CARCINOGENIC RISK ASSESSMENT OF GROUNDWATER ASSOCIATED HEAVY METALS VIA INGESTION EXPOSURE

BY

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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 FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF BACHELOR OF SCIENCE (B.Sc.) IN SCIENCE LABORATORY TECHNOLOGY (GEOLOGY & MINING TECHNIQUES OPTION)

OCTOBER, 2025.

CERTIFICATION

This is to certify that this project entitled "**CARCINOGENIC RISK ASSESSMENT OF GROUNDWATER ASSOCIATED HEAVY METALS VIA INGESTION EXPOSURE**" was carried out and authored by **Precious Ikponwosa OMOREGBE** with matriculation number LSC2007338 in the Department of Science Laboratory Technology, Faculty of Life Sciences, University of Benin. This Bachelor of Science (B.Sc.) thesis has undergone thorough evaluation and has been duly approved by:

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

DEDICATION

I dedicate this work to God who gave the inspiration for this work, and had also enabled this work to see the light of day.

ACKNOWLEDGEMENT

My immense and profound gratitude to God Almighty for His marvelous help to me throughout the duration of this research. I make bold to say that Jesus began and completed this project work by Himself through me. He made available every human vessel and technological tool needed for this work to see the light of day.

Without His guidance, this accomplishment would not have been possible. The completion of this research work has been made possible through the unwavering support of my family, friends, teammates, supervisor and lecturers. I deeply appreciate all the encouragements and assistance.

TABLE OF CONTENTS

LIST OF TABLES

ABSTRACT

This study assessed the carcinogenic risks of heavy metals in groundwater from Akoko-Edo, Edo State, with a focus on ingesting exposure. Atomic Absorption Spectrophotometry (AAS) was used on fifteen groundwater samples to detect lead (Pb), chromium (Cr), and zinc (Zn). The measured amounts were compared to WHO (2017) and EPA (2009) limits. Chromium values (0.0135-1.1015 mg/L) above permitted limits in numerous samples, whereas lead levels (0.0009-0.0353 mg/L) marginally exceeded norms in several areas. Zinc levels (0.0020-1.9683 mg/L) remained within acceptable ranges. TCR levels for adults (2.96 × 10^{-3}) and children (6.10 × 10^{-4}), indicating increased lifelong cancer risks, particularly from chromium exposure. The study suggests that heavy metal contamination has a major impact on the area's groundwater, which poses possible health risks through consumption. Continuous monitoring and the supply of alternative clean water sources are advised to reduce public health hazards.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Water is an indispensable resource for the survival of humans and other living organisms. Of the total global water supply, freshwater constitutes merely 3% and out of this, only about 0.01% is accessible for human use in domestic, agricultural and industrial contexts. Approximately one-third of the global population resides in regions experiencing moderate to severe water stress. The dual pressures of growing populations and dwindling freshwater availability have intensified the problem of water scarcity across various regions worldwide (Younesi-Baneh *et al.,* 2024). According to projections by the World Health Organization (WHO), by the year 2025, nearly 50% of the global population will face significant challenges related to water availability (Khalid *et al.,* 2020).

Groundwater, which comprises at least half of the Earth's freshwater reserves, serves essential roles in drinking, irrigation and industrial operations (Yahaya *et al.,* 2021). It provides safe drinking water for nearly one-third of the global population (Sadeghi *et al.,* 2018). This preference is due to its favorable microbiological characteristics, acceptable taste, smell and appearance, as well as its ease of treatment and generally stable quality (Edokpayi *et al.,* 2018). Nevertheless, numerous investigations have identified groundwater contamination from a wide array of pollutants. Among these, heavy metals (HMs) and their derivatives have received notable attention. These contaminants are introduced into groundwater from both natural processes (such as interactions with rock formations, soil composition, topography and seawater intrusion) and anthropogenic sources (including industrial discharges, mining activities, sewage effluent and agricultural practices), all of which deteriorate water quality (Younesi-Baneh *et al.,* 2024).

HMs in treated drinking water are especially concerning due to their persistence in trace amounts and their potential to cause chronic, cumulative health effects. These risks have led to the classification of certain heavy metals as hazardous substances on the 2007 Comprehensive Environmental Responses, Compensation and Liability Act Priority List (Zhao *et al.,* 2023; Saleh *et al.,* 2019). Their high toxicity at low concentrations, resistance to biodegradation, potential for forming even more toxic organic compounds, environmental persistence and bioaccumulation in body tissues make them particularly dangerous (Younesi-Baneh *et al.,* 2024). They interfere with biological systems by targeting specific cellular components, thereby overriding the body's natural regulatory mechanisms. Human exposure to HMs primarily occurs through drinking water, although inhalation and dermal absorption are also recognized pathways (Fakhri *et al.,* 2018; Razak *et al.,* 2015).

While trace levels of some HMs are vital for physiological processes, acting as co-factors and catalysts in enzymatic reactions, excessive amounts can be harmful (Yahaya *et al.,* 2021; Eleem *et al.,* 2021). Their accumulation in water bodies also degrades aesthetic properties, leading to public concerns. Even concentrations below regulatory thresholds can inhibit key biological functions (Younesi-Baneh *et al.,* 2024). Elements such as iron, copper, zinc, chromium, cobalt, selenium, vanadium and molybdenum are essential for growth and reproductive health; however, their overaccumulation can lead to toxicity (Abedi-Sarvestani *et al.,* 2019). Excessive levels of metals like aluminum and copper in drinking water have been associated with conditions such as Alzheimer’s disease (Abedi-Sarvestani *et al.,* 2019; Liu *et al.,* 2019) and gastrointestinal disturbances. Another set of HMs including arsenic, lead, cadmium, mercury and nickel, exert toxic effects at even lower concentrations (Sadeghi and Noroozi, 2021). Ingesting arsenic and cadmium can result in diseases such as cancer and allergic reactions, with arsenic exposure being specifically linked to cancers of the bladder, lungs and prostate (Wongsasuluk *et al.,* 2014). Chronic cadmium exposure has been implicated in disorders of the cardiovascular, skeletal and renal systems, while antimony exposure has also been associated with heart diseases. Lead has demonstrated teratogenic effects in pregnant women and can cause anemia in both children and adults. Mercury has been linked to the onset of autoimmune diseases (Younesi-Baneh *et al.,* 2024).

The intensification of industrial and agricultural activities has increased the release of these hazardous metals into water, soil and the atmosphere, posing serious threats to human health. Consequently, assessing and managing these health risks is crucial and should be prioritized within sustainable development agendas (Maleki and Jari, 2021). Health Risk Assessment (HRA) serves as a crucial tool for estimating and quantifying the potential health impacts of pollutants like heavy metals in aquatic ecosystems. Over recent decades, it has been extensively applied in scientific research to raise public awareness and guide policy-making authorities (Mohammadi *et al.,* 2019; Emmanuel *et al.*, 2022). HRA typically follows four structured steps: identifying hazards, evaluating exposure levels, assessing dose-response relationships and characterizing risk attributes (Hu *et al.*, 2020).

