SPATIAL AND TEMPORAL DISTRIBUTION OF SELECTED METALS IN THE SALT RIVER CATCHMENT, CAPE TOWN, SOUTH AFRICA

by

ZIKHONA MENZE

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Department of Conservation and Marine Sciences, Faculty of Applied Science at the Cape Peninsula University of Technology

Supervisor: Prof RG Snyman

Co-supervisors: Prof JP Odendaal and Prof R Toefy

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DECLARATION

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

15/02/2026

Signed **Date**

ABSTRACT

The Liesbeek and Black Rivers are two major urban tributaries in the Salt River catchment. The Salt River enters the ocean at Paarden Island, Table Bay, Cape Town. A multitude of pollution sources are found along the banks of these rivers, including industries, household waste, sewage treatment plants, golf course and informal settlements, which continue to threaten the water and sediment quality of these rivers. The catchment has been severely modified and canalized, increasing flooding events and sediment loads downstream. Despite the multitude of pollution sources surrounding the heavily urbanised Salt River catchment and the risk pollutants such as metals pose to aquatic ecosystems, no comprehensive study on metal pollution in this catchment has been published to date. This study investigated the spatial and temporal distribution of metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in water and sediments the Liesbeek, Black, and Salt Rivers by comparing new data (2022) with unpublished 2006 data, as well as by comparing wet and dry seasons and selected sampling stations. The objectives of the study were to assess contamination levels, identify the potential sources of pollution, and evaluate the spatial and temporal trends in metal concentrations over a sixteen years period. Two sampling stations were selected in each of the Liesbeek and Black Rivers, and one in the Salt River (due to most parts of the latter being canalised). Physicochemical parameters were measured at each sampling station by means of a handheld water multimeter. Sediment grain size analysis was also done for each sampling station, using sieves, a sieve shaker and the Wentworth scale (1922). Five replicates of water and sediment samples were collected at each of the sampling stations for metal analysis. Samples and blanks were digested in a heat block, using nitric acid and then filtered through 6 mm and 0.45μm filter paper. An Inductively Coupled Mass Spectrometer (ICP-MS) was used to determine metal concentrations at Stellenbosch University Central Analytical Facility. Results showed that physicochemical parameters increased downstream, with higher values observed in the lower Black River and Salt River, compared to the Liesbeek River. This trend is likely due to varying seasonal water levels, urban runoff, pollutants and canalisation. The study highlighted metals of particular concern in the Liesbeek, Black, and Salt Rivers that exceeded the recommended quality guidelines. According to the new risk-based freshwater quality guidelines (Odume *et al.* 2024), Al, Cu and Fe in this study were classified under the critical impact category and Mn and Cd under the moderate impact category. This indicated that the water quality is unacceptable and could lead to high mortality rates among aquatic organisms. Al, Cu, Fe, Mn and Pb, exceeded permissible levels of the Canadian Interim Sediment Quality Guidelines (CCME, 2002) at most of the lower sampling stations, which may have long term consequences on aquatic species' and human health. Urbanization, industrial discharges, household waste, sewage, stormwater runoff, and illegal dumping were identified as potential sources of metals. There were no clear temporal trends of increasing or decreasing metal concentrations observed across years (2006 and 2022). Distinct seasonal (wet and dry) patterns were however noted, with higher concentrations of metals such as Al, Fe, and Pb during the wet season of 2022 and a shift towards higher concentrations of metals like Cd, Cr, and Mn during the dry season of 2006. These patterns are likely due to a combination of seasonal environmental conditions (e.g. rainfall, flow speed, water level and evaporation), and increased input from surrounding sources. No clear spatial trends were observed for metals in river water, but some of the sampling stations, especially the Liesbeek River station 1 and areas downstream in the Black and Salt Rivers, showed high metal concentrations associated with household waste, atmospheric deposition, road runoff and industrial activities. The highest sediment metal levels were observed at the Black River station 2, located near industrial areas, roads, and a wastewater treatment plant and at the Liesbeek River stations, which has fewer major metal sources. The latter indicates that domestic pollution, litter and atmospheric deposition are important sources of metal contamination in urban rivers. Even though there were no clear long-term trends observed in this study, the findings highlight the importance of continued monitoring and pollution management strategies to mitigate the risks posed by metal contamination in the Salt River catchment and urban catchments in general. Attention should be given to smaller urban rivers and tributaries, such as the Liesbeek River, as they may be at greater risk than previously assumed.

Keywords: metals, pollution, physicochemical, sediment quality, water quality, Liesbeek River, Black River, Salt River, catchment, Cape Town.

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KEY ACRONYMS

DWAF: Department of Water Affairs and Forestry

CCME: Canadian Council of Ministers of the Environment

ISQG: Interim Sediment Quality Guidelines

CSQG: Canadian Sediment Quality Guidelines

ICP-MS: Inductively Coupled Plasma Mass Spectrometry

TWQR: Target Water Quality Range

CHAPTER 1: INTRODUCTION

1.1 Background

Water is regarded as the greatest natural resource to support all animals, plants, and human beings as they all rely on water for survival (Kazi *et al*., 2009; Molekoa *et al*., 2021). Surface freshwater is used for various crucial purposes which include drinking, irrigation, animal farming, recreation and habitats for water-living organisms (Edokpayi *et al*., 2016). About 0.01% of the world's water is made up of freshwater, that supports 100 000 species out of 1.8 million species (Dudgeon *et al*., 2006). Matthews (2016) stated that freshwater ecosystems such as lakes, ponds, rivers, streams, springs and wetlands are habitats to about 126 000 species. In South Africa water is used for various important reasons such agriculture activities (52%) mining, industries, power generation (12,5%), domestic, municipal uses (12%) and for maintaining estuaries and rivers (15%) (Holtzhausen, 2002; Jackson *et al.*, 2009).

Water quality plays a vital role in determining the ecological conditions and functions of water bodies (Liu *et al*., 2011). Rivers play a crucial role in meeting the needs of humans, animals, and plants. Despite this, river health is being threatened by unsustainable development (Liu *et al*., 2011). Urban rivers are surrounded by numerous potential sources of pollution such as industries, agriculture, domestic sources of pollution, as well as urban runoff via stormwater. The effect of pollution remains one of the main threats to rivers worldwide. Its effects need to be understood and addressed effectively (Jackson *et al*., 2007). The Liesbeek, Black and Salt Rivers flow mostly through urban areas of Cape Town, where numerous human activities may result in negative impacts on the condition of the river system. However, the degree of pollution, specifically metal pollution, remains relatively unknown for these rivers.

1.2 Threats to Rivers: A focus on pollution

Pollution of water is caused by various anthropogenic factors, many of them due to a high rate of human population growth, such as industries, urbanization, agricultural expansion, lack of environmental awareness, untreated sewage from industries, municipal waste, and the use of non-biodegradable pesticides including chemical fertilizers (Edokpayi *et al*., 2014; Reddy *et al*., 2015; Dudgeon, 2019). The world is struggling with various water quality issues arising from eutrophication, salinization, sedimentation, microbial pollution, including toxic pollution issues (Plessis, 2017).

The global sanitation and pollution crisis affects humans and ecosystems worldwide due to pollution of rivers by wastewater discharge from various sources such as household waste, air pollution, runoff and sewage (Wen *et al*., 2017). Pruss *et al*. (2002) reported that diseases such as diarrhoea are caused by untreated sewage that contains pathogens. The accumulation of pollutants in rivers promotes the growth of microbial bacteria that leads to oxygen depletion consequences of this affects the whole river system (Sirota *et al*., 2013). A study by Eneh & Eneh (2014) showed that 40% of Africans do not have adequate water sources and about 60% lack sanitation facilities, and in turn severely impacts human health and that of animals.

Challenges related to sustainable use of water resources are likely to be worsened by population growth and climate change (Musie & Gonfa, 2023). Urban streams are very important and delicate systems that can be evaluated by the impact of urban basins and routes (Wilmot, 2015). The state and health of rivers are in jeopardy, particularly in urban areas, necessitating more research to rehabilitate and sustain the state and quality of rivers (King *et al*., 2003). Water is a vital and scarce resource in South Africa. Therefore, it is essential to carefully manage it for future generations (King *et al*., 2003). Anthropogenic factors such as waste discharge, industrial effluents, medical waste, gas and particulate emissions from cars, oil spills, paving materials, domestic sewage, pharmaceutical waste, agricultural activities use of fertilizers, manures and pesticides may act synergistically (Bannerman *et al*., 1993; Pitt *et al*.,1995; Marsalek *et al*., 1999; Jackson *et al*., 2007).

Urban rivers are artificialized, resistant surfaces which are combined with heavily engineered drainage (Gilbert, 2015). Hydrological pathways have been transformed and the quantity and speed at which water flows have increased, which results in pollution finding its way into river systems (Gilbert, 2015). Surface water is a crucial source of water for both humans and animals all over the world (Nkqenkqa *et al*., 2017). This author mentioned that surface water is polluted and contaminated by a variety of causes, including mining, farming, and landfill operations, as well as human activities such as illegal dumping. Nkqenkqa *et al*. (2017) reported that during rainy seasons, the illegal dumping, municipal waste, and domestic waste reach the river system through runoff which results in degraded water quality.

The profile of water quality variables changes significantly within the spatial extent of the catchments or tributaries. As a result, it is important to have background knowledge and understanding of water quality variables in rivers since they play a significant role in meeting human, plant and animal needs. Generally, the natural environment and aquatic habitats have provided humans with numerous benefits. However, these attributes have also put a strain on the ecological form and river functioning (King *et al*., 2003) such as water flow, water quality, and water quantity.

Deterioration of water quality and ecological conditions is a typical trend in rivers and streams around the world as humans demand more water resources than their capacity (Musie & Gonfa, 2023). Natural processes such as precipitation rate, weathering processes, soil erosion and exploitation of water resources and human activities including exploitation of water resources, urban and industrial activities continue influencing surface water quality (Singh *et al*., 2005). King *et al*. (2003) stated that human intervention on the natural state of rivers has transformed river flow, which resulted in transforming water quality and quantity through altering drainage patterns and chemical constituents.

The demand and need for good quality water in South Africa is increasing (WRC, 2001; River Health Programme, 2005). Some of the rivers have been modified for various purposes such as irrigation in agricultural areas, industries, and most importantly for drinking purposes. Wuana & Okieimen (2011) and Sankhla *et al*. (2016) stated that environmental contamination is increasing every day, and they cause concern to local users due to the increase of industrialization, population growth, exploitation of natural resources, agriculture, and domestic waste runoff. Removal of natural vegetation in rivers increases the speed of runoff and that leads to soil erosion (Dudgeon, 2019). Population decline of aquatic species in the freshwater ecosystem is caused by habitat degradation (Reid *et al*., 2019). In support of this statement Dudgeon *et al*. (2006) also found that the threat to freshwater biodiversity is caused by habitat degradation through flow modification.

1.3 Metal pollution in rivers

Metals are usually present in only trace concentrations in the environment and are found in less than 1% of the earth's crust (Jackson *et al*., 2007). However, metals in the environment become a concern if found in higher-than-normal concentrations, since they tend to accumulate in living beings over time, i.e. they increase in life forms faster than they are broken down (metabolized) or excreted. Addo-Bediako *et al*. (2021) confirmed that metals are regarded as a great threat due to their potential for bioaccumulation and biomagnification within the bodies of aquatic organisms at concentrations higher than that of their environment.

Metals are reported to be very toxic and dangerous, as a result, they pose serious health risks when consumed by humans and animals (Reish & Oshida, 1987; Edokpayi *et al.*, 2014). Zhou *et al*. (2008) stated that it is important to ensure that metal concentrations do not exceed normal levels as it may consequently have detrimental long-term impacts on human health, including aquatic animals. Metal pollution in river systems has become a primary problem of public health concern because of their toxicity and persistence in the environment (Reddy *et al*., 2015; Addo-Bediako *et al*., 2021).

There is a positive correlation between metal distribution in aquatic environments and population density and urbanisation through largely uncontrolled inputs from industrial activities (Conrad *et al*., 2007; Shang *et al*., 2015). Transportation of metals in runoff from mines, industries and agricultural land, and the growth of human settlements next to riverine systems, have a detrimental effect on both water quality and river biota (Mimba *et al*., 2018; Addo-Bediako & Rasifudi, 2021). Industrial emissions such as sulphur dioxide and nitrogen dioxide reduce pH and increases aluminium, while agriculture, deforestation, sewage works, atmosphere emissions of nitrogen oxides (No_X) increase nitrogen & phosphorus (Malmqvist & Rundle, 2002).

Land preparation, burning, ploughing, fertilization, biocide application and livestock rotation may all have negative impacts on the quality of the receiving water bodies by contributing excessive nutrients and suspended solids through runoff (Dallas & Day, 1993). Agricultural fertilizers are a major source of metals in soils, which are eroded and transferred into catchment basins, where they are adsorbed by particulate matter such as sand and gravel (Van Stormbroek, 2007). A previous investigation on freshwater showed that agricultural and anthropogenic practices can influence the transport of metals into water (Chetty & Pillay, 2019). The mining industry releases essential and non-essential metals that are causing serious hazards to the environment throughout the world. These metals are released during, for example, mineral processing, production of exploitation remains, and the transport of acidic metal-rich effluents (Faria *et al*., 2008).

Sediments are primary metal carriers in the aquatic environments due to the chemical properties they possess, namely particle characteristics, as well as processes they experience, such as precipitation and desorption/adsorption (Fukue *et al*., 2006; Rath *et al*., 2009). According to Nemati *et al*. (2011), metal contamination within sediments is considered a primary environmental concern as it has the potential to cause remobilisation and bioaccumulation in aquatic organisms. This could also impact human health through food chains by means of benthic organisms (Shang *et al*., 2015). According to Calderon (2000) and Jarup (2002) excessive lead and cadmium consumption, even at relatively low levels, could lead to renal dysfunction, neurological, bone and cardiovascular diseases, as well as different cancers. The short-term impacts of high cadmium concentrations consist of nausea, diarrhoea, vomiting, muscle cramps, renal failure, convulsion, salivation, sensory disturbances, shock and liver injury (Hazards Centre & People's Science Institute, 2006). The Hazards Centre & People's Science Institute (2006) further stated that the impacts of short-term exposure to copper includes irritation of the eyes, nose and throat, as well as a flu-like sickness known as metal fume fever.

The most dangerous metals that are widespread and known to be harmful to humans and aquatic organisms are mercury, cadmium, and lead (Nriagu, 1988). A study found that the concentration of metals and length of introduction impact the chemical action within the river system and higher concentrations of metals are expected to initiate stress proteins like metallothioneins or evasion components (Rajalakshmi & Mohandas, 2005). Studies on metal pollution in rivers could easily overlook physicochemical changes, thus it is very crucial to understand the reactions that might be taking place in the water. Furthermore, physicochemical factors in the river can easily affect and change aquatic ecosystems and the toxicity of metals significantly (Alloway & Ayres, 1997).

Alloway & Ayres (1997) postulated that there may be a possibility that river sediment in a locality suspected of being polluted may have developed from rocks with high concentrations of certain metals and other chemicals. These metals include Pb, Cu, or Zn (Alloway & Ayres, 1997). These authors found that the natural enrichment of metals at higher concentrations in rivers may still give rise to harmful effects in organisms and humans. It is therefore important to determine the local background concentrations of metals to ascertain whether the concentrations in the water and sediment under investigation are significantly higher than natural concentrations of the investigated area (Alloway, 1995).

Sherrell & Rose (1999) suggested that despite the significance of metals in river biological systems, the processes governing metal concentrations in streams are still generally not clearly known. Jackson *et al*. (2007) reported that metal concentrations may become dangerous to the environment if they surpass a set of limitations, namely Water Quality Guidelines, General Effluent Standards and Water Quality Management Areas that were set for the prevention, control and reduction of water pollution (World Health Organisation, 1991; DWAF, 1996). Water quality guidelines were mainly formed to provide services that are aligned with the law with regards to the protection, preservation and improvement of aquatic environments (DWAF, 1996; CCME, 2002).

Fourie (2005) stated that the Eeste/Kuils River catchment area faces a multitude of environmental concerns, such as organic pollution (bacteria contamination), recreational risks, habitat destruction, water treatment (WWTWs), rural encroachment and rising watershed urbanization. As runoff and storm water drain from surrounding areas, all pollutants and bacteria (faecal pollution) are dumped into the river and therefore the rivers act as a dumping site for all these pollutants. The lack of riparian habitats serving as natural filters, it is impossible to eliminate or reduce potentially harmful bacteria (Fourie, 2005).

1.4 Effects of seasonality and physicochemical features on metal concentrations.

1.4.1 *Seasonality*

River flow is a function of factors such as precipitation, interflow, surface flow, pumped inflow, groundwater flow and outflow. The seasonal variation of these factors strongly impacts flow rates and thus the concentration of pollutants within the river water (Vega *et al*., 1998). Unlike industrial and municipal wastewater discharges, which are considered a polluting source, seasonal runoff on the other hand is highly impacted by climate (Vega *et al*., 1998). The regional climate's impact on the flow of Western Cape rivers is complicated: these rivers are highly influenced by changes in rainfall, which impacts flash floods and drought frequency and as well as evaporation rates due to temperature variations (Lakhraj-Govender & Grab, 2019). Milly *et al*. (2008) stated that river flow changes because of the shifts in rainfall and increased frequency of extreme events.

Temperature is considered as a crucial parameter because of its direct impact on chemical reactions, reaction rates, biota, and sustainable use of water for human beings (Metcalf & Eddy, 2004). The most favourable temperature ranges from 25ºC to 35ºC for many biological activities such as bacteria (Mathebula, 2015). Mathebula (2015) stated that the aerobic digestion and nitrification processes end in bacteria when the temperature rises to 50ºC. In comparison, this author also mentioned that methane producing bacteria becomes inactive with some nitrifying bacteria losing their viability, when temperature reduces to 15ºC. Moreover, temperature gives rise to toxicity of potency due to certain chemicals namely, cyanide, zinc and phenols making microorganisms more vulnerable to their potency (Mathebula, 2015).

According to Lakhraj-Govender & Grab (2019) spatio-temporal distribution of rainfall could potentially be altered through climate change. As a result, the supply and demand of water resources could be significantly impacted and lead to devastating consequences, particularly in an already water-stressed country such as South Africa. According to these authors the Intergovernmental Panel on Climate Change (IPCC) stated that there is strong evidence of climate change resulting in reduced renewable surface water. Lakhraj-Governder & Grab (2019) stated that a change in precipitation magnitude and frequency is considered one of the most consequential impacts of climate change.

Furthermore, an increase in temperature could result in higher evaporation levels, spatio-temporal runoff and storage of water resources (Lakhraj-Govender & Grab, 2019). Survival, phenology, disease outbreaks and species distribution are transformed by increasing freshwater temperature (Parmesan, 2006; Hermoso, 2017; Krabbenhoft *et al*., 2014; Bassar *et al*., 2016). Climate change increases water temperature, affects interaction between aquatic organisms, affects the hydrological cycle and reduces the quality of freshwater ecosystems (Reid *et al*., 2019).

Hester & Doyle (2011) stated that unnatural temperature fluctuations can cause detrimental effects on aquatic biota. It is evident that temperature plays a vital role within the aquatic environment and is therefore important to monitor. According to the research study conducted by Khan *et al*. (2006) climate change may cause an increase in global temperature and may make aquatic species more sensitive to toxic metals. The study by Sokolova & Lannig (2008) on temperature effect, revealed that ecological toxicology provided evidence that the temperature of the environment can influence the tolerance to metals in aquatic ectotherms. Moreover, increasing anthropogenic pollution of aquatic environments, interactions between environmental temperature and metal pollution have a significant impact on physiological tolerance to both stressors and can limit the survival and distribution of ectotherm population (Sokolova & Lannig, 2008).

Khan *et al*. (2006) and IPCC (2001) found that the presence of the current trends of environmental pollution and global warming, differences between and within species in the influence of temperature on the toxicity of metals can have a significant impact on the survival of sensitive species and persons. In addition, when water bodies become too warm, they can pose the greatest impact on riverine species and thus will make it hard for the species to adapt and may disperse to cooler habitats (Dudgeon, 2019). Contaminant toxicity increases due to warmer temperatures. In addition, water abstraction by humans reduces the capacity of rivers to dilute pollutants (Wang *et al*., 2019).

During the wet season, surface runoff from different land activities such as settlements, dumpsites, industrial and agricultural activities, together with dilution because of increased precipitation, can lead to variations in metal concentrations in rivers (Edokpayi *et al*., 2014). These authors indicated that during the dry season evaporation from water bodies result in increases in concentrations of contaminants, as the dilution factor is removed due to low water volume and less to no rainfall. Edokpayi *et al*. (2017) also showed that metal levels in rivers are affected in the wet season by storm water runoff from the surroundings in the river catchment, and this usually results in higher levels of metal contamination. These authors added that increased dilution caused by increased water volume and flow is one of the factors that impact the concentrations of metals in a river during the wet season. Whereas, during the dry season, metal concentrations may increase due to low water volume and flow, largely as a result of evaporation from water bodies (Edokpayi *et al*., 2017).

Similarly, Fosso-Kankeu *et al*. (2016) stated that there are significant seasonal differences in different parameters measured in surface water. A decrease in metal concentrations was observed during the wet season compared to the dry season. Lower metal concentrations were recorded in the wet season, which could be due to the water dilution effect from frequent and heavy rainfall events. A study that was done in China found that the values of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in the dry season (October to March) were significantly higher compared to those in the wet season (April to September) (Deng *et al*., 2018). Another study found similar results, where dissolved nitrogen and phosphorus levels in the river water were relatively higher in the dry season than in the wet season (Li *et al*., 2009). In contrast, Wang *et al*. (2010) showed that the wet season had higher concentrations of nutrients and metals than the dry season in water bodies. Matshakeni (2016) found that the current state of water quality in the Eerste River shows that turbidity, nitrates, nitrogen, and ammonia were higher than the South African water quality targets as recommended by DWAF (1996) nitrogen 0.5 mg/L and ammonia 0.007 mg/L.

1.4.2 *Physicochemical parameters*

Water quality can be determined through a combination of parameters, namely chemical parameters (electrical conductivity, total solids, dissolved oxygen, suspended solids, biological oxygen demand, etc) and physical parameters (pH, temperature, salinity, etc) (Korkanc *et al*., 2017). There are numerous chemicals/materials such as suspended solids, salts, organic material, metals, pesticides, and excessive nutrients that play a significant role in polluting water bodies and changing the physical and chemical properties of river water, in turn threatening human, animal and plant health, and ecosystem functioning in general. Field *et al*. (1998) reported that pollutants increase physical, chemical, and biological stress in water bodies, which further transfer these pollutants to the ocean and affect aquatic life and human health.

Physical and chemical parameters of rivers can be either high or low depending on various impacts within the river system, for example chemical parameters can be high due to disposal of waste into the river (Korkanc *et al*., 2017). Dallas & Day (2004) found that changes in water pH have a wide-ranging impact on water chemistry, and thus on a receiving river, e.g., from one river to another, but they are hard to evaluate since pH can shift constantly over periods as brief as 24 hours. pH can be used to determine whether the water status is acidic or alkaline (Alam *et al*., 2007). The standard water pH levels range between 6.5 mV to 9 mV and they can be considered as either high or low depending on the degrees and influence (Al-Badaii *et al*., 2013).

Water quality results for the River Enborne in the United Kingdom showed that the overall water chemistry was fed by calcareous groundwater from the chalk aquifer, as demonstrated with the high alkalinity, high calcium content and high conductivity (Halliday *et al*., 2014). Azrina *et al*. (2006) found that the Langat River in Malaysia had abnormal levels of nitrogen, total solid suspension, biochemical oxygen demand, and dissolved oxygen and were above their local water quality guidelines. A recent study conducted in South Africa (Western Cape, Limpopo, Eastern Cape, Northwest, Northern Cape, Free State, Kwa-Zulu Natal and Mpumalanga) and Mozambique (Gaza) showed higher concentrations of nitrite, chloride, sulphate and total dissolved solids that were above the national standard limit (Verlicchi & Grillini, 2020).

Korkanc *et al*. (2017) conducted a study in Akkaya Dam in Turkey where they found high levels of various chemical parameters at a sampling station where untreated domestic wastewater was disposed into the river system. Gauthier *et al*. (2006) stated that changes in water chemistry do not affect toxicity similarly for individual metals. Various investigations have been conducted to quantify the effects of individual water physicochemical parameters on metal toxicity (Alsop & Wood, 1999; Hollis *et al*., 2000; Pyle *et al*., 2002; Okonkwo & Mothiba, 2004). Temperature is one of the parameters that can be used to describe the health and functioning of an aquatic environment (Awe *et al*., 2020). Numerous environmental parameters such as alkalinity, hardness, pH, dissolved oxygen, temperature, turbidity, carbon dioxide, magnesium salts, phosphates and chelating agents can impact the toxicity of metals to aquatic species (National Research Council, 1972; Wang, 1987).

Electrical conductivity is described as a measurement of electrical current in water (Mathebula, 2015). This researcher mentioned that dissolved ions such as chloride anions and calcium cations including the size of the ions directly influence conductivity and it is changed by temperature because of the influence of the temperature on the viscosity of water. Mathebula (2015) further stated that there is often a close correlation between electrical conductivity and total dissolved Salts concentration for a particular water type. Natural electrical conductivity and total dissolved salts in rivers are dictated by geological and atmospheric conditions. However, anthropogenic activities such as industrial effluent, water reuse, and irrigation may result in increased total dissolved salts and electric conductivity (Belcher & Grobler, 2016). Electrical conductivity is easier to measure; therefore, it is usually used to estimate the level of compounds or salts dissolved in the water (Belcher & Grobler, 2016). These values indicate the natural salt content of the rivers. There can usually be large seasonal variability in electrical conductivity values, which are associated with increased runoff from the catchments during winter (Belcher & Grobler, 2016).

pH is one of the crucial parameters for natural and wastewater hydrogen ion concentration. Bezuidenhout (2013) stated that pH is regarded as the intensity of acidity in a water body. Geological and atmospheric influences determine the relative proportions of the major ions, and pH of natural waters. South African freshwaters are mostly relatively well-buffered with more or less neutral pH values ranging from 6 mV to 8 mV. Relatively small changes in pH levels are not often lethal but could lead to fecundity and reduced growth rates (Belcher & Grobler, 2016). Belcher & Grobler (2016) stated that industrial effluents, acid precipitation, and acid mine drainage often result in increased pH levels.

In terms of dissolved oxygen and chemical oxygen demand, temperature, atmospheric pressure and the saturation capacity regime in the water body is connected to the amount of dissolved oxygen (Mathebula, 2015). The author also noted that as water temperature increases, the solubility of dissolved oxygen decreases, leading to a reduction in its concentration (Mathebula, 2015). This happens due to increased metabolic rates, as well as respiration, and oxygen demand of aquatic biota resulting in high water temperature.

A study conducted in the Liesbeek and Black Rivers found that suspended solids found in water consist of organic and inorganic matter, such as particles, clay, minerals and a mixture of living organisms and decayed products (DWAF, 1996). The total suspended matter in a river is usually indicative of the degree of soil erosion associated with the river (DWAF, 1996). Therefore, activities which accelerate soil erosion would result in increased suspended solids in the river. According to the target water guidelines, total suspended solids should not exceed 10% of the background total suspended solids concentrations at a specific site and time (DWAF, 1996; Belcher & Grobler, 2016). Long term observations showed a decreasing trend in the amount of suspended solids measured within the two rivers (Yunus *et al*., 2021).

Belcher & Grobler (2016) found that inorganic nitrogen has a stimulatory impact on aquatic plant growth and algae. Belcher & Grobler (2016) indicated that the inorganic intermediate in converting ammonia to nitrate (NO_3^-) is nitrite (NO_2), which is toxic to aquatic organisms. Out of the two forms, nitrate is more stable and often more abundant in the aquatic environment. Nitrate and nitrite are often measured together. These authors also mentioned that the Black River had a median value of 1.4 mg/L for NO_2/NO_3^-, which was slightly elevated due to treated wastewater discharge. The Liesbeek River, on the other hand, had a median value of 0.6 mg/L. However, these values are still considered low compared to target values (Belcher & Grobler, 2016). Nitrogen is found abundantly in nature and is important for many biochemical processes. Belcher & Grobler (2016) stated that inorganic nitrogen comes in different forms, such as ammonia (NH_3), ammonium (NH_4^+), nitrites (NO_2) and nitrates (NO_3^-).

