HUMAN HEALTH RISK ASSESSMENT OF GROUNDWATER ASSOCIATED HEAVY METALS VIA DERMAL EXPOSURE, OLUKU.

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A PROJECT SUBMITTED TO THE DEPARTMENT OF SCIENCE LABORATORY TECHNOLOGY, FACULTY OF LIFE SCIENCES, UNIVERSITY OF BENIN, BENIN CITY, IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF BACHELOR OF SCIENCE DEGREE (B.Sc) IN SCIENCE LABORATORY TECHNOLOGY (GEOLOGY AND MINING TECHNIQUES)

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CERTIFICATION

This is to certify that this undergraduate project work titled "**HUMAN HEALTH RISK ASSESSMENT OF GROUNDWATER ASSOCIATED HEAVY METALS VIA DERMAL EXPOSURE**" was submitted and presented by Okeke Emmanuel SOMTOCHUKUWU with matriculation number LSC1907362 in the Department of Science Laboratory Technology, Faculty of Life Sciences, University of Benin, Benin City. In a partial fulfillment of the requirements for the award of Bachelor of Science Degree in Science Laboratory Technology.

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DEDICATION

I dedicate this project to the Almighty God for His ideas and wisdom while working on this project. I also dedicate this project to my wonderful family for the love and support throughout the course of this project.

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ABSTRACT

This study assessed the human health risks associated with heavy metals in groundwater from Oluku, Edo State, Nigeria, with a focus on dermal exposure. Groundwater, a primary domestic water source, is vulnerable to contamination by both natural and anthropogenic activities, including industrial discharge, agricultural runoff, and improper waste disposal. Key heavy metals analyzed included zinc (Zn), cadmium (Cd), manganese (Mn), iron (Fe), and Lead (Pb). Fifteen groundwater samples were collected and analyzed using atomic absorption spectrometry (AAS) following standard procedures. Concentrations were compared against World Health Organization (WHO, 2017) and Nigerian Standard for Drinking Water Quality (NSDWQ, 2007) limits, while potential human health risks were estimated using the United States Environmental Protection Agency (USEPA, 2004) Human Health Risk Assessment (HHRA) framework. Results indicated that zinc (Zn) and iron (Fe) were present at relatively higher levels, with mean concentrations of 3.05 mg/L and 1.53 mg/L, respectively, while lead (Pb) and cadmium (Cd) recorded concentrations of 0.604 mg/L and 0.462 mg/L, exceeding WHO and NSDWQ limits. Chronic Daily Intake (CDI) and Hazard Quotient (HQ) analyses revealed that non-carcinogenic risks from Zn, Fe, and Mn were minimal. However, Pb and Cd posed significant health risks, particularly for children, who exhibited higher exposure levels due to lower body weight and greater dermal contact. Carcinogenic risk assessment further indicated that both Pb and Cd exceeded acceptable USEPA limits, with cadmium presenting the highest lifetime cancer risk. The study concluded that Fe and Zn likely originated from natural geogenic sources within the Benin Formation, while Pb and Cd contamination was predominantly anthropogenic, linked to industrial, domestic, and agricultural activities. The uneven spatial distribution of metals highlighted the influence of proximity to pollution sources. These findings underscore the urgent need for continuous groundwater monitoring, effective waste management, and public health interventions to mitigate exposure risks in Oluku, ensuring the safety of groundwater resources for domestic use.

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Groundwater is a significant source of safe drinking water and fulfills a substantial portion of the home and irrigation requirements in numerous countries. Water is an indispensable resource that supports all forms of life on Earth. Among the various water sources available, groundwater remains the most reliable for domestic, agricultural and industrial purposes, particularly in developing countries such as Nigeria (Nwankwoala, 2011; Offodile, 2002). It is often preferred over surface water due to its natural filtration through soil and rock layers, which enhances its microbial and chemical quality (Oborie and Olorunfemi, 2015).

However, the quality of groundwater has been increasingly threatened by anthropogenic activities such as industrialization, poor waste disposal, agricultural runoff and urbanization. These activities introduce toxic substances including heavy metals into groundwater systems (Edet & Offiong, 2002; Tchounwou et al., 2012). Heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and zinc (Zn) are of particular concern because they are non-biodegradable, persist in the environment, and bioaccumulate through the food chain (Jaishankar *et al*., 2014; Saha *et al*., 2017).

Exposure to these metals, even at low concentrations, can have severe health implications. Lead is associated with neurological and cognitive disorders, especially in children. Cadmium causes and damages the liver, mercury affects the nervous system and excess zinc can cause gastrointestinal distress (Tchounwou *et al*., 2012; Jaishankar *et al*., 2014; Li *et al*., 2023).

To quantify the potential human health effects of exposure to heavy metals, researchers use the Human Health Risk Assessment (HHRA) model developed by the United States Environmental

Protection Agency (USEPA, 1989). This framework evaluates both carcinogenic and non-carcinogenic risks through exposure pathways such as ingestion and dermal contact. While HHRA has been applied extensively in Asia and Europe, there are relatively few studies assessing groundwater-related risks in many parts of Nigeria (Olalekan *et al.*, 2019; Aendo *et al.*, 2022).

The Oluku area of Benin City, known for its mixed residential and small-scale industrial activities, relies heavily on boreholes and wells for domestic use. With increasing urbanization and poor waste management, it is crucial to investigate the potential health risks associated with heavy metals in groundwater sources within this region.

1.2 Study Area

The study will be conducted Oluku located in Ovia North-East Local Government Area of Edo State, Nigeria. It serves as a major gateway from Benin City to other southwestern states such as Ondo and Ekiti. The area lies within the Benin Formation, characterized by lateritic soils composed mainly of silty and clayey sands. The tropical climate of Oluku is marked by distinct wet and dry seasons, which influence groundwater recharge and contamination dynamics (Oborie and Olorunfemi, 2015).

Groundwater remains the primary source of water for most residents due to the unreliable quality and availability of surface water. However, the proximity of residential wells to refuse dumps, automobile workshops and small-scale industries raises concerns about possible contamination by heavy metals and other pollutants.

1.3 Aim of the Study

The primary aim of this study is to assess the human health risks associated with heavy metals in groundwater sources used for domestic purposes with a focus on identifying potential health impacts and informing groundwater management strategies.

1.4 Objectives

The specific objectives of the study are to:

1. Determine the concentrations of selected heavy metals (Pb, As, Cd, Cr, Hg and Zn) in groundwater samples from Oluku and its environs.
2. Compare the observed concentrations with the permissible limits set by the World Health Organization (WHO, 2017) and the Nigerian Standard for Drinking Water Quality (NSDWQ, 2007).
3. Estimate both carcinogenic and non-carcinogenic health risks for adults and children using the Human Health Risk Assessment (HHRA) model.
4. Identify potential sources and pathways of heavy metal contamination in the study area.
5. Recommend measures to mitigate health risks and improve groundwater safety in Oluku.

1.5 Statement of the Problem

In Nigeria, there is a widespread assumption that groundwater is inherently safe for drinking. Consequently, most households consume water from boreholes and hand-dug wells without prior treatment or laboratory testing (Akinbile and Yusoff, 2011). However, several studies have revealed elevated concentrations of heavy metals in groundwater across Nigerian cities, including Lagos, Port Harcourt and Benin City (Ocheri *et al*., 2014; Olalekan *et al*., 2019).

Despite these findings, many of the studies have focused solely on determining metal concentrations without estimating their potential health risks to humans. This presents a significant gap, as the actual exposure risk depends not only on concentration but also on consumption rate, body weight, and duration of exposure (USEPA, 1989; Saha *et al*., 2017). Without comprehensive risk assessment, communities remain unaware of the potential chronic effects of consuming contaminated groundwater, such as kidney failure, neurological impairment or cancer.

Moreover, in regions like Oluku where groundwater is the predominant source of drinking water and local industries discharge untreated waste the possibility of heavy metal migration into aquifers is high. The absence of continuous monitoring and risk-based studies means that residents may be unknowingly exposed to harmful contaminants. Addressing this problem through a risk assessment framework will not only fill existing research gaps but also guide local authorities in enforcing groundwater safety regulations (Li *et al*., 2023; Aendo *et al*., 2022).

1.6 Justification of the Study

Groundwater is a vital source of drinking water for millions of Nigerians, yet its safety is often compromised by anthropogenic pollution and inadequate monitoring (Oborie and Olorunfemi, 2015). Most existing studies in Nigeria have primarily focused on measuring concentrations of contaminants without translating these data into human health implications (Olalekan *et al.*, 2019).

This study applies the HHRA framework to provide a more comprehensive understanding of groundwater safety in Oluku. The results will offer valuable insights for policymakers, environmental regulators, and public health officers to implement effective mitigation strategies. Furthermore, the findings will raise community awareness about the potential dangers of consuming untreated groundwater and serve as a baseline for future research and policy interventions on groundwater management and public health protection.

