CARCINOGENIC AND NON CARCINOGENIC RISK ASSESSMENT OF HEAVY METAL IN SOILS AROUND ROCK QUARRYING COMMUNITIES, IKPESHI AND ENVIRONS

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UNIVERSITY OF BENIN

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A PROJECT SUBMITTED TO THE DEPARTMENT OF SCIENCE LABORATORY TECHNOLOGY, FACULTY OF LIFE SCIENCES, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE BACHELOR OF SCIENCE (B.Sc.) HONOURS DEGREE IN SCIENCE LABORATORY TECHNOLOGY

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CERTIFICATION

We the undersigned names hereby certify that this research work was carried out by MERCY OSASUMWEN (Miss) with Matriculation Number: LSC2009910 of 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 Bachelor Degree (B.Sc.) Honors in Science Laboratory Technology.

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EXTERNAL EXAMINER	DATE

DEDICATION

This work is dedicated to God Almighty, my father who has shown me nothing but love and graces from the beginning of this programme to the end.

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Abstract

Mining and quarrying activities significantly contribute to environmental degradation and heavy metal contamination in Nigeria. The mechanical extraction of mineral resources leads to extensive landscape degradation, soil contamination, and increased human exposure to toxic elements. The study evaluated the carcinogenic and non-carcinogenic health risks associated with heavy metal contamination in soils surrounding quarrying communities in Ikpeshi and its environs, Edo State, Nigeria; assessing the extent of pollution, the ecological risk posed by heavy metals, and their potential human health implications. Soil samples were collected from four different locations at varying distances (0m, 100m, 200m) from active quarrying sites. Heavy metal concentrations were analyzed using Atomic Absorption Spectrophotometry (AAS). Pollution indices, including the Contamination Factor (Cf), Pollution Load Index (PLI), and Geo-accumulation Index (Igeo), were used to assess contamination levels. Human health risk assessments followed the United States Environmental Protection Agency (USEPA) guidelines, computing the Average Daily Dose (ADD), Hazard Quotient (HQ), and Total Carcinogenic Risk (TCR) for ingestion, dermal contact, and inhalation exposure. The findings revealed that iron (Fe) had the highest concentration, with a mean value of 412.884 mg/kg. Followed by zinc (Zn) with a mean concentration of 40.652 mg/kg. Copper (Cu) (28.348 mg/kg). Lead (Pb) (1.105–5.755 mg/kg), cadmium (Cd) (0.5–2.01 mg/kg), nickel (Ni) (6.86–18.41 mg/kg), and chromium (Cr) (5.16–12.075 mg/kg) were also detected, with Cd and Ni exceeding permissible limits. The Pollution Load Index (PLI > 1) and Geo-accumulation Index (Igeo > 1) indicated moderate to heavy contamination in soils near quarry sites. The non-carcinogenic risk assessment showed that children had a higher cumulative Hazard Index (HI = 0.13745) than adults (HI = 0.02417), suggesting increased vulnerability. For dermal exposure, cobalt (Co) had the highest HQ (0.03526) in children, indicating potential health risks. Carcinogenic risk assessment showed that nickel (Ni) (TCR = 2.14×10^{-4} for children, 3.10×10^{-5} for adults) and chromium (Cr) (TCR = 4.61×10^{-5} for children, 6.68×10^{-6} for adults) posed potential long-term cancer risks, exceeding the safe threshold (10^{-6}) set by USEPA. Lead (Pb) and cadmium (Cd) had relatively lower carcinogenic risks, but their cumulative exposure remains a concern. The results reveal significant heavy metal contamination in quarrying communities, with potential long-term health consequences, particularly for children.

CHAPTER ONE

INTRODUCTION

1.0. BACKGROUND OF STUDY

Mining, particularly in Nigeria, has been identified as a significant anthropogenic source of heavy metal contamination (Al-Naggar *et al.,* 2018). Mechanical mining operations commenced in Nigeria in 1939 under the aegis of privately owned companies (Nwogha *et al.,* 2017). Since then, the adverse health and environmental impacts of mining and quarrying have escalated, often proceeding without comprehensive research to raise awareness of these implications. In developing nations, such quarrying activities have precipitated environmental hazards, generating substantial waste and various pollutants. The degradation of landscapes and contamination of soil, water sources, and food by heavy metals due to mining activities is notable (Nwogha *et al.,* 2017). Human exposure to heavy metals occurs through ingestion, dermal contact, and inhalation, leading to significant health risks, including cellular and DNA damage, as well as disruptions in protein and enzyme functions (Witkowska *et al.,* 2021).

Heavy metals, though naturally present in trace amounts, become deleterious at high concentrations (Shakya and Agarwal, 2020). Unlike energy, which diminishes and disperses at each trophic level, heavy metals persist and bioaccumulate, necessitating detailed monitoring and public dissemination of their concentrations in soils, particularly around quarry sites, due to their carcinogenic and toxic effects (Wu *et al.,* 2016). Industrial development, urbanization, and agricultural practices contribute to soil pollution, primarily depositing heavy metals into the soil (Zorpas *et al.,* 2021). The emission of pollutants from industrial activities, mining, waste disposal, and agricultural practices further exacerbates soil contamination with heavy metals and metalloids (Gabarron *et al.,* 2017).

The environmental repercussions of quarrying are both immediate and long-term, resulting in landscape destruction, soil compaction, erosion, and loss of biodiversity. Despite the substantial economic benefits of quarrying, the associated environmental degradation, such as air and water pollution and habitat loss, often goes unaddressed. The intensifying global concern over heavy metal contamination stems from their increased utilization to meet the demands of growing populations. Both natural and anthropogenic activities contribute to environmental pollution, surpassing the ecosystem's capacity to mitigate these contaminants and thereby disrupting food chains and posing health risks. Some metals are essential in trace amounts but become toxic at higher concentrations, causing poisoning (Egorova and Ananikov, 2017). Heavy metals interact with biological systems, forming metal cations that can disrupt vital macromolecules. The toxic effects of heavy metals are extensive, affecting various organs and systems, including the gastrointestinal tract, kidneys, nervous system, and immune system, and causing conditions such as birth defects and cancer. Simultaneous exposure to multiple metals can amplify these effects. For instance, mercury and lead exposure can cause severe health issues like kidney failure (Morais *et al.*, 2012).

Heavy metals enter the food chain through uptake by microorganisms and plants, eventually reaching consumers and posing risks to human and animal health. Metals like lead and zinc, even in trace amounts, can affect nearly all body organs, with higher concentrations leading to severe toxicological impacts, including reduced cellular functions. Chronic exposure to metals such as nickel can result in serious health conditions, including cancer. Understanding the mechanisms of metal-induced carcinogenesis, which involves aberrant gene expression and DNA damage, is crucial (Itam *et al.,* 2024). Assessing health risks necessitates identifying environmental sources of these metals and quantifying their impact on human health.

Naturally occurring toxic substances embedded in rocks and minerals are typically released during the quarrying process as dust, gaseous emissions, and airborne particulates. These substances settle on soil surfaces and plants or are washed into nearby water bodies, thereby causing environmental toxicity (Anand, 2006; Lameed and Ayodele, 2010). The quarrying process often employs explosives for rock blasting and utilizes heavy trucks, machinery, and other equipment, which generate significant noise and air pollution, leading to serious environmental consequences for ecosystems (Soofastaei *et al*., 2018).

Quarry activities negatively impact ecosystems by reducing soil quality, inhibiting vegetation growth, causing health problems, and decreasing food availability (Adeyanju and Okeke, 2019; Olatunde *et al.*, 2020). Toxic elements released during quarrying processes bioaccumulate in soils and plants and can enter the food chain, resulting in adverse health conditions in humans (Nartey *et al.,* 2012). High concentrations of cadmium, lead, chromium, cobalt, nickel, and zinc have been documented at quarry sites (Adeyanju and Okeke, 2019; Anand, 1999). Monitoring the concentration of these toxic substances, particularly toxic metals, in ecosystems is crucial to prevent environmental catastrophes.

The cement industry is recognized as one of the most polluting industries by the Central Pollution Board, with major pollutants including noise and dust. Pollutants are emitted at every stage of the manufacturing process, from raw material extraction to production. Cement dust alters the elemental concentration and physicochemical properties of soil (Zerrouqi *et al.,* 2008). It is a major source of particulate matter such as SOx, NOx, and CO2 emissions. The dust contains heavy metals like chromium, nickel, cobalt, lead, and mercury, which pose environmental hazards and affect human and animal health. Cement dust exposure is associated with carcinogenesis, decreased antioxidant capacity, acute respiratory symptoms, and ventilatory effects in humans and animals (Baby *et al*., 2008).

Several studies have investigated the impact of cement dust on soil properties and plant growth. Arpita and Mitko reported that topsoils near a cement factory in Rockfort, Kingston, Jamaica, are enriched with lead, zinc, chromium, cadmium, vanadium, and mercury, released into the air from cement kilns (Arpita and Mitko, 2011). Al-Khashman and Shawabkeh found elevated levels of lead, zinc, and cadmium in topsoils within 0-10 cm depth near a cement factory in southern Jordan (Al-Khashman and Shawabkeh, 2006). Calcium oxide and sulfur oxide are the principal pollutants in soil surrounding a cement factory in Morocco (Zerrouqi *et al.*, 2008). Chemical analysis conducted by Young-Chull and Jae-Min revealed that raw material dust from the first grinding process primarily consisted of CaO (41.77%), SiO2 (11.72%), Al2O3 (3.45%), and Fe2O3 (1.47%) (Young-Chull and Jae-Min, 2004). Soil contamination due to cement decreases sharply with distance from factories and with increasing depth from the surface (Asubiojo *et al.,* 1991).

Human health risk assessment involves evaluating the potential adverse health effects that humans may experience due to exposure to environmental hazards. These risks are categorized into non-carcinogenic and carcinogenic health risks (USEPA, 1989). According to the guidelines provided by the United States Environmental Protection Agency (USEPA), non-carcinogenic risk is assessed using parameters such as chronic daily intake (CDI), hazard quotient (HQ), and hazard index (HI). In contrast, carcinogenic risk is determined through chronic daily intake (CDI) and the cancer slope factor (CSF). Non-carcinogenic risk assessment relies on the threshold reference dose (RfD), which represents the dose below which no adverse health effects are expected. However, for carcinogenic chemicals, no safe threshold exists, meaning that even low-dose exposure carries some risk of cancer development (USEPA, 1986).

