





Comparative Analysis of Heavy Metal Concentrations and Potential Health Risks Across Varied Land-Use Zones in Ado-Ekiti, Southwest Nigeria

Samson I. Emumekpor¹, Adeniyi J. Adewumi^{2*}

¹ Department of Environmental Management, University of Hertfordshire, AL 10 9AB Hertfordshire, United Kingdom

² Department of Geological Sciences, Achievers University, PMB 1030, Owo, Nigeria

* Correspondence: Adeniyi J. Adewumi (adewumiadeniyi@achievers.edu.ng)

Received: 05-01-2023

Revised: 06-06-2023

Accepted: 06-18-2023

Citation: S. I. Emumekpor and A. J. Adewumi, "Comparative analysis of heavy metal concentrations and potential health risks across varied land-use zones in Ado-Ekiti, Southwest Nigeria," *Acadlore Trans. Geosci.*, vol. 2, no. 2, pp. 113–131, 2023. <https://doi.org/10.56578/atg020205>.



© 2023 by the author(s). Published by Acadlore Publishing Services Limited, Hong Kong. This article is available for free download and can be reused and cited, provided that the original published version is credited, under the CC BY 4.0 license.

Abstract: An investigation was conducted to determine potential threats of heavy metal contaminants in soil samples from Ado-Ekiti, Southwest Nigeria, across distinct land-use zones. Five soil specimens were systematically gathered from each of the following locales, representing heightened anthropogenic activities: marketplaces, motor parks, schools, mining sites, and residential regions. Using an atomic absorption spectrometer, the soil samples' chemical compositions were scrutinized with a focus on elements such as As, Cu, Cd, Cr, Co, Ni, Pb, Zn, and Fe. Indices, including the geo-accumulation (Igeo), contamination factor (CF), and pollution load index (PLI), were employed for contamination assessment of metals in the soils. Furthermore, Ecological and Human Health Risk Assessments (HHRA), following the United States Environmental Protection Agency (USEPA) guidelines, were carried out to establish the probability of detrimental impacts of heavy metals in the soils on human and environmental health. Mean concentrations (mg/kg) across all zones for As, Cu, Cd, Cr, Co, Ni, Pb, Zn, and Fe were 1.16, 20.44, 2.18, 7.52, 2.18, 4.67, 18.57, 66.71, and 207.21 respectively, with the arsenic and cadmium concentrations exceeding permissible levels. A PLI value exceeding one suggested heavy metal-induced degradation in the studied area. Chromium presented notable environmental hazards, and the majority of detected metals were traced back to anthropogenic sources. Oral ingestion of soil metals resulted in hazard index (HI) values exceeding one for children across all zones, indicating their susceptibility to non-carcinogenic health risks. Consequently, vigilant monitoring of heavy metal levels is advocated to mitigate potential health hazards and ensure the health of the community.

Keywords: Ado-Ekiti; Contamination assessment; Ecological risk assessment; Health risk assessment; Heavy metals; Soils

1 Introduction

Urbanization, a socio-economic phenomenon involving the expansion of cities and migration of populations from rural to urban areas, represents a dominant trend in contemporary global development [1]. This process is typically incited by perceived opportunities for economic improvement, advancements in industrialization and modernization, as well as the promise of enhanced living conditions [1, 2]. Urban landscapes are often marked by a wide spectrum of economic possibilities, augmented access to education and healthcare, and a rich array of cultural and recreational activities [2]. It is these attributes that tend to entice individuals to vacate rural landscapes in search of a more prosperous and enhanced life quality.

From a global perspective, the trend of urbanization is discernible across both developed and developing nations, albeit with differing causes and effects [3]. In developed countries, urbanization largely results from industrialization and technological advancements, leading to a transition from agricultural economies towards industries focused on services and manufacturing [4, 5]. Conversely, developing countries tend to experience a more rapid rate of urbanization, propelled by factors such as population growth, rural-to-urban migration, and the expansion of industry and infrastructure [2].

The increasing prominence of urban environments engenders a multitude of outcomes. While offering avenues for economic growth, innovation, and cultural exchange, urbanization also precipitates socio-economic disparities, environmental degradation, resource scarcity, and issues pertaining to urban infrastructure [5]. Therefore, comprehensive understanding of the interplay between urbanization and the environment is pivotal in devising strategies for sustainable urban development [2].

As urban environments continue to burgeon, they exert profound environmental implications [1]. Deforestation and habitat destruction, water resource strain, contamination, and air pollution are among the key environmental repercussions of urbanization [1–3]. Specifically, loss of vegetation not only disrupts ecosystems but also exacerbates climate change due to a decrease in carbon sequestration and a rise in greenhouse gas emissions. In parallel, escalating demand for freshwater for domestic, industrial, and agricultural purposes strains water resources and exacerbates water scarcity [3]. This is coupled with water contamination caused by an influx of pollutants such as heavy metals, chemicals, and sediment from urban runoff [1–3].

Urban areas, being hubs of industry, transportation, and energy consumption, are often associated with high levels of air pollution [6, 7]. The dense concentration of automobiles and industrial operations leads to an increase in the emission of particulate matter, nitrogen oxides, sulfur dioxide, among other pollutants. These elements not only jeopardize human health but also contribute to climate change [6]. The implementation of cleaner technologies, improvement of public transportation systems, and adoption of renewable energy sources represent potential avenues for ameliorating pollution levels in urban areas [6].

Moreover, urbanization poses significant waste management challenges. Urban areas generate large volumes of waste encompassing solid waste, hazardous waste, and technological waste [7]. Mismanaged waste disposal contributes to pollution, soil contamination, and greenhouse gas emissions [6, 7]. In this light, initiatives promoting recycling, composting, waste reduction, alongside efficient waste collection and disposal systems are essential for minimizing the environmental impact of urban waste [8].

Soil, as a critical resource, sustains plant growth and ecological vitality [1]. Its status, however, can be severely compromised by pollutants, particularly heavy metals including lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), and nickel (Ni) [9]. While trace amounts of these metals are naturally present in soil, anthropogenic activities have exponentially increased their concentrations, eliciting grave environmental apprehensions [9]. Both natural and anthropogenic processes have been implicated in heavy metal introduction into soils [1, 9]. Natural contributors encompass rock weathering, volcanic eruptions, and atmospheric deposition [1]. However, human-induced activities—such as industrial emissions, mining and smelting operations, agricultural practices (including fertilizers and pesticides usage), inefficient waste management, wastewater discharges, and atmospheric deposition originating from industrial and vehicular emissions—are major drivers of elevated soil heavy metal levels [1].

Heavy metal pollution in soils poses significant environmental and health risks [10–12]. Stunted plant growth, impaired plant metabolism, and decreased agricultural productivity are direct impacts of heavy metal accumulation in soil [10]. Furthermore, bioaccumulation of these metals within the food chain presents threats to animal health and population stability [11]. Predominantly, this occurs when animals ingest contaminated plants, soil, or other organisms, leading to metal accumulation within their tissues. This can subsequently impair reproductive success, immunological function, and overall well-being, and may also lead to population decreases among vulnerable species [11].

Human health is similarly jeopardized by heavy metal contamination in soils [11–13]. Exposure routes include direct ingestion of contaminated soil (especially in children), inhalation of dust particles containing heavy metals, consumption of food grown on polluted soils, and contact with contaminated water sources [12]. The neurodevelopmental effects of heavy metals such as lead and mercury are particularly concerning, with potential implications for cognitive and behavioural outcomes in children [12]. Similarly, adults may experience cognitive impairments, memory loss, and neurological disorders [12]. Certain heavy metals, including arsenic, cadmium, and chromium, have been identified as carcinogenic or potential carcinogens [13]. Thus, chronic exposure to heavy metals can increase the risk of developing malignancies such as lung, liver, and kidney cancers [12, 13]. Moreover, heavy metals can accumulate in the kidneys and liver, causing long-term organ damage [12, 13]. The inhalation of dust from heavy metal-contaminated soil can also trigger respiratory ailments such as coughing, wheezing, bronchitis, and asthma [14].

Given these concerns, measures such as soil washing, phytoremediation, and the implementation of stricter industrial and agricultural practices are necessary to mitigate heavy metal contamination [15]. Regular soil quality monitoring and the introduction of appropriate safety measures are essential for managing the ecological and health risks associated with heavy metal pollution in soils [15].

Ecological Risk Assessment (ERA) provides a systematic framework for evaluating the potential adverse impacts of stressors, such as heavy metals, on ecosystems [9]. This approach allows for a comprehensive understanding of the threats posed by various environmental contaminants to both ecosystems and their biological constituents [1, 9]. ERA informs decision-making processes and environmental management practices, thereby supporting the preservation

of ecosystem health.

Similarly, Health Risk Assessment (HRA) serves as a systematic approach to gauge potential adverse health effects associated with exposure to hazardous substances or conditions [16]. It aids in the quantification and understanding of risks associated with specific hazards, thereby informing the development of risk management strategies [1]. HRA considers factors such as exposure pathways, substance toxicity, and individual susceptibility to provide crucial insights for decision-making processes related to public health policies, environmental regulations, and risk management strategies [9]. Ultimately, the implementation of ERA and HRA tools aids in safeguarding public health and environmental integrity, while facilitating sustainable land and resource management.

