Assessment of Potential Temporal Impacts of Land use Activities on Water Quality of the Luvuvhu River Catchment, South Africa

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A dissertation Submitted to the Department of Earth Sciences, Faculty of Sciences, Engineering and Agriculture in Fulfilment of the Requirements for the degree of Master of Earth Sciences in Hydrology and Water Resources.

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DECLARATION

I hereby declare that this dissertation submitted for the degree, Master of Earth Sciences in Hydrology and Water Resources, at the University of Venda is mine and the dissertation has not previously been submitted to any other institution of higher education. Furthermore, all the sources cited are acknowledged and indicated through in-text referencing and a comprehensive list of references.

Shibambu TH **Date** **23/02/2023**

DEDICATION

I dedicate this work to the Almighty God who gave me the strength, knowledge, ability, and integrity to complete this dissertation. I also dedicate this study to my late grandmother Anna Chauke and my future generation. I further dedicate this dissertation to my family, for their countless prayers, unconditional support, and everlasting love.

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This dissertation is the work of the Almighty God, and I will continue to give him glory and honour for the favour, guidance, and grace he has shown me in completing this study. The road travelled was made easy with him by my side. I would like to express my sincere appreciation to the following people for their outstanding support, guidance and tolerance, their contribution to the completion of this research, and for making this research possible.

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- I am indebted to the South African National Parks (SANParks) scientists (Dr E. Ridell) and staff, for granting permission to carry out part of this study in their conserved area.
- To my research assistant, Tshidumo Milliscent, I would like to appreciate your continued support throughout this study which made it possible for me to complete it with a controllable workload and courage.
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ABSTRACT

River health is crucial to benefit from the full resource potential of surface water bodies. This benefit becomes compromised when there's high water quality degradation in the system. Considering the South African context, the use of untreated river water for domestic uses such as laundry, recreation, and crop irrigation, is a common practice in various urban and rural communities. The Luvuvhu River Catchment (LRC), in Limpopo Province, South Africa, serves as an essential water resource for the communities within the catchment. Thus, the main focus of this study was to assess the impacts of land use activities on the water quality of the Luvuvhu River Catchment (LRC). This was achieved by analysing the spatiotemporal variation of river water, sediment quality and the potential ecological as well as human health risks associated with the river water and sediments.

Sediment and water samples were collected from 22 sampling sites along the Luvuvhu River Catchment between November 2020 and October 2021. Water samples were analysed for physicochemical parameters, nutrients, major metals and heavy metals, while sediments were analysed for heavy metals only. Physicochemical and nutrients data analysed consisted of pH, total dissolved solids (TDS), turbidity, temperature, dissolved oxygen (DO), salinity, biological oxygen demand (BOD), chemical oxygen demand (COD), electrical conductivity (EC), nitrate (NO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}), and phosphate (PO_4^{3-}). Samples were digested using microwave acid digestion (EPA 3051) and analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometer (ICP-MS) for major metals (Na, Mg, K, and Ca) and heavy metals (Mn, Fe, Al, Cr, Cu, Zn, As, Co, Ni, Mo, Ba, Hg, Cd, and Pb), respectively. The study examined the spatial distribution of these parameters using the Interpolated Distance Weighted (IDW) method on Esri ArcGIS Pro software. The findings were compared to South African Water Quality Guidelines and the World Health Organization.

The results show that the water quality fluctuated during the sampling period. Some parameters such as turbidity, EC, nitrate, Al, Mn, and Fe exceeded the drinking water standards. The findings also show spatiotemporal differences in water quality. The upstream catchment of the river is predominantly covered by agricultural activities and land use becomes more naturally vegetated in the downstream catchment inside the Kruger National Park. Further, the study reveals that the Luvuvhu River Catchment receives a significant amount of pollutants from the upstream and midstream reaches as well as upstream rivers in the Limpopo River before the confluence of the Luvuvhu River. The quality of water further

degrades towards the downstream catchment along the gradient as the river flows through various land use activities. It is therefore, concluded that upstream activities and other tributaries of the Limpopo River have a significant impact on the river's water quality. The quality of water in some sampling sites are not suitable (higher than the Department of Water Affairs and Forestry guidelines) for agricultural use and protection of aquatic ecosystems due to elevated concentrations of some parameters such as Hg, Cu, Mn, Fe, and Al. Generally, about 72% of the metals in sediments and water are higher during the wet season than the dry season. It is also found that high runoff during the wet season act as a transporting mechanism for pollutants though some parameters are not seasonally influenced.

The statistical tools used were able to analyse the water quality data of the river and provided meaningful and relevant information about the river. Multivariate Principal Component Analysis (PCA) revealed substantial anthropogenic contributions of metals in sediment and Cluster Analysis (CA) revealed three classes indicating three major anthropogenic (land use activities) contributions. While the Pollution Load Index (PLI), Enrichment Factor (EF), Contamination Factor (C^i_f) and Geo-accumulation Index (I_{geo}) indicate that the level of contamination is low to moderate in most of the sediment samples. In consideration of the potential ecological risk, the LRC sediments show low potential ecological risk. Also, chronic daily intake of metals because of ingestion was below the recommended guidelines. The overall hazard index for children and adults did not exceed the recommended limit (HI < 1) indicating no or low health risk (non-carcinogenic). The carcinogenic risks of As, Pb and Cd at various sampling sites via ingestion were lower than 10^{-6} indicating no or low risk to develop cancer. This study recommends further studies to be conducted in specific time frames to limit heavy metal content and to prevent further pollution of catchment ecosystems including Kruger National Park by future industrialisation and urbanisation processes upstream of the catchment.

Keywords: *Land use activities; Luvuvhu River Catchment (LRC); Heavy metals; human health risks; Principal Component Analysis (PCA)*

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ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
ATSDR	Agency for Toxic Substances and Diseases Registry
BOD	Biological Oxygen Demand
C_f	Contamination factor
C_d	Degree of contamination
COD	Chemical Oxygen Demand
DNA	Deoxyribonucleic acid
DO	Dissolved oxygen
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
EC	Electrical conductivity
GIS	Geographic Information Systems
HM	Heavy metals
ICP-MS	Inductively coupled plasma mass spectrometer
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
IDW	Interpolated Distance Weighted
ISQG	Interim Sediments Quality Guidelines
KNP	Kruger National Park
LULC	Land use and land changes
HNO_3	Nitric acid
PCA	Principal component analysis
RI	Potential ecological risk index
SANParks	South African National Parks
TDS	Total dissolved solids

USEPA	United States Environmental Protection Agency
WHO	World Health Organisation

CONFERENCES/WORKSHOPS AND PUBLICATIONS FROM THE DISSERTATION

This work contributed to the knowledge gap, environmental education and data need for water quality issues in the Luvuvhu River Catchment. Several workshops were held in collaboration with different stakeholders:

- **USAID Workshop (27th July 2022 to 05th August 2022)**
  Stakeholders involved include the Department of Water and Sanitation (DWS), Kruger National Park, and the United States Agency for International Development (South Africa).
  "Impacts of land use activities on water quality of the Luvuvhu River Catchment".
- **Wits Famelab training workshop (11th – 12th March 2020)**
  "Impacts of land use activities on water quality and associated human and ecological risks".

Proposed output journal papers (in progress):

First paper

Title: Spatial distribution and ecological risk assessment of heavy metals in sediments of the Luvuvhu River Catchment, South Africa.

Authors: Shibambu, T.H., Kahler, D.M., Rose, K., Riddell, E., Oyebanjo OM., Edokpayi, J.N.

Second paper

Title: Impacts of anthropogenic activities on water quality and associated human health risk in Luvuvhu River Catchment, South Africa.

Authors: Shibambu, T.H., Kahler, D.M., Rose, K., Riddell, E.; Oyebanjo OM., Edokpayi, J.N.

CHAPTER 1: INTRODUCTION

1.1 Background of the study

Land use activities associated with the local geomorphology and soil properties affect water quality and hydrological processes of a river system at large thus affecting the ecological integrity of aquatic ecosystems (Bwapwa, 2018). The major anthropogenic factors driving land-use changes are the overutilisation of agricultural lands, industrial development, and rapid urbanisation within catchments (Namugize *et al.,* 2018). Studies have validated that a significant relationship exists between land use activities and water quality characteristics either at the catchment or basin level (Dlamini *et al.,* 2021; Mandal *et al.,* 2019; Nemugize *et al.,* 2018). In concurrence, Nemugize *et al.* (2018) report that anthropogenic activities have different negative influences on the water quality of a river system, as they may lead to an increase in the concentration of pollutants such as heavy metals (HMs) in river sediments and water.

Globally, the adverse impacts of heavy metals in water resources have become an environmental concern for both developing and developed countries (Aydin *et al.,* 2021). In addition, Zhuang *et al. (*2016) state that heavy metals are considered pollution of concern since they are difficult to degrade once disposed into the natural environment. As a result of their persistence in water and sediments, heavy metals consequently affect the ecological environment negatively and human health at large (Proshad *et al.,* 2019). Based on the environmental conditions and biogeochemical processes of the river, sediments serve as essential absorbers of heavy metals (Li *et al.,* 2017). In some instances, the concentration of heavy metals in sediments generally reflects the quality of the river or water body (Proshad *et al.,* 2019).

Although river sediments may adsorb heavy metals, this process cannot permanently remove or fix them from water (Li *et al.,* 2017). Researchers such as Islam *et al. (*2017) and Proshad *et al. (*2019) report that heavy metals may desorb from sediments causing ecological problems when the river condition changes. In this regard, heavy metals may be incorporated into food chains due to their environmental persistence (Li *et al.,* 2020). For instance, Nickel (Ni), Copper (Cu), Zinc (Zn), Chromium (Cr), and Lead (Pb) have been reported in sediments, micro-invertebrates, and water of Oyun River, Ilorin, Kwara State, Nigeria (Opeyemi *et al.,* 2022). The study reported that Pb poses the highest ecological risk to the environment, even at a very low concentration.

Water quality is regarded as an important ecological factor for environmental health as well as human health (Gumbo *et al.,* 2016). According to Aydin *et al. (*2021) rivers are essential natural resources that provide water for a variety of organisms and help to sustain aquatic life as well as humans. Aydin *et al. (*2021) further state that a healthy environment (e.g., rivers) supports the proper ecological functions of organisms and their ecosystem services. However, the rapid population growth, economic development, urbanisation, and industrialisation has increased the pollution of several water bodies (DWS, 2018). Some of the tributaries of the Luvuvhu River which is one of the major tributaries of the Limpopo River have been reported to be polluted with heavy metals (Edokpayi *et al.,* 2016). According to the study, pollution around some parts of the LRC is a result of the intensified release of pollutants from agricultural activities, urban, industrial, and domestic wastes (Edokpayi *et al.,* 2016). All these land-use activities contribute to a steady decline in water quality in terms of ecological functions and water use within the LRC. However, no comprehensive water quality study has been conducted for the entire catchment focusing on water quality with a specific interest in heavy metals as pollutants of concern. Otherwise, the pertinence of the current study.

Surface water pollution has been noted as globally related to human health problems, which became a significant matter (Centers for Disease Control and Prevention, 2018). Health problems such as cancer and respiratory problems may arise from the consumption of river water that contains several toxic metals (Proshad *et al.,* 2018). Also, several metals such as Zn, Fe and Cu are fundamentally important for the systematic body development and functions of living organisms (Proshad *et al.,* 2018). However, some of these metals cause toxicity at higher levels (Li *et al.,* 2020). Heavy metals like Cd, Pb and Hg are exceptionally toxic for both human and aquatic life even at low concentrations. In developing countries including South Africa, the provision of clean and safe drinking water remains a concern. Therefore, it is important to understand the dynamic effects of water quality on consumers (human health risk assessment).

Though several studies have been conducted evaluating the impacts of land use activities on water quality in rivers, little information is known about the impacts of heavy metals in the LRC. Therefore, it is very imperative to assess land-use activities as a major contributor of heavy metals in the Luvuvhu River.

1.2 Problem statement

South Africa is ranked the 30th driest country in the world and water is regarded as a scarce resource in the country (Dlamini *et al.,* 2021). The overconsumption of limited freshwater resources has led to water scarcity (Petersen *et al.,* 2017). This problem is exacerbated by

increased water pollution cases recorded across the country (Petersen *et al.,* 2017). Water quality affects water supply and increases water demand. This is a concern in a country such as South Africa wherein there are no well-developed water quality monitoring systems despite the deteriorating condition of many river systems. Also, data on water quality is limited due to inconsistent sampling at monitoring stations, this may be a result of a lack of resources (such as funding and expertise) within the water management areas (WMA) or water institutions to properly isolate the problem and identify and implement appropriate corrective actions.

Evaluation and identification of spatial variability of water pollution sources provide insight into how water interacts with the environment. Though various methods have been researched and developed to quantify and assess the impacts of neighbourhood land-use activities on rivers (Mlotshwa, 2018; Nemugize *et al.,* 2018), research on the assessment of spatiotemporal variability of water quality in river systems is particularly lacking in South Africa. Luvuvhu River Catchment is one of the Vhembe District's major water sources and one of the few perennial river systems in Limpopo Province, and its water quality is not often monitored. Such monitoring is often considered to play an important role in river health management (DWA, 2011). The Luvuvhu River system is currently facing water quality problems due to land activities such as landfill sites, illegal dumping, agricultural activities, urban wastewater disposal and effluents (DWA, 2011). However, some of these activities (agricultural and industrial activities) are important economic drivers in this region. Dahms *et al. (*2017) add that land use activities are believed to be the largest contributor to water quality deterioration. Bwapwa *et al. (*2018) highlight that one of the major problems in South African rivers is agricultural activities which are associated with eutrophication due to nutrient enrichment.

More than 90% of the population in the LRC is classified as rural, mostly living in villages and informal settlements, while most of the urban population is in Thohoyandou town (DWA, 2013). Mainly, communities within the catchment utilise the river water for fishing, irrigation, drinking, and recreational activities (DWA, 2011). However, current water conditions may be unsuitable for such domestic purposes and may endanger people's health. Therefore, there is a risk of water quality deterioration from human activities. Increased water pollution could pose a public health problem in the future if no action is taken. Studies have shown that pollutants can accumulate in the water body, particularly in sediments for long period and this leads to incorporation into the aquatic food webs, posing a potential toxic risk to predatory mammals, birds, fish, and humans (Dlamini *et al.,* 2021). Therefore, the aquatic ecosystem and human health in the Luvuvhu River system are under great threat which proposes a risk assessment to be undertaken (Edokpayi *et al.,* 2016; Kändler *et al.,* 2017; Vrebos *et al.,* 2017; Yu *et al.,* 2016).

1.3 Motivation

Over the past decades, there has been an upsurge in water pollution, especially in developing countries, and South Africa is no exception as one of Africa's emerging countries, confronting water scarcity issues. Thus, the quality of available water resources is of great concern and needs to be treated in a conservative manner (Dlamini *et al.,* 2021). For water scarcity not to hinder economic development, it is important for water management areas or catchment management agencies to improve, control and manage water pollution. Poor water quality might lead to water-related diseases, infections of aquatic organisms, high water treatment costs and a reduction in agricultural production (Dahms *et al.,* 2017). In concurrence, DWA (2013) writes that pollution of available water resources is significantly affecting many people more specifically those living in rural areas such as the LRC rural dwellers.

Due to an increase in water shortage in rural areas around the catchment, consumption of river water has become an option for villages living around the course of the river. The use of river water as a source may be induced by people's perception of water quality, which is based on its taste, odour, and colour (Benameur *et al.,* 2022; Hu *et al.,* 2022). These individuals are often categorised as vulnerable hybrid water users, using both nearby rivers and dams for domestic needs (Mlotshwa *et al.,* 2018). This might lead to increased health concerns as the quality of water consumed and personal health is inseparable (Karunanidhi *et al.,* 2022). Therefore, the researcher found it fit to incorporate the possible health risks of consuming untreated river water within the study area.

Although several studies have been conducted in the LRC, such studies have been reporting the hydrological phenomenon and not focusing on the concentrations of heavy metals in water and sediments and potential risks which are very crucial (Mazibuko *et al.,* 2021; Ramulifho *et al.,* 2019; Thavhana *et al.,* 2018). This study aims to provide information on the suitability of water for different purposes for rural communities relying on the Luvuvhu River. Concerns have been expressed about heavy metal pollution in Dzindi, Madanzhe, Ngwedi, Mvudi, Tshinane, and Lunwenwe rivers (Edokpayi *et al.,* 2014; Edokpayi *et al.,* 2016; Luvhimbi, 2018). This has triggered attention for heavy metal pollution assessment to be undertaken in the Luvuvhu River Catchment.

According to the Department of Water and Sanitation report (2018), it is important that metals are measured using the inductively coupled plasma mass spectroscopy (ICP-MS) instrument so that the detection limit is fine enough to detect materials in low concentrations. Many previous studies around the Luvuvhu River did not use ICP-MS for analysis; so, in this study, ICP-MS is used for metal analysis. However, a study conducted by Genthe *et al. (*2018a) conclude that the timing of sample collection skewes the results and recommend that

additional samples should be taken from different seasons to supplement findings. Therefore, to supplement data in this study, sampling was conducted every month for one year to determine how pollution varies with dry, short rain and long rain seasons. Additionally, information on heavy metals in South African rivers is limited, particularly in the Luvuvhu River, and there are little data available on river pollution (DWS, 2013), especially data on metals and metalloids (DWS, 2013).

In 2013, the DWA released a gazette for classes and resource quality objectives standards of water resources for the Luvuvhu/Letaba Water Management Areas (WMA). Since the release of this gazette, few studies (Luvhimbi, 2018; Tshililo *et al.,* 2021) have been conducted to compare the current values to the standards set, so this is the first study to determine whether water pollution in the Luvuvhu River is below or above the standards set. The Gazette also reports that constituents of concern, which have a toxicological effect, include arsenic, copper, fluoride, molybdenum, nitrate, sodium, toxic algae, cadmium, mercury, lead, selenium, pathogens, and pesticides (DWA, 2013). Where possible, many of these constituents have been included in the water quality assessment done in this study.

About 1.2 million people in developing countries face water scarcity issues (Balkhair, 2016) and this has resulted in a heavy dependence on the untreated use of rivers for daily needs (Govender, 2016). Using polluted river water to irrigate crops is a prevalent practice in developing countries such as South Africa. However, this practice is of great concern as pollutants such as heavy metals may enter the food chain via this medium (Alia *et al.,* 2015). According to Govender (2016), an estimated 10 percent of the global population consumes crops irrigated with contaminated river water. Therefore, it is critical to contemplate the impact of contaminated water used for irrigation on crop quality. This is because of its potential implications for food security and ultimately human health. Considering the LRC in this context, a third of the upper catchment is primarily used for agriculture with forestry being the most dominant activity in the Soutpansberg Mountains (DWS, 2016). Therefore, assessing the water quality of the study area benefits emerging fruit farmers and crop producers who ply their trade on the catchment of the Luvuvhu River.

The current study aims to apply water quality indices (mathematical techniques) to simplify and make an important contribution to water resource monitoring. This study is in alignment with Mlotshwa's (2018) view that multivariable statistics may be used to identify spatial and temporal trends in river systems and provide a scientific foundation for water management practices. Based on this knowledge, this study assesses the state of water quality and suitability of the Luvuvhu River system for different water uses. Furthermore, this study evaluates spatiotemporal variability and uses geographic information systems and statistical

methods to examine factors affecting river water quality. Ultimately, the study's findings are critical in informing policies for the future management of the Luvuvhu River and other rivers in South Africa.

Rapid land use and land cover changes have occurred in the LRC over the past years (Singo *et al.,* 2016). These changes have a direct negative influence on water quality in reservoirs and rivers as they regulate stream flow and increase flooding. To the best of the current researcher's knowledge, there is no comprehensive catchment study that has been conducted to assess the impact of land use activities on water quality, to date. Furthermore, the LRC is one of the rivers rich in biodiversity, and as such, this study has the potential to provide findings applicable to biodiversity protection more especially in the Kruger National Park (KNP) which is downstream of the catchment. Moreover, assessing the potential ecological risk of pollutants such as heavy metals from the Luvuvhu River is beneficial to the Luvuvhu/Letaba Water Management Area (WMA) and KNP.

1.4 Objectives

1.4.1 Main objective

To assess the spatial temporal impacts of land use activities on water quality and sediments of the Luvuvhu River Catchment (LRC), Limpopo River Basin, South Africa.

1.4.2 Specific objectives

- To determine physicochemical parameters (e.g., COD, DO, pH, turbidity, temperature, Electrical Conductivity, TDS, salinity, BOD), in the water of the LRC.
- To determine the concentration and possible sources of heavy metals, nutrients and major ions in sediments and river water of the LRC.
- To evaluate the potential ecological and human health risks of heavy metals in river sediments and water.
- To classify and calculate the surface area of major land use activities in the LRC.

1.5 Research questions

- What are the physiochemical parameters evident in the water of the LRC?
- What is the concentration and possible causes of heavy metals, nutrients and major ions in sediments and river water of the LRC?

- What are the potential ecological and human health risks of heavy metals in river sediments and water?
- What are the spatial distribution and surface area of major land use activities in the LRC?

1.6 Description of the study area

1.6.1 Location

The LRC falls under the Luvuvhu-Letaba WMA (DWS, 2016). The Luvuvhu River flows for about 200 km before reaching the larger Limpopo River inside the Kruger National Park (Nare *et al.,* 2013). It is part of the Limpopo Basin, an international watercourse shared by Botswana, Mozambique, South Africa and Zimbabwe (Mashinye, 2018). The Catchment is located between latitudes 22°10'01''S and 23°20'50''S and longitudes 29°45'45.16''E and 31°28'10.02''E (Figure 1.1) with an area of approximately 5 941 km^2.

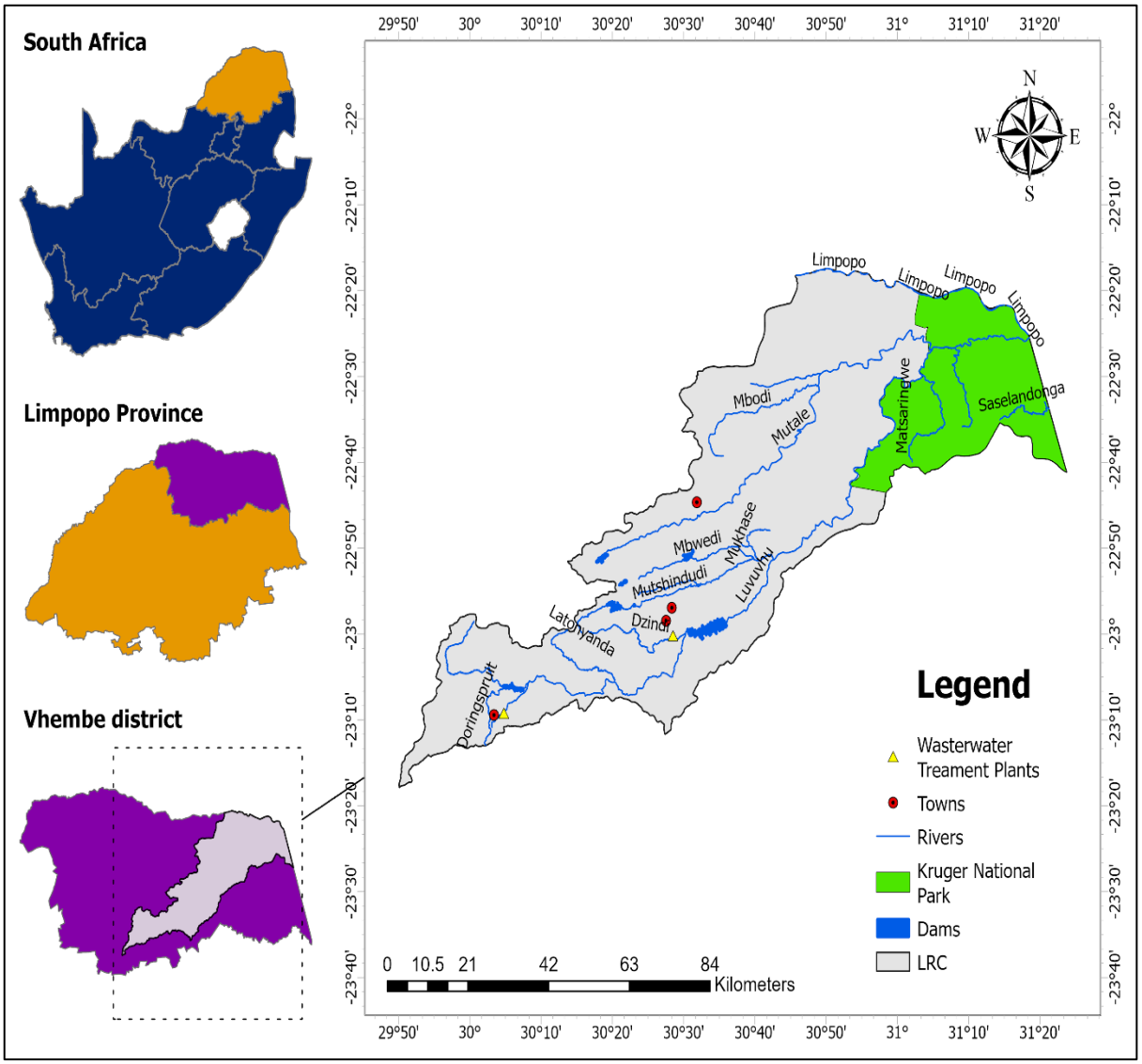

Figure 1.1 Map of the study area.

1.6.2 Geology

The geology of the region is diverse and complicated, with primarily igneous and metamorphic rocks in the south and sedimentary rocks covering the northern part of the catchment (DWA, 2012). A good quality coal deposit exists in the northern part of KNP near Tshikondeni (Mashinye, 2018). Moreover, the southern portion of the catchment is covered with high mineral rich bushveld igneous rocks (DWA, 2012). The formation, with the exception of sandy aquifers in the Limpopo River valley, has a relatively poor water-bearing capacity. It is also worth noting that a wide spectrum of soil occurs in the LRC, with sandy soil being the most common (Figure 1.2).

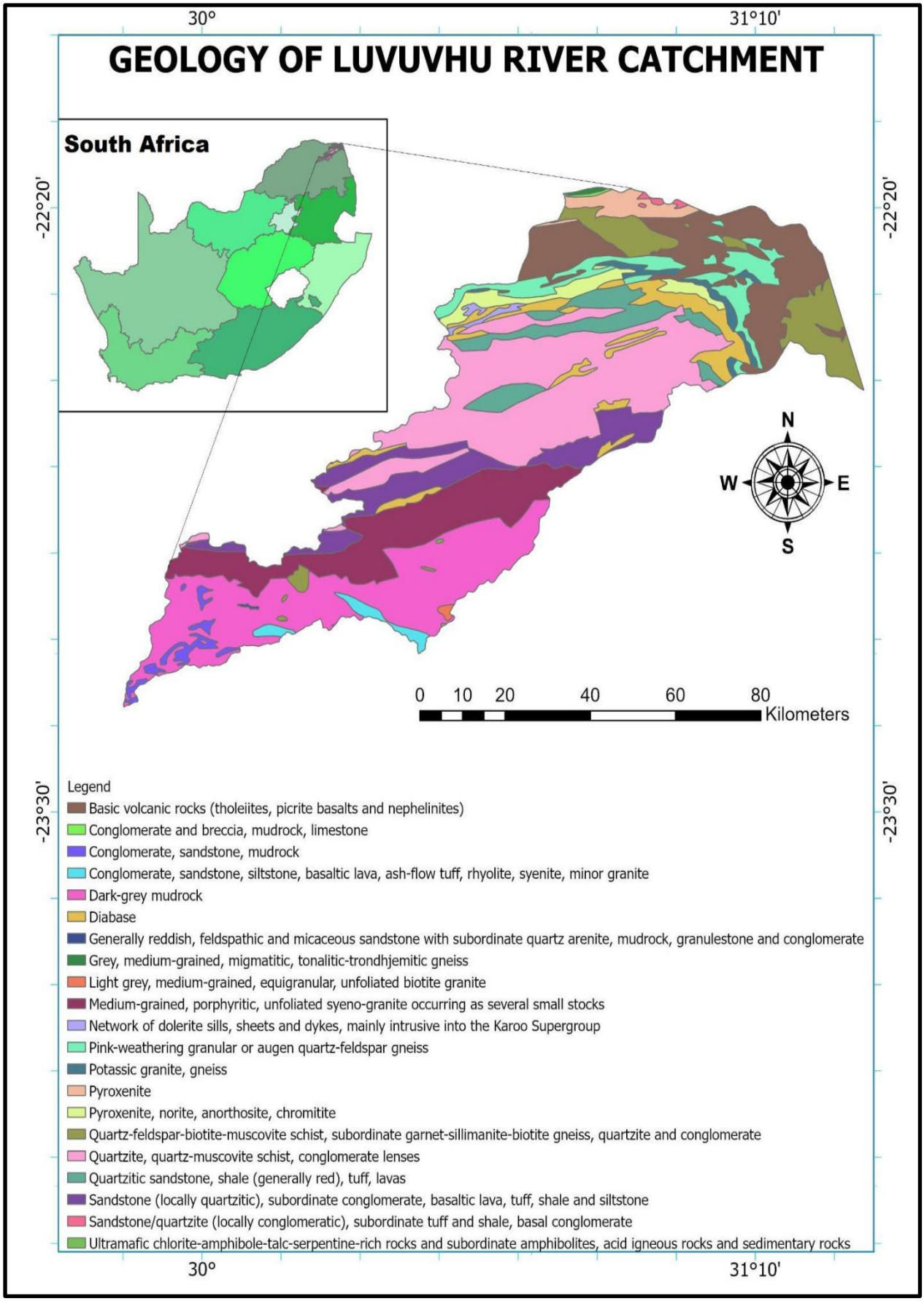

Figure 1.2: Detailed geology of the study area.

1.6.3 Climate

The LRC is situated in the northern part of the Limpopo Province, which is predominantly characterised by a sub-tropical, semi-arid arid climate (DWA, 2012). As shown in Figure 1.3, the average temperature is about 25°C for the entire catchment with the mean annual temperature ranging from 18°C in the mountainous areas to more than 28°C in the eastern and northern parts of the catchments. High temperatures occur generally in January and low temperatures in July (Nemaxwi *et al.,* 2019).

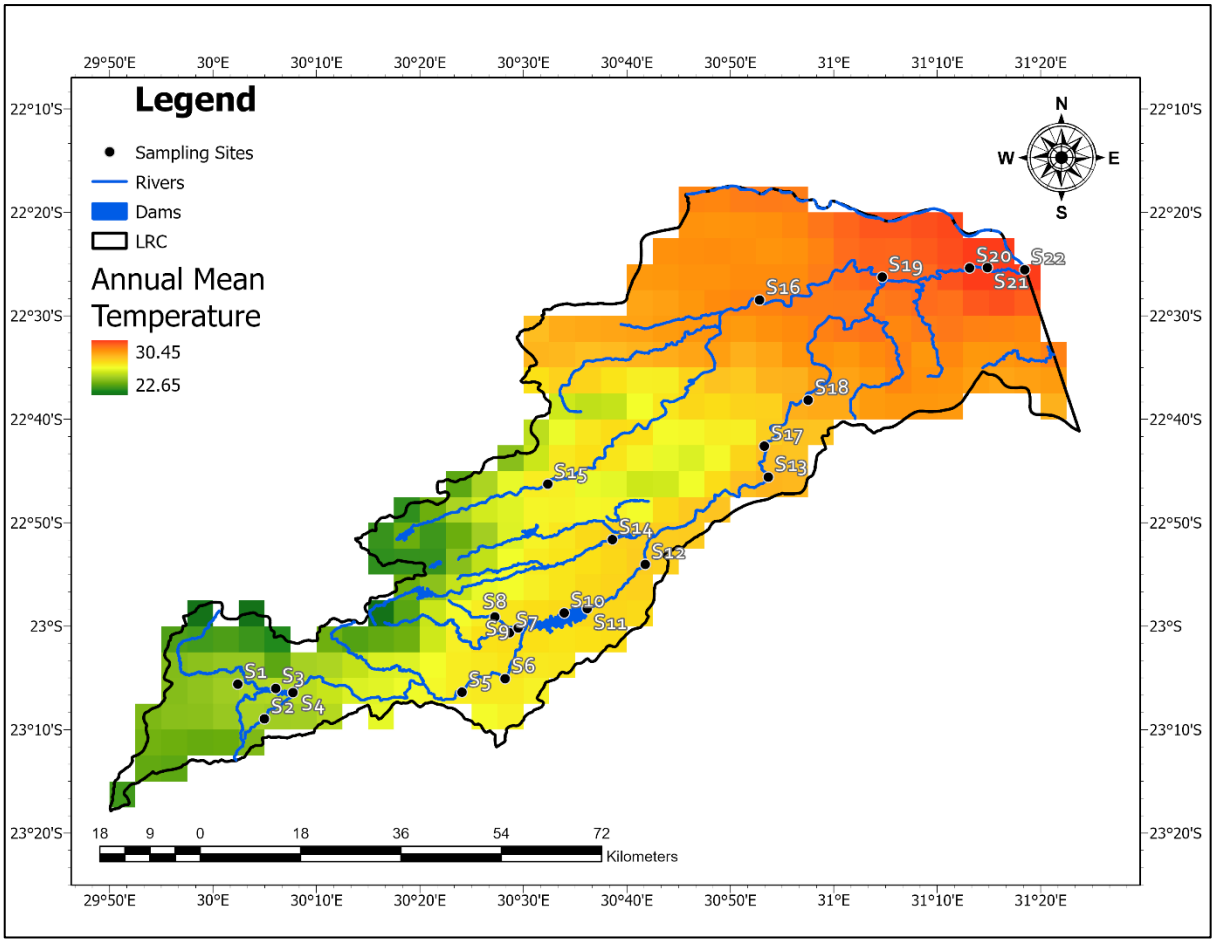

Figure 1.3: Annual mean temperature within the LRC (WorldClim data, 2022).

The catchment receives rainfall mostly in summer, which is from October to March (World Climate data, 2022). The rainfall within the catchment is strongly influenced by the topography of the area and peaks during January and February (DWA, 2012). Although the topography of the area varies considerably between 200 m to 1 500 m, the average annual rainfall is 608 mm, and the average annual runoff is about 520×106 m^3 (DWA, 2012). Further, Mashinye (2018) highlights that maximum rainfall occurs in the upper part of the catchment in the Soutpansberg mountains, with little rainfall downstream in the KNP (Figure 1.4). In his study, Mashinye (2018) further affirms that the mean total evaporation is estimated to be 1 678 mm.

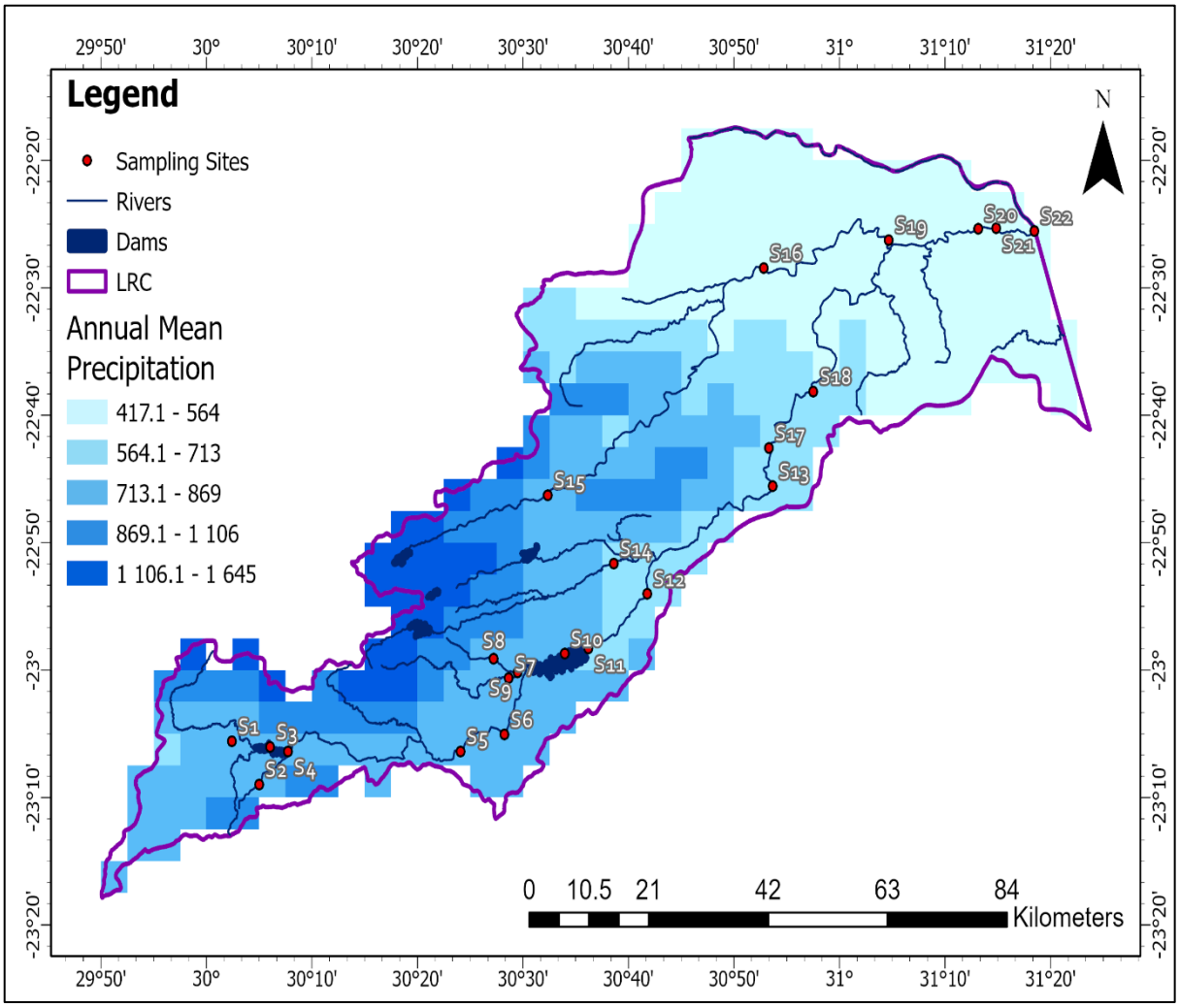

Figure 1.4: Annual mean precipitation in the LRC (WorldClim 1970-2000).

1.6.4 Hydrology

According to DWS (2018), the Luvuvhu River and all its major tributaries are perennial in nature. The river and some of its tributaries originate in the Soutpansberg mountains, and join the greater Limpopo River, which discharges into the Indian Ocean in Mozambique (DWA, 2012). Also, the confluence of the Luvuvhu and Limpopo rivers forms the common point where South Africa borders with both Zimbabwe and Mozambique (DWA, 2012). In this regard, major tributaries include the Mutshindudi River, Dzindi River, Mbwedi River, Mutale River, Mvudi River, Madandzhe River, and Latonganda River (Figure 1.1 above). Dams in the LRC include Albasini, Nandoni, Mambedi, Tshakhuma, Damani, Vondo and Phiphidi (Mashinye, 2018).

1.6.5 Population and land use activities

The entire Luvuvhu River Catchment has a population of about 1 million people (Stats SA, 2010). The LRC is composed of undeveloped scattered rural settlements and several peri-urban areas (Nemaxwi *et al.,* 2019). The main urban areas around the LRC include Thohoyandou, Sibasa, Malamulele and Makhado. The catchment mainly consists of rural settlements, forestry, commercial agriculture, subsistence farming, and conservation areas (i.e., the Kruger National Park). According to Nemaxwi *et al.* (2019), plantations cover the upper reaches of the Luvuvhu River catchment descending towards the Albasini Dam.

There are limited mining activities around the catchment with large coal deposits found in the Mutale area where coal mining activities by the Tshikondeni Colliery owned by Exxaro are take place (DWA, 2011). Most of the catchment area remains under natural vegetation for livestock and game farming with severe overgrazing being prevalent in many areas. Much of the central and north-western areas of the catchment area are largely undeveloped, with scattered rural villages where the people are mainly dependent on the river for water supply. The Waterval sewage plant, Vuwani oxidation ponds, Vuwani and Thohoyandou sewage plants, and Elim sewage plant are all located upstream of Nandoni dam (Gumbo *et al.,* 2016).

CHAPTER 2: LITERATURE REVIEW

2.1 Preamble

The quality of water in rivers plays an important role in ecological functioning. Good water quality generally means a well-functioning ecological system; however, the aquatic ecosystem is at risk because of water pollution in rivers. Further, the lack of access to safe and clean water for domestic purposes has consequently led to people utilising water from rivers without prior treatment in South Africa, especially in rural areas (Luvhimbi, 2018). Most of these rivers are polluted with pollutants, for instance, heavy metals that are detrimental to the aquatic ecosystem as well as human health, and these pollutants are not treated by readily available and affordable point-of-use technologies (Addo-Bediako, 2020). This chapter reviews literature related to heavy metal pollution and nutrients in rivers, impacts of land use activities on water quality, potential ecological risks and human health risks associated with heavy metals. The chapter also covers methods applicable for heavy metals analysis in water and sediments were also reviewed.

2.2 Previous studies around the world

In their assessment of the impact of land use on water quality in the upper Nisa catchment in the Czech Republic and Germany, Kändler *et al. (*2016) stipulate that land use is one of the important factors affecting the water quality in catchments. From their study, agricultural land, forest, grassland, settlements, and arable land were the major land use observed. It is also important to highlight that the water samples collected were analysed for a total of 25 parameters, including nutrients, major ions, major elements and traces of heavy metals. From the analysis, Kändler *et al.* (2016) report that water quality is particularly affected by the portions of settlement areas and arable land and Zn and Cd are the major pollutants of concern. Thus, concluding that densely populated areas reduce water quality despite high proportions of forests.

In a similar vein, Dlamini *et al. (*2021) study the effects of land use on surface water quality in the lower uMfolozi floodplain system, of KwaZulu-Natal. From their assessment of assessing the seasonal variation of some selected water and soil properties within the system, Dlamini *et al. (*2021), report that most of the chemical parameters analysed are within the recommended limits set by the South African Agricultural Water Quality (SAWQ), Irrigation Water Quality Guidelines, apart from Chloride, Sodium, and EC near cultivated sites. Their study submits that most water quality variables measured meet the SAWQ recommended

guidelines and they recommend continuous monitoring of soil and water quality to provide timely data for management purposes.

In a similar study, Dahms *et al. (*2017) assesses the ecological risk of trace elements in the sediments from the Nyl River system in Limpopo, through application of various ecological risk indices such as the pollution factor, geo-accumulation, pollution load index and enrichment factor. Dahms *et al. (*2017) report that that nickel (Ni) concentrations exceed Canadian sediment quality guidelines by a factor of 1.36 and 1.83, respectively. This implies that metal values were generally lower near the headwaters of rivers and higher downstream.

In another study on the impacts of land use and land cover changes on water quality in the uMngeni River catchment in Kwa-Zulu Natal, Namugize *et al. (*2018) indicate that land use and land cover change are the main drivers of water quality problems in watercourses and impoundments. Land-use changes were assessed using Geographic Information Systems (GIS) tools and statistical analyses for the years 1994, 2000, 2008 and 2011 based on changes over time of eight land use and land changes (LULC) classes and available water quality information. Namugize *et al. (*2018) submit that water quality in uMngeni River have deteriorated over time due to increased land use activities and an increase in nutrients and E. coli entering water bodies, although concentrations fluctuated with time. This implies that natural vegetation decreased with an increase in settlements (urban).

Similarly, Luvhimbi (2018) in Limpopo Province of South Africa assesses the quality of water and ecological risk associated with heavy metals in the sediments of Mutshundudi, Madanzhe, Tshinane, Lunwenwe, and Ngwedi Rivers. The study found that the risk of each metal in all sites were in the order of Cd > Ni > Cu > Pb > Zn > Cr > Mn > Fe. In this study, a comparison of heavy metal concentration to the Interim Sediment Quality Guidelines (ISQG) shows that none of these metals have the potential to adversely affect aquatic species or the environment at all sampling sites. Luvhimbi (2018) concludes that the water from these rivers is unsuitable for human consumption and requires further treatment before use.

Edokpayi *et al. (*2014) also investigates heavy metal pollution in the Dzindi River, in Limpopo province to evaluate the current water quality of the Dzindi River. Edokpayi et al (ibid) analysed the concentration of heavy metals (Fe, Cu, Zn, Pb, Cr, Al, and Mn) using a Perkin Elmer Flame Atomic Absorption Spectrophotometer (AAS), and the results of the study show that the average concentrations of all the metals investigated are higher than the recommended levels of the Department of Water Affairs and Forestry (DWAF, 1996) for the protection of aquatic life and domestic water use except for copper. Drawing from this, it is evident that during their study Dzindi River was polluted with heavy metals and which makes the water not useful for domestic purposes without treatment due to the probable health effects it may have on the

user. However, the water was suitable for irrigation purposes. According to Edokpayi *et al. (*2014), pollution at the Dzindi River may be due to high sediment inflow to the river during rainfall, poorly planned informal settlements, uncontrolled deforestation, poor agricultural practices, and effluents from a wastewater treatment plant.

Still in Limpopo, Gumbo *et al. (*2016) study the impact on the Water Quality of Nandoni dam downstream of Municipal Sewage Treatment Plant in the Vhembe District by determining the physicochemical and microbiological parameters in water. The purpose of the study was to assess the ecological impact of effluent discharged downstream of the municipal plants on the water quality of the Nandoni Water Reservoir (a reservoir along the LRC), South Africa. The results of the study indicate that physicochemical and microbial values were higher than the Department of Water Affairs and Forestry (DWAF) and World Health Organisation (WHO) guidelines. It is concluded that the continued discharge of effluent may render the raw water supply unsuitable for human consumption and lead to eutrophication due to nitrate enrichment and proliferation of harmful algal blooms and schistosomiasis infections in the long term (Gumbo *et al.* 2016).

Okonkwo and Mothiba (2005), investigate physicochemical characteristics and pollution levels of heavy metals in the Dzindi, Madanzhe and Mvudi rivers in Thohoyandou. Their results indicate that the concentration of Cd and Pb were higher than the international guidelines acceptable for drinking water and Cd was found to be posing a serious potential risk to aquatic organisms.

2.3 Water quality

Water quality refers to the physical, chemical, biological and aesthetic characteristics of water, usually with regard to its suitability for an intended use (DWAF, 2004). These properties are influenced or controlled by substances suspended or dissolved in water. In general, natural water quality varies from place to place due to seasonal changes, climate changes, and types of soils, rocks and surfaces that it flows on. The quality of the water source is vital since it determines the usability of the water source for different uses such as agricultural, domestic, and industrial activities (DWA, 2012).

Any specific water use has certain requirements for chemical, physical, or biological characteristics (DWA, 2012). Consequently, water quality is defined by a range of variables which limit its use. Nevertheless, ecological systems depend on the quality of the freshwater body for survival and growth (Dahms *et al.,* 2017). Water quality is influenced by both human activities and natural processes (DWAF, 2004). Deteriorating water quality leads to increased

treatment costs of potable and industrial process water as well as decreased agricultural yields due to increased salinity of irrigation water.

2.3.1 Water quality concerns in the Luvuvhu/Letaba WMA

According to the water quality report released by the DWA (2011), several water quality concerns were raised in Luvuvhu/Letaba WMA. Most of these factors impacting water quality were mainly from land-use activities as shown in Table 2.1.

Table 2.1: Water quality issues and concerns in the Luvuvhu/Letaba WMA (DWA, 2013).

Water quality issues	Driver (causes)	Effect
Eutrophication (nutrient enrichment)	Wastewater treatment works, Intensive agriculture fertiliser use, and dense urban sprawl, un-serviced sewage.	Algal growth, smell, toxic algae, taste and odour, irrigation system clogging, aesthetics, recreational water users.
Toxicants	Pesticides (subtropical fruits, nuts) industry	Fish kills and bioaccumulation.
Salinisation	Mines (operational and decommissioned), wastewater treatment works, agricultural (intensive irrigation)	Increased water treatment costs, soil salinity, and irrigation system clogging.
Turbidity	Informal dense settlements urbanisation, mining, agriculture, point source discharge	Dam sedimentation, water treatment costs, irrigation clogging
Microbial Pollution	Wastewater treatment works, informal dense settlements	Recreational users (human health), washing and bathing
Altered flow regime	Dams and weirs, Inter-basin transfers	Increased turbidity (erosion), algal growth, water temperature increase, dissolved oxygen changes, fish kills, and habitat

	reduction due to changed environmental flows.

2.3.2 Factors affecting water quality in catchments.

2.3.2.1 Anthropogenic factors

Population growth in recent decades has led to an increased demand for economic development such as human settlement and food production and forestlands are being converted to settlement and agricultural areas to meet human needs (Damanik-Ambarita *et al.,* 2018). Some areas drained by river systems have been changed into urban areas. In many regions, rivers have been adjusted to build reservoirs to provide food (e.g., fish), drinking water, electricity and water for agriculture (Borowski, 2022; Petsch *et al.,* 2022). Furthermore, industrial activities have grown widely and continue to consume large amounts of available water resources (Hojjati-Najafabadi *et al.,* 2022; Wang *et al.,* 2022). These anthropogenic activities adversely affect the quantity and quality of water and the ecosystem services of water bodies (Damanik-Ambarita *et al.,* 2018).

The major anthropogenic factors affecting water quality in the LRC are commercial agricultural activities, sand mining and urban run-off including sewage discharges (DWA, 2013). From their findings, DWA (2013) submits that the water quality concerns in the LRC are at times high concentrations of Nitrates, Pesticides (Persistent Organic Pesticides), Ammonia, and Phosphates because of agricultural activities. Further, a recent report by the Department of Water Affairs (2018) stipulates that there have been concerns expressed about the cumulative impacts of wastewater discharge and the long-term impacts on communities and aquatic ecosystems. DWA (2013) raise concerns about the potential impacts of agricultural chemicals on the irrigation return flows from intensive irrigation farming in the upper catchment.

LRC typically comprise multiple types of land use with varying sizes and spatial distributions. However, pressures on stream water may arise from different types of land use at different spatial scales. Bodies of water such as rivers and dams act as receivers of (wastewater) water discharged from settlements, agriculture, and industrial areas (Ferreira *et al.,* 2016). In this regard, surface water is often affected by agricultural runoff, which can change the composition of sediments and nutrient concentrations (Popescu *et al.,* 2022). Manfrin *et al.* (2016) and Shah *et al.* (2022) state that forest has a positive influence on water quality, whereas residential and agriculture-related land uses are mostly associated with a negative influence on water quality.

In a study by Damanik-Ambarita *et al.* (2018), agricultural and residential areas were potential sources of nutrient richness in surface waters that could lead to eutrophication. Agriculture also reduces oxygen levels, alter river channels and embankments, alter riparian vegetation types, increase erosion and sediment influx, and increase turbidity (Shah *et al.,* 2022). Moreover, increased human settlements and urban runoff around some areas in the LRC show clear negative effects on water quality, and increased heavy metal concentrations (Edokpayi *et al.,* 2016). This signals that the high salinities are also ascribed to irrigation activities at the vegetation plantation in Levubu (DWA, 2013).

Wastewater discharged by domestic and industrial activities has been reported to negatively affect water quality in rivers (Popescu *et al.,* 2022). In addition, urban wastewater treatment plants that discharge to local rivers were considered as point sources of pollution deteriorating water quality (Richards *et al.,* 2022). The progressive acidification and eutrophication of surface water resources, occurring either separately or in combination, is a country water quality concern (Dlamini *et al.,* 2021). In concurrence, Edokpayi *et al.* (2022) indicated that pollution in one of the tributaries of the Luvuvhu River is due to human activities such as car wash, animal grazing and farming, which poses health risks to communities using the rivers for various domestic chores.

2.3.2.2 Natural factors

Several natural factors affect water chemistry. Karr *et al.* (2022) state that rivers are living systems that are transformed by a multitude of chemical and biological processes. However, water chemistry may be described through several categories which include major ions, dissolved gases, microelements and organic substances. All these factors give the water quality properties such as salinity, alkalinity, acidity and hardness.

All metals are natural elements of the environment and are found in varying levels in the earth's crust. Due to the geological weathering of the bedrock, metals are released into surface water affecting its quality. Richards *et al.* (2022) indicate that the natural breakdown of a bedrock material through weathering and chemical processes is a natural process that affects water quality. In a study to determine the impacts anthropogenic activities on the water quality of the Cauvery River, RamyaPriya and Elango (2022) state that bedrock is the principal source of all Phosphorus, and in some instances also contributes to Nitrogen in a river. In a watercourse, groundwater act as a source of water through groundwater discharge into the river. Generally, groundwater contains high hardness and minerals which consequently affect the water chemistry of a river.

Other natural factors that affect water chemistry include seasonal changes in rainfall, interflow and surface runoff, all these factors have a significant impact on river discharge and the number of pollutants entering a river system (Li, 2018). The water chemistry of a river is also governed by climate, distance from the sea and the amount of soil cover present.

2.4 Main water users in LRC

Irrigation is the largest water use sector in the LRC, especially in the middle and upper Luvuvhu sub-area where extensive irrigation takes place (DWA, 2011). Farmers relying on water from the Luvuvhu River may experience a range of impacts because of changes in water quality (DWA, 2013). Also, livestock is another important water user in the LRC since it is a basic source of work and income for many of the poor people living in the catchment. The population in the upper and middle part of the catchment is largely rural settlements which depend on livestock as a source of food and income (DWA, 2011). The quantity of water used in a catchment is not significantly influenced by livestock watering. However, it is important that there are rules that ensure enough water supply for livestock and water pollution may results in harmful impacts on livestock.

Domestic use of water in the Luvuvhu River system includes drinking, food and beverage preparation, bathing, personal hygiene, and washing, for example, dishes and laundry. As regulated in the National Water Act, 1998 (Act 107 of 1998) Section 21j, recreational water use falls under the 11 water uses (DWA, 2011). Recreational activities vary from place to place and may have a direct impact on the quality of the water resources. Most obvious are activities such as powerboating, sailing and swimming which may have quality or pollution impacts (DWA, 2011). Other recreational activities include fishing and boating. Generally, water suitable for recreational activities is water that is suitable for domestic, ecological and irrigation use. However, recreational activities such as boating affect the quality of water through oil spills.

A transboundary river is a river that crosses at least one political border, either a border within a nation or an international boundary (Anik *et al.,* 2022). The LRC falls within the Limpopo River Basin, which is shared by South Africa, Botswana, Zimbabwe and Mozambique. It is significant to highlight that water development in South Africa directly affect Mozambique's water resources as the Limpopo River flows into Mozambique where it discharges into the Indian Ocean. Water utilisation in the LRC is governed through the Luvuvhu/Letaba WMA and management, and use of the watercourse within the Limpopo River Basin (LRB) are facilitated by the Limpopo Water Course Commission, established in November 2003 as a Joint international co-operation (DWA, 2011).

2.5 Heavy metals (HMs)

The term HMs refers to metallic chemical elements that are relatively dense and toxic or poisonous even at low concentrations and these metals have a specific gravity of more than 5.0, five times higher compared to water (Pham *et al.,* 2022). This group of metals is considered to have an atomic weight in the range of 63.5-200 (Tomáš *et al.,* 2021). Examples of heavy metals of concern in the aquatic environment include Iron (Fe), Lead (Pb), Arsenic (As), Zinc (Zn), Cadmium (Cd), Chromium (Cr), Thallium (Tl), Copper (Cu), Nickel (Ni) and Mercury (Hg) (Wang *et al.,* 2017). These metals are natural elements of the Earth's crust and are durable elements such that they cannot be destroyed or degraded. Copper, Zinc and Selenium are known to be vital for maintaining the metabolism system of the human's body (Shen *et al.,* 2021). However, they can be detrimental at higher concentrations.

Heavy metals are toxic to living organisms because they tend to bioaccumulate (Zhang *et al.,* 2019). Nevertheless, they are useful in many applications, i.e., Copper is used in a wide range of materials such as water pipes, kitchenware and roofing materials. Zinc is used in the manufacturing of paints and chemicals, while chromium-incorporated compounds are used as anti-corrosives in the oil industry. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into rivers, lakes, streams, and groundwater.

2.5.1 Toxicity of some heavy metals

HMs are well known for their toxicity in the environment, although some of these elements are critical for growth in many living organisms, but at a very low concentration (Zhang *et al.,* 2019). Excessive levels of these metals are detrimental and due to their bioaccumulation ability in organisms and sediments, they pose a long-term threat to the aquatic environment and human health (Yona *et al.,* 2018). Their accumulation and concentration depend on hydrographic factors such as salinity, DO, pH, and temperature (Yona *et al.,* 2018). The existence of these metals in high levels in the aquatic environment might cause damage to the life and functional activities of aquatic organisms and death (Edokpayi *et al.,* 2017).

Heavy metal toxicity may occur through dermal exposure, inhalation or ingestion. Effects may vary due to the degree of individual exposure, duration and type of element exposed to (Bharti and Sharma, 2022). Environmental conditions also contribute a significant role on the toxicity of heavy metals since they control the chemical speciation of elements (Zaynab *et al.,* 2022). Also, the toxicity is either chronic or acute and may cause both local and systemic effects (Zaynab *et al.,* 2022).

2.5.1.1 Mercury (Hg)

Mercury is a naturally occurring element which is liquid at room temperature (Bonotto *et al.,* 2018). It exists in three forms i.e., metallic, organic and inorganic form (Yang *et al.,* 2020). All forms of Hg are very toxic and induce toxic effects on mammals even at low levels (Yang *et al.,* 2020). The Agency for Toxic Substances and Diseases Registry (ATSDR, 2015) categorises mercury as the third toxic substance to public health in the priority list of hazardous substances. Mercury is released into the natural environment via different anthropogenic activities which include municipal wastewater discharge, agricultural activities, industrial waste discharge, mining and incineration (Kumari *et al.,* 2020).

Most discharged mercury waste is found in water resources such as rivers, lakes, dams and oceans (Kumari *et al.,* 2020). In the aquatic environment, Hg is taken up by microorganisms and transformed into methylmercury (Al-Sulaiti *et al.,* 2022). In addition, Wang *et al. (*2021), state that the major route of exposure to methylmercury is the consumption of contaminated aquatic animals. According to Wang *et al.* (2021), the toxicity of Hg depends on its chemical form. Naturally, mercury does not occur in living organisms and has no known essential functions in the human body. Acute toxicity may result in fatigue, fever, and clinical signs of pneumonitis (Nemery, 2022). Additionally, acute exposure to inorganic mercury also leads to lung damage (Kumari *et al.,* 2020).

Psychologically and neurologically affected individuals because of Hg effects begins to show symptoms such as depression, memory loss, tremor, anxiety, hypertension and gingivostomatitis after long-term exposure to Hg (Nemery, 2022). In the 1940s, in Minamata, south-west Japan, mercury was a responsible toxin for Minamata disease due to its discharge by a nearby chemical plant into the sea surrounding the village which affected many fishes (Sudsandee *et al.,* 2017; Yang *et al.,* 2020). Long-term exposure to Hg affects the central nervous system, and brain functions, and causes chromosomal and deoxyribonucleic acid (DNA) damage (Wang *et al. (*2021). Mercury also causes adverse reproductive problems in animals and humans (Adelakun *et al.,* 2020). In agreement, Kumari *et al.* (2020) indicate that exposure to a high dose may be fatal within 2-4 weeks after the onset of symptoms and consumption of food polluted with metallic mercury, which may cause damages to the kidneys.

2.5.1.2 Lead (Pb)

Lead is one of the natural elements found abundantly on the Earth's crust and it has a high malleability and low melting point, and due to its physical properties, it is used in many industries (Figure 2.1) (Stets *et al.,* 2018). Further, Rehman *et al. (*2018) note that drinking water, food, smoking and industrial processes are the main sources of exposure to Pb. Pb has no known important functions in the human body (Rehman *et al.,* 2018). According to

Queiroz *et al. (*2019), it is a carcinogenic metal and highly toxic and its consumption or exposure may cause several chronic health risks such as stomach cancer, abdominal pain, lung cancer, blood pressure, headache, gliomas and kidney damage. In support, Rehman *et al. (*2018) state that acute exposure to Pb may cause fatigue, renal dysfunctional and vertigo (Rehman *et al.,* 2018).

Figure 2.1: Various sources of lead pollution in the environment (Adapted from Zulfiqar et al., 2019).

Also in agreement, Alam *et al. (*2019). Affirm that long-term exposure to high Pb levels may cause miscarriage in pregnant women, brain damage, and consequently lead to death and anaemia. (Pb toxicity is more vulnerable to children both before and after birth because children absorb Pb more rapidly than adults (USEPA, 2011). The World Health Organisation (WHO) recommends a safe limit of 0.01 mg/L in drinking water. Nevertheless, plant (vegetables and crops) Pb pollution also occurs through the uptake from soil and ambient air while animals may be exposed to Pb-polluted plants via ingestion (Louie, 2019). However, aquatic organisms ingest Pb from sediments and water (Kumar *et al.,* 2022).

2.5.1.3 Arsenic (As)

Arsenic is a naturally occurring element and one of the most abundant in the Earth's crust (Alamdar *et al.,* 2018). In the Earth's crust, it is known as the 20th most abundant element and ranked as the number one toxic element on the list of most hazardous substances to public health (ATSDR, 2013). Arsenic occurs in three forms: inorganic (arsenite), organic (arsine), and elemental form. Despite being naturally occurring, it is released through natural activities such as volcanic activity, forest fires, soil and rock erosion and geothermal waters (Figure 2.2) (Raju *et al.,* 2022). Apart from natural sources, its application in insecticides, glass, animal

feeds, pesticides, ceramics, wood preservatives, herbicides and other possible sources also account for its anthropogenic contribution (Figure 2.2) (Alamdar *et al.,* 2018).

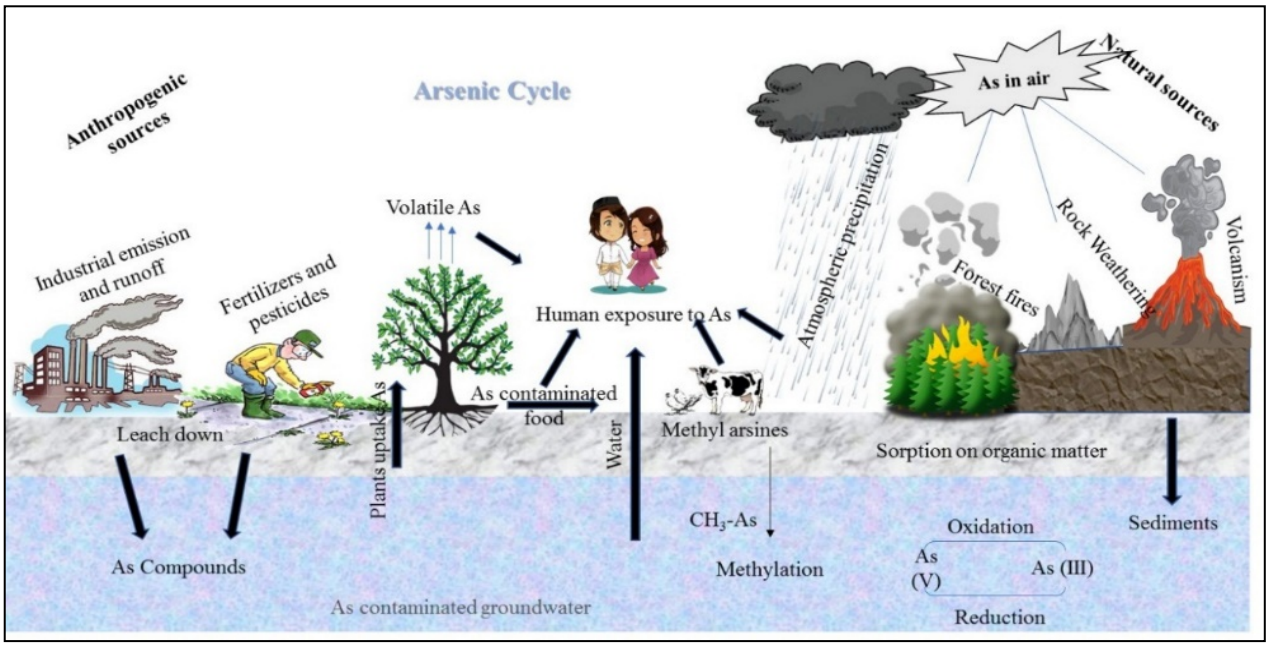

Figure 2.2: Arsenic cycle in the environment (Shahid et al., 2018).