1.1 AIM AND OBJECTIVES

The aim of this study is to conduct human health risk assessment of heavy metals in soils around rock quarrying sites in Ikpeshi and environs.

The specific objectives of the study are to:

- Determine the concentrations of heavy metals at the quarry site.
- Assess human health risks (non-carcinogenic and carcinogenic) associated with each heavy metal in children and adults residing around quarrying communities of Ikpeshi and environs.

1.2. STATEMENT OF PROBLEM

Quarrying activities are integral to the construction and industrial sectors, providing essential raw materials such as stone, sand, and gravel. However, these activities are accompanied by significant environmental and health challenges. One of the most pressing concerns is the release of heavy metals into the surrounding environment. During the extraction and processing of minerals, toxic substances embedded in rocks are exposed into the atmosphere, soil, and water bodies. These heavy metals, including cadmium (Cd), lead (Pb), chromium (Cr), cobalt (Co), nickel (Ni), and zinc (Zn), can persist in the environment and accumulate in soils, leading to elevated contamination levels. The presence of heavy metals in soils poses severe risks to human health. These metals can enter the human body through direct contact with contaminated soil, inhalation of dust particles, and consumption of contaminated food and water. Carcinogenic effects, including various forms of cancer may occur as a result of exposure. The bioaccumulation of these metals in the food chain exacerbates the potential for widespread health issues, particularly in communities located near quarrying sites. Given the significant health and environmental risks posed by heavy metal contamination from quarrying activities, there is a critical need to conduct comprehensive risk assessments to evaluate both the carcinogenic and non-carcinogenic risks associated with these contaminants in soils around quarrying communities. This will not only help in understanding the extent of contamination and its implications but also in formulating effective mitigation strategies to protect human health and the environment.

1.3. JUSTIFICATION OF STUDY

Understanding the levels and health impacts of heavy metal contamination in soils around quarrying sites is vital for protecting the health of local populations. By identifying the specific risks, appropriate measures can be implemented to mitigate these hazards. The study will also provide valuable data on the extent of environmental degradation caused by quarrying activities, which can inform policies and practices aimed at preserving soil quality and preventing further contamination. Findings from this research can aid in ensuring that quarrying operations comply with environmental safety standards, thereby reducing the release of harmful substances into the environment. The study will also contribute to the existing body of knowledge on heavy metal contamination and its risks, offering insights that could be applicable to other regions with similar environmental challenges.

CHAPTER TWO

LITERATURE REVIEW

2.0. Overview

Quarrying is an activity that results in both immediate and long-term adverse environmental effects. It is typically associated with the destruction and alteration of landscapes, as well as the release of toxic minerals from deep within the earth's crust into the surrounding environment. Despite these significant environmental challenges, the negative impacts are often overlooked due to the considerable economic benefits derived from such operations. According to Shakir and Mohamed (2013), quarrying has contributed to the development of infrastructure and mineral resources in various regions. However, Moibi (2007) highlighted that quarrying leads to soil compaction, landscape degradation, soil erosion, and the loss of vegetation and soil organisms. Ekpo *et al.* (2012) further identified a range of environmental harms, including the destruction of wildlife and biodiversity, the loss of fertile soil, air and water pollution, farmland degradation, health risks, pollution-induced migration, and damage to aquatic ecosystems. Additionally, multiple studies (Ekpo *et al.*, 2012; Ezenwa *et al.,* 2014; Tiimub *et al.*, 2015; Nwogha *et al.*, 2017) have reported increased concentrations of heavy metals in soil and plants due to quarrying activities. Significantly higher metal concentrations in quarry dust compared to control samples in the Ashanti region of Ghana (Tiimub *et al.,* 2015) Heavy metal contamination is an increasingly serious global concern, driven by the heightened use and processing of these metals to meet the demands of a rapidly growing population. Both natural processes and human activities contribute to environmental contamination, often releasing more pollutants than ecosystems can effectively handle (Nwogha *et al.,* 2017). This can result in widespread health issues, mortality, and disruptions to food chains. While some metals are essential in trace amounts for normal bodily functions, excessive exposure can lead to toxic effects (Egorova and Ananikov, 2017). Heavy metals frequently interact with biological systems by losing electrons and forming metal cations, which bind to nucleophilic sites on vital macromolecules. The acute and chronic toxic effects of heavy metals can impact various organs, leading to gastrointestinal and kidney dysfunction, nervous system disorders, skin lesions, vascular damage, immune system impairment, birth defects, and cancer. Exposure to multiple metals simultaneously can have cumulative toxic effects (Fernandes Azevedo *et al.*, 2012; Cobbina *et al.*, 2015). In particular, high levels of exposure to mercury and lead can cause severe health complications, including abdominal pain, bloody diarrhea, and kidney failure (Bernhoft, 2012). Heavy metals such as lead, aluminum, mercury, copper, cadmium, nickel, and arsenic are first absorbed by microorganisms such as phytoplankton, bacteria, and fungi, and then enter the food chain through larger organisms. Eventually, by consuming crops grown in contaminated soils, these metals enter the human and animal food chain, posing significant health risks (Cimboláková, 2020).

2.1. Brief history of mining in Nigeria

Mechanical mining in Nigeria commenced in 1939, spearheaded by privately-owned companies (Nwogha *et al.,* 2017). Since its inception, there has been a steady increase in both health-related issues and environmental degradation resulting from mining and quarrying activities, often occurring with little to no comprehensive research to raise awareness of their detrimental impacts on human health and the environment. In regions like Akamkpa Local Government Area, mechanized quarrying has been practiced for several decades. Such activities, particularly in developing nations like Nigeria, have led to significant environmental hazards, producing vast amounts of waste and various pollutants. The long-term effects of mining, particularly quarrying, have left landscapes ravaged, while fertile lands, water sources such as wells, streams, and rivers, as well as food supplies, have become vulnerable to contamination by minerals and heavy metals (Nwogha *et al.*, 2017).

2.2. Sources of heavy metals

Several studies indicate that heavy metal pollution in the environment primarily originates from two sources: natural (geogenic) and anthropogenic. Geogenic sources refer to the naturally occurring heavy metals found in the earth's crust, which result from processes such as weathering, soil erosion, and volcanic activity (OyeyemiK *et al.,* 2018). In contrast, anthropogenic sources of heavy metal contamination arise from human activities, including mineral mining, exploration, smelting, industrial manufacturing, pharmaceutical discharges, and the use of metals and metal-containing compounds in domestic and agricultural contexts (Sayadi and Torabi, 2009).

2.3. Spatial distribution of heavy metals

The analysis of spatial distribution, identification of contamination sources, and evaluation of soil quality are particularly significant (Anake *et al.,* 2018; Patel *et al.,* 2006) . The presence of heavy metals in soil is typically affected by various environmental factors, including the type of parent rock and soil characteristics (Sarlak, 2015; De Miguel, 2007), as well as anthropogenic activities such as industrial manufacturing, transportation, and farming. Large land areas can become contaminated with heavy metals released from waste incineration, industrial effluents, and the use of fertilizers, pesticides, and sewage sludge containing heavy metals (Usikalu *et al.,* 2015; Usikalu *et al.,* 2017). When multiple contamination sources exist and their byproducts are dispersed, the spatial variation in heavy metal concentrations can help pinpoint potential contamination sources and inform remediation strategies. Evaluating environmental quality based on heavy metal concentrations in soil requires the application of various pollution indices, such as the geoaccumulation index, pollution load index, potential ecological risk index, and Nemerow index (see Supplementary Materials). Utilizing geostatistical multivariate analysis through geographic information systems (GIS) provides more insightful and precise data. In studies on soil pollution, it's important to consider the economic implications alongside sampling and analysis, as frequent and dense sampling can be impractical. To mitigate these issues, spatial interpolation techniques are employed to create maps that depict the spatial distribution of contamination. One effective geostatistical method, known as "Kriging," is currently applied to describe and predict the spatial variability of specific soil parameters and to estimate values in areas that have not been sampled (Senesil *et al.,* 1999; Imperato *et al.,* 2003; McGrath *et al.,* 2004). Traditional statistical methods require that the data adhere to several assumptions, such as having independent observations and being based on extensive and repeated sampling. Research on the environmental geochemistry of heavy metals has significantly progressed over the past few decades due to their toxic effects and persistence in the environment (Bai *et al.,* 2010; Yang *et al.,* 2011).

Recently, principal component analysis has been applied across various disciplines to investigate soil, particularly regarding heavy metal pollution. This analysis is useful because it reveals the relationships among different heavy metals across various spatial dimensions and assesses the relative significance of each metal (Goovaerts, 1992; Webster *et al.,* 1994). A common approach to characterize soil pollution is to identify concentrations that exceed the background threshold levels specific to a geological area (Chen *et al.,* 1997). Elevated levels of certain heavy metals can result from natural contamination, such as the mineralogy and chemical composition of the parent rock, or from anthropogenic sources, including agricultural practices and the discharge of wastewater from industrial and urban areas into rivers and streams.

2.4. Health impacts of heavy metals

Heavy metals can enter the human body through ingestion, skin absorption, or inhalation. These toxic metals are a significant concern for human health due to their capacity to damage cellular membranes, alter DNA structure, and interfere with protein functions and enzymatic activities. Heavy metals can infiltrate the food chain through plant uptake, contamination during food processing, or trophic transfer (Witkowska *et al.,* 2021). Although these metals occur naturally in trace amounts, they become hazardous to humans and other organisms when present in high concentrations (Shakya and Agarwal, 2020). Unlike energy, which diminishes as it progresses through trophic levels, heavy metals persist and accumulate in ecosystems, emphasizing the need for rigorous monitoring of metal concentrations in soil, particularly around quarry sites, to ensure food safety and minimize health risks, including carcinogenic effects. These metals are present in trace amounts in natural water bodies, yet many are toxic even at low concentrations. At elevated levels, both essential and non-essential heavy metals can disrupt cellular functions, compromise enzyme activity, and damage DNA integrity (Wu *et al.,* 2016).

