WATER QUALITY ASSESSMENT AND POTENTIAL ECOLOGICAL RISK OF TRACE METALS IN SEDIMENTS OF SOME SELECTED WETLANDS ACROSS LIMPOPO PROVINCE; SOUTH AFRICA

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By

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DECLARATION

I Stanley Skhuna Ndlovu with student number 11512859, hereby declare that this dissertation submitted to the Department of Geography and Environmental Sciences for the award of a master's degree in Environmental Science at the University of Venda is my concept in design and implementation. This study has not been previously submitted to this or other institutions. All references cited have been fully acknowledged and are in the list of references.

Signature: Date: 03-March-2023

DEDICATIONS

I would like to dedicate this study to my parents; my father and mother Lion and Martha Ndlovu. I want to appreciate you because you tried, by all means, to make me who am I today and you never turned your back on me even during the period of storms. I also dedicate this study to my late brother Paul Ndlovu who saw the beginning of this study but unfortunately could not see the completion because death snatched him from us.

ACKNOWLEDGEMENT

I would like to thank the Almighty God who gave me the strength to conduct this study from the beginning to the completion. Moreover, my gratitude to my supervisor Prof Edokpayi JN who fought from all angles to guide and assist me with whatever was required throughout the project. Also, I would want to appreciate DST-NRF for supporting this study. My gratitude to Dr. Adeeyo O. A who also assisted me in most aspects of this study I would also want to thank Mr. Mahlaule N.A who also guided me closely from the beginning of this study to the completion. Mr. Mudau L and Mr. Netshinanani M also appreciated helping me during the sample collection, preparations, and analysis. Last but not least I would like to appreciate all my friends who offered me support during the period of this study. I would like to appreciate my daughters Shiluba and Vukona Ndlovu who kept on supporting me to finish this study.

ABSTRACT

Wetlands are one of the most crucial resources since they provide diverse benefits to the ecosystem. Therefore, South Africa has put in place policies and guidelines to safeguard these valuable resources. This study was conducted to evaluate water quality and the potential ecological risk due to trace metals in sediments across wetlands in Limpopo Province. The samples' physicochemical parameters were tested in the field and the laboratory. All the instruments used to test the physicochemical parameters of the water samples were calibrated first and all the measurements were done in triplicate. The water and sediments samples were digested following the method recommended by US EPA 3015 for aqueous samples and 3050 for sediments samples, respectively. This was done to dissolve the metals that cannot are insoluble in neutral pH but soluble in acidic pH. For trace metals, the digested samples were analysed using inductively coupled plasma mass spectrometry (ICP-MS). Sediment quality guidelines standards for the protection of aquatic life were studied and compared with the threshold effect levels (TEL) and probable effect levels (PEL) as well as effect range-low (ERL) and effect range median (ERM). The potential ecological risk index (PERI) for sediment was studied using indices. The removal efficiency of pollutants from one of the wetlands was calculated to check if the wetland still performs its function. Most concentrations for both the physicochemical parameters and trace metals were within the recommended standards for irrigation and aquatic ecosystem by the Department of Water and Sanitation (DWS) standards formerly referred to as DWAF. However, the dissolved oxygen levels recorded were below the World Health Organisation guideline standard (5 mg/L) in the water of all sampled sites as it reported to be ranged between 0.773±0.155 (W4) to 3.88±1.00 mg/L (W10). In addition, Iron, and manganese exceeded the DWAF irrigation and aquatic protection threshold limit in all wetlands. Fe and Mn varied between W8-12973.62 62 µg/L and W1-77.42 62 µg/L Sediment quality guidelines standards presented levels below the threshold effect levels and effect range-low in most samples. However, few samples presented levels above the threshold effect levels and effect range-low but below the probable effect levels and the effect range median. Most of the sites presented low levels of risk index (RI) values, excluding W3 and W12 which presented a very high risk index (RI) value. The contamination factor values of Cr levels recorded at some sites (W3, W5, W9, W11, W12, W15, and W16), presented extremely high levels greater than CF>32 of toxicity to aquatic biota. Level of contamination (CD) values presented extremely high risk greater than 32 of contamination to 46.67% of sites.

Phangami wetland was found to be efficient in reducing the pollution burden of wastewater disposed into the wetlands and recorded acceptable reduction efficiencies for most of the metals recorded.

Keywords: water quality, physicochemical parameters, trace metals sediments, potential ecological risk, removal efficiency, wetlands, contamination factor, risk index.

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LIST OF ABBREVIATIONS AND ACRONYMS

Abbreviations	**Acronyms**
T_r^i	Toxic Response Factor
µg/L	Micrograms per Litre
µs/cm	Microsiemens/centimeter
Ag	Silver
Al	Aluminium
As	Arsenic
Ba	Barium
Be	Berellium
BOD	Biochemical Oxygen Demand
C_1	Initial Concentration
C_2	Final Concentration
Cd	Cadmium
CD	Degree of Contamination
CF	Contamination Factor
Co	Cobalt
Cr	Chromium
Cs	Caesium
Cu	Copper
DAFF	Department of Fishery and Forest
DO	Dissolved Oxygen
DWAF	Department of Water Affairs and Forestry
EC	Electrical Conductivity
ERL	Effect Range-Low
ERM	Effect Range-Median
Fe	Iron
Ga	Gallium
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
Mg/kg	Milligram per Kilogram

mg/L	Milligrams per Litre
Mn	Manganese
Ni	Nickel
NTU	Nephelometric Turbidity Units
^{o}C	Degrees Celsius
Pb	Lead
PEL	Probable Effect Levels
PERI	Potential Ecological Risk
Rb	Rubidium
SANS	South African National Standards
SANS	South African National Standards
Se	Selenium
SP	Sampled Point
SQGs	Sediments Quality Guidelines
Sr	Strontium
TDS	Total Dissolved Solids
TEL	Threshold Effect Levels
Tl	Thallium
TN	Total Nitrogen
TP	Total Phosphorus
TSS	Total Suspended Solids
U	Uranium
V	Vanadium
W	Wetland
WHO	World Health Organization
Zn	Zinc

OUTPUTS OF THIS STUDY

Tittle	Publication	Status
Wetland resources in South Africa: threats and metadata study.	Adeeyo, A.O., **Ndlovu, S.S.**, Ngwagwe, L.M., Mudau, M., Alabi, M.A. and Edokpayi, J.N., 2022. Wetland resources in South Africa: threats and metadata study. Resources, 11(6), p.54. https://doi.org/10.3390/resources11060054	Published in Resources
Assessment of water and sediments quality some in some selected wetlands across Limpopo Province; South Africa	Ndlovu, S.S., Edokpayi, J.N. (2023). Assessment water and sediments quality some in some selected wetlands across Limpopo Province; South Africa	On going
Trace metals removal efficiency using Phangami wetland, Limpopo Province, South Africa.	Ndlovu, S.S., Edokpayi, J.N., Matsa T (2023). Trace metals removal efficiency using Phangami wetland, Limpopo Province, South Africa.	On going

CHAPTER ONE: INTRODUCTION

1.1 Background Information

Water is a necessary and life-sustaining resource for all life forms (Khatri and Tyagi, 2015). This implies that all living organisms require water for survival. Only 3% of the water on earth is freshwater, with 2% locked up in ice caps and glaciers, and the remaining 1% accounting for all freshwater sources for the survival of every living creature (Sharma and Bhattacharya 2017). Surface water is a critical freshwater resource because many water treatment facilities around the world draw water from it. Surface water offers numerous benefits to the communities that live in its course (Madilonga et al., 2021). Surface water includes water from streams, rivers, lakes, and wetlands. Wetland is generic term used to define the universe of wet habitats including swamps, marshes, bogs, ferns and seasonal logged areas. Wetlands are economically important to the communities that surround them because they provide numerous benefits and ecosystem services that no other ecosystem can (Adeeyo et al., 2022; Rebelo et al., 2019). Wetlands typically provide important ecosystem services such as water provision, water purification, water regulation, and many others, which include cultural services (Rebelo et al., 2019). Wetlands also provide habitat, food, and refuge for aquatic and terrestrial ecosystems and they serve as natural hydrologic buffers against natural hazards like floods and droughts (Jaramillo et al., 2019). Wetlands are important sources of freshwater for domestic and agricultural use, as well as a means of livelihoods and food security of many local communities (Jaramillo et al., 2019). The benefits of wetlands to the surrounding community include livestock feeding, grazing, and irrigation of several crops including maize, sugarcane as well as vegetables. Moreover, some construction companies draw water from wetlands during the construction of buildings and roads while some community members use water from wetland to wash their vehicles.

Wetlands also participate in numerous significant geochemical cycling processes, which include the cycling of carbon and other major and trace elements (Deng et al., 2022; Jaramillo et al., 2019). Many industrial wastewaters carry a large variety of pollutants into the water environment, which makes a great threat to the ecological environment and human health (Temesgen et al., 2018). However, in rural areas, some communities are using wetlands as dumping sites since they do not consider wetlands as a major resource that needs their protection. Some of anthropogenic influences on the sustainability of South African wetlands are presented in Figure 1.1.

Heavy metals like Cr, Ni, Cu, As, Cd, and Pb are regarded as systemic toxicants since they are capable of bioaccumulating in the major human body and are known to cause various organ injuries even at trace levels. Although, some trace metals are essential for human survival such as calcium, the intake of these micronutrients can be injurious or even fatal when consumed in large quantities (Prasad et al., 2021).

A global public health concern is chronic heavy metal poisoning, which affects millions worldwide, as well as diseases caused by contaminated water, which have killed over 1.6 million children globally (Fernandez-Luqueno et al., 2013). Metals are distributed between the water and sediments phases after they have entered the surface water bodies. Only a trace amount of the metals is dissolved in water, with the majority being adsorbed in the sediments (Edokpayi et al., 2022). Changes in some physicochemical characteristics of wetlands sediments like pH and salinity can result in the release of heavy metals from sediments into the underlying water column (Dan et al., 2022; Chu et al., 2015). Water resources and water quality are critical for human survival, the ecological environment, economic development, and regional sustainability (Tong et al., 2021; Xiao et al., 2019). Sediment monitoring is critical because it serves as a proxy indicator for assessing the potential ecological risk of aquatic ecosystems (Edokpayi et al., 2022; Knox et al., 2016). A strong link between sediments and environmental health, as well as carbon sequestration, has been shown in studies by Dalu et al. (2020).

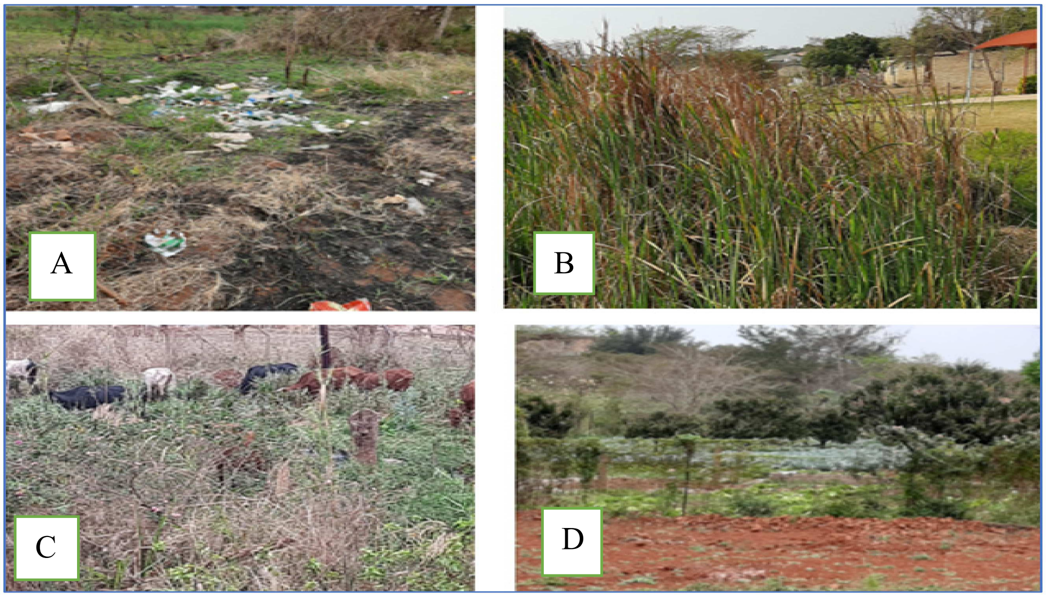

Figure 1. 1: Anthropogenic effects in wetlands. **A**-Solid waste deposition; **B**-Building within the wetland; **C**-Grassing in wetland; **D**-Plantation of crops within the wetland (Adeyoo et al., 2022).

1.2 Problem Statement

Wetland loss is estimated to be roughly 50% globally, with 35% to 50% of wetlands already lost or severely degraded in South Africa (De-Klerk et al., 2016). According to SANBI (2013), human activities threaten 48% of South Africa's wetland ecosystem. The discharge of raw and partially treated sewage discharge is among the leading causes of pollution in South African wetlands (Adeeyo et al., 2022). Wetlands in South Africa are being transformed into agricultural lands and residential areas, and nearly half of the country's wetlands have been lost (Adeeyo et al., 2022). Expedited population growth, social and urban advancement, and industrial growth all impose substantial demands on water resources, increasing the risk of contamination and depletion (Senoro et al., 2022). The discharge of both anthropogenic and natural substances into the aquatic environment is affecting water quality in wetlands. High levels of trace metals in the aquatic environment pose a significant risk to human health and ecosystems (Papagiannaki et al., 2022). South Africa has put in place policies and guidelines to safeguard these valuable resources. However, such guidelines are ineffective because most people are more concerned with meeting their own needs than preserving nature. There is a poor perception of people to the importance of wetlands hence unwanted are often disposed into them. Wetlands are being destroyed on a daily basis rather than being protected as freshwater resources, which is a major issue, particularly in rural areas where surface water resources are the primary source of water for the communities (Shibambu, 2016). The waste disposed in wetlands consists of toxic substances such as heavy metals which are non-biodegradable. These metals affect the aquatic ecosystem and can enter the food chain through the consumption of fish and other aquatic plants, therefore, the contamination of surface water by these metals may have an impact on other environmental counterparts (Proshad et al., 2021). In addition, eating food that was irrigated by polluted water that is beyond the irrigation threshold limit might also result in various diseases which are associated with high levels of metals.

The province of Limpopo has plenty of wetlands; however, some community members use these wetlands as dumping grounds instead of understanding the services they provide. Wetlands are also affected by these factors, which increase pollution levels as well as reduce dissolved oxygen levels. It was therefore necessary to study physicochemical parameters of these wetlands and trace metal levels in order to understand their current state.

1.3 Motivation

This study is of paramount importance because it focuses on the quality of water and sediments in wetlands across Limpopo province. Moreover, there is truly little information documented about the water quality of wetlands in South Africa and Africa. Based on the information reported in the literature, wetlands perform a variety of complex ecological processes and provide services that no other ecosystem can (Rebelo et al., 2019). Wetlands are important physical and social features of a country's natural capital, as well as ecosystem service providers for both local and national societies (George and Ngole-Jeme, 2022). These ecosystem services can be quantified to monetary value and incorporated into the economy. In 2011, natural wetland ecosystems were valued at 47.4 trillion dollars worldwide (Davidson et al., 2019). Wetlands are a significant source of freshwater for both agricultural and residential use, as well as for many local communities' livelihoods and food security (Jaramillo et al., 2019). South Africa has been reported as a water-scarce country due to the characteristic of low rainfall. Therefore, the water resources available have to be well-conserved to help with this problem of water scarcity (Adeeyo et al., 2022). Wetlands also act as a buffer of pollutants and recharge rivers and streams with purified water. Moreover, hundreds of plants and animals get their food sources from wetlands (Hammer et al., 2020). Wetlands need to have water and sediments which are below the quality guidelines standards to sustain the biodiversity and provide various ecosystem services to the surrounding communities. Because South Africa is a water-scarce country, water quality is a top priority (Matodzi et al., 2021). This study reports on the quality of the water in wetlands used for various purposes such as irrigation, livestock feeding, aquatic life protection as well as domestic use. Also, the sediment quality and the potential ecological risk of metals reported.

1.4. Objectives of the Study

1.4.1 Main objective

To evaluate water quality and the potential ecological risk due to trace metals in sediment across wetlands in Limpopo Province, South Africa.

1.4.2 Specific objectives

1. To determine the physicochemical and trace metals levels in water and sediments of wetlands across Limpopo Province.
2. To evaluate the potential ecological risk of metals in sediments of wetlands across Limpopo Province.
3. To investigate the trace metals removal efficiency using Phangami wetland.

1.5 Research Questions

I. What are the levels of physicochemical and trace metals in water and sediments of wetlands across Limpopo Province?

II. What is the potential ecological risk of metals in sediments of wetlands across Limpopo Province?

III. How efficient is Phangami wetland in trace metals removal?

1.6 Description of the Study Area

The study area comprises of selected wetlands across Limpopo Province (Figure 1.1) which is located in the North-East of South Africa bordering Botswana, Zimbabwe, and Mozambique. The area coverage of Limpopo province is 12.5 million hectares. Limpopo province is known for its temperature changes throughout the year. The average temperature varies between approximately 18° C (winter) and 28° C (summer) and elevation of Limpopo province is between approximately 200 m and approximately 2100 m. The average rainfall in Limpopo province ranges from less than 200 mm in low-lying areas to more than 1000 mm in high-lying areas, and it is highly seasonal, with rain in the summer and dry periods in the winter. Environmental gradients allow diverse vegetation types in the Limpopo Province (Scheiter et al., 2018). The Samples were collected in Waterberg, Mopani, Vhembe, Capricorn and Sekhukhune districts as shown in Figure 1.1.

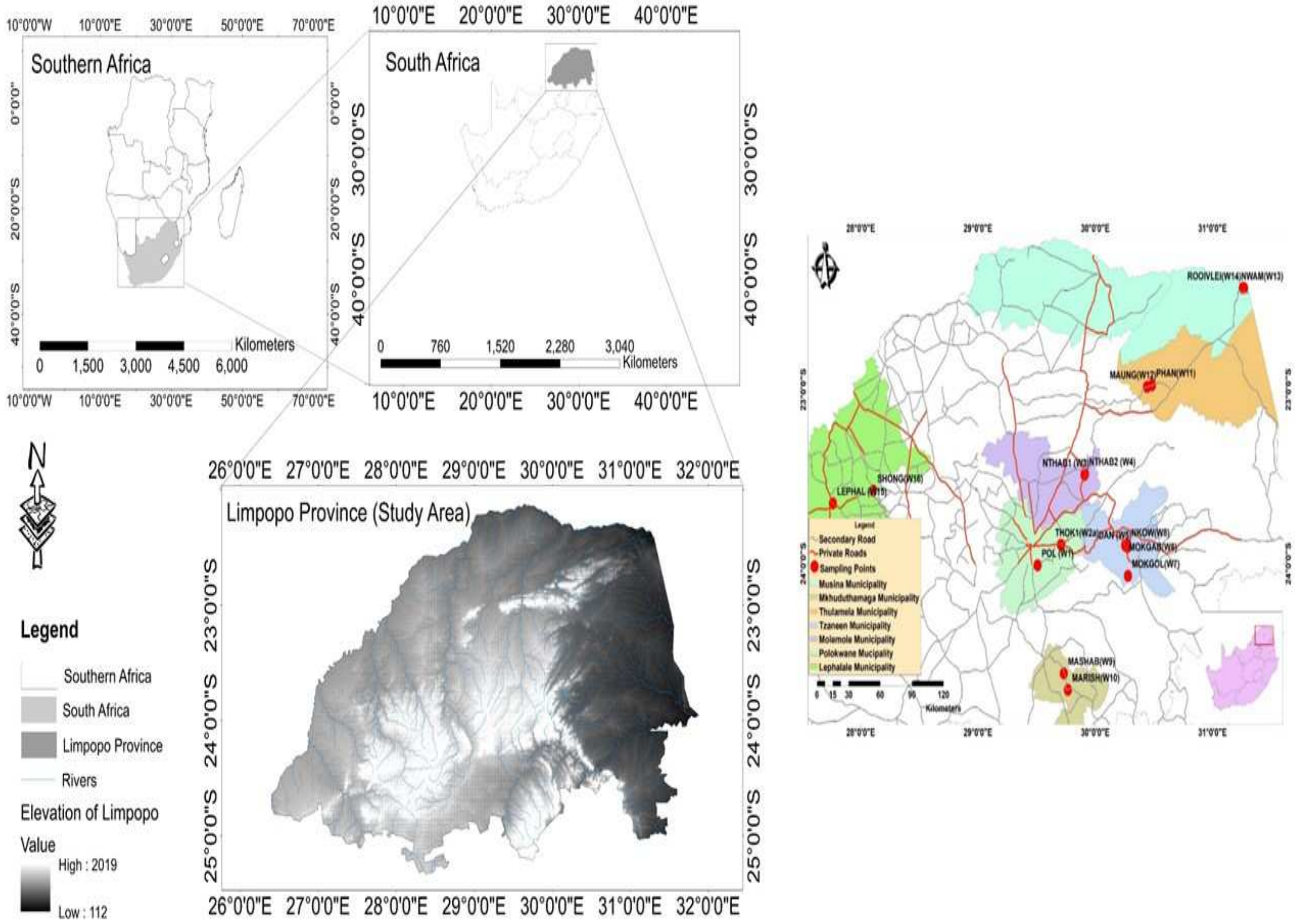

Figure 1. 2: Maps of the study area showing South Africa, Limpopo Province and the sampled wetlands.