In addition, this research is justified by the urgent need for region-specific health risk data. Many Nigerian groundwater studies generalize findings across broad geographic zones, neglecting local hydrogeological and anthropogenic factors that can significantly alter contamination dynamics. By focusing specifically on Oluku, this study provides localized evidence that can guide targeted interventions and community education programs aimed at reducing health risks associated with groundwater consumption (Nwankwoala, 2011; Tchounwou *et al.*, 2012).

1.7 Limitations of the Study

Every research has its constraints and this study is not exempted. One major limitation is funding and resource availability, which may restrict the number of groundwater samples collected and the frequency of sampling. As a result, the spatial and temporal variability of heavy metal concentrations across different parts of Oluku may not be fully represented. Similarly, sampling was limited to the dry season, which means potential seasonal fluctuations in groundwater quality during the rainy season could not be captured (Akinbile and Yusoff, 2011).

Another limitation arises from the scope of the Human Health Risk Assessment (HHRA), which in this study focuses primarily on the ingestion exposure pathway. Other potential routes, such as dermal contact or bioaccumulation through the food chain, were excluded due to time and resource constraints (USEPA, 1989; WHO, 2017). Furthermore, the risk assessment models applied are based on international standard parameters that may not perfectly reflect local conditions such as community-specific water consumption rates, diet, and physiological differences (Saha *et al.,* 2017).

Despite these limitations, the study provides reliable and valuable baseline data on groundwater contamination and associated health risks in Oluku. The findings can serve as a foundation for future, more comprehensive investigations that incorporate multiple exposure pathways and seasonal variations.

CHAPTER TWO

LITERATURE REVIEW

2.1 Groundwater

Groundwater refers to the portion of water stored beneath the Earth's surface within soil pores, rock fractures and aquifers. It forms through the downward percolation of precipitation and surface water until it reaches the saturated zone, where all available spaces are filled with water. This subsurface resource represents almost 30 percent of the world's accessible freshwater, making it one of the most dependable water supplies for domestic, agricultural, and industrial purposes (Todd and Mays, 2005). Because groundwater is filtered naturally through layers of soil and rock, it generally contains fewer pathogens and suspended solids than surface water, which explains its preference for drinking and household use in many regions (Oborie and Olorunfemi, 2015).

In developing countries like Nigeria, groundwater plays a critical role in daily life. Municipal water systems are often poorly maintained or absent, leaving boreholes, hand-dug wells and springs as the principal water sources for households and small businesses (Nwankwoala, 2011). Groundwater's reliability during dry seasons, when rivers and streams shrink or disappear, enhances its importance. However, the same factors that make groundwater accessible also make it vulnerable to contamination. Rapid urbanization, waste mismanagement, leachates from dumpsites, and infiltration of agricultural chemicals threaten aquifer quality in many Nigerian cities, including Benin City and its environs (Akinbile and Yusoff, 2011; Edet and Offiong, 2002).

Hydrogeologically, groundwater movement and storage depend on the permeability and porosity of the geologic materials in which it resides. Coarse-grained sands and sandstones facilitate infiltration and recharge, whereas fine-grained clay and shale impede flow. Oluku, situated within the Benin Formation, is dominated by lateritic and sandy soils that promote percolation but provide limited protection against contaminants migrating from surface sources (Adewumi *et al*., 2021; Offodile, 2002). Understanding these physical conditions is essential for assessing groundwater vulnerability and for designing monitoring or protection programs.

Groundwater's domestic use is widespread and indispensable. It provides drinking water for over two billion people globally and supplies almost half of all household water consumption (FAO, 2021). In rural and peri-urban communities, it is used for cooking, bathing, cleaning, sanitation and small-scale gardening. The relative affordability of wells and boreholes, compared with large-scale public water networks, makes groundwater an accessible option for low-income populations. However, contamination by heavy metals or pathogenic microorganisms can transform this lifeline into a health hazard. Studies across sub-Saharan Africa have reported high levels of lead, cadmium, and arsenic in domestic wells located near waste dumps and industrial zones (Olalekan *et al*., 2019; Aendo *et al*., 2022). These findings highlight the need for continuous monitoring and public education on groundwater safety.

Beyond households, groundwater is also vital for industrial use. Many manufacturing sectors—food and beverage production, textiles, pharmaceuticals, and energy generation—depend on groundwater for processing, cooling, and cleaning operations. Its stable temperature and consistent chemical composition make it especially suitable for industries that require high-purity water (Liu *et al*., 2020). In industrial hubs such as Benin City, groundwater provides an inexpensive and readily available input that sustains economic productivity. Nevertheless, unregulated abstraction and inadequate waste disposal by factories can deplete aquifers and introduce pollutants such as heavy metals, hydrocarbons, and solvents, compromising both industrial and domestic supplies (Saha *et al*., 2017; Li *et al.,* 2023).

The contribution of groundwater to global food security and industrial growth cannot be overstated, yet over-exploitation and pollution threaten its sustainability. Excessive pumping lowers water tables, causes land subsidence, and can draw in contaminated surface water or saline intrusion in coastal zones. Similarly, improper waste management enables toxic substances to infiltrate aquifers, endangering human health and ecosystems (Tchounwou *et al*., 2012). To safeguard this critical resource, effective groundwater governance must integrate scientific monitoring, community participation and enforcement of environmental standards (UNESCO, 2022; FAO, 2021). Sustainable groundwater management is therefore not only a technical challenge but also a socio-economic necessity for long-term environmental resilience and public well-being.

Risk assessment provides a quantitative approach for evaluating potential adverse health effects from chronic exposure to toxic metals without necessarily linking to cancer outcomes. The United States Environmental Protection Agency (USEPA) framework employs the Hazard Quotient (HQ) and Hazard Index (HI) as indicators of health risk and has been extensively applied in groundwater studies across Asia, Africa and the Middle East (Anyanwu *et al*., 2018). Dermal exposure assessment is particularly critical for vulnerable groups such as children who have thinner skin, greater skin surface area relative to body weight and higher exposure frequency during daily activities. Studies in Egypt’s northwestern desert, for instance, reported that children experience significantly higher non-carcinogenic risks ($HI > 1$) compared to adults, highlighting the importance of incorporating this pathway into risk evaluations (Omali *et al*., 2023).

2.2 Sources of Heavy Metal Contamination in Groundwater

Heavy metal contamination in groundwater arises from both natural and anthropogenic sources, each contributing to the spatial and temporal variability of pollution levels across different regions. Understanding these sources is essential for accurately assessing the extent of contamination, identifying high-risk areas and formulating effective mitigation and management strategies. Natural sources primarily include the weathering and dissolution of metal-bearing minerals, leaching from geological formations and volcanic activity, while anthropogenic contributions stem from mining, industrial discharge, agricultural runoff and improper waste disposal. Differentiating between these origins helps determine the dominant contamination pathways and guides remediation efforts. Recent studies emphasize that integrated geochemical and hydrogeological analyses are necessary for source identification and pollution control, particularly in regions where both natural and human activities interact to influence groundwater quality (Vesković and Onija, 2025).

2.2.1 Natural Sources

Natural geological processes play a vital role in the accumulation of heavy metals in groundwater through interactions between water, rocks, minerals and soils. These processes include weathering, leaching and various geochemical reactions that mobilize metals under specific environmental conditions (Ravenscroft *et al.*, 2009). Heavy metals such as Lead (Pb), chromium (Cr) and ZI (Zn) occur naturally in particular rock types like ultramafic formations, which are rich in nickel and chromium, and sedimentary deposits that contain arsenic-bearing minerals. In regions such as Bangladesh and West Bengal, India, naturally occurring arsenic within alluvial aquifers has led to severe groundwater contamination, with concentrations frequently exceeding the World Health Organization (WHO) guideline limit of 10 µg/L. Under reducing conditions, the presence of arsenite enhances arsenic mobility and toxicity, contributing to widespread exposure risks in affected communities (Ravenscroft *et al*., 2009).

Volcanic and geothermal activities also introduce heavy metals into groundwater. Metals such as mercury (Hg) and cadmium (Cd) may enter aquifers through volcanic ash, fumarolic emissions or geothermal fluids. In the East African Rift Valley, geothermal systems have been identified as major sources of elevated mercury and Arsenic levels in groundwater, driven by high subsurface temperatures and hydrothermal interactions (Anawar *et al*., 2013). Additionally, the weathering of sulfide minerals like pyrite (FeS_2), which contains iron (Fe) and arsenic, or galena (PbS), which contains lead (Pb), contributes to metal release into groundwater. The degree of metal mobilization depends on several factors, including pH, redox potential and aquifer mineralogy. Acidic groundwater ($pH < 6$) typically enhances the solubility of metals such as Pb and Cd, leading to higher contaminant concentrations (Kaur *et al*., 2020).