Nitrates are rapidly transformed into organic nitrogen in plant cells when entering aquatic systems. According to Belcher & Grobler (2016) unionised ammonia (NH_3) is toxic to aquatic organisms when exceeding the water quality guideline value of 0.007 mg/L (CCME, 1991, CCME, 2010). Its toxicity increases as pH levels decrease, in other words water becomes more acidic and temperature rises. Although ammonium ions (NH_4^+) have little to no toxicity, it contributes to eutrophication. Ammonium does not have any guidelines or standards set. However, the level thereof provides a good indication of pollution levels within the river, particularly as a result of treated wastewater discharge (Belcher & Grobler, 2016). Due to the discharge of treated wastewater within the Black River, the median value of ammonia is 5.7 mg/L. This exceeds the target values of 0.019 mg/L as stipulated by the CCME (2010).

In aquatic ecosystems an ecological impact of ammonia may occur through chronic toxicity to fish populations and benthic invertebrates due to reduced reproductive capacity (Belcher & Grobler, 2016). The impacted populations may die out over time if there is not continual recruitment from unaffected populations (Belcher & Grobler, 2016). Belcher & Grobler (2016) found that the impacts of toxicity on aquatic ecosystems may extend for kilometres below large wastewater treatment works discharge. It is very difficult to determine the impacts on fish populations as many species are mobile. Since benthic invertebrates are not very mobile during most of the life cycle, they are better indicators of the impacts (Costa *et al*., 2020; Mezgebu, 2022).

1.5 Metal pollution in South African rivers: A focus on the Western Cape and urban Cape Town rivers

In the Western Cape, South Africa, urbanization has resulted in the expansion of informal settlements, where residents face a severe lack of crucial resources to sustain livelihoods. In addition, insufficient sanitation and lack of proper sewage disposal systems can result in the release of potentially dangerous compounds into river systems. Urban rivers are the most heavily used and polluted rivers on the planet (Jackson *et al*., 2007). According to Dallas & Day (1993) agriculture and forestry may have an impact on the environment, by adding nutrients, dissolved, and suspended solids into receiving water bodies.

Even though many Western Cape rivers are urban rivers with numerous possible sources of metal pollution, only a few studies on the pollution of these rivers have been published to date. Gqomfa *et al*. (2023) and Ward (2014) found that the main disturbances in rivers are derived from urban development pressures, deterioration of stormwater quality, transitions between basins, alteration of channels and flows, mismanaged informal settlements, agricultural practices, return flow turbidity, and nutrient content. Water pollution from several nonpoint sources such as farms, roadways, urban and suburban landscapes remain uncontrollable (Brown & Froemke, 2012).

Three of the largest and/or most studied rivers close to Cape Town are the Berg River (Paarl), Diep River (Milnerton) and Eerste River (Stellenbosch). The Berg River is one of the biggest rivers in the Western Cape Province, it is located within the Berg Management Area, and its region is classified as a rich biodiversity hotspot (Goldblatt & Manning, 2002). This river provides water to nearby towns, cities, rural settlements, and farms for personal use, irrigation, and recreational purposes (Jackson *et al*., 2007). However, as the river flows downstream water quality decreases due to agricultural activities, urban stormwater, discharge from wastewater treatment and runoff from informal settlements with a lack of proper sanitation services (Bate & Snow, 2007).

A study conducted in the Berg River showed that the water quality was influenced by certain factors such as high concentrations of phosphate and silicate that were suspected to result from the anthropogenic nutrient inputs from domestic and industrial activities (Benamer, 2014). Benamer (2014) also found that Cd and Zn were the most mobile and bioavailable during the study. Jackson *et al*. (2013) stated that rivers exposed to industrial runoff, for example the Berg River, contain the highest metal concentrations.

The Diep River catchment has an estimated length of 65 km and is surrounded by both residential and industrial areas (Shuping, 2008; Paulse *et al*., 2009). The Diep River is a key freshwater environment near Cape Town. In addition, this river is surrounded by many potential sources of metal pollution including an oil refinery, sewage treatment plants, industries, densely populated formal and informal residential settlements, and a landfill site (Shuping, 2008; Shuping *et al*., 2011).

Siltation resulting from the soil erosion within the Diep River Rietvlei system has increased substantially over the past years, resulting in extensive erosion (Grindley & Dudley, 1988, Paulse *et al*., 2009). These authors reported that during floods, it is thus considered a storage area for sediment rich water. In addition, the vegetation in the vlei intensifies the rate of sedimentation, particularly in areas where treated sewage water is released (Grindley & Dudley, 1988). The catchment consists of Swartland and Sandveld regions within the Western Cape's western lowland area. Shuping (2008) stated that due to the flat topography of the catchment, it is suitable for agriculture and urban development.

Furthermore, cultivation, such as wheat and grain crops, currently expands more than 90% of the catchment (Shuping, 2008). In addition, vineyards and orchards are also increasing in the area (Shuping, 2008). There are currently three wastewater treatment works discharging into the Diep River at Malmesbury, Kraaifontein and Milnerton (Shuping, 2008). Visserhok, which is a large landfill site, as well as several other general waste stations, which receive hazardous wastes, are located within the vicinity of the river (Shuping, 2008). An incinerator is also used to dispose of medical wastes at Vissershok (Shuping, 2008).

The detected metal concentrations in water of the lower Diep River were higher than the DWAF guidelines for freshwater ecosystems (DWAF, 1996; Shuping, 2008). Concentrations of metals, such as Fe, Zn and Al were higher compared to those measured in other similar South African studies (Shuping, 2008). The lower Diep River ecosystem appears to be threatened by metal pollution, especially within the vicinity of the sensitive Rietvlei Nature Reserve as the surrounding industries and urban areas give rise to metal contamination (Shuping, 2008). These metals are settled in the sediments more rapidly than they are washed downstream. High concentrations of metals are accumulated by plants such as *Bolboschoenus maritimus* closer to the mouth of the river, thus reducing the impact on the estuary (Shuping, 2008). Shuping (2008) concluded that these metals have, however, not been taken out of the ecosystem, and still pose a threat to the ecosystem through decomposition of plants, as well as through food chains where the metals are transferred and released.

Previous research conducted by Snyman (1996) and Reinecke *et al*. (2002) showed that the Eerste River was unpolluted even though the physicochemical parameters of the river were influenced by runoff from the Stellenbosch municipal area, industries and agricultural land. A more recent study by Matshakeni (2016) found that the Eerste River's water quality declined downstream of Stellenbosch. Another study conducted in the Kuils River by Melato (2011) found higher concentrations of Al, Cu, Mn and Zn and were higher than the DWAF (1996) guidelines. Furthermore, in the lower reaches of the Eerste River, it is joined by the highly polluted Kuils River system (Ngwenya, 2006).

The Melato (2011) study conducted in the Kuils River revealed higher concentrations of metals in water and sediments due to input from the surrounding urban and agricultural activities. The water quality has been degraded due to a range of land uses such as agricultural areas with intensive irrigation (DWAF, 2004), as well as domestic and industrial uses (Somers & Nel, 2003; Ngwenya, 2006). The Kuils River receives effluent from *Bellville (14.7 million cubic metres/annum) and Zandvliet (16.8 million cubic metres/annum*) wastewater works (DWAF, 2004; River Health Programme, 2005). Ngwenya (2006) found significant trends of increased/decreased pH, electrical conductivity, phosphate, chemical oxygen demand, nitrite and nitrate, which serve as evidence that the water quality is degraded. The water quality of the Plankenburg River is classified as poor since it carries high levels of pollutants coming from the stormwater and wastewater from the Khayamandi informal settlement and Stellenbosch (River Health Programme, 2005).

1.6 The Liesbeek, Black and Salt Rivers

The Liesbeek, Black and Salt Rivers flow mostly through urban areas of Cape Town, where human activities may be negatively impacting the condition of river systems. The Liesbeek and Black River are tributaries supplying water to the Salt River (Whittemore *et al*., 2004). The Liesbeek River rises from the eastern slopes of Table Mountain and flows through the natural fynbos of Kirstenbosch National Botanical

Garden (Gilbert, 2015; Crisp, 2016; Aziz, 2020). The Black River covers an area of about 254 km² draining the Tygerberg Hills flows through the north-western parts of the Cape Flats and south-facing slope of Table Mountain through Pleistocene sands and Malmesbury marine sediments and then joins the Liesbeek River to form the Salt River (Haniff, 2003).

The Salt River starts after the confluence of the Black and Liesbeek River. The Gilbert (2015) study revealed that the middle and lower reaches of the Black and Salt Rivers are heavily polluted due to wastewater discharge, runoff from stormwater, and litter disposal. Parts of these rivers flow via informal settlements where there are numerous sources of pollution. In addition, pollution in this river could result from the railway line and runoff from the road. Many parts of this river are also canalised (Gilbert, 2015; Belcher & Grobler, 2016). The Liesbeek River is fed by several streams running down the eastern slopes of Table Mountain before reaching its confluence with the Black River, thus forming the Salt River, from which point it flows northwards to where it transfers water into the Atlantic Ocean at Paarden Island (Whittemore *et al*., 2004; Gilbert, 2015; Aziz, 2020).

A previous study found that urbanisation had an impact on the lower reaches of the Black River where mostly human activities, unsustainable development and high demand for space takes place (Fisher-Jeffes *et al*., 2017). Previous investigations provided evidence that the Liesbeek and Black Rivers are suffering from unsustainable development (Gilbert, 2015; Crisp, 2016). Crisp (2016) stated that the upper reaches of the Liesbeek River are less disturbed, due to the fact that it is surrounded by low density residential housing and land use, unlike in the lower reaches where mostly human activities, and urbanisation play a significant role in degrading the quality and functioning of the rivers. According to Belcher & Grobler (2016) most of Cape Town's rivers are urbanized, canalised and heavily transformed due to industrial activities and high human population. The Salt and the Black Rivers mostly consist of hardened/paved surfaces; both rivers' natural states have been altered. The upstream section of the Liesbeek River is not as modified compared to the Black and Salt Rivers, even though parts of this river are also canalised (Belcher & Grobler, 2016).

1.7 Research questions

- What is the current water quality, in terms of metal concentrations, water pH, temperature, salinity and oxygen content, in the Black, Liesbeek and Salt Rivers?
- How does the current water quality differ from the water quality of these rivers in 2006?
- How do metal concentrations in these three rivers differ between the wet and dry seasons?
- What are the possible sources of metal pollutants along the banks of these three rivers?

1.8 Research objectives

- To determine water quality in terms of temperature, pH and conductivity in the Liesbeek, Black and Salt Rivers.
- To determine the most prominent metals responsible for the contamination of water and sediments in the Liesbeek, Black and Salt Rivers.
- To determine the temporal variations in metal concentrations in terms of years (2006) and seasons (wet and dry) in the Liesbeek, Black and Salt Rivers.
- To determine spatial variations in metal concentrations between selected sampling stations in the Liesbeek, Black and Salt Rivers.

CHAPTER 2: MATERIALS AND METHODS

2.1 Sampling station selection

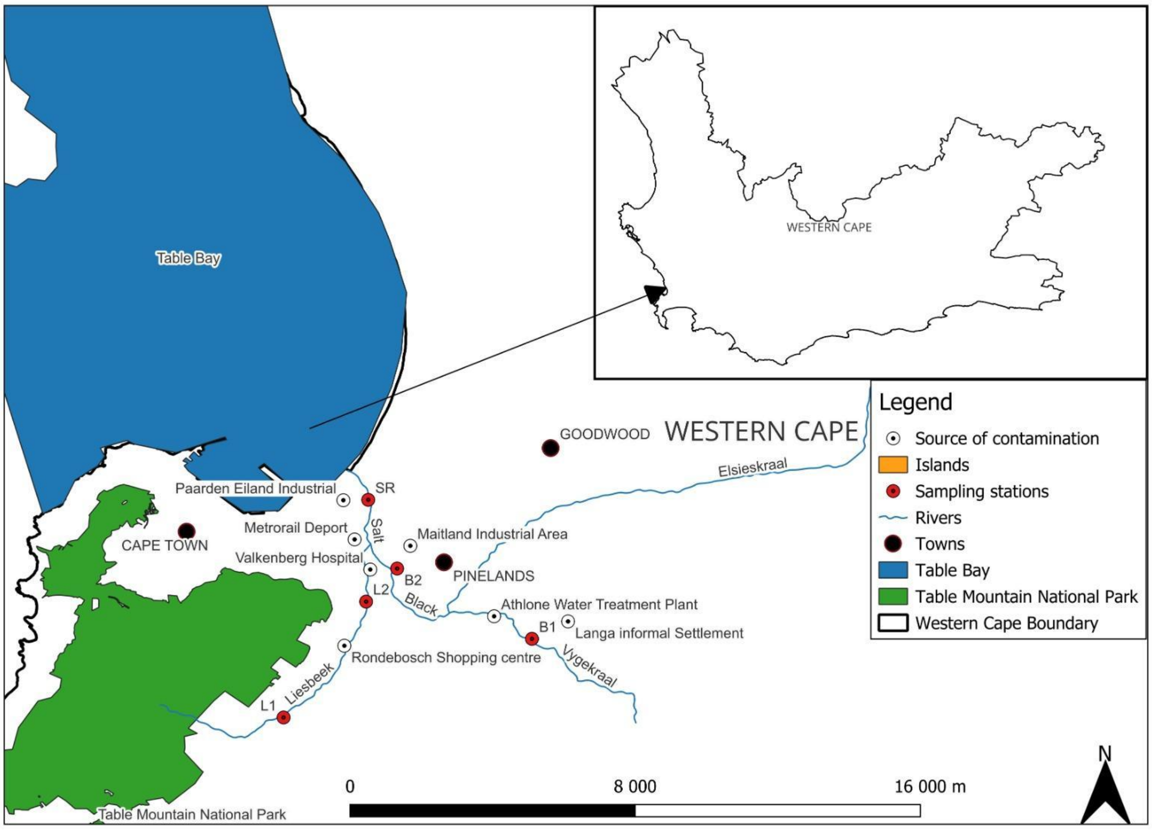


Figure 1: Map showing the sampling stations. The red points indicate the sampling stations in the Liesbeek, Black and Salt Rivers.

This study was carried out in three selected rivers around Cape Town (Liesbeek, Black and Salt Rivers) (Fig. 1). The Black, Liesbeek and Salt Rivers are situated in the Western Cape Province, South Africa. Sampling stations were chosen to include the upper and lower sections of the Liesbeek and Black Rivers to trace the possible sources of metal pollution. The Salt River has one station after the confluence of the Liesbeek and Black Rivers. These stations were selected based on the hydrodynamics, the magnitude of anthropogenic activities and practical and safety considerations, as well as the positions of the stations used in an unpublished 2006 study. The Liesbeek River's first station (L1) was used as a reference station because there are the least anthropogenic activities compared to the other sampling stations. Global Positioning Systems (GPS) was used to record coordinates of each sampling station to ensure that the same locations were sampled during both sampling occasions (wet and dry seasons).

The first sampling station in the Liesbeek River was located about 1.8 km from the Kirstenbosch National Botanical Garden (Fig.1). This station was used as a reference station because there is little disturbance in the area around that section of the river due to a low density of residential housing and less intense land use. The second sampling station in the Liesbeek River was situated in the formal residential area of Rosebank. This section of the river is canalised as a result of engineering interventions. This sampling station is surrounded by development that include formal housing, business premises, and sports grounds.

The first sampling station in the Black River is located at Nantes Park in Athlone and flows in a north-westerly direction (Fig 1). Station 1 in the Black River was in its natural state and was not canalised. The second station is situated close to Black River Parkway, just south of the Raapenberg Bird Sanctuary (Fig. 1). This section of the river is impacted by urban and industrial pollution sources from the surrounding areas close to the river. A wastewater treatment works is located about 3 km upstream from this sampling station.

The Salt River sampling station was located after the confluence of the Black and Liesbeek Rivers, adjacent to the Koeberg Interchange that links a highway with other major roads at Paarden Island (Fig. 1). This section of the river seems to have various other sources of pollution due to the industries in this area.

2.2 Sample collection

In 2006, a CPUT study was initiated on metal contamination in the Liesbeek, Black and Salt Rivers (Batena, 2006 Unpublished). Sampling was done and samples were analysed, however, no data analyses were performed. These data will now form part of the present study. This was done through comparisons of the data that was collected in 2006 and new data for 2022. Together with comparisons between wet and dry periods and between consecutive selected sampling stations in the rivers, a clearer picture will be established regarding the scope of metal contamination in these rivers and the Salt River catchment as a whole, as well as of temporal changes in metal concentrations due to land use intensity and climatic factors.

The sampling was done twice during a period of one year, to represent the wet and dry seasons, namely winter/early spring 2022 (high rainfall period) and summer/early autumn 2022 (very low rainfall period). Two sampling stations were selected in each of the rivers except for the Salt River catchment. Each sampling station was given an identification code and sampling stations were determined using a GPS. During each sampling, water temperature (ºC), electric conductivity, pH, dissolved oxygen and salinity were measured at each sampling station with a handheld YSI water multimeter. The multimeter was suspended in the water for at least ten seconds before measurements of the physicochemical parameters were taken. Five replicate water samples were randomly taken using a plastic container in the flowing water. Grab samples of the sediment (top 5 cm) were taken. Like with the water, five replicates were taken of the sediment from each sampling station. Each sample was placed in a plastic container and labelled. Samples were stored in the laboratory at the Cape Peninsula University of Technology, in the freezer at -18ºC. All sample preparation for metal analysis was done according to the methods described by Odendaal & Reinecke (1999) and Shuping *et al*. (2011).

2.2.1 *Acid Digestion*

2.2.1.1 Water samples

Before the process of digestion commenced, water samples were thawed. Then ten ml of each sample was digested in 5 ml 65% nitric acid at 40°C in a Grant UBD heating block. This was done for one hour and thereafter the temperature was increased to 120°C for 3 hours. A "blank" that did not contain river water was prepared in the same way. The acid was cooled and then filtered through Whatman No.6 (90 mm) filter paper, which was collected in labelled volumetric flasks. Each digested sample was diluted to 20 ml by adding distilled water and then filtered through 0.45 μm cellulose nitrate membrane micro-filter (Millipore) paper. A syringe was used and the solutions were collected in pill vials. Two ml subsamples were then pipetted into plastic centrifuge tubes and they were then diluted to 10 ml using distilled water. Finally, the samples were refrigerated until the metal analysis took place.

2.2.2.2 Sediment samples

The sediment samples were dried in an oven for 48 hours at 60°C and then sieved before weighing. Using a balance, 0.2 to 0.3 g subsamples were taken from the dried sediment and placed in labelled test tubes. A "blank" with no sediment, was also prepared. The heating blocks were heated to 40°C; 10 ml nitric acid (65%) was then added to each subsample and to the blank. The samples were heated for one hour at 40°C, then the temperature was increased to 120°C for three hours. All flasks, vials and tubes were labelled carefully. The cooled samples were filtered through Whatman No.6 (90 mm) filter paper, after which they were diluted to 20 ml using distilled water. Then the samples were filtered through 0.45 µm cellulose nitrate membrane filter paper using a needle and a syringe, as for the water samples. A 1 ml subsample of each was then pipetted into labelled centrifuge tubes and diluted to 10 ml with distilled water. Samples were refrigerated for later analysis.

2.3 Metal analysis

All samples and blanks were analysed using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at Stellenbosch University. The following metals were analysed: Aluminium, Cadmium, Copper, Iron, Cobalt, Chromium, Manganese, Zinc, Lead and Nickel.

Metal concentrations in water samples were calculated using the following formula:

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

Metal concentrations in sediment samples were calculated using the formula:

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

Concentrations are expressed as mg/kg dry mass for sediment samples and mg/L for water samples.

2.4 Sediment grain size analysis

Grain size is defined as the size of the individual grains of the sediments (Poppe *et al.*, 2000). Grain size analysis plays a crucial role in determining the impacting mechanical properties within the river system by defining the sedimentary environment and it gives a clear understanding into the physical regime. Poppe *et al.* (2000) mentioned that grain size analysis aids in distinguishing the sediment's regular distribution of grain size within the river system.

Soil particles are categorized in various sizes, using the Wentworth (1922) grade scale. According to this scale, gravel-sized particles have a nominal diameter of 2 mm, sand-sized particles range from <2 mm to >62.5 μm in diameter, silt-sized particles range from <62.5 μm to >4 μm in diameter, and clay is <4 μm.

For this investigation sediment samples were thawed overnight. After thawing a small portion of each of the sediment samples of about 50 g was taken from using a tablespoon and thereafter was placed into four separate petri dishes. The petri dishes were then arranged in heated oven shelves. Samples were dried in an oven for 48 hours at 30°C. Once the sediments were dry, they were cooled before sieving. The samples were separated and graded mechanically through a series of aluminium sieves of different mesh sizes, as proposed by the Wentworth scale (Wentworth, 1922).

Aluminium sieve jars were used to sieve the dry sediments. This was done to classify each of the sediment samples according to their sediment sizes. The sieves were arranged and stacked on top of one another according to their sizes, from the biggest mesh size on top to the smallest mesh size at the bottom and placed on a sieve shaker. The sieve sizes were 500 μm, 250 μm, 125 μm and 63 μm. Sediments were sieved for 10 minutes on the shaker. The sieve jars were moved to a clean area for weighing. The balance was tared to zero before each layer of sediment from the sieve was weighed. The sieves were carefully separated, each containing a portion of the sediment sample. Each sieved layer was emptied onto white paper and placed in separate containers. This was to prevent grains from being lost through transference.

The layers were then individually weighed and recorded per layer (mesh size) on a spreadsheet and converted into a percentage of grain size distribution.

Table 2.4.1: The percentage of different grain sizes in sediment samples from each of the sampling stations in the Liesbeek and Black Rivers. The Salt River is canalised; hence no sediment samples were collected.

Sampled stations	**Coarse sand**	**Medium sand**	**Fine sand**	**Very fine sand**
L1D22S	97.7%	2.0%	0.2%	0.0%
L2D22S	71.3%	25.7%	3.0%	0.0%
B1D22S	38.0%	39.7%	20.8%	1.4%
B2D22S	32.7%	16.0%	38.2%	13.1%

2.5 Statistical analyses

The results were analysed with the use of the PRIMER and SigmaPlot statistical software packages. Statistical analysis identified the variations of the findings of the study, for example which metals played a significant role or contributed to the differences between the Liesbeek, Black and Salt Rivers. PRIMER was used to investigate the similarities and the dissimilarities of metals at each of the selected sampled stations and for the years 2006 and 2022. Clarke & Gorley (2006) stated that PRIMER consists of various univariate, graphical and multivariate methods that could be used to test the similarities, dissimilarities, distance of samples and this study used PCA, ANOSIM, SIMPER and CLUSTER ANALYSIS as measures. Eigenvalues and Eigenvectors of metals were produced using PCA (principal component analysis). The significant differences of metals between wet and dry seasons, the sampled stations, 2006 and 2022 were evaluated using ANOSIM. SIMPER looked at the average squared distance and contributions of each of the metals in the sediments and in the water samples, between the sampling sites.

Environmental data was transformed in order to justify the Euclidean distance as a dissimilarity measure on normalised data. To produce a similarity matrix all data were log x + 1, transformed, normalised and Euclidean distance was used. In addition, cluster analysis using the transformed, normalised data produced dendrograms to visualise the distance between the samples of the analysed metals. In addition, the metal samples were plotted using Multi-dimensional scaling (MDS) as another method to visualise the distances between the samples of the measured metals for the sampled stations, seasons and the years 2006 and 2022.

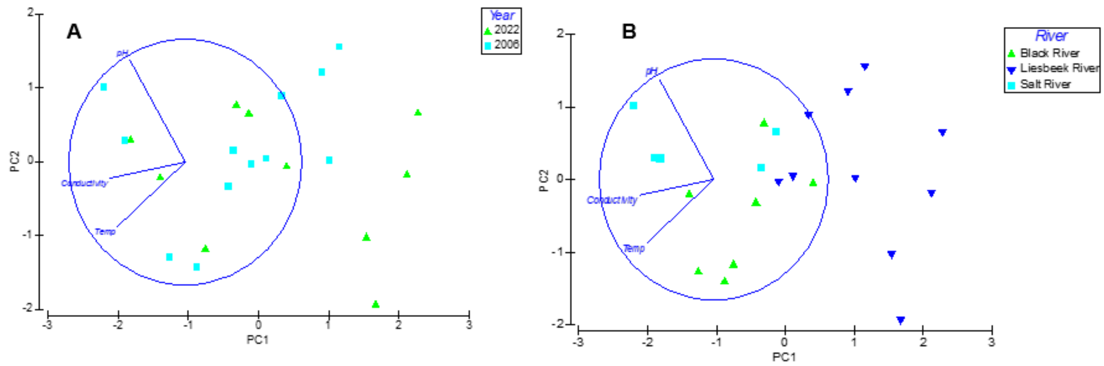
SigmaPlot was used to carry out the descriptive analyses to describe the data used for this study. To determine the seasonal and spatial variations in metal concentrations in the sediment and in water samples one-way analysis ANOVA was performed. The data was imported from MS Excel into SigmaPlot and analysed using one way ANOVA with a Tukey post-hoc test to assess significant differences. The p-value was considered significant if it was less than 0.05 and the results were interpreted based on the significance levels. SigmaPlot results showed the finer detail between all the sampling stations/seasons/years (2006 & 2022). Compliance with environmental standard quality guidelines for water (DWAF, 1996; Odume *et al*., 2024) and sediment (CCMA, 2002) were used to compare metal concentrations with the acceptable standard quality guidelines.

CHAPTER 3: RESULTS

3.1 Physicochemical parameters

3.1.1 Physicochemical parameters

Principal component analysis was used to map the distances between samples, this allows visual identification of similar clusters of samples, in this case, samples that have similar physicochemical factors. Figure 3.1.1.1 shows the results analysed using PRIMER.



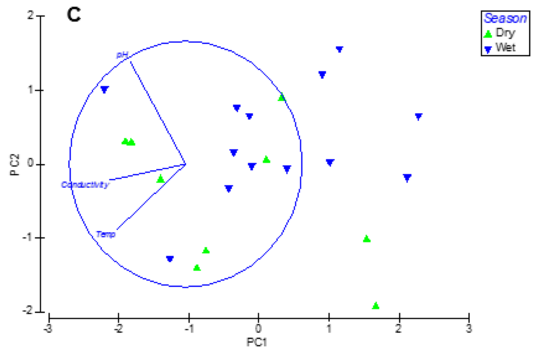


Figure 3.1.1.1: Principal component analysis (PCA) of physicochemical parameters (pH, conductivity and temperature) of the water samples for all samples, using Euclidean distance. The analysis was performed after log x+1 transformation and normalisation of the physicochemical water parameters. PCA ‘A’ used year as a factor, ‘B’ used river as a factor and ‘C’ used season as a factor.

PC1 accounted for 56.3% and PC2 for 27.7% of the variation. Together PC1 and PC2 accounted for 83.9% of the variation which showed that the PCA is a good reflection of the data (Table 3.1.1.1). The samples showed very little clustering in terms of year (PCA A), samples from 2006 and 2022 did not show any groupings. There were some separations of samples for the stations (PCA B) but they were not distinct groupings and the same was found for season. The vectors superimposed on the PCA showed the direction in which the 3 physicochemical factors change in the samples (only 3 were utilised as these were the factors measured in both years). For PCA B (chosen because it shows the most clustering), Temperature was shown to be higher in the Black River samples and lower in Liesbeek and Salt Rivers; conductivity was higher in the Salt and Black Rivers compared to the Liesbeek and pH, although differences were negligible, were higher in the Salt River.

Table 3.1.1.1: Eigenvalues and the amount of variation represented by each principal component.

Eigenvalues			
PC	Eigenvalues	%Variation	Cum.%Variation
1	1.69	56.3	56.3
2	0.83	27.7	83.9
3	0.483	16.1	100.0

The ANOSIM (Analysis of similarity) of the physicochemical factors of the water samples showed no significant difference between 2006 and 2022 (Global R: 0.08, p = 0.116), this is evident in PCA A (Fig. 3.1.1.1).

An ANOSIM using rivers as a factor showed a significant difference in the sample statistic (Global R: 0.53, p = 0.001), some clustering was found in PCA B (Fig.3.1.1.1).

An ANOSIM using wet and dry season demonstrated no significant differences in the physicochemical water parameters, sample statistics (Global R: 0.119, p = 0.061); PCA C demonstrated the lack of grouping of samples according to season (Fig.3.1.1.1).

Table 3.1.1.2: SIMPER (Similarity Percentage) of the physicochemical water parameters in the years 2006 and 2022. Data was log x+1 transformed, normalised and a resemblance matrix using Euclidean distance was used in the analysis. This table represents the average dissimilarity using year as a factor. The average squared distance = 6.31.

