QUANTITATIVE AND HEALTH RISKS ASSESSMENTS OF SELECTED HEAVY METALS IN OGBA RIVER, BENIN CITY, NIGERIA

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AN UNDERGRADUATE DISSERTATION SUBMITTED TO THE DEPARTMENT OF ENVIRONMENTAL MANAGEMENT AND TOXICOLOGY, FACULTY OF LIFE SCIENCES, UNIVERSITY OF BENIN, BENIN CITY, EDO STATE, NIGERIA; IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR AWARD OF BACHELOR OF SCIENCE (B.Sc.) DEGREE IN ENVIRONMENTAL MANAGEMENT AND TOXICOLOGY

OCTOBER, 2025.

CERTIFICATION

This is to certify that this research titled "**Quantitative and Health Risks Assessments of Selected Heavy Metals in Ogba River, Benin City, Nigeria"** was carried out by **INEGBENEHI FAVOUR EGHONGHON (MISS)** and presented to the Department of Environmental Management and Toxicology, Faculty of Life Sciences, University of Benin, Benin City; in partial fulfilment of the requirements for the award of Bachelor of Science (B.Sc.) in Environmental Management and Toxicology. It was conducted under suitable conditions, was carefully supervised and subsequently approved as having met the requirements for the award of a Bachelor of Science degree in Environmental Management and Toxicology.

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DATE

Prof. (Mrs.) E. T. Aisien
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DATE

DECLARATION

I **INEGBENEHI FAVOUR EGHONGHON (MISS)** declare that "**Quantitative and Health Risks Assessments of Selected Heavy Metals in Ogba River, Benin City, Nigeria"** is my work and that all sources that I have used or quoted have been acknowledged using complete references and that this work has not been submitted before for any other degree at any other University.

INEGBENEHI FAVOUR EGHONGHON **DATE**

DEDICATION

This work is dedicated to God Almighty for His divine guidance, strength, and protection throughout the course of this project.

ACKNOWLEDGEMENT

I wish to express to my deepest and profound gratitude to Almighty God for His grace, guidance, sustenance, and protection over me throughout the period of my study.

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ABSTRACT

Heavy metal contamination of freshwater bodies poses a significant environmental and public health concern, particularly in urban regions with increasing anthropogenic activities. This study aimed to evaluate the concentrations and health risks of selected heavy metals in the Ogba River, Benin City, Nigeria. Water samples were collected across three locations (upstream, midstream, and downstream) over three months to assess both spatial and temporal variations. The samples were analyzed for copper (Cu), chromium (Cr), nickel (Ni), lead (Pb), manganese (Mn), and cadmium (Cd) using an atomic absorption spectrophotometer. The data were analysed using SPSS version 22, and descriptive statistics and one-way ANOVA were employed to assess variations, with $p < 0.05$ considered statistically significant. Results revealed that Ogba River water showed elevated levels of Cr, Ni, Pb, Mn, and Cd, often exceeding WHO and, in some cases, NESREA permissible limits, while Cu remained within safe limits. Children had higher Chronic Daily Intake (CDI) values than adults. Hazard Quotient (HQ) indicated low risk for Cu, Ni, and Mn, but potential non-carcinogenic risk from Cr, Cd, and Pb. Combined Hazard Index (HI) exceeded 1 at all stations, with children more vulnerable. Incremental Lifetime Cancer Risk (ILCR) for Cr, Cd, and Pb surpassed USEPA limits, with Cr posing the highest cancer risk. In conclusion**,** Ogba River is contaminated with heavy metals exceeding safe limits and posing health risks, particularly to children. Immediate monitoring and pollution control are needed to protect human health and the river ecosystem.

CHAPTER ONE

1.0. INTRODUCTION

Water bodies around the world play different roles in supporting ecosystems and human settlements (Dubois *et al*., 2018). Rivers, in particular, serve as an interface between the environment and human activity. They support biodiversity, provide potable water, irrigate farmlands, sustain fisheries, and enable economic development in the communities they pass through (Wang and He, 2022). However, the growing pressures of industrialization, population expansion, and poor waste disposal practices have increasingly exposed river systems to pollution, affecting their ecological integrity (Choudhury *et al*., 2022). Among the various pollutants threatening the health of riverine systems, heavy metals have emerged as a group of particularly concerning contaminants due to their persistence, toxicity, and bioaccumulative properties (Kumar *et al*., 2022).

Heavy metals refer to metallic elements that have relatively high atomic weights and densities. These include, among others, lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), copper (Cu), arsenic (As), manganese (Mn), nickel (Ni), and zinc (Zn) (Balali *et al*., 2021). While some of these metals are essential micronutrients at trace levels, excessive concentrations in aquatic systems can result in toxic effects to both aquatic organisms and human consumers (Kolarova and Napiórkowski, 2021). Unlike many organic pollutants, heavy metals do not degrade or disintegrate over time; rather, they accumulate in sediments and biological tissues, posing long-term environmental and health hazards. Their continuous presence in water bodies means that even passive discharges or minor contamination that accumulates can lead to chronic exposure risks (Tufail *et al*., 2022).

Sources of heavy metals in aquatic systems are many and often related. These include industrial sources, improper disposal of electronic waste, leaking sewage systems, runoff from agricultural lands, and atmospheric deposition from vehicle exhausts (Saravanan *et al*., 2024). In regions with limited regulations, these sources often go unchecked, leading to gradual and often unnoticed degradation of river systems. As rivers pass through urban and rural landscapes, they act as collectors of materials from these various sources, often transporting contaminants across long distances (Mishra, 2023). In developing countries such as Nigeria, the rapid pace of urban development and insufficient environmental infrastructure has significantly increased the risk of water pollution. The expansion of cities often outpaces the development of waste treatment facilities, resulting in the discharge of untreated or poorly treated wastewater into nearby rivers (Aliyu and Amadu, 2017). Similarly, the use of chemical fertilizers and pesticides in agriculture, without proper controls or education, leads to runoff that introduces harmful substances into aquatic ecosystems. In such settings, rivers become both lifelines for communities and receivers of their waste (Weldeslassie *et al*., 2018). More so, climate and seasonal patterns influence the distribution and concentration of heavy metals in river systems. During the rainy season, increased runoff can introduce large amounts of metals from surface sources, diluting or elevating their concentrations depending on the volume and nature of the pollutants. In contrast, during the dry season, lower water levels can lead to higher concentrations of metals due to reduced dilution (Nguyen *et al*., 2020).

The Ogba River is a prominent river located in Edo State, southern Nigeria. It flows through several communities, including parts of Benin City, one of Nigeria's major urban centers. The river holds great importance for residents along its banks, serving domestic, agricultural, recreational, and in some cases, spiritual purposes. Its accessibility makes it a convenient source of water for washing, bathing, irrigation, and fishing. However, this same accessibility makes it vulnerable to various forms of anthropogenic influence (Enaruvbe and Atafo, 2019). The encroachment of informal settlements, markets, automobile workshops, and small-scale industries along its course has increased the volume and diversity of waste entering the river

(Onyima *et al*., 2025). With the growing human population and corresponding economic activities along the Ogba River, the quality of its water has come under increasing pressure. Residences that lack proper sewage systems often discharge waste into nearby drainage channels that feed into it (Enaruvbe and Atafo, 2019). Moreover, roadside mechanics and auto repair workshops with proximity to the river contribute used engine oil, metal scrap, and battery acid to the runoff during rainfall. These materials are rich in heavy metals such as lead, cadmium, and chromium (Gupta, 2020). Similarly, the use of phosphate-rich fertilizers and herbicides in nearby agricultural lands results in the introduction of metals like arsenic and zinc through leaching and runoff (Akhtar *et al*., 2021).

This study was carried out to assess the selected heavy metals levels in the Ogba River and evaluate the associated health risks posed to locales that rely on it as a source of water for drinking and other domestic purposes. The precarious challenge of residents using the water is due to the failed infrastructure and the collapse of the Edo State Water Works. In the absence of alternative water sources, people are left with little choice but to use polluted water for everyday activities (Yeboah *et al*., 2024). Despite the visible decline in water quality, lack of awareness and limited health literacy mean that many residents may not recognize the risks they are exposed to. In such settings, education plays a role in changing behaviour and promoting practices that reduce pollution and exposure (Simonds *et al*., 2019). Hence, monitoring the levels of heavy metals in rivers like Ogba is a necessary step toward public health protection. The study will provide an empirical basis for understanding the current state of the water body and tracking changes over time. Also, it will help to identify pollution hotspots and determine which activities are most responsible for the contamination. Therefore, the results of the study can be used to raise awareness among community members, promote safer practices, and guide the formulation of sustainable water resource management strategies. In essence, this study will contribute to both environmental protection and public health improvement.

1.1. Aim and Objectives of Study

This study aims to assess the concentrations of selected heavy metals in the Ogba River and evaluate the associated health risks.

The specific objectives of the study are:

1. To determine the concentrations of selected heavy metals (Cu, Cr, Ni, Pb, Mn, and Cd) in water samples from the Ogba River.
2. To evaluate the spatial variation of selected heavy metals across upstream, midstream, and downstream stations of the Ogba River.
3. To assess the temporal variation of selected heavy metals in the Ogba River water.
4. To compare the concentrations of heavy metals with the World Health Organization (WHO) permissible limits to determine compliance and potential health risks.
5. Assess the non-carcinogenic and carcinogenic health risk indices for the heavy metals.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1. Heavy Metals

Metals are naturally occurring elements found throughout the environment. They are substances with high electrical conductivity and readily lose electrons to form positively charged ions known as cations. Metals are present in various parts of the earth, including the atmosphere, the earth's crust, water bodies, and within living organisms such as plants and animals. Of the 35 naturally existing metals, 23 are considered heavy metals because they have a specific density greater than 5 g/cm^3 and an atomic weight exceeding 40.04 (Duffus, 2021). These heavy metals include Cu, Cr, Ni, Pb, Mn, and Cd (Duffus, 2021). Heavy metals are known not only for their high density but more importantly for their toxic effects on the environment and living organisms (Li *et al*., 2017).

Certain heavy metals, such as Co, Cr, Cu, Fe, Mg, Mo, Mn, Ni, Se, and Zn, are considered essential nutrients because they support various physiological and biochemical processes in the human body. When present in insufficient amounts, these metals can lead to deficiency-related diseases or syndromes. However, when consumed in excessive quantities, they may cause acute or chronic toxicity (Li *et al*., 2017). Many toxic heavy metals, including Pb, Tl, Cd, and Sb, are commonly associated with industrial activities and significantly contribute to environmental pollution. Thallium, although less common in nature, has more severe toxic effects than many other heavy metals and is known to cause hair loss (alopecia) in humans (Karbowska, 2016). The harmful impacts of heavy metals often surpass their benefits. For instance, high levels of Sb and Cr exposure have been linked to cancer development (Sun *et al*., 2015), Pb poisoning can result in intellectual impairment in children, Hg exposure causes Minamata disease, and Cd poisoning leads to itai-itai disease. Additionally, heavy metals may damage specific organs, causing kidney, liver, nervous system, skin, and cardiovascular toxicity. To minimize the risk of such toxic effects, it is essential for individuals to limit their exposure, particularly by avoiding industrial zones with high heavy metal emissions (Hou *et al.*, 2013). Due to their wide use in household, industrial, and agricultural activities, the extensive presence of metals in the environment poses significant concerns about their potential impact on human health. While exposure to large amounts of metals, such as in occupational settings, can lead to toxicity affecting several organ systems, the seriousness of the health effects depends on various factors. These include the specific type and chemical form of the metal, the route and length of exposure, and, importantly, an individual's level of vulnerability (Jan *et al.*, 2011). In terms of a health perspective, the pathophysiology of metals depends primarily on the generation of oxidative stress, which is characterized by;

(a) Increased Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) production;

(b) Depletion of intracellular antioxidant stores and free-radical scavengers; and

(c) Inhibition or reduction of the activity of enzymes that contribute significantly to the metabolism and detoxification of reactive oxygen species (Jan *et al.*, 2011).

Many treatment procedures have been developed to counteract the toxicity of heavy metals. Natural products are being efficiently used to treat the adverse consequences (Tchounwou *et al.*, 2012). Medicinal herbs and natural products for the treatment of various diseases have been around for almost the entire history of mankind. One of the most significant advantages of traditional or plant-based medicine seems to be its perceived effectiveness, as well as its low frequency of severe adverse responses and its relatively cheap cost. Experimentally induced heavy metal toxicity in laboratory animals was significantly reduced using a variety of medicinal herbs and natural products (Bhattacharya, 2018).

2.1.1. Classification of Heavy Metals

Heavy metals have been classified into two types: essential and non-essential. Essential Heavy metals are less toxic at low concentrations, and they act as a coenzyme in biological processes. For example, hemoglobin and myoglobin consist of Fe, while vitamin B12 consists of Co. Non-essential heavy metals are highly toxic even at very low concentrations; they are non-biodegradable and cause severe toxic effects to living organisms (Kim *et al.*, 2019).

Table 2.1. Classification of Heavy Metals (Kim *et al.*, 2019).

