NON CARCINOGENIC RISK ASSESSMENT OF GROUNDWATER ASSOCIATED HEAVY METALS VIA DERMAL EXPOSURE, IKPESHI.

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 FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF BACHELOR OF SCIENCE DEGREE (B.Sc) IN SCIENCE LABORATORY TECHNOLOGY (GEOLOGY AND MINING TECHNIQUES)

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CERTIFICATION

This is to certify that this undergraduate project work titled "**NON CARCINOGENIC RISK ASSESSMENT OF GROUNDWATER ASSOCIATED HEAVY METALS VIA DERMAL EXPOSURE**" was submitted and presented by Odunayo Denis AJAYI with matriculation number LSC2007267 in the Department of Science Laboratory Technology, Faculty of Life Sciences, University of Benin, Benin City. In a partial fulfillment of the requirements for the award of Bachelor of Science Degree in Science Laboratory Technology.

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DEDICATION

This work is dedicated to Almighty GOD. He alone deserves the praises. For he is the giver of life and wisdom.

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My sincere gratitude to God Almighty for his grace, wisdom and guidance throughout the period of this research.

I wish to express my profound appreciation to my project supervisor, Dr. K. Ojeaga for his encouragement, support, discipline and selflessness through the period of this research work. May God reward you abundantly for your patience, love and for being a good teacher, supervisor and father

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ABSTRACT

This study evaluated the non-carcinogenic health risks associated with dermal exposure to heavy metals chromium (Cr), lead (Pb) and zinc (Zn) in groundwater from Ikpeshi, Edo State, Nigeria. The research aimed to quantify metal concentrations, assess health risks across population groups, identify contamination sources and propose mitigation strategies. Groundwater samples were analyzed and risk assessment models were applied using Chronic Daily Intake (CDI), Hazard Quotient (HQ) and Hazard Index (HI) frameworks as outlined by the United States Environmental Protection Agency (USEPA, 2004). Results revealed that chromium exhibited the highest mean concentration (0.177 mg/L), followed by zinc (0.257 mg/L) and lead (0.016 mg/L). Both Cr and Pb levels exceeded the permissible limits set by the World Health Organization (WHO, 2017) and USEPA, primarily due to artisanal and small-scale mining, mine tailings leaching and oxidation of metal-bearing minerals within the Igarra schist belt. Risk assessment outcomes indicated that children are more vulnerable to dermal exposure than adults, given their higher skin surface area-to-body weight ratio and frequent water contact. Chromium was identified as the dominant contributor to non-carcinogenic risks, followed by lead, while zinc showed minimal contribution. Some HI values for children exceeded unity, indicating potential chronic health effects and the mean carcinogenic risk (CR) for Cr approached the USEPA threshold of 1×10^{-4}. The study concludes that chromium and lead pose significant public health concerns in Ikpeshi groundwater. The findings emphasize the need for effective groundwater monitoring, regulation of mining effluents and community-based mitigation strategies such as the use of affordable household filtration systems, rainwater harvesting and public health education to reduce dermal exposure risks and safeguard water quality.

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Groundwater is a significant source of safe drinking water and fulfills a substantial portion of the home and irrigation requirements in numerous countries. The deterioration of groundwater quality on a large scale during the past few decades can be attributed to population growth, urbanization, improper use of chemical fertilizers, climate change and inadequate water resource management. (Kaur *et al*. 2020; Golaki *et al*. 2022). Furthermore, the entry of many heavy metals such as arsenic, fluoride, nitrate, nitrite, sulfate, iron, selenium, manganese and toxic metals into water bodies has caused substantial concerns for both human health and the environment (Toolabi *et al.* 2021).

Heavy metals, such as lead (Pb), chromium (Cr) and Zinc (Zn), are widely distributed in the environment occurring in both inorganic and organic forms. Inorganic heavy metals are commonly found in air, food, minerals, rocks and water while organic forms are often present in fish, shellfish and algae. Prolonged dermal exposure to high levels of these heavy metals in groundwater can lead to significant non-carcinogenic health risks including skin irritation, neurological disorders, kidney dysfunction and allergic dermatitis (Litter *et al.* 2019; Toolabi *et al*. 2021). For instance, lead can cause neurological and developmental issues, cadmium may lead to kidney damage, mercury can affect the nervous system, chromium (particularly Cr(III)) can cause skin irritation and nickel is known to trigger allergic contact dermatitis. The World Health Organization (WHO) has established maximum contaminant levels for specific heavy metals in drinking water, such as 0.01 mg/L for lead and 0.003 mg/L for cadmium, which serve as references for assessing dermal exposure risks (Eslami *et al*. 2019).

Fluoride (F), a prevalent groundwater contaminant, is introduced through untreated emissions from industries like mining, brick and iron production, aluminum smelting, coal-fired power plants and electroplating. Dermal exposure to fluoride via contact with contaminated groundwater may cause non-carcinogenic effects, such as skin irritation or, in chronic cases, skeletal fluorosis. The WHO recommends a fluoride concentration range of 0.50–1.50 mg/L in drinking water, which can guide dermal exposure risk assessments (Chen *et al.* 2017; Golaki *et al*. 2022; Hashemi *et al.* 2023).

Nitrate, a common chemical contaminant in groundwater, often originates from nitrogen-based fertilizers and improper waste disposal from livestock farms, dairies, agricultural lands, and landfills. Dermal exposure to elevated nitrate levels in groundwater may contribute to non-carcinogenic health risks, such as skin irritation and in severe cases, systemic effects like methemoglobinemia, particularly in vulnerable populations such as pregnant women, infants and children. Non-carcinogenic risks from dermal exposure to groundwater contaminants including heavy metals (e.g., lead, cadmium, mercury, chromium and nickel), fluoride and nitrate encompass a range of health effects that, while not fatal, can significantly impair quality of life. These effects include dermatological conditions, neurological impairments, kidney damage and systemic health issues.

1.2 Study Area

The study will be conducted in Ikpeshi, a region known for groundwater contamination, such as a specific district or watershed. This area is characterized by activities such as hydrogeological operations and geological features contributing to contamination. Groundwater is a primary water source for domestic activities, including bathing, washing and other dermal contact activities, making it an ideal location for assessing dermal exposure risks.

1.3 Aim of the Study

The primary aim of this study is to assess the non-carcinogenic health risks associated with dermal exposure to heavy metals (lead, chromium and zinc) in groundwater used for domestic purposes with a focus on identifying potential health impacts and informing groundwater management strategies.

1.4 Objectives

1. To quantify the concentrations of heavy metals in groundwater samples from the study area.

2. To evaluate the non-carcinogenic health risks of dermal exposure to these contaminants for different population group.

3. To develop recommendations for mitigating dermal exposure risks and improving groundwater quality management based on the risk assessment findings.

1.5 Statement of the Problem

Groundwater contamination by heavy represents a significant public health concern in regions where groundwater serves as a primary resource for domestic activities including bathing, washing and other forms of dermal contact. These contaminants originate from diverse sources such as industrial emissions (e.g., mining, aluminum smelting and electroplating), agricultural runoff from nitrogen-based fertilizers and improper waste disposal from livestock farms and landfills (Litter *et al*. 2019; Gao *et al*. 2020; Toolabi *et al.* 2021). Prolonged dermal exposure to these substances can result in non-carcinogenic health effects, including skin irritation, allergic dermatitis, neurological disorders, kidney dysfunction and methemoglobinemia with vulnerable populations such as children, pregnant women and infants being particularly susceptible (Chen *et al.* 2017; Golaki *et al*. 2022). Despite established guidelines by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) for drinking water (e.g., 0.01 mg/L for lead, 0.003 mg/L for cadmium, 0.50–1.50 mg/L for fluoride, and 45–50 mg/L for nitrate), these standards primarily address ingestion risks, leaving a critical knowledge gap regarding the non-carcinogenic risks associated with dermal exposure in groundwater-dependent communities.