Drinking water accessed from wells, rivers and springs are a major source of Arsenic exposure to humans in different regions of the world (Raju *et al.,* 2022). Furthermore, Khosravi-Darani *et al. (*2022) posit that Arsenic has no colour, odour or taste so, which makes it too difficult to detect exposure by the naked eye. Therefore, human exposure to Arsenic includes both natural and man-made sources (food, air, water, and soil) (Khosravi-Darani *et al.,* 2022). Water used for drinking purposes in countries lsuch as China, India, Taiwan, Pakistan, Brazil, Vietnam, Mexico, Hungary, Canada, Chile, Bangladesh, Ghana, Zimbabwe and Burkina Faso has been found to contain inorganic arsenic up to 4,000 $\mu g.L^{-1}$, affecting over 200 million people worldwide (Mudzielwana *et al.,* 2019; Shaji *et al.,* 2021).

Its availability in large quantities poses a threat to the environment as well. The inorganic forms of Arsenic are lethal to living organisms (Khosravi-Darani *et al.,* 2022). Excessive intake of inorganic Arsenic causes acute toxicity leading to severe disturbances of the central nervous system, cardiovascular system, and gastrointestinal symptoms and may result in death (Sarkar and Paul, 2016). Individuals with increasing exposure to Arsenic through drinking water exhibit an excess risk of mortality from kidney, bladder, and lung cancer (Pál *et al.,* 2022). For Pál *et al. (*2022), the black foot disease reported on the southwest coast of Taiwan was noted to be caused by long-term exposure (for more than eighty years) in drinking water from an artesian well containing a high concentration of ArsenicIn addition, Khosravi-Darani *et al.* (2022) indicate that Arsenic is a protoplasmic poison which primarily affects the sulfhydryl

group of cells resulting in malfunctioning of the cell enzymes, cell respiration and mitosis. Drawing from the fact that drinking water is one of the primary routes of exposure, the WHO and the United States Environmental Protection Agency (USEPA) set the maximum limit level to 0.010 mg/L in drinking water (Sarkar and Paul, 2016).

2.5.1.4 Cadmium (Cd)

According to the Agency for Toxic Substances and Diseases Registry (ATSDR, 2012) ranking, cadmium is the 7th most toxic substance. It is a by-product of zinc and lead production and has a variety of applications in different industries. It is used mostly in rechargeable batteries, plastic, metal coating, and pigments (Ishchenko *et al.,* 2018). Humans are exposed to cadmium via ingestion and inhalation (ATSDR, 2012). Inhalation of cadmium may be due to smoking tobacco and diffuse pollution such as refined petroleum products, detergents, and phosphate fertilizers also contain some quantities of cadmium (Mohite *et al.,* 2022). Cd is highly toxic to both animals and plants as well as many micro-organisms (Ma *et al.,* 2020). It does not degrade when discharged into the environment to a product less toxic, which contributes to its bioaccumulation in invertebrates and vertebrates (Ma *et al.,* 2020).

According to Mohite *et al. (*2022), Cadmium has the capacity to accumulate in the human body and remain in the body for many years (10-30 years) (Mohite *et al.,* 2022). It can cause severe damage to the lungs due to breathing at high levels, particularly for smokers (Mondal *et al.,* 2022). Consuming large quantities of cadmium may lead to stomach irritation consequently causing diarrhoea. Long-term exposure also leads to renal dysfunction and allergies in humans. ATSDR (2012) shows that Cd also affects the brain, bones, and central nervous system. A study by Gupta and Gupta (2022) reveals that women are rich in cadmium than men and it could enter the embryo through the placenta, destroying its morphological structure and resulting in foetal growth restriction. Cadmium also affect Calcium (Ca) absorption, the activity of osteoclasts, increase bone resorption, and impair kidney functions which indulge the development of osteoporosis (Reyes-Hinojosa *et al.,* 2019). Due to its toxicity, the WHO (2004) recommends safe levels of Cd in drinking water to be 0.003 mg/L.

During and after World War II, inhabitants of the Jinzu River basin in Toyama Prefecture Japan experienced a well-known chronic Cd poisoning disease called Itai-Itai disease (Aoshima, 2016). The root cause of this disease was found to be the consumption of water and rice contaminated with Cd from discharges of a local zinc-mining operation in Toyama Prefecture (the leading industrial prefecture on the Japan sea coast) (Figure 2.3). It is characterised by severe pain resulting from osteomalacia; the name, itai itai disease, means ouch!!, ouch!! or painful in English. Between 1967 and 2011, 196 cases of itai itai disease had been officially recognised by the Japanese government (Dutta and Sharma, 2019).

Figure 2.3: (a) Effects of Itai-Itai disease (Dutta and Sharma, 2019) and (b) Villagers of Sanhe village in Guangxi show swollen hands suspected of being caused by cadmium (https://tinyurl.com/2m5y2psc).

2.5.1.5 Chromium (Cr)

Chromium is found in three forms: gas, solid and liquid and it occurs in the environment in several oxidation states from Cr2 to Cr6 (Tumolo *et al.,* 2020). It occurs because of the burning of coal and oil, and petroleum from Ferro chromite refractory materials (Figure 2.4). Studies have indicated that the hexavalent-Cr6 state is toxic to humans, plants, and animals and thus the most prevalent state found in industrial settings and the environment (Singh *et al.,* 2022; Suleman, 2022). Chromium is extensively used in various applications including paint and pigment production, wood preservation, paper and pulp production, electroplating, chemical production and metallurgy (Figure 2.4) (Perraki *et al.,* 2021). These industries contribute a major role in Cr pollution which poses adverse effects on ecological and biological species (Suleman, 2022). Agricultural activities also increase chromium pollution by increasing toxic levels in the environment.

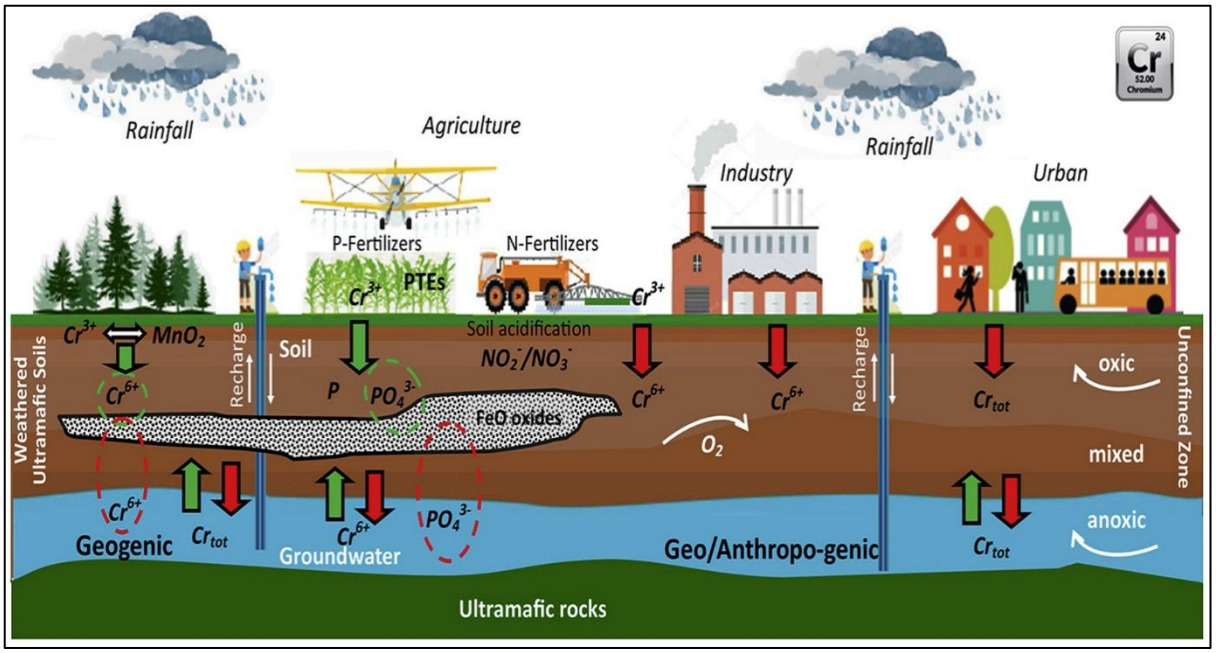

Figure 2.4: Schematic representation of the major sources of Cr (VI) in surface waters (Adopted from Perraki et al., 2021).

Humans are often exposed to high levels of Cr due to the accumulated Cr in aquatic life such as fish (Mavunda, 2016). Numerous experiments have reported various chromium toxicity in fish species such as reduced total lipid, glycogen and total protein concentration in the muscle, liver, and gill of rohu, Labeo rohita (Islam *et al.,* 2020). There is a risk of nerve damage, kidney damage, and liver damage following long-term exposure to Chromium (Alvarez *et al.,* 2021). Inhaling high levels of Cr through occupational exposure may give rise to nose irritation, nose ulcers and breathing problems such as wheezing, asthma or shortness of breath (Mavunda, 2016) while consuming water rich in Cr causes dermatological problems. Damage to DNA replication and inhibition of protein synthesis is one of the genomic system problems associated with Cr exposure (Alvarez *et al.,* 2021). In plants, Cr toxicity causes necrosis and leaf chlorosis (Onyemesili *et al.,* 2020). On the other hand, Chromium phytotoxicity also causes inhibition of seed germination, depressed biomass, and reduction in root growth (Onyemesili *et al.,* 2020). The International Agency for the Research on Cancer (2020) categises Cr (VI) as a group 1 human carcinogenic substance.

2.5.2 Methods for Heavy Metals analysis

Several studies have detailed various approaches for heavy metals analysis in biological, food, and environmental samples (Edokpayi *et al.,* 2018; Sudsandee *et al.,* 2017; Wang *et al.,* 2020). Analytical techniques often require preparation or pre-treatment of samples with acids before analysis to remove or digest unwanted particles.

2.5.2.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is a form of mass spectrometry that detects metals and some non-metals at a concentration very low as one part in 10^{-15} (part per quadrillion) on non-interfered low-background isotopes (Bilqis *et al.,* 2022). The system achieves this by ionising the sample in an inductively coupled plasma and separating and quantifying these ions with a mass spectrometer. It is used in a variety of industries including, but not limited to, environmental monitoring, geochemical analysis, metallurgy, pharmaceutical analysis, and clinical research (Bilqis *et al.,* 2022).

Compared to atomic absorption spectroscopy, ICP-MS is fast, precise and sensitive (Luvhimbi, 2018). The ICP-MS technique also has a multi-element character and a high sample throughput (Liu *et al.,* 2021). Disadvantages and weaknesses of ICP-MS detection are the occurrences of non-spectral and spectral interferences and the high operating costs. In several studies, sediments and water samples were analysed for Cu, Cd, Cr, Pb, and Ni using inductively coupled plasma mass spectrometry (Table 2.2).

Table 2.2: Principles, analysis and application of ICP MS.

Technique	Principle	Type of analysis	Applications	References
Inductively coupled plasma with mass spectrometry (ICP-MS)	-Argon plasma is used as an ion source –Used for separating ions based on their mass-to-charge ratio	Simultaneous multielement analysis	-Widely used -Isotope determination	Zhu *et al.,* 2019; Kormoker *et al.,* 2019; Wang *et al.,* 2020; Leventeli *et al.,* 2019; Sojka *et al.,* 2018

2.5.2.2 Inductively Coupled Plasma–Optical Emission Spectrometer (ICP-OES)

ICP-OES is an instrument used in elemental analysis which uses the emission spectra of a sample to identify and quantify the elements present (Khan *et al.,* 2022). It is an optical emission spectroscopy technique using an inductively coupled plasma to produce excited atoms and ions that produce electromagnetic radiation with certain wavelength characteristics (Luvhimbi, 2018). The plasma has a high temperature (10000K) and electron density, and this energy is utilized in the excitation-emission of the sample. An element's concentration is determined by the intensity of this emission.

Advantages of this procedure include high sample throughput enabling efficient analysis of large batches, simultaneous measurement of multiple elements within each sample, analysis that complements techniques such as X-ray fluorescence (XRF), and wide dynamic linearity

range, low chemical and matrix interference effects (Khan *et al.,* 2022). ICP-OES' disadvantages include the fact that it requires a highly sensitive and high-resolution spectrometer, which is an expensive instrument to buy and to operate (Liu *et al.,* 2021). Several studies used ICP-OES for metal analysis (Dahms *et al.,* 2017; Gab-Allah *et al.,* 2021; Manard at al., 2021).

2.5.2.3 Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry is a type of an analytical system used to measure the concentration of various elements. This technique is aimed at measuring high concentrations in samples and uses wavelengths of light that are specifically absorbed by elements (Perelonia *et al.,* 2021). Atoms of various elements absorbs specific wavelengths of light, corresponding to the energy required to propel an electron from one energy level to another (Harvey, 2019). In AAS, the sample is atomised into free atoms in a vapour form, and a beam of electromagnetic radiation emitted by the excited atoms passes through the vaporised sample (Harvey, 2019).

The advantages of using AAS are low spectral interferences, very high precision, direct analysis of some types of liquid samples, low cost, and very small sample sizes (Frohlich *et al.,* 2021). The main disadvantages of AAS are only solutions can be analysed, less sensitivity compared to graphite furnaces, relatively large sample quantities are required (1-3 ml) and problems with refractory elements (Chemistry Net, 2018). In their studies, Edokpayi *et al.* (2014) and Abrham, and Gholap (2021) use AAS to determine the level of selected heavy metals in water and sediment samples.

2.6 Indices for evaluating the toxic level of heavy metals in sediments and water.

2.6.1 Potential Ecological Risk Index (RI)

The RI approach was proposed in 1980 by Hakanson from a sedimentological perspective to evaluate the properties and environmental fate of heavy metal pollutants. This methodology was developed to assess the ecological risk based on the notion that the sensitivity of an aquatic ecosystem rely on its productivity (Acharjee *et al.,* 2022). This procedure also assesses the level of heavy metal contamination in the sediment, depending on the toxicity of the heavy metal and the response of the environment. The RI of heavy metals could be computed by the following equations:

$$C_f = C_0^i / C_n^i \qquad (2.1)$$

$$C_d = \sum C_f^i \quad (2.2)$$

$$E_r^i = T_r^i \times C_f^i \quad (2.3)$$

$$RI = \sum E_r^i \quad (2.4)$$

Where C_f^i is the pollution factor; C_0^i is the concentration of the metal in the sediment sample; C_n^i is the reference value for metals; C_d is the degree of pollution; E_r^i is the monomial potential ecological risk factor; T_r^i is the toxic response factor of a given element, which accounts for its sensitivity and toxic requirement (Table 2.3); and RI is the sum of all risk factors of metals analysed from the sediment. The standards to evaluate the potential ecological risk factor E_r^i and potential ecological RI is given in Table 2.3 below.

Table 2.3: Values used to interpret the risk factor E_r^i and RI as proposed by Hakanson (1980).

Comprehensive pollution index	Comprehensive pollution level	E_r^i	Eco-risk factor Grade	RI	Eco-risk index grade
$C_d < 5$	Low	$E_r^i < 40$	Low	RI < 150	Low
$5 \leq C_d < 10$	Moderate	$40 \leq E_r^i < 80$	Moderate	150 ≤ RI <300	Moderate
$10 \leq C_d < 20$	High	$80 \leq E_r^i < 160$	Considerable	300 ≤ RI < 600	High
$C_d \geq 20$	Very high	$160 \leq E_r^i < 320$	High	RI ≥ 600	Very high
		$E_r^i \geq 320$	Very high		

Extracted from Zhang *et al.,* 2017.

2.6.2 Index of Geo-Accumulation (I_{geo})

The I_{geo} method accounts for pollution by comparing the regional background and current concentration of that individual metal in sediment (Cui *et al.,* 2022). The I_{geo} was proposed by Müller (1979) and can be computed using the equation:

$$I_{geo} = log_2\left(\frac{C_n}{1.5B_n}\right) \quad (2.5)$$

Where I_{geo} is a single factor pollution index, C_n and B_n are the concentrations of the selected heavy metal in the bottom sediments and the geochemical background value, respectively ($mg.kg^{-1}$). A factor of 1.5 is applied for probable variation in the background data due to lithological conditions (Sojka *et al.,* 2018). I_{geo} values are interpreted as presented in Table 2.4.

Table 2.4: Values that are used to interpret the Index of Geo-Accumulation

Index values	Sediment condition
$I_{geo} \leq 0$	Practically unpolluted
$0 < I_{geo} \leq 1$	Unpolluted to moderately polluted
$1 < Igeo \leq 2$	Moderately polluted
$2 < I_{geo} \leq 3$	Moderately to heavily polluted
$3 < I_{geo} \leq 4$	Heavily polluted
$4 < I_{geo} \leq 5$	Heavily to extremely polluted
$I_{geo} > 5$	Extremely polluted

Extracted from Liu *et al. (*2018) &Sojka *et al. (*2018.

2.6.3 Enrichment Factor (EF)

EF is an index that quantifies the anthropogenic impact of the concentration of a given metal (Cui *et al.,* 2022). EF is based on the proportion of the determined metal concentration to the background geochemical value of the metal. To account for background geochemical concentration, EFs are normalised to Fe or Al content in sediments. The normalised EF is calculated according to the equation below:

$$EF = \frac{\left(\frac{C_x}{C_{Fe}}\right)_{sediment}}{\left(\frac{C_x}{C_{Fe}}\right)_{background}} \quad (2.6)$$

Where (C_x/C_{Fe}) sediment is the ratio of the concentration of element x (C_x) to that of Fe (C_{Fe}) in sediment samples and (C_x/C_{Fe}) background is the ratio from the reference background (Sojka *et al.,* 2018). EF consists of five classes which are EF < 2 being minimal enrichment, EF = 2–5 moderate enrichment, EF = 5–20 significant enrichment, and EF = 20–40 very high

enrichment whilst EF > 40 is extreme enrichment (Yi *et al.,* 2016). An EF value less than 1 reflects the remobilisation and loss of that element compared to the normalising element or indicates that the concentration of the normalising element is overestimated. An EF value of 1 indicates a predominantly natural origin of the element in the sediment, while an EF value above 1.5 indicates enrichment due to natural sources (bio input) or anthropogenic influences.

2.6.4 Pollution Load Index (PLI)

The PLI is an index proposed by Tomlinson *et al.* (1980). This method is used to assess pollutant concentration of heavy metals in sediments (Luvhimbi, 2018). It functions together with pollution factor (Contamination Factor) values that indicate the pollution potential of individual metal as shown in equation 7.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots CF_n)^{\frac{1}{n}} \quad (2.7)$$

However, Sojka *et al.* (2018) expanded the equation to:

$$PLI = \left(\frac{C_{n1}}{B_{n1}} \times \frac{C_{n2}}{B_{n2}} \times \dots\dots\dots \times \frac{C_{ni}}{B_{ni}}\right)^{\frac{1}{i}} \quad (2.8)$$

Where C_n/B_n is the ratio of selected elements to their background values and *i* is the number of elements. The empirical formula provides simple comparisons of site average heavy metal contamination (Rauf *et al.,* 2022). According to Sojka *et al.* (2018), a PLI value of 0 denotes perfection, PLI less than 1 denotes no pollution, and PLI greater than 1 indicates pollution.

2.6.5 Risk Assessment Code (RAC)

The index RAC is used to assess the transport of heavy metal according to their chemical fractions (Liu *et al.,* 2018). The RAC is expressed by the following equation:

$$RAC = C_m/C_{total} \times 100\% \quad (2.9)$$

Where C_m is the metal concentration, C_{total} is the total metal concentration in sediment. According to the values of RAC, the classification of ecological risk of RAC is shown in Table 2.5.

Table 2.5: RAC classification categories (Liu *et al.,* 2018).

Category	RAC (%)	Risk
1	<1	No risk
2	1-10	Low risk
3	11-30	Medium risk
4	31-50	High risk
5	>50	Very high risk

2.7 Assessment of Human health risk

According to the USEPA (2012), human health risk assessment is considered to characterise potential adverse human health effects due to exposure to environmental hazards. This procedure makes use of statistics, science and engineering to measure and identify a hazard, it also determines probable routes of exposure and finally uses that data information to compute a numerical value to represent the potential risk to humans (Shams *et al.,* 2022). Risk pathways for human exposure to individual metal could be through three major pathways including dermal absorption through skin exposure, direct ingestion through drinking water, and inhalation via mouth and nose (USEPA, 2012). Based on this assessment, the risk is classified into two elements: either non-carcinogenic or carcinogenic. Each classification has its procedure to be followed when calculating the potential risks (Shams *et al.,* 2022).

Carcinogenic metals are believed to have no effective threshold. This assumption implies that there is a probability of developing cancer upon exposure to carcinogenic contaminant over a lifetime and therefore, there is no safe threshold for exposure to carcinogenic metals (Bamuwamye *et al.,* 2022). Also, non-carcinogenic metals are assumed to have a threshold; a dose below which no adverse health effects will be observed (Bamuwamye *et al.,* 2022).

CHAPTER 3: METHODOLOGY

3.1 Research design

This chapter presents the methods of the study in alignment with the research objectives presented in Chapter 1. The study collected water and sediment samples from different locations in the Luvuvhu River Catchment to evaluate water and sediment quality. The results of this study were compared to the Department of Water Affairs and Forestry (DWAF) guidelines for the protection of the aquatic ecosystem and the South African National Standards (SANS) guidelines for safe drinking water as a reference for metals as well as the World Health Organisation (WHO) standards. In addition, various mathematical indices were applied to identify potential environmental and human health risks from heavy metal pollution.

3.2 Sampling, preparation, and storage

3.2.1 Water samples collection and insitu physico-chemical analysis

A total of seven hundred and fifty-six (756) samples were collected between the period of November 2020 and October 2021 from twenty-two (22) different sampling points (Figure 3.1). Sampling points were selected based on factors such as the major land use activity along the river, access to the river and confluence points (Luvuvhu River with its tributaries). Not all the rivers within the catchment were assessed since sampling the entire catchment could be difficult within the stipulated timeframe, only the main river and major tributaries were sampled. Three (3) water samples were collected from each sampling site monthly following the procedure described by the United States Environmental Protection Agency (USEPA,2004).

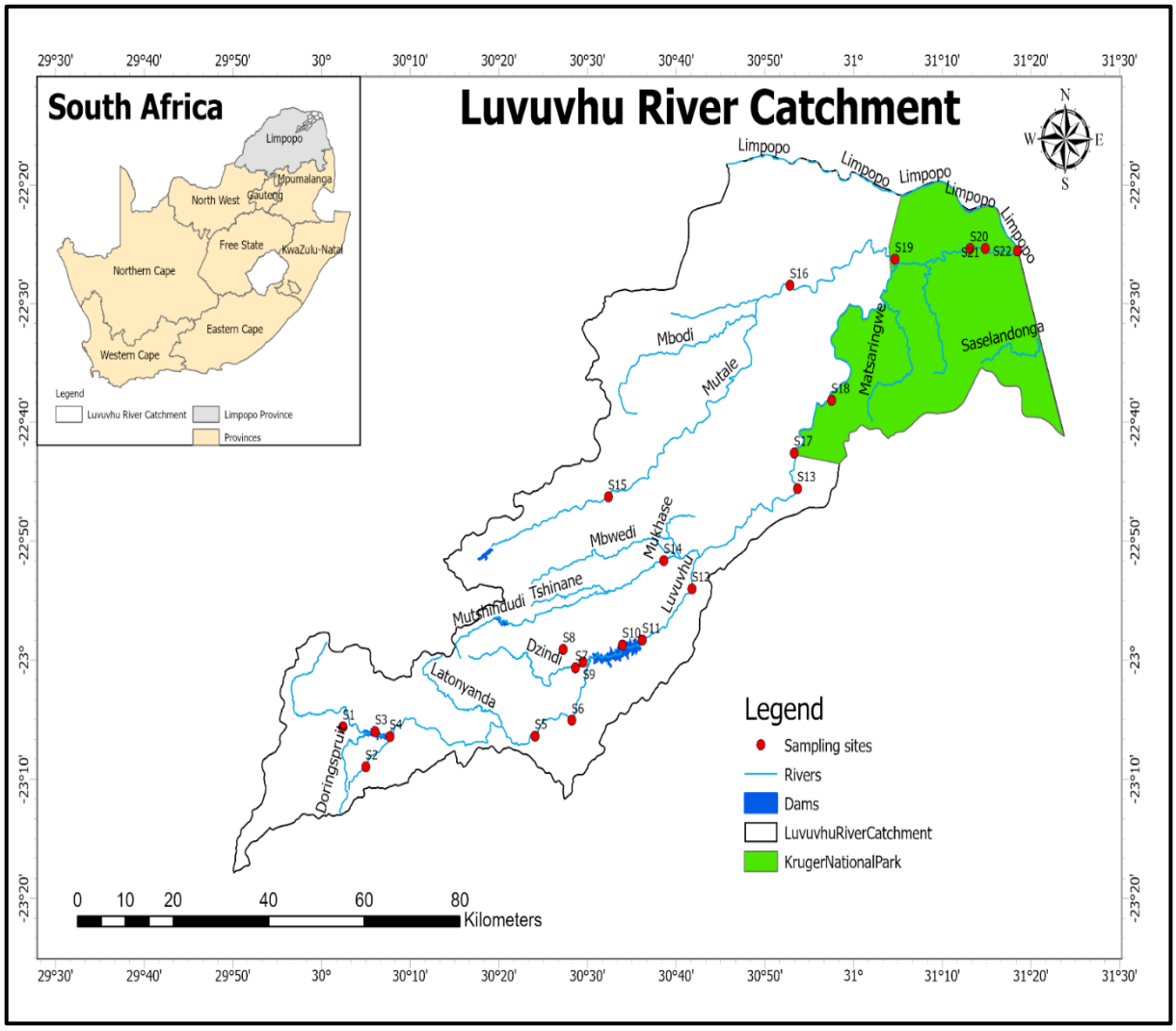

Figure 3.1: Location of sampling sites within the study area

Samples were collected in 500 mL polyethene bottles in triplicates. Sampling bottles were pre-cleaned with deionised water then rinsed with 65% concentrated nitric acid (HNO_3) and then again with deionised water. Further, the sampling bottles were rinsed with river water three times before sampling in the field. Each sample was collected at the site approximately at the river centre where there is high flow with bottle mouth facing upstream to avoid contamination and at a depth of about 2 cm. Samples were collected at an interval of 5 minutes to give each sample a unique identity or allow any disturbed sediment to flow or settle away. Each sample for total trace metal determination was acidified with HNO_3 (5%). After collection, each sample was clearly labelled with the exact date, time, name of the river, geographical coordinates of the sampling site and sampling site name for identification. All samples were kept in a mobile refrigerator at 4°C and transported to the University of Venda, Department of Earth Sciences where they were preserved at 4°C in a refrigerator before analysis (Figure 3.2).

Figure 3.2: Samples in a mobile refrigerator.

Physico-chemical parameters such as temperature, pH, electric conductivity (EC), dissolved oxygen (DO), total dissolved solids (TDS), salinity and turbidity were measured onsite using the YSI Professional Plus multiparameter (YSI Incorporated, Yellow Springs, USA), Waterproof ExStik EC 500 II (Extech, Teledyne FLIR, South Africa) and Extech TB 400 (Extech, Teledyne FLIR, South Africa), respectively.

3.2.2 Sediment sampling

Representative samples from 22 different points of surface sediments were collected from November 2020 to October 2021 at the same sampling points of water collection. A total of 252 sediment samples were collected during the sampling period. Each month, one sediment sample was collected at each sampling point using a 1 kg polythene bag. The sampling procedure followed in this study was adopted from the USEPA (2014).

To ensure no contamination from sampling bags, they were pre-washed with deionised water then with 10% v/v of concentrated HNO_3 and then rinsed numerous times with deionised water. Sediment samples were collected using a shovel and scoop and only the top 2–3 cm was scooped, transferred to pre-cleaned polythene bags, and sealed. All samples were labelled with the date, site name and the river name. After sampling, samples were kept at 4°C inside the mobile refrigerator and transported to the laboratory for further analysis at the

University of Venda. The same condition of 4°C was maintained in the laboratory until sample preparation for digestion.

3.2.3 Physico-chemical analysis (BOD and COD)

Water samples were analysed for BOD_5 (BOD after 5 days) in the laboratory. Briefly, samples were transferred into pre-cleaned BOD bottles and incubated for 5 days at 20°C. Samples were removed from the incubator after 5 days and analysed for available dissolved oxygen using the YSI Professional Plus multiparameter and all the readings were recorded in mg/L. BOD_5 was computed using the following equation:

$$BOD_5 = DO_i - DO_5 \quad (3.1)$$

Where DO_i is the initial amount of dissolved oxygen (mg/L) and DO_5 is the final amount of dissolved oxygen measured after 5 days of incubation (mg/L).

Chemical oxygen demand (COD) was also measured in the laboratory using the Spectroquant Pharo 100 spectrophotometer (Merck, South Africa). The methodology for COD analysis in this study was adopted from Camlab (2016). However, water samples were shaken thoroughly before use and a pipette was used to measure the sample into the COD vials (the vials had pre-measured reagents present with a measuring range of 0-1500 ppm). A blank sample was also prepared using deionised water. All samples were labelled with a marker for identification and were added into a thermoreactor (AquaLytic, AL125, Germany) and the instrument was set to the required temperature of 150°C for 2 hours (Figure 3.3).

Figure 3.3: Samples in thermoreactor for COD analysis.

COD vials were removed from the thermoreactor after 2 hours and allowed to cool for several minutes (approximately 30-45 minutes). The Spectroquant Pharo 100 spectrophotometer was then used to measure COD and the instrument was calibrated with the blank vial before analysing digested samples. The correct COD programme for a specific COD range (0-1500 nm) was selected and the blank vial was wiped with a clean cloth before inserting it into the photometer. Other vials were also wiped and analysed after calibration and the COD readings were recorded on a datasheet in mg/L.

3.3 Nutrients in water samples

Preserved water samples were homogenised and filtered through a 0.45 µm membrane filter using a syringe into 15 mL filter tubes. Major nutrients such as NO_3^-, SO_4^{2-}, Cl^-, and PO_4^{3-} were analysed in the filtrate sample using an ion chromatography instrument (850 IC Professional Ion Chromatography, Metrohm AG, Herisau, Switzerland). The apparatus was calibrated before to analysis using multielement standards of 1 mg/L, 5 mg/L, 10 mg/L and 50 mg/L of the anion of interest.

3.4 Heavy metals and major metals determination in water samples

For element analysis, the study followed the modified method reported by EPA method 3005A, 1992 for metals analysis in water samples. A 45 mL aliquot of the well-mixed sample was transferred to a vessel and 5 mL of 65% concentrated HNO_3 (trace metal grade) was added to the digestion vessel. The vessel was wiped with a dry cloth or tissue and put into the microwave digestor, and the solution was heated at a temperature of 170°C for 40 minutes. The solution was then removed from the microwave and allowed to cool down for 20 minutes. After cooling, samples were filtered through a 0.45 µm membrane filter to remove silicates and other insoluble material that could clog the nebuliser of the analyser. The filtrate solution was then transferred to a volumetric flask (100 mL) and filled up to 100 mL with Milli-Q water. Digested water samples were analysed for major metals (Na, Mg, K, and Ca) with ICP-OES and heavy metals (Zn, Al, Cr, Mn, Cd, Ba, Co, Fe, Cu, As, Mo, Hg, Ni, Pb) with ICP-MS. Each sample was analysed in triplicate to eradicate any batch-specific errors.

3.5 Heavy metals determination in sediment samples

Preparations for the determination of total concentration in sediment sample was performed according to the method described in USEPA Method 3051. Sediment samples were first dried in the oven at a temperature of 60°C for 48 hours. Each sample was grounded to a fine powder

and then sieved through 250 µm stainless steel mesh. Sieved samples were stored in pre-cleaned polyethene containers until digestion and analysis. Microwave-assisted acid digestion was employed for sediments digestion as explained by USEPA method 3051.

Briefly, all digestion vessels and volumetric ware were carefully cleaned with dilute acids (HNO_3 and HCl) for at least 24 hours and rinsed with deionised water before analysis. Storage containers were also cleaned by leaching with more dilute acids (HCl) (approximately 10% V/V) and then rinsed them with Milli-Q water and air-dried at room temperature. A well-mixed sieved sample was weighed to 0.5 g into the pre-cleaned digestion vessels equipped with a pressure relief mechanism (Figure 3.4). 9 mL of concentrated HNO_3 was added to the vessels and an additional volume of 3 mL of HCl was added to the solution as well. The solution was gently swirled before closing the vessel and the vessels were sealed and transferred to the microwave digestor.

Figure 3.4: CEM microwave digestor

The solution was digested using the Microwave Accelerated Reaction System One (MARS 1, CEM, Charlotte, NC USA) at a temperature greater than 175°C for 10 minutes (Figure 3.4). The digested solution was cooled for approximately 20 minutes and the filtrates were diluted to 50 mL with Milli-Q water and then transferred to 50 mL tubes and centrifuged at 3000rpm for 10 minutes. The centrifuged samples were stored in special containers for metal analysis. The total metal concentration of Mn, Fe, Al, Cr, Cu, Zn, As, Co, Ni, Mo, Ba, Hg, Cd, and Pb was determined using the ICP-MS. The analytes were analysed in triplicate to eliminate any batch-specific errors.

3.6 Ecological risk assessment

3.6.1 Potential ecological risk index (RI)

The RI was introduced to assess the impact of one or more factors on the ecosystem of the study area as described in Section 2.6.1. This method accounted for a risk index (RI) that reflects the sensitivity of the community and its toxic response. The RI of heavy metals in sediment samples was computed using equations (2.1-2.4) as described in chapter 2.6.1. The reference values used for Hg, Cd, As, Cu, Pb, Cr, Zn, and Mn in sediment samples were 0.25, 0.30, 13, 45, 70, 90, 95 and 850 mg/kg, respectively (Hakanson, 1980; Turekian and Wedepohl, 1961) and the toxic-response factors for Hg, Cd, As, Pb, Cu, Cr, Mn, and Zn were 40, 30, 10, 5, 5, 2, 1, and 1, respectively (Hakanson, 1980). The RI results were evaluated based on the standard values provided in Table 2.3.

3.6.2 Geo-accumulation Index (*Igeo*)

To understand the current environmental status and trace metal pollution extent with respect to the natural environment, the *Igeo* was used. The index was computed following the method explained in Section 2.6.2. The average shale values were obtained from Turekian and Wadepohl (1961) and results were interpreted using Table 2.4.

3.6.3 Enrichment factor (EF)

The current study applied EF to assess the pollution level and the possible anthropogenic impact on sediments of the LRC. To differentiate anthropogenic from natural components in this study, metal concentration was normalised for the textural property of sediments with respect to Fe. Iron was chosen as a normalisation element because of its origin being exclusively lithospheric and it is an important adsorbent in soils and is a quasi-conservative tracer of the natural metal-bearing phases in a river and coastal sediments (Cui *et al.,* 2022). According to Yi *et al.* (2016), the normalised EF is used to distinguish metal sources emanating from natural and anthropogenic means. The normalised enrichment factor of metals in sediments in this study was computed using equation (2.6) described in Section 2.6.3. The background values of heavy metals were adopted from the world average shale values as reported by Turekian and Wadepohl (1961). Several studies also quantified the degree and extent of metal contamination using the average shale values (Decena *et al.,* 2018; Hasimuna *et al.,* 2021; Shu *et al.,* 2021). Further, EF values were interpreted according to five classes explained in Section 2.6.3.

3.6.4 Pollution Load Index (PLI)

To account for anthropogenic influences in the study area, the Pollution Load Index was employed. The index was used to provide a complete picture of overall pollution by indicating the toxicity status of a particular site or location. The Contamination Factor (CF) values indicating the contamination potential of each element were determined as shown in equation 2.8. The PLI results were interpreted as explained by Rauf *et al.* (2022) and Sojka *et al.* (2018).

3.7 Assessment of human health risks

Various formulas were applied to the data collected to assess the health risk of heavy metals in water samples. The potential risk of each toxic metal was based on the quantification level and was expressed as either a non-carcinogenic or carcinogenic health risk. The two parameters (non-carcinogenic or carcinogenic) were computed using the methods below:

3.7.1 Non-carcinogenic risks

In this study, the common exposure pathways considered were ingestion and dermal absorption routes. The non-carcinogenic risks due to these two routes were determined using the chronic daily intake (CDI) or average daily dose (ADD) of water. CDI estimates the extent of exposure to heavy metal contaminations and was computed using the following equation:

$$CDI_{ingestion} = \frac{C_w \times IR \times EF \times ED \times CF}{BW \times AT} \qquad (3.2)$$

Where, $CDI_{ingestion}$ is the Chronic Daily Intake through ingestion (µg/(kg·day)); Cw is the concentration of heavy metal in water (mg/L); IR is the average daily intake rate of water (L/day); EF is the exposure frequency (day/year), BW is the body weight (kg), ED is the exposure duration (year), CF is the conversion factor and AT is the average time (day).

$$CDI_{dermal} = \frac{C_w \times \mathrm{SA} \times K_p \times \mathrm{ET} \times IR \times EF \times ED \times CF}{BW \times AT} \qquad (3.3)$$

Where CDI_{dermal} represents the exposure dose through dermal absorption (µg/(kg·day)); Cw is the concentration of heavy metals in water (mg/L); SA is the exposure area of skin (cm^2); *Kp* is the dermal permeability coefficient of pollutants in water (cm/h); and ET is the exposure time (h/day). Description for AT, BW, ED, EF, and Cw are in equation 3.2. In this study, Kp values for Cu, Fe, As, Mn, Hg, and Cd were 0.001, while 0.004 for Pb, 0.002 for Cr and Mo, 0.0006 for Zn, and 0.0002 for Ni, respectively (Li *et al.,* 2017; Madilonga *et al.,* 2021). The input parameters in the CDI formula are shown in Table 3.1.

Table 3.1: The input parameters in the CDI formula.

Exposure parameters	Value		Unit	References
	Adult	**Children**		
IR	2.0	0.64	L/day	USEPA (2011)
EF	350	350	Days/year	USEPA (2011)
ED	30	6	Years	USEPA (2011)
CF	1×10^{-6}	1×10^{-6}	*	US EPA (2004)
BW	70	15	Kg	USEPA (2011)
AT	25500	25500	Days	DEA South Africa (2010)
ET	0.58	1	Hours/day	USEPA (1989)
SA	18000	6600	cm^3	USEPA (1989)

** Means a unitless parameter*

Therefore, the non-carcinogenic risk was computed by estimating the hazard quotient (HQ) as shown in the equations.

$$HQ_i = \frac{CDI_i}{RfD_i} \quad (3.4)$$

$$HI = \sum_{i=1}^{n} HQ_i \quad (3.5)$$

Where, HQ_i is the hazard quotient of heavy metals via dermal absorption or ingestion; CDI_i is the Chronic Daily Intake (μg/(kg·day)); RfD is the reference oral dose for each metal (Table 3.2) and HI is the hazard index (Koki *et al.,* 2015). The value of HI was interpreted according to observations reported from several studies which indicated that if HI = 1 or HI < 1, no adverse human health risks would be expected to occur and when the HI > 1, there is a significant risk level (Bamuwamye *et al.,* 2022; Kormoker *et al.,* 2022; Shams *et al.,* 2022).

Table 3.2: Reference oral dose for each metal.

Metal	RfD (mg/kg/day)	Reference
Ba	7.0×10^{-2}	US EPA 2006
Fe	3×10^{-1}	US EPA 2006
Mo	2×10^{-2}	US EPA 2006
Mn	5×10^{-3}	US EPA 2006
Cu	4.0×10^{-2}	USEPA (2011)
Pb	3.5×10^{-3}	USEPA (2011)
Cd	1.0×10^{-3}	USEPA (2011)
As	3 x 10-4	USEPA IRIS 2011
Cr	3 x 10-3	USEPA IRIS 2011
Hg	3.0 x 10-4	USEPA IRIS 2011
Ni	2.0 x 10-2	USEPA IRIS 2011
Zn	0.3	USEPA IRIS 2011

3.7.2 Carcinogenic Risks

In this study, the carcinogenic risks through ingestion were calculated by multiplying CDI with cancer slope factor (SF) (Kormoker *et al.,* 2022) as shown in the equation below:

$$Cancer\ risk = CDI \times SF \qquad (3.6)$$

Where CDI is the chronic daily intake and SF is the cancer slope factor. Acceptable cancer risk values were interpreted in the range of 10^{-6} to 10^{-4}. If its value is less than 10^{-6}, it can be ignored and unacceptable if it exceeds 10^{-4}. SF values used in this study are shown in Table 3.3 below.

Table 3.3: Slope factor value constants used in this study.

Parameter	Value for both adults and children	References
	SF (mg/kg/day)	
Pb	0.0085	DEA South Africa (2010)
Cd	6.1	DEA South Africa (2010)
As	1.50	USEPA IRIS 2011

3.8 Reclassification of land use data in the study area from 73 classes to 6 classes (land-use map)

Before sampling, a reconnaissance survey was conducted using Google Earth Pro and field observations to assess different land use across the catchment. For detailed analysis and mapping, the 20m resolution, raster format South African National Land-Cover 2020 (SANLC 2020) dataset generated from the multi-seasonal 20m resolution Sentinel 2 satellite imagery was used for reclassification. The imagery reclassification analysis was done using the Esri ArcGIS Pro software. According to the Department of Environment, Forestry, and Fisheries (DEFF) (2021), the imagery used represents the full temporal range of available imagery acquired by Sentinel 2 during the period of 01 January 2020 to 31 December 2020 and the overall map accuracy for the SANLC 2020 dataset, calculated from 6835 reference points, is 85.47%. Land use classes were reclassified into 6 new classes i.e., forest, shrub and grassland, water bodies, barren land, agriculture, settlement/built-up, and mines and quarries and their quantities were also computed. The original land use types were reclassified to simplify the data such that it could be more readable and reflect the activities of interest to the study. Thereafter, sampling sites (GPS points) were then overlayed into the land use map using ArcGIS Pro. The spatial variations of water quality parameters with land use were compared to connect the quality and attributes of water use events with their physical locations.

3.9 Statistical analysis

Data in this study were statistically analysed using the statistical package SPSS 25 (International Business Machines Corporation Armonk, NY) and XLSTAT 2022.2.1. The standard deviations and means of the measured parameters in water and sediments were computed. A multivariate analysis method with Principal Component Analysis (PCA) was used to identify potential sources of contamination (anthropogenic and natural) using Rstudio 2022.12.0. Principal Component Analysis was applied to all the datasets. Cluster analysis was used to identify spatial variations and similarities between sites based on water quality parameters. Analysis of variance was carried out to assess mean significant differences of studied parameters between the two seasons (dry and wet season) using the Mann-Whitney test. Also, Microsoft Excel 2019 was used for other computations and sketching graphs.

CHAPTER 4: RESULTS AND DISCUSSION OF PHYSICOCHEMICAL PARAMETERS, MAJOR AND HEAVY METALS IN WATER SAMPLES

4.1 Spatial distribution of different land use and their classification

The land use map derived from the 2020 South African National Land Use Classes is shown in Figure 4.1. It was expected that the results of land use mapping of LRC would provide information on land use quantification, aerial distribution of various land uses and identification, and classification.

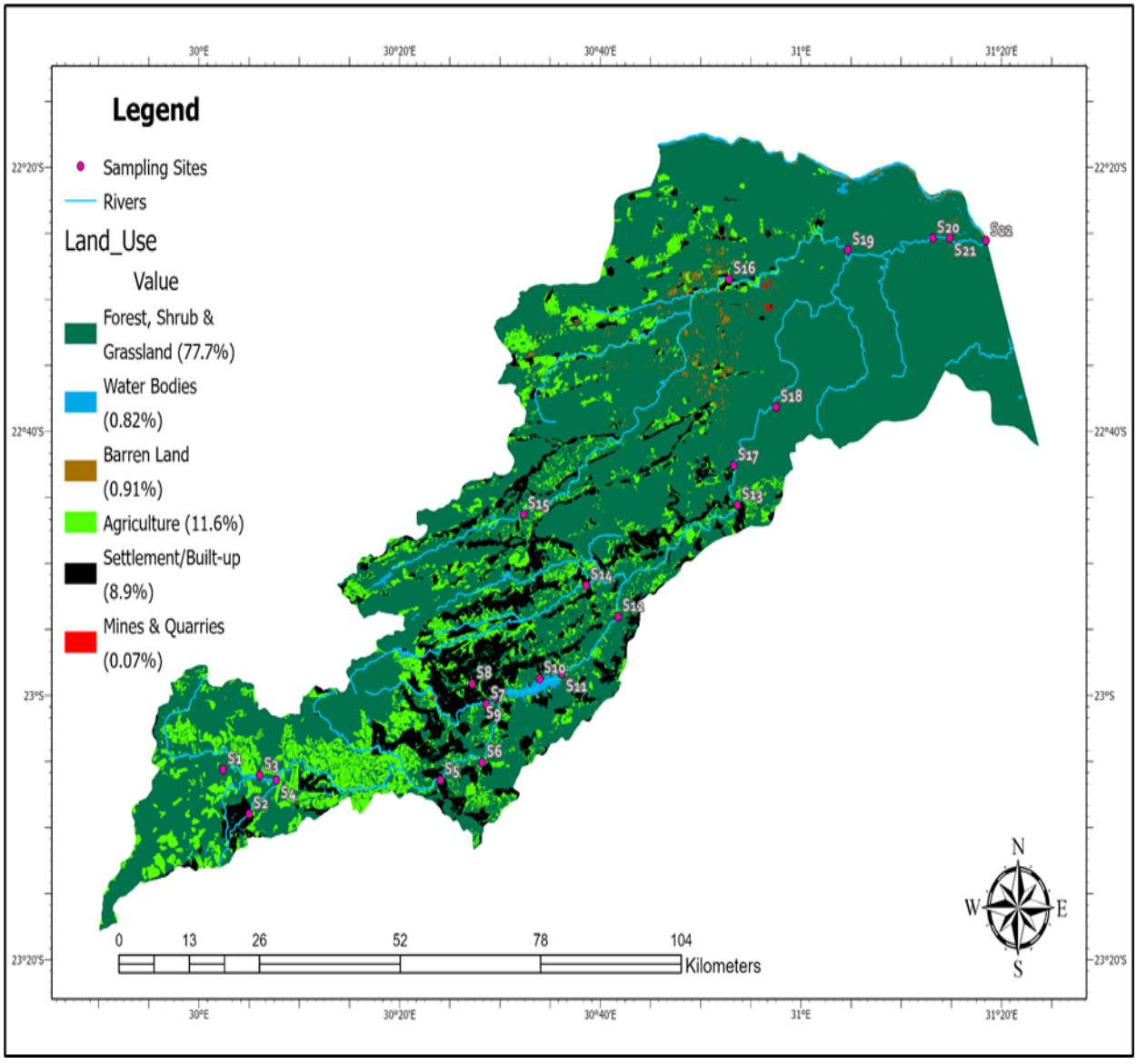

Figure 4.1: Land use map of LRC (2020).

Land use classes were classified into 6 categories: (i) forest, shrub and grassland, (ii) water bodies, (iii) barren land, (iv) agriculture, (v) settlement/Built-up and (vi) mines and quarries. Of

the classified categories, the highest category was forest, shrub and grassland contributing 77.7% of the total area of the catchment followed by agriculture with 11.6% and settlement/built-up with 8.9%. Similar land-use patterns were also identified in Chunati wildlife sanctuary, Bangladesh by Kamrul *et al.* (2018). In the context of this study, forest, shrub and grassland contributed a high percentage largely because of the conservation area (KNP) in the northeastern part of the catchment. Nevertheless, 3 components of the catchment representing various land use activities were identified during the sampling period as shown in Table 4.1.

Table 4.1: Land use activities identified.

Sampling sites	Description and activities
	Upstream
S1	Vehicle traffic and commercial farming
S2	Residential, sewage effluents, vehicle traffic, and dumping site
S3	Commercial farming and car wash
S4	Commercial farming and vehicle traffic
S5	subsistence farming, brickworks, car wash, residential, and vehicle traffic, and sewage effluents
	Midstream
S6	Commercial farming, vehicle traffic, car wash, laundry, and brickworks
S7	Residential, subsistence farming, laundry, and vehicle traffic
S8	Vehicle traffic, gas or fuel station, subsistence farming, car wash, brickworks, and urban and residential, commercial
S9	Sewage effluent, brickworks and subsistence farming
S10	Residential, car wash, and subsistence farming
S11	Car wash, subsistence farming, laundry, Vehicle traffic, recreational activities
S12	Car wash, vehicle traffic, laundry, dumping site, and subsistence farming
S13	Laundry, car wash, subsistence and commercial farming, vehicle traffic, and residential
S14	Subsistence farming, laundry, vehicle traffic, and car wash
S15	Residential, subsistence farming, car wash, laundry, and vehicle traffic
	Downstream
S16	Vehicle traffic, laundry, and subsistence farming
S17	Conserved area (KNP)
S18	Conserved area (KNP)
S19	Conserved area (KNP)
S20	Conserved area (KNP) and vehicle traffic
S21	Conserved area (KNP)
S22	Conserved area (KNP)

4.2 Physicochemical analysis in water samples

Descriptive statistics results from the average values (Appendix 4.1) of the studied physicochemical parameters from 22 sampling sites are exhibited in Table 4.2. The analysed parameters were temperature, pH, turbidity, EC, salinity, DO, TDS, BOD, COD, nitrate, phosphate, and chloride. In general, the physicochemical quality of the water was found good except in a few sampling sites as tailored against the World Health Organisation (WHO) and the South African National Standards (SANS) guidelines for water analysis.

Table 4.2: Descriptive statistics of average physicochemical parameters for all studied sample sites.

Parameters	Unit	Min	Max	Mean	Std. Dev	WHO std	SANS
Temperature	ºC	18.23	27.19	22.93	2.40	*	*
pH		7.49	9.24	8.40	0.52	6.5-8.5	≥5 to ≤9.7
Turbidity	NTU	4.67	151.04	44.17	42.30	<5	≤5
EC	µS/cm	178.24	394.96	252.63	41.73	400	≤170
DO	mg/L	3.06	4.22	3.65	0.35	*	*
TDS	mg/L	184.40	306.53	222.79	34.81	600	≤1200
BOD	mg/L	1.14	1.92	1.42	0.21	*	*
COD	mg/L	2.99	22.55	12.48	5.14	*	*
Nitrate	mg/L	0.51	11.27	2.14	2.23	5	≤11
Phosphate	mg/L	0.42	0.84	0.59	0.14	6.5	*
Sulphate	mg/L	0.94	7.92	2.31	1.48	250	≤250
Chloride	mg/L	6.46	22.79	11.12	3.37	250	≤300
Salinity	mg/L	83.72	223.67	123.62	28.77	*	*

* Represent no standard value, Std. Dev represents standard deviation.

4.2.1 Temperature

River water temperature is an essential physical property that plays a dynamic role in the aquatic environment because it represents the water body's heat concentration (Elassassi *et al.,* 2022). It is also important because it influences the reproduction of aquatic organisms, the solubility of organic matter, and the amount of DO in water (Georginia *et al.,* 2020). As shown in Table 4.2, the average water temperatures recorded ranged between 18.23 ºC and 27.19 ºC with a mean value of 22.93 ºC (Figure 4.2). The recorded temperature values in this study

fall within the WHO standard of <40 ºC (WHO, 2011). Higher temperatures were recorded in sites inside KNP which is close to Zimbabwe and Mozambique which usually records higher average temperatures (about 32 ºC and above) than South Africa (Chanza and Musakwa, 2022). Several studies indicated that high water temperatures can be because of the hot climate and that also affects DO level (Elassassi *et al.,* 2022; Jane *et al.,* 2021; Song *et al.,* 2019).

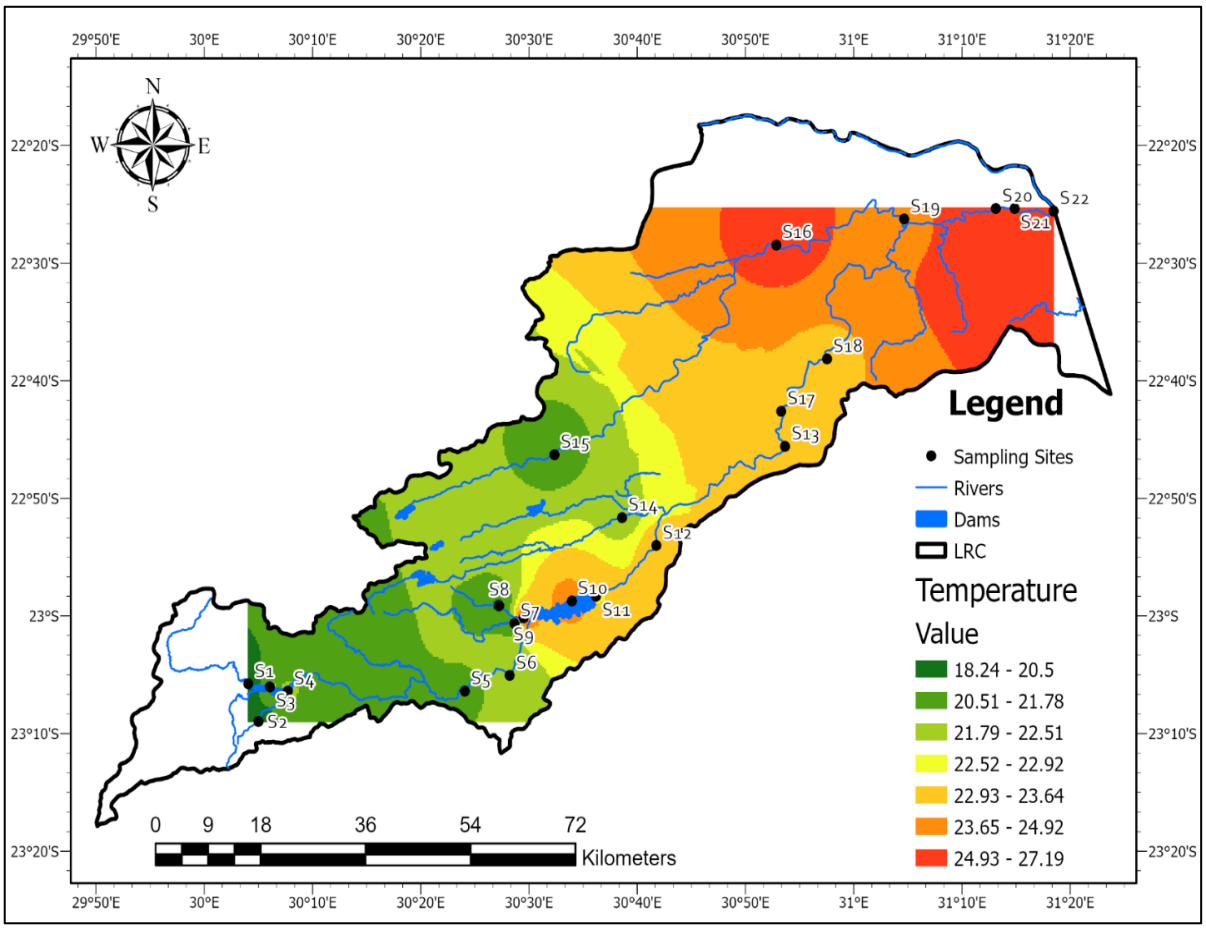

Figure 4.2: Spatial variation of temperature across the LRC.

According to the geospatial map in Figure 4.2, a drastic variation was recorded between sampling sites located upstream and downstream of the catchment. In comparison, downstream sampling sites recorded higher temperatures than upstream and midstream sampling sites. Site S20, which is part of the KNP (conserved area) recorded the highest temperature (27.19 ºC) whereas S1 (located within the agricultural zone) recorded the lowest temperature (18.24 ºC), respectively. These results are similar to those of Hasan *et al.* (2022) from the Turag River in Bangladesh in their study.

In the current study, the geographic location of the two catchment components (upstream and downstream) also played a major role in variation although the downstream part is mainly

consisting of forest, shrubs and grassland, a few settlements and agricultural areas. However, the midstream part of the catchment appeared to be the point of transformation between upstream and downstream. Agricultural activities showed fewer impacts on water temperature as compared to human settlements (Figure 4.3).

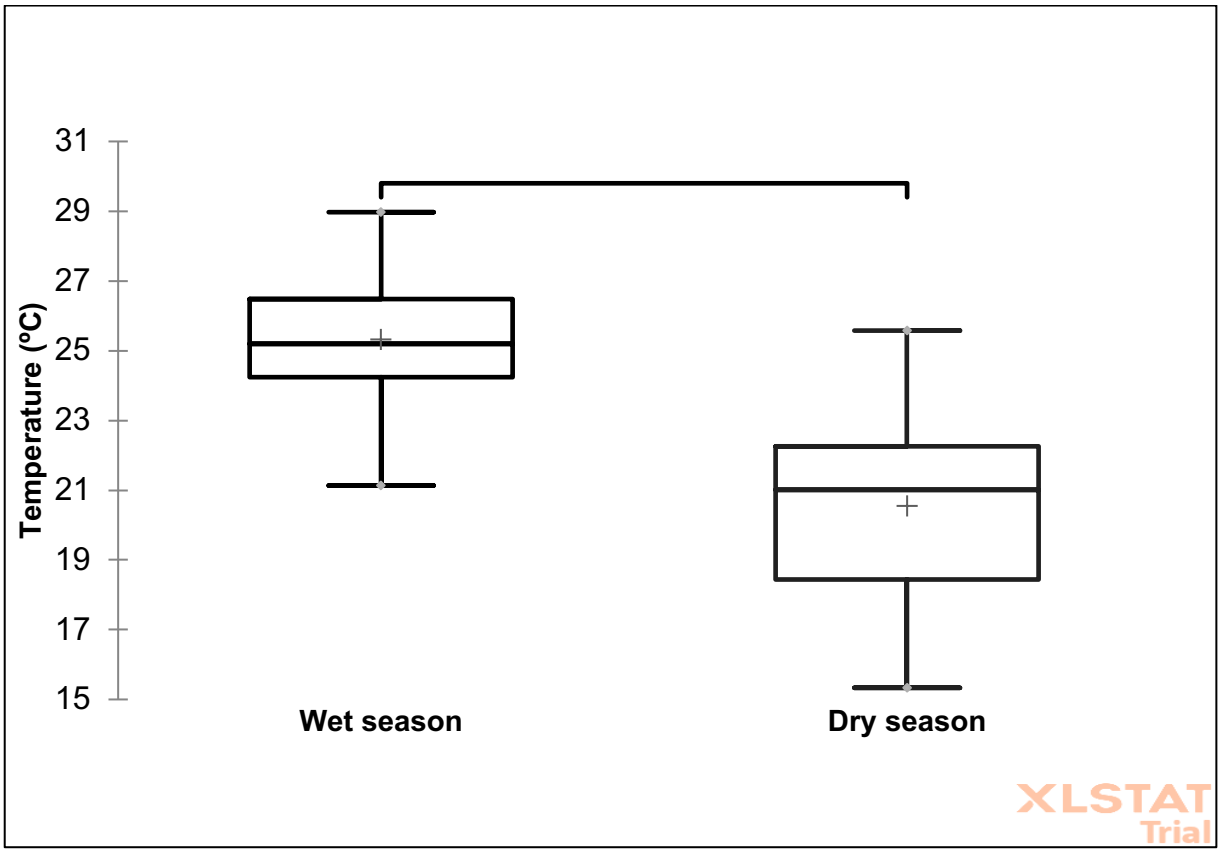

Figure 4.3: Box and whisker plots of seasonal variation of temperature in the LRC.

From Figure 4.3, temperature values obtained from the LRC varies from 15.33 ºC to 25.58 ºC and mean value of 20.54 ºC during the dry season and 21.13 ºC to 28.97 ºC with a mean value of 25.32 ºC during the wet season. Similar results are also observed in the Lower uMfolozi Floodplain System, South Africa by Dlamini *et al.* (2021). The data showed statistically significant variation ($p<0.05$) between the mean values of the wet and dry seasons, and the wet season recorded higher temperatures than the dry season. This condition is normal for regions that receive high solar radiation (summer) during the wet season such as the LRC. These results are different from those reported by Georginia et al, (2020) in Mini-Ezi Stream in Elele-Alimini, Emohua Local Government Area of Rivers State Nigeria, which recorded high temperatures during the dry season and vice versa. However, the observed values in terms of seasonal variation fall within the WHO standard of <40 ºC (WHO, 2011).

4.2.2 pH

The pH value is a measure of the hydrogen ion activity in a water sample (DWAF, 1996). However, the pH value of 7 is regarded as neutral. In water quality (drinking water), pH values ranging from 6.5-8.5 indicate the good status of water quality condition (WHO, 2011). As shown in Table 4.2, the analysis showed that the average values of pH ranged from 7.49 to 9.24 with a mean value of 8.40. The pH values reported in this study were within the South African National Standards (SANS) of 5 to 9.7. These values varied from site to site as shown in Figure 4.4 below.