Essential (Harmless)	**Non-Essential (Toxic)**
Zinc (Zn)	Chromium (Cr)
Copper (Cu)	Lead (Pb)
Iron (Fe)	Arsenic (As)
Cobalt (Co)	Mercury (Hg)
	Cadmium (Cd)

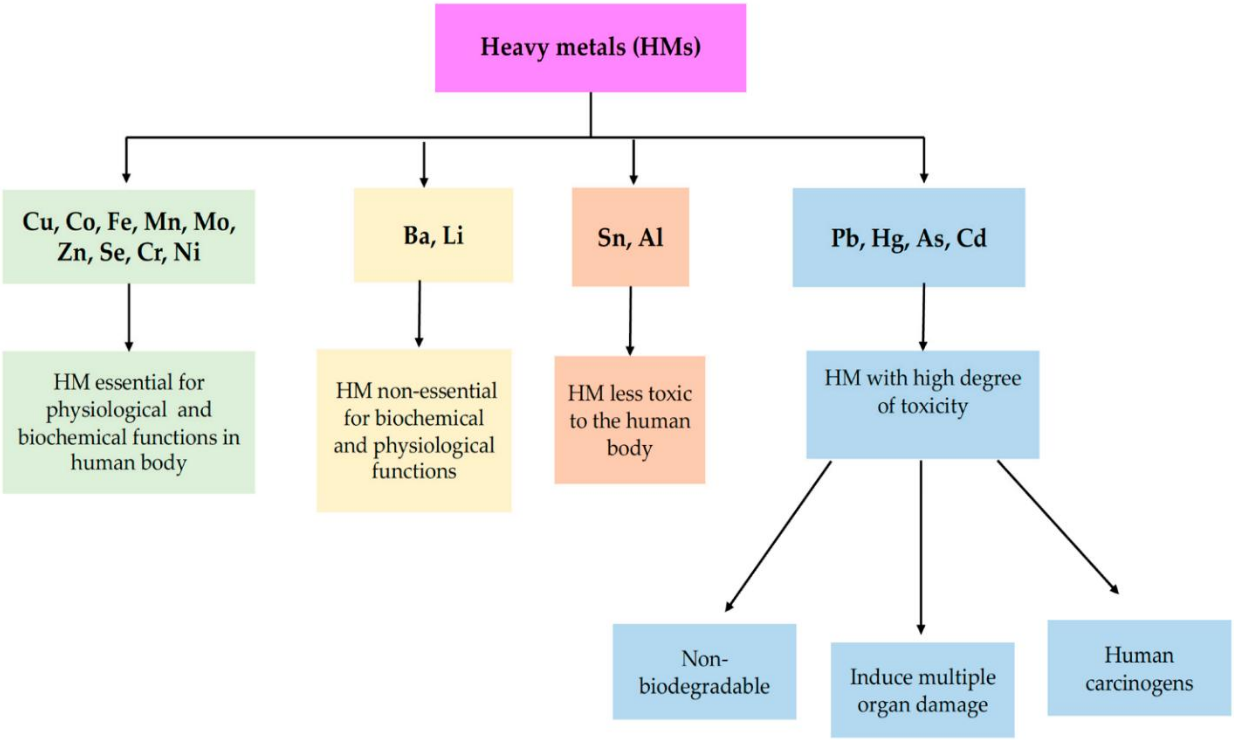

Figure 2.1: Classification of heavy metals based on their role in the human body (Filipoiu *et al*., 2022)

2.2. Sources of Human Exposure to Heavy Metals

Heavy metals are naturally found in the environment, but the major sources of human exposure are linked to human activities such as mining, industrial operations, agricultural practices, improper disposal of solid waste, discharge of municipal wastewater, and incineration (Rahimzadeh *et al.*, 2017). In the Earth's crust, heavy metals are present as ores and are extracted as minerals through mining. Some heavy metals, Fe, Zn, As, Co, Ni, and Pb, are commonly found in sulphide ores, while others, such as Mn and Al, are typically present in oxide forms. Additionally, metals like Co, Fe, and Cu can occur in both oxide and sulphide forms. During mining, these metals are released into the environment, where they accumulate in soil and are transported through the air and water to residential areas (Ohiagu *et al.*, 2016). Industrial activities also release heavy metals into the air during combustion and into the soil and water bodies through waste discharge. Various industrial products, including batteries, coatings, cosmetics, and paints, contain heavy metals and serve as additional exposure sources. These metals are further spread through environmental processes such as erosion, surface run-off, and acid rain (Engwa *et al.*, 2015). In agriculture, the use of fertilizers, herbicides, pesticides, manure, wastewater for irrigation, and other soil enhancement methods contributes to heavy metal contamination. These practices result in the build-up of toxic metals in the soil and air, which are absorbed by plants and later enter the human body through food consumption (Enyoh *et al.*, 2020).

2.3. Heavy Metals and the Environment

Heavy metals are naturally present in the environment and are essential in small amounts for biological functions, but they can become harmful when they accumulate in living organisms. Common environmental heavy metal pollutants include Hg, Cd, As, Cr, Ni, Cu, and Pb (Hayat *et al.*, 2018). Cadmium is introduced into the environment through both natural processes and human activities. It can enter the aquatic system via industrial discharges, runoff, and accumulation in soil and sediments. Humans and animals can be exposed to Cd through various routes, including contaminated food, water, and air. Cadmium has no known beneficial role in plant metabolism or growth (Hayat *et al*., 2018).

Mercury is another highly toxic heavy metal found throughout the biosphere. Its presence in the atmosphere is increasing due to human activities. In aquatic environments, mercury can transform into methylmercury, a highly poisonous form, when it interacts with sediments (Gworek *et al*., 2020). Methylmercury enters the human body mainly through consumption of fish, seafood, or wildlife that have accumulated the toxin from contaminated microorganisms. Once absorbed, it enters the bloodstream and can lead to various neurological disorders (Rice *et al*., 2014). Lead, a naturally occurring but non-biodegradable metal, is typically found in low concentrations in nature. However, its levels in the environment are rising due to human actions such as industrial production, mining, and the burning of fossil fuels. Exposure to Pb in amounts above safe limits poses serious health risks. Children are especially vulnerable, and their contact with lead-contaminated dust can result in more severe cases of lead poisoning (Loh *et al*., 2016).

Manganese is one of the most abundant toxic heavy metals and occurs in different oxidation states in the natural environment. When methylcyclopentadienyl manganese tricarbonyl (MMT), a fuel additive, is burned, manganese oxides are released into the atmosphere. While Mn plays important roles in various bodily functions, excessive exposure can lead to significant health risks (O'Neal and Zheng, 2015). Chromium is both toxic and carcinogenic. In nature, it is typically found in two stable oxidation forms: Cr (III) and Cr (VI). Among the two, Cr (III) is considered less dangerous. These forms can transform into one another during industrial processes, although the conversion of chromium (VI) to chromium (III) is less harmful due to the reduced toxicity of chromium (III) (O'Neal and Zheng, 2015). Cobalt has both positive and negative effects on human health. In small amounts, it is usually harmless, but high levels released into the environment can lead to serious health outcomes, including death. Nickel is a naturally occurring metal with widespread industrial applications. It is released into the environment from both natural sources and human activities (Li *et al.*, 2016a). Exposure to Ni has been linked to numerous health problems, including allergic reactions, respiratory cancers, and damage to the kidneys and heart due to inhalation of contaminated air (Genchi *et al.*, 2020).

Copper is an essential trace element required for proper biological functions. It supports vital plant processes such as chlorophyll production, photosynthesis, and carbohydrate and protein metabolism. A lack of copper disrupts these functions, while excessive amounts can lead to toxicity (Schwartz *et al.*, 2003). Zinc is a widely distributed essential metal involved in numerous enzymatic reactions, acting as a cofactor. The toxic effects of zinc depend on the exposure route and quantity. Major sources of Zn in the environment include smelting and mining activities. A significant portion of Zn pollution comes from mineral processing, which impacts both ecosystems and living organisms (Zhang *et al.*, 2012).

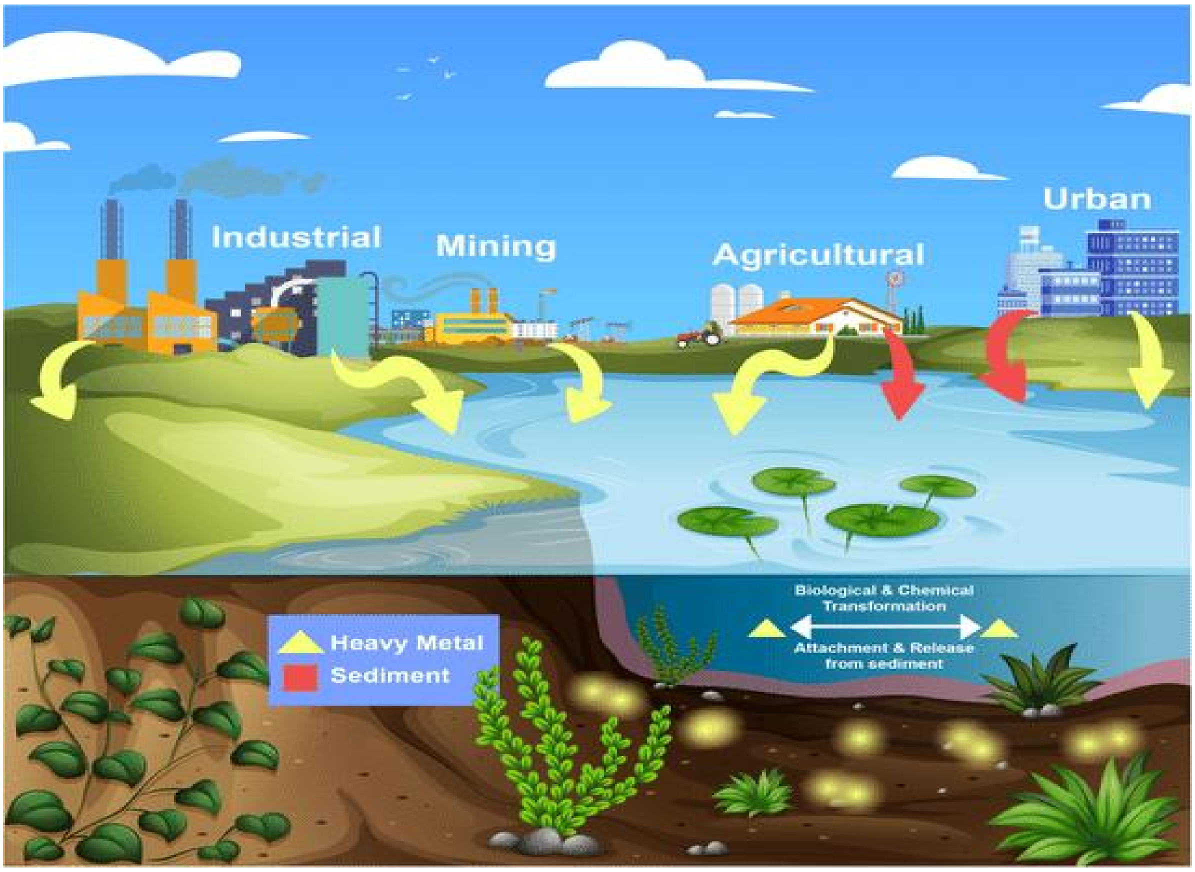

Figure 2.2: Heavy Metals and the Environment (Mishra *et al*., 2022)

2.4. Heavy Metals and the Aquatic Environment

Heavy metals in aquatic environments pose significant environmental and health concerns due to their persistence and toxicity. Once introduced into water bodies, these metals tend to bind with suspended particles and settle into sediments, creating long-term reservoirs of contamination. The behaviour and fate of heavy metals in aquatic systems are influenced by various physicochemical factors such as pH, temperature, redox potential, and the presence of organic matter (Ali *et al*., 2019). For example, lower pH levels often increase the solubility of metals, making them more bioavailable and toxic to aquatic organisms (Brezonik *et al*., 2020). These metals can accumulate in sediments and aquatic organisms through processes like adsorption and uptake, leading to bioaccumulation and biomagnification along the food chain (Ali and Khan, 2019). Fish and other aquatic species can concentrate metals in their tissues, which not only affects their health and reproductive capabilities but also poses risks to humans and wildlife that consume them (Isangedighi and David, 2019). Chronic exposure to heavy metals in aquatic environments has been linked to disruptions in enzyme activity, oxidative stress, and even genetic mutations in aquatic organisms. Moreover, heavy metals can affect the microbial communities in water and sediments, altering nutrient cycling and ecosystem functioning (Nowicka, 2022). Due to their non-biodegradable nature, heavy metals remain in the environment for extended periods, and their concentrations can fluctuate seasonally, often increasing during rainy seasons because of runoff and erosion. These factors collectively make heavy metal pollution in aquatic environments a complex challenge that requires continuous monitoring and effective management strategies to protect both ecosystem health and public safety (Girgis *et al*., 2019).

2.5. Sources of Heavy Metals in Rivers

2.5.1. Natural Sources (Geological Weathering, Soil Erosion)

Heavy metals naturally enter rivers through processes such as geological weathering and soil erosion. Over time, the breakdown of rocks and minerals releases metals like copper, zinc, and nickel into surrounding soils and water bodies (Wu *et al.*, 2020). Rainfall and surface runoff then transport these metals into rivers, especially during heavy rains when soil erosion intensifies. While these natural contributions are usually gradual and occur within a balanced ecosystem, they establish a baseline level of metals in the water. However, natural events such as landslides or volcanic activity can lead to sudden increases in metal concentrations (Zhang and Wang, 2020).

2.5.2. Anthropogenic Sources

1. **Industrial Discharges**: Industrial activities are major contributors to heavy metal pollution in rivers. Factories involved in mining, metal processing, chemical manufacturing, and textile production often release wastewater containing heavy metals directly into nearby water bodies (Mokarram *et al.*, 2020). Without proper treatment, this wastewater can contain toxic levels of metals such as lead, cadmium, chromium, and mercury. These metals accumulate in river sediments and aquatic organisms, posing significant risks to ecosystems and human health (Xia *et al.*, 2018). In many developing regions, enforcement of environmental regulations is weak, and untreated or poorly treated industrial effluents continue to degrade water quality. The proximity of industries to rivers often makes these waterways the primary recipients of heavy metal contamination (Xiao *et al.*, 2021).
2. **Agricultural Runoff (Fertilizers, Pesticides)**: Agricultural activities contribute to heavy metal contamination in rivers mainly through runoff from fertilizers and pesticides. Many chemical fertilizers contain trace amounts of metals like As, Cd, and

Pb, which can leach into the soil and eventually reach water bodies through rainwater runoff (Kaur and Sinha, 2019). Similarly, pesticides and herbicides may contain heavy metals as active ingredients or impurities. When applied excessively or improperly, these chemicals wash into rivers and streams, introducing toxic substances that can harm aquatic life. Agricultural runoff often increases during the rainy season, carrying sediments and metals from farmlands into nearby rivers, thus influencing both water quality and sediment composition (Soleimani *et al.*, 2023).

3. **Domestic Sewage and Waste Disposal**: The discharge of untreated or partially treated domestic sewage is another significant source of heavy metals in rivers. Household wastewaters often contain metals originating from household products, plumbing materials, detergents, and discarded electronics (Tariq and Mushtaq, 2023). In communities lacking adequate sanitation infrastructure, sewage is frequently discharged directly into rivers or through drainage systems that empty into water bodies (Kebonye *et al.*, 2017). Solid waste dumping, including batteries, paint cans, and other metal-containing refuse, also contributes to heavy metal pollution when rains wash these contaminants into rivers. This continuous input of metals from domestic sources exacerbates pollution levels, especially in densely populated urban areas (Kumar *et al.*, 2023).
4. **Urbanization and Informal Settlements**: Rapid urbanization and the growth of informal settlements near riverbanks often lead to increased heavy metal pollution. These settlements typically lack proper waste management systems, resulting in the disposal of domestic and industrial wastes directly into nearby rivers (Gqomfa *et al.*, 2023). Runoff from roads and urban surfaces can carry metals from vehicle emissions, tire wear, and construction materials into water bodies. Informal workshops and small-scale industries operating within these areas add to the contamination load by

releasing untreated waste. The combined effect of these activities in urban areas significantly alters the chemical composition of rivers, reducing water quality and increasing health risks for residents (Gqomfa *et al*., 2022).