CHAPTER TWO: LITERATURE REVIEW

2.1 Preamble

This chapter report on the detailed review of literature concerning wetlands globally with specific reference to those in South Africa.

2.2 Wetland Description and Characteristics

Wetlands are a type of environment that can be found from coastal flats to high mountain ranges (Kingsford et al., 2016). Wetlands are surrounded or filled with shrub vegetation (Bass and Evans, 2000). According to Gebresllassie et al. (2014), wetlands have a wide range of geographical and temporal properties because they change with the seasons, from dry to moist, and vary geographically due to topography and temperature. The presence of water, distinct soils that differ from upland soils, and vegetation adapted to saturated conditions distinguish wetlands (Rai, 2008). Because of their flat topography and abundant vegetation, which trap pollutants in settling sediments, wetlands are known for their pollution-reduction properties (Shivambu, 2016). The presence, characteristics, biodiversity, and productivity of wetlands are all influenced by their hydrology (Moshiri et al., 2020) Meadows, swamps, and aquatic vegetation are three major vegetation types found in overwater wetlands, all of which serve as habitats for various bird species (Zhang et al., 2021). The main biological component of wetland vegetation is macrophytes. They not only absorb contaminants directly into their tissues, but they also function as filtration catalysts by enhancing ecological diversity in the root zone and facilitating a variety of chemical and metabolic reactions that aid purification (Rai, 2008).

2.3 Natural Wetlands

Bezabih and Mosissa, (2017) defined wetlands as areas of marsh, ponds, and swamps with static or moving water that is fresh, brackish, or salty, including seawater, whether natural or artificial, permanent, or temporary. There are numerous issues caused by wetlands change, including the extinction and decrease of wild flora and fauna, loss of natural soil nutrients, decrease in water quality, and loss of aquatic biota (Bezabih and Mosissa, 2017). Regardless of the fact that natural wetlands provide crucial habitats for a varied set of animals and provide important ecosystem services, the majority of them have been lost due to anthropogenic activities, and as a result, wetland construction has become a common mitigation method (Draver and Richter, 2016). However, Kurzabaum et al. (2012) reported that wetlands are neither entirely land nor entirely water, but instead combine elements of both aquatic and terrestrial ecosystems. The Vhembe biosphere consists of numerous wetlands that assist as wildlife habitats and provide dynamic ecosystem services including improving the quality of water. However, anthropogenic activities continue to degrade or destroy some of these wetlands, causing them to decline at an alarming rate (Dalu and Chauke, 2019).

2.4 Wetland’s Types and Classifications

The classification of wetlands is based on their biophysical characteristics, including their plant species, soils, hydrology, animals, function, and value (Ollis et al., 2015). Various purposes can be served by classification, such as mapping, planning, acquisition, and regulation (Ollis et al., 2013; Ellery et al., 2016). The Cowardin system categorizes wetlands into five categories: marine, tidal, lacustrine, palustrine, and riverine based on the landscape, vegetation, and hydrologic regime (United Nations Environmental Protection Agency, 2021). Wetlands are classified as marine, estuarine, or inland based on their proximity to the open ocean; however, there is a fourth category called an artificial wetland, which is man-made but functions similarly to the natural types (Ollis et al., 2016; Makopondo et al., 2020). Figure 2.1 depicts the classification of wetlands, highlighting the various relationships between the various classification structures.

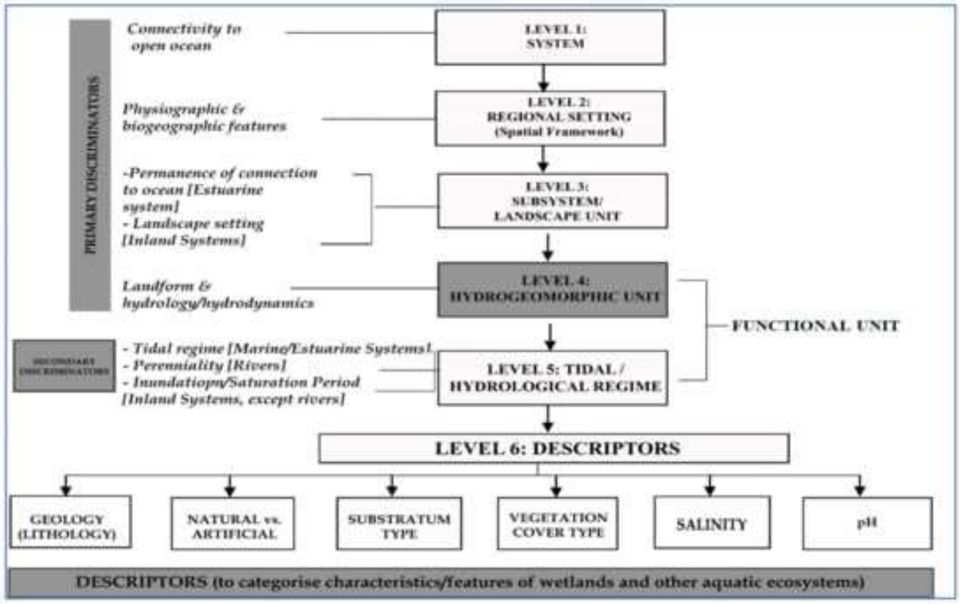

Figure 2. 1: A conceptual overview of the classification system used to classify wetlands and other aquatic ecosystems (Ollis et al., 2015).

There are four levels of spatial organization in the tiered system: marine at the broadest scale (Level 1), regional at the second and third levels, and hydrogeomorphic at the fourth level. South Africa’s climate has a profound effect on estuaries. They are influenced by global warming characteristics such as temperature rise, precipitation, sea level rise, storm disturbance, pH, and carbon dioxide levels (James et al., 2013). This feature classification was presented along with the biogeographical region category to generate 46 estuarine ecosystem types for South Africa.

2.4.1 Marine wetlands

The marine system is the open sea part of the continental shelf and/or its related shoreline, which extends up to 10 meters at low tide (Ollis, et al., 2015). Wetlands along the coast and in open coast areas, estuaries, tidal flats, coral reefs, mangrove forests, and coastal lagoons are all examples of marine and coastal wetlands. A further classification was made in 2011 by the SANBI into three types of marine habitats in South Africa: offshore, inshore, and coastal habitat. Offshore zones include both pelagic and benthic zones. Inshore zones have rocky or unconsolidated substrate. The third category, coastal areas, is further subdivided into rocky coast, mixed coast, and sandy coast. Marine wetlands are vital habitats for fish, dugongs, and sea turtles. Pig face, sea rush, marine couch, creeping book weed, and swamp weed are among the plants found here (Adeyoo et al., 2022). The marine groups are classified into 14 categories based on wave exposure, geology, grain size, and/or beach state (Adeyoo et al., 2022). These classifications are used to regionalize the classes, along with biogeographical differences (based on the delineation of marine "ecozones" and "ecoregions"). This will result in 136 marine and coastal habitats, 41 of which are shallow and less than 5 m deep, where marine and coastal wetlands are common (Makopondo et al., 2020; SANB, 2009).

2.4.2 Estuarine wetlands

In estuary wetlands, water bodies are partially enclosed and generally do not open up to the sea except on a decadal or seasonal basis. There are four types of estuarine systems: bays, river mouths, lakes, and estuaries that are permanently open or temporarily open. Current approaches to the classification system developed for the 2011 National Biodiversity Assessment (NBA) of estuaries consider four physical characteristics: size, mouth state (permanently or temporarily open/closed), salinity structure (fresh or mixed), and catchment type (turbid, black, or clear based on the colour of the inflowing river) (Van Niekerk and Turpie, 2012). Many South Africa's estuaries have river catchments that differ from adjacent marine inshore conditions in that they are calm, sheltered, and shallow. They serve as important nurseries for a variety of marine fish species.

The climate in South Africa has a significant impact on estuaries. They are influenced by global warming characteristics such as temperature rise, rainfall, sea level rise, storm disturbance, pH, and carbon dioxide (James et al., 2013). This feature classification was presented alongside the biogeographical region category to generate 46 estuarine ecosystem types for South Africa. The mentioned estuarine habitats have been outlined: water surface (estuary channel), rock, sand, and mudflats. The respective plant communities have been noted: intertidal/subtidal macroalgal, submerged macrophytes, intertidal/supratidal saltmarsh, reed sand sedges, mangroves, and swamp forest (Van Niekerk, et al., 2020). Table 1 lists the estuaries in South Africa that have some level of protection. According to van Niekerk and Turpie (2012), estuaries should target 84 fish species and 35 bird species. *Acanthopagrus berda, Ambasssis natalensis, Caranx papuensis, Elops machnata, Lichia amia, Liza alata, Pseudorhombus arsius, Solea bleekeri, Terapon jarbua, Syngnathus acus, and Valamguli seheli* are among the fish species. Great white pelican, greater flamingo, grey plover, red knot, sanderling, swift tern, little tern, mangrove kingfisher, pink backed pelican, and squacco heron are among the bird species.

2.4.3 Inland wetlands

Inland systems are distinguished from marine and coastal wetlands by the fact that they have no connection to the sea. Unlike marshes and wet meadows, which have marine exchanges and/or tidal influences, inland wetlands do not have such influences (Makopondo et al., 2020). The dominant plant species in these wetlands are herbaceous plants, while shrubs and trees are dominant in swamps (Adeyoo et al., 2022). Table 2.1 shows some of South Africa's Ramsar sites, as well as their wetland types and locations. Wetlands in KwaZulu-Natal are classified into three-level categories consisting of 16 wetland types based on the national wetland vegetation description (Rivers-Moore and Goodman, 2010). These Ramsar sites are well-protected except Orange River Mouth in the Northern Cape and Verlorenvlei in the Western Cape, which are not formally protected (Adeyoo et al., 2022). Wetlands are valuable, but they are disappearing because of impoundment, irrigation, hydroelectricity generation, food insecurity, population growth, and alien invasive biota (Mitchell et al., 2013).

Table 2. 1: Some of the South African Ramsar sites (Adeyoo et al., 2022)

Wetland’s Name	Wetland’s Type	Location
De Mond Nature Reserve (Heuningnes Estuary)	Estuary	Western Cape
Makuleke Wetlands	Floodplain	Limpopo
The Ndumo Game Reserve	Floodplain	KwaZulu-Natal
Nylsvley Nature Reserve	Floodplain	Limpopo
Verlorenvlei	Highland wetland	Western Cape
De Hoop	Costal lake	Western Cape
Langebaan	Estuary	Western Cape
Wilderness lakes	Costal lake	Western Cape
Verlorenvlei	Highland wetland	Western Cape
Orange River Mouth	Estuary	Northern Cape
Lake Sibaya	Costal lake	KwaZulu-Natal
Ntsikeni	Highland wetland	KwaZulu-Natal
Barberspan	Barberspan	North West
Natal Drankensberg	Estuary	KwaZulu-Natal
Kosi Bay	Costal lake	KwaZulu-Natal
ST. Lucia	Estuary	KwaZulu-Natal
Verloren Vallei Nature Reserve	Highland wetland	Mpumalanga

2.5 Functions of Wetlands

Based on the studies conducted, wetlands provide a wide range of ecological benefits, including improved water quality, climate regulation, nutrient processing, carbon sequestration, recreation, and habitat improvement (Souliotis, I. and Voulvoulis, etal., 2022; Kennedy and Mayer, 2002) There are macrophytes found in natural wetland ecosystems that serve as major storage sites for carbon and nutrients (Hardwick et al., 2022). Wetlands can store water during the rainy seasons and discharge it during the dry season which contributes to helping farmers living in semi-arid areas opportunities to grow crops all year round and improve food security and incomes (Jogo and Hassan, 2010). Except for farmers benefiting from water stored in wetlands, it also assists local communities to have access to water for domestic purposes in those dry seasons as more water is stored in wetlands. Ardon et al. (2010) reported that wetlands can act as a drought relief system, they also can export and retain nutrients and sediments, protect soil, control erosion, sustain stream flow, fish nurseries, and recharge groundwater, recreation, and tourism together with cultural value.

According to Reddy et al. (2010), wetlands serve as material sources, drains, and transformers which include serving as a site for the transformation of nutrients such as nitrogen (N) and phosphorus (P). It has been shown that Wetlands provide a range of ecosystem goods and services, including temporary floodwater storage, attenuation of flood peaks, and erosion control via sediment trapping and storage. Fishing, grazing, and subsistence farming are all supported by biodiversity as well as the harvesting of reeds and medicinal plants as part of agriculture (Rountree et al., 2008). Furthermore, wetlands act as a habitat for organisms such as aquatic plants, fish, mammals, reptiles, amphibians, invertebrates, and waterbirds (Kingsford et al., 2016).

2.6 Water Quality in Wetlands

Based on the study conducted by Jia et al. (2016), many wetlands have been destroyed or severely damaged because of reduced inflow and pollution. Given the increasing levels of watershed degradation across the country, a higher-level strategy to assess wetland conditions by wetland type is required before beginning to prioritise conservation measures at the regional level (Rivers-Moore and Cowden, 2012).

A healthy, functional wetland is essential for environmental and public health protection as stated by Phethi and Gumbo (2019). However, these wetlands continue to be degraded every day in various forms by different activities that temper their water quality. When wetlands are degraded or lost, they have an impact on the environment, human health, biodiversity, regional climate, and regional ecological security. Reddy et al. (2010) indicated that changes in wetlands' basic functions can lead to poor water quality and increasing nutrient and pollutant loads in surrounding aquatic systems.

According to Haidary et al. (2013), the forest plays a critical role in preventing the loss of nutrients from soils. Additionally, the study revealed that there was a direct relationship between the proportion of urban areas within the catchment of the wetlands, assessing the effects of four land uses, and the annual mean of nutrients such as Total nitrogen (TN), NO_2, Total dissolved solids (TDS), and Electrical conductivity (EC) in the wetland waters (Baloshi et al., 2019). Furthermore, the study demonstrates that when the number of agricultural areas grows, the annual mean of NO_{2-} and TN in the wetland site increases. As a result, urban and agricultural regions were regarded as landscape elements that harmed water quality. The results of water parameters revealed a substantial positive association between the proportion of urban areas within the wetlands' watershed and EC ($r= 0{,}67\ p<0{,}01$), TDS ($r= 0{,}69\ p <0{,}01$), and NO_{2-} ($r= 0{,}50\ p<0{,}05$) (Haidary et al., 2013).

A study by Huang et al. (2017) shows that wetlands protect water quality by trapping sediments and retaining excess nutrients and other pollutants such as heavy metals, where the slow velocity of water in wetlands allows the sediments to settle to the bottom where wetlands plants hold the accumulated sediments in place. Construction of roads or impoundments has a negative impact on wetland aquatic species by restricting access to marshes and changing hydrologic conditions, resulting in changes in nutrients, vegetation, and animals, as well as a reduction in diversity and water quality. Furthermore, studies indicated that although concentrations can be substantially modified by soil type, wetland type, hydro-meteorological regimes, and other factors, phosphorus can be an essential indicator of anthropogenic influences, including agricultural and residential stressors that lead to eutrophication (Huang et al., 2017).

According to Kingsford et al. (2017), the water quality of wetlands has been reduced due to poor farming practices, pesticide use, altered hydrology, and also eutrophication. Deterioration of water quality is due to the leaching of nutrients from soils to rivers and then to lakes as indicated by Geng et al. (2021). Human involvement such as the building of dams, draining of wetlands, and diversion of flow has a significant impact on water quality (Bartram and Balance, 1996). The summary of process type and major processes affecting water quality is presented in Table 2.2 below.

Table 2. 2: Processes affecting water quality (Yerubandi et al., 2016; Ren et al., 2019)

Process type	Major process within water body	Water body
Hydrological	Dilution Evaporation Percolation and leaching	All water bodies Surface water Groundwater

	Suspension and settling	Surface water
Physical	Gas exchange with atmosphere	Mostly rivers and lakes
	Volatilisation	Mostly rivers and lakes
	Adsorption/ desorption	All water bodies
	Heating and cooling	Mostly rivers and lakes
	Diffusion	
Chemical	Photo-degradation	
	Acid base reactions	All water bodies
	Redox reaction	All water bodies
	Dissolution of particles	All water bodies
	Precipitation of minerals	All water bodies
	Ionic exchange	Groundwater
Biological	Primary production	Surface water
	Microbial die-off and growth	All water bodies
	Decomposition of organic matter	Mostly rivers and lakes
	Bioaccumulation	Mostly rivers and lakes
	Bio-magnification	Mostly rivers and lakes

2.7 Major Pollution of the Wetland Ecosystem

Pollution is the introduction of elements, compounds, and energy into the environment at a concentration that affects its biological functioning or that pose an unacceptable risk to humans or other target linked to the environment (Briffa et al., 2020; Fernandez-Luqueno et al., 2013). The introduction of heavy metals into the environment originates from natural and anthropogenic sources (Zhang et al., 2020). The anthropogenic sources may include industrial wastewater, domestic wastewater discharge, and agricultural activities that contain a high concentration of metals which are often discharged into waterways.

According to Shibambu (2016), the most common industrial and agricultural pollutants in South Africa are pesticides, hazardous metals, trash hot water, and agricultural fertilizers. There are also common contaminants found in urban wastewater, particularly in informal areas with no sewage or suitable water filtration facilities. Furthermore, studies indicated that wetlands have been turned into a wasteland, where people dump all sorts of garbage. Therefore, contributes to a high rate of pollution of water in wetlands which also affects the physicochemical parameters. The destruction of wetlands as freshwater resources is a major issue, especially in rural areas where surface water is the predominant source of water.

2.8 South African Wetland Policy, Legislation, and Institutional Framework (Guidelines Nexus)

In the absence of water and environmental legislation, the 1983 Conservation of Agricultural Resources Act was the most effective means of preserving South Africa's wetlands outside of conservation areas. Despite being outdated, it is still used today for regulating the drainage of wetlands, agriculture, and vegetation. Agriculture, Fisheries, and Forestry (DAFF) is given clear mandates to conserve wetlands and wisely use them in order to ensure the long-term viability of agricultural resources. As part of its environmental management policy (Adeyoo et al., 2020; Rebelo and Guerreiro, 2016; DEAT, 1998), the government aims to protect both the present and future generations' right to a healthy and safe environment.

As a result of the provisions of the National Environmental Management Act of 1998, these rights and values were protected. According to the Act, "sensitive, fragile, dynamic, or stressed ecosystems, such as coastal, estuarine, and similar systems, require extra care in management and planning." According to the National Environmental Management Act, activities that may have serious environmental consequences must comply with the following regulations (DEA, 2010). Among the operations covered are the construction of aquaculture facilities, dams, canals, and infrastructure for water transfer, dredging, filling, and excavating in wetlands, and peat extraction. From a policy standpoint, the National Water Policy (Adeyoo et al., 2022) and one of its statutory manifestations, the 1998 National Water Act, are significant attempts to preserve wetlands. These have been praised for their explicit recognition that water resources are more than just water, that aquatic ecosystems are the resource base on which all other uses rely, and that healthy ecosystems strengthen the long-term viability of water use (Lemineet al., 2022; Adeyoo et al., 2022). The Act includes three sets of Resource Directed Measures to protect aquatic ecosystems and ensure environmentally sustainable development and use of water resources. South Africa, as a founding member of the Convention on Wetlands of International Importance, especially as a waterbird's habitat, and due to its location on Africa's southern tip. Furthermore, South Africa has a unique duty to coordinate international wetland conservation strategies in Southern Africa through the management of transborder resources like water and wildlife, as well as to promote global wetland conservation.