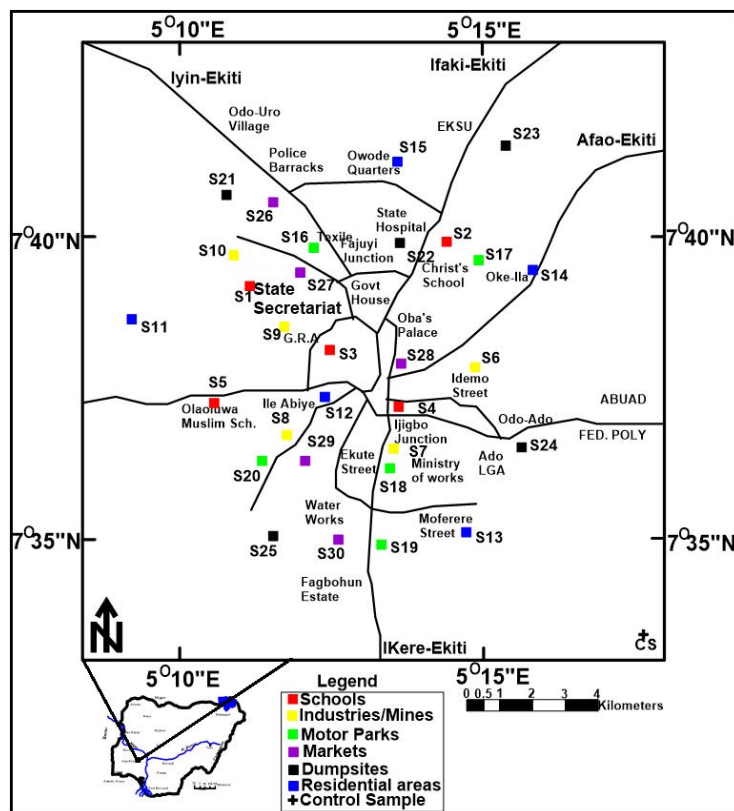


Figure 1. Map indicating the study area

While ERA evaluates the potential ecological damage, HRA is utilized to determine risks posed to human populations [17]. A shared goal of these methodologies is to identify and mitigate hazards affecting both environmental and human health. Pollutants, including heavy metals, pesticides, industrial chemicals and atmospheric pollution, potentially impact both ecological systems and human health [17]. Through ERA and HRA, risks presented by these pollutants are evaluated by examining their hazards, exposure routes, and possible adverse effects [9, 16]. Exposure routes that impact both ecological and human health are acknowledged within these frameworks [16]. Contamination of soil, air, or water can expose both ecological and human systems through ingestion, inhalation, or dermal contact [17]. This commonality allows for a thorough analysis of exposure possibilities and associated risks. The potential for contaminant transmission within ecosystems is recognized within ERA and HRA methodologies [9]. These contaminants may bioaccumulate throughout the food chain, affecting a myriad of organisms, including humans. The impact of pollutants on ecological receptors, such as plants, animals, and aquatic species, which may serve as a source of exposure for higher trophic levels, is considered in ERA [1]. HRA takes into account health risks associated with consuming contaminated organisms or exposure to polluted environmental media. The utilization of distinct methodologies within these frameworks is noted [17]. Although sharing certain characteristics, ERA and HRA deploy unique approaches and endpoints aligned with their respective aims. ERA frequently employs ecological models, population assessments and ecological outcomes such as population abundance, species diversity or reproductive success [18]. HRA makes use of toxicological data, exposure assessments, and health endpoints such as cancer risks, non-cancer risks, or hazard quotients (HQs) [18]. By applying both ERA and HRA, a study may thoroughly evaluate and mitigate contamination risks [16]. While ERA aims to safeguard ecosystems and non-human organisms, HRA focuses on protecting human populations [9]. The combined application of ERA and HRA allows for a comprehensive evaluation of environmental and health risks, enabling informed decision-making,

risk mitigation strategies, and the formation of effective regulatory measures to safeguard both the environment and human health [17–19].

Ado-Ekiti (The geographical location and boundaries of the study area are depicted in Figure 1), an eminent city situated in Nigeria's southwestern region, is currently undergoing an influential transformation marked by significant population growth and rapid industrialization. This expansion has precipitated profound impacts on the environmental constituents of the area, notably the water, soils, flora, and dust [20].

Historical data indicate a robust population surge from 99,923 in 1959 to 400,090 in 2006 [20]. As delineated by Macrotrends [21], this growth trajectory has continued unabated, with the population reported at 536,000 in 2023 and projected to escalate to 824,000 by 2035.

Ado-Ekiti, the capital city of Ekiti State, is geographically characterized by latitudes 7°34'N to 7°44' N and longitudes 5°11' E to 5°18' E. It is encompassed by several satellite settlements [22]. Notably, Iworoko is situated approximately 16 kilometers north, while Are-Ekiti and Afao-Ekiti lie approximately 16 kilometers east of the city. Iyin-Ekiti and Igede-Ekiti, located to the west, are around 20 kilometers distant, and to the south, approximately 18 kilometers away, lies Ikere-Ekiti. As a central hub within the state, Ado-Ekiti is interconnected with a network of routes that extend to other regions.

The city's socio-economic and political significance has been reflected in the growth of its population, which is projected to reach 1.11 million by 2030, based on an existing annual growth rate of 4% [20]. An overwhelming majority of 82% of this populace is expected to reside in the urban core.

In terms of its physical geography, the city's elevation is quite prominent, with an average height of 390 meters above sea level in the southeast along the Ureje stream, and approximately 540 meters above sea level in the northeastern extremities. The landscape is characterized by rounded inselbergs and steep-sided hills, with slope angles ranging from 33° to 44°.

Typical of the Southwestern Nigerian climate, Ado-Ekiti experiences distinct wet and dry seasons, with peak rainfall recorded between July and September. Notably, the inception and conclusion of the rainy season are often marked by intense thunderstorms, predominantly occurring in the afternoons and occasionally at night [23].

Temperature variations are minimal, with an annual mean temperature of approximately 27°C and a deviation of merely 3.7°C between February, the warmest month, and August, the coolest month. This agreeable climate fosters tree cultivation and supports a variety of year-round recreational activities.

Geologically, the region is dominated by Precambrian crystalline rocks of igneous and metamorphic origin. It is composed of migmatite gneiss, granite gneiss, granite, and charnockites, embodying the basement rocks of Southwestern Nigeria. Key industries thriving in the city span across paints, agriculture, agro-allied sectors, construction, pharmaceuticals, food and beverages, and financial institutions.

Several studies have been undertaken to evaluate pollution levels in the city's environmental media [24–26]. However, none have focused on the potential ecological and health impacts of heavy metals in urban soils. In addition, no research has examined the levels of heavy metals across various land uses within the region and their potential implications for human health and the environment. This study endeavors to fill this knowledge gap by examining heavy metal contamination in soils within Ado-Ekiti City. Furthermore, it presents the first investigation into potential ecological and health risks associated with the presence of heavy metals in the local soil. The primary objectives are to: (1) assess the ecological and health risks associated with metals in the media; and (3) identify potential sources of metals using multivariate statistical methods. The intention is to heighten awareness among city inhabitants about the increasing levels of heavy metals in their soil environment and the potential health implications.

2 Methodology

2.1 Sample Procurement

An initial reconnaissance was executed to gain an intimate understanding of the designated sampling locations. Local inhabitants provided requisite permissions, and advance notification was issued preceding the sampling ventures. An array of thirty soil specimens was gathered from six divergent land-use categories, incorporating waste disposal sites, educational institutions, market areas, industrial/mining zones, residential sectors, and vehicular parks. A non-systematic sampling methodology facilitated the acquisition of these specimens. Comparative control samples were obtained from an area approximately 5 kilometers south of the primary study zone. This region was selected due to the absence of extensive human activity and urbanization, factors known to contribute to an escalation in soil contaminants. Specimens were collected and sealed within suitably marked plastic bags utilizing a sterile hand trowel.

Around 10 kg of each specimen was retrieved at a subsurface depth of 10 cm employing a sterile hand auger. Each sampling point's geographical coordinates were recorded utilizing an eTrex Garmin GPS. To ensure a high degree of data fidelity and reliability, all equipment, including the hand auger and trowel, was meticulously cleaned with distilled water and air-dried between each sampling to prevent potential cross-contamination from unknown sources.

2.2 Laboratory Preparation of Samples

Ensuring sample integrity, each of the retrieved soil samples was distinctively segregated and aptly marked. Subsequent to their collection, a natural air-drying process was implemented for these samples at ambient temperature over a one-week duration within the laboratory confines until complete desiccation was attained. Upon complete drying, an allotment of 100 g from each sample was weighed utilizing an electronic balance and subsequently pulverized into a fine powder using a mortar and pestle.

For the purpose of fractionating the material based on particle sizes, the powdered specimens were subjected to mechanical sieving, implemented for a duration of 15 minutes at 70 revolutions per minute, utilizing a sedimentological sieve in conjunction with an agitator. The resulting fractions smaller than 25 mm were carefully amassed and stored in appropriately labeled miniaturized ziplock plastic bags to minimize potential sample contamination.

To further mitigate sample contamination from unidentified sources, the mortar and pestle employed in the pulverization process were meticulously cleansed with ultra-pure water and subsequently oven-dried prior to their utilization in processing each sample. In addition, the sieves were thoroughly washed with distilled water and air-dried before their application in the size fractionation of each sample.

2.3 Physicochemical Analysis of Samples

The pH value of the soil samples was measured employing a pH meter. An allotment of twenty grams of air-dried soil, subjected to a 2 mm sieve, was transferred into a 100 milliliter beaker. To this, 5 ml of distilled water was introduced and the resulting mixture was agitated intermittently every 30 minutes, totaling a duration of 30 minutes. Subsequent to the stabilization of the pH meter reading, the pH value in water was noted.

The Organic Matter Content (OMC) of the soil samples was ascertained utilizing the methodology delineated by Walkey and Black [27]. To assess the electrical conductivity (EC) of the samples, five grams of soil were combined with 5 ml of distilled water in a cylinder. The EC probe, calibrated at 25°C employing a standard salt solution (1.41 dS/m), was set to deliver a reading of 1.4. A quantity of 29.5 ml of mixed soil, devoid of air gaps owing to gentle tapping, was introduced into a plastic mixing vial. Subsequent to the careful insertion of the EC probe, the EC value was measured, ensuring the suspension of soil particles in the solution to prevent settling.

Prior to analyses, the samples were subjected to digestion via the aqua regia method. One gram of each sample, weighed using an electronic scale, was placed in Teflon tubes along with a 1:3 mixture of nitric acid (HNO₃) and hydrochloric acid (HCl). These tubes were then placed in steel canisters and heated for a duration of 16 hours at a temperature of 110°C. Following this, the canisters were heated on a hotplate until the digestate was nearly dry. Subsequent to the addition of 5 cc of acids to the nearly dry digestates, the digestion process was completed. The digestion products were diluted 1:50 with ultrapure water, and the digested samples were then analyzed utilizing a Buck Scientific Atomic Absorption 210VGP instrument.

2.4 Contamination Evaluations

Assessment of contamination levels in the water and soil samples involved the use of numerous indices including the Igeo, enrichment factor (EF), CF, PLI, contamination degree (CD), ecological risk index (ERI), potential ecological risk index (PERI), and health risk assessments.

2.5 Igeo

The degree of metal contamination in the soils was evaluated through the application of the Igeo, providing a comparison of their enrichment levels with background values. The Igeo was calculated utilizing Eq. (1), with classifications according to Muller [28] presented in Table 1.

$$I_{geo} = \log_2 \frac{C_n}{1.5 \times Bn} \quad (1)$$

where, C_n denotes the concentration of the metal in the test material, and Bn represents the concentration of the metal in the background sample. The fixed value of 1.5 is incorporated to account for potential variances in background values arising from lithological differences in the soils.

2.6 EF

The EF was ascertained by contrasting the target element to a reference element exhibiting minimal variability, for this study, Iron (Fe) was elected. Eq.(2) encapsulates the EF computation, further divided into five contamination levels [29, 30].

$$EF = \frac{\left(\frac{Metal}{RE}\right)_{Soil}}{\left(\frac{Metal}{RE}\right)_{Background}} \quad (2)$$

Table 1. Classification of Igeo [28]

S/N	Range	Level
1.	$I_{geo} < 0$	Clean
2.	$0 \leq I_{geo} < 1$	Clean to slightly Polluted
3.	$1 \leq I_{geo} < 2$	Slightly Polluted
4.	$2 \leq I_{geo} < 3$	Slightly to Moderately Polluted
5.	$3 \leq I_{geo} < 4$	Moderately Polluted
6.	$4 \leq I_{geo} < 5$	Moderately to Heavily Polluted
7	$I_{geo} \geq 5$	Heavily Polluted

where, RE represents the concentration of the reference metal. The EF facilitates the classification of contamination levels: EF 2 corresponds to minimal to low enrichment, EF between 2 and 5 signifies moderate enrichment, EF between 5 and 20 signifies significant enrichment, EF between 20 and 40 signifies very high enrichment, and EF greater than 40 signifies extremely high enrichment [29, 30].