The global human population continues to grow rapidly, bringing with it significant challenges, one of which is the vast and escalating volume of solid waste generated and discarded. As a result, numerous nations, especially those in the developing world, grapple with the complexities of effective waste management. In these countries, solid waste is predominantly deposited in open dumpsites, often lacking the necessary infrastructure or technical capability for proper management (Adewole, 2009). Typically, peripheral areas of urban settlements which may later integrate into residential and commercial zones due to urban sprawl are selected for landfill sites. In Nigeria, inefficient waste disposal remains a pressing environmental issue, with open dumping being the prevalent practice. Unfortunately, sanitary landfills are rare, even among those administered by governmental waste management bodies. These landfills often harbor hazardous substances, including heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and other persistent organic pollutants (POPs), which can contaminate surrounding soils and subsequently leach into groundwater systems (Anetor *et al.,* 2008; Oyeku and Eludoyin, 2010).

For many populations, particularly those outside major river basins, groundwater serves as a crucial source of potable water. However, contamination of this resource due to landfill leachate has long been recognized as a significant public health concern. Pathways such as surface runoff, subsurface groundwater flow and precipitation-induced infiltration facilitate the migration of harmful substances from landfill sites to nearby groundwater and residential areas (Sulaimon *et al.,* 2015). The composition, toxicity, and potential risk posed by landfill leachate are influenced by factors such as the nature of the waste and the presence (or absence) of impermeable liners and leachate collection systems (Ludwig *et al.,* 2003; Adeolu *et al.,* 2009). When these toxic leachate constituents enter water bodies or accumulate in food chains via aquatic organisms or agricultural products, they pose substantial risks to ecosystems and human populations alike (Koki *et al.,* 2015).

Heavy metal pollution is particularly alarming due to the persistent nature, bioaccumulative properties and toxicity of these elements, even at trace concentrations. Their presence in the environment can severely compromise ecological systems and human health (Olagunju *et al.,* 2020). Non-essential heavy metals such as lead (Pb), chromium (Cr) and cadmium (Cd) are particularly worrisome. Pb exposure has been associated with various health issues including pulmonary cancer, cognitive impairment in children, anemia and kidney damage. Cr and Cd, on the other hand, are known for their hepatotoxic, neurotoxic, nephrotoxic and carcinogenic effects (Olagunju *et al.,* 2020). While zinc (Zn) and copper (Cu) are necessary micronutrients for physiological functions, excessive Zn can hinder respiratory efficiency (Cooper, 2008) and an overload of Cu may disrupt thyroid hormone synthesis and adrenal hormone regulation (Olagunju *et al.,* 2020). Nickel (Ni) presents a dual nature beneficial in trace amounts but harmful in excess. It is recognized as a carcinogen and facilitates the activity of pathogenic organisms that utilize nickel-dependent enzymes (Zambelli and Ciurli, 2013).

Iron (Fe), although vital in numerous biochemical and signaling processes, can induce oxidative stress in its redox-active state by binding to cellular thiol groups (Haddad, 2012). Consequently, the management of municipal solid waste, which often contains significant concentrations of these metals, is a major focus for environmental scientists, public health professionals, policy makers and regulatory authorities. A crucial step in addressing such environmental contaminants involves measuring the extent of pollutant loads. Global regulatory bodies like the World Health Organization (WHO), the United States Environmental Protection Agency (USEPA) and the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) establish permissible thresholds for various pollutants, beyond which environmental quality is deemed compromised and potentially hazardous. Within the fields of ecotoxicology and environmental health, risk assessment entails evaluating the possible detrimental effects on ecosystems and human populations exposed to toxic substances. Various risk assessment frameworks have been developed to quantitatively analyze environmental hazards, delineate exposure pathways and assess potential risks (Lushenko, 2010).

In Nigeria, the majority of environmental and health risk assessments have centered on mining environments, aquatic life and edible crops (Olagunju *et al.,* 2020). However, there remains a notable lack of comprehensive studies concerning risk assessment in relation to landfill sites. While a limited number of studies such as that by Adesewa and Morenikeji (2017) on metal concentrations at the Awotan landfill exist, they often fall short of evaluating the associated health and ecological risks.

1.2 Statement of the Problem

The widespread reliance on groundwater for domestic and drinking purposes, especially in peri-urban and rural communities, raises significant health concerns in the face of increasing environmental contamination. Anthropogenic activities such as improper waste disposal, agricultural runoff, industrial discharges and unregulated land use have resulted in the release of heavy metals into groundwater aquifers. These metals, some of which are known carcinogens, can persist in the environment, bioaccumulate through the food chain and pose long-term health risks when ingested over time. Ingestion remains the primary route of exposure to these contaminants for many individuals, particularly in regions where groundwater serves as the sole or major source of potable water. The toxicological consequences of chronic exposure to heavy metals such as arsenic (As), lead (Pb), cadmium (Cd) and chromium (Cr) include mutagenicity, organ toxicity and increased cancer risk. Despite regulatory efforts, populations in many developing regions remain vulnerable. Understanding the carcinogenic potential of heavy metals through quantitative risk assessment frameworks is therefore critical to safeguard human health and inform public health interventions. This therefore necessitates a comprehensive evaluation of groundwater quality with particular emphasis on ingestion-related exposure pathways.

1.3 Aim and Objectives

The aim of this study is to evaluate the carcinogenic risks posed by heavy metals present in groundwater sources through ingestion exposure.

The objectives are:

i. To determine the concentrations of selected heavy metals in groundwater samples from the study area.
ii. To compare the measured concentrations with standard permissible limits for drinking water.
iii. To determine the chronic daily intake (CDI) of heavy metals via ingestion for adults and children.
iv. To determine the carcinogenic risk (CR) of the detected heavy metals to human health.

1.4 Justification of the Study

Groundwater quality assessment in the context of carcinogenic heavy metal contamination is a critical undertaking in environmental and public health research. Given the dependence on groundwater for drinking, cooking and other domestic purposes, evaluating the ingestion-related cancer risks posed by heavy metals is not only timely but also imperative. This study is justified by the need to generate empirical data that supports informed decision-making among groundwater users. The findings will contribute to a better understanding of carcinogenic risks associated with groundwater ingestion. By identifying areas of elevated carcinogenic risk, this study provides a foundation for proactive interventions and promotes the sustainable management of groundwater resources for present and future generations.

CHAPTER TWO

LITERATURE REVIEW

2.0 Overview

Groundwater is widely regarded as an essential and readily available source of potable water in numerous parts of the world, primarily due to its low microbial content and general accessibility (Bodrud-Doza *et al.*, 2019; Rahman *et al.*, 2021). In Bangladesh, it constitutes the main drinking water source for approximately 98% of the population (Hasan *et al.*, 2022; Shamsudduha *et al.*, 2011). In recent decades, there has been a notable escalation in the demand for groundwater, driven by factors such as rapid population growth, the deterioration of surface water quality and associated environmental challenges (Bodrud-Doza *et al*., 2019; Islam *et al.*, 2017). A significant issue that has gained attention among researchers and policy formulators is the contamination of groundwater by potentially toxic metals (PTMs) of geogenic origin (Tajwar *et al.*, 2024). The geochemical weathering of rocks and minerals facilitates the mobilization of various trace elements into groundwater systems. These include nickel, arsenic, iron, copper, manganese, boron, zinc, lead, cadmium, aluminum and chromium (Rango *et al.*, 2009; Tajwar and Uddin, 2021). Anthropogenic activities such as industrial development, urban sprawl, indiscriminate waste disposal and extensive agricultural practices further exacerbate the problem by introducing PTMs into shallow groundwater reservoirs (Tajwar *et al*., 2024).