Variable	Average value 2006	Average value 2022	% Contribution	Cumulative %
pH	-0.451	0.376	36.32	36.32
Temperature	-0.308	0.257	32.93	69.25
Conductivity	5.57E-02	-4.64E-02	30.75	100

The SIMPER analysis of the physicochemical factors between the two sampling years, 2006 and 2022 (Table 3.1.1.2) showed that pH accounted for 36.32% of the differences between the two years, with temperature accounting for 32.39%, and conductivity accounted for the least difference at 30.75%. pH and temperature had the largest impact on the differences between the two years, while conductivity contributed very little to the differences between the two years.

Table 3.1.1.3: The measured physicochemical parameters in the water samples from in the Liesbeek, Black and Salt Rivers during each sampling occasion for both seasons: wet and dry. ND = no data collected. First letters = river (Liesbeek, Black & Salt), numbers 1 and 2 = stations, letters D & W = dry and wet seasons, 06 & 22 = years at which data was collected (2006 and 2022) and W = water sample.

Sampling Stations	Temp (℃)	Conductivity (µS/cm)	pH	Dissolved oxygen (mg/L, ppm)	Salinity (ppt, PSU)
L1D06W	20.2	170.7	7.84	ND	ND
L1D22W	19.9	160.2	6.96	2.05	0.09
L1W06W	14.4	191	7.8	ND	ND
L1W22W	13.3	131.7	7.28	2.54	0.08
L2D06W	22	269	7.57	ND	ND
L2D22W	21.1	194.5	6.65	1.44	0.10
L2W06W	15.5	233	7.73	ND	ND
L2W22W	14.6	185.4	7.03	2.84	0.11
B1D06W	27	927	7.21	ND	ND
B1D22W	25.1	954	7.24	0.56	0.47
B1W06W	20.2	985	7.4	ND	ND
B1W22W	15.7	967	7.26	2.63	0.59
B2D06W	ND	ND	ND	ND	ND
B2D22W	24.3	1240	7.66	0.58	0.63
B2W06W	ND	ND	ND	ND	ND
B2W22W	16.5	1029	7.69	2.30	0.61
S1D06W	27	976	8	ND	ND
S1D22W	25	1274	7.93	0.80	0.63
S1W06W	18.3	1024	7.52	ND	ND
S1W22W	16.3	949	7.62	2.69	0.57

3.1.2 Physicochemical parameters for 2022 only

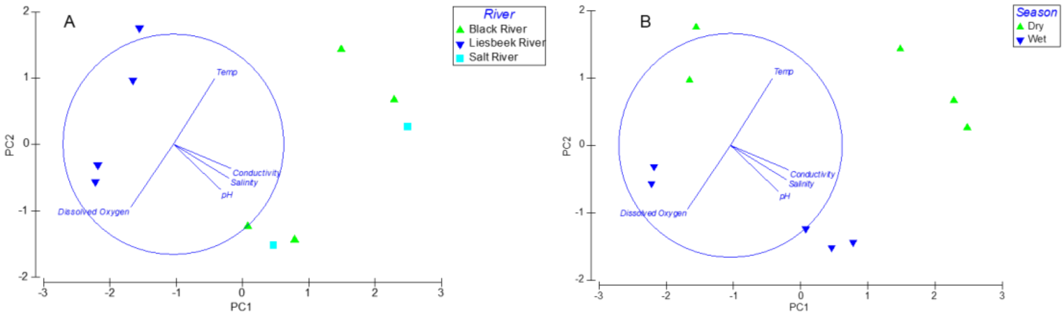


Figure 3.1.2.1: Principal component analysis (PCA) using Euclidean distance of physicochemical parameters (dissolved oxygen, pH, salinity, conductivity and temperature) of the water samples for 2022. The analysis was performed after log x+1 transformation and normalisation of the data.

PC1 accounted for 65.0% of the variation, PC2 accounted for 28.7%, together PC1 and PC2 accounted for 93.7%. "A" used the river as a factor and "B" used the season as a factor. A shows a clear separation of the Liesbeek River samples from those of the Salt and Black Rivers, while B shows a separation of the samples of the wet and dry seasons. In PCA A, generally conductivity, salinity and pH are highest in the Salt and Liesbeek Rivers, while the lower dissolved oxygen and higher temperatures are characteristics of the Black River samples. Generally, in PCA B, temperature, conductivity and salinity are higher in the dry season. The ANOSIM for the 2022 samples only were very similar to those found when both 2006 and 2022 samples were used. The ANOSIM between rivers showed a significant difference in the physicochemical water parameters between stations (Global R: 0.654, p = 0.008) (Fig. 3.1.2.1). The ANOSIM between seasons showed no significant differences in the physicochemical water parameters (Global R: 0.352, p = 0.071) (Fig. 3.1.2.1).

Table 3.1.2.2: SIMPER (Similarity Percentage) of the physicochemical parameters in the wet and the dry seasons in the year 2022. A resemblance matrix using Euclidean distance was used in the analysis. This table represents the average dissimilarity using the wet and dry seasons as a factor. The average squared distance = 11.82.

Variable	**Average value Dry**	**Average value Wet**	**% Contribution**	**Cumulative %**
Temperature	0.872	-0.872	28.07	28.07
Dissolved Oxygen	-0,794	0,794	25,90	53,97
pH	-0.123	0.123	15.48	69.46
Conductivity	7,35E-2	-7,35E-2	15,32	84,77
Salinity	-1,48E-2	1,48E-2	15,23	100,00

The SIMPER physicochemical analysis (Table 3.1.2.2) between the wet and dry season for 2022. The physicochemical water parameters that contributed to the dissimilarities at all rivers were temperature (28.07%), dissolved oxygen (25.90%), pH (15.48%), conductivity (15.32%) and salinity (15.23%). The averaged dissimilarity was a distance of 11.82 (Table 3.1.2.1). Temperature, conductivity, pH, dissolved oxygen and salinity of the water were measured at each sampling station during the wet and the dry seasons. Table 3.1.1 shows the physicochemical data.

3.2 Metal concentrations in water

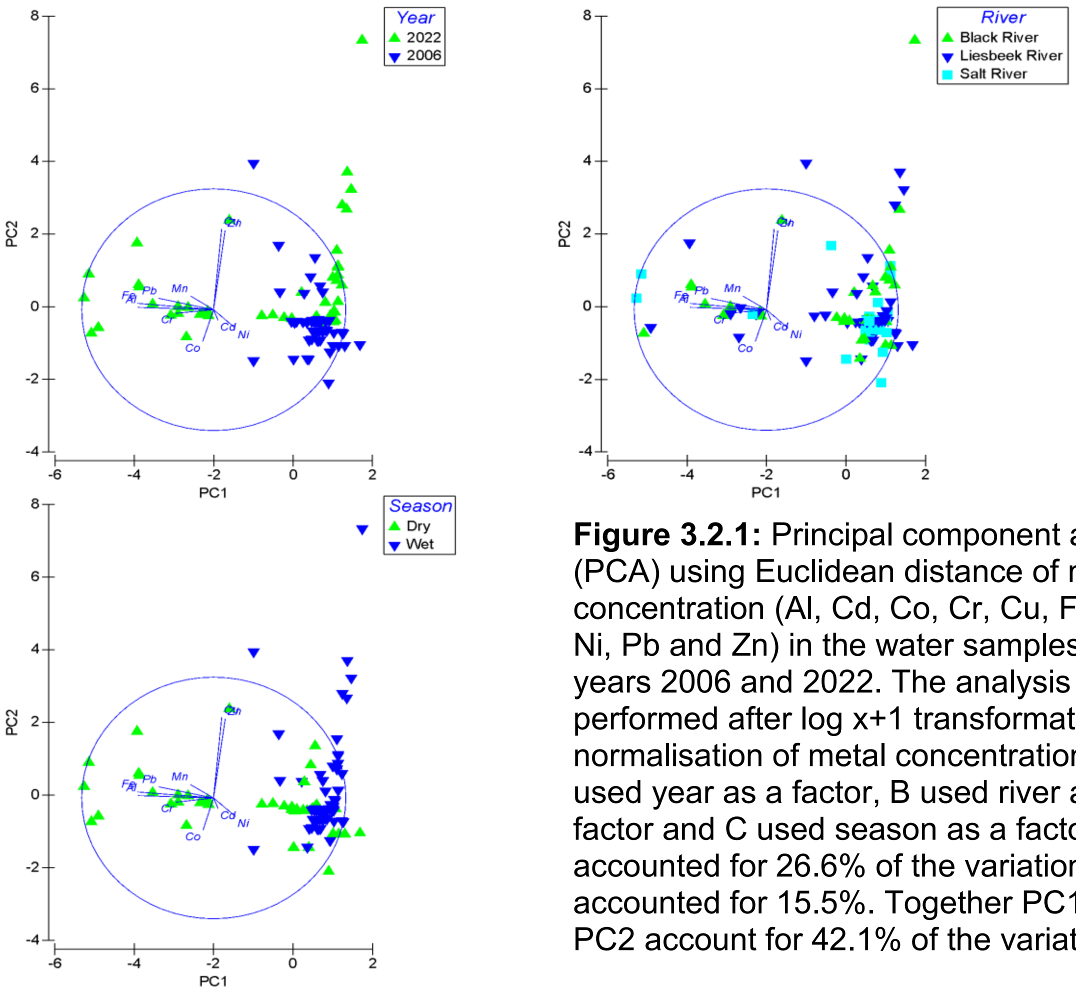


Figure 3.2.1: Principal component analysis (PCA) using Euclidean distance of metal concentration (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the water samples in the years 2006 and 2022. The analysis was performed after log x+1 transformation and normalisation of metal concentrations. A used year as a factor, B used river as a factor and C used season as a factor. PC1 accounted for 26.6% of the variation, PC2 accounted for 15.5%. Together PC1 and PC2 account for 42.1% of the variation.

Table 3.2.1: Eigenvalues and the amount of variation represented by each principal component.

Eigenvalues			
PC	Eigenvalues	%Variation	Cumulative% Variation
1	2.66	26.6	26.6
2	1.55	15.5	42.1
3	1.23	12.3	54.4
4	1.12	11.2	65.6
5	1.02	10.2	75.8

An ANOSIM of the years 2006 and 2022 showed a significant difference in the metal concentration in the water (Global R: 0.162, p = 0.001) PCA A (Fig. 3.2.1) also showed some clustering of samples, although not definitive, evidenced by the low R value. An ANOSIM between sampled rivers (Global R: 0.011, p = 0.034) showed no significant difference, while an ANOSIM between the dry and the wet seasons (Global R: 0.199, p = 0.001) was significant, again no definitive clustering also evident by the low R value.

Table 3.2.2: SIMPER (Similarity Percentage) of the metal concentrations in the water in the years 2006 and 2022. A resemblance matrix using Euclidean distance was used in the analysis. This table represents the average dissimilarities between the two years. The average squared distance = 22.24.

Variable	Average value 2022	Average value 2006	% Contribution	Cumulative %
Fe	0.579	-0.483	12.10	12.10
Al	0.532	-0.444	11.74	23.84
Cu	0.391	-0.326	10.82	34.66
Pb	0.259	-0.216	10.02	44.68
Cr	-0.345	0.287	10.00	54.58
Mn	0.124	-0.103	9.90	64.58
Zn	6.62E-2	-5.52E-2	9.08	73.66
Cd	-0.323	0.269	9.05	82.71
Co	-0.211	0.176	8.80	91.51

The SIMPER analysis of the metal concentrations in the water samples in the years 2006 and 2022 (Table 3.2.2). The metals that were most responsible for the dissimilarities between the two years were Fe (12.10%), Al (11.74%), Cu (10.82%), Pb (10.02%) and Cr (10.00%). The low average percentages of all the metals showed that none of the metals in the water samples were dominant and the large Euclidean distance of 22.24 demonstrated very little clustering of samples.

Table 3.2.3 illustrates the comparisons of the mean and the standard deviation of the metal concentrations in the water in all sampled stations.

Table 3.2.3: The means and standard deviations of the metal concentrations in water (mg/L). The first letters represent the river's name [Liesbeek (L), Black (B) & Salt (S)], numbers 1 and 2 represent stations, letters D and W represent dry and wet seasons, 06 & 22 represent years (2006 and 2022) and ND = No data collected.

Sampling Stations	**Al**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
L1D06W	0.323 ±0.041	0.000 ±0.000	0.000 ±0.000	0.084 ±0.020	0.000 ±0.000	0.506 ±0.158	0.009 ±0.002	0.000 ±0.000	0.000 ±0.000	0.073 ±0.075
L1D22W	40.774 ±26.629	0.000 ±0.000	0.002 ±0.003	0.060 ±0.045	0.057 ±0.127	79.938 ±60.355	0.000 ±0.000	0.000 ±0.000	0.015 ±0.033	0.000 ±0.000
L1W06W	0.180 ±0.110	0.003 ±0.002	0.002 ±0.004	0.121 ±0.085	0.020 ±0.044	0.709 ±0.189	0.028 ±0.007	0.000 ±0.000	0.060 ±0.054	0.152 ±0.132
L1W22W	0.114 ±0.030	0.000 ±0.000	0.000 ±0.000	0.001 ±0.000	0.113 ±0.156	0.214 ±0.057	0.007 ±0.001	0.006 ±0.007	0.000 ±0.000	0.040 ±0.041
L2D06W	0.254	0.000	0.002	0.045	0.000	0.074	0.001	0.032	0.000	0.000

Sampling Stations	**Al**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
	±0.049	±0.000	±0.004	±0.031	±0.000	±0.038	±0.001	±0.043	±0.000	±0.000
L2D22W	8.148 ±7.820	0.000 ±0.000	0.001 ±0.002	0.012 ±0.015	0.032 ±0.073	14.640 ±12.453	0.799 ±1.786	0.000 ±0.000	0.035 ±0.034	0.000 ±0.001
L2W06W	0.060 ±0.054	0.003 ±0.002	0.000 ±0.000	0.055 ±0.017	0.000 ±0.000	0.293 ±0.143	0.011 ±0.001	0.000 ±0.000	0.000 ±0.000	0.000 ±0.000
L2W22W	0.353 ±0.685	0.000 ±0.000	0.000 ±0.000	0.002 ±0.000	0.051 ±0.093	0.558 ±0.796	0.011 ±0.006	0.004 ±0.004	0.001 ±0.002	0.060 ±0.084
B1D06W	0.410 ±0.079	0.000 ±0.000	0.000 ±0.000	0.074 ±0.032	0.000 ±0.000	0.257 ±0.127	0.049 ±0.005	0.016 ±0.035	0.000 ±0.000	0.000 ±0.000
B1D22W	45.838 ±28.413	0.000 ±0.000	0.001 ±0.002	0.130 ±0.080	0.016 ±0.036	69.080 ±45.073	0.381 ±0.853	0.000 ±0.000	0.027 ±0.031	0.000 ±0.000
B1W06W	0.140 ±0.152	0.002 ±0.002	0.002 ±0.004	0.052 ±0.011	0.000 ±0.000	0.155 ±0.026	0.039 ±0.008	0.000 ±0.000	0.000 ±0.0000	0.024 ±0.053
B1W22W	0.054	0.000	0.000	0.001	0.071	0.118	0.018	0.005	0.000	0.062

Sampling Stations	**Al**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
	±0.049	±0.000	±0.000	±0.000	±0.073	±0.039	±0.002	±0.006	±0.000	±0.071
B2D06W	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND
B2D22W	20.666 ±18.259	0.000 ±0.000	0.000 ±0.000	0.017 ±0.012	0.000 ±0.000	19.566 ±16.123	0.000 ±0.000	0.000 ±0.000	0.051 ±0.055	0.000 ±0.000
B2W06W	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND
B2W22W	0.280 ±0.247	0.000 ±0.000	0.000 ±0.000	0.003 ±0.001	0.150 ±0.174	0.665 ±0.292	0.037 ±0.003	0.014 ±0.009	0.000 ±0.000	0.102 ±0.198
S1D06W	0.281 ±0.162	0.000 ±0.000	0.004 ±0.005	0.049 ±0.024	0.000 ±0.000	0.282 ±0.072	0.033 ±0.003	0.032 ±0.043	0.000 ±0.000	0.000 ±0.000
S1D22W	16.800 ±18.503	0.000 ±0.000	0.000 ±0.000	0.040 ±0.042	0.000 ±0.000	31.927 ±35.818	0.000 ±0..000	0.000 ±0.000	0.126 ±0.139	0.009 ±0.021
S1W06W	0.220	0.004	0.000	0.037	0.000	0.134	0.043	0.000	0.000	0.000

Sampling Stations	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
	±0.110	±0.002	±0.000	±0.018	±0.000	±0.049	±0.008	±0.000	±0.000	±0.000
S1W22W	0.060 ±0.052	0.000 ±0.000	0.000 ±0.000	0.001 ±0.001	0.037 ±0.072	0.250 ±0.060	0.025 ±0.002	0.007 ±0.006	0.000 ±0.000	0.026 ±0.053

3.2.1 Comparison of metal concentrations in the water

In order to test for statistical differences between the sampling stations, seasons and years, one-way ANOVA and Mann-Whitney Rank Sum Tests were performed (Appendix, Table 1 to 33). One-way ANOVA was used to test the statistical differences between the sampling stations, while the Mann-Whitney Rank Sum Test was used to test the statistical differences between the wet and dry seasons as well as the differences between the years (2006 and 2022).

3.2.1.1 Comparisons between the years 2006 and 2022

Aluminium: Statistically significant differences were found for all comparisons between 2006 and 2022 (p-value = 0.008 and 0.032), except for L1W06W versus L1W22W, L2W06W versus L2W22W, B1W06W versus B1W22W and S1D06W versus S1D22W (Appendix Table 1). Most significantly different comparisons for mean Al concentrations were higher in 2022 in comparison with 2006 (Table 3.2.3).

Cadmium: This metal showed no significant differences between the years 2006 and 2022 for most of the comparisons. The p-values ranged between 0.151 and 1.000. The only significant difference observed was for S1W06W versus S1W22W with a p-value of 0.032 (Appendix Table 4), with 2006 having the highest mean Cd concentration (Table 3.2.3).

Cobalt: There were no significant differences found for any of the comparisons; p-values ranged from 0.31 to 1.0 (Table 3.2.3; Appendix Table 6).

Chromium: Significant differences were observed during the wet season sampling: L1W06W versus L1W22W, L2W06W versus L2W22W, B1W06W versus B1W22W, and S1W06W versus S1W22W ($p = 0.008$). Dry season comparisons did not show significant differences: L1D06W versus L1D22W, L2D06W versus L2D22W, B1D06W versus B1D22W, and S1D06W versus S1D22W. These p-values ranged between 0.056 and 0.841 (Appendix Table 8). For all comparisons with significant differences, the mean Cr concentrations were the highest in 2006 (Table 3.2.3).

Copper: There were no significant differences between the year 2006 and 2022. The p-values ranged between 0.151 and 1.000 (Table 3.2.3; Appendix Table 13).

Iron: Significant differences were found for L1D06W versus L1D22W, L1W06W versus L1W22W, B1D06W versus B1D22W, and S1W06W versus S1W22W (p = 0.008). There were no significant differences for L2D06W versus L2D22W, L2W06W versus L2W22W, B1W06W versus B1W22W, and S1D06W versus S1D22W. The p-values ranged between 0.151 and 1.000. For most significantly different comparisons, mean Fe concentrations were higher in 2022 in contrast with 2006 (Table 3.2.3; Appendix Table 15).

Manganese: Significant differences were found for L1D06W versus L1D22W, L1W06W versus L1W22W, B1W06W versus B1W22W, S1D06W versus S1D22W, and S1W06W versus S1W22W (p = 0.008). There were no significant differences for L2W06W versus L2W22W, L2D06W versus L2D22W, and B1D06W versus B1D22W. The p-values ranged between 0.151 and 0.841 (Appendix Table 20, Appendix). For most comparisons with significant differences, the mean Mn concentrations were the highest in 2006 (Table 3.2.3).

Nickel: Significant differences were found for L1W06W versus L1W22W, L2W06W versus L2W22W, B1W06W versus B1W22W, and S1W06W versus S1W22W (p = 0.008). There were no significant differences for L1D06W versus L1D22W, L2D06W versus L2D22W, B1D06W versus B1D22W, and S1D06W versus S1D22W. The p-value ranged between 0.310 and 1.000 (Appendix Table 25). For all comparisons with significant differences, the mean Ni concentrations were the highest in 2022 (Table 3.2.3).

Lead: Significant differences were found for L2D06W versus L2D22W, and S1D06W versus S1D22W (p = 0.032). There were no significant differences for L1D06W versus L1D22W, L1W06W versus L1W22W, L2W06W versus L2W22W, B1D06W versus B1D22W, B1W06W versus B1W22W, and S1W06W versus S1W22W. The p-values ranged between 0.151 to 1.000 (Appendix Table 27). For all comparisons with significant differences, the mean Pb concentrations were the highest in 2022 (Table 3.2.3).

Zinc: A significant difference was found for L2W06W versus L2W22W (p = 0.032), with 2022 significantly higher than 2006. There were no significant differences for L1D06W versus L1D22W, L1W06W versus L1W22W, L2D06W versus L2D22W, B1D06W versus B1D22W, B1W06W versus B1W22W, S1D06W versus S1D22W, and S1W06W versus S1W22W. The p-values ranged between 0.151 to 1.000 (Appendix Table 30) (Table 3.2.3).

3.2.2.2 Comparisons between seasons

Aluminium: Statistically significant differences were found for all seasonal comparisons ($p<0.05$), except for S1D06W versus S1W06W, B2D22W versus B2W22W and S1D22W versus S1W22W (Appendix Table 2). For all significantly different comparisons, mean Al concentrations were generally higher in the dry season, in comparison with the wet season (Table 3.2.3).

Cadmium: There were no significant differences for most seasonal comparisons: L1D06W versus L1W06W, L2D06W versus L2W06W, B1D06W versus B1W06W, L1D22W versus L1W22W, L2D22W versus L2W22W, B1D22W versus B1W22W, B2D22W versus B2W22W, and S1D22W versus S1W22W ($p = 0.151$ and 1.000). A significant difference was only found for S1D06W versus S1W06W, dry season was the highest with this comparison ($p = 0.032$) (Appendix Table 5).

Cobalt: There were no statistically significant differences for any of the seasonal comparisons. The p-values ranged between 0.310 and 1.000 (Table 3.2.3; Appendix Table 7).

Chromium: There were no significant differences for the following seasonal comparisons: L1D06W versus L1W06W, L2D06W versus L2W06W, B1D06W versus B1W22W, S1D06W versus S1W06W, and S1D22W versus S1W22W ($p = 0.310$ to 0.690). Significant differences were found for L1D22W versus L1W22W, B1D22W versus B1W22W, and B2D22W versus B2W22W ($p = 0.008$) (Appendix Table 9). For all significantly different comparisons, mean Cr concentrations were always higher in the dry season (Table 3.2.3).

Copper: There were no significant differences for any of the seasonal comparisons. The p-values ranged between 0.151 to 1.000 (Table 3.2.3; Appendix Table 14).

Iron: Significant differences were found for certain seasonal comparisons: L2D06W versus L2W06W, S1D06W versus S1W06W, L1D22W versus L1W22W, B1D22W versus B1W22W, and B2D22W versus B2W22W ($p = 0.032$ to 0.008). Other comparisons did not differ significantly: L1D06W versus L1W06W, B1D06W versus B1W06W, L2D22W versus L2W22W, and S1D22W versus S1W22W. These p-values ranged between 0.151 to 0.690 (Appendix Table 16). For most of the significant different comparisons, the mean Fe concentrations were higher in the dry season (Table 3.2.3).

Manganese: Statistically significant differences were found in the following seasonal comparisons: L1D06W versus L1W06W, L2D06W versus L2W06W, S1D06W versus S1W06W, L1D22W versus L1W22W, B2D22W versus B2W22W, and S1D22W versus S1W22W ($p = 0.008$ and 0.032). There were no significant differences in seasonal comparisons for B1D06W versus B1W06W, L2D22W versus L2W22W, and B1D22W versus B1W22W. These p-values ranged between 0.151 to 0.095 (Appendix Table 21). For all the comparisons with significant differences, the mean Mn concentrations were the highest in the wet season (Table 3.2.3).

Nickel: Statistically significant differences in seasonal comparisons were found for L1D22W versus L1W22W, L2D22W versus L2W22W, B1D22W versus B1W22W, B2D22W versus B2W22W, and S1D22W versus S1W22W ($p = 0.008$). There were no significant differences for any of the seasonal comparisons of 2006. These p-values ranged between 0.310 to 1.000 (Appendix Table 26). For most comparisons with significant differences, the mean Ni concentrations were mostly higher in the wet season (Table 3.2.3).

Lead: A statistically significant difference in seasonal comparisons was only found for S1D22W versus S1W22W ($p = 0.032$). There were no significant differences for L1D06W versus L1W06W, L2D06W versus L2W06W, B1D06W versus B1W06W, S1D06W versus S1W06W, L1D22W versus L1W22W, L2D22W versus L2W22W, B1D22W versus B1W22W, and B2D22W versus B2W22W. The p-values ranged between 0.151 and 1.000 (Appendix Table 28). For all comparisons with significant differences, the mean Pb concentrations were higher in the dry season (Table 3.2.3).

Zinc: Significant differences were found for L1D22W versus L1W22W, and B1D22W versus B1W22W ($p = 0.032$). There were no significant differences in seasonal comparisons for L1D06W versus L1W06W, L2D06W versus L2W06W, B1D06W versus B1W06W, S1D06W versus S1W06W, L2D22W versus L2W22W, B2D22W versus B2W22W, and S1D22W versus S1W22W. The p-values ranged between 0.056 to 1.000 (Appendix Table 31). For all comparisons with significant differences, the mean Zn concentrations were higher in the wet season (Table 3.2.3).

3.2.1.2 Comparisons between sampling stations

Aluminium: There were no statistically significant differences for any of the seasonal comparisons. The p-values ranged between 0.073 and 0.998 (Appendix Table 3, Table 3.2.3).

Cadmium: There were no statistical significant differences between any of the sampling stations p-values of 0.151 and 1.000.

Cobalt: There were no statistical significant differences between any of the sampled stations p-values of 0.310 and 1.000.

Chromium: There were statistically significant differences between most sampling stations: B1D22W versus L2D22W, B1D22W versus B2D22W, B1D22W versus S1D22W, L1W06W versus S1W06W, B2W22W versus B1W22W, and B2W22W versus L1W22W (p-values ranged between 0.002 and 0.008). There were no significant differences found between other study station comparisons. These p-values ranged between 0.80 to 1.000 (Appendix, Table 10, 11 and 12). For most comparisons with significant differences, the mean Cr concentrations were higher at the first and second stations of the Black River during the dry season of 2022 and the first station of the Liesbeek River during the wet season of 2006 (Table 3.2.3).

Copper: There were no statistical significant differences found between any of the sampling stations p-values of 0.310 and 1.000.

Iron: Statistical significant differences were found for L1D06W versus L2D06W, L1D06W versus B1D06W, L1D06W versus S1D06W, S1D06W versus L2D06W, L1W06W versus S1W06W, L1W06W versus B1W06W, and L1W06W versus L2W06W (p = 0.001 to 0.038). There were no statistical significant differences between other sampling stations. The p-values ranged between 0.091 and 1.000 (Appendix Table 17, 18 and 19). For all comparisons with significant differences, the mean Fe concentrations were higher at the first station of the Liesbeek River during the wet and the dry season of 2006 and at the first station of the Salt River during the dry season of 2006 (Table 3.2.3).

Manganese: Statistical significant differences were found between most sampling stations: B1D06W versus L2D06W, B1D06W versus L1D06W, B1D06W versus S1D06W, S1D06W versus L2D06W, S1D06W versus L1D06W, S1W06W versus L2W06W, S1W06W versus L1W06W and B1W06W versus L2W06W, L1W06W versus L2W06W, B2W22W versus L1W22W, B2W22W versus L2W22W, B2W22W versus B1W22W, B2W22W versus S1W22W, S1W22W versus L1W22W, S1W22W versus L2W22W, S1W22W versus B1W22W, B1W22W versus L1W22W, and B1W22W versus L2W22W (p-value = 0.001 to 0.020). There were no significant differences found for L1D06W versus L2D06W, S1W06W versus B1W06W, B1W06W versus L1W06W, and L2W22W versus L1W22W (p-value = 0.018 to 0.855) (Appendix Table 22, 23 and 24). For most comparisons with significant differences, the mean Mn concentrations were higher at the first station of the Black River during the dry and the wet seasons of 2006, at the first station of the Salt River during the wet season of 2006 and the first and second station of the Black River during the wet and the dry seasons of 2022 (B1D06W, B1W06W, S1W06W, B1W22W, and B2W22W) (Table 3.2.3).