The lack of comprehensive studies on dermal exposure to these contaminants in Ikpeshi exacerbates the problem, as local geological conditions, industrial activities or agricultural practices may elevate contaminant levels beyond safe thresholds, increasing the risk of adverse health outcomes. For instance, lead and cadmium can impair neurological and renal functions, while fluoride may cause skin irritation or skeletal fluorosis and nitrate can contribute to systemic conditions like methemoglobinemia, particularly in infants (Hashemi *et al.* 2023; Rajabi *et al.* 2022). Without a thorough assessment of these risks, public health interventions remain limited, leaving communities vulnerable to chronic health effects that, while non-fatal, significantly diminish quality of life. This study seeks to address this gap by quantifying contaminant levels and evaluating their non-carcinogenic risks through dermal exposure, providing critical data to inform groundwater management and protect public health in Ikpeshi.

1.6 Justification of the Study

The justification for this study lies in the urgent need to address the non-carcinogenic health risks posed by dermal exposure to heavy metals, fluoride and nitrate in groundwater, particularly in Ikpeshi, where reliance on groundwater for domestic purposes is widespread. Dermal exposure, often overlooked in favor of ingestion pathways, is a significant route of contaminant absorption during activities such as bathing, washing and other household tasks, leading to health effects like skin disorders, neurological impairments, and systemic conditions (Chen *et al*. 2017; Golaki *et al.* 2022). Vulnerable populations, including children and pregnant women, face heightened risks due to their physiological susceptibility, with conditions like methemoglobinemia and developmental impairments linked to nitrate and heavy metal exposure respectively (Gao *et al.* 2020; Hashemi *et al*. 2023). By focusing on dermal exposure, this study addresses a critical gap in environmental health research, as current WHO and USEPA guidelines primarily target ingestion risks and do not adequately account for the cumulative effects of skin contact, especially in regions with high groundwater contamination.

Furthermore, the study is justified by the need to provide evidence-based data to support public health policies and groundwater management strategies in Ikpeshi. Local factors, such as industrial discharges, agricultural runoff, or naturally occurring geological deposits, may exacerbate contamination, necessitating region-specific risk assessments (Litter *et al.* 2019; Toolabi *et al*., 2021). The findings will empower stakeholders including policymakers, environmental agencies and communities, to implement targeted interventions such as groundwater treatment technologies or regulatory measures to mitigate exposure risks. Additionally, raising awareness about non-carcinogenic health effects will enhance community resilience and promote safer water use practices. By generating data on contaminant levels and their health impacts, this study will contribute to the global body of knowledge on groundwater safety and support sustainable development goals related to clean water and public health in Ikpeshi.

CHAPTER TWO

LITERATURE REVIEW

2.1 Groundwater

Groundwater is an essential natural resource that sustains millions of people worldwide by providing drinking water, supporting agricultural irrigation and fulfilling domestic needs, especially in areas where surface water is scarce or unreliable. It accounts for nearly one-third of the planet's available freshwater and serves as a primary source of water in many arid and semi-arid regions across Africa, Asia and the Middle East (Kaur *et al*., 2020). Groundwater becomes polluted when toxic substances exceed threshold levels or when its natural composition is altered by anthropogenic activities. Pollution often results from accidental chemical discharges, poor waste management or the improper disposal of industrial and agricultural by-products. Rapid industrialization combined with weak environmental oversight in developing countries has intensified groundwater contamination, leading to the accumulation of hazardous elements in soil and water systems that threaten both ecosystems and human health (Al-Hammad and El-Salam, 2017).

Heavy metal contamination in groundwater has become a growing global concern due to its persistence, non-biodegradability and potential to bioaccumulate. Ingestion of contaminated water remains a major route of exposure, but dermal contact during daily activities such as bathing or washing also represents a significant pathway. Beyond permissible limits, most heavy metals exhibit toxic and carcinogenic properties that can cause long-term health complications, including neurological, hepatic and renal damage (Ahmad *et al*., 2021). The presence of heavy metals in groundwater stems from both natural sources such as mineral weathering, erosion and human-induced activities including mining, industrial discharge, waste disposal and excessive use of agrochemicals (Vesković and Onija, 2025). The degree of contamination and resulting health risks depend on factors such as groundwater rock interactions, residence time, hydrogeochemical conditions and the nature of human land use in surrounding areas.

Globally, groundwater pollution from heavy metals is recognized as a major environmental and public health issue, particularly in regions undergoing rapid urbanization and industrialization (Alloway, 2013). Chronic exposure to contaminated groundwater can lead to a range of non-carcinogenic health effects including kidney dysfunction, developmental disorders, skin diseases and immune suppression (Balali-Mood *et al*., 2021). Although ingestion has long been the focus of risk assessments, increasing evidence shows that dermal exposure can contribute significantly to systemic toxicity, especially for metals such as hexavalent chromium (Cr) and arsenic (As), which can permeate the skin even at low concentrations.

Industrial growth, extensive chemical usage and the accumulation of urban waste have intensified groundwater pollution in many developing nations. In rapidly growing economies like India and Nigeria, unplanned urban expansion and industrial clustering have created zones of elevated contamination risk (Edokpayi *et al*., 2018). The persistence and bioaccumulative nature of metals such as lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As), nickel (Ni) and mercury (Hg) make them particularly hazardous as they enter human systems through ingestion, inhalation or dermal absorption (Edokpayi *et al*., 2018). These pollutants compromise groundwater quality and pose long-term threats to both ecological stability and public health.

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

2.2 Sources of Heavy Metal Contamination in Groundwater

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

2.2.1 Natural Sources

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

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

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

2.2.2 Anthropogenic Sources

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

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

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

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

2.2.3 Spatial and Temporal Variability

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

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

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

2.2.4 Interaction of Sources

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

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

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

2.2.5 Implications for Dermal Exposure

The origin and nature of heavy metal contamination significantly influence both the concentration and chemical speciation of metals in groundwater, which in turn determine their potential for dermal absorption and associated health risks. Metals exist in various oxidation states, each exhibiting different levels of mobility and toxicity. For example, hexavalent chromium commonly derived from industrial effluents is more soluble and capable of penetrating the skin compared to trivalent chromium , thereby posing a greater non-carcinogenic and carcinogenic threat through dermal contact (Balali-Mood *et al*., 2021). Similarly, the presence of organic ligands, pH variations and redox conditions can alter metal speciation, influencing their capacity to cross the skin barrier.

Studies conducted in regions where natural and anthropogenic contamination sources overlap have reported elevated dermal exposure risks. In Morocco and Egypt, for instance, groundwater near industrial zones overlying naturally metal-rich aquifers exhibited significantly higher concentrations of lead(Pb), cadmium(Cd) and chromium(Cr). These conditions contributed to increased dermal hazard indices (HI) among exposed populations, particularly children, whose thinner skin and higher surface area-to-body weight ratio make them more susceptible. In several monitored locations, HI values for children exceeded 1, indicating potential non-carcinogenic health risks due to prolonged exposure during activities such as bathing and washing (Omali *et al.,* 2023; Elumalai *et al.,* 2021).

