NON CARCINOGENIC RISK ASSESSMENT OF GROUNDWATER-ASSOCIATED HEAVY METALS VIA INGESTION EXPOSURE

BY

Joy Ewhere EBHORIA (Miss)
LSC2007280

DEPARTMENT OF SCIENCE LABORATORY TECHNOLOGY
FACULTY OF LIFE SCIENCES
UNIVERSITY OF BENIN

NOVEMBER, 2025

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A PROJECT WORK 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 OPTION).

NOVEMBER, 2025

CERTIFICATION

This is to certify that this undergraduate project work titled **NON-CARCINOGENIC RISK ASSESSMENT OF GROUNDWATER-ASSOCIATED HEAVY METALS VIA INGESTION EXPOSURE** was submitted and presented by **EBHORIA Joy Ewhere** with matriculation number **LSC2007280** in the Department of Science Laboratory Technology, Faculty of Life Sciences, University of Benin, Benin City.

Dr. K. OJEAGA	**Date**
(Project Supervisor)	
DR. P. O. ALONGE	**Date**
(Project Coordinator)	
PROF. J. O. OSARUMWENSE	**Date**
(Head of Department, SLT)	
External Examiner	**Date**

DEDICATION

I hereby dedicate this project to God almighty whose grace enabled me to complete my academic journey in the University of Benin, Edo State.

ACKNOWLEDGEMENTS

My sincere and deepest gratitude to the Almighty God for his infinite mercies and guidance that made this project a success.

My sincere appreciation goes to my project supervisor Dr. K Ojeaga, whose Intellectual guidance and patience Contributed immensely to the success of this research. Your Insight and mentorship have helped shape both this Project and my academic development.

My heartfelt appreciation to my Mum Mrs. Faith Ebhoria, my Grandma Mrs. Grace Ogbegie, my Uncles, my Siblings, for always being there for me and also for their care, love and support they have showed me throughout this years. God blesses you all..

I will also like to acknowledge Efe Olorunmo, Marilyn, Mary, and all my friends. Your unwavering support both financially, mentally and otherwise made it possible for me to go through school smoothly I'm forever grateful.

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ABSTRACT

Groundwater serves as a vital source of drinking water for millions worldwide, particularly in regions with limited access to treated surface water. However, its quality is increasingly compromised by contamination from heavy metals (HMs), which originate from both geogenic and anthropogenic sources. These metals pose significant non-carcinogenic health risks due to their persistence, bioaccumulation, and toxicity even at trace concentrations. This study evaluates the non-carcinogenic health risks associated with the ingestion of groundwater contaminated by heavy metals in the selected study area. Concentrations of key heavy metals including arsenic (As), cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), and zinc (Zn) were determined using standard analytical techniques. Spatial distribution patterns were analyzed to identify contamination hotspots. Health risk assessments were conducted for both children and adults using established models that calculate hazard quotients (HQ) and hazard indices (HI). The findings reveal varying degrees of exposure risk across age groups and sampling locations, underscoring the urgent need for targeted public health interventions and sustainable groundwater management strategies. This research contributes valuable data to environmental health science and supports policy development aimed at mitigating heavy metal exposure through ingestion pathways.

CHAPTER ONE

INTRODUCTION

1.0. BACKGROUND OF THE STUDY

Water plays a vital role in sustaining life for humans and other organisms. Despite its abundance on Earth, only about 3% of the total water is freshwater, and a mere 0.01% of this is readily available for human use (Hussain *et al.,* 2019). Approximately one-third of the global population resides in areas experiencing moderate to severe water stress. This situation is exacerbated by the dual pressures of water scarcity and a rapidly growing global population, which have intensified water challenges in many parts of the world (Enitan *et al.,* 2018). According to projections by the World Health Organization (WHO), nearly 50% of the world's population will be facing water shortages by the year 2025 (Khalid *et al.,* 2020).

Groundwater is a crucial component of the world's freshwater supply, providing at least half of this resource and serving various purposes such as drinking, agricultural irrigation, and industrial processes (Yahaya *et al.,* 2021). It supplies drinking water to roughly one-third of the global population (Sadeghi *et al.,* 2021). Its widespread use is attributed to favorable attributes such as low microbial contamination, acceptable aesthetic qualities, and ease of treatment, including desirable physical characteristics like taste, color, and odor (Edokpayi *et al.,* 2018). However, research has revealed that groundwater is vulnerable to pollution from a range of contaminants. Among these, heavy metals (HMs) have received considerable attention due to their persistence and harmful effects. These metals originate from both geogenic sources (such as rock-water interactions, geological formations, soil type, and seawater intrusion in coastal zones) and anthropogenic activities (including industrial discharge, mining operations, agricultural runoff, and wastewater release), all of which can deteriorate groundwater quality (Solgi and Jalili, 2021; Shakerkhatibi *et al.,* 2019; Eleem *et al.,* 2021; Singh *et al.,* 2022; Krishna *et al.,* 2014).

Heavy metals are considered particularly hazardous in drinking water, even after undergoing standard treatment processes, due to their cumulative and chronic toxic effects at low concentrations (Zhao *et al.,* 2023). The significant health hazards posed by these substances have warranted their inclusion on the 2007 CERCLA Priority List of Hazardous Substances (Saleh *et al.,* 2019). Key characteristics of HMs that contribute to their toxicity include their high potency at minimal doses, resistance to biodegradation, tendency to form more harmful organic complexes, long-term environmental persistence, and bioaccumulation in human tissues (Dong *et al.,* 2020; Muhammad *et al.,* 2011; Hamid *et al.,* 2022; Huang *et al.,* 2020). Their harmful effects arise from interactions with specific cellular structures that disrupt normal biological functions (Wang *et al.,* 2018).

Human exposure to heavy metals primarily occurs through ingestion of contaminated drinking water, although inhalation and dermal absorption also contribute (Fakhri *et al.,* 2018; Razak *et al.,* 2015). Some heavy metals are essential micronutrients, playing catalytic roles in metabolic reactions. Nonetheless, when present at elevated levels, they can become toxic to humans (Yahaya *et al.,* 2021; Eleem *et al.,* 2021). Excessive accumulation of these metals not only poses serious health risks but also diminishes the aesthetic quality of drinking water, resulting in public concern (Hu *et al.,* 2020). Even concentrations below regulatory limits can impair physiological functions (Rasool *et al.,* 2016). Elements such as iron, cobalt, copper, zinc, chromium, vanadium, selenium, and molybdenum are necessary for biological growth and reproduction; however, their excess can result in toxicity (Abedi-Sarvestani *et al.,* 2023).

In particular, elevated levels of aluminum and copper in drinking water have been linked to neurological conditions like Alzheimer's disease (Abedi-Sarvestani *et al.,* 2023; Liu *et al.,* 2019) and gastrointestinal complications (Alidadi *et al.,* 2019). Toxic heavy metals such as arsenic, lead, mercury, cadmium, and nickel are especially hazardous even at low concentrations (Sadeghi and Noroozi, 2018). Ingestion of arsenic and cadmium can cause

allergic reactions and increase cancer risks, with long-term arsenic exposure being associated with cancers of the bladder, lungs, and prostate (Wongsasuluk *et al.,* 2014). Chronic exposure to cadmium has been implicated in disorders of the cardiovascular, skeletal, and renal systems, while antimony exposure has been connected to heart disease (Alidadi *et al.,* 2019). Lead toxicity is particularly harmful to pregnant women and developing fetuses and is also associated with anemia (Abedi-Sarvestani *et al.,* 2019). Mercury exposure has been linked to autoimmune disorders that compromise human health (Fallahzadeh *et al.,* 2017).

As human industrial and developmental activities intensify globally, so does the generation of pollutants like heavy metals, leading to widespread contamination of air, water, and soil and posing severe health risks. These dangers highlight the urgent need to address and integrate heavy metal risk management into health and sustainability frameworks at the community level (Maleki and Jari, 2021).