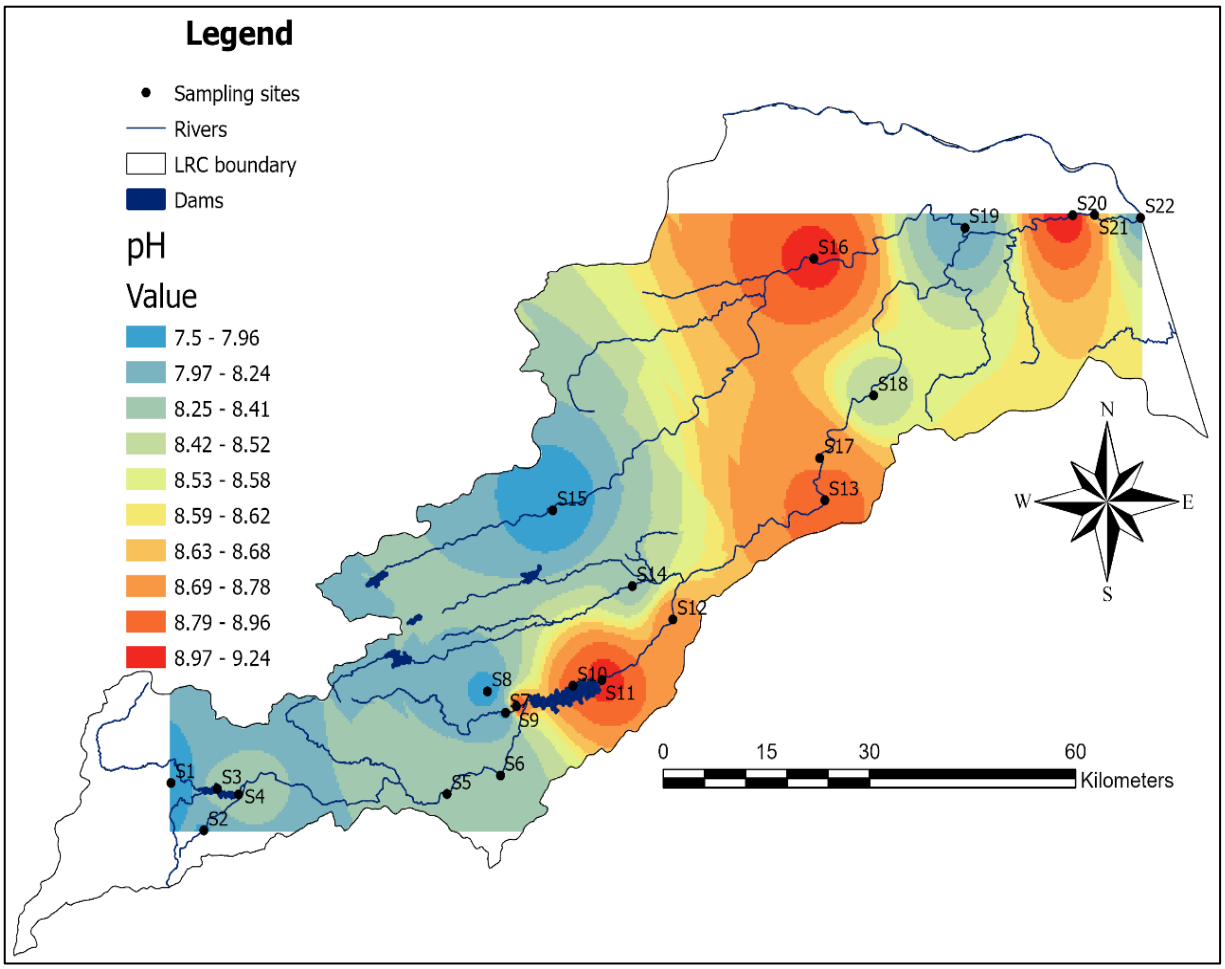

Figure 4.4: Spatial distribution of pH values between sampling sites.

The Interpolated Distance Weighted (IDW) map presented in Figure 4.4 shows the spatial distribution of pH in the LRC during the sampling period. IDW shows similarity in pH values measured from all the upstream sites (S1, S2, S3, S4, S5) and some parts of the mid-stream sites (S6, S7, S8, S14, S15) and downstream sites (S18, S19, S22) ranging between 7.5 and 8.52, respectively. Alternatively, mid-stream sites (S9, S10, S11, S12, S13) and downstream

sites (S16, S17, S20, S21) also display correlative results ranging from 8.53 to 9.24. Nevertheless, the highest pH value was recorded at site S20 (downstream).

According to Soliman *et al.* (2022), the optimum and suitable pH values for fish growth and health should be in the range of 6 to 9 and fish mortality could be recorded outside of this range. Furthermore, water with high and low pH values is very harmful to a variety of aquatic life. However, pH values observed in the current study are within the recommended range for fish growth and health. At all sampling sites, the mean values of pH are greater than 7.00, indicating the slightly alkaline nature of the river systems. In addition, high pH prevents most micronutrients and heavy metals from being taken up by plants and becomes available at lower pH levels. Therefore, the highest pH values recorded in this study were higher than the DWAF (1996) standard of 6.5 to 8.4 for crop irrigation.

Although, there is a significant variation in pH values across all the sites, which could be linked to changes in land use i.e., agricultural activities and animal wastes in upstream sites, wastes from municipalities, industries and residential (urbanisation and rural settlement) in mid-stream sites and rural settlement, wild animal wastes and mining activities in downstream sites. Consequently, the geospatial map (Figure 4.4) shows that agricultural land use areas recorded slightly lower pH values when compared to settlement/Built-up. High pH values from sites near settlement/built-up could be attributed to various wastes disposed of in river systems or near the riverbank (Madinga, 2021).

Moreover, mean pH values show low regression correlation between the two seasons (R^2 = 0.10) and no significant variation ($p>0.05$) between wet and dry seasons (Figure 4.5). The values of pH varied from 7.55 to 9.17 with a mean of 8.33 in the wet season and 7.24 to 9.89 with a mean of 8.48 in the dry season, respectively. The river water was slightly alkaline, which is higher than the report of Dlamini *et al.* (2021) from Lower uMfolozi Floodplain System, South Africa. This may be due to the presence of bicarbonate and the biodegradation of wastes in the soil that may have been washed into river systems by rainfall (Seng *et al.,* 2018). However, the observed pH values in this study are typical for such river systems not badly impacted (Parvathy *et al.,* 2022).

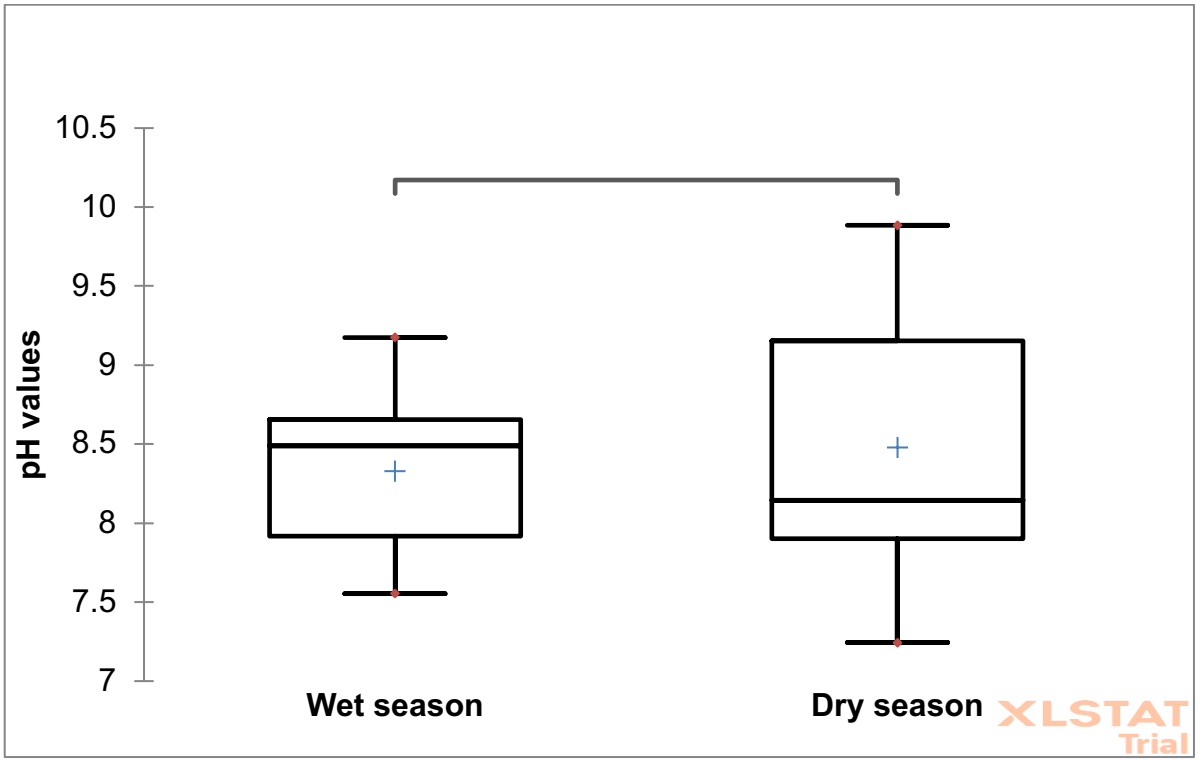

Figure 4.5: Box and whisker plots of pH values during the dry and wet seasons.

4.2.3 Turbidity

Turbidity of river water refers to the degree of cloudiness in water caused by suspended and fine insoluble particles (Wokoma *et al.,* 2017; Duru *et al.,* 2018). The turbidity of river water is also an approximate measure of pollution intensity (Duru *et al.,* 2018). As shown in Table 4.2, the average values of turbidity range from 4.67 to 151.04 NTU with a mean of 44.17 NTU. High turbidity values were recorded in site S22 (Figure 4.6). In general, high values were recorded in downstream sites; S17, S18, S20, S21, and S22 except for S19 and S16 which show variation in values. High turbidity in downstream sites could be attributed to animals waddling in water (Figure 4.7). According to the IDW map below, agricultural areas (upstream) show low turbidity values as compared to other land uses. However, the lowest turbidity values are recorded in S10 (4.67 NTU) located mid-stream of the catchment. This could be attributed to the stagnant condition of the water at Nandoni Dam (S10) which allows sedimentation or settling to occur leaving the water appearing clearer.

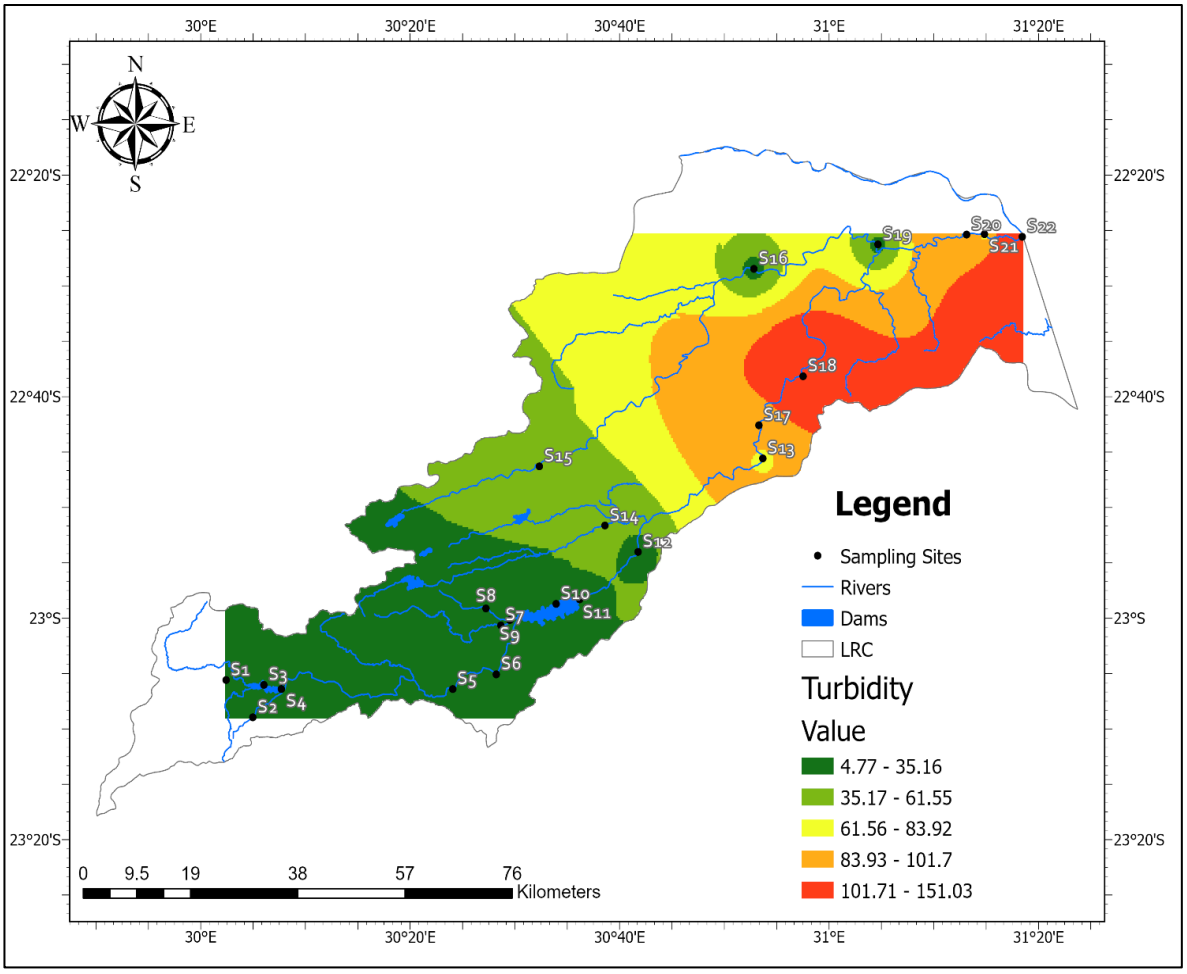

Figure 4.6: Spatial variation of turbidity values in water samples.

Figure 4.7: Animal waddling in Luvuvhu River at KNP

Additionally, the IDW shows a huge spatial variation trend in the midstream sites where the main land use activity is settlement/built-up with few agricultural activities. This was expected due to various discharges coming from settlement/built-up areas. The results obtained in this study were higher than those reported for Lake Msingazi in KwaZulu-Natal near Matenjiwa (2019). The average values were also above 5 NTU standard for drinking purposes by WHO and SANS. However, a statistically significant variation ($p<0.05$) is also observed between seasons, as highlighted in Figure 4.8.

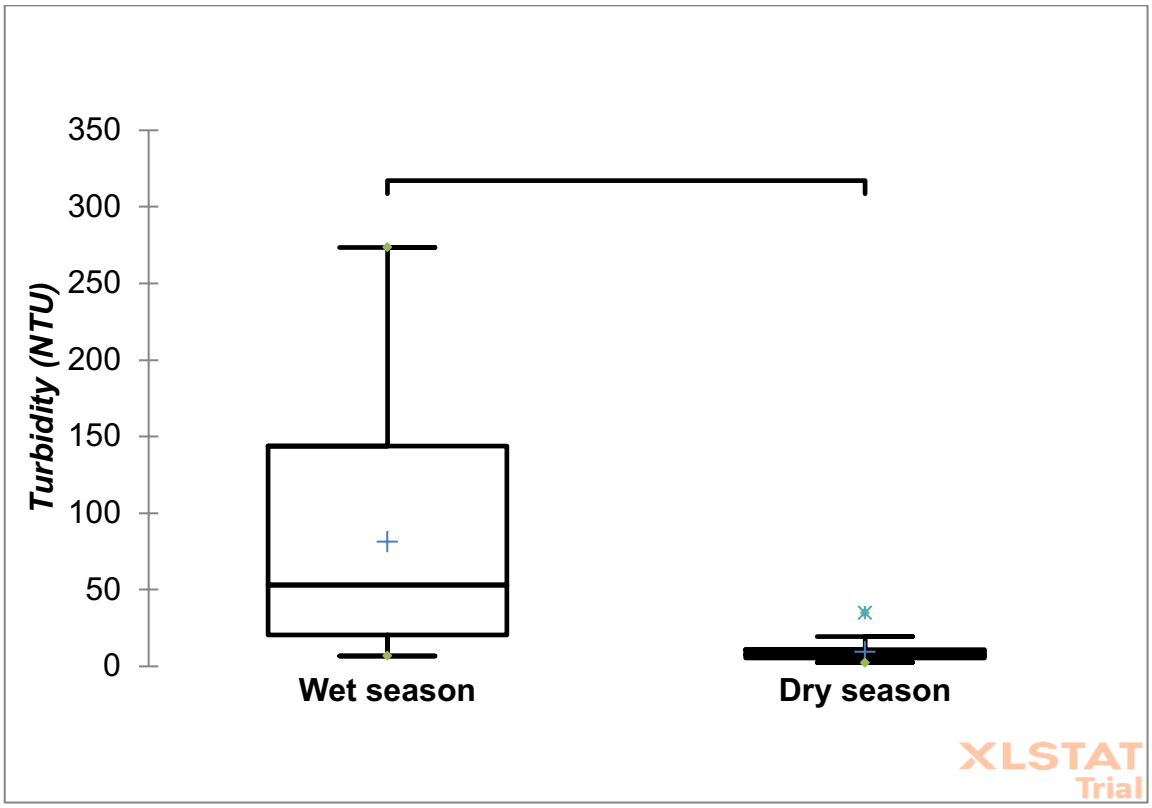

Figure 4.8: Box and whisker diagram for turbidity during the dry and wet seasons.

As shown in Figure 4.8, turbidity values were significantly higher in the wet season than in the dry season. This could be attributed to high runoff-carrying sediments during the wet season (Georginia *et al.,* 2020; Seng *et al.,* 2018). The turbidity values, ranged from 6.77 to 273.49 NTU with a mean of 81.42 NTU in the wet season and 2.54 to 34.97 NTU with a mean value of 9.40 in the dry season, respectively. The recorded values are beyond WHO's permissible limit and SANS of 1 NTU for drinking purposes. Banda (2020) also reports turbidity values from the Umgeni River catchment, Kwazulu-Natal, South Africa which was higher than the permissible limit though the results of their study were higher than the results of this study. Philibert *et al.* (2022), indicate that high turbidity in water cause reduced transparency of water due to the presence of particles such as silt or clay, plankton, finely divided organic matter, or other microscopic organisms and thus affecting the biological productivity of aquatic

organisms. Moreover, the South African Water Quality Guidelines do not have turbidity regulation for crop irrigation at the moment (DWAF, 1996).

4.2.4 Salinity

Descriptive results as presented in Table 4.2 reveals that the average salinity values ranged from 83.72 mg/L to 223.67 mg/L with a mean value of 123.62 mg/L from all the sampling sites. The concentration of salinity in a water body is essential to aquatic life but only certain species can survive in water with high salinity. Besides, some aquatic species can live in saline environments, but many cannot survive when the salinity levels are very high. Based on the results obtained from this study, the highest concentration of salinity is recorded at site S2, and the lowest concentration was recorded at S14. High salinity values across site S2 could be attributed to sewage effluents along the stream. The IDW map as presented in Figure 4.9 also show spatial variation amongst the sampling sites.

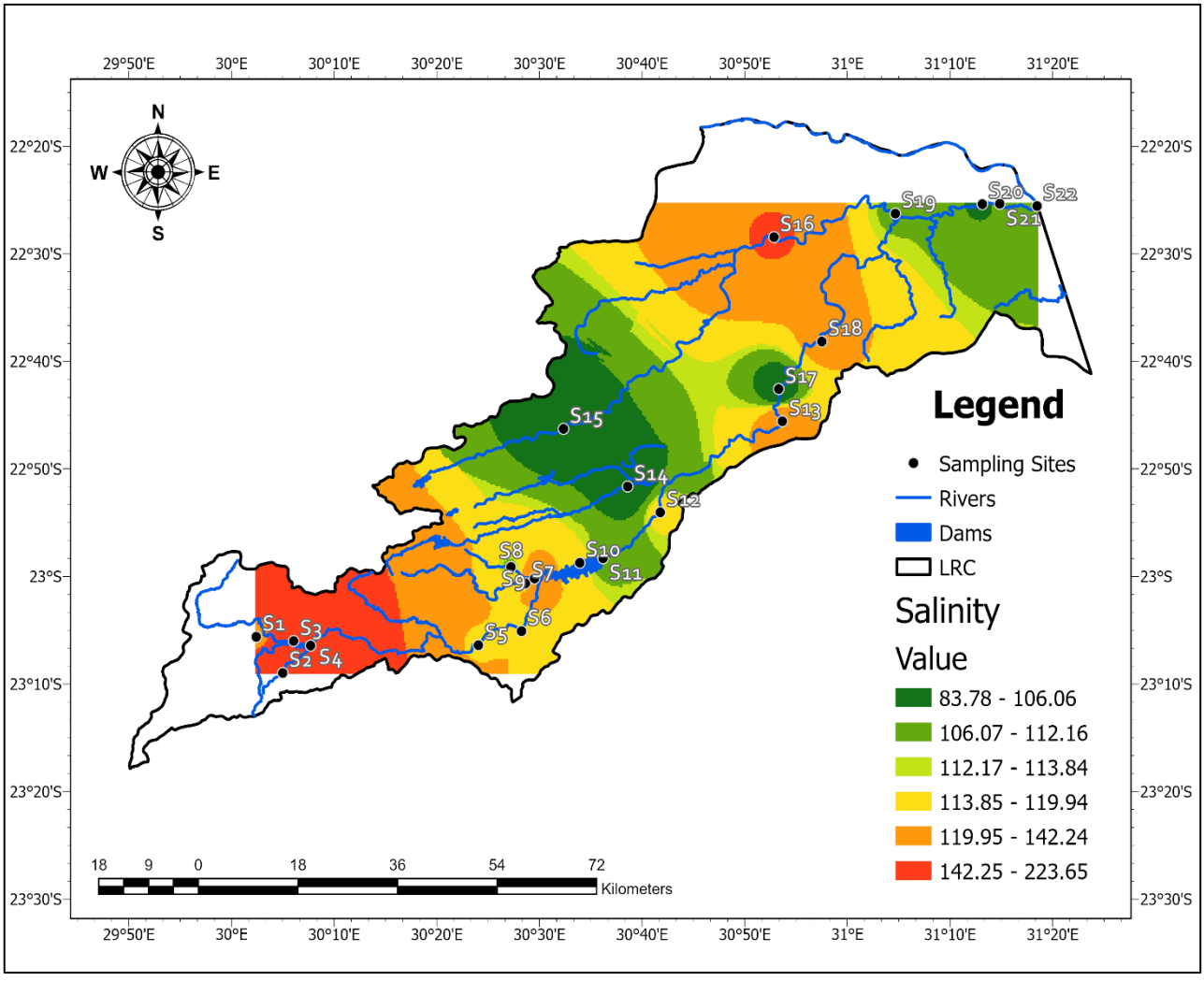

Figure 4.9: Spatial variation of salinity in water samples.

From the IDW map results, high salinity concentrations are recorded from the upstream part of the catchment where most of the land uses are mainly agriculture. Thus, agricultural activities contributed more to salinity values than other land uses. Several studies also stated that agricultural activities (irrigation practices) can cause a significant increase in salinity and TDS levels because of nitrates and phosphates (Tas, 2019; Tokatli, 2019). However, a substantial diversity of salinity values is also observed across the midstream component of the catchment where there's a mixture of land uses (Figure 4.9).

In terms of seasonal variations, a statistically significant difference ($p<0.05$) was observed between seasons (Figure 4.10). Salinity concentrations were significantly high at site S2 (273.17 mg/L) during the dry season, which could be due to the discharge of sewage effluents into the water body (Karringmelk Spruit) associated with low river flows (Saha *et al.,* 2022). Huang *et al.* (2022) indicated that the net result of the change in sediment adsorption and microbial processing is that during the low flow season, salinity increases.

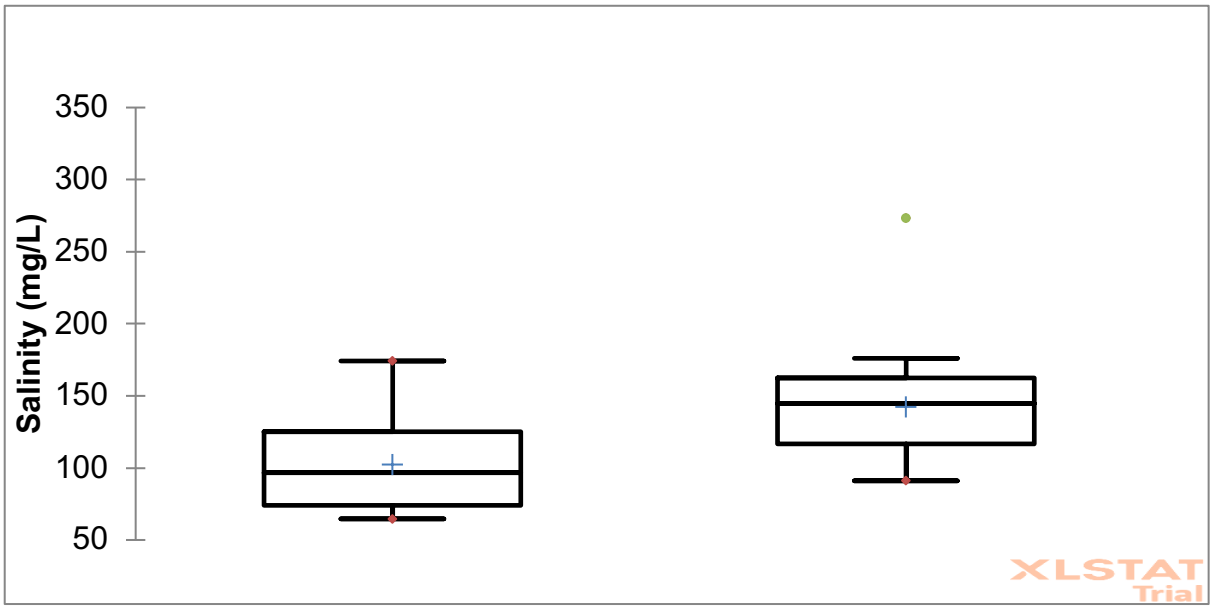

Figure 4.10: Box and whisker plots of seasonal variation of salinity concentration in the LRC.

Furthermore, the average salinity values ranged from 64.64 mg/L to 174.17 mg/L with an average value of 102.12 mg/L in the wet season and 91.04 mg/L to 273.17 mg/L with a mean value of 142.35 mg/L in the dry season (Figure 4.10). These results were higher than those obtained from surface water in Umhlatuzana River, Ethekwini, South Africa (Webster, 2020), Terme River, Turkey (Ustaoğlu *et al.,* 2021), and Giresun Province, northeastern Turkey (Aydin *et al.,* 2021). Consequently, such significant-high salinity values would pose a threat to aquatic ecosystem within the study area, as salinity affects the quantity of dissolved oxygen in the water.

4.2.5 Dissolved Oxygen (DO)

Almost all the water samples collected downstream (i.e., S18, S16, S19, S20, S21, S22) showed considerably low DO values (Figure 4.11). The minimum value was recorded from S21 (3.06 mg/L), and the maximum was noted in S11 (4.22 mg/L). The lowest values reported in site S21 might be due to high temperatures in the northeastern part of the catchment as well as animal wastes combined with the microbial decomposition of the organic matter (Arora and Keshari, 2021). In general, the midstream sites showed considerably high values of DO which could be attributed to low-mid temperatures across the area and turbulence flow (DWAF, 1996).

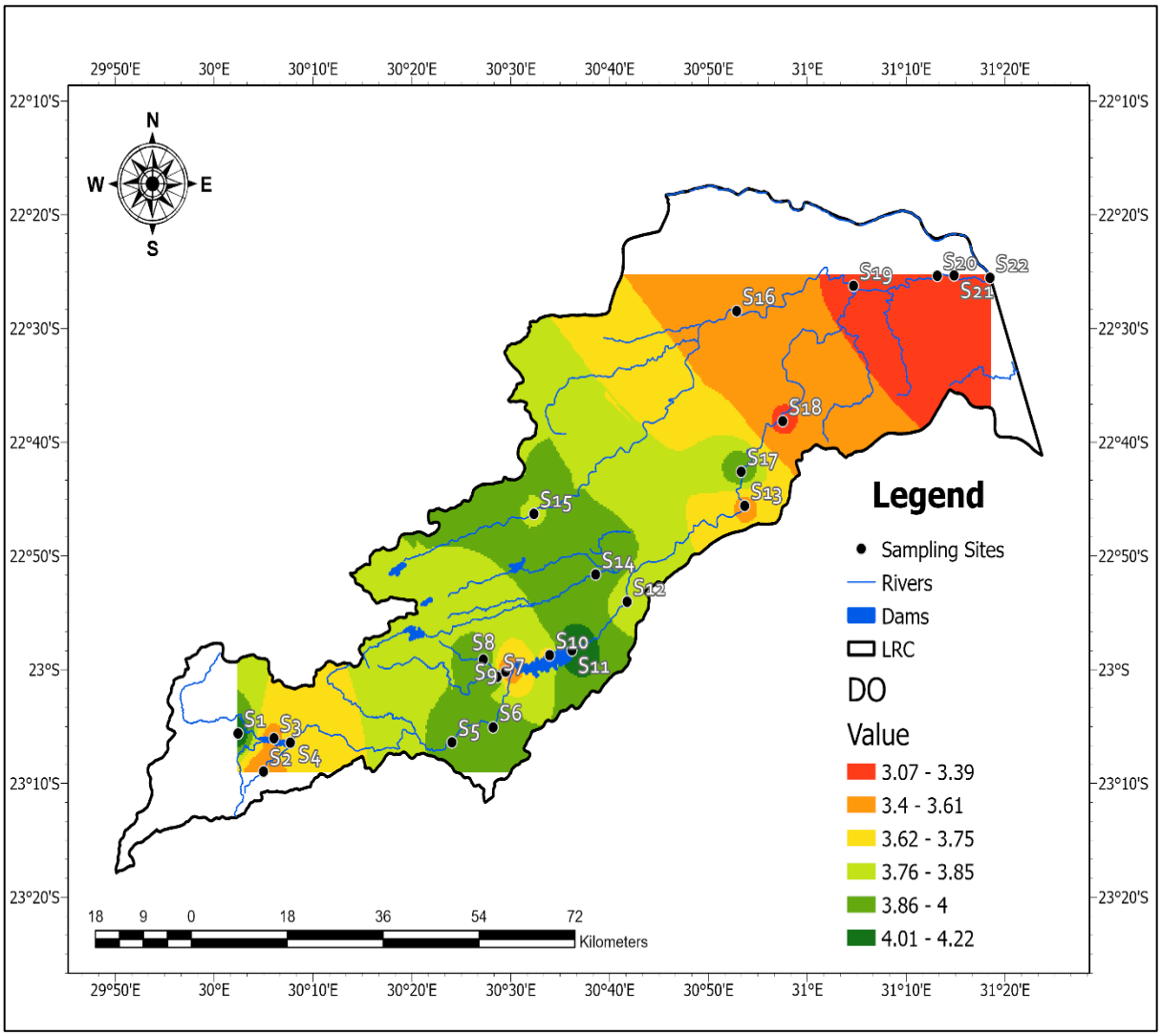

Figure 4.11: Spatial variation of DO in water samples.

Several studies also indicate that high temperature reduces oxygen holding capacity in water (Jindal *et al.,* 2022; Semy *et al.,* 2020; Ustaoğlu *et al.,* 2021). Worldclim (2022) reports higher temperatures across the north-eastern part of the catchment which correlates to the results

obtained in this study (Figure 4.11). However, the results of this study are lower than those reported by Webster (2020) for the Umhlatuzana River in Ethekwini. Ferahtia *et al.* (2021) also report results in a similar range in their study of surface water quality assessment in the semi-arid region of El Hodna watershed, Algeria. The reduction of DO in water might indicate a high nutrient load and organic matter pollution (Jindal *et al.,* 2022). Overall, the average values of DO were lower than the recommended value of 5 mg/L (DWAF, 1996) for the protection of aquatic life. In South Africa, there are no guideline standards for DO requirements for crop irrigation water though DO in the irrigation water improves a plant's overall health by increasing nutrient uptake and conversion efficiency.

However, statistically significant variation ($p<0.05$) between seasons (dry and wet) were recorded (Figure 4.12). The average values of DO vary between 3.67 and 5.85 mg/L with a mean value of 4.91 mg/L during the wet season and 2.21 and 3.36 mg/L with a mean value of 2.73 mg/L during the dry season. The highest values were recorded during the wet season, though high temperatures were also recorded during this season. The recorded value recorded indicates that the river water within the study area can still sustain fish and other aquatic life in the river at a moderate level during the wet season (Prambudy *et al.,* 2019).

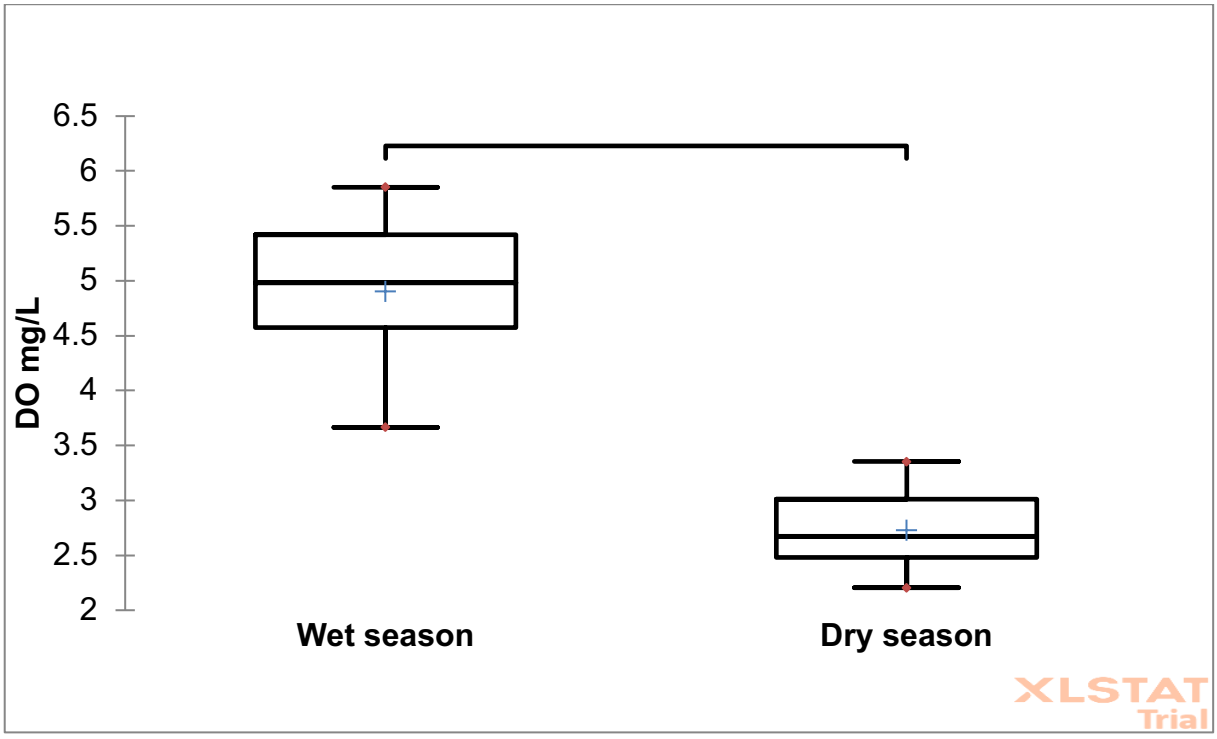

Figure 4.12: Box and whisker plots of seasonal variation of DO in the LRC.

The depletion of DO during the dry season could be due to microbial decomposition of the excessive organic matter discharged into the river during this low flow period (Xu *et al.,* 2022). The amount of DO could also be attributed to high salinity during the dry season. Studies also

reported similar effects of salinity in the water, implying that the amount of DO highly depends on the salinity of water such that oxygen is low in high saline waters and vice versa (Muoi *et al.,* 2022). The results reported in this study differ from the study reported by Xu *et al.* (2022) in Yangzong Lake, China, where DO abundance was high in the dry season and DO abundance was low in the wet season. Low DO in the river increases adverse effects on the biota (Hong *et al.,* 2022). Therefore, the average amount of DO measured in this study during the dry season implied high stress on the aquatic ecosystem. This could lead to the death of fish in the river system (Hong *et al.,* 2022). For example, a fish was found dead at site S20 inside KNP (Figure 4.13) during the sampling period and based on the geospatial map (Figure 4.11), it could be observed that the site reported low DO levels.

Figure 4.13: Dead fish found in Kruger National Park during sample collection.

4.2.6 Biological oxygen demand (BOD) and chemical oxygen demand (COD)

In water quality assessment, BOD is defined as the measure of the amount of dissolved oxygen removed from water by aerobic bacteria for their metabolic requirements during the breakdown of organic matter (Alewi *et al.,* 2021). It is normally used to determine organic

pollution in wastewater and surface water (Prambudy *et al.,* 2019). On the other hand, COD is the measure of the amount of oxygen needed and required for the oxidation of both inorganic and organic material in water bodies (Prambudy *et al.,* 2019). However, a low concentration of COD indicates that water is still in a good condition and a high concentration indicates a deterioration of water quality.

As shown in Table 4.2, the average concentration of BOD ranged from 1.14 to 1.92 mg/L with a mean value of 1.42 mg/L. The highest value of BOD was observed at site S17 (1.92 mg/L) and the lowest was at site S18 (1.14 mg/L) (Figure 4.14) and these results were within the WHO standards (5 mg/L). The low BOD level is probably because there are some total nutrients discharged into the river which affects BOD (Alewi *et al.,* 2021). However, most downstream sites show a low concentration of BOD as compared to other parts of the catchments. In addition, a discrepancy variation was observed at midstream sites, and this could be attributed to different land use within this area (waste discharged into the river as well as sewage effluents and fertilisers from agriculture) (Abdullahi *et al.,* 2021). In comparison, the results of this study are lower than those of a study conducted by Motholo (2014) in dams and Rivers of Qwaqwa in the Free State Province. The overall spatial result indicates that the LRC is within the desirable and suitable range.

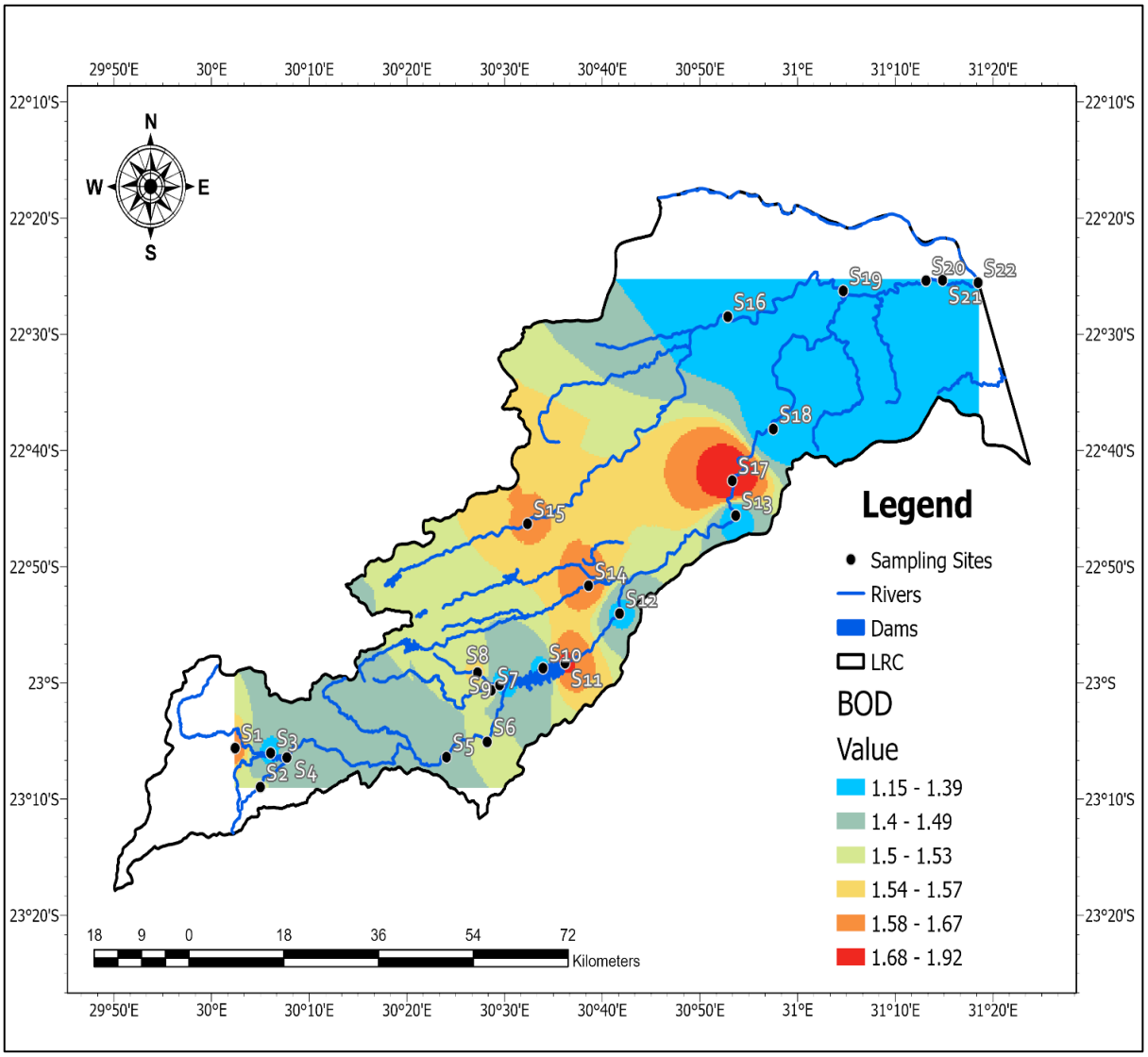

Figure 4.14: Spatial variation of BOD levels across sampling sites.

In this study, BOD results also show a significant variation ($p<0.05$) in concentration during the wet and dry seasons. Mean BOD levels ranged from 0.85 to 2.58 mg/L with an average of 1.61 mg/L in the wet season and 0.47 to 1.25 mg/L with an average of 0.87 mg/L in the dry season (Figure 4.15). Prambudy *et al.* (2019) report that BOD has been found positively correlated to domestic sewage (organic pollution) and thus could indicate the presence of microbial activities in the water bodies (LRC). Based on the results observed in this study, BOD values are reported high in the wet season than in the dry season and this is different from the results reported in water of Prancak Village, Sepulu District, Bangkalan (Daroini *et al.,* 2020). The high BOD during the wet season may be due to high runoff containing sewage, animal wastes, and fertilisers.

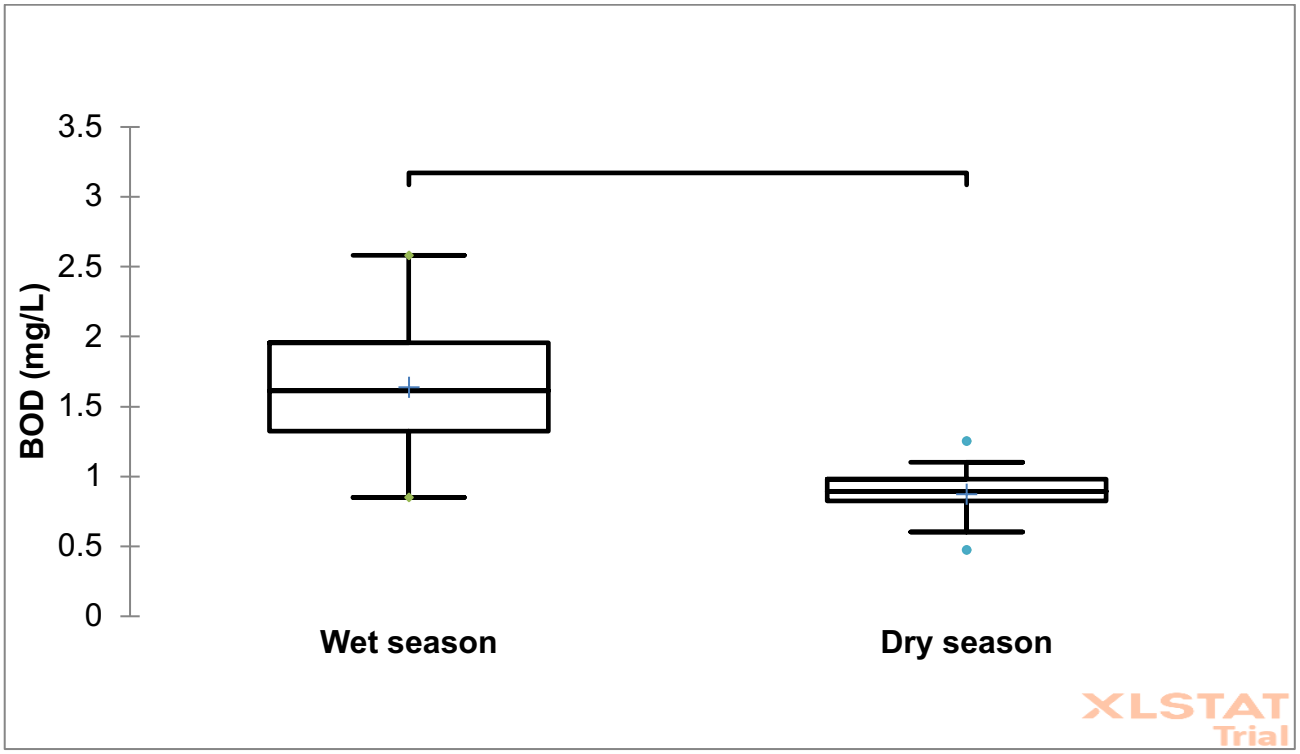

Figure 4.15: Box plot showing the seasonal variation of BOD values in the LRC.

Furthermore, the COD observed ranged between 2.99 to 22.55 mg/L with an average value of 12.48 mg/L (Table 4.2). Results show a significant variation in COD values between sampling sites. However, the highest value was measured in the midstream and may be attributed to the discharge of wastewater into the river upstream of S9. As shown in Figure 4.15, it is noted that COD values vary the most where there is a mixture of land uses. According to Prambudy *et al. (*2019), a high concentration of COD represents deteriorated water quality, and a low concentration indicates better water quality. Therefore, in the context of this study, COD levels are considerably low, and this indicate good water conditions. The highest recorded values are within the DWAF (1996) guideline standard.

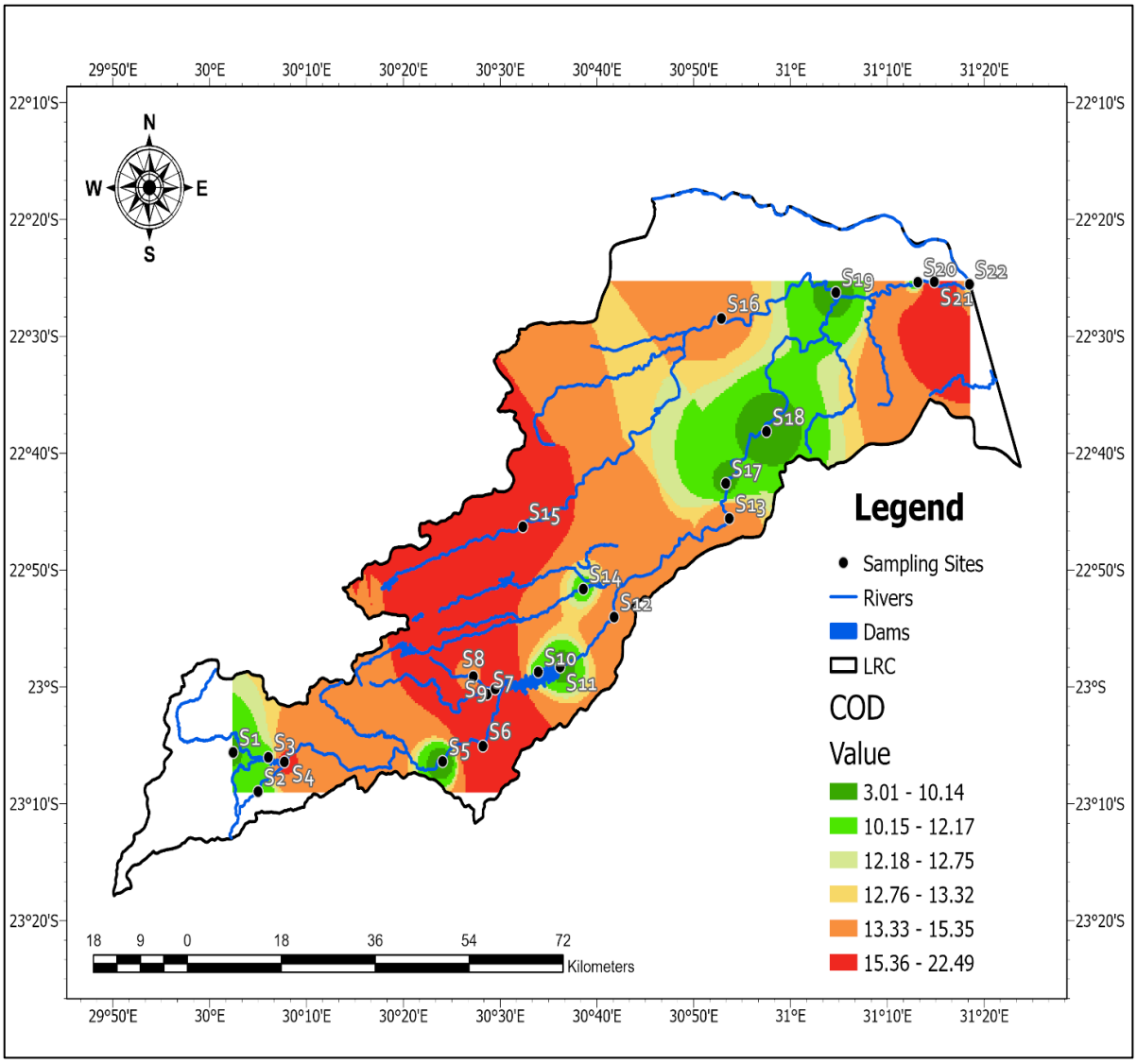

Figure 4.15: Spatial variation of COD in water samples.

There was a general seasonal variation in COD values across all the sampling sites. There was no statistically significant variation ($p>0.05$) between seasons. However, COD concentration ranged between 1.84 and 36.37 mg/L with a mean of 10.78 mg/L during the wet season and between 2.71 and 29.50 mg/L with a mean value of 13.16 mg/L during the dry season (Figure 4.16). The seasonal results are within the DWAF (1996) guideline standard. Nevertheless, the highest COD concentration was observed during the wet season which could have been influenced by high rainfall runoff containing an elevated organic matter contained in the discharge. However, these results are lower than those report in a similar study of Naidoo (2013) in the Ethekwini Metropolitan Area at Kwa-Zulu Natal.

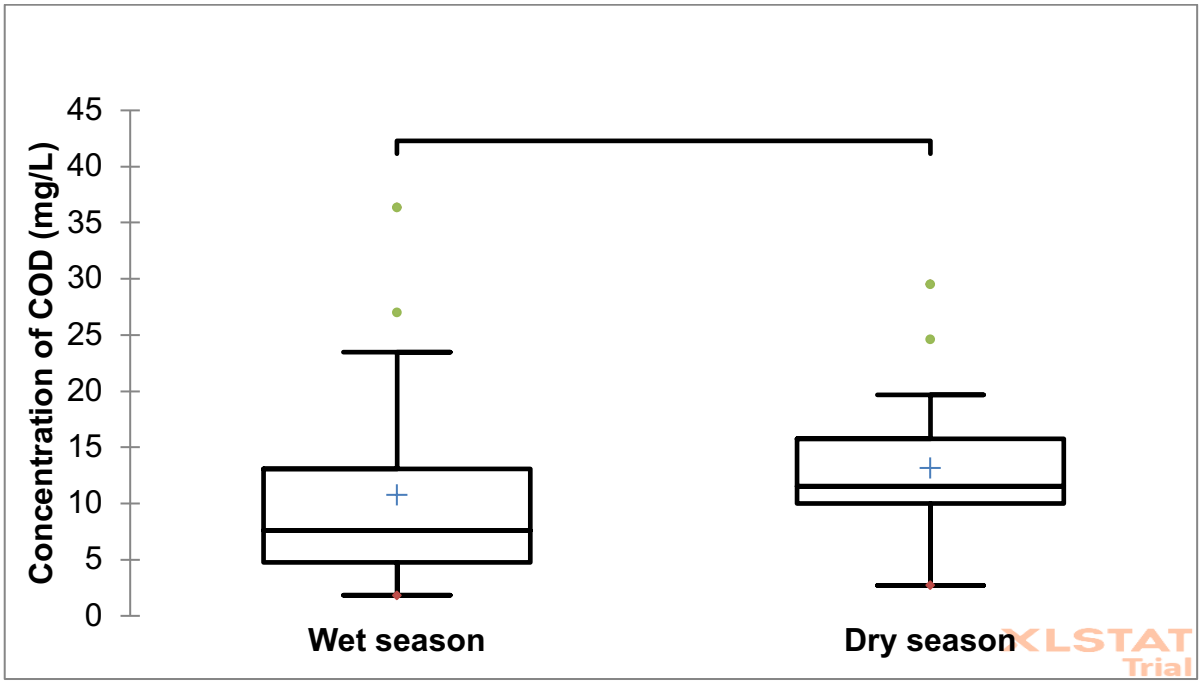

Figure 4.16: Box plot showing the seasonal variation of COD values in the LRC.

4.2.7 Nitrate

As stated by Meride and Ayenew (2016) and Sharma *et al. (*2022), nitrate is one of the major water quality parameters responsible for causing blue baby syndrome in infants. Its sources are industrial wastes, sewage and nitrogenous fertilisers (Meride and Ayenew, 2016). According to the WHO (2011), the maximum recommended limit of nitrate in drinking water is 36 mg/L. As shown in Table 4.2, the average results showed that the concentration of nitrate ranged from 0.51 to 11.27 mg/L in the LRC with a mean value of 2.14 mg/L. These results indicate that nitrate levels in all areas of the study area were below the permissible limits recommended by WHO (2011) and SANS. Figure 4.17 shows the spatial distribution of nitrate levels during the sampling period through the IDW map.

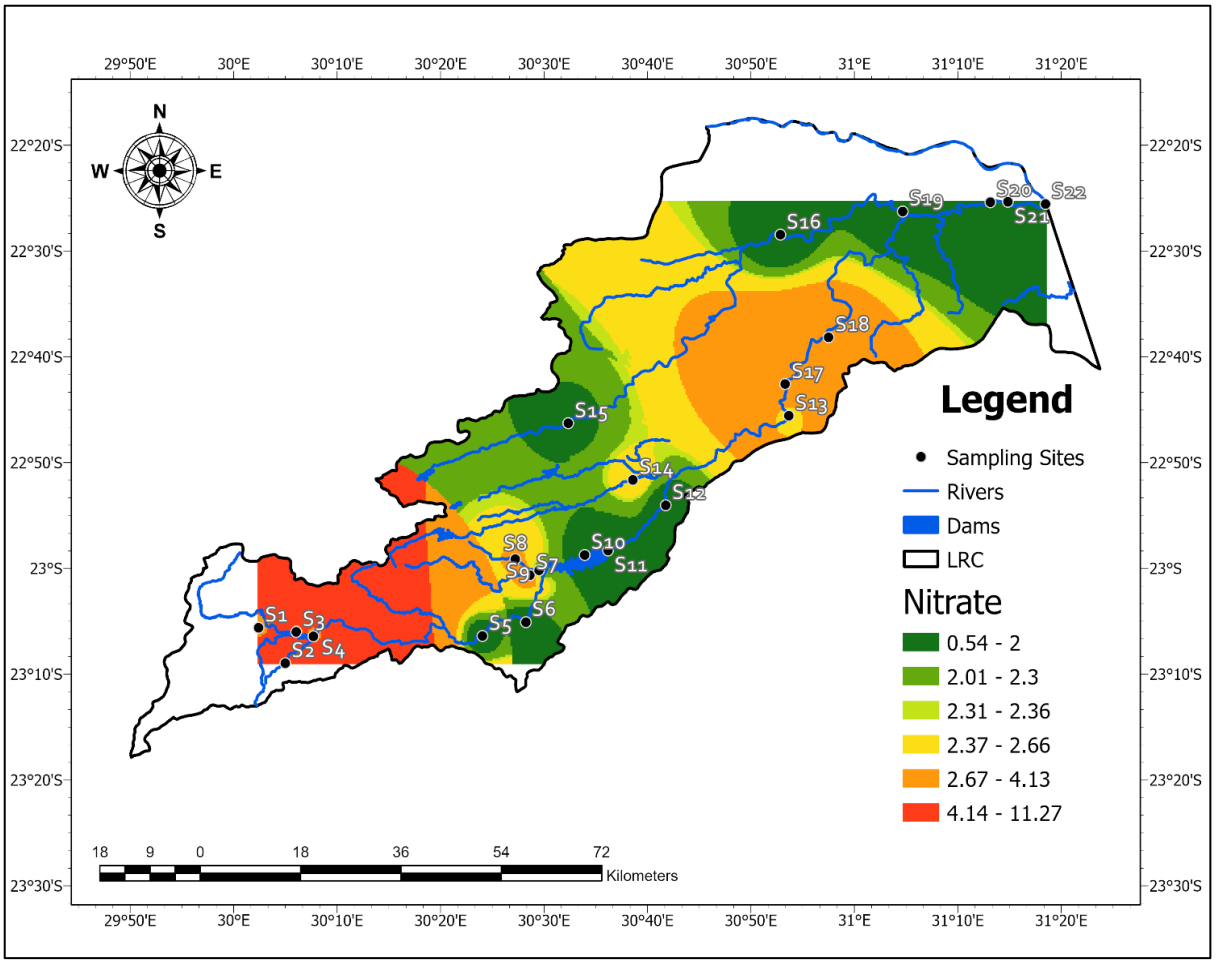

Figure 4.17: Spatial distribution of nitrate levels in the LRC.

It is evident from Figure 4.17 that nitrate levels are high upstream where the main land use is agriculture. Sharma *et al. (*2022), indicate that high concentrations of nitrate in their study area could be linked to human activities and the likely sources are sewage and NPK fertilisers. Therefore, the high levels of nitrate in some parts of the LRC might be associated with such agricultural sources. A notable variation in nitrate levels was also observed in the midstream part of the catchment where there are mixed land-use activities (Figure 4.17). Nevertheless, the highest nitrate values were measured at site S2 and the lowest at site S10. The high concentration of nitrate in S2 could be due to the sewage discharge into the river. Similar results were also reported in the Umgeni River, South Africa (Banda and Kumarasamy, 2020) but higher than the report of Chatanga *et al.* (2019) in the Mohokare River in Lesotho.

The mean reported concentration of nitrate for the LRC (2.14 mg/L) is lower than other agriculturally impacted rivers such as Umfolozi River in KwaZulu-Natal Province (Nunes *et al.,* 2019), Mvudi River in Limpopo Province (Gumbo *et al.,* 2016), Chiredzi and Runde Rivers in Zimbabwe (Nhiwatiwa *et al.,* 2017), and the Danube River in Europe (Ismail and Robescu, 2019), respectively. Additionally, a statistically significant variation ($p \leq 0.05$) was recorded

between the wet and dry seasons. From Figure 4.18, the average values of nitrate in surface water of the LRC ranged from 0.58 to 6.03 mg/L with a mean value of 2.10 mg/L in the wet season and 0.38 to 16.50 mg/L with a mean value of 2.01 mg/L in the dry season. Site S2 recorded an unusually high concentration of nitrate during both seasons. This may be due to sewage runoff and human waste being discharged into streams (Abija *et al.,* 2018). Compared to other studies, the highest value recorded during the wet season was higher than the results of Motholo (2014) in the Metsimatsho River in the Free State Province of South Africa. However, the seasonal values measured in this study were within the SANS recommended limits.

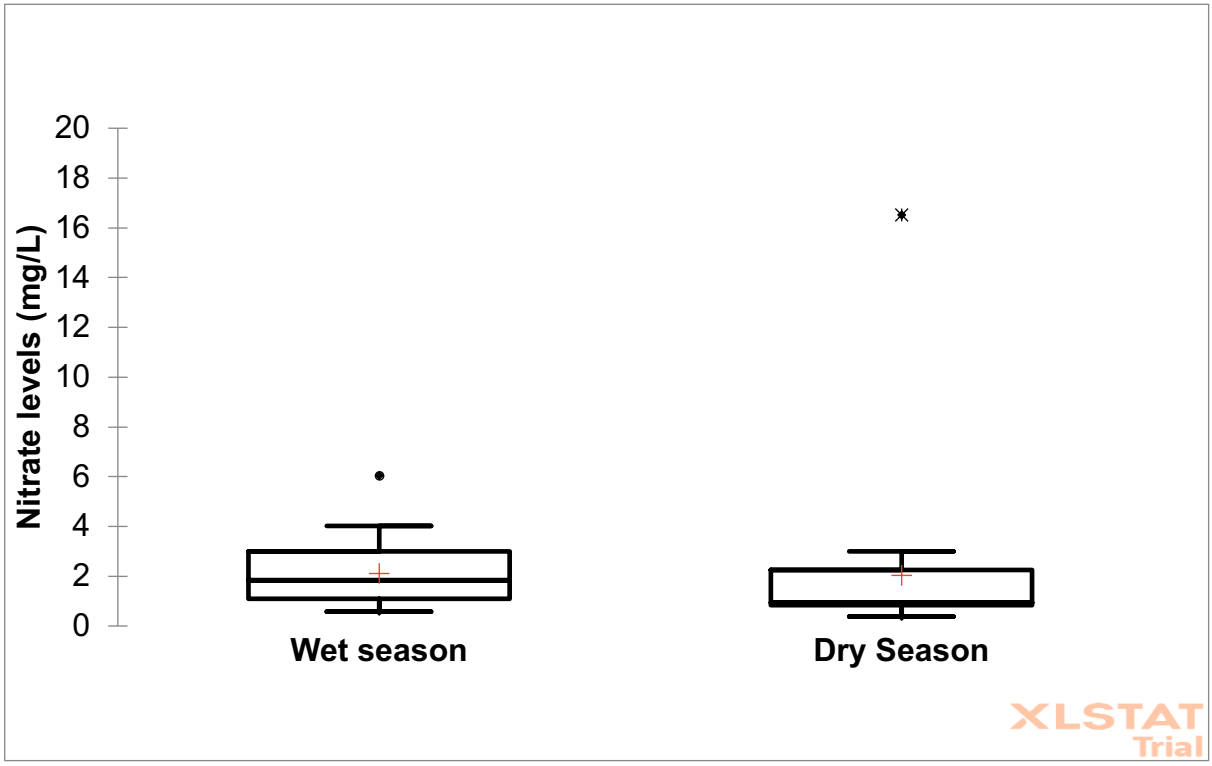

Figure 4.18: Box and whisker plots of seasonal variation of nitrate in water samples.

4.2.8 Phosphate

In water systems, phosphate can be found as a free ion and as salt in the terrestrial environment that is used in detergents as water softeners (Abija *et al.,* 2018). It can be found in different forms i.e., inorganic form (polyphosphates and orthophosphates) or organic form (organically bound phosphates) (Muoi *et al.,* 2022). Despite its morphology, phosphate is an imperative nutrient in water quality assessment and serves as a measure of anthropogenic and biological pollution liable for the development of eutrophic conditions in aquatic ecosystems (Jayasiri *et al.,* 2022). As shown in Table 4.2, the concentration of phosphate in this study ranged from 0.42 to 0.84 mg/L with an average value of 0.59 mg/L. The highest

phosphate concentrations were observed at site S12 and the lowest at site S15. However, the observed results also varied spatially as shown in Figure 4.19.