5. **Small-Scale Industries and Automobile Workshops**: Small-scale industries and automobile repair workshops, commonly located along riverbanks, contribute heavily to heavy metal contamination. These establishments generate waste containing metals such as Pb, Cd, and Cr from battery disposal, used engine oil, brake pads, and metal scraps (Deb *et al*., 2021). In many cases, waste disposal practices are informal and unregulated, with contaminants directly entering rivers through runoff or accidental spills. The heavy metals from these sources accumulate in sediments and aquatic organisms, leading to toxic conditions. Because these activities are often scattered and numerous, they can collectively cause significant pollution that is difficult to control without targeted interventions (Bansah *et al*., 2018).

2.6. Common Heavy Metals of Concern in Water Bodies

2.6.1. Mercury (Hg)

Mercury is regarded as the most toxic among the heavy metals and has become increasingly present in the environment due to human-related activities such as agriculture, municipal wastewater discharge, mining, incineration, and industrial wastewater release (Jan *et al*., 2009). It occurs in the environment in various forms, each with different levels of toxicity and bioavailability. These include elemental or metallic mercury, inorganic salts, and organic mercury compounds. In its elemental form, Hg appears as a liquid metal. It has been widely used in devices for measuring temperature, such as thermometers and pyrometers, in mercury arc and fluorescent lamps, and as a catalyst. Its applications also extend to battery production, industrial processes such as those in the pulp and paper industry, and notably in dental amalgams.

Mercury enters the atmosphere primarily through activities like mining and the combustion of materials. It reaches water bodies and soil through erosion of natural sources, industrial discharges, and runoff from landfill areas. Once inhaled, the average half-life of mercury in the human body is around 60 days. Exposure to high levels of metallic mercury can lead to a range of health issues, including damage to the lungs, irritation of the mucous membranes, nausea, vomiting, diarrhea, skin reactions, increased heart rate or blood pressure, kidney problems, and serious neurological disorders (Asano *et al.*, 2000). Intellectual disorder that leads to behavioural changes, anxiety, depression, tremors, and reduced coordination of muscles are common neurological symptoms. Inorganic mercury exists either as mercuric (Hg^{2+}) or mercurous (Hg^{+}) form. Having greater solubility in water, their toxic consequences are much greater compared with the elemental (Hg). Inside the body, it has a half-life of 40 days (Bates, 2003).

2.6.2. Arsenic (As)

Arsenic is a naturally occurring metalloid that is widely distributed throughout the environment. Although it ranks as the 20th most abundant element in the Earth's crust, it is considered the most hazardous substance in terms of public health risk. Its widespread presence in elemental, inorganic, and organic forms across the globe makes it one of the most concerning environmental and health-related metals (Hughes *et al.*, 2011). Arsenic is found in more than 200 mineral forms, with about 60% existing as arsenates (AsV), 20% as sulfides or sulfosalts, and the remaining 20% as arsenites, arsenides, oxides, silicates, and elemental arsenic (Mandal and Suzuki, 2002).

Natural sources of arsenic include volcanic eruptions, rock weathering, geothermal water, and forest fires. Besides these natural pathways, human-related activities such as the use of arsenic in animal feed, the production of glass and ceramics, application of herbicides and pesticides, wood preservation, and various metallurgical processes contribute significantly to arsenic pollution. Humans are commonly exposed to arsenic through soil, air, water, and food (Kaur *et al.*, 2011). Marine-based food products often contain high levels of arsenic, and rice, a globally consumed food, frequently carries As, making dietary exposure more common. This is especially concerning for infants who rely heavily on rice-based baby foods. According to the World Health Organization (WHO), the safe limit for the As in white rice is 200 µg/kg, while brown rice has a maximum allowable limit of 400 µg/kg (Sohn, 2014). Arsenic is classified as a Group I carcinogen, and its contamination in drinking water represents a major environmental and health crisis worldwide. Countries such as Bangladesh, India, and China have reported widespread arsenic-related water toxicity (Kulshrestha *et al.*, 2014). It is estimated that approximately 200 million people are exposed to arsenic mainly through contaminated drinking water that exceeds the recommended safety limits (Ramos-Chavaz *et al.*, 2015).

2.6.3. Lead (Pb)

Lead, a toxic element of significant health concern, has been introduced into the environment in large amounts through human activities, despite its naturally low geochemical mobility. This has resulted in its widespread distribution across the globe (Oehlenschläger, 2002). In deep ocean waters, Pb concentrations range from about 0.01 to 0.02 µg/L, while in surface ocean waters, levels are approximately 0.3 µg/L (Castro-González and Méndez-Armenta, 2008). Today, Pb is still used in various applications such as roofing sheets and protective screens against X-rays and radioactive emissions. Like many other pollutants, lead is widespread and can exist in the environment as metallic Pb, inorganic ions, or salts (Oehlenschläger, 2002). Lead serves no essential biological function in humans. Major sources of human exposure to Pb include food, air (especially from lead dust originating from petrol), and drinking water. Plants can become contaminated by absorbing Pb from the air and soil, and animals may consume these contaminated plants. Humans, in turn, may ingest

Pb through consuming contaminated plant or animal products. Additional exposure may occur by using containers or pottery glazed with lead-based materials. In humans, approximately 20 to 50 percent of inhaled inorganic Pb and 5 to 15 percent of ingested inorganic Pb is absorbed. Organic Pb compounds are more readily absorbed, with about 80 percent of inhaled organic Pb and a significant portion of ingested organic Pb entering the body. Once absorbed, Pb circulates in the bloodstream and is distributed across soft tissues, blood, and mineralizing tissues such as bones and teeth. In adults, over 95 percent of the body's total Pb burden is stored in bones and teeth. Children are particularly vulnerable to Pb exposure due to their faster growth and metabolism, which makes their developing nervous systems especially susceptible to damage (Castro-González and Méndez-Armenta, 2008).

2.6.4. Chromium (Cr)

Chromium is a naturally occurring heavy metal found in the earth's crust and in seawater, and it is frequently used in various industrial processes (Tchounwou *et al*., 2012). It exists in several oxidation states, ranging from –2 to +6, but the trivalent (Cr III) and hexavalent (Cr VI) forms are the most stable and commonly encountered in the environment. While Cr (III) plays an essential role in trace amounts for normal lipid and protein metabolism, including acting as a cofactor in insulin function (Vincent, 2019), Cr (VI) is highly toxic and has been associated with numerous health disorders. The International Agency for Research on Cancer (IARC) has classified hexavalent Cr as a Group I occupational carcinogen, indicating a strong link to cancer in exposed individuals (Loomis *et al*., 2018). Outside occupational settings, the general population is primarily exposed to Cr through the ingestion of contaminated food and water or through skin contact with chromium-containing products (Nickens *et al*., 2010). Industrial activities such as metallurgy, chemical manufacturing, and refractory production contribute significantly to Cr pollution, releasing large quantities of the metal into the air, soil, and groundwater. Over time, Cr can bioaccumulate in the human body, leading to a variety of health issues. These include skin conditions, kidney damage, neurological disorders, gastrointestinal problems, and an increased risk of cancers affecting organs such as the lungs, bladder, kidneys, bone, and thyroid (Fang *et al*., 2014).

2.6.5. Cadmium (Cd)

Cadmium, though relatively uncommon, occurs naturally in the environment, particularly in soil and mineral forms such as sulphides, sulphates, carbonates, chlorides, and hydroxides, as well as in water sources. Industrial operations can significantly increase Cd levels in air, water, and soil, thereby elevating human exposure to this toxic metal (Jiang *et al*., 2015). One of the primary routes of Cd intake is through the consumption of contaminated food. Additionally, cigarette smoking has been identified as a major contributor to Cd accumulation in the body, often resulting in higher levels in the blood and urine. The presence of cadmium in polluted water can interfere with essential biological processes and may lead to a range of short- or long-term health problems (Cao *et al*., 2018). According to the International Agency for Research on Cancer (IARC), Cd is classified as a Group 1 carcinogen, indicating that it is cancer-causing in humans (Kim *et al*., 2020). Individuals working in industries such as battery manufacturing, alloy production, glass making, and electroplating are at particular risk of occupational exposure. Due to these risks, some countries regularly monitor airborne Cd levels to protect public health. Studies have also shown that staple foods like rice, grains, and seafood can be contaminated with cadmium, posing a dietary risk (Chunhabundit, 2016).

2.6.6. Nickel (Ni)

Nickel is a naturally occurring metal that enters aquatic environments through both geological and human-driven processes. It can be released into rivers through weathering of rocks and soils, but industrial sources such as electroplating, mining, stainless steel production, and fossil fuel combustion often contribute more significantly to elevated nickel levels in water. In aquatic systems, Ni exists in both particulate and dissolved forms, and its mobility is influenced by factors such as pH, salinity, and organic matter content (Genchi *et al.*, 2020). While trace amounts of Ni are essential for certain biological processes in plants and animals, excessive exposure can be toxic. In humans, high concentrations of Ni may lead to allergic reactions, respiratory issues, and potential carcinogenic effects, particularly through inhalation or ingestion of contaminated water or food. The bioaccumulation of Ni in aquatic organisms also raises ecological concerns, as it may disrupt aquatic food webs and affect biodiversity (Begum *et al.*, 2022).

2.6.7. Cobalt (Co)

Cobalt is a trace element that can enter river systems through both natural processes and anthropogenic activities such as mining, smelting, and the disposal of electronic and industrial waste (Barrio *et al.*, 2018). Although Co is essential in small amounts for vitamin B12 synthesis and metabolic functions in humans and animals, excessive concentrations in aquatic environments can be harmful. Elevated Co levels can originate from industrial effluents, especially from metal processing and battery manufacturing plants (Genchi *et al.*, 2023). In rivers, Co can bind to sediments or remain in dissolved form, depending on environmental conditions like redox potential and organic content. Chronic exposure to cobalt-contaminated water may affect aquatic life by impairing reproductive and enzymatic functions. In humans, excessive intake can lead to cardiomyopathy, thyroid dysfunction, and neurological effects (Genchi *et al.*, 2023).

2.6.8. Copper (Cu)

Copper is commonly used in electrical wiring, plumbing, and industrial machinery, and as such, it often finds its way into river systems through industrial discharges, corrosion of copper-containing pipes, and agricultural runoff from fungicide use (Roy *et al.*, 2018). Although Cu is an essential trace element involved in enzymatic functions in both humans and aquatic organisms, its excessive presence in water can be highly toxic (Kaur *et al.*, 2023).

In aquatic environments, elevated Cu levels can damage fish gills, disrupt reproductive cycles, and inhibit the activity of microorganisms crucial for nutrient cycling. In humans, long-term exposure to high copper levels through drinking water can cause gastrointestinal irritation, liver and kidney damage, and, in extreme cases, neurological problems. The toxicity of Cu is influenced by water hardness and pH, with soft, acidic waters generally increasing its bioavailability and harmful effects (Teschke, 2024).

2.6.9. Zinc (Zn)

Zinc is a metal widely used in galvanization, alloy production, and various industrial processes. It often enters aquatic environments through industrial effluents, mining activities, and runoff from agricultural lands treated with zinc-containing fertilizers or pesticides (Kania and Saternus, 2023). Although Zn plays a vital role in cellular metabolism and immune function in both humans and aquatic life, elevated levels can lead to toxicity. In rivers, zinc can bind to suspended particles or remain dissolved, depending on pH and other water chemistry factors. High concentrations can disrupt aquatic ecosystems by impairing fish growth, reproduction, and enzymatic activity (Chasapis *et al*., 2020). For humans, excessive ingestion of zinc-contaminated water may lead to symptoms such as nausea, vomiting, abdominal cramps, and, in severe cases, interference with Cu metabolism and immune dysfunction (Senol and Sahin, 2023).

2.6.10. Iron (Fe)

Iron is one of the most abundant metals in the Earth's crust and is commonly found in rivers, especially in areas with iron-rich soils or mining activity. It can enter river systems through natural leaching, erosion, and anthropogenic sources like industrial discharge and wastewater from steel manufacturing (Eldesoky *et al*., 2025). Although Fe is essential for oxygen transport and enzyme functions in living organisms, excess Fe in water can lead to serious ecological and infrastructural issues (Hirota, 2019). In aquatic systems, Fe often precipitates as ferric hydroxide, creating reddish-brown deposits that can clog fish gills, smother benthic habitats, and disrupt photosynthesis by covering aquatic plants and sediments (Peng *et al.*, 2017). For humans, high Fe concentrations in drinking water can cause unpleasant taste, staining of household fixtures, and, in rare cases, contribute to conditions like hemochromatosis if consumed over long periods. The bioavailability and environmental behaviour of Fe are influenced by factors such as oxygen levels, pH, and organic matter, making its monitoring critical for maintaining both ecological balance and water quality (Milman, 2021).

2.7. Heavy Metal Toxicity

2.7.1. Neurotoxicity

Consumption of arsenic leads to cognitive impairment in the central nervous system and is associated with various neurological disorders, including neurodevelopmental alterations and an increased risk of neurodegenerative diseases. Arsenic poisoning also disrupts synaptic transmission and the balance of neurotransmitters (Garza-Lombó *et al.*, 2019). The neurotoxic effects of arsenic involve the activation of multiple apoptotic pathways. Specifically, arsenic and its methylated metabolites promote caspase-dependent apoptosis in neural cells through MAPK signaling pathways such as ERK2, JNK, and p38, which engage intrinsic mitochondrial apoptotic mechanisms. Additionally, As triggers an increase in intracellular calcium levels that further promotes apoptosis. Alternatively, apoptosis may also occur through the activation of autophagy, which involves stimulation of AMPK and inhibition of the mammalian target of rapamycin (mTOR). Autophagy is a cellular process that maintains homeostasis by forming double-membraned autophagosomes, which engulf cellular components and eventually degrade them after fusing with lysosomes (Garza-Lombó *et al.*, 2019). Neurotoxicity caused by Cd has been linked to several neurodegenerative disorders such as amyotrophic lateral sclerosis, Parkinson’s disease, Alzheimer’s disease, and multiple sclerosis (Branca *et al.*, 2018).