2.9 Potential Ecological Risks of Trace Metals in Wetland

Pollution of wetlands by trace metals has some deadly impacts on biodiversity such as a decrease in the biodiversity and malformation of aquatic organisms (de Carvalho Aguir et al., 2016). Pollutants are transferred to aquatic organisms and eventually to the human being through bioaccumulation and biomagnification in food chains (Sadeghi et al., 2021). The modern ecological status of the aquatic ecosystem can be determined by estimating the existence and distribution of trace metals in sediments and organisms (Sadeghi et al., 2021). The potential ecological risk of trace metals can be determined using the potential ecological risk index (PERI). In ecological risk assessment, sediment background values are used to predict future risks, identify areas of risk, and determine if human health was adversely affected by trace metals (Zhao et al., 2023). The index, equations, and classification presented in Table 2.3 are used by the authors to calculate the PERI.

Table 2. 3: Indices adopted from Hakanson (1980)

Index	Equation	Classification
CF	$C_f^i = \frac{C_i}{C_o}$	**CF** < 1 (low risk)
		1 ≤ CF < 3 (moderate risk)
		3 ≤ CF < 16 (considerable risk)
		CF ≥ 32 (very high risk)
CD	$CD = \sum_{I=l}^{n} CF$	**CD** < 8 (low risk of contamination)
		8 ≤ CD < 16 (moderate risk of contamination)
		16 ≤ CD < 32 (considerable risk of contamination)
		CD≥ 32 (very high degree of contamination)
E_r^i	$E_r^i = T_r^i \times C_f^i$	E_r^i < 40 (low ecological risk)
		40 ≤ E_r^i < 80 (moderate ecological risk)
		80 ≤ E_r^i < 160 (considerable ecological risk)
		160 ≤ E_r^i < 320 (high ecological risk)

		E_r^i < 320 (very high ecological risk)
RI	$RI = \sum_{I=l}^{n} E_r^i$	**RI** < 150 (low ecological risk)
		150 ≤ RI < 300 (moderate ecological risk)
		300 ≤ RI < 600 (considerable ecological risk)
		RI ≥ 600 (very high ecological risk)

2.10 Potential Health Effects of Metals on Living Organisms

Trace metals cannot be metabolised by the body rather they gather in adipose tissues, muscles, bones, and joints which cause health difficulties and diseases (Vasseghian et al., 2022). Some trace metals have shown beneficial effects on humans but their increasing concentration above the threshold is bound to have harmful effects on humans (Sayadi et al., 2015). The effects of metals are presented in Table 2.3.

Table 2. 4: Potential health effects of metals on living organisms (Sandeep et al., 2019; Kumar et al., 2022)

Heavy metal	Toxic effects (human being)	Toxic effects (plants and microorganisms)
Lead	Anemia, brain damage, anorexia, malaise, loss of appetite, Liver, kidney, gastrointestinal damage, mental retardation in children	Disturbs photosynthesis, growth, and chlorosis, reduces enzyme activities and seed germination, and oxidative stress in plants. Degeneration of proteins and nucleic acid and hinders enzyme activities and transcription.
Copper	neurotoxicity, and acute toxicity, dizziness, diarrhea	Cu influences the chlorosis, oxidative stress and impedes growth of plants. Dislocate cellular role and hinders enzyme activities in microorganism.
Cadmium	Kidney damage, bronchitis, Gastrointestinal disorder, bone marrow, cancer, lung insufficiency, hypertension,	Chlorosis, decline in plant nutrient, growth, and seed germination. Impairment nucleic acid, hinders cell division and transcription, carbon and nitrogen mineralization, and denaturation of protein in microorganisms.

	Itai–Itai disease, weight loss	
Zinc	Causes short term-metal-fume fever," gastrointestinal distress	
Mercury	Damage to nervous system, protoplasm poisoning, corrosive to skin, eyes, muscles, dermatitis, kidney damage	Distresses anti-oxidative system and photosynthesis, increases lipid peroxidation, persuaded genotoxic impact, reduces plant growth, yield, nutrient uptake and homeostasis and oxidative stress. Diminution population size, denature protein, unsettle cell membrane and enzyme role in microorganism
Nickel	Chronic bronchitis, reduced lung function, lung cancer,	Reduces chlorophyll content, enzyme activities and growth and nutrient uptake. Dislocate cell membrane, and impedes enzyme activities in microorganism.
Arsenic	Bronchitis, dermatitis, bone marrow depression, hemolysis, hepatomegaly,	Impairment cell membrane, reduction of growth and roots extension and production, restricts with perilous metabolic routes, fertility, yield, and fruit production is lost and oxidative stress. Arsenic causes enzyme deactivation in microorganisms.

2.11 Degradation of Wetland

The increase in population growth and industrialisation in China has set remarkable threats and pressure on coastal wetlands for the past 60 years (Chenet al., 2022; Sun et al., 2015). Swamps, salt marshes, estuaries, gulfs, and mangroves were badly destroyed in the past 20 years (Sun et al., 2015). The development of floodplain ecosystems and water resources has degraded wetlands (Kingsford et al., 2016). In North America and Europe, agriculture and urbanization have destroyed and damaged a number of wetlands (Sun et al., 2015). The leading causes of wetlands degradation are afforestation, malaria control, drainage for agriculture, river regulation, over-exploitation of groundwater resources, and infrastructure development (Bhatt, 2022; Kingsford et al., 2006).

Wetlands in South Africa are in critical condition, with more than 65% threatened and more than 50% destroyed (George and Ngole-Jeme, 2022). This is primarily because of anthropogenic activities (Nel and Driver, 2012). Wetlands and rivers in South Africa suffer from nutrient pollution caused by poorly treated sewage water discharges. According to a study conducted in the Rietvlei Nature Reserve wetland, Hartbeesfontein waste treatment plant effluent discharges, informal settlements, and agricultural lands are contributing to the ecosystem's pollution (Botha, 2015). Since agriculture in wetlands provides income to both rural and urban residents, it also contributes to wetland deterioration. Hence, human activities constitute the most significant factor influencing wetlands in the studied area. This has an adverse effect on how wetlands function ecologically. According to Sinthumule and Netshisaulu (2022), in Thohoyandou wetlands are not constantly inundated, and without government prohibitions, the local council has allotted certain business and residential plots within wetlands for development over the previous 10-15 years. Therefore, this has aided in the destruction and deterioration of wetlands.

Based on the reported information, there are no studies reported about wetlands water and quality in Limpopo province, hence there was a need for this study to be conducted.

CHAPTER THREE: METHODOLOGY

3.1 Preamble and Research Design

This chapter describes the procedure and integrated methods that were used to collect and

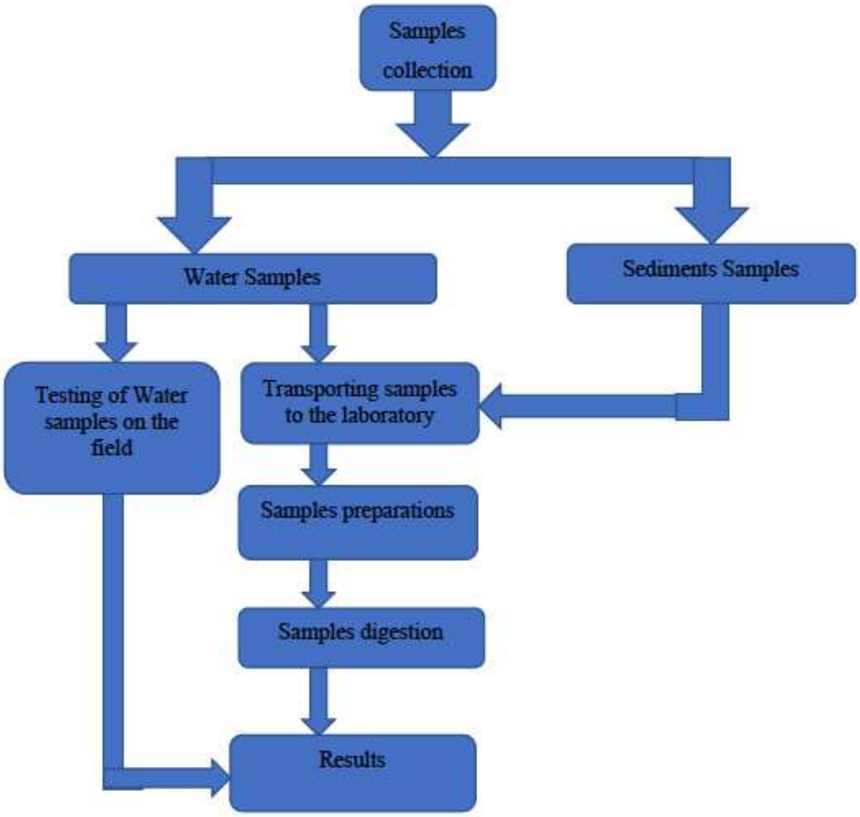

Figure 3. 1: Schematic Representative of Research Design

This study used descriptive research design which provides the information about the types of data collected and how the data was analysed. Moreover, this study used primary, secondary, and secondary data. To determine the physicochemical and trace metals levels in water and sediments of wetlands across Limpopo Province. The water and sediment samples were collected in 17 and 16 wetlands, respectively. The sampled sites were chosen randomly and based on the accessibility of the wetlands. Plastic bottles and mini-garden spade were used to collect the water and sediments sampled, respectively. For water samples, some physicochemical parameters were tested on the field while some were analysed in the lab. For trace metals analyses, water and sediments samples were prepared and digested following methods recommended by US EPA 3015 for aqueous samples and EPA methods 200.2 and 3050 on sediments samples, respectively. The samples were sent to University of Johannesburg for analysis using ICP-MS

To evaluate the potential ecological risk of metals in sediments of wetlands across Limpopo Province. Various indices adopted from Hakanson were used to rate the toxicity of selected metals based on the sediments guidelines standards.

To investigate the trace metals removal efficiency using Phangami wetland. Water samples were collected for four weeks before and after rain. The samples were collected between September and October 2021. Water quality improvement and trace metal removal efficient of a wetland were also calculated.

3.2 Sampling of Water and Sediments

For metals and sediments analyses, water samples were collected from 17 natural wetlands across Limpopo Province whereas sediments samples were collected from 15 wetlands (Table 3.1). The sampled site were chosen randomly and based on the accessibility. The water samples were collected using 500 ml plastic bottles (transparent). The plastic bottles were washed with tap water and detergent, and then rinsed with tap water followed by deionised water before use. Before sampling, the bottles were rinsed with field water and all the samples were collected during the dry season. The water samples were collected in duplicate. The samples for metal analysis were added with a few drops of nitric acid before being stored for analysis. This was done to prevent or minimize the growth of the microorganisms in the samples. The Chemistry reason for adding HNO_3 acid in water samples is that metals may not become oxidised and may not be adsorbed on the surface of the walls of container. The sediment samples were collected using a mini-garden shovel and kept in a sterile zipper plastic bag. The shovel was washed with the deionized water followed by the water from the wetland. All the samples were collected approximately in the middle of the wetlands. Some of the physicochemical parameters were tested in the field. The samples were placed in a cooler box with ice and transported to the laboratory for further analysis.

Table 3. 1: Location of the study area

District	Local municipality	Wetland area	Coordinates	Activities contributing to pollution	Characteristics of the wetland
Capricorn	Polokwane	Polokwane (W)1	-24,010, 29.510	Animals drinking water and animals droppings	Dense vegetation; including Water hyacinth; Flowing water
		Kga-Thoka (W2a)	-23.892, 29.709	Dumping of cans and bottles	Dense vegetation
		Kga-Thoka (W2b)	-23.892, 29.712	Dumping of cans and bottles	Dense vegetation; Flowing water
	Molemole	Nthabiseng (W3)	-23.49, 29.911	Solid waste and cow gung disposal, livestock feeding	Less vegetation; static water
		Nthabiseng (W4)	-23.892, 29.712	Sewage linkage (urine)	Dense vegetation; static water
Mopani	Tzaneen	Dan (W5)	-23.905, 30.276	Livestock feeding and cow dung	Dense vegetation; Flowing water
		Mokgabeng (W6)	-23.895, 30.257	Detergents resulting from washing of clothes	Dense vegetation; Flowing water
		Mokgolobotso(W7)	-24.071, 30.281	Plastic were disposed near the wetland	Dense vegetation; Flowing water
		Nkowankowa(W8)	-23.891, 30.276	Detergents from a car wash near the wetland	Dense vegetation; Flowing water
Sekhukhune	Mkhudutham aga	Mashabela(W9)	-24.631, 29.734	Livestock feeding, cow dung	Dense vegetation; Flowing water

		Marishane(W10)	-24.726, 29.769	Livestock feeding, cow dung	Less vegetation, Flowing water
Vhembe	Thulamela	Phangami(W11)	-22.974, 30.486	Sewage was channeled direct in to the wetland and agricultural activities within the wetland	Dense vegetation; Flowing water
		Maungani(W12)	-22.984, 30.443	Washing of vehicles, construction wastes as well as pumpers and plastic disposal	Dense vegetation; Flowing water
	Musina	Nwambi(W13)	-22.416, 31.271	Animals droppings and dung within the wetland	Less vegetation; static water
		Rooivlei(W14)	-22.416, 31.260	Animals dropping and dung	Less vegetation; static water
Waterberg	Lephalale	Lephalale (W15)	-23.654, 27.764	Plastic wastes	Dense vegetation; Flowing water
		Shongoane(W16)	-23.580, 28.108	Residential area	Less vegetation; Flowing water

3.3 Characterisation of Water Samples

Following sample collection, physicochemical parameters including pH, electrical conductivity, total dissolved solids, salinity, turbidity, DO, temperature, and BOD were measured. Extech multimeter (EC 400 Extech Instruments, Nashua, NH, USA) was used to measure TDS, EC, and Salinity (Figure 3.1). The instrument was calibrated before use based on the manufactures' guide. pH was measured using a pH meter (Thermo Scientific Orion Star) (Figure 3.1). Before the measurement, the pH meter was calibrated with standard solution buffers of 4.01, 7.01, and 10.01. The samples' turbidity was determined using a turbidity meter (TB, 400, Extech Instruments, Nashua, NH, USA) (Figure 3.1). Moreover, DO meter (BOECO portable DO/temp model DO-580) (Figure 3.1) was used to test DO and temperature on the field as well as the BOD in the laboratory. Before BOD was tested, 100 mL of the water samples were kept in a dark place for 5 days. To obtain the BOD, the formula DO1-DO5 was employed. DO1 is the level of Oxygen treated in the field and DO5 is the level of Oxygen after the incubation of samples for 5 day. Thereafter the mean and standard deviation of each set were calculated and recorded in the Table.

3.4 Microwave Digestion of Water Samples

The samples were digested following the method recommended by US EPA 3015 for aqueous samples. This was done to dissolve the metals that cannot are insoluble in neutral pH but soluble in acidic pH.45 mL of water samples were added to the digestion vessel. Then, 5 mL of HNO_3 was transferred into the MarsOne digestion vessel and mixed with the water sample. The samples were swirled and after swirling, the vessels were sealed and properly placed in the MarsOne microwave system according to the manufacturer's recommended guidelines. Then, the samples were centrifuged at 250 rpm for 20 minutes. At the end of the microwave program, the samples were allowed to cool for a minimum of 5 minutes before removing them from the MarsOne microwave system. Finally, the samples were filtered using a syringe filter, labeled based on the location, and transferred into 15 mL centrifuge tubes for trace metal analysis. Trace metal analyses were analyzed using Inductively Coupled Plasma mass spectrometry (ICP-MS).

Figure 3. 2: Instrument used to measure physicochemical parameters of water samples in this study.

3.5 Microwave Digestion of Sediments Samples

This procedure was conducted based on the method recommended by EPA methods 200.2 and 3050 on sediments samples. This was done to dissolve the metals that cannot are insoluble in neutral pH but soluble in acidic pH. The wet sediment samples were oven-dried and sieved using a 125-micrometer sieve. The wet samples were dried in 60 ^{o}C for 24 hours. Then, 0.5 g of sediments were measured using analytical balance and transferred into the digestion vessels. Thereafter, 9 mL of HNO_3 acid was added followed by 3 mL of HCl and the mixture was swirled gently before the vessels were closed. After swirling, the vessels were sealed properly and placed in the MarsOne microwave system (Figure 3.2b) according to the manufacturer's recommended guidelines. Thereafter, the samples were centrifuged for 10 minutes at 250 rpm. The samples were allowed to cool for 5 minutes. Then, the samples were transferred into a 50 mL centrifuge tube and filled with deionized water to make 50 mL. Thereafter, the samples were filtered using syringe filters and transferred into 15 mL centrifuge tubes as presented in Figure 3.2a. Finally, the samples were analysed using ICP-MS.

Figure 3. 3: Microwave Digestion used to digest water and sediments samples in this study. **A**-Digestate; **B**-MarsOne digester.

3.6 Sediments Quality Compliance Study

The sediment quality in this study was categorised using trace metals results and compared with the sediments quality guidelines (SQG) values presented below in Table 3.2. Where TEL and PEL denote the threshold and probable effect levels, respectively (Edokpayi et al., 2022). The abbreviations ERL and ERM stand for effect range-low and effect range-median, respectively. TEL and ERL are the concentrations below which metal will rarely pose a toxic effect on aquatic organisms in both SQGs guidelines, while PEL and ERM are the concentrations above which adverse effects will occur. The values between TEL-PEL and ERL-ERM represent concentrations where an adverse effect is likely while the concentrations above PEL and ERM represent the toxic effects.

Table 3. 2: Sediments quality guidelines standards used to assess the toxicity of metals in sediment

Heavy metals(mg/kg)	**TEL**	**PEL**	**ERL**	**ERM**	**REFERENCES**
As	7.2	41.6	8.2	70	Pekey (2004); Long (1995)
Cd	0.6	3.5	1.2	9.6	CCME (2001); Long (1995)
Cr	37.3	90	81	370	CCME (2001); Long (1995)
Cu	35.7	197	34	270	CCME (2001); Long (1995)
Ni	15.9	42.8	20.9	51.6	Pekey (2004); Long (1995)
Pb	35	91.3	46.7	218	CCME (2001); Long (1995)
Zn	123	315	150	410	CCME (2001); Long (1995)

3.7 Potential Ecological Risk Evaluation of Heavy Metals in Sediments

The Potential Ecological Risk Evaluation (PERI) method, suggested by Swedish scientist Hakanson (1980), was employed to determine the environmental effect of heavy metals. It represents the ecological responsivity of heavy metal concentrations (Kumar et al., 2020). The contamination factor (CF) and toxic response coefficient (Tr) of the metals are used to calculate PERI (Table 3.3). It is computed using the following equations:

$$RI = \sum_{I=l}^{n} E_r^i \qquad (3.1)$$

Where E_r^i denotes a single metal's potential ecological risk coefficient and is defined as

$$E_r^i = T_r^i \times C_f^i \qquad (3.2)$$

Where T_r^i represents the toxic response factor for a given metal. C_f^i refers to the contamination factor and is used to measure the level of contamination of sediments by trace metals. The C_f^i is computed using equation (3.3).

$$C_f^i = \frac{C_i}{C_o} \qquad (3.3)$$

Where C_i denotes the concentration of each metal in the sediments and C_o denotes the background value of trace metals in the sediments. Turekian and Wedepohl's (1961) shale average concentrations of trace metals in global sediments were used in this study because there are no background values for trace metals in South African sediments (Shabalala et al., 2013).

$$CD = \sum_{I=l}^{n} CF \tag{3.4}$$

The level of contamination is typically calculated as the sum of the CF for all metals in each study site.