Soil composition and geochemical interactions also influence the natural release of heavy metals into groundwater. Soils rich in organic matter or clay minerals have a strong capacity to adsorb metals, which can later be released depending on changes in soil pH or ionic composition. In tropical regions, lateritic soils abundant in iron oxides often release Fe and trace metals such as Ni and Cr into groundwater during intense rainfall or fluctuating redox conditions (Nikalje *et al*., 2021). Collectively, these natural processes underscore the significance of geological and geochemical factors in shaping the baseline concentrations of heavy metals in groundwater systems worldwide.

2.2.2 Anthropogenic Sources

Human activities are the predominant contributors to heavy metal contamination in groundwater, largely driven by industrialization, urbanization, agriculture and inadequate waste management. These sources introduce metals at concentrations far exceeding natural background levels, posing serious environmental and public health threats. Industrial sectors such as mining, smelting, electroplating, textile production and chemical manufacturing release substantial quantities of metals like lead (Pb), chromium (Cr) and zinc (Zn) through untreated or poorly treated effluents. Studies in Egypt's northwestern desert region, for example, identified industrial discharge as a major source of groundwater pollution with Heavy Metal Pollution Index (HPI) values exceeding 100 and Metal Index (MI) values above 6, indicating severe contamination (Omali *et al.,* 2023).

Agricultural practices are another significant pathway for heavy metal introduction into groundwater. The widespread use of phosphate fertilizers, pesticides and irrigation with contaminated surface water introduces metals such as chromium, zinc and lead into aquifers. Phosphate-based fertilizers often contain trace quantities of Cd that leach into groundwater over time. In the Malwa region of Punjab, India, agricultural runoff has been linked to elevated concentrations of iron, Cadmium, lead and nickel with hazard index (HI) values exceeding 2, suggesting potential non-carcinogenic risks (Kaur *et al*., 2020). Additionally, the use of wastewater for irrigation, common in peri-urban areas of developing countries, mobilizes metals from soils into groundwater, further worsening contamination levels.

Improper waste disposal is another key anthropogenic factor. Leachates generated from landfills, electronic waste and automobile scrap yards infiltrate groundwater, introducing heavy metals such as lead and arsenic. A study conducted in Ibadan, Nigeria, reported lead(Pb) concentrations ranging from 0.1 to 0.3 mg/L in groundwater near automobile repair clusters levels significantly higher than the World Health Organization (WHO) limit of 0.01 mg/L attributed to leakage from used oil, batteries and metallic debris (Omali *et al.,* 2023). Urban runoff also serves as a critical contamination pathway, as rainfall washes heavy metals from roads, industrial zones and construction sites into the subsurface. In Shiraz, Iran, unplanned urban expansion and inadequate sewage systems have contributed to groundwater contamination with some heavy metals, though most samples still exhibited hazard index (HI) values below one, indicating low non-carcinogenic risk (Omali *et al.,* 2023).

Mining operations represent one of the most severe anthropogenic sources of heavy metals in groundwater. Extraction and processing of minerals such as gold, copper and coal produce acid mine drainage and metallic tailings that infiltrate aquifers. In South Africa, extensive gold mining has resulted in widespread contamination of groundwater with arsenic, cadmium and mercury, with recorded pH levels as low as 3 promoting metal solubility and mobility (Tchounwou *et al*., 2012). Furthermore, atmospheric deposition from industrial emissions and fossil fuel combustion contributes additional heavy metal inputs. Smelter dust, fly ash and coal combustion residues release lead, mercury and nickel particles that settle on soil surfaces and are subsequently leached into groundwater, as observed in several industrial regions of China (Alloway, 2013). Collectively, these human-driven activities have significantly altered groundwater chemistry, creating persistent contamination hotspots that demand comprehensive monitoring and remediation efforts.

2.2.3 Spatial and Temporal Variability

The spatial and temporal distribution of heavy metals in groundwater is influenced by several interacting factors, including proximity to contamination sources, hydrogeological conditions, land use patterns and seasonal variations. Spatial variability reflects differences in local geology, aquifer permeability and anthropogenic pressure, such as industrial emissions or agricultural runoff. Geographic Information System (GIS)-based studies have demonstrated that groundwater near industrial estates, landfills and mining zones typically exhibits significantly higher metal concentrations compared to rural or less disturbed areas. For example, a hydrogeochemical study in Qatar revealed that heavy metal concentrations were elevated near industrial clusters and waste disposal sites, with Heavy Metal Pollution Index (HPI) values ranging between 50 and 200, indicating moderate to high levels of contamination (Kadhem *et al*., 2020).

Temporal variability is often governed by seasonal and long-term environmental changes that affect metal mobility and transport in aquifers. During wet or monsoon seasons, elevated infiltration and leaching rates enhance the dissolution and migration of metals such as lead(Pb), cadmium(Cd) and nickel(Ni) from surface soils into groundwater. In northern India, seasonal monitoring indicated that lead and cadmium concentrations increased by approximately 25% during the monsoon period compared to the dry season due to enhanced percolation and runoff processes (Kaur *et al*., 2020). Similarly, in tropical regions with alternating wet and dry periods, fluctuating redox conditions can alter the solubility and speciation of metals, influencing their availability and toxicity.

Long-term temporal trends are also shaped by sustained industrialization, urban expansion and land-use transformation. Studies in Iran have shown that over several decades, groundwater concentrations of chromium and nickel have increased significantly in urbanizing areas, attributed to persistent effluent discharge and inadequate wastewater management (Barzegar *et al*., 2017). Such findings underscore that both spatial and temporal dynamics must be integrated into groundwater monitoring and management frameworks to accurately assess contamination risks and design effective remediation strategies.

2.2.4 Interaction of Sources

The interaction between natural and anthropogenic sources often intensifies heavy metal contamination in groundwater, creating complex geochemical dynamics that complicate risk assessment and remediation efforts. In many cases, naturally occurring metals within geological formations are mobilized or concentrated through human activities that alter subsurface chemical conditions. For instance, in arsenic-affected regions of Bangladesh and West Bengal, India, excessive groundwater abstraction for irrigation has modified redox conditions, promoting the reductive dissolution of arsenic-bearing minerals and enhancing arsenic mobility in aquifers (Mukherjee *et al*., 2019). This anthropogenically driven geochemical disturbance amplifies the natural release of arsenic and increases its bioavailability in groundwater.

Similar synergistic interactions are observed in other regions, where naturally metal-rich soils are subjected to human-induced contamination. In Nigeria, for example, the combination of iron-rich lateritic soils and leachates from automobile and industrial wastes contributes to elevated levels of lead(Pb), cadmium(Cd) and nickel(Ni) in groundwater. The concurrent influence of natural and anthropogenic inputs often leads to metal co-contamination, resulting in more complex toxicity profiles and environmental persistence (Olagunju *et al*., 2020).

These interactions are further mediated by local environmental parameters such as pH, redox potential, organic matter content and aquifer recharge rates, all of which affect metal solubility, speciation and transport. Under acidic or reducing conditions, many metals exhibit increased mobility, while high organic content can form complexes that either enhance or inhibit transport depending on the dominant species. Consequently, understanding the interplay between natural geological processes and anthropogenic activities is essential for accurately predicting contamination behavior, assessing exposure risks and designing site-specific mitigation strategies (Anawar *et al*., 2013).

2.3 Heavy Metals of Concern in Groundwater

Heavy metals are dense metallic elements that occur naturally in the Earth's crust but become toxic when they accumulate beyond permissible limits. Unlike organic pollutants, they do not degrade or decompose, making them persistent in the environment. In groundwater, these metals may originate from both natural geologic formations and human activities such as industrial discharge, mining, and waste disposal. The six major heavy metals of environmental concern in groundwater are lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and zinc (Zn) (Li *et al*., 2023; Jaishankar *et al*., 2014).

Lead (Pb) is one of the most toxic heavy metals commonly found in contaminated groundwater. It is mainly introduced through corrosion of lead-based pipes, battery recycling, paints, and industrial effluents (Saha *et al*., 2017). Once released into the environment, lead (Pb) can persist for decades and migrate through soil layers into aquifers. In the human body, lead (Pb) accumulates in the bones, liver, and brain where it interferes with the synthesis of hemoglobin and the functioning of the central nervous system (Jaishankar *et al*., 2014). Chronic exposure leads to anemia, cognitive impairment, and reduced IQ levels in children, while in adults it causes hypertension and kidney dysfunction (Li *et al*., 2023; WHO, 2017). Because lead (Pb) has no biological function, even small concentrations in drinking water can cause severe health effects over time.

Cadmium (Cd) is another hazardous heavy metal found in groundwater, primarily introduced through industrial waste, phosphate fertilizers, electroplating, and mining activities (Nouri *et al*., 2018). It is often mobilized from soils into groundwater under acidic conditions where it remains soluble and bioavailable. Cadmium (Cd) tends to accumulate in the kidneys, liver, and bones causing renal failure, osteoporosis, and skeletal deformities with long-term exposure (Saha *et al*., 2017; WHO, 2017). The “Itai-Itai” disease reported in Japan is a classic example of cadmium (Cd) poisoning through contaminated water and food (Tchounwou *et al*., 2012). Because of its high toxicity and mobility in the environment, cadmium (Cd) is classified as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC).

