AKENTEN APPIAH-MENKA UNIVERSITY OF SKILLS TRAINING AND ENTREPRENEURIAL DEVELOPMENT

CONTAMINATION LEVELS, SOURCE APPORTIONMENT AND HUMAN HEALTH RISKS ASSESSMENT OF TOXIC ELEMENTS FROM A MINING DISTRICT

BY

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A Thesis submitted to the School of Graduate Studies, Akenten Appiah-Menka University of Skills Training and Entrepreneurial Development in partial fulfillment of the requirements for the award of a Master of Philosophy degree in Chemistry Education.

SEPTEMBER, 2024

DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original work and that no part of it has been presented for another degree at this university or elsewhere.

Candidate's Name: ....

Signature: .... Date: ....

Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were supervised in accordance with the guidelines on supervision of thesis laid down by the Akenten Appiah-Menka University of Skills Training and Entrepreneurial Development.

Principal Supervisor's Name: ....

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DEDICATION

I dedicate this thesis to the Almighty God, my dear late parents, and my entire family for their love, inspiration, and unflinching support throughout my education.

ACKNOWLEDGMENT

Firstly, I want to thank God for giving me strength, health, and guidance throughout this journey.

I would like to express my sincere gratitude to my supervisor Dr. Opoku Gyamfi for having faith in me, and for his guidance and support. I also want to thank Prof. Kofi Sarpong; head of the Chemistry Education Department for his support and words of encouragement.

I want to give special thanks to Akenten Appiah-Menka University of Skills and Entrepreneurial Development, Mampong campus for allowing me access to their laboratory facilities during my research.

A very special thanks goes to my late parents Mr. and Mrs. Alhassan who raised me and nurtured me into the man that I became. To my lovely wife Rahinatu Ibunan, thank you so much, your encouragement and prayers saw me through this study.

ABSTRACT

While artisanal and small-scale mining is important to local economies, their operations pose significant environmental and public health risks because they release potentially toxic elements (PTEs) into the ecosystem. This study examines the contamination, sources apportionment, and associated human health risks of PTEs at Manwe in the Wa East District of Ghana. An X-ray Ray Fluorescence (XRF) analyzer was used to measure PTE concentrations in sixty-five soil samples collected from key artisanal mining sites in the study area except mercury which was determined using Lumex mercury analyzer. Other parameters measured were pH, electrical conductivity, and organic matter content. The pH values in the samples ranged from 5.30 to 8.67, indicating that the soil varies significantly whereas some parts are slightly acidic, others are somewhat alkaline. The region has low organic content, with a mean organic matter content of 2.3% and an average electrical conductivity of 125.0 µS/cm, indicating moderate salinity levels. These parameters provide important context for the behaviour and mobility of PTEs in their environment.

The mean PTE concentrations found in the soil samples were As (405.740 mg/kg), Pb (3.797 mg/kg), V (67.46 mg/kg), Ni (29.93 mg/kg), Cd (20.45 mg/kg), Co (104.83 mg/kg), Hg (40.46 mg/kg), Cr (40.46 mg/kg), Cu (27.28 mg/kg), Hg (0.35 mg/kg) and Zn (28.69 mg/kg). The results revealed that concentrations of As, Cd, Cr, Hg, and Co in the sampled areas were significantly higher than the crustal average, raising concerns about environmental contamination from mining activities.

Environmental pollution indices were used to assess the degree of contamination using models such as the geochemical load index, enrichment factor, contamination factor (CF), and pollution load index, which revealed that the soils were heavily polluted by Cd, moderately polluted by Co, and unpolluted by other elements. EF showed the soil was significantly enriched by Cd (220.0), while As (10.36) and Co (15.40) are moderately enriched. The CF indicated low contamination for the majority of the metals studied, except As (3.06) and Co (5.52) which are significantly contaminated, while Cd (68.16) showed high contamination. The value of PLI > 1 (2.2) suggests the soil is polluted as a result of the mining activities.

The principal component analysis (PCA) used to predict the sources of these PTEs revealed significant anthropogenic contributions of mercury, arsenic, cobalt, and cadmium, resulting in elevated PTE levels in the soil. These anthropogenic activities included mining, pesticide and phosphate-based fertilizer application, vehicular and grinding mills, auto mechanic workshops, with natural sources accounting for only a small portion.

Using human health risk assessment models, the elements' total hazard index (HI) for ingestion and dermal contact in adults and children was greater than one, indicating a likely non-carcinogenic health risk effect. The cancer risk (CR) value for ingestion and dermal exposure pathways exceeded permissible limits ($1 \text{ x } 10^{-6}$ to 1×10^{-4}), posing health risks to residents. The levels of these PTEs were discovered to pose a significant risk to both adults and children, with children being more susceptible to exposure, primarily through oral ingestion and skin contact. Arsenic and cadmium were identified as the most dangerous elements, with long-term exposure potentially leading to cancer, kidney damage, and neurological disorders.

This study recommends that adequate attention be directed toward a thorough risk assessment of PTEs in the study area.

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LIST OF ABBREVIATIONS/ACCRONYMS/SYMBOLS

ADD	Average Daily Dose
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
CCME	Canadian Council of Ministers of the Environment
CF	Contamination Factor
CRM	Certified Reference Material
DEA	Drug Enforcement Administration
DNA	Deoxyribonucleic Acid
GDP	Gross Domestic Product
EC	Electrical Conductivity
EF	Enrichment Factor
IARC	International agency for Research on Cancer
ICI	Industrial Combustion Industries
IQ	Intelligent Quotient
Igeo	Index of Geoaccumulation
MCA	Multi Channel Analyser
MCL	Maximum Contaminant level
NEI	National Emissions Inventory
NPI	Nemerow Pollution Index
OM	Organic Matter
PCA	Principal Component Analysis
PERI	Potential Ecological Risk Index
PI	Pollution Index
PPM	Part Per Million
PTE	Potentially Toxic Element
RfD	Reference Dose
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency

WHO	World Health Organisation
XRF	X-Ray Fluorescence

CHAPTER ONE

INTRODUCTION

19.1 Background

The crucial settings where rock, air, and water meet are soils. The weathering of parent rocks and pedogenesis are the two processes that contribute potentially toxic elements (PTEs) to soils. Potentially toxic elements are inherently present in soils at an intrinsic level that is unrelated to human activity (Pourret and Hursthouse, 2019). In recent years, potentially toxic elements have become a global issue (Stolte et al., 2016). However, the prevalence of potentially toxic elements in both contaminated and unpolluted environments varies geographically, leading to changes in their concentration (Morais et al., 2012).

Human activity has contributed to an increase in the natural soil content in recent decades (Alloway, 2013). Potentially toxic elements in soils are mostly caused by humans and can be found in agricultural products, sewage sludge, metalliferous mining and smelting, industries, and the combustion of fossil fuels. PTEs continue to be one of the main risks to soil worldwide, originating from both point and nonpoint sources (Stolte et al., 2016). The environment may be contaminated with hazardous elements due to a variety of natural causes. As per Mihankhah et al. (2020), surface mineralization, atmospheric deposition, and forest fires are examples of natural processes.

Because of the possible effects on our surroundings and general wellness, the existence of potentially toxic elements in soil is a global concern. According to Babatunde et al. (2014), among the most significant problems with the environment concerns the contamination of the ecosystem by potentially toxic elements. Potentially hazardous substances found in the soil gradually make their way up the food chain via plants and pose a health concern to humans, animals, and plants when they bioaccumulate in their tissues. Potentially toxic elements are among the most dangerous pollutants according to Boran and Altynok (2010) because of their toxicity. The scenario is the same in Ghana, where industrialization, mineral exploration, and farming practices have led to environmental pollution. However, a lot of these PTEs, particularly at trace levels, are extremely toxic in high quantities and are essential to biological cycles. Elevated concentrations of components with potential toxicity degrade environmental quality, impacting both human and animal existence (Ideriah et al., 2010). Because PTEs can alter the composition and functionality of the soil ecosystem, their growing presence in soil has raised worries about environmental quality (Kirpichtchikova et al., 2006). For example, the Wa East district in Ghana has a significant probability of being contaminated with potentially toxic elements because of small-scale artisanal mining activity.

The contribution of the mineral industry to Ghana’s GDP is about 6%, with 90% of all mineral exports coming from the country's gold mining industry with an annual production of roughly 80.5 tons (Karn et al., 2021). The harmful effects of mining on the environment are well-known throughout the world (Cordy et al., 2013). Mining operations, no matter how big or small, can contaminate the soil in nearby communities. There has been prior reporting on the negative consequences of Ghana's gold mining industry, such as issues with regulation, ecological and economic impacts, and social instability (Ros–Tonen et al., 2021).

For centuries, artisanal mining has been a widely used mining technique across the globe. Although the process has benefits, there is a risk to human health because it leaves behind potentially toxic elements in the soil. One crucial step in determining and assessing the possible health risks connected to contaminant exposure is risk assessment for the safety of people.

19.2 Problem Statement

It is well known that artisanal mining operations add to the buildup of PTEs in soil, which has a serious detrimental effect on the wellbeing of man. These PTEs can seriously jeopardize the health of communities in the region, particularly if there is regular contact with contaminated soil. The European Commission has classified PTEs such as As, Cd, Pb, Hg, and Zn as elements that are of major concern to living organisms due to their dangerous effects (Wu et al., 2003).

Because of their toxicity, persistence, and bioaccumulation, PTEs are considered to be among the most dangerous chemical pollutants. Loska and Wiechuła (2003) stated that PTEs have a significant impact on the environment because rather than being eliminated by self-purification, they build up in reservoirs and eventually make their way into the food chain. Due to geological processes or human activities like mining, PTEs, including Al, Ca, Cd, Cr, Cu, Fe, Pb, and Zn, are released into soils (Sharma & Tyagi, 2013). Even at low concentrations, PTEs can cause variety of diseases and disorders by interfering with metabolic processes in living things (Pehlivan et al., 2009).

The Wa East District of Ghana is emerging as a hotspot for artisanal small-scale gold mining

(ASGM), a practice known to contribute significantly to the release of PTEs into the environment. Despite being the food basket of the Upper West Region and a major agricultural hub for other parts of the country, the impact of mining-related contamination on soil quality and human health remains largely unexamined in this area. Mining activities in the district involve men, women, and children, raising concerns about widespread exposure to PTEs, which can have severe ecological and human health implications. However, research on PTEs contamination in the district is scarce, with most national discourse and media coverage on illegal mining focusing on the southern part of Ghana. This lack of attention limits awareness, policy interventions, and mitigation strategies tailored to the unique socio-environmental conditions of Wa East. Therefore, a comprehensive study on the concentration, source apportionment, and human health risks of PTEs in the district's soils is crucial for assessing the extent of contamination and its potential effects on public health and food safety.

19.3 Objectives of the Study

The purpose of the project is to evaluate the risks to human health posed by PTEs found in soils of artisanal mining sites in some communities in Wa East District. The study's goal, seeks to:

1. Examine the levels of PTEs in the selected communities' soils
2. Ascertain the physicochemical parameters such as pH, organic matter content, and electrical conductivity of the soil
3. Assess the human health risk within the district
4. Estimate the contamination/pollution status indices in the study area using pollution indices.
5. Predict the sources of potentially toxic elements within the research area
6. Evaluate the potential ecological risks within the research area

19.4 Justification of the Study

The mining industry, including artisanal mining, has been known to cause environmental degradation due to pollution from the release of toxic metals and metalloids into the environment. Mining operations may cause trace elements to accumulate in the soil, which could seriously jeopardize people's health (Nahmani et al., 2013). Depending on the concentration, length of exposure, and mode of exposure, there are different health risks to humans when exposed to these potentially toxic elements (Hassani et al., 2019).

Tchounwou et al., (2012) suggests that exposure to hazardous substances like mercury, lead, and arsenic can raise the risk of neurological conditions, cancer, and other chronic illnesses. Furthermore, exposure to these harmful elements increases the risk of negative health effects for children, pregnant women, and other sensitive subpopulations (Nordberg et al., 2014).

The need for this study is underscored by several critical factors. First, ASGM is a major contributor to soil contamination, releasing PTEs such as lead (Pb), arsenic (As), mercury (Hg), and cadmium (Cd), which pose long-term risks to ecosystems and human health. Given that Wa East is a key agricultural zone, the bioaccumulation of these elements in crops could have far-reaching consequences for food security and public health. Moreover, the involvement of vulnerable groups including women and children in mining activities increases the likelihood of direct exposure through inhalation, ingestion, and dermal contact. The limited research on PTE contamination in northern Ghana means that policymakers and local authorities lack data to implement targeted interventions. Furthermore, the national discourse on illegal mining has largely neglected the Wa East District, leading to inadequate regulatory oversight and environmental management efforts. This study will fill this critical knowledge gap by providing empirical data on PTE concentrations, identifying their primary sources, and assessing their potential health risks to residents. The findings will be instrumental in informing sustainable mining practices, environmental remediation efforts, and public health policies tailored to the region’s needs.

19.5 Significance of this Research

The study's findings will;

- show the concentrations of PTEs from Artisanal mining sites in the Wa East district
- help residents of these communities to take prevent measures from exposing themselves to these PTEs
- be useful to stakeholders in deciding the kind of measures to enact to mitigate the impact of artisanal mining in these communities
- serve as a baseline for future reference

19.6 Limitations of this study

The outcomes of this research may be constrained by the availability of historical data on soil conditions, potential variations in sample collection techniques, and the focus solely on the Wa East District, limiting the generalisability of results to other geographical regions.

19.7 Organisation of the Study

This research is organized into Titles and Subtitles, which are further divided into five chapters. Listed below is a description of each chapter's content.

The study's background, problem statement, justification, research question, and goals and objectives are all included in Chapter 1.

The Second chapter offers an extensive literature review that starts with an outline of various mining techniques. The causes of heavy metal pollution and the behavior of PTEs in soils are also covered, as is a brief discussion of mining operations and their environmental effects.

Standards for heavy metal pollution are finally presented and earlier research on heavy metal in soils is discussed.

Chapter Three Methodology: The first part of this chapter is divided into six sections that each describe the study area. These include the study area, soils, vegetation, climate, geology, and hydrological features. The second part outlines the main research techniques and processes that were employed to carry out the investigation. This chapter gives a detailed explanation of field sampling, sample preparation, and the XRF technique. These approaches' rationale is provided, along with a list of the difficulties they present. Included is the methodology for analyzing soil contamination.

The results of the soil analysis of elements, geo-accumulation index, and risk assessment index are tabulated and discussed in the fourth chapter. The effects on ecological systems as well as communities are also discussed. The final chapter has the findings of the research, accompanied by suggestions that stem from these conclusions.

CHAPTER TWO

LITERATURE REVIEW

20.1 Introduction

A research review is essential because it provides context for the entire investigation and enables analysis and conclusion-making. A variety of data regarding the main ideas and broader area of study has been gathered and examined closely. This information has been collected from books, journals, reports, newspapers, and websites. These sources were obtained using a variety of search strategies and search engines, including Science Direct and Google Scholar.

20.2 Theoretical Review

In terms of methodology, both quantitative and qualitative research approaches were used to achieve the study's goals and objectives and offer an answer to the issues being investigated.

The quantitative approach concentrated on finding out the metal concentrations, while the qualitative approach assessed these concentrations in the context of the region's geography and determined the risks associated with these concentrations and the land use in which they have taken place.

The degree of PTE contamination in the local soil was assessed qualitatively using the geo-accumulation index (Igeo). The Igeo aids in identifying the source of the soil contamination: biological processes or human activity.

When selecting the analytical method of XRF Spectroscopy for the quantitative measurements, the literature and the background of the sample's makeup were taken into consideration because this non-destructive technique can provide rapid and accurate elemental analysis of various samples, including soil samples.

Under consideration were the PTEs: arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), titanium (Ti), vanadium (V), and zinc (Zn). A certified reference material (CRM) was additionally examined to confirm the analytical procedure and assess the degree of accuracy of the results.

20.3 Potentially Toxic Elements

The growth and biological functions of plants and animals depend on several elements, including Fe, Mn, Co, Ni, Zn, and Cu. When these elements' concentrations exceed thresholds, living things may exhibit phytotoxic symptoms. However, some elements are extremely hazardous and have no known biological purpose in plants or animals. These elements fall into three categories: non-metals (like Sb), metalloids (like As and Sb), and metals (like Cd, Pb, Ag, Sr, and Cr) (Caporale et al., 2016). Because of anthropogenic processes, these components are present in the land ecosystem at high amounts. All of these elements have the potential to be hazardous, whether they are necessary for plant and animal nutrition or not. For this reason, they are collectively known as "potentially toxic elements," or PTEs (Antoniadis et al., 2019)

Another way to think of Potentially toxic elements is as a subset of elements with metallic characteristics. It consists of actinides, lanthanides, certain metalloids, and transition metals. Suciu et al., (2008) further classified potentially toxic elements as those with a density greater than 4 gcm^{-3} by using density as a defining characteristic. In terrestrial and freshwater ecosystems, chemical elements with densities greater than 4 g/cm^3 may also be present in a variety of soils, rocks, and water (Adelekan & Abegunde, 2011).

Yahaya et al. (2012), and others, a potentially toxic element is defined as any fairly dense element that, even at small amounts is harmful or lethal. Consequently, potentially toxic elements are chemical elements known to have a specific gravity whose value is approximately five times higher than that of water, which is 1 at 4°C. Another way to think of specific gravity is as the density of a particular volume of a solid material divided by the volume of water. According to another school of thinking, PTEs are naturally occurring particles found in rocks with a density of at least 6.0 gcm^{-3}, substantially greater than the mean soil density of 2.65 gcm^{-3}. Nonetheless, pollution usually results in elevated concentrations (Asio, 2009). Thus, according to Obodai et al. (2011) and Yahaya et al. (2012), they can be characterized as a group of metals as well as metalloids having a density that is five times denser than water or greater than 4 gcm^{-3}.

Potentially toxic elements (PTEs) are chemical elements that when present in elevated concentrations, can be harmful to living organisms and ecosystems. Common examples include PTEs like Lead, cadmium, mercury, and arsenic (Nordberg et al., 2014). According to Tangahu et al. (2011), elements having metallic characteristics and an atomic number higher than 20 are typically classified as PTEs.One of the enduring pollutants found in the environment most frequently, PTEs fall into the essential or non-essential category.

20.4 Essential and Non-Essential Trace Elements

According to Duce and Bush (2010), metals are widely found in both biological systems and nature, and they can be classified as either biochemically functional or toxicological.

According to Theron et al. (2011), PTEs are made up of different groups of elements, some of which are non-essential cofactors for different enzymes and others of which are essential. Essential trace elements are substances that are necessary for the survival of living things and optimum well-being. In both plants and animals, the essential PTEs perform biochemical and physiochemical functions. They are significant components of several important enzymes which are crucial to several redox processes.

Metallic traces such as Cu, Mo, and Zn are essential components required in trace amounts by living organisms for metabolic processes, according to Singh et al. (2011). Their specific functions and ability to act as catalysts or structural elements of large molecules within the body make them essential for life and optimal health.

Medical researchers have discovered the importance of metals like Cr, Cu, Fe, Mn, and Zn, in the prevention and treatment a variety of illnesses. Essential trace elements have been shown to be effective in treating a variety of diseases, including kidney, gastrointestinal, genetic, and cardiovascular. Essential elements can be considered possible contaminants once they build up and get to harmful quantities, even though humans and other organisms require them (Cai et al., 2012). However, PTEs like As, Cd, Hg, and Pb are considered non-essential trace elements because they can be toxic even at very low concentrations and have no beneficial effects on humans (Vieira et al. (2011).

20.5 Properties of PTEs

According to Kirpichtchikova et al. (2006), soils serve as the primary repository for PTEs that are discharged into the environment, and their levels in soils endure for an extended duration even after their initial introduction. According to Housecroft and Sharpe (2008), PTEs have several characteristics, including the capacity to conduct heat, and electrical resistance that is directly correlated with temperature. The background concentration of metals varies geographically, and the characteristics of the metals themselves as well as the effects of the environment control their distribution (Khlifi & Hamza-Chaffai, 2010).

According to Sillanpaa, (1979), because the characteristics of soils are shaped by their parent material, the concentration of elements in soils and of the crustal earth vary greatly among the different types of rock. However, in addition to the made up of the geological natural material, other dominant factors during the soil formation process ascertain the trace element concentrations that are naturally present in the soil.

In that specific environment, the chemical composition and form of PTEs which can include free metal ions and metal complexes determines their mobility, bioavailability, and toxicity (Singh et al., 2011).

For instance, a compound's toxicity or non-toxicity can differ significantly in its biological activity, and it's critical to understand whether and how harmful forms of a substance are generated within biological systems. One or more of the elements may predominate in physical exchanges within global geochemical cycles due to differences in their physical properties. Analogously, decomposition rates and the local transportation of different elements can be significantly influenced by their chemical composition (Natusch and Hopke, 1983).

PTEs are typically found in the water-soluble soil solution or the solid state of the environment of soil. They are mobile and hazardous in the aqueous phase, but immobile and innocuous in the solid state (Ogundiran and Osibanjo, 2009). PTEs are not always contained in the environment once they are released into it. For instance, plants, animals, and humans may absorb metals if they are added to soil in their dissolved form or they may filter through the soil profile and reach groundwater.

The form that a heavy metal is in, rather than its total concentration, determines its potential for toxicity (Wuana and Okieimen, 2011). For example, the mobility, bioavailability, and toxicity of a metal in soil may vary depending on its state of oxidation. Metals with multiple oxidation states, like Cr, Cu, and As, can exhibit different behaviors in soil. Reduced Cr (III) in soils, for instance, is comparatively immobile and non-hazardous whereas oxidized chromium (4) has high mobility and is exceedingly hazardous to living organisms. As for arsenic, pentavalent (As (V)) is less toxic than trivalent (As(III)) (Naja and Volesky, 2009). Table 2.1 lists the predominant species of the PTEs as soil pollutants considered in this study.