2.7 CF

For evaluating soil contamination with individual elements, the CF was employed. Eq. (3) is utilized for the computation of CF and is further divided into four classes, as depicted in Table 2.

$$CF = \frac{\text{Metal Concentration}}{\text{Concentration of Element in Background Soils}} \quad (3)$$

Table 2. Classification of contamination factor [31]

S/N	CF Value	Contamination Factor Level
1.	$CF < 1$	Low contamination factor indicating low contamination
2.	$1 \leq CF < 3$	Moderate contamination factor
3.	$3 \leq CF < 6$	Considerable contamination factor
4.	$6 \geq CF$	Very high contamination factor

2.8 CD

An aggregate measure of environmental contamination, termed the CD , considers the contamination factors of all substances under investigation. Eq. (4) is employed for the computation of CD , further divided into four categories (Table 3).

$$C_d = \sum_{i=1}^n C_f^i \quad (4)$$

where, C_d represents the degree of contamination and C_f denotes the contamination factor.

Table 3. Classification of CD [31]

S/N	CF Value	Contamination Factor Level
1	$CD < 8$	Low degree of contamination
2.	$8 \leq CD < 16$	Moderate degree of contamination
3.	$16 \leq CD < 32$	Considerable degree of contamination
4.	$CD \geq 32$	Very high degree of contamination

2.9 PLI

The PLI, used to estimate the extent of metal contamination at each test site, was evaluated using Eq. (5) as per Tomilson et al. [32]. A PLI value less than one indicates an unpolluted site, while values exceeding one suggest a degradation in site quality [32].

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n} \quad (5)$$

where, n denotes the total number of metals investigated, and CF signifies the contamination factor computed using Eq. (3). The PLI serves as a straightforward and uniform methodology for the assessment of site quality. A PLI value equal to 1 is indicative of an optimal environmental state, characterized by baseline pollution levels. Conversely, a PLI value surpassing 1 signifies a decline in site quality, pointing towards escalated levels of pollution [32].

2.10 Environmental Risk Assessments

The ERI was employed to evaluate heavy metal contamination in soil and its correlation to ecological and environmental consequences. Toxic-response factors (TRi) for Cu, Zn, Cd, Cr, Ni, and Pb were incorporated in the calculation of Ecological Risk (ER). The computation of RI is depicted in Eq. (6), and the PERI is determined by the sum of potential ER of each element Eq. (7) [31, 33].

$$E_R = T_R \times C_F \quad (6)$$

$$PERI = \sum_{i=1}^m E_R \quad (7)$$

where, T_R stands for the toxic-response factor, while C_F denotes the contamination of a single element factor. T_R values for Zn, Cr, Cu, Pb, and Cd are 1, 2, 5, 5, and 30. The criteria for evaluating the PERI are delineated in Table 4.

Table 4. Criteria for classifying PERI

S/N	ER	Low Risk	Moderate Risk	Considerable Risk	High Risk	Significantly High Risk
1	ER	< 40	40 – 80	80 – 160	160 – 320	> 320
2.	RI	< 150	150 – 300	300 – 600	≥ 600	

2.11 Health Risk Assessments

In order to quantify the potential hazards and exposure pathways associated with heavy metals in contaminated soils, health risk assessments were conducted. Guidelines from a myriad of American literature sources [34] were employed for the calculation of the average daily intake (ADI) of heavy metals through soil ingestion, inhalation, and dermal contact. Eqs. (8)-(10) were utilized to derive the ADI for each exposure pathway, incorporating factors such as heavy metal concentrations, ingestion rates, exposure frequency, exposure duration, body weight, and inhalation rates [34].

$$ADI_{ing} = \frac{C \times IR \times EF \times ED \times CF}{BW \times AT} \quad (8)$$

$$ADI_{inh} = \frac{C_S \times IR_{air} \times EF \times ED}{BW \times AT \times PEF} \quad (9)$$

$$ADI_{dems} = \frac{C_S \times SA \times FE \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (10)$$

Table 5 outlines various parameters used in the calculation of heavy metal exposure.

2.12 Assessment of Non-Carcinogenic Risks

The dimensionless value, HQ, was used for assessing non-carcinogenic risks, indicating the potential likelihood of experiencing adverse health effects. The HQ was calculated using an equation established by the USEPA [36].

$$HQ = \frac{ADI}{RfD} \quad (11)$$

where, the HI represents the summation of all HQs linked to specific metals, as stipulated by USEPA guidelines [34]. The mathematical representation of HI is given by Eq. (12):

$$HI = \sum_{k=1}^n HQ_k = \sum_{k=1}^n \frac{ADI_k}{RfD_k} \quad (12)$$

where, HQ_k , ADI_k , and RfD_k are the heavy metal k values. If the HI value is less than one, adverse health effects are unlikely to be experienced by the exposed population. Conversely, a value surpassing one signals potential concerns regarding non-carcinogenic consequences [34].

Table 5. Utilized exposure parameters in health risk assessment for soil across multiple exposure pathways

S/N	Parameters	Unit	Child	Adult	References
1.	Body Weight (<i>BW</i>)	Kg	15	70	[35]
2.	Exposure Factor (<i>EF</i>)	days/year	350	350	[35]
3.	Exposure Duration (<i>ED</i>)	Year	6	30	[35]
4.	Ingestion Rate (IR)	mg/day	200	100	[35]
5.	Inhalation Rate (IRair)	m ³ /day	10	20	[35]
6.	Skin Surface Area (<i>SA</i>)	cm ²	2100	5800	[35]
7.	Soil Adherence Factor (<i>AF</i>)	mg/cm ²	0.2	0.07	[35]
8.	Dermal Absorption Factor (<i>ABS</i>)	None	0.1	0.1	[35]
9.	Dermal Exposure Ratio (<i>FE</i>)	None	0.61	0.61	[35]
10.	Particulate Emission Factor (<i>PEF</i>)	m ³ /kg	1.3×10^9	1.3×10^9	[35]
11.	Conversion Factor (<i>CF</i>)	kg/mg	10^{-6}	10^{-6}	[35]
12.	Average Time (<i>AT</i>) For-Carcinogens For Non-Carcinogens	Days	365×70 $365ED$	365×70 $365ED$	[35]

Note: ADInh: This denotes the average daily ingestion of heavy metals through soil, expressed in milligrams per kilogram per day;

C/CS: This refers to the concentration of heavy metals in the soil, measured in milligrams per kilogram of soil;

IR: This represents the ingestion rate, defined as the frequency of consumption, given in milligrams per day;

EF: This term stands for exposure frequency, which is the number of exposure days per year;

ED: This signifies the exposure duration, or the total period of contact with the contaminant, expressed in years;

BW: This variable corresponds to the body weight of the affected individual, measured in kilograms;

AT: This is the averaging time, which is the period over which exposure is averaged, given in days;

PEF: This stands for the particle emission factor, quantified in cubic meters per kilogram of soil;

ADInh: This defines the average daily intake of heavy metals inhaled from the soil, given in milligrams per kilogram per day;

IRair: This denotes the rate of inhalation, quantified in cubic meters per day;

CF: This term represents the conversion factor, which is used to convert units, given in kilograms per milligram.

2.13 Estimation of Carcinogenic Exposure

The calculation of carcinogenic hazards considers the escalating probability of an individual developing cancer over a lifetime due to potential contact with carcinogens. This increased lifetime cancer risk can be estimated as demonstrated in Eq. (13):

$$Risk_{pathway} = \sum_{k=1}^n ADI_k CSF_k \quad (13)$$

where, risk is a dimensionless parameter denoting an individual's lifetime probability of cancer development. The terms ADI_k and CSF_k represent the average daily intake and the cancer slope factor of the k th heavy metal respectively, both quantified in milligrams per kilogram per day. These computations are made for each of the n metals under investigation. The tendency factor converts the typical daily intake of a heavy metal over a lifetime into the cumulative risk of cancer acquisition [34]. As depicted in Eq. (13), the overall additional cumulative cancer risk for an individual is derived by summing the contributions from various heavy metals through different exposure routes.

$$Risk_{(total)} = Risk(ing) + Risk(inh) + Risk(derm) \quad (14)$$

Table 6. RfD and CSF for various heavy metals in units of (mg/kg/day)

S/N	Heavy Metal	Oral RfD	Dermal RfD	Inhalation RfD	Oral CSF	Dermal CSF	Inhalation CSF	References
1.	As	$3E-4$	$3E-4$	$3E-4$	$1.5E+0$	$1.5E+0$	$1.5E+1$	[34, 35]
2.	Pb	$3.6E-3$	-	-	$8.5E-3$	-	$4.2E-2$	[35]
3.	Cd	$5E-4$	$5E-4$	$5.7E-5$	-	-	$6.3E+0$	[34, 35]
4.	Cr	$3E-3$	-	$3E-5$	$5E-1$	-	$4.1E+1$	[34, 35]
5.	Co	$2E-2$	$5.7E-6$	$5.7E-6$	-	-	$9.8E+0$	[35]
6.	Ni	$2E-2$	$5.6E-3$	-	-	-	-	[35]
7.	Cu	$3.7E-2$	$2.4E-2$	-	-	-	-	[35]
8.	Zn	$3E-1$	$7.5E-2$	-	-	-	-	[35]

where, Risk(ing), Risk(inh), and Risk(dermal) represent the risk contributions through ingestion, inhalation, and dermal contact respectively. As shown in Table 6, the evaluation of both non-carcinogenic and carcinogenic risks associated with toxic metals is conducted using RfD (Reference Dose) and CSF (Cancer Slope Factor) values, primarily sourced from the Department of Environmental Affairs (South Africa) [35] and the USEPA [37].

2.14 Statistical Techniques

Chemical analysis data from samples were subjected to statistical evaluation utilizing the 22.0 version of SPSS™. Descriptive analysis, principal component analysis (PCA), hierarchical cluster analysis, and bivariate analysis were performed on the data, which were normalized prior to the analyses. In statistical investigations such as these, normalization of data ensures that different variables with different scales of measurement are made comparable, which is integral to many statistical techniques.

3 Results

3.1 Heavy Metal Concentrations in Soils

The concentrations of heavy metals in soils from Ado, Ekiti are tabulated in Table 7 and visually represented in Figure 2. A range of heavy metals was assessed, namely: As, Cu, Cd, Cr, Co, Ni, Pb, and Zn. In the proximity of school zones, the usual concentrations of these metals were recorded as follows (in mg/kg): As (0.82), Cu (17.03), Cd (0.76), Cr (3.80), Co (1.80), Ni (2.68), Pb (0.51), Zn (58.52), and Fe (228.38). Similarly, soils from mining sites demonstrated mean concentrations of the mentioned heavy metals in the order of As (1.19), Cu (17.43), Cd (1.69), Cr (9.06), Co (3.00), Ni (4.94), Pb (24.59), Zn (69.63), and Fe (201.88). Residential areas showcased average concentrations (in mg/kg) of As (1.09), Cu (20.80), Cd (1.45), Cr (10.23), Co (2.31), Ni (5.79), Pb (21.25), Zn (65.66), and Fe (202.29).