Arsenic (As) contamination in groundwater is largely due to natural geologic processes and to a lesser extent anthropogenic sources such as pesticide use and industrial effluents. In many parts of Asia and sub-Saharan Africa, arsenic (As) occurs naturally in sedimentary aquifers rich in iron oxides and sulfides that release it under reducing conditions (Mukherjee *et al*., 2022). Chronic exposure to arsenic (As) causes severe health effects including skin pigmentation, cardiovascular disorders, and cancers of the bladder, lung, and liver (Li *et al*., 2023; Smith *et al*., 2000). Arsenic (As) toxicity is of particular concern because its inorganic forms, especially arsenite (As^{3+}) and arsenate (As^{5+}), are highly mobile and bioavailable in groundwater. The World Health Organization (WHO, 2017) recommends a maximum permissible limit of 0.01 mg/L for arsenic (As) in drinking water.

Chromium (Cr) occurs naturally in two stable oxidation states trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}). While the trivalent form is an essential micronutrient required for glucose metabolism, the hexavalent form (Cr(VI)) is toxic and carcinogenic (Jaishankar *et al*., 2014). Chromium (Cr) pollution of groundwater mainly originates from tanneries, textile processing, electroplating, and stainless-steel manufacturing industries (Saha *et al*., 2017). The ingestion of water containing Cr(VI) can cause liver damage, gastric ulcers, respiratory disorders, and cancers (Tchounwou *et al*., 2012). Chromium (Cr) compounds are also known to cause allergic skin reactions and genetic mutations in prolonged exposures. Due to its persistence and toxicity, WHO (2017) recommends that total chromium (Cr) concentrations in drinking water should not exceed 0.05 mg/L.

Mercury (Hg) is a highly toxic heavy metal that exists in elemental, inorganic, and organic forms. It is released into the environment through artisanal gold mining, industrial discharges, and the improper disposal of mercury-containing equipment such as thermometers and fluorescent lamps (Li *et al.,* 2023; Clarkson and Magos, 2006). In groundwater, mercury (Hg) can transform into methylmercury a highly toxic compound that bioaccumulates through the aquatic food chain. Human exposure to mercury (Hg) through contaminated water leads to neurological and developmental damage, particularly in fetuses and young children (Tchounwou *et al*., 2012). Long-term exposure affects the kidneys and causes tremors, memory loss and impaired coordination (WHO, 2017). Even at low concentrations, mercury (Hg) poses a significant risk to human and ecosystem health due to its bioaccumulative nature.

Zinc (Zn), unlike other heavy metals, is an essential micronutrient required for enzyme activation and immune function. However, at elevated concentrations, zinc (Zn) becomes toxic to humans and aquatic organisms. Its main sources include galvanization, metal plating and the corrosion of zinc-coated pipes (Jaishankar *et al*., 2014). Excessive ingestion of zinc (Zn) through groundwater can cause nausea, vomiting, abdominal pain, and interference with copper absorption in the body (Tchounwou *et al*., 2012). Although zinc (Zn) is generally less toxic than other heavy metals, its presence in groundwater above the WHO (2017) limit of 3 mg/L may indicate contamination from industrial or urban waste. Continuous exposure to elevated zinc (Zn) levels can alter metabolic functions and contribute to oxidative stress in living cells.

In summary, the presence of lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and zinc (Zn) in groundwater presents a serious threat to environmental and public health. Their toxicity, persistence, and ability to bioaccumulate make them critical indicators of water quality. Assessing their concentrations and health implications is essential for understanding the extent of groundwater pollution and implementing effective management strategies in areas like Oluku where boreholes and wells serve as primary water sources (Aendo *et al*., 2022; Olalekan *et al*., 2019).

2.4 Health Risk Assessment Associated with Groundwater

Human health risk assessment (HHRA) is a scientific process used to estimate the likelihood of adverse health effects resulting from exposure to environmental contaminants such as heavy metals in groundwater. It involves identifying hazards, determining the extent of exposure, assessing toxicity, and characterizing the overall risk to human populations (USEPA, 1989). Groundwater is a major source of drinking water in most developing countries including Nigeria, yet it is often contaminated by toxic substances from industrial and agricultural activities (Olalekan *et al*., 2019). These contaminants, particularly heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and zinc (Zn), can accumulate in the human body through ingestion and bioaccumulation over time. The HHRA framework provides a quantitative means of estimating both carcinogenic (cancer-causing) and non-carcinogenic (non-cancer) risks associated with such exposure (Li *et al*., 2023).

Non-carcinogenic risk assessment focuses on determining the likelihood of health effects other than cancer from short- or long-term exposure to contaminants. It is typically expressed as a hazard quotient (HQ), which compares the estimated daily intake of a contaminant to a reference dose (RfD) a safe level of exposure below which no adverse health effects are expected (USEPA, 1989; WHO, 2017). When the HQ exceeds 1, it suggests a potential health risk. Chronic exposure to heavy metals through groundwater can lead to various non-carcinogenic effects such as kidney failure (from cadmium (Cd)), neurological damage (from lead (Pb)), and liver or skin disorders (from arsenic (As) and chromium (Cr)) (Tchounwou *et al*., 2012). Mercury (Hg) affects the central nervous system causing tremors and impaired coordination, while high levels of zinc (Zn) can cause nausea, abdominal pain, and interference with copper metabolism (Jaishankar *et al*., 2014).

These risks are often more severe in children than adults due to their lower body weight and higher rate of water consumption relative to body mass (Aendo *et al*., 2022).Carcinogenic risk assessment, on the other hand, estimates the probability of developing cancer over a lifetime due to exposure to carcinogenic contaminants. It is expressed as cancer risk (CR) and calculated by multiplying the average daily dose of a contaminant by its slope factor (SF) a parameter that quantifies the relationship between exposure and cancer risk (USEPA, 1989). Carcinogenic risks associated with groundwater exposure are primarily linked to metals such as arsenic (As), cadmium (Cd), chromium (Cr) and in some cases lead (Pb) (Li *et al*., 2023;Mukherjee *et al*., 2022). Arsenic (As) is well known for its link to skin, bladder, and lung cancers, while cadmium (Cd) exposure increases the risk of kidney and prostate cancers. Hexavalent chromium is classified as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC) and has been associated with stomach and respiratory cancers. The acceptable lifetime cancer risk range established by the USEPA is between 1×10^{-6} (one in a million) and 1×10^{-4} (one in ten thousand) (USEPA, 1989).

Both carcinogenic and non-carcinogenic risks depend on several exposure factors such as contaminant concentration in water, ingestion rate, exposure duration, frequency, and body weight. In many Nigerian communities, where people depend on untreated groundwater, these factors are often underestimated leading to higher actual risk levels (Olalekan *et al.,* 2019). Moreover, the synergistic effects of multiple metals can amplify toxicity beyond the impact of individual elements (Saha *et al.,* 2017). The application of HHRA in contaminated regions like Oluku is therefore vital for quantifying real health threats, identifying vulnerable populations such as children and pregnant women, and guiding environmental health policies. By integrating chemical analysis with risk modeling, HHRA provides a scientific basis for decision-making and public health protection against both cancer and non-cancer outcomes arising from groundwater contamination.

2.5 Health Effects of Heavy Metal Exposure

The health impacts of exposure to heavy metals in groundwater have been well documented across scientific and medical literature. Heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and zinc (Zn) pose serious risks even at low concentrations because of their tendency to bioaccumulate in human tissues and organs (Jaishankar et al., 2014; Tchounwou *et al*., 2012). Once ingested through drinking water, these metals bind to proteins and enzymes, disrupting normal physiological processes. The severity of health effects depends on factors such as metal type, concentration, exposure duration, age, and nutritional status. Children and pregnant women are particularly vulnerable since heavy metals can cross the placental barrier and interfere with developmental processes (Li *et al*., 2023; WHO, 2017).

Lead (Pb) exposure through contaminated groundwater primarily affects the central nervous system, kidneys, and blood-forming organs. It interferes with enzyme systems that regulate heme synthesis, resulting in anemia and reduced oxygen transport (Jaishankar *et al.,* 2014). In children, chronic exposure leads to cognitive impairment, reduced IQ, and behavioral disorders, while in adults it contributes to hypertension, kidney damage, and infertility (Saha *et al*., 2017). Cadmium (Cd) primarily targets the kidneys and skeletal system. Long-term exposure leads to renal dysfunction, calcium loss, and bone demineralization resulting in skeletal deformities (WHO, 2017). It is also a known carcinogen linked to lung and prostate cancers (Tchounwou *et al*., 2012). Because cadmium (Cd) has a long biological half-life (10–30 years), it remains in the human body for extended periods causing cumulative toxicity (Li *et al*., 2023).