Lead: Significant differences were found for L1W06W versus S1W06W, L1W06W versus B1W06W, and L1W06W versus L2W06W (p = 0.015). There were no significant differences found for L2W06W versus S1W06W, L2W06W versus B1W06W, and B1W06W versus S1W06W (p-value = 0.151 to 1.000) (Appendix Table 29). For all comparisons with significant differences, the mean Pb concentrations were higher at the first station of the Liesbeek River during the wet season of 2006 (Table 3.2.3).

Zinc: Significant differences were found for L1D06W versus S1D06W, L1D06W versus B1D06W, L1D06W versus L2D06W, L1W06W versus S1W06W, and L1W06W versus L2W06W (p = 0.018 to 0.034). There were no significant differences for L2D06W versus S1D06W, L2D06W versus B1D06W, B1D06W versus S1D06W, L1W06W versus B1W06W, B1W06W versus S1W06W, B1W06W versus L2W06W, and L2W06W versus S1W06W (p = 0.051 and 1.000) (Appendix Table 32 and 33). For all comparisons with significant differences, the mean Zn concentrations were higher at the first station of the Liesbeek River during the wet and dry seasons of 2006 (Table 3.2.3).

3.3 Metal concentrations in sediments

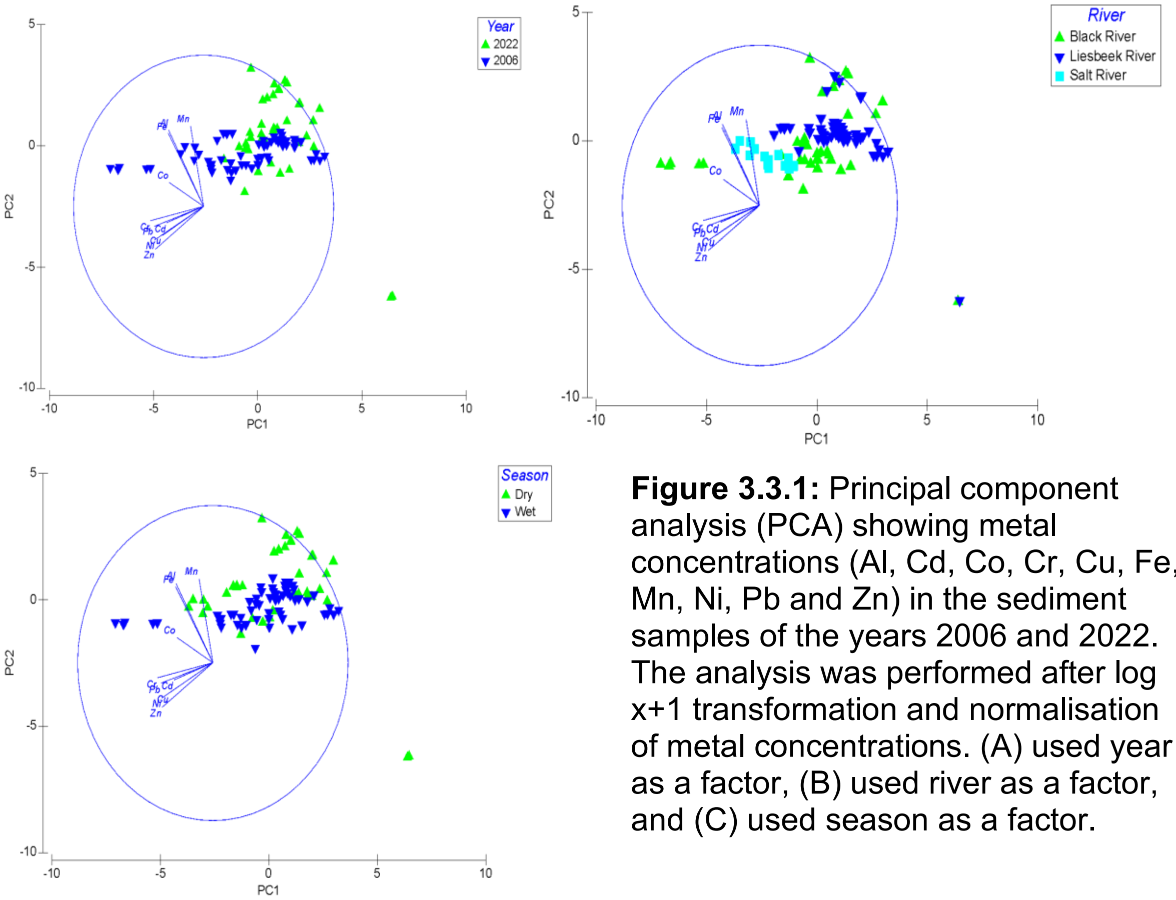


Figure 3.3.1: Principal component analysis (PCA) showing metal concentrations (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the sediment samples of the years 2006 and 2022. The analysis was performed after log x+1 transformation and normalisation of metal concentrations. (A) used year as a factor, (B) used river as a factor, and (C) used season as a factor.

Table 3.3.1: Eigenvalues and amount of variation represented by each principal component.

Eigenvalues			
PC	Eigenvalues	%Variation	Cumulative %Variation
1	5.15	51.5	51.5
2	1.79	17.9	69.4
3	0.985	9.9	79.3
4	0.685	6.8	86.1
5	0.55	5.5	91.6

The principal component eigenvalues and % variation are shown in (Table 3.3.1) shows that PC1 contributes 51.5% to the variation, while PC1 and PC2 together account for 69.4% of the variation. The samples are grouped as in the cluster analysis (Fig 3.3.1). 69.4% of the metal concentration in the sampled sediment. The superimposed vectors show almost an even distribution of the different metals causing the separation of samples, however quite notable on PCA A is the Al and Fe which is separating the 2022 and 2006 samples.

Table 3.3.2: SIMPER (Similarity Percentage) of metal concentrations in the sediments using years 2006 and 2022 as a factor. A resemblance matrix using Euclidean distance was used in the analysis. The following table represents the average dissimilarity using 2006 and 2022 as a factor. The average squared distance = 22.17.

Variable	**Average value 2022**	**Average value 2006**	**% Contribution**	**Cumulative %**
Mn	0.282	-0.188	11.14	11.14
Zn	-0.551	0.368	11.08	22.22
Al	-0.156	0.104	10.87	33.09
Fe	-0.205	0.137	11.82	43.90
Pb	-0.526	0.351	10.16	54.06
Cu	-0.474	0.316	9.99	64.05
Cr	-0.41	0.274	9.60	73.66
Ni	-0.469	0.313	9.46	83.12
Co	-3.07E-2	2.05E-2	9.20	92.32

SIMPER looked at each of the metal concentrations in the sampled sediments by determining which metal contributed the most to the dissimilarity between the year 2006 and 2022. The results of the SIMPER analysis (Table 3.3.2) showed that the metals that were mostly responsible for the dissimilarity between the years 2006 and 2022 were Mn (11.14%), Zn (11,08%), Al (10.87%), Fe (11.82%) and Pb (10.16%). The percentage differences of these metals were very similar, showing that there was no specific metal that was responsible for the differences between the seasons. The average dissimilarity was 22.17.

Table 3.3.3: SIMPER (Similarity Percentage) of the metal concentrations in the sediment samples, the wet and the dry seasons were used as a factor. A resemblance matrix using Euclidean distance was used in the analysis. Table 3.3.3 represents the average dissimilarities between the wet and the dry seasons. Average squared distance 13.03.

Variable	Average value Dry	Average value Wet	% Contribution	Cumulative %
Mn	0.43	-0.286	11.88	11.88
Zn	-0.539	0.359	11.36	23.24
Al	-0.165	0.11	10.94	34.18
Fe	-5.47E-2	3.65E-2	10.79	44.98
Co	0.143	-9.56E-2	10.00	54.97
Pb	-0.137	9.11E-2	9.53	64.50
Cr	-0.25	0.167	9.51	74.01
Ni	-0.262	0.175	9.19	83.20
Cu	-6.07E-3	4.04E-3	8.73	91.93

The SIMPER analysis (Table 3.3.3) showed that the metal concentrations in the sediments which displayed the highest dissimilarity between the dry and wet seasons were Mn (11.88%), Zn (11.36%), Al (10.94%), Fe (10.79%) and Co (10.00%). The average dissimilarity was 21.96 (Table 3.3.4

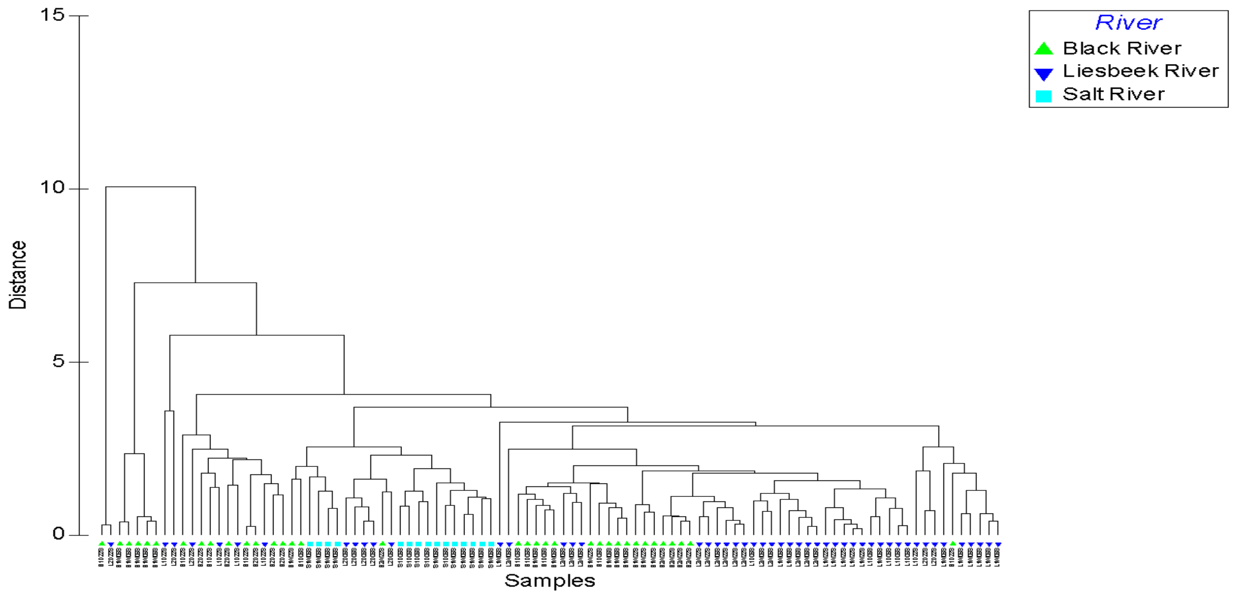


Figure 3.3.2: Dendrogram representing the cluster analysis of metal concentrations in the sediment samples of each sampled station in the Liesbeek, Black and Salt Rivers. These data were log x + 1 transformed, normalised and Euclidean distance was used in the analysis. Each of the samples is labelled according to the station name. Refer to figure 1 (MAP) for the location of each station.

The dendrogram (Fig. 3.3.2) was used to visualise the data, by clustering the samples which were similar. There was some overlap in the clustering of some of the samples from the different rivers. However, the general trend shows that the samples from the Salt River grouped with those of the Black River and that the Black River and Liesbeek River clustered separately from each other. An ANOSIM between rivers showed a significant difference in the metal concentrations in the sediments (Global R: 0.269, p = 0.001).

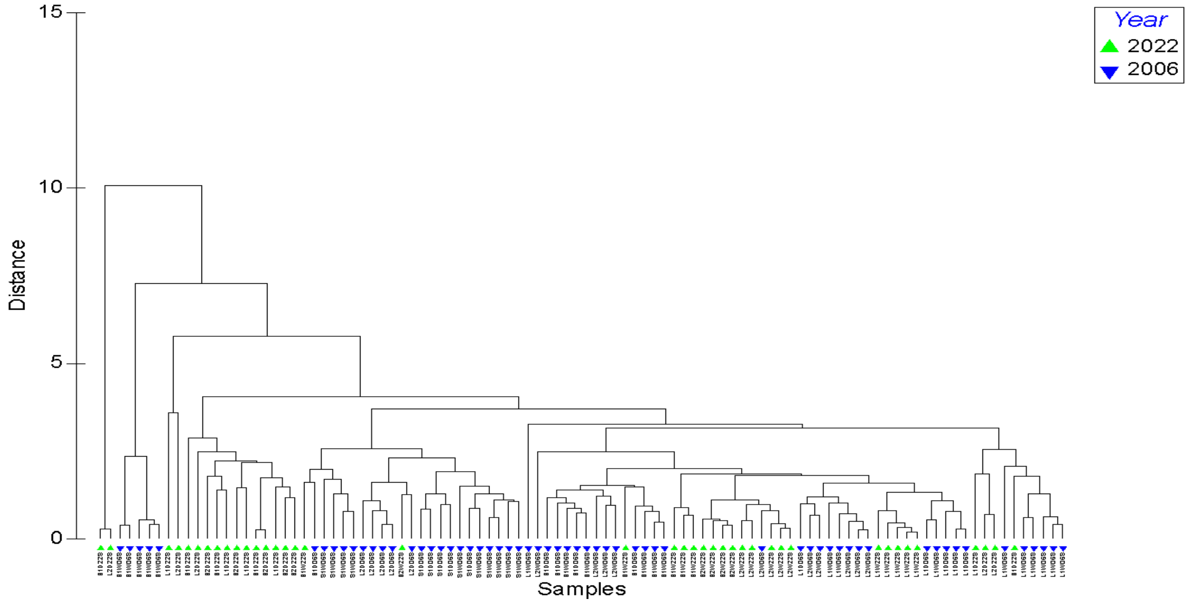


Figure 3.3.3: Dendrogram representing the cluster analysis of the metal concentrations in the sediments of each sampling station in the Liesbeek, Black and Salt Rivers using 2006 and 2022 as a factor. Samples were log x+1 transformed, normalised and Euclidean distance was used in the analysis.

Cluster analysis showed that the metal concentrations in the sediment samples in 2006 grouped separately from the metal concentrations in the sediment samples in 2022. This gives an indication that the 2006 and 2022 metal concentrations in the sediment samples were different from each other and that the metal concentrations in the sediment samples changed over 15 years (Fig. 3.3.3). An ANOSIM of the metal concentrations in the sediments using 2006 and 2022 as factors showed a significant difference in the metal concentrations (Global R: 0.121, p = 0.001).

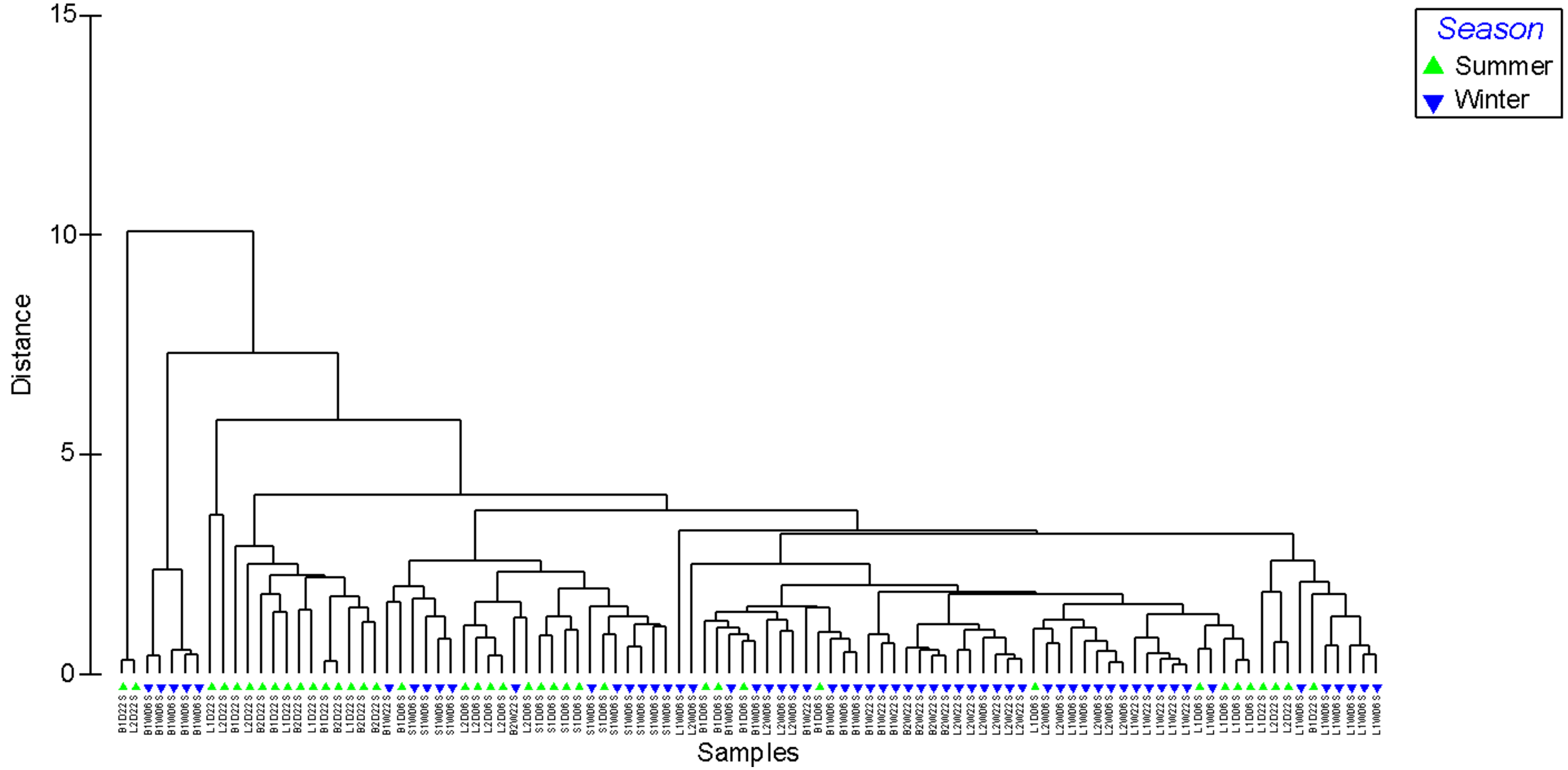


Figure 3.3.4: Dendrogram representing the cluster analysis of the metal concentrations in the sediment of each sampling station using the wet and dry seasons as a factor. Samples were log x + 1 transformed, normalised and Euclidean distance was used in the analysis. The cluster analysis shows that the samples collected during the wet season group separately from those collected during the dry season (Fig 3.3.4). An ANOSIM between the metal concentrations in the sediment using wet and dry season as a factor showed that there was a significant difference between the dry and the wet seasons (Global $R = 0.174$, $p = 0.001$).

Table 3.3.4 illustrates the comparisons of the mean and the standard deviation of the metal concentrations in the sediments in all sampled stations.

Table 3.3.4: The means and standard deviations of the metal concentrations in the sediments (mg/kg). The first letters represent rivers' names (Liesbeek (L), Black (B) & Salt (S)), numbers 1 and 2 represent stations, D & W (dry and wet) seasons, 06 & 22 represent years (2006 and 2022) and S represents sediment. ND = No Data.

Sampling Stations	**Al**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
L1D06S	1422.278 ±150.262	0.000 ±0.000	0.189 ±0.013	2.262 ±0.511	0.422 ±0.742	1807.977 ±244.044	10.372 ±1.906	1.010 ±0.638	2.124 ±1.457	3.005 ±0.789
L1D22S	1521.756 ±755.094	0.015 ±0.027	1.752 ±2.684	1.472 ±1.431	2.140 ±2.937	3405.208 ±1874.989	339.553 ±312.411	0.000 ±0.000	1.978 ±2.753	1.323 ±2.958
L1W06S	647.678 ±35.297	0.000 ±0.000	0.077 ±0.106	0.227 ±0.228	0.231 ±0.342	680.066 ±92.012	4.334 ±0.380	0.788 ±1.079	0.000 ±0.000	1.801 ±0.913

Sampling Stations	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
L1W22S	1726.828 ±167.161	0.007 ±0.004	0.569 ±0.102	3.126 ±0.432	0.000 ±0.000	2870.239 ±685.238	28.426 ±4.448	1.296 ±0.483	2.442 ±0.533	10.356 ±4.614
L2D06S	1951.4590 ±164.863	0.249 ±0.055	1.030 ±0.132	7.256 ±2.451	8.550 ±8.487	7541.875 ±425.732	35.885 ±6.354	1.753 ±0.708	58.519 ±27.693	45.116 ±9.069
L2D22S	1186.667 ±719.356	0.009 ±0.017	2.786 ±5.076	0.330 ±0.738	0.000 ±0.000	1795.385 ±1697.591	190.660 ±382.188	0.000 ±0.000	1.076 ±0.985	0.000 ±0.000
L2W06S	1284.628 ±177.924	0.000 ±0.000	0.192 ±0.140	5.364 ±6.529	1.735 ±0.787	2541.716 ±491.757	16.189 ±3.708	1.537 ±1.614	15.544 ±12.014	11.688 ±1.766
L2W22S	1835.378 ±218.481	0.024 ±0.005	0.539 ±0.086	5.430 ±2.621	0.000 ±0.000	3690.257 ±864.818	17.977 ±3.007	1.306 ±0.309	7.669 ±1.303	28.252 ±2.765

Sampling Stations	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
B1D06S	890.864 ±132.084	0.000 ±0.000	0.239 ±0.101	4.356 ±1.121	42.384 ±88.492	2315.532 ±330.404	10.471 ±1.418	1.937 ±1.572	43.159 ±33.131	58.278 ±17.173
B1D22S	1303.079 ±927.971	0.022 ±0.025	0.640 ±0.994	0.986 ±0.913	5.129 ±7.906	3278.727 ±3527.942	627.839 ±775.643	0.000 ±0.000	3.903 ±4.212	0.000 ±0.000
B1W06S	1059.371 ±90.618	0.000 ±0.000	0.159 ±0.089	3.366 ±0.999	5.723 ±1.835	2022.593 ±202.591	10.874 ±1.350	0.809 ±1.107	24.177 ±13.346	49.842 ±6.044
B1W22S	749.858 ±170.309	0.060 ±0.028	0.269 ±0.056	3.356 ±0.989	18.100 ±34.835	996.939 ±208.585	4.838 ±1.187	0.787 ±0.234	8.324 ±7.130	51.871 ±26.655
B2D06S	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND

Sampling Stations	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
B2D22S	1432.049 ±524.216	0.012 ±0.015	0.719 ±0.048	1.315 ±1.308	8.153 ±13.396	3435.386 ±1559.571	711.607 ±262.429	0.000 ±0.000	3.972 ±2.764	0.980 ±2.190
B2W06S	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND
B2W22S	1835.208 ±166.473	0.079 ±0.023	0.719 ±0.048	5.690 ±1.082	3.296 ±7.370	2987.375 ±611.643	13.473 ±1.877	2.203 ±0.387	19.684 ±5.675	75.635 ±15.615
S1D06S	1607.855 ±144.975	0.047 ±0.067	2.298 ±0.316	15.596 ±4.631	27.277 ±4.930	4448.697 ±408.211	65.205 ±34.187	9.540 ±2.169	89.405 ±45.366	134.421 ±36.852
S1D22S	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND

Sampling Stations	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
S1W06S	1035.210 ±90.786	0.000 ±0.000	1.106 ±0.450	4.678 ±1.447	42.609 ±37.559	1637.612 ±224.341	15.701 ±5.360	2.365 ±0.873	35.334 ±25.734	117.200 ±28.441
S1W22S	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND

3.3.1 Comparisons of metal concentrations in the sediments

Comparisons of metal concentrations in the sediments, in order to test for statistical differences between the sampling stations, seasons and years, one-way ANOVA and Mann-Whitney Rank Sum Tests were performed (Appendix Table 34 to 77). One-way ANOVA was used to test the statistical differences between the sampling stations, while Mann-Whitney Rank Sum Test was used to test the statistical differences between the wet and the dry seasons as well as the differences between the years 2006 and 2022.

3.3.1.1 Comparisons between years 2006 and 2022

Aluminium: Significant differences were found for L1W06S versus L1W22S, L2D06S versus L2D22S, L2W06S versus L2W22S, and B1W06S versus B1W22S ($p = 0.016$ and 0.008). There were no statistical differences for L1D06S versus L1D22S, and B1D06S versus B1D22S. These p-values ranged between 0.222 and 0.690 (Appendix Table 34). For most comparisons with significant differences, the mean Al concentrations were higher in 2022 compared to 2006 (Table 3.3.4).

Cadmium: Significant differences were found for L1W06S versus L1W22S, L2W06S versus L2W22S, and B1W06S versus B1W22S ($p = 0.008$ and 0.032). There were no significant differences for L1D06S versus L1D22S, L2D06S versus L2D22S and B1D06S versus B1D22S. These p-values ranged between 0.151 and 0.841 (Appendix Table 39). For all significant differences, mean Cd concentrations were higher in 2022 in contrast with 2006 (Table 3.3.4).

Cobalt: Significant differences were found for L1W06S versus L1W22S, L2W06S versus L2W22S, and B1W06S versus B1W22S ($p = 0.008$ and 0.016). There were no significant differences for L1D06S versus L1D22S, L2D06S versus L2D22S, and B1D06S versus B1D22S. These p-values ranged between 0.310 to 0.690 (Appendix Table 42). For most comparisons with significant differences, the mean Co concentrations were the highest in 2022 (Table 3.3.4).

Chromium: Significant differences were found for L1W06S versus L1W22S, L2D06S versus L2D22S, and B1D06S versus B1D22S ($p = 0.008$). There were no significant differences for L1D06S versus L1D22S, L2W06S versus L2W22S, and B1W06S versus B1W22S. These p-values ranged between 0.151 to 1.000 (Appendix Table 47). Generally, 2006 had the highest mean Cr concentrations (Table 3.3.4).

Copper: Significant differences were found for L2D06S versus L2D22S and L2W06S versus L2W22S, and ($p = 0.008$). There were no significant differences for L1D06S versus L1D22S, L1W06S versus L1W22S, B1D06S versus B1D22S and B1W06S versus B1W22S. These p-values ranged between 0.320 to 0.690 (Appendix Table 51). For all comparisons with significant differences, the mean Cu concentrations were the highest in 2006 in comparison with 2022 (Table 3.3.4).

Iron: Significant differences were found for L1W06S versus L1W22S, L2D06S versus L2D22S, L2W06S versus L2W22S, and B1W06S versus B1W22S ($p = 0.008$). There were no statistical differences for L1D06S versus L1D22S and B1D06S versus B1D22S. These p-values ranged between 0.151 and 0.690 (Appendix Table 54). For most significant different comparisons, mean Fe concentrations were higher in 2022 than in 2006 (Table 3.3.4).

Manganese: Significant differences were found for L1W06S versus L1W22S, and B1W06S versus B1W22S ($p = 0.008$). There were no significant differences for L1D06S versus L1D22S, L2D06S versus L2D22S, L2W06S versus L2W22S, and B1D06S versus B1D22S. These p-values ranged between 0.151 to 0.690 (Appendix Table 59). For all significantly different comparisons, mean Mn concentrations were higher in 2022 compared to 2006 (Table 3.3.4).

Nickel: Statistical significant differences were found for L1D06S versus L1D22S, L2D06S versus L2D22S and B1D06S versus B1D22S ($p = 0.008$ to 0.032). There were no statistical differences for L1W06S versus L1W22S, L2W06S versus L2W22S and B1W06S versus B1W22S ($p = 0.421$ and 0.690) (Appendix Table 64). For most comparisons with significant differences, the mean Ni concentrations were the highest in 2006 (Table 3.3.4).

Lead: Significant differences were found for L1W06S versus L1W22S, L2D06S versus L2D22S, and B1D06S versus B1D22S ($p = 0.008$). There were no significant differences for L1D06S versus L1D22S, L2W06S versus L2W22S, and B1W06S versus B1W22S. These p-values ranged between 0.056 to 0.690 (Appendix Table 68). For most comparisons with significant differences, the mean Pb concentrations were the highest in 2006 (Table 3.3.4).

Zinc: Significant differences were found for L1W06S versus L1W22S, L2D06S versus L2D22S, L2W06S versus L2W22S, and B1D06S versus B1D22S (p = 0.008). There were no significant differences for L1D06S versus L1D22S, and B1W06S versus B1W22S. These p-values ranged between 0.151 to 0.690 (Appendix Table 73). For most comparisons with significant differences, the mean Zn concentrations were the highest in 2006 (Table 3.3.4).