In soils from motor parks, the mean concentrations (in mg/kg) were as follows: As (1.25), Cu (25.17), Cd (1.76), Cr (5.50), Co (1.42), Ni (5.01), Pb (20.69), Zn (64.77), and Fe (203.34). In contrast, dumpsite soils exhibited mean concentrations (in mg/kg) of As (1.84), Cu (30.62), Cd (2.31), Cr (12.21), Co (12.15), Ni (6.43), Pb (28.28), Zn (89.02), and Fe (182.09). Lastly, soils from markets generally contained mean As (1.45), Cu (26.11), Cd (5.25), Cr (9.00), Co (2.35), Ni (4.94), Pb (24.59), Zn (69.63), and Fe (201.88) concentrations, respectively (in mg/kg).

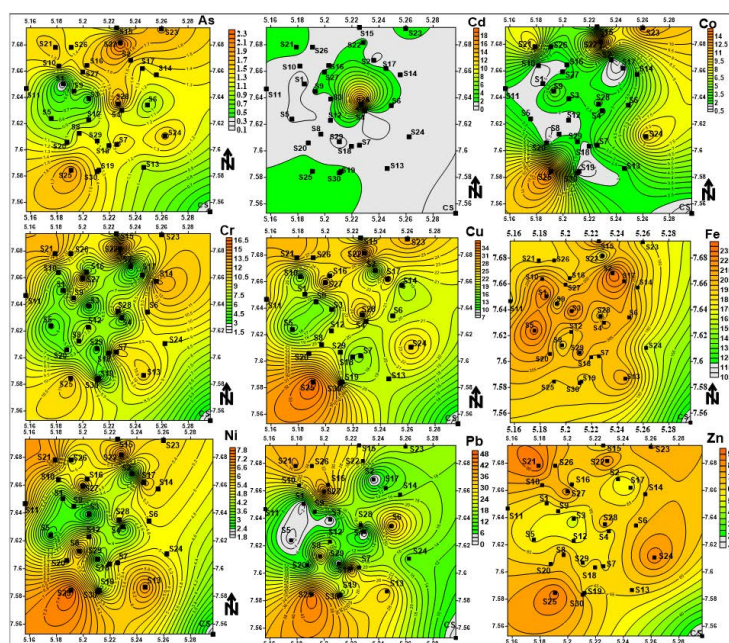


Figure 2. Heavy metal spatial distributions in Ado-Ekiti soils

3.2 Contamination Assessments

Igeo

The Igeo, EF, and CF values across various locations are summarized in Table 8. For dumpsite soils, the Igeo averages varied between 0.73 (Fe) and 4.05 (Co). For motor park soils, the range was from 0.89 (Fe) to 3.09 (Pb). School soils demonstrated a mean Igeo ranging from -1.95 (Pb) to 1.93 (Zn), whereas in market soils, the range was from -0.87 (Fe) to 2.76 (Pb). Residential soils had an average Igeo varying from -0.88 (Fe) to 3.40 (Pb), and in mining areas, the range was from -0.88 (Fe) to 3.55 (Pb).

Table 7. Heavy metals (mg/kg) in soils of Ado-Ekiti metropolis based on land-use

Land Use	Statistics	pH	EC	OMC	Sand (%)	Silt (%)	Clay (%)	As	Cu	Cd	Cr	Co	Ni	Pb	Zn	Fe
Schools	Min.	6.36	116.00	0.99	43.00	15.00	32.00	0.11	13.82	0.52	2.85	1.04	1.99	0.41	52.28	212.26
	Max.	7.69	268.00	1.63	49.00	22.00	42.00	1.53	20.36	1.08	4.73	2.48	3.18	0.75	62.83	236.8
	Avg.	6.98	174.40	1.36	46.40	18.60	35.00	0.82	17.03	0.76	3.80	1.80	2.68	0.51	58.52	228.38
	±SE	±0.23*	±27.77	±0.11*	±1.07*	±1.29*	±1.79*	±0.25*	±1.39*	±0.10*	±0.36*	±0.27*	±0.21*	±0.06*	±1.92*	±4.31*
	Benin City [38]	6.31	268.80	-	-	-	-	+0	11.02	6.86	6.42	-	1.72	9.26	11.02	389.70
Mining areas	Min.	6.38	143.00	1.18	45.00	13.00	31.00	0.86	15.10	1.16	6.72	1.06	3.34	10.44	61.83	190.40
	Max.	6.96	287.00	1.68	53.00	22.00	35.00	1.47	20.43	2.44	11.10	4.32	6.47	36.12	75.30	215.46
	Avg.	6.70	198.80	1.48	48.40	18.40	33.20	1.19	17.43	1.69	9.06	3.00	4.94	24.59	69.63	201.88
	±SE	±0.11*	±27.45	±0.11*	±1.33*	±1.50*	±0.66*	±0.13*	±1.06*	±0.24*	±0.80*	±0.65*	±0.52*	±4.42*	±2.92	±4.54*
	Ihero [39]	-	-	-	-	-	-	1.77	59.00	0.14	4.74	8.48	6.53	30.61	22.44	56300.00
Residential areas	Min.	6.76	139.00	0.72	41.00	18.00	31.00	0.95	17.59	1.02	7.68	1.48	5.05	15.00	58.81	186.34
	Max.	6.94	261.00	1.81	51.00	21.00	39.00	1.32	25.18	1.86	13.2	4.26	6.91	31.62	70.88	220.69
	Avg.	6.85	206.60	1.24	46.00	19.20	34.80	1.09	20.80	1.45	10.23	2.31	5.79	21.25	65.66	202.29
	±SE	±0.33*	±23.54	±0.19*	±1.61*	±0.58*	±1.28*	±0.07*	±1.24*	±0.15*	±1.06*	±0.51*	±0.35*	±3.16*	±2.17*	±6.09*
	Changsha [40]	-	-	-	-	-	-	-	37.30	0.52	86.50	-	28.70	37.40	144.40	-
Motor Parks	Min.	6.34	156.00	0.81	41.00	15.00	32.00	1.00	17.00	1.20	3.75	1.00	4.00	4.92	56.33	189.76
	Max.	6.96	261.00	1.69	48.00	24.00	42.00	1.55	25.52	5.14	7.29	1.92	6.00	36.78	70.40	225.06
	Avg.	6.76	215.80	1.12	43.80	19.60	36.60	1.25	21.57	1.76	5.50	1.42	5.01	20.69	64.77	203.34
	±SE	±0.11*	±17.66	±0.16*	±1.16*	±1.50*	±1.66*	±0.09*	±1.52*	±0.19*	±0.57*	±0.18*	±0.33*	±6.05*	±2.43*	±6.29*
	Gombe [41]	-	-	-	-	-	-	-	-	-	0.09	-	6.02	12.13	19.87	58.68
Dumpsites	Min.	6.25	119.00	0.69	44.00	16.00	32.00	1.56	25.50	1.00	8.91	9.34	4.93	11.94	80.63	167.79
	Max.	6.93	205.00	1.95	48.00	22.00	36.00	2.30	35.79	2.60	16.60	14.82	7.77	46.44	95.38	194.23
	Avg.	6.58	151.00	1.24	46.80	19.40	33.80	1.84	30.62	2.31	12.21	12.15	6.43	28.28	89.02	182.09
	±SE	±0.12*	±15.16	±0.20*	±0.97*	±0.98*	±0.74*	±0.14*	±1.88*	±0.14*	±1.28*	±1.17*	±0.52*	±6.31*	±2.49*	±4.40*
	Sunyani [42]	-	-	-	-	-	-	0.41	-	0.29	-	-	-	0.54	0.38	78.04
Markets	Min.	6.54	168	0.69	42.00	14.00	31.00	1.19	20.21	0.64	4.38	1.34	3.07	0.41	62.08	189.48
	Max.	7.95	247	1.37	52.00	24.00	40.00	1.96	28.58	19.22	12.51	3.36	6.21	44.22	85.28	213.89
	Avg.	6.98	212.20	1.03	46.80	18.40	34.80	1.45	26.11	5.25	9.00	2.35	4.94	25.83	74.95	200.18
	±SE	±0.26*	±12.79	±0.13*	±1.63*	±1.81*	±1.53*	±0.13*	±1.53*	±3.50*	±1.31*	±0.35*	±0.54*	±7.36*	±3.71*	±4.25*
	Enugu [43]	-	-	-	-	-	-	-	46.40	1.58	-	-	0.54	42.10	-	597.50
CS	1	6.65	205.65	0.69	53.00	15.68	31.32	0.30	8.28	0.52	2.00	0.60	2.00	2.45	16.26	112.58
USEPA [44]								0.11	270.00	0.48	11.00		72.00	210.00	1100	

[38]: Biose et al. 2021; [39]: Laniyan and Adewumi 2020; [40]: He et al. 2021 [41]: Magaji et al. 2019; [42]: Agbeshie et al. 2020; [43]: Ekere and Ukoha, 2013; CS: Control Sample; SE: Standard Error; *p < 0.01; **p > 0.01

EF

In the case of dumpsite soils, EF values for metals ranged from 5.64 (Ni) to 28.64 (Co) on average, while for motor park soils, the range was from 3.02 (Co) to 16.71 (Pb). School soils exhibited a mean EF ranging from 0.36 (Pb) to 14.38 (As), and for market soils, the range was from 3.89 (Zn) to 20.99 (Pb). In residential areas, the average EF ranged from 2.94 (Zn) to 16.69 (Pb), and in mining areas, the range was from 3.12 (Zn) to 19.49 (Pb).

CF

For dumpsite soils, the average CF values for metals ranged from 1.66 (Fe) to 16.87 (Co), while for motor park soils, the range was from 1.85 (Fe) to 10.72 (Pb). School soils demonstrated a mean CF ranging from 0.27 (Pb) to 3.82 (Zn), and for market soils, the range was from 1.82 (Fe) to 13.39 (Pb). In residential areas, the average CF ranged from 1.84 (Fe) to 11.02 (Pb), and in mining areas, the range was from 1.84 (Fe) to 12.25 (Pb).

PLI and CD

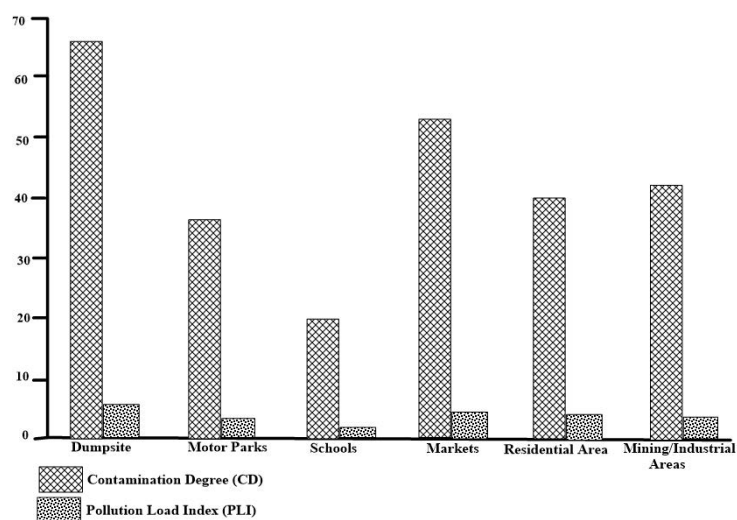
The average values of the CD for heavy metals in dumpsites, motor parks, schools, markets, residential areas, and mining areas were found to be 65.89, 36.44, 19.45, 52.88, 39.52, and 41.94, respectively (Figure 3). These figures indicate a very high degree of heavy metal contamination in soils from dumpsites, motor parks, markets, residential areas, and mining areas. Conversely, soils from school areas displayed a significant level of heavy metal contamination. The average PLI values were calculated to be 5.82, 3.37, 1.72, 4.25, 3.81, and 3.86 for the same respective locations (Figure 3).