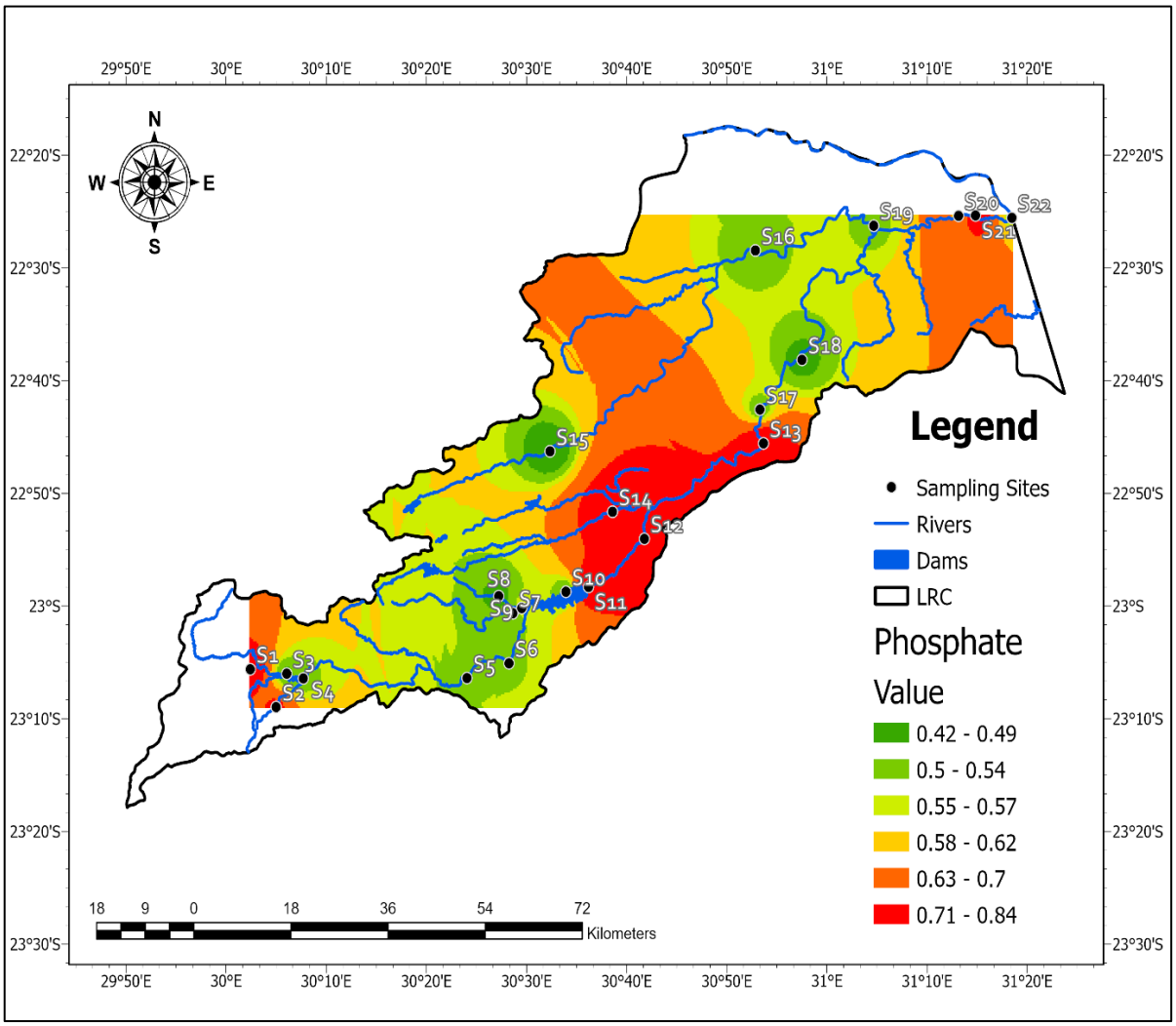

Figure 4.19: Spatial variation of phosphate in the LRC.

The IDW map revealed a dynamic spatial variation in phosphate values where most upstream sites (S3, S4, and S5) showed low values and a minority of midstream sites (S11, S12, S12, and S13) showed high values. Based on the results of this study, settlement/Built-up showed high contribution impacts on phosphate levels. According to Jayasiri *et al.* (2022), the elevated concentration of phosphate in water has been linked to species composition changes, increased rate of plant growth, and proliferation of planktonic and epibenthic algae, leading to the shading of higher plants. Additionally, downstream sites showed considerably similar results of phosphate except for sites S20 and S21. However, a notable reason underlying the difference in concentration could be associated with the unique behaviour of phosphate in shallow water (Muoi *et al.,* 2022). Phosphate absorbs quickly at the surface of sediments and re-enters the water column (Hong *et al.,* 2022).

Interestingly, the results reported in this study were lower than in other areas such as the Crocodile River in Mpumalanga Province, South Africa (Meyer and Antwerpen, 2015), Mekong Delta, Southern Province of Vietnam (Hong *et al.,* 2022), and Forcados River, Western Niger Delta, Nigeria (Abija *et al.,* 2018). Nonetheless, the findings of this study were within the acceptable limits of the WHO (2011). However, a statistically significant difference ($p<0.05$) was also noted between seasons (Figure 4.20).

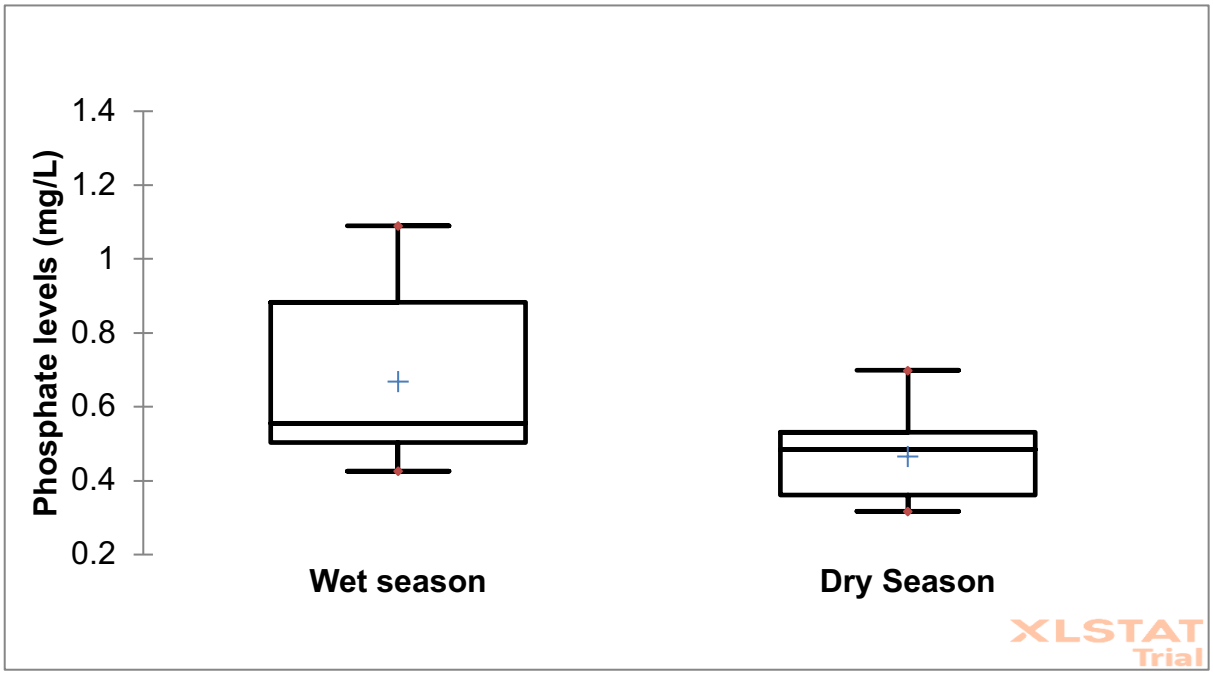

Figure 4.20: Box and whisker plots of seasonal variation of phosphate levels.

Seasonal variation of phosphate showed higher levels of phosphate in the wet season (1.09 mg/L) than during the dry season (0.70 mg/L) while the mean value was 0.67 mg/L in the wet season and 0.47 mg/L in the dry season (Figure 4.20). During the wet season, site S12 recorded the highest level of phosphate compared to other sites whereas site S2 recorded the highest phosphate level in the dry season. The high levels of phosphate might be due to irrigation practices, surface water runoff, laundry, and car washing around these areas (Jian *et al.,* 2016). The results obtained in this study conform to the report of Garcia-Rodriguez *et al.* (2014) in Swartkops River, Eastern Cape province of South Africa but are incongruence with the report of Georginia *et al.* (2020) in Mini-Ezi Stream in Elele-Alimini, Emohua Local Government Area, Nigeria. However, the highest results obtained in both seasons were higher than 5 µg/L (DWAF, 1996) which would increase the likelihood of alga and other plant growth.

4.2.9 Sulphate

According to Hong *et al.* (2022), sulphate level in natural waters is an essential consideration in determining their suitability for industrial and public supplies. It is also common in the aquatic environment due to its wide distribution in different natural environments since it plays a role in biogeochemical cycles (Wang and Zhang, 2019). Table 4.2 shows that the average sulphate values reported in this study ranged from 0.94 to 7.92 mg/L, with an average of 2.31 mg/L. Site S2 recorded an unusually higher level of sulphate (7.92 mg/L) compared to other sites (Figure 4.21). The lowest level of sulphate was recorded at the site S6 (0.94 mg/L).

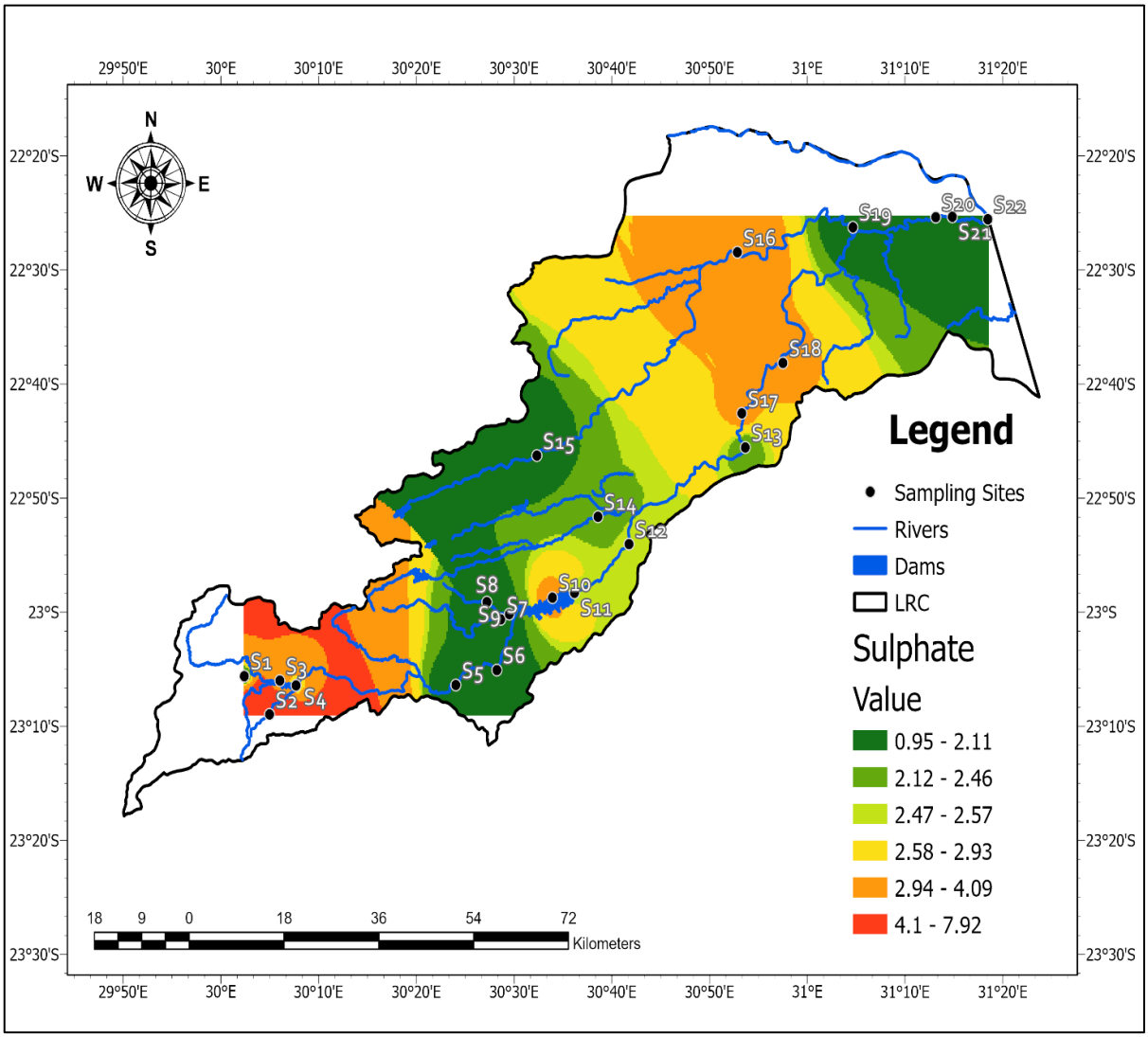

Figure 4.21: Spatial variation of sulphate levels in the LRC.

As shown in Figure 4.21, there was a significant variation in sulphate levels across the catchment with most of the upstream sites showing high values as compared to midstream and downstream sites. However, the IDW map also showed some similar patterns between

the midstream and downstream sites. Higher concentrations of sulphate in the upstream sites could be linked to the main land use activity (agricultural practices) and sewage effluents. Wang and Zhang (2019) also stated that fertilisers and sewage effluents are some of the anthropogenic sources contributing to sulphate levels in the aquatic environment.

Moreover, low values were observed downstream at S19, S20, S21 and S22 where the main land use activity is conservation (KNP). This, therefore, suggest the sorption reaction taking place in the river system downstream. However, the recorded average values were below the WHO (2004) limit of 250 mg/L for drinking water. Based on the results of this study, the concentrations of sulphate in the water samples are not likely to cause human health issues or threat to the aquatic ecosystem.

Furthermore, the concentration of sulphate in the LRC ranged from 0.76 to 6.58 mg/L with a mean value of 1.96 mg/L in the wet season and 0.98 to 9.26 mg/L with a mean of 2.66 mg/L in the dry season (Figure 4.22). The t-test results showed no statistically significant seasonal difference ($p>0.05$), but higher values were recorded in the dry season. The results conform to the report of Abija *et al.* (2018). The results of this study were below the results reported in Mvoti River System, Kwazulu Natal, South Africa (Sukdeo, 2010), Deduru Oya river basin of Sri Lanka (Jayasiri *et al.,* 2022) and Mekong Delta, Vietnam (Hong *et al.,* 2022), but were within the WHO (2011) recommended value (100 mg/L) for surface water. Otene and Alfred-Ockiya (2019) stated that sulphate levels below the recommended value do not show any characteristics of eutrophication, since sulphate, nitrate and phosphate levels control eutrophication and algal growth in the river ecosystem.

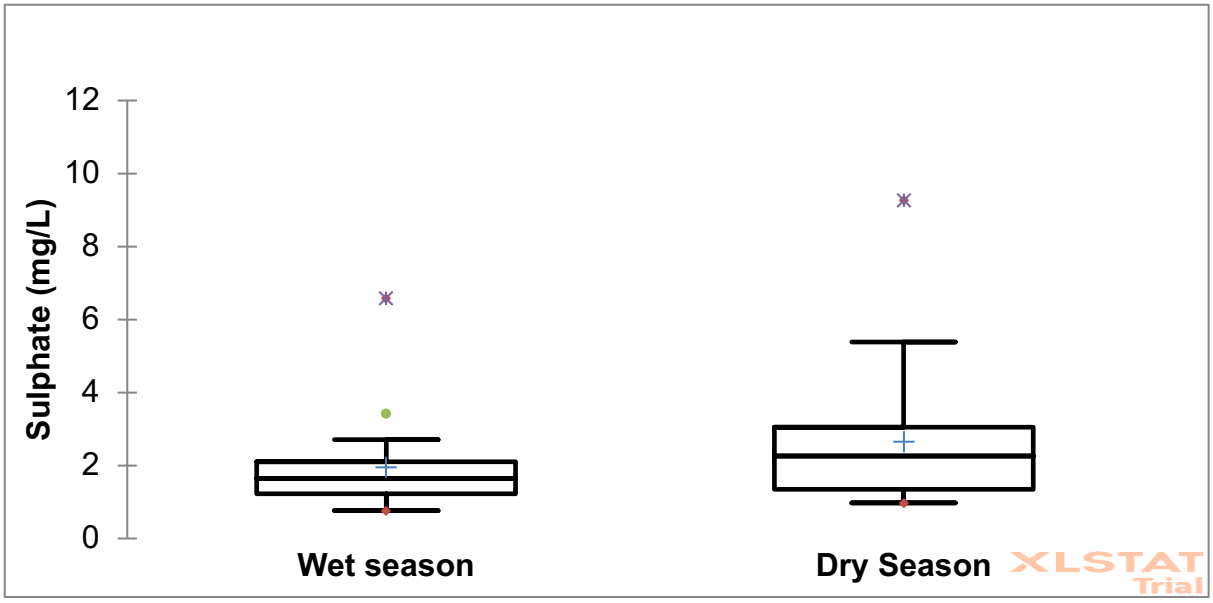

Figure 4.22: Box and whisker plots of seasonal variation of sulphate in the LRC.

4.2.10 Chloride

Chloride (Cl^-) is a naturally occurring element that is common in most natural waters and is most often found as a component of salt (sodium chloride) or in some cases in combination with potassium or calcium. Its occurrence in surface water can result from various sources such as weathering of soils, salt used for road de-icing, salt-bearing geological formations, and attribution from wastewaters. From the results shown in Table 4.2, it was found that the concentrations of chloride ranged between 6.46 to 22.79 mg/L in the water samples with an average value of 11.12 mg/L. The highest chloride concentration was measured at sampling site S2 and the lowest at S14. The high presence of chloride along site S2 could be due to sewage effluents, road runoff, and agricultural runoff (Johnstone *et al.,* 2022; Sorichetti *et al.,* 2022). Moreover, the IDW maps presented in Figure 4.23 show the spatial distribution of chloride in the LRC during the sampling period.

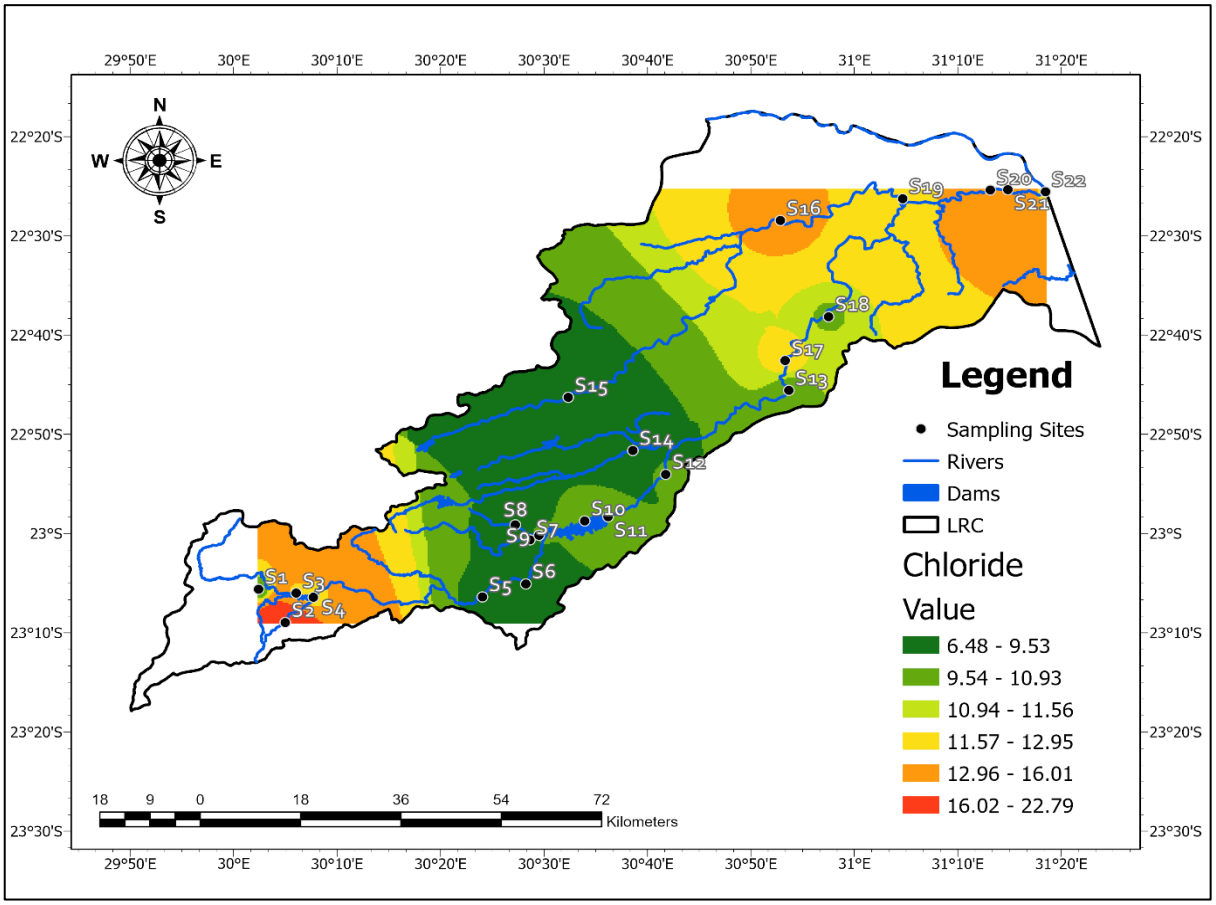

Figure 4.23: Spatial distribution of chloride in the LRC.

Generally, midstream land use activities showed low values of chloride as compared to other sites. The results also show that there is a gradual increase in chloride concentration in the sites located downstream suggesting the contribution of wastes joining at different locations

from upstream and midstream (Muoi *et al.,* 2022). This could be attributed to the discharge of wastes downstream as the river system flows towards those sampling sites. Chloride concentrations reported in this study were lower than those reported in Touws and Duiwe Rivers, Gouritz Water Management Area, Western Cape of South Africa (Petersen *et al.,* 2017) and Hex River in the Rustenburg Area, South Africa (Mavunda, 2016). The results reported in this study are consistent with those of Seth *et al.* (2016) from the Himalayan River, Kumaung Region, Uttarakhand, India.

Stets *et al.* (2018) indicated that high chloride concentration can result in water being unsuitable for drinking, livestock watering and unpalatable. Seth *et al.* (2016) also indicated that excess chloride concentration gives a salty taste to water and may result in osteoporosis, hypertension, asthma, and renal stones. In the present study, it was found that chloride concentration is well within the recommended limits by WHO (2011) for drinking purposes and DWAF (1996) for the protection of the aquatic ecosystem. In addition, the Wilcoxon statistical test showed no significant difference between the two seasons ($p > 0.05$), with the dry season recording higher values than the wet season (Figure 4.24).

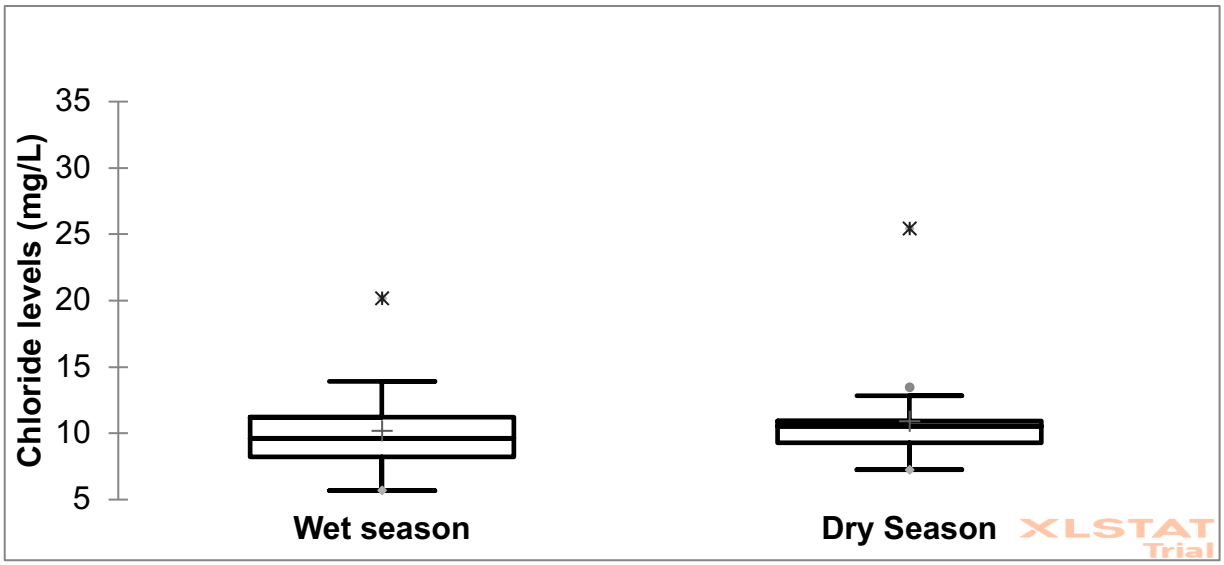

Figure 4.24: Box and whisker plots of seasonal variation of chloride concentration in the water samples.

From the analysis results as shown in Figure 4.24, the values of chloride obtained in this study ranged from 5.67 to 20.15 mg/L with a mean of 10.19 mg/L in the wet season and 7.25 to 25.42 mg/L with a mean of 10.89 mg/L in the dry season. Omuku *et al.* (2022) also reported a similar pattern where chloride concentration increased most dramatically during the dry season. The highest concentrations of chloride were recorded at site S2 in both seasons. This could be attributed to the dissolution of salt deposits, sewage effluents and irrigation runoff

since settlements/Built-up and agricultural activities are the major land uses around the area. In comparison with other previous studies, the results obtained in this study were lower than those reported in the Mutangwi River, Limpopo Province, South Africa (Madilonga *et al.,* 2021), Mooi River, North West Province, South Africa (Koekemoer *et al.,* 2021), Crocodile River, South Africa (Kunene, 2022) but higher than those reported in Mini-Ezi Stream in Elele-Alimini, Emohua Local Government Area of Rivers State, Nigeria (Georginia *et al.,* 2020). However, it is noticed that the concentration of chloride was well below the permissible standards (WHO and SANS).

4.3 Spatiotemporal variations of major and heavy metals in water samples

The analytical results including dissolved major and trace metals (heavy metals) from the 22 sampling sites along the LRC are presented in Table 4.3. The concentration of heavy metals in river water varied across sampling sites during the sampling period.

Table 4.3: Statistical description of heavy metal and major metals concentrations in the LRC water samples compared with water quality standards for drinking and protection of aquatic life.

Metal	Min	Max	Mean	Std. Dev	SANS	DWAF	WHO
			Heavy metals				
Hg	0.01	0.05	0.02	0.01	≤6	≤ 0.04	6
As	0.11	0.43	0.19	0.09	≤10	≤ 10	10
Pb	0.30	1.84	0.79	0.50	≤10	≤ 0.2	-
Cd	0.00	0.05	0.01	0.01	≤3	≤ 0.15	3
Cr	1.03	2.86	1.90	0.53	≤50	≤ 7	50
Cu	2.89	8.44	4.50	1.15	≤2000	≤ 0.3	2000
Al	0.13	7.49	1.22	1.57	≤0.3	≤ 0.15	-
Mn	30.26	169.32	92.41	40.48	≤100	≤ 180	80
Fe	0.64	2.48	1.37	0.45	≤2	≤10% bv	-
Co	0.45	2.50	1.01	0.48	-	-	-
Ni	1.42	9.97	3.61	2.35	≤70	-	70
Zn	11.25	27.41	18.59	3.87	≤5000	≤ 2	-
Mo	0.08	0.43	0.18	0.09	-	-	-
Ba	23.76	70.69	43.06	12.07	≤700	-	-

				Major metals			
Na	5.67	18.53	8.51	2.48	≤200	-	200
Mg	3.93	16.23	6.79	2.38	100	-	50
K	0.49	2.65	1.19	0.50	-	-	200
Ca	7.32	21.16	11.01	2.97	-	-	75

**All values are in µg/L except for Na, Mg, K, Ca, Al, and Fe which are in mg/L, bv and Std. dev represents background value and standard deviation, respectively. – represent no standard for that element.*

4.3.1 Mercury (Hg) concentration in water

The average concentrations of mercury (Hg) was ranging between 0.01 µg/L and 0.05 µg/L with a mean value of 0.02 µg/L (Table 4.3). Spatially, the highest Hg concentration was found at site S11 and the lowest at sites S16, S17 and S19 (Figure 4.25). The measured values of Hg did not exceed the WHO and SANS standard of 6 µg/L for domestic uses but higher than the DWAF recommended limit for protecting aquatic life. Therefore, the reported Hg levels could constitute ecological issues for the aquatic ecosystem within the LRC. Bonotto *et al.* (2018) indicated that Hg pollution of water bodies exerts significant human and ecosystem health impacts due to high toxicity. Additionally, exposure to metals such as mercury can trigger autoimmune development, in which a person's immune system attacks cells (Manyatshe, 2017). However, KNP might be subjected to significant ecological risks due to the availability of high Hg levels upstream of the park.

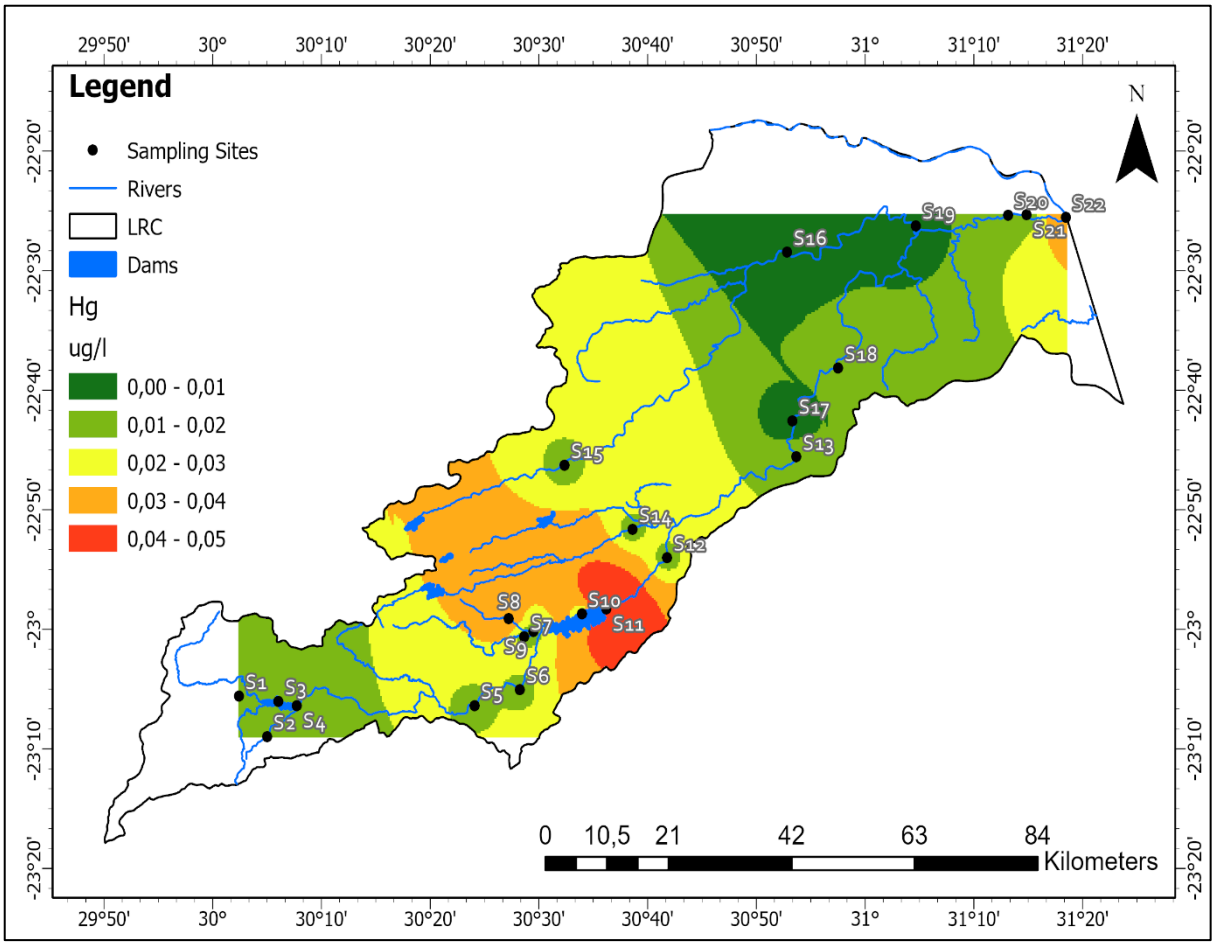

Figure 4.25: Spatial distribution of Hg in water samples of the LRC

A seasonal significant difference ($p < 0.05$) was also observed amongst the water samples (Figure 4.26). The maximum concentration of Hg (0.08 µg/L) was found during the wet season than in the dry season. The highest concentration of Hg was observed at site S11 which could be attributed to car washing (petroleum) at the site. The results of the current study were lower than the report of Genthea *et al.* (2018b) in the Lower Olifants River catchment area, South Africa and Mozambique.

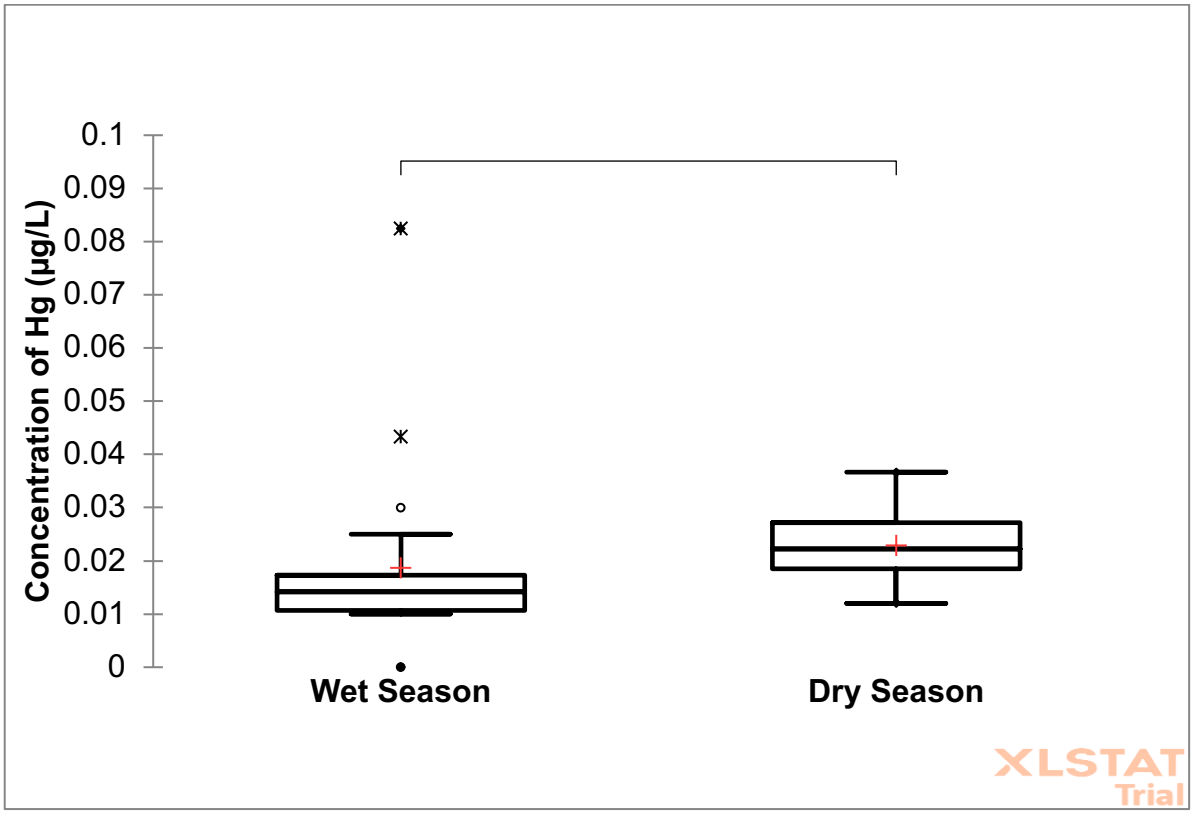

Figure 4.26: Box and Whisker diagram showing the seasonal variation of Hg in water samples.

4.3.2 Arsenic (As) concentration in water

Arsenic (As) is one of the metalloids that are toxic to freshwater and marine aquatic life, and it is known to be carcinogenic (DWAF, 1996; Zhang *et al.,* 2019). One of the major sources of As pollution in river systems are mining activities (David *et al.,* 2020). However, its relationship with anthropogenic activities in mining areas is often difficult to characterise since the high concentrations found in environmental matrices may be a product of its natural distribution (David *et al.,* 2020). In this study, mean As concentrations ranged from 0.11 to 0.43 µg/L, with an average of 0.19 µg/L. Spatially, the highest concentration of As was found at site S21 (downstream inside KNP) whereas the lowest value was found at site S15 (midstream) (Figure 4.27).

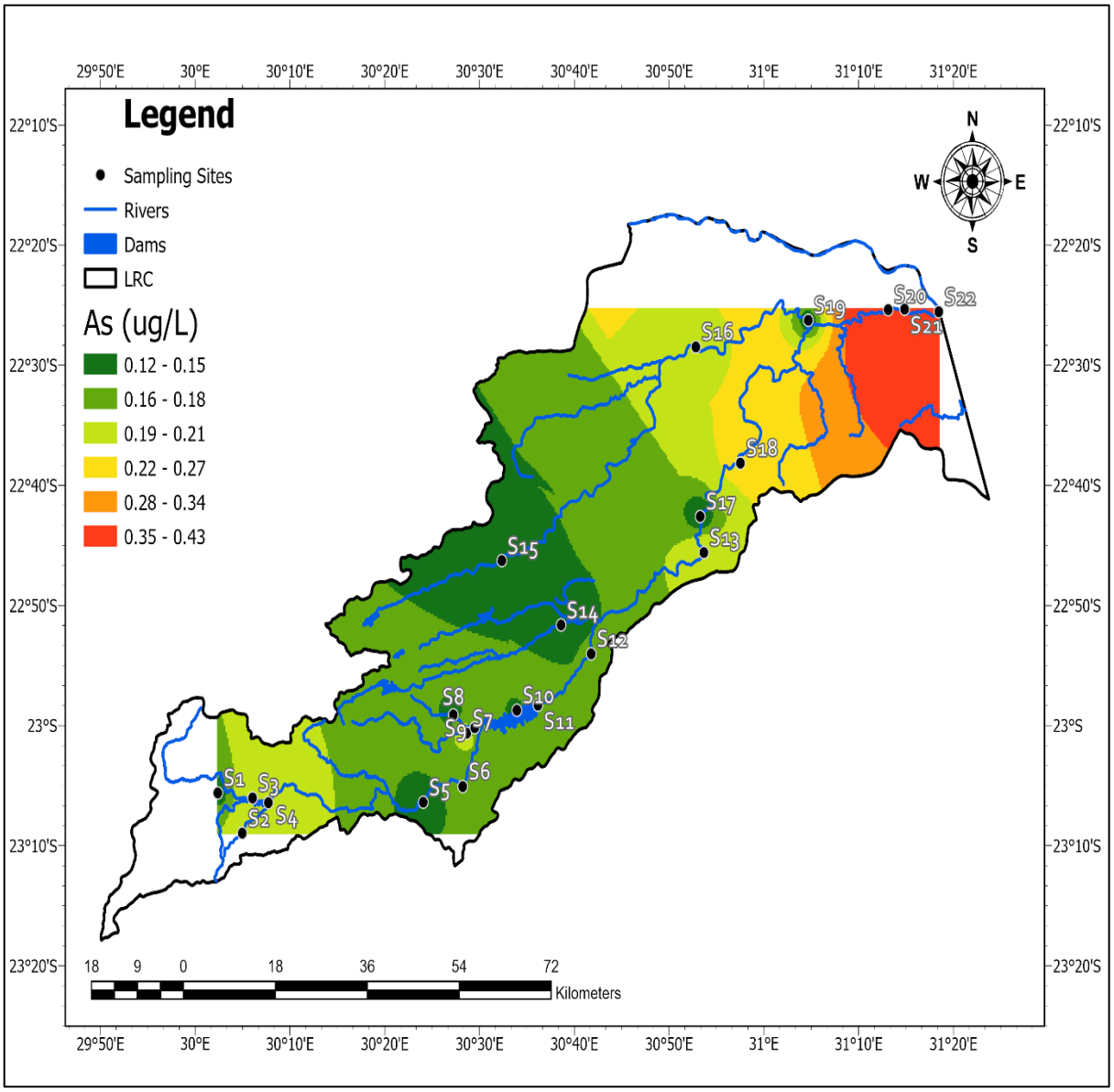

Figure 4.27: Spatial variation of As in LRC water samples.

The results recorded were within SANS, WHO, and DWAF standards for domestic water use and the protection of aquatic life. Also, these results were lower than the report of Manyatshe (2017) from the Mooi River at Potchefstroom, South Africa. However, the Mann-Whitney statistical test showed a statistically significant variation ($P<0.05$) between seasons, with higher concentrations (0.68 µg/L) recorded during the wet season than in the dry season (Figure 4.28).

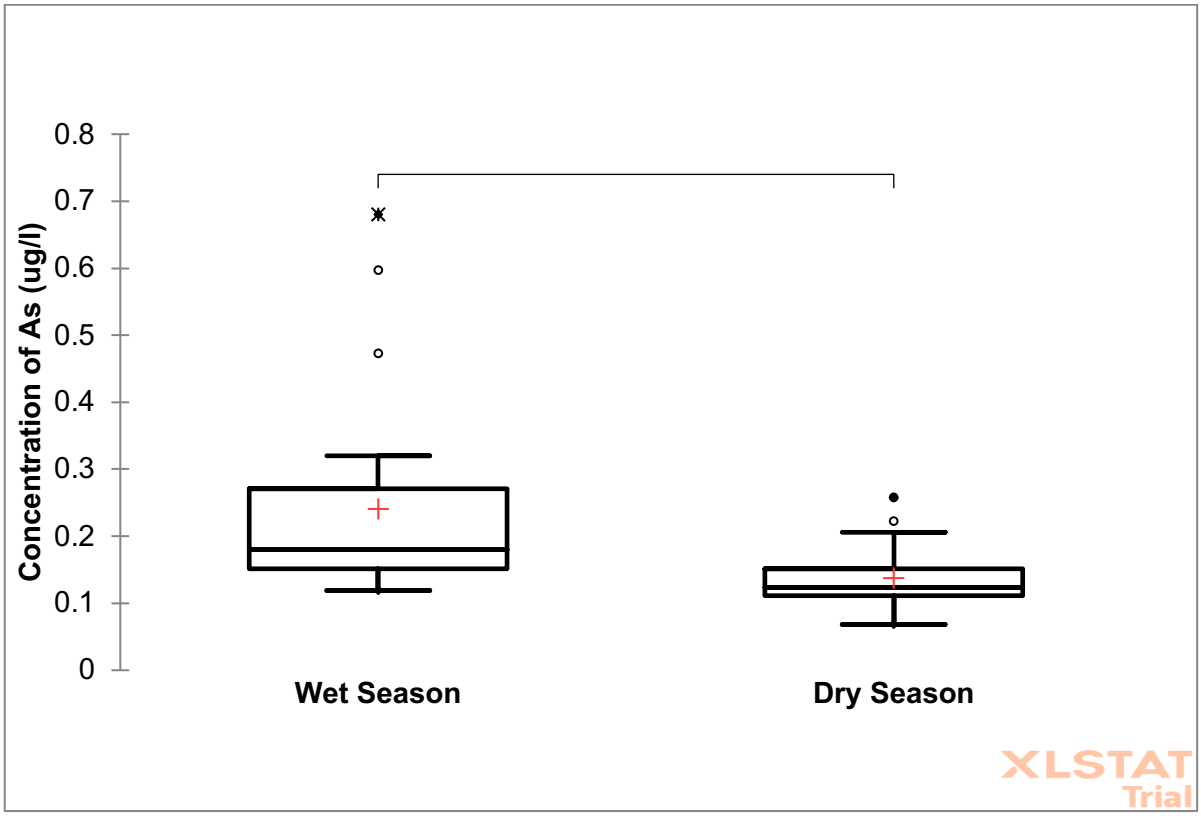

Figure 4.28: Seasonal variations of As concentration in water samples.

4.3.3 Lead (Pb) concentration in water

As shown in Table 4.3, mean concentrations of lead (Pb) in water samples ranged from 0.30 µg/L to 1.84 µg/L, with an average of 0.79 µg/L. The determined concentration of Pb complied with the SANS recommended limit for domestic purposes but did not comply with the DWAF standard value of 0.2 µg/L for protecting the aquatic ecosystems. A similar result was also reported by Edokpayi *et al.* (2017) in Nzhelele River, South Africa. The findings of this study were lower than the results reported in the Halda river, Bangladesh (Islam *et al.,* 2020). As shown in Figure 4.29, upstream and midstream sites showed a similar pattern of Pb concentrations except for site S7 which is highly impacted by domestic sewage effluents from the Thohoyandou Wastewater Treatment plant. However, higher concentrations of Pb have been observed downstream within the KNP, potentially posing an ecological risk to the aquatic ecosystems of this protected area.

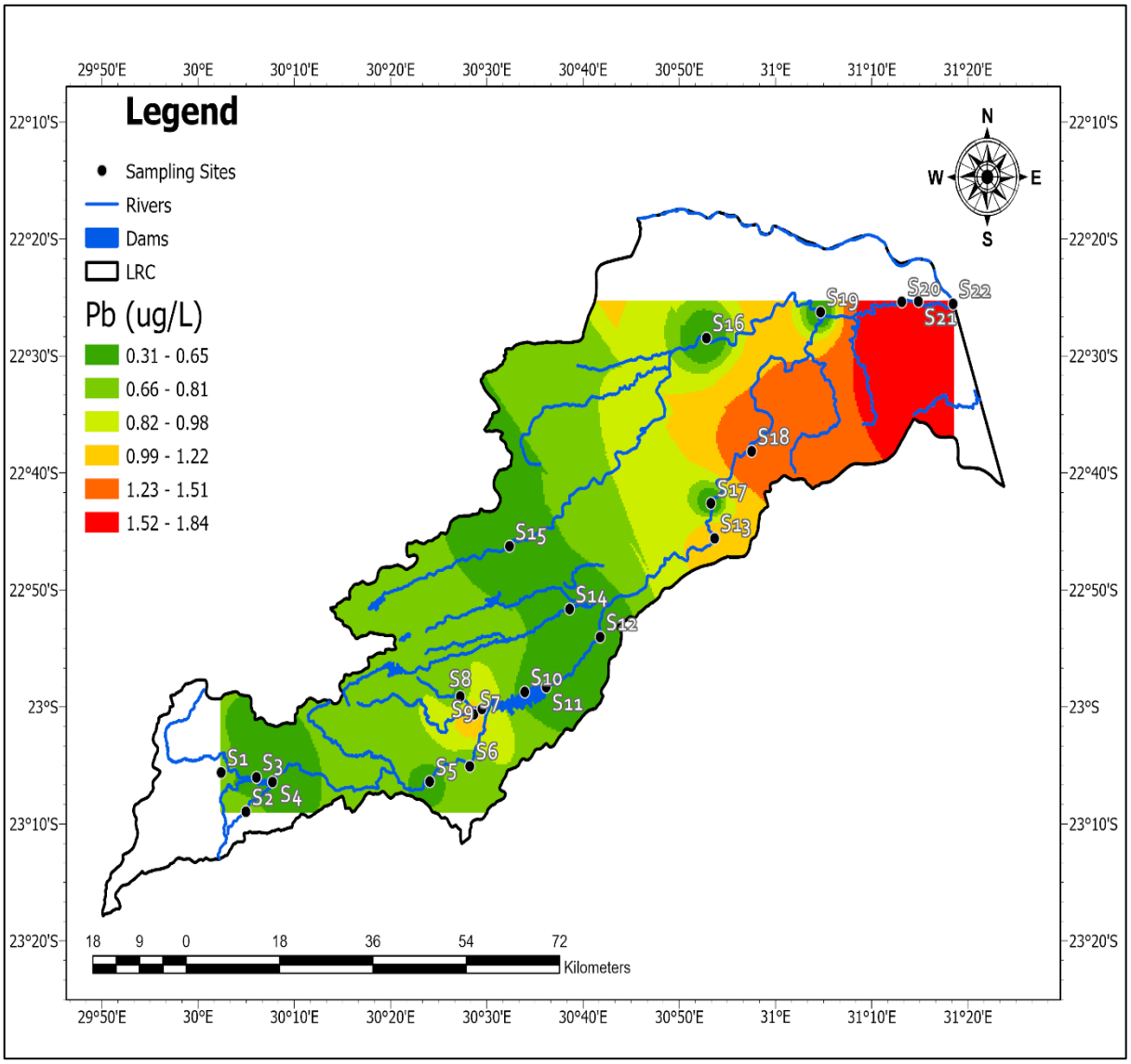

Figure 4.29: Spatial distribution of Pb in water samples of the LRC.

Additionally, the Man-Whitney test showed a statistically significant difference between seasons. The highest concentration of Pb (2.99 µg/L) was found during the wet season (Figure 4.30) which could be due to high runoff containing Pb materials from agricultural lands and sewage into the rivers. Nyamukamba *et al.* (2019) also found a low concentration of lead in Emfuleni Local Municipality and Johannesburg Metropolitan Municipality, South Africa. The reported levels were within the target water quality range (0.2 mg/L) for irrigation water use, aquaculture, and livestock watering (DWAF, 1996).

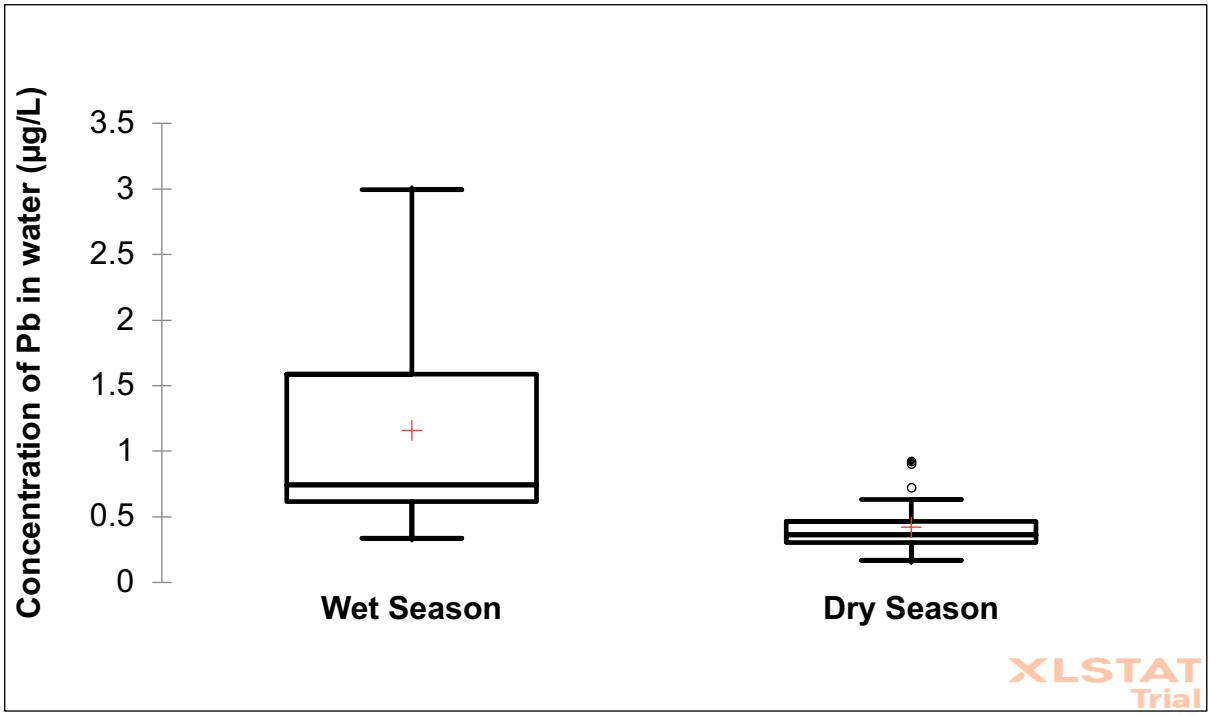

Figure 4.30: Box and whisker plots of seasonal variation of Pb concentrations in water samples of the LRC.

4.3.4 Cadmium (Cd) concentration in water

In this study, mean concentrations of cadmium (Cd) were also observed to vary from below the limit of detection to 0.05 µg/L, as shown in Table 4.3. A higher Cd concentration was observed at site S22 (0.05 µg/L) (Figure 4.31). Comparing average Cd concentrations in water samples to available guidelines, Cd was found to comply with WHO, SANS, and DWAF standards. Therefore, Cd levels measured in water samples do not pose a potential health problem (Edokpayi *et al.,* 2017). High concentrations of Cd at site S22 could be attributed to the pollution input from upstream rivers in the main Limpopo River. Islam *et al.* (2020) indicated that upstream human activities such as industrial and domestic sewage effluents into the river contribute to pollution downstream of the river.

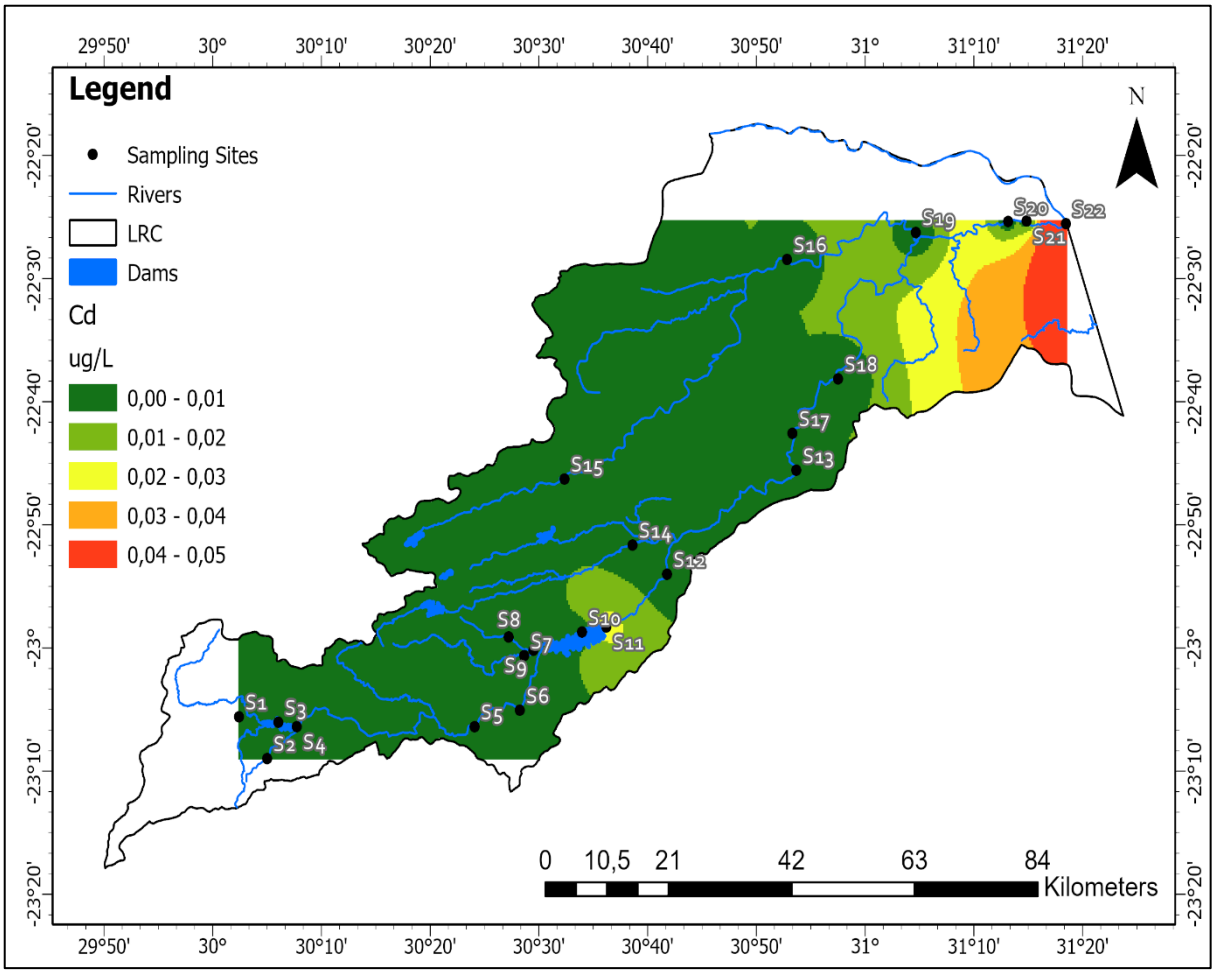

Figure 4.31: Spatial distribution of Cd concentration in water samples.

Nevertheless, the concentrations of Cd in water samples varied significantly ($p < 0.05$) between the two seasons (Figure 4.32). Higher Cd concentrations (0.09 ug/L) in water samples were measured only during the wet season and may be related to higher rainfall, followed by increased runoff of Cd-bearing constituents from agricultural lands and semi-industrial areas into rivers (Edokpayi *et al.* 2017). However, the observed results were lower than the report of Nyamukamba *et al.* (2018) in Emfuleni Local Municipality and Johannesburg Metropolitan Municipality, South Africa. The quality of water was found suitable for agricultural uses (irrigation water use) based on Cd concentrations. Moreover, the maximum concentration of Cd was higher than the agricultural guideline for use in aquaculture (DWAF, 1996).

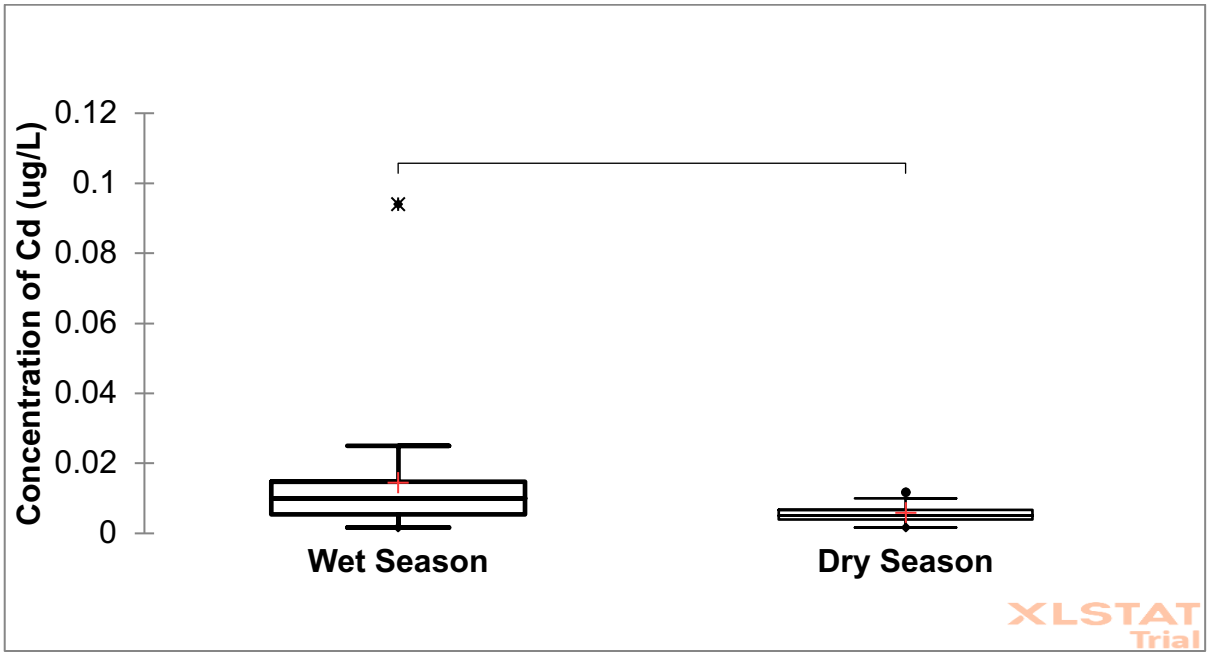

Figure 4.32: Box and Whisker diagram showing the seasonal variation of Cd in water samples.

4.3.5 Chromium (Cr) concentration in water

The average concentrations of chromium (Cr) were ranging from 1.03 to 2.86 µg/L with a mean value of 1.90 µg/L. A notable spatial variation was observed across all the sampling sites as shown in Figure 4.33. The IDW map results showed that high Cr concentrations were more dominant in the upstream and downstream sites than in midstream sites (Figure 4.33). Based on these findings, agriculturally and settlement/built-up dominated areas showed high influence on Cr concentrations than other land uses. However, the sources of Cr may include raising chromium levels in wastewater as well as geological processes (Tomolo *et al.,* 2020). The highest recorded Cr concentration was observed at site S22 (KNP) and the lowest was recorded at site S8. This high record of Cr at site S22 could be attributed to the fact that the site is located downstream of the catchment where there is an inflow of different rivers upstream of the Limpopo River as well as the geology of the area (Tomolo *et al.,* 2020).

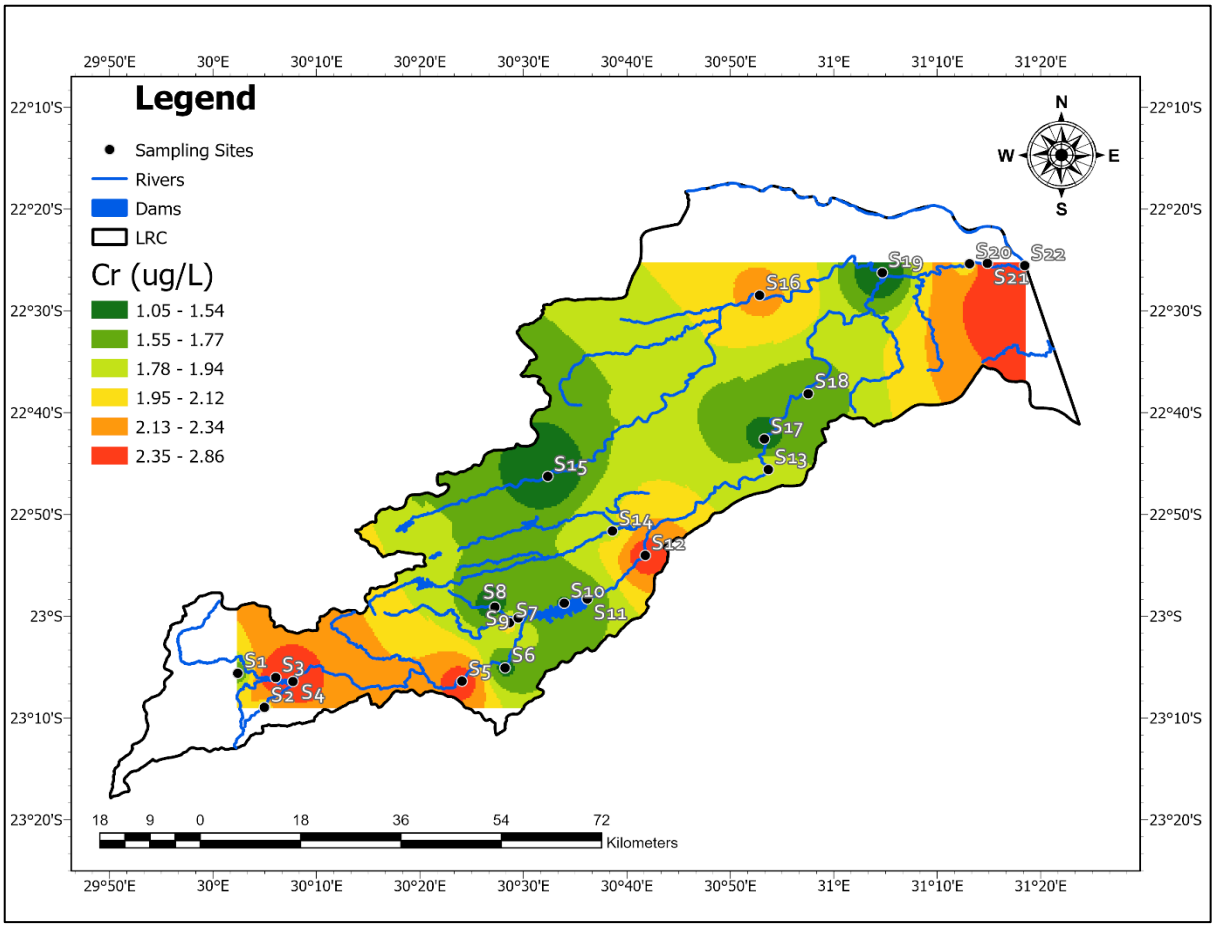

Figure 4.33: Spatial variation of Cr concentrations in the LRC.