3.3.1.2 Comparisons between the wet and the dry seasons

Aluminium: Statistical significant differences for seasonal comparisons were found for L1D06S versus L1W06S, L2D06S versus L2W06S, S1D06S versus S1W06S, and L2D22S versus L2W22S (p = 0.008 and 0.032). There were no significant differences for B1D06S versus B1W06S, L1D22S versus L1W22S, B1D22S versus B1W22S and B2D22S versus B2W22S (p = 0.056 - 0.690) (Appendix Table 35). For all significantly different comparisons, mean Al concentrations were higher in the dry season of both 2022 and 2006 (Table 3.3.4).

Cadmium: Significant differences were found for B2D22S versus B2W22S (p = 0.008). There were no significant differences for L1D06S versus L1W06S, L2D06S versus L2W06S, B1D06S versus B1W06S and S1D06S versus S1W06S, L1D22S versus L1W22S, L2D22S versus L2W22S and B1D22S versus B1W22S. These p-values ranged between 0.056 to 1.000 (Appendix Table 40). For most comparisons with significant differences, the mean Cd concentrations were the highest in the wet season of 2022 (Table 3.3.4).

Cobalt: Statistical significant differences were found for L2D06S versus L2W06S, and S1D06S versus S1W06S (p = 0.008). There were no statistical differences for L1D06S versus L1W06S, and B1D06S versus B1W06S, L1D22S versus L1W22S, L2D22S versus L2W22S, B1D22S versus B1W22S, and B2D22S versus B2W22S. These p-values ranged between 0.151 and 1.000 (Appendix Table 43). For most significantly different comparisons, mean Co concentrations were higher in the dry season of 2006 (Table 3.3.4).

Chromium: Significant differences were found for L1D06S versus L1W06S, S1D06S versus S1W06S, L2D22S versus L2W22S, B1D22S versus B1W22S, and B2D22S versus B2W22S ($p = 0.008$ and 0.016). There were no significant differences for L2D06S versus L2W06S, B1D06S versus B1W06S, and L1D22S versus L1W22S. These p-values ranged between 0.151 to 0.095 (Appendix Table 48). For all comparisons with significant differences, the mean Cr concentrations were higher in the dry season of 2006 and wet season of 2022 (Table 3.3.4).

Copper: Significant differences were found for L2D06S versus L2W06S ($p = 0.008$). There were no significant differences for L1D06S versus L1W06S, B1D06S versus B1W06S, and S1D06S versus S1W06S, L1D22S versus L1W22S, L2D22S versus L2W22S, B1D22S versus B1W22S, and B2D22S versus B2W22S. These p-values ranged between 0.222 to 1.000 (Appendix Table 52). For most significantly different comparisons, mean Cu concentrations were higher in the dry season of 2022 and dry season of 2006 (Table 3.3.4).

Iron: Significant differences were found for L1D06S versus L1W06S, L2D06S versus L2W06S and S1D06S versus S1W06S ($p = 0.008$). There were no statistical differences for B1D06S versus B1W06S, L1D22S versus L1W22S, L2D22S versus L2W22S, B1D22S versus B1W22S and B2D22S versus B2W22S ($p = 0.151$ to 0.841) (Appendix Table 55). For all comparisons with significant differences, the mean Fe concentrations were the highest in the dry season of 2022 and 2006 (Table 3.3.4).

Manganese: Significant differences were found for L1D06S versus L1W06S, L2D06S versus L2W06S, S1D06S versus S1W06S, and B2D22S versus B2W22S ($p = 0.008$). There were no statistical differences for B1D06S versus B1W06S, L1D22S versus L1W22S, L2D22S versus L2W22S, and B1D22S versus B1W22S. These p-values ranged between 0.151 to 0.690 (Appendix Table 60). For all significantly different comparisons, mean Mn concentrations were higher in the dry season of 2022 and 2006 (Table 3.3.4).

Nickel: Statistical differences were found for S1D06S versus S1W06S, L1D22S versus L1W22S, L2D22S versus L2W22S, B1D22S versus B1W22S, and B2D22S versus B2W22S (p = 0.008). There were no significant differences for L1D06S versus L1W06S, L2D06S versus L2W06S and B1D06S versus B1W06S. These p-values ranged between 0.310 to 0.841 (Appendix Table 65). For most comparisons with significant differences, the mean Ni concentrations were higher in the wet season in 2022 and dry season in 2006 (Table 3.3.4).

Lead: Significant differences were found for most seasonal comparisons: L1D06S versus L1W06S, L2D06S versus L2W06S, S1D06S versus S1W06S, L2D22S versus L2W22S, and B2D22S versus B2W22S (p = 0.008 and 0.032). There were no significant differences for B1D06S versus B1W06S, L1D22S versus L1W22S, and B1D22S versus B1W22S. These p-values ranged between 0.151 and 0.421 (Appendix Table 69). For all significantly different comparisons, mean Pb concentrations were higher in the wet season in 2022 and in the dry season in 2006 (Table 3.3.4).

Zinc: Significant differences were found for L2D06S versus L2W06S, L1D22S versus L1W22S, L2D22S versus L2W22S, B1D22S versus B1W22S, and B2D22S versus B2W22S (p = 0.008). There were no statistical differences for L1D06S versus L1W06S, B1D06S versus B1W06S, and S1D06S versus S1W06S. These p-values ranged between 0.095 to 0.548 (Appendix Table 74). For most comparisons with significant differences, mean Zn concentrations were higher in the dry season of 2006 and wet season of 2022 (Table 3.3.4).

3.3.1.3 Comparisons between the sampling stations

Aluminium: Statistical significant differences were found for most sampling stations comparisons: L2D06W versus B1D06W, L2D06W versus L1D06W, L2D06W versus S1D06W, S1D06W versus B1D06W, L1D06W versus B1D06W, L2W06S versus L1W06S, L2W06S versus S1W06S, L2W06S versus B1W06S, B1W06S versus L1W06S, S1W06S versus L1W06S, L2W22S versus B1W22S, B2W22S versus B1W22S, and L1W22S versus B1W22S (p = 0.001 to 0.026). There were no statistical differences for the S1D06W versus L1D06W, and B1W06S versus S1W06S (p = 0.238 to 0.986) (Appendix Tables 36, 37 and 38). For all comparisons with significant differences, the mean Al concentrations were higher at the first and second station of the Liesbeek River during the dry season of 2006, at the second station of Liesbeek River during the wet season of 2006, at the first station of the Black River during the wet season of 2006 and at the first station of the Salt River during the dry and the wet seasons of 2006 (L2D06S, S1D06S, L1D06S, L2W06S, B1W06S, and S1W06S) (Table 3.3.4). There were no significant differences between the sampled stations for the dry season of 2022.

Cadmium: Statistically significant differences were found for B2W22S versus L1W22S, B2W22S versus L2W22S, B1W22S versus L1W22S and B1W22S versus L2W22S (p = 0.001 and 0.028) (Appendix Table 41). The Black River had the highest mean Cd concentrations compared to the Liesbeek River (Table 3.3.4).

Cobalt: Significant differences were found for S1D06S versus L1D06S, S1D06S versus B1D06S, S1D06S versus L2D06S, L2D06S versus L1D06S, L2D06S versus B1D06S, S1W06S versus L1W06S, S1W06S versus B1W06S, S1W06S versus L2W06S, B2W22S versus B1W22S, B2W22S versus L2W22S, B2W22S versus L1W22S, L1W22S versus B1W22S and L2W22S versus B1W22S (p = 0.001 to 0.031). There were no significant differences for B1D06S versus L1D06S, L2W06S versus L1W06S, L2W06S versus B1W06S, and B1W06S versus L1W06S (p = 0.880 to 0.997) (Appendix Tables 44, 45 and 46). For most comparisons with significant differences, the mean Co concentrations were higher at the first station of the Salt River during the wet and the dry seasons of 2006 and at the second station of the Black River during the wet season of 2022 (Table 3.3.4).

Chromium: Significant differences were found for most sampling station comparisons: S1D06S versus L1D06S, S1D06S versus B1D06S, S1D06S versus L2D06S, and L2D06S versus L1D06S, (p = 0.001 to 0.044). There were no significant differences for L2D06S versus B1D06S, B1D06S versus L1D06S, B2W22S versus L1W22S, B2W22S versus B1W22S, B2W22S versus L2W22W, L2W22S versus L1W22S, L2W22S versus B1W22S, and B1W22S versus L2W22S. These p-values ranged between 0.072 and 0.618 (Appendix Tables 49 and 50). For all comparisons with significant differences, the mean Cr concentrations were higher at the first station of the Salt River during the dry season of 2006 and at the second station of the Liesbeek River during the dry season of 2006, the mean Cr concentrations were higher in the second station of Liesbeek River and second station of Black River during the wet season of 2022 (Table 3.3.4).

Copper: Significant differences were found for S1W06S versus L1W06S, S1W06S versus L2W06S, and S1W06S versus B1W06S (p = 0.013 to 0.031). There were no significant differences for B1W06S versus L1W06S, B1W06S versus L2W06S, and L2W06S versus L1W06S. These p-values ranged between 0.966 to 0.999 (Appendix Table 53). For all significantly different comparisons, mean Cu concentrations were higher at the first station of the Salt River during the wet season of 2006 (Table 3.3.4).

Iron: Significant differences were found for L2D06S versus L1D06S, L2D06S versus B1D06S, L2D06S versus S1D06S, S1D06S versus L1D06S, S1D06S versus B1D06S, L2W06S versus L1W06S, L2W06S versus S1W06S, B1W06S versus L1W06S, S1W06S versus L1W06S, L2W22S versus B1W22S, B2W22S versus B1W22S and L1W22S versus B1W22S (p = 0.001 and 0.002). There were no statistical differences for B1D06S versus L1D06S, L2W06S versus B1W06S, and B1W06S versus S1W06S, L2W22S versus L1W22S, L2W22S versus B2W22S and B2W22S versus L1W22S (p = 0.054 to 0.991) (Appendix Tables 56, 57 and 58). For most comparisons with significant differences, the mean Fe concentrations were higher at the second station of the Liesbeek River during the dry and the wet seasons of 2006, at the first station of the Salt River during the dry and the wet seasons of 2006 and at the first station of the Black River during the wet season of 2006 and second station of Liesbeek River dry season of 2006 (Table 3.3.4).

Manganese: Significant differences were found for S1D06S versus L1D06S, S1D06S versus B1D06S, L2W06S versus L1W06S, S1W06S versus L1W06S, B1W06S versus L1W06S, L1W22S versus B1W22S, L1W22S versus B2W22S, L1W22S versus L2W22S, L2W22S versus B1W22S and B2W22S versus B1W22S (p = 0.001 and 0.031). There were no significant differences for S1D06S versus L2D06S, L2D06S versus L1D06S, L2D06S versus B1D06S, B1D06S versus L1D06S, L2W06S versus B1W06S, L2W06S versus S1W06S, S1W06S versus B1W06S and L2W22S B2W22S. These p-values ranged between 0.073 to 0.996 (Appendix Tables 61, 62 and 63). For all comparisons with significant differences, the mean Mn concentrations were higher at the second station of the Liesbeek River during the dry and the wet seasons of 2006, at the first station of the Salt River during the dry and the wet seasons of 2006, and at the first station of the Black River during the wet season of 2006, higher mean Mn concentration were also observed at the first station of Liesbeek River during the wet season of 2022 (Table 3.3.4).

Nickel: Significant differences were found for S1D06S versus L1D06S, S1D06S versus L2D06S, S1D06S versus B1D06S, B2W22S versus B1W22S, B2W22S versus L1W22S and B2W22S versus L2W22S (p = 0.001 to 0.007). There were no significant differences for B1D06S versus L1D06S, B1D06S versus L2D06S, L2D06S versus L1D06S, L2W22S versus B1W22S, L2W22S versus L1W22S and L1W22S versus B1W22S (p = 0.153 to 1.000) (Appendix Table 66 and 67). For most significantly different comparisons mean Ni concentrations were higher at the first station of the Salt River during the dry season of 2006 (Table 3.3.4).

Lead: Significant differences were found for S1D06S versus L1D06S, S1W06S versus L1W06S, B2W22S versus L1W22S, B2W22S versus L2W22S, and B2W22S versus B1W22S (p = 0.001 to 0.013). There were no significant differences for S1D06S versus B1D06S, S1D06S versus L2D06S, L2D06S versus L1D06S, L2D06S versus B1D06S, B1D06S versus L1D06S, S1W06S versus L2W06S, S1W06S versus B1W06S, B1W06S versus L1W06S, B1W06S versus L2W06S, L2W06S versus L1W06S, B1W22S versus L1W22S, B1W22S versus L2W22S, and L2W22S versus L1W22S. These p-values ranged between 0.051 to 0.996 (Appendix Tables 70, 71 and 72). For all comparisons with significant differences, the mean Pb concentrations were higher at the first station of the Salt River during the dry and wet seasons of 2006 (Table 3.3.4).

Zinc: Significant differences were found for S1D06S versus L1D06S, S1D06S versus L2D06S, S1D06S versus B1D06S, B1D06S versus L1D06S, L2D06S versus L1D06S, S1W06S versus L1W06S, S1W06S versus L2W06S, S1W06S versus B1W06S, B1W06S versus L1W06S, B1W06S versus L2W06S, B2W22S versus L1W22S, B2W22S versus L2W22S, and B1W22S versus L1W22S (p = 0.001 and 0.026). There were no significant differences for B1D06S versus L2D06S, L2W06S versus L1W06S, B2W22S versus B1W22S, B1W22S versus L2W22S, and L2W22S versus L1W22S. These p-values ranged between 0.118 to 0.752 (Appendix Tables 75, 76 and 77). For all comparisons with significant differences, the mean Zn concentrations were higher at the first station of the Salt River during the dry and wet seasons of 2006, at the first station of the Black River during the dry and the wet seasons of 2006, and at the second station of the Liesbeek River during the dry season of 2006, for the wet season of 2006 the station with highest mean Zn concentration was Salt River station 1 and during the wet season of 2022 the highest mean was observed at Liesbeek River station 2 (Table 3.3.4).

CHAPTER 4: DISCUSSION

4.1 Comparison with environmental quality guidelines

Water and sediment quality guidelines play a crucial role in determining the water quality, health and functioning of a river system (Odume *et al*., 2024). The DWAF (1996) Target Water Quality Range (TWQR), risk-based water quality guidelines for freshwater ecosystems (Odume *et al*., 2024), and the interim freshwater sediment quality guidelines of the Canadian Council of Ministers of the Environment (CCME, 2002) are examples of environmental quality guidelines that assist in environmental monitoring. When employed in environmental management, they can also assist in ensuring that water is safe for drinking purposes and recreational use, as well as protecting public health, aquatic biota and ecosystems from toxic pollutants (DWAF, 1996, Odume *et al*., 2024).

4.1.1 *Water quality guidelines*

Table 3.1.1.1.1 shows the physicochemical parameters measured from the three rivers and their respective sampling stations. The results showed that for all parameters (temperature, conductivity, pH, dissolved oxygen and salinity), the measurements taken did not exceed the respective South African TWQR of the Water Quality Guidelines for Aquatic Ecosystems (DWAF, 1996). The physicochemical parameters were within the set water quality guidelines, indicating that they are unlikely to pose significant risks to aquatic species.

New risk-based South African water quality guidelines for freshwater ecosystems were developed by Odume *et al*. (2024). These recently developed guidelines were designed as a trigger value should metals exceed a guideline value. These guidelines were established primarily utilizing toxicological data produced through species sensitivity distribution (Odume *et al*., 2024) (Appendix Table 78) and is what will be used in this study for metal concentrations in water, together with the DWAF (1996) guidelines. Should the metal concentrations exceed the recommended guidelines remedial actions can then be taken to prevent negative impacts that could potentially arise (Odume *et al*., 2024).

Mean (± SD) metal concentrations, measured in the water samples from the three rivers and their respective sampling stations, during each sampling occasion are shown in Table 3.2.3. The results showed that the mean Al concentrations measured across the different sampling stations in 2006 and 2022 ranged from 0.060 ± 0.052 mg/L to 0.410 ± 0.079 mg/L and from 0.054 ± 0.049 mg/L to 45.838 ± 28.413 mg/L, respectively, and fell within the critical impact category. These concentrations were all above the TWQR (0.01 mg/L) as stipulated in the South African Water Quality Guidelines for Aquatic Ecosystems (DWAF, 1996). Additionally, when compared to the new Water Quality Guideline values of 2024 (Odume *et al*., 2024), the sampling stations fell within the largely natural category (>0.0070 mg/L to 0.119 mg/L) (Liesbeek River station 1 wet season both years; Liesbeek River station 2 wet season 2006; Black River station 1 wet season both years; Salt River station wet season 2022), the moderate impact category (>0.119 mg/L to 0.218 mg/L) (Black River station 2 wet season 2022), and the large impact category (>0.218 mg/L to 0.475 mg/L) (Liesbeek River station 2 wet season 2022; Liesbeek River station 2 dry season 2006; and Black River 1 dry season 2006). The mean Al concentrations were mostly extremely high during the dry season of 2022 and above the upper limit of the critical impact category (>0.475 mg/L to 0.880 mg/L).

Results of the water quality analysis indicated that no Cd was detected during 2022, at any of the rivers' sampling stations, for either of the seasons. This was also true for the 2006 dry season. In comparison, mean Cd concentrations during the wet season of 2006 ranged from 0.002 ± 0.002 mg/L to 0.003 ± 0.002 mg/L. For all sampling stations in 2006 results were above the TWQR (>0.0004) mg/L (DWAF, 1996) and fell within the moderate impact category (>0.0022 mg/L to 0.0054 mg/L) of the new water quality guidelines (Odume *et al*., 2024). Mean Co concentrations varied during both the dry and wet seasons of 2006 (0.000 ± 0.000 mg/L to 0.004 ± 0.005 mg/L) and 2022 (0.000 mg/L ± 0.000 mg/L to 0.002 ± 0.003 mg/L). Cobalt was undetected at most sampling stations, and those above the detection limit were generally below the TWQR guideline of 0.0024 mg/L (DWAF, 1996) and fell within the natural category

(<0.0024 mg/L) (Liesbeek River station 1 wet season both years; Liesbeek River station 2 dry season both years; Black River station 1 wet season 2006; and Salt River dry season 2006), when compared to the guidelines of Odume *et al*. (2024).

The mean Cr concentrations varied during both the dry and wet seasons of 2006 and 2022 (0.037 ± 0.018 mg/L to 0.121 ± 0.085 mg/L) and 2022 (0.001± 0.001 mg/L to 0.130 ± 0.080 mg/L), and most of the sampling stations were above the set TWQR (>0.007 mg/L) (DWAF, 1996). When compared to the new freshwater quality guidelines as stipulated by Odume *et al*. (2024), the results fell within the natural category (<0.000 mg/L to 0.0082 mg/L) (Liesbeek River station 1 & 2 wet season 2022; Black River station 2 wet season 2022; and Salt River wet season 2022), the largely natural category (<0.0082 mg/L to 0.0841 mg/L) (Liesbeek River stations 1 & 2 dry and wet seasons both years; Black River station 1 dry and wet seasons 2006; Salt River dry season 2006) and the moderate impact category (>0.0841 mg/L to 0.214 mg/L) (Liesbeek River station 1 wet season 2006; Black River station 1 dry season 2022).

Copper was not detected at most of the sampling stations during both the dry and wet seasons of 2006, except for the Liesbeek River station 1 wet season (0.020 ± 0.044 mg/L). Mean Cu concentrations during the dry and wet seasons of 2022 ranged from 0.016 ± 0.036 mg/L to 0.057 ± 0.127 mg/L during the dry season and from 0.037 ± 0.072 mg/L to 0.150 ± 0.174 mg/L during the wet season. These mean concentrations were above the TWQR (>0.0014 mg/L) (DWAF, 1996). Furthermore, the results fell within the largely natural category (<0.00036 mg/L to 0.0058 mg/L) (Liesbeek River station 1 wet season 2006; Liesbeek River station 1 & 2 dry season 2022; Black River station 1 dry and wet seasons 2022; and Salt River dry season 2006) and the critical impact category (>0.0601 mg/L) (Liesbeek River station 1 wet season 2022; Black River station 2 wet season 2022) as stipulated in the new water quality guidelines (Odume *et al*., 2024).

The mean Fe concentrations during the dry and wet seasons ranged from 0.074 ± 0.038 mg/L to 0.709 ± 0.189 mg/L in 2006 and from 0.118 ± 0.039 to 79.938 ± 60.355 mg/L in 2022. These concentrations were below the set TWQR of 0.9 mg/L (DWAF,

1996) and fell within the largely natural category (<0.0036 mg/L to 0.122 mg/L) (Liesbeek River station 2 dry season 2006), and the moderate impact category (>0.122 mg/L to 0.391 mg/L) (Liesbeek River station 1 wet season 2006; Black River station 1 & 2 dry and wet seasons 2006; Salt River dry season 2006) as stipulated in Odume *et al*. (2024). The mean Fe concentrations at the Liesbeek River station 1 dry season for both years, Liesbeek River station 1 wet season 2006, Liesbeek River station 2 dry and wet seasons of 2022, with Black River stations 1 & 2 dry and wet seasons 2022, and Salt River wet season 2022 were all above the critical impact category guideline value (>4.1 mg/L) (Odume *et al*., 2024).

The mean Mn concentrations varied throughout the wet and dry seasons of 2006 from 0.001 ± 0.001 mg/L to 0.049 ± 0.005 mg/L and those of 2022 from 0.000 ± 0.000 mg/L to 0.799 ± 1.786 mg/L. Most sampling stations were below the set TWQR of 0.18 mg/L (DWAF, 1996), except for the Liesbeek River station 2 and the Black River station 1 dry season of 2022. Compared to the guidelines by Odume *et al.* (2024), the results fell within the natural category (<0.0457 mg/L) (Liesbeek River stations 1 & 2 dry season 2006; Black River stations 1 & 2 dry and wet seasons 2006; Black River stations 1 & 2 wet season 2022; Salt River wet and dry seasons both years), the largely natural category (<0.0457 mg/L to 0.306 mg/L) (Black River station 1 dry season 2022), and the moderate impact category (>0.306 mg/L to 0,605 mg/L) (Liesbeek River station 2 dry season 2022).

The results showed that there was no Ni detected during the 2006 wet season and 2022 dry season at any of the rivers' sampling stations. Variations in concentrations of this metal were observed during the dry season of 2006 and the wet season of 2022. DWAF (1996) does not have a guideline value for Ni. When compared to the guidelines of Odume *et al*. (2024), mean concentrations fell within the natural category (<0.0042 mg/L) (Liesbeek River stations 1 & 2 wet seasons 2022; Black River stations 1 & 2 wet seasons 2022; Salt River wet season 2022) as well as the largely natural category (<0.0042 mg/L to 0.0690 mg/L) (Liesbeek River station 2 dry season 2006; Black River station 1 dry season 2006; Salt River dry season 2006).

Lead was not detected at most of the sampling stations during the dry and wet seasons of 2006 and 2022. It was, however, detected at the Liesbeek River station 1 during the 2006 wet season (0.060 ± 0.054 mg/L). At stations where this metal was detected during the dry season of 2022, concentrations varied from 0.014 ± 0.009 mg/L to 0.126 ± 0.139 mg/L. All the stations where Pb was detected, concentrations were above the TWQR of 0.0012 mg/L (DWAF, 1996), and fell within the large impact category (<0.0032 mg/L to 0.158 mg/L) (Liesbeek River stations 1 & 2 dry season 2022; Liesbeek River station 1 wet season 2006; Liesbeek River station 2 wet and dry seasons 2022; Black River station 2 dry season 2022; Salt River dry season 2006) (Odume *et al*., 2024).

Zinc was not detected at most of the sampling stations during the dry season of 2006, except at the Liesbeek River station 1 (0.073 ± 0.075 mg/L). During the wet season of 2006 Zn was only detected at the Liesbeek River station 1 (0.152 ± 0.132 mg/L) and Black River station 1 (0.024 ± 0.053 mg/L). There were no Zn detected at most of the sampling stations during the dry season of 2022, except at the Salt River sampling station (0.009 ± 0.021 mg/L). Zinc was found during the 2022 wet season sampling at the Liesbeek River stations 1 & 2 (0.040 ± 0.041 mg/L and 0.060 ± 0.084 mg/L, respectively), Black River stations 1 & 2 (0.062 ± 0.071 mg/L and 0.102 ± 0.198 mg/L, respectively), and the Salt River sampling station (0.026 ± 0.053 mg/L). Mean concentrations of Zn were above the TWQR of 0.002 mg/L (DWAF, 1996) and fell within the largely natural category (<0.0027 mg/L to 0.101 mg/L) (Liesbeek River station 1 dry and wet season 2006; Liesbeek River station 1 wet season 2022; Black River stations 1 & 2 wet season 2022; Salt River wet and dry seasons 2022) as stipulated in the risk-based South African Water Quality Guidelines for Freshwater Ecosystems (Odume *et al*., 2024).

4.1.2 *Sediment quality guidelines*

When metal concentrations exceed the sediment quality guidelines, they can significantly impact the structure, functioning and health of aquatic ecosystems (CCME, 2002; Edokpayi *et al*., 2017). Recent studies conducted by Vivien *et al*. (2020) and Mohajane & Manjoro (2022) indicated that most aquatic organisms rely on sediment quality for their well-being, as sediment serves as a habitat, particularly for benthic species. If sediment quality is affected by metal contaminants, they could pose detrimental effects on these organisms, potentially affecting population size and even reproductive cycles (Suresh *et al*., 2012; Islam *et al*., 2018; Mohajane & Manjoro, 2022). Suresh *et al*. (2012) further stated that the sediment contamination could potentially alter species communities and diversity, particularly affecting macroinvertebrates as these organisms are more vulnerable to the effects of contamination (Li *et al*., 2020; Mohajane & Manjoro, 2022).

Mean (± SD) metal concentrations measured in sediments from the three rivers during each sampling occasion are shown in Table 3.3.4. These concentrations were compared to the Canadian Interim Sediment Quality Guidelines (CCME, 2002). It should be noted that there are no such guidelines for South Africa. Only mean concentrations of Cd, Cr, Cu, Ni, Pb and Zn were compared to the CCME (2002), as these quality guidelines do not cover all the selected metals discussed in this study.

Findings from the sediment quality assessment showed that mean Cd concentrations in the Liesbeek, Black and Salt Rivers varied between sampling stations in 2022 (0.007 ± 0.004 mg/kg to 0.079 ± 0.023 mg/kg). There was no Cd detected at most sampling stations in 2006, except at the Liesbeek River station 2 (0.249 ± 0.055 mg/kg) and Salt River (0.047 ± 0.067 mg/kg). Cadmium detected at those sampling stations fell within the permissible sediment quality guidelines (0.6 mg/kg) (CCME, 2002). The mean Cr concentrations varied across sampling stations during the dry and wet seasons ranging from 0.227 ± 0.228 mg/kg to 15.596 ± 4.631 mg/kg in 2006, and from 0.330 ± 0.738 mg/kg to 5.690 ± 0.102 mg/kg in 2022, respectively. Mean concentrations were within the permissible sediment quality guideline (37.3 mg/kg) (CCME, 2002).

Analysis of the sediment showed that the mean Cu concentrations varied during the dry and wet seasons ranging from 0.231 ± 0.231 mg/kg to 42.609 ± 37.559 mg/kg in 2006, and from 2.140 ± 2.937 mg/kg to 18.100 ± 34.835 mg/kg in 2022, respectively. However, no Cu was detected at the Liesbeek River stations 1 and 2 during the dry season of 2022. Most sampling stations where Cu was found were within the acceptable sediment quality criteria (35.7 mg/kg) as stipulated in the Canadian Interim Sediment Quality Guidelines (CCME, 2002), except for the Black River station 1 (42.384 ± 88.492 mg/kg) dry season and Salt River station (42.609 ± 37.559 mg/kg) wet season of 2006. All the sampling stations where Ni was detected, were within the permissible sediment quality guideline (52 mg/kg) as stipulated by McCready *et al*. (2006). The mean Ni concentrations varied during the dry and wet seasons ranging from 0.788 ± 1.079 mg/kg to 9.540 ± 2.169 mg/kg in 2006 and from 0.000 ± 0.000 mg/kg to 2.203 ± 0.387 mg/kg in 2022, respectively.

Sediment quality assessment results showed that the mean Pb concentrations ranged from 0.000 ± 0.000 mg/kg to 89.405 ± 45.366 mg/kg in 2006 and from 1.978 ± 2.753 mg/kg to 19.684 ± 5.675 mg/kg in 2022. Most sampling stations within the permissible sediment quality guideline of 35 mg/kg (CCME, 2002). Except for the Liesbeek River station 2 (58.519 ± 27.693 mg/kg), Black River station 1 (43.159 ± 33.131 mg/kg) and the Salt River station (89.405 ± 45.366 mg/kg) during the dry season of 2006, as the mean Pb concentrations were higher than the sediment quality guideline (CCME, 2002). The mean Zn concentrations varied during the dry and wet seasons ranging from 1.801 ± 0.913 mg/kg to 134.421 ± 36.852 mg/kg in 2006 and from 0.000 ± 0.000 mg/kg to 75.635 ± 15.615 mg/kg in 2022, respectively. Mean concentrations mostly fell within the acceptable 123 mg/kg guideline as stipulated in the Canadian Quality Guidelines (CCME, 2002), except for the Salt River station (134.421 ± 36.852 mg/kg) during the dry season of 2006.