Arsenic (As) exposure, particularly through groundwater, is one of the most severe environmental health concerns worldwide. Chronic ingestion of arsenic (As) leads to a condition known as arsenicosis, characterized by skin lesions, hyperpigmentation, and thickening of the palms and soles (Smith *et al*., 2000). Prolonged exposure is also associated with cancers of the skin, bladder, liver, and lungs (Mukherjee *et al*., 2022). Arsenic (As) disrupts metabolic enzymes and generates oxidative stress, leading to DNA damage and impaired cell repair mechanisms. Chromium (Cr) exposure, especially in its hexavalent form, causes respiratory irritation, liver and kidney damage, and is classified as a human carcinogen by the International Agency for Research on Cancer (IARC). Continuous exposure to chromium (Cr) through drinking water can result in gastric ulcers, dermatitis, and immune suppression (Saha *et al*., 2017).

Mercury (Hg) and zinc (Zn) also have distinct health implications. Mercury (Hg) is neurotoxic and can damage the brain and nervous system, particularly in fetuses and young children. It is converted by microorganisms into methylmercury, a compound that bioaccumulates in the food chain and affects cognitive and motor development (Clarkson and Magos, 2006). Long-term mercury (Hg) exposure leads to tremors, memory loss, and kidney damage. Zinc (Zn), though essential for enzyme function and immune regulation, becomes harmful at high concentrations. Excess zinc (Zn) intake through contaminated groundwater can cause nausea, abdominal cramps, and interference with the absorption of essential trace elements like copper (Tchounwou *et al*., 2012). Elevated zinc (Zn) levels are often an indicator of industrial pollution from galvanization and metal plating processes.

The combined or synergistic effects of multiple heavy metals in groundwater can amplify health risks beyond the sum of their individual toxicities. For example, concurrent exposure to lead (Pb) and cadmium (Cd) increases the likelihood of kidney damage while the interaction of arsenic (As) and chromium (Cr) enhances carcinogenic potential (Olalekan *et al*., 2019; Aendo *et al*., 2022). The World Health Organization (WHO, 2017) and United States Environmental Protection Agency (USEPA, 1989) have established guideline values to limit exposure to these metals. However, in many developing regions such as Nigeria, these standards are often exceeded due to inadequate regulation and poor monitoring. Understanding the mechanisms and health implications of heavy metal exposure is therefore essential for developing risk-based groundwater management strategies and protecting public health.

2.6 Groundwater Contamination in Nigeria

Groundwater contamination has become a major environmental and public health concern in Nigeria due to rapid urbanization, population growth, and industrialization. Although groundwater is often regarded as safer than surface water because of its natural filtration through soil and rock layers, studies have shown that it is increasingly being polluted by both natural and anthropogenic activities (Oborie and Olorunfemi, 2015). The absence of proper waste management systems and the indiscriminate disposal of refuse and industrial waste contribute significantly to this problem. In major Nigerian cities such as Lagos, Port Harcourt, Benin City and Kano, leachates from open dumpsites, effluents from factories, and sewage discharge have introduced heavy metals including lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and zinc (Zn) into aquifers (Ocheri *et al*., 2014; Akinbile and Yusoff, 2011). These contaminants persist for long periods because heavy metals are non-biodegradable and can accumulate in groundwater to toxic levels.

The extent of groundwater contamination in Nigeria varies across regions depending on industrial activities, geology and land use practices. In the southwestern region, groundwater contamination is largely attributed to urban runoff and leachate infiltration from refuse dumpsites, while in the northern regions, it is often linked to mining and agricultural activities (Adewumi *et al*., 2021; Olalekan *et al*., 2019). For instance, studies in Akure and Ilorin have revealed high levels of lead (Pb) and cadmium (Cd) in groundwater near dumpsites (Akinbile and Yusoff, 2011). In the Niger Delta, petroleum refining and gas flaring release heavy metals such as chromium (Cr) and mercury (Hg) which seep into nearby water sources (Aendo *et al*., 2022). These contaminants not only degrade groundwater quality but also pose serious health risks to local populations who depend on untreated borehole and well water for domestic use.

Agricultural practices have also been identified as significant contributors to groundwater contamination in rural and peri-urban communities. The excessive use of fertilizers, herbicides, and pesticides introduces nitrates and trace metals into the soil that gradually leach into groundwater reserves (Nouri *et al*., 2018). Furthermore, livestock waste, septic tanks, and open defecation in rural areas increase the microbial and chemical load of groundwater. The high mobility of these contaminants, combined with Nigeria's porous sandy soil types, facilitates their infiltration into aquifers (Offodile, 2002). This situation is aggravated by the lack of effective environmental monitoring systems and the absence of strict enforcement of national water quality standards such as those provided by the Nigerian Standard for Drinking Water Quality (NSDWQ, 2007).

Several studies across Nigeria have demonstrated that the concentration of heavy metals in groundwater frequently exceeds the permissible limits set by the World Health Organization (WHO, 2017) and NSDWQ (2007). For example, Oborie and Olorunfemi (2015) reported elevated concentrations of lead (Pb), cadmium (Cd) and zinc (Zn) in borehole water samples from parts of Edo and Delta States, while Olalekan et al. (2019) found similar results in groundwater from southwestern Nigeria. These findings suggest that groundwater contamination is not limited to industrial zones but also occurs in rural areas due to diffuse sources of pollution such as agricultural runoff and natural mineral dissolution. Such widespread contamination highlights the urgent need for comprehensive water quality monitoring and risk-based management approaches to safeguard public health.

The growing dependence on groundwater in Nigeria for drinking and irrigation, coupled with weak regulatory frameworks, has intensified the risks associated with contamination. The lack of regular testing, poor maintenance of boreholes, and limited public awareness of groundwater safety exacerbate the problem. To protect groundwater resources, integrated management strategies are needed, including the proper siting of waste disposal facilities, enforcement of industrial effluent treatment regulations and public education on safe groundwater use (Nwankwoala, 2011; FAO, 2021). Strengthening institutional capacity and adopting scientific tools such as Human Health Risk Assessment (HHRA) can provide a more comprehensive understanding of contamination risks and help guide effective policy decisions across the country.

2.7 Research Gaps and Global Studies

Globally, groundwater pollution by heavy metals has been widely reported and remains one of the most significant environmental and public health challenges of the 21st century. As populations expand and industrial activities increase, groundwater systems have become vulnerable to contamination from both natural and anthropogenic sources (UNESCO, 2022). Studies conducted in Asia, Africa, Europe, and the Americas reveal that heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and zinc (Zn) are common groundwater pollutants found at concentrations exceeding international safety limits (Li *et al*., 2023; Jaishankar *et al*., 2014). For instance, research in Bangladesh and India has shown widespread arsenic (As) contamination affecting millions of people through drinking water, leading to severe health disorders including skin lesions and cancers (Mukherjee *et al*., 2022). Similarly, elevated levels of cadmium (Cd) and lead (Pb) have been detected in groundwater across China and Southeast Asia where industrial effluents, mining operations, and agricultural runoff are major contributors (Liu *et al*., 2020).

In Europe and North America, groundwater contamination by heavy metals is primarily linked to industrial and mining legacies. In Italy, studies have identified high concentrations of chromium (Cr) and nickel in groundwater near tanneries and metal-processing plants (Bianchini *et al*., 2020). In Poland and the Czech Republic, abandoned mining sites have contributed to long-term contamination of aquifers with lead (Pb) and cadmium (Cd) (Nocoń *et al*., 2021). In the United States, the U.S. Geological Survey has reported the occurrence of arsenic (As) and uranium in groundwater in the southwestern states, posing carcinogenic health risks to rural communities (Rodriguez et al., 2018). These findings indicate that even in regions with strong environmental regulations, legacy pollution and industrial waste continue to pose significant threats to groundwater quality and human health.

African studies have equally demonstrated the growing risk of heavy metal contamination in groundwater. In Ghana, Aendo *et al*. (2022) reported that lead (Pb), cadmium (Cd) and chromium (Cr) concentrations in groundwater exceeded World Health Organization (WHO) permissible limits, posing both carcinogenic and non-carcinogenic risks to residents. Similar studies in Kenya, South Africa and Egypt revealed high concentrations of mercury (Hg) and arsenic (As) in groundwater near mining and industrial zones (Elumalai *et al*., 2021; Nouri *et al*., 2018). In Nigeria and other West African countries, the lack of effective environmental management and rapid urban expansion have exacerbated groundwater contamination from waste dumps, oil spills, and agricultural runoff (Olalekan *et al*., 2019). These findings highlight that heavy metal pollution in groundwater is a widespread issue in developing countries where environmental regulation and monitoring are often inadequate.