Table 3.3: Toxic response factor and shale average values of trace metals in sediment

Element	Toxic response factor	Shale average
As	10[a]	20[b]
Cd	30[ab]	0.3[be]
Cr	2[ac]	90[e]
Cu	5[ab]	45[be]
Co	5[d]	19[e]
Fe	1[c]	46700[e]
Mn	1[abc]	850[ae]
Ni	5[ac]	68[e]
Pb	5[ab]	20[be]
Zn	1[abc]	95[be]

(Proshad et al., 2022)a; (Avkopashvili et al., 2022)b; (Edokpayi et al., 2022)c; (Kumar et al., 2021)d; (Turekian and Wedepohl, 1961)e

3.8 Wetland Trace Metals Removal Efficiency

To achieve objective three, the water samples were collected before the rain (four weeks) and after rain (four weeks) following the procedure presented above in subsection 3.2. The samples were collected between September and October (2021) and it rained for about 4day toward the end of September. However, 4 points were selected for sampling in the wetland (one point up-stream, two points in mid-point, and one point down-stream just before the wetland discharge its water to the river. Physicochemical parameters and trace metals preparations and analysis were conducted following the procedure used in sections 3.3 and 3.4, respectively. To check if the wetland is still efficient in pollutants removal, the physicochemical parameters and the trace metals levels were analysed from the collected samples and calculated using equation 3.5 as presented below:

$$\%R = \frac{C_1 - C_2}{C_1} \times 100 \qquad (3.5)$$

$\%R$ stands for the percentage removal whereas C_1 *and* C_2 shows the initial and final concentration of physicochemical and trace metals concentration, respectively.

CHAPTER FOUR: ASSESSMENT OF WATER AND SEDIMENTS QUALITY IN SOME SELECTED WETLANDS ACROSS LIMPOPO PROVINCE, LIMPOPO PROVINCE, SOUTH AFRICA

4.1 Preamble

This chapter presents and discusses data on water and sediment quality as well as the potential ecological risk of sediments in wetlands across Limpopo Province.

4.2 Physicochemical Parameters Analysis

4.2.1 Temperature

Temperature is an important physical element that influences chemical and biological processes in water (Manikannan et al., 2011). This suggests that when the temperature of water bodies changes, it influences the rate at which some metals dissolve and also influences some processes in the aquatic ecosystem which are specific to some organisms. The average temperature of water collected from various wetlands ranged between 16.83±0.23 to 25.87±0.15 °C as shown in Table 4.1. The mean temperature recorded in this study was similar to the one reported by Abir (2014) in Rudrasagar wetland, India. A study conducted by Rahimi et al. (2023) also found the mean temperature levels (21.4 ^{o}C) to be within the range of this study in the water of Amirkalayeh Wetland in Northern Iran. The recommended standard of temperature in surface water set by WHO is 30^{o}C (WHO, 2011). However, there are no DWAF threshold limits for livestock watering and aquatic life. This suggests that the water from the wetlands will not result in adverse effects associated with temperature when used for aquatic life, livestock feeding, and domestic purposes.

4.2.2 Turbidity

The turbidity value of water determines its clarity, and highly turbid water indicates the presence of suspended particulates, colloidal compounds, and microbes (Edokpayi et al., 2016). Higher turbidity levels are often associated with higher levels of disease-causing microorganisms such as viruses, parasites, and some bacteria (DWAF, 1996). The mean and standard deviation of turbidity of the water from the sampled wetlands varied between 2.99±0.17 and 174.67±3.05 NTU (Table 4.1). The high values of turbidity recorded in this study could be due to surface runoff and solid waste deposited in the wetlands, as some of the wetlands are currently used as dump sites by the community around them. The water from the wetlands may result in adverse impacts when used for domestic purposes without treatment. It is commonly reported that some of these wetlands waters are often consumed by animals and humans during water scarcity without any form of treatment. All the water samples were above the turbidity aesthetic (≤1) and operational (≤5) standards, however, W11 meets the operational value (SANS, 2015). 50% of the sampled wetlands complied with the DWAF value for aquaculture water use (25 NTU) (DWAF, 1996). This suggests that the water from 50% of the wetlands could result in adverse effects when used for aquacultural purposes. Compared to Gbogbo and Otoo (2015) in coastal wetland areas in Ghana, whose average turbidity was 290 NTU, this study found lower average turbidity.

4.2.3 Electrical conductivity (EC)

The electrical conductivity of water measures its total ionic concentration. Cl^-, Na^+, K^+, and other cations all influence this variable in some way. Water with high conductivity is unfit for human consumption as well as industrial use (Singh and Noori, 2022). As shown in Table 4.1, the mean and standard deviation of EC recorded in water samples ranged from 61.27±0.15 (W5) to 1088.67±0.58 µS/cm (W4). The recorded mean levels of conductivity in this study were lower than the SANS drinking water guidelines standard of 170000 µS/cm. The mean EC in the water of the wetlands varied between wetlands. There was a high mean EC level (7580 S/cm) reported by Heisi et al. (2022) in Blesbokspruit wetland water in South Africa that was above this study's levels, but below the SANS drinking water standard. The recorded mean level in this study would not result in negative impacts associated with conductivity when the water was used for domestic purposes due to its compliance. However, this water cannot be recommended for domestic because conductivity is not the only parameter used to determine the suitability of water for consumption.

4.2.4 potential Hydrogen (pH)

Potential Hydrogen (pH) is a measure of acidity or alkalinity based on the concentrations of hydrogen ions (H^+) in water (Abir, 2014). The mean and standard deviation values of pH of the sampled wetlands water varied between 7.15±0.02 (W13) and 8.69±0.07 (W14). The pH results recorded in the water of this study were slightly neutral to alkaline and the average value was higher than the one reported by George and Ngole-Jeme (2022) in Khubelu wetland (Lestho) (6.59±0.37) which was slightly neutral. In Amirkalayeh wetland water in Northern Iran, Rahimi et al. (2023) reported a pH value of 7.7 which was within the range of this study. All wetlands under the study wetlands fell within the DWAF irrigation (6.5-8.5) standard and aquacultural standard (6.5-9.0), domestic (6-9), SANS (5.0-9.7), respectively (DWAF, 1996; SANS, 2015). However, there is no DWAF standard for livestock watering, irrigation, aquaculture, and the protection of aquatic life. The pH levels recorded would not cause toxic metals to solubilise and have a high impact on the aquatic biota provided the wetland remains within that pH range.

4.2.5 Salinity

Highly saline waters "alter the geochemical cycles of major elements such as carbon, iron, nitrogen, phosphorus, silicon, and sulfur" (Herbert et al., 2015; Mateo-Sagasta et al., 2017), with overall effects on ecosystems (Mateo-Sagasta et al. 2017). In the study area, the mean and standard deviation of salinity of sampled wetlands water ranged between 40.70±1.06 and 1386.67±15.28 mg/L (Table 4.1). The lowest value of salinity was obtained in W5 whereas the highest was detected in W4. However, the recorded level of salinity was below the threshold limit set by WHO in the surface water of 120 mg/L (WHO, 2011; Davies and Ekperusi, 2021). High levels of salinity tend to affect the biodiversity of microorganisms, algae, plants, and animals (Lorenz, 2014). In addition, high salinity levels can irritate the eyes of humans and cause chlorosis in plants (Madilonga et al., 2021; Pawari and Gawande, 2015). Most surface water tends to have low salinity as compared to groundwater. However, there is no recommended level of salinity set by DWAF and SANS in surface water. Gbogbo and Otoo (2015) reported very low mean salinity levels (3.4×10^{-6} mg/L) in coastal wetland areas in Ghana, as opposed to this study's range.

4.2.6 Total dissolved substances (TDS)

In the study area, the mean TDS and standard deviation recorded ranged from 61.267±0.153 to 1139.00±14.73 mg/L as presented in Table 4.1. The lowest concentration of TDS was recorded in W5 and the highest in W4. The TDS reported by George and Ngole-Jeme (2022) in Khudelu wetland; Lesotho (277.80±125.29 mg/L) was within the range of this study. Similarly, the results recorded by Abir (2014) in Rudrasagar wetland, India which was 133.8±38.36 mg/L was also within the range of the results recorded in this study. The DWAF recommended levels are: 1000-3000 mg/L (livestock watering), 40 mg/L (irrigation), and (DWAF, 1996). However, the WHO recommended level for TDS in the surface water is 250 mg/L (WHO, 2011; Davies and Ekperusi, 2021). The water from sampled wetlands complied with the DWAF recommended standards of livestock watering use since the concentrations in those wetlands were within the recommended limits. Therefore, the water might not have adverse effects associated with TDS when used for livestock watering. The water from the sampled wetlands did not comply with the DWAF irrigation threshold limit. Therefore, adverse effects are likely to occur when this water is used for irrigation. However, 56% of the wetlands exceeded the WHO guideline standards for TDS in surface water while 48% complied with these standards.

4.2.7 Dissolved Oxygen (DO)

Dissolved oxygen is a critical water quality criterion for aquatic life's survival in aquatic environments. The amount of oxygen dissolved in water is referred to as dissolved oxygen. It is an excellent method for determining the physical, chemical, and biological state of water (Singh and Noori, 2022). This chemical parameter varied between 0.773±0.155 (W4) to 3.88±1.00 mg/L (W10) (Table 4.1). It was also determined that the mean DO level was 5.4 mg/L at Zoarvlei, Cape Town, South Africa, which differs from those determined in this study. As compared with Gbogbo and Otoo (2015) which recorded 7.87±1.55 mg/L. The high biological activity associated with the decomposition of organic matter could also have resulted in low DO levels in the wetland water. These microorganisms consume more oxygen in the water due to high concentrations of pollutants in wetlands as compared to rivers and streams. The required oxygen level in a well-functioning aquatic ecosystem is 5 mg/L (WHO, 2011). The DO recorded in this study did not comply with regulatory standards thus causing stress to living organisms in this ecosystem.

4.2.8 Biological dissolved Oxygen (BOD)

The BOD is used to quantify the amount of organic material in an aquatic environment that promotes microorganism growth. The BOD is the amount of dissolved oxygen (DO) consumed by aerobic microorganisms to break down organic materials in water (Günter and Alpat, 2019). Elevated organic matter in surface waters raises the BOD to oxidize the organic matter (Khullar and Singh, 2022). BOD ranged between 0.01±0.07 to 2.65±0.17 mg/L. The minimum was in W11 and the maximum was in W12. In all sampled points the concentrations of BOD were lower than the DO as presented in Table 4.1. This might attribute to the fact that there was a microorganism that was depleting DO in water samples as they were degrading the contaminants. Water bodies with a lower BOD will be deficient in oxygen, which can stress and kill aquatic organisms whereas a higher BOD presents a healthier status for water bodies with various aquatic species.

Table 4. 1: Physicochemical parameters' mean, and standard deviation recorded in wetlands water with their corresponding guidelines standards.

	PHYSICOCHEMICAL PARAMETERS	Temperature (°C)	pH	EC (µs/cm)	TDS (mg/L)	Salinity (mg/L)	Turbidity (NTU)	DO (mg/L)	BOD (mg/L)
WETLANDS CODE	W1	19.17±0.06	7.99±0.03	583.3±0.58	418.67±0.577	284.67±3.22	7.88±0.07	2.76±0.08	1.11±0.06
	W2a	20.67±0.31	7.50±0.12	810.00±2.65	563.00±5.00	382.00±8.19	30.77±1.80	2.70±0.02	1.04±0.03
	W2b	19.17±0.06	7.99±0.03	583.33±0.58	418.67±0.577	284.67±3.22	7.88 ± 0.07	2.76 ± 0.08	1.11 ± 0.06
	W3	20.10±0.10	7.72±0.04	406.47±19.34	310.67±0.58	208.67±0.58	2.99±0.17	2.86±0 .06	1.15±0.01
	W4	20.27±0.06	8.06±004	2873.00±12.10	1088.67±0.58	1386.67±15.28	165.67±3.51	0.77±0.16	0.62±0.14
	W5	22.77±0.42	8.10±0.06	84.97±0.21	61.27±0.15	40.70±1.06	40.13±1.61	2.30±0.07	2.17±0.06
	W6	25.87±0.15	7.74±0.18	134.27±2.14	85.03±0.82	57.40±0.20	33.83±3.29	1.98±0.02	0.27±0.05
	W7	23.93±0.15	7.76±0.02	293.00±0.57	192.00±13.86	132.67±1.53	5.34±0.74	2.18±0.01	0.49±0.04
	W8	24.90±0.10	7.39±0.03	399.00±1.00	370.57±34.66	259.33±7.02	174.67±3.06	2.09±0.01	0.39±0.13
	W9	19.03±0.31	7.15±0.02	1050.33±4.73	725.00±15.00	527.00±1.00	172.33±0.58	2.21±0.01	0.61±0.06
	W10	18.07±0.06	7.38±0.18	243.13±3.56	179.00±1.00	119.00±2.00	35.97±0.05	2.91±0.05	1.13±0.00
	W11	19.00±0.00	7.00±0.08	586.67±1.53	313.00±1.00	81.67±1.16	1.90 ± 0.08	0.79 ± 0.08	0.01±0.17
	W12	19.73±0.15	7.13±0.16	240.20±0.17	142.67±0.57	104.33±0.06	10.83±0.06	3.88±1.00	2.76±0.08
	W13	23.97±0.87	8.69±0.07	586.67±1.53	313.00±1.00	284.57±3.53	81.67±1.16	1.90±0.08	0.79±0.08
	W14	22.60±0.35	8.08±0.07	1269.67±6.66	1139.00±14.73	625.33±3.79	130.00±1.00	1.40 ± 0.06	0.16±0.06
	W15	16.83±0.23	7.27±0.11	330.27±1.00	241.00±1.00	160.33±1.53	16.72±0.62	2.43 ± 0.10	0.79±0.14
	W16	18.13±0.06	7.66±0.11	320.27±0.61	247.33±2.08	152.00±6.00	18.73±0.63	2.61±0.06	1.07±0.05
WATER QUALITY GUIDELINES STANDARDS	DWAF (1996) IRRIGATION STD	—	6.5-8.4	—	40	—	—	—	—
	DWAF (1996) LIVESTOCK WATTERING. STD	—	—	—	1000-3000	—	—	—	—

	DWAF (1996) THE PROTECTION. OF AQUATIC. LIVE STD	—	—	—	—	—	—	80*-120 of Saturation	—
	DWAF (1996) AQUALTURE STD	—	6.5-9.0	—	—	—	25	6-9-Cold-Water Spp & 5-8-Interm.& Warm Spp.	—
	DWAF (1996) DOMESTIC. WATER STD	—	6-9	—	≤450	—	≤1	—	—
	SANS (2011) DRINKING WATER STD	—	5-9.7	170 000	≤1200	—	≤1-Aesthetic ≤5-Operational	—	—
	WHO (2011) DRINING. WATER STD	30	—	1700	250	120	—	5	—

4.3 Trace Metals Levels in Wetlands Water

The trace metals' mean results were obtained from gas and no gas mode of the ICP-MS (Table 4.1).

4.3.1 Arsenic (As)

Arsenic is referred to as a "soft poison" or "death metalloid" because it kills people gradually after entering the human body (Proshad et al., 2021; Nawab et al. 2018). The concentration of As in the sampled points varied between 0.01-1.79 µg/L (Table 4.2) during the period of sampling. The lowest and highest levels were obtained in W12 and W4, respectively. These levels were below the regulatory threshold limits for the protection of aquatic life (≤ 10 µg/L), livestock watering (≤ 1000 µg/L), aquaculture (≤ 50 µg/L), and irrigation (≤ 100 µg/L) water uses (DWAF, 1996), drinking water (≤ 10 µg/L) (SANS, 2015; WHO, 2011). Therefore, the water from all sampled wetlands will not have negative impacts associated with Arsenic when used for the above-mentioned uses. Arsenic exposure to humans has been linked to a variety of disorders, posing a significant threat to people's health, economic, and social well-being, particularly in the world's less-developed countries (Fatoki and Badmus, 2022). In this study, As levels were lower than the mean levels (280 g/L) reported by Cohen et al. (2001) in coastal wetland water in California.

4.3.2 Cadmium (Cd)

Cadmium is a dangerous metal because it can pose a health threat to humans and aquatic life (Madilonga et al., 2021). The concentrations of Cd in the sampled points were found to be below the detection limit as presented in (Table 4.2). This might attribute to the fact that the samples were collected in less industrialised areas. Fatoki et al. (2001) reported that for area, not highly industrialised, trace metal concentrations in the body of water are typically low for most metals. Therefore, these concentrations complied with the DWAF recommended standards for the protection of aquatic life (≤ 150 µg/L), livestock watering (≤ 10 000 µg/L), and irrigation (≤ 10 000 µg/L) water uses (DWAF, 1996) as well as the SANS and WHO standard drinking water which for ≤ 3 µg/L (SANS, 2015; WHO, 2015). Thus, health risk linked to Cd is not expected with the use of water from these wetlands. Wetland water concentrations of Cd in this study are similar to those reported by Menon et al. (2023) (BDL), Kole wetland, South India. However, the Cd levels in this study were lower than those reported by Cohen et al. (2001) from coastal wetland water in California.

4.3.3 Lead (Pb)

When present in extremely low concentrations, Pb is known to be extremely toxic to benthic organisms (Zhao et al., 2023). Lead concentrations of water from wetlands varied between BDL-1.86 μg/L (Table 4.2). Low levels of Pb might be attributed to the fact that most of the wastes dumped in wetlands did not consist of this metal. Pb levels in this study were lower than those reported by Cohen et al. (2001) (160 g/L) in California coastal wetland water. The SANS and WHO threshold limit of Pb in drinking water is ≤ 10 μg/L (SANS, 2015; WHO; 2011). Water containing more than 10 μg/L Pb has been linked to several diseases, including memory loss, brain damage, and anemia as reported by Ayandiran et al. (2018). The threshold limit recommended for livestock watering is ≤ 0.1 and ≤ 0.5 μg/L for all other livestock, respectively (DWAF, 1996). Moreover, DWAF also recommended ≤ 200 μg/L (irrigation), ≤ 0.2 μg/L (for the protection of aquatic life), and ≤ 10 μg/L (aquaculture). Therefore, this study has recorded lower levels that complied with DWAF recommended limits for several water uses except for the protection of aquatic life and livestock watering. Therefore, the waters from the sampled wetlands would be suitable for aquacultural and irrigation purposes.

4.3.4 Uranium (U)

An excess of uranium can cause adverse effects on the kidney when it is nephrotoxic (Sahoo et al., 2020). The concentrations of U in the water from the sampled wetlands ranged between 0.03-8.93 μg/L as indicated in Table 4.2, respectively. There may be anthropogenic sources that enhance its levels in the environment, such as the exploitation of minerals, mining, industrial activities, fossil fuel uses, and municipal waste releases (Sahoo et al., 2020). Therefore, in the water of the sampled wetlands, U could results from domestic wastewater since most of the wastewater treatment plants discharge their effluent in waterways that are connected to wetlands. The recorded levels of U in wetlands were below the SANS and WHO drinking water standard of ≤ 30 μg/L (SANS, 2015; WHO, 2011). However, there is no Uranium DWAF threshold in surface water. It has been reported that uranium binds to proteins and nucleotides in the human body and accumulates mainly in the kidney and skeleton (Sahoo et al., 2020). The gastrointestinal tract absorbs about 0.1 to 6% of ingested uranium from adults, according to a study by Zamora et al. (1998).

4.3.5 Aluminium (Al)

Once Al is introduced in neutral to basic pH ranges, it is a non-critical metal; however, there is significant concern once this metal is available in excessive amounts. (DWAF, 1996). The concentration of Al obtained in the wetland's water ranged between 55.34-902.03 µg/L as shown in Table 4.2. The minimum value of Al was found in the water of W11, and the maximum was obtained in W10. High levels of Al recorded in this study could result from the construction materials dumped within the wetlands. The concentrations of Al were found to be within the required limits of DWAF for irrigation and livestock watering water use (≤ 5000 µg/L) (DWAF, 1996). Conversely, Al levels in the wetlands did not comply with the DWAF guideline value for the protection of aquatic life (≤ 05 µg/L). 65% of the samples complied with the SANS regulatory limit (≤ 300 µg/L) of drinking water (SANS, 2015; WHO 2011). Many authors published studies on trace metal levels but did not look into Al levels in wetlands water.

4.3.6 Chromium (Cr)

Since chromium has a high redox potential and complex chemistry in its electronic shell, it can be converted from a certain oxidation state to another, mostly Cr^{+3} and Cr^{+6}, which are the most stable forms of chromium, and these two forms of chromium are interchangeable (Kapoor et al., 2022). Industrial effluent discharge is the major source of chromium in the environment followed by urban run-off (Udofia et al., 2015). The average concentrations of Cr in all sampled points were found to range between BDL-4.33 µg/L (Table 4.2). The concentration of (Cr) was BDL in 43.78 % of the sampled water in the wetlands. Cr levels recorded in wetlands water were below the SANS and WHO threshold limit of drinking water which is ≤ 50 µg/L (SANS, 2015; WHO, 2011). This study found lower mean Cr levels in the water than Cohen et al. (2001) found in California coastal wetland water.