Health Risk Assessment (HRA) provides a systematic approach to estimating and quantifying the potential health impacts of pollutants, especially heavy metals, in aquatic systems. It has gained prominence in recent years as a tool for raising public awareness and guiding policy decisions (Mohammadi *et al.,* 2019; Emmanuel *et al.,* 2022). The HRA process comprises four key steps: identifying potential hazards, assessing exposure levels, evaluating dose-response relationships, and characterizing the nature and magnitude of the risk (Hu *et al.,* 2020). Groundwater remains a fundamental natural resource, indispensable for domestic consumption, agriculture, industry, and other sectors of the economy (Bodrud-Doza *et al.,* 2019). Due to its general freedom from pathogenic organisms and its widespread availability, groundwater has become the primary source of drinking water in numerous countries across the globe (Kumar *et al.,* 2019; Rahman *et al.,* 2021a). In Bangladesh, for instance, nearly 98% of the population relies on groundwater for their drinking water needs (Shamsudduha *et al.,* 2019). The increasing demand for groundwater has been driven by rapid population

growth and the growing pollution of surface water sources in recent years (Islam *et al.,* 2017; Bodrud-Doza *et al.,* 2019). However, concerns have emerged due to the contamination of groundwater by naturally occurring potentially toxic metals (PTMs), which has become a pressing issue for scientists and policy-makers worldwide (Bundschuh *et al.,* 2017; Nwankwo *et al.,* 2020; Tomašek *et al.,* 2022). Elements such as arsenic (As), copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), boron (B), lead (Pb), cadmium (Cd), and nickel (Ni) are considered potentially toxic and can leach into groundwater through natural geochemical processes, such as the weathering of rocks and minerals (Singh, 2005; Rango *et al.,* 2009). Human-induced activities like urban development, industrial operations, improper waste disposal, and agricultural practices also contribute to the presence of PTMs in shallow aquifers (Kumar *et al.,* 2016; Pugazhendhi *et al.,* 2018; Bhattacharjee *et al.,* 2019).

These PTMs are typically dense, non-degradable, persistent in the environment, and capable of bioaccumulating even at low concentrations, making them hazardous to both ecosystems and human health (Ali *et al.,* 2019). Long-term consumption of water contaminated with such metals can lead to a variety of health problems, including but not limited to hypertension, cancer, vascular disorders, restrictive lung conditions, gastrointestinal bleeding, neurological impairments, and reproductive health issues, especially when the concentration of these metals exceeds safe limits (Rahman *et al.,* 2022). For instance, excessive copper (Cu) in drinking water may result in digestive issues such as nausea and diarrhea, and can cause damage to liver tissues (USNRC, 2000). Elevated levels of iron (Fe) in water may impart a metallic taste and contribute to fatigue, joint pain, and weight loss (Ahmed *et al.,* 2019).

Exposure to chromium (Cr) at high concentrations can affect multiple body systems, including blood, liver, kidneys, and the nervous and cardiovascular systems, and may even result in death (Adimalla and Li, 2018). Cadmium (Cd) is recognized as a carcinogen, with chronic exposure associated with kidney damage, bone demineralization, and respiratory

complications (Bernard, 2008; Belabed and Soltani, 2018). Long-term ingestion of manganese (Mn) through drinking water may lead to neurological deficits, cognitive decline, and even DNA damage (WHO, 2011; Rahman *et al.,* 2022). Chronic intake of zinc (Zn) has been linked to symptoms such as stomach cramps, anemia, and vomiting. Other metals such as lead (Pb), mercury (Hg), and boron (B) also present substantial health hazards when present in groundwater (Rahman *et al.,* 2022).

Given these concerns, it becomes essential to monitor and assess contaminants in groundwater to understand how environmental pollution may affect human health (Tirkey *et al.,* 2017; Rahman *et al.,* 2020). In this regard, health risk assessments (HRAs) play a crucial role, providing a scientific framework for examining the potential health impacts of pollutants and their pathways of exposure (Tirkey *et al.,* 2017; Rahman *et al.,* 2020). In the case of Bangladesh, studies have found excessive concentrations of PTMs such as arsenic (As), iron (Fe), manganese (Mn), boron (B), and fluoride (F^-) in various regions, with arsenic being identified as the predominant contaminant (Ahmed *et al.,* 2004; Islam *et al.,* 2017; Rahman *et al.,* 2018; Rahman *et al.,* 2021a, b). Particularly in coastal and deltaic plains, arsenic levels in shallow aquifers (<150 m) frequently exceed 10 µg/L, and between 60–80% of tubewells in these areas have been found to be contaminated (Ahmed et al., 2004). Additionally, the elevated salinity in both shallow and deep aquifers across several coastal regions further limits the suitability of groundwater for human consumption (Shamsudduha *et al.,* 2019).

1.1. AIM AND OBJECTIVES

The aim of this study is to evaluate the non-carcinogenic health risks associated with the ingestion of groundwater contaminated by heavy metals within the study area.

The objectives are:

- To determine the concentration levels of selected heavy metals in groundwater sources within the study area.
- To analyze the spatial variation and distribution patterns of these heavy metals across different sampling locations.
- To assess the non-carcinogenic health risks associated with the ingestion of contaminated groundwater
- To evaluate the susceptibility to heavy metal exposure via ingestion in both Children and Adults

1.2. STATEMENT OF THE PROBLEM

Groundwater is a crucial resource for domestic consumption, agriculture, and industrial use in many parts of the world, especially in rural and peri-urban settings where access to treated surface water is limited. However, its quality is increasingly threatened by contamination from naturally occurring geogenic sources and anthropogenic activities, leading to the release of potentially toxic metals (PTMs) such as arsenic, cadmium, lead, chromium, and others. These heavy metals are non-biodegradable, persist in the environment, and can bioaccumulate in human tissues, even at trace concentrations. In many developing countries, including regions in South Asia and Africa, groundwater is often consumed without adequate treatment, and the local population remains unaware of the risks associated with prolonged ingestion of contaminated water. Despite growing evidence of heavy metal pollution in groundwater and its implication for public health, there is still a gap in understanding the non-carcinogenic health risks specifically associated with ingestion exposure pathways. Furthermore, vulnerable populations, including children and the elderly, may face heightened risk due to physiological susceptibility and prolonged exposure durations. In the absence of continuous surveillance, risk assessments, and effective water quality monitoring,

communities remain exposed to health hazards such as kidney damage, liver dysfunction, neurological impairments, and developmental issues in children, all of which are associated with long-term ingestion of heavy metal-contaminated water. The lack of comprehensive data on heavy metal concentrations and health risk assessments in many under-resourced regions elevates the challenge, making this study both timely and necessary.

1.3. JUSTIFICATION OF THE STUDY

The increasing prevalence of heavy metals in groundwater, coupled with their known toxicological impacts, highlights the urgency for scientific investigations that can accurately assess health risks associated with their ingestion. Unlike carcinogenic risk assessments, which focus on long-term cancer potential, non-carcinogenic risk assessments address immediate and chronic physiological effects that can compromise one's quality of life. This study is particularly relevant in areas where groundwater is the principal source of drinking water, and where water quality monitoring is inconsistent. By quantifying the levels of PTMs and assessing their health implications through established exposure models, the study will contribute valuable data to environmental health science and public health risk management. The outcomes of this research will help raise public awareness, and guide remediation efforts. The disaggregation of risk by age group also enables targeted interventions.

CHAPTER TWO

LITERATURE REVIEW

2.0. CONCEPTUAL OVERVIEW

Any substance, whether naturally occurring or anthropogenically introduced, that has the potential to cause adverse health outcomes is classified as a hazard (Järup, 2003). Among the most critical pollutants threatening groundwater quality are heavy metals, which pose significant health hazards upon exposure (Sun *et al.,* 2010). While certain heavy metals such as iron and zinc are essential micronutrients that support human physiological functions (Adeyemi *et al.,* 2021), others including cadmium, lead, and mercury, exhibit high toxicity and can be detrimental to human health even at low concentrations. Prolonged consumption of contaminated groundwater is associated with various long-term health effects. According to the (WHO, 2020), approximately 20 percent of global cancer incidences and up to 70 percent of all diseases worldwide are linked to the ingestion of polluted water**.** Heavy metals infiltrate groundwater systems through multiple pathways. Prominent among these are domestic wastewater discharge, leachates from landfills, and atmospheric deposition (Tayebi *et al.,* 2020).