Comparative global assessments show that regions with rapid industrialization and weak waste management systems are more vulnerable to heavy metal contamination. The World Health Organization (WHO, 2017) and the Food and Agriculture Organization (FAO, 2021) have emphasized the need for integrated groundwater management and the application of Human Health Risk Assessment (HHRA) frameworks to evaluate exposure and safeguard public health. Research from various continents confirms that chronic exposure to heavy metals in groundwater can lead to both carcinogenic and non-carcinogenic health effects including kidney damage, neurotoxicity and cancers of the bladder, liver, and lungs (; Li *et al*., 2023; Tchounwou *et al.,* 2012). Understanding these global patterns provides a valuable foundation for evaluating groundwater contamination risks in local contexts such as Oluku, Benin City, where industrial and domestic activities continue to pose potential threats to water quality and community health.

2.8 Future Directions

Future research on groundwater contamination and heavy metal risk assessment should focus on developing more advanced and region-specific monitoring and mitigation strategies. Although numerous studies have examined the presence of heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and zinc (Zn) in groundwater, there remains a significant gap in continuous surveillance and spatial mapping, especially in developing nations (Li *et al*., 2023). The integration of Geographic Information Systems (GIS) and remote sensing technologies into groundwater monitoring can improve the detection of pollution hotspots and provide valuable insights into contamination trends (Kumar *et al*., 2020). Additionally, future research should prioritize long-term data collection and modeling to predict the movement and transformation of heavy metals under changing climatic and land-use conditions. Such approaches will enhance understanding of contaminant dynamics and inform proactive groundwater management policies.

Emerging analytical technologies present opportunities for more precise and rapid detection of heavy metals in groundwater. Techniques such as inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF) and portable spectrometers allow for real-time quantification of trace metals at low concentrations (Zhou *et al*., 2021). Combining these tools with machine learning algorithms can facilitate automated identification of contamination sources and prediction of future risk scenarios. Furthermore, research into low-cost and eco-friendly remediation techniques such as the use of biochar, microbial consortia, and nanomaterials offers sustainable solutions for heavy metal removal from groundwater (Bhattacharya et al., 2021). These innovations are especially crucial in regions like Nigeria, where financial and infrastructural limitations often hinder large-scale treatment efforts.

Another promising direction involves strengthening the application of Human Health Risk Assessment (HHRA) frameworks by integrating probabilistic and cumulative risk models. Traditional deterministic models often underestimate exposure variability among different age groups and communities (Aendo *et al*., 2022). Future HHRA studies should therefore incorporate demographic, behavioral, and socioeconomic factors to better capture real-world exposure conditions. Moreover, there is a growing need to investigate the combined effects of multiple contaminants since most groundwater sources are exposed to a mixture of metals and organic compounds. Multi-contaminant risk modeling can provide more accurate estimations of cumulative health impacts and guide more effective intervention strategies (Li *et al*., 2023).

Finally, achieving sustainable groundwater management requires strong policy implementation, public participation, and international collaboration. Governments and environmental agencies should strengthen regulations on industrial waste disposal and enforce routine groundwater quality assessments. Public awareness campaigns are also essential to educate communities on the risks of heavy metal exposure and encourage safe water practices. Collaborative efforts between universities, research institutions, and international bodies such as the World Health Organization (WHO) and the United Nations Educational, Scientific and Cultural Organization (UNESCO) can facilitate capacity building and knowledge sharing (UNESCO, 2022). Integrating scientific innovation with sound policy and community engagement will be critical to securing safe groundwater resources for future generations.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Geology Of The Study Area

Oluku is situated in Ovia North-East Local Government Area of Edo State, Nigeria, along the Benin–Ore–Lagos expressway. The area lies within the Benin Formation, which forms part of the Coastal Plain Sands of the Niger Delta sedimentary basin. This formation is predominantly composed of coarse to medium-grained sand, gravel, and interbedded clay lenses that enhance groundwater storage and transmission (Offodile, 2002). The sandy nature of the soil provides high permeability, allowing easy infiltration of surface water and potential contaminants into the aquifer system.

The region is characterized by a humid tropical climate with distinct wet (April–October) and dry (November–March) seasons. Average annual rainfall ranges between 1,800 and 2,200 mm, and mean annual temperature is approximately 27°C (Nwankwoala, 2011). The topography is gently undulating with elevations of 60–80 meters above sea level. Groundwater occurs under both unconfined and semi-confined conditions within the sandy aquifer zones. However, the high permeability of the formation makes the groundwater highly susceptible to contamination from agricultural runoff, industrial discharge, and domestic waste leachates.

The vegetation is primarily tropical rainforest with a mixture of secondary forest and derived savannah. The hydrogeological setting favors significant groundwater recharge through infiltration during the wet season. However, unregulated waste disposal and increasing human settlement around Oluku have contributed to groundwater quality deterioration, especially in shallow wells and boreholes near waste dumps and industrial facilities (Adewumi *et al*., 2021). This geological background provides a foundation for understanding contamination pathways and groundwater behavior in the study area.

3.2 Materials

- Portable Multiparameter Probe
- Insulated Coolers
- Total Dissolved Solids
- Inductively Coupled Plasma-Mass Spectrometer
- Sterilized polyethylene bottles
- Field notebook
- Personal Protective Equipment (PPE)
- pH meter
- Data Analysis Software
- Laboratory reagents
- Thermometer

- Labels
- Geographical Information System
- Membrane filters

3.3 Methodology

3.3.1 Sample Collection

A total of fifteen (15) groundwater samples were collected from various locations near mining sites in Oluku, Ovia North-East Local Government Area, Edo State. The sampling points were strategically selected based on their proximity to mining and domestic activities, as well as the extent of local dependence on groundwater for daily use.

For sample collection, clean 1-liter polyethylene bottles were used. Before sampling, the bottles were pre-treated by soaking in 10% nitric acid (HNO_3) and rinsing thoroughly with deionized water. At each sampling point, bottles were further rinsed with the groundwater to be collected to ensure sample purity and minimize contamination. The wells were allowed to flow or stabilize briefly before sampling to avoid collecting stagnant water. Once collected, the bottles were tightly sealed to prevent leakage and external contamination (Odukoya and Abimbola, 2010). The wells were allowed to flow or stabilize briefly before sampling to avoid collecting stagnant water. Once collected, the bottles were tightly sealed to prevent leakage and external contamination (Odukoya and Abimbola, 2010).

To preserve the samples, a few drops of concentrated nitric acid (HNO_3) were added to maintain the pH below 2. The samples were immediately stored in ice-filled coolers at approximately 4°C to inhibit chemical and biological reactions. All samples were transported to the laboratory and analyzed within 48 hours of collection. The entire sampling and preservation process adhered strictly to the standards of the American Public Health Association (APHA, 2012), the World Health Organization (WHO, 2017), and the United States Environmental Protection Agency (USEPA, 1989) to ensure reliability and prevent contamination.

3.3.2 Sample Analysis

To evaluate trace metal concentrations, a total of 15 groundwater samples were subjected to analysis. Each sample was initially passed through a 0.45 µm membrane filter to eliminate suspended particles that might interfere with the accuracy of the metal analysis. This filtration step is essential to ensure reliable results by removing materials that could skew readings.

After filtration, the samples were placed into clean, clearly labeled containers to avoid any form of cross-contamination. A 50 mL portion from each sample was then acidified with concentrated nitric acid (HNO_3) to undergo acid digestion, following the procedures outlined by APHA (2005). This step is critical for breaking down residual organic matter and releasing metals that may be bound to solid particles. The samples were gently heated in digestion vessels for complete dissolution of all metal content without causing metal loss.

Atomic Absorption Spectrometry (AAS) was used to detect and quantify the toxic metals present. This analytical technique is known for its sensitivity and specificity, making it ideal for identifying trace levels of metals in water (Utah *et al.,* 2018). This advanced analytical technique was chosen for its high sensitivity, precision and suitability for detecting trace levels of metals in water. The analytical procedures strictly followed the guidelines and protocols outlined by the American Public Health Association (APHA, 2005) and the United States Environmental

Protection Agency (USEPA, 2013). Quality assurance and control measures were implemented during analysis including the use of blanks, replicate samples and calibration standards to ensure the reliability and validity of the results.

3.4. Health Risk Assessment

The primary objective of a health risk assessment is to evaluate the potential adverse health effects on residents resulting from the ingestion of contaminated groundwater. This process focuses on understanding the extent to which individuals may be exposed to pollutants and their susceptibility to associated health impacts. Consequently, identifying vulnerable populations and implementing strategies to minimize exposure to heavy metals is crucial.

In this study, the Hazard Quotient (HQ), Hazard Index (HI) and Incremental Lifetime Cancer Risk (ILCR) were calculated to estimate both non-carcinogenic and carcinogenic health risks associated with groundwater assumptions. The assessment was conducted specifically for adults and children.

For heavy metals (HMs) in groundwater sources, ingestion and dermal contact are recognized as the primary exposure pathways for humans (Saha *et al*., 2017). In this study, the health risks associated with these two exposure routes were assessed for adults and children using the Health Risk Assessment (HRA) model recommended by the United States Environmental Protection Agency (USEPA). Adults were considered the general population, while children were treated as a sensitive sub-group due to their higher vulnerability to toxic substances. In this study, seven heavy metals were analyzed and are classified into non-carcinogenic (Fe, Cu, Zn) and carcinogenic (Cr, Cd, Pb, Ni) categories.