4.3.7 Beryllium (Be)

Beryllium normally occurs in low concentrations in natural surface waters; the typical concentration range varies between a few nanograms to a few micrograms per liter (Mogobe et al., 2016). The levels of Be in all the sampled wetlands ranged between BDL-0.21 µg/L (Table 4.2). The lowest levels were observed in W3 and W11 while the highest was in W10. The concentrations of Be in all sampled points complied with the DWAF irrigation standard which is ≤ 100 µg/L (DWAF, 1996), for all sampled points. However, there is no DWAF recommended levels for domestic, aquatic life, aquaculture, and livestock watering water uses. The water of the sampled wetlands might not have Beryllium-associated negative impacts when used for irrigation purposes.

4.3.8 Cobalt (Co)

The average Co concentration varied between 0.19-7.27 µg/L as indicated in Table 4.2. The highest value of Co was found in W14 and the lowest value in W10. There was a slight variation in Co levels across the water samples from wetlands in Limpopo Province. Detergents were reported to contain trace metals such as Co and others. The concentrations of Co complied with the DWAF recommended standard for livestock watering (≤ 1000 µg/L) and irrigation water uses (≤ 50 µg/L), respectively (DWAF, 1996). However, there is no recommended required standard set by DWAF for the protection of aquatic life, aquaculture, and domestic water uses. This suggests that the negative effects associated with Co are unlikely to occur when water from wetlands is used for various purposes. Many authors reported on trace metal levels but did not investigate Co levels in wetlands water.

4.3.9 Copper (Cu)

A high intake of Cu has been linked to several health problems, including anemia, liver and kidney damage, and stomach and intestinal irritation (Andem et al., 2015). The average concentrations of Cu in the samples were found to be below the detection limit of ICP-MS (Table 4.2). Cu could be sourced from road runoff and deposition from the atmosphere (Kacholi and Sahu, 2018). These levels were also below the DWAF recommended limits for aquaculture (≤ 5 µg/L), for the protection of aquatic life (≤ 3 µg/L), domestic water use, and irrigation (≤ 20 µg/L), respectively (DWAF, 1996). In addition, the DWAF recommended levels of livestock watering are ≤ 500 µg/L (Sheep and pre-weaned calves), ≤ 1000 µg/L (Cattle), and ≤ 5000 µg/L (Horses, Pigs, and Poultry) (DWAF, 1996) were not exceeded. Moreover, the results recorded in the study area were also below the SANS (≤ 1000 µg/L) and WHO drinking water standards, respectively (≤ 2 000 µg/L) (SANS, 2015; WHO, 2011). Heisi et al. (2022) found a high mean Cu level (10.7 g/L) in Blesbokspruit wetland water in South Africa, which was above the range of this study's Cu levels. The wetlands water in the study area would not cause any negative impact with use. However, the water might not be recommended for drinking purposes since many parameters need to be tested to recommend water for consumption purposes.

4.3.10 Iron (Fe)

The concentrations of Fe in the wetland water ranged from 77.42-12973.62 µg/L. The lowest level of Fe in the water of the sampled wetlands was recorded in W1 whereas the highest level was in W8 (Table 4.2). The Fe concentrations obtained in the water of wetlands were below the DWAF recommended limits of ≤ 10 000 µg/L (for livestock watering) and ≤ 5000 µg/L (for irrigation) (DWAF, 1996), except for the water from W8. In addition, the water from the wetlands exceeded the domestic water use (100 µg/L) except for the water from W1 (DWAF, 1996). However, the Fe levels recorded in this study did not comply with the DWAF recommended limit for aquaculture (≤ 10 µg/L) (DWAF, 1996). Moreover, 88.24% of the water from wetlands was above the SANS recommended standards of drinking water for aesthetic (≤ 300 µg/L) and chronic health (≤ 2 000) (SANS, 2015). However, the water from all sampled wetlands was below the chronic health limit excluding W8 which has the highest Fe value. High concentrations of Fe in the sampled wetlands could have resulted from the rust of wastes containing Fe which were dumped within the wetlands. Therefore, another source of Fe in the water of the sampled wetlands could be detergents. This is because most of the wetlands sampled in this study were closer to the residential area where detergents are used and disposed of carelessly daily and these detergens are transported into the wetland through runoff after rainfall event. However, (W8) might cause some iron adverse effects if the water from it is used for irrigation and drinking. Fe levels reported by Menon et al. (2023) from Kole wetland water (1848 g/L), South India, was within the range of this study.

4.3.11 Manganese (Mn)

The concentrations of Mn in the water of the sampled wetlands varied from 29.64-3449.95 µg/L (Table 4.2). The minimum value of Mn was recorded in W1 and the maximum value in (W9). These wetlands were used for dumping plastics, bottles, pumps, rotten food, dead pets, and construction waste, which may have contributed to the Mn levels recorded. Only the water from W1 complied with the DWAF recommended limits for domestic use (≤ 50 µg/L). W1 and W3 also complied with the DWAF guideline for aquaculture use (≤ 100 µg/L), and the protection of aquatic life water (≤ 180 µg/L), respectively while 88 % of the wetlands recorded higher levels of Mn which did not comply with the DWAF guidelines for various water use. The SANS threshold limit for Mn in drinking water is ≤ 100 µg/L for aesthetic and ≤ 400 µg/L for chronic health concerns, respectively (SANS, 2015). However, the water from wetlands was found to be above the DWAF recommended standard of irrigation (≤ 20 µg/L) but lower than the DWAF recommended limits of livestock watering (≤ 10 000 µg/L). The high concentrations of Mn are concerning because their combined effect with Fe and Al can significantly impact its use for laundry (Edokpayi et al., 2014).

4.3.12 Nickel (Ni)

The average levels of Ni in the water of wetlands varied between 1.61 and 7.27 µg/L (Table 4.2). The concentration of Ni was found to be lower than the DWAF recommended limits in all wetlands for livestock watering (≤ 1000 µg/L) and irrigation (≤ 200 µg/L), respectively (DWAF, 1996). Heisi et al. (2022) found Ni levels that were higher than those found in this study in the Blesbokspruit wetland in South Africa (41500 g/L). The SANS and WHO recommended level of drinking water is ≤ 70 µg/L (SANS, 2015; WHO, 2011). However, there is no limit of Ni for aquaculture water uses and for the protection of aquatic life set by DWAF. Therefore, the water from all sampled wetlands can be used for livestock watering and irrigation without the potentially adverse impacts resulting from Ni.

4.3.13 Selenium (Se)

The average concentrations of Se in the water of the sampled wetlands ranged between below BDL-1.14 µg/L (Table 4.2). The mean Se levels measured in this study's water were lower than the Se levels (210 g/L) reported in California coastal wetland water by Cohen et al. (2001). The levels of Se in water were below the DWAF recommended standards for domestic water (≤ 20 µg/L), livestock watering (≤ 50000 µg/L), for the protection of aquatic life (≤ 2 µg/L), and irrigation (≤ 20 µg/L) water uses (DWAF, 1996). The SANS and WHO recommended level of drinking water is (≤ 40 µg/L) (SANS, 2015; WHO, 2011). Se in the water from wetlands would not result in adverse effects associated with Se when used for the above-mentioned water uses.

4.4.14 Vanadium (V)

A high concentration of V in the environment has adverse effects on plants, animals, and humans (Wu et al., 2022). The average concentrations of V in water ranged from BDL-23.31 µg/L as indicated in Table 4.2. The lowest V level was detected in (W9) while the highest level was obtained in (W10). These levels were below the DWAF recommended limits for domestic 1000 µg/L), livestock watering (≤1 000 µg/L), and irrigation water use (≤ 100) µg/L, respectively (DWAF, 1996). Ashayeri and Keshavarzi (2019) found low levels of V (1.02) in Shadengan wetland in Iran, which were within the range of levels found in this study.

4.4.15 Zinc (Zn)

Zn is a common and mobile element found in natural waters in both dissolved and suspended forms (Kacholi and Sahu, 2018). The levels of Zn in water from sampled wetlands varied between

13.50-20.99 µg/L with the minimum value obtained in W15 and the maximum value in W13. The Zn levels obtained in this study might result from the galvanised roofing sheets and detergents that flow through runoff into the wetlands since most of these wetlands were located near residential areas. The Zn levels measured in this study's water were above the Zn levels (140 µg/L) reported by Cohen et al. (2001) in California coastal wetland water in the United States. The results obtained in this study complied with DWAF recommended standard for livestock watering (≤ 20000 µg/L), irrigation (≤ 1000 µg/L), aquaculture (≤ 30 µg/L), and domestic water use (≤ 30000 µg/L) (DWAF, 1996). The Zn water quality target range for drinking water is ≤ 3500 µg/L for SANS and ≤ 3000 µg/L for DWAF, respectively (SANS, 2015 and WHO, 2011). Therefore, negative impacts associated with Zn are not anticipated with water use.

4.4.16 Trace metals without DWAF water quality guidelines standards

Ga, Rb, Sr, Ag, Cs, Ba, and Ti were also analyzed; however, they do not have a threshold effect since they are unlikely to impact the aquatic biota. These trace metals ranged between BDL (Ag)-583.54 µg/L (Ba). Most of these trace metals recorded a concentration of less than 1 µg/L except Ba, Sr, and Rb.

Table 4. 2: Trace Metals levels (µg/L) recorded in wetland water with their corresponding guidelines standards

SAM. C	Be	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Rb	Sr	Ag	Cd	Cs	Ba	Tl	Pb	U
W1	0.06	60.36	0.20	BDL	29.64	77.42	0.19	1.61	BDL	15.58	0.02	0.37	0.38	1.37	343.86	0.07	BDL	0.05	224.70	0.01	BDL	8.93
W2a	0.06	336.20	5.09	0.52	102.25	320.69	1.15	3.40	BDL	18.79	0.13	0.31	0.21	3.21	353.08	0.02	BDL	0.13	130.17	0.02	1.20	0.15
W2b	0.13	567.9	6.73	1.01	510.63	684.18	4.46	8.80	BDL	14.66	0.31	1.04	0.36	3.35	267.23	0.05	BDL	0.13	113.92	0.03	0.75	1.32
W3	0.01	58.71	0.88	BLD	91.42	975.70	0.81	8.29	BDL	313.18	0.02	0.33	0.54	1.90	219.12	0.02	BDL	0.04	46.57	0.00	BDL	0.09
W4	0.06	115.27	3.98	4.33	468.28	263.24	2.68	17.91	BDL	15.62	0.06	1.79	0.53	58.88	364.09	0.46	BDL	0.73	158.82	0.01	BDL	0.66
W5	0.15	802.45	0.81	0.06	966.12	2232.71	5.72	3.38	BDL	101.31	0.21	0.10	0.46	4.71	47.64	0.04	BDL	0.06	103.84	0.01	0.27	0.13
W6	0.03	148.84	0.76	BLD	324.55	1155.37	1.91	2.45	BDL	29.03	0.06	0.07	0.07	2.43	111.45	0.98	BDL	0.06	51.96	0.01	0.89	0.04
W7	0.09	261.51	1.45	0.04	258.20	3421.84	3.00	2.21	BDL	48.49	0.15	0.17	0.60	4.24	60.78	0.11	BDL	0.06	163.44	0.03	0.86	0.08
W8	0.09	345.64	3.22	0.58	1071.18	12973.62	3.30	2.48	BDL	48.49	0.21	0.46	1.08	1.92	227.26	0.39	BDL	0.06	246.85	0.01	1.83	0.10
W9	0.15	142.38	BDL	BLD	3449.95	2005.49	4.26	3.56	BDL	14.87	0.31	0.75	0.44	1.39	294.33	0.03	BDL	0.09	90.04	0.01	BDL	0.48
W10	0.21	902.03	23.31	3.11	1295.96	2812.12	7.27	13.46	BDL	79.93	0.45	0.50	0.60	1.97	329.92	0.00	BDL	0.04	583.54	0.01	1.30	1.30
W11	0.01	55.34	1.70	BLD	372.52	1714.52	1.92	2.04	BDL	95.36	0.07	0.13	0.20	2.95	78.72	0.03	BDL	0.07	52.16	0.01	BDL	0.03
W12	0.03	88.67	0.06	BLD	500.58	552.34	3.14	1.88	BDL	7.93	0.02	0.01	BLD	1.11	46.71	0.12	BDL	0.06	53.92	0.00	BDL	0.08
W13	0.08	449.38	12.08	1.65	759.10	2917.17	4.19	8.83	BDL	1619.50	0.30	0.62	1.14	2.12	179.91	0.01	BDL	0.06	120.76	0.00	0.69	0.33
W14	0.17	867.22	0.74	0.46	329.34	2812.12	0.75	1.67	BDL	157.26	0.49	0.37	0.64	4.16	78.66	BDL	BDL	0.15	97.48	0.01	BDL	0.43
W15	0.05	71.11	1.02	BDL	386.82	2495.76	1.95	5.26	BDL	5.83	0.03	0.88	0.18	1.60	136.84	0.41	BDL	0.21	171.35	0.01	BDL	2.96
W16	0.05	132.03	0.37	BDL	1614.59	708.50	1.59	4.88	BDL	30.69	0.10	0.48	0.34	3.50	137.41	0.24	BDL	0.13	172.91	0.01	BDL	0.57
DWAF (1996) IRRIG. STD	≤100	≤5000	≤100	≤20	≤20	≤50	≤50	—	≤100	—	—	≤100	≤20	—	—	—	—	—	—	—	≤200	—
DWAF (1996) LIVESTOCK WAT. STD	—	≤5000	—	≤10000	≤10000	≤10000	≤1000	—	≤50-5000	—	—	≤1000	≤50000	—	—	—	—	—	—	—	≤0.01	—
DWAF (1998) AQUAC. STD	—	≤30	—	—	≤100	≤100	—	—	≤5	—	—	≤50	≤30	—	—	—	—	—	—	—	µg/L	—
DWAF AQUAT. STD	—	≤5	—	≤180	≤50	—	—	—	≤0.3	—	—	≤10	≤2	—	—	—	—	—	—	—	≤0.2	—
DWAF (1996) DOMESTIC	—	≤150	—	—	≤50	≤100	—	—	≤1000	≤10	—	≤10	≤20	—	—	—	—	—	—	—	—	—

USE WATER STD																					
SANS (2015) DRINK. WATER STD	—	≤300	—	≤50	≤300-≤2000	≤500	—	≤70	≤1000	≤3500	—	≤10	≤40	—	—	—	≤3	—	≤700	—	≤10	≤30
WHO ((2011) DRIN.WATER STD	—	≤900	—	≤50	≤400	—	—	≤70	≤2000	≤3000	—	≤10	≤40	—	—	—	≤3	—	≤700	—	≤10	≤30

4.5 Sediment Quality Analysis

The results of this study were discussed and compared with the Canadian Council of Ministers of the Environment (CCME) sediment quality guidelines (SQGs) for the protection of aquatic life and those of the marine and estuarine reported by Long et al. (1995). The TEL and PEL denote the threshold and probable effect levels, respectively. The abbreviations ERL and ERM stand for effect range-low and effect range-median, respectively (Edokpayi et al., 2022). TEL and ERL are the concentrations below which metal will rarely have no toxic effect on aquatic organisms in both SQGs guidelines, while PEL and ERM are the concentrations above which adverse effects will occur. The values between TEL-PEL and ERL-ERM represent concentrations where an adverse effect is likely to occur.

4.5.1 Arsenic (As)

The levels of As in sediments ranged between 1.04 and 20.96 mg/kg as shown below in Table 4.3. There was a variation of levels of As in sediments of the wetlands across Limpopo province. In most wetlands, As levels in sediments were below the TEL (7.2) mg/kg) and PEL (41.6 mg/kg) limit. In contrast, W3 exceeded the TEL limit but fell within the PEL limit. Furthermore, since levels of sediment in the sampled wetlands tracked within ERL (8.2 mg/kg) and ERM (70 mg/kg), except for W3, the ERL limit was exceeded but the ERM limit was below, suggesting that adverse effects are likely to occur to aquatic organisms in this area. The results reported by Raji et al. (2021) in sediments from wetlands of Rietspruit, South Africa (223.1 mg/kg) was higher than the results of this study also exceeded the PEL and ERM sediments quality guidelines. The results reported by Kinimo et al. (2018) (15.5 mg/kg) in wetland sediments around gold mining activities in central-southern and southeastern Côte d'Ivoire were within the range of the results recorded in this study. The As sediments levels reported by Gbogbo and Otoo (2015) in the sediments from coastal wetland water (0.0067 mg/kg) in Ghana were lower than the range levels recorded in the water from this study.

4.5.2 Cadmium (Cd)

Cadmium was not detected in most of the wetlands' sediments in the sampled wetland. The Cadmium sediments ranged from BDL to 0.04 mg/kg as indicated in Table 4.3. The sediments from all the sampled wetlands were below the threshold limit reported by CCME (2001) which are TEL (0.6 mg/kg) and PEL (3.5 mg/kg). Similarly, the sediments concentrations also complied with ERL (1.2 mg/kg) and ERM (9.6 mg/kg) as stated by Long et al. (1995). Therefore, the negative impacts associated with Cd will rarely take place in all sampled points. In a study conducted by

Raji et al. (2021) in Limpopo Province, wetlands of Rietspruit, (3.5 mg/kg) showed higher levels of Cd as compared to the results of this study. Gbogbo and Otoo (2015) found lower Cd levels (0.043 mg/kg) in sediments from coastal wetland sediments in Ghana than in this study.

4.5.3 Lead (Pb)

In all sampled wetlands, Pb levels varied between 3.79 and 42.49 mg/kg in the sediments (Table 4.3). All sediments from the sampled sites complied with the TEL threshold limit except sediments from W1. These sediments will rarely harm the aquatic organisms with respect to the levels of Pb recorded. Based on the SQGs reported by Long et al. (1995) the sediments from the sampled wetlands were below the ERL and ERM threshold limits. This implies that the sediments from all sampled wetlands will hardly pose threats to aquatic organisms. Raji et al. (2021) reported high Pb levels in sediments from Rietspruit wetlands, Limpopo Province, South Africa than those recorded in this study, thus exceeding TEL, PEL, and ERL sediment quality guidelines but below the ERM standard.

4.5.4 Chromium (Cr)

The average Cr level in sediments of the sampled wetlands varied from 1.01-99.90 mg/kg (Table 4.3). Cr levels in sediments of most sampled points were below the TEL threshold level of 37.3 mg/kg indicating no risk to the ecosystem except for W3, W5, W9, W11, and W14. The level of Cr in the sediments in W3, W5, W9, and W11 ranged between the threshold limit of TEL (37.3 mg/kg) and PEL (90 mg/kg) as stated by CCME (2001) meaning that they could pose moderate risk to the ecosystem. However, the level of Cr in W14 Cr exceeds the PEL threshold which implies that there would be negative effects on the ecosystem in relation to the Cr level recorded in that site. Based on the threshold limit stated by Long et al. (1995), Cr levels in the sediments of most wetlands were lower than the ERL limit also suggesting that toxic impacts will hardly occur. Among the sampled wetland (sediments), only the sediments in W3 and W14 were exceeding the ERL limit. However, W3 and W14 ranged between ERL (81 mg/kg) and ERM (370 mg/kg) threshold limits implying that toxic impacts are likely to occur. W3 and W14 are depressions wetlands and they have no sufficient macrophytes that to absorb pollutants. The Cr levels reported by Ashayeri and Keshavarzi (2019) in sediments from Shadengan wetland (57.62), Iran was within the range of the results recorded in this study.

4.5.5 Copper (Cu)

The levels of Cu in sediment from the sampled wetlands varied between 1.40 and 152.96 mg/kg as shown in Table 4.3. 73% of the sampled points were below the TEL (35.7 mg/kg). This suggests that they will not pose harm to living organisms habiting the sediments. However, the levels of Cu in 27% of the sampled sediments are likely to result in adverse effects since they exceeded the TEL limit of (197 mg/kg). The index value by Long et al. (1995) showed that most of the sediments recorded levels below the ERL levels while 23% recorded values between the ERL and ERM indicated a moderate impact on the ecosystem. Kinimo et al. (2018) reported results in wetland sediments of Central-Southern and Southeastern Côte d'Ivoire (44.3 mg/kg) which were within the range of this study's results. This suggests that it is very much likely to have Cu in wetlands sediments.