The evaluation of potential health outcomes resulting from such exposures is typically conducted through risk assessment; a structured methodology that estimates the likelihood and severity of adverse effects arising from contact with hazardous substances (Bailey *et al.,* 2020). The United States Environmental Protection Agency (US EPA, 2020) outlines four essential components of this process: hazard identification, dose-response assessment, exposure assessment, and risk characterization. Beyond risk characterization, it is imperative to implement strategies for mitigating identified risks, a phase referred to as risk management.

Hazard identification involves the detection of pollutants within environmental media. Dose-response assessment seeks to determine the toxicological relationship between the level of exposure and the severity of health effects. Exposure assessment examines the frequency, duration, and intensity of human contact with these contaminants (Sheikhi Alman Abad *et al.,* 2021). Finally, risk characterization integrates the data from previous steps to quantify both non-carcinogenic and carcinogenic risks, yielding hazard indices (HI), hazard quotients (HQ), and cancer risk estimates for both children and adults (Rahman *et al.,* 2020; Miranzadeh-Mahabadi *et al.,* 2020). Groundwater constitutes a fundamental element of the Earth's hydrosphere and functions as a principal source of potable water for a considerable segment of the world's population. Its relevance is not limited to domestic consumption; it also supports agricultural productivity through irrigation, underpins various industrial operations, and contributes significantly to the maintenance of ecological integrity. Nonetheless, the integrity of groundwater resources is increasingly compromised by the intrusion of pollutants, particularly heavy metals. These contaminants, which originate from both natural geogenic sources and human-induced activities, present substantial threats to public health and environmental sustainability (Alloway, 2013; Smedley and Kinniburgh, 2002). Heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), and mercury (Hg) are notable for their high atomic weight and toxicity, even at trace concentrations. Their environmental persistence and tendency to bioaccumulate in biological systems enhance their potential for harm. Common sources of heavy metal pollution in groundwater include industrial effluents, agricultural leachates, inadequate waste management practices, and metal-rich geological formations (Nriagu and Pacyna, 1988; Jarup, 2003).

The spatial heterogeneity of heavy metal concentrations in groundwater is shaped by an array of determinants such as regional geology, hydrogeological settings, land use practices, and anthropogenic activities. For instance, areas underlain by mineralized bedrock may naturally

exhibit elevated metal levels in groundwater. In contrast, territories subjected to intensive agricultural and industrial development tend to display contamination driven by human activities. Given these complex interactions, systematic studies are essential to accurately characterize the spatial distribution of heavy metals and identify regions at risk (Smedley and Kinniburgh, 2002).

Recent technological developments have significantly enhanced the capacity to investigate the spatial distribution of groundwater contaminants with higher resolution and accuracy. Tools such as Geographic Information Systems (GIS), remote sensing technologies, and geostatistical modeling now play pivotal roles in detecting contamination hotspots and elucidating spatial patterns of metal dispersion. These methodologies allow for the integration of multifaceted datasets, including hydrogeological characteristics, land use patterns, and locations of potential pollution sources, thereby facilitating the construction of detailed spatial frameworks for groundwater quality assessment (Goovaerts, 1997; Burrough and McDonnell, 1998). Empirical investigations from various global regions continue to reveal significant heavy metal contamination in groundwater systems. Studies in industrial zones of China, for example, have reported alarming concentrations of metals like cadmium and lead, which have raised public health concerns for local populations (Xiang *et al.,* 2021). Likewise, research conducted in Indian agricultural districts has identified the deleterious effects of excessive agrochemical application, with arsenic and chromium frequently surpassing permissible limits in sampled wells (Shaji *et al.,* 2021).

2.1. SOURCES OF HEAVY METAL CONTAMINATION

Contamination of groundwater by heavy metals originates from a combination of natural and human-induced sources, each playing a critical role in determining the extent and spatial

variability of these pollutants. Identifying and understanding these sources is essential for designing effective control measures and minimizing associated health risks.

2.1.1. Geogenic Sources

Geological processes significantly influence the occurrence of heavy metals in groundwater. The natural weathering and dissolution of rocks and minerals that contain metallic constituents, such as arsenic, lead, mercury, and cadmium, contribute to the release of these elements into the subsurface water systems. For instance, minerals like pyrite (FeS_2) and arsenopyrite (FeAsS), when exposed to oxidative conditions, can mobilize arsenic into adjacent aquifers (Smedley and Kinniburgh, 2002). Additionally, geothermal activity in volcanic regions facilitates the introduction of elements such as mercury and antimony into groundwater (Nriagu and Pacyna, 1988).

In regions with soils enriched in metal-bearing minerals, elevated metal concentrations in groundwater are often attributed to natural leaching processes. These processes are largely controlled by local hydrogeochemical conditions, including pH and redox potential, which affect the solubility and transport of metals (Alloway, 2013). For example, the arsenic contamination in groundwater across parts of Bangladesh and West Bengal, India, has been linked to the geochemical characteristics of the alluvial sediments in these areas (Smedley and Kinniburgh, 2002). Heavy metals occur in trace amounts throughout the Earth's crust, distributed among various elemental groups based on their environmental roles and technological applications. Common elements include oxygen, silicon, aluminum, iron, calcium, sodium, magnesium, potassium, and titanium, which form the bulk of soil matrices. Others are classified as nonmetals (e.g., hydrogen, carbon, nitrogen), precious metals (e.g., gold, silver, platinum), rare earth elements (e.g., lanthanum, neodymium), and radioactive elements (e.g., uranium, thorium). Metals of concern in health risk assessments include

cadmium, chromium, copper, nickel, lead, zinc, arsenic, mercury, cobalt, manganese, vanadium, iron, antimony, molybdenum, and barium (Miletic *et al.,* 2023).

In terms of abundance within the Earth's crust, the typical order follows: aluminum > iron > titanium > manganese > barium > strontium > vanadium > chromium > nickel > zinc > copper > cobalt > scandium > lead > boron > tin > arsenic > molybdenum > antimony > cadmium > mercury > selenium > bismuth. The composition and concentration of heavy metals under investigation vary depending on the pollution source and soil characteristics, but the most frequently studied include cadmium, arsenic, chromium, copper, mercury, nickel, lead, and zinc, owing to their pronounced toxicological relevance (Rehman *et al.,* 2018). Understanding the origins of these contaminants is vital for tracing their dispersion patterns within soil systems (Zhang *et al.,* 2021). While natural pedogenic processes largely dictate heavy metal content in soils, anthropogenic influences are increasingly dominant in urbanized areas. This shift is especially noticeable in industrially developed cities, where human activities significantly alter soil chemistry (Miletic *et al.,* 2023).

2.1.2. Anthropogenic Sources

Human actions have markedly increased the introduction of heavy metals into groundwater, particularly through industrial, agricultural, and urban activities.

2.1.2.1 Industrial Activities

Industries are among the foremost contributors to heavy metal pollution. Mining and metal processing activities, such as smelting, often discharge large volumes of heavy metals like lead, cadmium, copper, and zinc into the environment. These metals may infiltrate groundwater through tailing ponds, waste disposal sites, and surface water runoff (Shaji et al., 2021). Furthermore, effluents from manufacturing sectors including electroplating, battery

production, and chemical industries frequently contain high levels of heavy metals, which can migrate into subsurface water systems if not properly treated (Jarup, 2003).

2.1.2.3 Agricultural Practices

Agriculture also plays a pivotal role in groundwater contamination, particularly through the use of agrochemicals and organic amendments. Phosphate-based fertilizers often carry cadmium as a trace impurity, which can be leached into groundwater over time (Singh et al., 2010). Likewise, pesticides with arsenic compounds have been widely used in herbicides and insecticides, contributing to subsurface contamination. The application of sewage sludge and animal manure both of which may contain metals such as copper and zinc further intensifies the risk of metal leaching into groundwater sources (Alloway, 2013).