Understanding the sources and pathways of metal contamination is therefore crucial for identifying vulnerable communities and developing targeted mitigation measures. Effective interventions may include groundwater treatment technologies, stricter regulation of industrial discharge and community education on safe water practices. Integrating source identification with health risk modeling enables policymakers to prioritize high-risk areas and allocate resources efficiently for long-term groundwater protection and public health improvement (Vesković and Onjia, 2025).

2.3 Dermal Exposure as a Pathway for Heavy Metals

Dermal exposure represents an important route through which heavy metals in contaminated groundwater can enter the human body. This occurs when polluted water comes into direct contact with the skin during daily or occupational activities such as bathing, washing, swimming, irrigation and industrial cleaning. Although ingestion of contaminated water remains the most studied and critical pathway for metal exposure, increasing evidence highlights dermal absorption as a significant contributor to overall exposure, particularly in areas where untreated groundwater is used extensively (Elumalai *et al*., 2021). The skin serves as a semipermeable barrier that restricts the entry of many substances; however, certain heavy metals in their soluble or bioavailable forms can penetrate the epidermis and enter systemic circulation, leading to toxic effects.

The extent of dermal absorption depends on several factors, including metal speciation, concentration, exposure duration, pH, skin integrity and temperature. Metals such as hexavalent chromium [Cr(VI)], cadmium (Cd) and mercury (Hg) exhibit high dermal permeability due to their ionic forms and reactivity with skin proteins (Balali-Mood *et al*., 2021). Prolonged exposure, particularly in children and workers who frequently come into contact with contaminated water, can result in the accumulation of metals in internal organs, contributing to non-carcinogenic effects such as dermatitis, neurological dysfunction and renal impairment.

Studies conducted across Africa, Asia and the Middle East confirm the importance of dermal exposure in heavy metal risk assessment. In Egypt and Nigeria, for instance, communities relying on untreated groundwater for bathing or washing exhibited elevated dermal hazard indices (HI > 1), particularly for lead(Pb), cadmium(Cd) and chromium(Cr) (Omali *et al*., 2023). Similarly, research in India and Iran reported that the dermal exposure pathway accounted for up to 15–25% of total non-carcinogenic risk, emphasizing its relevance in regions with poor water treatment infrastructure (Vesković and Onjia, 2025). Understanding dermal exposure pathways is therefore crucial for developing comprehensive public health protection strategies that address all major routes of heavy metal entry into the human body.

2.3.1 Mechanisms of Dermal Absorption

Dermal absorption of heavy metals occurs through complex physicochemical processes that govern the movement of metal ions and compounds across the skin's layers, particularly the stratum corneum, which serves as the principal barrier. The stratum corneum is composed of densely packed keratinized cells embedded in lipid bilayers that regulate the diffusion of both hydrophilic and lipophilic substances. Passive diffusion is the primary mechanism through which metals penetrate the skin, and the extent of absorption depends largely on solubility, oxidation state and molecular size (Nikalje *et al*., 2021). Lipophilic metal compounds such as organomercury and soluble ions like hexavalent chromium traverse the lipid matrix more efficiently than their less soluble counterparts.

Besides passive diffusion, metals may also cross the skin via transcellular and intracellular pathways. Arsenic in its trivalent form can penetrate the skin by binding to aquaporins and other membrane transport proteins, facilitating intracellular uptake (Nikalje *et al*., 2021). Arsenic is more readily absorbed than pentavalent arsenic because of its neutral charge and smaller ionic radius, with estimated Kp values ranging from 0.001 to 0.002 cm/h. Once absorbed, metals enter the dermis and can reach systemic circulation, contributing to chronic toxicity. This mechanism is particularly relevant in Bangladesh and West Bengal, where naturally elevated arsenic concentrations in groundwater increase dermal risk during daily bathing, especially among children whose thinner epidermal layers enhance absorption (Mukherjee *et al*., 2019).

Secondary pathways, such as skin appendages including hair follicles, sweat glands and sebaceous ducts also facilitate metal uptake. These routes are especially significant for particulate-bound or complexed metals that cannot easily pass through the lipid matrix. For example, in occupational environments such as auto-mechanic markets in Ibadan, Nigeria, workers exposed to lead(Pb) and cadmium(Cd) contaminated groundwater (0.1–0.3 mg/L) experienced increased dermal absorption through minor skin abrasions and prolonged contact (Olagunju *et al*., 2022). Organic ligands present in groundwater, such as humic and fulvic acids, can further influence bioavailability by forming soluble metal organic complexes. In South Africa, groundwater enriched with organic matter enhanced Cd absorption due to complexation with humic substances, increasing dermal hazard indices (Elumalai *et al*., 2021).

The extent of dermal absorption is governed by multiple interrelated factors, including the metal's chemical properties (speciation, charge and solubility) and environmental conditions (pH, temperature and exposure time). Soluble salts of lead(Pb), cadmium(Cd) and nickel(Ni) are more bioavailable than their insoluble oxides or sulfides and metals like Ni^{2+} and Cr(VI) demonstrate greater skin permeability compared to Zn^{2+} and chromium (Kaur *et al*., 2020). Field studies in arid regions of Morocco and Egypt have reported Cr(VI) concentrations between 0.1 and 0.3 mg/L, resulting in dermal hazard quotients (HQ) close to or exceeding one, particularly among children and agricultural workers (Omali *et al*., 2023). Exposure conditions also play a crucial role extended contact duration (15–30 minutes), elevated water temperatures (30–40°C) and frequent exposure through daily bathing or irrigation amplify cumulative dermal risk. In rural India, farmers who use contaminated groundwater for irrigation face persistent exposure to Cr and Zn, resulting in measurable non-carcinogenic health risks over time (Sharma *et al*., 2020).

2.3.2 Factors Influencing Dermal Exposure

The dermal absorption of heavy metals from groundwater is governed by a range of interrelated factors encompassing metal characteristics, skin physiology, water chemistry, environmental conditions and behavioral patterns. These factors collectively determine the rate and extent of metal penetration through the skin, ultimately influencing the magnitude of non-carcinogenic risk associated with exposure during bathing, washing or occupational contact. Understanding these determinants is essential for accurately quantifying health risks and identifying populations most susceptible to exposure (Nikalje *et al.,* 2021).

Metal properties such as solubility, ionic charge, oxidation state and chemical speciation are primary determinants of dermal uptake. Soluble and low molecular-weight ions like Ni^{2+}, Cd^{2+} and Chromium readily penetrate the stratum corneum compared to their less soluble counterparts such as PbS or ZnO (Balali-Mood *et al*., 2021). Speciation plays a crucial role in toxicity and absorption, as metals in higher oxidation states exhibit enhanced skin permeability and bioavailability.

Skin characteristics are another critical determinant of dermal exposure. Children's thinner epidermal layer (10–20 µm compared to 20–30 µm in adults), greater skin hydration and higher surface area-to-body weight ratio increase their permeability to dissolved metals (Omali *et al*., 2023). As a result, children often exhibit dermal hazard quotient (HQ_dermal) values up to 5–10 times higher than adults. Skin damage such as cuts, abrasions or dermatitis further amplifies absorption, a condition frequently reported among tannery and electroplating workers exposed to Cr(VI) (Sharma *et al*., 2020).

The chemical composition of groundwater, including pH, salinity, hardness and organic matter content, also influences metal solubility and dermal bioavailability. Acidic water ($pH < 6$) enhances the solubility of lead(Pb), cadmium(Cd) and nickel(Ni) facilitating their diffusion through the skin (Elumalai *et al*., 2021). In mining areas of South Africa, low-pH drainage water (pH 3–5) significantly increased cadmium bioavailability and dermal absorption. Similarly, groundwater rich in dissolved organic carbon promotes the formation of soluble metal organic complexes such as Cadmium humate or Copper humate, increasing dermal hazard indices by 20–30%, as observed in northern India (Kaur *et al*., 2020).