3.3 Origins of Soil Contamination

Comprehensive exploration of potential sources of metals was executed utilizing a range of methodologies including bivariate correlation (BC), principal component analysis (PCA), and hierarchical cluster analysis (HCA).

Table 8. Mean heavy metal Igeo, EF, and CF in soils from various land-uses

Indices	Land-Use/Activities	As	Cu	Cd	Cr	Co	Ni	Pb	Zn	Fe
Igeo	Dumpsites	2.83	1.96	2.50	2.71	4.05	1.71	3.71	2.54	0.73
	Motor Parks	2.28	1.47	2.08	1.56	0.93	1.36	3.09	2.08	0.89
	Schools	1.23	1.12	0.84	1.05	1.25	0.45	-1.95	1.93	1.06
	Markets	2.49	1.75	2.67	2.22	1.64	1.31	2.76	2.28	0.87
	Residential Areas	2.09	1.41	1.66	2.45	1.57	1.57	3.40	2.05	0.88
	Mining Areas	2.19	1.16	2.01	2.29	1.88	1.32	3.55	2.18	0.88
EF	Dumpsites	12.27	6.73	9.69	11.35	28.64	5.64	24.49	4.42	1.00
	Motor Parks	14.35	4.25	6.63	4.59	3.02	3.93	16.71	2.89	1.00
	Schools	14.38	3.01	2.53	2.88	3.42	1.89	0.36	2.31	1.00
	Markets	14.40	5.26	20.45	7.68	5.09	3.98	20.99	3.39	1.00
	Residential Areas	14.40	4.03	5.54	8.65	4.98	4.33	16.69	2.94	1.00
	Mining Areas	14.40	3.47	6.45	7.63	6.45	3.94	19.49	3.12	1.00
CF	Dumpsites	7.21	3.96	5.71	6.68	16.87	3.33	14.66	5.82	1.66
	Motor Parks	4.93	2.79	4.34	3.01	1.97	2.59	10.72	4.23	1.85
	Schools	3.21	2.20	1.87	2.11	2.50	1.39	0.27	3.82	2.08
	Markets	5.69	3.38	12.96	4.92	3.27	2.56	13.39	4.89	1.82
	Residential Areas	4.55	2.69	3.58	5.20	3.21	2.86	11.02	4.29	1.84

**Figure 3.** The severity of contamination from metals (CD) and the level of pollution load index (PLI) in soils

Strong relationships were revealed between several metal pairs through bivariate correlation analysis (Table 9), notable among which were Ni-Cr ($r=0.76$), Pb-Cr ($r=0.62$), Pb-Ni ($r=0.76$), and Zn-Cr ($r=0.71$), among others.

The HCA highlighted distinct clustering amongst the samples. Specifically, the first cluster, which comprises 10% of the total component, includes samples 1, 5, and 2. The second cluster, accounting for 7% of the total, encompasses samples 3 and 4 (Figure 4). The third and largest cluster, representing 60% of the total component, involves samples 6 to 10, 22 to 30, and 16 to 21, and 17. Lastly, the fourth component, which comprises 23% of the total, includes samples 11 to 15, and 18 to 19.

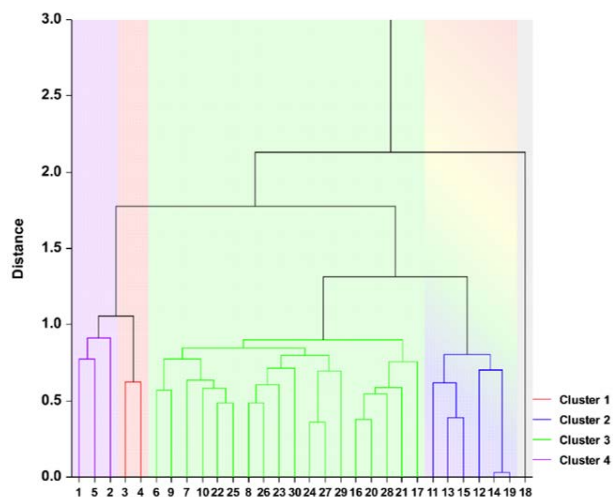
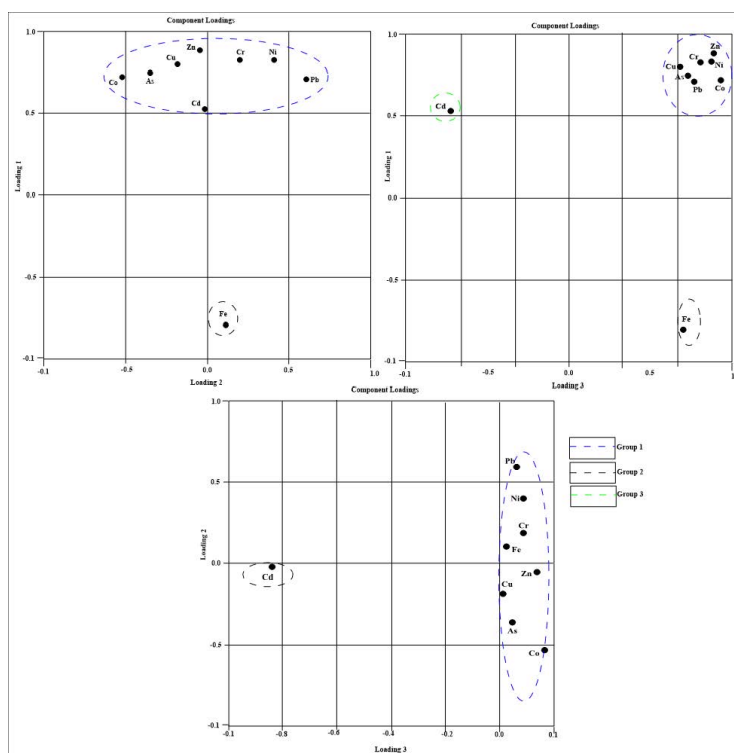
Furthermore, PCA was employed to plot loading 1 against loading 2 (Figure 5), indicating that Co, As, Cu, Zn, Cr, Ni, Pb, and Cd form a coherent group, with Fe being an outlier. When loading 1 was plotted against loading 3, Co, As, Cu, Zn, Cr, Ni, and Pb were found to coalesce into a single group, with Fe and Cd appearing as independent entities. A similar pattern was observed in the plot of loading 2 against loading 3, wherein Co, As, Cu, Zn, Cr, Ni, Pb, and Fe form one group, whereas Cd emerges as a distinct group.

3.4 Environmental Risk Evaluation

In an attempt to understand the environmental implications of these findings, an ecological hazards index of heavy metals present in the studied soils is generated (Figure 6). The data illustrates environmental risks (ER) associated with Cu ranging from 11.02 (schools) to 16.89 (markets), while those for Cd extend from 56 (schools) to

Table 9. Heavy metal bivariate association in soils

	Cr	Ni	Pb	Co	Cu	Zn	As	Fe	Cd
Cr	1.00								
Ni	0.76	1.00							
Pb	0.62	0.76	1.00						
Co	0.63	0.48	0.30	1.00					
Cu	0.58	0.70	0.50	0.67	1.00				
Zn	0.71	0.68	0.66	0.72	0.73	1.00			
As	0.53	0.56	0.42	0.62	0.63	0.61	1.00		
Fe	-0.65	-0.56	-0.47	-0.57	-0.56	-0.69	-0.60	1.00	
Cd	0.20	0.14	0.11	0.08	0.31	0.19	0.38	-0.21	1.00

**Figure 4.** Hierarchical cluster analysis of heavy metals in soils**Figure 5.** Metal principal component analysis (PCA) in soils

a concerning 388.74 (markets). Further analysis indicates a varied total index of risk (RI) across the region, ranging from 76.40 (schools) to a startling 487.35 (markets).

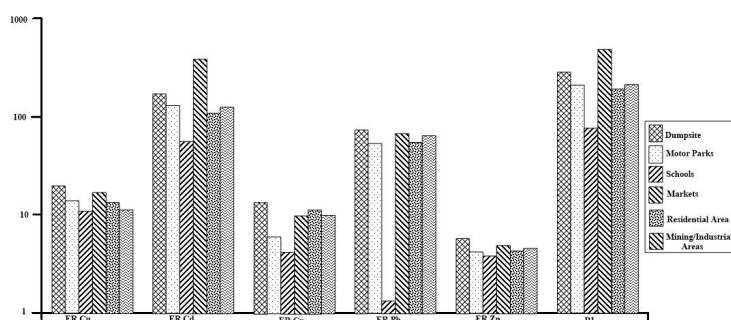


Figure 6. Ecological risk and heavy metal risk index in soils

3.5 Health Risk Assessment of Heavy Metals

Figures 7 and 8 delineate the outcomes of the health risk assessment for heavy metals present in the soils from the studied region. For children, the HQ, a measure indicative of non-carcinogenic health threats posed by heavy metals through oral consumption (in mg/kg/day), varies, spanning from 1.95E+0 (at the dumpsite) to 2.13E+0 (in markets) (Figure 7). Similarly, for inhalation, the HQ fluctuates between 1.39E-6 (schools) and 7.78E-6 (dumpsite). Cutaneous exposure to heavy metals in soils demonstrates a HQ range from 8.00E-2 (Motor Park) to 3.42E-1 (dumpsite). The resulting HI extends from 2.11E+0 to 2.29E+0, indicating substantial variation.