Persistent Toxic Materials (PTMs), measured in mgL^{-1}, are characterized by their high density, environmental persistence, resistance to natural degradation and tendency to bioaccumulate. These properties make them particularly dangerous to human health, even at minimal concentrations (Ali *et al*., 2019). Ingestion of water contaminated with such metals can result in a spectrum of serious health effects, including hypertension, carcinogenesis, vascular dysfunction, respiratory impairment, gastrointestinal bleeding, neurotoxicity and reproductive disorders (Tajwar *et al.,* 2024). Among these, arsenic is known to produce chronic health conditions such as gastrointestinal disturbances, suppressed hematopoiesis, muscular fatigue, dermatological reactions, cutaneous malignancies and various internal cancers, especially of the liver, lungs and bladder. Arsenic exposure is also associated with cardiovascular and neurological complications (Hughes, 2003). According to available data (Council, 2000), elevated copper concentrations in drinking water can induce symptoms like nausea, abdominal pain, diarrhea and hepatic damage. Chronic chromium exposure has been associated with hematological abnormalities and damage to the kidneys, liver, central nervous system, gastrointestinal tract, and cardiovascular system, with potentially fatal outcomes (Adimalla and Li, 2019). Long-term exposure to high manganese levels has been implicated in neurological dysfunction and cognitive decline, alongside genotoxic effects. Excess boron intake through drinking water may cause serious health issues, including irritability, seizures, diarrhea, vomiting, skin eruptions and pharyngeal ulcers in infants. Adults may exhibit symptoms such as erythema, vomiting, nausea and diarrhea (EPA, 2008). Aluminum ingestion has been correlated with non-carcinogenic effects, including Alzheimer’s disease, dementia, kidney failure and bone and brain pathologies. Furthermore, the occurrence of iron, mercury, lead and cadmium in groundwater also presents significant health concerns (Tajwar *et al.,* 2024).

There is an increasing global consensus on the necessity to rigorously monitor groundwater quality and assess its associated health risks. This approach is critical for understanding the link between environmental contaminants and public health outcomes (Tirkey *et al.,* 2017; Rahman *et al.,* 2020). Comprehensive assessments in Bangladesh have revealed alarmingly high concentrations of toxic metals and metalloids, such as arsenic, iron, manganese, boron and fluoride, in both soil and groundwater across diverse regions (Tajwar *et al.,* 2024). Of particular concern is the high arsenic content in shallow aquifers within coastal and deltaic zones, frequently surpassing the World Health Organization's recommended threshold of 10 μg/L, thereby posing significant health threats (Ahmed *et al.*, 2004). Moreover, elevated salinity levels in both shallow and deep coastal aquifers further compromise groundwater portability. These conditions intensify water scarcity for an estimated 6.5 to 24.4 million individuals residing in these vulnerable coastal communities (Shamsudduha *et al.*, 2019).

2.1 Emergence and Environmental Threats of Brownfield Sites

The acceleration of urban development alongside the recent enforcement of industrial restructuring policies has led to the proliferation of brownfield sites in numerous urban areas. These brownfields, which refer to previously utilized industrial or commercial lands suspected of contamination, have become increasingly common (Hammond *et al.*, 2021). Their presence not only restricts the sustainable utilization of land resources but also presents substantial threats to both human health and ecological stability. For example, it has been reported that over 5,000 brownfield locations across major Chinese cities are either contaminated or suspected of contamination with hazardous substances (Briffa *et al.*, 2020). Among these substances, heavy metals (HMs) have garnered global concern due to their pronounced toxicity, carcinogenic nature, high mobility and resistance to natural degradation processes (Ettler, 2016). A significant body of literature attributes smelting operations as a major anthropogenic contributor to HM emissions, with observed concentrations in affected surface soils often reaching several thousand milligrams per kilogram. Smelting sites are particularly challenging because of their persistent and prolonged discharge of HMs, with these contaminants typically present as primary pollutants, embedded in matrices of complex chemical and mineralogical composition, unevenly distributed and located within geologically and hydrogeologically intricate settings that complicate pollutant transport pathways (Zeng *et al.*, 2023). Consequently, soil and groundwater pollution arising from smelting-related heavy metal contamination remains a critical issue confronting contemporary environmental management (Zhu *et al.,* 2022).

2.2 Complexities of Pollutant Transport in Subsurface Environments

To design effective and site-specific remediation strategies, it is essential to understand the transport dynamics of pollutants within soil and groundwater systems, especially as these subsurface environments function as a unified, interconnected entity (Zeng *et al.,* 2023). However, predicting pollutant migration in these systems is inherently difficult due to the concealed and discontinuous nature of aquifers, in combination with the heterogeneous physical properties of soils (Tabelin *et al.,* 2018). Furthermore, once pollutants infiltrate the subsurface, their spatial and temporal behavior is influenced by a complex interplay of factors such as pH, redox conditions, microbial activity, presence of complexing ligands and the mineralogical composition of soil or aquifer sediments (Zhang *et al.*, 2022*)*. Specifically at smelting sites, heavy metals introduced into the environment can undergo diverse physicochemical and biological interactions at the solid–liquid interface, facilitating their migration through various mechanisms such as diffusion, complexation, advection, leaching and interactions between surface and groundwater systems (Zeng *et al.,* 2023).

2.3 Governing Processes in Heavy Metal Migration

The intricate interplay between heavy metals and the physical, chemical and biological attributes of the subsurface media, along with its inherent heterogeneity, severely hampers accurate forecasting of HM behavior and fate within soil-groundwater systems. Prior investigations have examined the transformation and migration of HMs, highlighting the governing physical, chemical and biological processes within the subsurface environment (Zeng *et al.*, 2023). Physical processes such as advection, convection, dispersion, surface evaporation and filtration modify the spatial distribution and intensity of pollution without altering the total HM mass (Zeng *et al.,* 2023). In contrast, chemical processes such as dissolution and precipitation, redox transformations, adsorption and desorption, ion exchange, complexation, and hydrolysis significantly influence HM concentrations and speciation (Dai *et al.*., 2018; Tabelin *et al.*, 2022). Similarly, biological processes involving microbial activity and plant uptake can promote the biodegradation, transformation, or complexation of these metals (Zeng *et al.*, 2023).