Soil contamination by heavy metals is often a consequence of human activities such as industrialization, urbanization, and the use of sewage sludge, compost, and chemical fertilizers. Once released into the environment, these metals predominantly accumulate in the soil (Zorpas *et al.,* 2021). Heavy metal contamination can also arise from emissions in industrial zones, mining operations, waste disposal, combustion of diesel and coal, lead-based paints, agricultural practices involving fertilizers and pesticides, and atmospheric deposition (Gabarron *et al*., 2017). Unlike organic pollutants, which degrade through microbial oxidation into carbon dioxide, heavy metals do not undergo such processes, remaining in the soil for prolonged periods (Bolan and Duraisamy, 2003).

The environmental contamination by heavy metals is a growing concern, as it has been shown to cause a wide range of adverse effects on living organisms. Increased economic activities, driven by population growth and urbanization, have been associated with the rising levels of heavy metals in the environment. In many African countries, anthropogenic sources are the primary contributors to heavy metal pollution. For instance, mercury pollution is prevalent in Algeria, arsenic in Namibia and South Africa, tin in Nigeria and the Democratic Republic of Congo, and copper in Zambia, all largely resulting from mining and quarrying activities (Taylor *et al.,* 2005). Among the various anthropogenic sources, Pradhan *et al*. (2020) argue that mining and quarrying operations release the largest quantities of heavy metals into the environment. Heavy metals are primarily distributed from the bloodstream to various tissues within the body (Florea *et al.*, 2006). For instance, lead is transported by red blood cells to organs such as the liver and kidneys and is later redistributed to the teeth, bones, and hair, typically as a phosphate salt (Morais *et al.*, 2012). Cadmium initially binds to blood cells and albumin, but later attaches to metallothionein within the kidney and liver tissues. Arsenic, after being distributed to the lungs via the bloodstream, accumulates in the heart, lungs, liver, kidneys, muscles, neural tissues, and also in the skin, nails, and hair. Heavy metals like lead and zinc have been linked to a wide range of health issues, including both hematological and neurological disorders (Tchounwou, 2014). Even in trace amounts, lead poses significant health risks, as it can affect nearly every organ in the body. In excessive amounts, zinc becomes toxic, leading to reduced rates of cell division and the disruption of the processes of cell division and photosynthesis (Fisher *et al.,* 1981).

Chronic exposure to nickel and its compounds can result in serious health consequences, such as lung fibrosis, kidney and cardiovascular diseases, and cancers of the respiratory tract (Zambelli *et al.,* 2016). Another crucial aspect of chronic exposure to heavy metals is their carcinogenic potential. Although the precise mechanisms are not fully understood, it is believed that disruptions in genomic integrity and gene expression play a role. Carcinogenic metals like arsenic, cadmium, and chromium can interfere with DNA synthesis and repair processes, contributing to their toxic and carcinogenic effects (Koedrith *et al.*, 2013). The toxicity and potential for carcinogenicity of heavy metals depend on the dosage. In health risk assessments, it is essential to identify potential environmental sources of these toxic agents and estimate the level of risk they pose to individuals in contact with the environment. Additionally, determining the specific health consequences of exposure is critical (Khan *et al.,* 2015). Increased levels of arsenic in limestone negatively affect both plants and humans. Exposure to arsenic can lead to damage to vital organs, including the brain, liver, and kidneys, and is also associated with an increased risk of cancer (Srinivasa *et al.,* 2007; Anake *et al.,* 2018). Lead, which can originate from dust particles or aerosols, is highly toxic and serves as a systemic toxicant that impacts various body systems, including the neurological, hematological, gastrointestinal, reproductive, cardiovascular, and renal systems (Patel *et al.,* 2006). Elemental mercury, a widely distributed environmental toxicant, can cause numerous changes in body tissues, leading to adverse health outcomes (Sarlak, 2015). When absorbed through environmental exposure, mercury accumulates in the kidneys, neurological tissues, and liver, resulting in effects such as neurotoxicity, nephrotoxicity, and gastrointestinal issues (De Miguel *et al.,* 2007).

2.5. Effects of Heavy Metal Contamination on Plant Physiology and Nutrient Dynamics

Fruits and vegetables play a critical role in daily nutrition due to their richness in proteins, carbohydrates, vitamins, minerals, and fibers (Baghaie and Fereydoni, 2019). Diets high in fruits and vegetables are associated with numerous health benefits, including reduced blood pressure, lower risks of heart disease and stroke, prevention of certain cancers, and protection against eye and digestive issues. In light of these benefits, the World Health Organization (WHO) recommends a daily intake of at least 400 grams of fruits and vegetables (excluding starchy tubers like potatoes) (WHO, 2004). Despite their nutritional importance, vegetables are also known to absorb substantial amounts of toxic metals from the environment (Xiong, 1998; Cobb *et al*., 2000). These metals accumulate in various parts of plants, including roots, stems, fruits, grains, and leaves. Heavy metals, due to their toxicity, persistence, and non-degradability, pose a significant environmental threat, especially in urban regions (Zwolak *et al.,* 2019). Elevated levels of these metals in agricultural soils and plants largely stem from human activities such as mining, smelting, waste disposal, vehicle emissions, sewage, and the use of pesticides, herbicides, and fertilizers. The application of agrochemicals and wastewater for irrigation has been frequently cited as a primary source of metal contamination in vegetables (Mahmood and Malik, 2014; Chauhan and Chauhan, 2014). The extent of heavy metal absorption by plants depends on several factors, including the plant species and soil properties such as pH, organic matter content, moisture, temperature, and nutrient availability (Onakpa *et al.*, 2018). In addition to soil-to-plant transfer, metals can also accumulate through aerial deposition on leaf surfaces, where they become trapped by surface hairs or cuticle structures. Accumulation of heavy metals in edible plants poses severe health risks (Mahmood and Malik, 2014), including cellular damage, enzymatic disruptions, as well as neurotoxic and carcinogenic effects (Jomova *et al.,* 2011). Additionally, the presence of toxic metals in food can significantly reduce essential nutrients like vitamin C, leading to weakened immune function, impaired physiological processes, and malnutrition-related disabilities (Liu *et al*., 2005).

2.6. Exposure for average dose estimation

Body weight plays a significant role in determining the absorbed dose of contaminants per kilogram of body mass. USEPA (2011) prescribes an average body weight of 20 kg for children and 70 kg for adults, reflecting differences in metabolic rates and susceptibility to contaminants. Both children and adults are assumed to have an exposure frequency (EF) of 365 days per year, following the assumption of daily contact with contaminated media (Ferreira, 2005). However, exposure duration (ED) varies significantly, with children exposed for an average of 10 years and adults for 70 years (USEPA, 2011). This distinction accounts for the cumulative exposure period and potential lifetime risk assessment.

The ingestion of soil or dust particles is a primary exposure route, particularly for children due to hand-to-mouth activities. The USEPA (2011) estimates an ingestion rate of 200 mg/day for children and 100 mg/day for adults, highlighting the greater susceptibility of children to soil-borne contaminants. Inhalation exposure is influenced by physiological differences in respiratory rates. Children, with an estimated inhalation rate of 10 m^3/day, have lower pulmonary intake than adults, who inhale 20 m^3/day (Huang et al., 2015). These values reflect activity levels and lung capacity differences between age groups. The dermal pathway considers the exposed skin surface area (SA) and the soil adherence factor (SAF). Children have an estimated SA of 2800 cm^2, whereas adults have a larger surface area of 3300 cm^2 (USEPA, 2011). The soil adherence factor, representing the amount of soil retained per unit skin area, remains constant at 0.2 mg/cm^2 for both groups (USEPA, 2011). The dermal absorption factor (ABS) accounts for the fraction of contaminants that penetrate the skin upon contact. A value of 0.001 is assigned to both children and adults, indicating minimal dermal absorption of most contaminants (Du *et al*., 2013). The exposure duration is converted into total exposure time by multiplying ED by 365 days, ensuring consistency in risk assessment calculations (USEPA, 2011). The particle emission factor (PEF), which represents the resuspension of soil particles into the air, is estimated at 1.316×10^{-9} m^3/kg, reflecting the atmospheric dispersion of contaminants (USEPA, 2011). The combination of these parameters provides a comprehensive framework for assessing exposure risks to contaminants, particularly in soil environments. Children, due to their lower body weight, higher ingestion rates, and increased susceptibility to toxic effects, are at greater risk of adverse health outcomes compared to adults. Therefore, regulatory guidelines emphasize protective measures and risk assessments tailored to vulnerable populations (USEPA, 2011; Ferreira, 2005; Huang *et al.*, 2015; Du *et al.*, 2013).

2.7. Reference dose (RFD) (Mg/kg/day) of heavy metals via ingestion, inhalation and dermal Exposure route

Lead (Pb) and Cadmium (Cd) are of particular concern due to their relatively low RFD values, especially for dermal exposure, with Pb having a RFD dermal of 0.000525, indicating its potential to cause significant health impacts even at low exposure levels (Zheng *et al.*, 2020). Inhalation exposure to Pb and Cd is also notable, with RFD Inhalation values of 0.0035 and 0.001 respectively, highlighting potential respiratory health risks. For Cadmium (Cd), the CSF value of 1.7 further indicates the carcinogenic potential, with the metal's ingestion and inhalation routes warranting close attention in risk assessment frameworks (Muirhead *et al.*, 2015). Nickel (Ni), with an RFD Inhalation of 0.025 and CSF of 0.5, also presents significant carcinogenic risks, particularly through ingestion and dermal exposure. Metals such as Iron (Fe) and Copper (Cu), which exhibit comparatively higher RFD values, suggest lower immediate risk through these pathways, though prolonged exposure could still have cumulative health effects (Muirhead *et al*., 2015).

CHAPTER THREE
MATERIALS AND METHOD

3.1. REGIONAL GEOLOGY

Ikpeshi, located in the Akoko-Edo Local Government Area of Edo State, Nigeria, lies within the southwestern section of the Nigerian Basement Complex, which is a part of the broader Pan-African mobile belt, a geological zone formed through the amalgamation of the West African Craton and the Congo Craton. The geology of this region is characterized by a complex sequence of Precambrian crystalline rocks, typical of the Nigerian Basement Complex, and sedimentary formations from the Cretaceous period. The Nigerian Basement Complex is composed predominantly of migmatite-gneiss, quartzites, schists, and granitic intrusions, formed through various tectonothermal events. These rocks were subjected to polycyclic metamorphism, tectonic deformation, and magmatic intrusions, particularly during the Pan-African orogeny, approximately 600 million years ago. The rocks in the Ikpeshi area, specifically, consist of a combination of the Precambrian Basement Complex and sedimentary rocks of Cretaceous age. The Precambrian rocks are primarily schists, granites, and gneisses, while the sedimentary formations, which belong to the Anambra Basin, consist of limestone, marble, and shale deposits (Sanni *et al.,* 2023).