2.1.2.4 Urbanization and Waste Disposal

Urban expansion, coupled with inadequate waste disposal, constitutes another significant pathway for heavy metal entry into groundwater. Leachates from landfills and open dumps often contain a mixture of hazardous metals that can infiltrate aquifers. Additionally, urban runoff from roads, buildings, and atmospheric deposition carries contaminants originating from vehicular emissions and construction materials (Nriagu and Pacyna, 1988). The growing challenge of electronic waste (e-waste) also poses a serious environmental concern, as discarded devices frequently release harmful metals such as mercury, cadmium, and lead (Cobbing, 2008).

2.1.2.5 Domestic and Municipal Contributions

Domestic wastewater and municipal effluents can also introduce metals into groundwater systems. Improperly managed septic tanks may lead to leaching of metals like copper and

lead, particularly from plumbing infrastructure. In cases where municipal wastewater is inadequately treated, residual trace metals may persist and contaminate nearby groundwater resources (Turekian and Wedepohl, 1961).

2.2. HEALTH RISK ASSESSMENT

Health risk assessment (HRA), also referred to as human health risk assessment (HHRA), is a systematic approach employed to evaluate the likelihood of adverse health effects resulting from exposure to environmental pollutants such as heavy metals (Miletic *et al.,* 2023). The assessment involves several key steps, beginning with hazard identification, which focuses on determining the nature and extent of toxic elements in soil or sediment environments. Given their pervasive presence and toxicological significance, heavy metals are often the primary targets of such assessments (Raj *et al.,* 2022). Each metal has a defined threshold intake level, beyond which harmful effects are likely to occur. As such, determining their concentrations in environmental media is critical. The risk assessment framework incorporates exposure assessment, which considers exposure frequency, duration, and relevant pathways. Three main exposure routes are typically examined: oral ingestion of contaminated particles, inhalation of airborne particulates, and dermal contact with polluted soil (Miletic *et al.,* 2023).

The final stage of HRA is risk characterization, which synthesizes the exposure data to estimate the magnitude and likelihood of health outcomes. Individuals from various age groups may be susceptible; however, most risk models differentiate between children and adults to account for variations in physiological parameters and exposure patterns (Kan *et al.,* 2021). Health impacts associated with heavy metal exposure are broadly categorized as either carcinogenic or non-carcinogenic. Consequently, comprehensive risk assessments typically address both categories. Non-carcinogenic risks are quantified using the Hazard Index (HI), while carcinogenic risks are evaluated through the Total Carcinogenic Risk (TCR)

metric. These indices serve as benchmarks for interpreting contamination severity and the potential for adverse health effects. Classification of HI and TCR values allows for the systematic determination of health risk levels posed by contaminated soils and sediments (Miletic *et al.,* 2023).

2.3. ANALYTICAL METHODS FOR DETECTING HEAVY METALS

2.3.1. Atomic absorption spectroscopy (AAS)

Atomic Absorption Spectroscopy (AAS) remains one of the most extensively utilized methods for quantifying heavy metals due to its high sensitivity, accuracy, and operational simplicity. This technique is grounded in the principle that free atoms in a ground state absorb light at characteristic wavelengths. When a sample is atomized in a flame or graphite furnace, the metal atoms absorb ultraviolet or visible radiation, and the extent of absorption is measured to determine the metal concentration (Welz and Sperling, 1999). AAS is particularly effective in detecting trace levels of elements such as cadmium, copper, zinc, and lead. It is capable of achieving detection limits in the parts-per-billion (ppb) range, making it suitable for environmental monitoring. While flame AAS is commonly used for analyzing samples with relatively high concentrations, Graphite Furnace AAS (GFAAS) offers enhanced sensitivity and is preferred for ultra-trace level detection (Skoog *et al.,* 2013).

2.3.2. Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively Coupled Plasma Mass Spectrometry combines a high-temperature plasma source with a mass spectrometer to achieve exceptional sensitivity in multi-element analysis. In this method, the plasma converts atoms in the sample into ions, which are then separated by their mass-to-charge ratios and quantified (Jarvis *et al.,* 1992). ICP-MS can routinely attain detection limits in the parts-per-trillion range, support rapid sample throughput, and measure

numerous elements in a single run. Its ability to distinguish isotopic signatures also makes it invaluable for tracing contamination sources and transport pathways (Thomas, 2001).

2.3.3. Inductively coupled plasma optical emission spectrometry (ICP-OES)

Also known as ICP-Atomic Emission Spectroscopy, ICP-OES introduces the sample into an argon plasma where the constituent atoms are excited and emit light at element-specific wavelengths. The emitted light intensity is measured to derive concentrations (Boss and Fredeen, 2004). ICP-OES offers a wide linear dynamic range and robustness in complex matrices, making it suitable for elements with high excitation energies. Though its detection limits are higher than those of ICP-MS, it remains a mainstay for routine monitoring of metals such as arsenic, mercury, and selenium in environmental waters (Dean, 2019).

2.3.4. X-Ray Fluorescence (XRF) spectroscopy

XRF spectroscopy determines elemental composition by measuring the characteristic secondary X-rays emitted after primary X-ray excitation. This noninvasive, rapid technique requires minimal sample preparation, and portable instruments enable on-site screening of groundwater samples (Jenkins, 1999). XRF effectively detects metals like lead, chromium, and nickel, but its relatively higher detection limits compared with AAS or ICP-MS may restrict its use in ultra-trace analyses (Kalnicky and Singhvi, 2001).

2.3.5. Electrochemical methods

Techniques such as Anodic Stripping Voltammetry and Differential Pulse Voltammetry concentrate metal ions onto an electrode surface, then measure the current produced during their electrochemical oxidation. These approaches achieve high sensitivity and selectivity for metals including lead, cadmium, and mercury. Their low cost and portability make them

attractive for field deployment, although careful calibration and potential interference from other ions must be addressed (Wang, 2006; Brett and Brett, 1993).

2.3.6. High-performance liquid chromatography coupled with mass spectrometry (HPLC-MS)

HPLC-MS pairs chromatographic separation of metal species with the sensitive detection capabilities of mass spectrometry. By isolating individual oxidation states or inorganic and organic forms of metals, it enables detailed speciation analysis. This is crucial for understanding the differing bioavailability and toxicological profiles of metal species in groundwater (Kersten and Kulik, 2011; Garcia-Alonso and Rodriguez-Gonzalez, 2013).

2.4. NON-CARCINOGENIC RISK ASSESSMENT

2.4.1. Average daily dose (ADD)

Calculating the average daily dose of heavy metals represents a foundational step in both carcinogenic and non-carcinogenic risk assessments. ADD estimates the daily intake of contaminants via ingestion, inhalation, and dermal contact (Miletic *et al.,* 2023). Because inhalation often contributes minimally to total exposure, some studies focus only on ingestion or combine ingestion and dermal pathways (Zhou *et al.,* 2018). Synonymous terms include chronic daily intake (CDI), average daily intake (ADI), daily intake of metals (DIM), and exposure (Exp). When distinguishing risk types, non-carcinogenic exposure is denoted ADD, while LADD (lifetime average daily dose) refers to carcinogenic calculations (Cui *et al.,* 2020). Occasionally, total daily dose (ADD_total) aggregates all pathways directly within risk indices (Zhou *et al.,* 2022).

2.4.2. Reference dose (RfD)

The reference dose specifies the estimated daily exposure level to a heavy metal that is unlikely to produce adverse effects over a lifetime. Expressed in $mg \cdot kg^{-1} \cdot day^{-1}$ for ingestion and dermal routes, and sometimes in $mg \cdot m^{-3}$ for inhalation, RfD values are pathway-specific. Standardized RfDs for metals such as cadmium, arsenic, chromium, copper, nickel, lead, and zinc are published by regulatory bodies like the U.S. EPA IRIS. While cadmium, arsenic, chromium, copper, nickel, lead, and zinc are most frequently assessed, data on mercury, manganese, cobalt, vanadium, molybdenum, barium, iron, and antimony are less abundant (Miletic *et al.,* 2023; Wang *et al.,* 2022).

2.4.3. Hazard quotient (HQ) and Hazard index (HI)

The Hazard Quotient quantifies the non-carcinogenic risk for an individual pathway by dividing the ADD by the corresponding RfD. Summing HQs across all pathways yields the total HQ for a given metal. The Hazard Index further aggregates HQs for all metals under consideration, providing a composite measure of cumulative non-carcinogenic risk. Both HQ and HI are dimensionless ratios; values below one imply acceptable risk, whereas values above one indicate potential health concerns and the need for intervention (Miletic *et al.,* 2023).