4.5.6 Nickel (Ni)

The levels of Ni in the sediment samples from the selected wetlands ranged between 2.38 and 48.30 mg/kg as presented in Table 4.3. There was a variation of Ni levels in the sediment samples ranging from extremely low to very high. 80% of the sampled points were below the TEL threshold limit of (18 mg/kg)). Therefore, the sediments from these points will rarely pose adverse impacts on aquatic species. However, the sediments from 20% of the sampled points which are above TEL limits were lower than the PEL limits, indicating that they are likely to result in negative effects on the ecosystem. Moreover, 60% of the sampled sites complied with the ERL (20.9 mg/kg) and ERM (51.6 mg/kg) threshold limit reported by Long (1995). Thus, the sediments from these wetlands are unlikely to pose threat to aquatic species. However, the sediments from 40% of the sampled point are likely to pose threat to aquatic biota since their sediment levels ranged between the ERL and the ERM SQGs. The levels of Ni in sediments reported by Kinimo et al. (2018) in wetland sediments (29.7 mg/kg), Central-Southern, and Southeastern Côte d'Ivoire were within the range of the results recorded in this study.

4.5.7 Zinc (Zn)

The levels of Zn in the sediments ranged between 14.66 (W2b) and 178.65 mg/kg (W3) as presented in Table 4.3. All the sediments from the sampled wetlands complied with the SQGs reported by CCME (2001) (TEL 123 mg/kg and PEL 315 mg/kg) except W3 which varied between the TEL and PEL guidelines standards. Similarly, sediments in most sampled wetlands complied with the guidelines stated by Long et al. (1995) ERL (150 mg/kg) and ERM (410 mg/kg) excluding W3. This suggests that these wetlands are unlikely to cause the negative effect associated with

Zn in all sampled wetlands while W3 is likely to pose negative impacts. The Zn sediments levels reported by Ashayeri and Keshavarzi (2019) in Shadengan wetland (51.9 mg/kg), Iran was within the range of the results of this study.

4.5.8 Trace metal without sediments quality guidelines standards

The following metals are frequently not thought to have a negative impact on aquatic organisms, so they are excluded from the majority of SQGs and they have been recorded in the following concentration. Fe (684.18-41626.85 mg/kg), Mn (69.22-2003.61 mg/kg), Co (3.78-32.63 mg/kg), Se (0.90- 6.83 mg/kg), V (7.69-100.39 mg/kg), Be (0.23-0.38 mg/kg), Ga (0.98-10.39 mg/kg), Sr (5.23- 35.08 mg/kg), Ag (0.01- 0.12 mg/kg), Cs (0.15-2.55 mg/kg), Ba (24.74 -100.93 mg/kg), Al (887.74-26420.60 mg/kg), U (0.21-15.62 mg/kg), and Ti (0.02 - 0.20 mg/kg). The results of these trace metals are shown in Table 4.3.

Table 4. 3: Trace metals recorded in sediments (mg/kg) wetlands with SQGs

SAM. C	Be	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Rb	Sr	Ag	Cd	Cs	Ba	Tl	Pb	U
W1	0.36	2659.96	23.13	9.74	419.07	9290.24	11.43	18.52	38.20	49.21	2.13	2.30	1.91	4.94	35.08	0.04	BDL	0.51	104.64	0.05	42.49	7.47
W2a	0.35	1431.62	18.00	6.65	197.37	6291.95	5.67	3.52	26.09	54.62	1.17	1.59	0.90	5.33	15.12	0.03	BDL	0.22	52.45	0.04	7.05	0.66
W2b	0.13	567.90	6.73	1.01	510.63	684.18	4.46	8.80	BDL	14.66	0.31	1.04	0.36	3.35	267.23	0.05	BDL	0.13	113.92	0.03	0.75	1.32
W3	0.36	6376.02	100.39	88.02	1226.37	34360.85	32.63	29.21	83.03	178.65	10.39	20.96	21.79	17.19	75.12	0.12	BDL	0.75	345.77	0.16	5.45	2.37
W4	0.37	1707.21	19.09	14.71	241.32	5549.73	7.70	10.55	15.03	26.09	1.62	2.26	2.81	7.11	22.84	0.04	BDL	0.56	72.78	0.07	9.65	0.33
W5	0.37	2400.21	99.04	43.64	660.13	27280.02	27.53	16.92	52.62	51.04	3.43	1.38	1.88	1.73	11.39	0.04	BDL	0.15	81.52	0.04	6.24	0.22
W6	0.38	1865.64	17.18	14.71	1219.29	25153.86	7.68	8.28	11.84	38.27	3.68	4.59	6.83	5.05	24.06	0.03	BDL	0.43	178.25	0.04	15.63	15.62
W7	0.35	887.74	21.66	13.20	76.31	8116.84	6.04	8.71	15.23	66.19	0.98	2.04	1.30	2.70	12.54	0.04	BDL	0.18	69.86	0.02	13.07	13.70
W8	0.36	1405.26	7.69	7.20	2003.61	27264.14	3.78	2.38	7.98	24.76	2.76	4.46	5.50	3.95	19.59	0.02	BDL	0.31	227.91	0.03	6.68	0.85
W9	0.30	10502.03	105.42	38.18	877.24	41626.85	39.06	32.80	152.96	62.81	6.99	1.95	2.90	24.91	12.39	0.06	BDL	2.31	175.49	0.20	6.13	0.27
W10	0.30	2610.05	21.03	13.82	69.22	6933.29	3.79	4.41	1.40	21.34	1.40	1.93	0.95	2.65	5.80	0.01	BDL	0.16	24.74	0.03	4.02	0.21
W11	0.36	12289.48	43.34	35.55	175.24	16447.26	10.87	20.30	13.60	62.98	5.37	2.16	1.83	17.05	10.16	0.07	BDL	0.92	84.27	0.11	11.02	0.44
W12	0.37	26420.60	61.45	99.90	553.96	26069.48	19.37	48.30	24.08	55.60	9.07	2.52	2.44	28.64	17.62	0.04	BDL	2.55	100.60	0.15	9.30	0.60
W13	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
W14	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
W15	0.23	6872.64	23.85	65.01	83.65	6735.37	5.59	34.53	2.50	16.43	2.76	5.10	1.65	6.05	5.23	0.02	BDL	0.43	25.52	0.03	3.79	0.34
W16	0.31	18933.11	28.40	26.61	92.75	11228.97	5.90	19.75	4.92	45.24	6.02	6.35	1.79	15.96	8.97	0.02	BDL	0.87	100.93	0.08	7.47	0.28
TEL	—	—	—	37.3	—	—	—	15.9	35.7	123	—	—	7.2	—	—	—	0.6	—	—	—	35	—
PEL	—	—	—	90	—	—	—	42.8	197	315	—	—	41.6	—	—	—	3.5	—	—	—	91.3	—
ERL	—	—	—	81	—	—	—	20.9	34	150	—	—	8.2	—	—	—	1.2	—	—	—	46.7	—
ERM	—	—	—	370	—	—	—	51.6	270	410	—	—	70	—	—	—	9.6	—	—	—	218	—

4.6 Potential Ecological Risk of Sediments from Wetlands

The potential ecological risk of metals was discussed following various indices by Hakanson (1980). The model assigns specific values to determine whether the sediments will result in adverse impacts on aquatic biota or not. The specific values of the indices are presented in chapter 3.

4.6.1 Contamination factor (CF) and the degree of contamination (CD)

The contamination factor CF risk index calculated for the majority of the metals revealed a CF<1 (Table 4.4) indicating a minimal risk of those metals to aquatic biota. In sediment samples, metals like Cd, Cu, Fe, and Ni had CF values of less than one from all sampled wetlands. This interpretation agrees with the sediment quality guidelines because most the metals were recorded at levels lower than the TEL and ERL values. However, Cr levels were high in the sediments of some sampled points and could cause considerable risk to aquatic biota. Some metals from the sampled points showed a moderate risk for As (W3=1.05 mg/kg), Co (W3=1.72 mg/kg; W5=1.45 mg/kg; W9=2.06 mg/kg; W12=1.02 mg/kg), Mn (W3=1.36 mg/kg; W6=1.35 mg/kg; W8=2.23 mg/kg), Pb (W1=2.12 mg/kg) and Zn (W3=1.88 mg/kg). According to the above-presented levels, Cr is the only metal that could highly impact the aquatic biota while Pb, As, Co, Mn, and Zn may potentially result in adverse impacts on aquatic species in some of the sites.

The degree of contamination CD as a result of the cumulative impacts of the metals was also calculated. The results of the degree of contamination factor are illustrated in Table 4.4. CD levels of <8 mg/kg present a low degree of contaminants from the sediment and these levels were obtained at W1=4.40 mg/kg, W2a=1.87 mg/kg, and W2b=0.16 mg/kg respectively. This implies that the sediments from the sampled wetlands were in good condition to sustain aquatic biota. The CD levels recorded in the sediments from W7, W8, and W10 displayed a moderate degree of contamination (8≤CD<16 mg/kg). This suggests that these sediments were likely to cause harm to the aquatic species over a long period. The sediments from W4=16.56, and W6=18.66 showed a considerable degree of contamination (16≤CD<32), implying that the adverse effects were likely to occur in the aquatic species from the sampled wetlands. Conversely, most of the sampled wetlands (W3=95.56 mg/kg; W5=47.56 mg/kg; W9=43.70 mg/kg; W11=38.41 mg/kg; W12=104.05 mg/kg; and W15=66.67 mg/kg) presented a CD value >32 mg/kg which presents an extremely high degree of contamination. This suggests that the sediments from these wetlands were toxic to aquatic species as presented by Hakanson (1980). This study's CD results are consistent with those reported by Vetrimurugan et al. (2019) in KwaZulu-Natal beach sediments of South Africa, where most samples showed considerable enrichment of metal contamination.

Table 4. 4: CF and CD values of each metal in all sampled points (mg/kg)

SAMPLE CODE	**CF VALUE**										**CD VALUES**	**RATINGS**
METAL	As	Cd	Cr	Cu	Co	Fe	Mn	Ni	Pb	Zn		
W1	0.12	BLD	0.11	BLD	0.60	0.20	0.47	0.27	2.12	0.52	4.40	Low risk of contaminates
W2a	0.08	0.09	0.07	0.00	0.30	0.13	0.22	0.05	0.35	0.57	1.87	Low risk of contaminations
W2b	0.08	BDL	0.01	BDL	0.23	0.01	0.60	0.13	0.04	0.15	0.16	Low risk of contaminates
W3	1.05	0.10	88.02	0.00	1.72	0.73	1.36	0.43	0.27	1.88	95.56	Very high degree of contaminations
W4	0.11	0.03	14.71	0.00	0.41	0.12	0.27	0.16	0.48	0.27	16.56	Considerable risk of contamination
W5	0.07	BLD	43.64	BLD	1.45	0.58	0.73	0.25	0.31	0.54	47.56	Very high degree of contaminations
W6	0.23	0.12	14.71	0.00	0.40	0.53	1.35	0.12	0.78	0.40	18.66	Considerable risk of contamination
W7	0.10	0.04	13.20	0.00	0.32	0.17	0.08	0.13	0.65	0.70	15.40	Moderate risk of contamination
W8	0.22	BLD	7.20	BLD	0.20	0.58	2.23	0.04	0.33	0.26	11.05	Moderate risk of contamination
W9	0.10	0.06	38.18	0.00	2.06	0.88	0.97	0.48	0.31	0.66	43.70	Very high degree of contaminations
W10	0.10	BLD	13.82	BDL	0.20	0.15	0.08	0.06	0.20	0.22	14.83	Moderate risk of contamination
W11	0.11	0.12	35.55	0.00	0.57	0.35	0.19	0.30	0.55	0.66	38.41	Very high degree of contaminations
W12	0.13	0.07	99.90	0.00	1.02	0.55	0.62	0.71	0.47	0.59	104.05	Very high degree of contaminations
W13	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
W14	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
W15	0.26	BLD	65.01	BDL	0.29	0.14	0.09	0.51	0.19	0.17	66.67	Very high degree of contaminations
W16	0.32	BLD	26.61	BDL	0.31	0.24	0.10	0.29	0.37	0.48	28.72	Considerable risk of contamination

4.6.2 Toxic response factor (E_r^i) and potential ecological risk (RI)

The toxic response factor E_r^i was also computed, and it was found that all the metals values as well as their points were <40 mg/kg, presenting a low potential ecological risk except Cr in some sampled points as shown in Table 4.5. Sediments from some sampled points were W9=76.36 mg/kg, W11=71.10 mg/kg, and W16=53.22 mg/kg showing a Cr moderate risk (40≤$E_r^i < 80$). This shows that these sediments could harm the aquatic biota over a period of period. A considerable risk (80≤ $E_r^i < 160$) was observed in W15=130.02 mg/kg. This implies that the sediments are likely to pose adverse effects on the aquatic ecosystem. The sediments in W3 and W12 were

176.04, and 199.80 mg/kg respectively, showing an elevated risk $(160 \leq E_r^i < 320)$. Therefore, the sediments from the sampled wetlands are toxic to aquatic biota. The results of the toxic response factor are illustrated below in Table 4.5.

Similarly, the potential ecological risk RI that is associated with each site was also calculated, and all sites except W3 and W12 were present in levels that would not pose an ecological risk (RI<150 mg/kg). The RI values of sediments in this study did not correspond to the one reported by (2022) in India, Colombia, Saudi Arabia and China (RI≥600), which signified the high ecological risk of heavy metals contamination in these countries. However, low ecological risk was observed in Malaysia, Azerbaijan, Iran, Kenya, Sri Lanka, Turkey, and Australia due to HMs in sediments (RI<150).

Table 4. 5: ER and RI values of each metal in the water from wetland

ER AND RI VALUES (mg/kg)											RI VALUES (mg/kg)	RATINGS
SAMP.CO	As	Cd	Cr	Cu	Co	Fe	Mn	Ni	Pb	Zn		
W1	1.15	BLD	0.22	BDL	3.01	0.20	0.52	1.36	10.62	0.52	17.09	Low ecological risk
W2a	0.79	0.00	0.15	0.00	1.49	0.13	0.57	0.26	1.76	0.57	5.72	Low ecological risk
W2b	0.80	BDL	0.02	BDL	1.17	0.01	0.60	0.65	0.19	0.15	3.59	Low ecological risk
W3	10.48	0.00	176.04	0.00	8.59	0.73	1.88	2.15	1.36	1.88	203.11	Moderate ecological risk
W4	1.13	0.00	29.42	0.00	2.03	0.12	0.27	0.78	2.41	0.27	36.43	Low ecological risk
W5	0.69	BLD	87.27	BLD	7.24	0.58	0.54	1.24	1.56	0.54	99.66	Low ecological risk
W6	2.29	0.00	29.42	0.00	2.02	0.53	0.40	0.61	3.91	0.40	39.58	Low ecological risk
W7	1.02	0.00	26.41	0.00	1.59	0.17	0.70	0.64	3.27	0.70	34.50	Low ecological risk
W8	2.23	BLD	14.39	BLD	0.99	0.58	0.26	0.18	1.67	0.26	20.56	Low ecological risk
W9	0.98	0.00	76.36	0.00	10.28	0.88	0.66	2.41	1.53	0.66	93.76	Low ecological risk
W10	0.97	BLD	27.64	BLD	1.00	0.15	0.22	0.32	1.01	0.22	31.53	Low ecological risk
W11	1.08	0.00	71.10	0.00	2.86	0.35	0.66	1.49	2.76	0.66	80.94	Low ecological risk
W12	1.26	0.00	199.80	0.00	5.10	0.55	0.59	3.55	2.33	0.59	213.77	Moderate ecological risk
W13	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
W14	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
W15	2.55	BLD	130.03	BLD	1.47	0.14	0.17	2.54	0.95	0.17	138.02	Low ecological risk
W16	3.17	BLD	53.22	BLD	1.55	0.24	0.48	1.45	1.87	0.48	62.46	Low ecological risk

4.7 Conclusion

Most of the water (physicochemical parameters) from the sampled wetlands complied with the DWAF guidelines standards for irrigation, livestock feeding, aquaculture, and the protection of aquatic life, as well as the SANS (drinking water standard), and WHO (surface water quality standard). However, DO levels were lower than the WHO surface water quality guidelines standard in 100% of the wetlands. Similarly, metals in most of the wetlands' water complied with the water quality target. The trace metal Cu and Cd recorded extremely low levels However, some trace metals (Mn, Fe, and Al) were at high concentrations in some wetlands, exceeding some of the water quality target ranges. High levels of these metals is believed to have been due to anthropogenic activities in and around the wetlands. The metals in sediments from most sampled wetlands also complied with the SQGs. 33% of the water from the wetlands showed a very high risk of contamination, indicating a very bad environment for aquatic organisms relying on those sediments. The metals showed a low risk of RI values, excluding Cr which was at very high risk. The CF values of Cr recorded levels (CF>32) at some sites, presented and extremely high levels of toxicity to aquatic biota and, the CD values presented an extremely high risk of contamination in 46.67% of these sites. The levels recorded in sediments were above the ones in the water.

CHAPTER FIVE: WATER QUALITY IMPROVEMENT AND TRACE METAL REMOVAL EFFICIENCY USING PHANGAMI WETLAND

5.1 Preamble

In this chapter, Phangami wetland was chosen to evaluate the efficiency of the wetland in water quality improvement and trace metal removal efficiency.

5.2 Description of the Study Area

5.2.1 Location

The area of study is a wetland ecosystem in the Thulamela local municipality, which is located in the Thohoyandou section of the Vhembe district municipality in Limpopo province as presented in Figure 5.1. The study area is located at a wetland along the Phangami area, with its upstream located at Ha Magidi village of geographical units of 22° 57' 22" S and 30° 28' 48" E. And the midstream is located, at Thohoyandou block G Phangami area of geographical coordinates of 22° 58' 0" S and 30°28' 53 " E. The downstream is located at Thohoyandou East alongside the Maniini road of geographical coordinates 22°58 ' 54" and 30°27 ' 45 " E.

Thohoyandou is known for its extreme temperature changes that occur throughout the year. The average midday temperatures range from 22.9-30.3 °C in summer and 17-22 °C in winter, according to the monthly distributions of average daily maximum temperatures. July is the region's coolest month, with an average nighttime temperature of 7.5 °C. Thohoyandou gets 752 mm of rain every year on average, with most of it falling in the middle of the summer. It receives the least amount of rain 4 mm in June and the most 154 mm in January. Rainfall is seasonal, falling between October and March. Summer rains account for more than 80% of total rainfall, whereas winter rains account for only about 20% (Durowoju et al., 2019).

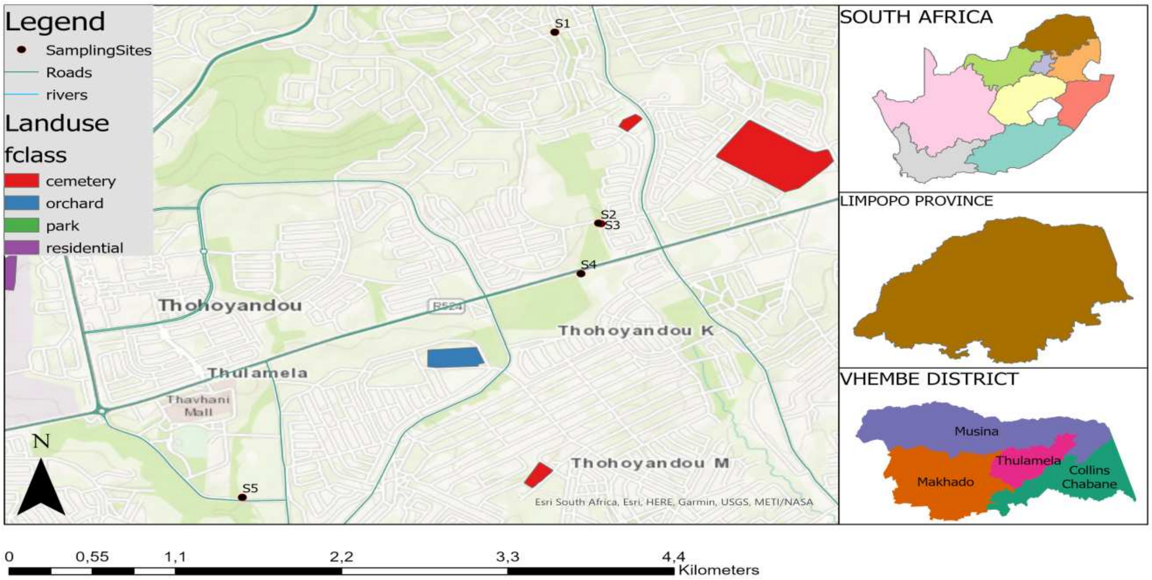

Figure 5. 1: Study area map of the study area

5.3 The Physicochemical Parameters of Water Sample

5.3.1 Dissolved Oxygen (DO)

The concentration of dissolved oxygen depends on the physical, chemical, and biological activities of the body of water (Akinfolarin et al., 2020). The dissolved oxygen level was measured, and it varied from 0.33-1.58 mg/L in the dry season. During the wet season, the DO level ranged from 1.14-2.62 mg/L (Appendix A.1). The dissolved oxygen improved in the wet season compared to the dry season, as it recorded the highest mean and standard deviation as indicated in Table 5.1. The presence of several living microorganisms in water, such as algae and common reeds, could be one reason for the higher oxygen levels during the rainy season (Matodzi et al., 2021). Moreover, the water received by the wetland during the wet season should have contributed to dilution the contaminants in the wetland. According to the t-test analysis of the dry and wet seasons, DO levels varied significantly ($p<0.05$) during the dry and wet seasons, demonstrating that the wetland had a favorable effect on increasing DO levels as the seasons changed. The DO increases from the upstream but when it reaches the point after the wastewater discharge it decreases drastically in both the wet and the dry seasons. The components of the wastewater negatively influence the DO of water, which can negatively impact the aquatic organisms living in that area on the wetland. But after the wastewater discharge, downstream there was an improvement of dissolved oxygen again as it increases the values for both the dry and rainy seasons.