2.7.2. Nephrotoxicity

Cadmium-induced nephrotoxicity results in severe clinical symptoms such as glucosuria, Fanconi-like syndrome, phosphaturia, and aminoaciduria (Reyes *et al.*, 2013). Direct exposure of the kidneys affects the proximal tubular epithelium, leading to elevated cadmium levels in urine, aminoaciduria, increased β2-microglobulinuria, glucosuria, and reduced phosphate reabsorption in the renal tubules. Excessive exposure can cause renal tubular acidosis, kidney failure, and hypercalciuria (Daniel *et al.*, 2013). Lead has harmful effects on multiple organs, but the kidneys are particularly affected. Acute lead nephropathy leads to dysfunction of the proximal tubules, causing a Fanconi-like syndrome. Chronic Pb nephropathy is characterized by tubular hyperplasia, interstitial fibrosis, tubular atrophy, renal failure, and glomerulonephritis. Acute Hg exposure damages the kidneys by causing acute tubular necrosis and manifests with clinical symptoms such as acute shortness of breath, altered mental state, abdominal pain, excessive salivation, tremors, vomiting, chills, and low blood pressure. Chronic Hg exposure causes damage to the epithelial cells and necrosis in the pars recta of the proximal tubule. Symptoms of mercury-induced chronic kidney injury include tubular failure, increased urinary excretion of albumin and retinol-binding protein, and a nephritic condition marked by membranous nephropathy (Lentini *et al.*, 2017). Excretion of thallium sulphate through the kidneys is slow and may take up to two months after ingestion. Kidney toxicity is indicated by albuminuria and haematuria. However, thallium poisoning does not result in a significant decline in overall kidney function (Yumoto *et al.*, 2017).

2.7.3. Carcinogenicity

Arsenic induces epigenetic changes, DNA damage, alterations in the expression of the p53 protein, histone modifications, DNA methylation, and decreased expression of p21. Exposure to arsenic increases cancer risk by binding to DNA-associated proteins and slowing down the DNA repair process (Garcia-Esquinas *et al*., 2013). Lead is a carcinogen that damages DNA repair mechanisms, disrupts cellular tumour regulatory genes, and alters chromosomal structure and sequence through the release of reactive oxygen species (ROS). It interferes with transcription by displacing Zn from certain regulatory proteins (Silbergeld *et al*., 2000). Mercury produces a high amount of reactive oxygen species due to its peroxidative activity, which supports pro-tumour signaling and cancer cell growth. These ROS can promote carcinogenesis by damaging cellular proteins, lipids, and DNA, causing cellular injury (Zefferino *et al*., 2017). Nickel acts as a carcinogen by regulating various mechanisms involved in cancer development, such as gene regulation, transcription factor activity, and free radical production. It influences the expression of specific long non-coding RNAs, mRNAs, and microRNAs. Nickel also participates in the methylation of promoter regions and downregulation of the MEG3 gene, which enhances the modulation of hypoxia-inducible factor-1, both contributing to carcinogenesis (Zhou *et al*., 2017).

2.7.4. Hepatotoxicity

Lead's toxicity to liver cells is well documented. Exposure to lead increases oxidative stress, which leads to liver damage. When combined with organic solvents, which share similar properties with Pb, liver injury can also occur. Chronic exposure to Pb can be harmful to liver cells, causing glycogen depletion and cellular infiltration that may lead to chronic cirrhosis (Malaguarnera *et al*., 2012). Cadmium primarily targets the renal cortex and liver in humans (Bernard, 2004). During acute exposure, Cd accumulates in the liver and is associated with various liver dysfunctions. It disrupts the cellular redox balance, causing oxidative stress and damage to liver cells. Both acute and chronic cadmium-induced hepatotoxicity can result in liver failure and increase cancer risk (Hyder *et al.*, 2013). Copper is known to accumulate in the liver, especially in Wilson's disease. High Cu levels can cause oxidative stress, making hepatic Cu build-up both a diagnostic sign and a cause of disease. Elevated Cu levels are also found in cholestatic liver diseases, but these result from reduced biliary Cu excretion and do not cause liver infection (Yu *et al.*, 2019).

2.7.5. Skin Toxicity

Long-term exposure to As is linked to various skin conditions such as hyperkeratosis, hyperpigmentation, and several forms of skin cancer. Among these, hyperpigmentation is the most common skin change resulting from extended arsenic exposure. Arsenic can also lead to Bowen's disease, an early form of skin cancer. Arsenic-induced hyperkeratosis often appears extensively on the palms and soles but can also affect other areas such as the legs, toes, fingers, arms, and backs of the hands. Some lesions caused by hyperkeratosis and Bowen's disease have the potential to progress into invasive cancers (Huang *et al.*, 2019). Mercury and compounds containing Hg are responsible for various skin infections, including acrodynia, also known as pink disease, a common dermatological condition where the skin turns pink following exposure to heavy metals, especially mercury (Horowitz *et al.*, 2002).

2.7.6. Immunological Toxicity

Both acute and chronic exposure to lead cause various harmful effects on the immune system, leading to increased allergies, infectious diseases, autoimmune disorders, and cancer. Lead exposure has been associated with a higher risk of lung, stomach, and bladder cancers in several population groups (Hsiao *et al.*, 2011). It stimulates the production of B and T cells as well as enhances MHC activity. Lead can affect both cellular and humoral immune responses by altering T-cell functions, which increases susceptibility to autoimmunity and hypersensitivity. Exposure to cadmium in occupational and environmental settings may suppress the immune system, depending on the level and duration of exposure. Low levels of cadmium exposure tend to enhance humoral immune responses, but the effects of higher exposure levels are not fully understood. Nonetheless, activities such as phagocytosis, natural killer cell function, and host resistance to infections are generally reduced in most cases (Mishra *et al.*, 2022).

2.7.7. Reproductive Toxicity

Arsenic is recognized as a reproductive toxin in humans and causes abnormalities in experimental animals, especially neural tube defects (Wang *et al.*, 2006). Inorganic arsenic negatively affects male reproduction by decreasing the weights of the testes, accessory sex organs, and the sperm count in the epididymis. In addition to reducing sperm production, exposure to inorganic arsenic alters levels of testosterone and gonadotropins and disrupts the steroidogenesis process (Kim and Kim, 2015). In females, As exposure has been linked to a higher risk of endometrial cancer. During pregnancy, arsenic impairs endometrial angiogenesis, which is essential for embryo development. This impairment can lead to symptoms such as endometriosis, reduced fertility, premature birth, infertility, and spontaneous abortions (Milton *et al.*, 2017).

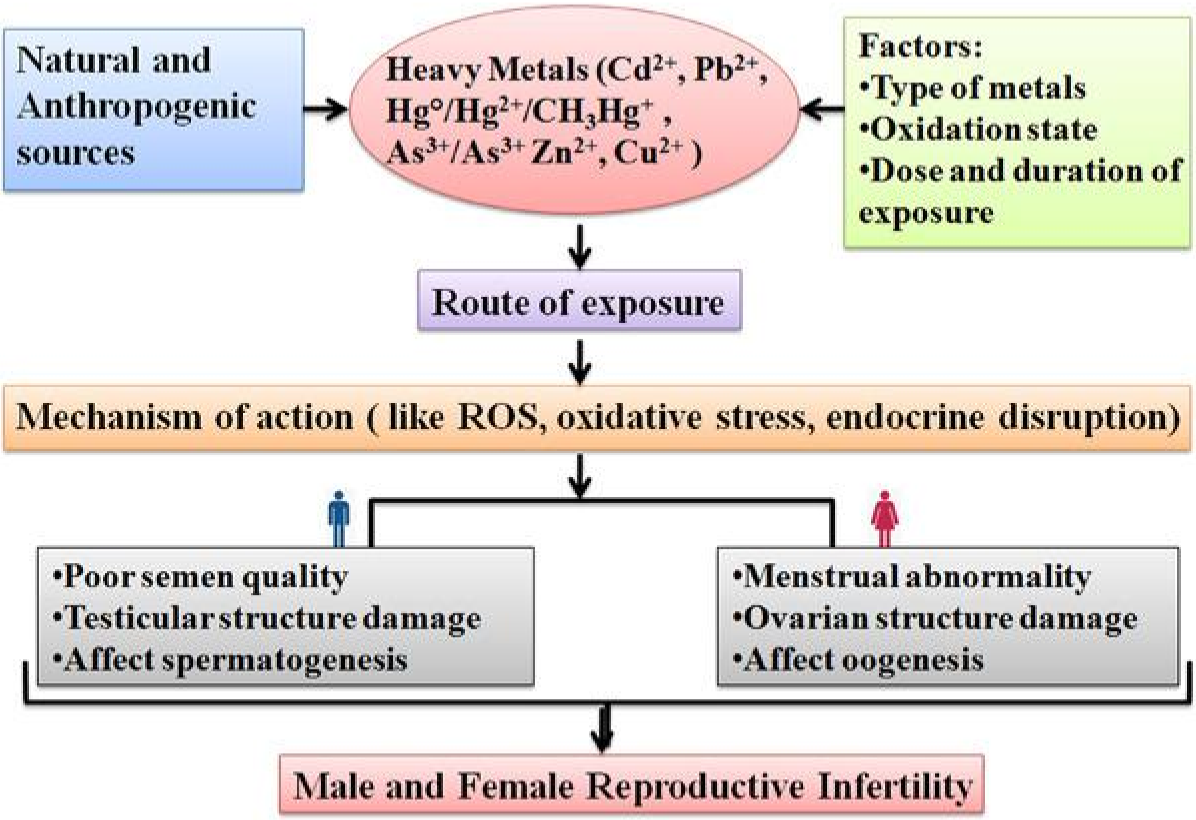

Figure 2.3: General effect of heavy metals on reproductive health (Milton *et al*., 2017)

2.8. Biochemical Mechanism of Heavy Metal Toxicity

When heavy metals are ingested through food or water into the body, they are acidified by the acidic medium of the stomach. In this acidic medium, they are oxidized to their various oxidative states (Zn2^{+}, Cd2^{+}, Pb^{2+}, As^{2+}, As^{3+}, Ag^{+}, Hg^{2+}, etc.), which can readily bind to biological molecules such as proteins and enzymes to form stable and strong bonds. The most common functional group that heavy metals bind to is the thiol groups (SH group of cysteine and SCH3 group of methionine). Cadmium has been shown to inhibit human thiol transferases such as thioredoxin reductase, glutathione reductase, and thioredoxin in vitro by binding to cysteine residues in their active sites (Chrestensen *et al*., 2021). Heavy metal-bound proteins may be a substrate for certain enzymes. In such situations, the heavy metal-bound protein fits into an enzyme in a highly specific pattern to form an enzyme-substrate complex and thus cannot accommodate any other substrate until it is freed. As such, the product of the substrate is not formed as the enzyme is blocked, and therefore, the heavy metal remains embedded in the tissue, leading to dysfunctions, abnormalities, and damage in the body (Faller *et al*., 2015). Inhibition of thiol transferases leads to increased oxidative stress and cell damage. For example, toxic As present in fungicides, herbicides, and insecticides can attack –SH groups in enzymes to inhibit their catalytic activity. Also, heavy metal toxicity may be induced by the replacement of a metalloenzyme by another metal ion of similar size. Cadmium displaces Zn and Ca ions from Zn finger proteins and metalloproteins (Faller *et al*., 2015). For instance, Cd can replace Zn in certain dehydrogenating enzymes, leading to Cd toxicity. Such replacement can convert the enzyme structurally to an inactive form and completely alter its activity (Sharma *et al*., 2008). It was also observed that when protein misfolds in the presence of heavy metals, the misfolded protein could not be rescued in the presence of reduced glutathione or EDTA chelator. The order of heavy metals in terms of their efficacy in folding inhibition is Hg > Cd > Pb, and correlates with the relative stability of their monodentate complexes with imidazole, thiol, and carboxylate groups in proteins (Tamas *et al*., 2014). Heavy metal may cause proteins to aggregate, as arsenite-induced protein aggregation was observed and shown to be concentration-dependent. Also, the aggregates contained a wide variety of proteins enriched in functions related to metabolism, protein folding, protein synthesis, and stabilization (Tamas *et al*., 2014).

2.9. Heavy Metal Pollution in Nigerian Rivers

A study conducted in selected rivers across Southwest Nigeria assessed the concentrations and potential human health risks of five heavy metals: Mn, As, Cr, Cd, and Pb. The study involved seasonal sampling and analysis of water from multiple rivers using atomic absorption spectrophotometry, following digestion with a di-acid mixture of nitric acid and perchloric acid in a 9:4 (v/v) ratio. Water samples were collected during both the rainy and dry seasons to compare seasonal variations in metal concentrations. Results revealed that the concentrations of all five heavy metals were generally higher during the dry season, except for arsenic in Dandaru (0.012 mg/L) and Asejire (0.016 mg/L), which showed a slight increase during the rainy season. Among the metals analysed, Mn consistently had the highest mean concentration across all rivers in both seasons. Further analysis of the annual mean concentrations showed the following descending order of prevalence: Mn > Cr > Cd > Pb > As. This trend was consistent across all the sampled rivers. The study also evaluated the potential health risks associated with exposure to these metals through direct ingestion of river water. The human health risk assessment found that both the hazard index (HI) and hazard quotient (HQ) values for cadmium and arsenic exceeded the safe threshold of 1.0 in all the rivers, indicating a significant carcinogenic risk from long-term consumption.

Additionally, the cancer risk (CR) values for arsenic via ingestion surpassed the remedial target of 1×10^{-6}, suggesting the need for urgent public health attention. Chronic daily intake (CDI) calculations further highlighted that chromium and manganese posed the greatest exposure risks across the four rivers sampled, emphasizing the necessity for continuous monitoring and mitigation strategies to protect local communities (Adesiyan *et al*., 2018).

A study conducted between December 2017 and November 2018 assessed the heavy metal content of a Nigerian river across six different stations. The primary aim was to evaluate the water quality for drinking purposes using heavy metal pollution indices. Due to the complexity of interpreting multiple water quality parameters, the study adopted an index-based approach to simplify the analysis. Two key indices were used: the Heavy Metal Pollution Index (HPI) and the Contamination Index (Cd). Eight heavy metals were analyzed using standard procedures, and their concentrations were compared against the Nigerian Drinking Water Quality Standard. The results revealed that Fe, Cd, and Pb exceeded permissible limits in several locations. Additionally, Mn, Cr, and Ni were found to surpass the allowable limits during the dry season at specific stations, while Cu and Zn remained within safe limits across all samples. Statistical analysis indicated that heavy metal concentrations during the dry season were significantly higher ($p < 0.05$) compared to the wet season. The HPI results showed that all stations recorded values above the critical threshold of 100, with stations 1 and 4 through 6 exhibiting particularly elevated pollution levels. The Contamination Index (Cd) further revealed that station 3 had low contamination risk, station 2 had medium contamination risk, and stations 1, 4, 5, and 6 had high contamination potential. These indices effectively reflected the influence of anthropogenic activities such as sand mining, bathing, laundry, and other human interactions with the river. Based on the findings, the study concluded that the water from the river was not suitable for drinking, highlighting the urgent need for remediation and stricter environmental controls (Anyanwu and Umeham, 2020).