3.2. LITHOLOGIC UNITS

3.2.1 Migmatite-Gneiss Complex: This forms the oldest and most extensive rock unit in the area. The migmatite-gneiss complex, as in many parts of southwestern Nigeria, consists of banded gneisses and migmatites, characterized by alternating felsic and mafic mineral bands. These rocks are the result of high-grade metamorphism and partial melting, associated with the Pan-African tectonothermal events (Rahaman, 1988).

3.2.2 Granite and Granitic Gneisses: Granitic intrusions within the migmatite-gneiss complex are common in Ikpeshi, forming massive outcrops in some parts. These rocks are typically coarse-grained and made up of quartz, feldspar, and biotite, with some occurrences of hornblende. The granitic intrusions are linked to Pan-African tectonic activities that caused extensive reworking and emplacement of granitic bodies within the Nigerian Basement Complex (Oyewole and Ofuyah, 2017).

3.2.3 Schists: Schists in the Ikpeshi area are part of the metasedimentary assemblages and consist mainly of muscovite and biotite schists. These rocks represent medium-grade metamorphic rocks derived from shale and siltstone precursors, which were deformed and metamorphosed during the Pan-African orogeny. Schists in this area also contain important mineral resources, such as quartz veins, which have been explored for their economic value (Oyewole and Ofuyah, 2017).

3.2.4. Cretaceous Sedimentary Formations: Overlying the crystalline basement rocks in some parts of Ikpeshi are sedimentary units, primarily limestone and marble, which belong to the southern extension of the Anambra Basin. The Cretaceous limestone and marble deposits in Ikpeshi are of high quality and form the basis of the local cement and marble industries (Sanni *et al*., 2023).

3.3. MINERAL DEPOSITS

Limestone and Marble: The Cretaceous limestone and marble deposits in Ikpeshi are of high purity and have been extensively exploited for the production of cement and other construction materials. These carbonate rocks are the primary economic driver in the region, attracting both local and foreign investors.

3.3.1. Quartz and Feldspar: Quartz veins and pegmatites associated with the granite and schist formations are an important source of industrial minerals. Quartz is utilized in the glass and ceramics industries, while feldspar is used in the production of ceramics and as a flux in the glass-making process.

3.3.2. Kaolin and Clay Deposits: In addition to quartz veins, the area is distinguished by its significant deposits of clay and kaolin, which have a broad range of applications. Their notable properties, including swelling capacity, adsorption, ion exchange, and large surface area, make them valuable for various purposes. These materials are employed in geophagy, contemporary pottery, construction, water purification, as well as in the manufacture of ceramics and bricks (Oyedoh *et al.,* 2023).

3.4. LOCAL GEOLOGY

The study area, Ikpeshi and its environs, is located within the southwestern part of the Nigerian Basement Complex. The study area is positioned approximately between latitudes 7°07'59"N and longitudes 6°12'25"E and is part of Igarra schist belt of southwestern Nigeria. The region is characterized by basement rocks, including the Migmatite Complex, Gneiss, and Schist. Overlying the crystalline basement rocks in some parts of Ikpeshi are sedimentary units, primarily limestone and marble which make up part of the mineral resources, alongside Quartz, Feldspar and clay minerals (Sanni *et al*., 2023).

3.5. MATERIALS

1. Soil sampling equipment

2. GPS device

3. Sample containers

4. Deionized water

5. PPE

6. Acid-washed polyethylene bags

7. Laboratory reagents (Nitric acid, Hydrogen peroxide)

8. Atomic Absorption Spectrophotometer (AAS)

9. pH meter

10. Analytical balance

11. Digestion apparatus

12. Data analysis software

13. Statistical software (SPSS)

14. Carcinogenic and non-carcinogenic risk assessment models (USEPA risk models)

3.6. METHOD

3.6.1 Sample collection

Soil samples were gathered from four different locations surrounding the quarry sites. The first location (MS1), serving as the control, was situated away from the quarry. The second location (MS2) was directly within the quarry (0m), while the third (MS3) and fourth (MS4) locations were positioned 100m and 200m from the quarry, respectively. At each site (0m, 100m, 200m, and the control), 50g of soil was sampled using a hand auger from a depth of about 0–15 cm and placed in clean polyethylene bags for further testing. In the lab, the samples were air-dried, sieved to pass through a mesh of less than 0.25 mm, and heated in an electric oven at approximately 40°C for 30 minutes. The fine powder produced was stored in desiccators before the heavy metal analysis.

3.6.2. Determination of heavy metal concentration at study site

The levels of Lead (Pb), Chromium (Cr), Copper (Cu), Cadmium (Cd), Cobalt (Co), Nickel (Ni), Vanadium (V), Zinc (Zn), Selenium (Se), and Arsenic (As) were measured using atomic absorption spectrophotometry (AAS) as outlined by (Itam *et al.,* 2024). Several indices were employed to evaluate the present pollution levels, along with the assessment of both carcinogenic and non-carcinogenic risks, using the models specified below.

3.6.3. Pollution indices

The pollution indicators applied in this study to assess soil contamination included the contamination factor (Cf), degree of contamination (Cd), geo-accumulation index (Igeo), and pollution load index (PLI).

3.6.4. Contamination factor (Cf)

The contamination factor for the site was calculated using the formula outlined by (Hakanson, 1980).

$$C_f = \frac{C_{metal}}{C_{backgrund}}$$

Where: Cf = contamination factor, Cf < 1 = low contamination factor, Cf ≤1<3 = Moderate contamination factor, 3≤ Cf < 6 = considerable contamination factor, Cf ≥ 6 = Very high contamination factor.

3.6.5. Degree of contamination (Cd)

The degree of contamination (Cd) was calculated following the method proposed by Hakanson (1980), using the equation provided below.

$$C_d = \sum_{i=1}^{n} C_f$$

Where: Cd<7 = low degree of contamination, 7≤Cd<14 = moderate degree of contamination, 14 ≤ Cd < 28 = considerable degree of contamination, Cd ≥28 = very high degree of contamination.

3.6.6. Pollution load index (PLI)

The pollution load index (PLI) for the heavy metals analyzed in this study was determined using the formula described by (Tomlinson *et al*., 1980), as shown below.

$$PLI = (CF_1 \text{ x } CF_2 \text{ x } CF_3 \text{ x} \ldots \text{x } CF_n)^{1/n}$$

Where: PLI<1 = No metal pollution, PLI = 1 = Baseline levels of pollutants, PLI >1= indicates a polluted condition.

3.6.7. Geo-accumulation index (Igeo)

The geo-accumulation index (Igeo) was computed following the method outlined by (Muller,

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 * B_n}\right)$$

1969).

The variable Cn represents the measured concentration of the metal n in the soil, while Bn denotes the reference or geochemical background concentration of metal n (mg/kg) in the soil. A factor of 1.5 is applied to account for possible variations in background values and minor anthropogenic influences. The geo-accumulation index (Igeo) is classified as follows:

Class 0: Igeo < 0 = practically uncontaminated, Class 1: 0 < Igeo < 1 = uncontaminated to moderately contaminated, Class 2: 1 < Igeo < 2 = moderately contaminated, Class 3: 2 < Igeo < 3

= moderately to heavily contaminated, Class 4: 3 < Igeo < 4 = heavily contaminated, Class 5: 4 < Igeo < 5 = heavily to extremely contaminated, Class 6: Igeo > 5 = extremely contaminated.

3.6.8. Ecological risk factors and index

The ecological risk factor for the control soil (i.e., soil from outside the quarry site) and soils collected at 0m, 100m, and 200m from the quarry site was calculated following the method proposed by (Hakanson, 1980).

$$Er = TR \times CF$$

$$RI = \sum_{i=1}^{n} E_r$$

Where: Er = ecological risk factor, TR = toxicity of heavy metals, CF = pollution factor, RI = ecological risk index, RI< 150 <300 = low risk, 150 ≤ RI = moderate Risk, 300≤ RI <600 = considerable risk, IR ≥600 = very high risk.

3.6.9. Human health risk assessment of heavy metals in quarry site; determination of the average daily dose

The average daily dose was calculated by taking into account the different exposure pathways for humans, including ingestion, inhalation, and dermal absorption. The assessment aimed to evaluate both the carcinogenic and non-carcinogenic risks associated with exposure to heavy metals, following the methodology outlined by (Zglobicki and Telecka, 2021). The risk was quantified using the equations provided below:

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

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

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

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

Where C = the Concentration of metal (e.g. µg/kg, mg/kg); Ring = ingestion rate, Rinh = 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).

3.6.10. Determination of the hazard quotient (HQ) and index (HI) or non-carcinogenic risk

This assessment measures the risks linked to exposure to non-carcinogenic substances. The hazard quotient (HQ) is calculated as the ratio of exposure to the oral reference dose (RFD) in mg/kg/day; if the HQ exceeds one, it indicates a potential for adverse health effects from the substance in question. The USEPA Region 3 provides guidelines for using HQ to estimate risks. Additionally,

$$HQ = \frac{ADD}{RfD} \quad (4)$$

the hazard index (HI) is used to evaluate the overall risk associated with exposure to the total heavy metals present in the samples. Developed by the USEPA, the HI is computed by summing the individual HQ values for all the heavy metals analysed.

HQ represents the hazard quotient, with specific components defined as follows: HQinh is the hazard quotient for inhalation, HQing is the hazard quotient for ingestion, HQdem is the hazard quotient for dermal absorption, and HQt is the total summation of hazard quotients from all exposure routes. The hazard index (HI) summarizes these risks. An HQ value greater than 1 indicates a potential for health effects, while an HQ value less than 1 suggests no possibility of health effects. Similarly, an HI value of less than 1 indicates a very low risk, an HI between 1 and 4 suggests that risk effects are possible, and HI values exceeding 4 indicate a high risk level.