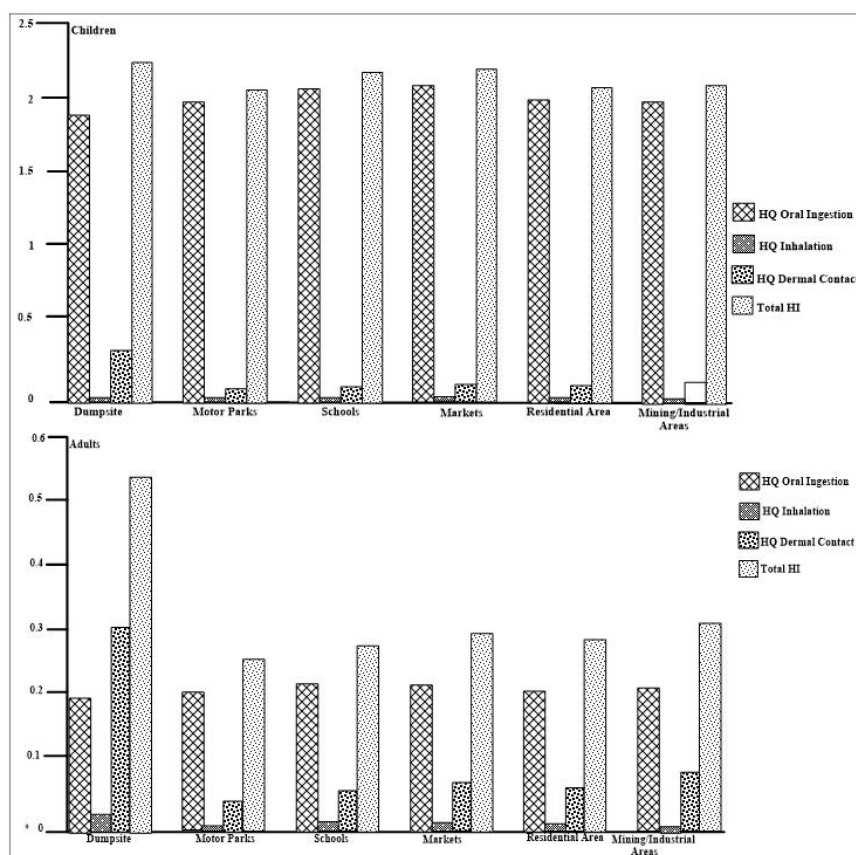


Figure 7. Non-cancerous health risks associated with metals that are found in soils

Considering adults, the HQ for non-carcinogenic health hazards from oral ingestion oscillates between 2.08E-1 (dumpsite) and 2.28E-1 (markets). For inhalation, the HQ values range from 4.62E-3 (schools) to 2.59E-2 (dumpsite). The HQ associated with cutaneous contact with contaminated soils extends from 4.74E-2 (Motor Park) to 3.20E-1 (dumpsite), while the HI varies from 2.69E-1 to 5.55E-1 (Figure 7).

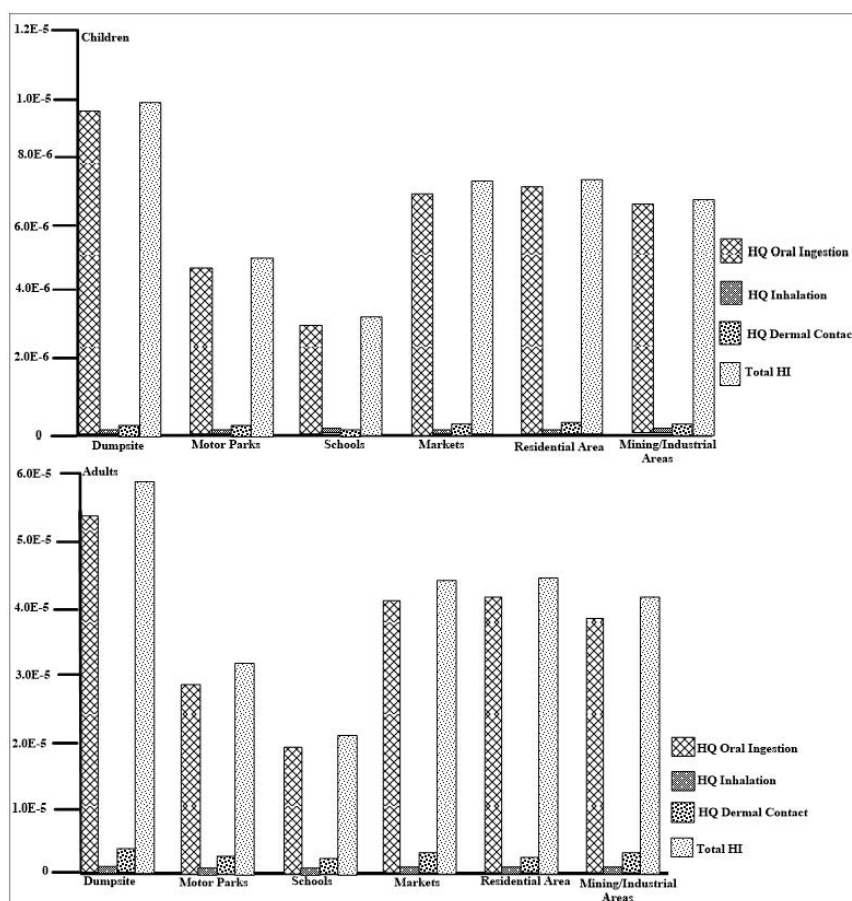


Figure 8. Cancerous health hazards of toxic metals in soils

In terms of carcinogenic health hazards, the HQ for children consuming the contaminated soil orally (in mg/kg/day) varies from $3.47\text{E-}6$ (schools) to $9.98\text{E-}6$ (dumpsites), and for inhalation, it extends from $7.68\text{E-}9$ (schools) to $2.71\text{E-}8$ (dumpsite). Cutaneous exposure to heavy metals in soils exhibits a HQ range of $1.72\text{E-}7$ (schools) to $3.87\text{E-}7$ (dumpsite) (Figure 8). The resultant HI fluctuates between $3.65\text{E-}6$ to $1.04\text{E-}5$.

For adults, the HQ for carcinogenic health hazards via oral ingestion extends from $1.86\text{E-}6$ (schools) to $5.34\text{E-}6$ (dumpsites), whereas for inhalation, it spans from $1.75\text{E-}8$ (schools) to $5.99\text{E-}8$ (dumpsite). Cutaneous contact with heavy metal-infused soils exhibits a HQ range from $1.79\text{E-}7$ (schools) to $4.01\text{E-}7$ (dumpsite), while the HI varies from $2.05\text{E-}6$ to $5.80\text{E-}6$ (Figure 8). These findings highlight the potential health risks posed by heavy metal contamination and call for urgent remedial measures.

4 Discussion

An examination of the heavy metal concentrations in the soils from the study region brings forward several comparisons to findings from other regions. The soils in schools of this region were reported to hold higher Cu, Ni, and Zn concentrations compared to those in Benin City, Nigeria, as noted by Biose et al. [38]. A comparative analysis with soils from Nigeria's Ijebu region reveals that the extraction districts of the region under study show greater Cd, Cr, and Zn concentrations [39]. A higher Cd content was observed in the residential soils of this region compared to that documented in Changsha, China [40]. It was also noticed that As, Cd, Pb, Zn, and Fe concentrations in the soils from dumpsites were greater than those reported in Gombe, Nigeria [41]. Interestingly, the car parks' soils in this area had higher Cr, Pb, Ni, Fe, and Zn concentrations than those reported in Sunyani, Nigeria [42]. Higher Cd and Ni concentrations were observed compared to an industrial market in Enugu, Nigeria [43]. Of note, the As and Cd concentrations in the soils were found to exceed the standards set by USEPA for schools, mining sites, residential areas, motor parks, and markets. The As, Cd, and Cr contents in the soils from dumpsites were noted to be higher than the recommended limits.

The distribution of As in soils was found to follow the order: dumpsites > markets > motor parks > mining regions > residential areas > schools. The distribution pattern for other metals was identified as follows: Cu: markets > motor parks > residential areas > mining areas > schools, Cd: marketplaces > dumpsites > car parks >

mining zones > residential zones> schools, Cr: dumpsite > residential areas> mining areas > marketplaces > motor parks > school, Co: dumpsites > mining areas > markets> residential areas > schools > automobile parks, Ni: dumpsite> residential areas > motor parks > mining areas > market > school, Pb and Zn: dumpsite > markets > mining areas > residential areas> motor parks > school, and Fe: school > motor parks> residential areas > mining areas > marketplaces> dumpsite.

Fe contamination in dumpsite soils ranged from unaffected to slight, with Cu and Ni indicating slight pollution. As, Cd, Cr, and Zn were found to cause moderate to significant pollution, whereas Pb caused severe pollution. In motor park soils, Co and Fe indicated unpolluted to moderate contamination, while Cu, Cr, and Ni presented moderate pollution. Pb was found to cause heavy pollution in these soils. School soils were found to be unpolluted by Pb but significantly polluted by Cd and Co. As, Cu, Cr, Ni, Zn, and Fe indicated mild contamination. In marketplace soils, Fe ranged from unpolluted to moderately contaminated, whereas Cu, Co, and Ni showed substantial pollution. Residential soils ranged from unpolluted to moderately polluted by Fe, slightly polluted by Cu, Cd, Co, and Ni, moderately to heavily polluted by As, Cr, and Zn, and heavily polluted by Pb.

The level of enrichment in dumpsite soils showed moderate enrichment for Zn, high enrichment for As, Cu, Cd, Cr, and Ni, and extremely high for Co and Pb. Car park soils were found to be slightly enriched in Cu, Cr, Co, and Ni, but depleted in As, Cd, Pb, and Zn. School soils exhibited minor enrichment for Ni and Pb, moderate for Cu, Cd, Cr, Co, and Zn, and high for As. Market soils displayed modest enrichment for Ni and Zn, substantial for As, Cu, Cr, and Co, and very high for Cd and Pb. Residential soils showed slight enrichment for Cu, Co, Ni, and Zn, while As, Cd, Cr, and Pb showed high enrichment. Excavation soils ranged from slightly tainted by Fe to moderately polluted by Cu, Co, and Ni, while As, Cd, Cr, and Zn indicated slight to significant pollution, and Pb was found to cause severe pollution. These findings emphasize the severity of heavy metal pollution in different areas, warranting an immediate response.

In line with the classification proposed by Hakanson [31], an assessment of heavy metal pollution across different land uses revealed that dumpsite soils demonstrated a moderate degree of Fe pollution, while significant contamination was observed for Cu, Cd, Ni, and Zn. Furthermore, As, Cr, Co, and Pb were identified as pollutants of substantial concern. Soils derived from motor parks were mildly polluted by Cu, Co, Ni, and Fe, but displayed significant contamination from As, Cd, Cr, and Zn. These soils were notably tainted by Pb to a considerable extent. As and Zn were the principal contaminants in school soils, with a significant level of pollution exhibited by Cu, Cd, Cr, Co, Ni, and Fe. Pb pollution in these soils, however, was comparatively moderate.

An examination of the market soils revealed mild pollution by Ni and Fe, while As, Cu, Cr, Co, and Zn emerged as substantial pollutants. An alarmingly high level of Cd and Pb contamination was observed in these soils. In the residential areas, soils displayed moderate contamination by Cu, Ni, and Fe, with As, Cd, Cr, Co, and Zn contributing significantly to pollution. Pb was found to contaminate these soils highly. Soils in mining areas showed minimal influence from Fe but substantial contamination by Cu and Ni. Furthermore, As, Cd, Cr, Co, and Zn contributed significantly to the pollution of these soils, with Pb identified as an extremely high contaminant. The contamination degree and PLI indicate that heavy metals pose threats to soils across all land-use categories.

A consideration of bivariate correlations revealed that a majority (over 60%) of the area's soils were subjected to analogous geochemical processes. Negative associations of Fe with other heavy metals underscored the significant influence of geogenic processes in the release of this metal. However, PCA analysis indicated that Fe and Cd contamination in soils potentially originated from both geogenic and anthropogenic sources [37]. The bustling metropolitan region of Ado-Ekiti in Nigeria, characterized by rapid growth and an assortment of human-related activities, is a major contributor to the release of heavy metals into the soil. These activities include but are not limited to painting, agriculture, construction, pharmaceutical production, and food and beverage services.