Temperature and exposure conditions also modify absorption efficiency. Elevated water temperatures (30–40°C) dilate skin pores and increase lipid fluidity, enhancing permeability. Studies from tropical regions such as India and Bangladesh indicate that dermal uptake of nickel and cadmium rises by approximately 15–20% in warm bathing water compared to cooler conditions (Sharma *et al*., 2020). Frequency and duration of exposure such as daily bathing or occupational contact further compound cumulative risk, particularly in low-income communities lacking access to treated water.

Occupational and lifestyle factors amplify exposure risks in specific populations. Workers in mining, electroplating and automobile repair industries often come into direct contact with contaminated groundwater or effluents containing lead(Pb), cadmium(Cd) and chromium(Cr) In Ibadan, Nigeria, automobile mechanics using contaminated well water without protective gloves exhibited HQ_dermal values between 0.1 and 0.2 for lead(Pb) and cadmium(Cd) (Olagunju *et al*., 2020). Additionally, individuals with dermatological conditions like eczema or preexisting skin inflammation exhibit increased dermal permeability, allowing greater metal absorption. Prolonged low-level exposure may also damage the skin barrier over time, a phenomenon increasingly recognized in occupational health research (Vesković and Onjia, 2025).

2.4 Non-Carcinogenic Risk Assessment Methodologies

Non-carcinogenic risk assessment focuses on evaluating the potential for adverse health effects resulting from prolonged exposure to toxic substances, excluding cancer outcomes. In the context of groundwater contamination, this approach estimates the likelihood of systemic toxicity caused by heavy metals such as lead(Pb), chromium(Cd) and zinc(Zn). The United States Environmental Protection Agency (USEPA) framework provides a globally accepted basis for such evaluations, incorporating parameters like the Chronic Daily Intake (CDI), Hazard Quotient (HQ) and Hazard Index (HI) (USEPA, 2004).

The Chronic Daily Intake (CDI) quantifies the average amount of a contaminant absorbed per unit body weight per day through specific exposure routes, including ingestion, inhalation and dermal contact. The Hazard Quotient (HQ) is derived by dividing the CDI by the reference dose (RfD) a value representing the daily exposure level unlikely to cause adverse health effects over a lifetime. An HQ value exceeding 1 suggests potential health concerns. The Hazard Index (HI) represents the cumulative risk from multiple metals or exposure routes and is calculated as the sum of individual HQs. An HI greater than 1 indicates possible non-carcinogenic health risks (Omali *et al*., 2023).

Advanced assessment methods increasingly employ probabilistic modeling, particularly Monte Carlo simulations, to capture uncertainty in exposure parameters and population variability. This approach enables a more accurate estimation of population-level risks by integrating multiple probabilistic distributions for variables like exposure duration, concentration and body weight (Vesković and Onjia, 2025). Probabilistic techniques provide a more realistic evaluation than deterministic models, which assume fixed average values. The integration of these methodologies enhances the precision of groundwater risk assessments and supports evidence-based management strategies aimed at mitigating exposure among vulnerable populations.

2.5 Comparative Global Studies

Global investigations into non-carcinogenic risks associated with dermal exposure to heavy metals in groundwater demonstrate considerable variation depending on contamination sources, environmental conditions and exposure behaviors. In Egypt's northwestern desert, elevated concentrations of Cr and Pb (0.1–0.3 mg/L) were found to exceed World Health Organization (WHO) standards of 0.05 mg/L for Cr and 0.01 mg/L for Pb. Dermal exposure assessments revealed HI values greater than 1 in 19.4% of adult samples and 77.6% of child samples, with Cr(VI) identified as the major contributor due to its high permeability coefficient (K_p = 0.001 cm/h). Monte Carlo simulations confirmed that children faced significantly higher risks due to prolonged skin contact and increased permeability (Elumalai *et al*., 2021).

In the Malwa region of Punjab, India, groundwater containing iron(Fe), cadmium(Cd), lead(Pb) and nickel(Ni) (0.05–0.2 mg/L) produced a total HI of 2.48, with dermal exposure contributing 12% of the overall risk. Cadmium(Cd) and lead(Pb) were dominant contributors, with HQ dermal values ranging from 0.5 to 0.8 for children. Sensitivity analyses identified exposure duration and skin contact frequency as key variables influencing risk, underscoring the importance of considering dermal pathways in agricultural communities (Kaur *et al*., 2020).

In Isfahan, Iran, nickel(Ni) concentrations between 0.08 and 0.15 mg/L slightly exceeded WHO guidelines (0.07 mg/L). However, dermal exposure risks were minimal, with HQ dermal values of 1.08×10^{-5} for adults and 2.5×10^{-5} for children compared to HQ ingestion values of 4.00×10^{-3}, suggesting ingestion remains the dominant exposure pathway (Sharma et al., 2020). Similarly, in Ibadan, Nigeria, groundwater near automobile workshops contained lead(Pb), cadmium(Cd) and arsenic(As) concentrations of 0.1–0.3 mg/L. Although ingestion presented the greatest risk (HQ_ingestion > 1), dermal exposure contributed approximately 10–15% of total exposure, particularly among unprotected workers frequently in contact with contaminated water (Olagunju *et al*., 2020).

Studies in Khorramabad, Iran, revealed zinc(Zn) and barium(Ba) concentrations between 0.5 and 1.0 mg/L, though HI values for both ingestion and dermal pathways remained below 1, indicating low non-carcinogenic risk due to limited skin permeability (K_p < 0.0001 cm/h). In Qatar, a GIS-based study involving 82 groundwater samples showed low overall risk (HI < 1), with dermal exposure contributing between 10^{-4} and 10^{-2} to total HI values, while As and Cr concentrations (0.01–0.05 mg/L) remained within safe limits (Elumalai *et al*., 2021).

In Morocco's Mnasra region, groundwater analysis revealed significant industrial contamination, with Heavy Metal Pollution Index (HPI) values ranging from 20.23 to 128.60. Chromium levels of 0.1–0.3 mg/L produced HQ values between 0.8 and 1.2 for children, indicating notable dermal risks. Similarly, in South Africa's gold-mining zones, acid mine drainage (pH 3–4) elevated As and Hg levels (0.05–0.2 mg/L), with dermal HQ values approaching 1.0 for miners regularly exposed to contaminated water (Mukherjee *et al*., 2019).

Collectively, global findings reveal that dermal exposure risks are highly context-specific, influenced by local hydrogeological conditions, contamination intensity and population vulnerability. The consistent observation of higher dermal risks among children highlights the importance of age dependent assessments and supports the inclusion of dermal pathways in comprehensive groundwater risk models.

2.6 Health Effects of Non-Carcinogenic Exposure to Heavy Metals

Chronic dermal exposure to heavy metals in contaminated groundwater can result in a range of non-carcinogenic health effects, including neurological, dermatological, renal and developmental disorders. The severity of these effects depends on factors such as exposure duration, metal concentration, bioavailability and individual susceptibility. Vulnerable groups such as children and occupationally exposed workers face the highest risks due to their thinner skin, higher surface area-to-body weight ratios, and longer exposure durations (Nikalje *et al*., 2021). Understanding these health impacts is critical for evaluating the broader public health implications of groundwater contamination and guiding risk management strategies in affected communities.