Results of the current study were lower than those reported in Nzhelele River, South Africa (Edokpayi *et al.,* 2017) and Blyde and Steelpoort River water, South Africa (Addo-Bediako, 2020). In comparison with the study conducted by Edokpayi *et al.* (2016) in the Mvudi River, the concentration of the current study was found higher, and this indicate progressive contamination of the water quality of this catchment. Furthermore, the results obtained from this study were within the recommended guideline for irrigation water use and livestock watering (DWAF, 1996). Additionally, the Mann-Whitney statistical test also showed a significant difference ($p < 0.05$) between the levels recorded in the wet and dry seasons (Figure 4.34). Higher concentrations were recorded in the wet season rather than the dry season. According to the standards by SANS, DWAF, and WHO for drinking water, domestic water and protection of the aquatic ecosystem, the measured concentration of Cr was below the toxicity levels as shown in Table 4.3. These results, therefore, suggest that the water quality of the LRC can be classified as uncontaminated with respect to the recorded Cr values.

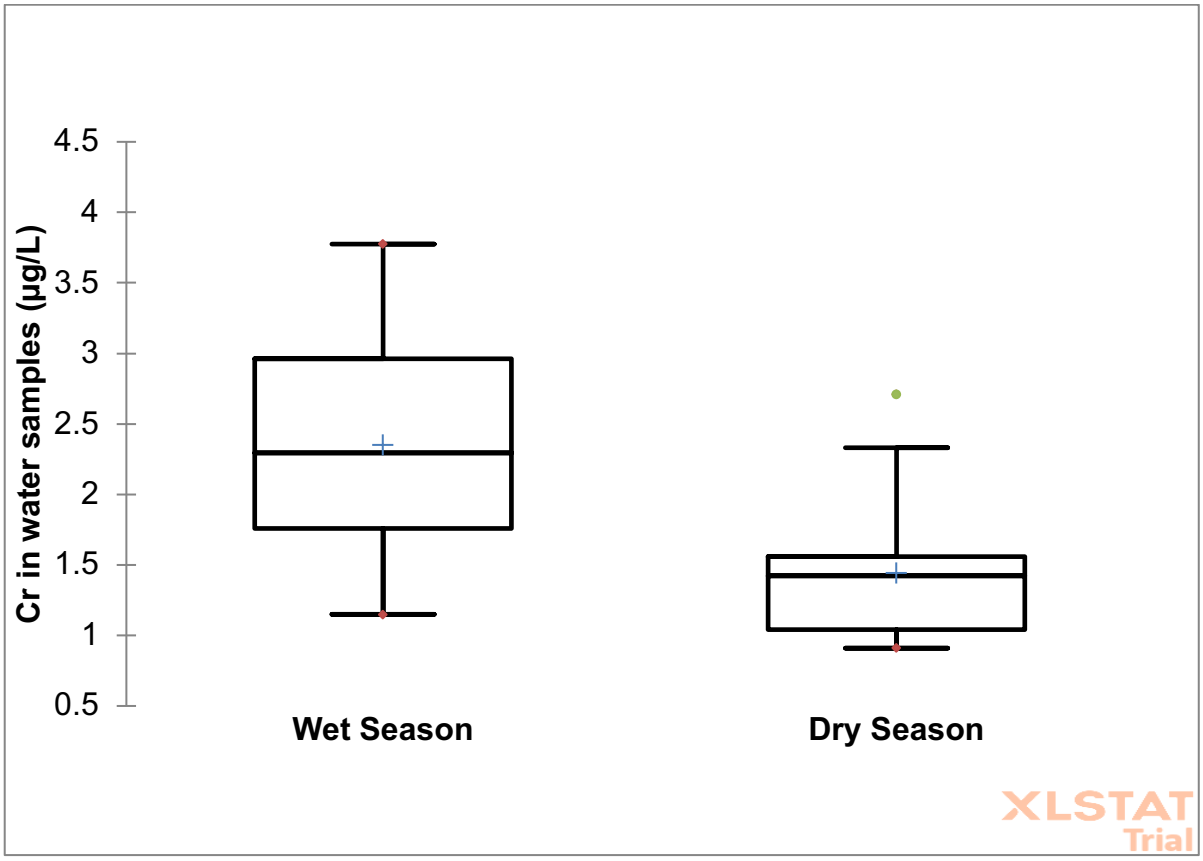

Figure 4.34: Box and whisker plots of seasonal variation of Cr in water samples.

4.3.6 Concentration of copper (Cu) in water

Average concentrations of copper (Cu) ranged from 2.89 to 8.44 µg/L and was lower than the WHO and SANS recommended limit for domestic purposes (Table 4.3). Spatially the highest concentrations of Cu were observed at sampling site S22 whereas the lowest value was observed at site S8 (Figure 4.35). The higher concentration of Cu at site S22 could be attributed to the inflow into the Limpopo River from tributary rivers such as the Olifants River which is heavily polluted with heavy metals and other pollutants (Addo-Bediako, 2023). All the average reported values were higher than the DWAF standard (0.3 µg/L) for the protection of an aquatic ecosystem. This, therefore, indicates potential ecological concern for biodiversity inside the KNP because high Cu concentrations are anticipated. Braz-Mota *et al.* (2018) stated that Cu plays an imperative role in the biological metabolic processes of a living organism, but its presence in high concentrations can adversely affect aquatic organisms.

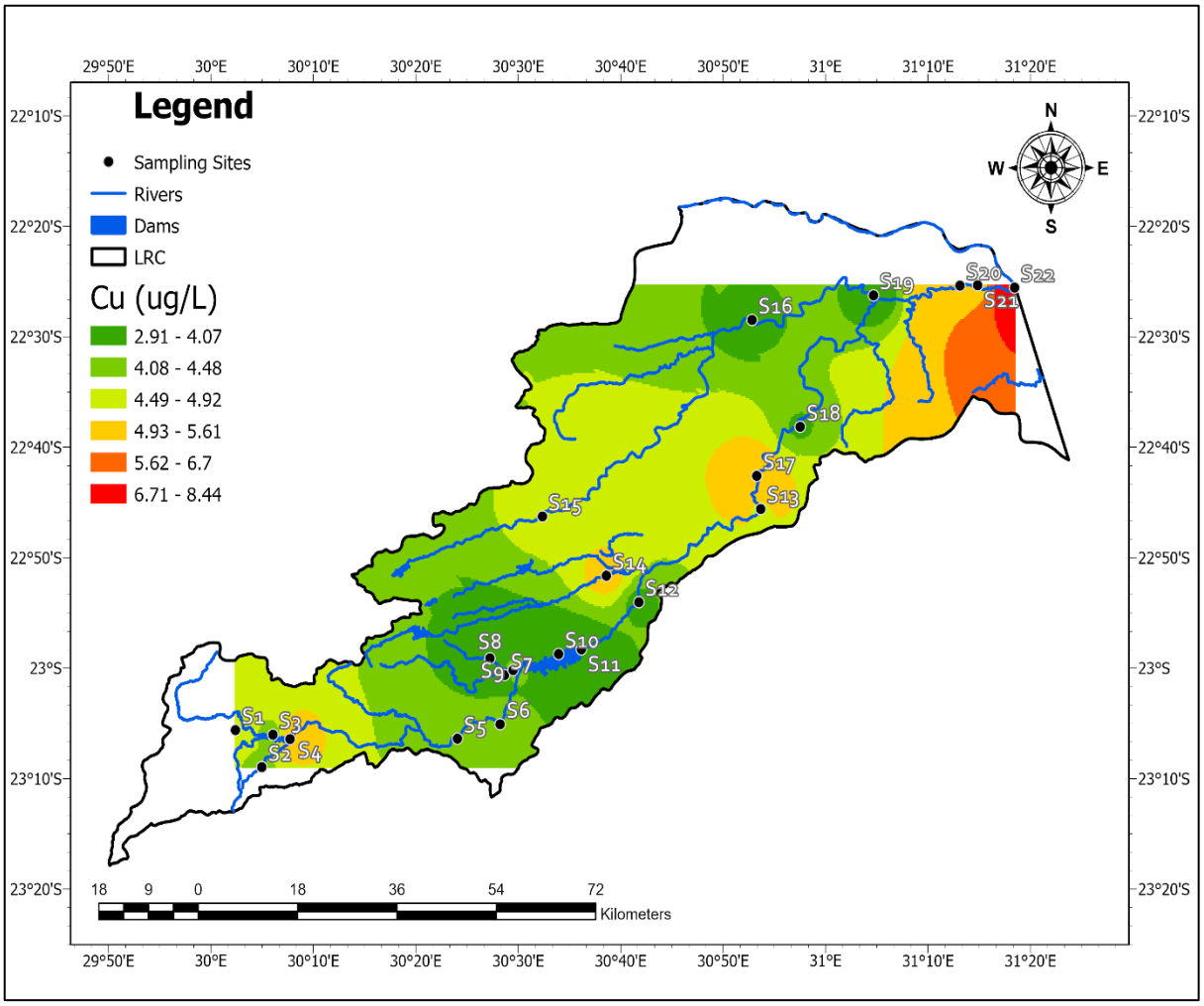

Figure 4.35: Spatial distribution of Cu in water samples

The highest recorded concentrations of Cu was higher than the reported concentration in Moses River, South Africa (WRC, 2011). Also, the concentration of Cu in the study area were higher than those of another study conducted in Tepi Town, Southwest Ethiopia, where the concentration of Cu in a nearby stream ranged between the detection limit and 0.03 µg/L (Mekonnen *et al.,* 2020), however, was lower than other findings in the Syrdarya Basins, Uzbekistan, which was reported by Ernazarovna and Sattorovich (2020). Furthermore, higher Cu concentrations were detected in water samples from the wet season (11.38 µg/L) compared to the dry season (5.497 µg/L) (Appendix 4.4). The mean difference of Cu in the water samples differed significantly ($p < 0.05$) for both seasons (Figure 4.36). However, the highest seasonal concentration of Cu was found below the DWAF standard for agricultural use (irrigation water and livestock watering). Based on Cu concentrations, the quality of water was found unsuitable for aquaculture use as it exceeded the target water quality range of < 0.005 mg/L.

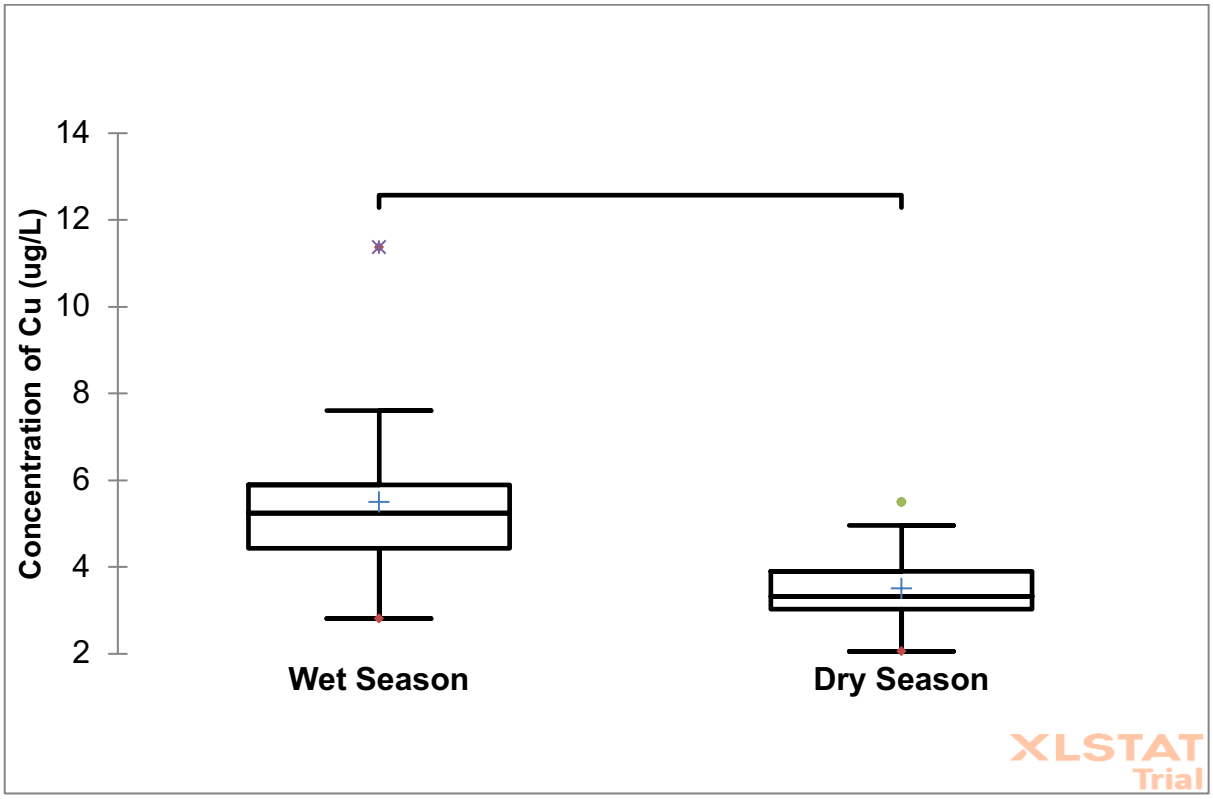

Figure 4.36: Seasonal variations of Cu concentration in water samples.

4.3.7 Concentration of Aluminium (Al) in water samples

The average concentrations of aluminium (Al) in water samples ranged from 0.13 to 7.49 mg/L with an average of 1.22 mg/L. The highest concentration was measured at site S11 and the lowest at site S17. The geospatial map as shown in Figure 4.37 showed variation in Al concentration amongst sampling sites. The IDW map showed that most of the sampling sites were below 3.14 mg/L except for site S11 (midstream) which is located downstream of Nandoni Dam. Karananidi *et al.* (2022) stated that the main source of Al in surface waters is leaching from the soils. However, this process depends on the pH of the river water (Senze *et al.,* 2021). Krupińska (2020) also indicated that Al salts are also used in wastewater treatment processes, lake reclamation and water treatment plants for drinking purposes.

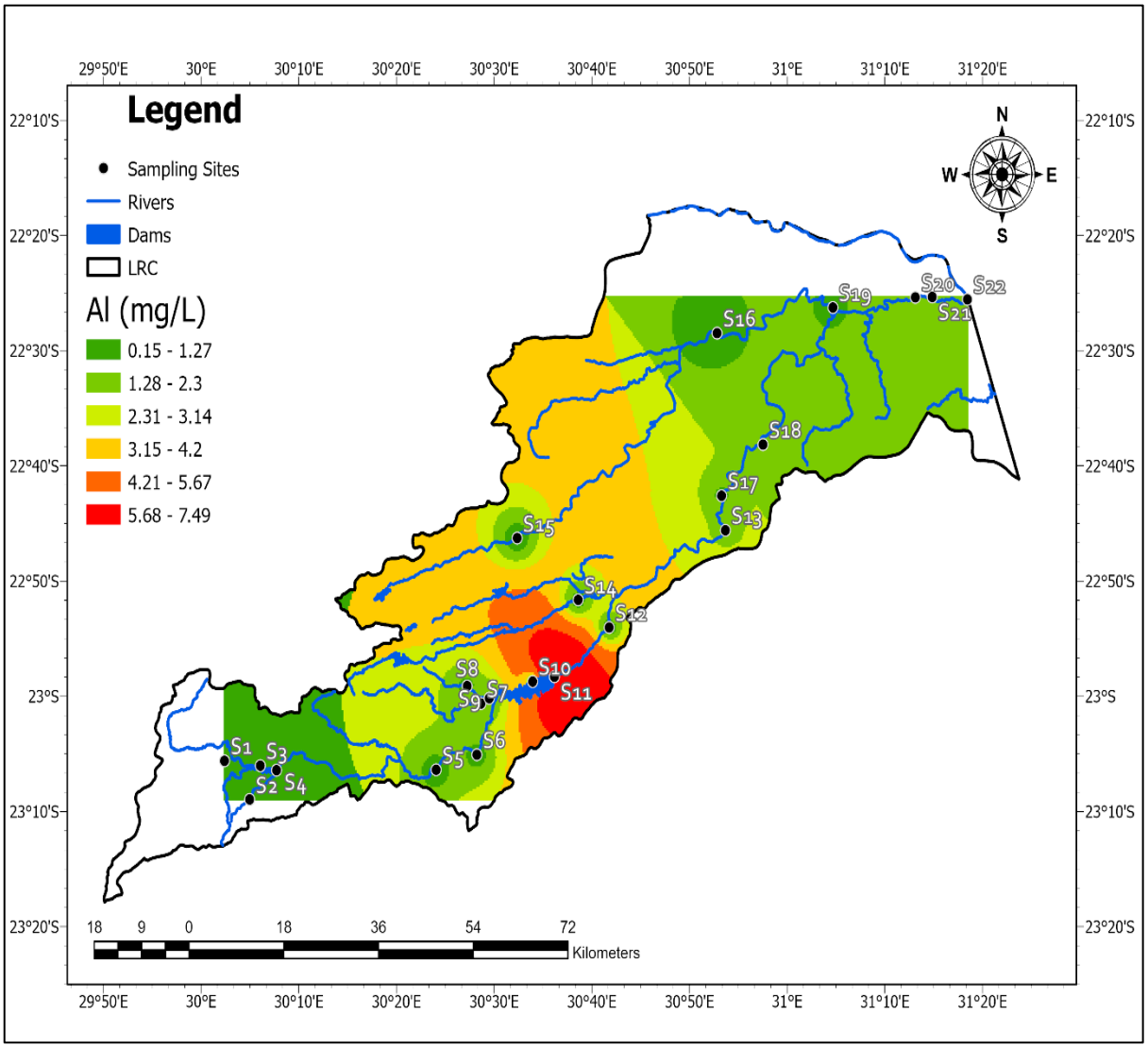

Figure 4.37: Spatial variation of Al in water samples in the LRC.

Al concentrations measured in this study exceeded the value (0.005 mg/L) recommended by the DWAF to protect aquatic ecosystems. Edokpayi *et al.* (2017) stated that Al is generally soluble at acidic pH values and is toxic to certain aquatic species. The WHO does not have a recommended value for Al in drinking water because Al is considered not harmful to humans at low concentrations. However, studies have shown that there are indications that excess Al in the body is associated with various disease syndromes such as Alzheimer's disease (Edokpayi *et al.,* 2017; Edokpayi *et al.,* 2014; Krupińska, 2020). The reported results were also higher than the SANS standard of 0.3 mg/L for drinking purposes at some sites. The results obtained from this study were lower than those reported in Mun River, Northeast Thailand by Liang *et al.* (2019) and higher than those reported in Dzindi River, Limpopo Province by Edokpayi *et al.* (2014). Moreover, the concentrations of Al also exceeded the recommended

value (0.15 mg/L) for domestic uses set by DWAF (1996). It also exceeded the DWAF standard (5 mg/L) for water uses in irrigation at some sampling sites.

Figure 4.38 shows the overall seasonal variation of Al concentrations in water samples. The concentration of Al in the water samples differed significantly ($p<0.05$) demonstrating that its concentrations varied between seasons. The highest concentrations of Al were observed during the wet season than in the dry season. Edokpayi *et al.* (2014), also reported a similar trend in the Mvudi River (a tributary of the Luvuvhu River), Limpopo Province. This may be related to rain runoff that can easily carry Al-bearing material into rivers discarded by villagers living in the catchment, explaining the higher concentrations measured during the rainy season (Edokpayi *et al.,* 2017). The elevated bioavailability of Al concentration in water has been noted to be toxic to a wide range of aquatic organisms since Al can interfere with calcium metabolism and sodium homeostasis leading to neuromuscular dysfunction (DWAF, 1996).

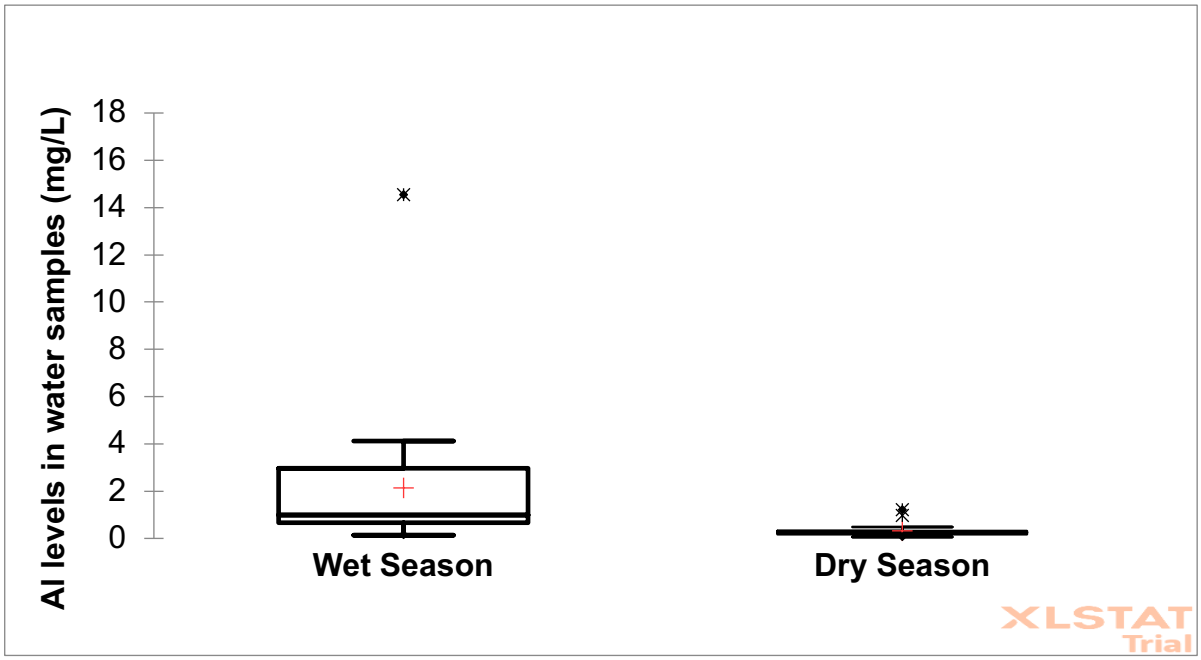

Figure 4.38: Box and whisker plots of seasonal variation of Al in water samples.

4.3.8 Manganese (Mn) concentration in water

According to Edokpayi *et al.* (2016), manganese (Mn) plays a variety of roles in the physiological processes of living organisms, including humans. The presence of Mn in high concentrations in drinking water constitutes a nuisance with characteristics of staining properties and metallic taste (Edokpayi *et al.,* 2016). In the current study, the average concentration of Mn ranged between 30.26 to 169.32 µg/L. These concentrations complied with the DWAF recommended limit of 180 µg/L for protecting aquatic life but exceeded the

WHO and SANS standards for domestic water uses. The Mn concentrations reported in this study did not exceed those reported by Nyamukamba *et al.* (2019) Emfuleni Local Municipality and Johannesburg Metropolitan Municipality, South Africa. The spatial distribution of Mn was also observed across all the sampling sites indicating drastic variation in concentrations between sites (Figure 4.39).

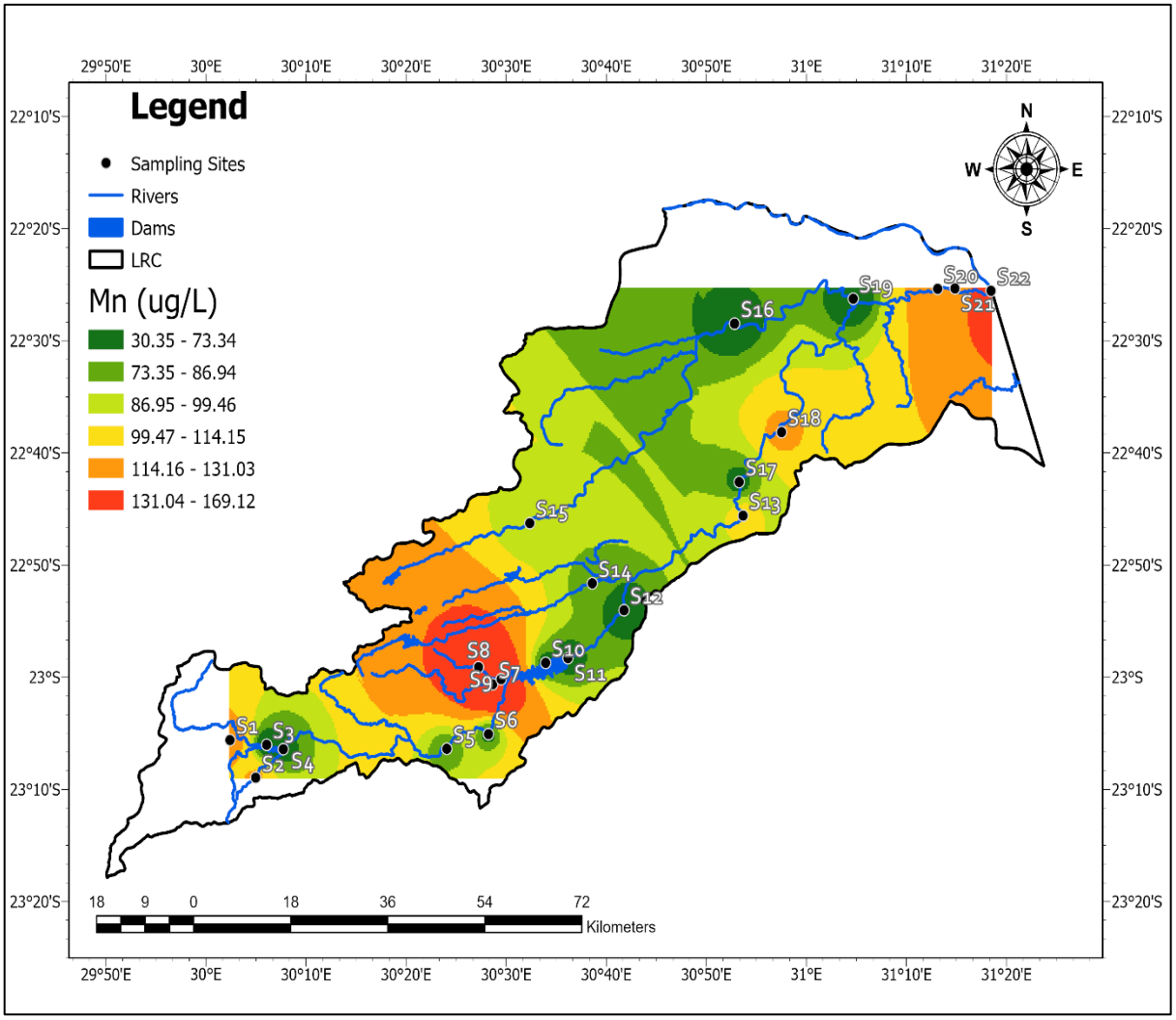

Figure 4.39: Spatial distribution of Mn levels in water samples.

Spatially, the highest concentration (169.32 µg/L) of Mn was observed from site S7 and the lowest was observed from site S3. The observed high concentration at site S7 was due to wastewater effluents from a nearby wastewater treatment plant. As shown in Figure 4.39, it is observed that high concentration of Mn was also recorded at site S22 which is inside the KNP. Thus, the aquatic ecosystem at KNP might be at risk in the longer term if this substantial increase at downstream sites continues to increase over time. However, the water quality was found suitable for irrigation water use (target water quality value < 0.02 mg/L) and livestock watering (<10 mg/L) but higher than the target water quality range (0.1 mg/L) for aquaculture.

According to the statistical test (Mann-Whitney) results, the seasonal recorded values differ significantly ($p < 0.05$). Comparatively, the highest concentrations of Mn were observed during the wet season than in the dry season (Figure 4.40). The presence of high concentration of this metal in the wet season may be related to the heavy influx of runoff derived from the land into the river (Thangamalathi and Anuradha, 2018). The findings of this study were higher than those reported by Islam *et al.* (2020) in Halda river, Bangladesh.

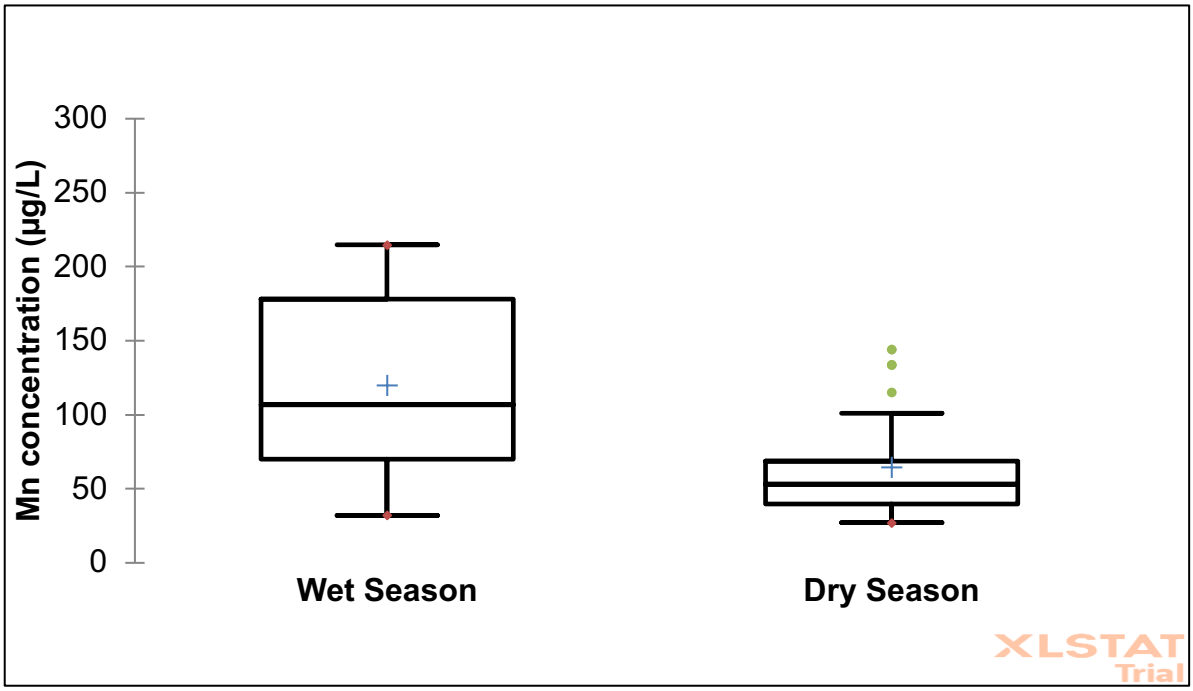

Figure 4.40: Box and whisker plots of seasonal variation of Mn in water samples.

4.3.9 Concentration of iron (Fe) in water

The average concentrations of iron (Fe) in water samples ranged from 0.64 mg/L to 2.48 mg/L and the maximum recorded value exceeded the SANS recommended limit for drinking water. When the average concentrations of Fe in the LRC water samples were compared with the study of Addo-Bediako and Rasifudi (2021) in the Ga-Selati River, a tributary of the Olifants River in Limpopo Province, South Africa, it was observed that the concentration of Fe was lower than those reported in their study. Spatially, the highest recorded value of Fe was observed at site S14 and the lowest was observed at site S17 (Figure 4.41). For sampling sites inside the KNP, high concentrations were observed at site S22 which could be a result of upstream land use activities along the Limpopo River.

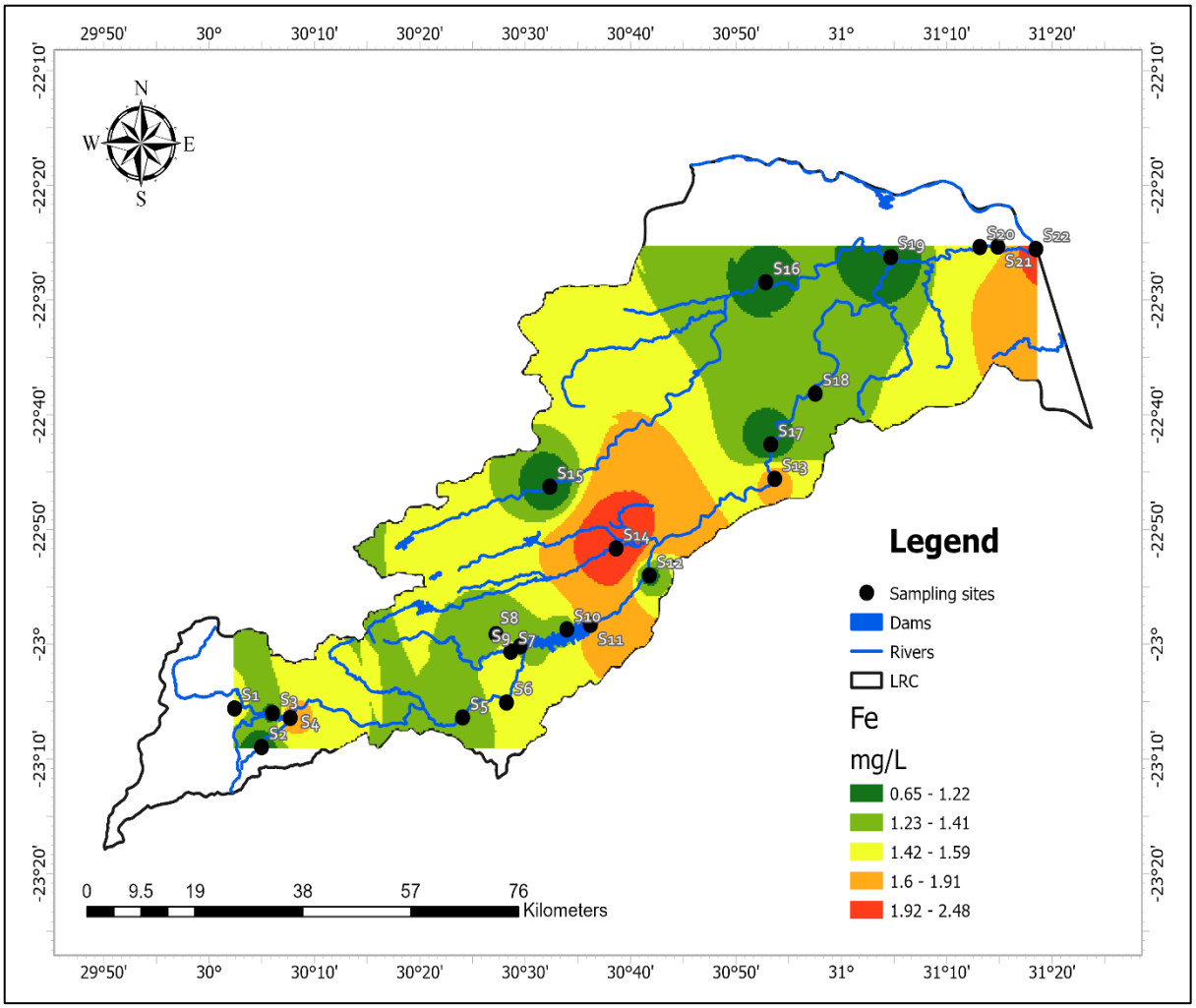

Figure 4.41: Spatial distribution of Fe in water samples of the LRC

In addition, higher Fe concentrations were measured in the wet season (3.31 mg/L) water samples than in the dry season (1.67 mg/L), and this variance was statistically significant ($p<0.05$) (Figure 4.42). However, these findings are not in consonant with the results reported in Nzhelele River, Limpopo Province by Edokpayi *et al.* (2017) and Mun River, Northeast Thailand by Liang *et al.* (2019). The obtained results were within the recommended guideline value for irrigation water use (Target Water Quality Range ≤ 5.0) and livestock watering but exceeded the standard for agricultural use in aquaculture (DWAF, 1996).

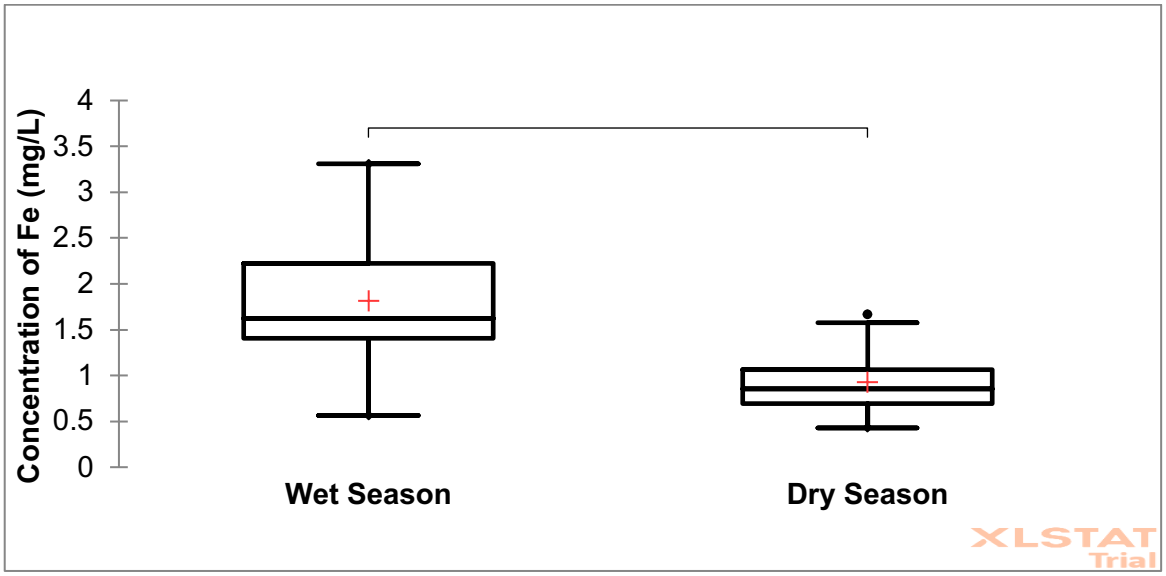

Figure 4.42: Seasonal variation of Fe concentrations in water samples

4.3.10 Concentration of Cobalt (Co) in water samples

As stated by Liu *et al.* (2017) and Suh *et al.* (2016), cobalt (Co) is also a poisonous metal that can cause cancer and consequently threaten human life. Besides being harmful, it also plays a major role in biological processes as a constituent of vitamin B12 (Li *et al.,* 2018). In contrast, the 13th Report on Carcinogens (ROC) lists cobalt sulfate and cobalt tungsten carbide as hard metals and powders reasonably expected to be carcinogenic to humans (National Toxicology Program, 2014). From this study, average concentrations of Co ranged from 0.45 µg/L to 2.50 µg/L and a mean value of 1.01 µg/L. Currently, there is no standard value for Co concentration in drinking water. When compared with a study conducted in the Lower Olifants River catchment area, South Africa and Mozambique (Genthe *et al.,* 2018b), the concentrations of Co observed from this study were lower than those results but higher than the report of the Water Research Commission (WRC, 2011) from Moses River, South Africa and Ernazarovna and Sattorovich (2020) from Small Rivers of The Syrdarya Basins, Egypt. Spatially, the distribution of Co concentrations did not differ significantly from site to site (Figure 4.43).

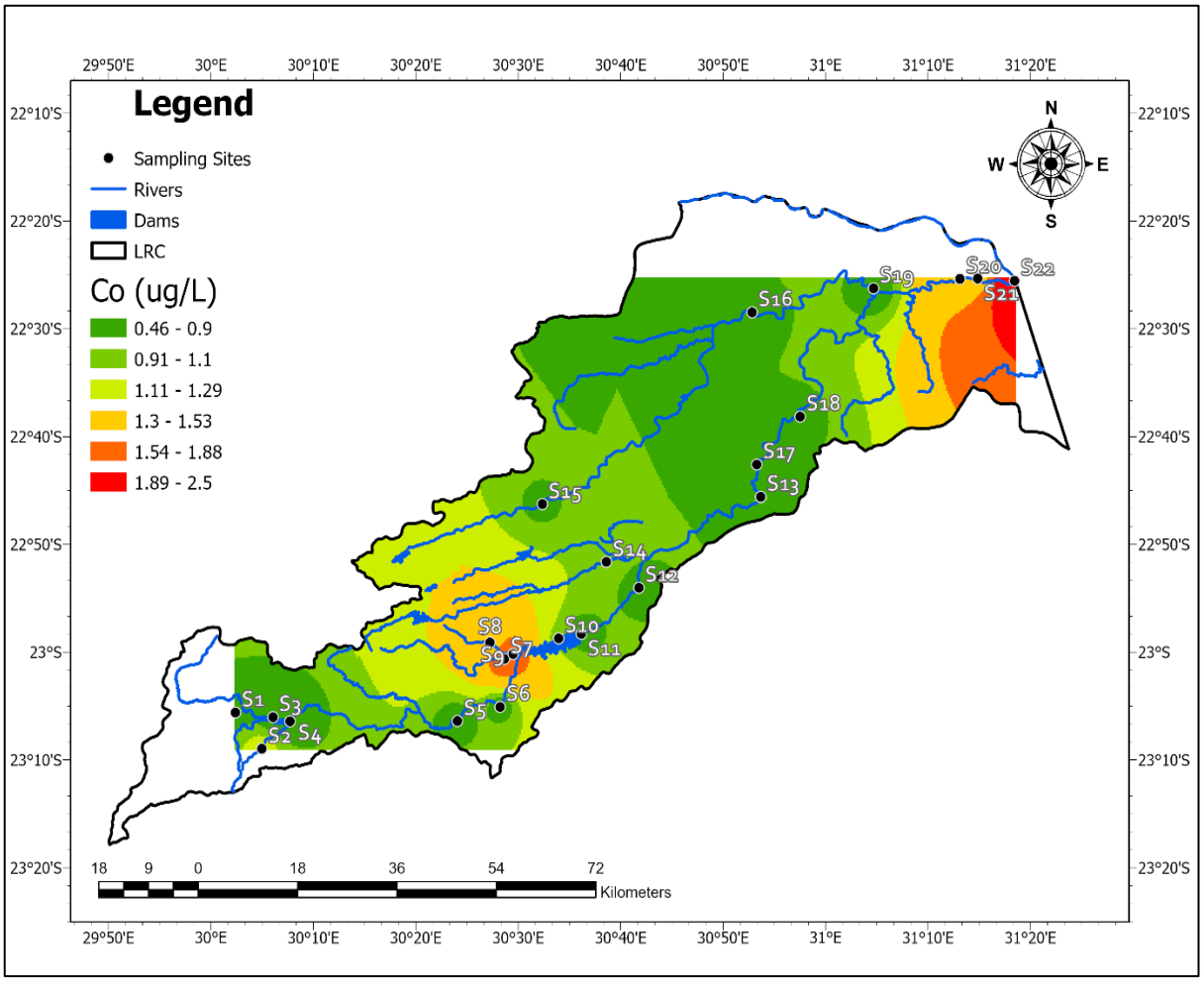

Figure 4.43: Concentration of Co in water samples.

Meanwhile, the highest Co concentration was noted at site S22 (2.50 µg/L) and the lowest at site S11. These results indicate that Co has a similar spatial pattern, perhaps signifying that they were influenced by the same source or input except for S22 (Li *et al.,* 2018). However, the statistical test showed a significant variance ($p < 0.05$) seasonally with the wet season showing the highest concentrations of Co than the dry season (Figure 4.44). Additionally, the concentration of Co complied with the DWAF standard for agricultural use (livestock watering and irrigation water use).

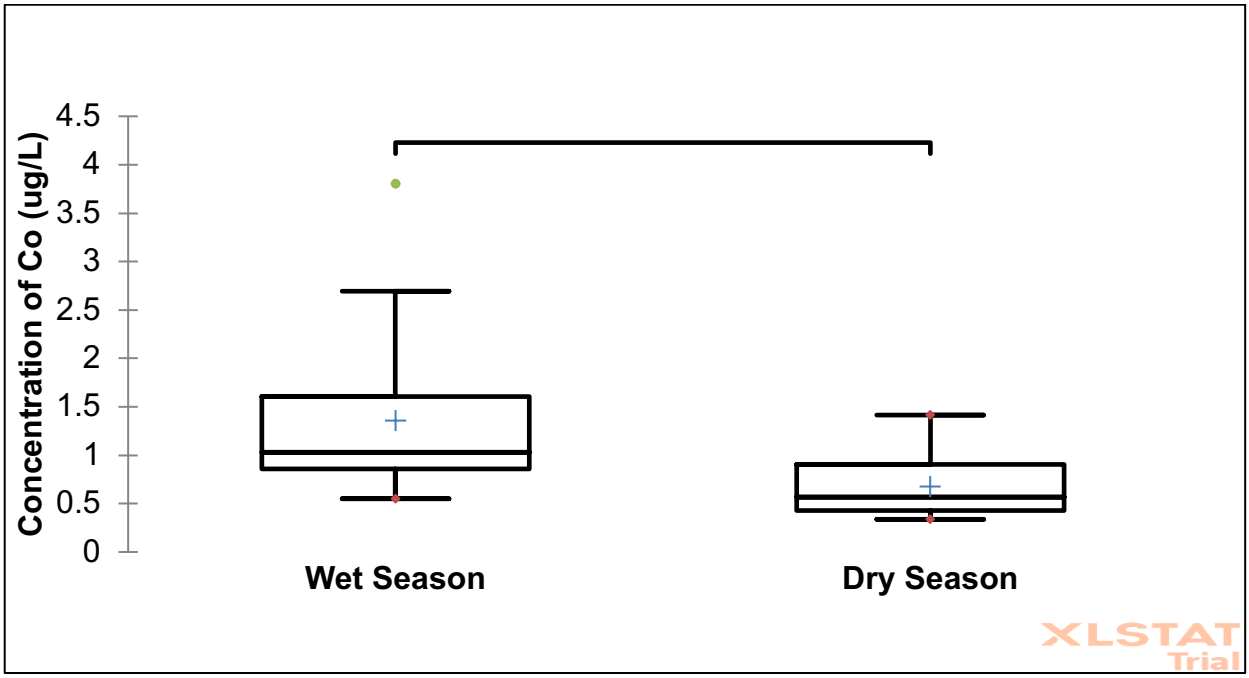

Figure 4.44: Seasonal variation of Co concentration in water

4.3.11 Concentration of Nickel (Ni) in water samples

As Table 4.3 show, the average concentration of nickel (Ni) in water samples from the LRC varied between 1.42 and 9.97 µg/L. The highest concentration was measured at site S22 and the lowest at the site S19 (Figure 4.45). Anthropogenic pressures, point or non-point sources, and geochemical processes in the region are likely responsible for this spatial variation (Bhuyan and Bakar, 2017; Sadeghi *et al.,* 2022). The results obtained in this study are similar to the report of (Islam *et al.,* 2020). Ni concentrations at all sampling sites were lower than SANS and WHO drinking standards (< 70 µg/L). There is no DWAF standard for Ni in river water for the protection of aquatic life. Brix *et al.* (2017) stated that several studies have addressed plausible mechanisms of Ni toxicity in aquatic eukaryotes (e.g., fish and invertebrates) that are typically the focus of aquatic environmental risk assessment.

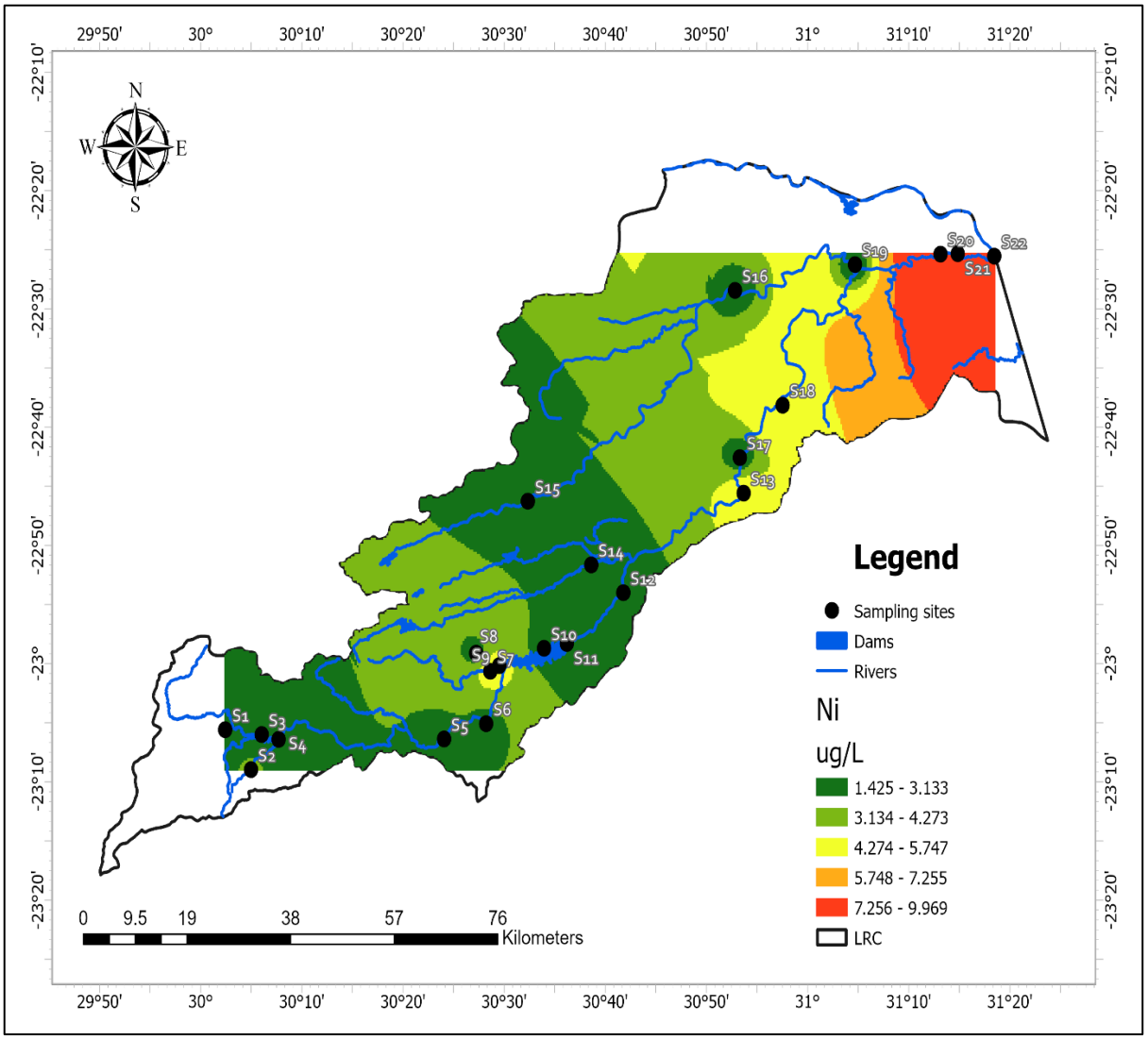

Figure 4.45: Spatial distribution of Ni in water samples.

Statistical results also showed a significant difference ($p<0.05$) between seasons. The high concentrations of Ni were reported during the wet season than in the dry season with the highest recorded value being 17.13 µg/L (Figure 4.46). High rainfall runoff could be linked to the seasonal variability of Ni in water samples. The concentration of Ni was found suitable for agricultural uses such as irrigation water and livestock watering based on the DWAF standard (Target Water Quality Range) of 1 mg/L and 0.2 mg/L, respectively.

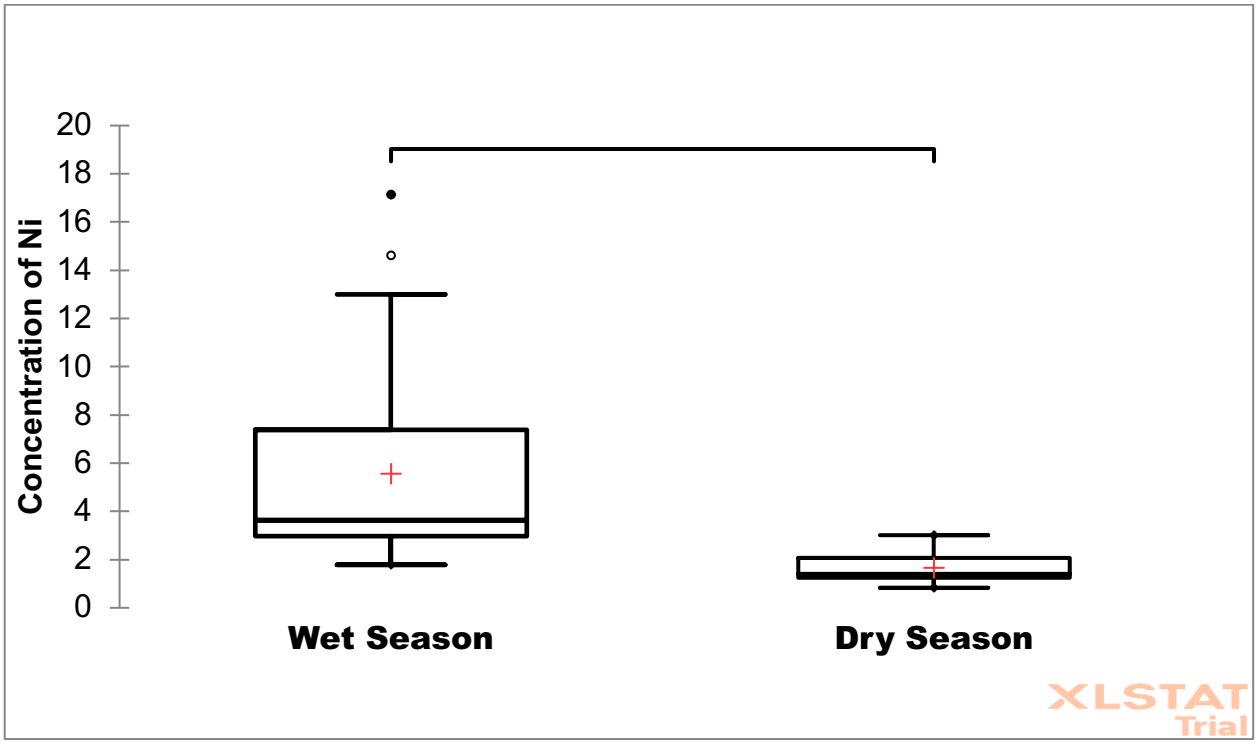

Figure 4.46: Seasonal variation of Ni in water samples

4.3.12 Concentration of Zinc (Zn) in water samples

Zinc (Zn) average concentrations in the river water samples ranged from 11.25 to 27.41 µg/L with a mean value of 18.59 µg/L (Table 4.3). Average zinc concentrations did not exceed SANS standards for domestic water use but exceeded DWAF limits for aquatic ecosystem protection. There is no WHO standard value for Zn for domestic uses. Nevertheless, the highest concentrations were found at site S22 and the lowest at site S17 (Figure 4.47). Similarly, high concentrations of Zn were also reported in the Ga-Selati and Olifant Rivers, Limpopo Province of South Africa (Addo-Bediako and Rasifudi, 2021; Genthe *et al.,* 2018b). Compared to other studies, the results obtained from this study exceeded those reported by Ernazarovna and Satorovich (2020) in Small Rivers of The Syrdarya Basins, Egypt and Mun River, Northeast Thailand (Liang *et al.,* 2019). In addition, higher Zn concentrations were found in river water samples during the wet season than during the dry season, but this variance was not statistically significant (Appendix 4.5). The reported results were also lower than the target water quality range set by the DWAF (1996) for agricultural use in irrigation (1.0 mg/L) and livestock watering (<20 mg/L).

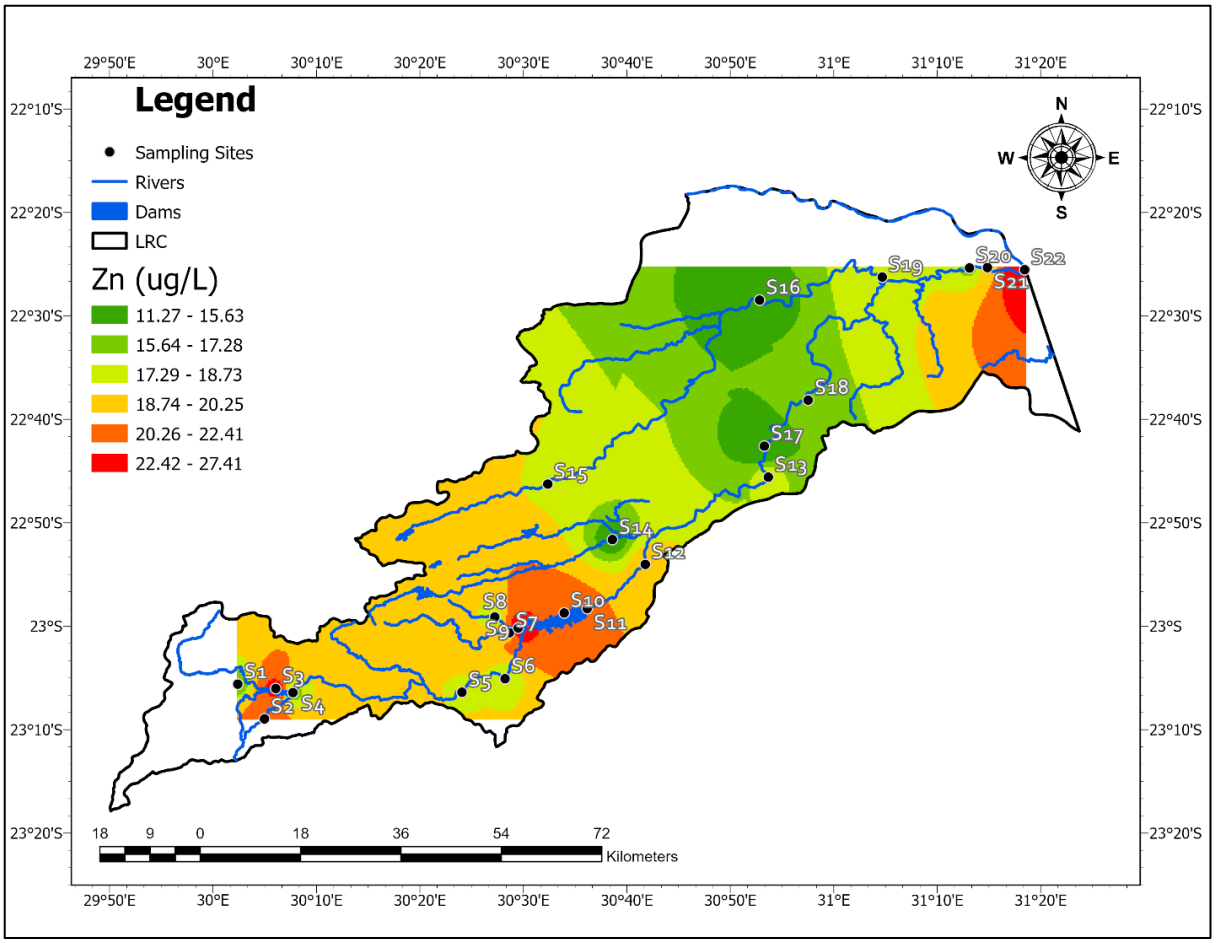

Figure 4.47: Spatial distribution of Zn concentration in river water samples

4.3.13 Concentration of molybdenum (Mo) in water

Average concentrations of molybdenum (Mo) in water samples ranged between 0.43 µg/L and 0.08 µg/L. Spatially, the highest concentration was measured at site S22 and the lowest was measured at site S15 (Appendix 4.6). There are no guideline values for Mo in river water either for domestic purposes or for the protection of the aquatic ecosystem. Zhang *et al.* (2022) indicated that Mo is a necessary microelement for plants and animals, but an excessive concentration of Mo has adverse effects. Several studies have shown that excessive intake of molybdenum may cause damage to the kidney, and reproduction function, as well as affect fish growth (Chen *et al.,* 2020; Feng *et al.,* 2020; Tang *et al.,* 2019; Wang *et al.,* 2016). In addition, higher Mo concentrations were detected in wet season water samples compared to the dry season (Appendix 4.7). However, this variance was statistically significant ($p < 0.05$). In comparison, the current reported results were lower than those reported by WRC (2011) in Olifants River Catchment in South Africa. The concentration of Mo was below the DWAF guideline for agricultural uses (irrigation water use and livestock watering).

4.3.14 Concentration of barium (Ba) in water

As shown by Peana *et al.* (2021), Barium (Ba) is an element that occurs naturally and the 14th most common element on the Earth's crust. Zoroddu *et al.* (2019) stated that Ba does not have a recognised biological role in humans but it appears to be essential for some organisms proper growth, such as *desmid green alga Closterium moniliferum* containing vesicles with barium sulfate in the crystalline form as barite (Krejci *et al.,* 2011). In the current study, the spatial distribution of Ba concentrations ranged from 23.76 to 70.69 µg/L (Appendix 4.8). The WRC (2011) also reported similar Ba concentrations from Olifants River, South Africa. The highest Ba concentration was measured at site S2 and lowest at the siteS14. Environmental contamination due to Ba has been linked to domestic waste containing Ba such as personal care products, cosmetics, plastics, adhesives, and ceramics which could be one cause of high Ba levels at site S2 (Peana *et al.,* 2021). Moreover, the Man-Whitney statistical test showed no significant difference between seasons (Appendix 4.9). Furthermore, there are no guidelines for Ba in water for agricultural uses and protection of aquatic life however, the reported concentrations were lower than the SANS recommended value.

4.3.15 Concentration of sodium (Na) in water

As shown in Table 4.3, the findings of the current study showed that the average concentration of sodium (Na) in the river water samples ranged between 5.67 and 18.53 mg/L with a mean value of 8.51 mg/L. The highest recorded value was obtained at sampling site S2 whereas the lowest value was recorded at site S14. However, a significant spatial distribution of Na was also observed between various sampling sites as shown in Figure 4.48.