3.6.11. Carcinogenic risk assessment

The carcinogenic risk (CR) was assessed following the methodologies outlined by (Maeaba *et al*., 2019) to evaluate the likelihood of developing cancer from exposure to heavy metals such as arsenic (As), nickel (Ni), lead (Pb), cadmium (Cd), cobalt (Co), and chromium (Cr). The equations

$$CR = ADD \times SF \quad (1)$$

Where CR = cancer risk. ADD = average daily dose and SF = cancer slope factor

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

provided below were utilized to estimate the carcinogenic risk for each exposure pathway.

Where TCR, CR, and SF represent total carcinogenic risk (no unit), carcinogenic risk (no unit), and slope factor for carcinogenic potentially toxic elements (PTEs) (mg/kg/d), respectively. Safe TCR values should fall within the range of 1×10^{-6} to 1×10^{-4}, which indicates an acceptable standard reflecting no significant risk to human health (Itam *et al.,* 2024). Conversely, values equal to or less than 1×10^{-3} suggest a potential for cancer development.

3.6.12. Statistical analysis

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

CHAPTER FOUR

PRESENTATION OF RESULTS

The results of the physicochemical and heavy metal analysis of soil samples at a depth of 0-15 cm across the study area are presented in Table 4.1- 4.10. The concentrations of Fe, Zn, Cu, Pb, Cd, Mn, Ni, Cr, and Co were analyzed, alongside physicochemical parameters such as pH, electrical conductivity (EC), organic carbon (OC), and organic matter (OM). These values were compared against international standards, including the World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA), to assess the potential health and environmental risks posed by heavy metal contamination.

Table 4.1: Physicochemical and Heavy Metal Parameters of Soil Samples (0-15 cm Depth)

(mg/kg)

Parameter	Min Conc	Max Conc	Mean Conc	Standard Error (±)	Control Sample	WHO Limit	EPA Limit
Fe	317.875	839.08	412.884	14.56	162.98	-	-
Zn	27.225	97.455	40.652	3.21	13.03	300	200
Cu	18.205	67.74	28.348	2.67	8.48	36	30
Pb	1.105	5.755	2.163	0.32	0.625	85	50
Cd	0.5	2.01	1.041	0.14	0.315	3	2
Mn	4.03	14.3	7.544	0.87	1.46	-	-
Ni	6.86	18.41	12.550	1.02	2.29	35	25
Cr	5.16	12.075	9.169	0.94	2.455	100	70
Co	3.86	13.845	7.182	1.11	2.09	-	-
pH	5.4	7.78	6.796	0.32	-	5.5-7.5	6.5-8.5
EC (μS/cm)	751	13531.5	2875.05	123.45	-	-	-
OC (%)	1.95	6.91	4.32	0.67	-	-	-
OM (%)	2.41	12.9	7.05	0.89	-	-	-

Table 4.2. Exposure parameters for average dose estimation.

PARAMETERS	CHILDREN	ADULTS	Unit	REFERENCE
Body weight (BW)	**20**	**70**	**Kg**	**USEPA, 2011**
Exposure frequency (EF)	**365**	**365**	**Days/year**	**Ferreira, 2005**
Exposure duration (ED)	**10**	**70**	**Year**	**USEPA, 2011**
Ingestion rate (IR)	**200**	**100**	**mg/day**	**USEPA, 2011**
Inhalation rate	**10**	**20**	**m^3/day**	**Huang et al., 2015**
Skin surface area (SA)	**2800**	**3300**	**cm^3**	**USEPA, 2011**
Soil adherence factor (SAF)	**0.2**	**0.2**	**mg/cm^3**	**USEPA 2011**
Dermal Absorption factor (ABS)	**0.001**	**0.001**	**None**	**Du, et al., 2013**
Average time (AT)	**ED × 365**			**USEPA, 2011**
Particle emission factor (PEF)	**1.316×10^{-9}**		**m^3/kg**	**USEPA, 2011**

Table 4.3. Reference dose (RFD) (Mg/kg/day) of Heavy Metals via ingestion, inhalation and dermal Exposure route used for non-carcinogenic health risk Assessment and cancer slope factor (CSF) used for carcinogenic health risk Assessment. (Jin *et al*., 2023; Huang, *et al.*, 2022; Kamuda, *et al.*, 2016).

Heavy metal	Pb	Zn	Cu	Fe	Cd	Mn	Ni	Cr
RFD Inhalation	0.0035	0.35	0.045	0.8	0.001	0.0014	0.025	0.00003
RFD Ingestion	0.0035	0.3	0.04	0.7	0.001	0.024	0.02	1.5
RFD dermal	0.000525	0.3	0.04	0.7	0.00001	0.00096	0.02	0.003
CSF	0.0085	-			0.38		1.7	0.5

Table 4.4. Summary of the carcinogenic and Non-carcinogenic health risk for selected heavy metals in soil within Ikpeshi for children via ingestion.

METALS	CDI(children)	HQ	CR
Fe	4.14×10^{-3}	5.86×10^{-3}	-
Zn	4.10×10^{-4}	1.36×10^{-3}	-
Cu	2.83×10^{-4}	7.07×10^{-3}	-
Pb	2.16×10^{-5}	6.18×10^{-3}	1.83×10^{-7}
Cd	1.04×10^{-5}	1.04×10^{-2}	3.95×10^{-6}
Mn	7.5×10^{-5}	3.12×10^{-3}	-
Ni	1.25×10^{-4}	6.27×10^{-3}	2.13×10^{-4}
Cr	9.16×10^{-5}	6.10×10^{-5}	4.58×10^{-5}
Co	7.18×10^{-5}	3.59×10^{-3}	-
		$\sum HQ = 0.13745$	

Table 4.5. Summary of the carcinogenic and non-carcinogenic health risk for selected heavy metals in soil within Ikpeshi for Adults via ingestion.

METALS	CDI (Adults)	HQ	CR
Fe	5.89×10^{-4}	8.41×10^{-4}	-
Zn	5.80×10^{-5}	1.93×10^{-4}	-
Cu	4.04×10^{-5}	1.01×10^{-3}	-
Pb	3.09×10^{-6}	8.83×10^{-4}	2.62×10^{-8}
Cd	1.48×10^{-6}	1.48×10^{-3}	5.65×10^{-7}
Mn	1.07×10^{-5}	4.48×10^{-4}	-
Ni	1.79×10^{-5}	8.95×10^{-4}	3.04×10^{-5}
Cr	1.31×10^{-5}	8.73×10^{-6}	6.54×10^{-6}
Co.	1.02×10^{-5}	5.1×10^{-4}	-
		$\sum HQ = 0.02417$	

Table 4.6. The Hazard quotient (HQ) and the carcinogenic risk (CR) was computed for children through dermal Exposure route.

METALS	CDI (children)	HQ	CR
Fe	1.150×10^{-5}	1.65×10^{-5}	-
Zn	1.138×10^{-6}	3.79×10^{-6}	-
Cu	7.93×10^{-7}	1.98×10^{-5}	-
Pb	6.056×10^{-8}	1.15×10^{-4}	5.14×10^{-10}
Cd	2.91×10^{-8}	2.91×10^{-2}	1.105×10^{-8}
Mn	2.11×10^{-7}	2.20×10^{-4}	-
Ni	3.51×10^{-7}	1.75×10^{-5}	5.967×10^{-7}
Cr	2.56×10^{-7}	8.53×10^{-5}	1.28×10^{-7}
Co	2.01×10^{-7}	0.03528	-
		$\sum HQ=0.06485$	

Table 4.7. The hazard quotient (HQ) and the carcinogenic risk (CR) was computed for Adults through dermal Exposure route.

METALS	CDI (Adults)	HQ	CR
Fe	3.89×10^{-6}	5.56×10^{-6}	-
Zn	3.83×10^{-7}	1.277×10^{-6}	-
Cu	2.67×10^{-7}	6.68×10^{-6}	-
Pb	2.03×10^{-8}	3.88×10^{-5}	1.73×10^{-10}
Cd	9.81×10^{-9}	9.81×10^{-4}	3.72×10^{-9}
Mn	7.11×10^{-8}	7.40×10^{-5}	-
Ni	1.183×10^{-7}	5.91×10^{-6}	2.01×10^{-7}
Cr	8.64×10^{-8}	2.88×10^{-5}	4.32×10^{-8}
Co	6.77×10^{-8}	0.01188	-
		∑HQ= 0.01302	

Table 4.8. Summary of the hazard quotient and carcinogenic risk for Children through inhalation route

METALS	CDI (Children)	HQ	CR
Fe	1.569×10^{-5}	1.96×10^{-5}	-
Zn	1.54×10^{-6}	4.41×10^{-6}	-
Cu	1.077×10^{-6}	2.39×10^{-5}	-
Pb	8.22×10^{-8}	2.34×10^{-5}	6.99×10^{-10}
Cd	3.95×10^{-8}	3.95×10^{-5}	1.50×10^{-8}
Mn	2.86×10^{-7}	2.04×10^{-4}	-
Ni	4.77×10^{-7}	1.90×10^{-5}	8.11×10^{-7}
Cr	3.48×10^{-7}	0.01162	1.74×10^{-7}
Co	2.73×10^{-7}	0.04790	-
		∑HQ = 0.05985	

Table 4.9. Summary of the hazard quotient and carcinogenic risk for Adults through inhalation route.

METALS	CDI (Adults)	HQ	CR
Fe	8.96×10^{-6}	1.12×10^{-5}	-
Zn	8.82×10^{-7}	2.52×10^{-6}	-
Cu	6.15×10^{-7}	1.36×10^{-5}	-
Pb	4.49×10^{-8}	1.34×10^{-5}	3.99×10^{-10}
Cd	2.26×10^{-8}	2.26×10^{-5}	8.59×10^{-9}
Mn	1.638×10^{-7}	1.17×10^{-4}	-
Ni	2.72×10^{-7}	1.09×10^{-5}	4.63×10^{-7}
Cr	1.99×10^{-7}	0.00663	9.95×10^{-8}
Co	1.55×10^{-7}	0.0273	-
		$\sum HQ = 0.03412$	

Table 4.10. Summary of the Harzard index and the total Carcinogenic risk (TCR) through all exposure routes (ingestion, dermal and inhalation) for both children and Adults.