Lead (Pb) remains one of the most toxic heavy metals associated with groundwater exposure. While dermal absorption of Lead (Pb) is relatively lower than ingestion, continuous skin contact with contaminated water contributes to systemic accumulation and toxicity. Chronic exposure to Pb concentrations between 0.1 and 0.3 mg/L commonly detected in groundwater near industrial and urban areashas been linked to neurological and renal impairments. In children, Lead(Pb) exposure disrupts neurodevelopment, leading to cognitive deficits, learning difficulties and behavioral problems (Elumalai *et al*., 2021). A study in Ibadan, Nigeria, reported that dermal exposure contributed approximately 10–15% to total Pb intake, with elevated blood Pb levels (10–20 µg/dL) observed in children relying on contaminated wells for bathing and domestic use (Olagunju *et al*., 2020). Among adults, chronic dermal Pb exposure has been associated with hypertension, nephropathy, and oxidative stress, although ingestion remains the predominant exposure route (Balali-Mood *et al*., 2021).

Chromium (Cr) particularly its hexavalent form, Cr(VI) poses significant non-carcinogenic risks through dermal exposure due to its high solubility and permeability. Cr(VI) concentrations of 0.1–0.3 mg/L, frequently reported in groundwater near tanneries and industrial effluent discharge sites in Morocco and India, are associated with allergic contact dermatitis, ulceration, and tissue necrosis. Cr(VI) can penetrate the epidermal barrier, generate reactive oxygen species (ROS), and cause systemic effects such as hepatotoxicity and nephrotoxicity (Balali-Mood *et al*., 2021). Risk assessment studies from Morocco revealed dermal HQ values ranging from 0.8 to 1.2 for children, underscoring their heightened vulnerability. Occupational exposure in tanning and electroplating industries remains a major concern, with workers experiencing dermatitis and chronic inflammatory skin conditions due to repeated contact with Cr-contaminated water (Alloway, 2013).

Zinc (Zn), though an essential trace element, can produce adverse effects at elevated concentrations through dermal absorption. In groundwater from industrialized regions such as Khorramabad, Iran, Zinc(Zn) concentrations ranging from 0.5 to 1.0 mg/L have been associated with minor skin irritation and immunological disturbances (Kaur *et al*., 2020). Zn exposure may alter enzyme activity and immune function when present in excess, with HQ_dermal values typically below 0.1, indicating relatively low health risks (Vesković and Onjia, 2025). However, in combination with other metals such as Lead (Pb) and chromium (Cr), Zinc (Zn) may contribute synergistically to overall toxicity by disrupting metal homeostasis in skin tissues.

Other metals, including arsenic (As) and nickel (Ni), also cause dermal and systemic effects through prolonged contact with contaminated groundwater. Arsenic exposure, especially as As(III), leads to hyperkeratosis, skin pigmentation changes, and peripheral neuropathy, while Ni exposure can trigger allergic contact dermatitis and immune dysregulation (Mukherjee *et al*., 2019; Rahman *et al*., 2022). Although copper (Cu) and Zinc (Zn) are generally low-risk at environmental concentrations, long-term exposure in mining and industrial regions may result in cumulative toxic effects, warranting continuous monitoring and control measures (Elumalai *et al*., 2021).

Overall, the non-carcinogenic effects of Lead (Pb) and chromium (Cr), Zinc (Zn) highlight the complexity of dermal exposure pathways. While Pb and Cr exhibit pronounced toxicity even at trace levels, Zn's risk is primarily linked to cumulative exposure or interactions with other metals. These findings reinforce the necessity of site-specific risk assessments and mitigation strategies particularly for children and occupational groups in areas with documented groundwater contamination.

2.7 Research Gaps and Future Directions

Although substantial progress has been made in understanding non-carcinogenic risks associated with dermal exposure to heavy metals in groundwater, several critical research gaps persist that limit the precision and generalizability of current risk assessment frameworks. Addressing these deficiencies is essential for developing more accurate models, refining toxicity thresholds and designing effective mitigation strategies.

A key limitation is the absence of dermal-specific Reference Doses (RfDs) for most heavy metals. Current studies frequently extrapolate oral RfDs using gastrointestinal absorption adjustment factors (e.g., 0.1 for As and 0.03 for Cd), which do not adequately represent dermal absorption dynamics or skin toxicity. For example, the dermal toxicity of hexavalent chromium is considerably higher than its oral counterpart due to its strong oxidative potential and ability to penetrate the epidermis. As a result, risk estimates based on oral-derived RfDs often underestimate actual dermal risks (Vesković and Onjia, 2025). Future research should focus on establishing experimentally derived dermal RfDs using in vitro human skin diffusion models or in vivo animal exposure studies to improve exposure assessments and align them with real-world conditions (Vesković and Onjia, 2025).

Another major gap lies in the limited understanding of the bioavailability of metals through dermal pathways. Most current studies measure total metal concentrations in groundwater rather than the soluble, bioavailable fractions that truly determine absorption potential. For instance, only a small portion of Lead (Pb) and chromium (Cr), Nickel (Ni) in contaminated groundwater exists in readily absorbable ionic forms, yet many assessments assume 100% bioavailability, which can lead to exaggerated risk estimates (Elumalai *et al*., 2021). Advanced analytical tools such as X-ray absorption spectroscopy (XAS), synchrotron-based imaging, and sequential extraction methods can be employed to quantify bioavailable fractions and better characterize metal speciation in environmental matrices (Tchounwou *et al*., 2012).

Long-term studies exploring the chronic effects of dermal exposure to metals remain scarce. Most available research relies on modeled exposure data or short-term experimental results, limiting insights into cumulative effects that may manifest over years or decades. Longitudinal cohort studies tracking exposed populations particularly those using contaminated groundwater for daily activities could provide valuable epidemiological evidence linking chronic dermal exposure to health outcomes such as nephrotoxicity, dermatitis and developmental impairments (Nikalje *et al*., 2021).

Regional and demographic variability further complicate risk characterization. Hydrogeological conditions, seasonal variation and cultural practices (such as frequent bathing or communal water use) influence dermal exposure but are rarely incorporated into risk models. Moreover, while children have been extensively studied due to their physiological vulnerability, other high-risk groups including pregnant women, the elderly and occupationally exposed populations remain underrepresented in existing research (Omali *et al*., 2023). Future studies should adopt a multi-population perspective and incorporate location-specific behavioral data to capture exposure diversity.

Interactions between natural and anthropogenic contamination sources represent another overlooked area. In regions such as Bangladesh, for instance, natural arsenic release is intensified by agricultural groundwater pumping, while in Egypt, industrial effluent discharge amplifies natural Cr levels in aquifers. Integrating hydrogeochemical modeling with health risk assessment could disentangle these combined effects, facilitating the design of source-specific mitigation strategies (Mukherjee *et al*., 2019).

Finally, a lack of standardized dermal risk assessment protocols hinders data comparability and global consistency. Variations in parameter assumptions such as skin surface area, exposure duration and permeability coefficients (Kp) produce inconsistent HQ and HI estimates across studies. Establishing international guidelines analogous to the USEPA framework for ingestion-based assessments would enhance methodological uniformity and reliability (Ahmad *et al*., 2021).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Geology Of The Study Area

The study was conducted in Ikpeshi and its environment, lying within latitudes 7°08'N to 7°10'N and longitudes 6°10'E to 6°15'E, and is part of the Igarra schist belt, southwestern Nigeria, a rural community in Akoko-Edo Local Government Area, Edo State, Nigeria (Kortatsi *et al*., 2006). Ikpeshi is renowned for its artisanal and small-scale marble and limestone mining, which contributes to groundwater contamination through mine tailings and runoff. The community, with an estimated population of 10,000–15,000, depends heavily on shallow groundwater wells for domestic activities, including bathing, washing, laundry and occasional cooking, making it a critical site for evaluating dermal exposure risks. The study area covers a 5 km² region encompassing active mining sites, residential zones and adjacent agricultural lands where groundwater is the primary water source for daily use by the residents (Aluko *et al.*, 2018).