2.4 Determinants and Modeling of Heavy Metals

The fate and mobility of heavy metals in the subsurface are largely governed by two critical factors: the physical and structural characteristics of soils and aquifers and the specific concentrations and chemical forms of the metals involved. Laboratory column experiments, combined with numerical simulations, have been used to explore heavy metal behavior. For instance, (Dai *et al.,* 2018) investigated lead (Pb) immobilization in smelting site soils but concluded that such experimental setups may inadequately represent the spatial heterogeneity encountered in real-world settings. To address this limitation, (Tabelin *et al*., 2022) applied a combination of geochemical modeling and simulation to track the movement of acid mine drainage and associated heavy metals in a legacy mine site in Japan. In another approach, researchers proposed integrating various spatial datasets including lithological, hydrogeological, geophysical, geotechnical and chemical information using data fusion methods. Their work at a contaminated military airfield in Italy successfully delineated hydrogeological and geophysical structures, as well as the spatial-temporal behavior of organic contaminants. Isotopic analysis, along with other groundwater tracing techniques, is another effective tool for investigating subsurface HM migration (Zhang *et al.,* 2022). These methods provide valuable insights into aquifer configurations, groundwater flow dynamics and pollutant dispersion, groundwater age and provenance and interactions between groundwater and soil or aquifer matrices (Zeng *et al.*, 2023).

2.5 Techniques in Heavy Metal Transport Analysis

Establishing precise models for contaminant transport requires extensive, consistent and long-term acquisition of diverse datasets. Recent advances in three-dimensional (3D) visualization techniques have significantly enhanced our capacity to model subsurface pollutant behavior. These tools are now being utilized to examine contamination at industrial sites, enabling the accurate delineation of pollution plumes. For example, researchers in successfully superimposed multiple HM contamination plumes and clearly mapped the boundaries of different metal pollutants. Furthermore, 3D modeling supports the effective integration of pollutant data with various auxiliary sources. (Ciampi *et al.,* 2022) demonstrated the usefulness of such integration in managing, visualizing and analyzing hydrogeological conditions, contamination data and risk assessments at an industrially impacted location. Combining 3D modeling with simulation tools, machine learning algorithms and other analytical methods has shown promise in addressing challenges related to spatial heterogeneity, sparse sampling and random variability in contaminated environments. (Tao *et al.,* 2019) investigated differences between artificial neural networks and 3D kriging methods to resolve heterogeneity issues in contamination prediction. It is important to note that the environmental impact, mobility and toxicity of heavy metals are not solely determined by their total concentrations but also by their chemical speciation, especially the form in which they first enter the environment. Different chemical species of the same metal can behave in distinct ways, influencing their environmental persistence, bioavailability and ecological risks (Zeng *et al.,* 2023).

2.6 Mechanism of Action

Arsenic (As), cadmium (Cd), chromium (Cr) and nickel (Ni) are classified as Group 1 carcinogens by the International Agency for Research on Cancer (IARC) due to their established roles in human carcinogenesis. These heavy metals induce oxidative stress by generating reactive oxygen species (ROS), which damage cellular macromolecules, particularly DNA, lipids and proteins. This oxidative damage disrupts tumor suppressor gene function, impairs DNA repair mechanisms such as nucleotide excision repair (NER) and alters enzymatic activities involved in cellular metabolism. For instance, arsenic has been shown to induce global DNA hypomethylation and silence tumor suppressor genes, while hexavalent chromium (Cr VI) causes DNA-protein crosslinks that interfere with transcription and replication. The risk of exposure is often influenced by the contamination source, with studies reporting increased cancer incidence among individuals working in heavy metal-polluted industrial areas (Sankhla *et al.,* 2016).

2.7 Sources of Heavy Metal Contamination in Groundwater

2.7.1 Natural Sources

Heavy metals naturally occur in the earth's crust and may be introduced into aquatic systems through various geophysical and geochemical processes such as rock weathering, volcanic activities and water percolation through mineralized zones (Bagul *et al.*, 2015). Volcanic eruptions and geothermal emissions contribute to the dispersion of these metals into rivers, lakes and aquifers. Moreover, the presence of trace metals in groundwater is often linked to the geogenic composition of rocks and soils. In addition, mining activities whether artisanal or large-scale have the potential to introduce heavy metals directly or indirectly into water bodies across different regions of the world (Liu *et al.,* 2008).

2.7.2 Anthropogenic Sources

Human-induced contamination arises from both small-scale and industrial-scale activities that extract and process metallic ores. Since the onset of industrialization, mining operations and metal refinement have significantly increased heavy metal loadings in surface and groundwater systems. Various forms of waste including domestic effluent, agricultural runoff and vehicular emissions also contribute trace metals into environmental compartments. Major anthropogenic sources include:

a) Metallurgical processes such as smelting and ore refining.

b) Mining and excavation activities.

c) Combustion of fossil fuels.

d) Industrial effluent discharge.

e) Improper disposal of household wastes.

f) Vehicular emissions and auto exhaust.

g) Application of agrochemicals containing metal-based compounds (Mahipal and Rajeev, 2019).

2.7.2.1 Mining Activities

Heavy metals embedded in geological materials can leach into water systems, particularly when these materials are disturbed by anthropogenic operations like mining. During periods of intense rainfall or flooding, heavy metals may be washed out from exposed lithologies, leading to contamination. This effect is amplified by mining-induced landscape alterations, often resulting in phenomena like acid mine drainage, which significantly deteriorate water quality (Sankhla *et al.*, 2016).

2.7.2.2 Mineral Extraction and Processing

The processes involved in mineral extraction and ore beneficiation generate large quantities of waste that often contain elevated levels of toxic metals. These wastes, including tailings and leachates, present a significant risk to groundwater systems. The mechanical and chemical procedures used to concentrate ores tend to increase the surface area for leaching, which facilitates the release of heavy metals into the environment (Sankhla *et al.*, 2016).

2.7.2.3 Electronic Waste

Electronic waste (e-waste) contains a range of toxic substances, including heavy metals, carcinogens and persistent organic pollutants. Improper disposal and recycling of electronic products can lead to severe environmental contamination. Without regulatory oversight, the heavy metals in e-waste can leach into soil and water, posing risks to human health and ecosystems. Health disorders related to e-waste exposure include gastrointestinal, immune, dermatological, respiratory, endocrine, and neurological diseases, including cancer (Sankhla *et al.*, 2016).

2.8 Spatial Distribution of Heavy Metals

The spatial assessment of heavy metals in groundwater is critical for understanding contamination patterns, especially where groundwater serves as a primary source for drinking and irrigation. (Arslan and Ayyildiz-Turan, 2015) conducted an extensive study involving the collection of groundwater samples from 78 wells during the dry season (July 2012), which were subsequently analyzed for 17 heavy metals, including Pb, Zn, Cr, Mn, Fe, Cu, Cd, Co, Ni, Al, As, Mo, Se, B, Ti, V and Ba. To map the spatial distribution of these metals, the authors employed three geostatistical interpolation techniques: Inverse Distance Weighting (IDW), Radial Basis Function (RBF) and Ordinary Kriging (OK). Cross-validation metrics, including Root Mean Squared Error (RMSE) and Mean Absolute Error (MAE), were used to determine the most appropriate interpolation method for each metal, enhancing the reliability of spatial predictions.