2.5. HEALTH IMPACTS OF HEAVY METALS IN GROUNDWATER

Heavy metals such as lead, arsenic, cadmium, and mercury pose severe health hazards even at low concentrations. Lead exposure impairs neurological development in children, leading to cognitive deficits and behavioral disorders, and in adults it can cause cardiovascular and renal dysfunction (Lanphear *et al.,* 2005). Chronic arsenic exposure is linked to skin, lung, and bladder cancers, as well as cardiovascular disease, diabetes, and dermatological

conditions (Smith *et al.,* 2002). Cadmium accumulation leads to renal damage, skeletal weakening, and elevated cancer risk by disrupting calcium homeostasis (Nordberg, 2009). Mercury primarily targets the nervous system, with organic forms like methylmercury accumulating in food chains and causing neurobehavioural abnormalities (Clarkson and Magos, 2006).

2.6. ECOLOGICAL EFFECTS OF HEAVY METAL CONTAMINATION

2.6.1. Bioaccumulation and biomagnification

Heavy metals such as lead, cadmium, mercury, and arsenic accumulate within organisms faster than they can be eliminated, a process known as bioaccumulation. Through successive trophic transfers, biomagnification leads to increasingly higher concentrations in predatory species. Aquatic ecosystems are particularly vulnerable, with mercury exemplifying this phenomenon by reaching harmful levels in fish and wildlife, and ultimately impacting human consumers (Chen *et al.,* 2012).

2.6.2. Toxicity to aquatic life

Even trace amounts of heavy metals disrupt enzymatic functions, reproductive biology, and morphology in fish and invertebrates. Cadmium and lead interfere with osmoregulation, increasing mortality and reducing biodiversity in freshwater environments (Pandey and Madhuri, 2014; Gall *et al.,* 2015).

2.6.3. Soil–plant interactions

Irrigation with contaminated groundwater allows heavy metals to accumulate in soils and be taken up by crops, inhibiting seed germination, root development, and overall biomass production. These metals also impair beneficial soil–microbe interactions, such as those with

mycorrhizal fungi, which are essential for nutrient uptake (Nagajyoti *et al.,* 2010; Göhre and Paszkowski, 2006).

2.6.4. Effects on soil microbial communities

Heavy metals reduce microbial biomass and metabolic activity, impairing nutrient cycling and soil fertility. The selective pressure of metal toxicity can also favor resistant strains, leading to shifts in community composition and ecological imbalance (Zhao *et al.,* 2014; Rajapaksha *et al.,* 2012).

2.6.5. Implications for human health

Ecological disruptions caused by heavy metal contamination ultimately feed back into human health risks through contaminated food and water supplies. In the Niger Delta of Nigeria, industrial discharges and oil spills have elevated groundwater concentrations of lead, cadmium, and arsenic, posing serious health threats in communities relying on these water sources (Nwankwoala and Ememu, 2018).

2.7. RELATED LITERATURE

(Nkpaa *et al.,* 2017) conducted an extensive investigation into the concentration of heavy metals in groundwater sources across six coastal communities in Gokana, Rivers State. The study focused on evaluating the potential health risks posed to the local population through ingestion and dermal pathways by employing standard non-carcinogenic and carcinogenic risk assessment frameworks. The concentration ranges reported for manganese (Mn), nickel (Ni), lead (Pb), cadmium (Cd), and chromium (Cr) were 0.02–0.86, 0.16–0.19, 0.03–0.10, 0.02–0.03, and 0.01–0.17 mg/L, respectively. All these levels exceeded the permissible limits established for safe drinking water. In assessing non-carcinogenic risk, the study

utilized the average daily dose (ADD) and dermal absorbed dose (DAD) models, which revealed that Mn, Ni, and Pb posed significant health concerns through ingestion. Notably, the hazard index (HI) values for Cd and Cr via the ingestion route were greater than 1.0, suggesting a high potential for adverse health effects.

(Kapoor *et al.,* 2024) conducted a comprehensive assessment of heavy metal contamination in groundwater by analysing 34 water samples from various blocks within the Rupnagar district of Punjab, India. The study employed chronic daily intake (CDI) and hazard quotient (HQ) models to evaluate potential health risks associated with metal ingestion. The analysis revealed that aluminium recorded the highest concentration in the Nurpur Bedi block, reaching 36.43 mg/L. Arsenic levels were measured at 0.09 mg/L in Ropar and 0.068 mg/L in Anandpur Sahib, while cadmium peaked at 0.041 mg/L in Nurpur Bedi. The Morinda block exhibited the highest concentration of selenium at 0.0038 mg/L. Lead was consistently detected across all surveyed blocks, with the highest concentration of 2.176 mg/L observed in Chamkaur Sahib. The HQ values for aluminium, arsenic, and lead exceeded one in nearly all locations, suggesting considerable non-carcinogenic health risks through ingestion. Notably, the hazard index (HI) for adults was highest in Nurpur Bedi at 2.66, indicating potential adverse health effects due to cumulative exposure to multiple metals. Although the study also addressed carcinogenic risks using Incremental Lifetime Cancer Risk (ILCR) metrics, its findings concerning non-carcinogenic exposure are particularly significant. The presence of arsenic, chromium, and lead was associated with elevated cancer risks, while a one-way ANOVA confirmed statistically significant differences in the concentrations of iron, arsenic, and aluminium ($p < 0.05$).

(Mohammadi *et al.,* 2019) assessed the concentration of eight heavy metals in forty drinking water samples collected from the distribution system in Khorramabad, Iran. The concentrations recorded for the metals were all found to be within the permissible limits set

by the United States Environmental Protection Agency (EPA) and the World Health Organization (WHO), indicating that the water was of acceptable quality for human consumption. In terms of chronic daily intake (CDI) values for adults, the metals were ranked in decreasing order as zinc, barium, lead, nickel, chromium, copper, cadmium, and molybdenum. The study employed health risk assessment models focusing on non-carcinogenic outcomes by calculating the hazard quotient (HQ) for ingestion and dermal exposure routes. Results indicated that both the combined hazard quotient (HQing + HQderm) and the overall hazard index (HI) values were below the threshold of concern, suggesting no significant non-carcinogenic risk from daily consumption or dermal absorption of the water. Among the two pathways, ingestion was identified as the dominant route of exposure. Despite the absence of non-carcinogenic health risks, the study reported that carcinogenic risks associated with lead, chromium, cadmium, and nickel exceeded the acceptable limit of 1×10^{-6}, thereby indicating potential long-term health hazards from chronic exposure.

(Jafarzadeh *et al.,* 2022) investigated the concentrations of selected heavy metals, specifically chromium (Cr), cadmium (Cd), and lead (Pb), in groundwater samples collected from 89 active wells in Saravan city. The study utilized the Hazard Quotient (HQ) method in combination with Monte Carlo Simulation (MCS) comprising 10,000 iterations to evaluate non-carcinogenic health risks associated with these metals across four population subgroups: adults, teenagers, children, and infants. The concentrations of Cr, Pb, and Cd in the water samples ranged from 0.49 to 20 µg/L, 0.1 to 58.34 µg/L, and 0.11 to 12.8 µg/L, respectively. The mean HQ values derived from ingestion exposure were all below the safety threshold of one, with lead ranging from 0.0018 to 0.0023, chromium from 0.0112 to 0.0186, and cadmium from 0.0370 to 0.0615. These findings indicate that, at the observed concentrations, the risk of non-carcinogenic health effects due to oral exposure to these metals is minimal across all age categories. Sensitivity analysis further demonstrated that the concentration of

heavy metals was the most influential variable in estimating non-carcinogenic risk for all population groups. The authors suggested that while the risk was within acceptable limits, there is need for broader investigations involving larger sample sizes.