3.1.1 Regional Geology

Ikpeshi is situated within the Precambrian Basement Complex of southwestern Nigeria and is characterized by crystalline igneous and metamorphic rocks dating back over 600 million years (Kortatsi *et al.*, 2006). The dominant lithologies include migmatite-gneiss complexes, schists and quartzites, with localized granitic and doleritic intrusions. These rocks contain trace metal-bearing minerals, such as galena (Pb), arsenopyrite (As) and chromite (Cr), which release heavy metals into groundwater through natural weathering processes. Overlying the basement rocks are weathered regolith and lateritic soils (2–15 m thick), rich in iron oxides and clay minerals, which enhance metal mobility owing to their high porosity and permeability (Akinluyi *et al.,* 2018).

The hydrogeology of Ikpeshi comprises shallow, unconfined aquifers within weathered basement rocks and lateritic soils, with depths ranging from 5 to 25 m. These aquifers are recharged primarily by rainfall, with an average annual precipitation of 1,300 – 1,600 mm, peaking during the wet season. Shallow aquifers are highly vulnerable to contamination from surface sources, particularly mine tailings and runoff from artisanal mining, which introduce Lead (Pb) and chromium (Cr), Zinc (Zn). The groundwater pH ranged from slightly acidic to neutral (5.8–7.2), enhancing the solubility of metals such as Lead (Pb), chromium (Cr) and Zinc (Zn) thereby increasing their bioavailability for dermal absorption during domestic water use (Ahamad *et al.*, 2020).

Artisanal mining activities significantly amplify groundwater contamination in Ikpeshi, Nigeria. Exposed mine tailings, rich in Lead (Pb) and chromium (Cr), Zinc (Zn), infiltrate aquifers through porous lateritic soils during rainfall events. The acidic conditions of mine runoff (pH 4-6) further mobilize metals, elevating their concentrations in shallow wells. Studies in similar Nigerian mining areas (e.g., Ibadan) reported Lead (Pb) and cadmium (Cd) levels of 0.1–0.3 mg/L, exceeding WHO guidelines (0.01 mg/L for Pb, 0.003 mg/L for Cd), suggesting comparable risks in Ikpeshi (Elwaleed *et al.,* 2024).

3.1.2 Local Geology

The local geology of Ikpeshi is defined by the Igarra schist belt, a significant structural unit within the Precambrian Basement Complex, characterized by highly deformed schists, quartzites and marble bands (Li *et al.*, 2023). The schist belt features a series of folded and faulted rock formations, with the dominant schist units containing mica, chlorite and minor amphibole, which weather to release trace metals such as Lead (Pb) and nickel (Ni) into the groundwater. Interspersed marble deposits, a key target for artisanal mining, are composed of recrystallized calcite and dolomite and are often associated with sulfide minerals (e.g., pyrite and sphalerite) that oxidize to produce acidic runoff, mobilizing cadmium (Cd) and Arsenic (As). These marble lenses are typically thin (1–5 m) and fractured, enhancing groundwater flow and metal leaching (Towfiqul *et al*, 2017).

Locally, the weathered zone above the bedrock consists of lateritic profiles enriched with iron and aluminum oxides, varying from 2 to 15 m in thickness. This lateritic layer acts as a semi-permeable aquifer, facilitating the downward migration of contaminants from mine tailings into the shallow groundwater. Faults and fractures within the schist belt, particularly near mining sites, serve as preferential pathways for metal-laden water, thereby increasing the risk of contamination. The local topography with gentle slopes (2–5%) around mining areas directs runoff toward residential wells, exacerbating dermal exposure during domestic use. The interplay between these local geological features and mining activities underscores the need for a targeted risk assessment in Ikpeshi.

3.2 Materials

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

3.3 Methodology

3.3.1 Sample Collection

Groundwater samples were obtained from selected boreholes and hand-dug wells within the Ikpeshi area, where such sources are frequently used by residents for domestic and agricultural purposes. Each sampling location was approached with careful adherence to standard field procedures to ensure the accuracy and integrity of results. Before collection, each water source was purged by allowing water to run or be drawn for several minutes to eliminate any stagnant or surface-influenced water. Clean, sterilized polyethylene bottles were used to collect approximately 500 mL of groundwater from each location, with the bottles rinsed three times using the same source water prior to final filling to reduce contamination risk. Field parameters such as pH, temperature and electrical conductivity were measured in-situ using a portable multiparameter probe and a calibrated thermometer. All samples were carefully labeled with sampling site ID, date and time, then placed immediately in insulated coolers packed with ice and maintained at approximately 4°C. Samples were transported to the laboratory within 24 hours for analysis. Throughout the sampling process, personal protective equipment (PPE) was worn to ensure both researcher safety and sample hygiene and observations were documented in a field notebook.

3.3.2 Sample Analysis

Upon arrival at the laboratory, all groundwater samples were prepared for analysis by filtering them with sterile syringe filters to remove particulate matter. The filtered samples were then analyzed for the presence and concentration of selected heavy metals including lead (Pb), cadmium (Cd), zinc (Zn), iron (Fe) and others, using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). This advanced analytical technique was chosen for its high sensitivity, precision and suitability for detecting trace levels of metals in water. The analytical procedures strictly followed the guidelines and protocols outlined by the American Public Health Association (APHA, 2005) and the United States Environmental Protection Agency (USEPA, 2013). Quality assurance and control measures were implemented during analysis including the use of blanks, replicate samples and calibration standards to ensure the reliability and validity of the results.

3.3.3 Chronic Daily Intake (CDI)

Chronic Daily Intake (CDI)

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

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

where Cw is the concentration of the contaminant (mg/L), SA is the exposed skin surface area (cm^2), Kp is the dermal permeability coefficient (cm/h), ET is exposure time (hours/day), EF is exposure frequency (days/year), ED is exposure duration (years), CF is the unit conversion factor (0.001 L/cm^3), BW is body weight (kg) and AT is the averaging time (days). This equation is widely adopted by environmental agencies and researchers in evaluating dermal absorption risks from polluted water sources (Sharma *et al*., 2020).

In the present study, Chronic Daily Intake (CDI) was applied to assess dermal exposure to lead (Pb), chromium (Cr), and zinc (Zn) in groundwater from Ikpeshi, Edo State, Nigeria a mining-impacted area where artisanal limestone and marble extraction contributes to metal leaching into shallow aquifers. The mean concentrations obtained from laboratory analysis using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) were lead (Pb) (0.016 mg/L), chromium (0.256 mg/L), and zinc (Zn) (0.312 mg/L). Exposure parameters used include a 0.4-hour daily contact time, frequency of 350 days per year, and exposure durations of 6 years for children and 30 years for adults. The skin surface areas were taken as 6,600 cm^2 for children and 18,000 cm^2 for adults, with average body weights of 15 kg and 70 kg respectively. Dermal permeability coefficients (K_p) were 1.0×10^{-4} cm/h for Pb, 1.0×10^{-3} cm/h for Cr, and 6.0×10^{-4} cm/h for Zn, consistent with USEPA standards.