Moreover, multivariate statistical techniques such as Cluster Analysis (CA) and Factor Analysis (FA) were utilized to discern spatial groupings among the sampling locations and to identify the principal components contributing to groundwater contamination. The results indicated that iron (Fe) and manganese (Mn) concentrations exceeded World Health Organization (WHO) guidelines for drinking water in nearly all locations, with several sites also surpassing Food and Agriculture Organization (FAO) standards for irrigation. Elevated concentrations of aluminum (Al), arsenic (As) and cadmium (Cd) were likewise reported, posing additional health concerns. Cluster analysis categorized the groundwater into three distinct groups based on their elemental composition, while factor analysis extracted five latent factors that accounted for 73.39% of the total variance. These were grouped as follows:

Factor 1: Se, Ti, Cr, Mo

Factor 2: Ni, Mn, Co, Ba

Factor 3: Pb, Cd

Factor 4: B, V, Fe, Cu

Factor 5: As, Zn

This study illustrates the effectiveness of combining spatial interpolation methods with multivariate statistics in delineating the distribution and identifying potential sources of heavy metal contamination in groundwater systems (Arslan and Ayyildiz-Turan, 2015).

2.9 Heavy Metals in Water and Their Impact on Human Health

2.9.1 Arsenic (As)

Arsenic exposure is associated with a spectrum of toxicological outcomes, including symptoms that may mimic autoimmune disorders such as Guillain-Barre syndrome. It is considered among the most hazardous environmental and public health concerns due to its high toxicity and carcinogenicity. Arsenic exists in various chemical forms, commonly as oxides, sulfides and salts of elements like iron, sodium and calcium. It is the 20th most abundant element in the Earth's crust, frequently occurring in arsenate and arsenite forms, both of which are harmful to living organisms. Arsenic toxicity impairs cellular respiration, disrupts mitotic processes and inactivates essential enzymes by binding to sulfhydryl groups. Exposure can result from accidental ingestion, contaminated food, or polluted drinking water and has been linked to cardiovascular diseases, liver damage, reproductive disorders and endocrine disruption (Mahipal and Rajeev, 2019).

2.9.2 Lead (Pb)

Lead is a highly toxic element that poses severe health risks even at low exposure levels. It enters the human body primarily through ingestion of contaminated water and food, or via inhalation of particulate matter from lead-based paints or vehicle exhaust. Lead can also leach from plumbing systems in older buildings. Accumulation of lead in the body can cause neurological mpairments, renal dysfunction and cognitive decline. Mechanistically, lead exerts neurotoxicity through disruption of neurotransmission, lipid peroxidation and oxidative stress. It binds irreversibly to sulfhydryl groups of enzymes, thereby impairing antioxidant defense systems. Lead's ability to mimic calcium ions allows it to cross the blood–brain barrier, targeting critical brain regions such as the hippocampus and cortex and contributing to disorders like Alzheimer's disease, Parkinsonism and developmental delays (Mahipal and Rajeev, 2019).

2.9.3 Nickel (Ni)

Nickel is a naturally occurring element found in trace amounts in biological tissues. However, high levels of exposure particularly through contaminated drinking water can lead to significant health risks. While dietary intake remains the primary exposure route, soluble nickel compounds such as chlorides and sulfates are more readily absorbed in the gastrointestinal tract. Nickel toxicity targets multiple organ systems, including the kidneys, lungs, cardiovascular system and immune response. It has been linked to conditions such as contact dermatitis, pulmonary fibrosis and cancers of the respiratory tract. Studies have demonstrated nickel-induced liver toxicity, nephropathy and hematological abnormalities in both humans and animals. Although definitive reproductive toxicity in humans has not been established, experimental evidence in animals indicates possible adverse effects (Mahipal and Rajeev, 2019).

2.9.4 Chromium (Cr)

Chromium is a widely distributed metal that exists in various valence states, with hexavalent chromium (Cr (VI)) being the most toxic and carcinogenic form. Environmental contamination primarily arises from industrial activities such as metal plating, leather tanning and pigment production. Cr (VI) can enter aquatic systems through effluent discharge and atmospheric deposition. Human exposure to chromium compounds can lead to multi-organ toxicity including respiratory, gastrointestinal, renal and dermatological effects. Cr (VI) is particularly hazardous because of its ability to cross cell membranes and generate reactive intermediates that damage DNA. Documented health impacts include nasal ulcers, intestinal lesions, anemia, reproductive toxicity and increased cancer risk, especially of the respiratory system (Mahipal and Rajeev, 2019).

2.9.5 Zinc (Zn)

Zinc is an essential trace element crucial for cellular function, enzyme activity, and immune competence. However, both deficiency and excessive exposure can have significant health implications. Zinc deficiency affects nearly two billion people globally, especially in developing regions and is associated with impaired growth, delayed sexual maturation, increased susceptibility to infections and poor wound healing. Zinc-dependent enzymes play vital roles in metabolic and regulatory processes and inadequate intake is often linked to malabsorption syndromes, liver and kidney diseases, diabetes, and malignancies. Clinical manifestations of zinc deficiency include stunted growth, dermatitis, impaired taste and vision, anorexia and compromised immune response (Dutta and Sarma, 2015).

2.10 Related Literature

In a comprehensive study conducted in the Kurdistan Province of Iran, (Younesi *et al.*, 2024) investigated the concentrations of 20 heavy metals in groundwater sources across rural communities. The study involved the collection and analysis of 155 groundwater samples from wells and springs using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), a highly sensitive technique for trace metal quantification. The findings revealed elevated levels of arsenic (As), cobalt (Co), copper (Cu) and molybdenum (Mo), with maximum concentrations of 7.90, 0.22, 2.48 and 1.68 μg/L respectively, recorded in the cities of Qorveh, Sanandaj, Baneh & Qorveh. A Health Risk Assessment (HRA) was performed to evaluate both carcinogenic and non-carcinogenic risks across age groups. Although most HM concentrations fell within permissible limits, arsenic and lithium posed notable non-carcinogenic risks to children, accounting for over 48% of the total hazard index (HI) across the ten cities studied. Alarmingly, Qorveh was the only city where the HI for adults surpassed the threshold value of 1.0, reaching 1.23. Furthermore, a significant carcinogenic risk was attributed to lead (Pb), with a risk index of 7.3×10^{-3}, far exceeding the acceptable threshold of 10^{-4} . These findings underscore the critical need for periodic groundwater monitoring and the implementation of remediation strategies to prevent adverse health outcomes.

Similarly, in a study conducted in Qatar, (Manawi *et al.*, 2024) assessed the spatial variations in heavy metal concentrations and their associated health risks using 82 groundwater samples collected from various locations across the country. The researchers applied Geographic Information System (GIS) tools to map spatial variations and employed multiple health risk models, including the Hazard Index (HI), the Nemerow Comprehensive Pollution Index (NCPI) and the Incremental Lifetime Cancer Risk (ILCR). Heavy metals such as silver (Ag), manganese (Mn), chromium (Cr), vanadium (V), molybdenum (Mo) and strontium (Sr) were analyzed. The chronic daily intake (CDI) of these metals via ingestion and dermal contact ranged from 1.4×10^{-5} to 6.7×10^{-1} mg/kg/day. The NCPI ranged from 0 to 4.39, while the HI and ILCR values were recorded between 0–3.2 and 5.6×10^{-4} to 5.5×10^{-2}, respectively. The elevated values of both non-carcinogenic and carcinogenic indices reflect considerable exposure risks for residents, warranting urgent attention from regulatory authorities. Notably, the study represents one of the few detailed assessments of groundwater-related HM toxicity in the Gulf region and establishes a valuable baseline for future environmental surveillance.