The high concentrations of the Cu, Pb and Zn could have been due to several factors such as waste disposal, excessive nutrients, and storm water runoff from the road (Dassenakis *et al*., 1995). The rivers selected for this study are likely to be impacted by the aforementioned factors. Soil characteristics play a major role in adsorbing metals (Dassenakis *et al*., 1995). Soils have been observed to become contaminated and retain and accumulate metals resulting from various activities, including industrial emissions, the disposal of untreated wastewater, the use of leaded petrol as well as atmospheric deposition (Wuana & Okieimen, 2011). The current study found that the Black River sediment consisted of high fine and very fine sand particles, these soils are known to have a high nutrient holding capacity, high adsorption and poor drainage (Gilbert, 2015), which may have contributed to the high Cu and Pb concentrations. Additionally, since the second station of the Black River is in close proximity to major roads and a golf course, the irrigation and maintenance activities from the golf course and stormwater runoff from the road could have contributed to the high metal concentrations observed in the sediments.

The high metal concentrations detected in the sediment indicate a significant environmental concern. Given that higher concentrations were observed at sites with high levels of anthropogenic activities, it is postulated that sources of pollution could have resulted from the sewage treatment works, golf course, household waste from the southern suburbs, industrial activities, urban runoff, and waste from informal settlements in the surrounding areas. The Black and Salt Rivers are situated relatively close to an industrial area and wastewater treatment plants. Due to these reasons waste could have drained into these rivers and influenced the concentrations of metals. The Liesbeek River is situated in the southern suburbs of Cape Town and may thus receive domestic wastewater effluents from the surrounding residential areas.

4.1.3 *Metals not represented in the sediment quality guidelines*

Apart from the comparisons with the sediment quality guidelines, metals that were not included in the Canadian sediment quality guidelines were compared with previous studies. The metals that were not included in the Canadian sediment quality guidelines were Al, Fe, Co, and Mn.

The study conducted by Desrosiers *et al*. (2009) provided sediment quality guidelines for Al (12.0 mg/kg), Fe (18.0 mg/kg) and Mn (1.1 mg/kg). The mean concentrations for Al, Fe and Mn measured in the present study were higher than these stated detection limits at all the sampling stations. Mean Al concentrations measured in 2006 and 2022 ranged from 647.678 ± 35.297 mg/kg to 1035.210 ± 90.786 mg/kg and from 749.858 ± 170.309 mg/kg to 1835.378 ± 218.481 mg/kg, respectively. Mean Fe concentrations varied across wet and dry seasons ranging from 680.066 ± 92.012 mg/kg to 4448.697 ± 408.211 mg/kg in 2006 and from 996.939 ± 208.585 mg/kg to 3690.257 ± 864.818 mg/kg in 2022, respectively. Mean Mn concentrations differed between 2006 and 2022 and ranged from 4.334 ± 0.380 mg/kg to 65.205 ± 34.187 mg/kg and from 4.838 ± 1.187 mg/kg to 711.607 ± 262.429 mg/kg, respectively.

Aluminum, Iron and Manganese concentrations were high in sediment samples suggesting potential contamination of the sediments through the adsorption of these metals. Given that Al and Fe are naturally occurring elements, their high levels were expected relative to other metals (Mohajane & Manjoro, 2022). There are numerous factors that could have influenced the elevated concentrations of Al, Fe and Mn in the sediments such as extra inputs of waste from the sewage treatment works, industrial waste and waste from surrounding areas, e.g household waste (Khan *et al*., 2017).

Other studies on metal concentrations found similar results. Metals of concern that had higher concentrations when compared with the sediment quality guidelines were Cr, Cu, Fe, Zn, Mn and Ni with Mn and Zn exceeding the acceptable limit value as indicated by Addo-Bediako *et al*. (2021). Metals are vital as they play a significant role in the environment, but if they exceed set quality guidelines, they pose a risk to aquatic organisms and humans and may even cause irreversible effects on the food web. High Al concentrations may lead to Alzheimer disease as it is known to be neurotoxic (Edokpayi *et al*., 2016). Cadmium can pose a toxic risk to freshwater organisms. In addition, Fe supports living organisms with protein and enzymes, but increased concentrations can cause anaemia and fatigue, especially in young children and pregnant women and it is also known to cause hemochromatosis, if consumed in high concentrations (Edokpayi *et al*., 2016; Abdulla *et al*., 2020; Feng *et al*., 2022; Jiao *et al*., 2022).

The Diep and Berg Rivers have been extensively studied, with high concentrations of metals such as Al, Fe, Zn, Cu, and Pb found in the sediments (Jackson *et al*., 2009; Jackson *et al*., 2007). A study that was conducted at the Plankenburg and Diep Rivers in the Western Cape, South Africa, found that the Al (19 179.0 mg/kg) and Fe (106 379.5 mg/kg) mean concentrations were above the set sediment quality guidelines as recommended by Canadian sediment quality guidelines, respectively (CCME, 2001; Jackson *et al*., 2009). These authors stated that the sources of pollution were not identified although runoff from the industrial and residential areas was suspected to have contributed to the elevated metal concentrations in the sediments. Another study conducted by Jackson *et al*. (2007) in the Berg River, Western Cape, South Africa had key findings that showed high mean concentrations of Al (17 448.8 mg/kg and 26 473.3 mg/kg). The authors stated that the high concentrations of Al and Fe in Berg River sediment could have resulted from leaching of household waste from residential areas as well as unmanaged waste from surrounding informal settlements, which subsequently settled and accumulated among the sediments. These results were not very different from the results in the present study as sampling stations with high metal concentrations were those that were in close proximity to industries, residential areas and surrounding informal settlements.

4.2 Sources and effects of metals

The metals selected in this study were compared to South African Water Quality Guidelines (DWAF, 1996), together with the new set of recently developed risk-based water quality guidelines for freshwater ecosystems (Odume *et al*., 2024), and the Canadian Interim Sediment Quality Guidelines (CCME, 2002). These guidelines were established to monitor water quality, structure, functioning and health of river ecosystems (DWAF, 1996; CCMA, 2002; Odume *et al*., 2024). Selected metals were assessed against these quality guidelines to determine whether they meet or exceed the stated quality guideline values. The established sediment quality guidelines indicate that elevated metal concentrations can pose significant risks to both aquatic and human health (Algul & Beyhan, 2020). The increase in metal concentrations in the water and sediment is a major concern since metals can bioaccumulate (Gao & Chen-Tung, 2012; Addo-Bediako, 2020). Population growth and urbanisation are some of the factors that contribute to metal pollution in water bodies globally (Scarf *et al*., 1985; Briffa *et al*., 2020). Human activities play a significant role in affecting the water quality and functioning of water bodies and their ecosystems. This may cause irreversible effects on the functioning and structure of river systems. Moreover, the environmental and health risks posed by metal contaminants are exacerbated by their chemical persistence and potential for bioaccumulation. Edokpayi *et al*. (2016), Edokpayi *et al*. (2017), and Niba & Sakwe (2018) have raised critical concerns about the direct discharge of metal pollutants into freshwater ecosystems, emphasizing the threat they pose to aquatic organisms and public health.

For Liesbeek River station 1 dry season both years, Liesbeek River station 1 wet season 2006, Liesbeek River station 2 dry and wet seasons 2022, household waste and rainwater runoff from roads, construction sites, litter and waste from vagrants could have spiked the concentrations of these metals for Black River station 1 & 2 dry and wet seasons 2022 and Salt River wet season 2022 the rise of these metals could have been caused by the discharge of untreated sewage, improper disposal of waste, especially in the informal settlements. Waste from factories and industries adjacent to these rivers could have contributed to the increase in metal concentrations. As noted in DWAF (1996) biotic and abiotic components depend on the health of the river for survival. With that being said, freshwater ecosystems, structure and function is highly threatened particularly with pollution (DWAF, 1996). This could mean that human activities, changes in climate, air pollution, hydrological cycle and household waste could have influenced the Fe concentrations. Addo-Bediaki *et al*. (2021) stated that high metal concentrations in water have a potential of bioaccumulating within the bodies of aquatic organisms, which can cause fatal effects on species health, which might lead to mortality of aquatic organisms.

When metals exceed recommended quality guidelines it can cause harmful effects to both humans and animals such as weakening their immune system, causing multi organ cancer and cardiovascular system problems (Bathla & Jain, 2016; Noor *et al*., 2024). In addition, a previous study that examined the effects of Cr noted that a high concentration of this metal has the potential to cause cancer when an organism is exposed to it, while Cd causes itai-itai disease and other metals such as Cr, Cu and Fe to name a few are known to be toxic if are found in high levels and can cause nephrotoxicity, hepatotoxicity and skin toxicity (Mitra *et al*., 2022). Aziz *et al*. (2023) found that high metal concentration could cause major problems to the affected individuals/aquatic organisms by affecting their organs, neurological system, liver, lungs, kidneys, stomach, skin and reproductive systems even if the exposure is at low levels can still cause damage to animals and humans.

A study conducted by Snyman (1996) at the Eerste River, Western Cape, investigated the uptake and distribution of selected metals in the freshwater crab (*Potamonautes perlatus*). The study found variations of metals concentration between tissues, with the carapace identified as the primary storage site for Mn, Zn, and Pb. Based on these findings, the author suggested that *P. perlatus* could serve as a potential biomonitor for environmental pollution in aquatic environments. These results highlight the detrimental effects that metal exposure may have on the health and population of aquatic species. In addition, Snyman *et al*. (2002) examined the uptake and distribution of Cu in *Potamonautes perlatus* at the same location, Eerste River. Their findings indicated that the digestive gland exhibited the highest Cu mean concentrations. Furthermore, they noted that smaller crabs accumulated more Cu compared to larger individuals, suggesting a size dependent variation in metal accumulation. Similarly, Schuwerack *et al*. (2006) conducted study on the freshwater crab (*Potamonautes warren*) and results showed that the crab was exposed to high concentrations of Zn, Cd, Cu, and Pb. The results from this study, like the previous ones, emphasize the potential risks posed by metal contamination on freshwater organisms, further supporting the notion that such species could be affected by pollutant exposure in their natural habitats (Snyman, 1996; Snyman *et al*., 2002; Schuwerack *et al*., 2006).

Edokpayi *et al*. (2016) reported that high mean Mn concentration may cause memory lapses and reduced memory and concentration as it targets the brain and central nervous system in young children. Lead is known to cause negative effects, it can lead to kidney damage, high blood pressure and anemia, furthermore it is a threat to public health. It has the potential to build up in the body, normally affecting younger children, causing mental and physical retardation (DWAF, 1996; CCME, 2002; Edokpayi *et al*., 2016). A study conducted at the Olifants River, Limpopo Province, investigated metal bioaccumulation in the muscle tissue of rednose labeo (*Labeo* *rosae*) (Jooste *et al*., 2014). The findings revealed high concentrations of Pb and Cr in the species, with levels exceeding the recommended health risks threshold that indicated potential health risks for possible consumers of this species.

CSIR (2010) and Mwangi (2014) found several factors that are the contributing factors to the degradation of water quality in South African rivers such factors include eutrophication, salinization and acidification. These factors can be relevant to the Salt River catchment and are known to influence metal concentrations by increasing metal bioavailability and toxicity to aquatic organisms due to urban runoff, industrial activities (Stokes *et al*., 1985). Some of the selected metals such Al, Fe, Cr and Cu observed at the Salt River catchment were above the TWQR and falling in the higher categories, especially the moderate impacted category and critically impacted category.

4.3 Temporal comparison of metal concentrations (years and seasons) in the Black, Liesbeek and Salt Rivers

4.3.1 *Physicochemical parameters*

The PCA revealed overlap of samples between the years using physicochemical parameters as variables (Fig. 3.1.1.1). The ANOSIM results confirmed this, no significant dissimilarities were found between 2006 and 2022 PCA (A) (Global R: 0.08, p = 0.116) (Fig. 3.1.1.1). In addition, according to the ANOSIM results there were no significant dissimilarities between the wet and dry seasons (Global R: 0.119, p = 0.061) (Fig. 3.1.1.1). Both PCA's (A & C) demonstrated a lack of groupings between years (2006 & 2022) and the wet and dry seasons. The SIMPER was utilized to quantify the percentage dissimilarity of the physicochemical parameters in the water samples. Table 3.1.1.2 summarised the physicochemical parameters and highlighted the parameters which were most important in contributing to the dissimilarities between the years. The pH contributed the highest percentage (30.75%), then temperature (32.39%) and then conductivity (30.75%) to the difference between the years. Dissolved oxygen and salinity were not analysed as variables across years, due to the lack of data for 2006.

Higher water temperatures were consistently recorded for 2006 compared to 2022. This could have been due to seasonal fluctuations, runoffs from the road and pollution. In addition, this could simply have been due to natural annual temperature fluctuations. However, higher water temperatures can also result from factors such as thermal discharge, riparian vegetation modification and land use (Dallas, 2008). All of these are likely factors within the Salt River catchment.

Conductivity and pH also decreased from 2006 to 2022. It has been shown and is well known that runoff from different sources significantly impact parameters such as conductivity and pH (Reinecke *et al.,* 2002; Baralkiewicz *et al*., 2014, Magwaza, 2017; Wang *et al*., 2017). In the present study, possible increased runoff between 2006 and 2022, could have been responsible for the decrease in conductivity and pH. According to Magwaza (2017), faster flows shorten water residence time, limiting mineral weathering and ion release. Of all physicochemical parameters measured, only temperature and dissolved oxygen showed clear seasonal trends, with temperature being predictably consistently higher during the dry, hot season, and dissolved oxygen being consistently higher during the wet season (only for 2022, no data available for 2006). The latter is mainly due to increased water flow rate and turbulence, which increases oxygen content.

It is important to monitor and manage physicochemical parameters such as temperature, pH, conductivity, salinity and dissolved oxygen, as they are crucial to the health of aquatic ecosystems and the safety of freshwater for human consumption. Even if the physicochemical parameters are within the quality guideline ranges, they have direct impacts on metal bioavailability (Olaniran *et al*., 2013; Mebane, 2023) and bioaccumulation (Schafer *et al*., 2015; Edokpayi *et al*., 2016), which can lead to high body metal loads in aquatic biota and toxic effects on various levels of biological organisation.

4.3.2 *Metal concentrations in water*

Metal concentrations in water for the years 2006 and 2022 were analysed using PRIMER (PCA, ANOSIM, SIMPER) and SigmaPlot (ANOVA). The PCA illustrated the grouping of the metal samples using the years as factors (2006 and 2022) (Fig. 3.2.1). PC1 and PC2 accounted for 42.1% of the total variation in metal concentrations (Table 3.2.1). The ANOSIM indicated significant differences between 2006 and 2022 with a p-value of 0.001 (R=0.162). The SIMPER (similarity percentage) analysis identified the metals that were most responsible for the dissimilarities (Table 3.2.2), namely, Fe, Al, Cu, Pb and Cr (together responsible for 54.58% of the dissimilarity). ANOSIM determined that the metals were significantly different between 2006 and 2022. Despite various significant differences in individual metal concentrations between 2006 and 2022, there were no clear trends of increasing or decreasing metal concentrations, when considering the metals as a group. ANOSIM results for water samples indicated significant differences between the wet and dry seasons for both years (Global R: 0.199, p = 0.001). The SIMPER showed that the metals that contributed most to these dissimilarities (Table 3.2.2) were Fe (12.10%), Al (11.74%), Cu (10.82%), Pb (10.02%) and Cr (10%).

A comparative analysis of metal concentrations in the Liesbeek, Black, and Salt Rivers between 2006 and 2022 revealed notable temporal and seasonal variations, particularly for the wet seasons. The results from 2022 indicated significant shifts in metal accumulation patterns compared to 2006, suggesting the influence of evolving environmental pressures and intensifying anthropogenic activities over the 16-year period. These shifts were especially seen during the wet season of 2022, where seasonal increased water inflow likely influenced the transport, redistribution, and deposition of metals within the river systems (Osakwe *et al*., 2014; Pandey & Singh, 2017). Vega *et al*. (1998) also showed that the concentration of pollutants in river water changes with the seasons due to fluctuations in precipitation.

In the wet season of 2022, high concentrations of Al, Fe, and Pb were detected, whereas Cd, Cr, and Mn levels were comparatively higher during the dry season of 2006 (Fig. 3.2.1; Table 3.2.2 and 3.2.3). This contrast could have resulted due to differing hydrological and geochemical conditions between seasons and years, which may have altered metal mobilization and bioavailability (Landner & Reuther, 2005; Chalov *et al*., 2015; Maphanga *et al*., 2024). The changes observed during the wet season of 2022 highlight the potential role of increased surface runoff and stormwater flow in modifying metal transport dynamics, supporting that the hydrological changes contributed to seasonal fluctuations in metal contamination (Xue *et al*., 2015; McGrane, 2016; Addo-Bediako *et al*. 2021; Kumar *et al*., 2024).

Previous studies reinforce these findings. Addo-Bediako *et al*. (2021) and Fadlillah *et al*. (2023) reported high wet season concentrations of Cr, Fe, and Zn, with Fe levels exceeding water quality guidelines. Other researchers have found that rainfall surface runoff is a major pathway for metal pollutants entering aquatic systems, as contaminants are washed from surrounding areas, including industrial areas and informal settlements into rivers (Edokpayi *et al*., 2017; Guo *et al*., 2019). This mechanism was relevant to this study area, where the selected rivers were adjacent to areas characterized by high population densities, diverse land uses, informal housing developments next to the Black River station 2 and varied waste management infrastructure (Aziz, 2020; Gqomfa *et al*., 2022). Such socio-environmental factors likely contributed to the observed variations in metal concentrations across the sampling stations in 2006 and 2022.

This statement is further supported by literature which found that elevated metal accumulation in aquatic systems was a result of poor waste management, illegal waste dumping, canalisation of rivers, and climatic events such as droughts (Edokpayi *et al*., 2016; Plessis, 2017; Mohajane & Manjoro, 2022). The proximity of certain rivers, particularly the Black and Salt Rivers to industrial activities, coupled with inadequate waste services in informal settlements, exacerbates the influx of metals, especially at stations such as Black River Station 2. These factors collectively indicate a link between human activities and hydrological processes in shaping metal contamination profiles.

Hydrological and biogeochemical processes further influence metal behaviour in aquatic systems. Arheimer and Liden (2000) and Stutter *et al*. (2008) highlight how altered flow regimes and nutrient loading can enhance metal accumulation during periods of high runoff. Conversely, Robson (2014), Lloyd *et al*. (2016), and Guo *et al*. (2019) noted that chemical and biological transformations during the dry season such as oxidation reduction reactions can change metal accumulation, potentially increasing their toxicity or mobility. These processes can significantly impact aquatic ecosystems and human health, especially in systems where metals persist at low but bioaccumulative concentrations.

The need for proactive water quality management becomes imperative. An understanding of the factors influencing metal dynamics both natural and anthropogenic is essential for assessing environmental risks and developing informed strategies for sustainable river management and aquatic ecosystem protection.

4.3.3 *Metal concentrations in the sediments*

The data for the metal concentrations in the sediments of 2006 and 2022 were statistically analysed using PRIMER (ANOSIM, PCA, SIMPER and Cluster) and Sigmaplot (ANOVA). Cluster analysis was used to visualise the samples, log x + 1 transformed, normalised data and Euclidean distance was used in the analysis. The factors used were season, year and station, samples with similar concentrations of metals grouped together. The ANOSIM results showed significant differences between 2006 and 2022 (Global R: 0.121, $p = 0.001$), which was also evident in the cluster groupings of the samples. The PCA results showed a good reflection of data of the metal concentrations in the sediment, PC1 accounted for 51.5%, PC2 accounted for 17%, together accounted for 69.4% and two eigenvalues >1 (Table 3.3.1). Mn (11.14%), Zn (11.08%), Al (10.87%), Fe (10.82%) and Pb (10.16%) contributed to the dissimilarities between the years, according to SIMPER results (Table 3.3.2). This study revealed seasonal fluctuating trends rather than consistent increases or decreases over time. The metal contaminations may have changed due to seasonal environmental factors. In the comparison between 2006 and 2022, the highest metal concentrations, notably of Cr, Cu, Ni, Pb and Zn, were observed in the 2006 dry season, whereas in 2022 the highest metal concentrations were observed during the wet season. Several studies on metal contamination were conducted in South African rivers and demonstrated that concentrations differ significantly with seasonal changes. A study of the Nzhelele River in Limpopo Province reported significantly higher concentrations of Al, Fe, Cd, Cr, Cu, and Zn in sediments during the wet season (Edokpayi *et al*., 2017). In contrast, a study in the Jukskei River in Gauteng, revealed higher metal concentrations of Fe and Cd during the dry season sampling and persistent Pb in both seasons (Mukwevho *et al*., 2025). These authors suggested that these concentrations were attributed to anthropogenic inputs, amongst others, effluent discharges from wastewater treatment facilities. Such increased inputs due to higher runoff, as well as factors such as soil leaching, higher transport rates and adsorption to fine sediment particles, may all have contributed to the high metal concentrations observed in the sediment (Turner *et al*., 2004; Wang & Li, 2011; Chen *et al*., 2016; Melako *et al*., 2022; Melako *et al*., 2023).

The highest concentrations of Al, Cd, Co, Fe, and Mn were observed in the sediment across the studied sites in 2022. These results found that the metal pollutant load in 2022 has increased compared to 2006, particularly for Al, Fe, and Cr. Additionally, a temporal comparison further revealed that in 2006, high metal concentrations of Al, Fe, and Mn were more noted during the dry season, while in the wet season of 2022, higher concentrations of Al, Cr, Fe, Ni, Pb, and Zn were observed. The comparative data reflected a significant variation in metal contamination increasing from 2006 to 2022, indicating a potential decline in sediment quality and broader riverine health. This deterioration is likely linked to intensified anthropogenic pressures such as land use changes, urban expansion, and habitat degradation over the years (Mauck & Warburton, 2014; Mwangi, 2014; Wan *et al*., 2014; Namugize *et al*., 2018; Ballut-Dajud *et al*., 2022; Kola *et al*., 2025).

There are several ways in which metals are transported from the water column into the sediment. A major route is settling and adsorbing to sediment particles (Que *et al*., 2024). It can also be due to increased decomposition due to increased animal deaths or rotting vegetation. This could have resulted due to lower flow rates rather than in strong flow: in this case metals observed in 2006 in the sediments could have been a result of the lower flow rates during the dry season. In addition, metals could persist for long periods, especially if they are not remobilized by changes in environmental conditions (Afzaal *et al*., 2022; Ashayeri *et al*., 2023). Higher metal concentrations in the dry season of 2006 could have resulted from factors such as less water dilution, low water level and lower water flow rate.

Aquatic vegetation removal is an important management strategy in the freshwater ecosystem, it plays an imperative role in reducing excessive plant growth, especially non-native plant species. This process restores water flow, keeps areas open, reduces nutrient overload, and supports ecological health (River Health Programme, 2005; Hill & Coetzee, 2017). These authors stated that vegetation removal aids in enhancing flow, improving light and oxygen conditions, reducing buildup of organic matter, sediments, and restoring habitat for aquatic fauna. The alteration of the Liesbeek and Black Rivers due to the removal of alien aquatic vegetation such as purple loosestrife (*Lythrum salicaria*) and water hyacinth (*Pontederia crassipes*), aimed at managing water flow, reducing pollution, and enhancing riparian habitats may have influenced the increased settling and adsorption of metals in the sediments. As identified in this study, sediment particles within the Black River consist mostly of fine and very fine particles which are known to have high adsorption capacities for metals; this might have possibly contributed to the high concentrations of metals in the Black River sediment. Metals could also come via contaminated sediment particles from upstream sources during increased flow (Frogner-Kockum *et al*., 2020; Zhang *et al*., 2023; Que *et al*., 2024). This study has observed higher metal concentrations during the wet season of 2022 which could be due to contaminated sediment particles from upstream sources during the increased flow, resulting in more metals settling in the sediments of these rivers. This could be particularly true for Al and Fe, as they make up part of the clay particle structure (Karathanasis, 2006; Kome *et al*., 2019) and can be released and washed downstream from upstream.

Depending on the solubility, mobility and persistence, metal concentrations in freshwater environments are increased in sediment and aquatic life (Kumar *et al*., 2013; Yao *et al*., 2014; Nyantakyi *et al*., 2019). Vivien *et al*. (2020) stated that most aquatic organisms' health depends on the quality of the sediments, especially the benthic bottom dwelling organisms. According to the State-of-Rivers Report for the Western Cape, the application of the South African Scoring System (SASS) classified the Black River, Salt River, and the lower reaches of the Liesbeek River as being in a poor ecological condition (River Health Programme, 2005). This degraded status indicates significant detriment of benthic macroinvertebrate communities, including taxa of high sensitivity, which are adversely affected by the water and sediment contamination. This study noted the detrimental impacts of sediment bound pollutants within these rivers.

4.4 Spatial comparison of metal concentrations between the Black, Liesbeek and Salt River stations

4.4.1 *Physicochemical parameters*

All water physicochemical parameters, except dissolved oxygen, increased downstream, with higher values observed in the Black River and Salt River compared to the Liesbeek River. This difference may be attributed to multiple factors, including natural geomorphological variation, litter from informal settlements, domestic waste, waste from the sewage treatment plant and pump stations, runoff from the two golf courses, heated industrial effluent, and illegal dumping.

Dallas (2008) stated that most of the Western Cape's lowland rivers pass through industries, residential areas, agricultural land and wastewater treatment plants, which could change the river's thermal regime. The highest recorded temperature was 27 °C at the Salt River station and Black River Station 1, while the lowest temperature of 19.9 °C was observed at Liesbeek River Station 1. In comparison, the maximum temperature of 20.2 °C was also recorded at Black River Station 1, with the lowest temperature of 13.3 °C again occurring at Liesbeek River Station 1. The relatively lower temperatures observed in the Liesbeek River may have been caused by the geomorphological and ecological characteristics of its upper reaches, where riparian vegetation and overhanging riverbanks provide shading (Meek *et al*., 2013). This canopy cover likely reduces solar radiation penetration, thereby limiting thermal input and contributing to lower ambient water temperatures (Ali & Patnaik, 2019). The higher temperatures of the Salt and Black Rivers, on the other hand, may be due to a combination of canalisation, reduced canopy cover, industrial effluent and slower flow rates due to natural flow regimes and anthropogenic impacts such as litter, sludge and alien vegetation. (Palmer & O'Keeffe, 1989; Dallas, 2008; Lorenzo-Gonzalez *et al.,* 2023).

Electrical conductivity and salinity values varied markedly between sampling stations. The highest conductivity and salinity values were measured at the Salt River sampling station (1274µS/cm and 0.63ppt respectively) and the lowest values (131.7µS/cm and 0.08ppt respectively) at the Liesbeek River Station 1. This is probably due to the Salt River sampling station being located in the lowest section of the river, with more solutes and possibly also some estuarine influx (Taljaard *et al*., 2009; Whitfield *et al*., 2006; James *et al*., 2013; Van Niekerk *et al*., 2022). According to Russell & Randall (2017), the balance between marine and freshwater inflow (volume and timing) and evaporation primarily determine salinity in estuarine lakes. Their study found high freshwater salinity due to the opening of the estuary.

Similar results were found for pH, the Salt River had the highest pH value (8), while the lowest value (6.65) was recorded at Liesbeek River Station 2. This downstream increase in pH could have resulted from high concentrations of dissolved solutes and pollutants such as nutrients and ions derived from urban runoff, sewage, or industrial discharges (Glinska-Lewczuk *et al*., 2016). These authors stated that these sources often lead to an increase in alkalinity (for example via bicarbonate or carbonate ions) or a shift in chemical equilibria in ways that increase pH values. They also stated that urban land use greatly influences river chemistry in urbanized catchments; higher levels of nutrients, ammonium, and other ions are correlated with high pH downstream compared to upstream sections.