Ecological risk assessments suggested that Cu, Cr, and Zn in the area's soils impose a minor ecological risk, while Cd presents a risk ranging from moderate to severe. Pb, on the other hand, poses a minor to moderate ecological risk. An evaluation of overall risk confirmed that heavy metals in the soils of this region pose varying levels of ecological risks, ranging from low to extremely high. Of all the categories of land use, soils derived from schools were found to be the least at risk from heavy metal environmental impacts, while market soils were the most vulnerable.

The ecological repercussions of excessive metal content in plants have multiple facets. It can hamper plant growth and productivity [9], interfere with various physiological processes [30], and subsequently reduce agricultural yields. It is noteworthy that accumulated metals such as Cd and Pb in edible parts of the plants pose potential health risks [39]. Additionally, plants growing in polluted soils or metal-rich environments may become vectors of contamination in the food chain.

Excessive metal content in plants can also lead to environmental contamination [9]. Metals accumulated by plants may be released back into the environment through pathways such as leaf litter, root exudates, or decomposition, contributing to soil degradation, water contamination, and damage to other organisms [45]. Furthermore, bioaccumulation and biomagnification can lead to the transfer of metals to higher trophic levels [39].

Mitigating the effects of excessive metals in plants in this region could involve strategies such as phytoremediation,

soil remediation, and correct waste disposal methods [46]. Moreover, the implementation of legislation to monitor and regulate metal emissions and contamination levels is crucial in managing and preventing metal pollution.

The health risk assessment conducted within this study highlighted the susceptibility of children to non-carcinogenic health hazards due to the presence of heavy metals in soils. Despite this, no discernable carcinogenic health hazards associated with these heavy metals in soils were identified for either adult or children populations. Health implications connected with As include increased instances of gastrointestinal discomfort, such as vomiting and diarrhea [47, 48]. Symptoms such as nausea, abdominal discomfort, and diarrhea can be induced by acute Cu poisoning, while chronic exposure may lead to liver and kidney damage [49]. Similarly, heightened Cd levels in the body can trigger acute poisoning symptoms including nausea, vomiting, abdominal discomfort, and diarrhea [48].

Cr is recognized as a human carcinogen when inhaled, with the potential for inducing severe respiratory irritation, gastrointestinal consequences, and damage to the liver and kidneys at high doses [48]. High levels of Co, either inhaled or ingested, can cause respiratory difficulties such as asthma-like symptoms and shortness of breath. Long-term exposure to Co dust or fumes can trigger lung and heart issues, along with skin allergies [48]. Nickel exposure, through inhalation or skin contact, can induce allergic reactions such as dermatitis or respiratory sensitization. Long-term Ni exposure has been associated with an increased risk of lung and nasal cancers [50].

Lead toxicity can have widespread effects on the human body, especially in children, potentially causing developmental delays, behavioral problems, a decrease in IQ, and hearing impairment. Adult Pb exposure can result in cardiovascular effects, renal damage, and reproductive issues [48]. Acute Zn ingestion or inhalation can induce symptoms of nausea, vomiting, and abdominal discomfort, while chronic exposure can disrupt the absorption of copper and iron, leading to deficiencies in these essential minerals. Nausea, vomiting, and gastrointestinal discomfort may result from children ingesting excessive amounts of Fe [44]. Diseases of iron overload, such as hemochromatosis, can lead to the accumulation of excess iron in organs, potentially causing organ damage and an increased risk of liver disease, cardiovascular complications, and diabetes [44, 48]. Despite adults being less vulnerable to these non-carcinogenic health issues, the study suggests potential future health problems for individuals residing near dumpsites.

Within the confines of this investigation, only a limited number of samples were analyzed, potentially hindering a comprehensive understanding of heavy metal content in the soils of Ado-Ekiti. However, valuable insights were gained into the concentrations of toxic metals present in soils across areas impacted by varying human activities. For a more comprehensive understanding of how increased urbanization influences soil heavy metal content, it is suggested that a more detailed geochemical study be undertaken, incorporating the collection and analysis of closely spaced samples. A seasonal-based study could also be considered to determine any temporal fluctuations in heavy metal content within the city's soils.

Another constraint of this investigation is the limited number of metals analyzed. The research focused on only nine heavy metals within soil samples. In future studies, the inclusion of all available heavy metals, as well as major and minor oxides and radionuclides, could offer a more thorough understanding of the pedogeochemical processes in the area. Such an approach would provide a more comprehensive perspective on the potential ecological and health risks associated with these heavy metals.

Additionally, the sole use of the atomic absorption spectrometer (AAS) as an analytical technique in this study may have resulted in a potential underestimation of metal concentrations due to the limitations of this instrument. Consequently, future analyses should consider incorporating more advanced geochemical instruments, such as the inductively coupled plasma-mass spectrometer (ICP-MS) and X-Ray fluorescence (XRF), to ensure greater accuracy.

5 Conclusions

This investigation delineates the abundance, severity, origins, and potential ecological and health repercussions of metallic elements present in the urban soils of Ado-Ekiti. The analysis confirmed concentrations of As and Cd surpassing permissible thresholds across various urban spaces including marketplaces, schools, mining locales, residential zones, motor parks, and waste disposal sites. This points to significant pollution through these heavy metals. Contrastingly, levels of Cu, Cr, Co, Ni, Pb, Zn, and Fe were detected within recommended bounds. Pollution indices, as indicated by the Igeo, EF, CF, and PLI, ranged from negligibly low to extremely high, reflecting considerable environmental contamination attributable to intensified local anthropogenic activity.

Ecological risk evaluations underscored the potentially harmful environmental effects of heavy metals, with Cd posing a particularly significant risk. Risk assessments also suggested that urban dwellers are more likely to be exposed to non-carcinogenic health hazards as opposed to carcinogenic ones, with children found to be more susceptible to non-cancerous health conditions compared to adults.

Anthropogenic activities in Ado-Ekiti appear to contribute significantly to the enrichment of heavy metals in local soils. The rapid urban expansion witnessed in the region has fueled industrialization, elevating the quantities of toxic metals in the environment. Concurrently, an urbanized cityscape has led to a surge in waste generation stemming from varied human activities such as mining, household activities, and other industrial processes, leading

to escalating contamination levels in urban soils.

The environmental implications of such heavy metal contamination are manifold. Contaminated urban soils may pose significant threats to local flora, which can bioaccumulate these toxic elements. The resultant metal-laden plant life could substantially impair the health of consumers. Further, heavy metals in the contaminated soils can potentially degrade both surface and groundwater quality, while aerosols originating from such soils may pose a major threat to local air quality.

A comprehensive approach, involving the enforcement of stricter regulations on industrial operations that emit heavy metals or generate waste, is required. These operations should be obliged to employ pollution-reducing technologies and practices, such as effective waste management, treatment, and recycling. Encouragement for the adoption of greener manufacturing processes and the substitution of heavy metals with safer alternatives where feasible is also necessary. Rigorous rules and procedures for the disposal of hazardous waste, particularly heavy metal-rich waste, need to be strengthened and strictly enforced.

Simultaneously, an emphasis on recycling and proper waste disposal to curtail the release of heavy metals into the environment is warranted. Investments in the development of infrastructure and technologies for hazardous waste processing, storage, and disposal should also be encouraged. Moreover, fostering public awareness about the risks associated with heavy metal exposure and the importance of preventive measures is crucial. Dissemination of educational resources and training programs for individuals, communities, and professionals such as farmers, industrial workers, and waste management personnel can significantly aid in mitigating the environmental and health impacts of heavy metal contamination.

Author Contributions

Conceptualization, S.I.E. and A.J.A.; methodology, A.J.A.; software, A.J.A.; validation, S.I.E. and A.J.A.; formal analysis, A.J.A.; investigation, S.I.E. and A.J.A.; resources, S.I.E. and A.J.A.; data curation, S.I.E. and A.J.A.; writing—original draft preparation, A.J.A.; writing—review and editing, A.J.A.; visualization, A.J.A. All authors have read and agreed to the published version of the manuscript.

Data Availability

Not applicable.

Acknowledgements

The authors appreciate the management of Achievers University, Owo, Nigeria for providing equipment used for sample collections.

Conflicts of Interest

The authors declare no conflict of interest.

References

- [1] A. J. Adewumi, “Heavy metals in soils and road dust in Akure City, Southwest Nigeria: pollution, sources, and ecological and health risks,” *Expo. Health.*, vol. 14, no. 2, pp. 375–392, 2022. <https://doi.org/10.1007/s12403-021-00456-y>
- [2] D. A. Pupilampu and Y. A. Boafo, “Exploring the impacts of urban expansion on green spaces availability and delivery of ecosystem services in the Accra Metropolis,” *Environ. Chall.*, vol. 5, no. 100283, 2021. <https://doi.org/10.1016/j.envc.2021.100283>
- [3] L. T. Molina, T. Zhu, W. Wan, and B. R. Gurjar, “Impacts of megacities on air quality: Challenges and opportunities,” *Oxford. Res. Encycl. Environ. Sci.*, 2020. <https://doi.org/10.1093/acrefore/9780199389414.013.5>
- [4] F. Perera, “Pollution from fossil-fuel combustion is the leading environmental threat to global pediatric health and equity: Solutions exist,” *Int. J. Environ. Res. Public. Health.*, vol. 15, no. 1, p. 16, 2018. <https://doi.org/10.3390/ijerph15010016>
- [5] I. Manisalidis, E. Stavropoulou, A. Stavropoulos, and E. Bezirtzoglou, “Environmental and health impacts of air pollution: a review,” *Front. Pub. Health.*, vol. 8, no. 14, 2020. <https://doi.org/10.3389/fpubh.2020.00014>
- [6] S. O. Oyedepo, “Energy and sustainable development in nigeria: the way forward,” *Energy. Sustain. Soc.*, vol. 2, no. 1, pp. 1–17, 2012. <https://doi.org/10.1186/2192-0567-2-15>
- [7] H. I. Abdel-Shafy and M. S. Mansour, “Solid waste issue: Sources, composition, disposal, recycling, and valorization,” *Egypt. J. Petrol.*, vol. 27, no. 4, pp. 1275–1290, 2018. <https://doi.org/10.1016/j.ejpe.2018.07.003>