Table 2.1: Prevalent PTEs found in the soil

PTE	**Prevalent soil species**
As	AsO_4^{3-}, As O_3^{2-},
Cd	Cd^{2+}
Cr	CrO_4^{2-}, $Cr3+$
Cu	Cu^{2+}
Mn	MnO_2
Hg	$(CH_3)_2Hg$, Hg^{2+}
Ni	Ni^{2+}
Pb	Pb^{2+}
Ti	TiO_2
V	V_2O_5
Zn	Zn^{2+}

Eugenio et al., (2018)

Inhalation, skin contact absorption, and ingestion are the major routes PTEs can enter the human body (Adelekan and Abegunde, 2011; Rajaganapathy, 2011). They also accumulate in crops, soils, and aquatic organisms (Obodai et al., 2011; Wuana and Okieimen, 2011). Before becoming accessible to living things, PTEs can persist in a range of biological and chemical colloids for extended periods (Adelekan and Abegunde, 2011; Friedlova, 2010). They do not deteriorate over time because they are not biodegradable. An organism may become biomagnified with PTEs if its excretion rate is slower than its intake. Accordingly, they may start to pose a threat to both people and animals (Adelekan and Abegunde, 2011; Harikumar et al., 2010). In addition to having high densities, PTEs are found close to the bottom of the list of elements on the periodic table, per Obodai et al. (2011).

20.6 Effects of PTEs

Due to the exponential growth in the use of potentially toxic elements in various industrial, agricultural, household, and technological applications, their distribution throughout the environment has increased significantly, raising concerns about possible health effects (Tchounwou et al., 2012). Humans' exposure to PTEs has consequently significantly increased. They asserted that several variables, such as the amount, mode of exposure, and chemical species, in addition to the exposed people's age, gender, genetics, and nutritional status, affect how harmful PTEs are. Because PTEs have been shown to cause harm to human organs even at low exposure levels, USEPA and IARC have designated them as human carcinogenic substances.

According to Bhagure and Mirgane (2010), the persistence of PTEs can lead to bioaccumulation and biomagnifications, which expose certain organisms to higher levels of exposure than what is found in the environment alone. For example, microorganisms can transform and volatilize elements such as selenium and mercury (USDA and NRCS, 2000). As reported by Yildiz et al. (2010); harmful toxicological effects may result from increased exposure of marine and terrestrial organisms to harmful elements. For example, Minamata disease and itai-itai disease, which are caused by mercury and cadmium poisonings, respectively, can be mentioned (Azimi et al., 2006).

The distribution, concentration, and chemical modification of metals due to human activity may make them more toxic. However, compared to their normal background values, the activities may cause the metal concentrations to increase (Adelekan and Abegunde, 2011). Though little is known about the combined effects of PTEs and other chemicals, they may produce dangerous cocktail combinations. According to Rajaganapathy, (2011). Water quality deteriorates when PTEs are present, ultimately impacting the health of humans.

Contamination by PTEs poses a threat to poor vegetation growth and reduces plant resistance to forest pests, agriculture, and other human food sources thereby influencing the growth of plants, microorganisms, and food quality (Ene et al., 2009). Their impact on microorganisms may result in reduced nitrogen fixation and litter decomposition, inefficient nutrient cycling, and impaired enzyme synthesis (Adelekan and Abegunde 2011).

There has been proof to support the theory that contaminated sites could allow toxic concentrations of PTEs to enter the food chain, according to Gall and Rajakaruna (2013).

Elevated levels of PTEs in food-producing plants and crops can be toxic to man and animals, resulting in illness both acute and long-term, and occasional fatalities (Appenroth 2010).

20.7 Sources of Potentially Toxic Elements in Contaminated Soil

People frequently use the term "soil contamination" interchangeably with "soil pollution." Subsequently, a formal definition for both of these words has been established. When a substance's or chemical's concentration rises above its naturally occurring background level, contamination occurs, even though it may not be dangerous. However, according to Eugenio et al., (2018) soil pollution is the term used to describe the occurrence of a material or chemical at a concentration higher than the background concentration, usually as a result of human activity, and negatively impacts any living things that are not the intended target. As stated differently by Chapman, (2007), while, not all contaminants are pollutants, all pollutants are contaminants.

Potentially toxic elements are widely present in the environment due to anthropogenic and natural activities and are exposed to living things through a variety of pathways (Wilson & Pyatt, 2007). Although PTEs are naturally occurring, most environmental contamination and human exposure are caused by human activities like metal mining and smelting, as well as industrial, residential, and agricultural use (He et al., 2005).

According to Greaney (2005), natural fluxes of metals like Pb, Hg, Zn, Cd, and Cu are in a ratio of 1:3 of magnitude lower than anthropogenic emissions into the atmosphere, and these metals are predicted to accumulate in natural reserves. PTEs like Cu, Cr, Pb, As, Hg, nickel, and zinc, not only contaminate the immediate environment in which they are produced, but they also tend to spread through the air and water and contaminate areas that are far from the source of pollution (Neilson and Rajakaruna, 2012). According to Khan et al. (2008), various anthropogenic activities aid the environmental release of PTEs. The reasons for these include rapidly expanding industrial areas, mine waste, metal waste disposal, paint, agricultural activities and combustion residues, petroleum product spills, and atmospheric release. Physical factors such as pH levels, temperature, adsorption, sequestration, and electrical conductivity affect their bioavailability (Hamelink, 1994). Wang et al., (2001) came to the conclusion that metal ions interact with components of cells, such as DNA and nuclear proteins, causing conformational changes in DNA that may result in cancer or cell death.

When igneous, sedimentary, and metamorphic rocks weather physically and chemically, as well as during volcanic activity, PTEs are discharged into both the water system and soils.

However, anthropogenic activities have recently increased the level of PTEs. According to D'Amore et al. (2005), human activity is responsible for the gradual acceleration and distribution of the naturally existing geochemical cycle of metals, which has accumulated above its predetermined background values. The increased production and deposition of metals in the environment brought on by human activity are typically more mobile and bioavailable than those found in natural events (Wuana & Okieimen, 2011).

When it comes to the production and deposition of PTEs, mining operations stand out predominantly because they produce enormous amounts of contaminated residues. Significant volumes of waste, whether be it soil, water, or air, are emptied or discharged into surrounding land during mining operations, creating soil pollution. Research on the distribution of PTEs in ecosystems reveals that soil in areas near mining and industrial sites has significantly higher concentrations of PTE pollutants (Asio, 2009, Karbassi et al., 2020).

20.7.1 **Waste Rock**

Waste rock is an excavated by-product of mining that is used to get at the ore, according to Hasan et al. (2019). It has mineral concentrations that are deemed as being too low to be economically extracted. To reduce transportation, waste rock is frequently kept in sizable heaps or dumps on the mine site (Servida et al., 2012). Non-economic waste rock frequently has a higher mineral concentration than the background, which can have serious negative effects on human health and the environment (Brown and Calas, 2011). PTEs found in waste rock can be released through leaching, which is made possible by drainage and precipitation, as well as natural weathering processes. PTEs are present in the waste material's fine particles and can be dispersed by wind and water erosion; the elements released will vary depending on the waste rock's mineral content (Pathania, 2016).

20.7.2 Mine Waste

Mine waste includes the soil and rocks left over after ore is extracted and processed. Although enormous waste is produced during mining, not all waste generated is regarded as hazardous.

However, waste has a significant mineral content, and improper management could put the environment and the surrounding community's health at serious risk (Muller, 2009). During the mining process, waste is produced at various points, and it persists until the mining is completed. The first stage of production in hard rock mining is called extraction, and it entails moving ore from the earth's surface to the surface while producing a significant amount of solid waste. The type of mineral content being extracted and the method of extraction used will determine different waste material qualities and volumes are produced (Politis et al., 2017). The three waste materials with the largest volume are acid mine drainage, tailings, and waste rock.

20.7.3 Tailings

Recovering all recyclable chemicals and reagents is an inefficient process during the extraction process. Usually, the tailings, the unprofitable and unrecoverable mineral and metal-based reagents for chemical reactions, and processing water are released into isolated reservoirs. However, poor management practices frequently cause these reservoirs to fail, releasing substantial quantities of tailings into the surrounding soil (Mileusnic et al., 2014).

Because tailings often contain high concentrations of hazardous substances, they are typically viewed as an environmental hazard (Ritcey, 1989). The type of ore and the extraction method used also have an impact on the properties and chemical composition of tailings (Fashola et al., 2016). Chemicals or water and gravity can be used to remove the ore from the mineral. The mineral rock is broken up into small pieces if chemical processing is used. Consequently, tailing particles will be minuscule (Eugenio et al., 2018).

20.8 Selected Potentially Toxic Elements

20.8.1 Cadmium (Cd)

This transition metal is a part of group 12 and period 5. Its atomic mass is 112.2, it melts and boils at 594 K, and 1038 K respectively, and its atomic number is 48. It has a density of 8.65 gcm^{-3}. Cadmium is a rare metal with small amounts in the earth's crustal and soils (Kabata Pendias and Pendias, 1985). The main sources of cadmium pollution are waste from both industries and municipalities. Due to its relative water solubility, cadmium exhibits greater mobility, bioavailability, and bioaccumulation rate. Cadmium's toxic effects on humans as well as the environment have been extensively documented, as it has no known biological uses. Cadmium poisoning was first linked to skeletal damage in Japan in the 1950s, marking the beginning of a long history of its health effects. The exposure resulted from cadmium-contaminated water used to irrigate local rice fields.

Although it is a necessary micronutrient for both plants and animals, it may lead to metabolic process malfunctions (Wuana and Okieimen, 2011). When coal and trash are burned without control, cadmium (Cd) is released into the atmosphere either directly or indirectly from plants or animals through the human food chain (Azimi et al., 2006). Using inputs in agriculture, such as pesticides and fertilizers, biosolids (sewage sludge), industrial waste disposal, and the buildup of air pollution raises the overall concentration of cadmium.

Joseph (2009) claims that both anthropogenic and natural activities have contributed significantly to the amount of Cd that has entered the environment, with anthropogenic activities accounting for three to ten times the amount of Cd that has entered the environment compared to natural activities. According to Peters et al. (2010), eating particular foods, breathing in cigarette smoke, and consuming emissions from industrial and waste management processes are the primary recognized origins of cadmium exposure in the United States. Joseph (2009) also noted that Cadmium is categorized as a human cancer-causing agent by the IARC, raising serious concerns about occupational and environmental exposure. The IARC also noted that the metal can remain in the body of an individual for 15 to 20 years due to cadmium's extraordinarily long half-life and propensity to continue having cancerous effects that persist long after environmental exposure. According to Singh et al., (2011), when cadmium bioaccumulates in edible plant tissue, it becomes one of the most hazardous PTEs that can make its way into the food chain.

Olawoyin et al. (2012) claim that cadmium adversely impacts the kidneys, lungs, and bones. Cadmium causes cancer through a variety of pathways, the most significant of which are aberrant gene expression, inhibition of DNA damage repair, oxidative stress induction, and inhibition of apoptosis (Joseph, 2009). According to Filipič and Hei (2004), studies have demonstrated that cadmium can cause DNA strand breaks, sister chromatid exchanges, chromosomal deviations, and DNA-protein crosslinks.

Kidney malfunction is the first sign of cadmium poisoning (Azimi et al., 2006). It has an impact on sperm, lowers birth weight, and is a contributing factor to hypertension and cardiovascular illnesses (Adelkan and Abegunde, 2011; Asio, 2009). Furthermore, disorders like neurotoxin, hypertension, liver dysfunction, carcinogenicity, teratogenicity, cramps, nausea, vomiting, respiratory problems, and unconsciousness can be brought on by exposure to Cd (Bhagure and Mirgane, 2010; Adelkan and Abegunde, 2011).

20.8.2 Zinc (Zn)

Zinc (Zn) is primarily found in +2 and 0 oxidation states. It is easily soluble at pH values between 7.0 and 7.5 and forms complexes with anions, amino acids, and organic acids. Zinc is easily absorbed at high pH levels and readily precipitates under reducing conditions. It can also precipitate with iron or manganese hydrous oxides (Hashim et al., 2011).

Mining operations, the mining and processing of cadmium, lead, and zinc ores, the production of steel, the burning of coal, and the burning of wastes all contribute to the discharge of zinc into the natural environment. Due to its mobility in the soil, zinc is made more available in soils by a number of processes, including the degradation of the base rock, atmospheric precipitation, plant and animal decay, and the use of wastewater for soil fertilization (Loska et al., 2005).

One essential trace mineral that we get from our food is zinc. Apart from iron, zinc is a plentiful trace element in the body that is present in all cells, a necessary food component, and a coenzyme in cells. Men, for example, require 15-20 mg of zinc per day. (WHO, 2009). Zinc raises the level of zinc by preventing the toxic effects of cadmium from occurring in the body. If zinc is present in the body, cadmium uses it extensively. When cadmium levels in the diet are high, there is typically a greater need for zinc.

In general, zinc is thought to be non-toxic. Even for brief periods of time, taking large oral doses of zinc can cause nausea, vomiting, and stomach cramps. Consuming excessive amounts of zinc over a period of weeks may harm the pancreas, lower lipoprotein (HDL) cholesterol, and induce anemia (ATSDR, 2007).

Wide-ranging effects of zinc deficiency include impaired neuropsychological functioning, delayed or stunted development, impaired reproduction, immune system disorders, dermatitis, ineffective wound healing, exhaustion, anorexia, and baldness. Zinc deficiency in agricultural soils affects agricultural output and quality worldwide. Zinc deficiency affects pregnant women more than it does the general population. Therefore, taking 25–30 mg of zinc supplements daily can improve pregnancy outcomes for this demographic. (Osendarp, 2003).

20.8.3 Arsenic (As)

The chemical symbol for the metalloid element arsenic is "As". Its intricate chemistry is comparable to that of phosphorous, despite being commonly referred to as a heavy metal (CCME, 2001). According to Mohan and Pittman (2007), arsenic is a brittle crystalline solid with a mass number of 74.9 g/mol, a specific gravity of 5.73 g/cm^3, melting and boiling points of 817 °C and 613 °C, and vapor pressure of 1 mm Hg at 372 °C. With an average level of 3-5 ppm, Due to geological factors, the level of arsenic in the crust of the earth varies greatly (ATSDR, 2007a). Its concentration depends on rock type and industrial activity. It is acknowledged as a well-known poison and one of the global hazardous substances.

According to Mohan and Pittman (2007), arsenic can be found in the -3, 0 valence oxidation states, +3, and +5. The two most prevalent mobile forms of arsenic are the anions arsenate ($AsO4^{3-}$) and arsenite (AsO_3^{3-}). Arsenic compounds have a high soil adsorption strength, which limits their migration even though they are easily soluble. The soluble arsenic's toxicity is determined by speciation. The most dangerous compounds are arsenic trioxide

(As_2O_3) and sodium arsenate (Na_3AsO_4) (Kabata-Pendias and Pendias, 1985). Given that soil contains arsenic in both additive and accumulated forms, plants may absorb it into the portions suitable for consumption. The degree of exposure has a wide range of consequences for human health.

The oxidation state and chemical species of arsenic play a major role in its toxic effects (Vaclavikova et al. 2008). Arsenic's inorganic compounds are typically thought to be more highly toxic than the majority of its organic counterparts (Chutia et al., 2009). kidney, Lung, bladder, and dermal disorders are caused by inorganic arsenic (Chutia et al., 2009). Human activities such as the use of chemical pesticides, mining and minerals processing, smelting lead, zinc, and copper, and disposing of waste all contribute to the presence of arsenic in soil (Mirlean et al., 2003).

For many years, the toxicity of arsenic in the following forms has been identified in the inorganic form: immunotoxicity (Sakurai et al., 2004), developmental and reproductive toxicity (Chakraborti et al., 2004), acute toxicity, sub-chronic toxicity, genetic toxicity, biochemical and cellular toxicity, and chronic toxicity (Mudhoo et al., 2011). According to Chen and Ahsan (2004), ingestion of arsenic doubled the risk of lung, bladder, and liver cancer deaths in Bangladesh. This suggests that arsenic may be a human carcinogen. Tchounwou et al., (2003) state that nearly every organ system is impacted by arsenic exposure, including the neurological, hepatobiliary, respiratory, dermatological, digestive, and cardiovascular systems

20.8.4 Copper (Cu)

Copper is found within the periodic table's fourth period and Group 11, a transition metal with the chemical symbol "Cu." The metal is reddish-brown and has a cubic crystal structure. Its specific density is 8.9 g/cm^3, atomic weight is 63.546 g/mol, melting and boiling points are 1083 and 2595 °C, respectively. Its atomic number is 29. There is an average concentration of 50 parts per million of copper (ppm) in the crust of the earth (Georgopoulos et al. 2011).

According to Georgopoulos et al. (2011), there are four different oxidation states for copper: Cu, Cu (I), Cu (II), and Cu (III). The Cu(III) is extremely uncommon. It can be found in many different minerals and rocks. According to Georgopoulos et al. (2011), copper is among the vital micronutrients needed for a variety of metabolic processes in both prokaryotes and eukaryotes.

According to Alaoui-Sossé et al. (2004), atmospheric deposition and emission of metal dust from human activity are the main causes of copper contamination in the environment. High copper concentrations in soils can also result from widespread pesticide use, careless sewage sludge application, mining, and smelting operations. It is necessary for the synthesis of red blood cells, the preservation of the nervous system's structure and function, and the biological electron transfer process—despite being toxic in excess (Medeiros et al., 2012). Since the liver is the first organ to receive Cu after it enters the bloodstream, chronic Cu toxicity predominantly impacts it. Hemolysis, liver cirrhosis, brain, renal tubule, and other organ damage are caused by it. (Chow & Gaetke, 2003).

20.8.5 Chromium (Cr)

There are three oxidation states for chromium (Cr): 0, +3, and +6, with +6 being the most common and toxic form. Chromate CrO_4^{2-} and dichromate $Cr_2O_7^{2-}$ are the most prevalent Cr (+6) compounds. Cr^{3+} is the most prevalent species at low pH values. Research has demonstrated that, in anaerobic conditions, Organic matter in the soil, sulfur, and Fe^{2+} can reduce Cr^{6+} to Cr^{3+} This explains why Cr^{6+} leaches as soil pH rises (Hashim et al, 2011). Among other things, chromium is widely used in paint production, production of wood preservatives, metallurgical operations, rubber, paper, cement, and floor coverings. It is also used in magnetic tapes.

The level of oxidation determines how dangerous chromium is. Cr $^{6+}$ readily penetrates cell membranes after absorption, whereas Cr $^{3+}$ cannot. According to reports, the hexavalent state is carcinogenic (Khopkar, 2006). After entering the cell, Cr $^{6+}$ quickly reduces to Cr $^{3+}$, at which point it attaches itself to macromolecules. After ingestion and parenteral absorption of various compounds, it was found in animal research that Cr primarily builds up in the bone marrow, kidney liver, and spleen; the species of chromium that causes this accumulation determines its spread. Elevated levels have been seen in human lungs, spleen, liver, and kidneys, followed by hilar lymph nodes (Janus, 1999).

Human allergic dermatitis, gastrointestinal bleeding, respiratory tract cancer, and skin ulcers can all result from exposure to chromium (Cr). According to the EPA, exposure to levels of chromium exceeding the (MCL) maximum contaminant level for short intervals of time can result in a variety of health effects, including ulceration and dermatitis. Chromium can cause lifelong defects at levels over the MCL, such as harm to the kidney, liver, circulatory system, and nerve tissues.

20.8.6 Lead (Pb)

The periodic table's group 4 and period 6 include the metallic element lead, whose chemical symbol is "Pb" (Al-Saleh et al., 2009). With an atomic weight of 207.19, specific gravity of 11.34 g/cm^3, melting point of 327.5 °C, and boiling point of 1725 °C, this blue-gray or silvery-grey metal has these properties. According to Harrison (2001) and Tangahu et al. (2011), lead is extensively and uniformly distributed in the environment, and its concentration in the crust of the earth is 12.5 mg/kg.

It is utilized in radioactive emissions, roofing sheets, and X-ray screens. Additionally, it is employed in the production of batteries, soldering supplies, pipes, and drains. Lead forms PbS, $PbSO_4$, and $PbCO_3$ when it reacts with elements like oxygen and sulphur (Wuana & Okieimen, 2011).

Lead is a toxicologically significant element that, despite its low geochemical mobility, It is heavily integrated into the environment by human activity (Oehlenschläger, 2002). According to Oehlenschlager (2002), the main sources of lead pollution in the environment are industrial production and its emissions, leaded gasoline used in vehicles, and smoke and dust emissions from coal and gas-fired power plants. Lead is found in the tissues and organs of all mammals, even though it has no biological value for humans (Förstner and Wittmann, 2012). Human exposure occurs via food and water. Several variables, including age and physiological state, affect absorption. The majority of the lead eventually accumulates in the skeleton after the metal is absorbed and is subsequently distributed to soft tissues like the brain, kidney, liver, and heart (Naja and Volesky, 2009).

A common environmental toxin, lead causes a variety of physiological, and biochemical, dysfunctions of the metabolism and behavior (Gurer & Ercal, 2000). Lead is not biodegradable like other PTEs, and once it gets into the soil, it exposes living things to it over an extended period. According to Cho-Ruk et al. (2006), there is insoluble lead pollution in the environment that poses a major risk to human health, specifically brain damage and retardation.

Due to their hand-to-mouth behaviors, higher respiratory rates, and higher gastrointestinal adsorption per unit body weight, children are more susceptible to lead poisoning than adults (Ahamed & Siddiqui, 2007). Lead toxicity is a global environmental public health concern. For instance, children exposed to lead exhibit lower intelligence quotient, attention span shortening, anxiety, and mental retardation in addition to developmental impairments. Additionally, the kidney, nervous system, and digestive system may be affected by lead exposure. Lead poisoning has been connected to persistent impairment of nervous systems, kidney dysfunction, and a reduction in hemoglobin synthesis, according to Ogwuebu and Muhanga (2003).

