend it in upcoming studies and the possibility of it being used as a biological monitor for the third source in Cu, Fe, Ni, Pb and Zn in the area of the Eerste River catchment. Some studies, such as Adesuyi et al. (2018); Sa'idu et al. (2013) and Ying et al. (2008), found the possibility of using some types of the same family as *Paspalum urvillei* as a biological monitor or phytoremediation after the accumulation of heavy metals in the tissue of the plant.

In *Persicaria lapathifolia*, the concentrations of Cu and Ni gave important results in water with our study without the third source at  $p < 0.001$ . *P. lapathifolia* also had good results with the soil as Cu, Fe, Pb, and Zn gave the values of correlation ( $\beta$ ) in the soil without the third source at  $p < 0.001$ . Accordingly, *P. lapathifolia* can be used as a prospective bio-monitor for Cu and Ni in the water in the area. In addition to that it can be used to monitor Cu, Fe, Pb and Zn contamination in the soil. We recommend it in future studies and the possibility of it being used *P. lapathifolia* as a biological monitor for third source with Cd, Cu, Fe, Fe, Pb and Zn in the Eerste River catchment. Baldantoni and Alfani (2016) confirmed that there is a promising future for *Persicaria lapathifolia* to be used as a lead biomonitor.

Based on previous information on plant species recommended as biomonitors for the specific heavy metals with each plant species. Samples are taken from the leaves of the plant, and the concentration of heavy metals is measured and computed in the equations in the statistical model to predict the concentration of heavy metals in water and soil in particular.

## 8.2 Synthesis

Most studies have used mineral concentrations in plant tissues to predict the heavy metal concentrations in soil only or in water only. However, in our study, we used, for the first time, the concentration of heavy metals in plant leaves to predict the concentration of heavy metals in water and in soil. The following elements or compounds exceeded the safety in some part of the water or soil of the Eerste River catchment:  $\text{NH}_4^+$ , Ni, Zn, Cu, Cd and Pb.

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