A study was conducted on Edagberi Creek to evaluate the concentration of heavy metals in surface water over a one-year period. Water samples were collected bimonthly from three distinct stations along the creek. Standard methods were employed in the treatment of the samples before analysis using AAS. The heavy metals analysed included Mn, Hg, Cd, Pb, Cu, Ni, Fe, Cr, and Zn. The results of the analysis showed that the concentrations of the metals, when arranged in increasing order, followed the pattern: Hg < Cd < Pb < Cr < Cu < Zn < Fe < Mn < Ni. Among the metals studied, Fe, Mn, and Ni were found to exceed the permissible limits set by the World Health Organization (WHO) for drinking water. In contrast, Hg, Cd, Pb, Cr, Cu, and Zn were all within acceptable limits based on the guideline provided by the same agency. To assess the level of pollution, a contamination factor test was applied using the WHO standards as a benchmark. The results indicated that the various heavy metals exhibited different degrees of contamination and fell into distinct pollution classifications across the sampling stations. This study demonstrated the presence of heavy metal pollution in Edagberi Creek and underscored the need for regular monitoring and control of pollutants in the area to ensure environmental and public health safety (Edori and Iyama, 2020).

A study was carried out on the Ebonyi River at Eha-Amufu in Enugu State, Nigeria, to assess heavy metal enrichment and evaluate the river's suitability for human consumption. The river serves as the primary source of drinking water for the surrounding community, yet limited information exists regarding its pollution status. To address this gap, a total of 54 water samples were collected from three distinct locations along the river during both the rainy and dry seasons. Standard analytical methods were employed to examine the physicochemical properties, mineral nutrient levels, and heavy metal concentrations in the water samples. Additionally, heavy metal pollution indices and heavy metal toxicity load assessments were applied to evaluate the potential health risks. The study found that all water samples exhibited slightly alkaline pH values ranging from 7.58 to 7.90 in both seasons. Sodium was the only mineral nutrient with a higher concentration during the rainy season, while magnesium showed the highest levels among the minerals, particularly in the downstream section, recording 8.41 mg/L in the dry season and 13.31 mg/L in the rainy season. The mean concentrations of trace metals such as Pb, Cd, As, Cu, Fe, Ni, Hg, and Mn were found to exceed the permissible limits for drinking water, whereas Zn and Mg remained within acceptable standards. Pearson's correlation coefficient analysis revealed significant associations between some physicochemical parameters and certain heavy metals, except for pH, suggesting that pH was not a primary factor influencing the distribution of heavy metals in the river. The findings highlight the need for consistent monitoring and implementation of mitigation strategies to protect public health and maintain the quality of the river water (Agwu *et al*., 2023).

A study was conducted to assess the levels of heavy metals: As, Cr, Pb, Cd, and Zn in both the water and sediment of River Kubanni Dam in Zaria, Nigeria. The concentrations of these metals were measured using a Microwave Plasma Atomic Emission Spectrophotometer (MPAES) model 4200. Results indicated that metal concentrations were generally higher in sediment samples compared to water. A positive correlation was observed between metal concentrations in sediment and water, except for Cr and Pb, which did not show a significant relationship. The concentration ranges in water (mg/L) were as follows: As (0.890 to 1.620), Cr (0.07 to 0.090), Pb (1.320 to 1.890), and Cd (0.078 to 0.098), all exceeding the permissible limits set by the World Health Organization (WHO). Furthermore, Cd levels in sediment (4.43 to 7.230 mg/kg) surpassed the standards established by the United States Environmental Protection Agency (USEPA), the average shale value (ASV), the toxicity reference value (TRV), and the threshold effect level (TEL). Pollution assessment indices such as the Heavy Metal Pollution Index (HPI) and Metal Index (MI) indicated that the river water was polluted with heavy metals, while the Geo-accumulation Index (Igeo) revealed that sediment pollution was primarily due to Cd contamination. Based on these findings, the study emphasized the urgent need to regulate waste dumping and wastewater discharge to prevent further degradation of the river's water and sediment quality (Okon *et al*., 2022).

A study was conducted on River Kaduna, a vital water source for farming, domestic, and industrial uses, to assess the concentration of selected heavy metals in its surface waters. The river experiences significant pollution due to industrial activities and other anthropogenic sources. Water samples were collected using the grab method from five points along the river: Bypass, Barnawa, Down Quarters, Kakuri-Makera drains, and Kudendan. Sampling was performed twice, once during the rainy season and again during the dry season, resulting in a total of six samples. The collected samples were analyzed in the laboratory for Cr, As, Fe, Cu, Ba, Al, Cd, CN, and Zn using AAS. The concentrations of these metals were then compared with the WHO recommended standards to determine the extent of pollution and assess the water quality. Results indicated that the levels of all metals exceeded the permissible limits set by the WHO. These finding suggests that River Kaduna has become heavily contaminated with heavy metals, primarily due to discharge from industrial effluents and municipal waste. The elevated concentrations pose serious ecological risks and potential health hazards to the communities relying on the river for water supply and other uses. The study highlights the urgent need for pollution control measures and effective waste management to protect the river's ecosystem and public health (Abui *et al*., 2017).

A study was conducted in the Ossiomo River in Benin City to evaluate the sediment pollution load of a river, recognizing that both natural and anthropogenic factors influence sediment quality. To identify the sources of contaminants, whether lithogenic or human-induced, a comprehensive analysis of sediment characteristics was carried out. Over a period from March 2015 to August 2016, a total of 360 sediment samples were collected monthly using an Eckman grab sampler. Nine heavy metals: Fe, Mn, Zn, Cu, Cr, Cd, Pb, Ni, and V were analyzed using standard analytical methods with strict quality control procedures. The concentrations of these metals showed individual variations, with statistically significant differences ($p < 0.05$) observed across some stations, while others showed no significant differences ($p > 0.05$). The metals were ranked in descending order of concentration as Fe > Mn > Zn > Cu > Cr > Cd > Pb > Ni > V. Most of the measured heavy metal levels exceeded both national and international standards when compared with their respective permissible limits. To assess the degree of contamination, Enrichment Factors (EF), Pollution Index (PI), and Nemerow Integrated Pollution Index (NIPI) were calculated. These indices revealed varying degrees of pollution, with EF values greater than 1 and both PI and NIPI values exceeding 3, indicating moderate to high levels of contamination. The study concluded that the sources of sediment pollution were primarily a combination of natural lithogenic origins and anthropogenic activities, highlighting the need for continued monitoring and pollution control strategies to protect the river ecosystem (Anani and Olomukoro, 2017).

A study was carried out to assess the heavy metal pollution status of several rivers and creeks located within oil-producing communities in Delta State, Nigeria. Water and fish samples were collected from six water bodies, namely the Egbokodo River in Warri, River Ethiope in Sapele, Urie River in Igbide Isoko, Asaba-Ase Creek, Aragba River in Abraka, and Uzere Creek. Both fresh water and ready-to-eat fish samples were analysed for heavy metals, including Pb, Cd, Mn, Cu, Fe, and Ni. The analysis showed that most heavy metal concentrations were marginally below the residual limits recommended by the WHO and the FEPA. However, iron, cadmium, and nickel were consistently detected across all samples regardless of the sampling location. Notably, nickel concentrations in fresh fish samples from

Aragba River (0.89 mg/kg) and Asaba-Ase Creek (0.7 mg/kg) exceeded the WHO standard limit of 0.6 mg/kg. Additionally, fresh fish from the River Ethiope exhibited manganese levels (0.57 mg/kg) slightly above the WHO-recommended limit of 0.5 mg/kg. These findings highlight localized contamination concerns and underscore the need for ongoing monitoring to ensure the safety of aquatic resources in these oil-producing regions (Ubiogoro and Adeyemo, 2017).

CHAPTER THREE

MATERIALS AND METHODS

3.1. Study Area

This study was carried out on the Ogba River in Benin City, Edo State, Nigeria. Edo State, one of Nigeria's 36 states, is situated in the southern part of the country and is one of the six states in the South-South geopolitical zone. It shares borders with Kogi State to the North East and East, Anambra State to the East, Delta State to the South, and Ondo State to the West and Northwest. The Niger River marks its Eastern boundary. The state's elevation ranges from 150 meters (500 feet) in the South to over 550 meters (1,800 feet) in the North. Covering approximately 10,400 square kilometers, the central Edo region features a rolling coastal plain interspersed with rivers and lies within a tropical rainforest zone. Benin City is located between latitudes 06° 19’ E to 6° 21’E and longitude 5° 34’E to 5^{o} of the equator. The average elevation above sea level is 78 meters. The region is made up of five (5) Local Government Areas: Egor, Ikpoba-okha, Oredo, Ovia North-East, and Uhunmwode.

The Ogba River is located on the southwestern outskirts of Benin City, in Edo State, Nigeria, within the tropical rainforest region of southern Nigeria. Geographically, it lies between Latitude 6.20°N and Longitude 5.34°E. The river is approximately 42 km long and is classified as a fourth-order (4^{o}) river. It originates from Ekenhuan and flows southeast through Ogba village, and eventually drains into the Ossiomo River, which flows into the

Benin River and subsequently into the Atlantic Ocean. The Ogba River catchment experiences distinct wet and dry seasons and serves as a source of drinking water while also receiving urban and agricultural runoff.

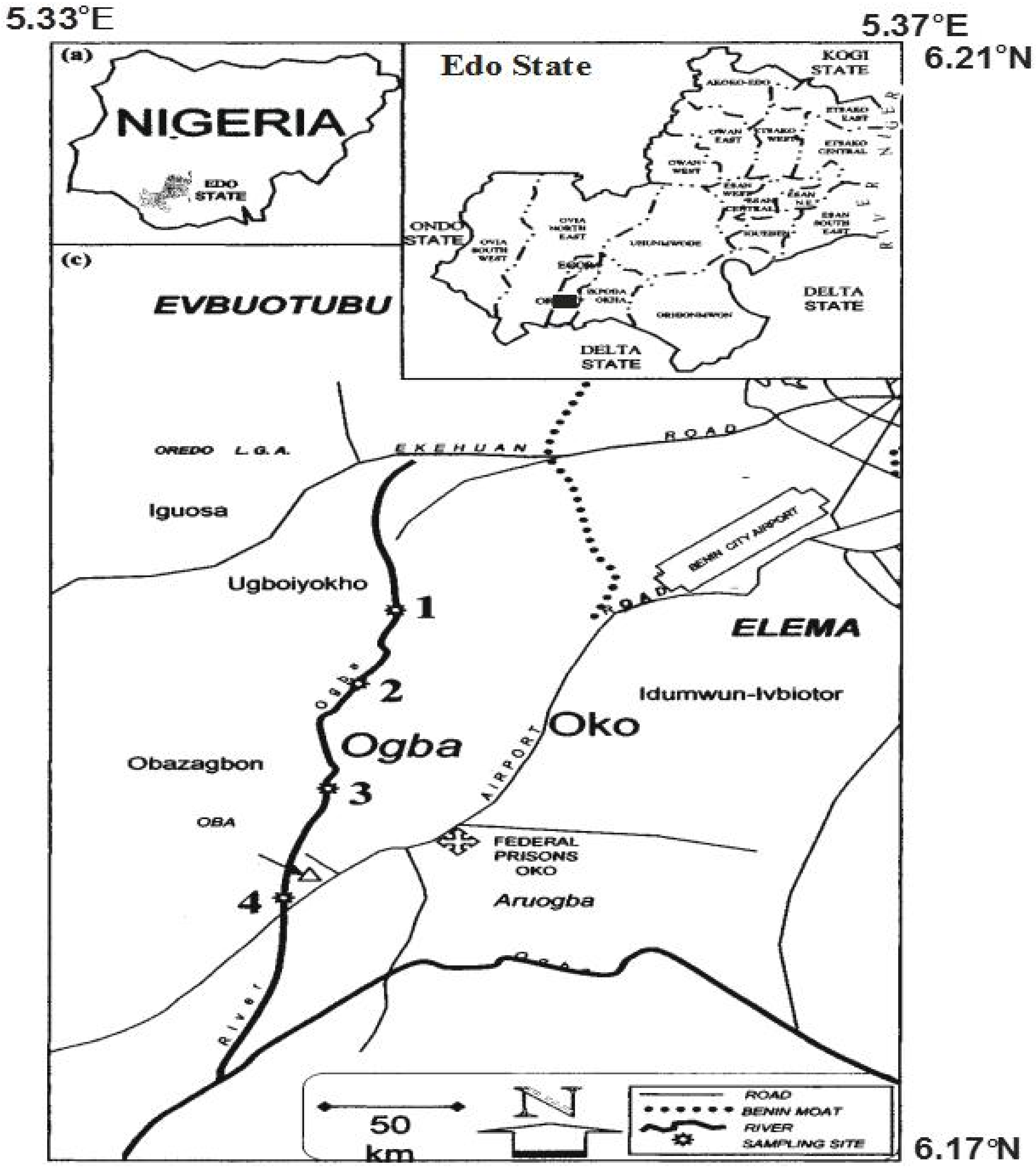

Figure 3.1: Map showing the Study area (Anyanwu, 2012)

3.1.1. Climate

Benin City, where the Ogba River is located, experiences a tropical rainforest climate, characterized by high annual rainfall, elevated humidity levels, and consistently warm temperatures throughout the year. The region exhibits two distinct seasons: a wet season, which typically spans from April to October, and a dry season, occurring from November to March. These climatic conditions significantly influence the hydrological dynamics and ecological characteristics of the Ogba River (Unuafe *et al.*, 2025).

3.1.2. Vegetation

The vegetation surrounding the Ogba River is representative of the tropical rainforest biome, known for its lush and biologically diverse flora. The riverbanks are lined with riparian forests featuring tall hardwood trees such as *mahogany* and *iroko*, along with dense undergrowth made up of shrubs, herbs, and climbing plants. However, anthropogenic pressures, including farming, settlement expansion, and urbanisation, have contributed to deforestation, vegetation loss, and habitat fragmentation in several portions of the river's catchment area (Unuafe *et al.*, 2025).