- [8] I. R. Abubakar, K. M. Maniruzzaman, U. L. Dano, F. S. AlShihri, M. S. AlShammari, S. M. S. Ahmed, and T. I. Alrawaf, "Environmental sustainability impacts of solid waste management practices in the global south," *Int. J. Environ. Res. Pub. Health.*, vol. 19, no. 19, p. 12717, 2022. <https://doi.org/10.3390/ijerph191912717>
- [9] A. J. Adewumi and T. A. Laniyan, "Contamination, sources and risk assessments of metals in media from Anka artisanal gold mining area, northwest nigeria," *Sci. Tot. Environ.*, vol. 718, no. 137235, 2020. <https://doi.org/10.1016/j.scitotenv.2020.137235>
- [10] S. Singh, P. Parihar, R. Singh, V. P. Singh, and S. M. Prasad, "Heavy metal tolerance in plants: role of transcriptomics, proteomics, metabolomics, and ionomics," *Front. Plant. Sci.*, vol. 6, p. 1143, 2016. <https://doi.org/10.3389/fpls.2015.01143>
- [11] J. Gall, R. Boyd, and N. Rajakaruna, "Transfer of heavy metals through terrestrial food webs: a review," *Environ. Monit. Assess.*, vol. 187, pp. 1–21, 2015. <https://doi.org/10.1007/s10661-015-4436-3>
- [12] J. Khatun, A. Intekhab, and D. Dhak, "Effect of uncontrolled fertilization and heavy metal toxicity associated with arsenic (As), lead (Pb) and cadmium (Cd), and possible remediation," *Toxicology*, p. 153274, 2022. <https://doi.org/10.1016/j.tox.2022.153274>
- [13] P. Fasinu and O. Orisakwe, "Heavy metal pollution in sub-Saharan Africa and possible implications in cancer epidemiology," *Asian Pac. J. Cancer Prev.*, vol. 14, no. 6, pp. 3393–3402, 2013. <https://doi.org/10.7314/apjcp.2013.14.6.3393>
- [14] K. Rehman, F. Fatima, I. Waheed, and M. S. H. Akash, "Prevalence of exposure of heavy metals and their impact on health consequences," *J. Cell. Biochem.*, vol. 119, no. 1, pp. 157–184, 2018. <https://doi.org/10.1002/jcb.26234>
- [15] L. Wang, J. Rinklebe, T. F. M. Tack, and D. Hou, "A review of green remediation strategies for heavy metal contaminated soil," *Soil Use Manage.*, vol. 37, no. 4, pp. 936–963, 2021. <https://doi.org/10.1111/sum.12717>
- [16] T. Bizjak, D. Kontić, and B. Kontić, "Practical opportunities to improve the impact of health risk assessment on environmental and public health decisions," *Int. J. Environ. Res. Public Health*, vol. 19, no. 7, p. 4200, 2022. <https://doi.org/10.3390/ijerph19074200>
- [17] J. Burger and M. Gochfeld, "Temporal scales in ecological risk assessment," *Arch. Environ. Contam. Toxicol.*, vol. 23, pp. 484–488, 1992. <https://doi.org/10.1007/BF00203814>
- [18] R. Van der Oost, J. Beyer, and N. P. Vermeulen, "Fish bioaccumulation and biomarkers in environmental risk assessment: a review," *Environ. Toxicol. Pharmacol.*, vol. 13, no. 2, pp. 57–149, 2003. [https://doi.org/10.1016/s1382-6689\(02\)00126-6](https://doi.org/10.1016/s1382-6689(02)00126-6)
- [19] G. Ginsburg and H. Willard, "Genomic and personalized medicine: foundations and applications," *Transl. Res.*, vol. 154, no. 6, pp. 277–287, 2009.
- [20] O. Oriye, "Urban expansion and urban land use in Ado Ekiti, Nigeria," *America. J. Res Comm.*, vol. 1, no. 2, pp. 128–139, 2013.
- [21] "Ado-Ekiti, Nigeria Metro Area Population 1950-2023," MacroTrends, 2023. <https://www.macrotrends.net/cities/21977/ado-ekiti/population#:~:text=The%20current%20metro%20area%20population,a%203.82%25%20increase%20from%202021>
- [22] "Nigeria National Census: Population Distribution by Sex, State, LGAs and Senatorial District: 2006 Census Priority Tables," National Population Commission (NPC), 2006. <http://www.population.gov.ng/index.php/publication/140-popn-distri-by-sex-state-jgas-and-senatorial-distr-2006>
- [23] W. O. Adebayo, *Weather and climate. Ado-Ekiti Region: A geographical analysis and master plan.* Lagos, Nigera: Alpha Prints, 1993.
- [24] I. I. Oguntimehin and J. O. Babalola, "The pollution status of some selected rivers in Ado-Ekiti, Nigeria," *Bio. Sci. PJSIR.*, vol. 50, no. 1, pp. 22–26, 2007.
- [25] E. I. Adeyeye, O. S. Shittu, O. J. Ayodele, and A. A. Ilori, "Heavy metal pollution potential in soil influenced by sawmill operations at Ado-Ekiti, Nigeria," *Bang. J. Sci. Ind. Res.*, vol. 53, no. 1, pp. 29–34, 2018. <https://doi.org/10.3329/bjsir.v53i1.135907>
- [26] O. T. Ogunmodede, E. Adewole, and A. A. Ojo, "Quantitative evaluation of soil properties pollution hazards in urban solid waste dump sites in Nigeria," *World.*, vol. 5, no. 1, pp. 5–15, 2015. <https://doi.org/10.5829/idosi.wjep.2015.5.1.9367>
- [27] A. J. Walkley and I. A. Black, "Estimation of soil organic carbon by the chromic acid titration method," *Soil Sci.*, vol. 37, pp. 29–38, 1936.
- [28] G. Muller, "Index of geoaccumulation in sediments of the rhine river," *GeoJ.*, vol. 2, no. 108-118, 1969.
- [29] N. Sezgin, H. K. Ozcan, G. Demir, S. Nemlioglu, and C. Bayat, "Determination of heavy metal concentrations in street dusts in istanbul E-5 highway," *Environ. Int.*, vol. 29, pp. 979–985, 2023. [https://doi.org/10.1016/S0160-4120\(03\)00075-8](https://doi.org/10.1016/S0160-4120(03)00075-8)

- [30] N. S. Duzgoren-Aydin, "Sources and characteristics of lead pollution in the urban environment of guangzhou," *Sci. Tot. Environ.*, vol. 385, no. 1–3, pp. 182–195, 2007. <https://doi.org/10.1016/j.scitotenv.2007.06.047>
- [31] L. Hakanson, "An ecological risk index for aquatic pollution control, a sedimentological approach," *Water. Res.*, vol. 14, no. 975–1001, 1980. [https://doi.org/10.1016/0043-1354\(80\)90143-8](https://doi.org/10.1016/0043-1354(80)90143-8)
- [32] D. L. Tomlinson, J. G. Wilson, C. R. Harris, and D. W. Jeffrey, "Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index," *Helv. Meer.*, vol. 33, no. 566–575, 1980.
- [33] Z. Wang, Y. Wang, L. Chen, C. Yan, Y. Yan, and Q. Chi, "Assessment of metal contamination in coastal sediments of the Maluan Bay (China) using geochemical indices and multivariate statistical approaches," *Mar. Pollut. Bull.*, vol. 99, no. (1–2), pp. 43–53, 2015. <https://doi.org/10.1016/j.marpolbul.2015.07.064>
- [34] "Risk Assessment Guidance for Superfund. Human Health Evaluation Manual (Part A)," U.S. Environmental Protection Agency, 1989. <https://www.epa.gov/risk/risk-assessment-guidance-superfund-rags-part>
- [35] "Department of environmental affairs: The framework for the management of contaminated land, South Africa," DEA 2010, 2023. <http://sawic.environment.gov.za/documents/562.pdf>
- [36] "Supplemental guidance for developing soil screening levels for superfund sites. office of solid waste and emergency response, Washington, D.C." United States Environmental Protection Agency (USEPA), 2002. <http://www.epa.gov/superfund/health/conmedia/soil/index.htm>
- [37] "Risk-based concentration table," United States Environmental Protection Agency (USEPA), 2008. <http://www.epa.gov/reg3hwm/risk/human/index.html>
- [38] E. Biose, C. F. Amaechi, and C. Nwaemene, "Heavy metal contents in topsoil of selected public primary schools playground in Benin Metropolis, Nigeria," *J. Appl. Sci. Environ. Manag.*, vol. 25, no. 2, pp. 173–182, 2021. <https://doi.org/10.4314/jasem.v25i2.6>
- [39] T. A. Laniyan and A. J. Adewumi, "Potential ecological and health risks of toxic metals associated with artisanal mining contamination in Ijero, southwest Nigeria," *J. Environ. Sci. Health.*, vol. 55, no. 7, pp. 858–877, 2020. <https://doi.org/10.1080/10934529.2020.1751504>
- [40] Y. He, Y. Zhang, C. Peng, X. Wan, Z. Guo, and X. Xiao, "Distribution characteristics and risk assessment of heavy metals in soil and street dust with different land uses, a case in Changsha, China," *Int. J. Environ. Res. Pub. Health.*, vol. 18, no. 20, p. 10733, 2021. <https://doi.org/10.3390/ijerph182010733>
- [41] B. Magaji, L. Danbature, Z. Shehu, M. Sani, A. Sani, and A. Abubakar, "Evaluation of some heavy metals in soils around major parks in Gombe Town, Nigeria," *Asian. J. Appl. Chem. Res.*, vol. 4, no. 4, pp. 1–5, 2020. <https://doi.org/10.9734/ajacr/2019/v4i430118>
- [42] A. A. Agbeshie, R. Adjei, J. Anokye, and A. Banunle, "Municipal waste dumpsite: Impact on soil properties and heavy metal concentrations, Sunyani, Ghana," *Sci. African.*, vol. 8, no. e00390, 2000. <https://doi.org/10.1016/j.sciaf.2020.e00390>
- [43] N. R. Ekere and O. P. Ukoha, "Heavy metals in street soil dusts of industrial market in Enugu, South East, Nigeria," *Int. J. Phy. Sci.*, vol. 8, no. 4, pp. 175–178, 2013. <https://doi.org/10.5897/IJPS12.719>
- [44] H. W. Yuen and W. Becker, *Iron toxicity*. In: StatPearls" Treasure Island (FL): StatPearls Publishing, 2023. <https://www.ncbi.nlm.nih.gov/books/NBK459224>
- [45] A. J. Adewumi, T. A. Laniyan, and P. R. Ikhane, "Distribution, contamination, toxicity, and potential risk assessment of toxic metals in media from Arufu Pb–Zn–F mining area, northeast Nigeria," *Toxin. Review.*, vol. 40, no. 4, pp. 997–1018, 2021. <https://doi.org/10.1080/15569543.2020.1815787>
- [46] O. D. Ogundele, A. J. Adewumi, and D. A. Oyegoke, "Phycoremediation: Algae as an effective agent for sustainable remediation and waste water treatment," *Environ. Earth. Sci. Res. J.*, vol. 10, no. 1, pp. 7–17, 2023. <https://doi.org/10.18280/eesrj.100102>
- [47] R. N. Ratnaike, "Acute and chronic arsenic toxicity," *Postgrad. Med. J.*, vol. 79, no. 933, pp. 391–396, 2003. <https://doi.org/10.1136/pmj.79.933.391>
- [48] M. Jaishankar, T. Tseten, N. Anbalagan, B. B. Mathew, and K. N. Beeregowda, "Toxicity, mechanism and health effects of some heavy metals," *Interdiscip. Toxicol.*, vol. 7, no. 2, p. 60, 2014. <https://doi.org/10.2478/intox-2014-0009>
- [49] N. Franchitto, P. Gandia-Mailly, B. Georges, A. Galinier, N. Telmon, J. L. Ducassé, and D. Rougé, "Acute copper sulphate poisoning: a case report and literature review," *Resuscitation*, vol. 78, no. 1, pp. 92–96, 2008. <https://doi.org/10.1016/j.resuscitation.2008.02.017>
- [50] G. Genchi, A. Carocci, G. Lauria, M. S. Sinicropi, and A. Catalano, "Nickel: Human health and environmental toxicology," *Int. J. Environ. Res. Public. Health.*, vol. 17, no. 3, p. 679, 2020. <https://doi.org/10.3390/ijerph17030679>