(Zabin *et al.,* 2008) conducted a study aimed at evaluating the concentration of selected heavy metals and fluoride in groundwater sourced from private wells in the Al-Baha region of Saudi Arabia. The primary objective was to determine the potential for non-carcinogenic health effects arising from exposure to these contaminants. The researchers collected water samples and analyzed them using standard protocols to assess chemical contamination. The elements consistently detected in all water samples included chromium, manganese, zinc, iron, and fluoride. These were subsequently subjected to toxicological risk analysis. The study considered ingestion and dermal contact as the principal exposure pathways, and chronic daily intake (CDI) values were calculated for each route. These values were then compared against health-based reference limits to evaluate potential risks. The results showed that the individual oral hazard quotient (HQ) values for manganese, chromium, and zinc were below one, indicating no significant non-carcinogenic health threat from these elements. However, certain samples exhibited oral HQ values for iron and fluoride that exceeded one, suggesting potential risk under chronic exposure. Additionally, when the combined effect of all detected contaminants was assessed using the hazard index (HI), some samples were found to have values greater than one for both ingestion and dermal pathways. This indicates a potential for cumulative non-carcinogenic health impacts among individuals consuming or coming into contact with the contaminated groundwater.

CHAPTER THREE

MATERIALS AND METHOD

3.0. REGIONAL GEOLOGY

Etsako West Local Government Area is located in the northern part of Edo State, Nigeria, approximately between latitudes 6° 45′ N and 7° 35′ N and longitudes 5° 55′ E and 6° 45′ E. Regionally, it forms part of the southwestern segment of the Nigerian Basement Complex, a major component of the Pan-African Trans-Saharan mobile belt that developed through the collision and suturing of the West African and Congo cratons (Rahaman, 1988; Dada, 2008). This tectonic domain is characterized by complex Precambrian crystalline rocks and subordinate Cretaceous sedimentary sequences. The basement complex is dominated by migmatite-gneiss complexes, quartzites, mica schists, and granitic intrusives that record multiple tectonothermal episodes (Rahaman, 1988; Ajibade and Woakes, 1989). These rocks have undergone repeated phases of high- to medium-grade metamorphism, deformation, and magmatism associated with the Pan-African orogeny, dated at approximately 600 ± 150 Ma (Dada, 2008). The Etsako West metamorphic domain, particularly around Igarra, is a key part of Nigeria's Migmatite–Gneiss Complex within the Pan-African mobile belt. (Udi *et al.*, 2023) documented syn- to late-tectonic intrusion of Pan-African granitoids (circa 600 Ma ± 150 Ma) that reportedly reactivated pre-existing E–W fault systems. (McCurry, 1971) described two primary deformation phases: D_1 (E–NE to W–SW) and D_2 (N–S), accompanied by migmatization, granite emplacement, and subsequent fracturing and faulting. The regional lithostratigraphy comprises migmatitic gneisses, schist belts, and granitoids. (Ajibade *et al.*, 1987) showed that syn-tectonic granites intrude both older basement and supracrustal cover, indicating significant crustal reworking. Regional geology further reflects pervasive foliation, isoclinal folding, and metamorphic conditions ranging from greenschist up to amphibolite

and localized granulite facies, especially where partial melting occurred. Stress analyses of the Igarra Schist Belt by (Udinmwen, 2017) identified two deformation episodes: first NE–SW, then E–W with the E–W trend being dominant and indicative of ductile to brittle deformation. Metamorphic pressure–temperature profiles across the Benin–Nigerian Shield corroborate a metamorphic gradient—from middle greenschist (approx. 400 °C) to upper amphibolite facies (680–750 °C), highlighting the region's significant tectonothermal evolution during the Pan-African event (Ephraim *et al.,* 2008).

3.0.1. Migmatite-gneiss Formations

At the site scale, exposures in Etsako West show that the migmatite-gneiss complex forms the principal basement unit. These rocks are typically banded and consist of alternating felsic and mafic layers (Obasi *et al.,* 2020). Petrographic descriptions from nearby mapped localities report quartz, K-feldspar and plagioclase in the felsic bands, and biotite and hornblende in the mafic bands. Locally the gneisses grade into migmatites with leucosome veins and granite injections, indicating partial anatexis during high-grade metamorphism. Supracrustal packages comprising schist, quartzite and calc-silicate rocks are commonly found adjacent to these gneissic bodies, demonstrating lateral juxtaposition of sedimentary protoliths and basement rocks during deformation (Adegbuyi *et al.,* 2018; Rahaman, 1988).

3.0.2. Granitoid Intrusions

Pan-African granitoids and associated porphyritic or coarse-grained granites are common intrusive phases in the Etsako West basement. Field relations indicate that many granitoid bodies were emplaced syn- to post-tectonically, producing sharp intrusive contacts, country-rock assimilation, and local development of granitic gneiss through deformation and metamorphism. Geochemical and regional petrogenetic studies of Pan-African granites in

Nigeria interpret these intrusions mainly as crustal melts produced by tectonothermal reworking during the Pan-African orogeny (Sanni *et al.,* 2023; Oyewole and Ofuyah, 2017).

3.0.3. Mineralogical Composition

The metacarbonate deposits of Enwan, Bekuma, and Ekpedo display a distinct mineralogical composition. Analyses reveal that the rocks at Enwan contain an average of 96.4% calcium carbonate and 3.6% magnesium oxide, while those from Ekpedo contain 58.5% calcium carbonate and 41.5% magnesium oxide. The Bekuma deposits hold 77.35% calcium carbonate and 13.1% magnesium oxide. Across all three locations, the primary minerals are calcite and dolomite, with calcite as the dominant phase. Additional minerals present include quartz, plagioclase, and muscovite, which occur in smaller proportions (Omotehinse and Taiwo, 2022; Nweke *et al.,* 2024).

3.0.4. Hydrogeological and Structural Controls on Groundwater

Hard-rock aquifers in Etsako West are strongly controlled by secondary permeability associated with fractures, weathered zones, and structural lineaments. Remote sensing and lineament mapping studies in Etsako West demonstrate a network of linear features that correspond to faults and shear zones. These lineaments often localize groundwater occurrence and influence recharge pathways in otherwise low-porosity basement rocks (Salami *et al.,* 2024).

3.1. LOCAL GEOLOGY

Ago-Isame is a village in Etsako West Local Government Area, Edo State, located at approximately **7.1321° N, 6.2027° E**. The village lies within the rugged, ridge-dominated terrain that characterizes the Etsako West domain. The area is part of the Precambrian

Nigerian Basement Complex and sits within the Pan-African mobile belt produced by the Neoproterozoic collision and suturing of the West African and Congo cratons (Rahaman, 1988; Dada, 2008). Ago-Isame is underlain by rocks of the Precambrian Basement Complex. The dominant lithologies of the Akoko-Edo region include migmatite-gneiss complexes, banded gneisses, schists and supracrustal sequences, subordinate quartzites, and various granitoid intrusions (Rahaman, 1988; Ajibade and Woakes, 1989).

3.2. MATERIALS

The materials and equipment used in the study included 75 cl plastic sampling bottles, portable calibrated meters, ultrapure nitric acid (HNO_3), ice-packed coolers, Atomic Absorption Spectrophotometer (AAS), analytical-grade stock solutions, standard laboratory glassware, distilled water, blanks, calibration standards for each metal, PPE, data analysis software, statistical software (SPSS).

3.3. METHODS

3.3.1 Sample Collection

Ten (10) groundwater samples were collected from boreholes distributed across the study area. Prior to collection, each sampling container (75 cl plastic bottles) was thoroughly rinsed with clean water. In situ measurements of physicochemical parameters, including pH, electrical conductivity (EC), temperature, total dissolved solids (TDS), and dissolved oxygen (DO), were taken using portable, calibrated meters. All samples were acidified to $pH < 2$ with ultrapure nitric acid (HNO_3) to prevent metal precipitation and adsorption to container walls, then stored at 4 °C in ice-packed coolers and transported to the laboratory for heavy metal analysis.