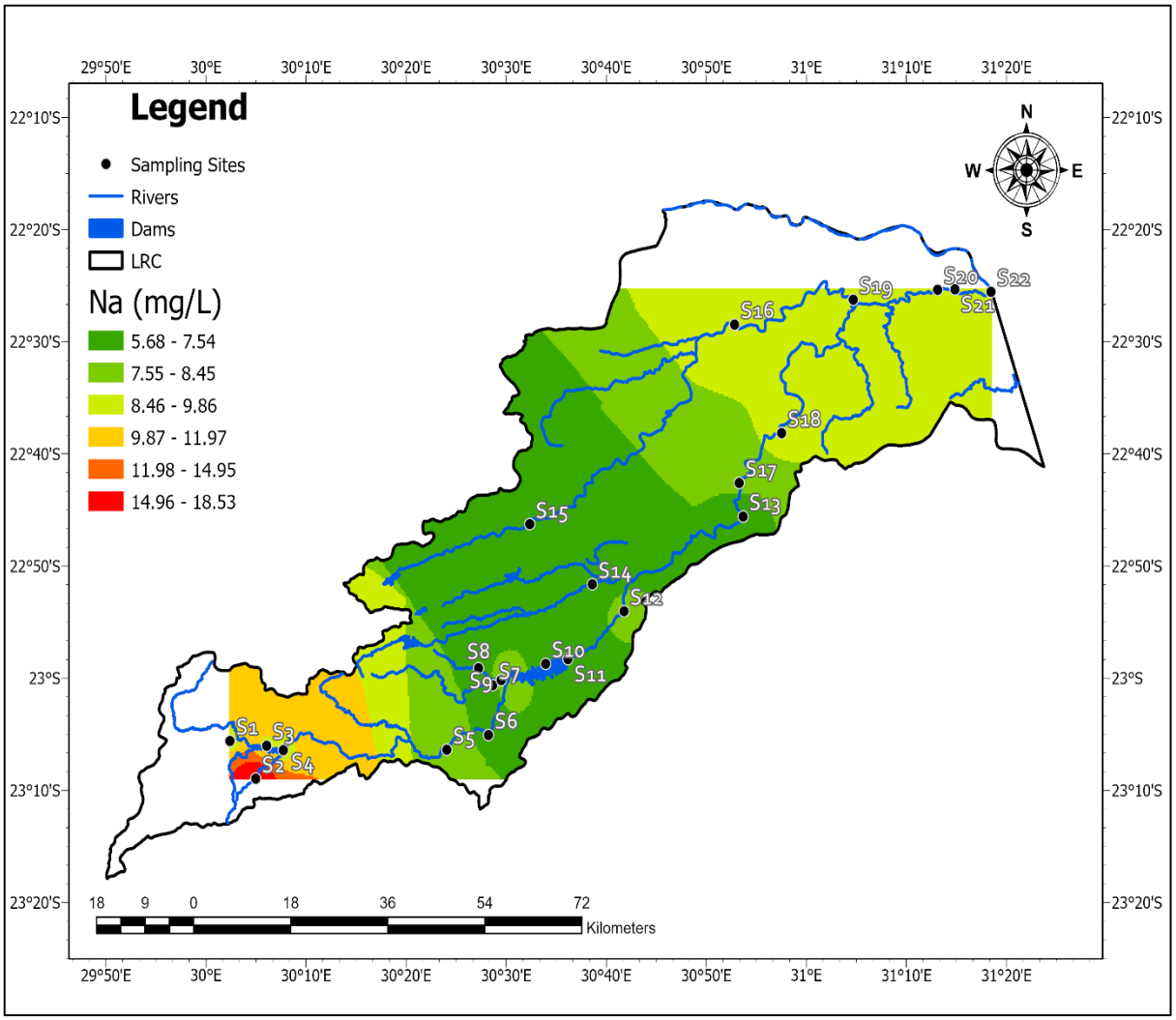

Figure 4.48: Spatial distribution of Na in the LRC.

Furthermore, the IDW map results, as shown above, indicates that the concentration of Na at upstream sites, especially S2 were higher than others and Na changes as the river flow midstream and downstream. This high record could be related to the fact that site S2 was located near the discharge point for domestic wastewater as such can contain a high concentration of major metals if the wastewater treatment plant is not complying with the regulations (Shubbar *et al.,* 2018). The reported results were below the SANS recommended value for drinking purposes. Generally, the obtained findings indicated that Na could not potentially pose human health issues. However, DWAF (1996) suggested that people suffering from renal, cardiovascular or hypertension diseases should abstain from Na intake.

Moreover, no significant difference was recorded between the wet and dry seasons ($p > 0.05$) (Figure 4.49). Nevertheless, the concentration of Na ranged between 5.84 and 20.20 mg/L with an average of 8.86 mg/L during the dry season and 5.50 and 16.85 mg/L with an average of 8.17 mg/L during the wet season.

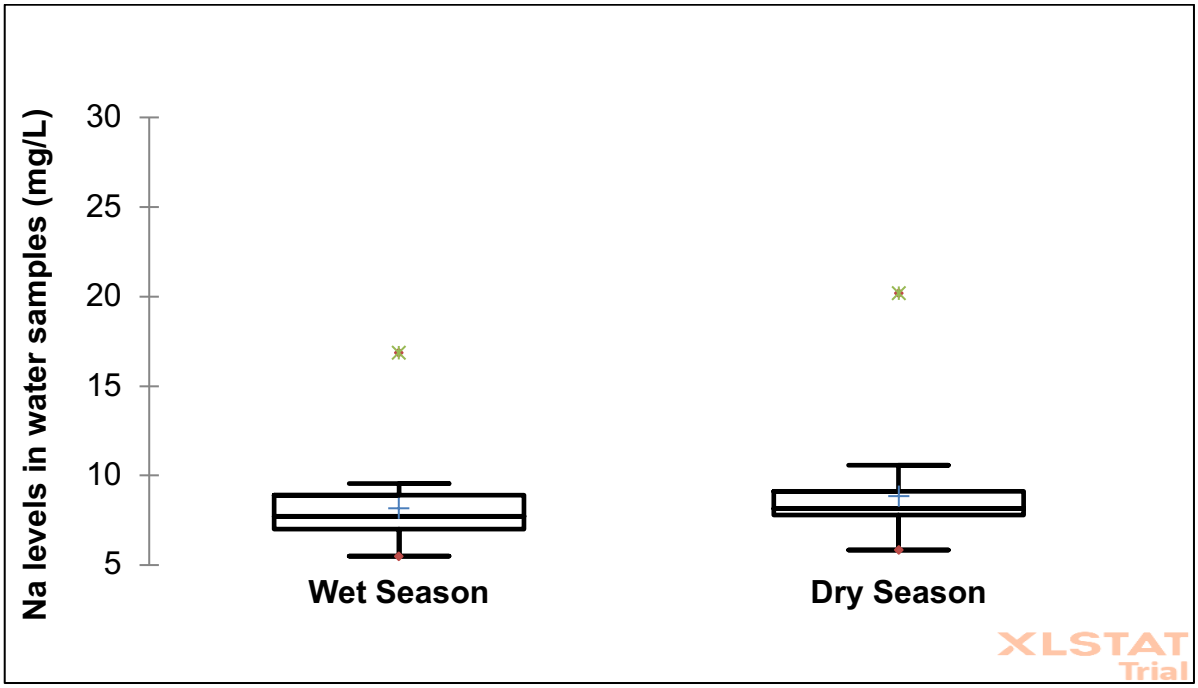

Figure 4.49: Box and whisker plots of seasonal variation of Na levels in water samples.

4.3.16 Magnesium (Mg) concentration in water

The average concentrations of magnesium (Mg) ranged from 3.93 to 16.23 mg/L with a mean value of 6.79 mg/L. The highest concentrations were observed at site S2 while the lowest concentrations were observed at sampling site S15. The recorded values varied spatially as shown in Figure 4.50. According to the IDW map results (Figure 4.50), high concentrations of Mg were observed upstream as compared to other parts of the catchment. The current reported values complied with the DWAF guideline for agricultural use (livestock watering).

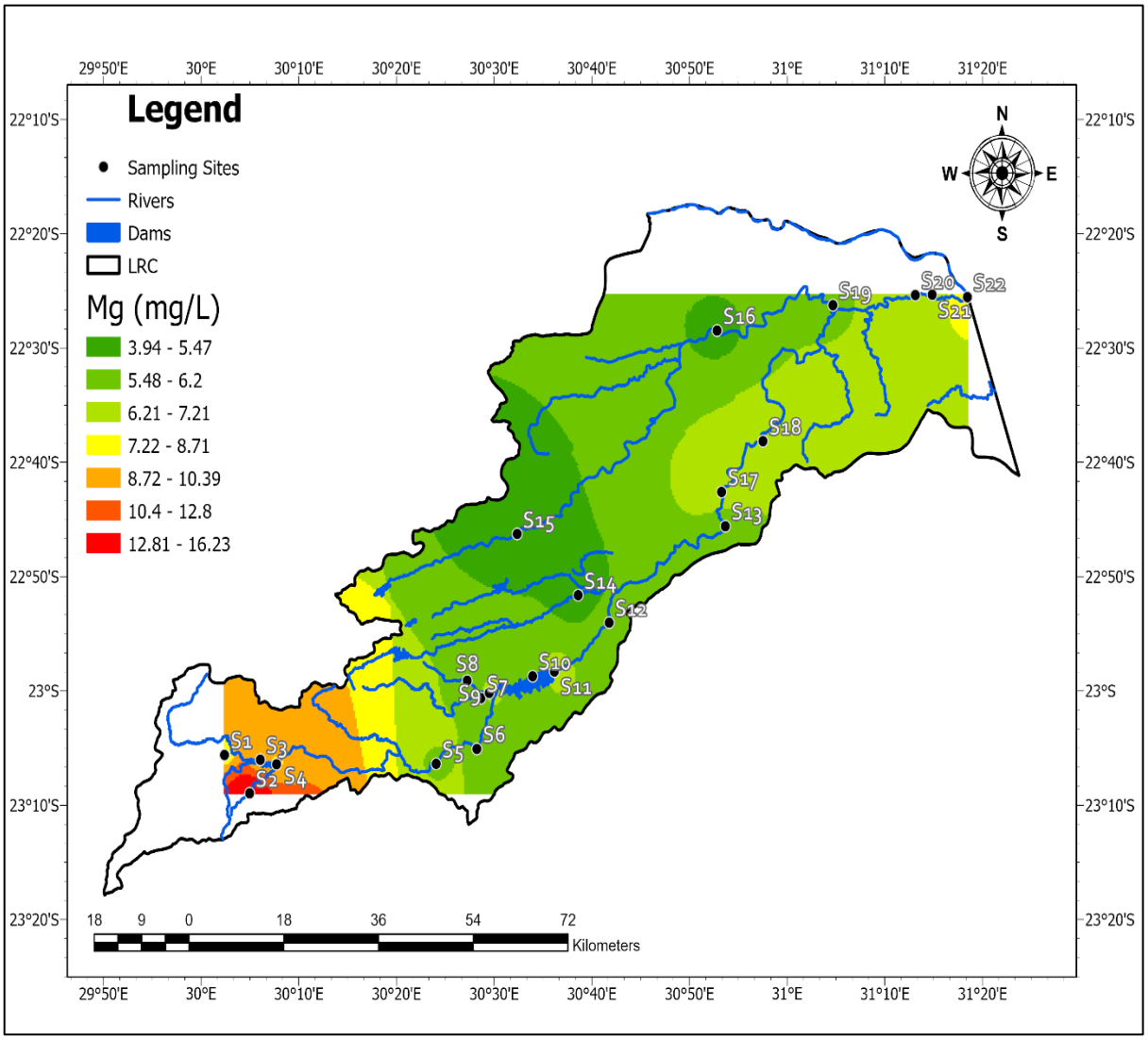

Figure 4.50: Spatial variation of Mg in LRC water samples.

The results showed that Mg concentrations in water samples showed no significant variation ($p > 0.05$) between seasons. During the wet season, the concentration ranged between 4.57 and 16.60 mg/L with an average value of 7.23 mg/L and in the dry season ranged from 3.20 to 15.87 mg/L with an average value of 6.36 mg/L (Figure 4.51). The average Mg values measured were slightly higher in the wet season than in the dry season. This may be due to dilution effects from rainfall that carry Mg-bearing material into the river (Bano *et al.,* 2022). The findings of this study were lower than those reported by Senze *et al.* (2021) from Nysa Szalona River, Poland.

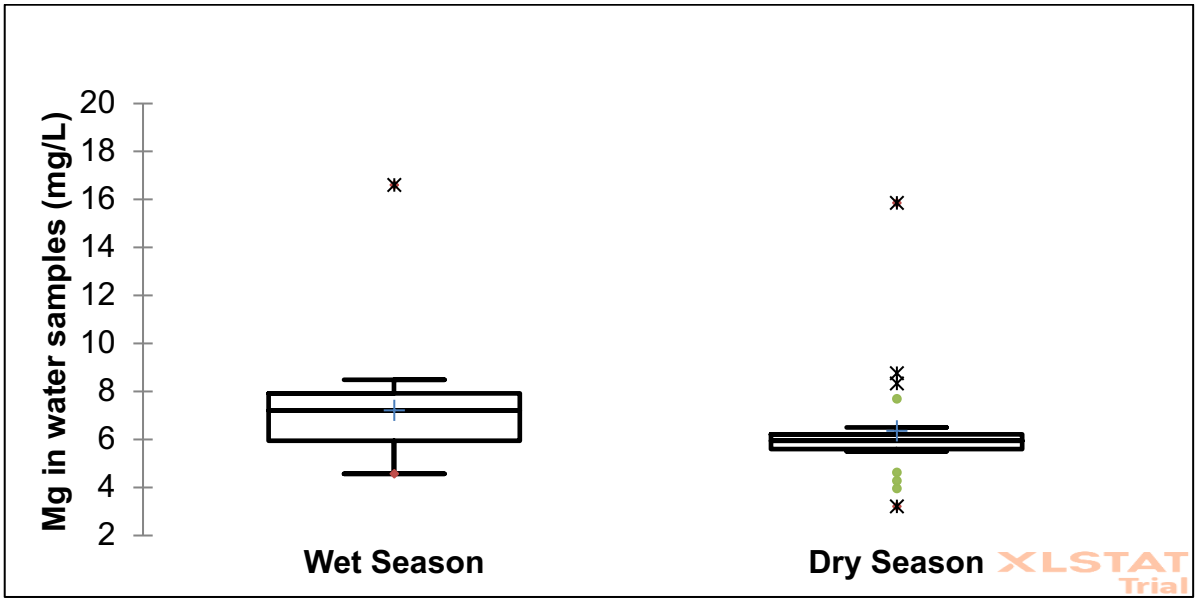

Figure 4.51: Box and whisker plots of seasonal variation of Mg in water samples of the LRC.

4.3.17 Potassium (K) concentration in water

The average concentrations of potassium (K) were in the range of 0.45-2.65 mg/L (Table 4.3). The computed mean value was 1.19 mg/L. There are no DWAF, SANS and WHO recommended values for K in drinking water and protection of aquatic ecosystems. The reported results were lower than those reported in the Bystrzyca river catchment, Poland by Skowron *et al.* (2018). The highest concentration was recorded at site S2, and the lowest concentration was recorded at site S15. Agricultural runoff, industrial and municipal sewage discharges are the familiar sources of potassium in river water (Skowron *et al.,* 2018). Furthermore, the results showed a statistically significant variation ($p<0.05$) between the wet and dry seasons, with the highest K concentration (2.90 mg/L) during the dry season.

4.3.18 Calcium (Ca) concentration in water

The average concentration of calcium (Ca) ranged from 7.32 to 21.16 mg/L with a mean value of 11.01 across all the sampling sites (Table 4.3). The highest concentration of Ca was recorded at site S2 and the lowest was recorded at S14. The high Ca concentration measured at site S2 could be attributed to domestic wastewater discharge from the sewage treatment plant upstream of this site. The average results obtained from this study were much higher than the global mean Ca concentration (4.0 mg/L) reported by Weyhenmeyer *et al. (*2019) from different freshwater bodies around the world including South Africa and Senze *et al. (*2021) from Nysa Szalona River, Poland. However, several studies indicated that the concentration of Ca in freshwaters is an essential driver of ecological community structure

(Hessen *et al.,* 2017; Jeziorski and Smol, 2017). Also, Hessen *et al. (*2017) further indicate that Ca is a valuable element for the population dynamics and growth of freshwater fauna and flora by prompting muscle contraction, intracellular signalling, enzymatic processes, and neuron activity. The Mann-Whitney test showed no statistically significant variance ($p > 0.05$) between the dry and wet seasons. However, the highest concentration Ca (23.89 mg/L) was recorded during the dry season. The concentration of Ca ranged from 6.57 to 23.89 mg/L during the dry season and 6.22 to 18.43 mg/L during the wet season.

4.4 Assessment of human health risk

4.4.1 Non-Carcinogenic Risks

Tables 4.4 and 4.5 show the carcinogenic and non-carcinogenic risk values of selected heavy metals for adults and children based on dermal absorption and ingestion exposure pathways. Ingestion and dermal absorption pathways are the major routes of exposure and the most imperative source of exposure to heavy metals from river water (USEPA, 2004). Metal-specific data was used to determine the CDI of heavy metals through both pathways. For both children and adults, the mean chronic daily intake showed that ingestion exposure poses more risk than dermal absorption exposure. Again, mean chronic daily intake was highest in adults than in children. This may be because adults have a higher average daily intake rate of water (L/day) than children. These results are similar to the report of Farhang (2020) on the Olifants River, South Africa. Compared to other metals, the mean $CDI_{ingestion}$ values revealed high uptake of Mn, Mo, Fe, and Ba for both adults and children. Thus, these metals could pose a high risk to water consumers. The CDI values obtained in this study are lower than those reported by Muhammad and Usman (2022) in the water of the Indus River and its tributaries, Northern Pakistan, and CDI was found to be high for Zn, Ni, and Cu.

Table 4.4: Hazard index (HI) and hazard quotient (HQ) of heavy metals in surface water from Luvuvhu River Catchment for Adults.

Metal	$CDI_{ingestion}$	CDI_{dermal}	$HQ_{ingestion}$	HQ_{dermal}	Cancer Risk
Pb	2.66×10^{-9}	2.46×10^{-11}	7.60×10^{-7}	7.02×10^{-9}	2.26×10^{-11}
Cd	1.28×10^{-10}	1.79×10^{-13}	1.28×10^{-7}	1.79×10^{-10}	7.83×10^{-10}
As	7.45×10^{-9}	2.89×10^{-12}	2.48×10^{-5}	9.64×10^{-9}	1.12×10^{-8}
Cu	1.32×10^{-9}	7.76×10^{-11}	3.31×10^{-8}	1.94×10^{-9}	-
Cr	7.45×10^{-9}	3.96×10^{-11}	2.48×10^{-6}	1.32×10^{-8}	-
Hg	8.20×10^{-10}	3.47×10^{-13}	2.73×10^{-6}	1.16×10^{-9}	-
Ni	2.12×10^{-9}	4.36×10^{-11}	1.06×10^{-7}	2.18×10^{-9}	-
Zn	7.29×10^{-9}	2.63×10^{-10}	2.43×10^{-9}	8.77×10^{-10}	-
Ba	2.27×10^{-8}	-	3.24×10^{-7}	-	-
Fe	4.40×10^{-8}	2.36×10^{-8}	1.47×10^{-7}	7.87×10^{-8}	-
Mo	8.54×10^{-8}	4.40×10^{-12}	4.27×10^{-6}	2.20×10^{-10}	-
Mn	1.71×10^{-7}	1.72×10^{-9}	3.41×10^{-5}	3.43×10^{-7}	-
HI	-	-	**7.00×10^{-5}**	**4.58×10^{-7}**	-

- *means no values were calculated.*

Table 4.5: Hazard index (HI) and hazard quotient (HQ) of heavy metals in surface water from Luvuvhu River Catchment for children.

Metal	$CDI_{ingestion}$	CDI_{dermal}	$HQ_{ingestion}$	HQ_{dermal}	Cancer Risk
Pb	3.96×10^{-10}	2.02×10^{-11}	9.89×10^{-9}	5.05×10^{-10}	4.78×10^{-14}
Cd	7.94×10^{-10}	5.62×10^{-12}	2.27×10^{-7}	1.61×10^{-9}	2.88×10^{-13}
As	3.83×10^{-11}	4.73×10^{-14}	3.83×10^{-8}	4.73×10^{-11}	1.18×10^{-12}
Cu	2.23×10^{-9}	7.84×10^{-13}	7.42×10^{-6}	2.61×10^{-9}	-
Cr	2.22×10^{-9}	9.83×10^{-12}	7.41×10^{-7}	3.28×10^{-9}	-
Hg	2.45×10^{-10}	9.14×10^{-14}	8.16×10^{-7}	3.05×10^{-10}	-
Ni	6.35×10^{-10}	1.28×10^{-11}	3.17×10^{-8}	6.39×10^{-10}	-
Zn	2.18×10^{-10}	7.28×10^{-11}	7.26×10^{-9}	2.43×10^{-10}	-
Ba	6.77×10^{-9}	-	9.68×10^{-8}	-	-
Fe	1.32×10^{-8}	6.14×10^{-9}	4.38×10^{-8}	2.05×10^{-8}	-
Mo	2.55×10^{-8}	1.06×10^{-12}	1.28×10^{-6}	5.28×10^{-11}	-
Mn	5.10×10^{-8}	4.36×10^{-10}	1.02×10^{-5}	8.72×10^{-8}	-
HI	-	-	**2.09×10^{-5}**	**1.17×10^{-7}**	-

- *means no values were calculated.*

Estimated hazard quotients (HQ) for children and adults are summarised in Table 4.4 and Table 4.5. Average values of hazard quotients for both adults and children were noted in the descending order of 1>Mn>As>Mo>Hg>Cr>Pb>Ba>Fe>Cd>Ni>Cu>Zn. The HQ showed values that were less than one indicating a tolerable level of non-carcinogenic adverse health risk. In this study, Mn showed the highest hazard quotient. This could be due to the fact that the concentration of Mn was reported higher than the recommended limit for drinking water use. Thus, Mn is the major element to cause health concerns in both adults and children. According to Qu *et al.* (2018), exposure to high levels of Mn can cause permanent neurological damage known as manganism, with symptoms such as tremors, difficulty walking, and facial muscle spasms. However, no known health effects of that nature have been reported within

the study area. A previous study by Madilonga *et al.* (2021), also computed an HQ <1 for the metals evaluated in the Mutangwi River, Limpopo Province, South Africa. Studies have suggested that even when heavy metal HQs for children are <1, they should not be ignored (da Silva Bonifácio *et al.,* 2021; Giandomenico *et al.,* 2016). According to Mafulul *et al.* (2022), children are highly susceptible to environmental contaminants because their body systems are not fully developed. This is particularly the case for Pb because no evidence has been found for a threshold below which no harmful effects occur (U.S. EPA 2004). Therefore, the human nervous system, especially that of a child or foetus, is very sensitive to low concentrations of Pb because the biological impacts of Pb are not yet fully understood (U.S. EPA 2004).

The hazard index (HI) of selected heavy metals was found below 1, which suggests no obvious non-carcinogenic hazard to consumers. However, the hazard index based on ingestion was greater than that of dermal absorption though dermal absorption exposure is most dominant in the area. Therefore, consuming this water without treatment poses more risk than swimming. Comparatively, the non-carcinogenic risk is higher for adults than for children in the study area. The results of this study are dissimilar from the report of Madilonga *et al.* (2021) where HI was found higher in children than adults. The results of this study were also lower than the report of Kamunda (2017) in water samples around a gold mining area in Gauteng Province, South Africa. Though the HI values for both children and adults were below the standard value of 1, long-term exposure and increased land use activities within the LRC would potentially raise a human health concern. The low HI observed in the water samples is due to the low concentrations of heavy metals in samples. The unpredictably low HI from exposure to heavy metals in water can be due to complex geological formations with high biological productivity (Aski *et al.,* 2022). According to de Souza-Araujo *et al.* (2022), in bodies of water that contain high biological productivity complexation with the participation of natural organic ligands is the dominant factor in the stabilisation of metals in a solution.

4.4.2 Carcinogenic risks

According to USEPA (2011), carcinogenic risks are regarded as the likelihood that a person will develop any form of cancer during their lifetime as a result of being exposed to carcinogenic hazards. In this study, the carcinogenic risk was computed for As, Cd and Pb as these metals are categorised as carcinogenic to children and adults (ASTDR 2012). For metals without known cancer slope factors, the risk was not calculated. Cancer risks for adults and children are shown in Tables 4.4 and 4.5. Carcinogenic values in the range of 10^{-6} to 10^{-4} indicate tolerable or acceptable risks to social stability and human health (Qasemi *et al.,*

2023). In this study cancer risks were negligible, as metal revealed cancer risks scores below the target of 10^{-6} (USEPA 2011).

Considering the ingestion exposure pathway, computed cancer risk values for adults were within the range of 2.26 x 10^{-11} to 1.12 x 10^{-8} and were 4.78 x 10^{-14} to 1.18 x 10^{-12} for children. As contributed more risk compared to Pb and Cd. The carcinogenic risks of Cd, Pb and As from ingestion pathways under study were much lower than standard values in children. These findings clearly indicate that adults are more vulnerable to health hazard associated with water consumption than children. These findings are dissimilar from the report of Madilonga *et al.* (2021) where the vulnerability was found amongst children than adults. However, several studies have shown that long-term exposures to drinking water containing As and Pb can cause carcinogenic effects, diabetes, skin lesions, hypertension, and neuropathy even if their concentrations are low (Qasemi *et al.,* 2023; Xiao *et al.,* 2019). The current results were also lower than the study of Kamunda (2017) in water samples collected around gold mining areas in Gauteng Province, South Africa.

CHAPTER 5: RESULTS AND DISCUSSION OF HEAVY METALS IN SEDIMENTS SAMPLES

5.1 Concentrations and distribution of metals in the surface sediments of the LRC.

Table 5.1 provides descriptive statistics (mean values) for Cu, Ni, Zn, Al, Cr, Co, As, Mo, Cd, Mn, Fe, Pb, Hg, and Ba in sediment samples from the LRC as well as the background reference values for protecting aquatic ecosystem. A total of 252 samples were collected from 22 different sites, which showed significant spatial distribution. As South Africa does not have sediment quality guidelines (SQG) for metal concentrations in freshwater sediments, the Canadian Council of Environment Ministers (CCME) SQG for freshwater sediments was used in this study (DEA, 2011; Edokpayi *et al.,* 2017).

Table 5.1: Descriptive stats for heavy metal concentrations in sediments of the LRC from 22 sampling sites.

Metal	Min	Max	Mean	Std. Deviation	ASV	ISQGs	PEL	TEL
Hg	0.01	0.02	0.01	0.003	*	0.17	0.49	0.174
As	0.42	0.89	0.62	0.12	*	13	17	5.9
Pb	2.99	22.65	7.66	4.12	20	35.0	91.3	30.2
Cd	0.01	0.11	0.03	0.02	0.3	0.6	3.5	0.68
Cr	25.21	112.75	54.76	19.54	90	37.3	90	52.3
Cu	9.21	52.20	25.90	10.00	45	35.7	197	18.7
Mn	0.11	1.69	0.40	0.33	850	-	-	460
Fe	14723.05	44812.96	24437.96	7443.81	46000	-	-	-
Co	5.14	31.20	13.02	5.53	19.01	-	-	-
Ni	12.50	49.62	25.31	9.54	50	-	35.9	15.9
Al	3878.43	14391.93	8788.63	2687.27	80000	-	-	-

Zn	11.09	35.45	19.47	5.41	95	123	315	124
Mo	0.09	0.29	0.17	0.05	2.6	-	-	-
Ba	37.55	93.34	59.79	16.07	580	-	-	-

*All metals, guidelines, and background values are in mg/kg. * = no background values, - = no guideline values, ISQGs = interim sediment quality guidelines of Canada, PEL = probable effect levels, ASV = Average Shale Values and TEL= the threshold effect level.*

5.1.1 Concentration of mercury (Hg) in sediment samples

The concentrations of Hg in all the sampling sites are presented in Appendix 4.13, which reveals no significant spatial variance. The concentrations of Hg in the sediment showed a similar value of 0.01 mg/kg at most sites except for sites S2 and S3 which recorded 0.02 mg/kg, respectively. Generally, Hg showed the highest average values upstream of the LRC. According to the New Hampshire Department of Environmental Services (NHDES) (2019) report, Hg can be found in the aquatic environment because of the burning of fossil fuels, soils, municipal or medical waste, and weathering of rocks. NHDES (2019) further stipulated that even low concentrations of Hg interfere with reproduction in fish-eating animals such as birds. Furthermore, the results of this study did not indicate a statistically significant variation ($p>0.05$) between seasons (Figure 5.1). However, the highest concentration (0.02 mg/kg) of Hg was observed during the wet season. A study by Mohajane and Manjoro (2022) from Molopo River, Northwest Province of South Africa, reported higher concentrations of Hg (0.59 mg/kg) than the current study. For Hg, all the analysed samples were within the minimal effect range, less than PEL and TEL. Thus, indicating low harmful effects to occur on sediment-dwelling fauna.

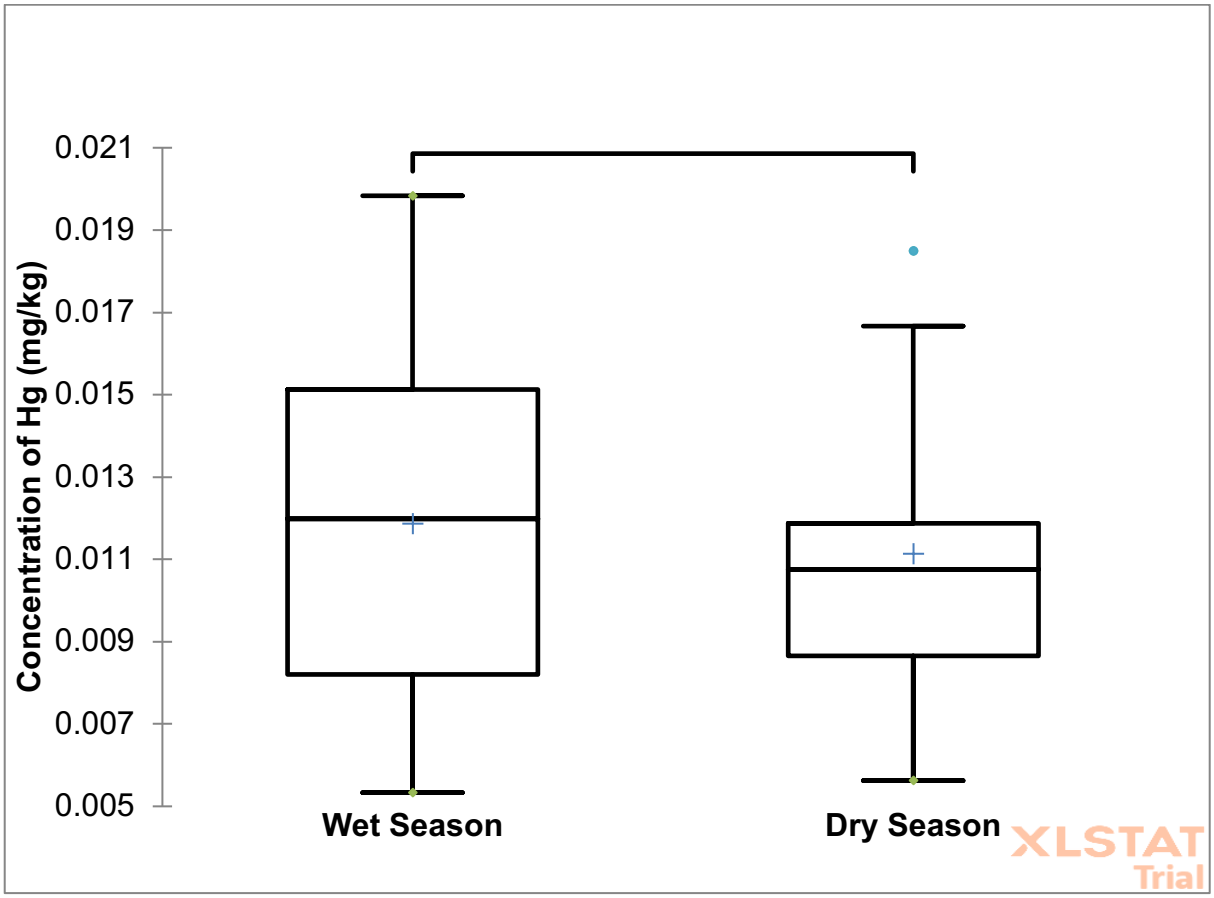

Figure 6: Box and whisker plots of seasonal variation of Hg in sediments samples of the LRC.

5.1.2 Concentration of arsenic (As) in sediment samples

Arsenic (As) is a naturally occurring chemical element widely distributed in the earth's crust (Tran *et al.,* 2018). In the environment, As levels differ by location and are found in different mediums viz. soil, air and water (Alamdar *et al.,* 2017). In this study, the average concentration of As ranged between 0.42 mg/kg and 0.89 mg/kg with a mean value of 0.62 mg/kg. The highest As concentration was measured at site S20 and lowest at site S10 (Figure 5.2). The results of this study show that the concentration of As at downstream sites (S20, S21, and S22) is much higher than at other sites, suggesting that downstream river flow, erosion of arsenic-containing rocks (geological formations), and rapid settlement activity (land use) contributes to As contamination in surface sediment. Interestingly, these results are lower than the ASV (Turekian and Wedepohl, 1961). The current reported results are also lower than the PEL and TEL, indicating no adverse effects can occur in the sediment-dwelling organisms. Moreover, no statistically significant temporal difference between seasons was recorded with the concentrations ranging from 0.38 to 1.02 mg/kg during the wet season and 0.44 to 0.86 mg/kg during the dry season, respectively. Generally, the results obtained in this study are lower than the report of Addo-Bediako and Rasifudi (2021) in sediments of Ga-Selati River,

South Africa ranging from 5–15 mg/kg and Addo-Bediako *et al.* (2021) in the sediments of Spekboom River, South Africa. The reported results also complied with the PEL and TEL guidelines.

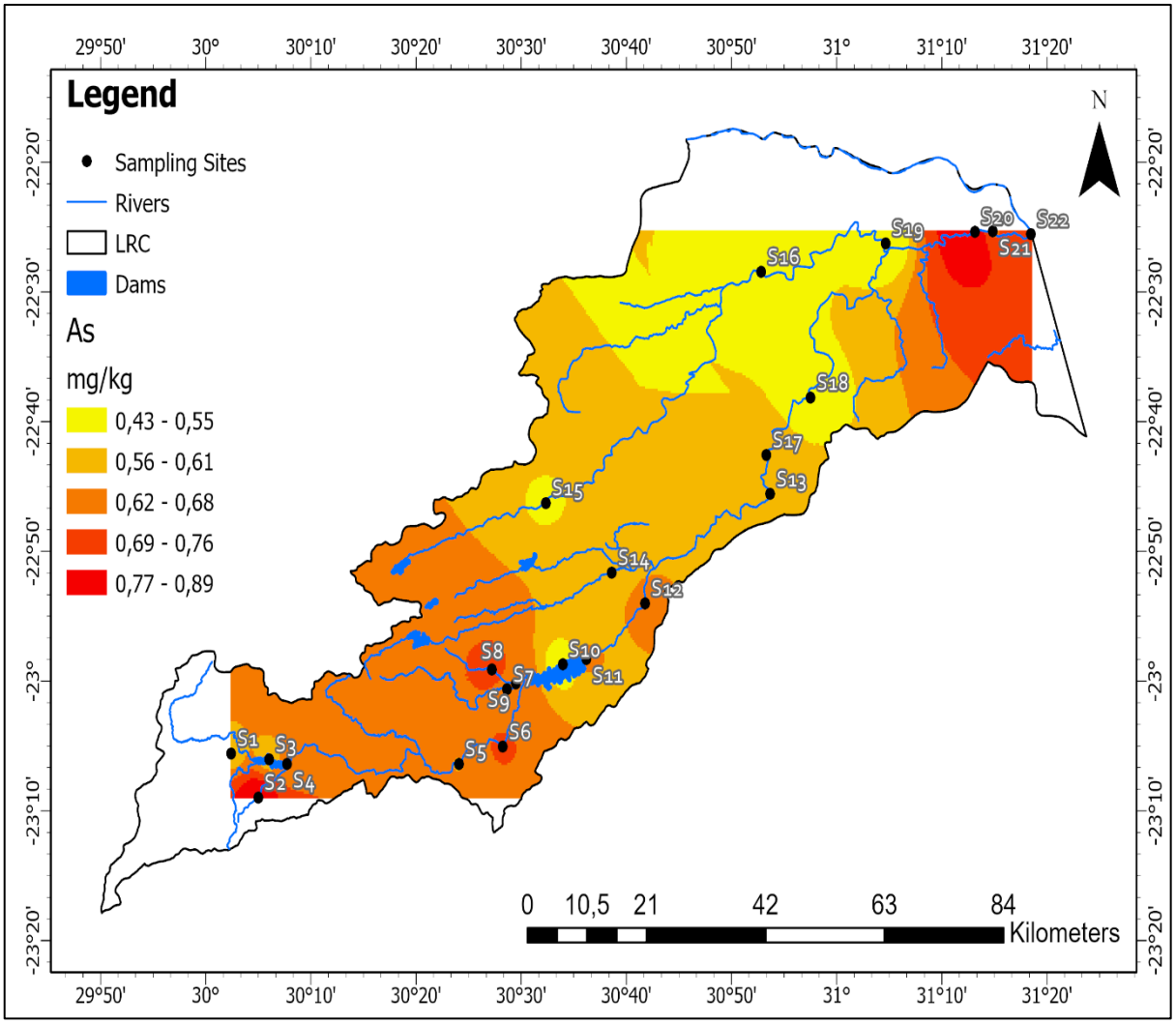

Figure 5.2: Spatial distribution of As in sediments samples.

5.1.3 Concentration of lead (Pb) in sediment samples

Lead is a non-essential, toxic metal and has no nutritional value for living organisms (Edokpayi *et al.,* 2016). In the current study, the highest Pb concentration was observed at site S2 (22.65 mg/kg) and the lowest at site S19 (2.99 mg/kg), with an average of 7.66 mg/kg, respectively. As shown in Figure 5.3, the concentration of Pb varied spatially. All the sampling sites recorded Pb values below the ASV of 20 mg/kg. Based on Li *et al.* (2018), the high concentrations of Pb could be from the source rocks. However, the high recorded level of Pb at site S2 could be attributed to land use activities (point and nonpoint sources, such as atmospheric deposition and municipal sewage runoffs) (Islam and Al-Mamun, 2017; Islam *et al.,* 2022).

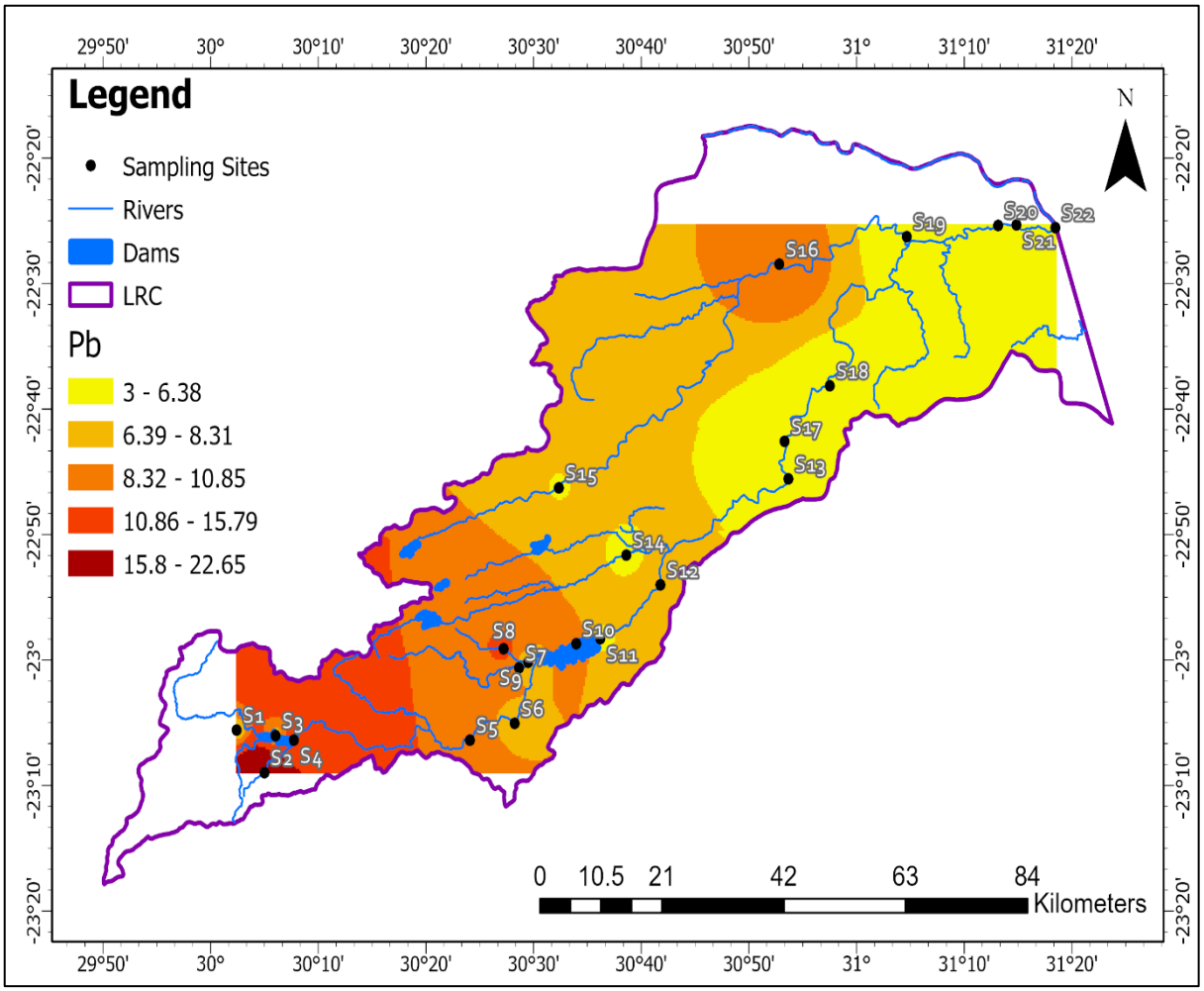

Figure 5.3: Spatial distribution of Pb in sediment samples.

The highest concentration of Pb (27.97 mg/kg) was observed during the dry season. Furthermore, the concentrations of Pb ranged between 2.80 and 17.66 mg/kg with an average value of 8.17 mg/kg during the wet season and 2.44 to 27.97 mg/kg with a mean value of 7.15 mg/kg, respectively (Figure 5.4). Also, these results showed no statistically significant variation ($p>0.05$). Although no statistically significant difference was observed, Pb was observed to be higher in the dry season compared to the wet season. This suggests that there may be changes in the organic profile due to deposition and/or resuspension, or fluctuations in redox and pH conditions (Ali *et al.,* 2022; Proshad *et al.,* 2019). The current results are higher than the report of Addo-Bediako *et al.* (2021) in the sediment samples of the Dwars River ranging from 2.4-4.2 mg/kg and Addo-Bediako (2020) in the Blyde and Steelpoort river sediments, South Africa. Furthermore, the highest Pb concentration measured was lower than PEL and TEL, so no adverse biological effects are expected, although a significant increase in Pb concentration could have adverse effects on sediment-dwelling organisms.

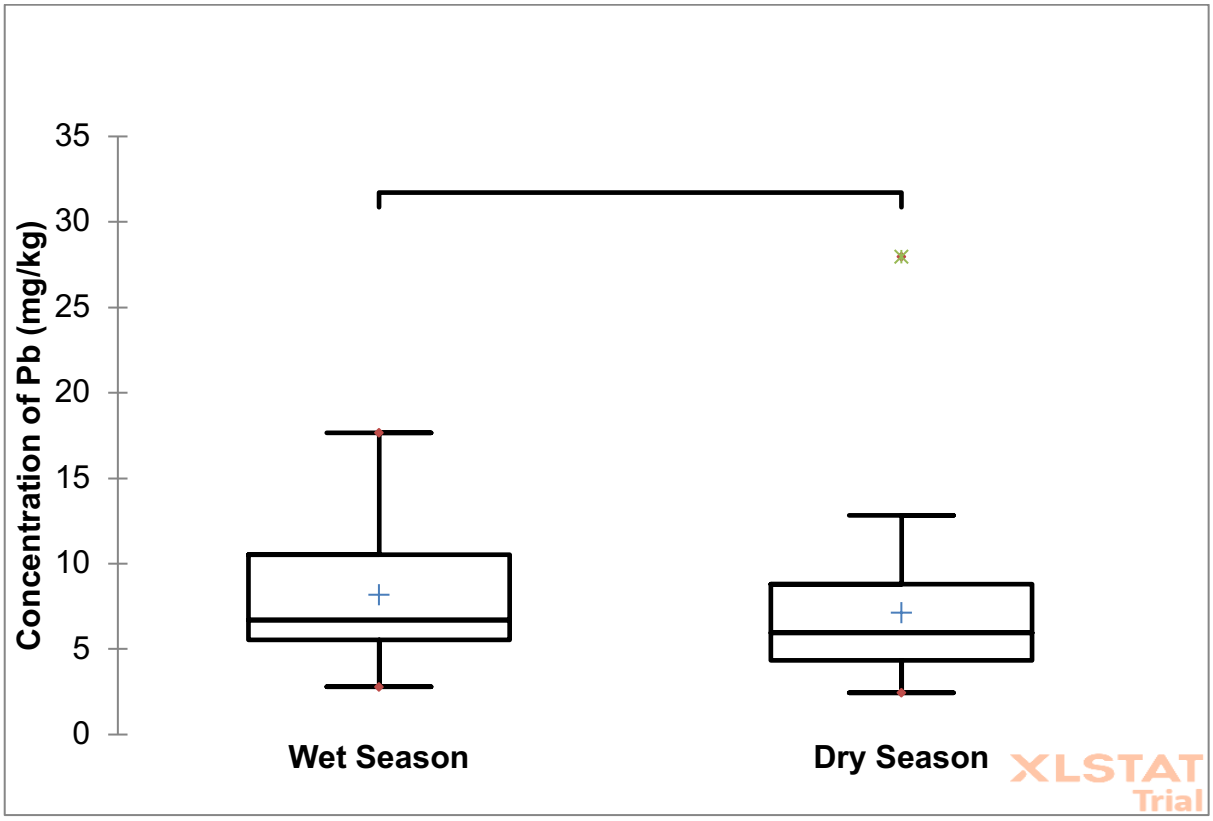

Figure 5.4: Box and whisker plots of seasonal variation of Pb in sediments samples.

5.1.4 Concentration of cadmium (Cd) in sediment samples

As reported by Edokpayi *et al.* (2016), Cd is an extremely toxic element and non-essential for marine and freshwater organisms. The spatial concentrations of Cd determined in this study ranged from 0.01 to 0.11 mg/kg with an average value of 0.03 mg/kg (Table 5.1). Figure 5.5 shows the spatial variation of Cd levels in the study area. Discharge of agricultural and domestic wastes could be linked to Cd pollution in S7 and S8. Further, the discharge of wastewater effluent may be the reason for the elevated concentration of Cd in the sediments at site S7. Kumar *et al. (*2015) report that Cd has the greatest tendency to remigrate from the sediment phase to the bioavailable pore water phase.

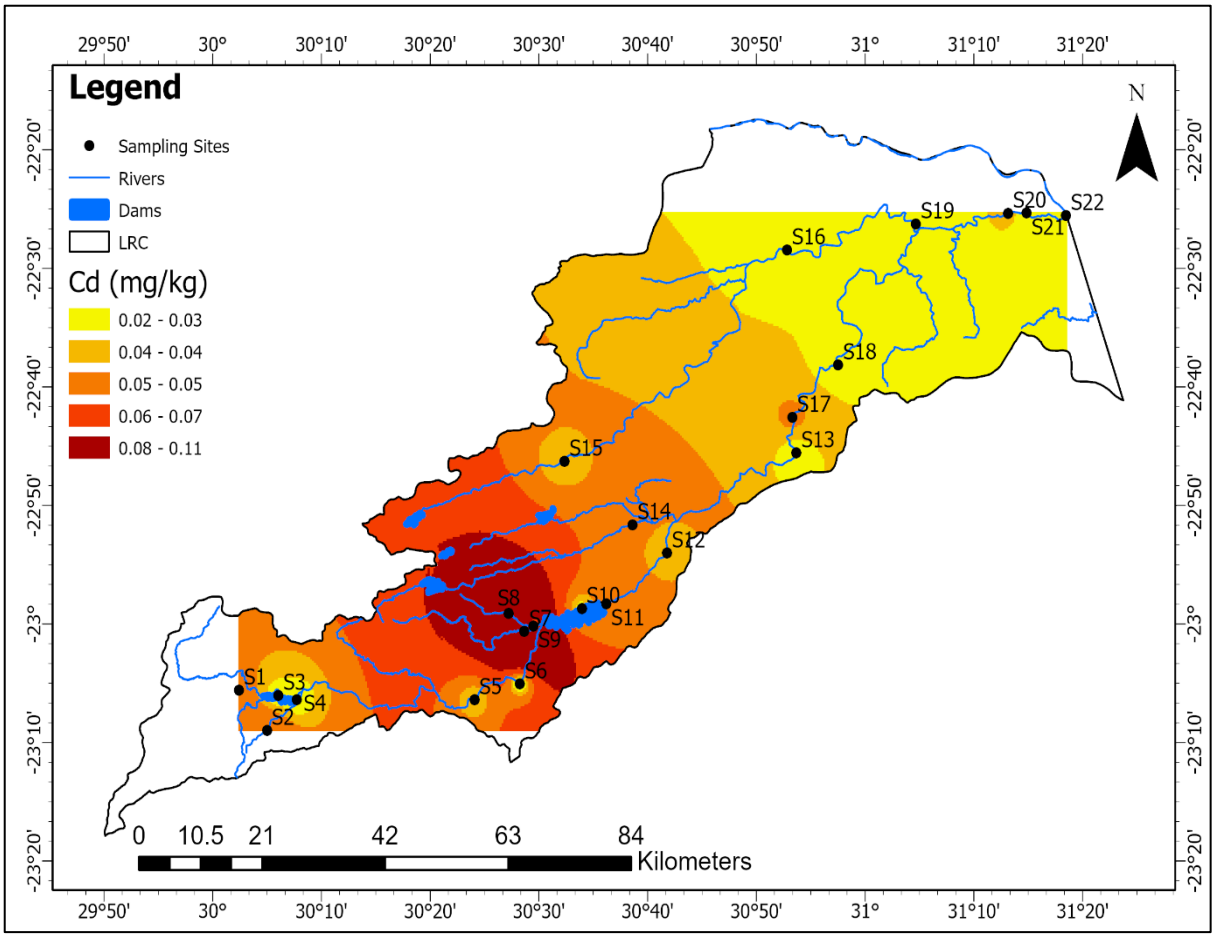

Figure 5.5: Spatial distribution of Cd in sediment samples

When comparing seasonal results, there was no statistically significant variation ($p>0.05$) observed between seasons (Figure 5.6). However, the highest concentration of Cd (0.12 mg/kg) was recorded during the dry season. The slightly elevated Cd levels in the dry season can be attributed to fluctuations in river water levels, where water inflow into rivers is generally inadequate in the dry season, leading to precipitation of pollutants in sediments (Ali *et al.,* 2016). The average concentration of Cd (0.03 mg/kg) measured in this study was lower than the report of Mohajane and Manjoro (2022) of 1.61 mg/kg from Molopo Riverin the North-West Province. A study by Izegaegbe *et al.* (2020) in the sediment of the Mhlathuze Estuary in the northern KwaZulu-Natal Province reported lower concentrations of Cd than this study. Conclusively, the recorded concentrations were in the minimal effect range (less than TEL) and none of the samples was in the probable effect range (PEL). Therefore, Cd concentrations would not impose adverse biological effects on sediment-dwelling organisms.

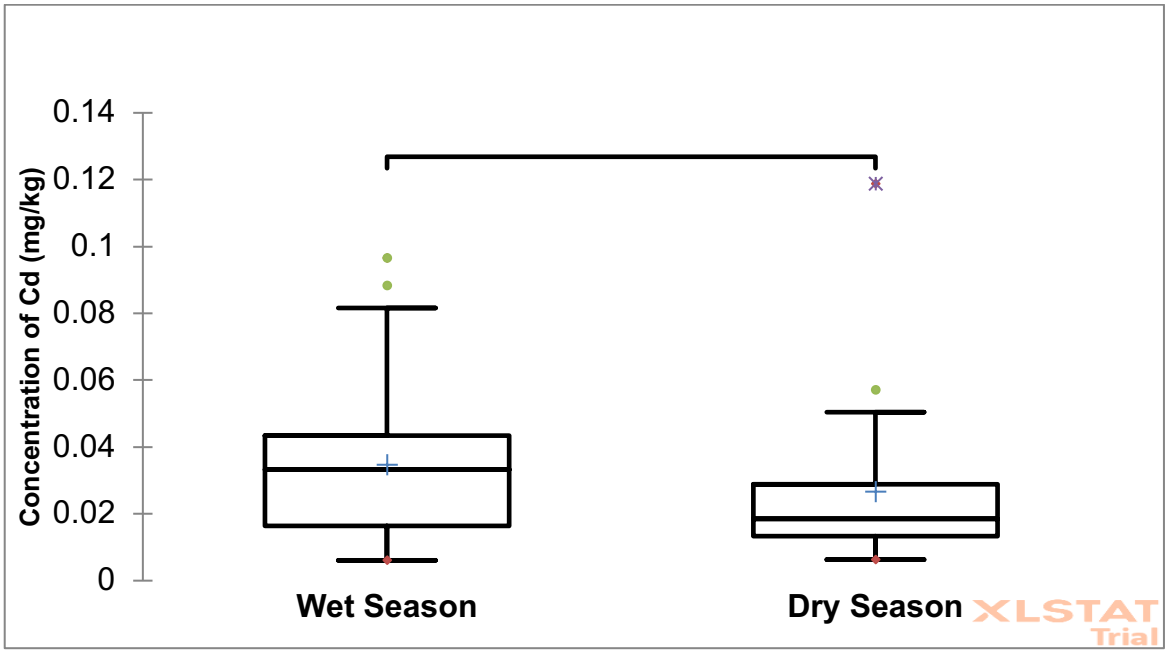

Figure 5.6: Box and whisker plots of seasonal variations of Cd concentration in sediment samples of the LRC.

5.1.5 Concentration of chromium (Cr) in sediment samples

Mean Cr concentrations in sediments ranged from 25.21 to 112.75 mg/kg, with an average value of 54.76 mg/kg (Table 5.1). Several sampling sites exceeded the CCME guideline value (37.3 mg/kg) for Cr in freshwater sediments. Spatially, the highest average Cr concentrations were observed in site S7 (midstream) and the lowest in site S16 (downstream) (Figure 5.7). According to Kormoker *et al.* (2019) and Kumar *et al.* (2015), higher anthropogenic influence and higher clay content (natural: concentration of Cr-bearing minerals) in the sediment can lead to a higher accumulation of Cr in the river sediments, and vice-versa. The elevated concentration of Cr noticed in this study was also higher than the reference background value (90 mg/kg) by Hakanson (1980). For Cr, about 50% of the samples were higher than the TEL range suggesting adverse biological effects upon sediment-dwelling organisms. However, these results rise an alarming concern for KNP as sites S20, S21, and S22 also showed concentrations higher than TEL. Concentration higher than the PEL range was only determined from one sampling site (S7) which indicates the high effects of this metal on the aquatic environment.

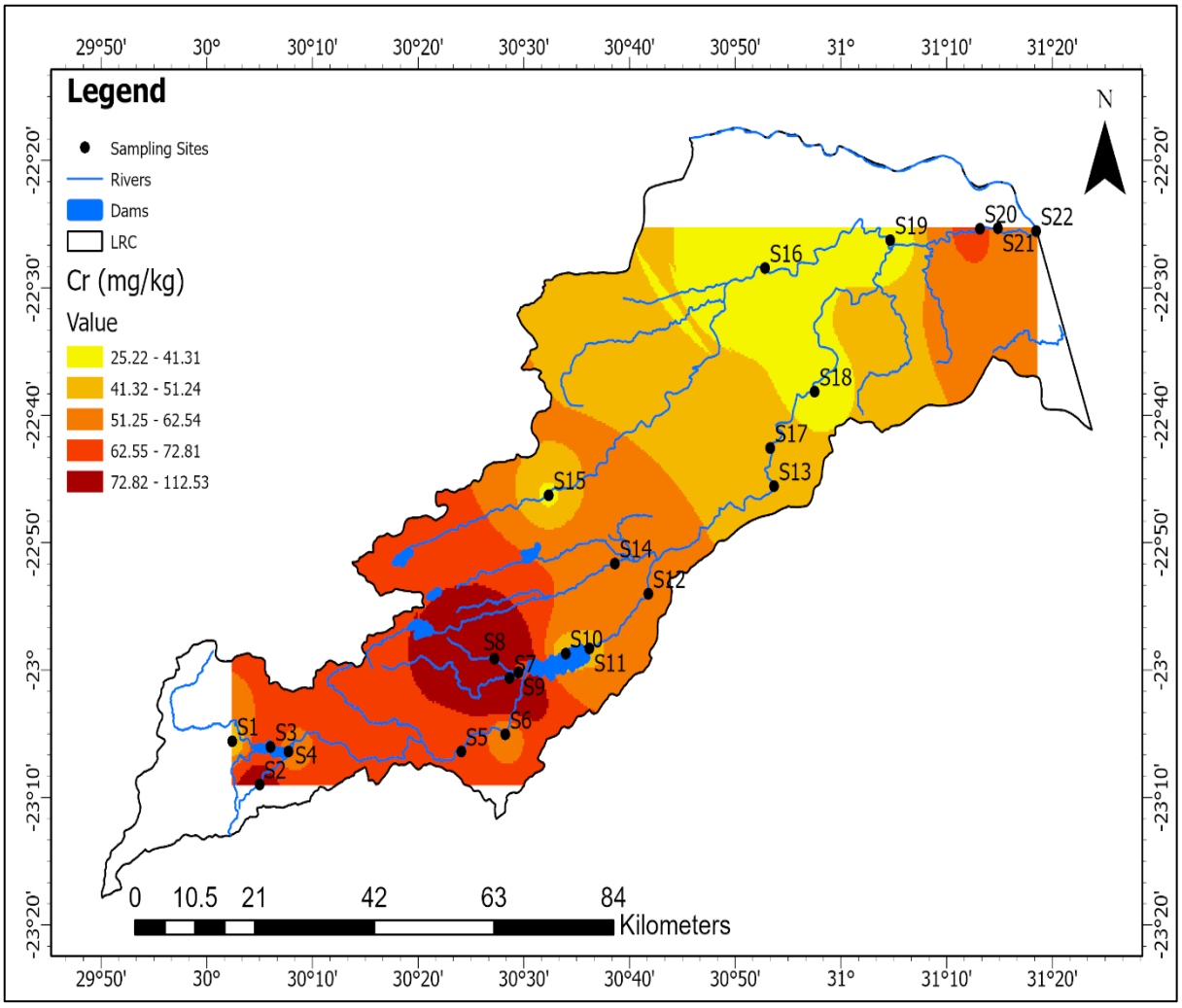

Figure 5.7: Spatial distribution of Cr concentration in sediments.

However, the difference in mean Cr concentration of sediment samples was not statistically significant ($p > 0.05$). However, the highest Cr concentration was in the dry season (119.74 mg/kg). Additionally, Cr concentrations ranged between 21.61 and 105.76 mg/kg in the wet season and 25.88 mg/kg to 119.74 mg/kg in the dry season, respectively (Figure 5.8). In general, the Cr concentrations in the sediments of the LRC are similar to those found in the sediments of Ga-Selati River in South Africa (Addo-Bediako and Rasifudi, 2021) but lower than the report of Addo-Bediako *et al.* (2021) in Spekboom River also in South Africa.

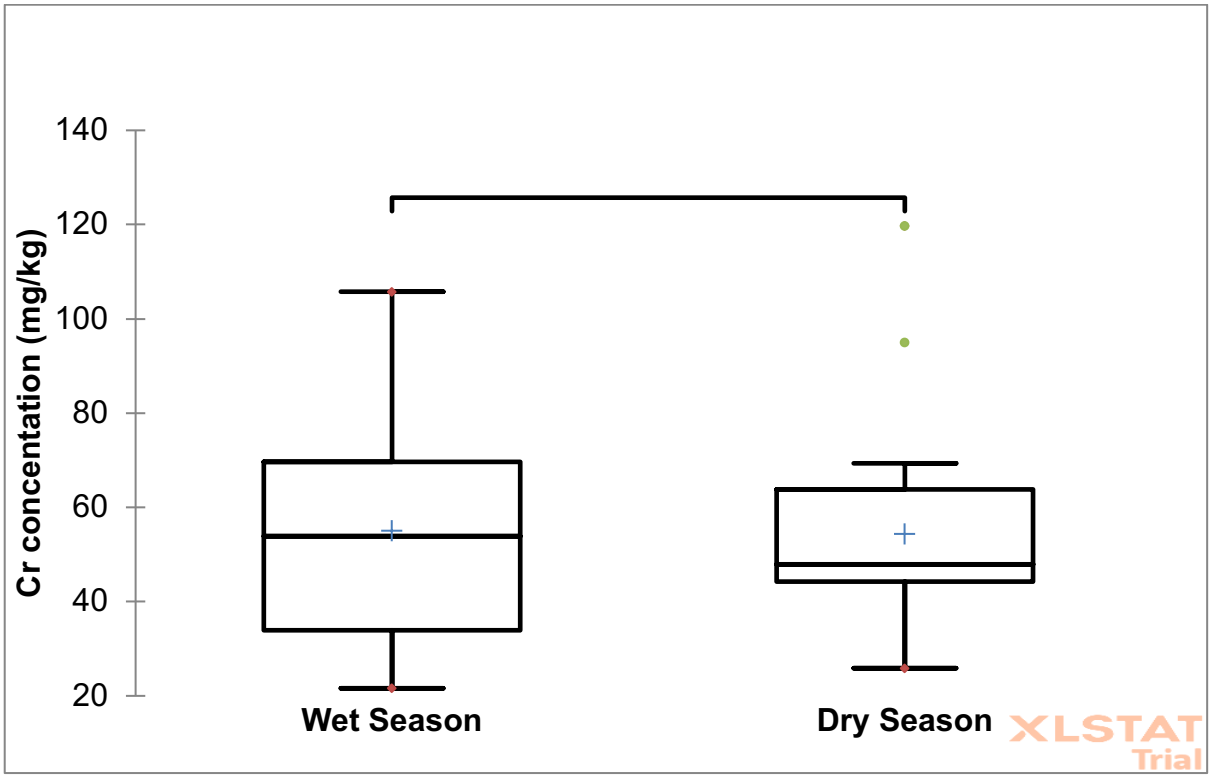

Figure 5.8: Box and whisker plots of seasonal variation of Cr concentrations in sediments of the LRC.