20.8.7 Mercury (Hg)

Mercury (Hg) is a hazardous material that has been extensively studied. It can be found in our environment's three different oxidation states (+2, +1, and 0). Mercury may be found in the alkylated species (methyl/ethyl mercury), depending on the alkalinity of the system, and both Hg^{2+} and Hg_2^{2+} are stable under oxidizing conditions. According to Goldman and Shannon (2001), pure mercury is a silver-white, lustrous metal that is either liquid or vapor at room temperature. Its atomic weight is 200.59 g/mol, its density is 13.53 g/cm^3, and its melting and boiling points are 38.83 °C and 356.73 °C. According to Acta and Ireland (1964), the mean concentration of mercury in the crust of the earth is 0.08 parts per million.

When it mixes with other substances like oxygen, sulfur, or chlorine, inorganic mercury compounds are created. Its low boiling point and easy vaporization are among its physical and chemical properties, which make it a useful material for dental amalgam, thermostats, and thermometers. It can be found in organic compounds, metallic elements, and inorganic mercury. Methylmercury is the most prevalent form of organic mercury found in the environment (Counter & Buchanan, 2004).

According to Gustin et al. (2000), mercury emissions from both natural and human activities can travel extensively through atmospheric routes, far from their anthropogenic source. Murray and Holmes (2004) report that the US Environmental Protection Agency (EPA) and the National Emissions Inventory (NEI) conducted an investigation that revealed that 52.7% of the mercury emissions in the region came from coal-fired electric utilities. The remaining percentage comes from other activities like the production of lime, the burning of medical waste, stationary internal combustion engines, mercury-cell chlor-alkali plants, toxic waste incinerators, and boilers.

Humans are exposed to mercury's many harmful health effects (Guzzi & La Porta, 2008). Humans and wildlife are frequently exposed to mercury, to the point where concerns are expressed about possible effects on the environment and human health worldwide (Scheuhammer et al., 2007).

The organic form of mercury, predominantly methylmercury, has been the most hazardous because of the health risks it poses, mostly from eating fish (Zahir et al., 2005). Furthermore, it accumulates in the kidney's tissues, which directly causes renal toxicity and diseases like nephrotic syndrome and protein urine (Goldman & Shannon, 2001).

Due to the possibility of harm to the development of the central nervous system, lungs, and kidneys, children are particularly vulnerable to mercury intoxication (Counter & Buchanan, 2004). Exposure to high levels of mercury can cause permanent damage to the developing fetus's kidneys, nervous system, and brain (Gautam et al., 2014).

Extended exposure to mercury vapour can result in kidney failure toxicity, skin rashes, eye irritation, elevated blood pressure, nausea, vomiting, diarrhea, and rashes.

Mercury is toxic to humans and almost all other living things in its various forms. Mercury can be found in the environment in three different forms: elemental, organic, and inorganic. Each form has a unique toxicity profile. The elemental mercury vaporizes at room temperature, which increases the likelihood of inhaling it. (Langford and Ferner, 1999). The most hazardous to human health is the organic form, which is soluble and mobile in soil (Zahir et al., 2005). The main means human beings are exposed to this type of mercury is through food. However, water as well as air can contribute significantly to the intake depending on concentration. There are two ionic forms of inorganic mercury compounds: mercury (I) and mercury (II). The latter typically dominate because they are more stable in their surroundings. Because inorganic mercury salts are soluble in water, they pose a greater risk to human health when ingested than elementary mercury (Langford and Ferner, 1999).

20.8.8 Nickel (Ni)

This metal is transitional, belonging to group 10 and period 4. Its atomic mass is 58.7, its melting point is 1726 K, its boiling point is 3005 K, and its atomic number is 28. Its density is 8.9 g/cm^3. Nickel occurs naturally in a variety of chemical forms, and the parent rocks and the formation of soil processes influence the amount of nickel in soil. Nickel levels in soils have increased due to human activities, including industrial and municipal waste discharge. It is an element that is necessary in small doses and found at very low levels in the environment; however, when the maximum allowable amounts are exceeded, it can be hazardous (Wuana and Okieimen, 2011).

The sources of soil contamination with nickel include the metal coating industries, the burning of fossil fuels, nickel extraction, and nickel electroplating. (Bhagure and Mirgane, 2010). Inhalation, drinking water, and eating tainted food are other ways that humans can come into contact with nickel (Ni) (Asio, 2009). Money, nickel for shield plates, vegetable oils, and burglar-proof vaults are among the products made with it (Asio, 2009). Exposure to nickel (Ni) can damage the liver, kidneys, and lungs. In addition, neurological system dysfunction, dermatitis, allergies, cancer, respiratory failure, birth defects, and heart failure can all be brought on by high Ni levels (Adelekan and Abegunde, 2011; Asio, 2009; Lenntech, 2010).

20.8.9 Cobalt (Co)

Cobalt (Co) is a d-block metal, it is a silver-gray, cubic crystal. In the periodic table, co is a transition metal that is a part of period 4 group 9. Its atomic mass is 58.9, its melting point is 1768 K, its boiling point is 3143 K, and its atomic number is 27. Cobalt exists in three valence states: 0, +2, and +3. (Kim et al., 2006). It is commonly found in nature in conjunction with nickel. There are two types of cobalt exposure: anthropogenic and natural. Dust carried by the wind, spray from the sea, volcanic eruptions, forest fires, and biogenic emissions from the continent and the ocean are the natural sources. In addition, anthropogenic sources include the mining and smelting of cobalt ores, the processing of cobalt alloys, the use of cobalt compounds, phosphate fertilizers, sewage sludge, and the burning of fossil fuels (Kim et al., 2006).

Cobalt settles on the soil upon its discharge into the atmosphere, but it can attach itself to particles in water or be absorbed directly into sediment.

Cobalt (Co) has several applications, including magnetic steels, electroplating, ground coats for porcelain enamels, and alloys for jet engines. Because cobalt is a component of vitamin B12, which is crucial for human health, it is significant for humans (Bhagure and Mirgane, 2010). It is also used to treat anemia in pregnant women because it promotes the production of red blood cells (Lenntech, 2010).

There is a discernible increase in cobalt absorption in people who are iron deficient (Kim et al., 2006). Inhaling or coming into contact with cobalt through the skin can cause humans to suffer from asthma of the bronchi, lung cancer, pneumonia, heart problems, thyroid gland damage, nausea, and diarrhea (Bhagure and Mirgane, 2010; Kim et al., 2006; Lenntech, 2010). Accordingly, exposure to cobalt in animals could affect their growth and ability to reproduce (Kim et al., 2006).

20.8.10 Selenium (Se)

According to Fordyce (2013), selenium is a naturally occurring metalloid that is detrimental in excess but an essential microelement required for humans, animals, and other living things to function normally. As a member of periodic table group 16, selenium is a chalcogen, which means that it behaves chemically like sulfur (Lenz & Lens, 2008). Its density is 4.809 g/cm3, atomic mass is 78.96, melting point is 220.5 °C, and boiling point is 685 °C. Its atomic number is 34. There are several allotropic forms of selenium (ATSDR, 2007). Fishbein, (1983), states that selenium occurs naturally in a variety of rocks and soils, where it can be found in quantities that vary between 0.1 and 2.0 ppm with a mean concentration of 0.05 ppm. Due to its photovoltaic and photoconductive properties, it is widely utilized for the manufacturing of photoelectric technology cells.

Fishbein (1983) identified four oxidation states for selenium: elemental selenium (Se^0), selenide (Se^{2-}), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}). While selenides (Se^{2-}) and elemental selenium (Se) are insoluble, selenium VI (as selenate, SeO_4^{2-}) and selenium IV (as selenide, SeO_3^{2-}),) are the most common mobile forms. Se is found in certain minerals, but it is most commonly found in metal sulphides (As, Cu, Pb, Hg, Ni, etc.), either in the mineral structure as selenide or by substituting the sulfur ion.

The reactivity and bioavailability of selenium are determined by both its chemical form and the total concentration of the element in soil. The dissolution and accessibility of Se to plants are significantly influenced by the pH and redox potential of the soil. Seldom does elemental selenium occur in nature; instead, it is mostly formed as a waste product of the refinement of copper (Fishbein, 1983). It is mostly linked to trace amounts of naturally occurring sulphides such as sphalerite, chalcopyrite, and pyrite (Wiberg et al., 2001). Metal sulphides produced by volcanic activity and volcanic rocks may also contribute to the natural pathway of selenium. Geologic materials such as phosphate-based rocks, and sulphide mineralization contain substantial amounts of selenium (Lenz & Lens, 2008). The amount of selenium in soils can vary based on processes that take place after the soil's formation, leaching, and the makeup of the underlying material. The amount of selenium in soils can vary based on processes that take place after the soil's formation and leaching. According to Simmons and Ager (2005), mining, irrigating crops, refining crude oil refining sulfide ore, and the combustion of coal are a few examples of anthropogenic sources of selenium.

Selenium has a significant protective effect against cancer, cardiovascular disease, and trace element toxicity. It is also a cellular antioxidant (Medeiros et al., 2012). However, at greater concentrations, selenium is harmful to humans and other living organisms. The quantity and chemical form of selenium that is consumed affects its toxicity to living things. Human selenosis usually has dermal or neurological effects, such as hair loss, unsteady gait, paralysis, and damaged skin and nails (Lenz & Lens, 2008).

20.9 Physicochemical parameters

20.9.1 pH

According to APHA (2005), Equation (2.1) illustrates how pH, a measurement of hydrogen ion concentration, is expressed as the logarithm of the reciprocal of hydrogen ion. pH is equal to -log (H^+)

$$pH = -\log (H^+). \tag{2.1}$$

The pH of the soil is considered to be one of the major factors affecting the levels of PTEs in the soil solution, as well as their movement and accessibility to plants (Alkorta et al., 2004).

According to Vamerali et al., (2010), the intensity of heavy metal mobilization is impacted by an increase in hydrogen ion concentration. In comparison to neutral or alkaline soils, highly acidic soils have substantially higher metallic element mobility. Metal mobility in low pH soils increases in the following order: Pb <Cu <Mn<Zn<Ni<Cd. Nonetheless, depending on the kind and quantity of organic matter present, the impact of pH on the mobility of metallic elements in the soil varies greatly. Prasad & Freitas, (2003) assert that there is a chance that PTE complex anions with higher mobility and bioavailability will occur in alkaline soils with a pH range.

In addition to facilitating the mobilization of PTEs, low soil pH also lowers the value of exchangeable cations and inhibits the ability of impacted microorganism populations to develop more intensely. The pH factor also affects the bioavailability of many metal ions by determining their activity in the water within the soil's pores. The pH level of crops is inversely correlated with the concentration of some metallic elements, such as cadmium.

20.9.2 Electrical conductivity

Electrical conductivity (EC) in soil refers to the ability of the soil to conduct electricity. It evaluates the soil's capacity to permit electrical current flow, which is influenced by the level of moisture and ion content of the soil. Usually, it is expressed in millisiemens per centimeter (mς/cm) or Siemens per meter (ς/m) (USDA) units. It is an important indicator of soil health and quality because it reflects the soil’s ability to retain and transmit water, nutrients, and salts. High EC values typically indicate high concentrations of soluble salts in the soil, which could be as a result of natural salinity or the accumulation of salts from fertilizers and other chemicals. Soils with finer texture such as clay, usually have higher EC compared to sandy soils, as they retain more water and nutrients. Electrical conductivity is influenced by soil density as well and it rises with soil density. Additional pore fluid provides additional electrolytic conductivity and additional ion mobility in surface conductivity is provided by clay minerals in sand, both of which raise the global effective conductivity.

20.9.3 Organic Matter Content

Metallic elements are actively retained by land that is rich in organic matter. Because of its various connections to the mineral phase, organic matter has a complex process for binding PTEs. The soil's ability to absorb minerals is significantly inferior to that of organic matter, Van Loon & Duffy, (2007).

Organic matter can render PTEs immobile or act as a catalyst for their release. The solubility of the corresponding organic matter affects the solubility of metal compounds that either form strong complexes with organic matter or are structural components of it. Its dissolution typically results in the distribution of more soluble and smaller products. This crucial component makes it possible for metal elements to move from the aqueous phase to the other (Bodar et al., 2006).

According to Gang et al., (2010), in temperate climates, a layer of decomposing organic litter, which is renewed annually, covers the mineral soil in forested areas. This process results in the production of small molecules such as stable, insoluble humic substances and organic acids. Since many metal ions have organic acids as ligands, these ions carry more water through the soil profile.

20.10 Soil Quality Standards

Understanding the background metal concentration is essential for identifying and controlling soil pollution. This type of information will clarify reference values for uncontaminated soil that are reasonable to anticipate well in advance of human activity-induced contamination. Unfortunately, only a few nations have access to this information (Herselman, 2007). Only by opting for appropriate reference values is it possible to assess the risk of contamination and develop standards for the highest permissible concentrations of PTEs in soils (Herselman, 2007). The allowable concentration limit of a soil pollutant is provided by soil quality standards to show when alterations in the characteristics of the soil become hazardous. Due to soil degradation, this situation may result in a loss of soil productivity (USDA, 2000). Water quality declines are relatively simple to measure; water is typically judged according to how suitable it is to drink, and air quality is determined according to how suitable it is to breathe. In contrast, a decrease in soil quality might not always be apparent or felt right away (Nortcliff, 2002). An additional issue with soil is that it does not react instantly to changes in the surrounding environment. Generally speaking, soil can at least partially mitigate the effects of potentially hazardous situations (Nortcliff, 2002).

20.11 X-ray Fluorescence (XRF) Analyzer

A Niton XL3t GOLDD+ field portable X-Ray Fluorescence (XRF) Analyser which works based on US-EPA Method 6200 (US-EPA, 2007) is composed of three main parts: an exciting radiation source (such as an X-ray tube or isotope), a way to present the sample in a repeatable manner, and a detector that includes an analytical software and multichannel analyzer (MCA). The spectrometer records the sample's X-ray spectrum during the measurement process, which consists of all of the compositional data. The data of the elemental concentrations in the material under test is derived from the spectrum and transformed into both qualitative and quantitative information. The foundation of XRF analysis is the phenomenon wherein the sample's constituent atoms, when excited by an external radiation source emit X-rays.

Willis and Lachance (2004) state that an atom of the sample material may eject one of its inner-shell electrons when it is struck by a gamma or sufficiently intense X-ray from an isotope or when it emits from an X-ray tube. One of the electrons from the higher energy shell fills the vacancy almost immediately (in less than 10^{-20} s). Because the energy released during the process is specific to each element (atom), it is referred to as a characteristic X-ray. This radiation is the result of the energy difference between the two energy shells involved in the process. The quantitative and qualitative components of XRF analysis are achieved by respectively measuring the energy and intensity of an element's characteristic X-rays.

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304SS
42 Match 9.6 01-04 22:38
Time 2.0
El   Min     %     Max    +/-
Fe  66.35  71.80  74.00   0.37
Cr  18.00  18.05  20.00   0.16
Ni   8.00   8.36  10.50   0.16
Mn   0.00   1.22   2.00   0.09
Cu   0.00   0.17   0.50   0.03
Mo   0.00   0.13   0.50   0.01
Co          0.28          0.03
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Fig. 2.1: A portable XRF Analyser

20.12 Other studies on PTEs pollution in mining areas

Many researchers and working groups looked into the effects of mineral extraction activities on soil quality locally as well as globally. Below is a brief overview of the prior research and relevant studies carried out:

Lee, Chon, and Jung (2001) conducted a study titled "Heavy metal contamination in the vicinity of the Daduk mine in Korea." Significant concentrations of the elements, particularly zinc and cadmium, were discovered by the authors in sediments and waters. A study on "Acid mine drainage arising from gold mining activity in Johannesburg, South Africa" was conducted in 2002 by Naicker, Cukrowska, and McCarthy. According to the study, heavy metal contamination is severe in the mining district's soil, surface water, and groundwater. Another study titled "Metal contamination of the environment by pacer and primary gold mining in the Adola region of Southern Ethiopia" was carried out in 2006 by Getaneh and Alemayehu. According to their analysis, the sediment samples obtained from the gold mining site contained high levels of PTEs toxic elements.

An investigation on "Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea" was carried out by Lim and colleagues in 2008. The concentration of PTEs, including arsenic, turned out to be higher than allowed from samples collected within the mine site, soil, and tailing samples. Rashed (2010) conducted a study on the "monitoring of contaminated toxic and PTEs, from mine tailings through age accumulation, in soil and some wild plants in Southeast Egypt." The findings show that as one gets farther away from the tailing, the concentration of PTEs in the soil, such as silver, mercury, zinc, lead, manganese, and chromium decreases. The overall findings, however, point to the extremely toxic nature of the plants and soil that surround the gold mine tailings, making them unfit for agriculture or grazing.

A study titled "Soil contamination by potentially toxic elements around Aljustrel (Portugal) mining area" was carried out by Candeias et al., (2011). The researchers discovered that soil samples had significantly higher concentrations of hazardous elements when compared to what was recommended for the European Union and Portugal.

A study by Mileusnic et al.,(2013), titled "Assessment of agricultural soil contamination by potentially toxic metals dispersed from improperly disposed tailings (Kombat mine) in Namibia" discovered that lead and copper had remarkably high concentrations in the soil among the seven elements examined.

The public, particularly those who live close to the contaminated area, is at high risk of developing cancer from heavy metal-polluted soil, according to the authors' conclusion.

Zhiyuan (2013) et al. conducted a review of soil heavy metal pollution from specific mines in China. The results show that potentially toxic elements released from mining operations severely contaminate the soils around the mining areas.

The public, specifically those who live close to the contaminated area, is at high risk of developing cancer from heavy metal-polluted soil, based on the authors' conclusion.

In 2014, Angelovicova and Fazekasova conducted a study to determine the level of heavy metal contamination in soil and water in a former mining area located in Rudnany, Slovakia. Copper and mercury levels in the soil samples were extremely high and significantly above the threshold values.

The Research work "Concentration levels of PTEs from gold mining in Lake Victoria revealed high levels of Cd, Pb, As, and Hg on soil samples" was carried out in Kenya by Ngure et al., (2014). From a comparison of benchmark soil samples taken seventy kilometers away from the site of mining, the researchers concluded that elevated levels of hazardous elements are a result of mining operations.

Elevated levels of lead (Pb) were found in the Vaderbijlpark, South Africa, study "Evaluation of heavy metal pollution in soil" carried out by Mthunzi et al., (2015). The study found that the primary cause of the pollution in the area is human activity and that the concentration of the metals under study decreases as one moves farther away from the industrial area. Also, According to Kamunda et al.'s (2016) study, "Health Risk Assessment of PTEs in Soils from Witwatersrand Gold Mining Basin, South Africa," the concentrations of chromium and arsenic were significantly higher than those of other nations worldwide as well as the South African standard.

Wei, J., et al., (2019) conducted a study titled "Concentration and pollution assessment of PTEs within surface sediments of the Raohe Basin, China". The results obtained indicate that most metal values were significantly higher than the corresponding background values.

Again, the 2020 study "Environmental Pollution from PTEs in Soil and Stream Near an Abandoned Mine in Korea" was carried out by Hwan and Yoonjin Lee. The study's findings revealed elevated levels of PTEs.

According to the studies outlined in the preceding paragraphs, PTEs pollution was a concern in various mining locations. The varying concentrations of PTEs in the soil resulted in varying environmental consequences for the surrounding areas. The significant toxicological consequences that extend beyond soils and affect various land uses and ecological systems make it imperative to highlight the high levels of metals found in plants as a result of mining, with implications for the agricultural sector, foraging, and environmental systems.

2.11 Chapter Summary

The literature on mining and PTEs contamination of soil was covered in this chapter. PTEs found on mining sites were thoroughly examined, along with their standards and effects. Prior research on mining-related heavy metal contamination has been done both domestically and worldwide, as shown in Section 2.9. In the Wa East District of Ghana's Upper West Region, no such study has been done before, so this study aims to fill that knowledge gap.

Thus, the purpose of this study is to offer this data.

Communities in the Study Area should be aware of the effects of living close to these illegal mining sites as well as the potentially toxic elements contamination these mines leave in their soil. This study should be viewed as the initial step toward reducing possible effects and creating a more wholesome environment for the local population and ecosystems in these communities.

CHAPTER THREE

METHODOLOGY

21.1 Introduction

This chapter provides background information on the specific research procedure that was followed and the study's methodological framework. The study area's sampling locations are described, and the comprehensive sampling protocols are also delineated. The approach for determining the environmental risk based on PTEs concentrations is provided in the second section of this chapter. In particular, the geo-accumulation index and the ecological threat index are looked at.

21.2 Study Area

The study was conducted in the Wa East District, which Legislative Instrument 1746 established in July 2004 by combining the former Wa District with other areas. In Ghana's Upper West Region, Wa East is part of the Guinea Savannah Agroecological Zone, which is distinguished by a combination of savannah and woodland terrain.

West Gonja borders the district to the southeast, Sissala East district to the north, and West Mamprusi to the northwest. It lies between longitudes 1º 10" W and 2º 5" W and latitudes 9º 55"N and 10º 25" N. Its landmass is approximately 4297.1 sq/km². The district makes up 17.3 % of the region's total landmass (18,478.4 sq/km³).

GSS, (2021) estimates that there are 91,457 people living in the district, 50.8 % of whom are women and 49.2 % of whom are men. The district's primary economic pursuits are agricultural production, hunting, and artisanal small-scale illicit mining.

The climate is tropical equatorial, and it prevails throughout northern Ghana. All year long, the temperatures are high, peaking in March and April. Temperatures could rise as high as 42 ºC during this time. In December and January, the temperature drops to as low as 22 ºC. The Harmattan occurs from November to April and is characterised by cold, dry, dusty winds with sporadic haze. The district experiences a single rainfall season from May to October. The average annual rainfall is 1,200 mm, with torrential, erratic, and stormy conditions. Heavy rains at the start and end of the season often cause damage to buildings and farms. One-time rainfall season does not allow for year-round farming. Farmers often become unemployed during the dry season, which lasts from November to May.