In Bangladesh, particularly in rural communities, groundwater serves as the principal source of drinking water. However, it has increasingly become a medium for toxic metal contamination, arising from both natural geochemical processes and anthropogenic influences. (Rahman *et al.,* 2022) conducted a study to assess the concentration of naturally occurring metals and evaluate the associated human health risks from consuming deep groundwater in Hatiya Island. The reliance on deep groundwater in this region is largely due to the contamination of shallow aquifers by arsenic, high iron content and salinity. During the fieldwork, only deep tube wells were observed and as a result, the researchers collected 17 groundwater samples from across the island. Five trace metals; magnesium (Mg), zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu) were quantified using Atomic Absorption Spectrophotometry (AAS). The metals were found in the following decreasing order of concentration: Mg > Zn > Fe > Mn > Cu. The measured concentrations for all metals, with the exception of iron, were within the permissible limits set by the World Health Organization (WHO, 2017), the Bureau of Indian Standards (BIS, 2012) and Bangladesh Drinking Water Standards (BDWS, 1997). Notably, 29.41% of the Fe samples exceeded the acceptable limits.

Water quality indices such as the Metal Evaluation Index (MEI) and the Contamination Degree (Cd) indicated that the groundwater was not contaminated. However, marginal pollution was observed in the mid-western region of the island based on the Metal Pollution Index (MPI) and Nemerow Pollution Index (NI). The results of the Hazard Quotient (HQ) for individual metal; Cu, Zn, Fe and Mn indicated no significant health risks via oral or dermal exposure. Furthermore, the Hazard Index (HI) values for cumulative exposure were all below the threshold value of 1, confirming the absence of non-carcinogenic risks for both adults and children. Nevertheless, children were found to be more susceptible to oral exposure risks, while adults exhibited higher vulnerability to dermal exposure.

(Ratnalu and Dhakate, 2021) assessed the levels of chromium contamination and associated health risks in groundwater. Groundwater samples were collected during three seasonal campaigns: July 2016, January 2017 and August 2017 and analyzed for heavy metal content, with a specific focus on chromium species. The researchers employed a health risk assessment framework that included hazard quotient (HQ), health hazard index (HHI), cancer risk (CR) and total cancer risk (TCR) to evaluate both carcinogenic and non-carcinogenic risks. Their findings indicated that concentrations of trivalent chromium (Cr^{3+}) exceeded the WHO permissible limit of 0.05 mg/L in a substantial portion of the samples; 35.38% (July 2016), 32.39% (January 2017) and 39.43% (August 2017). Similarly, hexavalent chromium (Cr^{6+}), a more toxic and carcinogenic species, was found to surpass permissible levels in 3.07% of samples in July 2016 and 26.76% in January 2017. Health risk analysis revealed that non-carcinogenic risks from ingestion pathways were notably higher than those from dermal exposure, particularly among children.

The hazard quotient (HQ) values for children were found to exceed safety thresholds, indicating elevated susceptibility. Moreover, the total cancer risk (TCR) values associated with both Cr^{3+} and Cr^{6+} were greater than the accepted threshold of 1.00E-04, signifying a substantial carcinogenic risk to the population. To elucidate the sources of contamination, the study applied Principal Component Analysis (PCA), which identified three to four principal factors contributing to metal loading, explaining 82.65%, 74.89% and 83.17% of the total variance for the three sampling periods, respectively. The study concluded by emphasizing the urgent need for strategic mitigation efforts, including broader-scale monitoring and equitable well distribution among neighboring communities, to minimize exposure and protect public health.

In a study conducted by (Adeyemi and Ojekunle, 2021), the concentrations of heavy metals in groundwater and their potential health impacts were assessed in two major industrial zones; Ota and Sagamu in Ogun State, Nigeria. Groundwater samples were collected from both hand-dug wells and boreholes during the rainy and dry seasons to account for seasonal variations. A total of 96 samples, 48 per season were analyzed using standard laboratory techniques to determine concentrations of lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), iron (Fe), zinc (Zn), copper (Cu) and manganese (Mn). The study revealed spatial and temporal variation in metal concentrations. In Ota, the average concentrations (mg/L) of Pb, Cd, Ni, Cr, Mn, Fe, Zn and Cu were 0.459, 0.006, 0.084, 0.016, 0.100, 0.709, 0.036 and 0.117, respectively. In Sagamu, the corresponding values were 0.450, 0.012, 0.082, 0.016, 0.165, 0.663, 0.031 and 0.146 mg/L. The metals followed a general concentration trend of Pb > Fe > Ni > Cr > Cd > Cu > Mn > Zn, indicating lead and iron as the dominant contaminants in both areas. Health risk assessment was conducted using the Hazard Index (HI) and Cancer Risk models.

The total HI values exceeded the critical threshold of 1.0 for all age groups, indicating significant non-carcinogenic risks. Infants, in particular, were identified as the most vulnerable demographic due to higher susceptibility. Additionally, the cumulative cancer risk values for the studied metals ranged from medium to extremely high levels, suggesting potential long-term carcinogenic effects associated with continued exposure. This study highlights the urgent need for environmental monitoring and regulatory interventions to reduce metal contamination in groundwater sources within industrial areas. It also emphasizes the importance of incorporating health risk models to assess both immediate and latent health consequences of groundwater pollution in rapidly industrializing regions.

In a recent study conducted by (Ayejoto and Egbueri, 2024), groundwater samples from two major urban centers Nnewi and Awka in southeastern Nigeria were analyzed for concentrations of nitrate and selected heavy metals, including lead (Pb), copper (Cu), cadmium (Cd) and iron (Fe). The research sought to evaluate the corresponding health risks to various demographic groups, including women, men and children, using established risk assessment protocols. Groundwater sampling involved the collection of ten samples from each locality, with subsequent physicochemical and toxicological analyses carried out using standard analytical methods. While the results indicated that nitrate concentrations remained within acceptable limits, all groundwater samples exhibited elevated levels of heavy metals exceeding recommended safety thresholds. The carcinogenic risk (CR) analysis revealed that approximately 40% of samples from Nnewi and 80% from Awka surpassed the safe exposure range of $\leq 1 \times 10^{-6}$ to 1×10^{-4}. This signifies a considerable cancer risk among groundwater users in these areas. Toxicity patterns varied between the two locations. In Nnewi, cadmium emerged as the most hazardous contaminant, followed by lead, copper and iron (Cd > Pb > Cu > Fe).