3.3.2. Laboratory Analysis

The concentrations of target heavy metals: Lead (Pb), Cadmium (Cd), Chromium (Cr), Arsenic (As), Nickel (Ni), Zinc (Zn), Copper (Cu), and Iron (Fe) were determined using Atomic Absorption Spectrophotometry (AAS). Prior to measurement, the instrument was calibrated with standard solutions prepared from analytical-grade stock solutions (1000 mg/L) of each metal. Blanks and replicate analyses were used to ensure precision and accuracy. Detection limits were determined for each metal to validate analytical sensitivity. Parameters such as Total Dissolved Solids (TDS), Total Hardness, and Alkalinity were determined using standard titrimetric and gravimetric methods as outlined by (APHA, 2017).

3.3.3. Human Health Risk Assessment: Ingestion Pathway

Human health risk assessment for heavy metals in groundwater was carried out in accordance with the United States Environmental Protection Agency (US EPA, 1989; 2004) guidelines, focusing on the ingestion exposure route. The methodology involved determining the **Chronic Daily Intake (CDI)**, estimating the of **non-carcinogenic risk** (Hazard Quotient, HQ) and **carcinogenic risk** (CR) for identified heavy metals.

3.3.4. Chronic Daily Intake (CDI)

The CDI through ingestion was determined using Equation (1):

$$CDI = C_w \times IR \times EF \times ED / BW \times AT$$

The variable C_w denotes the concentration of heavy metals in groundwater expressed in milligrams per litre (mg/L). The ingestion rate of water is represented by *IR* and measured in litres per day (L/day). *ER* refers to the exposure frequency in days per year, while *ED* indicates the exposure duration in years. Body weight is expressed as *BW* in kilograms (kg). The averaging time, denoted as *AT*, is calculated in days and differs depending on the type of

effect considered: for non-carcinogenic effects, *AT* equals *ED*, whereas for carcinogenic effects, it is set at 70 × 365 (Samaila *et al.,* 2024).

3.3.5. Ecological Risks of Heavy Metals in Groundwater

The ecological risk index (ERI) serves as an integrated measure for evaluating the potential ecological threats associated with heavy metal contamination in groundwater (Sharifi *et al.,* 2016). It is given as;

$$ERI = \sum_{i=1}^{n} T_i \times M_i / S_i$$

The parameter T_i represents the biological toxicity factor assigned to a specific heavy metal. The values of T_i are determined as Cu = Ni = Pb = Co = 5, Mn = Zn = 1, As = 10, and Cd = 30 (Hakanson, 1980; Sharifi *et al.,* 2016). The ecological risk index (ERI) is categorized into levels of severity, namely: low risk when ERI is less than 110; moderate risk when ERI ranges from 110 to less than 200; considerable risk when ERI lies between 200 and less than 400; and very high risk when ERI equals or exceeds 400 (Sharifi *et al.,* 2016).

3.3.6. Health Risks of Heavy Metals in Groundwater

The assessment of health risks followed the guidelines established by the United States Environmental Protection Agency (USEPA, 1989). In groundwater, exposure to heavy metals occurs primarily through ingestion and dermal absorption (Kim et al., 2004; Wu et al., 2009). To evaluate these risks, both cancer risk (CR) and hazard quotient (HQ) were applied as key indicators (USEPA, 2016; Wu *et al.,* 2018a; Lv *et al.,* 2019).

3.3.7. Determination of Non-Carcinogenic Risk

This assessment aims to measure the potential health implications arising from exposure to non-carcinogenic contaminants. The hazard quotient (HQ) is calculated by dividing the

estimated daily exposure dose by the oral reference dose (RfD), with both expressed in milligrams per kilogram per day (mg/kg/day). An HQ value exceeding one indicates the likelihood of adverse health outcomes resulting from contact with the contaminant. HQ = ADD/RFD

An HQ value greater than one signifies a potential for harmful health effects, while a value less than one indicates minimal risk. The average daily dose (ADD) was determined by considering multiple human exposure pathways, namely ingestion, inhalation, and dermal absorption (Zglobicki and Telecka, 2021). The associated risks were calculated using the equations presented below:

$$ADD_{ingestion} = \frac{C \times R_{ing} \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \ldots\ldots (1)$$

$$ADD_{inhalation} = \frac{C \times R_{inh} \times EF \times ED}{PEF \times BW \times AT} \quad \ldots\ldots (2)$$

$$ADD_{dermal} = \frac{C \times SA \times SL \times ABF \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \ldots\ldots (3)$$

Therefore, the total ADD can be evaluated by adding the ADD dermal +ADD inhalation + ADD ingestion.

Where C = Concentration of metal (µg/kg, mg/kg), R_{ing} = ingestion rate, R_{inh} = inhalation Rate, EF is Exposure Frequency (days/yr), SA = exposed skin area, ABF = the exposure duration (h/day), SL = the chemical-specific dermal permeability constant (cm/h), ED = Exposure Duration (yr), AT = Averaging Time (period over which exposure is averaged) (days), BW = Body Weight (kg).

The Hazard Index (HI) is utilized to evaluate the overall non-carcinogenic risk associated with concurrent exposure to multiple heavy metals detected in the analyzed samples. The HI is obtained by summing the individual Hazard Quotients (HQs) for each metal (Goumenou and Tsatsakis, 2019). The HQ represents the risk from a particular exposure pathway and is

classified as HQ_{inh} for inhalation, HQ_{ing} for ingestion, HQ_{derm} for dermal contact, and HQ_t as the total hazard quotient from all exposure routes combined.

$HQ_{ing} = CDI_{ing}/RFD_{ing}$

$HQ_{inh} = CDI_{inh}/RFD_{inh}$

$HQ_{derm} = CDI_{derm}/RFD_{derm}$

3.3.8. Hazard Index for Children and Adults

An HI value exceeding one indicates a potential risk to human health, while values less than one are typically regarded as posing minimal concern. The hazard index is determined using the following formula:

$$HI = \frac{C_{metal} \times IR \times EF \times ED}{RfD \times BW \times AT}$$

- $HI < 1$ implies an insignificant health risk,
- $1 \leq HI < 4$ suggests the possibility of risk, and
- $HI > 4$ indicates a high level of non-carcinogenic health risk.

3.3.9. Carcinogenic Risk Assessment

Carcinogenic risk (CR) was assessed following the method outlined by (Maeaba *et al.*, 2019) to estimate the lifetime probability of developing cancer due to exposure to carcinogenic heavy metals such as arsenic (As), nickel (Ni), lead (Pb), cadmium (Cd), cobalt (Co), and chromium (Cr). The subsequent equations were employed to calculate carcinogenic risk for the various exposure pathways:

$CR = ADD \times SF$…….....(1)

Where CR= Cancer risk, ADD = Average daily dose and SF = Cancer slope factor

$TCR = \sum CR = CR_{ing} + CR_{inh} + CR_{derm}$……………………………..……………(2)

TCR represents the Total Carcinogenic Risk, while CR denotes the individual Carcinogenic Risk. Based on established guidelines, a TCR value between 1×10^{-6} and 1×10^{-4} is regarded as acceptable, indicating no significant risk to human health (Itam *et al.,* 2024). Conversely, values equal to or greater than 1×10^{-3} may reflect an increased likelihood of cancer occurrence over a lifetime of exposure.

3.3.10. Statistical Analysis

The dataset, including all estimated parameters, was analyzed statistically to compute the mean and standard deviation. This was performed using the Statistical Package for the Social Sciences (SPSS).

CHAPTER FOUR

RESULTS

The results of the groundwater heavy metal analysis are presented in Tables 4.0.1-4.0.4. The concentrations of lead (Pb), chromium (Cr), and zinc (Zn) were determined across fifteen (15) groundwater samples and subsequently compared with the World Health Organization (WHO, 2011) and U.S. Environmental Protection Agency (U.S. EPA, 1992) guideline values to evaluate potential health implications. To further assess the non-carcinogenic risks associated with human exposure through groundwater ingestion, the chronic daily intake (CDI), hazard quotient (HQ), and hazard index (HI) were computed and analyzed.