A variety of heights of trees, shrubs, and grasses make up the vegetation. The district is home to a variety of common trees, including cashew, mango, ache apple, neem, kapok, shea, and baobab. Thirty percent of the natural vegetation has been destroyed as a result of annual bush burning, improper farming methods, careless tree cutting for fuel, the production of charcoal, and subpar animal husbandry techniques. The Ambalaara Forest Reserve, home to a variety of animal species including antelopes, baboons, monkeys, and lions, is another asset to the district. Because the vegetation is grassy and ideal for grazing, a lot of foreign Fulani herdsmen come into the district every year.

The district is known for its gold, iron, and bauxite deposits and is mostly composed of metamorphic and igneous rock. Thus, there are illegal mining operations in places like Bulenga, Duu, Joanfian, and Danyokura. The rocks' artistic qualities draw tourists, and they also present opportunities for a thriving quarrying industry (MOFA, 2021).

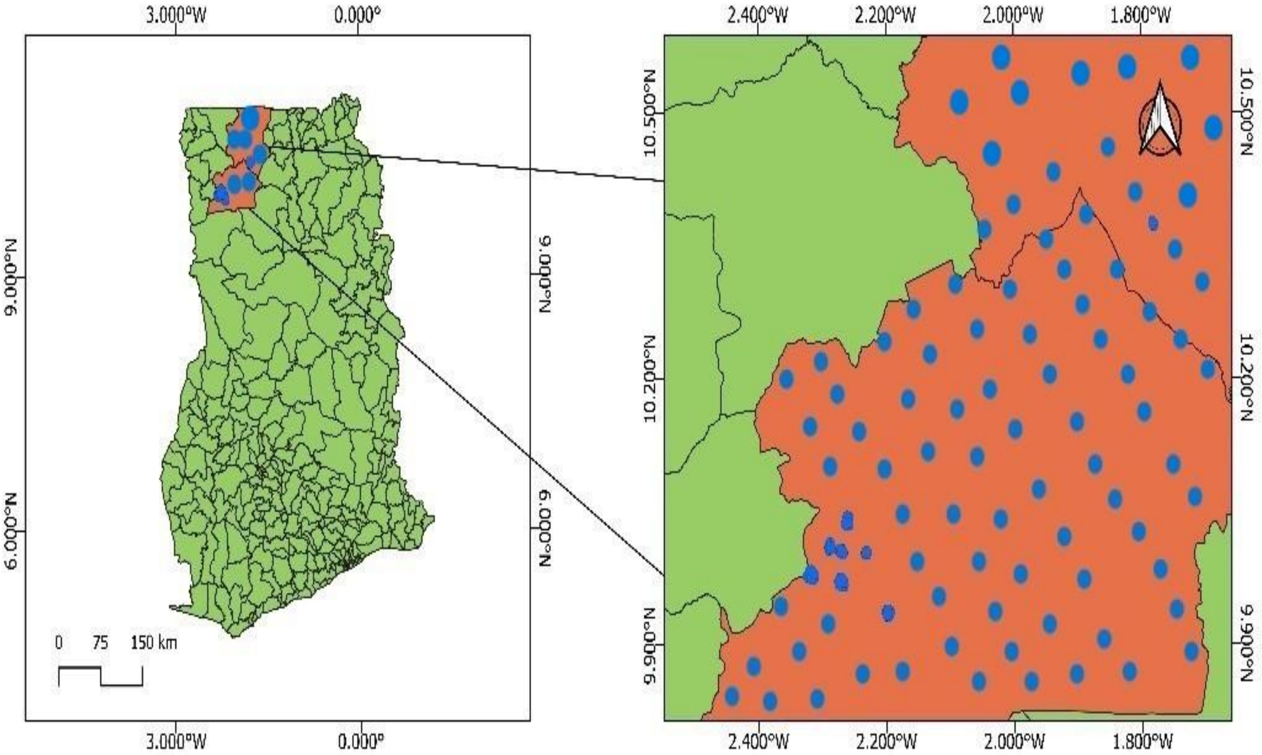


Fig. 3.1: A map showing the Wa East District

21.3 Activities at the study site

Investigating the activities at the artisanal mining sites in the Wa East District involved on-site observations and interviews with local miners. Common activities included surface excavation, crushing & milling, sluicing, sediment processing, motor vehicular mechanics, metal fabrication and welding. These activities, alongside using mercury in the extraction process, were documented to assess potential exposure pathways and their implications for human health risk in the study area.

21.4 Sampling Technique

Samples were collected from the identified 8 artisanal mining sites in the Wa East district using a purposive sampling technique. Samples were collected systematically from each artisanal mining site.

21.5 Sample collection, preparation, and storage

The main factors affecting the choice of sampling locations and procedures (sampling and handling) were the goals of the study, the areas of interest's accessibility, the areas' proximity to possible pollution sources, and the locations of environmental hotspots. Sixty-five composite soil samples in total were gathered from the communities' artisanal mining sites. (see Appendix Table 3.1 and Figure 3.1).

At an excavation depth of 0–15 cm, samples were taken with a dry plastic soil auger. This depth enhances human risk assessment since it is believed to be the layer that humans are most probably to encounter in their daily lives (Dodd et al., 2017).

The soil from each sampled location was thoroughly mixed in a 20 L plastic bucket. After obtaining a 500 g composite sample, it was sealed in identified zip lock bags. To reduce cross-contamination during sampling, after each sampling point, the digging tools were scrubbed with detergents and wiped with deionized water. Every sample collection location was GPS-identified using GPS Essentials version 4.5.24, by Micheal Schollmeyer; Seattle-USA, and appropriately labelled with the sampling locations. Table 3.1 in the appendix lists their exact sampling locations and sample identities.

The soil samples were air-dried for six days after being delivered to the lab to ensure proper drainage and reduce the moisture content below 20%.

This is due to the possibility that humidity content levels exceeding 20% for solid (powdered) samples could alter the structure of the soil upon which the XRF spectrometer has been adjusted and interfere with the results of the X-Ray Fluorescence determination (Kodom et al., 2010; EPA/ROC, 1998). Tools were thoroughly cleaned between samples using deionized water to prevent external contamination or contamination among the samples. After carefully removing debris, stones, and pebbles, the samples were processed into a powder and screened to an average particle size of 250 µm, which is the portion of soil that can stick to the skin, particularly the hands.

21.6 Determination of Soil Physiochemical Properties

Electrical conductivity and soil pH were measured from a 1:2 soil-to-water ratio supernatant using an Oakton PCSTestr35 multiparameter probe (Quebec, Canada) (Amponsah et al., 2022). The total organic matter in the samples was computed using the loss on ignition method (Darko et al., 2019). A crucible containing a 10 g portion of soil was preheated for two hours to 105°C. The samples were put into a Thermolyne muffle furnace that had been preheated to 550 °C for four hours after being allowed to cool to room temperature in a desiccator. The samples were taken out of the furnace, allowed to cool (overnight) at room temperature in a desiccator, and then weighed once more. The organic matter content was determined by taking the difference between its initial and the final weights. Three replicas of each analysis were completed.

21.7 Determination of Potentially Toxic Elements

Employing US-EPA Method 6200 (US-EPA, 2007), the Niton XL3t GOLDD+ field portable XRF analyzer (Massachusetts, USA) was used to analyze the sieved soil samples for metals except Hg. A polyethene container was filled to roughly three-quarters of its capacity with about 2 g of the sieved soil sample, and the XRF scanned the sample for 3 mins. The readings were averaged after each sample was run in triplicate (Darko et al., 2017).

21.7.1 Quality control

A triplicate run of the certified reference material NIST 2711a was used for the recovery analysis. This resulted in recoveries that were consistently within 10% of each target element's certified value. After analyzing ten replicates, the reproducibility was found to be satisfactory, with an average relative percent difference of less than 15% for every metal. The following elements have a limit of detection: As (<2 mg/kg), Cd (<3 mg/kg), Co (<10 mg/kg), Cr (<10 mg/kg), Cu (<6 mg/kg), Hg (<3 mg/kg), Mn (<12 mg/kg), Ni (<10 mg/kg), Pb (2 mg/kg), and Zn (<3 mg/kg). This limit is determined based on thrice the detector-estimated error in measuring the readings.

21.7.2 Determination of mercury concentration

The Lumex PYRO-915+ pyrometer was used to atomize mercury, and the RA-915 M Zeeman mercury analyzer (Lumex, St. Petersburg, Russia) used atomic absorption spectrometry to determine the amount of mercury in the soil. The sample's mercury content is determined using the integrated analytical signal, accounting for the pre-set calibration coefficient from the activated charcoal reference material (Cat: 500292 Lumex, Russia).

Each 0.5g soil sample was then put into the injection spoon of the PYRO-915+ attachment. The mercury analyzer was run at a rate of one liter per minute and has a detection limit of 0.0005 mg/kg.

21.8 Statistical analysis

Minitab 20.0 from Minitab, LLC, Pennsylvania, USA and JASP 0.18.1, a free open-source statistical program, were used for the statistical analyses. Data were assessed using international standards for soil quality. Based on their application in previous studies carried out in Ghana (Amponsah et al. 2022, Cao et al., 2020), the Dutch Intervention Values (VROM, 2000) and the Canadian Council of Ministers of the Environment (CCME, 2007) soil quality guidelines were chosen.

Since residential, agricultural, and artisanal mining are all part of the Wa East communities' land use scenario, when analyzing the data, the CCME guideline for residential land use was used.

21.9 Contamination Assessment Methods

Using the contamination factor, geo-accumulation index, enrichment factor, and potential ecological risk index, the possible effects of artisanal mining operations on elements or metal concentrations in the immediate environment were assessed (Qing et al., 2015).

21.9.1 Enrichment factor

The comparison of a measured element against a reference element forms the basis of the enrichment factor (EF) of an element in the samples under study. According to Turner and Simmonds (2006), a reference element is typically one with low occurrence variability, such as Al, Fe, etc. In this study, Fe served as the reference element. To distinguish PTEs from natural sources and those resulting from human activity, the enrichment factor is employed. This is calculated using the equation:

$$EF = \frac{M_s \times Fe_b}{M_b \times Fe_s} \tag{1}$$

where Mb and Feb are the pertinent background concentrations of the metal and Fe, and Ms and Fes are the concentrations of the metal and Fe in the soil sample. The mean elemental concentration in 12 control samples taken from the Wa Botanical Gardens was used to estimate the Mb for this investigation. According to Kowalska et al. (2018), an EF< 2 denotes insufficiency to minimal enrichment, 2–5 moderate enrichment, 5–20 significant enrichment, 20–40 very high enrichment, and >40 extremely high enrichment.

21.9.2 Geo-Chemical background index (Igeo)

By comparing the measured levels of PTE to the initial background level in the soil, the index of geo-accumulation (Igeo) is widely used to evaluate contamination. It is calculated using equation 2

$$\text{Igeo} = \log_2\left[\frac{M_s}{1.5M_b}\right] \tag{2}$$

where M_s represents the measured concentration of the element in soil being studied and B_b represents the geochemical background value of the measured element's concentration. The constant 1.5 is introduced to minimize the effect of possible variation in the background values which may be attributed to lithologic and anthropogenic input (Asare et al., 2019).

The Igeo data was evaluated using the following descriptive classes: ≤ 0 =unpolluted; 0–1= unpolluted to moderately polluted; 1–2 = moderately polluted; 2–3 = moderately to highly polluted; 3–4 = highly polluted; 4–5 = highly to extremely high polluted; and 5–6 extremely high polluted (Kowalska et al., 2018).

3.8.3 Contamination factor

The ratio of the metal concentration in the sample to the background concentration is known as the contamination factor (CF). The contamination factor was calculated using Equation 3 (Darko et al., 2017).

$$\text{CF} = \frac{M_c}{M_b} \tag{3}$$

Because the Botanical Gardens in Wa are immaculate and unaffected by human activity like mining, reference samples were taken there. According to Asamoah et al. (2021) there were four categories for soil contamination: uncontaminated (CF<1), moderate (CF=1-3), significant (CF=3-6), or highly contaminated (CF>6). The geochemical background values of different PTEs are provided in Table 3.1.

Table 3.1 : International average geochemical background values of various PTEs

PTE	As	Cu	Cd	Cr	Hg	Ni	Pb	Zn
Bn	20	2.98	0.62	5.82	0.15	3.43	2.99	12.0

Alloway, 1990

21.9.3 Risk Factor and Potential Ecological Risk Index

The potential ecological risk coefficient (Erf) or risk indices (RI) were calculated using the following formula to determine the ecological risk that each metal presents:

Erf or RI = Trf ×CF (4)

The contamination factor is CF, and the toxic response factor, or metal toxicity, is Trf. As = 10, Cd = 30, Cr = 2, Cu = Mn = Pb = 5, Ni = 6, and Zn = 1 are the Trf that are utilized (Hakanson, 1980). Low risk (Erf < 50), moderate risk (Erf = 50 - 100), significant risk (Erf = 100 - 300), high risk (Erf = 300 - 500), and very high risk (Erf ≥ 500) are the categories used to categorize ecological risk.

The degree of metal pollution was evaluated using the potential ecological risk index (PERI), which is the weighted average of the individual risk indices.

$$\text{PERI} = \sum_{i}^{n} (E_r f) \qquad (5)$$

where n represents how many metals were examined. Low risk (PERI ≤ 80), moderate risk (80 ≤ PERI ≤ 100), significant risk (100 ≤ PERI ≤ 150), high risk (150 ≤ PERI ≤ 300), and very high risk (PERI > 300) were the categories used in the literature-based categorization (Swarnalatha et al., 2015).

21.9.4 Pollution Load Index

The integrated pollution load index (PLI) is used to provide an evaluation of the sample's overall pollution status (Chen et al., 2001G). The PLI is determined by means of;

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots\dots\dots\dots . CF_n)^{1/n} \qquad (6)$$

According to Zhang et al., (2011), the pollution Load Index is classified as; Background Concentration PLI= 0, Unpolluted 0 < PLI=1, unpolluted to moderately polluted, 1 < PLI=2, Moderately polluted 2 < PLI=3, Moderately to highly polluted 3 < PLI=4, highly polluted 4 < PLI= 5 and Very highly polluted PLI > 5.

21.9.5 The Nemerow Pollution Index

The Nemerow Pollution Index (PNI) is a comprehensive pollution index that considers the highest and average values of the single-factor pollution index. These comprehensively suggest the role of more hazardous pollutants and depict the average pollution level of different pollutants in the soil. (Guan et al., 2014). According to Guan et al; (2014), to assess the overall level of heavy metal pollution in soil, the Nemerow Pollution Index (NPI) is usually employed. The Nemerow Pollution Index, frequently used to evaluate soil quality, also emphasizes the significance of the most contaminated element. The Nemerow Pollution Index combines multiple environmental factors into a single composite score to provide a way to measure pollution. It is coveted for its ability to integrate information from various contaminants, providing a comprehensive picture of the state of the environment in a particular location. It is determined by comparing the concentrations of various pollutants to the appropriate standard or allowable limits. In order to ensure that the final index reflects both average conditions and extreme pollution events, the Nemerow Pollution Index formula usually includes both the mean and the maximum values of the pollution indices for individual pollutants.

$$P_N = \sqrt{\frac{(P_1)^2 + P_{imax}^2}{2}} \qquad (7)$$

Where $P_N =$ comprehensive pollution index of the sampling point.

P_{imax} = maximum value of the single-item pollution index of the pollutants at the sampling point.

The Nemerow Pollution index is classified as; No pollution or very light pollution (PNI ≤ 1), Light pollution (1< PNI ≤ 3), Moderate pollution (1< PNI ≤ 10), Considerable Pollution (10 < PNI ≤ 50), Severe pollution (PNI > 50).

21.10 Human Health Risk Assessment

PTE pollution affects people and the natural environment differently depending on the chemical composition, amount, and frequency of exposure. Exposure to PTEs can happen by direct dietary consumption, inhalation, and skin absorption. The dosage obtained via every route is determined using equations (8) – (10). (Gyamfi et al; 2021)

The dosage intake for skin contact (Dderm) is determined by Equation 8, with the variables specified in **Table 3.2 and 3.3.**

$$\text{Dderm} = C \times \frac{SL \times SA \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{8}$$

The following equation gives the dose intake by ingestion (Ding):

$$\text{Ding} = C \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{9}$$

The following is the dose intake by inhaling soil particle (Dinh):

$$\text{Dinh} = C \times \frac{IngR \times EF \times ED}{PEF \times BW \times AT} \times 10^{-6} \tag{10}$$

Table 3.2: Reference dosage (RfD) according to Baptista et al. (2009) for specific PTEs through exposure routes

Element	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mn**	**V**	**Ni**	**Pb**	**Zn**
RfDinh	0.000086	0.0000507	0.0000057	0.0000285	0.040	0.000086	0.00143	0.0008	0.0206	0.00352	0.3
RfDing	0.0003	0.0005	0.01	0.003	0.037	0.0030	0.024	0.003	0.00186	0.036	0.3
Rfder	0.0003	0.0005	0.01	0.003	0.037	0.0030	0.024		0.00186	0.0036	0.3

Table 3.3: The exposure factors and the benchmark value of variables used to evaluate the risk of PTEs to human health

Factor	**Definition**	**Unit**	**Value**	
			Children	**Adult**
C	The concentration of elements in the sample	mg/kg	This study	This study
BW	Body weight	kg	15	70
EF	Exposure frequency	Days/year	350	250
ED	Exposure duration	Years	6	24
AT	Average time	Days	2190	8760
IngR	Ingestion rate	mg/day	200	100
InhR	Inhalation rate	m^3/day	10	10.4
PEF	Particulate emission factor	m^3/day	1.3×10^9	1.3×10^9
SA	Exposed surface area	cm2/day	5800	13110
AF	Skin adherence factor	mg/cm2/day	0.07	0.07
ABS	Skin absorption factor	no unit	0.01	0.01

VF	Volatilization factor	mg/kg	

US EPA, (2011) and DEA, (2010)

The organism is considered to be able to tolerate a reference dose or a manageable daily intake with little to no risk of negative health effects in risk assessments for non-carcinogenic toxicants. To determine the non-cancer or non-carcinogen risk of exposure, equation 11 is used. US-EPA, (2011).

$$HQ = \frac{DI}{RfD} \qquad (11)$$

where RfD is the reference dose for a specific element through a specific route, DI is the dose intake by a particular mode of exposure, and HQ is the hazard quotient for a specific path of exposure.

The hazard index (HI), which measures the overall risk of exposure through ingestion, inhalation, and dermal contact, is determined by equation 12.

$$HI = HQ_{ing} + HQ_{inh} + HQ_{derm} \qquad (12)$$

where HQ (ing, inh, and derm) stands for the hazard quotients of the exposure routes, and HI is the hazard index.

The total of each metal's hazard quotients over all potential exposure pathways is used to compute the hazard index (Coker et al., 2023).

One well-known method for assessing the risks that contaminants pose to health is the hazard index (Gyamfi et al., 2021). A value above one raises concerns about potential health effects, while an index below one indicates little to no non-cancerous impact or absence of harmful health risks.

21.10.1 Risk Assessment on Mercury

It is mentioned that in addition to being exposed to mercury through eating, drinking, and skin contact, individuals in the study area will also be in exposure to mercury through the atmosphere (Gyamfi et al; 2022). A vaporization-based risk assessment for mercury in soil was carried out for human health. The community is affected by the mining operations, which discharge PTEs into the soil, including mercury. These operations are situated close to farms and residential homes. Mercury exposure can have detrimental effects on the health of artisanal mine workers, non-miners, and vulnerable groups like women and children who might or may not be employed at these artisanal sites.

The amount of mercury that an organ is exposed to from the mercury-contaminated soil was determined to perform the exposure assessment. Similar to the other PTEs evaluated above using equations 8–10, Vapours from contaminated soils can also expose people to mercury. Direct exposure can occur frequently through skin contact with the soil, inhaling dust particles, and consuming the contaminated soil orally (Wang et al., 2001). The contamination by vapourization can be calculated by using the exposure parameters listed in Table 3.3 above.

The dose received through the vapourization pathway was calculated using equation 13;

$$D_{\text{vapour}} = C \times \frac{IngR \times EF \times ED}{VF \times BW \times AT} \times 10^{-6} \qquad (13)$$

21.10.2 Carcinogenic Health Risk Analysis

The carcinogenic assessment is computed as a product of the various average daily doses through the exposure pathways (ADDinh, ADDing, and ADDderm) and the cancer slope factor (CSF). Equation 14 used in the carcinogenic risk (CR) estimation process.

$$CR = ADD \times CSF \qquad (14)$$

Table 3.4: Values for Cancer slope factor CSF (mg/kg/day) for Carcinogenic elements

Element		**CSF (mg/kg/day)**	
	Inhalation	Ingestion	Dermal
As	4.3×10^{-3}	1.50	1.50
Cd	6.30	-	-
Cr	4.02	5×10^{-1}	2.0
Pb	4.2×10^{-2}	-	-

USEPA, 2011

CHAPTER FOUR

RESULTS AND DISCUSSIONS

22.1 Physicochemical Parameters

The physicochemical characteristics of soil samples taken from the research area are shown in Table 4.1. The pH levels, electrical conductivity (EC), and organic matter (OM) are among the parameters that were examined since they have a direct impact on the state of the soil in general and how well plants grow. These parameters are essential for assessing the quality and fertility of the soil.

Table 4.1: Physicochemical parameters of the soil

	Physicochemical parameters		
	EC(μς/cm)	**OM**	**pH**
Mean	125.113	2.299	7.044
Std. Deviation	103.250	1.045	0.708
Minimum	24.160	0.500	5.300
Maximum	544.200	6.500	8.670

The average pH of the soil is 7.04±0.71 with a standard deviation of 0.708, and the range of pH values is 5.30 to 8.67. The soil is generally neutral, with a mean pH of 7 being neutral. This is marginally higher than the average pH range of 4.10-7.40 of Ghana's Guinea Savanna ecological zone and the 4.50-7.40 pH of soils in the Upper West Region (MOFA, 2018).

The variability in the soil’s pH, however, points to potential shifts in the levels of acidity or alkalinity, which may affect the health of the soil and the availability of nutrients. These variations might have been caused by waste products or mine tailings from the extraction of minerals. While carbonate minerals can have an alkalizing effect, sulfide minerals in tailings have the potential to oxidize and produce sulphuric acid, which lowers pH. Once more, the operations conducted at the study sites frequently require the use of chemicals, like acids, which have the potential to seep into the nearby soils and alter their pH.