METALS	HI (children)	TCR (Children)	HI (Adults)	TCR (Adults)
Fe	5.89×10^{-3}	-	8.57×10^{-4}	-
Zn	1.368×10^{-3}	-	1.97×10^{-4}	-
Cu	7.11×10^{-3}	-	1.03×10^{-3}	-
Pb	6.30×10^{-3}	1.84×10^{-7}	9.35×10^{-4}	2.68×10^{-8}
Cd	3.95×10^{-2}	3.97×10^{-6}	2.48×10^{-3}	5.77×10^{-7}
Mn	3.55×10^{-3}	-	6.39×10^{-4}	-
Ni	6.30×10^{-3}	2.14×10^{-4}	9.11×10^{-4}	3.10×10^{-5}
Cr	1.176×10^{-2}	4.61×10^{-5}	6.67×10^{-3}	6.68×10^{-6}
Co	0.08675	-	0.03969	-

CHAPTER FIVE

DISCUSSION AND CONCLUSION

5.1. Heavy Metal Analysis

Soil pH is a fundamental physicochemical parameter that influences nutrient availability, microbial activity, and the mobility of heavy metals, thereby affecting soil quality and environmental sustainability (Brady and Weil, 2016). The pH of the soil samples ranged from 5.4 to 7.78, with a mean value of 6.796 and a standard error of ±0.32, indicating a predominantly slightly acidic to neutral condition. Compared to regulatory standards, the observed values align with the EPA limit of 6.5–8.5 and the WHO permissible range of 5.5–7.5, except for the lower bound of 5.4, which suggests localized acidity (WHO, 2017; USEPA, 2012). Soil acidity is particularly significant in heavy metal-contaminated environments, as it enhances the solubility and bioavailability of toxic metals such as Fe, Zn, and Cd, thereby increasing their environmental risks (Kabata-Pendias and Mukherjee, 2007). Conversely, near-neutral to slightly alkaline pH levels, as observed in some samples, may favor metal precipitation and adsorption onto soil colloids, reducing their mobility and potential uptake by plants (Alloway, 2013).

Iron (Fe) concentrations ranged from 317.875 to 839.08 mg/kg, with a mean of 412.884 mg/kg, exceeding the control sample value of 162.98 mg/kg, and while Fe is essential for plants, excessive levels can induce oxidative stress and disrupt soil microbial activity, with high concentrations often linked to industrial activities and ecological risks (Aluko *et al.*, 2018). Zinc (Zn) ranged from 27.225 to 97.455 mg/kg, with a mean of 40.652 mg/kg, remaining below the WHO (300 mg/kg) and EPA (200 mg/kg) limits, though excessive Zn can be toxic to plants and humans, particularly in areas near metal scrap recycling (Onanuga *et al.,* 2023). Copper (Cu) levels varied from 18.205 to 67.74 mg/kg, with a mean of 28.348 mg/kg, below the WHO (36 mg/kg) and EPA (30 mg/kg) limits, but excessive Cu can lead to plant toxicity and human health issues, often linked to industrial activities (Abdullahi *et al.,* 2021). Lead (Pb) ranged from 1.105 to 5.755 mg/kg, with a mean of 2.163 mg/kg, well below the WHO (85 mg/kg) and EPA (50 mg/kg) limits, yet even low Pb levels pose neurological and developmental risks, particularly for children, with contamination often presenting significant health concerns (Lawal *et al.,* 2017). Cadmium (Cd) ranged from 0.5 to 2.01 mg/kg, with a mean of 1.041 mg/kg, below the WHO (3 mg/kg) and EPA (2 mg/kg) limits, though as a known carcinogen, prolonged Cd exposure can cause kidney damage and bone disorders, primarily resulting from industrial contamination (Aluko *et al.,* 2018). Manganese (Mn) concentrations varied from 4.03 to 14.3 mg/kg, with a mean of 7.544 mg/kg, and while essential for plant and human health, excessive Mn exposure is linked to neurological effects, particularly when elevated due to industrial emissions (Onanuga *et al.,* 2023). Nickel (Ni) levels ranged from 6.86 to 18.41 mg/kg, with a mean of 12.550 mg/kg, below the WHO (35 mg/kg) and EPA (25 mg/kg) limits, though Ni exposure is associated with respiratory and carcinogenic risks, often stemming from industrial pollution (Abdullahi *et al.*, 2021). Chromium (Cr) concentrations ranged from 5.16 to 12.075 mg/kg, with a mean of 9.169 mg/kg, below the WHO (100 mg/kg) and EPA (70 mg/kg) limits, though the toxicity of Cr depends on its oxidation state, with hexavalent chromium (Cr^{6+}) being highly carcinogenic and industrial activities contributing to its presence in soil (Aluko *et al.*, 2018). Cobalt (Co) ranged from 3.86 to 13.845 mg/kg, with a mean of 7.182 mg/kg, and while essential in trace amounts, excessive Co exposure can have cardiotoxic and mutagenic effects, with elevated levels typically linked to industrial pollution (Abdullahi *et al.*, 2021).

5.2. Carcinogenic and Non-Carcinogenic Health Risks of Heavy Metals in Children via Ingestion

The CDI values reflect the estimated exposure of children to heavy metals via soil ingestion, measured in mg/kg/day. Among the metals analyzed, iron (Fe) exhibits the highest CDI at **4.14×10^{-3}**, followed by zinc (Zn) at **4.10×10^{-4}**, and copper (Cu) at **2.83×10^{-4}**. The lowest CDI is recorded for cadmium (Cd) at **1.04×10^{-5}**, indicating minimal exposure compared to other metals.

The hazard quotient (HQ) is used to assess potential non-carcinogenic health risks. An HQ value greater than 1 suggests a potential for adverse health effects (USEPA, 2011). In the present study, none of the individual heavy metals exceed this threshold. However, cadmium (Cd) presents the highest HQ at **1.04×10^{-2}**, followed by copper (Cu) at **7.07×10^{-3}** and lead (Pb) at **6.18×10^{-3}**. The cumulative hazard index (**$\sum HQ$**) for all metals is 0.13745, remaining below the safety threshold, suggesting that non-carcinogenic risks via ingestion are relatively low for children in the study area.

The cancer risk (CR) values estimate the probability of developing cancer over a lifetime due to exposure to carcinogenic heavy metals. According to the USEPA (2001) guidelines, acceptable cancer risk levels range between **10^{-6}** and **10^{-4}**. Among the metals analyzed, nickel (Ni) presents the highest CR value at **2.13×10^{-4},** which falls at the upper boundary of the acceptable risk range, indicating potential concerns for long-term exposure. Chromium (Cr) follows with a CR of **4.58×10^{-5},** while cadmium (Cd) and lead (Pb) exhibit lower CR values of **3.95×10^{-6}** and **1.83×10^{-7}** respectively. The presence of carcinogenic metals, particularly nickel and chromium, warrants further environmental and health monitoring to mitigate long-term exposure risks.

5.3. Carcinogenic and Non-Carcinogenic Health Risks of Heavy Metals in Adults via Ingestion

The CDI values indicate the estimated intake of heavy metals through soil ingestion (mg/kg/day). Among the analyzed metals, iron (Fe) exhibits the highest CDI at **5.89×10^{-4},** followed by zinc (Zn) at **5.80×10^{-5}** and copper (Cu) at **4.04×10^{-5}.** The lowest CDI is observed for cadmium (Cd) at **1.48×10^{-6}**, suggesting minimal exposure to this metal in comparison to others. However, even at low concentrations, certain metals, such as cadmium, are of concern due to their high toxicity and bioaccumulation potential (USEPA, 2011).

The HQ values represent the potential for non-carcinogenic health effects, with HQ > 1 indicating a possible health risk (USEPA, 2011). In this study, none of the individual metals exceed the threshold, implying that non-carcinogenic risks from soil ingestion remain within acceptable limits. However, cadmium (Cd) presents the highest HQ at **1.48×10^{-3}**, followed by copper (Cu) at **1.01×10^{-3}** and lead (Pb) at **8.83×10^{-4}**. The cumulative hazard quotient (∑HQ) for all metals is 0.02417, significantly below the safety limit, suggesting minimal immediate health risks for adults in the study area.

The carcinogenic risk (CR) values estimate the probability of developing cancer over a lifetime due to exposure to carcinogenic metals. According to USEPA (2001) guidelines, acceptable risk levels range from **10^{-6}** and **10^{-4}**. In this study, nickel (Ni) presents the highest CR value at **3.04×10^{-5}**, indicating a potential concern for long-term exposure. Chromium (Cr) follows with a CR of **6.54×10^{-6}**, while cadmium (Cd) and lead (Pb) exhibit lower CR values of **5.65×10^{-7} and 2.62×10^{-8}**, respectively. Although none of these values exceed the upper risk threshold of 10^{-4}, the presence of Ni and Cr within the acceptable range suggests that continuous exposure could pose long-term health risks (USEPA, 2011).

5.4. The Hazard Quotient (HQ) And The Carcinogenic risk (CR) for Children through Dermal Exposure

Among the metals analyzed, lead (Pb) stands out with the highest HQ value (1.15×10^{-4}), which suggests a significant non-carcinogenic health risk through dermal absorption, a finding consistent with established concerns regarding lead exposure in children, known for its neurotoxic effects (Zheng *et al.,* 2020). Similarly, nickel (Ni) and chromium (Cr) present noteworthy HQ values of 1.755×10^{-5} and 8.53×10^{-5}, respectively, indicating a potential health risk from prolonged dermal exposure, especially considering their toxicity at high concentrations (Muirhead *et al*., 2015). Notably, cobalt (Co) exhibits a particularly high HQ of 0.03526, highlighting its potential to cause health hazards even at lower concentrations, emphasizing the importance of monitoring exposure levels in vulnerable populations. On the other hand, iron (Fe), zinc (Zn), and copper (Cu) show relatively lower HQ values, indicating that while they contribute to CDI, they pose minimal health risks through dermal exposure under typical conditions. The CR values for Pb, Ni, and Cr indicate a potential for carcinogenic effects, although at relatively low levels, necessitating caution in environments where children may be exposed to contaminated materials. These results underscore the critical need for a comprehensive risk assessment framework that incorporates dermal exposure pathways, particularly in residential areas, playgrounds, and other environments where children may come into direct contact with contaminated surfaces (Muirhead *et al*., 2015; Zheng *et al.,* 2020).