In contrast, Awka showed a different toxicity profile, with lead and cadmium ranking as the most critical pollutants (Pb > Cd > Cu > Fe). These variations were accompanied by significant non-carcinogenic health hazards, particularly for children, who demonstrated greater susceptibility compared to adult groups. Cadmium and lead were consistently identified as the principal contributors to overall water quality degradation and public health risk in both regions. The findings by Ayejoto and Egbueri emphasize the need for continuous groundwater quality monitoring and the development of location-specific mitigation strategies. Additionally, the study highlights the critical vulnerability of children to heavy metal exposure and underscores the broader implications of groundwater contamination in urban and peri-urban settings in developing regions.

CHAPTER THREE

MATERIALS AND METHOD

3.1 Regional Geology

Akoko-Edo 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 Akoko-Edo 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).

3.1.1 Migmatite-Gneiss Formations

At the site scale, exposures in Akoko-Edo 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).

3.1.2 Granitoid Intrusions

Pan-African granitoids and associated porphyritic or coarse-grained granites are common intrusive phases in the Akoko-Edo 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).

3.1.3 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).

3.1.4 Hydrogeological and Structural Controls on Groundwater

Hard-rock aquifers in Akoko-Edo are strongly controlled by secondary permeability associated with fractures, weathered zones and structural lineaments. Remote sensing and lineament mapping studies in Akoko-Edo 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).

3.2 Local Geology

Ago-Isame is a village in Akoko-Edo 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 Akoko-Edo 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).

3.3 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).

3.4 Methods

3.4.1 Sample Collection

Fifteen (15) 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 the groundwater to be sampled. 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.

3.4.2 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).

3.4.3 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 non-carcinogenic risk (Hazard Quotient, HQ) and carcinogenic risk (CR) for identified heavy metals.

3.4.4 Chronic Daily Intake (CDI)

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

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

Where:

C_w = concentration of heavy metal in groundwater (mg/L)

IR = ingestion rate of water (L/day)

ER = exposure frequency (days/year)

ED = exposure duration (years)

BW = body weight (kg)

AT = averaging time (days) – for non-carcinogenic effects, AT = ED × 365;

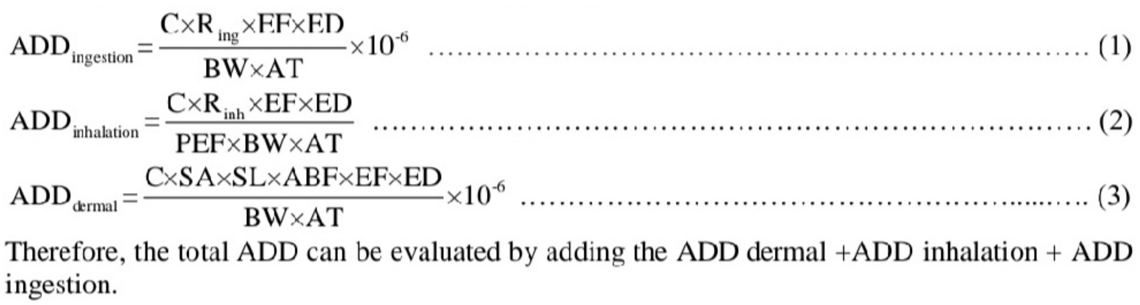
For carcinogenic effects, AT = 70 × 365 (Samaila *et al.*, 2024).

3.4.5 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.

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

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

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

3.4.6 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.

3.4.7 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.

3.4.8 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

4.0. Results

The results of the groundwater heavy metals analysis are presented in Tables 4.0.1–4.0.7**.** The concentrations of Pb, Cr and Zn, were measured across 15 groundwater samples (GW1-GW15). These results were compared against WHO and EPA standards to assess their Carcinogenic properties. The carcinogenic risk assessment was also carried out in children and adults to determine their level of risk.

4.1 Presentation of Data

Table 4.1: Concentration of heavy metals in groundwater samples (mg/L) and comparison with U.S. EPA and WHO Standard

Sample	**Pb (mg/L)**	**Cr (mg/L)**	**Zn (mg/L)**
GW1	–	0.0839	–
GW2	0.0108	0.0511	–
GW3	0.0057	0.1381	–
GW4	0.0257	0.0517	–
GW5	0.0040	0.0728	0.0287
GW6	0.0204	0.0977	–
GW7	0.0087	0.2051	0.0020
GW8	0.0150	0.2277	0.0183
GW9	–	0.0670	0.0044
GW10	0.0353	–	0.0152
GW11	0.0009	1.1015	0.1685
GW12	–	0.0704	1.9683
GW13	0.0227	0.2787	0.1002
GW14	0.0151	0.0135	0.0369
GW15	–	0.2718	–
Mean	0.0133	0.2076	0.1722
Standard Error (±)	0.0025	0.0715	0.1326
Maximum	0.0353	1.1015	1.9683
EPA Standard	0.015	0.1	5.0
WHO Standard	0.010	0.05	5.0

Table 4.2: Chronic daily intake (CDI) via ingestion pathway for adults

Metal	Mean Concentration (mg/L)	CDI (mg/kg/day)
Pb	0.0133	0.000379
Cr	0.2076	0.00591
Zn	0.1722	0.00490

Table 4.3: Chronic daily intake (CDI) via ingestion pathway for children

metal	Mean concentration (mg/L)	CDI (mg/kg/day)
Pb	0.0133	0.00177
Cr	0.2076	0.00119
Zn	0.1722	0.0115

Table 4.4: Hazard Quotient (HQ) and Hazard Index (HI) via Ingestion Exposure for adults

Metal	CDI (mg/kg/day)	RfD (mg/kg/day)	HQ
Pb	0.000379	0.0035	0.108
Cr	0.00591	0.003	1.970
Zn	0.00490	0.3	0.016
Hazard Index (HI)	-	-	**2.094**

Table 4.5: Hazard Quotient (HQ) and Hazard Index (HI) via Ingestion Exposure for children

Metal	CDI (mg/kg/day)	RfD (mg/kg/day)	HQ
Pb	0.00177	0.0035	0.506
Cr	0.00119	0.003	0.397
Zn	0.0115	0.3	0.038
Hazard Index (HI)	-	-	**0.941**

Table 4.6: Assumptions for exposure to heavy metals through drinking water

Exposure factors	Unit	Adults	children
ED	Years	30	6
EF	Days/year	365	365
IR	L/Day	2	1
BW	Kg	70	15
AT	Years	25,550	25,550

Table 4.7: Carcinogenic risk assessment via ingestion for adults

Metal	CDI	SF	CR
Pb	0.000379	0.0085	3.22×10^{-6}
Cr	0.00591	0.5	2.96×10^{-3}
TCR	-	-	2.96×10^{-3}

Table 4.8: Carcinogenic risk assessment via ingestion for Children

Metal	CDI	SF	CR
Pb	0.00177	0.0085	1.50×10^{-5}
Cr	0.00119	0.5	5.95×10^{-4}
TCR	-	-	6.10×10^{-4}