5.1.6 Concentration of copper (Cu) in sediment samples

Several studies have shown that Cu is potentially dangerous only when present in high concentration in an environmental media (Edokpayi *et al.,* 2016; Şaylan *et al.,* 2023). However, this element is essential for proper plant growth as it is a building block of various proteins and enzymes (Decena *et al.,* 2018). In this study, the average Cu levels in sediments ranged from 9.21 to 52.20 mg/kg, with an average of 25.90 mg/kg (Table 5.1). The highest concentration of Cu was observed from site S8 while the lowest was from site S19 (Figure 5.9). In addition, environmental Cu contamination is associated with suspected pesticide use and domestic wastewater at Site S8 (Decena *et al.,* 2018). Cu is widely used in the manufacturing of electrical wiring, roofing materials, alloys, pigments, cookware, and plumbing (Decena *et al.,* 2018). Mean Cu concentrations in stream sediments corresponded to the CCME specified limit of 37.5 mg/kg for Cu in freshwater sediments at all sampling points except sampling points S2 and S8. Edokpayi *et al.* (2016) also report a similar pattern in the sediments of Mvudi River, Luvuvhu River Catchment in Limpopo Province, South Africa. Additionally, the statistical test (Mann-Whitney) showed no significant difference between seasons. The concentrations of Cu ranged from 10.19 to 59.56 mg/kg during the wet season and 8.18 to 44.85 mg/kg during the dry season, respectively (Appendix 4.11). The observed Cu concentrations in this study did not exceed the ASV. However, 86.36% of sampling sites exceeded the TEL range for Cu thus

indicating the likelihood of biological effects occurring due to high concentrations of Cu in the LRC. For all the studied sites, none of the samples exceeded the PEL range.

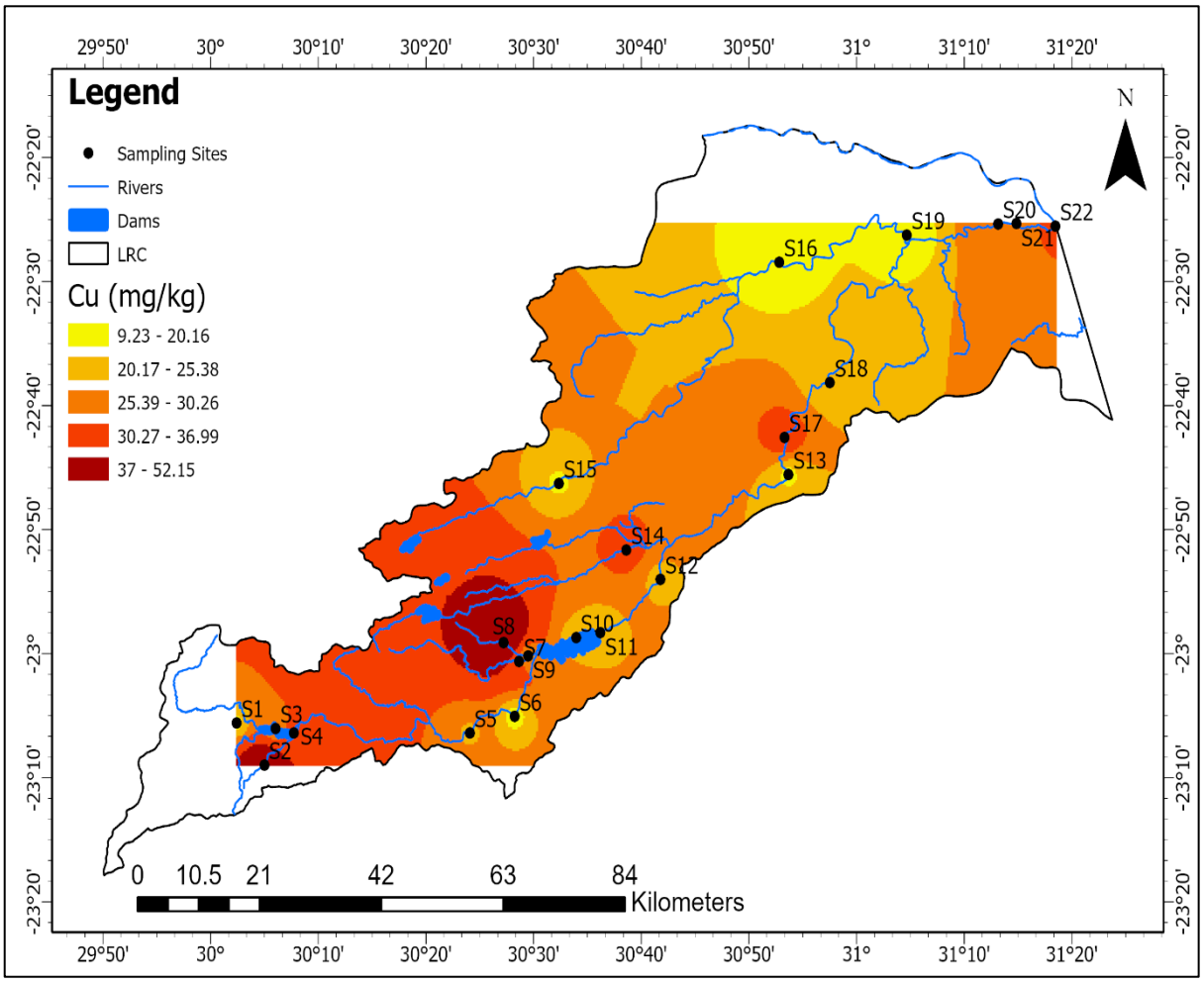

Figure 5.9: Spatial distribution of Cu in sediment samples

5.1.7 Concentration of aluminium (Al) in sediment samples.

The spatial average concentrations of Al in the sediments of the LRC ranged from 3878.43 to 14391.93 mg/kg with a mean value of 8788.63 mg/kg (Table 5.1). The highest Al concentration was observed at site S2 and the lowest at site S16 (Figure 5.10). Studies indicate that Al levels may be related to its significant abundance on Earth, and high concentrations of Al have been previously found in river systems in South Africa (Edokpayi *et al.,* 2016; Senze *et al.,* 2021). In addition, the use of Al-bearing materials in river basins may also be a source of high value, as villages along rivers do not have effective solid waste collection and disposal systems (Edokpayi *et al.,* 2017).

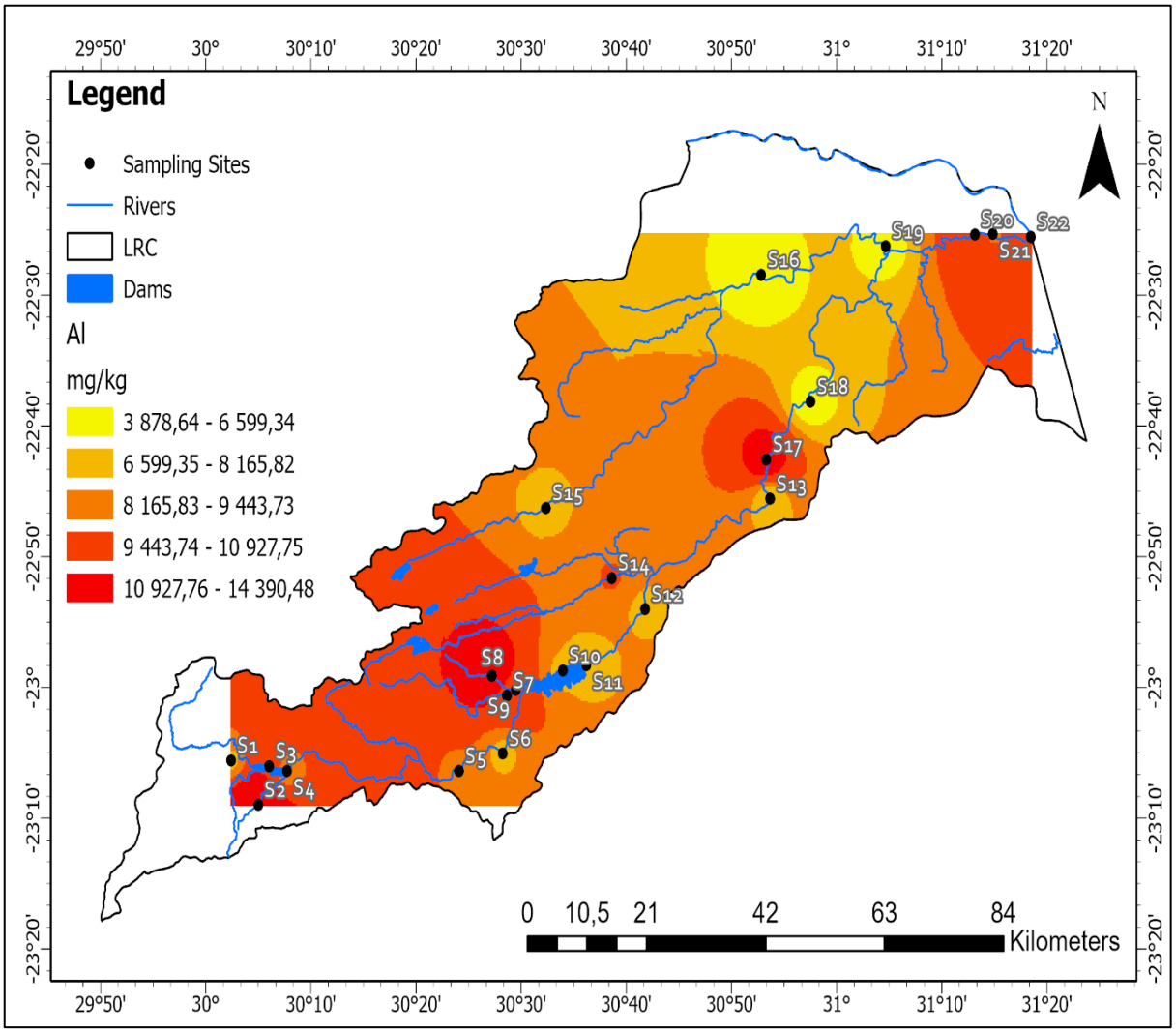

Figure 5.10: Spatial distribution of Al concentrations in sediment samples.

The concentration of Al did not significantly vary statistically ($p>0.05$) with seasons and the highest concentration was observed in the wet season (Figure 5.11). Therefore, when it rains, rainfall easily carry Al-bearing materials into rivers, which could explain the high concentrations observed during the wet season (Edokpayi *et al.,* 2017). At the time of conducting this study, Al was not assigned a reference value in this study as there are no guideline standards. When comparing the concentration of Al detected in this study with the study of Edokpayi *et al.* (2016) in Mvudi River, Limpopo, South Africa, it was found that these results were higher than for those reported but lower than that of WRC (2011) in the Lake Flag Boshielo, South Africa. Currently, there are no PEL and TEL guideline values for Al in sediment samples.

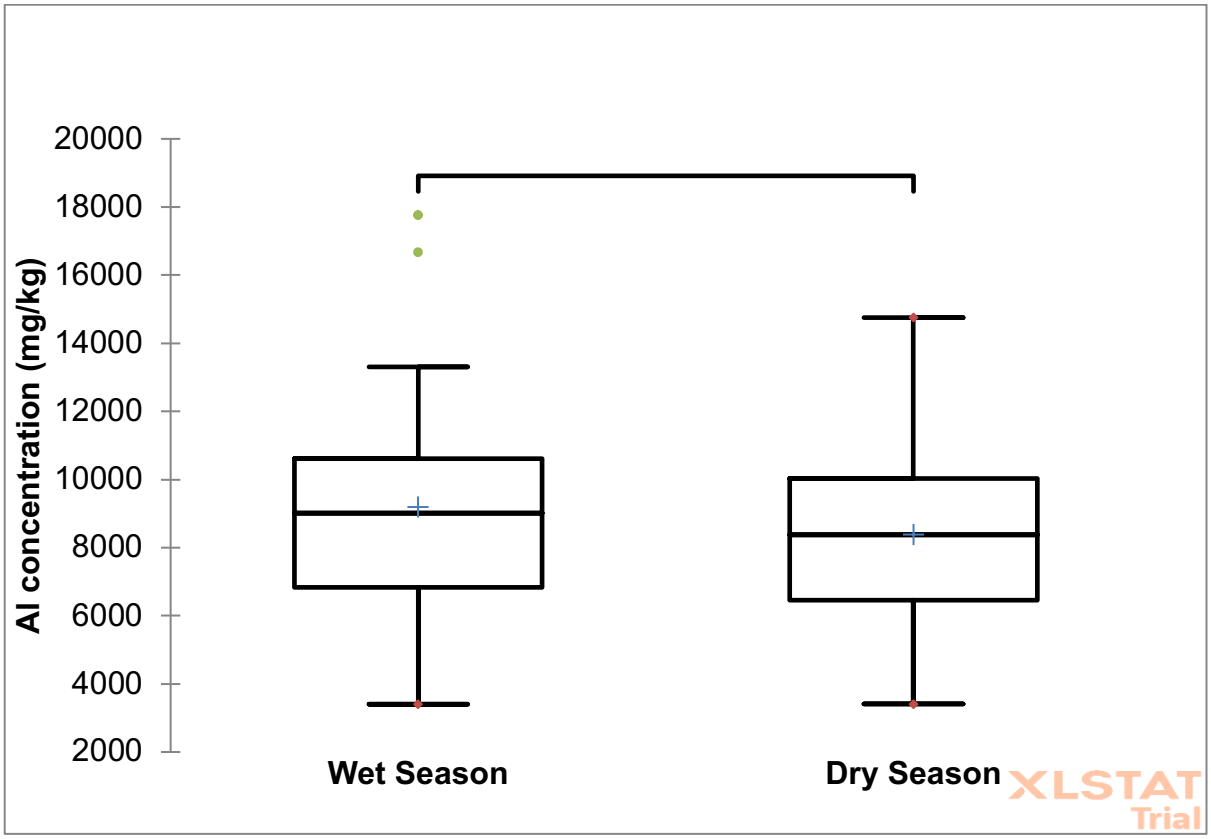

Figure 5.11: Box and whisker plots of seasonal variation of Al concentrations in sediments of the LRC.

5.1.8 Concentration of manganese (Mn) in sediment samples

An average value of 400.44 mg/kg was recorded for Mn, which is one of the least toxic metals. Its levels varied between 113.70 and 1687.64 mg/kg. The average lowest and highest Mn concentrations in the LRC sediments were found at site S19 (113.70 mg/kg) and site S8 (1687.64 mg/kg), respectively (Figure 5.12). However, Edokpayi *et al.* (2017) indicated that there are no CCME guidelines for Mn in freshwater sediments. The factors contributing to Mn in sediments could be a result of atmospheric deposition, geological weathering, and release from organic matter (Decena *et al.,* 2018). The concentration of Mn in LRC sediment samples did not differ significantly with season ($p>0.05$). Mn concentrations ranged from 128.64 to 1698.49 mg/kg, in the wet season, and 95.87 to 1676.78 mg/kg, in the dry season (Appendix 4.10). In previously published studies (Addo-Bediako *et al.,* 2021; Shezi *et al.,* 2022) Mn concentration determined in this study was compared to previously published studies in Spekboom River, South Africa and Kuils River, Cape Town, South Africa and was found to be higher than those studies. The recorded concentrations were lower than the TEL range, showing no adverse effects on sediment-dwelling organisms.

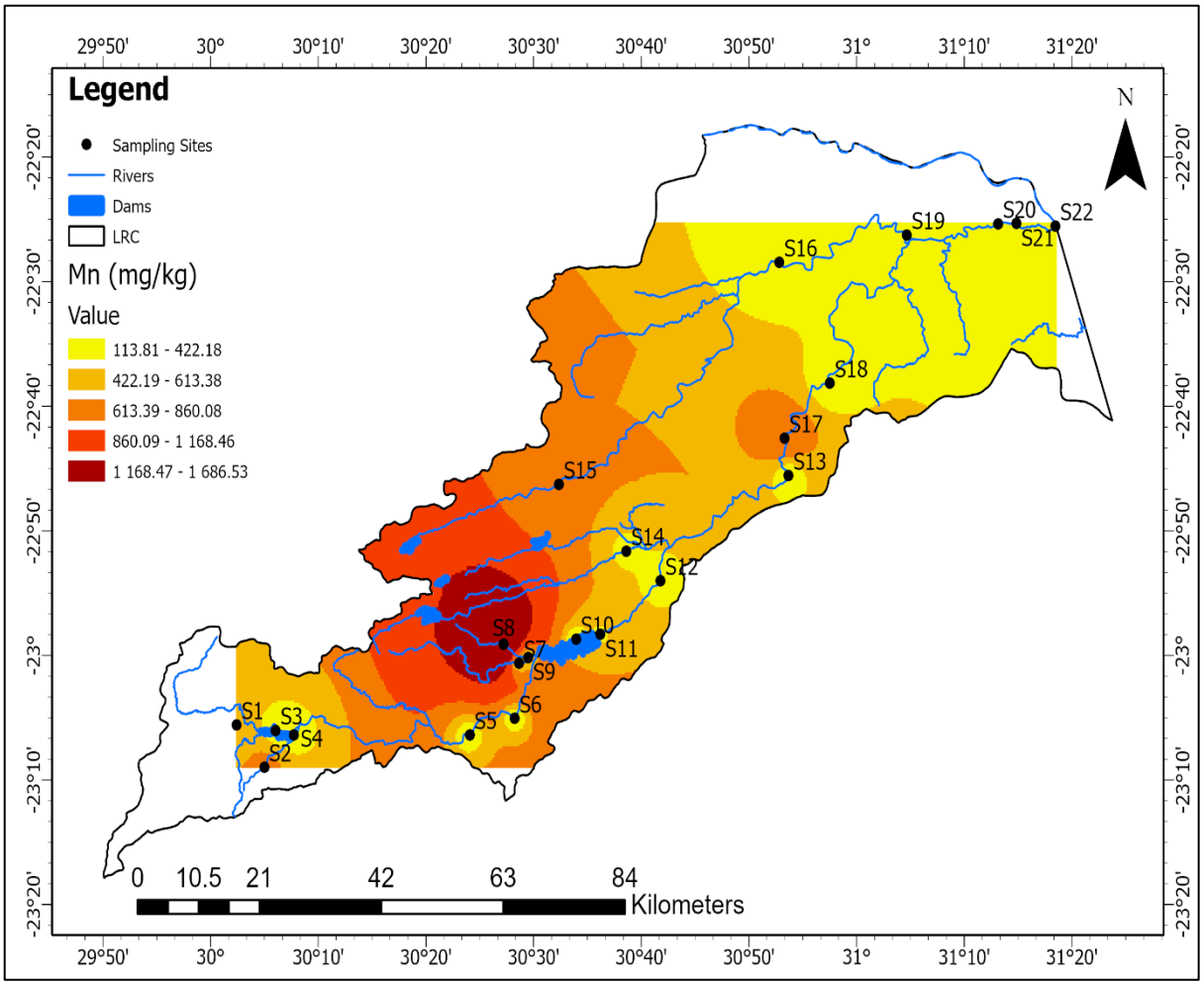

Figure 5.12: Spatial variation of Mn in sediment samples.

5.1.9 Concentration of iron (Fe) in sediment samples

Fe is an important element for humans and many living organisms and a component of many enzymes (haemoglobin and myoglobin) and proteins (Edokpayi *et al.,* 2016). Mean Fe concentrations ranged from 14723.05 to 44812.96 mg/kg with an average of 24437.96 mg/kg (Table 5.1). Mean Fe concentrations at sites S2 and S8 were much higher than at other sites (Figure 5.13), suggesting that anthropogenic activities in the upstream and midstream could have contributed to Fe contamination to surface sediments (Kormoker *et al.,* 2019). Other possible sources include erosion, weathering, and other natural sources. Decena *et al.* (2018) report that large-scale human activities such as agricultural activities, municipal solid waste, urban-industrial releases, and construction and demolition waste can also contribute to the abundance of Fe in a river ecosystem.

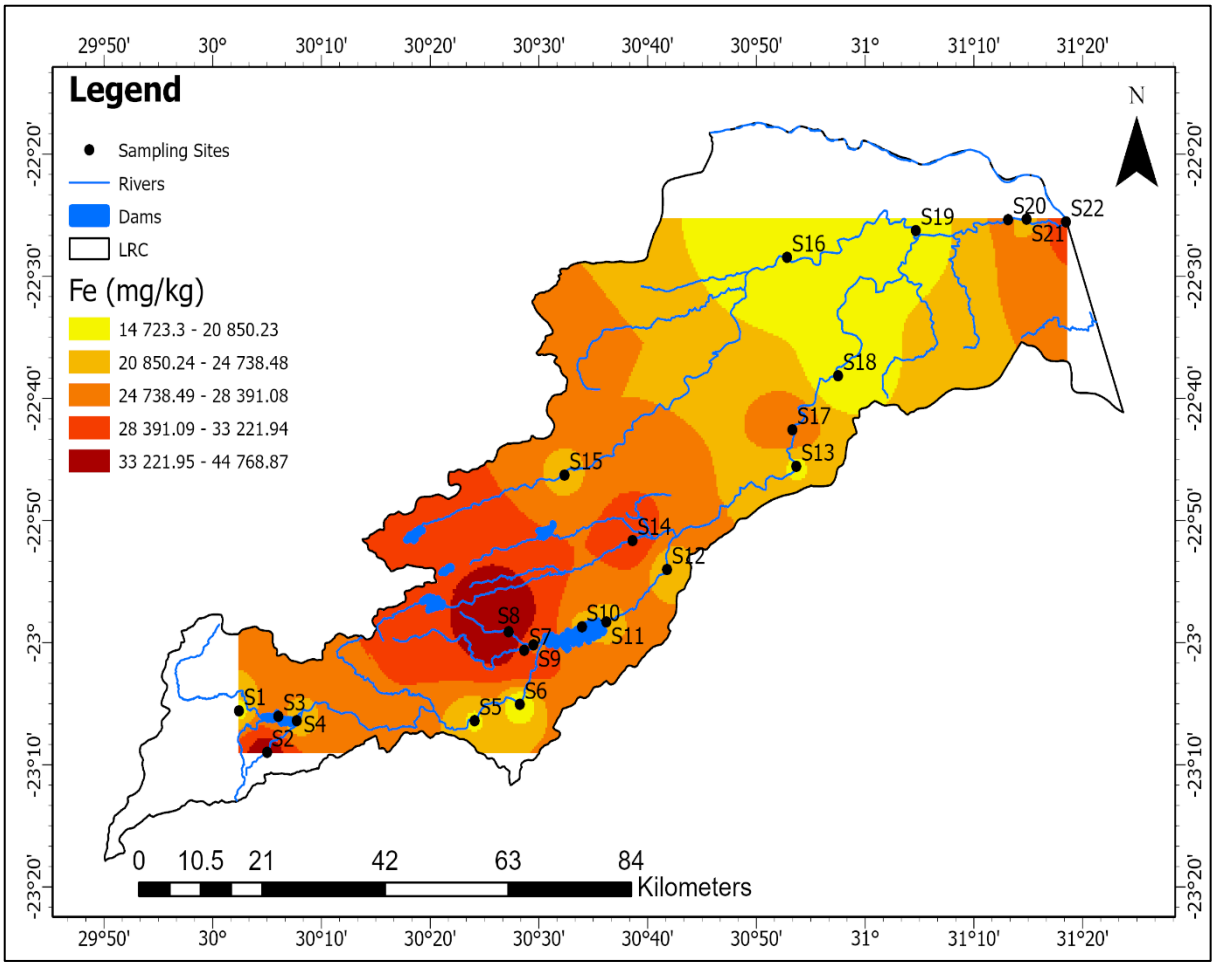

Figure 5.13: Spatial variation of Fe in sediment samples

In this study, the highest Fe concentration was observed at site S8 (44812.96 mg/kg). Though the levels determined in the current study were high, there is no CCME SQG value for Fe in freshwater sediment. Similar findings were also reported by Edokpayi *et al. (*2017) in Nzhelele River, Limpopo Province, South Africa and Hasimuna *et al. (*2021) in Solwezi and Kifubwa Rivers, Northwestern province, Zambia. In alignment with this statement, Omwen *et al. (*2018) report that Fe has indirect and direct effects on river ecology because it affects aquatic organisms by disrupting the osmotic regulation and normal metabolism. This study further stipulates that the combined effects of Fe contamination with other elements such as Cd, Pb, and Cr can degrade the diversity and abundance of various aquatic organisms, including fish. The average concentrations of Fe during the two seasons did not differ significantly ($p>0.05$) in this study. However, the highest concentration of Fe was recorded during the dry season. The current results were higher than the study of Shezi *et al.* (2022) in Kuils River, Cape Town, South Africa and Addo-Bediako and Rasifudi (2021) in Ga-Selati River, South Africa. Conclusively, Fe appeared to have the highest concentrations than any other heavy metal in this study.

5.1.10 Concentration of cobalt (Co) in sediment samples

Mean Co concentrations in sediments ranged from 5.14 to 31.20 mg/kg, with an average of 13.02 mg/kg. The highest Co concentration was observed at site S8 and the lowest Co concentration at site S19 (Figure 5.14). The average Co concentrations in most of the sites did not exceed the average shale value (ASV) of 19.01 mg/kg, except for sites S2 and S8. Similar findings are also reported in sediments of the Ona and Alaro rivers, an industrial area (Oluyole) in Southwestern Nigeria (Kolawole *et al.,* 2021). Seasonal observations of Co concentrations in sediment samples of the LRC showed no significant variation ($p > 0.05$) between the dry and wet seasons. However, the concentration of Co during the wet season ranged from 5.57 to 33.70 mg/kg and 4.59 to 28.71 mg/kg during the dry season. Comparatively, the results obtained in this study were lower than the report of Omwene *et al.* (2018) in the surface sediments of Mustafakemalpaş, Borate basin, Turkey.

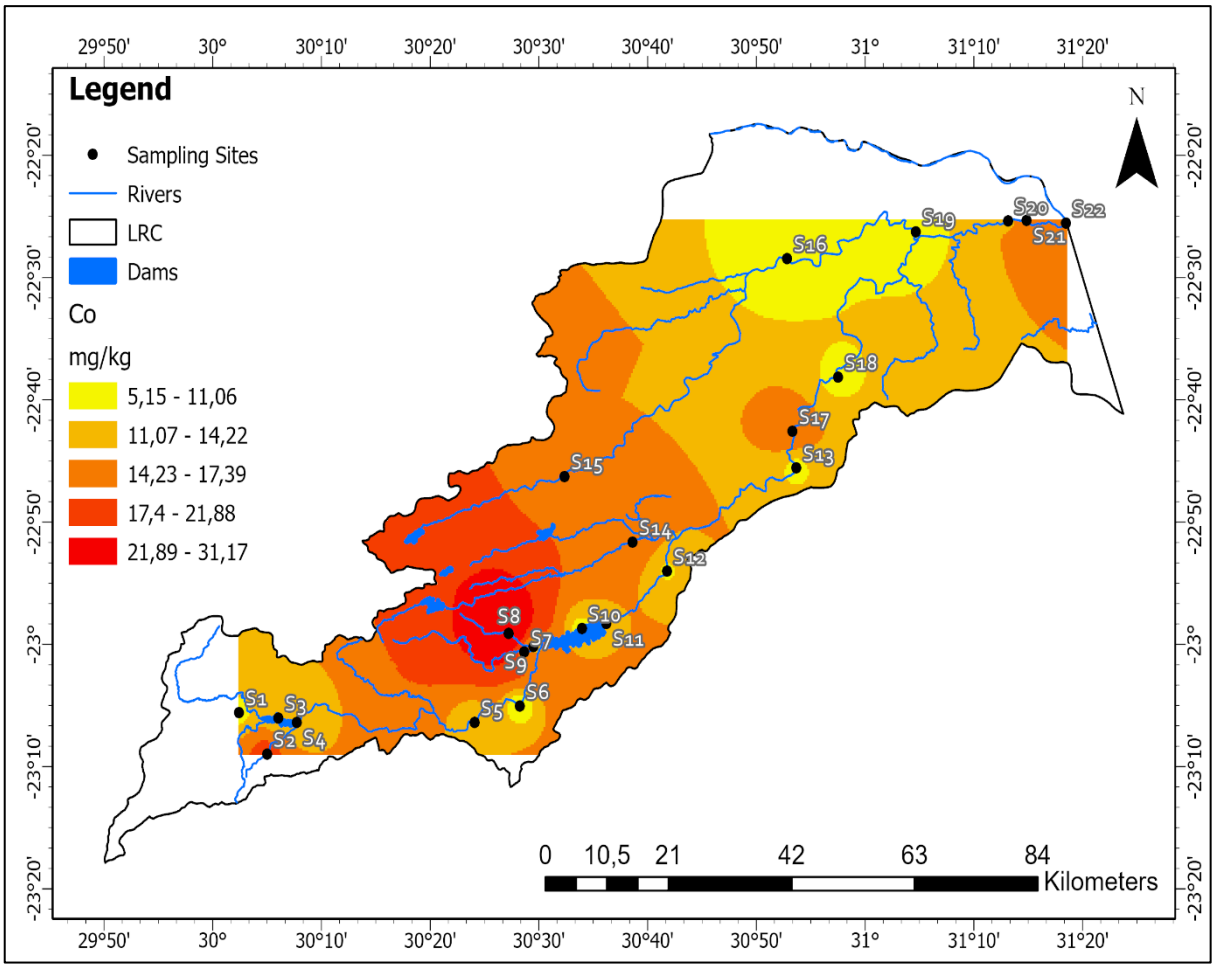

Figure 5.14: Spatial distribution of Co in sediment samples.

5.1.11 Concentration of nickel (Ni) in sediment samples

The spatial concentration of Ni in the sediment samples ranged from 12.50 to 49.62 mg/kg with a mean of 25.31 mg/kg (Figure 5.15). The highest Ni concentrations in sediment samples were measured at site S7 and lowest at site S16. An elevated level of Ni was observed near an urban area, which may be related to urban wastes entering sediment near the site (Islam *et al.,* 2018). The obtained results were significantly higher than the report of Izegaegbe *et al.* (2020) in sediment of the Mhlathuze Estuary, northern KwaZulu-Natal Province of South Africa. In addition, the main anthropogenic sources of Ni that have been identified are domestic sludge, fuel combustion, and agricultural waste (Decena *et al.,* 2018). Seasonal variation of Ni concentration showed no statistically significant variation ($p > 0.05$). Ni concentrations ranged from 11.94 to 50.11 mg/kg during the wet season and 12.06 to 49.13 mg/kg during the dry season, respectively. Compared to the ASV, the average Ni concentration in all the sites did not exceed the ASV of 50 mg/kg but was higher than the TEL value as shown in Table 5.1. Therefore, the highest reported Ni concentration would cause frequent adverse effects to sediments dwelling organisms. Gondwe (2022) also report that the concentration of Ni in Lake Ngami in Botswana to be lower than the current report. However, Addo-Bediako (2020) report a higher Ni concentration of 185 mg/kg in river sediment samples of the Blyde and Steelpoort rivers in South Africa.

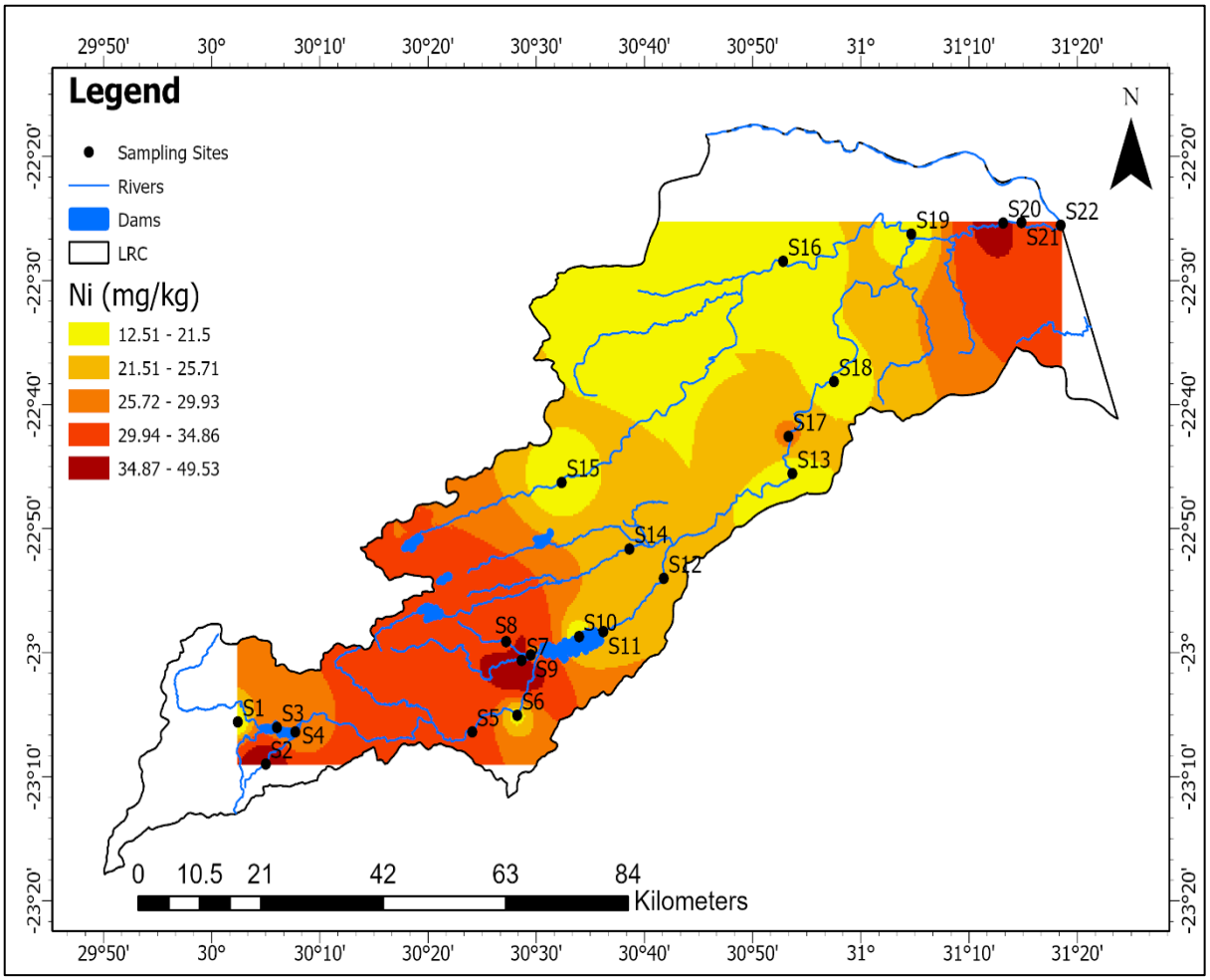

Figure 5.15: Spatial distribution of Ni in sediment samples

5.1.12 Concentration of zinc (Zn) in sediment samples

In living organisms, Zn serves much biological importance supporting many physiological functions (Edokpayi *et al.,* 2016). It has detrimental effects on humans and other organisms, when present at low or very high levels affecting most metabolic processes (Edokpayi *et al.,* 2016). Mean Zn concentrations in sediments in this study range from 11.09 to 35.45 mg/kg (Table 5.1), corresponding to the CCME limit of 123 mg/kg for aquatic ecosystem protection. The highest concentrations of Zn were recorded at sampling site S2 which could be linked to the discharge of domestic sewage waste while the lowest was at site S19 (Figure 5.16). Kumar *et al.* (2015) indicate that high levels of Zn could also be attributed to anthropogenic activities viz. industrial tailing, vehicular emissions, and irregular waste disposal.

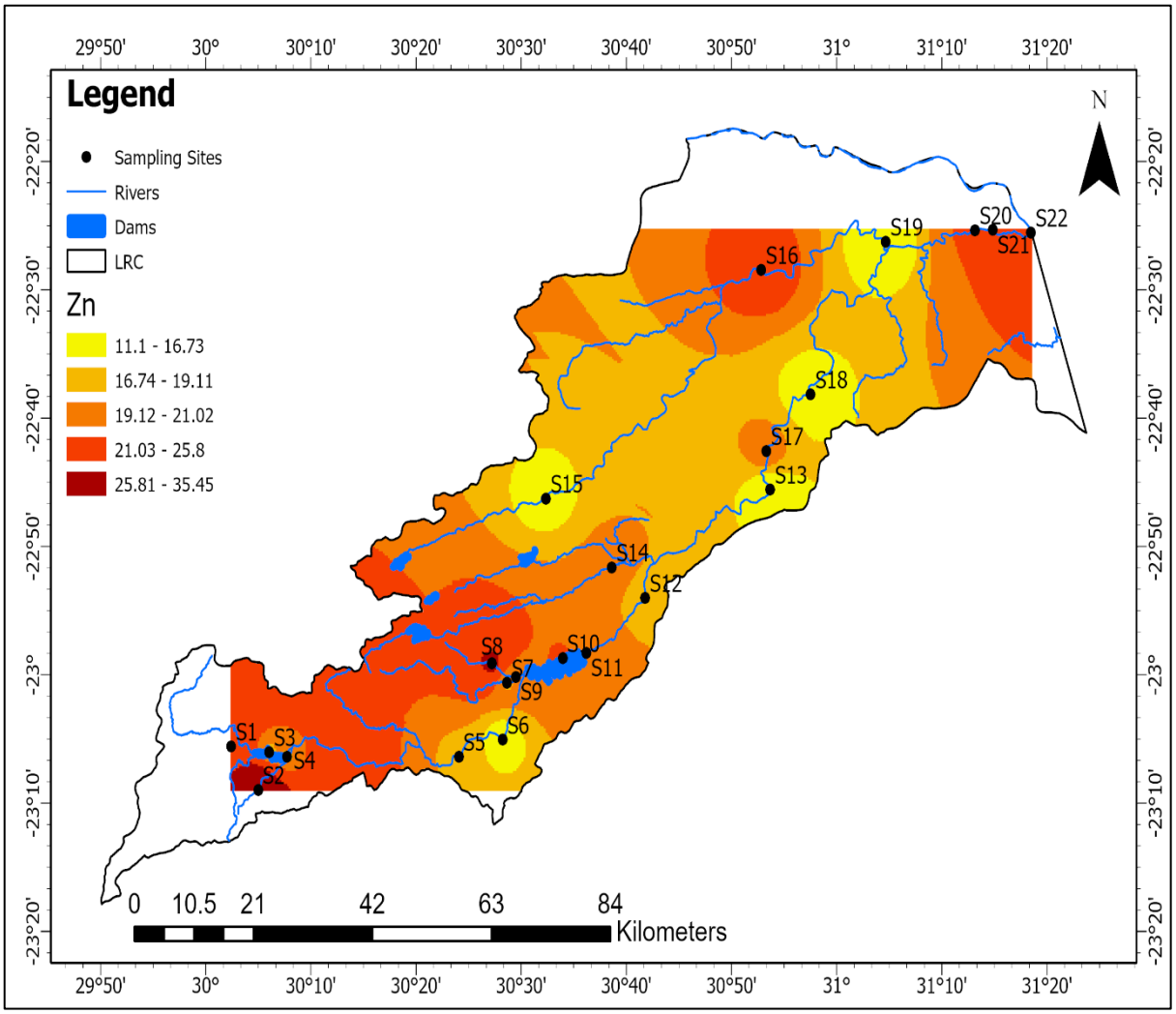

Figure 5.16: Spatial distribution of Zn in sediment samples.

The concentration of Zn in sediment samples did not change significantly with the season ($p>0.05$). Nevertheless, Zn concentrations in sediment samples ranged from 11.09 to 36.96 mg/kg in the wet season and from 8.72 to 38.958 mg/kg in the dry season (Figure 5.17). The average Zn concentration reported was lower than the PEL and TEL at all sampling sites as well as during both seasons. Thus, implying that the concentration of Zn reported cannot pose risk to the aquatic ecosystem. Different observations were also made by Addo-Bediako and Rasifudi (2021) in sediments of Ga-Selati River ranging from 14–52 mg/kg. When comparing these results with other studies around the globe, the concentrations of Zn in the study area were lower than those in the Spekboom River (Addo-Bediako *et al.,* 2021), Pearl River Delta, China (Zhao *et al.,* 2018), and Xiaobai River, in Baotou, China (Wang *et al.,* 2018).

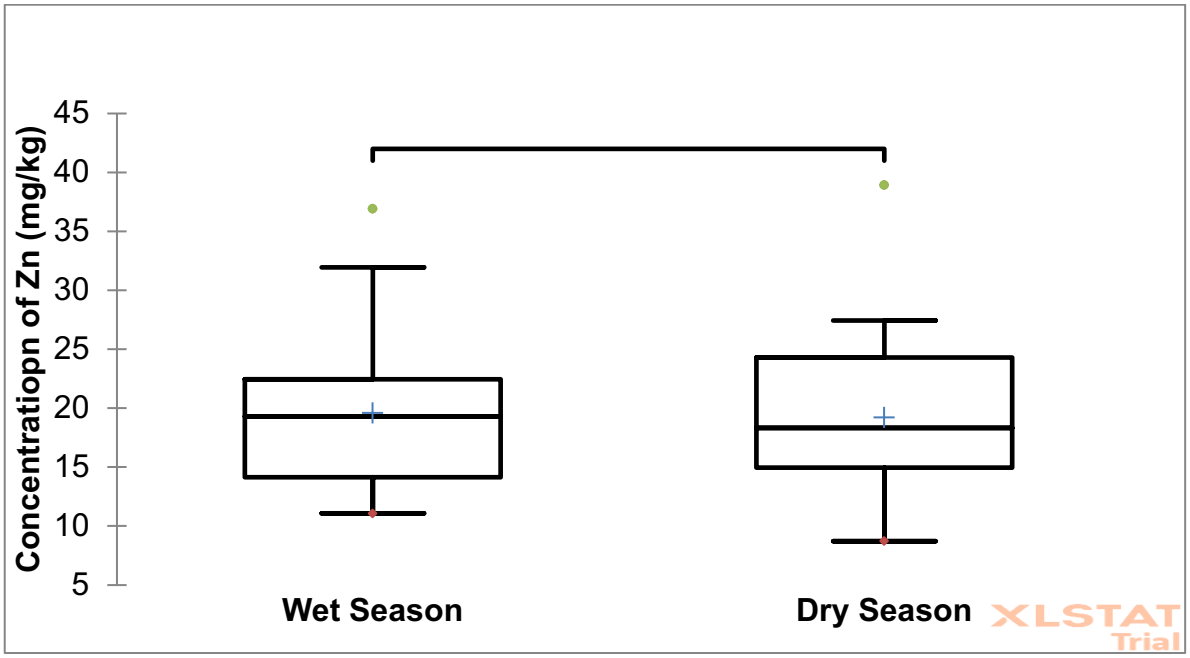

Figure 5.17: Box and whisker plots of seasonal variation of Zn in the sediment samples of the LRC.

5.1.13 Concentration of molybdenum (Mo) in sediment samples

The average concentration of Mo ranged between 0.09 and 0.29 mg/kg with a mean value of 0.17 mg/kg in sediment samples. The highest concentration of Mo was observed at site S8 and the lowest at site S18. Mo may be released into the environment from fossil fuel combustion, wastewater from industrial processes, ore transport, and domestic sewage (Tran *et al.,* 2018). A higher concentration of Mo recorded at site S8 indicates a possible source from wastewater discharges along the site. Additionally, the use of Mo compounds as catalysts, corrosion inhibitors, lubricants, smoke suppressants, flame retardants, and pigments may release them into the environment through various waste streams (Tran *et al.,* 2018). Once Mo enters a water body it attaches to sediment and be consumed by fish to cause harm. The statistical test shows no significance variance ($p>0.05$) between seasons. In the wet season, the average concentration of Mo ranges from 0.09 to 0.34 mg/kg with a mean value of 0.19 mg/kg and 0.07 to 0.29 mg/kg with a mean value of 0.15 mg/kg during the dry season, respectively. Mo concentrations in sediment during the wet season were slightly higher than dry possibly due to the higher runoff inflows during the wet season (Ali *et al.,* 2016). Conclusively, the results obtained in the study are lower than the WRC report (2011) in Olifants River in South Africa.

5.1.14 Concentration of barium (Ba) in sediment samples

Peana *et al. (*2021) reveal that Barium (Ba) compounds are persistent and usually remain in water sediment for a long. However, Peana *et al. (*2021) also indicate that Ba is not mobile and poses little risk to the environmental system. In this study, the highest average Ba concentration was observed at site S8 (93.34 mg/kg) while the lowest was at site S14 (37.55 mg/kg) with a mean value of 59.79 mg/kg, respectively. The concentrations of Ba varied spatially (Appendix 4.12). The measured concentrations of Ba were lower than the ASV of 580 mg/kg, indicating low concentrations of Ba as compared to the world average (ASV) concentration. Seasonal analysis show no significant variance ($p>0.05$) but the average concentrations of Ba in sediment was found as 26.85-105.80 mg/kg with a mean value of 62.71 mg/kg in the wet season and 33.48-96.93 mg/kg with a mean value of 56.87 mg/kg in the dry season (Figure 5.18). These results are lower than the report of the WRC (2011) in Lake Flag Boshielo in South Africa (337 mg/kg).

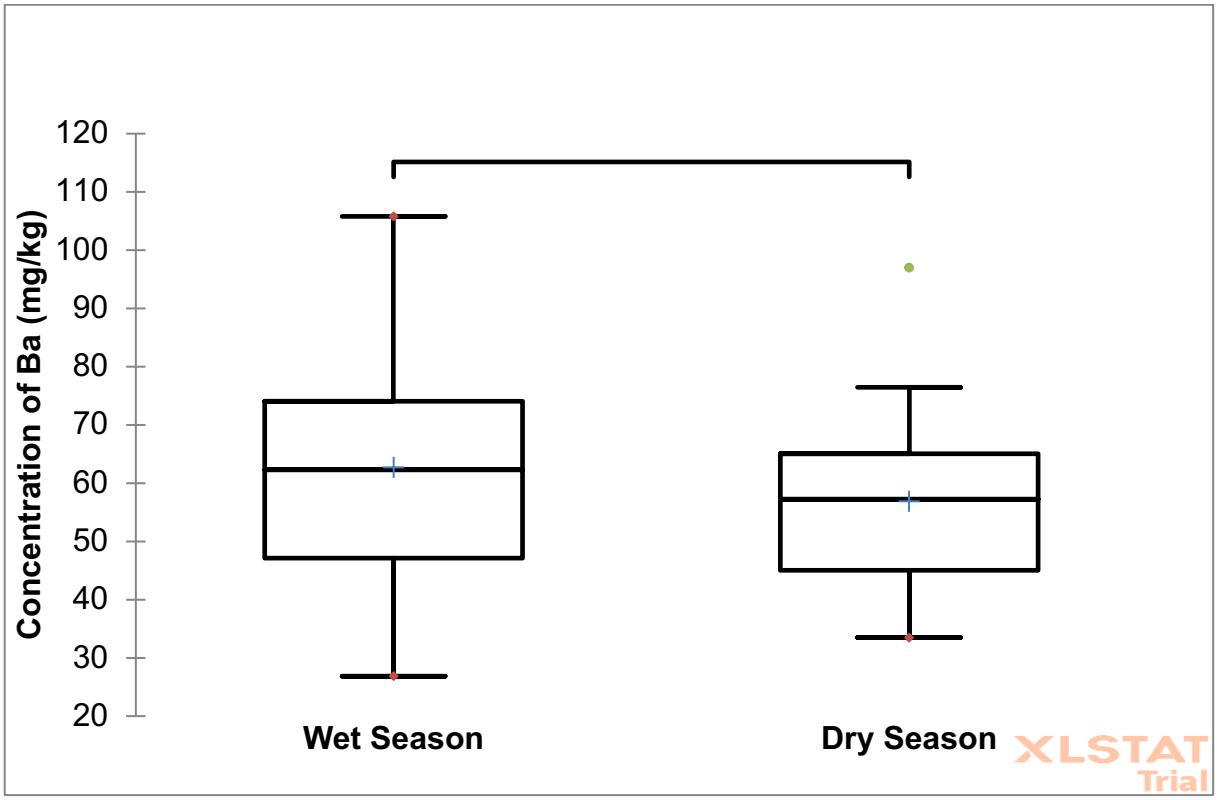

Figure 5.18: Box and whisker plots of seasonal variations of Ba concentration in sediment samples.

5.2 Assessment of the extent of heavy metal pollution in sediment using various indices

Since sediments typically act both as a sink and as a potential subordinate source of pollutants in the water column and organisms in the aquatic environment, their contamination may have

severe impacts on aquatic ecosystems (Wu *et al.,* 2017). Therefore, it is critical to understand the sources of pollutants in aquatic ecosystems and the extent of these pollutants to define pollution control measures (Hasimuna *et al.,* 2021). The Enrichment Factor (EF), Pollution Load Index (PLI), potential ecological risk index (RI), and geo-accumulation index (Igeo) were used to assess the extent of heavy metal contamination in sediments.

5.2.1 Enrichment factor (EF)

Enrichment factors are important indicators of geochemical similarities and trends or differences between sites. EF values were calculated from the average heavy metal concentrations from each site. Inclusively, the average EF values for all investigated metals indicated their accumulation in surface sediments of the Luvuvhu River Catchment. Based on the average enrichment factors for all metals examined from all sites, EF values were in the ascending order of Fe<Hg<As<Mo<Cd<Ba<Al<Zn<Ni<Pb<Mn<Cu<Cr<Co. The difference in EF values is shown in Table 5.2.

Table 5.2 Mean enrichment factor values of metals in sediment samples collected from the LRC

Sites	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Ba	Hg	Pb
S1	0.23	4.50	5.64	0.004	5.34	2.48	4.40	2.30	0.45	0.55	1.46	1.02	0.23	3.17
S2	1.52	5.01	4.50	0.004	5.57	3.37	5.71	2.07	0.37	0.58	0.84	0.87	0.24	6.29
S3	1.39	5.79	2.55	0.004	4.76	3.03	4.10	1.41	0.31	0.40	0.30	0.65	0.33	2.34
S4	1.60	6.10	3.01	0.005	6.03	3.93	7.22	1.97	0.49	0.94	0.48	1.21	0.27	5.88
S5	1.28	6.40	2.64	0.004	5.12	4.08	4.77	1.68	0.40	0.65	1.00	0.96	0.30	4.32
S6	1.24	5.98	2.37	0.004	3.94	3.07	4.12	1.33	0.58	0.63	0.34	1.13	0.23	3.94
S7	1.87	10.18	3.00	0.005	6.91	5.93	5.60	1.59	0.41	0.76	2.92	0.93	0.26	3.40
S8	1.93	4.79	11.59	0.006	9.58	2.64	6.77	1.67	0.32	0.65	1.41	0.94	0.21	3.45
S9	1.51	4.47	3.50	0.004	4.96	2.18	4.02	1.64	0.40	0.51	0.26	0.89	0.26	2.58
S10	1.81	4.50	2.05	0.005	4.89	2.32	4.98	2.37	0.34	0.62	0.66	0.88	0.26	5.00
S11	2.05	6.28	5.62	0.006	8.65	4.28	5.66	2.39	0.57	0.73	1.49	1.30	0.33	3.10
S12	1.67	6.84	3.37	0.005	5.85	3.53	5.42	1.99	0.51	0.95	0.92	1.12	0.32	3.94
S13	1.79	5.99	3.27	0.005	6.42	3.09	5.06	1.58	0.54	0.52	0.77	1.05	0.27	2.54
S14	1.95	5.41	3.57	0.006	7.35	2.75	6.09	1.78	0.37	0.45	1.12	0.54	0.20	2.30
S15	1.86	4.69	7.83	0.005	8.31	2.40	4.60	1.56	0.44	0.74	1.00	0.72	0.37	3.36
S16	2.24	5.78	3.00	0.006	5.58	3.79	5.50	4.96	0.73	0.83	1.59	1.45	0.29	10.36
S17	1.37	3.27	5.84	0.004	5.81	2.58	4.93	1.44	0.30	0.41	0.99	0.64	0.20	1.88
S18	1.92	6.67	4.05	0.006	8.80	4.56	7.54	2.36	0.64	0.57	0.86	1.22	0.38	3.08
S19	1.68	4.84	2.04	0.005	4.14	3.90	3.13	1.78	0.54	1.00	0.45	0.99	0.27	2.29
S20	1.35	5.56	3.20	0.004	5.46	4.15	4.41	1.64	0.50	0.48	0.77	1.06	0.19	2.36
S21	1.50	5.44	2.84	0.004	6.61	4.04	5.51	1.93	0.44	0.43	0.39	0.94	0.32	2.43
S22	1.78	5.11	3.51	0.005	6.50	3.56	5.36	1.92	0.42	0.39	0.43	0.95	0.22	1.94

EF values greater than 1.5 were observed at most sites, except for sites where low concentrations were detected in the sediment. This indicates that the elemental inputs at sites are most likely from natural sources (Islam *et al.,* 2018). In addition, most of the EF values are greater than 1, thus indicating a possibility of elements releasing into the river system. This possibility implies that the LRC sediments are also potential sources of pollution in the system. Enrichment values for Fe were lower than 1 indicating background concentration, hence posing no serious pollution to the river (Table 5.2). Enrichment values for Al, As, Mo, Cd, Ba, and Hg were lower than 3 which indicates less accumulation of these metals in the sediments of the LRC. As a result, there are few impacts of land use activities contributing to these elements within the catchment. EF values exceeding 3 were determined from Zn indicating moderate enrichment and may raise concerns for water pollution from this metal in the Luvuvhu River Catchment. The EF value for Zn was found higher at the downstream site (S16), with an EF value of 4.96, which could be attributed to anthropogenic activities such as agriculture (zinc compounds containing fungicides and insecticides) and vehicle traffic. A similar pattern of high EF values at downstream sites was also observed in the surface sediments of an Urban River, Philippines (Decena *et al.,* 2018).

EF values exceeding 5 for Ni and Cu are indicative of pollution which at some sampling sites could be attributed to land use sources. These findings indicated a substantial enrichment in the sediments. The highest EF values for Ni and Cu were obtained from sites S7 (5.93) and S18 (7.54). Decena *et al. (*2018) indicate that Cu enrichment may result from pollution sources such as discharge from sewers, urban runoff, and motor/auto repair shops which could be the case for the LRC. In addition, the accumulation of Ni at site S7 strongly suggests high inputs of this element from the wastewater treatment plant nearby which is the closest land-use activity.

The high enrichment values exceeding 9 for all the monitored sites were obtained from Co, Cr, Pb, and Mn, and it is sufficient evidence to assume that a very high proportion of pollution in the LRC sediments is primarily due to land use activities such as human settlement or urban wastes disposal sites (landfills). For Co, Cr, Pb, and Mn, the highest EF values were observed at sites S8 (9.58), S7 (10.18), S16 (10.36), and S8 (11.59). Based on the interpretation classes of EF values, these results indicated a highly significant enrichment (EF = 5-20) in the sediment samples. Furthermore, the bioavailability and toxicity of heavy metals in sediments depend on their chemical form and concentration (Ali *et al.,* 2022). Therefore, metals in sediments with high EF values have bioavailability and mobility potential in aquatic ecosystems in addition to more labile fractions in sediments (Ali *et al.,* 2019). The current results were lower than the results of Seifi *et al.* (2019) in sediments of the Persian Gulf.

5.2.2 Geo-accumulation Index (I_{geo})

Igeo is a pollution assessment index that predict the anthropogenic contributions of heavy metals in the environment. In this study, Figure 5.19 shows the Igeo values for all the investigated heavy metals based on ASV.

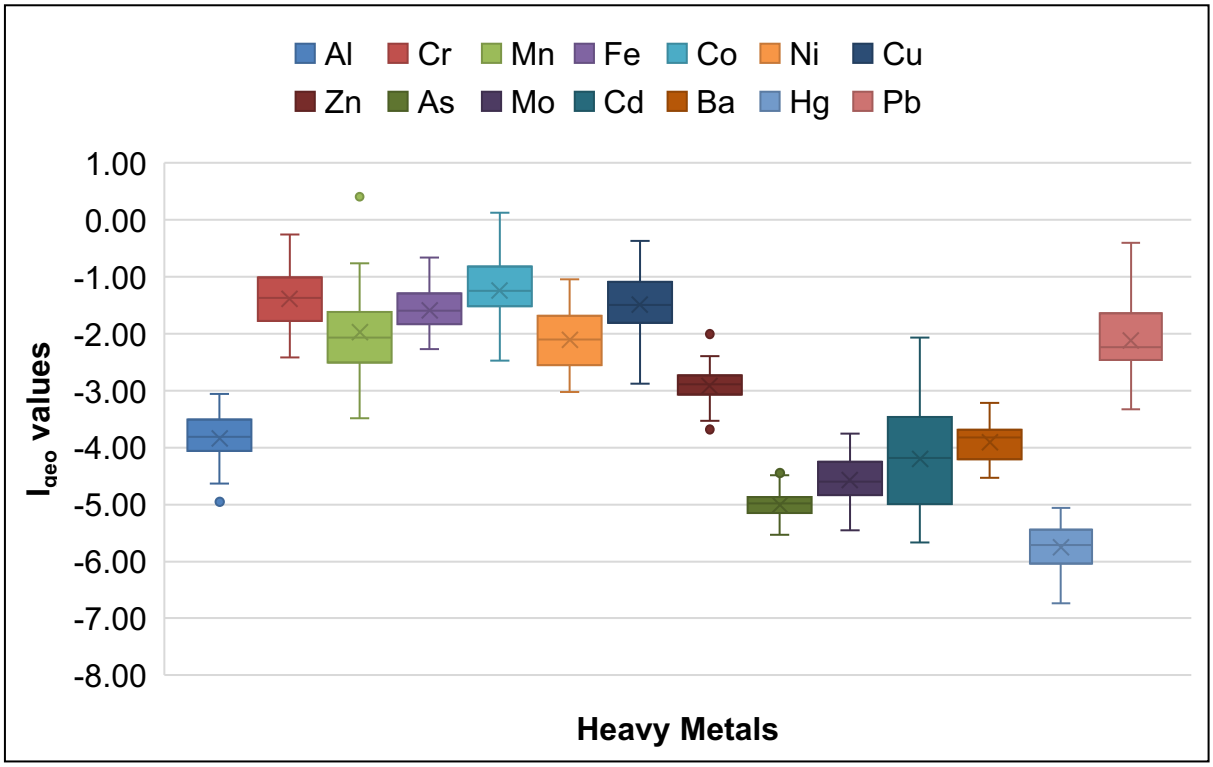

Figure 5.19: I_{geo} results of heavy metals in sediment samples collected from the LRC.

Among the metals examined, the overall Igeo values from all the sites showed an ascending order of Hg<As<Mo<Cd<Ba<Al<Zn<Pb<Ni<Mn<Fe<Cu<Cr<Co. As shown in Figure 5.19, the mean I_{geo} values for Hg, As, Mo, Cd, Ba, Al, Zn, Pb, Ni, Fe, Cu and Cr were below class 0 at all sampling sites, indicating that the sediments are not polluted with these heavy metals. Interestingly, the Igeo values of Mn and Co are below class 1 indicating that the sediments of the LRC were uncontaminated or moderately contaminated with these metals. Similar findings have been reported by Proshad *et al.* (2019) from in surface sediments of the Rupsa River in Bangladesh where most of the I_{geo} values show uncontaminated to moderately contaminated levels. For Mn and Co, the highest values of 0.40 and 0.13 were obtained from site S8, respectively. High Igeo values for Mn and Co may be the result of increased waste treatment pollution from household waste, engine/body shops, manganese pesticides, and municipal and agricultural runoff (Zahra *et al.,* 2014). The findings obtained from this study are lower than those reported in sediment in the Mhlathuze Estuary, KwaZulu-Natal, South Africa

(Izegaegbe *et al.,* 2020) and in surface sediments of the freshwater ecosystem in Zhenjiang City, China (Liu *et al.,* 2022).

5.2.3 Pollution Load Index (PLI)

PLI provide some comprehension of the quality of the environment that affects aquatic populations (Ali *et al.,* 2016). Furthermore, it provides useful information on the sediment pollution severity, helping decision-makers such as catchment managers in their decision-making (Su *et al.,* 2022). In addition, Ali *et al. (*2016) state that PLI values of less than 0 indicate a pristine environment, values between 0 and 1 indicate baseline levels of the pollutants, and values higher than 1 indicate pollution in the river system. The results of the Pollution Load Index (PLI) analysis are shown in Figure 5.20.

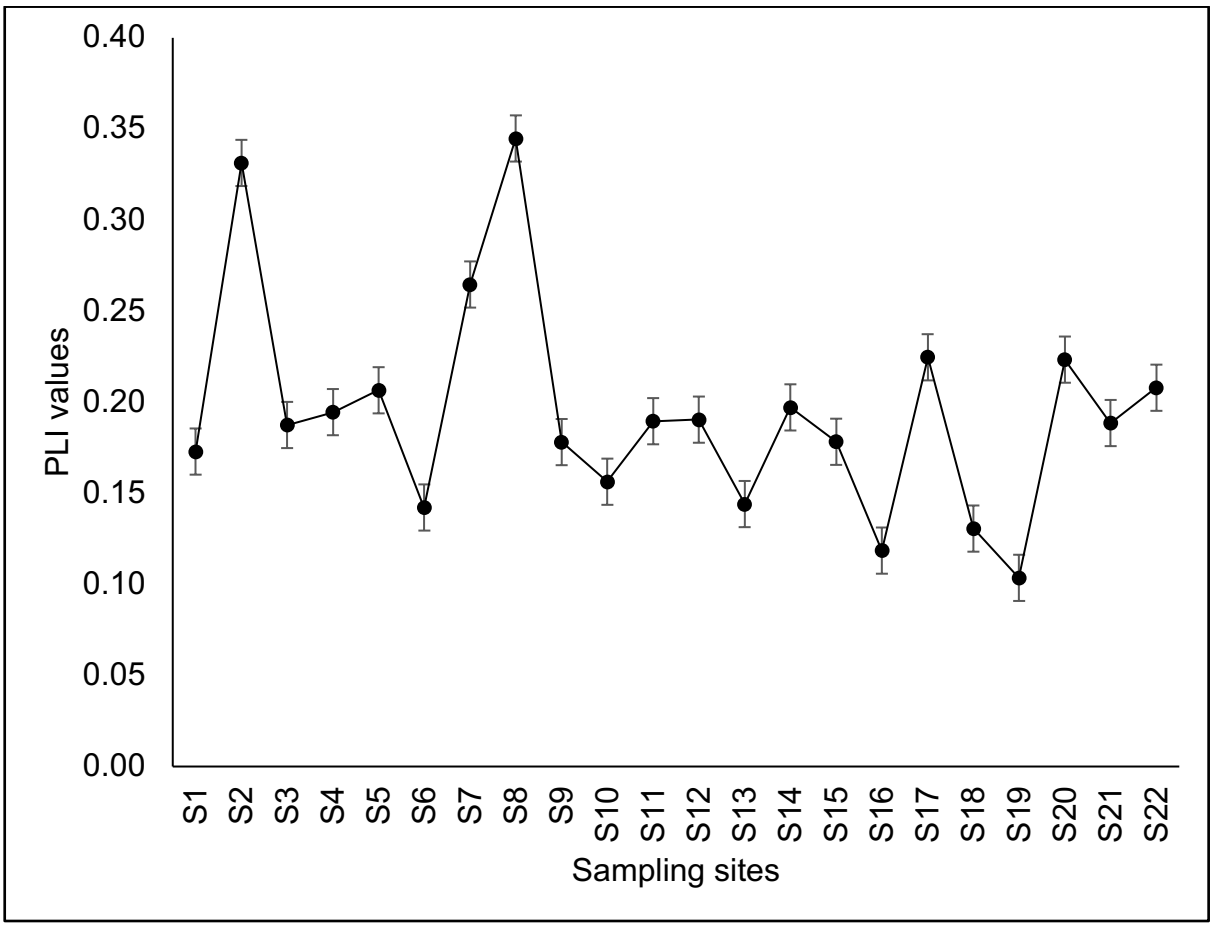

Figure 5.20: PLI values at various sites along the LRC

Within the LRC system, the PLI values did not exceed a value of 1 in all sites, implying no significant deterioration in the condition of the river system. However, the PLI values were between 0 and 1, indicating baseline levels of pollutants. The highest PLI value of 0.34 was recorded from site S8 which is mainly surrounded by vehicle traffic, gas, subsistence farming,

car wash, brickworks, urban and residential, and commercial. Among the investigated metals, the high PLI values at site S8 indicate that Cr, Mn, Fe, Co and Cu were the main contributors to sediment contamination. In a study by Proshad *et al. (*2019), it is also found that Cu is one of the metals contributing to sediment contamination in the surface sediment of the Rupsa River in Bangladesh. Therefore, while the impact of one metal can pose a small risk to aquatic ecosystems, the combination of all these metals raises serious ecological concerns (Ali *et al.,* 2016). The obtained result was lower than that of Izegaegbe *et al. (*2020) from the sediment samples collected in the Mhlathuze Estuary, KwaZulu-Natal, South Africa.