3.1.3. Geology

The geology of the Ogba River region is predominantly made up of top reddish earth, which consists mainly of ferruginized or lateralised clayey sand. This composition is typical of tropical weathering processes. Beneath the surface, the area is underlain by sedimentary geological formations such as the Benin Formation, alluvium, drift/topsoil, and the Azagba-Ogwashi Formation. These subsurface structures significantly influence the soil texture, groundwater movement, and overall hydrology of the Ogba River system (Unuafe *et al.*, 2025).

3.2. Sample Collection

Water samples for heavy metal analysis were collected from the Ogba River at Obaria, located just after the Ogba Zoo in Benin City, Nigeria. Sampling was conducted across three (3) months: July, August, and September. The sampling was conducted at three strategic points along the river course (upstream, midstream, and downstream) to assess spatial variation in heavy metal concentrations. The upstream sampling point was located near a bridge at coordinates 6°12′27″N, 5°40′56″E. The midstream sample was collected further along the same latitude and longitude (6°12′27″N, 5°40′56″E), while the downstream sample was taken at 6°12′27″N, 5°40′58″E. These sampling points were carefully chosen to reflect possible changes in water quality due to anthropogenic or natural influences along the river's course. At each location, water was collected in pre-cleaned 2-liter plastic bottles. The bottles were rinsed thoroughly with the river water at the site before the actual samples were collected to avoid contamination. After collection, the bottles were tightly sealed, labelled appropriately with the sampling point and date, and transported to the laboratory under cooled conditions for heavy metal analysis.

3.3. Wet Ashing of Sample

The method described by Victor Dmitrievich (2013) was used for the digestion of water samples before metal analysis. Specifically, 10 mL of each water sample was transferred into a clean Kjeldahl digestion flask. Subsequently, 10 mL of mixed acid (a 3:1 ratio of nitric acid and perchloric acid) was added to each flask. The flasks were heated gently for 20 minutes at 40 °C, then the temperature was raised to 100 °C for an additional 20 minutes to complete digestion. After digestion, the samples were allowed to cool to room temperature. 20 mL of distilled water was added to each digested sample, and the mixture was filtered using Whatman No. 42 filter paper into a 100 mL standard volumetric flask. The filtrate was then made up to the 100 mL mark with distilled water and stored in clean containers for heavy metal analysis.

3.4. Atomic Absorption Spectrophotometry (AAS) Analysis of Heavy Metals

The digested and filtered water samples were analyzed for Cu, Cr, Ni, Pb, Mn, and Cd using a Buck Scientific AAS (Model 210 VGP, Buck Scientific Inc., USA). Before sample analysis, the instrument was calibrated using a series of standard solutions for each metal prepared from certified stock solutions. Calibration curves were constructed by plotting absorbance against metal concentration, ensuring a linear correlation ($R^2 \geq 0.995$) for all metals. Each sample was aspirated into the aspiration chamber, and absorbance readings were recorded at the specific wavelengths recommended for each metal: Cu (324.8 nm), Cr (357.9 nm), Ni (232.0 nm), Pb (283.3 nm), Mn (279.5 nm), and Cd (228.8 nm). Background correction was applied when necessary to minimize interference. Blank samples containing only distilled water and reagents were analyzed to account for any background absorbance. Each sample and standard were analyzed in triplicate to ensure precision, and the mean absorbance was used for calculating metal concentrations. The metal concentrations in the water samples were determined from the calibration curves and expressed in mg/L.

3.5. Health Risk Assessment

Health Risk Assessment (HRA) was conducted to evaluate the potential adverse effects associated with exposure to heavy metals in the surface water of Ogba River, Benin City.

3.5.1. Exposure Pathway

The major route of exposure considered in this study was oral ingestion of contaminated water, as this represents the most likely means through which local residents may be exposed to heavy metals in the river.

3.5.2. Estimation of Chronic Daily Intake (CDI)

The Chronic Daily Intake (CDI) represents the amount of a particular heavy metal ingested daily through consumption of contaminated water. It was calculated using the following equation:

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \text{ …………….. eqn 1}$$

Where:

- **C** = Concentration of heavy metal in water (mg/L)
- **IR** = Ingestion rate (L/day)
- **EF** = Exposure frequency (days/year)
- **ED** = Exposure duration (years)
- **BW** = Body weight (kg)
- **AT** = Averaging time (days) (Adimalla *et al.*, 2020).

For non-carcinogenic risk, AT = ED × 365, while for carcinogenic risk, AT = 70×365. The parameters and their standard values used in this study are presented in Table 3.1.

Table 3.1: Exposure Parameters Used for Health Risk Assessment (LaKind *et al*., 2023).

Parameter	Unit	Adult	Child
Ingestion rate (IR)	L/day	2.0	1.0
Exposure frequency (EF)	days/year	365	365
Exposure duration (ED)	years	30	6
Body weight (BW)	kg	70	15
Averaging time (AT) non-cancer	days	10,950	2,190
Averaging time (AT) cancer	days	25,550	25,550

3.5.3. Non-Carcinogenic Risk Assessment

The non-carcinogenic risk for each metal was determined by computing the Hazard Quotient (HQ) using the equation:

$$HQ = \frac{CDI}{RfD} \text{ …………….. eqn 2}$$

Where RfD is the Reference Dose, which represents the maximum daily exposure to a substance that is unlikely to cause harmful effects during a lifetime (Eze *et al.*, 2021).

The Hazard Index (HI), representing the cumulative non-carcinogenic risk from all the metals, was obtained by summing the individual HQs as follows:

$$HI = \sum_{i=1}^{n} HQi \text{ …………….. eqn 3}$$

An HQ or HI value less than 1 indicates no significant health risk, whereas values greater than 1 suggest potential non-carcinogenic health effects (Eze *et al.*, 2021).

The RfD values used for the metals analyzed from Ogba River are shown in Table 3.2.

Table 3.2: Reference Dose (RfD) Values for Heavy Metals (Wong *et al.*, 2022).

Metal	**RfD (mg/kg/day)**
Cu	0.04
Cr	0.003
Ni	0.02
Mn	0.14
Cd	0.0005
Pb	0.00035

3.5.4. Carcinogenic Risk Assessment

This is usually estimated using the Incremental Lifetime Cancer Risk (ILCR). The ILCR is the possibility of a person developing any type of cancer over a lifetime as a result of daily exposure to a given daily amount of a carcinogenic element. The equation below was used for the calculation of the lifetime cancer risk (Eze *et al.*, 2021).

$ILCR = CDI \times SF$…………….. eqn 4

Where:

- CDI = Chronic daily intake (mg/kg/day)
- SF = Slope factor ((mg/kg/day) $^{-1}$)

The acceptable range of cancer risk, as recommended by the USEPA, lies between 1 × 10^{-6} (one in a million) and 1 × 10^{-4} (one in ten thousand) (Eze *et al.*, 2021).

The slope factors used for the carcinogenic metals in this study are presented in Table 3.3.

Table 3.3: Cancer Slope Factor (CSF) for Different Potentially Toxic Elements (Eze *et al.*, 2021).

Metal	**CSF (mgL^{-1} /day)**
Cu	NAD
Cr	41.00
Ni	0.84
Mn	NAD
Cd	6.10
Pb	8.50

NAD=No available data

Table 3.4 presents the National Environmental Standards and Regulations Enforcement Agency (NESREA) and WHO permissible limits for selected heavy metals in river water. According to the NESREA guideline values, the maximum allowable concentrations for Cu, Cr, and Ni are 1.0 mg/L, 0.5 mg/L, and 0.01 mg/L, respectively. Pb and Cd have permissible limits of 0.1 mg/L and 0.01 mg/L, indicating their high toxicity even at low concentrations. Mn has a permissible limit of 1.0 mg/L. The WHO guidelines set lower permissible limits for most of these metals, with Cu, Cr, and Ni at 2.0 mg/L, 0.05 mg/L, and 0.07 mg/L, respectively, while Pb and Cd are limited to 0.01 mg/L and 0.003 mg/L. The WHO range for Mn is 0.4–0.5 mg/L. These standard values from both regulatory bodies are used to evaluate the safety and quality of river water, ensuring that heavy metal concentrations remain within acceptable limits to protect human health and aquatic ecosystems (NESREA, 2009; World Health Organization, 2022).

Table 3.4: World Health Organization Permissible Limits for Heavy Metals in River Water

Metal	**NESREA Permissible Limit (mg/L)**	**WHO Permissible Limit (mg/L)**
Copper (Cu)	1.0	2.0
Chromium (Cr)	0.5	0.05
Nickel (Ni)	0.01	0.07
Lead (Pb)	0.1	0.01
Manganese (Mn)	1.0	0.4 – 0.5
Cadmium (Cd)	0.01	0.003

3.6. Statistical Analysis

Data obtained from the study were entered and analysed using Statistical Package for the Social Sciences (SPSS) version 22. Descriptive statistics such as means, standard deviations, frequencies, and percentages were computed to summarize the concentrations of heavy metals and physicochemical parameters across sampling points. For comparison between sampling locations (upstream, midstream, downstream), one-way analysis of variance (ANOVA) was performed to determine if there were statistically significant differences in heavy metal concentrations and water quality parameters. Where significant differences were detected, post hoc tests (e.g., Tukey's HSD) were applied to identify specific group differences. A p-value < 0.05 was considered statistically significant for all inferential tests.

CHAPTER FOUR

RESULTS

The results in Table 4.1 show that the concentration of Cu was higher at the midstream station (0.34 ± 0.10 mg/L) compared to the downstream (0.31 ± 0.07 mg/L) and upstream (0.24 ± 0.06 mg/L) stations; however, the difference was not statistically significant ($p = 0.645$), and all values were below the WHO (2.0 mg/L) and NESREA (1.0 mg/L) permissible limits for Cu. The concentration of Cr was significantly higher upstream (0.20 ± 0.01 mg/L) compared to midstream (0.12 ± 0.02 mg/L), while downstream concentration was 0.17 ± 0.02 mg/L. This variation was statistically significant ($p = 0.038$), and all observed Cr values exceeded the WHO limit of 0.05 mg/L but remained below the NESREA limit of 0.5 mg/L. For Ni, higher concentrations were recorded upstream (0.15 ± 0.02 mg/L) compared to midstream (0.12 ± 0.02 mg/L), while it was not detected downstream. Although this variation was not statistically significant ($p = 0.260$), the detected concentrations exceeded both the WHO (0.07 mg/L) and NESREA (0.01 mg/L) limits. The concentration of Pb was significantly higher midstream (0.26 ± 0.04 mg/L) and upstream (0.22 ± 0.03 mg/L) compared to downstream (0.11 ± 0.01 mg/L) ($p = 0.005$). All recorded Pb concentrations were well above both WHO (0.01 mg/L) and NESREA (0.1 mg/L) limits. Mn was detected only at the upstream station (0.62 ± 0.19 mg/L), exceeding the WHO guideline range of 0.4–0.5 mg/L but below the NESREA limit of 1.0 mg/L. For Cd, the highest concentration was observed midstream (0.16 ± 0.02 mg/L), followed by upstream (0.12 ± 0.01 mg/L) and downstream (0.11 ± 0.01 mg/L) (p = 0.105), with all values considerably exceeding both WHO (0.003 mg/L) and NESREA (0.01 mg/L) permissible limits.

Table 4.1: Heavy Metal Levels in the Surface Water of Ogba Rivers at the Different Sample Stations

Heavy Metal	**Upstream**	**Midstream**	**Downstream**	**F**	**p value**
Copper (mg/L)	0.24±0.06	0.34±0.10	0.31±0.07	0.447	0.645
Chromium (mg/L)	0.20±0.01b*	0.12±0.02a*	0.17±0.02*	4.338	0.038
Nickel (mg/L)	0.15±0.02*#	0.12±0.02*#	ND	1.429	0.260
Lead (mg/L)	0.22±0.03c*#	0.26±0.04c*#	0.11±0.01ab*#	6.619	0.005
Manganese (mg/L)	0.62±0.19*	ND	ND	-	-
Cadmium (mg/L)	0.12±0.01*#	0.16±0.02*#	0.11±0.01*#	2.476	0.105

Values shown represent Mean±SEM, ND=Not detected, letter a represents significant difference from upstream, letter b represents significant difference from midstream, letter c represents significant difference from downstream, $p \leq 0.05$ was considered statistically significant, Asterisks (*) denote values above the WHO permissible limit, Hash (#) denote values above the NESREA permissible limit.