Table 5. 1: Mean and standard deviation of DO from wetland water samples

Sampled points	Sites Description	DO (mg/L)	
		Dry season	**Wet Season**
SP1	Upstream	1.51±0.26	2.08±0.57
SP2	Before the sewage discharge	1.58±0.27	2.62±1.19
SP3	After the sewage discharge	0.33±0.20	1.14±0.90
SP4	After the sewage discharge	1.12±0.19	2.58±0.91

5.3.2 Temperature

The water temperature ranged from 18.58-24.67 ℃ throughout the wetland for both the dry and wet seasons (Appendix A.2). Aquatic organisms survive within a temperature of < 30 ℃ and the mean temperature recorded were all below 30 ℃, which indicates that the temperature is suitable for organisms living in the water for both seasons throughout the wetland. The temperature increased at the point after the wastewater discharge for both seasons with the mean and standard deviation values of 24.67±4.37 and 21.07±3.35, respectively (Table 5.2). This could be due to the organic matter present in the raw sewage discharged to the wetland absorbing more heat (Pipi et al., 2018). The temperature values were well within the Department of Water and Sanitation guidelines values for aquatic life preservation (5-30 ℃) (DWAF, 1996).

Table 5. 2: Mean and standard deviation of temperature ℃ between the dry and wet season

Sampled points	Sites Description	Temperature (℃)	
		Dry Season	**Wet season**
SP1	Upstream	20.62±2.63	19.88±1.35
SP2	Before the sewage discharge	21.93±2.83	19.67±1.60
SP3	After the sewage discharge	21.93±2.83	21.07±3.35
SP4	Downstream	20.19±2.42	19.58±1.60

5.3.3 potential of Hydrogen (pH)

The mean pH for both the dry and wet seasons of the Phangami wetland ranged from 6.95-7.39 (Appendix A.3). The pH increased at the point before the wastewater discharge for dry seasons with the mean and standard deviation values of 7.39±0.17 and 7.32 at the point after the sewage discharge for wet season, respectively (Table 5.3). In the aquatic environment, pH has a significant impact on metal speciation and bioavailability (Matodzi et al., 2021). The pH results were within the DWAF guidelines for irrigation of 6.5-8.4 (DWAF, 1996). There was no significant change in the pH across the dry and wet seasons (p>0.05). Total alkalinity and acidity, as well as runoff from nearby water releases, can change the pH of the water (Lawson, 2011).

Table 5. 3: Mean and standard deviation of pH between the dry and wet season

Sampled Points	Sites Description	Dry season	Wet season
SP1	Upstream	7.35±0.17	7.22±0.10
SP2	Before the sewage discharge	7.39±0.17	6.95±0.49
SP3	After the sewage discharge	7.26±0.08	7.32±0.26
SP4	Downstream	7.17±0.20	7.21±0.08

5.3.4 Turbidity

Turbidity measures the visibility of water and indicates how clear the water body is. This is determined by the total suspended solids and dissolved solids in the water sample (Akinfolarin et al., 2020). The obtained turbidity values for the dry season ranged from 11.05-102.46 NTU while that of the wet season ranged from 11.79-376.5 NTU (Appendix A.4). According to the results of the paired t-test analysis of dry and wet seasons, there was no significant difference between the results obtained during both seasons (p>0.05). The turbidity values improved from the upstream to the second sampling point in both seasons (Table 5.4). After the wastewater discharge to the wetland, the turbidity values increased again, and the highest point was during the wet season with the mean and standard value of 376.5±406.84 NTU. This may be due to surface run-off which transported sediment to the wetland as well as the total amount of waste. The wetland recorded a removal efficiency in the range of 15.54 - 95.68%. More removal was after the wastewater discharge to the wetland as there was an enormous difference in turbidity after the third point, showing that the wetland made an enormous impact in removing the pollutants before the downstream.

Table 5. 4: Mean and standard deviation of turbidity (NTU) between the dry and wet season

Sampled Points	Sites Description	Dry season	Wet season
SP1	Upstream	22.83±3.66	13.96±9.98
SP2	Before the sewage discharge	15.01±4.61	11.79±4.98
% Removal		34.25%	15.54%
SP3	After the sewage discharge	102.46±22.39	376.5±406.84
SP4	Downstream	11.05±1.52	16.25±12.23
% Removal		89.21%	95.68%

5.3.5 Total dissolved solids

The wetland recorded the total dissolved solids in the range of 199.5 - 567.75 mg/L during the dry season and 220.75-605.25 mg/L during the wet season (Appendix A.5). There was no significant difference in total dissolved solids in the wetland between the dry and wet seasons, according to the paired t-test analysis ($p>0.05$). There was an improvement from the upstream to the second point of the total dissolved solids in both seasons, however, after the point of sewage discharge, there was a sudden increase in the total dissolved solids. This shows that the wastewater discharge had an impact on the wetland because of the pollution that comes with the wastewater discharge to the wetland, as total dissolved solids are a measure of the content of inorganic and organic substances present in water (Lawson, 2011). Increased rainfall also increases these organic and inorganic compounds, which have negative impacts on dissolved oxygen and carbon dioxide. Hence the value of total dissolved solids during the wet season was higher than during the dry season. This value can increase in wet season because rain various types of wetland were transported to the wetlands by surface runoff. There was an improvement in total dissolved solids along the wetland as it was reduced from 62.86% to 35.78%. More removal was after the third point before the downstream with 60.67 %, and 62.86% reduction showing that the wetland was efficient in making the water quality better as shown in Table 5.5.

Table 5. 5: Mean and standard deviation of TDS (mg/L) between the dry and wet season

Sampled Points	**Sites Description**	**Dry season**	**Wet season**
SP1	Upstream	409.00±53.94	343.75±43.46
SP2	Before the sewage discharge	199.50±40.10	220.75±14.93
% Removal		51.22%	35.78%
SP3	After the sewage discharge	567.75±95.44	605.25±150.12
SP4	Downstream	223.25±44.20	224.75±8.26
% Removal		60.67%	62.86%

5.3.6 Electrical conductivity

The obtained values of electrical conductivity during the dry season ranged from 284.75-826.25 µs/cm and 318.75-814.25 µs/cm during the wet season (Appendix A.6). The values of electrical conductivity (EC) typically indicate the existence of dissolved ions in water, which can affect the taste of water as well as contribute to water hardness (Matodzi et al., 2021). There was no significant change in conductivity across the wetland between the two seasons as the value of $p<0.05$. The values of electrical conductivity (Table 5.6) were higher at the sampling point three for both seasons after the wastewater discharge with the mean values of 826.25±126.60 µs/cm and 814.25±281.64 µs/cm respectively. The high conductivity is due to dissolved particles and ions, which may have been overproduced as a result of garbage disposal, runoff, and effluent discharge (Akinfolarin et al., 2020). The values of electrical conductivity improved from the upstream to the midstream except during the point after wastewater discharge with a huge increase. But immediately it was reduced to 58.78% during the dry season and 60.30% during the wet season.

Table 5. 6: Mean and standard deviation of EC (µs/cm) between the dry and wet season

Sampled points	**Sites Description**	**Dry season**	**Wet season**
SP1	Upstream	608±64.09	520.5±49.83
SP2	Before the sewage discharge	284.75±45.47	318.75±22.38
% Removal		53.16%	38.76%
SP3	After the sewage discharge	826.25±126.60	814.25±281.64
SP4	Downstream	340.5±36.34	323.25±12.55

% Removal		58.78%	60.30%

5.3.7 Salinity

Salinity is a measure of all the salts dissolved in water. It ranges from 144.25-454 ppm for the dry season and from 151.25 to 425 ppm for the wet season (Appendix A.7). According to the paired t-test, there was no noticeable difference in salinity during the dry and wet seasons ($p>0.05$). The mean concentration for salinity in the third point of sampling for both seasons was high with values of 454±67.76 and 425±110.12 ppm (Table 5.7). Salinity was improving throughout the wetland from the upstream to the second point but had a huge increase at the third sampling point after the waste discharge. This may be due to the introduction of wastewater to the wetland, and this alters the function of the wetland, as the wetland now increases the concentration of salinity. But after this the wetland decreases again, showing that the wetland was able to improve the quality of water. The wetland showed a positive reduction in salinity for all the sampling points with the removal efficiency ranging from 39.13%-66.13%. This showed that the wetland was efficient in reducing the salinity of water in the wetland.

Table 5. 7: Mean and standard deviation of salinity (ppm) between the dry and wet season

Sampled Points	Sites Description	Dry season	Wet season
SP1	Upstream	289±28.61	248.5±27.08
SP2	Before the sewage discharge	144.25±1.70	151.25±10.88
% Removal		50.08%	39.13%
SP3	After the sewage discharge	454±67.76	425±110.12
SP4	Downstream	153.75±2.5	152.25±5.90
% Removal		66.13%	64.17%

5.3.8 BOD measurement throughout the wetland

BOD is referred to as the entire amount of oxygen required by aerobic bacteria to completely degrade organic wastes in water (Akinfolarin et al., 2020). The dry and wet seasons obtained BOD values that ranged from 0.08 to 0.72 mg/L and 0.37 to 0.95 mg/L (Table 5.8) and (Appendix A.8), respectively. According to the paired t-test analysis, there was no significant difference in BOD between the dry and the wet season on the wetland ($p>0.05$). The highest value of BOD is an indicator of a high level of organic pollution. And the wetland recorded the highest BOD at various points within the wetland.

Table 5. 8: Mean and standard deviation of BOD (mg/L) between the dry and wet season

Sampled Points	Sites Description	Dry season	Wet season
SP1	Upstream	0.72±0.07	0.95±0.97
SP2	Before the sewage discharge	0.12±0.04	0.46±1.15
SP3	After the sewage discharge	0.08±0.09	0.37±0.26
SP4	Downstream	0.18±0.14	0.80±0.49

5.4 Trace Metals Removal Percentage throughout the Wetland

5.4.1 Aluminium (Al)

The mean concentration of the first sampling point for Aluminium was 59.84±33.96 µg/L and 262.01±175.49 µg/L in the dry and the wet seasons, respectively (Table 5.9). Aluminium values (Appendix B.1) were well within the irrigation and livestock water quality target range of ≤ 5000 µg/L (DWAF, 1996). Conversely, the water from the sampled point exceeded the DWAF aquatic life water use (≤ 05 µg/L). The threshold limit of Al in drinking water is ≤ 300 µg/L (SANS, 2015 and WHO, 2011). The concentration of Al between the dry and wet seasons did not vary significantly ($p>0.05$). The mean concentration was higher after the wastewater discharge to the wetland as it recorded the value of 1975.64 µg/L and 3661.33 µg/L for the before rain and after rain, respectively. The reason could be the pollutants entering the wetland through surface runoff. These values were above the drinking water standards. The values of Al were however reduced after this point with 91.74% and 94.64% during the dry and wet seasons, respectively. This might attribute to the fact that the wetland was efficient in removing the Al between the third point and the final sampling point. The high reduction efficiency of aluminum was between the third sampling point and the fourth sampling point compared to the upstream and the second point. This is due to the increase in aluminum concentration after the wastewater discharge point.

Table 5. 9: Percentage removal of Aluminium (µg/L) throughout the wetland

Sampled Points	Sites Description	Dry season	Wet season
SP1	Upstream	59.84±33.96	262.01±175.49
SP2	Before the sewage discharge	78.28±21.28	253.03±110.40
% Removal		-30.81%	3.42%
SP3	After the sewage discharge	1975.64±1020.38	3661.33±4937.86

SP4	Downstream	163.06±156.22	196.24±91.52
% Removal		91.74%	94.64%

5.4.2 Chromium (Cr)

The concentration of Cr was mostly below the detection limit during the dry season as compared to the wet season (Table 5.10) and (Appendix B.2). The highest mean concentration of 16.73±22.92 µg/L was recorded at the discharge point in the wet season. There was no significant difference between the samples between the dry and rainy seasons, according to the paired t-test analysis (p>0.05). The value of Cr was not detected at the first and the second sampling point during the dry season. However, it increased at the third point which is a point after the wastewater discharge to the wetland. The increase of Cr after wastewater was reduced by 87.16% during the dry season, and this is an indicator that the wetland was efficient enough in removing Cr. The wetland showed the highest removal efficiency of chromium during the wet season (97.01%). The rich vegetation between the wastewater discharge site and the midstream point may have resulted in increased metal uptake by the plants, reducing Cr levels (Shibambu, 2018). Microalgae and bacteria could have also contributed to Cr uptake. As reported by Mubashar et al. (2020) algal–bacterial consortium removed 79%, 71%, and 62% at 5%, 10%, and 20% of Cr from different wastewater.

Table 5. 10: Percentage removal of Chromium (µg/L) throughout the wetland

Sampled Points	Sites Description	Dry Season	Wet season
SP1	Upstream	Not detected	1.23±0.49
SP2	Before the sewage discharge	Not detected	1.03±0.99
% Removal		Not detected	16.26%
SP3	After the sewage discharge	8.96±5.18	16.73±22.92
SP4	Downstream	1.1549±0	0.50±0.433
% Removal		87.16%	97.01%

5.4.3 Manganese (Mn)

Manganese levels reached the highest during the dry season at the third point which is the wastewater discharge (646.14 µg/L) while the lowest levels were recorded in the downstream. There was no significant change in Mn concentration between the dry and wet seasons (p>0.05). The Mn concentration (Table 5.11) and (Appendix B.3) do not meet the irrigation water quality target range of ≤ 0.02 mg/L (DWAF, 1996). The Mn removal efficiencies of the wetlands in both season ranged between 18.51 and 66.06%. This further shows that the wetland was efficient in removing manganese. Moreover, the presence of micro-algae present in wetlands might have contributed to the reduction of Mn as stated by Leong and Chang (2020).

Table 5. 11: Percentage removal of manganese (µg/L) throughout the wetland

Sampled Points	Sites Description	Dry season	Wet season
SP1	Upstream	576.19±304.72	644.82±273.83
SP2	Before the sewage discharge	235.96±147.93	260.04±36.27
% Removal		59,04%	59,67%
SP3	After the sewage discharge	646.14±397.15	507.67±254.74
SP4	Downstream	219.86±66.08	413.7±122.81
% Removal		66.06%	18.51%

5.4.4 Iron (Fe)

Iron concentrations were generally high in the wetland (Table 5.12) and (Appendix B.4) and all the points and did not meet the irrigation's target water quality range, which is ≤ 50 µg/L (DWAF, 1996) for both dry and wet season. The wetland showed an increase in Fe concentration during the rainy season with the highest mean of 8879.3±11524.64 µg/L. There was no significant difference in Fe content between the dry and rainy seasons in the wetland. The increase in Fe concentration may have been introduced by the wastewater discharge and as it moves downstream however there was a reduction of 75.87% in the dry season and 83.12% in the wet season. The presence of micro-algae, bacteria, fungi and, macrophytes present in wetlands might have contributed to the reduction of Fe (Perera et al., 2018; Batty and Younger, 2002). The initial increase of Fe levels from the upstream sites could be due to the leaching of Fe from soil and bedrocks in the wetlands as Fe levels are generally high in the soil of the study area (Makiel et al., 2022). Higher levels were recorded after wastewater discharge which was eventually reduced by the wetlands before the water was discharged into the river.

Table 5. 12: Percentage removal of Iron (µg/L) throughout the wetland

Sampled Points	Sites Description	Dry Season	Wet Season
SP1	Upstream	256.34±209.71	1075.59±579.83
SP2	Before the sewage discharge	1154.83±736.76	2274.22±564.64
% Removal		-350%	-311.43%
SP3	After the sewage discharge	5821.9±3172.04	8879.3±11524.64

SP4	Downstream	1405.37±827.71	1498±176.34
% Removal		75.87%	83.12%

5.4.5 Cobalt (Co)

Low amounts of Co were frequently measured through the sampling period in the range of 2.22–9.07 µg/L during the dry and wet seasons (Table 5.13) and (Appendix B.5). There was a significant change in Co during the dry season and the wet season ($p<0.05$). Co concentration decreased during the rainy season, which could be attributed to dilution effect due to increased precipitation. The levels of Co increased at the third sampling point due to wastewater discharge but was subsequently reduced by the wetland in both the dry (62.88%) and the wet season (79.52%). In comparison with the study by Shibambu (2016) in the evaluation of wetland water quality in Makhado oxidation ponds, the removal of cobalt was reported to be in the range of 50.46% to 99.01%. This shows that the cobalt in this wetland was removed efficiently by the wetland. Moreover, the presence of micro-algae present in wetlands might have contributed to the reduction of Co as stated by Leong and Chang (2020).

Table 5. 13: Percentage removal of Cobalt (µg/L) throughout the wetland

Sampled Points	**Sites Description**	**Dry Season**	**Wet Season**
SP1	Upstream	9.07±1.17	3.82±2.03
SP2	Before the sewage discharge	4.52±0.38	1.91±0.47
% Removal		50.16%	50%
SP3	After the sewage discharge	23.90±3.02	10.84±9.94
SP4	Downstream	8.87±1.33	2.22±0.63
% Removal		62.88%	79.52%

5.4.6 Nickel (Ni)

Throughout the study, nickel was mostly measured in low contents in the wetland with the highest recorded concentration of 24.04 µg/L during the wet season at the third point of sampling which is after a wastewater discharge while the second sampling point recorded the lowest at 8.52 µg/L during the same season as indicated in (Table 5.14) and (Appendix B.6), and met the irrigation water quality target range of ≤ 0.2 ppm (DWAF, 1996). According to the paired-test analysis, there was no significant change between the Ni concentration during the dry and rainy seasons ($p>0.05$). The wetland showed an improvement from the upstream to the second sampling point with a reduction of 34.57% for the dry season. There was an insignificance reduction of 4.69% during the wet season and since it was a wet period and the introduction of Ni into the wetland could have been caused by runoff in the area. The concentration of Ni increased again after the third point for both seasons. However, it showed an immediate reduction to the midstream of 32.30% and 26.42% for the dry and rainy seasons. This further shows that the wetland was effective in removing the Ni as its concentration was reduced again after the wastewater was discharged into the wetland.