Table 4.0.1: Concentrations of Heavy Metals (Pb, Cr, Zn) in Groundwater Samples (GW1–GW15)

Sample	Pb (mg/L)	Cr (mg/L)	Zn (mg/L)
GW1	-	0.09937	-
GW2	0.01973	0.05607	-
GW3	0.00522	0.12882	-
GW4	0.03018	0.04331	-
GW5	0.01858	0.07447	0.01274
GW6	0.02017	0.09413	-
GW7	0.00858	0.21138	0.01801
GW8	0.02770	0.22902	-
GW9	-	0.07813	0.00444
GW10	0.02781	-	0.02496
GW11	-	1.10335	0.15791
GW12	0.01094	0.07543	1.98149
GW13	0.01180	0.27310	0.09302
GW14	0.04621	0.01616	0.06410
GW15	-	0.23532	-
Mean	0.01513	0.18120	0.15711
Standard Error	0.00356	0.06935	0.13084
Minimum	0.00000	0.00000	0.00000
Maximum	0.04621	1.10335	1.98149
EPA Standard	0.01500	0.10000	5.00000
WHO Standard	0.01000	0.05000	3.00000

Table 4.0.2: Chronic Daily Intake (CDI), and Reference Dose (RfD) of Heavy Metals in Groundwater

Metal	Concentration (mg/L)	CDI (Adults) (mg/kg-day)	CDI (Children) (mg/kg-day)	RfD (mg/kg-day)
Pb	0.01513	0.000415	0.000967	0.0035
Cr	0.18120	0.004964	0.011584	0.0030
Zn	0.15711	0.004304	0.010044	0.3000

Table 4.0.3: Hazard Quotients (HQs) and Hazard Index (HI) for Adults and Children

Metal	HQ (Adults)	HQ (Children)
Pb	0.118434	0.276347
Cr	1.654795	3.861187
Zn	0.014348	0.033479
Hazard Index (HI)	**1.787577**	**4.171013**

CHAPTER FIVE

DISCUSSION, CONCLUSION RECOMMENDATION

5.1. DISCUSSION

5.1.1. Physico-Chemical Assessments

The results of concentrations of heavy metals (Pb, Cr, and Zn) analyzed in fifteen (15) groundwater samples (GW1-GW15) and their comparison with WHO (2011) and U.S. EPA (1992) standards are presented in Table 4.0.2. Lead (Pb) concentrations in the groundwater samples ranged from 0.0000 mg/L to 0.0462 mg/L, with a mean value of 0.0151 mg/L. The Pb levels in some locations such as GW4 (0.0302 mg/L) and GW14 (0.0462 mg/L) exceeded both the WHO permissible limit of 0.01 mg/L and the U.S. EPA limit of 0.015 mg/L, indicating localized contamination likely from anthropogenic sources. The elevated Pb values in these wells suggest that the surrounding environment may be influenced by urban runoff or leaching from metal-based infrastructure (Omonona *et al.,* 2020). Chromium (Cr) concentrations varied widely across the groundwater samples, ranging from 0.0000 mg/L to 1.1033 mg/L, with a mean concentration of 0.1812 mg/L. The highest Cr value was recorded in GW11 (1.1033 mg/L), which far exceeded both the WHO (0.05 mg/L) and U.S. EPA (0.1 mg/L) recommended limits. This significant exceedance implies a possible influence from anthropogenic sources. The presence of Cr above permissible limits in multiple samples highlights potential risks to human health (Ojeaga and Segine, 2025). Zinc (Zn) concentrations in the analyzed samples ranged from 0.0000 mg/L to 1.9815 mg/L, with a mean concentration of 0.1571 mg/L. The maximum Zn concentration occurred in GW12 (1.9815 mg/L), while most other samples exhibited minimal Zn levels. All observed Zn values remained well below the WHO (3.0 mg/L) and U.S. EPA (5.0 mg/L) guideline limits, suggesting that zinc contamination within the study area is minimal and within acceptable

limits for potable water. The relatively elevated Zn values in a few wells could be attributed to natural mineral dissolution, corrosion of galvanized pipes, or leaching from zinc-bearing rocks.

The mean concentrations of the metals followed a decreasing order of Cr (0.1812 mg/L) > Zn (0.1571 mg/L) > Pb (0.0151 mg/L). This sequence indicates that chromium is the most dominant element in the groundwater samples, followed closely by zinc, while lead occurs in relatively low concentrations. The dominance of chromium suggests a significant anthropogenic imprint, possibly from industrial and mechanical processes, whereas the presence of Zinc and Lead may reflect both geogenic contributions and human-induced contamination. This trend aligns with the hydrogeochemical patterns reported by Omonona *et al.* (2020) and Ojeaga and Segine (2025), who observed similar distributions of heavy metals in groundwater systems influenced by mixed natural and anthropogenic factors.

5.1.2. Non-Carcinogenic Risk Assessment

Human health risk evaluation is the process of assessing the nature and extent of potential adverse health effects in humans exposed to toxic metals in contaminated environments (Mohammadi *et al.,* 2019). In this study, the non-carcinogenic risks associated with exposure to lead (Pb), chromium (Cr), and zinc (Zn) through ingestion of groundwater were evaluated. The chronic daily intake (CDI) and hazard quotient (HQ) values for each metal were computed and are presented in Tables 4.0.3 and 4.0.4. The CDI values for the analyzed metals via ingestion for adults were 0.000415 mg/kg/day for Pb, 0.004964 mg/kg/day for Cr, and 0.004304 mg/kg/day for Zn, while those for children were 0.000967 mg/kg/day for Pb, 0.011584 mg/kg/day for Cr, and 0.010044 mg/kg/day for Zn. These results reflect the relative concentrations of the metals in groundwater and their potential contributions to human exposure. Among the analyzed metals, chromium exhibited the highest CDI values for both

adults and children, suggesting a higher exposure potential, while Lead recorded the lowest CDI in both cases, implying relatively lower bioavailability and mobility in groundwater.

The HQ values, derived as the ratio of CDI to the reference dose (RfD), provide a measure of the potential for non-carcinogenic health effects. The HQ values for adults followed a decreasing order of Cr (1.6548) > Pb (0.1184) > Zn (0.0143), whereas for children, the sequence was Cr (3.8612) > Pb (0.2763) > Zn (0.0335). The HQ values greater than the threshold (HQ > 1), particularly those observed for chromium, indicate potential health risks arising from prolonged ingestion of contaminated groundwater. Chromium's dominance in HQ values suggests its probable influence from anthropogenic sources (Omonona *et al.,* 2020).

The hazard index (HI), which represents the cumulative non-carcinogenic risk from simultaneous exposure to multiple metals, was 1.7876 for adults and 4.1710 for children. In both cases, HI values exceeded the threshold (HI > 1), indicating possible adverse health implications due to combined exposure effects, with children showing a higher susceptibility. This heightened risk among children may be attributed to their lower body weight, higher water intake relative to body mass, and developing physiological systems that increase vulnerability to toxic exposure (Wu *et al.,* 2024). Chromium's elevated HQ values largely drive the total HI, reaffirming that this element is the dominant contributor to overall risk. Continuous exposure to elevated chromium levels could result in dermatological effects, gastrointestinal distress, or damage to the liver and kidneys (Mohammadi *et al.,* 2019). The overall decreasing order of non-carcinogenic risk was Cr > Pb > Zn. Pb and Zn values, which remained below the threshold, suggest negligible risk at their current concentrations. (Ojeaga and Segine, 2025).

5.2. CONCLUSION

The assessment of heavy metals (Pb, Cr, and Zn) in groundwater revealed varying levels of contamination across the sampled locations. Chromium exhibited the highest concentrations, exceeding both WHO and U.S. EPA permissible limits in several wells, while lead showed moderate exceedances and zinc remained within safe limits. The dominance of chromium in the hydrochemical composition indicates significant anthropogenic input, likely from industrial discharges, metal corrosion, or leaching from contaminated soils. The non-carcinogenic risk assessment further demonstrated that both adults and children are potentially at risk of adverse health effects, with hazard index (HI) values exceeding the safety threshold (HI > 1). The higher risk levels among children highlighting their physiological vulnerability and greater exposure relative to body mass. Chromium contributed most significantly to the total risk, highlighting it as the principal contaminant of concern.

5.3. RECOMMENDATION

It is recommended that regular groundwater monitoring be instituted to track heavy metal concentrations and assess seasonal variations. Mitigation measures, control of industrial effluent discharge, and public sensitization on safe water use should be prioritized.

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