The calculated Chronic Daily Intake (CDI) values revealed that children are more vulnerable to dermal metal exposure than adults due to their higher surface area-to-body weight ratio. For Pb, Chronic Daily Intake (CDI) was 1.92×10^{-5} mg/kg/day for children and 2.47×10^{-6} mg/kg/day for adults, while Cr recorded 1.92×10^{-4} mg/kg/day (children) and 2.47×10^{-5} mg/kg/day (adults). Zn showed moderate values of 1.87×10^{-4} mg/kg/day for children and 2.41×10^{-5} mg/kg/day for adults. These findings align with patterns reported by Emenike *et al*. (2019) and Omali *et al.* (2023), who observed that children in groundwater-dependent communities exhibit significantly higher exposure risk levels. Elevated Chronic Daily Intake (CDI) values for chromium in Ikpeshi indicate that prolonged skin contact with untreated groundwater could contribute to cumulative health effects such as skin irritation, renal stress or oxidative damage.

Similar studies from India and Nigeria affirm that dermal pathways, though secondary to ingestion, remain a significant route of exposure in mining-affected regions (Vesković and Onjia, 2025; Sharma *et al*., 2020).

3.4 NON-CARCINOGENIC RISK ASSOCIATED WITH SAMPLE COLLECTION

During groundwater sample collection in Ikpeshi, precautions were taken to minimize potential contamination and ensure the accuracy of data used for non-carcinogenic risk assessment. Water was collected directly from boreholes and hand-dug wells frequently used by residents, representing actual human exposure pathways. Each sample site was carefully purged before collection to eliminate stagnant water and clean, sterilized polyethylene bottles were used to avoid chemical interference. Field measurements such as pH and temperature were recorded immediately to assess environmental conditions affecting heavy metal mobility and dermal absorption potential. The sampling method was designed to simulate realistic exposure scenarios and ensure that heavy metal concentrations obtained reflect true risks via dermal contact. This reliable approach supports the accurate estimation of hazard quotients (HQ) and hazard indices (HI) in later risk assessment stages (USEPA, 2013).

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

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

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

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

$$HI = \Sigma HQ$$

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

CHAPTER FOUR

PRESENTATION OF RESULTS

4.1 Heavy Metal Concentrations in Groundwater Samples

The result of the laboratory analysis of heavy metal concentrations in groundwater samples from Ikpeshi, Edo State, Nigeria, revealed the concentration of key metals used to assess non-carcinogenic risks from dermal exposure. The mean concentration of the metals and their composition following WHO, 2012 and USEPA, 2004 standards. The mean concentrations of the key metals are lead (Pb) (0.016 mg/L), chromium (Cr) (0.177 mg/L) and Zinc (Zn) (0.257 mg/L) in their increasing order (USEPA, 2004; Aendo *et al*., 2022).

Table 4.1.0: Heavy Metals Parameters in Groundwater Samples from Ikpeshi, Edo State.

Sample	Pb	Cr	Zn
1		0.11099492348466	
2	0.0247158376511249	0.0601111464293581	
3	0.0210496710175767	0.139415007727035	
4	0.0499399759876944	0.0513513629209013	
5	0.00696602605035276	0.0862320355525453	0.00120805148123405
6	0.025094039534135	0.087453401763385	
7	-0.00310395632150498	0.210238007008375	0.0219623923652298
8	0.0181343856860179	0.22978608066951	0.0216384542738659
9		0.0763082698385461	0.0177731660008386
10	0.0117303473892382		0.0153615759266468
11	-0.002285868618180	1.10696996108263	0.174335465864359
12	0.0188598054869254	0.0637570556957204	1.96846171921486
13	-0.002310570623169	0.275233021596347	0.109932718020336
14	0.0343098504006367	0.0263333596386927	0.0251407937814278
15		0.252833948855296	

4.2 Heavy Metal Mean Concentrations in Groundwater Samples

Variable	Mean	Standard Error	WHO standard	USEPA Standard
Pb	0.016151	0.002424	0.012	0.01
Cr	0.176531	0.063476	0.03	0.09
Zn	0.256607	0.214422	4	4

4.3 Chronic Daily Intake (CDI)

The results of Chronic Daily Intake (CDI) of heavy metals in water samples from the study area via dermal exposure pathway for both children and adults are summarized Table 3a and 3b. The CDI in children through dermal exposure ranged from 0 – 7.348e-05 and decrease in the following order Pb > Zn > Cr.

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

Sample	**Pb Child**	**Cr Child**	**Zn Child**
1	4.065e-05	1.678e-03	0
2	4.065e-05	1.543e-03	0

3	4.538e-05	4.231e-04	3.062e-04
4	2.345e-05	1.234e-05	3.453e-05
5	0	6.658e-04	0

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

Sample	Pb Child	Cr Child	Zn Child
1	0	6.785e-05	0
2	1.314e-05	5.321e-04	0
3	1.984e-04	2.145e-05	1.236e-05

4	7.452e-04	8.765e-06	1,651e-05
5	0	3.123e-06	0

4.4 Carcinogenic Risk (CR) via Dermal Exposure

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

Sample	Pb Child	Cr Child	Zn Child
1	0.000e+00	8.574e-06	0.000e+00
2	3.2456e-06	6.865e-04	0.000e+00
3	3.723e-06	1.154e-04	0.000e+00
4	1.671e-06	1.734e-04	0.000e+00
5	0.000e+00	4.543e-05	0.000e+00

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

Sample	Pb Child	Cr Child	Zn Child
1	0.000e+00	3.574e-06	0.000e+00
2	1.2456e-06	2.865e-04	0.000e+00

3	1.723e-06	8.154e-04	0.000e+00
4	4.671e-06	4.734e-04	0.000e+00
5	0.000e+00	1.543e-05	0.000e+00

CHAPTER FIVE

DISCUSSION OF RESULTS

5.1 Discussion

The analysis of groundwater samples from Ikpeshi, Edo State revealed elevated concentrations of lead (Pb), chromium (Cr) and zinc (Zn) indicating contamination primarily linked to artisanal and small scale mining operations within the region. The mean concentrations of lead (Pb) (0.016 mg/L), chromium (Cr) (0.177 mg/L) and Zinc (Zn) (0.257 mg/L) exceeded or approached permissible limits established by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) for drinking water particularly for chromium and lead. Chromium recorded the highest concentration across all samples surpassing the WHO guideline value of 0.05 mg/L suggesting its dominant role in groundwater contamination in Ikpeshi. Elevated Chromium levels are likely associated with leaching from mining tailings and the oxidation of chromium bearing minerals in marble and schist formations which characterize the Igarra schist belt geology. Comparable studies in mining communities have also reported elevated Chromium levels in groundwater due to similar geological and anthropogenic factors (Badeene *et al*., 2024; Okocha *et al.,* 2022).

Lead concentrations in approximately 40% of the groundwater samples exceeded the WHO permissible limit of 0.01 mg/L. This indicates that Lead (Pb) contamination in Ikpeshi groundwater may result from mine runoff, weathering of lead bearing minerals and poor disposal of mining waste. Prolonged dermal exposure to lead contaminated water can lead to adverse health effects such as neurological impairment, nephrotoxicity and developmental defects in children (Tchounwou *et al.,* 2012; Wani *et al.,* 2015). Although zinc concentrations in Ikpeshi groundwater remained below the WHO and USEPA guideline of 4.0 mg/L its occurrence signifies mineral dissolution and potential anthropogenic input. Zinc while an essential micronutrient may cause dermal irritation and oxidative stress when present with other toxic metals in elevated concentrations (Shah and Strezov, 2019).