3.5 Carcinogenic and Non-Carcinogenic Risk Assessment

3.5.1 Carcinogenic Toxicity

For carcinogenic metals like arsenic and chromium, cancer risk is assessed using the Cancer Risk (CR) formula, which incorporates the Cancer Slope Factor (CSF). The CSF represents the increased probability of developing cancer per unit of exposure, usually measured in risk per milligram per kilogram of body weight per day (mg/kg/day). This risk assessment follows the U.S. EPA guidelines that consider heavy metal ingestion (USEPA, 2013).

Chronic Daily Intake (CDI) estimates the average amount of a contaminant a person is exposed to daily over a specified time frame (Nyashanu *et al.*, 2020). The CDI value is then applied in the cancer risk calculation to estimate the likelihood of cancer developing from that exposure.

- Chronic Daily Intake (CDI):

The Chronic Daily Intake (CDI) is a critical parameter in environmental health risk assessments, representing the average amount of a contaminant absorbed daily per unit body weight over a specific exposure duration. In dermal exposure pathways, CDI quantifies the dose of pollutants, such as heavy metals, that penetrate the skin during contact with contaminated groundwater used for domestic activities like bathing and washing. The Chronic Daily Intake (CDI) provides a foundation for estimating both non-carcinogenic and carcinogenic risks associated with heavy metals in groundwater (USEPA, 2004). The general expression for dermal CDI is:

$$\text{CDI (ingestion)} = \frac{\text{C x IR x EF x ED}}{BW\ x\ AT}$$

Where:

C = Concentration of contaminant (mg/L)

IR = Ingestion Rate (L/day)

EF = Exposure Frequency (days/year)

ED = Exposure Duration (years)

BW = Body Weight (kg)

AT = Averaging Time (days)

$$\text{CDI dermal} = \frac{\text{Cw x SA x Kp x ET x EF x ED x CF}}{BW\ x\ AT}$$

Where:

C = Concentration of the contaminant

IR = Ingestion rate

EF = Exposure frequency

ED = Exposure duration

BW = Body weight

SA = Surface area

KP = Skin permeability coefficient

ET = Exposure time

- Cancer Risk (CR)

Carcinogenic Risk: This is commonly evaluated through the Incremental Lifetime Cancer Risk (ILCR), which quantifies the probability that an individual will develop cancer at some point during their lifetime as a result of continuous daily exposure to a carcinogenic substance (Saha *et al.*, 2017).

$$CR = CDI + CSF$$

Where, CSF is the Cancer Slope Factor

3.5.2 Non-Carcinogenic Risk

The non-carcinogenic risks associated with with heavy metal exposure are evaluated using the Hazard Quotient which represents the ratio of the estimated daily intake of a contaminant in its reference dose. To access the cumulative non carcinogenic risk from multiple exposure pathways, the Hazard Index is used. It is defined as the sum of the HQs for both ingestion and dermal contact route (Saha *et al.*, 2017). The relevant calculation equations are presented below:

$$HQ = {}^{ADD}/_{\mathrm{RfD}}$$

Hazard Quotient (HQ) is calculated using the formula, where ADD refers to the Average Daily Dose and RfD stands for Reference Dose. Both are typically measured in milligrams per kilogram of body weight per day (mg/kg/day).

Non-carcinogenic risk is evaluated by calculating the Hazard Index (HI), which reflects the total potential non-carcinogenic effects caused by all metals present. This is determined by following the EPA’s health risk assessment guidelines by adding the Hazard Quotient (HQ) values for all metals present, using the equation:

$$HI = \Sigma\ HQ$$

An HI value less than 1 is considered safe, while a value greater than 1 indicates the possibility that a potential non-carcinogenic risks may pose an expected health risk.

3.5. Statistical Analysis

The mean and standard deviation of the collected data for the various estimated parameters were statistically analyzed using SPSS.

CHAPTER FOUR

PRESENTATION OF RESULTS

4.1 Heavy Metal Concentrations in Groundwater Samples

The result of the laboratory analysis of heavy metal concentrations in groundwater samples from Oluku, Edo State, Nigeria, revealed the concentration of key metals in accessing health risks. The mean concentration of the metals and their composition following WHO, 2012 and USEPA, 2004 standards. The mean concentrations of the key metals are (Mn) (0.032 mg/L), cadmium (Cd) (0.462 mg/L), lead (Pb) (0.604 mg/L), iron (Fe) (1.53 mg/L) and zinc (Zn) (3.05 mg/L) in their increasing order (USEPA, 2004; Aendo *et al*., 2022).

Table 4.1: Parameters in Groundwater Samples

Sample code	Zinc (mg/L)	Iron (mg/L)	Manganese (mg/L)	Lead (mg/L)	Cadmium (mg/L)
1	5.70	3.22	0.04	0.76	0.58
2	5.73	3.28	0.04	0.74	0.58
3	1.63	0.50	0.03	0.55	0.42
4	1.65	0.51	0.03	0.53	0.42
5	0.53	0.16	0.02	0.44	0.33
6	0.67	0.21	0.02	0.48	0.36
7	3.57	1.20	0.03	0.68	0.5
8	3.47	1.24	0.03	0.66	0.49
9	1.57	0.33	0.03	0.54	0.41
10	3.62	0.91	0.03	0.67	0.50

4.2 Heavy Metal Mean Concentrations in Groundwater Samples

Variable	Average Mean (mg/L)	Standard Error (mg/L)	WHO Standard (2017)	NSDWQ Standard (2007)
Zinc (Zn)	3.05	1.07	3.00	3.00
Iron (Fe)	1.53	0.65	0.30	0.30
Manganese (Mn)	0.032	0.004	0.10	0.20
Lead (Pb)	0.604	0.053	0.01	0.01
Cadmium (Cd)	0.462	0.029	0.003	0.003

4.3 Chronic Daily Intake (CDI)

The results of Chronic Daily Intake (CDI) of heavy metals in water samples from the study area for both children and adults are summarized Table 3a and 3b.

Table 4.3a: CDI (mg/kg day) for Adults (selected samples)

Sample	Zn	Fe	Mn	Pb	Cd
S1	1.631E-1	9.200E-2	1.143E-3	2.171E-2	1.657E-2
S2	1.637E-1	9.371E-2	1.143E-3	2.114E-2	1.657E-2
S3	4.657E-2	1.429E-2	8.571E-4	1.571E-2	1.200E-2
S4	4.714E-2	1.457E-2	8.571E-4	1.514E-2	1.200E-2
S5	1.514E-2	4.571E-3	5.714E-4	1.257E-2	8.857E-3

Table 4.3b: CDI (mg/kg day) for Children (selected samples)

Sample	Zn	Fe	Mn	Pb	Cd
S1	3.807E-1	2.147E-1	2.667E-3	5.067E-2	3.867E-2
S2	3.820E-1	2.187E-1	2.667E-3	4.933E-2	3.867E-2
S3	1.087E-1	3.333E-2	2.000E-3	3.667E-2	2.800E-2
S4	1.100E-1	3.400E-2	2.000E-3	3.533E-2	2.800E-2
S5	3.533E-2	1.067E-2	1.333E-3	2.933E-2	2.067E-2

4.4 Carcinogenic Risk (CR) via Dermal Exposure

Table 4.4a: Carcinogenic Risk (CR) for Children (selected samples)

Sample	Zn	Fe	Mn	Pb	Cd
S1	0.000E+0	0.000E+0	0.000E+0	4.307E-4	2.359E-1
S2	0.000E+0	0.000E+0	0.000E+0	4.193E-4	2.359E-1
S3	0.000E+0	0.000E+0	0.000E+0	3.117E-4	1.708E-1
S4	0.000E+0	0.000E+0	0.000E+0	3.003E-4	1.708E-1
S5	0.000E+0	0.000E+0	0.000E+0	2.493E-4	1.261E-1

Table 4.4b: Carcinogenic Risk (CR) for Adult (selected samples)

Sample	Zn	Fe	Mn	Pb	Cd
S1	0.000E+0	0.000E+0	0.000E+0	1.846E-4	1.011E-1
S2	0.000E+0	0.000E+0	0.000E+0	1.797E-4	1.011E-1
S3	0.000E+0	0.000E+0	0.000E+0	1.336E-4	7.320E-2
S4	0.000E+0	0.000E+0	0.000E+0	1.287E-4	7.320E-2
S5	0.000E+0	0.000E+0	0.000E+0	1.069E-4	5.403E-2

Table 4.5a: HQ (Adults)