5.2.4 Potential ecological risk index (RI)

According to Hakanson (1980), there are four defined classes of contamination degree (C_d), and RI and five classes for E_r^i. The contamination factor and contamination degree (C_d) for each metal are shown in Table 5.3. The assessment of integrated contamination degree of sediment is based on the level of contamination (Proshad *et al.,* 2019). CF values less than 1 imply low pollution, and values between 1 and 3 imply moderate pollution. Considerable pollution is occurring when CF values are between 3 and 6, and higher than 6 indicates very high pollution. In this study, contamination was low in all sampling sites with CF<1, with an exception for Cu in sites S2 and S8, Cr at site S7 and Mn at site S8 which indicated moderate pollution in the system. Generally, across all sampling sites, pollution varies between low to moderate. To prevent further pollution risks, monitoring the concentration of Cu, Cr, and Mn in the riverine system is essential. Additionally, the values of C_d ranged from 0.93 to 4.87 with a mean value of 2.23. The highest obtained C_d value was lower than 5, indicating low sediment pollution.

Table 5.3: Degree of contamination and contamination factors of heavy metals in sediments collected from the LRC

Sites	Contamination factors (C_f^i)								C_d
	Cd	As	Cr	Cu	Zn	Mn	Pb	Hg	
S1	0.14	0.04	0.43	0.42	0.22	0.54	0.14	0.04	1.97
S2	0.15	0.07	0.90	1.03	0.37	0.81	0.50	0.07	3.90
S3	0.04	0.04	0.79	0.56	0.19	0.35	0.14	0.07	2.17
S4	0.05	0.05	0.61	0.72	0.20	0.30	0.26	0.04	2.22
S5	0.12	0.05	0.74	0.55	0.19	0.31	0.22	0.06	2.23
S6	0.03	0.05	0.55	0.38	0.12	0.22	0.16	0.03	1.55
S7	0.36	0.05	1.25	0.69	0.20	0.37	0.19	0.05	3.15
S8	0.24	0.06	0.82	1.16	0.29	1.99	0.26	0.06	4.87
S9	0.03	0.05	0.56	0.50	0.20	0.43	0.14	0.05	1.97
S10	0.06	0.03	0.43	0.47	0.23	0.20	0.21	0.04	1.67
S11	0.13	0.05	0.53	0.48	0.20	0.47	0.12	0.04	2.01
S12	0.09	0.05	0.65	0.52	0.19	0.32	0.17	0.05	2.04
S13	0.06	0.04	0.49	0.42	0.13	0.27	0.09	0.04	1.55
S14	0.13	0.04	0.65	0.73	0.21	0.43	0.12	0.04	2.36
S15	0.09	0.04	0.44	0.43	0.15	0.73	0.14	0.06	2.08
S16	0.08	0.04	0.28	0.27	0.24	0.15	0.22	0.02	1.29
S17	0.15	0.05	0.50	0.75	0.22	0.89	0.13	0.05	2.72
S18	0.05	0.04	0.40	0.46	0.14	0.25	0.08	0.04	1.46
S19	0.03	0.04	0.32	0.20	0.12	0.13	0.07	0.03	0.93
S20	0.11	0.07	0.76	0.60	0.22	0.44	0.14	0.04	2.38
S21	0.04	0.05	0.63	0.63	0.22	0.33	0.12	0.06	2.09
S22	0.06	0.05	0.67	0.70	0.25	0.46	0.11	0.05	2.36

C_d = Degree of contamination

The ecological risks and potential ecological hazard indices (RIs) for individual elements are shown in Table 5.4. The average potential ecological risk factors from heavy metals in sediments were in ascending order, Zn>Mn>As>Pb>Cr>Hg>Cu>Cd. Proshad *et al.* (2019) observe a different order of potential ecological risk factors in their study. Considering the potential ecological hazard factors (E_r^i) of individual elements, Cd and Cu showed the highest potential ecological hazard with ($\boldsymbol{E_r^i}$) factors ranging from 0.88 to 10.77 and 1.02 to 5.80,

respectively (Table 5.4). The highest E_r^i value of Cd was noted at sampling site S7 followed by S8, S2, S17 and S1. Islam *et al.* (2018) note that high E_r^i may be due to the use of phosphate fertilisers to agricultural lands adjacent to rivers, dumping of oily substances from materials, and urban waste disposal. The E_r^i results found in this study are lower than the report of Baah *et al.* (2022) in the sediment of Abuakwa South Municipal in Ghana.

Table 5.4: Contamination factors of heavy metals in sediment samples collected from Luvuvhu River Catchment

Sites	Potential ecological risk factor (E_r^i)							
	Cd	As	Cr	Cu	Zn	Mn	Pb	Hg
S1	4.19	0.43	0.86	2.11	0.22	0.54	0.68	1.41
S2	4.55	0.67	1.80	5.14	0.37	0.81	2.52	2.72
S3	1.24	0.42	1.57	2.78	0.19	0.35	0.71	2.88
S4	1.45	0.49	1.21	3.59	0.20	0.30	1.30	1.69
S5	3.45	0.47	1.48	2.75	0.19	0.31	1.11	2.25
S6	0.94	0.53	1.10	1.90	0.12	0.22	0.81	1.38
S7	10.77	0.50	2.51	3.45	0.20	0.37	0.93	2.07
S8	7.27	0.55	1.64	5.80	0.29	1.99	1.31	2.31
S9	0.98	0.50	1.11	2.50	0.20	0.43	0.71	2.05
S10	1.89	0.32	0.86	2.37	0.23	0.20	1.06	1.57
S11	3.75	0.48	1.06	2.38	0.20	0.47	0.58	1.79
S12	2.65	0.49	1.31	2.59	0.19	0.32	0.84	1.93
S13	1.91	0.44	0.99	2.08	0.13	0.27	0.47	1.44
S14	4.04	0.44	1.29	3.64	0.21	0.43	0.61	1.50
S15	2.82	0.41	0.88	2.16	0.15	0.73	0.70	2.20
S16	2.31	0.35	0.56	1.33	0.24	0.15	1.12	0.90
S17	4.50	0.46	0.99	3.74	0.22	0.89	0.63	1.98
S18	1.56	0.39	0.81	2.29	0.14	0.25	0.41	1.46

S19	0.88	0.35	0.63	1.02	0.12	0.13	0.33	1.11
S20	3.16	0.69	1.52	3.01	0.22	0.44	0.72	1.63
S21	1.33	0.50	1.25	3.17	0.22	0.33	0.62	2.33
S22	1.69	0.55	1.34	3.52	0.25	0.46	0.57	1.87

The spatial distribution of Potential Ecological Risk Index (RI) is shown in Figure 5.21. The order of RI in sediment samples was in the following ascending order S19>S16>S6>S18>S13>S9>S10>S21>S15>S3>S4>S22>S12>S1>S11>S20>S5>S14>S17 >S2>S7>S8 and the RI values for all metals revealed low potential ecological risks. However, site S8 in the present study exhibited higher ecological risks compared to other sites. Cd and Cu were the main contributors to high RI values at S8. As shown in Figure 5.21, it is noted that areas with mixed land-use activities were responsible for higher RI values. Thus, mixed land use activities may pose more threats to the aquatic ecosystem of the river. Upstream of the catchment also showed variation in RI values which could be driven by wastewater discharge and agricultural runoff into the system. Baah *et al.* (2022) state that the use of Cd-containing pesticides in agricultural lands and Cu-containing materials in residential areas is one of the main sources of Cd and Cu in sediments. Therefore, Cd and Cu should be the primary control pollutants in the LRC.

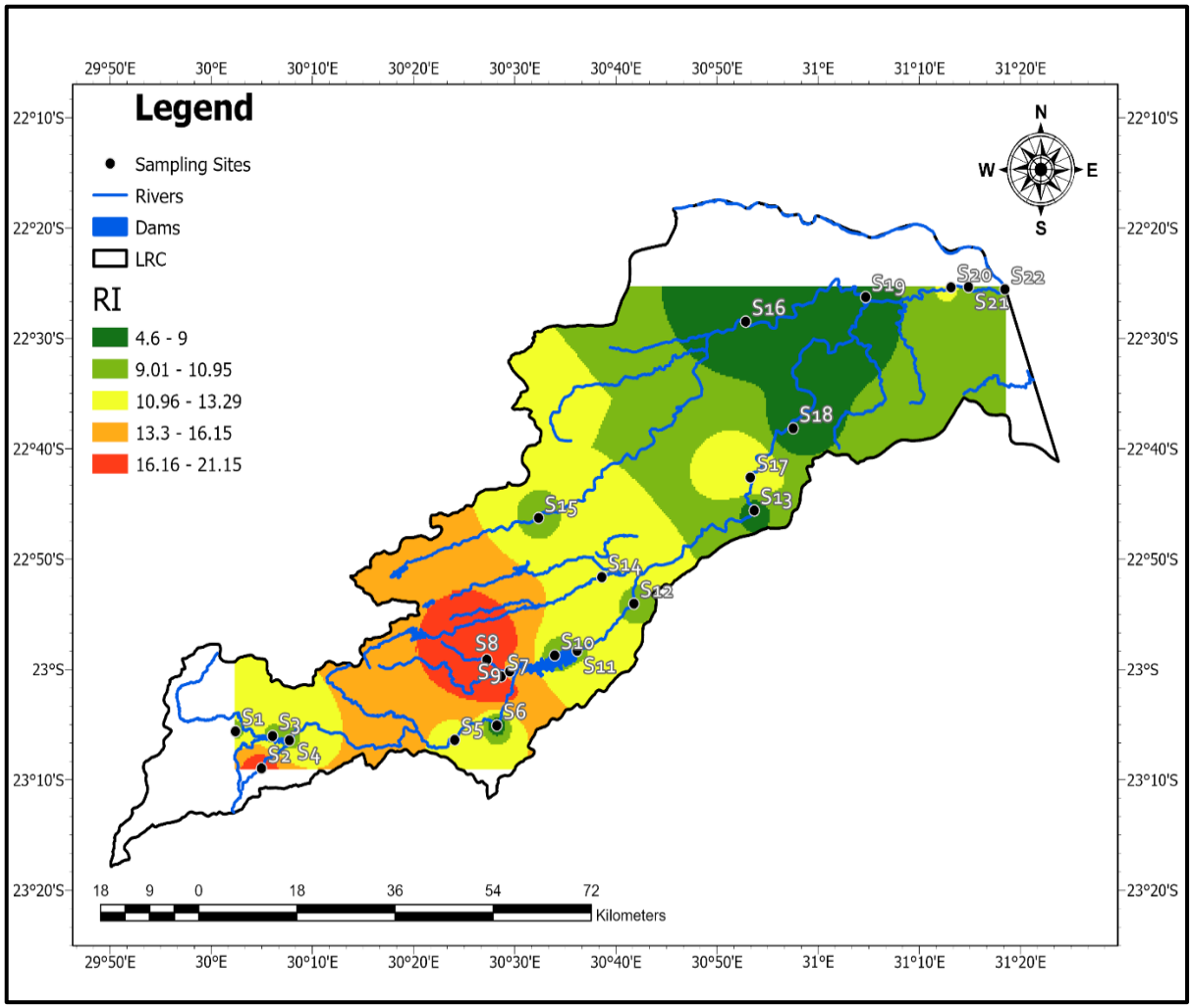

Figure 5.21: Spatial distribution of RI values in the LRC

Also, the geospatial map in the above Figure 5.21 indicate that areas close to wastewater treatment plants (indicated in red on the map) tend to have high RI as compared to other land use activities. Therefore, in this study wastewater treatment plants contributed more risk to the aquatic ecosystem. However, land use activities such as conservation (KNP) play a major role in restoring sediment quality within the LRC as low RI values were determined along those sites. Thus, the LRC system has the capability to recover sediment quality as it flows downstream towards the Limpopo River. This transition was observed from the midstream sites where the Nandoni dam exists which could be interrupting the continuity of sediment transport by trapping sediments and permitting sedimentation to occur resulting in a change in sediment quality. The obtained results from this study are lower than those reported in Nzhelele River, South Africa (Edokpayi *et al.,* 2017).

5.3 Multivariate statistical results (source identification for dissolved heavy metals)

PCA was applied to the heavy metal dataset (14 variables) according to the methodology described in chapter three using Rstudio 2022.12.0. PCA reduced the dimensionality of the data without losing important information by identifying the dimension factors and percentage of variance by the squared euclidean distance (Arora and Keshari, 2021). The dataset was transformed into a covariance matrix that provides the coefficient of variance for each sampling site.

5.3.1 Inertia distribution

Inertia in the first dimension indicates whether there is a strong relationship between the variables and suggests the number of dimensions to investigate. In this study, the first two dimensions of analysis represent 71.05% of the total dataset inertia. This means that 71.05% of the sites (or variables) cloud total variability is explained by the plane. This percentage is high, and the first plane represents an important segment of the data variability. The variability explained by this level is very important as this value is significantly larger than the reference value corresponding to 38.72% (the reference value is the 0.95 quantile of the inertia percentages distribution obtained by simulating 1411 data tables of equivalent size based on a normal distribution). From these remarks, it is probably not useful to interpret the next dimensions (Figure 5.22).

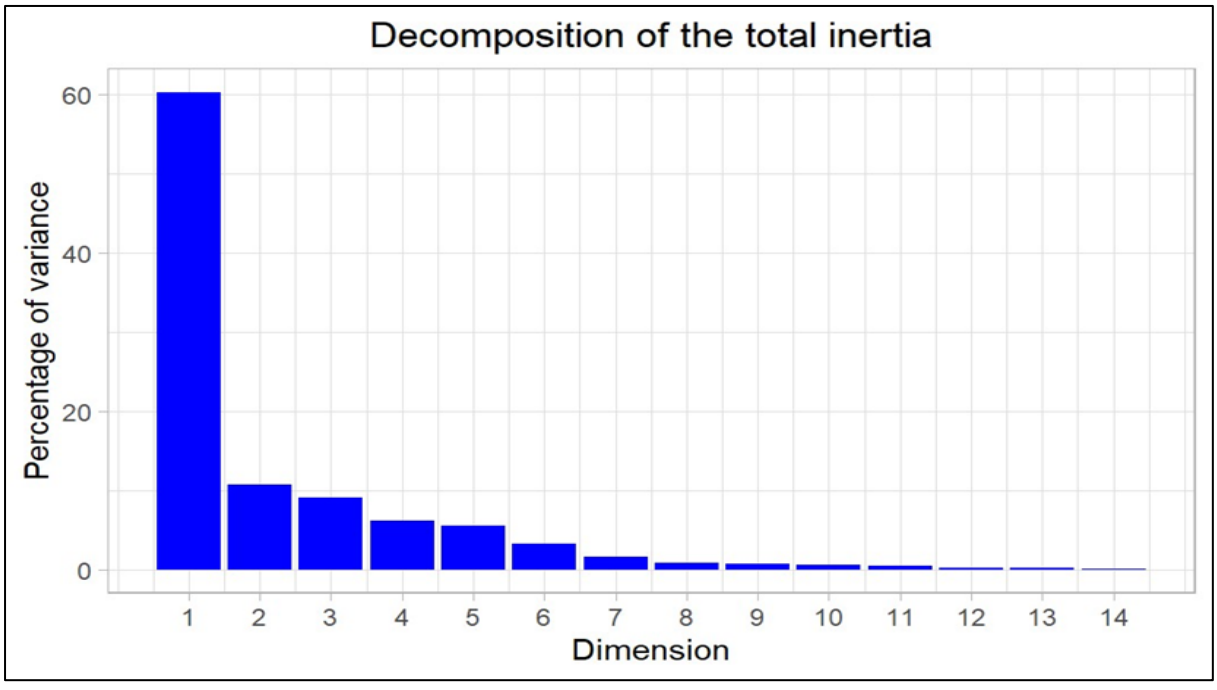

Figure 5.22: A bar graph showing the decomposition of the total inertia.

The first factor is major: it expresses itself 60.37% of the data variability (Figure 5.22). In such a case, the variability related to the other components might be meaningless, despite of a high percentage. An estimation of the right number of axis to interpret suggests restricting the analysis to the description of the first 1 axis. These axes present an amount of inertia greater than those obtained by the 0.95-quantile of random distributions (60.37% against 22.25%). This observation suggests that only this axis is carrying a real information. The description therefore refers to these axes (Figures 5.23 and 5.24).

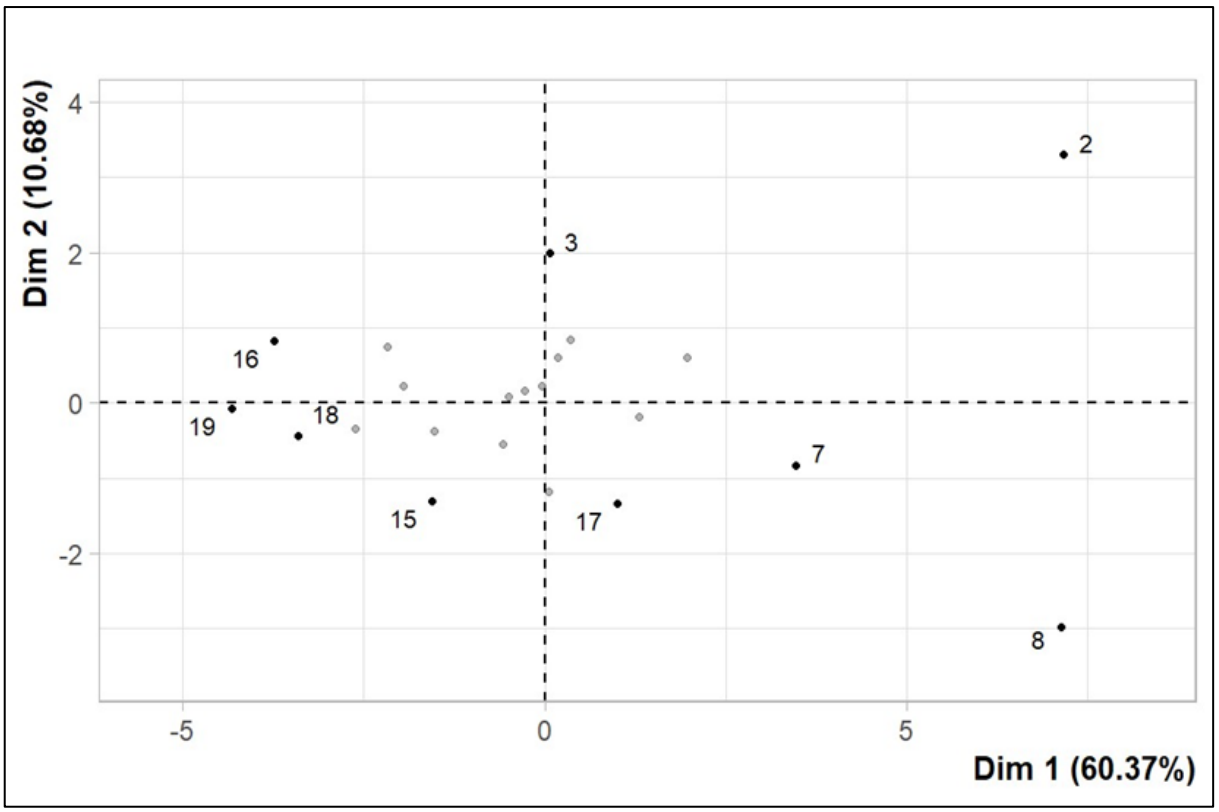

Figure 5.23: sites factor map (The labeled sites are those with the higher contribution to the plane construction).

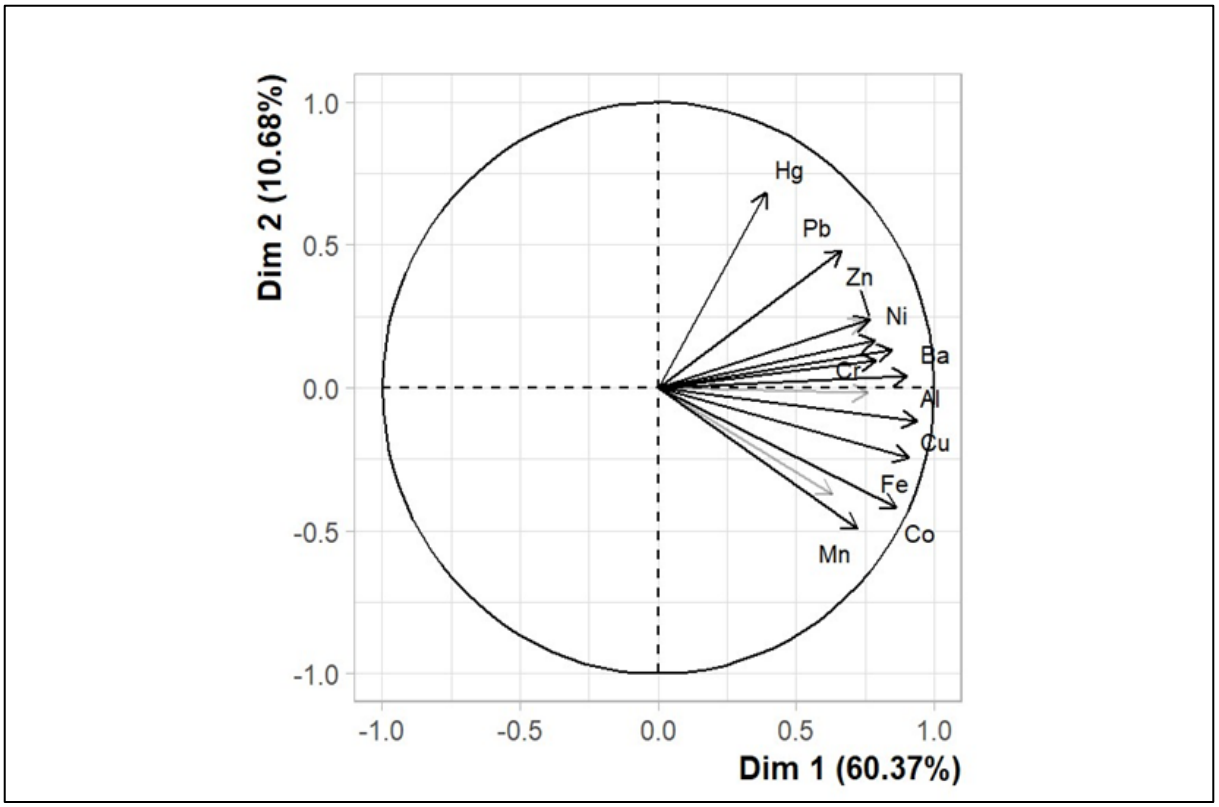

Figure 5.24: Variables factor map (The labelled variables are those the best shown on the plane).

The dimension 1 opposes sites such as 2 and 8 (to the right of the graph, characterised by a strongly positive coordinate on the axis) to sites such as 19, 18, 16 and 15 (to the left of the graph, characterized by a strongly negative coordinate on the axis). The group in which the site 8 stands (characterised by a positive coordinate on the axis) is sharing high values for the variables Mn, Co, Fe, Cd, Cu and Mo (variables are sorted from the strongest). The group in which the site 2 stands (characterised by a positive coordinate on the axis) is sharing high values for the variables Hg, Pb, Ni, As, Zn and Cr (variables are sorted from the strongest). Therefore, sites 8 and 2 shows similar sources based on dimension 1 but different sources based on dimension 2. This indicates that there is a mixed pollution sources of these metals along these sites which could be attributed to natural sources, urban runoff and wastewater discharge. According to the land-use map in Figure 4.1, it is observed that sites 8 and 2 are predominantly exposed to settlement/built-up which could explain the similarity in high values for these metals. Moreover, the group in which the sites 19, 18, 16 and 15 stand (characterised by a negative coordinate on the axis) is sharing low values for variables like Cu, Ni, Ba, Fe, Al, Cr, Mo, Co, Cd and Mn (variables are sorted from the weakest). This group includes Al and Fe, which are major elements in the Earth's crust and their concentrations showed relatively low values as compared to the ASV (background values) indicating their natural origin.

Therefore, the main contributing source at these sites could be natural sources or upstream agricultural activities as observed in Figure 4.1.

5.3.2 Classification

A multivariate statistical technique that allows variables to be grouped into clusters based on similarity or dissimilarity, such that each cluster indicates an explicit process within the system, is called cluster analysis (Kour *et al.,* 2021). According to Kour *et al.* (2021), CA classifies objects or variables such that each object or variable is similar to other objects or variables in a cluster concerning given selection criteria. In this study, the ascending hierarchical clustering (AHC) method was applied to identify similarities among heavy metals in sediments at various sampling sites. The classification made on sampling sites reveals 3 clusters (Figure 5.25).

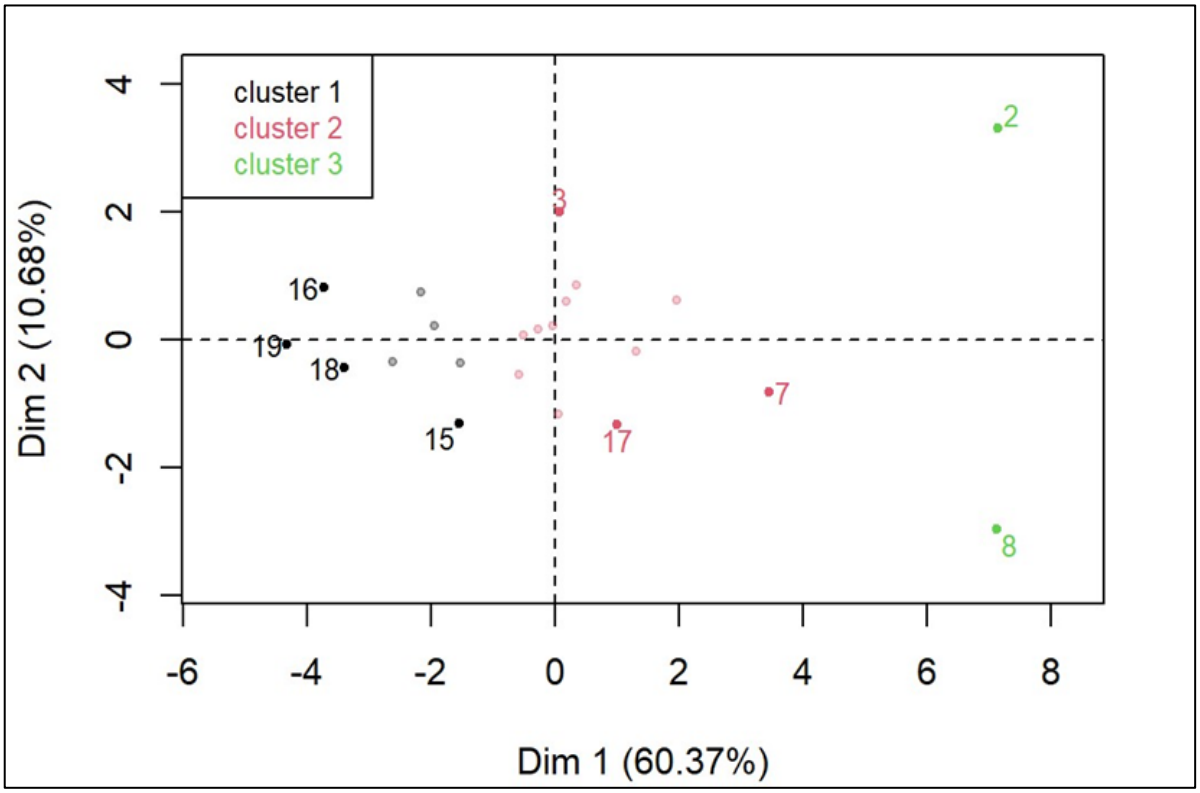

Figure 5.25: Ascending Hierarchical Classification of the sampling sites.

The cluster 1 is made of sites such as 15, 16, 18 and 19 of which 18 and 19 were inside KNP. This group is characterised by low values for the variables Ni, Al, Cr, Cu, Fe, Ba, As, Co, Zn and Mo (variables are sorted from the weakest). This similarity indicates same source of pollution along these sites. The cluster 2 is made of sites such as *3*, *7* and *17*. This group is characterized by high values for the variables; *Ni* and *Cr* (variables are sorted from the strongest). The cluster 3 is made of sites such as 2 and 8. This group is characterised by high values for variables such as Mn, Cu, Pb, Fe, Zn, Co, Mo, Ba, Al and As (variables are sorted

from the strongest). Based on these results, cluster 3 explains more variability in the analysed variables and thus cluster 3 can be regarded as the key contributor of heavy metals (variables) in the study area. Each cluster indicates a similarity in the concentration of metals obtained in this study. Thus, there could be three major sources of pollution within the study area. Nevertheless, the higher the similarity amongst sampling sites, the higher possibility of the same exhibiting source.

CHAPTER 6: CONCLUSION AND RECOMMENDATION

6.1 Conclusion

Physico-chemical parameters and concentrations of heavy metals in water and sediment, risk assessment (human and ecological), and possible sources of heavy metal in the Luvuvhu River Catchment were measured and evaluated. Various land use activities (human activities) influenced the water quality in the study area. Generally, physicochemical parameters results were within the SANS-recommended limits for drinking purposes except for Turbidity. Moreover, the study concludes that the mean heavy metal concentrations in the LRC water samples are decreasing in the order of Ca>Na>Mg>Fe>Al>K>Cr>Mn>Co>Ni>Cu>Zn>As>Mo>Cd>Ba>Hg>Pb. In the water samples from the river, 72.22% of metals (major and trace elements) showed higher levels during the wet season than in the dry season. Thus, runoff from settlements and lands might be a possible source of pollution during the wet season (rainy season) than the dry season. Nevertheless, the current trace metal concentrations have not yet reached levels that would be considered extreme. However, this study highlights that human activities have escalated the dissolution of heavy metals and other related pollutants into surface waters and sediments. This argument is supported by high contamination levels at measurement points receiving wastewater from sewage treatment plants and agricultural runoff. In conclusion, agriculture and settlement/built-up were the main land use activities affecting water quality in the LRC.

The study also found that the average heavy metal concentrations in the LRC sediments are decreasing in the order of Fe>Al>Mn>Ba>Cr>Cu>Ni>Zn>Co>Pb>As>Mo>Cd>Hg. Al and Fe concentrations were found highest in sediment samples, which may reflect their relative abundance in the Earth's crust. Additionally, higher concentrations were measured in the wet season than in the dry season in river sediment samples, except for Cd, Cr, Fe, Pb, and Zn. Possible sources of pollution in this catchment are partially treated water discharges from sewage treatment plants, runoff from settlements, runoff from agricultural land, landfills around the catchment, and atmospheric deposition. Except for Hg, metal levels in river water samples vary significantly from metal levels in sediment samples. Concentrations of Cr and Cu in sediments can have toxic effects on river aquatic organisms, whereas concentrations of Cd and Zn might not adversely affect them. Multivariate principal component analysis showed significant land use activities contributing to metals in the sediment. The enrichment factor, potential ecological risk, contamination factor, geo-accumulation index, and pollution load index indicated low to medium contamination of sediment by the studied heavy metals.

The Luvuvhu River Catchment water was found not suitable for drinking purposes without treatment as most of the WQI values exceed compliance levels. The study found that chronic daily intakes for adults were higher than for children. Non-carcinogenicity calculations of ingestion and dermal absorption exposure pathways to individual metals at all sampling sites do not pose a human carcinogenic risk. According to health risk assessments, the overall hazard index for children and adults does not represent non-carcinogenic risk (HI < 1). The carcinogenic risks assessment for As, Pb and Cd assumed that risk values are low (< 10^{-6}) resulting in no cancer risk to humans living within the study area, especially to children. Despite improvements in environmental protection measures, the growth rate of the LRC indicates that industrial, domestic and agricultural sources of pollution are likely to pose a growing problem in the future. This study provides baseline data for future studies on anthropogenic impacts in this region.

6.2 Recommendations

The findings acquired from this study made it possible to articulate the following specific recommendations:

- To study the combined impacts of human activities on regional environmental changes in the LRC, since river sediments may contain integrated information about environmental changes within their basins thus long-term observations of sediment geochemistry should be beneficial.
- A few parameters (microbial parameters) are desirable to cover the current status of the LRC as best as possible.
- A strategic plan should be developed to make local people aware of the pollution arising from the catchment rivers and how to protect the environment from this important problem.
- Initiate environmental programmes (environmental education) from primary school to decision makers, engaging all stakeholders to participate in pollution prevention and mitigation.
- Sites near sewage treatment plants are a priority site for environmental monitoring and control, and comprehensive risk assessment of heavy metals. This suggests that more investigation should be tailored to the assessment of the aquatic environment of rivers and the discharge of untreated municipal/industrial waste.
- There should be a continuous monitoring and identification of hotspot areas through the application of pollution indices since they are important for resource management priority setting and policy implementation.

- In addition, updated data on the state of elemental contamination are also desirable to set local guidelines on sediment quality and monitoring will not only address the issue of further accumulation and contamination with these metals but also addresses public health concerns arising from ingestion of these carcinogenic metals.

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APPENDICES

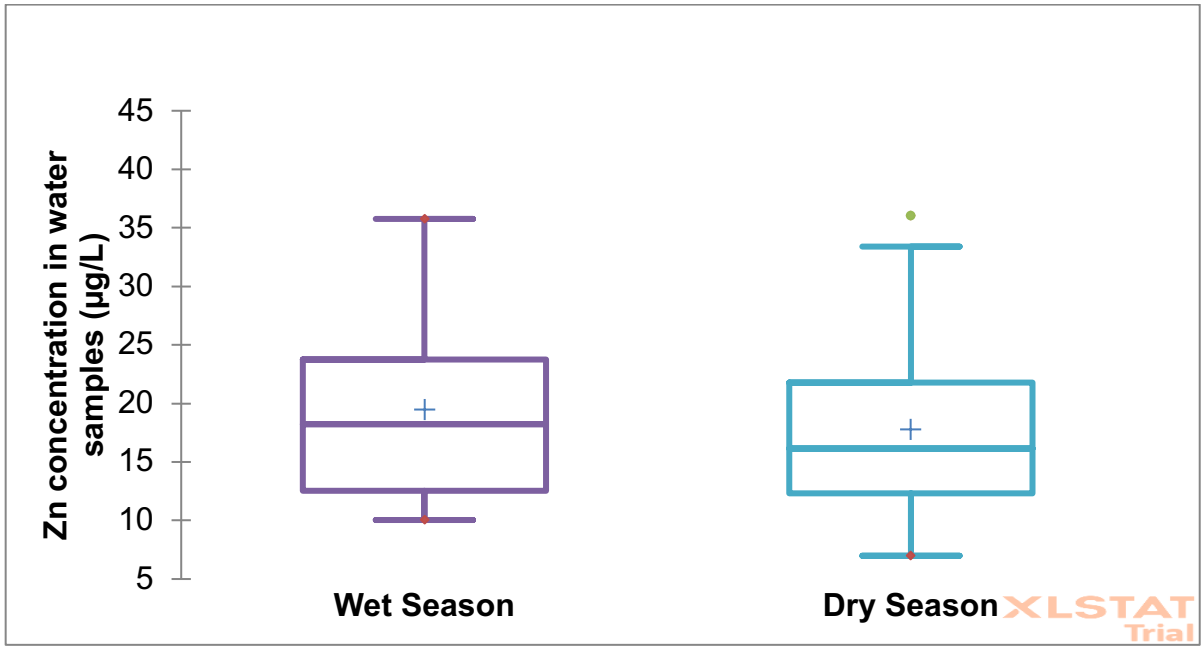
Appendix 4.1: Average value of metals in water samples

Sites	Na	Mg	K	Ca	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Ba	Hg	Pb
S1	8.57	7.75	0.64	13.05	0.25	1.62	124.70	1.48	0.79	1.83	4.88	15.74	0.13	0.21	0.01	32.01	0.02	0.70
S2	18.53	16.23	2.65	21.16	0.23	2.08	116.58	0.95	1.23	3.28	4.24	21.72	0.18	0.26	0.01	70.69	0.02	0.72
S3	9.30	8.42	1.83	13.13	0.39	2.55	30.26	1.08	0.73	2.36	4.06	23.63	0.21	0.24	0.00	44.14	0.02	0.44
S4	8.79	8.41	1.63	13.71	0.56	2.41	62.00	1.77	0.62	2.99	5.51	15.96	0.19	0.24	0.00	46.35	0.02	0.59
S5	7.73	6.04	1.31	11.63	0.46	2.47	71.57	1.28	0.61	2.74	4.40	18.40	0.13	0.14	0.01	46.16	0.02	0.57
S6	7.49	6.10	1.25	9.44	0.71	1.45	64.68	1.45	0.68	2.40	4.41	17.28	0.15	0.15	0.01	47.89	0.02	0.68
S7	6.93	5.86	0.72	9.36	1.81	2.09	169.32	1.68	1.70	4.76	3.92	18.57	0.20	0.14	0.01	38.87	0.02	1.31
S8	7.11	5.77	0.92	10.23	0.52	1.03	149.83	1.17	1.33	2.07	2.89	16.74	0.13	0.14	0.01	40.58	0.03	0.52
S9	8.31	6.47	1.28	10.78	0.74	1.67	139.17	1.05	1.63	4.56	4.30	25.81	0.14	0.13	0.01	49.99	0.02	0.63
S10	7.49	5.63	1.41	9.54	0.89	1.50	62.42	1.22	1.05	2.48	3.58	21.79	0.14	0.15	0.01	54.80	0.02	0.60
S11	7.24	6.51	1.50	11.03	7.49	1.67	51.04	1.87	0.45	1.65	3.20	20.53	0.17	0.33	0.02	53.90	0.05	0.38
S12	7.92	5.98	1.29	11.77	0.51	2.49	46.29	1.08	0.66	2.16	3.86	19.68	0.15	0.16	0.01	57.86	0.02	0.46
S13	7.22	5.53	0.99	9.02	2.25	1.94	105.63	1.67	0.91	4.84	4.89	18.11	0.20	0.31	0.01	36.43	0.02	1.09
S14	5.67	4.60	0.51	7.32	0.84	1.91	79.45	2.48	1.09	2.12	5.30	13.42	0.12	0.10	0.01	23.76	0.02	0.54
S15	6.30	3.93	0.49	7.94	0.57	1.09	86.69	0.86	0.83	2.30	4.74	18.50	0.11	0.08	0.01	25.51	0.02	0.44
S16	8.97	5.21	0.80	8.68	0.47	2.17	57.76	1.15	0.72	2.40	3.67	13.53	0.18	0.11	0.01	34.39	0.01	0.37
S17	7.58	6.90	1.02	14.28	0.13	1.36	63.29	0.64	0.58	1.70	5.43	11.25	0.12	0.12	0.00	55.65	0.01	0.30
S18	8.73	6.52	1.09	9.97	2.06	1.61	118.11	1.36	0.84	5.64	3.96	17.20	0.22	0.12	0.01	39.47	0.02	1.38

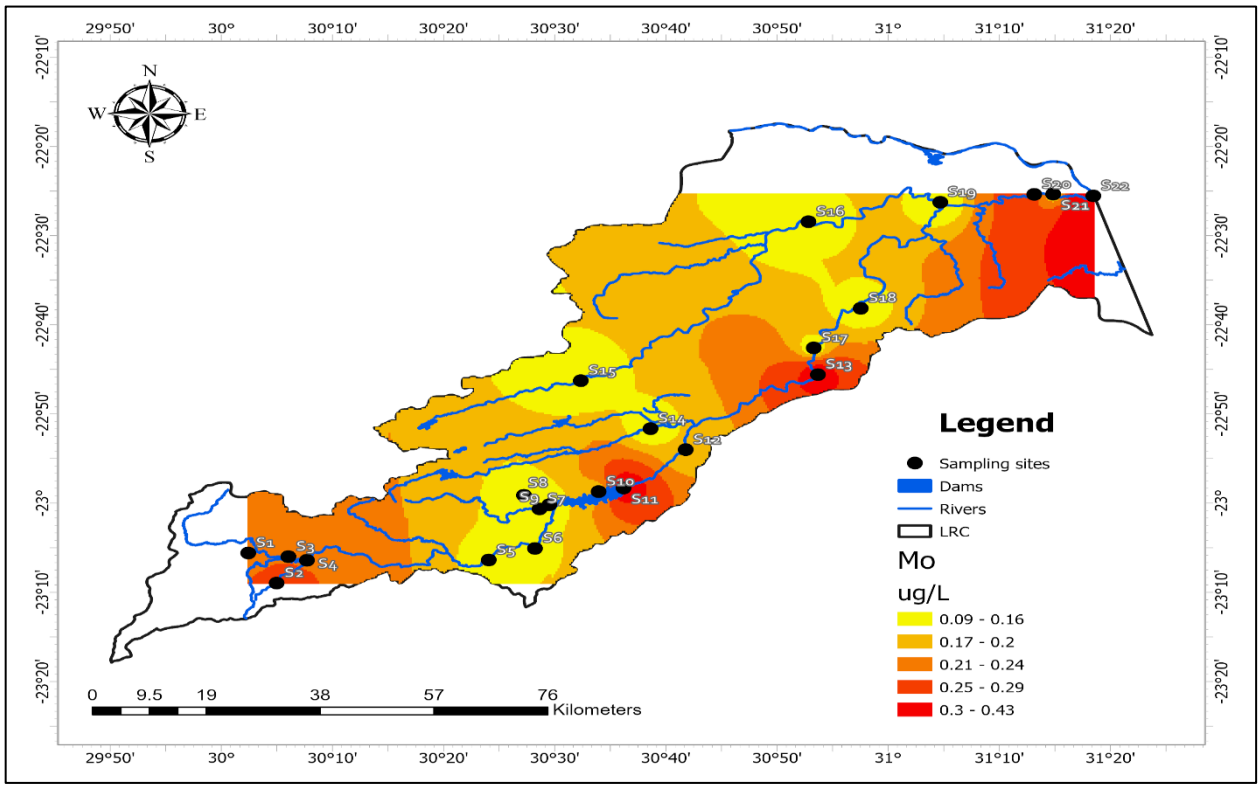
S19	9.34	5.97	0.58	7.46	0.14	1.18	44.97	0.76	0.60	1.42	3.33	17.79	0.13	0.10	0.01	24.34	0.01	0.32
S20	9.60	6.96	1.45	10.45	2.13	1.88	118.34	1.46	1.32	8.14	5.08	16.50	0.41	0.25	0.01	35.38	0.02	1.68
S21	9.77	7.12	1.37	10.62	1.99	2.74	113.64	1.57	1.31	7.66	5.01	19.42	0.43	0.14	0.01	34.62	0.02	1.84
S22	8.68	7.49	1.43	11.72	1.71	2.86	157.25	2.13	2.50	9.97	8.44	27.41	0.34	0.43	0.05	54.58	0.03	1.84

All values are in µg/L except for Na, Mg, K, Ca, Al, and Fe which are in mg/L

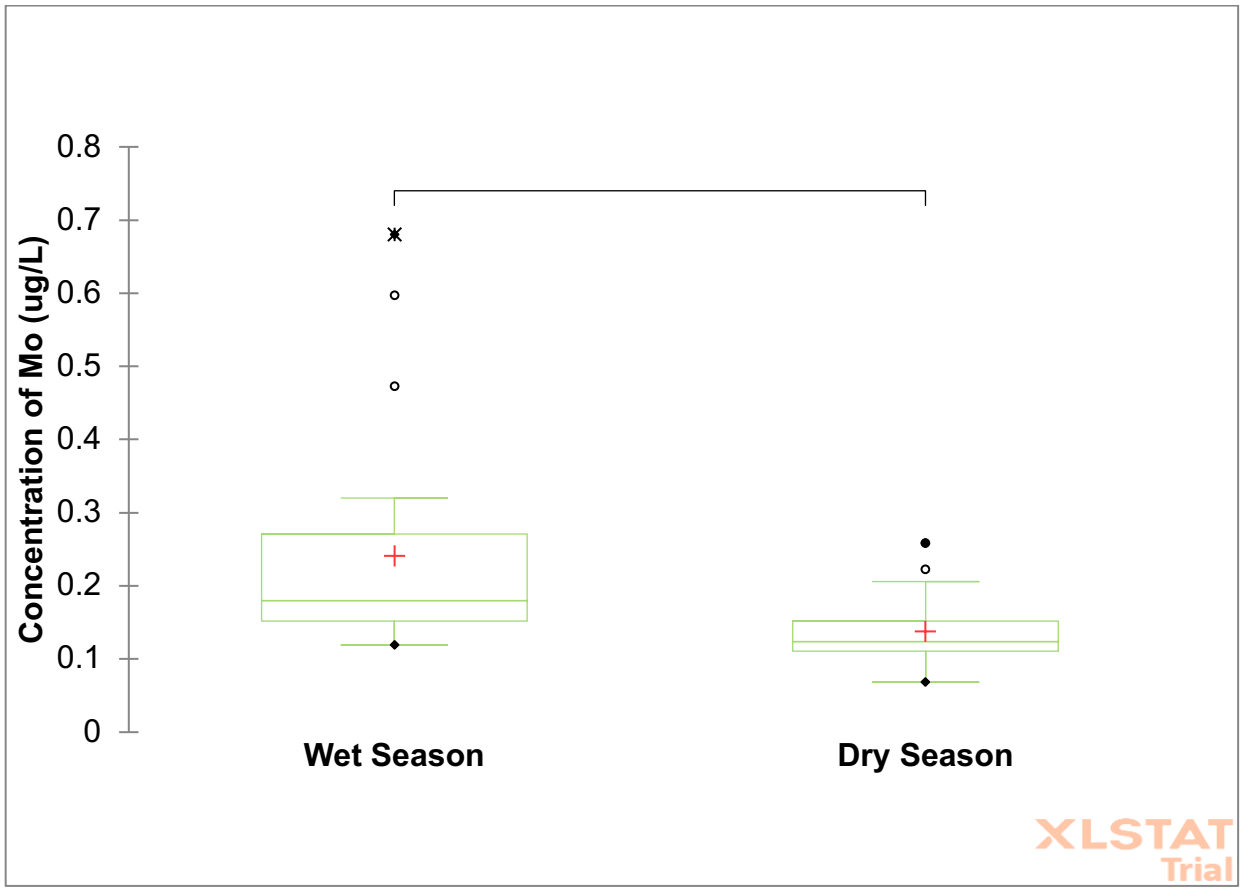
Appendix 4.2: Seasonal variation of Zn in water samples



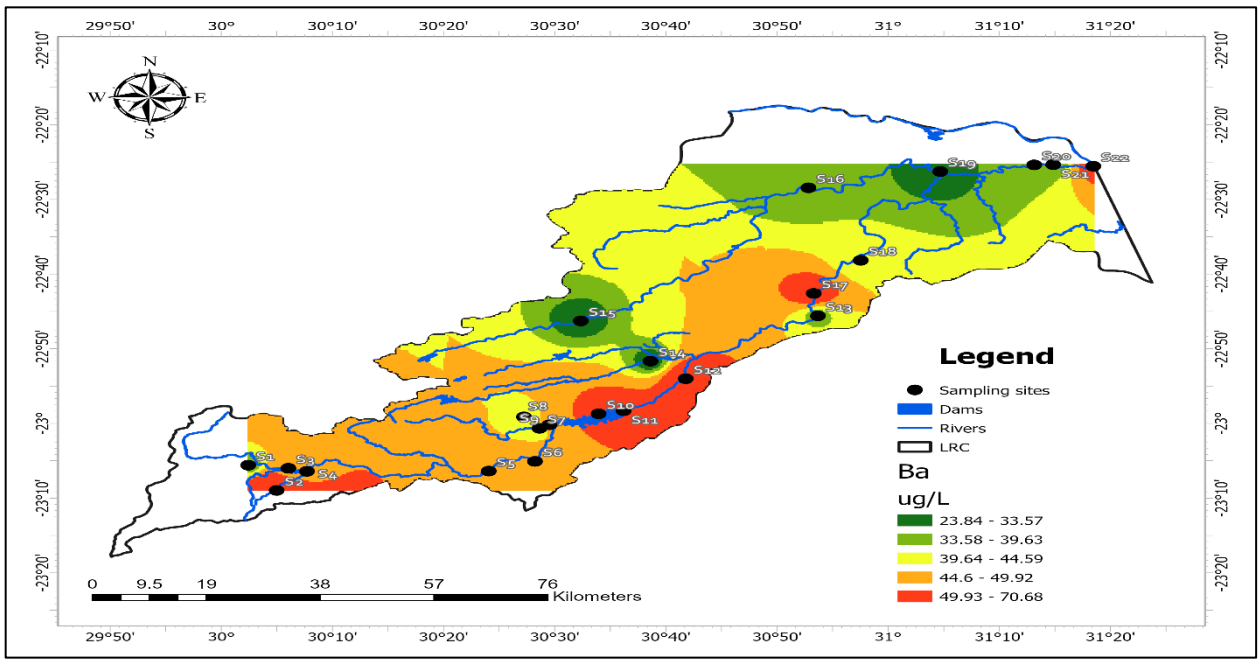
Appendix 4.3: Spatial distribution of Mo concentration in water samples



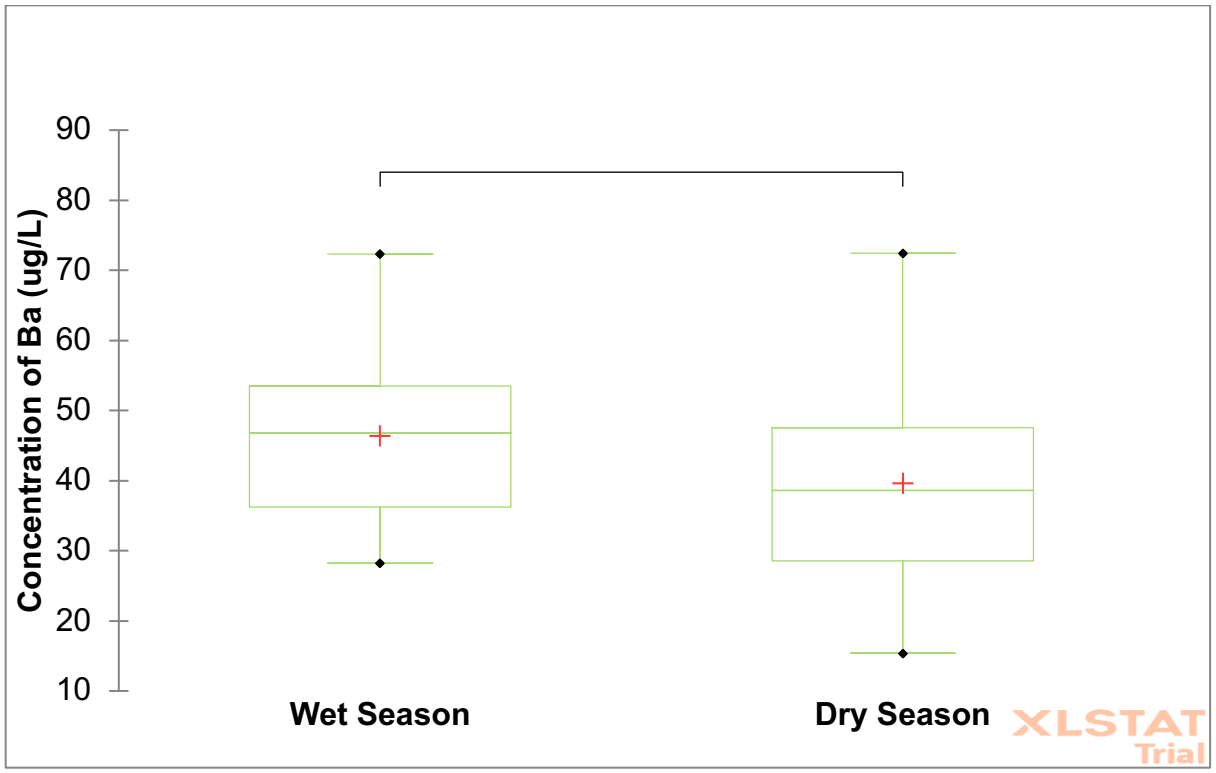
Appendix 4.4: Seasonal variation of Mo in water



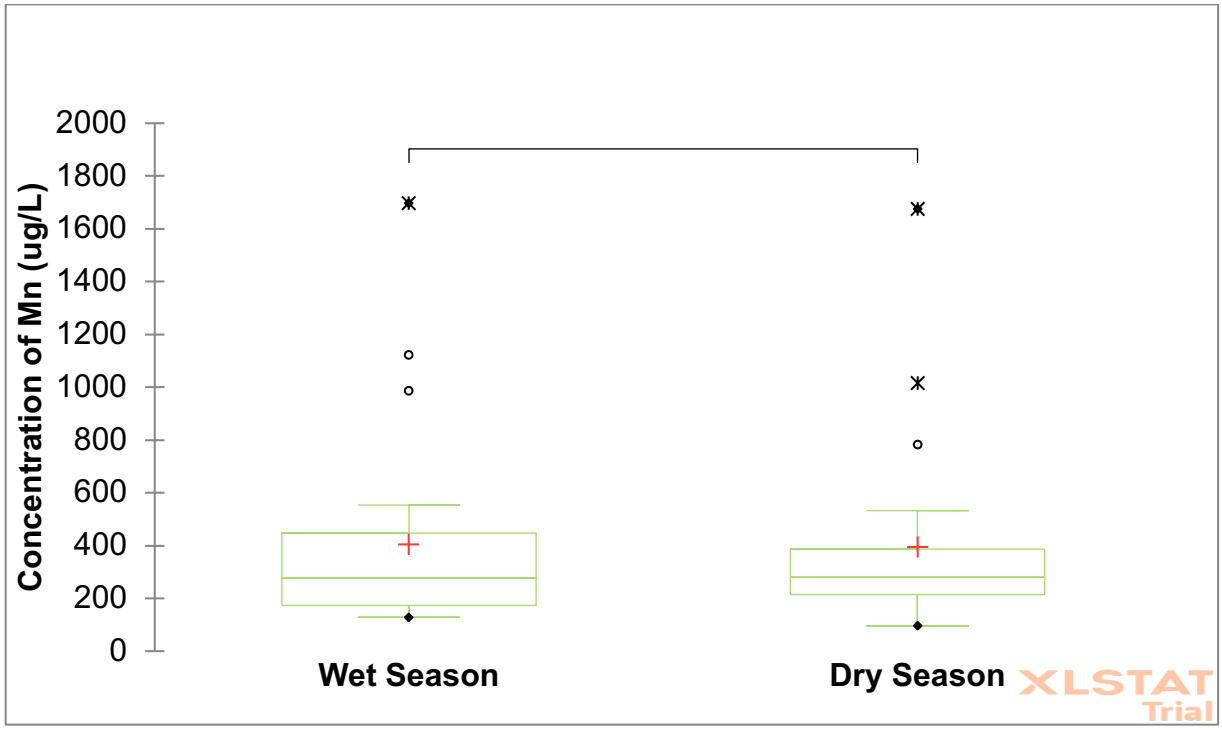
Appendix 4.5: Spatial distribution of Ba in water samples



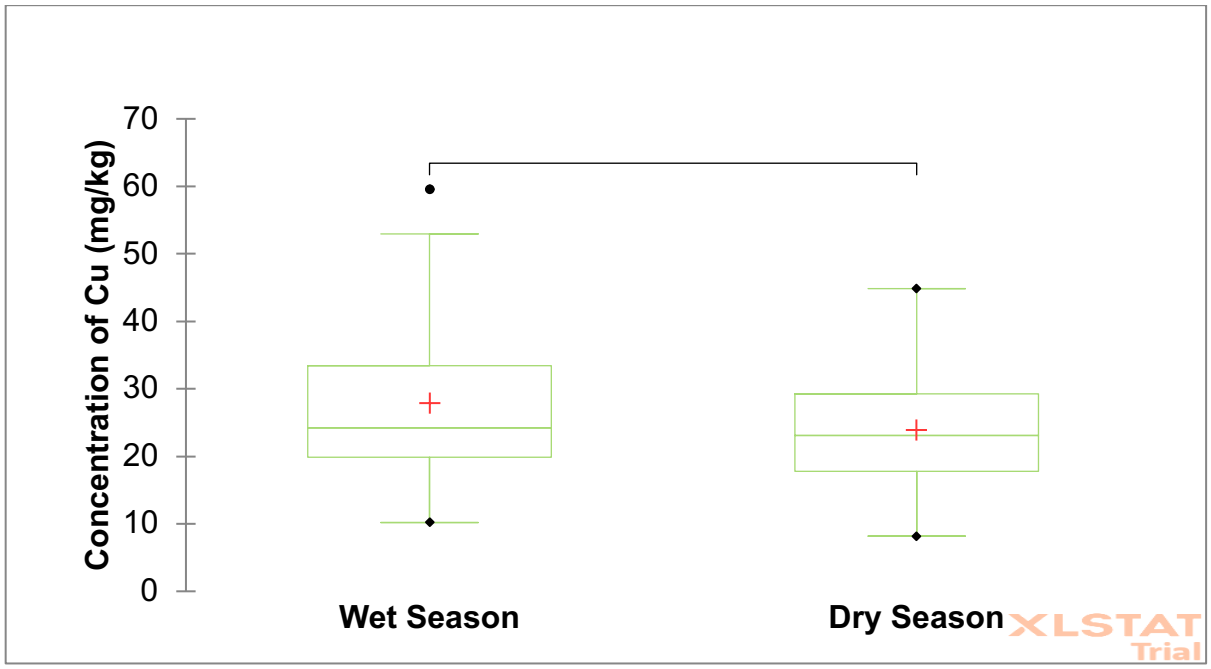
Appendix 4.6: Seasonal variation of Ba in water samples



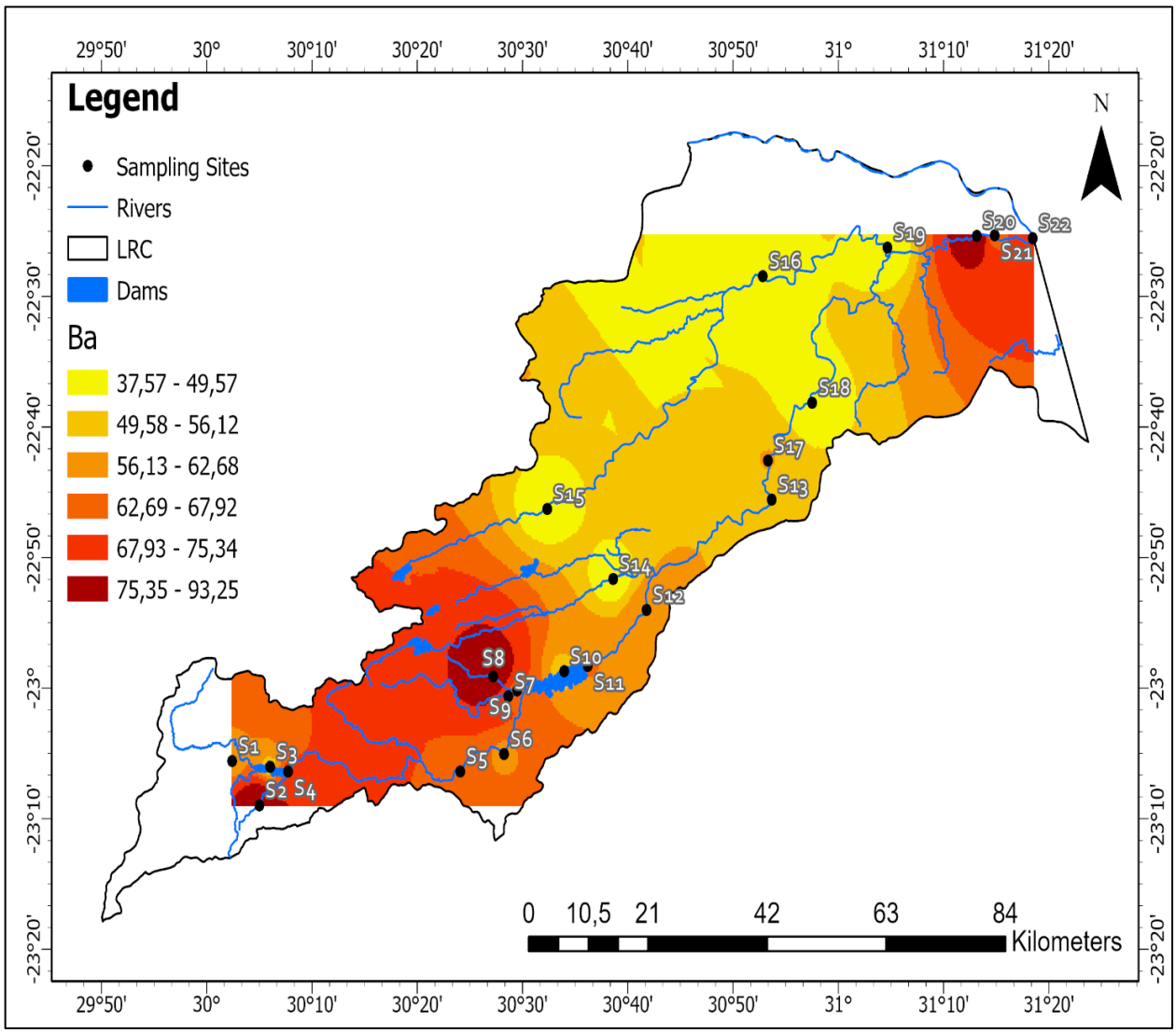
Appendix 4.7: Seasonal Variation of Mn in water samples



Appendix 4.8: Seasonal variation of Cu in sediment samples



Appendix 4.9: Spatial distribution of Ba in sediments



Appendix 4.10: Spatial distribution of Hg in sediments samples.