5.5. The Hazard Quotient (HQ) And The Carcinogenic Risk (CR) For Adults Through Dermal Exposure

The dermal exposure risk assessment for adults, based on the Chronic Daily Intake (CDI) values, further highlights the potential health risks of heavy metals through skin contact. Iron (Fe) exhibited a CDI of 3.89×10^{-6} mg/kg/day, resulting in a Hazard Quotient (HQ) of 5.55×10^{-6}, which suggests a minimal risk of non-carcinogenic health effects (USEPA, 2011). Zinc (Zn) had a CDI of 3.83×10^{-7} mg/kg/day and an HQ of 1.277×10^{-6}, indicating negligible non-carcinogenic risks. Copper (Cu), with a CDI of 2.67×10^{-7} mg/kg/day and an HQ of 6.68×10^{-6}, also suggests a minimal risk of adverse health effects (WHO, 2018). Lead (Pb), which has been associated with both non-carcinogenic and carcinogenic risks, showed a CDI of 2.03×10^{-8} mg/kg/day and an HQ of 3.88×10^{-5}, indicating a significant non-carcinogenic risk, with a Cancer Risk (CR) of 1.72 × 10^-10, suggesting an extremely low cancer risk (ATSDR, 2019). Cadmium (Cd) exhibited a CDI of 9.81×10^{-9} mg/kg/day, an HQ of 1.96×10^{-6}, and a CR of 3.72×10^{-7}, suggesting both non-carcinogenic and low carcinogenic risks (ATSDR, 2021). Manganese (Mn) showed a CDI of 7.11×10^{-8} mg/kg/day and an HQ of 7.40×10^{-5}, indicating a much higher potential for non-carcinogenic effects through dermal contact. Nickel (Ni) with a CDI of 1.18×10^{-7} mg/kg/day, an HQ of 5.91×10^{-6}, and a CR of 2.01×10^{-9}, points to a very low risk of both non-carcinogenic and carcinogenic health effects. Chromium (Cr) exhibited a CDI of 8.64×10^{-8} mg/kg/day and an HQ of 2.88×10^{-5}, indicating a significant non-carcinogenic risk, while its CR of 4.32×10^{-7} suggests a potential low carcinogenic risk (Zhao *et al.,* 2020). Cobalt (Co) had a CDI of 6.77×10^{-8} mg/kg/day and an HQ of 0.01188, signifying a non-carcinogenic risk based on dermal exposure levels (Zhao *et al*., 2020).

5.6. Carcinogenic Risk For Children Through Inhalation Route

The inhalation risk assessment for shows that metals such as **iron (Fe),** with a **Hazard Quotient (HQ)** of **1.96×10^{-5},** and **zinc (Zn),** with a **HQ** of **4.41×10^{-6}**, pose minimal non-carcinogenic risk, as their HQ values are well below the threshold of 1 (USEPA, 2011). **Copper (Cu),** with an **HQ** of **2.39×10^{-5}**, also indicates low risk, though it is slightly higher than that of iron and zinc (ATSDR, 2019). **Lead (Pb)**, with a **HQ** of **2.34×10^{-5},** similarly does not exceed the risk threshold, but despite its low non-carcinogenic risk, lead is a known neurotoxin, and even small amounts can adversely affect children's cognitive development (ATSDR, 2019). The **Cancer Risk (CR)** for lead is **6.98×10^{-10},** reflecting a low carcinogenic risk over long-term exposure (ATSDR, 2019). **Cadmium (Cd)** shows a **CR** of **1.50×10^{-8}**, indicating a potential carcinogenic risk, though its **HQ** is not available (WHO, 2018). **Manganese (Mn), nickel (Ni)**, and **chromium (Cr)** exhibit varying levels of risk, with **chromium** having an **HQ** of **0.01162**, which exceeds the threshold of 1, suggesting a significant non-carcinogenic risk through inhalation (Zhao *et al.,* 2020). **Nickel** presents a **CR** of **8.11×10^{-7},** suggesting a low but notable carcinogenic risk (Agency for Toxic Substances and Disease Registry [ATSDR], 2021). **Cobalt (Co),** with an **HQ** of **0.04790**, presents a potential non-carcinogenic risk, although the **CR** is not provided in this dataset. Overall, while metals like **iron, zinc,** and **copper** show little threat, metals like **chromium** and **cobalt** are of concern due to their higher toxicity and carcinogenic potential, especially for children living near quarry sites (USEPA, 2011; ATSDR, 2019; Zhao *et al*., 2020).

5.7. Carcinogenic risk for Adults Through Inhalation Route

The assessment of potential health risks from heavy metals in the inhalation pathway for adults reveals significant insights into exposure levels and the associated risks. The Chronic Daily Intake (CDI) for iron (Fe) was found to be 8.96×10^{-6} mg/kg/day, yielding a Hazard Quotient (HQ) of

1.12×10^{-5}, indicating a very low risk of adverse health effects (USEPA, 2011). Zinc (Zn), with a CDI of 8.82×10^{-7} mg/kg/day, results in an HQ of 2.52×10^{-6}, further suggesting minimal toxicity. Copper (Cu) showed a CDI of 6.15×10^{-7} mg/kg/day and an HQ of 1.36×10^{-5}, indicating a similarly low risk (WHO, 2018). Lead (Pb), a known carcinogen, exhibited a CDI of 4.69×10^{-8} mg/kg/day and an HQ of 1.34×10^{-5}, which suggests a potential non-carcinogenic risk, though the calculated Cancer Risk (CR) of 3.99×10^{-10} points to a very minimal cancer risk from lead exposure (ATSDR, 2019). Cadmium (Cd), with a CDI of 2.26×10^{-8} mg/kg/day, showed no HQ but a CR of 8.599×10^{-9}, signifying a low but present carcinogenic risk (ATSDR, 2021). Manganese (Mn) and chromium (Cr) exhibited no significant risk from inhalation exposure, with very low CDIs and HQ values far below the threshold of concern. Nickel (Ni), with a CDI of 2.72×10^{-7} mg/kg/day and an HQ of 1.09×10^{-5}, also presented a non-significant non-carcinogenic risk, but its CR of 4.63×10^{-7} indicates a potential carcinogenic risk. Cobalt (Co) had a CDI of 1.56×10^{-7} mg/kg/day, with a significantly higher HQ of 0.0273, pointing to a potential non-carcinogenic risk based on the exposure levels (Zhao *et al.*, 2020).

5.8. Hazard index And Total Carcinogenic Risk Through All Exposure Routes For Children And Adults

The hazard index (HI) and total carcinogenic risk (TCR) values for heavy metal exposure in Ikpeshi indicate varying health risks for children and adults through ingestion, dermal contact, and inhalation. Non-carcinogenic risks (HI) remain below the critical threshold of 1, with the highest values observed for cobalt (0.08675 in children and 0.03969 in adults), followed by cadmium and chromium, suggesting potential health concerns, particularly for children (Zhao *et al.,* 2020). Carcinogenic risk (TCR) assessments reveal that nickel poses the highest risk (2.14×10^{-4} in children and 3.10 × 10^{-5} in adults), exceeding the acceptable lower limit (10^{-6}) set by USEPA (2011), followed by chromium and cadmium. Although lead presents a relatively lower carcinogenic risk (1.84 × 10^{-7} in children and 2.68 × 10^{-8} in adults), its neurotoxic effects remain a significant concern (Aluko *et al.,* 2018).

5.9. Carcinogenic and Non-Carcinogenic Health Risks of Heavy Metals in Children via Ingestion

The CDI values reflect the estimated exposure of children to heavy metals via soil ingestion, measured in mg/kg/day. Among the metals analyzed, iron (Fe) exhibits the highest CDI at **4.14 × 10^{-3}**, followed by zinc (Zn) at **4.10 ×10^{-4}**, and copper (Cu) at **2.83 ×10^{-4}**. The lowest CDI is recorded for cadmium (Cd) at **1.04 ×10^{-5}**, indicating minimal exposure compared to other metals.

The hazard quotient (HQ) is used to assess potential non-carcinogenic health risks. An HQ value greater than 1 suggests a potential for adverse health effects (USEPA, 2011). In the present study, none of the individual heavy metals exceed this threshold. However, cadmium (Cd) presents the highest HQ at **1.04 ×10^{-2}**, followed by copper (Cu) at **7.07 ×10^{-3}** and lead (Pb) at **6.18 ×10^{-3}**. The cumulative hazard index (**∑HQ**) for all metals is 0.13745, remaining below the safety threshold, suggesting that non-carcinogenic risks via ingestion are relatively low for children in the study area.

The cancer risk (CR) values estimate the probability of developing cancer over a lifetime due to exposure to carcinogenic heavy metals. According to the USEPA (2001) guidelines, acceptable cancer risk levels range between **10^{-6}** and **10^{-4}**. Among the metals analyzed, nickel (Ni) presents the highest CR value at **2.13 ×10^{-4},** which falls at the upper boundary of the acceptable risk range, indicating potential concerns for long-term exposure. Chromium (Cr) follows with a CR of **4.58 $\times 10^{-5}$,** while cadmium (Cd) and lead (Pb) exhibit lower CR values of **3.95 $\times 10^{-6}$** and **1.83 $\times 10^{-7}$** respectively. The presence of carcinogenic metals, particularly nickel and chromium, warrants further environmental and health monitoring to mitigate long-term exposure risks.

5.10. Carcinogenic and Non-Carcinogenic Health Risks of Heavy Metals in Adults via Ingestion

The CDI values indicate the estimated intake of heavy metals through soil ingestion (mg/kg/day). Among the analyzed metals, iron (Fe) exhibits the highest CDI at **5.89 $\times 10^{-4}$,** followed by zinc (Zn) at **5.80 $\times 10^{-5}$** and copper (Cu) at **4.04 $\times 10^{-5}$.** The lowest CDI is observed for cadmium (Cd) at **1.48 $\times 10^{-6}$**, suggesting minimal exposure to this metal in comparison to others. However, even at low concentrations, certain metals, such as cadmium, are of concern due to their high toxicity and bioaccumulation potential (USEPA, 2011).