(The geological makeup of the parent material from which the soil is formed may be the cause of the majority of the samples' somewhat elevated alkalinity (Li et al., 2023), hampered leaching due to haphazard natural water flow and drainage patterns as either a result of the mining operations or from fluid and oil leaks from the machines that are maintained at the mining sites. Transmission fluids, car oils, and other fluids with alkaline content can leak and seep into the soil over time, possibly increasing the pH in the surrounding area. Elevated pH levels in soil encourage metal retention while reducing their solubility. The study sites exhibited a slightly elevated level of soil alkalinity, indicating that the PTEs had become insoluble and were being held in the soil.

The mean EC value is 125.113 µς/cm, with a standard deviation of 103.250 µς/cm. This indicates variability in the conductivity of the soil, possibly due to differences in mineral content or contamination levels.

Soil solution conductivity is mainly caused by dissolved ions, especially salts, which have an impact on electrical conductivity. Generally speaking, soils that have experienced human activity have higher electrical conductivity. Residues from the mining operations such as sulfides and salts can leach into the soil elevating the EC levels.

22.2 Potentially Toxic Elements in Soil Samples

Examining soil samples from artisanal mining sites for Potentially Toxic Elements (PTEs) reveals alarming concentrations of different PTEs. The descriptive statistics of the concentrations of elements that may be toxic in soil samples taken from the mining sites are shown in Table 4.2

Table 4.2: Descriptive Statistics of Concentrations of Potentially Toxic Elements

	Concentration (mg/kg)									
	As	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**V**	**Zn**
Mean	51.525	20.449	104.831	40.456	27.279	0.353	29.928	3.797	67.460	28.692
Std. Deviation	96.269	45.394	43.281	17.537	7.519	0.978	18.628	1.347	33.272	14.439
Minimum	2.560	2.560	50.790	5.150	12.350	0.004	17.820	2.960	14.770	8.770
Maximum	405.740	318.290	229.850	84.880	49.550	5.844	117.880	13.730	176.500	80.790

The following are the mean PTE concentrations found in the soil samples: As (405.740 mg/kg), Pb (3.797 mg/kg), Ni (29.928 mg/kg), V (67.460 mg/kg), Cd (20.449 mg/kg), Co (104.831 mg/kg), Hg (40.456 mg/kg), Cr (40.456 mg/kg), Cu (27.279 mg/kg), and Zn (28.692 mg/kg). The study area's soil's mean values of the hazardous elements declined in the following order: Co > V > As > Cr > Ni > Zn >Cu > Cd > Pb>Hg. The ranges were as follows: Co (50.790-229.850 mg/kg); V (14.770-176.500 mg/kg); As (2.560-5.740 mg/kg); Cr (5.150-84.880 mg/kg); Ni (17.820-117.880 mg/kg); Zn (8.770- 80.790 mg/kg); Cu (12.350-49.550 mg/kg); Cd (2.560-8.290 mg/kg) and Pb (2.960–13.730 mg/kg). The concentrations observed ranged from 0.004 mg Hg/kg to 50.790 mg Co/kg at the minimum and 5.844 mg Hg/kg to 405.740 As/kg at the maximum as shown in Figure 4.1.

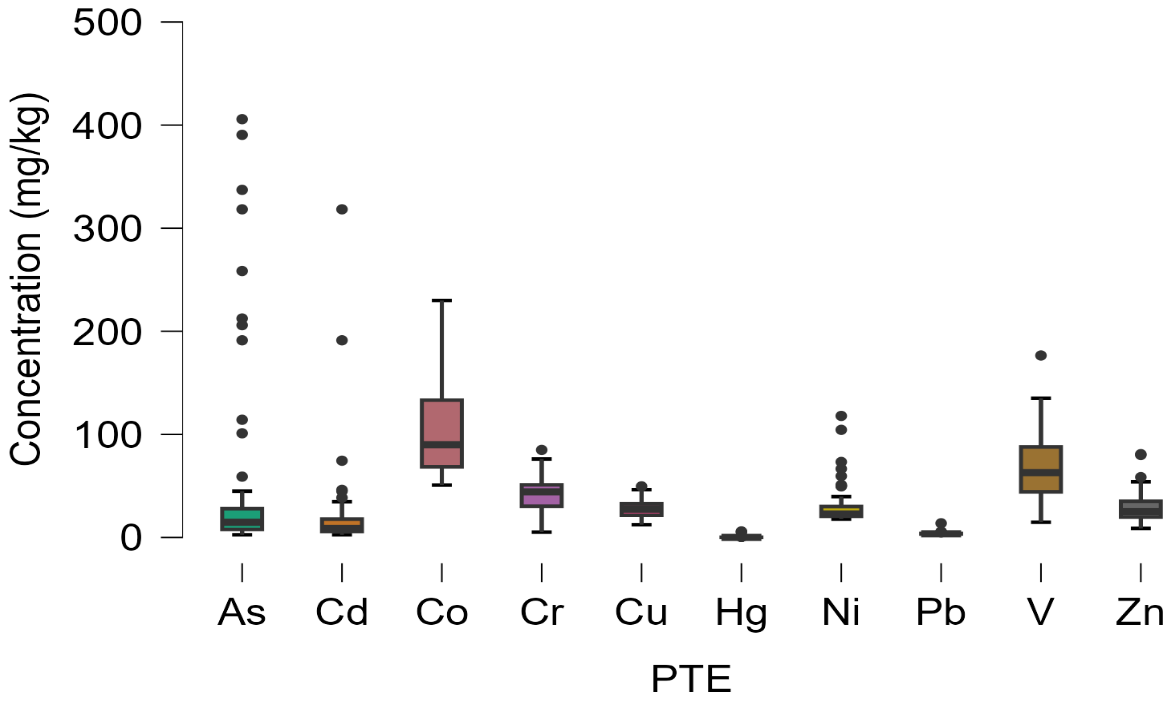


Fig. 4.1: Boxplot of PTEs concentrations in soils from artisanal mining sites

The data exhibits a broad range of variability, as indicated by the standard deviations, wherein certain elements display notably elevated levels of dispersion. Extremely high concentrations of some PTEs, like Co and V, are also highlighted by the minimum and maximum concentrations; Cobalt (Co) exhibits comparatively higher mean values than the other elements. The higher levels of Co can occur naturally due to geological processes or from anthropogenic activities. Potential human contributions in the study area are further indicated by the higher mean concentrations of As, Cd, and Co.

Furthermore, comparatively lower mean concentrations but higher maximum values were shown by potentially hazardous elements like As, Cd, and Co, suggesting localized contamination sources such as mining and agricultural activities. The concentrations of the PTEs are given in milligrams per kilogram (mg/kg). The World Health Organization (WHO), the Canadian Council of Ministers of the Environment (CCME), and any applicable local regulations are taken into consideration when comparing these levels to standards. The concentrations of As, Cd, and Co in the study area were higher than those recorded at mining sites in Ilesha, southwest Nigeria (Odukoya et al., 2018) and Tarkwa, Ghana (Bortey-Sam et al., 2015). These concentrations were also higher than those recorded in Pinggu County, China, (Zhao et al., 2017). Also, a study by Sadhu et al., (2012) on soil pollution by heavy metals in and around the Raniganj Area's open-pit mines, India showed lower concentrations of Cd, Ni, and Mn than the levels in the study area. Comparatively, there are higher levels of these potentially toxic elements at artisanal mining sites in Wa East, Ghana than similar sites at Raniganj Area in India.

Ghana does not have regulations outlining permissible metal concentrations in soil. The maximum acceptable levels of metals in unpolluted soils are indicated by the WHO target values, which are 0.8 mg Cd/kg, 50 mg Zn/kg, 36 mg Cu/kg, 100 mg Cr/kg, 85 mg Pb/kg, and 35 mg Ni/kg (FAO/WHO, 2007). The study sites were found to be contaminated with potentially toxic elements. As, Cd, and Co, except Cr and Pb, exceeded their target values. All other elements analysed were found to be below their respective target values.

Once more, comparing the PTE concentration in the study area's soil to threshold values for these elements in other nations as well as the World’s crustal averages for these elements, as Table 4.3 below illustrates, reveals that the average concentrations of toxic elements like As, Cd, Cr, and Co were all higher than the crustal average concentration of these elements, suggesting that the soil may have been contaminated with these elements. In contrast, all seven other elements that were analysed had concentrations below their respective crustal averages.

Additionally, the study area's mean As and Cd concentrations were higher than what Dutch and Canadian standards required. That is to say, for the Canadian standard, the target values for As and Cd were exceeded by 4 and 2 times, respectively. As and Cd, the Dutch standards, however, came in two and twenty-six times over their target values, respectively. On the other hand, the research region's soil samples had higher concentrations of As, Cr, Cu, and Cd than what was allowed in South Africa, a significant mining hub on the continent. In comparison, Cd surpassed its target value by 3 times, while As exceeded it by 9 times. Moreover, Cr and Cu surpassed their goal values by 6 and 2 times, respectively.

Cadmium, Cr, and As are potentially hazardous elements that present the biggest risk because of their extreme toxicity. Because of this, major concerns have been raised about the elevated levels of these elements in the study area’s environment. Plants can accumulate and absorb arsenic in soil, potentially affecting edible parts. Excessive exposure can result in several health problems, including skin problems, neurological issues, lung, liver, and kidney cancers, and even death (Ravenscroft et al. 2009).

Exposure to high levels of Cd can cause anaemia, kidney and lung problems, bone diseases, and excruciating joint pain. It may have an impact on sperm, lower birth weight, and be a contributing factor to hypertension and cardiovascular illnesses (Adelekan and Abegunde, 2011; Asio, 2009). Adelekan and Abegunde (2011) stated that disorders like dysfunction of the liver, nausea, cramps, respiratory issues, neurotoxicity, hypertension, carcinogenicity, and teratogenicity can also be brought on by Cd exposure.

Chromium cannot be broken down biologically, it persists in the environment. The risk of chromium's bioavailability, bio-mobility, and consequent toxicity rises when its content in surface soil rises as a result of pollution from different sources, such as gold mine tailings (Abdul-Wahab and Marikar, 2012).

22.2.1 Concentration of Mercury in Soil Samples

The overall mercury levels in this area are not alarming by this standard, as the mean mercury concentration of 0.353 mg/kg (Table 4.3) is well below the Canadian limit of 6.6 mg/kg. It is marginally over the Dutch limit (0.3 mg/kg), indicating a possible health risk. The average concentration, however, is noticeably greater than the background mercury level normally found in the Earth's crust 0.04 mg/kg), suggesting a possible anthropogenic effect or level of contamination.

The highest concentration value is still less than the Canadian standard, so it stays below this limit. It is significantly higher than the Dutch limit, suggesting that mercury contamination may be a serious problem in some areas. The highest concentration is substantially higher than the background level of the natural environment, implying the existence of hotspots with abnormally high mercury concentrations. According to Beckers and Rinklebe (2017), terrestrial species may have higher mercury burdens because they are partially or indirectly linked to the aquatic food chain, despite this, terrestrial ecosystems experience less pronounced mercury accumulation and poisoning than aquatic systems.

The minimum mercury concentration (0.004 mg/kg) is well below all three standards (Canada, Dutch, and crustal average Table 4.3) suggesting that some areas have very low or nearly natural levels of mercury in the soil.

The Significant variation in mercury concentrations across the sampled areas is indicated by the high standard deviation. This indicates that even though the average concentration might appear to be moderate, there are places where contamination is far higher.

Mercury levels in other craft small-scale mining sites are comparable to those found in this study. Mercury levels in Bogoso soils were reported by Adjorlolo-Gasokpoh et al. (2012) to be between 0.125 and 0.352 mg/kg. The average mercury concentration at the mining sites included in this study was 0.353 mg/kg (0.004-5.844 mg/kg), which is lower than the amount recorded by Rajaee et al. (2015), who assessed the mercury levels in household soil in Kejetia in 2010 and 2011. In 2010, the mean mercury concentration was reported at 4.78 mg/kg (0.096-40.969 mg/kg), while in 2011, it was 15.6 mg/kg (0.297-330 mg/kg). The Canadian soil quality guideline of 6.6 mg/kg for the protection of human and environmental health at residential sites was exceeded by the 2011 mercury levels from that study (CCME, 1999; Rajaee et al., 2015).

Table 4.3**:** Soil quality references for PTEs (mg/kg) of different nations and the world's crustal averages compared with the study area

PTE	**EU STD**[1]	**SOUTH AFRICA**[2]	**CANADA**[3]	**DUTCH**[4]	**CRUSTAL Avg**[5]	**WHO**[6]	**THIS STUDY**[7]
AS	-	5.8	12	29	1.5	-	51.5
Cd	3	7.5	10	0.8	0.1	0.8	20.4
Cr	100	6.5	64	100	83	100	40.5
Cu	140	16	63	36	25	36	27.3
Fe	-	-	-	-	35	-	-
Co	-	300	-	-	17	-	104.83
Mn	-	-	-	-	600	-	471.6
Ni	75	91	50	35	44	35	29.9
Pb	300	20	140	85	17	85	3.8
Zn	300	240	200	140	71	50	28.7
Hg	-	-	6.6	0.3	0.04		0.353

1: Zarcinas et al., 2004 2: FLCM, 2010 3: CCME, 1999 4: VROM, 2000 5: Hakanson, 1980
6: WHO/FAO, 2007 7: This study

22.3 Principal Component Analysis

The sources of PTEs in the soil samples from the Wa East artisanal mining areas were further determined by applying principal component analysis (PCA). Table 4.4 presents the PCA's findings. Table 4.5 shows the five main components that collectively explain 78.0% of the cumulative total variance for the various metals found in the soil samples in the source analysis. With a total variance of 20.1%, V, Ti, and Cr exhibited a significant correlation with the first component. This might be the outcome of human activity. Pb, Ni, and Mn had a total variance correlation of 17.3% with the second component. This could have been caused by exhaust emissions from nearby cars and machinery, but a strong correlation with Cu, Co, and Mn was indicated by the third factor, which also had a total variance of 17.3% (Figure 4.2). Once more, As, Cd, and Zn showed a significant correlation with the fourth component, with a total variance of 13.8% while the fifth component is Hg with just a variance of 9.5% which is most likely as a result of the mining activities. With 78.0% of the cumulative variance explained by the five components, it can be concluded that the interpretation is reliable considering these five components account for a significant proportion of the dataset's variability.

The low uniqueness values of V (0.064), Ti (0.105), and Zn (0.158) indicate that the components account for the majority of their variance. Additionally, the moderate uniqueness values of Pb (0.196) and Co (0.211) show that while the components define a significant portion of their variance, some remain undefined. Even though Mn (0.382) and Cu (0.315) have somewhat higher uniqueness values, PC4 still accounts for most of the explanation.

The third component shows comparable Zn loadings in the soil, indicating that both lithogenic and paedogenic origins contributed. This might have resulted from industrialized processes. This observation is consistent with the correlation findings, which point to a similar source.

Table 4.4: Component Loadings

	PC1	**PC2**	**PC3**	**PC4**	**PC5**	**Uniqueness**
V	0.888					0.064
Ti	0.831					0.105
Cr	0.790					0.261
Pb		0.869				0.196
Ni		0.777				0.274
Mn		0.657				0.382
Cu			0.821			0.315
Co			0.818			0.211
Zn			0.628	0.517		0.158
Cd				0.816		0.247
As				0.807		0.167
Hg					0.861	0.254

Note. Applied rotation method is varimax.

Table 4.5: Component Characteristics

	Rotated solution			
	Eigenvalue	**SumSq. Loadings**	**Proportion var.**	**Cumulative**
Component 1	3.621	2.414	0.201	0.201
Component 2	2.135	2.078	0.173	0.374
Component 3	1.354	2.069	0.172	0.547
Component 4	1.163	1.655	0.138	0.685
Component 5	1.092	1.148	0.096	0.780

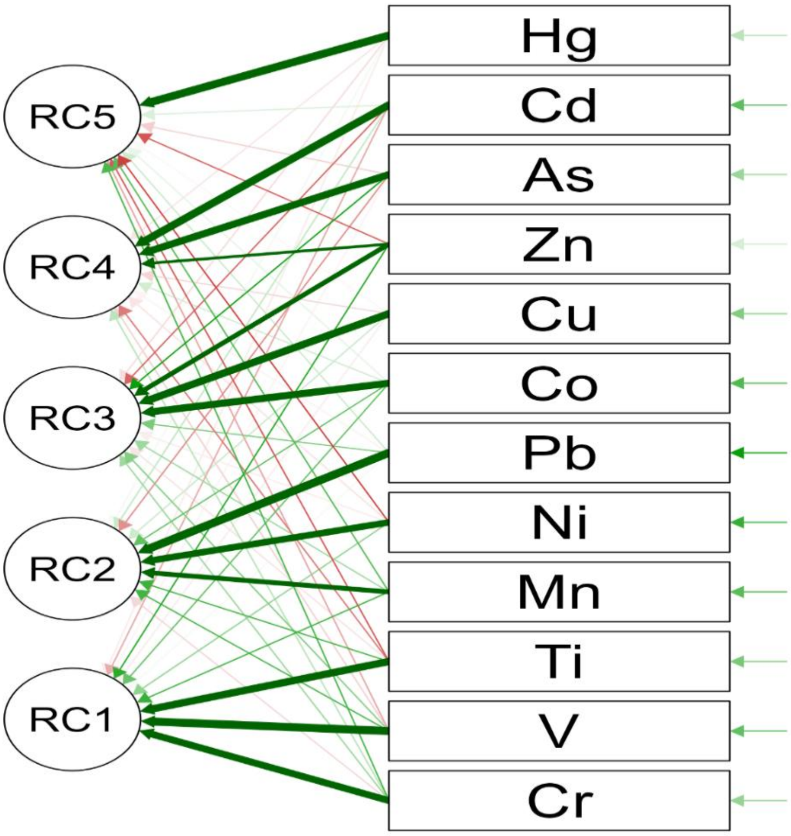


Figure 4.2: Path Diagram of PTEs

22.3.1 Source Apportionment of Potentially Toxic Elements

The PCA results identified five major components (Table 4.5), which collectively account for 78.0% of the source analysis's cumulative total variance for the various PTEs found in the soil samples. The PC1 contains V, Ti, and Cr; V. Cr is frequently associated with oil combustion and industrial emissions, particularly from the combustion of heavy fuel oils and coal. Cr is often linked to industrial emissions as well as non-anthropogenic sources such as the weathering of chromium-containing rocks, whereas Ti is primarily derived from natural sources such as crustal materials (Reimann et al., 2018). PC1 is likely a combination of industrial and natural sources, with contributions from fossil fuel combustion, metallurgical activities, and soil re-suspension.

Pb, Ni, and Mn strongly correlate with PC2; according to Lottermoser (2010), Pb contamination is frequently caused by improper handling of lead-rich ores, waste incineration, and improper disposal of mine tailings and lead-based products. In contrast, Ni and Mn are associated with metal ores mined at these sites, particularly in manganese or nickel-containing deposits. Nickel can also be introduced through the combustion of fossil fuels for equipment operation. PC2 identifies emissions from artisanal mining, metal processing, and vehicle emissions from fuels laced with methylcyclopentadienyl manganese tricarbonyl, a fuel addictive.

The third component consists of Cu, which is associated with copper-rich ores extracted from artisanal mining sites. Copper dust can also be produced through vehicular emissions from brake and tire wear on mining equipment and machinery, as well as metal smelting. While Co is frequently emitted through industrial sources such as mining, metallurgy, and battery production which is highlighted by its high EF value of 15.395. Zn can be released through rubber tire wear and galvanized steel corrosion. It is also found in fertilizers (Nriagu, 1989).

The presence of Cu, Co, and Zn in this component suggests that it was influenced by vehicular traffic particularly brake and tire wear, industrial activities involving metal processing, and, on some occasions, agricultural activities.

Again, As, Cd, and Zn exhibited a significant correlation with the fourth component; Cd is commonly associated with non-ferrous metal production, fossil fuel combustion, and waste burning. It is also found in phosphorus fertilizers. Cd may also be found in waste materials. As is frequently found in association with gold ores, particularly in areas where arsenopyrite exists. Arsenic may be released into the environment during artisanal gold mining, which often uses crude extraction and processing methods, as well as agricultural pesticide applications (Ncube, F., & Ncube., 2020). The EF values of Cd (220.012) and As (10.362) confirm the anthropogenic origin of these PTEs.

PC5 contains only mercury as its component; mercury at artisanal mining sites is most likely derived from an anthropogenic source related to its use in gold amalgamation, a common practice in small-scale gold mining. Mercury is combined with gold ores to create an amalgam, which is then heated to vapourize the mercury and release it into the environment. This component indicates the widespread use of mercury for gold recovery. The lack of proper control over mercury emissions causes significant environmental contamination in areas where artisanal mining occurs (Pacyna et al., 2010). An EF of 2.961 suggests that the levels of mercury in the soil are a result of anthropogenic activities.

The PCA components show that these elements come from a variety of natural and anthropogenic (agricultural, transportation, and industrial) sources. According to their respective sources, each component group's elements tend to co-occur in the environment, which aids in determining the relative significance of various emissions.

22.4 Correlation Analysis

The sources and routes of the PTEs are revealed by inter-element interaction (Xiaoyang et al, 2019). Coefficients of correlation analysis were used to determine the relationship in the study area. The findings of the PTEs’ concentration correlation coefficient analyses for all sampling sites are shown in Figure 4.3.