Sample	Zn	Fe	Mn	Pb	Cd
S1	5.438E-1	1.314E-1	8.163E-3	6.204E+0	1.657E+1
S2	5.457E-1	1.339E-1	8.163E-3	6.041E+0	1.657E+1
S3	1.552E-1	2.041E-2	6.122E-3	4.490E+0	1.200E+1
S4	1.571E-1	2.082E-2	6.122E-3	4.327E+0	1.200E+1
S5	5.048E-2	6.531E-3	4.082E-3	3.592E+0	8.857E+0

Table 4.5b: HQ (Children)

Sample	Zn	Fe	Mn	Pb	Cd
S1	1.269E+0	3.067E-1	1.905E-2	1.448E+1	3.867E+1
S2	1.273E+0	3.124E-1	1.905E-2	1.410E+1	3.867E+1
S3	3.622E-1	4.762E-2	1.429E-2	1.048E+1	2.800E+1
S4	3.667E-1	4.857E-2	1.429E-2	1.010E+1	2.800E+1
S5	1.178E-1	1.524E-2	9.524E-3	8.381E+0	2.067E+1

CHAPTER FIVE

DISCUSSION OF RESULTS

5.1 Discussion

The concentration of heavy metals in groundwater samples showed that zinc (Zn) and iron (Fe) were present at relatively higher levels compared to manganese (Mn), lead (Pb), and cadmium (Cd). The mean concentrations of Zn (3.05 mg/L) and Fe (1.53 mg/L) exceeded or were near the permissible limits of 3.00 mg/L and 0.30 mg/L respectively, while Pb (0.604 mg/L) and Cd (0.462 mg/L) were far above the World Health Organization (WHO, 2017) and Nigerian Standard for Drinking Water Quality (NSDWQ, 2007) limits of 0.01 mg/L and 0.003 mg/L. The higher levels of Pb and Cd suggest contamination from anthropogenic sources such as automobile workshops, waste dumps, corroded metal pipes, and agricultural runoff. Similar elevated Pb and Cd values have been reported in groundwater from urban and semi-urban regions of Nigeria, where poor waste management and industrial effluents contribute to contamination (Oyekunle *et al*., 2021; Ocheri *et al*., 2014).

The Chronic Daily Intake (CDI) results revealed that exposure to Zn, Fe, and Mn through drinking water was within the recommended daily limits, indicating no major non-carcinogenic risk from these metals. However, Pb and Cd recorded CDI values exceeding the USEPA (1989) threshold for both adults and children, with children showing higher exposure due to their lower body weight and higher ingestion rate per kilogram of body mass. This finding agrees with Jaishankar et al. (2014) and Li et al. (2011), who observed that children are more susceptible to heavy metal toxicity, particularly Pb, which affects neurological development, and Cd, which accumulates in the kidneys over time. The consistent elevation in Pb and Cd CDI values underscores the chronic exposure potential in the study area.

The Hazard Quotient (HQ) analysis showed HQ values below one for Zn, Fe, and Mn, suggesting minimal non-carcinogenic risks from these elements. Conversely, Pb and Cd exhibited HQ values significantly greater than one in both age groups, indicating potential non-carcinogenic health risks. The HQ values for Pb ranged up to 6.20 in adults and 14.5 in children, while Cd reached values as high as 16.6 and 38.7 respectively. These findings imply that prolonged consumption of this groundwater could cause neurological, hematological, and renal damage, as reported by Khan et al. (2013) in Pakistan and Olalekan et al. (2019) in southwestern Nigeria. The elevated HQ for Pb and Cd confirms that the water quality is not suitable for drinking without treatment.

The Carcinogenic Risk (CR) assessment revealed that both Pb and Cd posed potential cancer risks beyond acceptable USEPA limits ($1.0 \times 10^{-6} - 1.0 \times 10^{-4}$). The CR values for Pb ranged between 1.07×10^{-4} and 4.31×10^{-4}, while Cd ranged from 5.75×10^{-2} to 2.36×10^{-1}. These values are considerably higher than those found in less-impacted regions, suggesting a very high lifetime cancer risk, especially from Cd, which has a strong carcinogenic profile. Studies by Tchounwou et al. (2012) and Clarkson and Magos (2006) also identified Cd and Pb as potent carcinogens capable of inducing lung, kidney, and prostate cancers after long-term exposure through contaminated drinking water.

The results clearly indicate that Fe and Zn may have geogenic origins due to the lateritic soil composition of the Benin Formation, while Pb and Cd contamination is mainly anthropogenic. Similar geochemical associations between Fe, Zn, and soil parent materials have been documented by Offodile (2002) and Edet and Offiong (2002). The high variation among sampling points suggests that contamination is uneven, likely influenced by proximity to pollution sources. These findings are consistent with those reported by Oborie and Olorunfemi

(2015), who highlighted that industrial and household waste contribute significantly to heavy metal enrichment in Nigerian aquifers.

Overall, the combination of high concentrations, elevated CDI, HQ > 1 and excessive CR values for Pb and Cd indicate that groundwater from the study area poses both non-carcinogenic and carcinogenic health risks to residents. The results demonstrate the urgent need for remediation and strict monitoring of groundwater quality. Continuous ingestion of such water may lead to long-term health complications, particularly among children and pregnant women. Similar conclusions have been drawn by recent risk-based studies emphasizing the importance of applying Human Health Risk Assessment (HHRA) frameworks for groundwater safety evaluation (Badeenezhad *et al*., 2023; Li *et al*., 2011).

5.2 Conclusion

The study assessed the concentration of heavy metals zinc (Zn), iron (Fe), manganese (Mn), lead (Pb), and cadmium (Cd) in groundwater sources within the study area and evaluated their potential health risks. Results revealed that while Zn and Fe appeared in higher proportions, Pb and Cd concentrations far exceeded the permissible limits set by the World Health Organization (WHO, 2017) and the Nigerian Standard for Drinking Water Quality (NSDWQ, 2007). The Chronic Daily Intake (CDI) and Hazard Quotient (HQ) analyses confirmed that Pb and Cd pose significant non-carcinogenic risks, while the Carcinogenic Risk (CR) values for both metals were well above the acceptable range proposed by the United States Environmental Protection Agency (USEPA, 1989). These findings indicate that groundwater in the area is unsafe for drinking without adequate treatment.

The elevated Pb and Cd levels are primarily linked to anthropogenic sources such as improper waste disposal, corroded metal pipes, industrial runoff, and vehicular emissions, which leach into the subsurface. The presence of Fe and Zn in moderate excess likely reflects natural geogenic influence from the lateritic Benin Formation (Offodile, 2002; Edet and Offiong, 2002). The consistent pattern of high HQ and CR values, particularly among children, demonstrates the severity of exposure and aligns with previous research across Nigeria showing similar contamination trends (Olalekan *et al*., 2019; Ocheri *et al*., 2014).

In conclusion, the research underscores a dual contamination profile—geogenic enrichment of essential elements (Fe, Zn) and anthropogenic contamination by toxic metals (Pb, Cd). Continuous consumption of such groundwater presents both immediate and long-term health concerns, including neurological disorders, kidney dysfunction, and increased lifetime cancer risk (Jaishankar *et al*., 2014; Tchounwou *et al*., 2012). The study therefore affirms that urgent intervention through remediation, public education and consistent groundwater monitoring is essential to safeguard community health.

5.3 Recommendations

The findings of this research have clearly shown that groundwater in the study area contains elevated concentrations of toxic heavy metals, particularly lead (Pb) and cadmium (Cd), which pose both carcinogenic and non-carcinogenic health risks. It is therefore recommended that immediate actions be taken to ensure the safety of residents relying on these water sources. Groundwater used for domestic purposes should undergo adequate treatment before consumption. Appropriate purification techniques such as reverse osmosis, activated carbon filtration, and ion exchange systems are effective for reducing heavy metal concentrations to acceptable limits.

Regular cleaning and maintenance of boreholes and storage facilities are also essential to prevent recontamination through corroded pipes or tanks.

Government and environmental agencies should intensify monitoring and enforcement of regulations governing waste disposal and industrial effluents within the study area. The establishment of routine groundwater surveillance programs by the Nigerian Geological Survey Agency and the Federal Ministry of Environment will enable early detection of contamination. Such programs should be supported by local authorities and community water management committees to ensure compliance with national and international drinking water standards. The use of standardized monitoring frameworks such as the Human Health Risk Assessment (HHRA) approach recommended by the United States Environmental Protection Agency (USEPA, 1989) will enhance the accuracy and reliability of water safety evaluations.

Public awareness and education are equally critical in addressing groundwater contamination issues. Residents must be sensitized to the health dangers associated with prolonged exposure to Pb and Cd and encouraged to adopt household water treatment and safe waste disposal practices. Awareness campaigns can be integrated into local health programs to promote the use of alternative water sources and the importance of regular testing. In the long term, further studies should be conducted to assess seasonal variations in heavy metal concentrations and to develop low-cost, locally adaptable remediation technologies. Applying sustainable groundwater management strategies that combine scientific monitoring with community participation will ensure lasting protection of water resources and public health.

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