4.4.2 *Metal concentrations in the water*

No clear trends in metal accumulation between sampling stations and rivers were observed in 2006 and 2022. In all comparisons conducted in 2006, the mean Al concentrations differed across the sampling stations, with the highest concentrations recorded at station 1 of the Liesbeek River and the lowest at station 2 of the same river. Cobalt was detected at most sampling stations except at Black River station 2, with detections occurring at stations 1 and 2 of the Liesbeek River, Black River station

1, and the Salt River. Chromium concentrations varied across all sampling stations, with the highest recorded at Liesbeek River station 1 and the lowest at station 2 of the Liesbeek River. Copper concentrations were mostly detected in 2022 compared to 2006. Detections occurred at Liesbeek River stations 1 and 2, Black River stations 1 (exhibiting the lowest concentrations) and 2 (exhibiting the highest concentrations), and the Salt River station. In 2006 Cu were only detected at Liesbeek River station 1.

Iron concentrations differed in all sampling stations. The highest Fe concentrations were observed at Liesbeek River station 1 and the lowest at the same river's station 2. The mean Mn concentrations varied across all sampling stations, with the highest measured at Black River station 1 and the lowest at Liesbeek River station 2. Nickel was not detected at most sampling stations, except at the Salt River station, Black River station 1, and Liesbeek River station 2. The highest Ni concentrations were measured at the Salt River station and Liesbeek River station 2. Lead concentrations were not detected at any of the sampling stations, except at Liesbeek River station 1. Zinc was not detected at most of the sampling stations, except station 1 of the Black River and Liesbeek River station 1.

In the 2022 comparisons of sampling stations, the mean Al concentrations varied across stations, with the highest concentrations recorded at station 1 of the Black River during the dry season and the lowest measured at the same station during the wet season. No Cd was detected at any of the sampling stations. No Co was detected at most of the sampling stations, except at station 1 of the Black River and stations 1 and 2 of the Liesbeek River during the dry season. The highest concentrations of Co were recorded at station 1 of the Liesbeek River. Chromium concentrations varied across the sampling stations, with the highest concentrations recorded at station 1 of the Black River and the lowest at station 1 of the Liesbeek River. Copper concentrations also differed among sampling stations, with the highest found at station 2 of the Black River and the lowest at station 1 of the same river. Iron concentrations varied across the sampling stations, with the highest concentrations found at station 1 of the Liesbeek River and the lowest at station 1 of the Black River. Manganese concentrations varied across the sampling stations, with the highest recorded at station 2 of the Liesbeek River during the dry season and the lowest at station 1 of the same river during the wet season. Krueger *et al*. (2020) indicated that elevated concentrations of Fe and Mn can alter the odour, colour, and taste of water, potentially leading to health issues in people, including neurological disorders in young children.

Nickel was not detected at most of the sampling stations, except at stations 1 and 2 of the Liesbeek River and station 1 of the Black River during the wet season. The highest concentrations of Ni were detected at station 1 of the Liesbeek River. Lead was not detected at any of the sampling stations during the wet season, except at station 2 of the Liesbeek River. The highest concentrations of Pb were recorded at the Salt River station, while the lowest was found at station 1 of the Liesbeek River. Zinc was not detected at the Liesbeek and Black River stations during the dry season, except at the Salt River station. Zinc concentrations varied across the stations, with the highest concentrations recorded at station 2 of the Black River and the lowest at the Salt River station.

It was observed that station 1 of the Liesbeek River generally exhibited higher metal concentrations compared to some other sampling stations, despite being located away from major sources of pollution like industrial areas. This may suggest that pollutants in this area may be primarily derived from household waste, aerial deposition from air pollution (Bytnerowicz *et al*., 2003; Klimek *et al*., 2015; He *et al.,* 2023) and runoff from roads. In contrast, the Black and Salt Rivers seem to be exposed to numerous and major sources of pollution, such as from industrial waste and untreated sewage. For example, station 2 of the Black River is located close to and downstream of an informal settlement, the N2 highway, a golf course, and a wastewater treatment plant, which may have contributed to pollution in this river. As previously indicated, the CoCT (2011) stated that contamination caused by runoff, wastewater treatment plants and effluent discharge may pose a significant risk to the health of rivers in Cape Town. South African aquatic ecosystems significantly change due to various activities such as land use practices, sewage effluent, mismanagement of waste, vehicle emissions, sewage discharge, and atmospheric deposition from industrial processes. River flow regimes may also contribute to the accumulation of metals in freshwater ecosystems (Duffus, 1980; Dallas & Day, 1993; DWAF, 1996; Oberholster and Ashton, 2008; Mwangi, 2014). Given the industrial areas surrounding the Black and Salt Rivers, the environmental load from these activities may likely contribute to the accumulation of metals in these rivers.

Mwangi (2014) stated that most Cape Town rivers are threatened by various impacts from upstream to downstream originating from the various anthropogenic activities, human population growth, urbanisation and illegal dumping. The State-of-Rivers reports for the Diep, Hout Bay, Lourens and Palmiet Rivers (River Health Programme, 2003) and the central Cape Town rivers (including the Black, Liesbeek and Salt Rivers (River Health Programme, 2005), also stated that rivers in Cape Town are significantly impacted and degraded as a result of the previously mentioned activities. These reports further highlighted that water quality declines downstream, primarily as a result of human activities and urban development. The present results are mostly consistent with this statement, however, some of the highest metal concentrations were found in the Liesbeek River water samples and this indicates that domestic pollution, litter and atmospheric pollution play a much more important role in metal contamination than what is generally expected.

4.4.3 *Metal concentrations in the sediment*

Sediments play a crucial role in the inhabiting and sheltering of many aquatic species, serving as a breeding ground for a variety of aquatic organisms (Unlu *et al*., 2008). In addition, sediments play an important role in the functioning of biogeochemical cycles (Hoss *et al*., 2011). Sediment particles play a significant role as a primary source in the transportation and storage of potential toxic metals, and act as a sink of metal accumulation (Burton *et al*., 2006; Duran *et al*., 2012., Castillo *et al*., 2013; Superville *et al*., 2014; Zhang *et al*., 2014).

There were no clear trends of metal concentrations in the sediments between the sampling stations in the three rivers. The 2006 comparison of sampling stations revealed that the mean Al concentrations varied across the different stations, with the highest concentrations recorded at station 2 of the Liesbeek River and the lowest at station 1 of the same river. Cadmium was not detected at most of the sampling stations, except at station 2 of the Liesbeek River, where high Cd concentrations were measured and at the Salt River station, which exhibited the lowest concentration of

Cd. The mean Co concentrations varied across the sampling stations, with the highest observed at the Salt River station and the lowest at station 1 of the Liesbeek River. Chromium concentrations also varied across the sampling stations, with the highest recorded at the Salt River and the lowest at station 1 of the Liesbeek River. Mean Cu concentrations differed among the sampling stations, with the highest observed at the Salt River station and the lowest at station 1 of the Liesbeek River. Iron concentrations showed variation across the sampling stations, with the highest observed at the Salt River station and the lowest at station 1 of the Liesbeek River. Manganese concentrations were also highest at the Salt River station and lowest at station 1 of the Liesbeek River. Nickel concentrations also varied, with the highest observed at the Salt River station and the lowest at station 1 of the Liesbeek River. Lead concentrations exhibited variation across the sampling stations, with the highest recorded at the Salt River station and the lowest at station 1 of the Liesbeek River. The mean concentrations of Zn varied across the sampling stations, with the highest observed at the Salt River station and the lowest recorded at station 1 of the Liesbeek River.

Analysis of sampling stations in 2022 revealed variations in the concentrations of several metals. Aluminium concentrations exhibited the highest value at station 2 of the Liesbeek River and the lowest at station 1 of the Black River. For Cd, the highest concentrations were observed at station 2 of the Black River, while the lowest was recorded at station 2 of the Liesbeek River. Cobalt concentrations varied, with the highest observed at station 2 of the Liesbeek River and the lowest at station 1 of the Black River. Chromium concentrations differed, with the highest measured at station 2 of the Liesbeek River, and the lowest at the same station. Copper was undetected at station 2 of the Liesbeek River, as well as at station 1 of the same river. However, Cu was detected at the other sampling stations, with the highest concentrations observed at station 1 of the Black River and the lowest at station 1 of the Liesbeek River. Iron exhibited the highest concentrations at station 2 of the Liesbeek River and the lowest at station 1 of the Black River.

Manganese concentrations varied across sampling stations, with the highest concentrations measured at station 1 of the Black River during the dry season, and the lowest at the same station during the wet season. Nickel concentrations were detected only during the wet season, with the highest recorded at station 2 of the Black River and the lowest at station 1 of the same river. Lead concentrations varied across the sampling stations, with the highest recorded at station 2 of the Black River and the lowest at station 2 of the Liesbeek River. Zinc was undetected during the dry season at both station 2 of the Liesbeek River and station 1 of the Black River. At sampling stations where Zn was detected, the highest concentrations were observed at station 2 of the Black River, while the lowest was recorded at station 1 of the Liesbeek River.

Accumulation of metals in the Salt and Black Rivers could have resulted from local human activities along the riverbanks. Discharges and runoff from industrial and urban waste, roads, and sewage to name a few, may have contributed to the contamination of these rivers. The studied rivers are surrounded by many sources of metal pollution such as industries, a sewage treatment plant and household activities. These sources are suspected to have had an influence on the accumulation of metals in the rivers. A previous study on the Black River (Gilbert, 2015) found high concentrations of Cd, Cu, Pb and Zn and the author argued that the roadside, stormwater and industries gave rise to the accumulation of metals in the Black River.

Previous studies have found that sediments act as sinks of metals (Edokpayi *et al*., 2017; Algul & Beyhan, 2020). Finer sediment particles (silt and clay) adsorb more metals, and they serve as a sink and as a result metal concentrations are usually higher in sediments dominated by these particles (Abed, 2009; Huang *et al*., 2020). Grain size plays an important role in the transport and deposition of sediments (Maslennikova *et al*., 2012). The surface volume ratio of the grain size helps to determine whether the different sized sediment particles play a role in mechanical behaviour of metals. The Black River sediment was found to contain more fine and very fine particles, compared to Liesbeek River's predominantly coarse and medium particles. Interestingly, Liesbeek River station 2, with predominantly coarser sediments, often showed higher metal concentrations compared to other sampling stations. Metal concentrations were also often higher in the water in this river. This station is located in a high to medium income residential area with better waste management, proper waste facilities and proper sanitation, unlike the situation around the Black and Salt Rivers.

Finally, the impact of domestic pollution, litter, and atmospheric deposition is clearly reflected in the results from the Liesbeek River, where high metal concentrations were detected regardless of the absence of major industrial or point-source discharges. This suggests that urban inputs such as stormwater runoff from residential areas, road surfaces, and atmospheric deposition can substantially elevate metal loads even in smaller tributary systems. These findings reveal that small rivers (tributaries), in urban catchments, with no major industrial sources of metal pollution, may be at greater risk than previously suspected.

CHAPTER 5: CONCLUSION

- Physicochemical parameters (pH, temperature, and conductivity) were within the DWAF (2006) recommended TWQR, indicating that they do not pose significant risks to aquatic life. The temporal comparison of physicochemical parameters in the Black, Liesbeek, and Salt Rivers revealed some seasonal variations, although statistical analyses indicated no significant differences between the years or between the wet and dry seasons. Physicochemical parameters generally increased downstream, with higher values observed in the lower Black River and Salt River, compared to the Liesbeek River. This trend is likely due to varying seasonal water levels, urban runoff, pollutants, canalisation etc.
- The study highlighted metals of particular concern in the Liesbeek, Black, and Salt Rivers that exceeded the recommended quality guidelines, according to the new risk-based freshwater quality guidelines (Odume *et al*., 2024), Al, Cu and Fe in this study were classified under the critical impact category and Mn and Cd under the moderate impact category. This indicates that the water quality is unacceptable and could lead to high mortality rates among aquatic organisms. Al, Cu, Fe, Mn and Pb, exceeded the Canadian Interim Sediment Quality Guidelines' permissible levels (CCME, 2002) at some of the sampled stations. Notably the Liesbeek River station 2, Black River station 1 and Salt River were impacted by pollution, which may have long term consequences on aquatic species' and human health.
- The findings underscore the role of urbanization, industrial activities, and pollution sources such as untreated sewage, household waste, illegal dumping and stormwater runoff, as contributing factors to higher metal concentrations in both water and sediments.
- The temporal distribution of metals in the studied rivers were analysed using both historical and current data, providing an understanding into the ongoing challenges faced by these river systems due to continued pollution from human and anthropogenic activities. While no clear trends of increasing or decreasing metal concentrations were observed across years, distinct seasonal patterns were noted, with higher concentrations of metals such as Al, Fe, and Pb during

the wet season of 2022 and a shift towards higher concentrations of metals like Cd, Cr, and Mn during the dry season of 2006. This observation may reflect changing environmental conditions such as rainfall, water flow, water level, and evaporation, or human activities over the years.

- Spatial variations in metal concentrations were observed across the sampled stations, influenced by both natural processes and local human activities. No specific trends were observed for river water, but some of the sampling stations, especially the Liesbeek River station 1 and areas downstream in the Black and Salt Rivers showed high metal concentrations associated with household waste, atmospheric deposition, road runoff and industrial activities. The highest sediment metal levels were observed at the Black River station 2, located near industrial areas, roads, and a wastewater treatment plant and the Liesbeek River stations, despite much fewer metal pollution sources.
- The Liesbeek River has been identified as at risk, and the impact of domestic pollution, litter and atmospheric deposition on a small urban river with few major sources of metal pollution, was shown.
- The findings highlight the importance of continued monitoring and pollution management strategies to mitigate the risks posed by metal contamination in urban rivers and catchments.
- Pollution management in the Salt River catchment should focus on reducing the industrial discharges, reducing litter in the system, improving waste management systems, and restoring riparian habitats in order to filter and manage contaminants. In particular, various canalised sections of this catchment should be rehabilitated through removal of hard surfaces, and planting of riparian indigenous vegetation. Vegetation restoration will improve the rivers' natural status and aid in filtering pollutants and may contribute to habitat complexity and support macro-invertebrate diversity. It is also advised that collaboration with researchers, ecologists, the City of Cape Town and the public, may play a role in reducing pollution and further monitoring the rivers to maintain the health of these rivers. Additionally, promoting environmental education and community engagement is also essential to improve public awareness of the environmental challenges affecting our rivers and to foster collective responsibility in protecting aquatic ecosystems.

- Future research should not be limited to sampling water and sediments, but it should also include the assessment of indigenous macrophyte and macro-invertebrate bioindicators and the use of biomarkers of metal exposure. This integrated approach will provide knowledge on the toxicity and impact of metal bioaccumulation on aquatic biota. Studies should also include a wider range of relevant urban contaminants, including flame retardants, PAH's, microplastics and pharmaceuticals. There should be particular focus on the Liesbeek River and other smaller tributaries in this catchment.

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APPENDIX

Water concentration statistical comparisons

Statistical analysis was used to compare metal concentrations in water and sediments with respect to years (2006 versus 2022), seasons (wet versus dry) and sampling stations (stations per river and between rivers). One-way ANOVA was used to compare temporal data (years and seasons) and Mann-Whitney Rank Sum test was used to compare spatial data (stations). For all statistical analyses the confidence interval was set at 95% ($p<0.05$).

Aluminium

Table 1: The p-values determined by statistical comparisons of water aluminium concentrations between 2006 and 2022.ND = no data.

Al Water	L1D2 2W	L1W2 2W	L2D2 2W	L2W2 2W	B1D2 2W	B1W2 2W	B2D2 2W	B2W2 2W	S1D2 2W	S1W2 2W
L1D0 6W	**0.008**									
L1W0 6W		0.548								
L2D0 6W			**0.008**							
L2W0 6W				0.548						
B1D0 6W					**0.008**					
B1W0 6W						0.690				
B2D0 6W							ND			
B2W0 6W								ND		
S1D0 6W									0.690	
S1W0 6W										**0.032**

Table 2: The p-values determined by statistical comparisons of water aluminium concentrations between the wet and dry seasons. ND = no data.

Al Water	L1W0 6W	L2W0 6W	B1W0 6W	B2W0 6W	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	**0.032**									
L2D0 6W		**0.008**								
B1D0 6W			**0.008**							
B2D0 6W				ND						
S1D0 6W					0.841					
L1D2 2W						**0.008**				
L2D2 2W							**0.016**			
B1D2 2W								**0.008**		
B2D2 2W									0.151	
S1D2 2W										0.548

Table 3: Statistical comparisons of water aluminium concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2022.

Comparison	P	P<0.050
B1D22W vs. L2D22W	0.073	No
B1D22W vs. S1D22W	0.234	No
B1D22W vs. B21D22W	0.362	No
B1D22W vs. L1D22W	0.995	No
L1D22W vs. L2D22W	0.148	No
L1D22W vs. S1D22W	0.409	No
L1D22W vs. B2D22W	0.576	No
B2D22W vs. L2D22W	0.881	No
B2D22W vs. S1D22W	0.998	No
S1D22W vs. L2D22W	0.966	No

Table 4: The p-values determined by statistical comparisons of water cadmium concentrations between 2006 and 2022. ND = no data.

Cd Water	L1D2 2W	L1W2 2W	L2D2 2W	L2W2 2W	B1D2 2W	B1W2 2W	B2D2 2W	B2W2 2W	S1D2 2W	S1W2 2W
L1D0 6W	1.000									
L1W0 6W		0.151								
L2D0 6W			0.310							
L2W0 6W				0.151						
B1D0 6W					0.690					
B1W0 6W						0.310				
B2D0 6W							**ND**			
B2W0 6W								**ND**		
S1D0 6W									0.310	
S1W0 6W										**0.032**

Cadmium

Table 5: The p-values determined by statistical comparisons of water cadmium concentrations between the wet and dry seasons. ND = no data.

Cd Water	L1W0 6W	L2W0 6W	B1W0 6W	~~B2W0 6W~~	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	0.151									
L2D0 6W		0.151								
B1D0 6W			0.151							
~~B2D0 6W~~				ND						
S1D0 6W					**0.032**					
L1D2 2W						1.000				
L2D2 2W							0.310			
B1D2 2W								0.690		
B2D2 2W									1.000	
S1D2 2W										0.310

Table 6: The p-values determined by statistical comparisons of water cobalt concentrations between 2006 and 2022. ND = no data.

Co Water	L1D22W	L1W22W	L2D22W	L2W22W	B1D22W	B1W22W	B2D22W	B2W22W	S1D22W	S1W22W
L1D06W	0.310									
L1W06W		0.690								
L2D06W			1.000							
L2W06W				1.000						
B1D06W					0.690					
B1W06W						0.690				
B2D06W							ND			
B2W06W								ND		
S1D06W									0.310	
S1W06W										1.000

Table 7: The p-values determined by statistical comparisons of water cobalt concentrations between the wet and dry seasons. ND = no data.

Co Water	L1W0 6W	L2W0 6W	B1W0 6W	B2W0 6W	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	0.690									
L2D0 6W		0.690								
B1D0 6W			0.690							
B2D0 6W				ND						
S1D0 6W					0.310					
L1D2 2W						0.310				
L2D2 2W							0.690			
B1D2 2W								0.690		
B2D2 2W									1.000	
S1D2 2W										1.000

Table 8: The p-values determined by statistical comparisons of water chromium concentrations between 2006 and 2022. ND = no data.

Cr Water	L1D22W	L1W22W	L2D22W	L2W22W	B1D22W	B1W22W	B2D22W	B2W22W	S1D22W	S1W22W
L1D06W	0.151									
L1W06W		**0.008**								
L2D06W			0.056							
L2W06W				**0.008**						
B1D06W					0.310					
B1W06W						**0.008**				
B2D06W							ND			
B2W06W								ND		
S1D06W									0.841	
S1W06W										**0.008**

Chromium comparisons between seasons (wet and dry) Mann-Whitney Rank Sum Test

Table 9: The p-values determined by statistical comparisons of water chromium concentrations between the wet and dry seasons. ND = no data.

Cr Water	L1W0 6W	L2W0 6W	B1W0 6W	B2W0 6W	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	0.841									
L2D0 6W		0.690								
B1D0 6W			0.310							
B2D0 6W				ND						
S1D0 6W					0.421					
L1D2 2W						**0.008**				
L2D2 2W							0.690			
B1D2 2W								**0.008**		
B2D2 2W									**0.008**	
S1D2 2W										0.690

Chromium comparisons between stations ANOVA

Comparisons between stations in 2022 during dry season

Table 10: The p-values determined by statistical comparisons of water chromium concentrations between the sampled stations during the dry season of 2022.

Comparison	P	P<0.050
B1D22W vs. L2D22W	0.005	Yes
B1D22W vs. B2D22W	0.008	Yes
B1D22W vs. S1D022W	0.041	Yes
B1D22W vs. L1D22W	0.158	No
L1D22W vs. L2D22W	0.484	No
L1D22W vs. B2D22W	0.587	No
L1D22W vs. S1D22W	0.955	No
S1D22W vs. L2D22W	0.871	No
S1D22W vs. B2D22W	0.932	No
B2D22W vs. L2D22W	1.000	No

Table 11: The p-values determined by statistical comparisons of water chromium concentrations between the sampled stations during the wet season of 2006.

Comparison	P	P<0.050
L1W06W vs. S1W06W	0.044	Yes
L1W06W vs. B1W06W	0.118	No
L1W06W vs. L2W06W	0.138	No
L2W06W vs. S1W06W	0.925	No
L2W06W vs. B1W06W	1.000	No
B1W06W vs. S1W06W	0.951	No

Comparisons between stations in 2022 during wet season

Table 12: The p-values determined by statistical comparisons of water chromium concentrations between the sampled stations during the wet season of 2022.

Comparison	P	P<0.050
B2W22W vs. B1W22W	0.022	Yes
B2W22W vs. L1W22W	0.033	Yes
B2W22W vs. S1W22W	0.080	No
B2W22W vs. L2W22W	0.391	No
L2W22W vs. B1W22W	0.538	No
L2W22W vs. L1W22W	0.648	No
L2W22W vs. S1W22W	0.878	No
S1W22W vs. B1W22W	0.970	No
S1W22W vs. L1W22W	0.992	No
L1W22W vs. B1W22W	1.000	No

Table 13: The p-values determined by statistical comparisons of water copper concentrations between 2006 and 2022. ND = no data.

Cu Water	L1D22W	L1W22W	L2D22W	L2W22W	B1D22W	B1W22W	B2D22W	B2W22W	S1D22W	S1W22W
L1D06W	0.690									
L1W06W		0.548								
L2D06W			0.690							
L2W06W				0.151						
B1D06W					0.690					
B1W06W						0.151				
B2D06W							ND			
B2W06W								ND		
S1D06W									1.000	
S1W06W										0.310

Copper comparisons between seasons (wet and dry) Mann-Whitney Rank Sum Test

Table 14: The p-values determined by statistical comparisons of water copper concentrations between the wet and the dry seasons. ND = no data.

Cu Water	L1W0 6W	L2W0 6W	B1W0 6W	B2W0 6W	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	0.690									
L2D0 6W		1.000								
B1D0 6W			1.000							
B2D0 6W				ND						
S1D0 6W					1.000					
L1D2 2W						0.690				
L2D2 2W							0.421			
B1D2 2W								0.310		
B2D2 2W									0.151	
S1D2 2W										0.310

Iron comparisons between years (2006 and 2022) Mann-Whitney Rank Sum Test

Table 15: The p-values determined by statistical comparisons of water iron concentrations between 2006 and 2022. ND = no data.

Fe Water	L1D22W	L1W22W	L2D22W	L2W22W	B1D22W	B1W22W	B2D22W	B2W22W	S1D22W	S1W22W
L1D06W	**0.008**									
L1W06W		**0.008**								
L2D06W			0.151							
L2W06W				1.000						
B1D06W					**0.008**					
B1W06W						0.151				
B2D06W							ND			
B2W06W								ND		
S1D06W									0.690	
S1W06W										**0.032**

Iron comparisons between seasons (wet and dry) Mann-Whitney Rank Sum Test

Table 16: The p-values determined by statistical comparisons of water iron concentrations between the wet and the dry seasons. ND = no data.

Fe Water	L1W0 6W	L2W0 6W	B1W0 6W	B2W0 6W	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	0.151									
L2D0 6W		**0.008**								
B1D0 6W			0.151							
B2D0 6W				ND						
S1D0 6W					**0.032**					
L1D2 2W						**0.008**				
L2D2 2W							0.151			
B1D2 2W								**0.008**		
B2D2 2W									**0.008**	
S1D2 2W										0.690

Iron comparisons between stations ANOVA

Comparisons between stations in 2006 during dry season

Table 17: The p-values determined by statistical comparisons of water iron concentrations between the sampled study stations (Black, Liesbeek and Salt Rivers) during the dry season of 2006.

Comparison	P	P<0.050
L1D06W vs. L2D06W	<0.001	Yes
L1D06W vs. B1D06W	0.012	Yes
L1D06W vs. S1D06W	0.024	Yes
S1D06W vs. L2D06W	0.038	Yes
S1D06W vs. B1D06W	0.984	No
B1D06W vs. L2D06W	0.075	No

Comparisons between stations in 2022 during dry season

Table 18: The p-values determined by statistical comparisons of water iron concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2022.

Comparison	P	P<0.050
L1D22W vs. L2D22W	0.092	No
L1D22W vs. B2D22W	0.134	No
L1D22W vs. S1D22W	0.312	No
L1D22W vs. B1D22W	0.991	No
B1D22W vs. L2D22W	0.205	No
B1D22W vs. B2D22W	0.284	No
B1D22W vs. S1D22W	0.556	No
S1D22W vs. L2D22W	0.951	No
S1D22W vs. B2D22W	0.986	No
B2D22W vs. L2D22W	1.000	No

Comparisons between stations in 2006 during wet season

Table 19: The p-values determined by statistical comparisons of water iron concentrations between the sampled stations (Black, Liesbeek and Salt River) during the wet season of 2006.

Comparison	**P**	**P<0.050**
L1W06W vs. S1W06W	<0.001	Yes
L1W06W vs. B1W06W	<0.001	Yes
L1W06W vs. L2W06W	<0.001	Yes
L2W06W vs. S1W06W	0.206	No
L2W06W vs. B1W06W	1.311	No
B1W06W vs. S1W06W	0.993	No

Manganese comparisons between years (2006 and 2022) Mann-Whitney Rank Sum Test

Table 20: The p-values determined by statistical comparisons of water manganese concentrations between 2006 and 2022. ND = no data.

Mn Water	L1D22W	L1W22W	L2D22W	L2W22W	B1D22W	B1W22W	B2D22W	B2W22W	S1D22W	S1W22W
L1D06W	**0.008**									
L1W06W		**0.008**								
L2D06W			0.841							
L2W06W				0.310						
B1D06W					0.151					
B1W06W						**0.008**				
B2D06W							ND			
B2W06W								ND		
S1D06W									**0.008**	
S1W06W										**0.008**

Manganese comparisons between seasons (wet and dry) Mann-Whitney Rank Sum Test

Table 21: The p-values determined by statistical comparisons of water manganese concentrations between the wet and dry seasons. ND = no data.

Mn Water	L1W0 6W	L2W0 6W	B1W0 6W	B2W0 6W	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	**0.008**									
L2D0 6W		**0.008**								
B1D0 6W			0.095							
B2D0 6W				ND						
S1D0 6W					**0.032**					
L1D2 2W						**0.008**				
L2D2 2W							0.151			
B1D2 2W								0.151		
B2D2 2W									**0.008**	
S1D2 2W										**0.008**

Manganese Comparisons between stations ANOVA

Comparisons between stations in 2006 during dry season

Table 22: The p-values determined by statistical comparisons of water manganese concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the dry seasons of 2006.

Comparison	P	P<0.050
B1D06W vs. L2D06W	<0.001	Yes
B1D06W vs. L1D06W	<0.001	Yes
B1D06W vs. S1D06W	<0.001	Yes
S1D06W vs. L2D06W	<0.001	Yes
S1D06W vs. L1D06W	<0.001	Yes
L1D06W vs. L2D06W	0.018	No

Comparisons between stations in 2006 during wet season

Table 23: The p-values determined by statistical comparisons of water manganese concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2006.

Comparison	P	P<0.050
S1W06W vs. L2W06W	<0.001	Yes
S1W06W vs. L1W06W	0.020	Yes
S1W06W vs. B1W06W	0.855	No
B1W06W vs. L2W06W	<0.001	Yes
B1W06W vs. L1W06W	0.094	No
L1W06W vs. L2W06W	0.007	No

Comparisons between stations in 2022 during wet season

Table 24: The p-values determined by statistical comparisons of water manganese concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	**P**	**P<0.050**
B2W22W vs. L1W22W	<0.001	Yes
B2W22W vs. L2W22W	<0.001	Yes
B2W22W vs. B1W22W	<0.001	Yes
B2W22W vs. S1W22W	<0.001	Yes
S1W22W vs. L1W22W	<0.001	Yes
S1W22W vs. L2W22W	<0.001	Yes
S1W22W vs. B1W22W	0.012	Yes
B1W22W vs. L1W22W	<0.001	Yes
B1W22W vs. L2W22W	0.009	Yes
L2W22W vs. L1W22W	0.165	No

Nickel comparisons between years (2006 and 2022) Mann-Whitney Rank Sum Test

Table 25: The p-values determined by statistical comparisons of water nickel concentrations between 2006 and 2022. ND = no data.