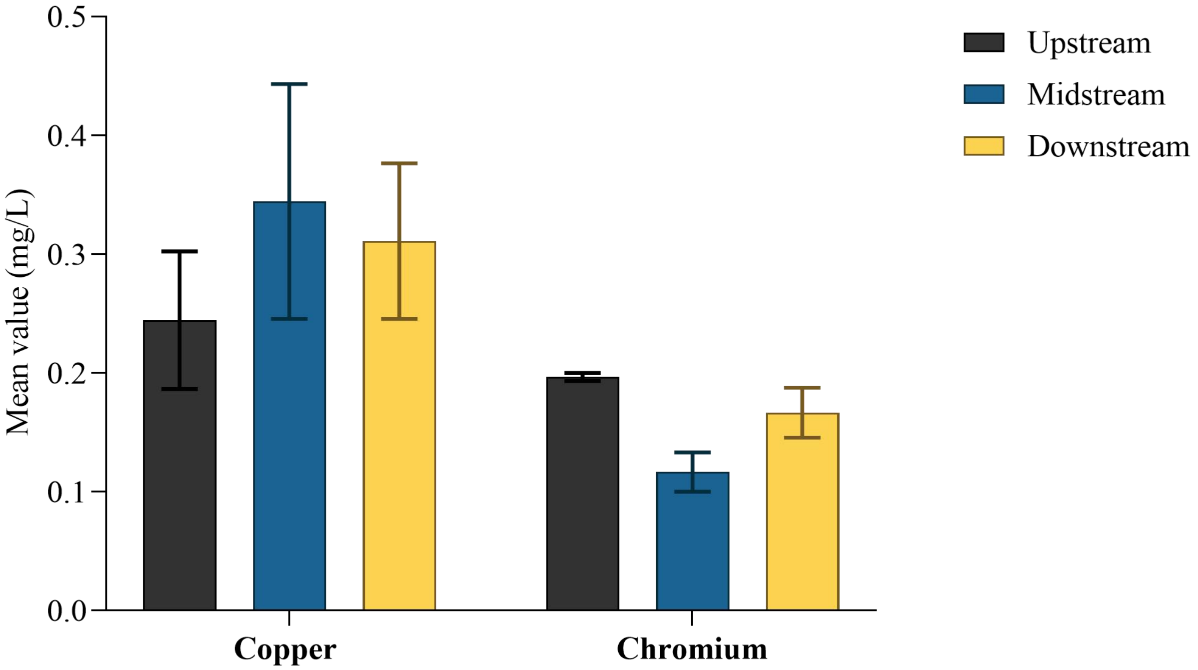

Figure 4.1: Chart showing the concentration of Cu and Cr across all stations

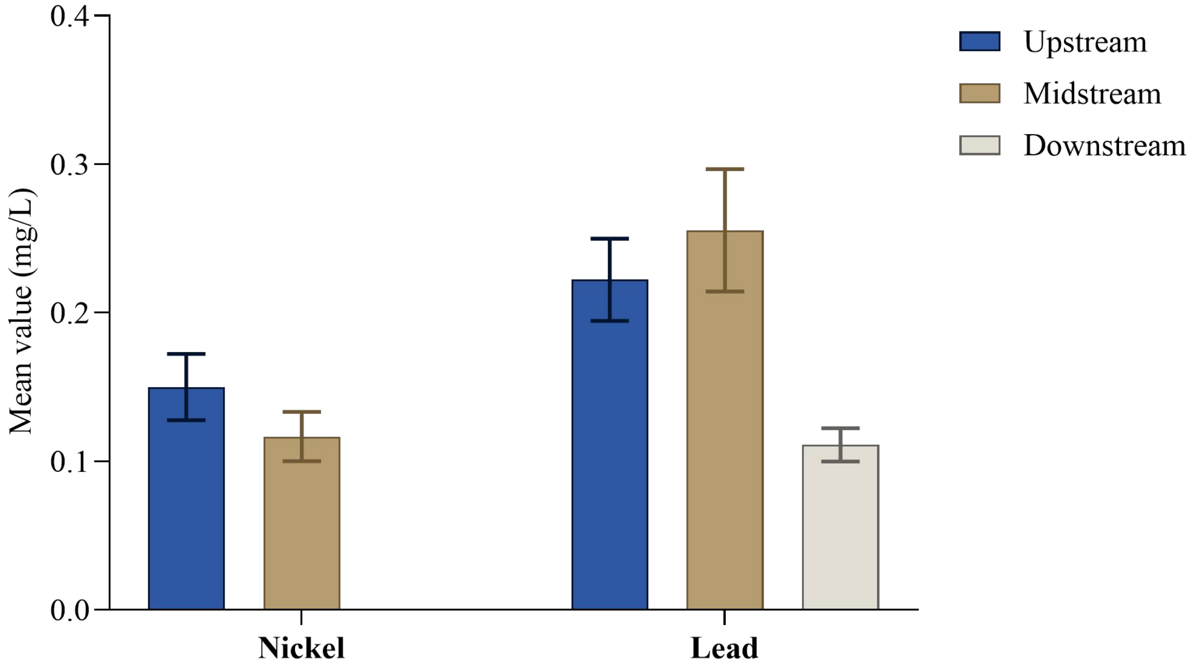

Figure 4.2: Chart showing the concentration of Ni and Pb across all stations

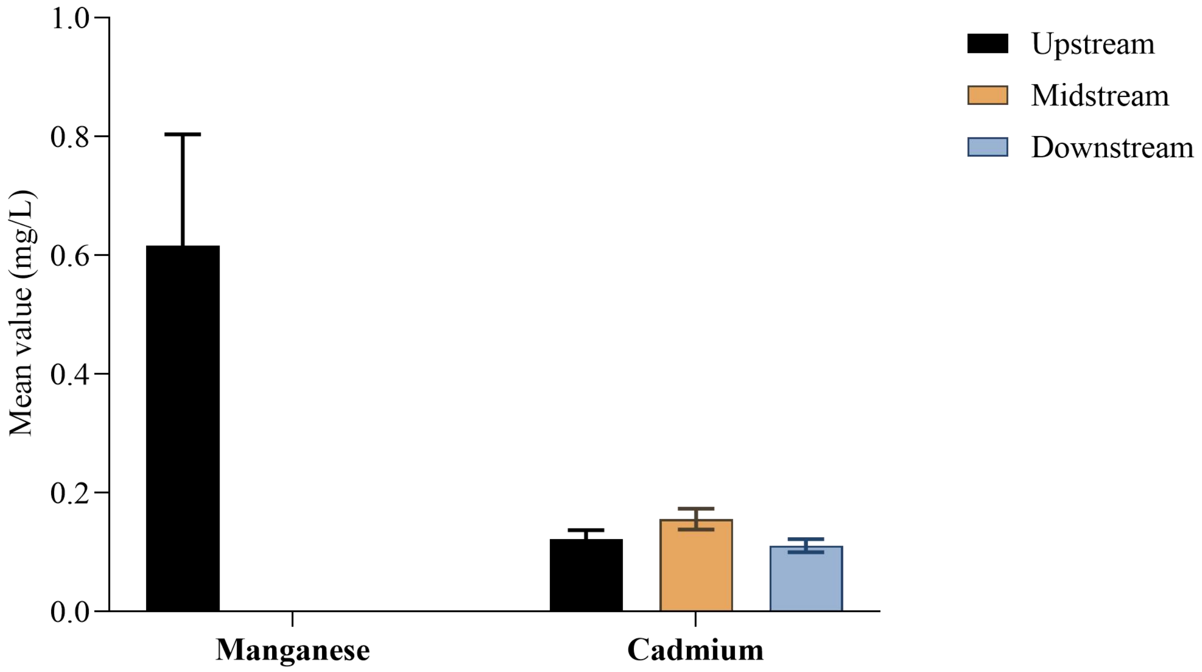

Figure 4.3: Chart showing the concentration of Mn and Cd across all stations

The concentration of Cu was highest in July (0.59 ± 0.04 mg/L) compared to August (0.13 ± 0.02 mg/L) and September (0.18 ± 0.01 mg/L) ($p < 0.001$), with all values remaining below the WHO (2.0 mg/L) and NESREA (1.0 mg/L) permissible limits. Cr was not detected in July but appeared in August (0.13 ± 0.02 mg/L) and September (0.17 ± 0.02 mg/L) ($p = 0.234$); all detected concentrations exceeded the WHO limit of 0.05 mg/L but were below the NESREA limit of 0.5 mg/L. The concentration of Ni was higher in July (0.17 ± 0.02 mg/L) and September (0.10 ± 0.01 mg/L) ($p = 0.010$), while not detected in August; all detected concentrations surpassed both the WHO (0.07 mg/L) and NESREA (0.01 mg/L) limits. For Pb, concentrations were higher in July (0.26 ± 0.05 mg/L) and August (0.20 ± 0.02 mg/L) compared to September (0.13 ± 0.02 mg/L) ($p = 0.042$), exceeding both WHO (0.01 mg/L) and NESREA (0.1 mg/L) limits. Mn concentration was highest in July (1.03 ± 0.03 mg/L) compared to August (0.20 ± 0.01 mg/L), while it was not detected in September ($p < 0.001$); the July concentration exceeded the WHO range of 0.4–0.5 mg/L but remained below the NESREA limit of 1.0 mg/L. Cd concentrations were highest in August (0.15 ± 0.02 mg/L), followed by September (0.13 ± 0.02 mg/L) and July (0.12 ± 0.02 mg/L) ($p = 0.513$), with all values considerably above both WHO (0.003 mg/L) and NESREA (0.01 mg/L) permissible limits (Table 4.2).

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Table 4.2: Monthly Variations of Heavy Metals in Water (mg/L) from Ogba River

Heavy Metal	July	August	September	F	p value
Copper (mg/L)	0.59±0.04bc	0.13±0.02a	0.18±0.01a	82.865	<0.001
Chromium (mg/L)	ND	0.13±0.02*	0.17±0.02*	1.560	0.234
Nickel (mg/L)	0.17±0.02*#	ND	0.10±0.01*	10.000	0.010
Lead (mg/L)	0.26±0.05c*#	0.20±0.02c*#	0.13±0.02ab*#	3.640	0.042
Manganese (mg/L)	1.03±0.03*#	0.20±0.01	ND	62.500	<0.001
Cadmium (mg/L)	0.12±0.02*#	0.15±0.02*#	0.13±0.02*#	0.692	0.513

Values shown represent Mean±SEM, ND=Not detected, letter a represents significant difference from July, letter b represents significant difference from August, letter c represents significant difference from September, $p \leq 0.05$ was considered statistically significant, Asterisks (*) denote values above the WHO permissible limit, Hash (#) denote values above the NESREA permissible limit.

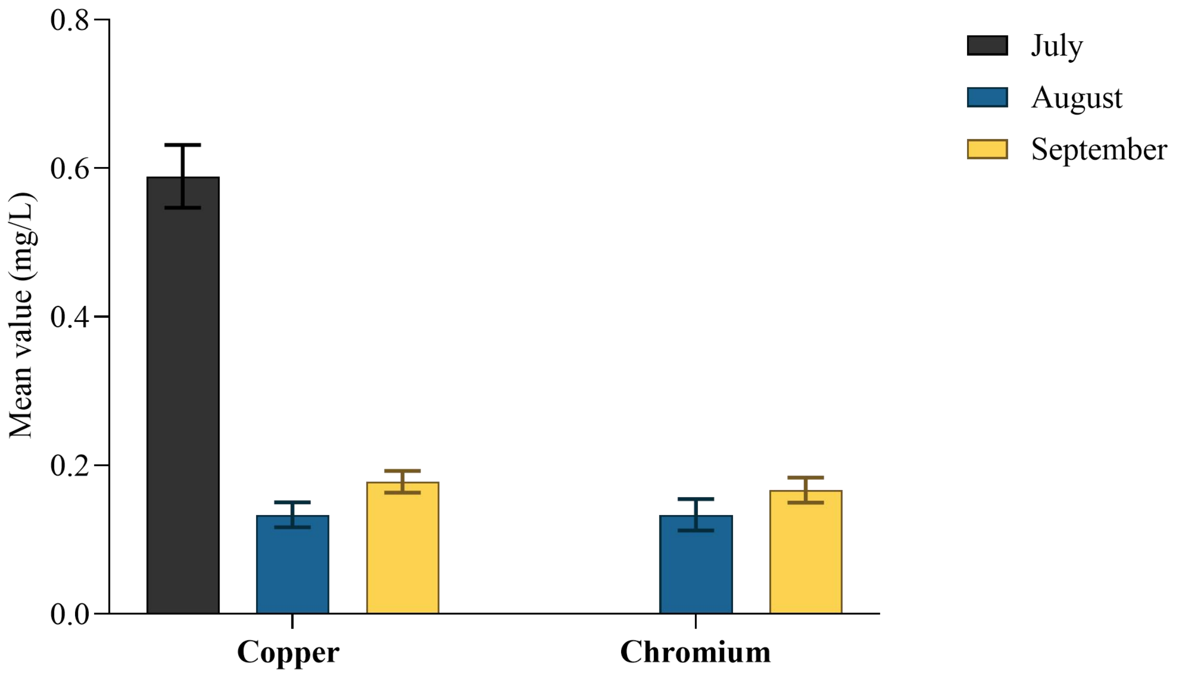

Figure 4.4: Chart showing the concentration of copper and chromium across all time periods.

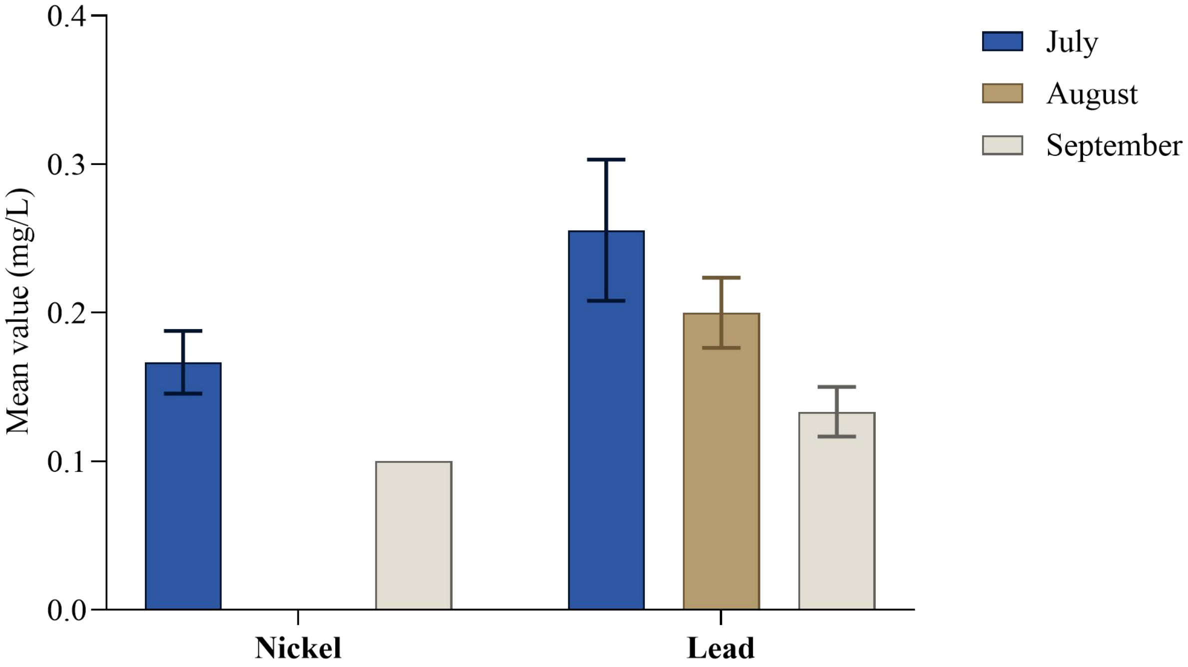

Figure 4.5: Chart showing the concentration of nickel and lead across all time periods.