Table 4.6: Pearson's Correlations

Variable	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn	Hg	Ti
As												
Cd	0.373**											
Co	0.291*	-0.134										
Cr	0.124	-0.040	0.262*									
Cu	0.151	-0.050	0.522***	0.151								
Mn	-0.119	0.008	0.404***	0.243	0.112							
Ni	-0.061	-0.100	0.157	0.005	0.040	0.300*						
Pb	-0.073	-0.008	0.336**	0.131	0.233	0.503***	0.583***					
V	-0.076	-0.141	0.412***	0.614***	0.215	0.432***	0.404***	0.290*				
Zn	0.689***	0.119	0.592***	0.222	0.385**	0.122	0.150	0.081	0.424***			
Hg	-0.048	-0.047	-0.047	0.055	-0.074	0.045	-0.064	0.008	-0.115	-0.165		
Ti	-0.220	-0.234	0.216	0.421***	0.009	0.356	0.475***	0.212	0.881***	0.241	-0.135	

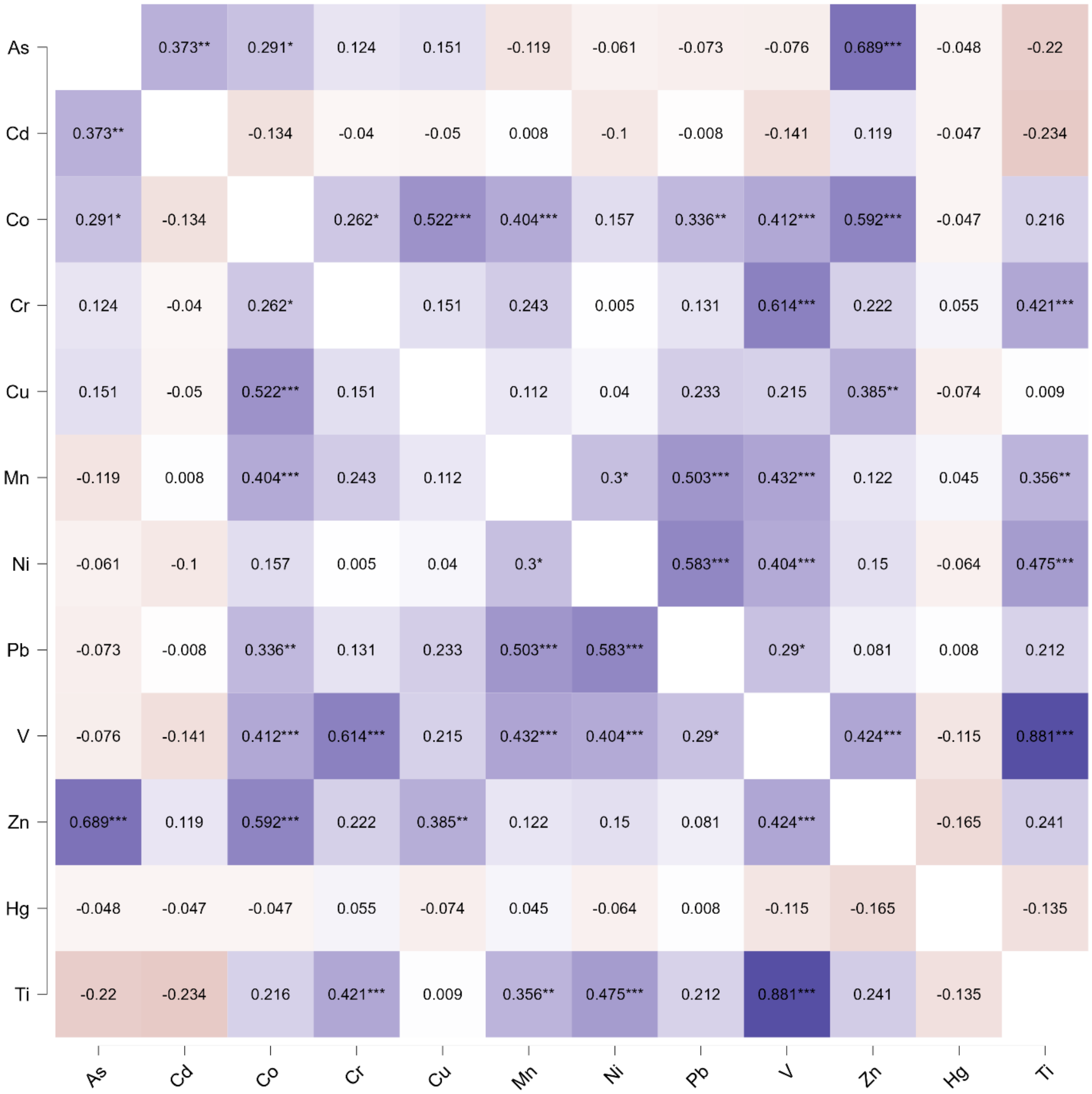
* p < .05, ** p < .01, *** p < .001

From table 4.6; a strong positive correlation (r = 0.689) between As and Zn indicates that higher zinc levels correlate with higher arsenic levels. The data indicates a moderate positive correlation (r = 0.373) between arsenic and cadmium levels, indicating a discernible but weak tendency for them to rise concurrently. There is a weak negative correlation (Pearson's correlation coefficients of -0.119 and -0.220, respectively) between As and Mn and As and Ti. This demonstrates the pairs' slight inverse relationship.

The strong positive correlation between Cr and V (r=0.614) suggests a strong relationship between higher levels of chromium and vanadium. Additionally, the fact that Cr and Ti have a somewhat positive correlation (r=0.421), indicating that higher chromium levels are connected to higher Ti levels, suggests that they are most likely from the same source.

Once more, Ti and V have a very strong positive correlation (r=0.881), suggesting that higher levels of titanium correlate with higher levels of vanadium. Zinc and arsenic show a strong positive correlation (r=0.689), indicating a possible link between higher zinc and arsenic levels.

In conclusion, Figure 4.3 illustrates the strong positive relationships that Ti and V, As and Zn, Co with Cu and Zn, Mn with Pb, and Cr with V exhibit. But a lot of other pairs, like As with Mn or Cd with Cu, have weak or insignificant correlations, indicating limited linear associations.



	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn	Hg	Ti
As		0.373**	0.291*	0.124	0.151	-0.119	-0.061	-0.073	-0.076	0.689***	-0.048	-0.22
Cd	0.373**		-0.134	-0.04	-0.05	0.008	-0.1	-0.008	-0.141	0.119	-0.047	-0.234
Co	0.291*	-0.134		0.262*	0.522***	0.404***	0.157	0.336**	0.412***	0.592***	-0.047	0.216
Cr	0.124	-0.04	0.262*		0.151	0.243	0.005	0.131	0.614***	0.222	0.055	0.421***
Cu	0.151	-0.05	0.522***	0.151		0.112	0.04	0.233	0.215	0.385**	-0.074	0.009
Mn	-0.119	0.008	0.404***	0.243	0.112		0.3*	0.503***	0.432***	0.122	0.045	0.356**
Ni	-0.061	-0.1	0.157	0.005	0.04	0.3*		0.583***	0.404***	0.15	-0.064	0.475***
Pb	-0.073	-0.008	0.336**	0.131	0.233	0.503***	0.583***		0.29*	0.081	0.008	0.212
V	-0.076	-0.141	0.412***	0.614***	0.215	0.432***	0.404***	0.29*		0.424***	-0.115	0.881***
Zn	0.689***	0.119	0.592***	0.222	0.385**	0.122	0.15	0.081	0.424***		-0.165	0.241
Hg	-0.048	-0.047	-0.047	0.055	-0.074	0.045	-0.064	0.008	-0.115	-0.165		-0.135
Ti	-0.22	-0.234	0.216	0.421***	0.009	0.356**	0.475***	0.212	0.881***	0.241	-0.135	

Fig 4.3: Pearson’s heatmap showing inter-element relationships

22.5 Pollution Indices

For the soil sample results from the study area, Table 4.7 shows the geochemical load index (Igeo), enrichment factor, contamination factor, and pollution load index.

Table 4.7: Mean Pollution Indices of Potentially Toxic Elements in Soil Samples

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Ti	V	Zn	Hg
Igeo	-0.211	4.467	1.764	-1.940	-1.363	-1.720	-1.925	-3.025	-1.632	-1.726	-2.468	-3.084
CF	3.063	68.164	5.517	0.450	0.606	0.555	0.440	0.190	0.561	0.519	0.302	0.882
EF	10.362	220.012	15.395	1.241	1.821	1.479	1.351	0.591	1.546	1.361	0.827	2.961
PERI	39.634	2044.923	27.587	0.899	3.031	0.555	2.201	0.949	0.561	1.038	0.302	35.266

Igeo= Geoaccumulation Index; CF = Contamination Factor; EF = Enrichment Factor; PERI = Potential Ecological Risk

Except for Cd and Co, all of the elements under analysis have negative mean Igeo values. Due to their negative values and Co's Igeo value of 1.764, all of these elements are either nearly unpolluted or have no background levels. On the other hand, the value of Cadmium (Cd) is positive (4.467), indicating a high to extremely high pollution level. The results further indicate that the soils at these artisanal mining sites are not polluted by As, Cr, Cu, Mn, Ni, Pb, Ti, V, and Zn.

According to contamination factor rankings, the soil samples from the artisanal mining sites were classified as significantly contaminated with As (3.063) and Co (5.517) and highly contaminated with Cd (68.164). The soil samples were also uncontaminated with Mn, Ni, Ti, Cu, Pb, Cr, V, and Zn.

With the enrichment factor, a crucial anthropogenic input is indicated by the extremely high enrichment of Cd (220.012) in the enrichment factor results (Table 4.7). Significant enrichment was seen in As and Co, with EF values of 10.362 and 15.395, respectively while the soil is moderately enriched by Hg with an EF value of 2.961. The EF values of the remaining elements are less than 2, suggesting a probable natural origin and a deficiency to minimal enrichment. The average EF's exceedance indicates that anthropogenic factors were the primary cause of Cd, As, and Co. According to Hogarh et al. (2016), the underlying goldbearing geology of the regions and the use of As in the extraction and processing of minerals may be responsible for the accumulation and enrichment of As, Cd, and Co. In a study conducted in Mahidasht, Iran, Atafar et al. (2010) linked the use of inorganic fertilizers to higher concentrations of As. The varied Igeo, CF, and EF values of the assessed PTEs across the study area suggest that different processes may have affected the processes affecting elemental accumulation and enrichment.

The research area is considered to be low-risk for all of the PTEs examined, according to the ecological risk assessment, except Cd, which poses a very high environmental risk to humans with a PERI of 2044.923 as indicated in Figure 4.4d.

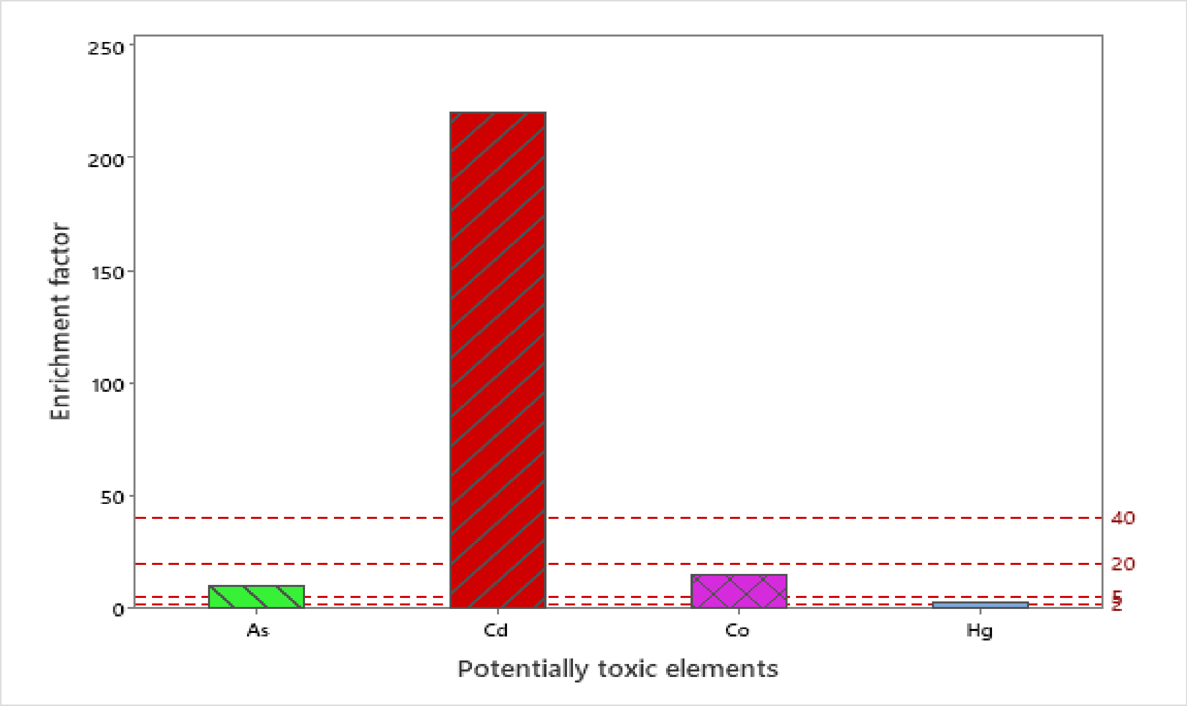


Fig. 4.4: Enrichment factor of PTEs

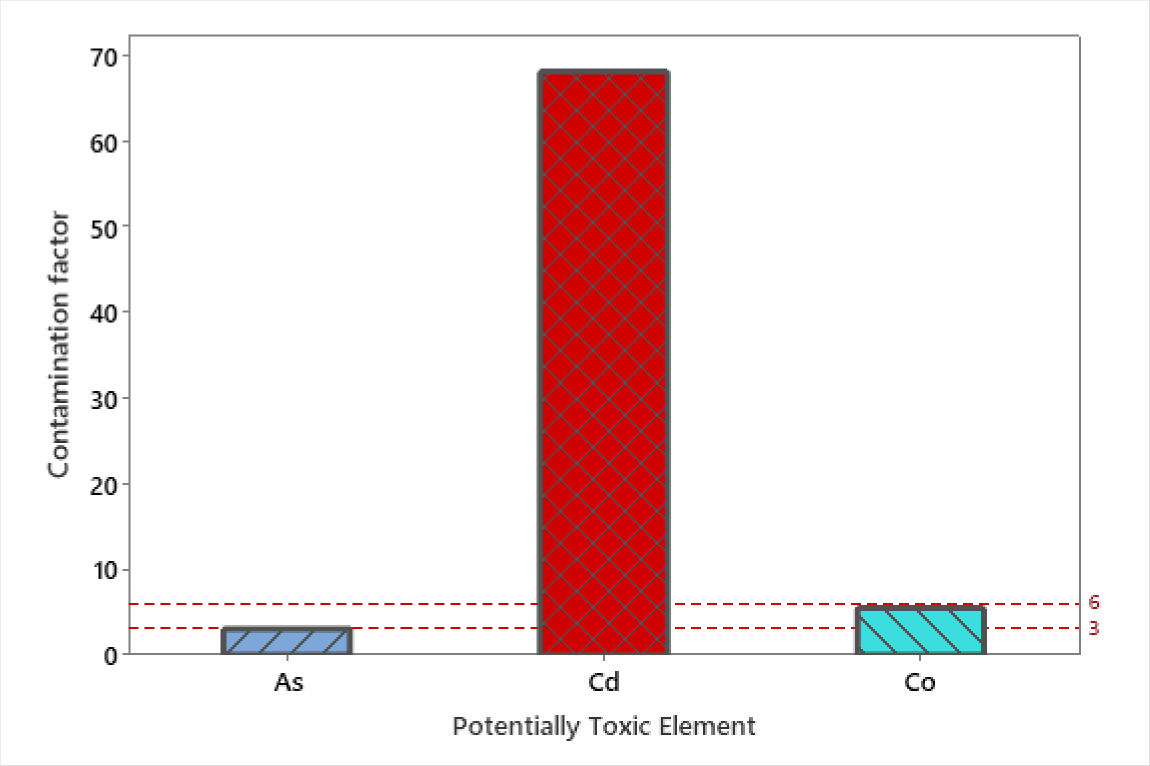


Fig. 4.5: Contamination factor of PTEs

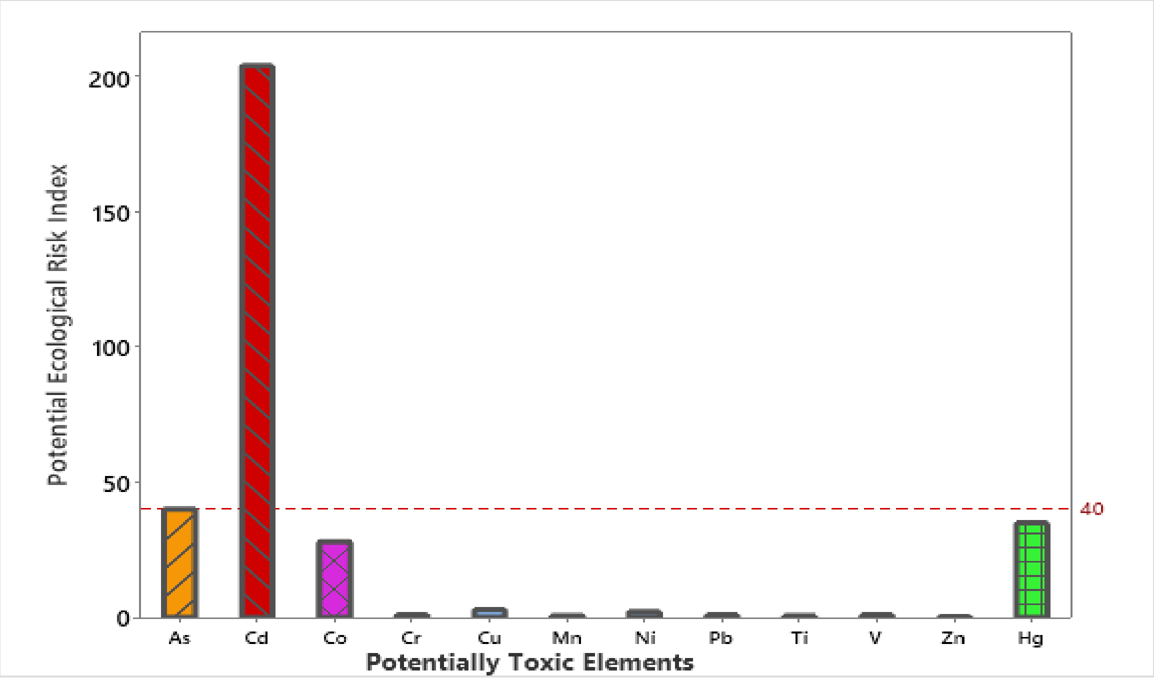


Fig. 4.6: PERI of PTEs

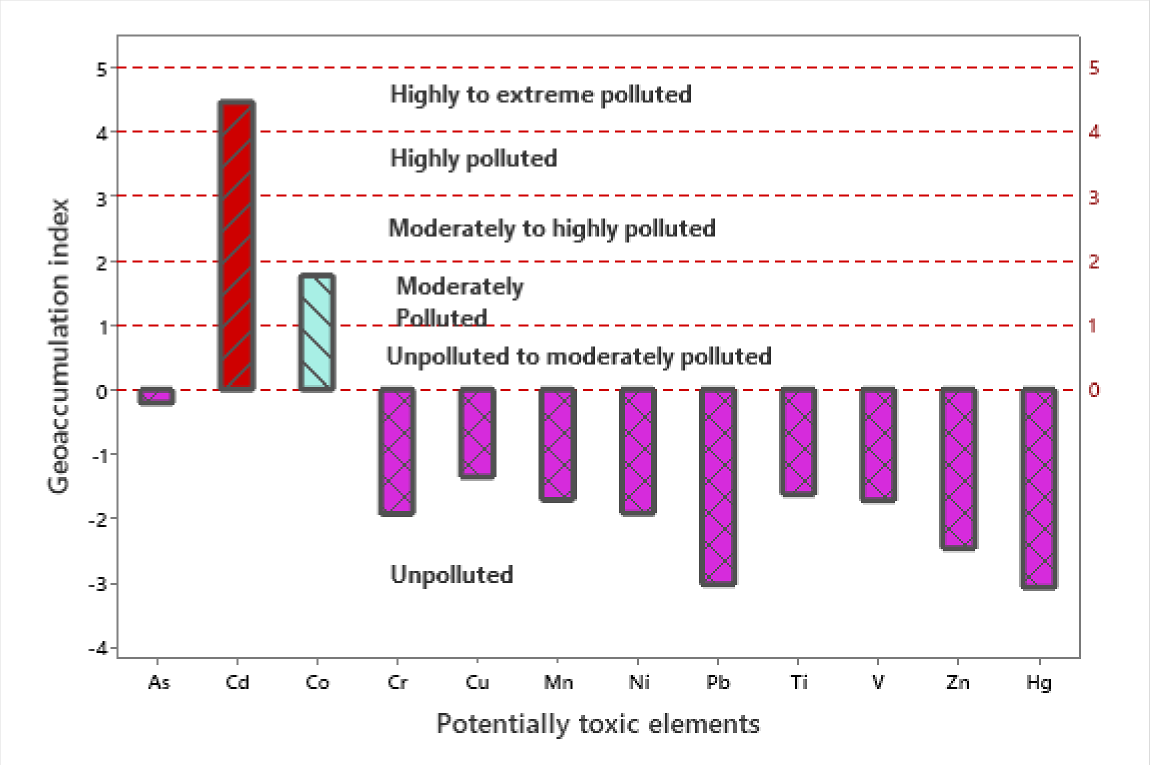


Fig. 4.7: Geoaccumulation index of PTEs

22.5.1 The Nemerow Pollution Index

The Nemerow Pollution Index provides a means to quantify pollution by integrating various environmental parameters into a single composite score. Table 4.8 gives the Nemerow Pollution Index for the various potentially toxic elements.

Table 4.8: Nemerow's Pollution Index

Metal	Cf	Cfmax	PNI
As	3.063	31.211	36.50
Cd	68.164	1060.961	751.76
Co	5.517	12.097	9.40
Cr	0.450	0.943	0.74
Cu	0.606	1.101	0.89
Hg	0.353	5.844	4.14
Mn	0.555	2.911	2.10

Ni	0.440	1.734	1.26
Pb	0.190	0.686	0.50
Ti	0.561	1.436	1.09
V	0.519	1.358	1.03
Zn	0.302	0.850	0.64

Cf= Contamination factor**, Cfmax=** Maximum Contamination Factor**, PNI=** Nemerow's Pollution Index

Table 4.8 above shows that there is very little or no contamination with potentially toxic elements like Cr, Cu, Zn, and Pb, while the findings show that V, Ti, Mn, and Ni are lightly polluted in the soil from the study area. Conversely, the study area exhibits moderate pollution as indicated by the PNI value of Hg and Co. The findings also show that these artisanal mining sites' soils and communities around these sites have been considerably polluted with As and severely polluted with Cd as shown in figure 4.5, which raises serious ecological concerns.