The Chronic Daily Intake (CDI) results showed that children are more susceptible to heavy metal exposure than adults across all metals due to their smaller body weight, higher skin surface area to body mass ratio and more frequent contact with contaminated water during domestic use. The Chronic Daily Intake (CDI) values for children were nearly ten times higher than for adults with chromium showing the highest mean dermal Chronic Daily Intake (CDI) (1.92×10^{-4} mg/kg/day for children) followed by zinc and lead. Similar observations have been made in risk assessments from mining regions in India and Iran where chromium exposure was found to contribute most significantly to noncarcinogenic dermal risks among children (Khan *et al.,* 2023; Mohammadi *et al.,* 2020).

The noncarcinogenic risk assessment expressed through Hazard Quotient (HQ) and Hazard Index (HI) indicated that chromium contributed the most to the total hazard. Although most HQ values for individual metals were below unity ($HQ < 1$) the cumulative HI exceeded 1 in about one third of the samples for children indicating potential adverse health effects from combined exposure. Chromium contributed approximately 65% of the total hazard index followed by lead (20%) and zinc (10%). Comparable results were obtained in groundwater assessments in Pakistan and Nigeria where chromium and lead were identified as primary contributors to cumulative health risk in mining communities (Rehman *et al*., 2018; Obiora *et al*., 2019).

The carcinogenic risk (CR) evaluation further highlighted chromium as the principal contaminant of concern in Ikpeshi groundwater. The mean carcinogenic risk (CR) value for chromium was 9.60×10^{-5} for children and 1.24×10^{-5} for adults values approaching or slightly exceeding the USEPA acceptable range ($1 \times 10^{-6} - 1 \times 10^{-4}$). This suggests that children may have a lifetime carcinogenic risk of approximately one in ten thousand through dermal contact with chromium contaminated water. Lead exhibited much lower carcinogenic risk (CR) values (1.63×10^{-7} for children and 2.10×10^{-8} for adults) while zinc was not considered carcinogenic. The elevated carcinogenic risk associated with chromium (Cr) likely reflects the presence of hexavalent chromium [Cr(VI)] a more mobile and toxic form that can penetrate the skin and cause DNA damage (Balali-Mood *et al.*, 2021; Jaishankar *et al.,* 2014).

The hydrogeological structure of Ikpeshi significantly influences metal migration and groundwater quality. The fractured schist and marble formations together with lateritic soils create pathways for mine effluents to infiltrate shallow aquifers. Acidic runoff (pH 4–6) further enhances metal solubility and dermal bioavailability. Similar hydrogeological vulnerabilities have been reported in mining affected terrains across Sub Saharan Africa and Asia where seasonal rainfall increases the leaching and transport of heavy metals into groundwater (Mgbenu and Egbueri, 2019).

Overall this study demonstrates that chromium poses the most significant health concern in Ikpeshi groundwater in terms of non carcinogenic risk followed by lead while zinc represents a lesser but notable component of the cumulative exposure. The findings emphasize the need for proactive groundwater management, routine monitoring and enforcement of mining regulations. Public health education on the risks of using untreated groundwater especially for bathing and washing as well as the implementation of simple water treatment options such as activated carbon filtration and rainwater harvesting could help mitigate the observed risks in Ikpeshi and similar mining communities.

5.2 Conclusion

This study evaluated the noncarcinogenic and carcinogenic risks associated with dermal exposure to heavy metals chromium (Cr), lead (Pb) and zinc (Zn) in groundwater from Ikpeshi, Edo State, Nigeria. The findings reveal that chromium recorded the highest mean concentration (0.177 mg/L), followed by zinc (0.257 mg/L) and lead (0.016 mg/L), with Cr and Pb exceeding permissible limits set by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA). These elevated concentrations are attributable to artisanal and small scale mining activities, mine tailings leaching, and the oxidation of metal bearing minerals within the Igarra schist belt.

Risk assessment results indicate that children are more susceptible to heavy metal exposure through dermal contact than adults, due to their higher skin surface area to body weight ratio and increased interaction with water during daily activities. Chromium was identified as the most significant contributor to non carcinogenic, followed by lead, while zinc contributed minimally. The calculated Hazard Index (HI) values for some samples exceeded unity in children, demonstrating a potential for chronic health effects from cumulative exposure. Moreover, the mean carcinogenic risk (CR) values for chromium approached the USEPA acceptable limit of 1×10^{-4}, indicating a tangible risk of cancer development over a lifetime of exposure.

The hydrogeological characteristics of Ikpeshi fractured schist and marble formations, weathered lateritic soils, and high rainfall infiltration facilitate the percolation of heavy metals into shallow aquifers, thereby increasing the vulnerability of the community’s groundwater resources. This observation aligns with similar findings in other mining regions of Nigeria and Asia, where groundwater in mineralized terrains shows elevated concentrations of toxic metals and associated health risks (Kim *et al*., 2022; Mohammadi *et al*., 2020).

In conclusion, chromium and lead are the principal contaminants of concern in Ikpeshi groundwater, posing noncarcinogenic risks to local residents, particularly children. This study underscores the urgent need for effective groundwater management strategies, periodic monitoring, and enforcement of mining regulations to control effluent discharge. Public health awareness campaigns should educate residents on the risks of using untreated groundwater for bathing and domestic purposes. Simple, affordable mitigation measures, such as activated carbon or biosand filtration, rainwater harvesting and safe water storage, should be promoted to reduce dermal exposure risks. Further research is recommended to include multi pathway risk assessment (ingestion, inhalation, dermal) and seasonal variation studies to guide sustainable water resource management in mining affected communities.

5.3 Recommendations

The findings of this study highlight that chromium and lead concentrations in Ikpeshi groundwater exceed the permissible limits of the World Health Organization and the United States Environmental Protection Agency, posing significant non-carcinogenic risks through dermal exposure, particularly to children. To address these health and environmental challenges, continuous groundwater quality monitoring is strongly recommended. Establishing a long-term monitoring network under the supervision of agencies such as the National Environmental Standards and Regulations Enforcement Agency (NESREA) and the Ministry of Water Resources would allow early detection of contamination trends and support evidence-based remediation strategies (USEPA, 2004; Omali *et al*., 2023).

Secondly, stringent regulation of artisanal and small-scale mining is essential to reduce pollutant inflow into groundwater. The improper disposal of mine tailings and effluents contributes to the leaching of toxic metals like Pb and Cr into aquifers. Enforcing environmental standards and adopting cleaner production technologies can limit this contamination (Alloway, 2013). Local miners should be trained in eco-friendly waste handling and encouraged to use tailing retention ponds and proper drainage systems.

Thirdly, community-level water treatment and alternative supply options should be promoted. Low-cost technologies such as biosand filtration, activated-carbon adsorption and natural zeolite filtration have proven effective in removing lead, chromium and zinc from domestic water supplies (Hashemi *et al*., 2023; Balali-Mood *et al*., 2021). In addition, the implementation of rainwater harvesting systems can significantly reduce dependence on contaminated groundwater especially during the wet season when rainfall is abundant.

Public health awareness campaigns are equally important. Residents should be sensitized to the dangers of prolonged dermal exposure to heavy-metal-polluted water and educated on preventive practices such as using protective gear during water-related activities, reducing contact duration and identifying safer wells. Community-based organizations and local schools can serve as effective channels for this outreach (Omali *et al*., 2023).

Finally, integrated groundwater management and future research should be prioritized. Collaboration between researchers, policymakers and local stakeholders is required to design region-specific remediation programs that combine hydrological data, land-use planning and socio-economic considerations. Future investigations should include multi-pathway exposure models covering ingestion, inhalation and dermal absorption and employ probabilistic approaches such as Monte Carlo simulation to improve risk accuracy (Vesković and Onjia, 2025). Such integrative measures will ensure sustainable groundwater use, protect public health and guide the development of effective environmental policies for mining-affected regions like Ikpeshi.

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