Table 5. 14: Percentage removal of Nickel (µg/L) throughout the wetland

Sampled Points	Sites Description	Dry Season	Wet Season
SP1	Upstream	13.65±13.80	8.94±6.37
SP2	Before the sewage discharge	8.93±4.81	8.52±13.18
% Removal		34.57%	4.69%
SP3	After the sewage discharge	12.97±16.26	24.04±16.59
SP4	Downstream	8.78±4.78	17.69±19.43
% Removal		32.30%	26.41%

5.4.7 Copper (Cu)

Copper was measured at extremely low levels and mostly it was under the limit of detection for most of the sampling points except the third sampling point which recorded the mean value of 19.94, and 6.45 µg/L during the dry and the wet season as indicated in (Table 5.15). The Cu levels at this point were due to the introduction of wastewater to the wetland and which increased the amount of Cu but immediately decreased at the final sampling point. This shows that there was metal uptake by plants, microalgae, and bacteria in the wetland before it reaches the final sampling point, and it was effective. The Cu concentration values (Appendix B.7) met the standard water quality range for irrigation set as ≤ 200 µg/L (DWAF, 1996). However, these levels exceeded the DWAF recommended limits for aquaculture (5 µg/L), and aquatic life (0.3 µg/L) (DWAF, 1996) but complied with the DWAF recommended levels of livestock watering 500- 5000 µg/L. Moreover, the results recorded in the study area were far below the SANS and WHO drinking water standards (≤ 2 000 µg/L) (SANS, 2015; WHO, 2011. The copper concentration did not demonstrate a significant change during the dry and rainy seasons ($p>0.05$). The reduction of copper was not detected as the concentration was lower for all points except SP3. According to Mengdzhi et al. (2009), Cu can be removed in a range of 69-99% in wetlands. Macrophytes, microalgae, fungi, and bacteria found in wetlands might be contributed to reducing trace metals in water.

Table 5. 15: Percentage removal of copper (µg/L) throughout the wetland

Sampled Points	Sites Description	Dry Season	Wet Season
SP1	Upstream	Not detected	Not detected
SP2	Before the sewage discharge	Not detected	Not detected
% Removal		-	-
SP3	After the sewage discharge	19.94±0.00	6.45±0.00
SP4	Downstream	Not detected	Note detected
% Removal		-	-

5.4.8 Zinc (Zn)

The level of Zinc was highest at the point after the wastewater discharge with the mean and standard deviation of 151.30±86.64 µg/L for the dry season and 170.58±174.2 µg/L for the wet season, respectively (Table 5.16). The results of this study are lower than the results presented by Rakib et al. (2022) in the surface water of a fish breeding river in Bangladesh which were 393 µg/L in the dry season and 62 µg/L in the wet season. There was no significant change in Zn concentration between the dry season and the rainy season ($p>0.05$). The value of zinc improved from the upstream to the second point of sampling for both seasons (Appendix B.8) and showed a removal efficiency of 67.07% and 48.3%. As the wetland further shows the removal of this Zn after the introduction of waste at the third point, this shows the positive effect the wetland has on the water quality as it reduces the Zn concentration in water. The removal of Zn can be in the range of 54-99% by wetland (Mengzhi et al., 2009).

Table 5. 16: Percentage removal of Zinc (µg/L) throughout the wetland

Sampled Points	Sites Description	Dry Season	Wet Season
SP1	Upstream	122.58±143.50	21.60±13.28
SP2	Before the sewage discharge	40.36±19.16	11.16±3.44
% Removal		67.07%	48.30%
SP3	After the sewage discharge	151.30±86.64	170.58±174.2
SP4	Downstream	85.60±95.42	12.89±10.6
% Removal		43.42%	92.44%

5.4.9 Arsenic (As)

Arsenic was measured at an extremely low concentration of < 1 μg/L in the wetland, and its concentration was reduced from the upstream to the second sampling point, showing that the metalloid uptake by plants in the wetland (Table 5.17) and (Appendix B.9). Arsenic in irrigation water has a target water quality range of ≤ 0.1 mg/L (DWAF, 1996), and the concentration was within that limit. The wetland did not show any significant change in arsenic between the dry and rainy seasons ($p>0.05$). There was an improvement in the arsenic concentration between the upstream and the second sampling point leading to a reduction of 88.88% and 45.45% for the dry and wet seasons. There was more removal efficiency during the dry season as compared to the rainy season as during the dry season, the discharged matter may have settled fully, allowing for plant uptake. The wetland showed positive removal for all points and this metal uptake may be due to the vegetation, micro-algae, and bacteria found in the wetland responsible for breaking down pollutants and improving the quality of water.

Table 5. 17: Percentage removal of Arsenic (μg/L) throughout the wetland

Sampled Points	Sites Description	Dry Season	Wet Season
SP1	Upstream	0.18±0.14	0.11±0.16
SP2	Before the sewage discharge	0.02±0.01	0.06±0
% Removal		88.88%	45.45%
SP3	After the sewage discharge	0.52±0.01	0.46±0.3
SP4	Downstream	0.03±0.01	0.08±0.06
% Removal		94.23%	82.60%

5.4.10 Lead (Pb)

In the wetland, lead levels were generally low with the highest concentration of 20.4 μg/L during the wet season at the third sampling point and the lowest concentration of 0.05 μg/L at the second sampling point during the dry season and were well within the target water quality range for irrigation set as of ≤ 0.2 mg/L. According to the paired t-test analysis, there was no observable difference during the dry and wet seasons ($p>0.05$). During the rainy seasons Pb increased in the wetland and again showed a huge increase in Pb concentration at the third point during the rainy season with the mean and standard value of 20.4±27.09 indicated in Table 5.18 b and (Appendix B.10). This is expected during the rainy season as runoff may have degraded matter with various chemical compositions, contributing to an increase in Pb concentration (Shibambu, 20016). The wetland showed a reduction of 31.16% to 82.6% of Pb throughout the wetland. According to Mengzhi et al. (2009), the efficient removal of Pb can be in a range of 95-99%. Its concentration varies, and its residence time has minimal bearing on it.

Table 5. 18: **Percentage removal of Lead (µg/L) throughout the wetland**

Sampled Points	Sites Description	Dry Season	Wet Season
SP1	Upstream	0.11±0.16	1.54±0.00
SP2	Before the sewage discharge	0.05±0	1.06±55.30
% Removal		54.54%	31.16%
SP3	After the sewage discharge	0.46±0.30	20.4±27.09
SP4	Downstream	0.08±0.06	7.95±6.50
% Removal		82.60%	61.02%

5.5 Major Human Activities and their Impacts along the Phangami Wetland

Anthropogenic events are the most common source of contamination and degradation alongside wetland and water resources. The wetland in the Phangami area plays an important part in the surrounding areas of Thohoyandou as it provides water to the communities and ensures there is enough water for livestock, and agricultural activities, as well as maintaining the water quality before it enters the river. However, as is the case elsewhere, the degradation of the wetland results in wetland not being able to fulfill their functions. In this chapter, the Phangami wetland was able to remove most of the trace metals as the concentration was higher downstream but was mostly high at the point before the downstream after wastewater discharge to the wetland.

More pollution was observed on the third sampling point of the wetland, just after wastewater discharge and this may have contributed to the increase in metal concentration recorded. The number of cans, tins, and bottles thrown in the wetland could be one of the causes of the increased metal concentration recorded. These metals can also be found in fertilizers, cleaning goods, and factories that are located outside of the community's wetland.

Another possibility of an increase in metals and pollution in the wetland can be the low-cost houses near the wetland, roofed with corrugated sheets around Ha Magidi village (Matodzi et al., 2021). Some of the pollutants like cement that contain toxic elements might result from the building within the wetland. The houses built within the wetland points to those more anthropogenic activities will take place as they will use the wetland as a wasteland, and a dumping place. Some of the sources of pollution in the wetland where the discharge of sewage, house construction, livestock feeding, and dumping of solid waste Figure 5.1 which increases the concentration of heavy metals within the wetland and disturbs the wetland in terms of improving the water quality.

Figure 5. 2: Anthropogenic effects along the wetland (Phangami): **A**-Sewage discharge; **B**-Livestock feeding; **C**-House built and construction waste; **D**-Solid waste.

A-sewage discharge in Phangami wetland

Along Phangami wetland, a channel discharging raw sewage direct into the wetland was observed during the period of the study.

5.6 Conclusion

The physicochemical characteristics did not alter significantly in general between the two seasons except for DO. Most physicochemical parameters were within the standard value of irrigation water, and this indicates that the water in the wetland can be used for irrigation. Although there was no significant difference in parameters between seasons, the rainy seasons were noted to record higher values for most of the parameters, and the third sampling point was found to be the one with a high amount of pollution as this was the discharge point to the wetland in both the dry and wet seasons. There was a significant reduction observed through most of the sampling points in the wetland and most trace metals were reduced along the wetland. Therefore, this concludes that the wetland was efficient in removing heavy metals by absorbing pollutants.

CHAPTER SIX: CONCLUSION AND RECOMMENDATION

6.1 Conclusion

Most of the water (physicochemical parameters) from the sampled wetlands complied with the DWAF guidelines standards for irrigation, livestock feeding, aquaculture, and the protection of aquatic life, as well as the SANS (drinking water standard) and WHO (surface water quality standard).

Lower levels of most metals were recorded in water and sediments of the wetlands across the Limpopo Province. Higher levels were generally recorded for Al, Fe and Mn. Most of the metals in the sediments recorded levels that comply with the CCME SQGs. Results from the indices computed showed that there is a likelihood of adverse ecological effect of metals on the wetland ecosystem due to the cumulative and synergistic effects of the metals.

Water quality improvement was also recorded from the detailed study performed using Phangami wetland. It was clearly shown that effluent from wastewater treatment plant adversely affect the ecological state of wetlands as higher levels of various contaminants were recorded after the discharge of wastewater effluent into the wetland. Wastewater should be treated adequately before their discharge to wetland which further helps to polish the quality before discharging such water into river systems.

6.2 Recommendations

South Africa should implement projects that teach communities about sustainable use and the significance of wetlands, as well as teach people about the indirect benefits of wetlands. The discharge of effluent from industries and wastewater treatment plants which is the major source of pollution should be regulated and monitored. Most of the wetland used as dumping sites for various types of pollutants such as construction waste, solid waste, pumpers and plastics. Then, the community in Limpopo Province should be taught about the negative effects associated with these contaminants. This will alert them about the contaminants that are not supposed to be dumped within the wetlands. With adequate funding, current and new personnel should be trained in environmental compliance monitoring and the application of laws, regulations, and policies. Therefore, measures should be put in place to reduce the further contamination of the water resources in the wetland ecosystem.

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APPENDICES

APPENDIX A: PHYSICOCHEMICAL PARAMETERS

Appendix A. 1: DO (mg/L) measurement throughout the wetland

SITES	W1	W2	W3	W4	MEAN	STDV	W5	W6	W7	W8	MEAN	STDV
	DRY SEASON						WET SEASON					
SP1	1.6	1.71	1.44	1.17	1.50	0.25	1.2	2.57	2.14	2.35	2.08	0.57
SP2	1.8	1.67	1.51	1.24	1.58	0.27	1.5	4.30	2.21	2.47	2.62	1.19
SP3	0.1	0.28	0.61	0.23	0.32	0.19	0.4	0.62	2.44	1.05	1.14	0.90
SP4	1.1	1.33	1.12	0.86	1.11	0.19	1.2	3.14	3.08	2.87	2.58	0.90

Appendix A. 2: Temperature (℃) measurement throughout the wetland

SITES	W1	W2	W3	W4	MEAN	STDV	W5	W6	W7	W8	MEAN	STDV
	DRY SEASON						WET SEASON					
SP1	20.86	23.03	16.9	21.7	20.63	2.63	18.7	20.8	18.73	21.27	19.88	1.35
SP2	21.6	25.1	18.3	22.73	21.93	2.82	18.9	20	18.03	21.76	19.67	1.60
SP3	22.7	30.2	20.03	25.76	24.67	4.36	19.6	24.14	17.06	23.5	21.07	3.34
SP4	20.16	21.5	16.8	22.28	20.18	2.42	18.2	20.23	18.36	21.53	19.58	1.60

Appendix A. 3: pH measurement throughout the wetland

SITES	W1	W2	W3	W4	MEAN	STDV	W5	W6	W7	W8	MEAN	STDV
	DRY SEASON						WET SEASON					
SP1	7.24	7.33	7.22	7.61	7.35	0.17	7.16	7.23	7.1	7.35	7.21	0.11
SP2	7.18	7.34	7.46	7.59	7.39	0.17	6.39	6.9	6.91	7.6	6.95	0.50
SP3	7.27	7.17	7.37	7.24	7.26	0.083	7.66	7.01	7.29	7.32	7.32	0.27
SP4	7.2	6.88	7.37	7.23	7.17	0.20	7.28	7.09	7.24	7.24	7.21	0.08

Appendix A. 4: Turbidity (NTU) measurement throughout the wetland

SITES	W1	W2	W3	W4	MEAN	STDV	W5	W6	W7	W8	MEAN	STDV
	DRY SEASON						WET SEASON					
SP1	27.7	18.81	22.4	30.83	22.83	3.67	26.5	3.64	16.92	8.78	13.96	9.98
SP2	18.87	19.14	11.02	19.73	15.01	4.61	18.37	7.52	12.88	8.39	11.79	4.97
SP3	92.76	136	90.53	108	102.46	22.39	979	114	148	265	376.5	406.84
SP4	9.96	13.3	10.48	23.9	11.05	1.52	33.7	6.07	15.34	9.89	16.25	12.24

Appendix A. 5: TDS (mg/L) measurement throughout the wetland

SITES	W1	W2	W3	W4	MEAN	STDV	W5	W6	W7	W8	MEAN	STDV
	DRY SEASON						WET SEASON					
SP1	390	396	363	487	409	53.94	377	385	313	300	343.75	43.46
SP2	154	218	181	245	199.5	40.10	241	219	205	218	220.75	14.93
SP3	628	590	427	626	567.75	95.44	549	828	500	544	605.25	150.12
SP4	198	246	176	273	223.25	44.20	231	225	213	230	224.75	8.26

Appendix A. 6: EC (µs/cm) measurement throughout the wetland

SITES	W1	W2	W3	W4	MEAN	STDV	W5	W6	W7	W8	MEAN	STDV
	DRY SEASON						WET SEASON					
SP1	550	567	623	692	608	64.09	540	550	446	546	520.5	49.83
SP2	260	251	277	351	284.75	45.46	350	312	297	316	318.75	22.38
SP3	930	838	645	892	826.25	126.59	793	1189	506	769	814.25	281.63

SP4	313	340	317	392	340.5	36.33	331	325	305	332	323.25	12.55

Appendix A. 7: Salinity (ppm) measurement throughout the wetland

SITES	W1	W2	W3	W4	MEAN	STDV	W5	W6	W7	W8	MEAN	STDV
	DRY SEASON						WET SEASON					
SP1	279	253	313	311	289	28.61	259	264	208	263	248.5	27.09
SP2	145	144	142	146	144.25	1.70	167	148	142	148	151.25	10.87
SP3	552	427	397	440	454	67.76	382	589	352	377	425	110.11
SP4	151	154	153	157	153.75	2.5	156	152	144	157	152.25	5.90

Appendix A. 8: BOD (mg/L) measurement throughout the wetland

SITES	W1	W2	W3	W4	MEAN	STDV	W5	W6	W7	W8	MEAN	STDV
	DRY SEASON						WET SEASON					
SP1	0.79	0.71	0.76	0.62	0.72	0.07	0.3	2.34	0.29	0.85	0.95	0.97
SP2	0.14	0.056	0.13	0.14	0.12	0.04	1.31	3.1	0.45	0.97	0.46	1.15
SP3	0.04	0.06	0.2	0	0.08	0.09	0.11	0.21	0.68	0.48	0.37	0.26
SP4	0.013	0.083	0.12	0.38	0.18	0.14	1.39	0.35	0.44	1.03	0.80	0.49

APPENDIX B: METALS DATA

Appendix B. 1: Aluminium measurement (ug/L) throughout the wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
SP1	Upstream	77.74	42.87	21.625	97.141	44.24	434.82	368.42	200.59
SP2	before the sewage discharge	52.70	83.466	73.148	103.79	226.5	159.55	213.22	412.85
SP3	After the sewage discharge	2944.6	2733.2	867.06	1357.7	11022.6	1287.67	501.66	1833.40
SP4	Downstream	144.0	11.061	116.10	381.11	321.1	112.80	146.19	204.88

Appendix B. 2: Chromium measurement (ug/L) throughout the wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
SP1	Upstream	<0.000	<0.000	<0.000	<0.000	<0.000	1.5925	1.4338	0.6679
SP2	Before the sewage discharge	<0.000	<0.000	<0.000	<0.000	1.0094	0.2825	0.3890	2.4476
SP3	After the sewage discharge	13.6089	13.099	3.282	5.8659	50.896	5.7441	1.9565	8.3082
SP4	Downstream	<0.000	<0.000	<0.000	1.1549	1.104	0.187	0.529	0.184

Appendix B. 3: Manganese measurement (ug/L) variation throughout the wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
SP1	Upstream	1000.8	546.89	476.71	280.39	551.35	953.15	429.97	421.3 8
SP2	Before the sewage discharge	53.033	252.76	223.88	414.18	233.93	312.2	236.87	257.17
SP3	After the sewage discharge	303.74	238.97	154.23	182.51	804.00	349.03	628.86	248.80
SP4	Downstream	964.53	66.037	754.14	799.87	465.95	530.79	414.10	243.96

Appendix B. 4: Cobalt measurement (ug/L) variation throughout the wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
SP1	Upstream	4.0024	1.9328	1.7623	1.3752	1.6966	6.5335	3.9832	3.0794
SP2	Before the sewage discharge	0.6240	1.3180	1.0685	1.5106	1.5514	1.8249	1.6714	2.5967
SP3	After the sewage discharge	8.3272	8.7726	2.7373	4.0652	25.478	4.6873	8.6921	4.5224
SP4	Downstream	3.0242	0.2785	2.3926	3.1754	3.1191	2.0722	2.0771	1.6173

Appendix B. 5: Iron measurement (ug/L) variation throughout the wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
SP1	Upstream	197.51	168.34	95.300	564.23	397.87	1721.4	1348.2	834.92
SP2	Before the sewage discharge	617.91	2235.7	992.31	773.40	1717.1	2319.6	2023.6	3036.6
SP3	After the sewage discharge	8460.9	8586.9	2421.9	3817.9	26114.	3903.1	1878.6	3621.5
SP4	Downstream	1630.8	345.99	1305.4	2339.3	1760.0	1444.9	1391.7	1395.4

Appendix B. 6: Nickel measurement (ug/L) variation throughout the wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
SP1	Upstream	34.193	6.3443	5.032	9.0298	5.1714	5.5374	18.460	6.6068
SP2	Before the sewage discharge	16.077	6.1729	6.0390	7.4287	2.4992	1.8716	1.4339	28.275
SP3	After the sewage discharge	13.999	11.400	3.5013	6.1813	44.909	28.717	6.6990	15.824
SP4	Downstream	2.8136	1.8652	10.529	36.648	45.200	2.7373	17.434	5.3689

Appendix B. 7: Copper measurement (ug/L) variation throughout the wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
SP1	Upstream	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000
SP2	before the sewage discharge	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000
SP3	After the sewage discharge	23.2142	16.68559	<0.000	<0.000	6.446249	<0.000	<0.000	<0.000
SP4	Downstream	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000

Appendix B. 8: Zinc measurement (ug/L) variation throughout the wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
SP1	Upstream	133.14	321.69	13.8364	21.635	41.364	12.803	16.201	16.020
S2	before the sewage scharge	45.011	58.187	13.1679	45.065	13.798	6.1054	12.535	12.194
SP3	After the sewage scharge	215.30	236.59	76.1727	77.126	79.627	71.567	431.40	99.721
SP4	Downstream	52.887	227.184	42.7492	19.541	26.088	6.1427	16.585	2.7158

Appendix B. 9: Arsenic measurement (ug/L) variation in a wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
SP1	Upstream	0.3303	0.1132	<0.000	0.0943	0.0188	0.0377	0.0283	0.3492
SP2	before the sewage discharge	0.0283	0.0094	<0.000	<0.000	<0.000	<0.000	<0.000	0.0566
S3	After the sewage discharge	0.7740	0.6324	0.3492	0.3304	0.9062	0.2737	0.2359	0.4059
S4	Downstream	<0.000	0.0377	0.0283	<0.000	0.1415	0.037	0.0094	0.1321

Appendix B. 10: Lead measurement (ug/L) variation throughout the wetland

Sites	Description	WEEK 1	WEEK 2	WEEK 3	WEEK 4	WEEK 5	WEEK 6	WEEK 7	WEEK 8
S1	Upstream	33.472	0.5168	<0.000	<0.000	<0.000	<0.000	<0.000	1.5416
S2	Before the sewage discharge	3.9234	<0.000	6.0159	<0.000	0.2576	<0.000	96.583	1.0633
S3	After the sewage discharge	6.23212	5.45682	15.214	33.035	17.847	4.4754	3.7229	7.9402
S4	Downstream	14.7873	<0.000	<0.000	<0.000	0.6083	9.3175	51.282	<0.000