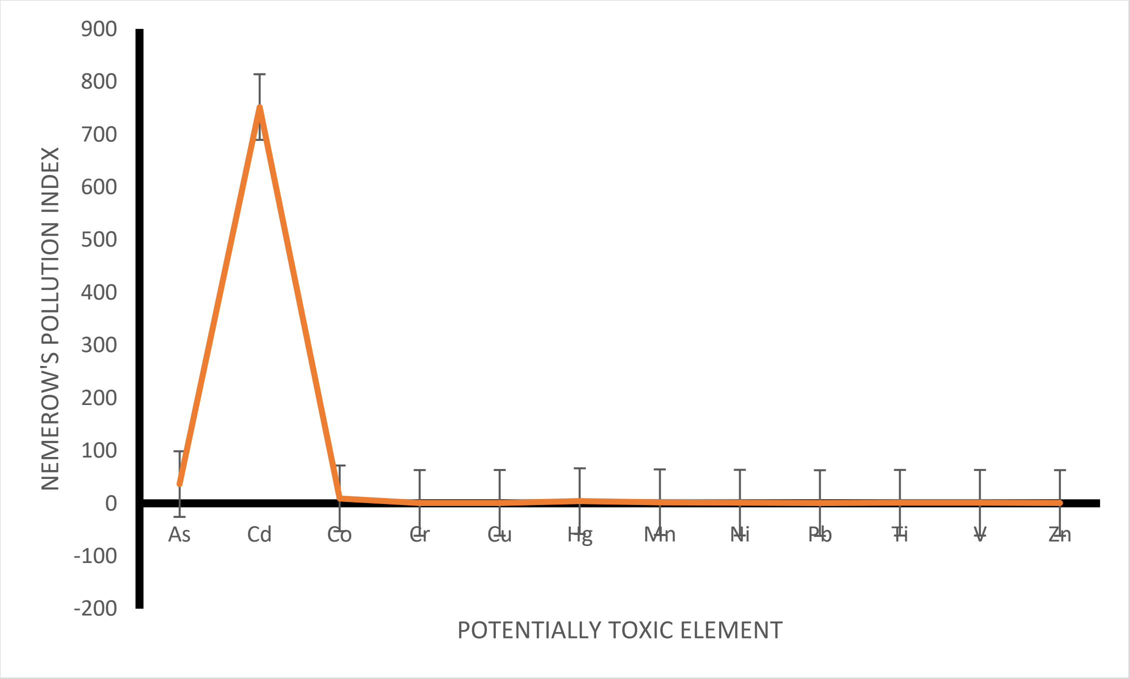


Fig. 4.8: Description of Nemerow's pollution index

22.5.2 Pollution Index

The pollution index is a measure used to quantify pollution in a specific area. It helps to assess the degree to which various pollutants are present compared to acceptable standards or baseline values. The pollution index analysis was done to provide a clear easy-to-understand indication of the pollution level and its potential impact on health and the environment. Table 4.9 displays the Pollution indices of the potentially toxic elements under study.

Table 4.9: Pollution Indices of PTEs and Pollution Load Index of Artisanal Mining Sites in Wa East

PTE	As	Cr	Cd	Cu	Hg	Pb	Ni	Co	Mn	Ti	V	Zn
PI	4.0	0.6	204.5	1.2	17.7	0.2	1.0	6.2	0.8	4.3	0.7	0.4
PLI	2.2											

PTE = Potentially toxic element; PI = Pollution index; PLI = pollution load index

Table 4.9 displays PTEs' Pollution Indexes in the decreasing order of Cd>Hg>Co>Ti>As>Cu>Ni>Mn>V>Zn>Pb. The As, Co, Hg, and Cd Pollution indexes show high contaminations with increasing PI values of 4.0, 6.2, 17.7, and 204.5, respectively, indicating high pollution and posing potential health or environmental risks to humans and other living organisms. The high Cd pollution level, as illustrated in Figure 4.6, reflects the levels recorded for Nemerow's pollution index. Cu and Ni also showed significant contamination of the study area with PI of 1.2 and 1.0, respectively. However, there was low Zn, Mn, Pb, and Cr contamination with PI 0.4, 0.8, 0.2, and 0.6, respectively.

The integrated pollution load index (PLI) measures the overall pollution level of the study area. A PLI value of 2.2 shows that the soil from the Wa East Artisanal Mining sites can be classified as moderately polluted. This suggests that the area is experiencing some pollution, likely from the mining activities. These results are in line with Yang et al.'s (2022) investigation of heavy metal contamination in a mining region northwest of Yunnan Province, China, where the pollution levels were comparable. Similar results were obtained by Bonah & Belford (2022) from their assessment of pollution indices in gold mining communities in Ghana's Central Region. They found out that the Peri of Cd was high pollution, Hg was medium pollution, and the rest were low risk.

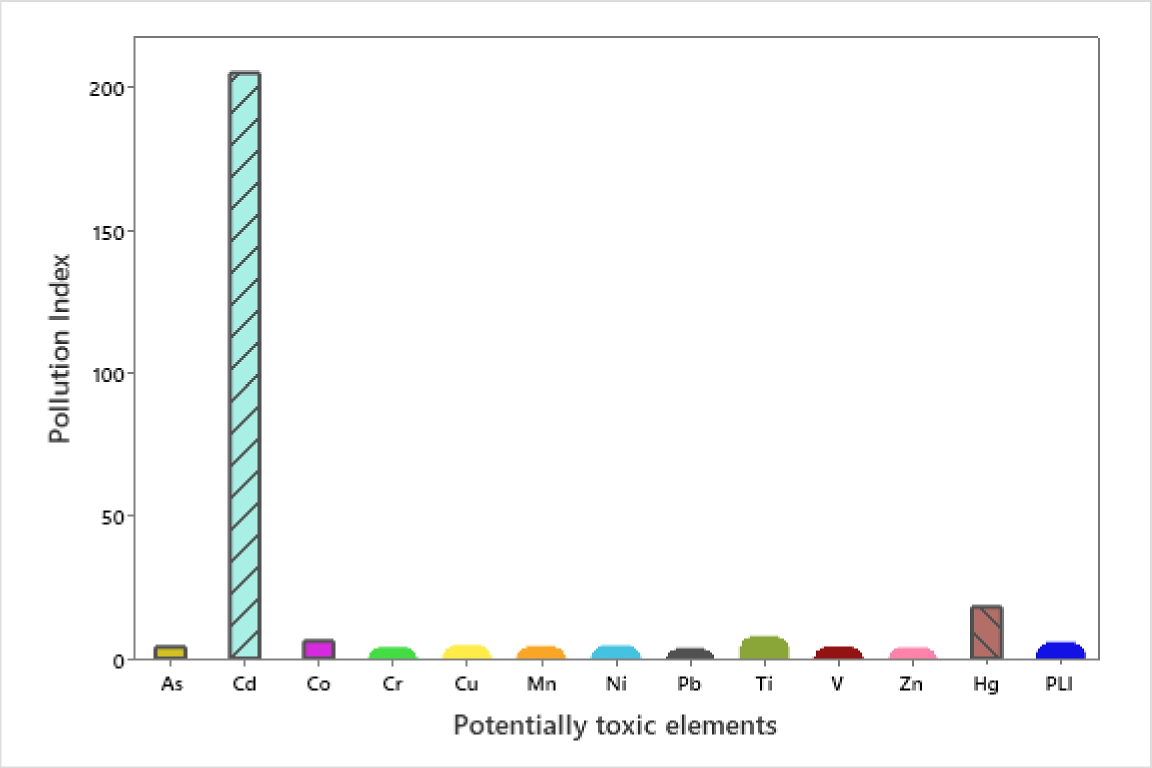


Fig 4.9: Description of Pollution Index

22.6 Non- carcinogenic Health Risk Analysis

The Average Daily Dose (ADDs) of PTEs for adults and children based on three different routes of exposure (inhalation, ingestion, and dermal contact) are shown in Table 4.10. For the ADDs of the PTEs, the exposure pathways are as follows: Ingestion, Dermal contact, and Inhalation. Similar studies on soils from Osogbo metropolis (Taiwo et al., 2019) and Abeokuta metropolis (Ogun state) in southwest Nigeria are consistent with this order. In a related study of soils in Bangladesh near an industrial area, the same order of exposure pathways is also reported (Kormoker et al; 2019).

For each of the three pathways, the ADD was less than the suggested RfDs for PTEs (Table 3.2) except, ADD for As and Ti through ingestion and Ti via dermal exposure pathway which exceeded the advised RfDs as displayed in Figure 4.7 and Table 4.10.

Table 4.10: Average Daily Dose (ADD) values in mg/kg/day for adults and children for PTEs through Various Exposure Routes

PTE	**AGE GROUP**	**ADD**			
		Inhalation	Ingestion	Dermal	Vapourisation
As	Child	5.647E-09	0.0006588	1.337E-05	
	Adult	2.534E-08	7.058E-05	6.477E-06	
Cd	Child	1.006E-08	0.0002615	5.307E-06	
	Adult	2.241E-09	2.801E-05	2.571E-06	
Co	Child	5.155E-08	0.0013403	2.721E-05	
	Adult	1.149E-08	0.0001436	1.318E-05	
Cr	Child	1.989E-08	0.0005172	1.05E-05	
	Adult	4.434E-09	5.542E-05	5.086E-06	
Cu	Child	1.341E-08	0.0003488	7.08E-06	
	Adult	2.99E-09	3.737E-05	3.429E-06	
Mn	Child	2.318E-07	0.0060279	0.0001224	
	Adult	5.167E-08	0.0006458	5.927E-05	
Ni	Child	0.0003826	1.472E-08	7.768E-06	
	Adult	4.1E-05	3.28E-09	3.762E-06	

Pb	Child	1.867E-09	4.854E-05	9.854E-07	
	Adult	4.161E-10	5.201E-06	4.773E-07	
Ti	Child	9.211E-07	0.0329648	9.23E-05	
	Adult	5.194E-07	0.0035319	1.409E-05	
V	Child	2.41E-08	9.241E-05	2.415E-06	
	Adult	1.359E-08	0.0008625	3.687E-07	
Zn	Child	1.411E-08	0.0003668	7.447E-06	
	Adult	3.144E-09	3.93E-05	3.607E-06	
Hg	Child	1.73E-10	4.51E-06	9.15E-08	6.96E-06
	Adult	3.86E-11	4.83E-07	4.43E-08	1.55E-06

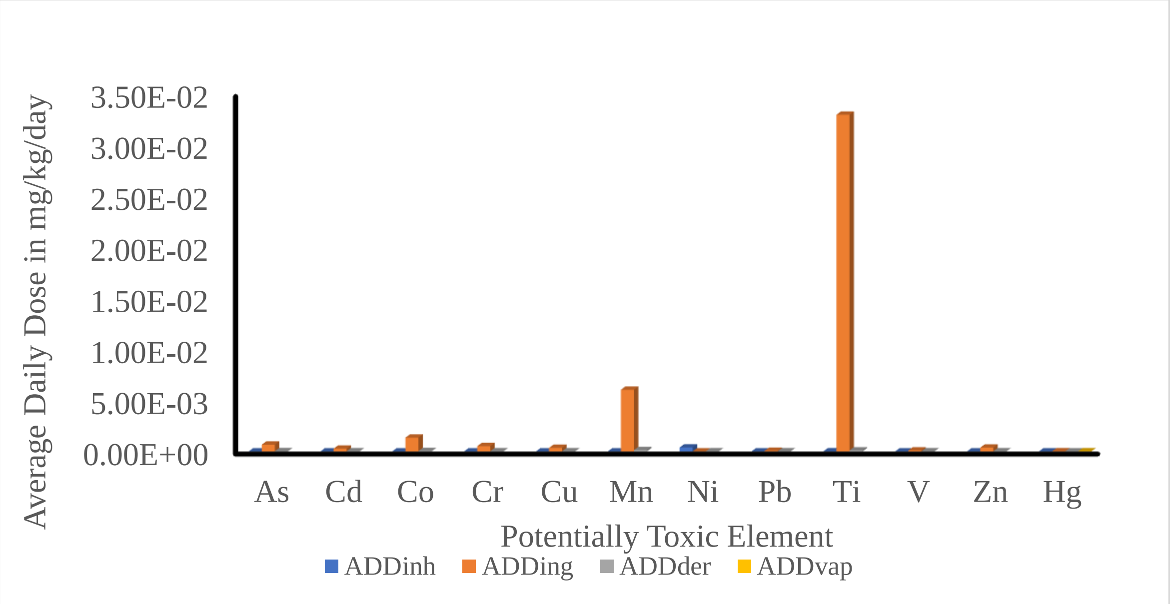


Fig. 4.10: Average daily dose for adult of PTEs through exposure pathways

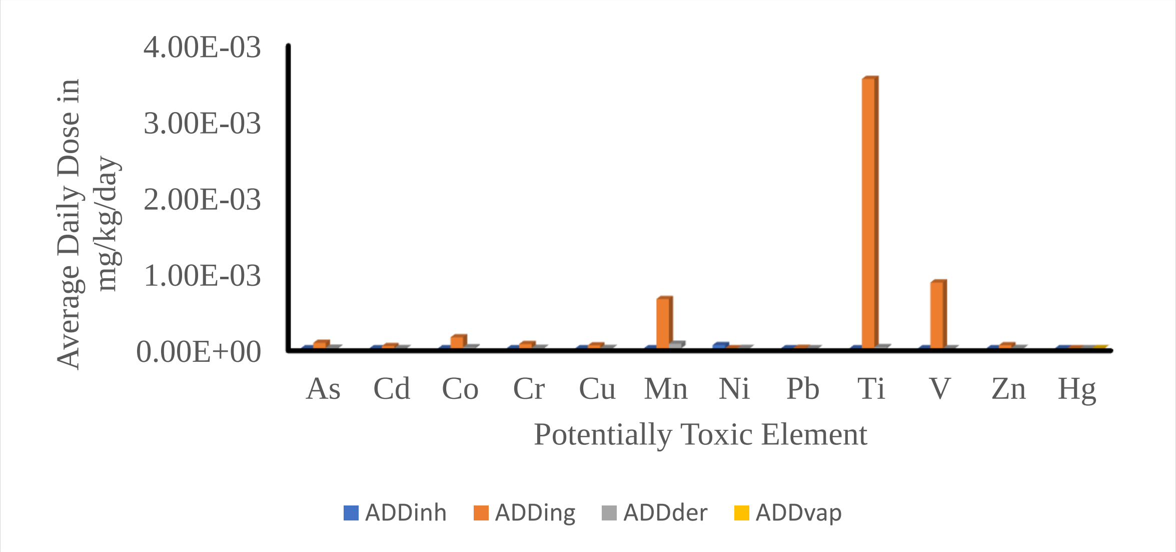


Fig. 4.11: Average daily dose for children of PTEs through exposure pathways

Table 4.11: Risk of non-carcinogenic exposure to PTEs in Wa East artisanal mining soils

PTE	**AGE**		**HQ**		
	GROUP	Inhalation	Ingestion	Dermal	Vapourisation
As	Child	0.0002946	2.195874	0.0445762	
	Adult	6.566E-05	0.2352722	0.0215909	
Cd	Child	0.0001983	0.5229027	0.0106149	
	Adult	4.42E-05	0.0560253	0.0051414	
Co	Child	0.0090439	0.1340304	0.0027208	
	Adult	0.0020155	0.0143604	0.0013179	
Cr	Child	0.000698	0.1724165	0.0035001	
	Adult	0.0001556	0.0184732	0.0016953	
Cu	Child	3.354E-07	0.0094264	0.0001914	
	Adult	7.474E-08	0.00101	9.269E-05	
Mn	Child	0.0001621	0.2511631	0.0050986	
	Adult	3.613E-05	0.0269103	0.0024696	
Ni	Child	7.144E-07	0.205721	0.0041761	
	Adult	1.592E-07	0.0220415	0.0020228	
Pb	Child	5.304E-07	0.0013484	0.0002737	
	Adult	1.182E-07	0.0001445	0.0001326	
Ti	Child	0.0107102	206.03005	8.3910421	
	Adult	0.0060396	22.074648	1.2811323	
V	Child	3.012E-05	0.2875021	0.219547	
	Adult	1.699E-05	0.0308038	0.0335201	
Zn	Child	4.703E-08	0.0012228	2.482E-05	
	Adult	1.048E-08	0.000131	1.202E-05	
Hg	Child	2.02E-06	0.001503	3.05E-05	
	Adult	4.49E-07	0.000161	1.48E-05	0.080969
HI	Child	0.027180467	209.8132	8.681796	0.018045
	Adult	8.37E-03	22.47998	1.349142	0.080969
					0.018045

The results for HQinh for both adults and children decreased in the following order, as indicated in Table 14: Ti > Co > As > Mn > Cd > V > Hg > Ni > Pb > Cu > Zn > Cr. While HQderm has the order of Ti > V > As > Cd > Mn > Ni > Co > Pb > Cu > Hg > Zn > Cr for both children and adults, HQing has the order of Ti > As > Cd > V > Mn > Ni > Co > Cu > Hg > Pb > Zn > Cr declined by both adults and children. The order of the determined hazard quotient (HQ) is inhalation first, followed by dermal contact, and then ingestion. This suggests that compared to dermal contact and inhalation, exposure through ingestion would present a substantial risk.

The HQing values of Ti and As for adults are 22.07 and 2.195, respectively, exceeding the limit of 1. For children, the values are 206.03 and 2.195, respectively (Table 4.11). Specifically, children's HQing values of As and Ti are higher than adults, suggesting that children are more vulnerable to the dangers of Ti and As in soils than adults are.

Furthermore, Ti's HQ value for adults, which represents uptake through oral ingestion, is 22.07, higher than unity, suggesting that adults who ingest Ti orally are vulnerable to non-carcinogenic risk.

Additionally, Ti has HQderm values of 1.28 and 8.39 for adults and children, respectively, suggesting that dermal contact with Ti does not present a carcinogenic risk to either adult or child. Conversely, the HQ values are less than 1 for adults and children who are at risk of exposure to Cd, Co, Hg, Mn, Cr, Pb, Cu, and Zn through skin contact, respiratory inhalation, and oral consumption. Also, the HQvap values for adults and children for mercury are less than 1 indicating they are all within permissible bounds and do not present a non-carcinogenic risk.

Again, Table 4.11's results showed that children were systematically more susceptible to PTEs in soil than adults were in all three routes of exposure examined as indicated in figure 4.8. This observation may be explained by kids being prone to absorb more toxic metals from the soil during recreation outside than adults do, which increases their vulnerability. (Ihedioha et al; 2017). Furthermore, because children have smaller bodies than adults, ingesting small particles in larger doses may have a greater effect on them (Jahandari, 2020).

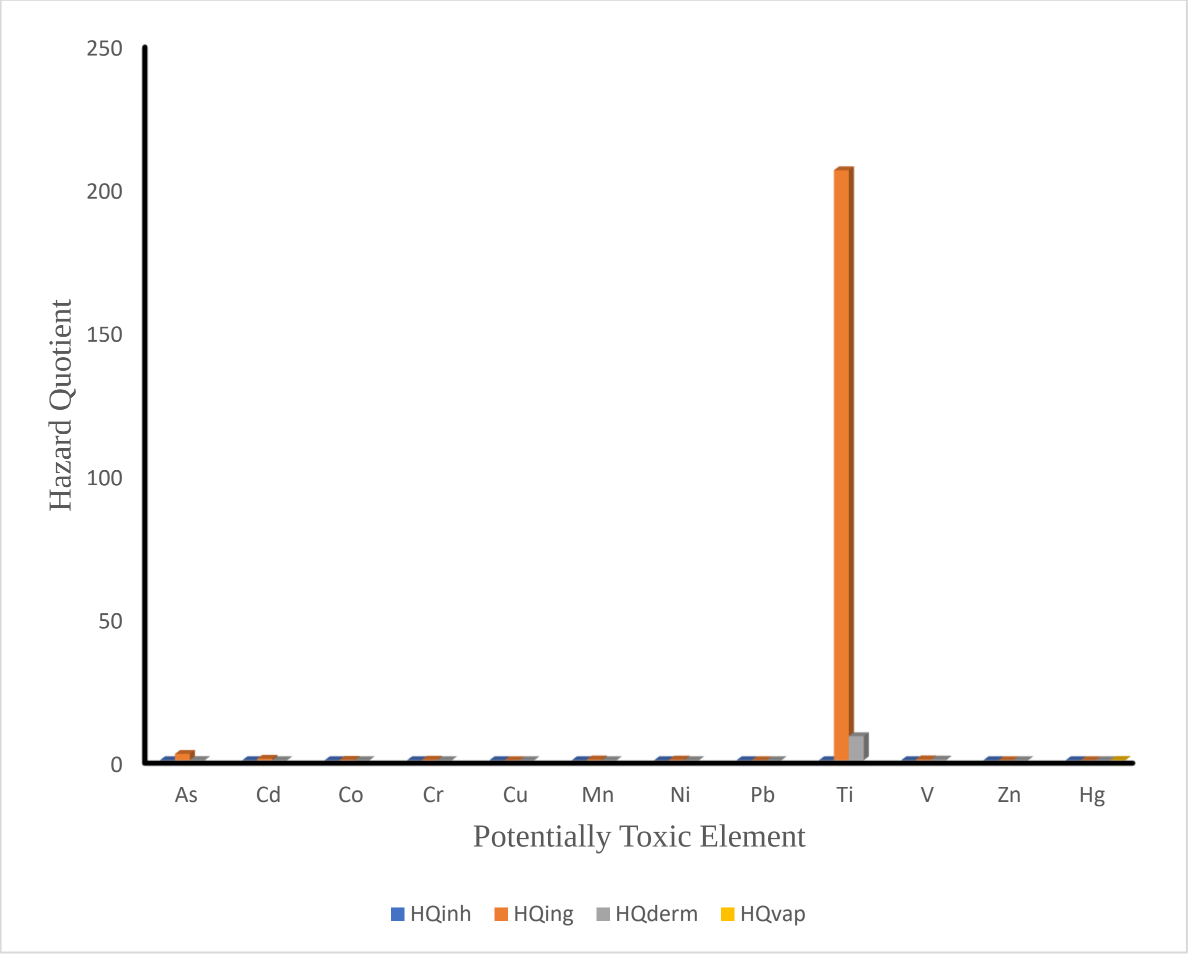


Fig. 4.12: Non-carcinogenic index for different exposure pathways

The total hazard index (HI) values showed that for inhalation, children (0.027) and adults (0.0083), for ingestion, children (209.81) and adults (22.47), and for dermal exposure, children (8.681) and adults (1.349). Both adults and children have inhalation hazard indices that are less than 1, meaning that there is little risk associated with inhalation exposure for either group. Nonetheless, children appear to be marginally more vulnerable than adults, as indicated by their slightly higher inhalation hazard index. With over 200% and 20% more than the permitted threshold for children and adults, respectively, the ingestion hazard indices for both adults and children are significantly above 1, indicating a high risk from ingestion exposure. In addition, As contributed 7.4% of the HI values of children upon oral intake, while Ti contributed 98.3% and 96.7% of the HI values of children for dermal and oral exposures, respectively. Once more, Ti was involved in 10.5% and 94.8% of adult’s HI values for oral and dermal exposures, respectively. The findings verified that the most prevalent PTEs that contribute most to the non-carcinogenic risk that children and adults in the study area face from oral and dermal exposures are Ti and As.