Ni Water	L1D22W	L1W22W	L2D22W	L2W22W	B1D22W	B1W22W	B2D22W	B2W22W	S1D22W	S1W22W
L1D06W	1.000									
L1W06W		**0.008**								
L2D06W			0.310							
L2W06W				**0.008**						
B1D06W					0.690					
B1W06W						**0.008**				
B2D06W							ND			
B2W06W								ND		
S1D06W									0.310	
S1W06W										**0.008**

Nickel comparisons between seasons (wet and dry) Mann-Whitney Rank Sum Test

Table 26: The p-values determined by statistical comparisons of water nickel concentrations between the wet and the dry seasons. ND = no data.

Ni Water	L1W0 6W	L2W0 6W	B1W0 6W	B2W0 6W	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	1.000									
L2D0 6W		0.310								
B1D0 6W			0.690							
B2D0 6W				ND						
S1D0 6W					0.310					
L1D2 2W						**0.008**				
L2D2 2W							**0.008**			
B1D2 2W								**0.008**		
B2D2 2W									**0.008**	
S1D2 2W										**0.008**

Lead comparisons between years (2006 and 2022) Mann-Whitney Rank Sum Test

Table 27: The p-values determined by statistical comparisons of water lead concentrations between 2006 and 2022. ND = no data.

Pb Water	L1D22W	L1W22W	L2D22W	L2W22W	B1D22W	B1W22W	B2D22W	B2W22W	S1D22W	S1W22W
L1D06W	0.690									
L1W06W		0.151								
L2D06W			**0.032**							
L2W06W				0.310						
B1D06W					0.151					
B1W06W						1.000				
B2D06W							ND			
B2W06W								ND		
S1D06W									**0.032**	
S1W06W										1.000

Lead comparisons between seasons (wet and dry) Mann-Whitney Rank Sum Test

Table 28: The p-values determined by statistical comparisons of water lead concentrations between the wet and the dry seasons. ND = no data.

Pb Water	L1W0 6W	L2W0 6W	B1W0 6W	B2W0 6W	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	0.151									
L2D0 6W		1.000								
B1D0 6W			1.000							
B2D0 6W				ND						
S1D0 6W					1.000					
L1D2 2W						0.690				
L2D2 2W							0.056			
B1D2 2W								0.151		
B2D2 2W									0.151	
S1D2 2W										**0.032**

Lead comparisons between stations ANOVA

Comparisons between stations in 2006 during wet season

Table 29: The p-values determined by statistical comparisons of water lead concentrations between the sampled stations (Black, Liesbeek, Salt Rivers) during the wet season of 2006.

Comparison	**P**	**P<0.050**
L1W06W vs. S1W06W	0.015	Yes
L1W06W vs. B1W06W	0.015	Yes
L1W06W vs. L2W06W	0.015	Yes
L2W06W vs. S1W06W	1.000	No
L2W06W vs. B1W06W	1.000	No
B1W06W vs. S1W06W	1.000	No

Zinc comparisons between years (2006 and 2022) Mann-Whitney Rank Sum Test

Table 30: The p-values determined by statistical comparisons of water zinc concentrations between 2006 and 2022. ND = no data.

Zn Water	L1D22W	L1W22W	L2D22W	L2W22W	B1D22W	B1W22W	B2D22W	B2W22W	S1D22W	S1W22W
L1D06W	0.151									
L1W06W		0.151								
L2D06W			0.690							
L2W06W				**0.032**						
B1D06W					1.000					
B1W06W						0.151				
B2D06W							ND			
B2W06W								ND		
S1D06W									0.690	
S1W06W										0.310

Zinc comparisons between seasons (wet and dry) Mann-Whitney Rank Sum Test

Table 31: The p-values determined by statistical comparisons of water zinc concentrations between the wet and dry seasons. ND = no data.

Zn Water	L1W0 6W	L2W0 6W	B1W0 6W	B2W0 6W	S1W0 6W	L1W2 2W	L2W2 2W	B1W2 2W	B2W2 2W	S1W2 2W
L1D0 6W	0.310									
L2D0 6W		1.000								
B1D0 6W			0.690							
B2D0 6W				ND						
S1D0 6W					1.000					
L1D2 2W						**0.032**				
L2D2 2W							0.056			
B1D2 2W								**0.032**		
B2D2 2W									0.310	
S1D2 2W										0.690

Zinc comparisons between stations ANOVA

Comparisons between stations in 2006 during dry season

Table 32: The p-values determined by statistical comparisons of water zinc concentrations between sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2006.

Comparison	P	P<0.050
L1D06W vs. S1D06W	0.034	Yes
L1D06W vs. B1D06W	0.034	Yes
L1D06W vs. L2D06W	0.034	Yes
L2D06W vs. S1D06W	1.000	No
L2D06W vs. B1D06W	1.000	No
B1D06W vs. S1D06W	1.000	No

Comparisons between stations in 2006 during wet season

Table 33: The p-values determined by statistical comparisons of water zinc concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2006.

Comparison	P	P<0.050
L1W06W vs. S1W06W	0.018	Yes
L1W06W vs. L2W06W	0.018	Yes
L1W06W vs. B1W06W	0.051	No
B1W06W vs. S1W06W	0.950	No
B1W06W vs. L2W06W	0.950	No
L2W06W vs. S1W06W	1.000	No

Sediment significant difference comparisons

Aluminium comparison between years Mann-Whitney Rank Sum Test

Table 34: The p-values determined by statistical comparisons of sediment aluminium concentrations between 2006 and 2022. ND = no data.

Al Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	0.690									
L1W06S		**0.008**								
L2D06S			**0.008**							
L2W06S				**0.016**						
B1D06S					0.222					
B1W06S						**0.008**				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Aluminium comparison between seasons (wet and dry) Mann-Whitney Rank Sum Test

Table 35: The p-values determined by statistical comparisons of sediment aluminium concentrations between the wet and dry seasons. ND = no data.

Al Sed	L1W06S	L2W06S	B1W06S	B2W06S	S1W06S	L1W22S	L2W22S	B1W22S	B2W22S	S1W22S
L1D06S	**0.008**									
L2D06S		**0.008**								
B1D06S			0.056							
B2D06S				ND						
S1D06S					**0.008**					
L1D22S						0.690				
L2D22S							**0.032**			
B1D22S								0.151		
B2D22S									0.222	
S1D22S										ND

Aluminium comparisons between stations ANOVA

Comparisons between stations in 2006 during 2006 dry season

Table 36: The p-values determined by statistical comparisons of sediment aluminium concentrations between sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2006.

Comparison	P	P<0.050
L2D06S vs. B1D06S	<0.001	Yes
L2D06S vs. L1D06S	<0.001	Yes
L2D06S vs. S1D06S	0.010	Yes
S1D06S vs. B1D06S	<0.001	Yes
S1D06S vs. L1D06S	0.238	No
L1D06S vs. B1D06S	<0.001	Yes

Comparisons between stations in 2006 during wet season

Table 37: The p-values determined by statistical comparisons of sediment aluminium concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2006.

Comparison	P	P<0.050
L2W06S vs. L1W06S	<0.001	Yes
L2W06S vs. S1W06S	0.013	Yes
L2W06S vs. B1W06S	0.026	Yes
B1W06S vs. L1W06S	<0.001	Yes
B1W06S vs. S1W06S	0.986	No
S1W06S vs. L1W06S	<0.001	Yes

Table 38: The p-values determined by statistical comparisons of sediment aluminium concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	**P**	**P<0.050**
L2W22S vs. B1W22S	<0.001	Yes
L2W22S vs. L1W22S	0.351	No
L2W22S vs. B2W22S	1.000	No
B2W22S vs. B1W22S	<0.001	Yes
B2W22S vs. L1W22S	0.352	No
L1W22S vs. B1W22S	<0.001	Yes

Cadmium comparison between years (2006 and 2022) Mann-Whitney Rank Sum Test

Table 39: The p-values determined by statistical comparisons of sediment cadmium concentrations between 2006 and 2022. ND = no data.

Cd Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	0.151									
L1W06S		**0.032**								
L2D06S			0.841							
L2W06S				**0.008**						
B1D06S					0.151					
B1W06S						**0.008**				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Cadmium comparison between seasons (wet and dry) Mann-Whitney

Table 40: The p-values determined by statistical comparisons of sediment cadmium concentrations between the wet and dry seasons. ND = no data.

Cd Sed	L1W06S	L2W06S	B1W06S	B2W06S	S1W06S	L1W22S	L2W22S	B1W22S	B2W22S	S1W22S
L1D06S	1.000									
L2D06S		0.690								
B1D06S			1.000							
B2D06S				ND						
S1D06S					0.310					
L1D22S						0.690				
L2D22S							0.151			
B1D22S								0.056		
B2D22S									**0.008**	
S1D22S										ND

Table 41: The p-values determined by statistical comparisons of sediment cadmium concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	P	P<0.050
B2W22S vs. L1W22S	<0.001	Yes
B2W22S vs. L2W22S	<0.001	Yes
B2W22S vs. B1W22S	0.408	No
B1W22S vs. L1W22S	0.002	Yes
B1W22S vs. L2W22S	0.028	Yes
L2W22S vs. L1W22S	0.502	No

Cobalt comparison between years (2006 and 2022) Mann-Whitney Rank Sum Test

Table 42: The p-values determined by statistical comparisons of sediment cobalt concentrations between 2006 and 2022. ND = no data.

Co Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	0.310									
L1W06S		**0.008**								
L2D06S			0.690							
L2W06S				**0.008**						
B1D06S					0.690					
B1W06S						**0.016**				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Cobalt comparison between seasons (wet and dry) Mann-Whitney Rank Sum Test

Table 43: The p-values determined by statistical comparisons of sediment cobalt concentrations between the wet and dry seasons. ND = no data.

Co Sed	L1W06S	L2W06S	B1W06S	B2W06S	S1W06S	L1W22S	L2W22S	B1W22S	B2W22S	S1W22S
L1D06S	0.151									
L2D06S		**0.008**								
B1D06S			1.000							
B2D06S				ND						
S1D06S					**0.008**					
L1D22S						0.690				
L2D22S							1.000			
B1D22S								0.690		
B2D22S									0.151	
S1D22S										ND

Cobalt comparisons between stations ANOVA

Comparisons between stations 2006 dry season

Table 44: The p-values determined by statistical comparisons of sediment cobalt concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2006.

Comparison	P	P<0.050
S1D06S vs. L1D06S	<0.001	Yes
S1D06S vs. B1D06S	<0.001	Yes
S1D06S vs. L2D06S	<0.001	Yes
L2D06S vs. L1D06S	<0.001	Yes
L2D06S vs. B1D06S	<0.001	Yes
B1D06S vs. L1D06S	0.970	No

Comparisons between stations in 2006 during wet season

Table 45: The p-values determined by statistical comparisons of sediment cobalt concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2006.

Comparison	P	P<0.050
S1W06S vs. L1W06S	<0.001	Yes
S1W06S vs. B1W06S	<0.001	Yes
S1W06S vs. L2W06S	<0.001	Yes
L2W06S vs. L1W06S	0.880	No
L2W06S vs. B1W06S	0.997	No
B1W06S vs. L1W06S	0.951	No

Table 46: The p-values determined by statistical comparisons of sediment cobalt concentrations between sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	**P**	**P<0.050**
B2W22S vs. B1W22S	<0.001	Yes
B2W22S vs. L2W22S	0.009	Yes
B2W22S vs. L1W22S	0.031	Yes
L1W22S vs. B1W22S	<0.001	Yes
L1W22S vs. L2W22S	0.925	No
L1w22S vs. B1W22S	<0.001	Yes

Chromium comparisons between years (2006 and 2022)

Table 47: The p-values determined by statistical comparisons of sediment chromium concentrations between 2006 and 2022. ND = no data.

Cr Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	0.310									
L1W06S		**0.008**								
L2D06S			**0.008**							
L2W06S				0.151						
B1D06S					**0.008**					
B1W06S						1.000				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Chromium comparisons between seasons (wet and dry)

Table 48: The p-values determined by statistical comparisons of sediment chromium concentrations between the wet and dry seasons. ND = no data.

Cr Sed	L1W0 6S	L2W0 6S	B1W0 6S	B2W0 6S	S1W0 6S	L1W2 2S	L2W2 2S	B1W2 2S	B2W2 2S	S1W2 2S
L1D0 6S	**0.008**									
L2D0 6S		0.151								
B1D0 6S			0.095							
B2D0 6S				ND						
S1D0 6S					**0.008**					
L1D2 2S						0.095				
L2D2 2S							**0.008**			
B1D2 2S								**0.016**		
B2D2 2S									**0.008**	
S1D2 2S										ND

Chromium comparisons between stations ANOVA

Comparison between stations in 2006 dry season

Table 49: The p-values determined by statistical comparisons of sediment chromium concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2006.

Comparison	P	P<0.050
S1D06S vs. L1D06S	<0.001	Yes
S1D06S vs. B1D06S	<0.001	Yes
S1D06S vs. L2D06S	<0.001	Yes
L2D06S vs. L1D06S	0.044	Yes
L2D06S vs. B1D06S	0.354	No
B1D06S vs. L1D06S	0.618	No

Comparison in stations 2022 wet season

Table 50: The p-values determined by statistical comparisons of sediment chromium concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	P	P<0.050
B2W22S vs. L1W22S	0.072	No
B2W22S vs. B1W22S	0.111	No
B2W22S vs. L2W22S	0.993	No
L2W22S vs. L1W22S	0.117	No
L2W22S vs. B1W22S	0.177	No
B1W22S vs. L2W22S	0.995	No

Copper comparisons between years (2006 and 2022)

Table 51: The p-values determined by statistical comparisons of sediment copper concentrations between 2006 and 2022. ND = no data.

Cu Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	0.690									
L1W06S		0.310								
L2D06S			**0.008**							
L2W06S				**0.008**						
B1D06S					0.421					
B1W06S						0.69**0**				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Copper comparisons between seasons (wet and dry)

Table 52: The p-values determined by statistical comparisons of sediment copper concentrations between the wet and dry seasons. ND = no data.

Cu Sed	L1W06S	L2W06S	B1W06S	B2W06S	S1W06S	L1W22S	L2W22S	B1W22S	B2W22S	S1W22S
L1D06S	0.841									
L2D06S		**0.008**								
B1D06S			0.222							
B2D06S				ND						
S1D06S					1.000					
L1D22S						0.310				
L2D22S							1.000			
B1D22S								1.000		
B2D22S									0.421	
S1D22S										ND

Copper comparisons between stations ANOVA

Comparisons between stations in 2006 during wet season

Table 53: The p-values determined by statistical comparisons of sediment copper concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2006.

Comparison	**P**	**P<0.050**
S1W06S vs. L1W06S	0.013	Yes
S1W06S vs. L2W06S	0.016	Yes
S1W06S vs. B1W06S	0.031	Yes
B1W06S vs. L1W06S	0.966	No
B1W06S vs. L2W06S	0.987	No
L2W06S vs. L1W06S	0.999	No

Iron comparisons between years (2006 and 2022)

Table 54: The p-values determined by statistical comparisons of sediment iron concentrations between 2006 and 2022. ND = no data.

Fe Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	0.151									
L1W06S		**0.008**								
L2D06S			**0.008**							
L2W06S				**0.032**						
B1D06S					0.690					
B1W06S						**0.008**				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Comparison between seasons (wet and dry)

Table 55: The p-values determined by statistical comparisons of sediment iron concentrations between the wet and dry seasons. ND = no data.

Fe Sed	L1W06S	L2W06S	B1W06S	B2W06S	S1W06S	L1W22S	L2W22S	B1W22S	B2W22S	S1W22S
L1D06S	**0.008**									
L2D06S		**0.008**								
B1D06S			0.151							
B2D06S				ND						
S1D06S					**0.008**					
L1D22S						0.841				
L2D22S							0.095			
B1D22S								0.151		
B2D22S									0.421	
S1D22S										ND

Iron comparisons between stations ANOVA

Comparison of stations in 2006 dry season

Table 56: The p-values determined by statistical comparisons of sediment iron concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2006.

Comparison	P	P<0.050
L2D06S vs. L1D06S	<0.001	Yes
L2D06S vs. B1D06S	<0.001	Yes
L2D06S vs. S1D06S	<0.001	Yes
S1D06S vs. L1D06S	<0.001	Yes
S1D06S vs. B1D06S	<0.001	Yes
B1D06S vs. L1D06S	0.157	No

Comparison of stations in 2006 wet season

Table 57: The p-values determined by statistical comparisons of sediment iron concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2006.

Comparison	P	P<0.050
L2W06S vs. L1W06S	<0.001	Yes
L2W06S vs. S1W06S	<0.001	Yes
L2W06S vs. B1W06S	0.054	No
B1W06S vs. L1W06S	<0.001	Yes
B1W06S vs. S1W06S	0.198	No
S1W06S vs. L1W06S	<0.001	Yes

Table 58: The p-values determined by means of statistical comparisons of sediment iron concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	**P**	**P<0.050**
L2W22S vs. B1W22S	<0.001	Yes
L2W22S vs. L1W22S	0.219	No
L2W22S vs. B2W22S	0.337	No
B2W22S vs. B1W22S	<0.001	Yes
B2W22S vs. L1W22S	0.991	No
L1W22S vs. B1W22S	0.002	Yes

Manganese comparisons between years (2006 and 2022)

Table 59: The p-values determined by statistical comparisons of sediment manganese concentrations between 2006 and 2022. ND = no data.

Mn Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	0.151									
L1W06S		**0.008**								
L2D06S			0.690							
L2W06S				0.421						
B1D06S					0.151					
B1W06S						**0.008**				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Manganese comparisons between seasons (wet and dry)

Table 60: The p-values determined by statistical comparisons of sediment manganese concentrations between the wet and dry seasons. ND = no data.

Mn Sed	L1W06S	L2W06S	B1W06S	B2W06S	S1W06S	L1W22S	L2W22S	B1W22S	B2W22S	S1W22S
L1D06S	**0.008**									
L2D06S		**0.008**								
B1D06S			0.690							
B2D06S				ND						
S1D06S					**0.008**					
L1D22S						0.222				
L2D22S							0.690			
B1D22S								0.151		
B2D22S									**0.008**	
S1D22S										ND

Manganese comparisons between stations (ANOVA)

Comparison of stations in 2006 dry season

Table 61: The p-values determined by statistical comparisons of sediment manganese concentrations between the sampled stations (Black, Liesbeek, Salt Rivers) during the dry of 2006.

Comparison	P	P<0.050
S1D06S vs. L1D06S	<0.001	Yes
S1D06S vs. B1D06S	<0.001	Yes
S1D06S vs. L2D06S	0.073	No
L2D06S vs. L1D06S	0.136	No
L2D06S vs. B1D06S	0.138	No
B1D06S vs. L1D06S	1.000	No

Comparisons of stations in 2006 wet season

Table 62: The p-values determined by statistical comparisons of sediment manganese concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2006.

Comparison	P	P<0.050
L2W06S vs. L1W06S	<0.001	Yes
L2W06S vs. B1W06S	0.094	Yes
L2W06S vs. S1W06S	0.996	No
S1W06S vs. L1W06S	<0.001	Yes
S1W06S vs. B1W06S	0.142	No
B1W06S vs. L1W06S	0.031	Yes

Table 63: The p-values determined by statistical comparisons of sediment manganese concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	**P**	**P<0.050**
L1W22S vs. B1W22S	<0.001	Yes
L1W22S vs. B2W22S	<0.001	Yes
L1W22S vs. L2W22S	<0.001	Yes
L2W22S vs. B1W22S	<0.001	Yes
L2W22S vs. B2W22S	0.107	No
B2W22S vs. B1W22S	0.001	Yes

Nickel comparisons between years (2006 and 2022)

Table 64: The p-values determined by statistical comparisons of sediment nickel concentrations between 2006 and 2022. ND = no data.

Ni Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	**0.032**									
L1W06S		0.421								
L2D06S			**0.008**							
L2W06S				0.690						
B1D06S					**0.032**					
B1W06S						0.690				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Nickel comparisons between seasons (wet and dry)

Table 65: The p-values determined by statistical comparisons of sediment nickel concentrations between the wet and dry seasons. ND = no data.

Ni Sed	L1W06S	L2W06S	B1W06S	B2W06S	S1W06S	L1W22S	L2W22S	B1W22S	B2W22S	S1W22S
L1D06S	0.841									
L2D06S		0.841								
B1D06S			0.310							
B2D06S				ND						
S1D06S					**0.008**					
L1D22S						**0.008**				
L2D22S							**0.008**			
B1D22S								**0.008**		
B2D22S									**0.008**	
S1D22S										ND

Nickel comparisons between stations ANOVA

Comparisons between stations in 2006 dry season

Table 66: The p-values determined by statistical comparisons of sediment nickel concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2006. and 2022.

Comparison	P	P<0.050
S1D06S vs. L1D06S	<0.001	Yes
S1D06S vs. L2D06S	<0.001	Yes
S1D06S vs. B1D06S	<0.001	Yes
B1D06S vs. L1D06S	0.734	No
B1D06S vs. L2D06S	0.997	No
L2D06S vs. L1D06S	0.841	No

Table 67: The p-values determined by statistical comparisons of sediment nickel concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	P	P<0.050
B2W22S vs. B1W22S	<0.001	Yes
B2W22S vs. L1W22S	0.006	Yes
B2W22S vs. L2W22S	0.007	Yes
L2W22S vs. B1W22S	0.153	No
L2W22S vs. L1W22S	1.000	No
L1W22S vs. B1W22S	0.165	No

Lead comparisons between years (2006 and 2022)

Table 68: The p-values determined by statistical comparisons of sediment lead concentrations between 2006 and 2022. ND = no data.

Pb Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	0.421									
L1W06S		**0.008**								
L2D06S			**0.008**							
L2W06S				0.690						
B1D06S					**0.008**					
B1W06S						0.056				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Lead comparisons between seasons (wet and dry)

Table 69: The p-values determined by statistical comparisons of sediment lead concentrations between the wet and dry seasons. ND = no data.

Pb Sed	L1W06S	L2W06S	B1W06S	B2W06S	S1W06S	L1W22S	L2W22S	B1W22S	B2W22S	S1W22S
L1D06S	**0.032**									
L2D06S		**0.032**								
B1D06S			0.421							
B2D06S				ND						
S1D06S					**0.032**					
L1D22S						0.151				
L2D22S							**0.008**			
B1D22S								0.310		
B2D22S									**0.008**	
S1D22S										ND

Lead comparisons between stations (ANOVA)

Comparisons between stations in the year 2006 dry season

Table 70: The p-values determined by statistical comparisons of sediment lead concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2006.

Comparison	P	P<0.050
S1D06S vs. L1D06S	0.002	Yes
S1D06S vs. B1D06S	0.132	No
S1D06S vs. L2D06S	0.428	No
L2D06S vs. L1D06S	0.051	No
L2D06S vs. B1D06S	0.865	No
B1D06S vs. L1D06S	0.204	No

Comparisons between stations in 2006 wet season

Table 71: The p-values determined by statistical comparisons of sediment lead concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2006.

Comparison	P	P<0.050
S1W06S vs. L1W06S	0.013	Yes
S1W06S vs. L2W06S	0.231	No
S1W06S vs. B1W06S	0.680	No
B1W06S vs. L1W06S	0.110	No
B1W06S vs. L2W06S	0.820	No
L2W06S vs. L1W06S	0.424	No

Comparisons between stations in 2022 wet season

Table 72: The p-values determined by statistical comparisons of sediment lead concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	P	P<0.050
B2W22S vs. L1W22S	<0.001	Yes
B2W22S vs. L2W22S	0.004	Yes
B2W22S vs. B1W22S	0.006	Yes
B1W22S vs. L1W22S	0.223	No
B1W22S vs. L2W22S	0.996	No
L1W22S vs. L1W22S	0.313	No

Zinc comparisons between years 2006 and 2022

Table 73: The p-values determined by statistical comparisons of sediment zinc concentrations between 2006 and 2022. ND = no data.

Zn Sed	L1D22S	L1W22S	L2D22S	L2W22S	B1D22S	B1W22S	B2D22S	B2W22S	S1D22S	S1W22S
L1D06S	0.151									
L1W06S		**0.008**								
L2D06S			**0.008**							
L2W06S				**0.008**						
B1D06S					**0.008**					
B1W06S						0.548				
B2D06S							ND			
B2W06S								ND		
S1D06S									ND	
S1W06S										ND

Zinc comparisons between seasons (wet and dry)

Table 74: The p-values determined by statistical comparisons of sediment zinc concentrations between the wet and dry seasons. ND = no data.

Zn Sed	L1W06S	L2W06S	B1W06S	B2W06S	S1W06S	L1W22S	L2W22S	B1W22S	B2W22S	S1W22S
L1D06S	0.095									
L2D06S		**0.008**								
B1D06S			0.548							
B2D06S				ND						
S1D06S					0.421					
L1D22S						**0.016**				
L2D22S							**0.008**			
B1D22S								**0.008**		
B2D22S									**0.008**	
S1D22S										ND

Zinc comparisons between stations (ANOVA)

Comparisons between stations 2006 dry season

Table 75: The p-values determined by statistical comparisons of sediment zinc concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the dry season of 2006.

Comparison	P	P<0.050
S1D06S vs. L1D06S	<0.001	Yes
S1D06S vs. L2D06S	<0.001	Yes
S1D06S vs. B1D06S	<0.001	Yes
B1D06S vs. L1D06S	0.004	Yes
B1D06S vs. L2D06S	0.752	No
L2D06S vs. L1D06S	0.026	Yes

Comparisons between stations 2006 during wet season

Table 76: The p-values determined by statistical comparisons of sediment zinc concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2006.

Comparison	P	P<0.050
S1W06S vs. L1W06S	<0.001	Yes
S1W06S vs. L2W06S	<0.001	Yes
S1W06S vs. B1W06S	<0.001	Yes
B1W06S vs. L1W06S	<0.001	Yes
B1W06S vs. L2W06S	0.004	Yes
L2W06S vs. L1W06S	0.710	No

Table 77: The p-values determined by statistical comparisons of sediment zinc concentrations between the sampled stations (Black, Liesbeek and Salt Rivers) during the wet season of 2022.

Comparison	P	P<0.050
B2W22S vs. L1W22S	<0.001	Yes
B2W22S vs. L2W22S	<0.001	Yes
B2W22S vs. B1W22S	0.118	No
B1W22S vs. L1W22S	0.004	Yes
B122WS vs. L2W22S	0.121	No
L2W22S vs. L1W22S	0.307	No

Table 78: The main standard categories of the new water quality guidelines (Odume *et al.* (2024).

Ecological category	Description of category	Water quality guideline value	Risk description
A	Natural	<= 0,0070 mg/L (0,0054 - 0,0086 95% CI)	<=1% chronic guideline Concentration of a water quality constituent most likely suitable for 99% or more of species. The risk of more than 1% of species being affected is low. Extremely sensitive species may still be affected.

B	Largely natural	<= 0,119 mg/L (0,0754 - 0,162 95% CI)	<=5% acute guideline Concentration of a water quality constituent most likely non-lethal for 95% or more of species. The risk of more than 5% of species being affected is low. Highly sensitive species may still be affected.
C	Moderate impact	<= 0,218 mg/L (0,150 - 0,286 95% CI)	<=10% acute guideline Concentration of a water quality constituent may cause mortality in a number of species. The risk of 10% or fewer of the species dying is high, with moderate impact on biodiversity and ecosystem functionality.

D	Large impact	<= 0,475 mg/L (0,303 - 0,647 95% CI)	<=20% acute guideline Concentration of a water quality constituent may cause mortality in a large number of species. The risk of 20% or less of the species dying is high, with a large impact on biodiversity and ecosystem functionality.
E	Serious impact	<= 0,880 mg/L (0,517 - 1,2 95% CI)	<=30% acute guideline Concentration of a water quality constituent may cause mortality in a very large number of species. The risk of 30% or less of the species dying is high, with serious impact on biodiversity and ecosystem functionality. Water

			quality is unacceptable.
F	Critical impact	>0,880 mg/L	>30% acute guideline concentration of a water quality constituent may cause mortality in a very large number of species. The risk of 30% or more of the species dying is high. Water quality is unacceptable.