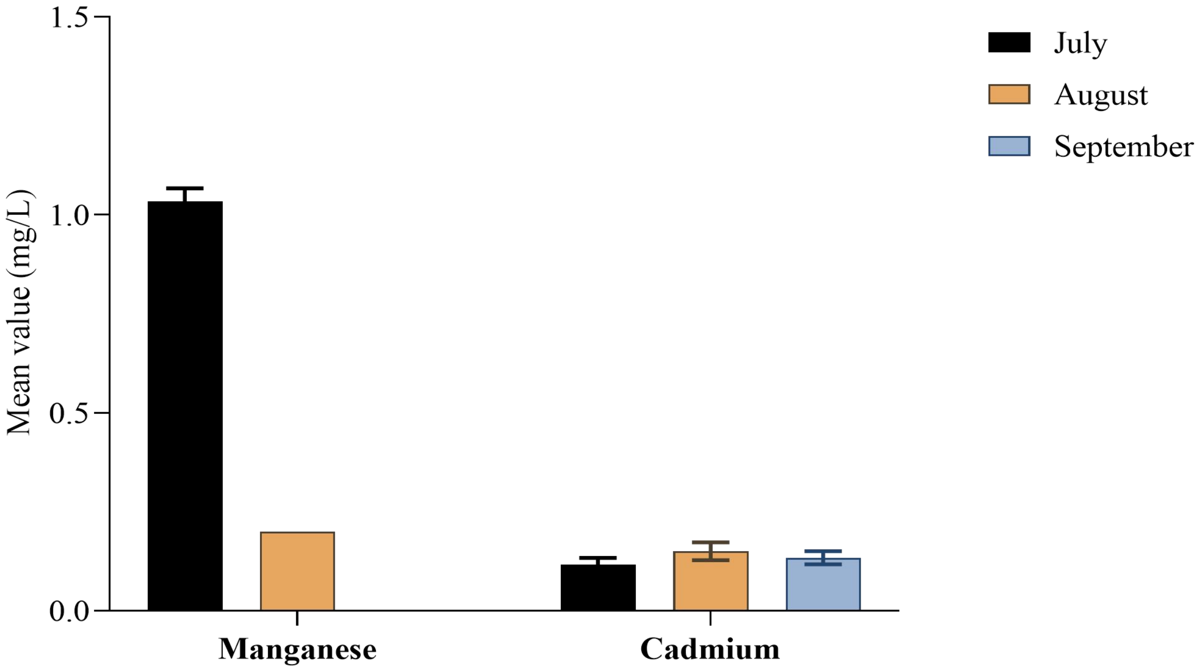

Figure 4.6: Chart showing the concentration of Mn and Cd across all time periods

The table presents the Chronic Daily Intake (CDI) of six heavy metals in water from Ogba River for adults and children at upstream, midstream, and downstream stations. CDI values are expressed in $\times 10^{-3}$ mg/kg/day. For all metals, children had higher CDI values than adults at the corresponding stations. Copper CDI ranged from 6.58 to 9.32 for adults and 15.34 to 21.74 for children. Chromium CDI ranged from 3.29 to 5.48 for adults and 7.67 to 12.79 for children. Nickel CDI ranged from 0.00 to 4.11 for adults and 0.00 to 9.59 for children. Lead CDI ranged from 3.01 to 7.12 for adults and 7.03 to 16.62 for children. Manganese was detected only at the upstream station, with CDI of 16.99 for adults and 39.63 for children. Cadmium CDI ranged from 3.01 to 4.38 for adults and 7.03 to 10.23 for children. The data indicate variations in CDI across metals, stations, and age groups (Table 4.3).

Table 4.3: Chronic Daily Intake (CDI) of Heavy Metals in Water Samples from Ogba River for Adults and Children (×10^{-3} mg/kg/**day)**

Metal	**Adult**			**Children**		
	Upstream	**Midstream**	**Downstream**	**Upstream**	**Midstream**	**Downstream**
Copper	6.58	9.32	8.49	15.34	21.74	19.82
Chromium	5.48	3.29	4.66	12.79	7.67	10.87
Nickel	4.11	3.29	0.00	9.59	7.67	0.00
Lead	6.03	7.12	3.01	14.06	16.62	7.03
Manganese	16.99	0.00	0.00	39.63	0.00	0.00
Cadmium	3.29	4.38	3.01	7.67	10.23	7.03

Note. CDI = Chronic Daily Intake. Values represent CDI (×10^{-3} mg/kg/day) for adults and children at upstream, midstream, and downstream stations of Ogba River.

The assessment of heavy metals in Ogba River revealed potential non-carcinogenic and carcinogenic risks for both adults and children. Hazard Quotient (HQ) values showed that Cu, Ni, and Mn were generally below 1, indicating low risk, whereas Cr, Cd, and Pb exceeded 1 at most stations, suggesting potential non-carcinogenic health effects (Table 4.4). Hazard Index (HI) values, which represent combined non-carcinogenic risk, were substantially above 1 for all stations, with children showing higher values than adults (upstream: 61.10 vs. 26.07; midstream: 71.32 vs. 30.58; downstream: 38.13 vs. 16.35), indicating increased vulnerability (Table 4.5). Incremental Lifetime Cancer Risk (ILCR) values for Cr, Cd, and Pb were above the USEPA acceptable range (1×10^{-6} to 1×10^{-4}), with Cr exhibiting the highest risk, while Ni posed negligible cancer risk (Table 4.6).

Table 4.4: Hazard Quotients (HQ) of Heavy Metals in Water Samples from Ogba River for Adults and Children

Metal	**Adult**			**Children**		
	Upstream	**Midstream**	**Downstream**	**Upstream**	**Midstream**	**Downstream**
Copper	0.165	0.233	0.213	0.383	0.543	0.495
Chromium	1.833	1.100	1.567	4.267	2.567	3.633
Nickel	0.205	0.165	0.000	0.480	0.385	0.000
Lead	17.143	20.286	8.571	40.286	47.429	20.000
Manganese	0.121	0.000	0.000	0.283	0.000	0.000
Cadmium	6.600	8.800	6.000	15.400	20.400	14.000

Note. HQ = Hazard Quotient. Values represent the ratio of Chronic Daily Intake (CDI) to the Reference Dose (RfD) for adults and children at upstream, midstream, and downstream stations of Ogba River. An HQ value less than 1 indicates that the exposure level is within the safe limit and unlikely to cause adverse non-carcinogenic health effects, while values greater than 1 suggest potential health risk.

Table 4.5: Hazard Index (HI) for Combined Non-carcinogenic Risk in Ogba River

Station	**Adult**	**Children**
Upstream	26.07	61.10
Midstream	30.58	71.32
Downstream	16.35	38.13

Note. HI represents the combined non-carcinogenic risk from exposure to heavy metals through water ingestion. Values above 1 indicate potential non-carcinogenic health risks for the population.

Table 4.6: Incremental Lifetime Cancer Risk (CR / ILCR) of Selected Heavy Metals in Ogba River

Metal	**Adult**			**Children**		
	Upstream	**Midstream**	**Downstream**	**Upstream**	**Midstream**	**Downstream**
Chromium	0.096	0.058	0.082	0.045	0.027	0.038
Nickel	0.001	0.001	0.000	0.001	0.001	0.000
Cadmium	0.009	0.011	0.008	0.004	0.005	0.004
Lead	0.022	0.025	0.011	0.010	0.012	0.005

Note. CR (or ILCR) = Incremental Lifetime Cancer Risk. Values represent the estimated probability of developing cancer over a lifetime due to exposure to carcinogenic heavy metals through water ingestion at the upstream, midstream, and downstream stations of Ogba River. According to USEPA guidelines, acceptable ILCR values range from 1×10^{-6} to 1×10^{-4}. Values below 1×10^{-6} are negligible, while values above 1×10^{-4} indicate potential cancer risk.

CHAPTER FIVE

5.1. Discussion

The evaluation of selected heavy metal concentrations in the Ogba River, Benin City provides essential information on the river's current ecological status and potential health implications for communities that depend on it for domestic, agricultural, and recreational purposes. Heavy metal pollution in surface water bodies has become a growing environmental concern, particularly in urban areas where industrial effluents, agricultural runoff, and domestic waste discharge contribute to contamination (Proshad *et al*., 2021). In this study, the variations in heavy metal concentrations across sampling locations and months were assessed to determine the extent of pollution and possible sources influencing metal accumulation in the river system. Human activities have been reported to increase the influx of heavy metals into aquatic ecosystems, leading to potential toxicity in aquatic organisms and disturbances in ecological balance (Sharma *et al*., 2025). In this study, the concentrations of selected heavy metals in the Ogba River, Benin City, varied across the upstream, midstream, and downstream stations, reflecting likely differences in human impact along the river course. Based on the World Health Organization (WHO) permissible limits and NESREA permissible limits (Ahmad *et al*., 2021; NESREA, 2009), the mean concentrations of Cu in all stations were within both WHO and NESREA limits, suggesting reduced contamination. Copper is an essential trace element for aquatic organisms, but excessive amounts can become harmful (Dawood, 2022). The slightly higher Cu concentration at the midstream compared to the upstream and downstream points could likely be due to domestic wastewater discharge, vehicular runoff, or corrosion of metallic materials entering the river (Bakyayita *et al*., 2019). Similar observations were reported in the Ikpoba River (Osa-Iguehide *et al*., 2016). Although Cu levels in the Ogba River were within safe limits, prolonged exposure can still cause liver and kidney damage in humans and impair gill function in fish (Egun *et al.*, 2024).

Chromium concentrations exceeded the WHO guideline of 0.05 mg/L at all stations but remained below the NESREA limit of 0.5 mg/L, with the highest level recorded upstream. This may likely result from auto-mechanic workshops, waste dumps, and small-scale industries releasing effluents into the river (Ore and Adebiyi, 2019). Elevated levels of hexavalent Cr (Cr^{6+}) are particularly dangerous because they can cause liver and kidney damage as well as genetic mutations. Continuous use of such contaminated water for domestic or agricultural purposes may therefore pose serious health risks (Yu *et al.*, 2021). Nickel exceeded both WHO and NESREA limits but was not detected downstream, suggesting point-source pollution from industrial or electroplating activities that gradually reduce through sedimentation and dilution. Obasohan *et al.* (2008) reported a similar pattern in the Ikpoba River, although their values for Ni were higher in the Ogba River. Long-term exposure to Ni can lead to allergic dermatitis, respiratory problems, and cardiovascular issues in humans, while in aquatic life, it may interfere with enzyme activity and reproduction (Genchi *et al.*, 2020). Lead concentrations exceeded both the WHO and NESREA limits at upstream and midstream stations, with lower but still significant levels downstream. The elevated Pb concentration midstream could likely originate from automobile emissions, lead-acid batteries, or leaching of paints and plastics (Gwenzi *et al.*, 2018). Lead is a non-essential and highly toxic metal that can accumulate in tissues. Prolonged exposure can cause anemia, neurological damage, kidney dysfunction, and developmental issues in children. The presence of Pb above safe limits indicates that Ogba River water is unsafe for drinking or domestic use without proper treatment (Generalova *et al.*, 2025). Manganese was detected only at the upstream station exceeding the WHO limit of 0.4–0.5 mg/L but below the NESREA limit of 1.0 mg/L. Its absence midstream and downstream could be due to dilution or sedimentation. The finding from this study contrasts with the study of Anyanwu (2012) in the Ogba River, who reported lower levels of Mn. While Mn is essential in small amounts, excessive exposure may cause neurological symptoms like Parkinson's disease and affect oxygen transport in fish (Peres *et al*., 2016). Cadmium concentrations exceeded both WHO and NESREA limits at all stations, with the highest recorded midstream. This may likely result from poor waste disposal, battery waste, and fertilizer runoff from surrounding areas. Cadmium is a cumulative poison that can cause kidney damage, bone loss, and cancer (Sharma *et al*., 2015).

The observed monthly variations in heavy metal concentrations in the Ogba River indicate that seasonal and anthropogenic factors likely influenced metal input and distribution across the study period. Cu recorded the highest concentration in July (0.59 mg/L) and declined thereafter, though all values remained below both WHO and NESREA limits. Chromium was undetected in July but appeared in August and September exceeding only the WHO limit but below NESREA limits. Nickel concentrations exceeded the WHO and NESREA limits in July and September with no detection in August. Lead concentrations were significantly higher in July and August compared to September, exceeding both WHO and NESREA limits. Manganese peaked in July, exceeding WHO limits but below NESREA limits, and was undetected in September. Cadmium remained consistently above both WHO and NESREA limits across months.

The assessment of heavy metal exposure in Ogba River revealed significant variations in Chronic Daily Intake (CDI) values, with children consistently exhibiting higher exposure than adults across all stations, reflecting their greater vulnerability due to lower body weight and higher relative water consumption. All metals calculated had elevated values. Hazard Quotients (HQs) exceeded 1 for Cr, Pb, and Cd at most stations, suggesting potential non-carcinogenic health risks, whereas Cu, Ni, and Mn posed lower immediate risk. The combined non-carcinogenic risk, expressed as Hazard Index (HI), was substantially higher in children than adults, with midstream showing the highest HI values, showing the vulnerability of younger populations.

In addition to non-carcinogenic risks, potentially toxic elements (PTEs) such as Cr, Cd, Ni, and Pb were assessed for carcinogenic potential, as these metals are known to magnify cancer risk in humans with long-term exposure. The Incremental Lifetime Cancer Risk (ILCR) values in this study revealed that Cr, Pb, and Cd posed the highest cancer risks, following the order Cr > Pb > Cd > Ni. According to Huang *et al.* (2008) and Alidadi *et al.* (2019), ILCR values less than 1×10^{-6} are considered unimportant and can be disregarded, while an ILCR value exceeding 1×10^{-4} is considered detrimental. This study revealed that all the ILCR values are greater than the safe ILCR range, meaning the estimated cancer risk for both adults and children is above the generally acceptable risk level. These findings, however, contrast with the study of Eze *et al.* (2021) in Njaba River, who reported no obvious risk to children and adults' health. Findings from this study revealed the potential long-term health consequences of chronic exposure to these heavy metals and the risk of developing carcinogenic effects due to their cumulative exposure over time.

5.2. Recommendations

1. Strengthen Pollution Control Measures: Enforce stricter regulations on industrial effluent discharge, automobile workshops, and waste disposal practices along the Ogba River to minimize heavy metal contamination.
2. Regular Monitoring: Implement continuous monitoring of heavy metal concentrations across the upstream, midstream, and downstream sections to detect pollution trends and guide timely interventions.
3. Public Health Education: Conduct awareness campaigns to educate local communities on the dangers of using untreated river water for domestic and agricultural purposes.
4. Waste Management Improvement: Promote proper waste segregation, recycling, and safe disposal of batteries, plastics, and electronic waste to reduce leaching of toxic metals.
5. Eco-Restoration Programs: Encourage bioremediation and phytoremediation initiatives using metal-absorbing plants to restore the river's ecological balance.

5.3. Conclusion

The findings of this study indicate that the Ogba River is contaminated with multiple heavy metals, particularly Cr, Ni, Pb, Mn, and Cd, with the exceedance of the WHO and NESREA permissible limits recorded. The Chronic Daily Intake (CDI), Hazard Quotients (HQ), Hazard Index (HI), and Incremental Lifetime Cancer Risk (ILCR) analyses revealed that children are more vulnerable than adults, with Cr, Cd, and Pb posing the highest carcinogenic and non-carcinogenic risks, while Ni presented negligible cancer risk.

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APPENDIX

Plate 1: Sample Collection Upstream

Plate 2: Sample Collection Midstream

Plate 3: Sample Collection Downstream