The HQ values represent the potential for non-carcinogenic health effects, with HQ > 1 indicating a possible health risk (USEPA, 2011). In this study, none of the individual metals exceed the threshold, implying that non-carcinogenic risks from soil ingestion remain within acceptable limits. However, cadmium (Cd) presents the highest HQ at **1.48 $\times 10^{-3}$**, followed by copper (Cu) at **1.01 $\times 10^{-3}$** and lead (Pb) at **8.83 $\times 10^{-4}$**. The cumulative hazard quotient ($\sum$HQ) for all metals is 0.02417, significantly below the safety limit, suggesting minimal immediate health risks for adults in the study area.

The carcinogenic risk (CR) values estimate the probability of developing cancer over a lifetime due to exposure to carcinogenic metals. According to USEPA (2001) guidelines, acceptable risk levels range from **10^{-6}** and **10^{-4}**. In this study, nickel (Ni) presents the highest CR value at **3.04**

$\times 10^{-5}$, indicating a potential concern for long-term exposure. Chromium (Cr) follows with a CR of **6.54 $\times 10^{-6}$**, while cadmium (Cd) and lead (Pb) exhibit lower CR values of **5.65 $\times 10^{-7}$ and 2.62 $\times 10^{-8}$**, respectively. Although none of these values exceed the upper risk threshold of 10^{-4}, the presence of Ni and Cr within the acceptable range suggests that continuous exposure could pose long-term health risks (USEPA, 2011).

5.11. The Hazard quotient (HQ) and the carcinogenic risk (CR) for children through dermal Exposure

Among the metals analyzed, lead (Pb) stands out with the highest HQ value (1.15×10^{-4}), which suggests a significant non-carcinogenic health risk through dermal absorption, a finding consistent with established concerns regarding lead exposure in children, known for its neurotoxic effects (Zheng *et al.*, 2020). Similarly, nickel (Ni) and chromium (Cr) present noteworthy HQ values of 1.755×10^{-5} and 8.53×10^{-5}, respectively, indicating a potential health risk from prolonged dermal exposure, especially considering their toxicity at high concentrations (Muirhead *et al*., 2015). Notably, cobalt (Co) exhibits a particularly high HQ of 0.03526, highlighting its potential to cause health hazards even at lower concentrations, emphasizing the importance of monitoring exposure levels in vulnerable populations. On the other hand, iron (Fe), zinc (Zn), and copper (Cu) show relatively lower HQ values, indicating that while they contribute to CDI, they pose minimal health risks through dermal exposure under typical conditions. The CR values for Pb, Ni, and Cr indicate a potential for carcinogenic effects, although at relatively low levels, necessitating caution in environments where children may be exposed to contaminated materials. These results underscore the critical need for a comprehensive risk assessment framework that incorporates dermal exposure pathways, particularly in residential areas, playgrounds, and other environments where children may come into direct contact with contaminated surfaces (Muirhead *et al*., 2015; Zheng *et al.*, 2020).

5.12. The Hazard quotient (HQ) and the carcinogenic risk (CR) for adults through dermal Exposure

The dermal exposure risk assessment for adults, based on the Chronic Daily Intake (CDI) values, further highlights the potential health risks of heavy metals through skin contact. Iron (Fe) exhibited a CDI of 3.89×10^{-6} mg/kg/day, resulting in a Hazard Quotient (HQ) of 5.55×10^{-6}, which suggests a minimal risk of non-carcinogenic health effects (USEPA, 2011). Zinc (Zn) had a CDI of 3.83×10^{-7} mg/kg/day and an HQ of 1.277×10^{-6}, indicating negligible non-carcinogenic risks. Copper (Cu), with a CDI of 2.67×10^{-7} mg/kg/day and an HQ of 6.68×10^{-6}, also suggests a minimal risk of adverse health effects (WHO, 2018). Lead (Pb), which has been associated with both non-carcinogenic and carcinogenic risks, showed a CDI of 2.03×10^{-8} mg/kg/day and an HQ of 3.88×10^{-5}, indicating a significant non-carcinogenic risk, with a Cancer Risk (CR) of 1.72 × 10^-10, suggesting an extremely low cancer risk (ATSDR, 2019). Cadmium (Cd) exhibited a CDI of 9.81×10^{-9} mg/kg/day, an HQ of 1.96×10^{-6}, and a CR of 3.72×10^{-7}, suggesting both non-carcinogenic and low carcinogenic risks (ATSDR, 2021). Manganese (Mn) showed a CDI of 7.11×10^{-8} mg/kg/day and an HQ of 7.40×10^{-5}, indicating a much higher potential for non-carcinogenic effects through dermal contact. Nickel (Ni) with a CDI of 1.18×10^{-7} mg/kg/day, an HQ of 5.91×10^{-6}, and a CR of 2.01×10^{-9}, points to a very low risk of both non-carcinogenic and carcinogenic health effects. Chromium (Cr) exhibited a CDI of 8.64×10^{-8} mg/kg/day and an HQ of 2.88×10^{-5}, indicating a significant non-carcinogenic risk, while its CR of 4.32×10^{-7} suggests a potential low carcinogenic risk (Zhao *et al.,* 2020). Cobalt (Co) had a CDI of 6.77×10^{-8}

mg/kg/day and an HQ of 0.01188, signifying a non-carcinogenic risk based on dermal exposure levels (Zhao *et al*., 2020).

5.13. Carcinogenic risk for Children through inhalation route

The inhalation risk assessment for shows that metals such as **iron (Fe),** with a **Hazard Quotient (HQ)** of **1.96×10^{-5},** and **zinc (Zn),** with a **HQ** of **4.41×10^{-6}**, pose minimal non-carcinogenic risk, as their HQ values are well below the threshold of 1 (USEPA, 2011). **Copper (Cu),** with an **HQ** of **2.39×10^{-5}**, also indicates low risk, though it is slightly higher than that of iron and zinc (ATSDR, 2019). **Lead (Pb)**, with a **HQ** of **2.34×10^{-5},** similarly does not exceed the risk threshold, but despite its low non-carcinogenic risk, lead is a known neurotoxin, and even small amounts can adversely affect children's cognitive development (ATSDR, 2019). The **Cancer Risk (CR)** for lead is **6.98×10^{-10},** reflecting a low carcinogenic risk over long-term exposure (ATSDR, 2019). **Cadmium (Cd)** shows a **CR** of **1.50×10^{-8}**, indicating a potential carcinogenic risk, though its **HQ** is not available (WHO, 2018). **Manganese (Mn), nickel (Ni)**, and **chromium (Cr)** exhibit varying levels of risk, with **chromium** having an **HQ** of **0.01162**, which exceeds the threshold of 1, suggesting a significant non-carcinogenic risk through inhalation (Zhao *et al.,* 2020). **Nickel** presents a **CR** of **8.11×10^{-7},** suggesting a low but notable carcinogenic risk (Agency for Toxic Substances and Disease Registry [ATSDR], 2021). **Cobalt (Co),** with an **HQ** of **0.04790**, presents a potential non-carcinogenic risk, although the **CR** is not provided in this dataset. Overall, while metals like **iron, zinc,** and **copper** show little threat, metals like **chromium** and **cobalt** are of concern due to their higher toxicity and carcinogenic potential, especially for children living near quarry sites (USEPA, 2011; ATSDR, 2019; Zhao *et al*., 2020).

5.14. Carcinogenic risk for Adults through inhalation route

The assessment of potential health risks from heavy metals in the inhalation pathway for adults reveals significant insights into exposure levels and the associated risks. The Chronic Daily Intake (CDI) for iron (Fe) was found to be 8.96×10^{-6} mg/kg/day, yielding a Hazard Quotient (HQ) of 1.12×10^{-5}, indicating a very low risk of adverse health effects (USEPA, 2011). Zinc (Zn), with a CDI of 8.82×10^{-7} mg/kg/day, results in an HQ of 2.52×10^{-6}, further suggesting minimal toxicity. Copper (Cu) showed a CDI of 6.15×10^{-7} mg/kg/day and an HQ of 1.36×10^{-5}, indicating a similarly low risk (WHO, 2018). Lead (Pb), a known carcinogen, exhibited a CDI of 4.69×10^{-8} mg/kg/day and an HQ of 1.34×10^{-5}, which suggests a potential non-carcinogenic risk, though the calculated Cancer Risk (CR) of 3.99×10^{-10} points to a very minimal cancer risk from lead exposure (ATSDR, 2019). Cadmium (Cd), with a CDI of 2.26×10^{-8} mg/kg/day, showed no HQ but a CR of 8.599×10^{-9}, signifying a low but present carcinogenic risk (ATSDR, 2021). Manganese (Mn) and chromium (Cr) exhibited no significant risk from inhalation exposure, with very low CDIs and HQ values far below the threshold of concern. Nickel (Ni), with a CDI of 2.72×10^{-7} mg/kg/day and an HQ of 1.09×10^{-5}, also presented a non-significant non-carcinogenic risk, but its CR of 4.63×10^{-7} indicates a potential carcinogenic risk. Cobalt (Co) had a CDI of 1.56×10^{-7} mg/kg/day, with a significantly higher HQ of 0.0273, pointing to a potential non-carcinogenic risk based on the exposure levels (Zhao *et al.*, 2020).

5.15. Hazard index and total carcinogenic risk through all exposure routes for children and adults

The hazard index (HI) and total carcinogenic risk (TCR) values for heavy metal exposure in Ikpeshi indicate varying health risks for children and adults through ingestion, dermal contact, and inhalation. Non-carcinogenic risks (HI) remain below the critical threshold of 1, with the highest values observed for cobalt (0.08675 in children and 0.03969 in adults), followed by cadmium and chromium, suggesting potential health concerns, particularly for children (Zhao *et al.,* 2020). Carcinogenic risk (TCR) assessments reveal that nickel poses the highest risk (2.14×10^{-4} in children and 3.10×10^{-5} in adults), exceeding the acceptable lower limit (10^{-6}) set by USEPA (2011), followed by chromium and cadmium. Although lead presents a relatively lower carcinogenic risk (1.84×10^{-7} in children and 2.68×10^{-8} in adults), its neurotoxic effects remain a significant concern (Aluko *et al.,* 2018).

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