CHAPTER FIVE

DISCUSSION, RECOMMENDATIONS AND CONCLUSION

5.1 Discussion

5.1.1 Physico-Chemical Assessments

The results of concentrations of heavy metals (Pb, Cr, and Zn) analyzed in 15 groundwater samples and their comparison with WHO (2011) and U.S. EPA (1992) standards are presented in Table 4.0.1. Lead (Pb) concentrations in the groundwater samples ranged from 0.0009 mg/L to 0.0353 mg/L, with a mean value of 0.0133 mg/L. The observed values in some locations (GW4 and GW10) slightly exceeded the WHO guideline value of 0.01 mg/L and were close to the U.S. EPA permissible limit of 0.015 mg/L, indicating possible anthropogenic contamination. Chromium (Cr) concentrations varied between 0.0135 mg/L and 1.1015 mg/L, with a mean value of 0.2076 mg/L. The maximum concentration observed (1.1015 mg/L) in sample GW11 far exceeded both the WHO (0.05 mg/L) and EPA (0.1 mg/L) limits, suggesting potential pollution from industrial effluents or corrosion of metallic components. Zinc (Zn) concentrations ranged from 0.0020 mg/L to 1.9683 mg/L, with an average value of 0.1722 mg/L. The maximum value (1.9683 mg/L) was recorded in sample GW12. All Zn concentrations remained well below the WHO and EPA guideline value of 5.0 mg/L, indicating that zinc contamination is minimal and within safe limits for potable use.

The mean concentrations of the investigated metals followed a decreasing order of Cr (0.2076 mg/L) > Zn (0.1722 mg/L) > Pb (0.0133 mg/L), indicating that chromium was the most dominant element in the groundwater samples, followed closely by zinc, while lead occurred in trace amounts. This trend reflects both natural and anthropogenic influences on groundwater chemistry (Ojeaga and Segine, 2025). Elevated chromium levels may be attributed to the dissolution of chromium-bearing minerals or infiltration of industrial wastes, while zinc may originate from the weathering of zinc-bearing rocks and corrosion of metallic pipes (Omonona *et al.*, 2020).

5.1.2 Human Health 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 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 based on U.S. EPA risk assessment models, as presented in Tables 4.0.2 and 4.0.3. The CDI values for the analyzed metals via ingestion for adults were 0.000379 mg/kg/day for Pb, 0.00591 mg/kg/day for Cr and 0.00490 mg/kg/day for Zn, while for children were 0.00177 for Pb, 0.00119 for Cr and 0.0115 for Zn. These values reflect the relative abundance of the metals in groundwater and their potential contribution to human exposure. Among the three metals, chromium exhibited the highest CDI value for adults and zinc for children, indicating greater exposure potential, while Lead recorded the lowest for adults and Chromium for children. The HQ values derived from the ratio of CDI to reference dose (RfD) revealed a decreasing order of Cr (1.970) > Pb (0.108) > Zn (0.016) and Pb (0.506) > Cr (0.397) > Zn (0.038) for adults and children respectively.

The calculated hazard index (HI), which represents the cumulative risk from simultaneous exposure to multiple metals, was 2.094 and 0.941 for adults and children respectively. Its elevated value in adults (HI > 1) indicates that long-term exposure to these metals, particularly chromium, could result in potential adverse health effects. In contrast, the lower HI value for children (HI < 1) indicates that, under current exposure conditions, the combined metal concentrations are less likely to induce significant carcinogenic health risks (Mohammadi *et al.*, 2019). Chromium's elevated HQ value (>1) (adults) signifies potential health concern, implying that exposure through ingestion could lead to effects such as skin irritation, ulceration and internal organ damage (Wu *et al.,* 2016). Conversely, HQ values for Pb and Zn were below the threshold. The hazard index for ingestion followed the same decreasing order as the HQ values: Cr > Pb > Zn, reaffirming that chromium contributes most significantly to the overall risk (Ojeaga and Segine, 2025).

5.1.3 Carcinogenic Risk Assessment

Carcinogenic risk (CR) evaluates the probability of an individual developing cancer over a lifetime due to exposure to carcinogenic contaminants (U.S. EPA, 2011). The results for both adults and children are presented in Tables 4.0.7 and 4.0.8. For adults, the CR values ranged from 3.22×10^{-6} for Pb to 2.96×10^{-3} for Cr, with a total carcinogenic risk (TCR) of 2.96×10^{-3}. Similarly, for children, CR values ranged from 1.50×10^{-5} for Pb to 5.95×10^{-4} for Cr, resulting in a TCR of 6.10×10^{-4}. According to the U.S. EPA (2011), acceptable carcinogenic risk levels range from 1×10^{-6} to 1×10^{-4}. Therefore, the CR values for chromium in both adults and children exceed the upper threshold of the acceptable risk range, indicating a significant carcinogenic potential associated with chromium exposure through ingestion. The carcinogenic risk order for ingestion exposure followed the trend Cr > Pb, suggesting that chromium contributed the most to the overall cancer risk burden, while lead posed comparatively minimal carcinogenic concern. The higher TCR value in adults compared to children indicates that adults are more susceptible to cumulative carcinogenic effects under the given exposure scenario, possibly due to prolonged exposure duration and bioaccumulation tendencies of chromium in the body (Dashtizadeh *et al.,* 2019).

5.2 Recommendations

The findings of this study carry significant implications for environmental and public health. The elevated concentrations of heavy metals; particularly chromium (Cr) and lead (Pb) in groundwater samples suggest that residents relying on these sources for drinking water may be exposed to chronic health risks. The ingestion pathway revealed that children face disproportionately higher risks due to their physiological vulnerability and behavioral exposure patterns. The calculated Hazard Index (HI) indicates that long-term consumption could lead to adverse health outcomes such as organ damage, immune dysfunction and developmental delays. The situation is further worsened by the Total Carcinogenic Risk (TCR) for adults and children. Both far exceeding the acceptable range. Implying a high probability of cancer development over a lifetime of exposure, particularly from Cr ingestion.

Given these risks, the following recommendations are proposed:

- Immediate intervention is required to mitigate exposure. This includes the provision of alternative drinking water sources, such as treated municipal water or bottled water.
- Installation of point-of-use filtration systems, such as activated carbon or reverse osmosis units, can significantly reduce heavy metal concentrations in household water supplies.
- Regular monitoring and surveillance of groundwater quality should be put in place, with periodic testing for heavy metals and other contaminants. This will enable early detection and timely response to emerging threats.
- Public health education campaigns should be launched to inform residents about the dangers of contaminated water and promote safe water handling practices.
- Further research is needed to assess additional exposure pathways such as dermal contact and inhalation and to evaluate the cumulative effects of multiple contaminants beyond Pb, Cr and Zn.

5.3 Conclusion

This study provides compelling evidence that groundwater in the sampled region is contaminated with heavy metals at levels that pose serious health risks. Chromium emerged as the most hazardous contaminant, with concentrations far exceeding regulatory limits and contributing to carcinogenic risks. Lead, though present at lower levels, remains a concern due to its cumulative toxicity and potential to cause irreversible damage, especially in children. Zinc, while generally within safe limits, showed elevated levels in isolated samples that warrant attention. The risk assessment revealed a high carcinogenic risk through ingestion exposure. Children are especially vulnerable, with risk levels significantly higher than adults. These findings highlight the urgent need for targeted interventions to address groundwater contamination and protect public health.

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