Children are more likely than adults to ingest hazardous substances, as indicated by their significantly higher ingestion hazard index in Figures 4.9 and 4.10. Both children's and adults' dermal hazard indices are significantly higher than the HI acceptable threshold of 1, indicating a high risk of dermal exposure. Children are more vulnerable to dermal exposure compared to adults much like with ingestion.

In contrast, both children and adults have a high risk from ingestion exposure, with children being at a particularly higher risk. Nevertheless, both children and adults have elevated risk from dermal exposure, with children again being especially vulnerable.

These HI values point to the necessity of interventions that, especially for the most vulnerable children, are primarily focused on lowering ingestion and dermal exposures. The HI found in this study is consistent with past findings from the arid northwest of China's Urad Houqi Area (Shui et al., 2018) and the Zuoxiguo antimony mining area, in Southwest China (Bai et al; 2023).

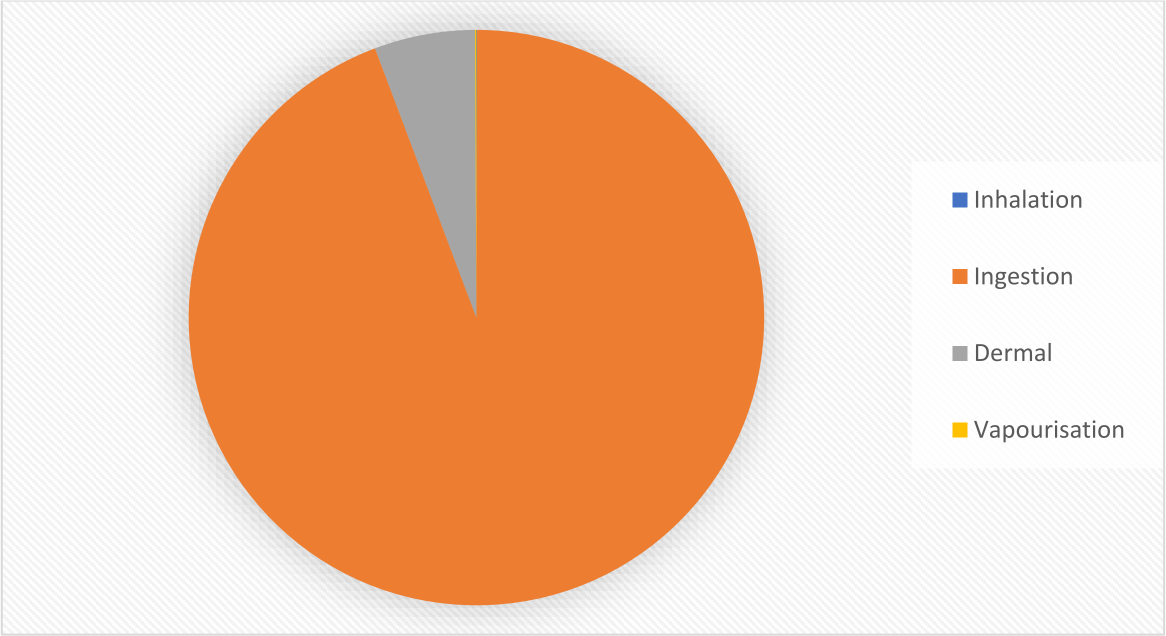


Fig. 4.13: Total Health Index for Adults

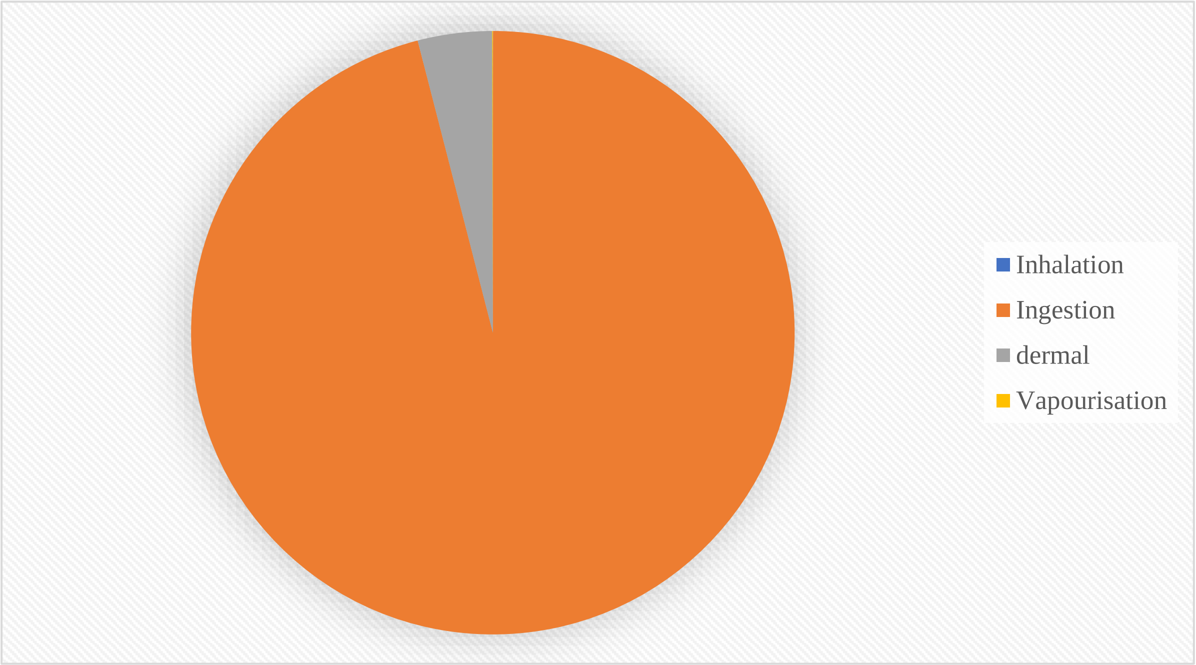


Fig. 4.14: Total Health Index for Children

22.7 Carcinogenic Health Risk Analysis

Figure 4.14 and Table 4.12 display the PTEs' individual carcinogenic health-risk indices (CR) and total carcinogenic health-risk indices (TCR).

Table 4.12: Risk of carcinogenic exposure to PTEs in Wa East artisanal mining soils

Group	CR	As	Cd	Cr	Pb	TCR
Adult	CRinh	1.09E-10	1.41E-8	1.78E-8	1.75E-11	3.19E-8
	CRing	1.06E-4	-	2.77E-2	-	2.78E-2
	CRderm	9.71E-6	-	1.02E-5	-	1.99E-5
Child	CRinh	2.43E-11	6.34E-8	7.99E-7	7.59E-11	8.63E-7
	CRing	9.88E-3	-	2.77E-2	-	3.76E-2
	CRderm	2.01E-5	-	2.10E-5	-	4.11E-5

The carcinogenic risk severity from PTEs in the soils of the Wa East artisanal mining sites for adults and children via three exposure pathways is ranked as follows: Ingestion >Dermal > Inhalation (Table 4.12).

Children are more at risk of developing cancer from PTEs than adults are, as shown by the higher CR values of various exposure modes for children compared to adults. For both adults and children, As and Cr have CR values exceeding 10^{-4}, indicating a carcinogenic risk from oral ingestion. Additionally, skin contact with As causes CR values to range from 10−6 to 10^{-4}, which is higher than the maximum allowable limit of 1×10^{-6} to 1×10^{-4} set by the USEPA and suggests a possible carcinogenic risk for both adults and children.

However, the CR values of Pb for adults and children after oral ingestion, as well as the values of As, Cd, and Pb following respiratory inhalation, are all less than 10^{-6}, which falls within the acceptable range for these values as illustrated in Figures 4.13 and 4.14, respectively.

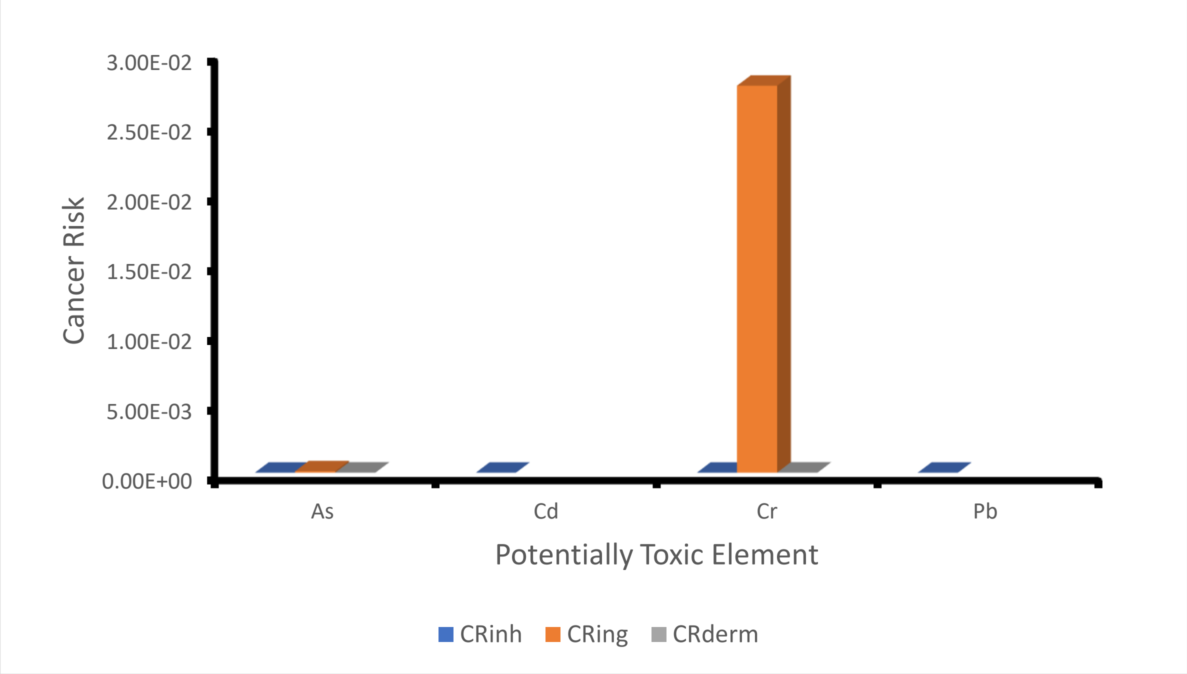


Fig. 4.15: Carcinogenic Index for Adults through different exposure routes

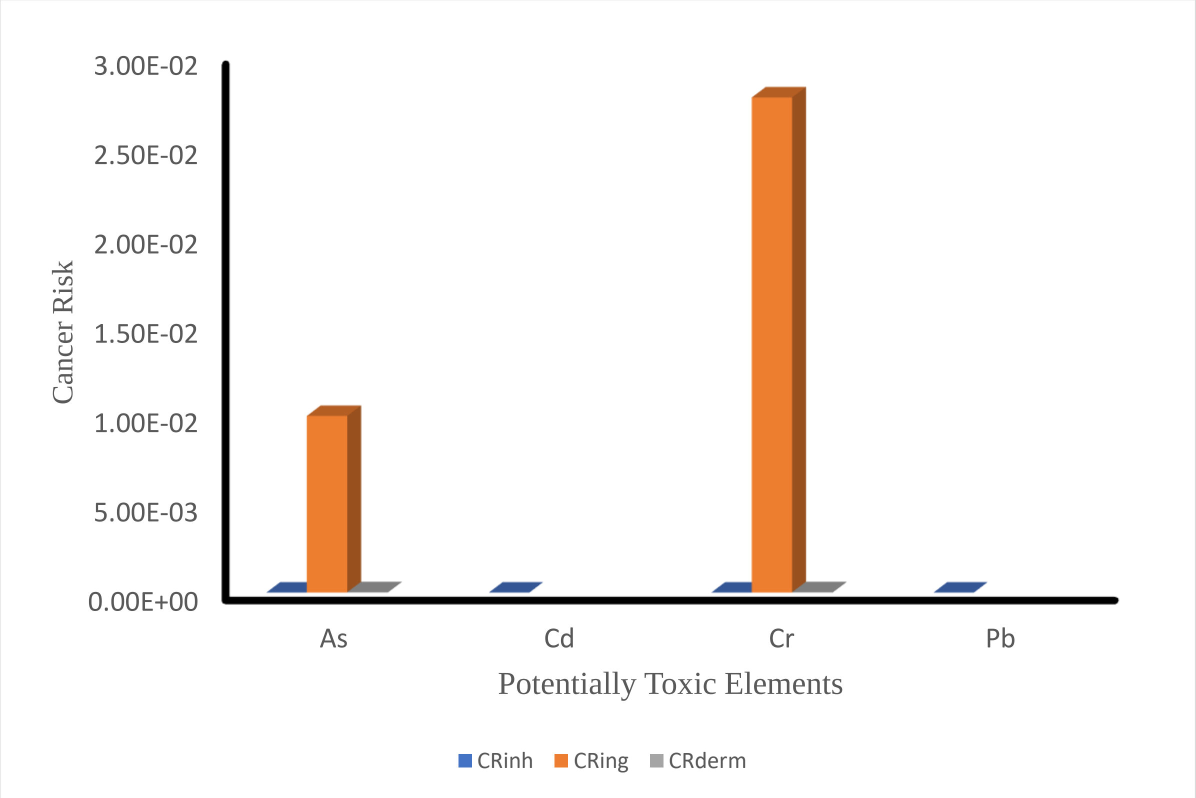


Fig. 4.16: Carcinogenic Index for Adults through different exposure routes

Additionally, the TCR following oral ingestion exceeds 10^{-4} in both adult and child cases, and the TCR following dermal exposure exceeds 10^{-6} in both cases. However, since the TCR after inhalation is less than 10^{-6} in both adults and children, there is no risk of cancer from inhalation. Also, it is evident that following oral ingestion by adults and children, Cr contributes 73.6% and 99.6% of the TCR values, respectively. Furthermore, As contributes 26.4% and 0.4% to the TCR values when ingested orally by adults and children. Again, Cr contributed 51.3% and 50.0% to the TCR following dermal exposure, while As contributed 48.7% and 50.0% for adults and children, respectively. This result shows that the primary pollutants posing the greatest cancer risk are Cr and As.

22.8 Summary of Results

Descriptive statistics on the average concentrations and standard deviations of PTEs in the study area are presented in this chapter. The average concentrations were contrasted with data from soil screening obtained in Australia, Canada, the Netherlands, Ghana, and South Africa.

Physicochemical parameters such as electrical conductivity, organic matter content, and pH were investigated. The sources and routes of potentially toxic elements are revealed by inter-element interaction using correlation analysis. PCA was used to determine the sources of potentially toxic elements, and four major principal components were identified. Pollution indices, including Nemerow's pollution index, were obtained from the PTEs, providing information on the pollution status at the study site.

Finally, a health risk analysis was carried out to identify contaminants, assess exposure risks, and provide valuable information to local communities about potential risks and precautions, thereby promoting public health and safety. Graphs of element concentrations, pollution indices, and health risks are also provided to back up the analysis.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

23.1 Introduction

The results and suggestions of the study are presented in this chapter. As a result, it highlights and summarizes the key research findings. There are also suggestions for tackling soil contamination in the examined areas and for further study.

23.2 Conclusions

There are a lot of operational and shut artisanal mining sites in Ghana. According to research, one of the main concerns with these mining areas' soils is PTE contamination. A dozen (12) PTEs were found to be present in the soil. The study also assessed the risks to human health, agricultural land, and neighboring ecosystems.

The soil is generally slightly alkaline with a mean pH of 7.04 and a range of 5.30-8.67. The study sites exhibited a slightly elevated level of soil alkalinity, indicating that the PTEs had become insoluble and remained stuck in the soil. A mean EC of 125.113 μς/cm and standard deviation of 103.250 μς/cm indicate variability in the soil due to contamination levels caused by anthropogenic activities.

The mean concentrations of the PTEs show a wide range of variability, as indicated by the standard deviations, with some elements exhibiting significantly higher levels of dispersion. The minimum and maximum concentrations highlight extremely high concentrations of some PTEs, such as Mn and Ti; titanium (Ti) has comparatively higher mean values than the other elements. Higher levels of titanium can occur naturally due to geological processes or through anthropogenic activities. The higher mean As, Cd, and Co concentrations in the study area may also indicate anthropogenic inputs. Furthermore, PTEs had decreased mean concentrations but higher maximums, such as As, Cd, and Co, indicated localized sources of contamination like mining.

Mining operations were identified by PCA as the primary source of pollution. Four primary elements were found to be responsible for 78.0% of the cumulative total variance of the source analysis for the various PTEs present in soil samples. V, Ti, and Cr significantly correlated with the first component, with a total variance of 20.1% which could be the result of human activity. There was a 17.3% total variance correlation between Pb, Ni, and Mn and the second component. This could have been caused by exhaust emissions from nearby cars and machinery, but a strong correlation with Cu, Co, and Zn was indicated by the third factor, which had a total variance of 17.3%. The fourth factor indicates a total variance of 13.8% with a strong correlation between Zn, As, and Cd with the fifth factor made of Hg accounting for 9.5% of the total variance which is likely as a result of the mining activities in the area. According to the PCA results, Pb, Cd, As, Zn, and Hg are primarily caused by anthropogenic activities such as mining, whereas V, Ni, Cr, Mn, Co, and Cu are primarily caused by the combined effects of soil-forming parent materials, mining operations, exhaust emissions from mine machinery, and agricultural activities.

The Igeo values of these PTEs also show no significant contamination, except Cd, which falls between high and extremely high pollution. Contamination factor (CF) values confirm the study area's significant and highly contaminated As and Co levels. The average Enrichment Factor (EF) indicates that anthropogenic factors were the primary cause of Cd, As, and Co contamination. The high EF values for Cd, As, and Co indicate that pollution in the study area exceeds the WHO critical limit.

With the exception of Cd, which the Igeo value confirms poses extremely high environmental risks to humans, the peri value indicates that the overall risk is low. Nemerow's pollution index shows the study area exhibits moderate pollution as indicated by the PNI value of Hg and Co. The findings also show that these artisanal mining sites' soils and communities around these sites have been considerably polluted with As and severely polluted with Cd, which raises serious ecological concerns, whereas a pollution load index (PLI) value of 2.2 classifies this region as moderately polluted.

For every PTE, except for ADDderm for Ti and ADDing for As and Ti, the ADD for the exposure pathways was less than the suggested RfDs.

The increasing order of the calculated hazard quotient (HQ) is inhalation first, followed by dermal contact, and then ingestion. This suggests that compared to dermal contact and inhalation, exposure through ingestion would present a substantial risk. In all three of the exposure routes studied, the HQ values demonstrated that children were effectively more exposed to PTEs in soil than adults were.

The total hazard index (HI) values showed that Both adults and children have inhalation hazard indices that are less than 1, meaning that there is little risk associated with inhalation exposure for either group. Nonetheless, children appear to be marginally more vulnerable than adults, as indicated by their slightly higher inhalation hazard index. With over 200% and 20% more than the permitted threshold for children and adults, respectively, the ingestion hazard indices for both adults and children are significantly above 1, indicating a high risk from ingestion exposure. The health risk results also showed that the ingestion pathway, followed by the dermal pathway, was the major contributor to non-carcinogenic risk in both adults and children. The least risky method was inhalation.

The PTEs are more likely to cause cancer in children than in adults, according to the carcinogenic risk analysis, which revealed that the CR values of various exposure modes were higher for children than for adults. The carcinogenic risk from oral ingestion and dermal exposure is indicated by As and Cr having CR values greater than 10^{-4}, which is higher than the maximum permissible limit for adults and children set by the US Environmental

Protection Agency. The CR values of Hg of adults and children following vaporization are lower than 10^{-6} indicating no carcinogenic risk.

Additionally, the TCR following oral ingestion and dermal exposure exceeds the range 10^{-6} to 10^{-4} in both adult and child cases. It is also evident that the contributions of Cr to the TCR values following oral ingestion by adults and children are 73.6% and 99.6%, respectively. Conversely, when taken orally by adults and children, As adds 48.7% and 24.4%, respectively, to the TCR values. Again, Cr contributed 51.3% and 50.0% to the TCR following dermal exposure, while As contributed 48.7% and 5.0% for adults and children, respectively. This result firmly shows that the ingestion route is the major contributor to excess lifetime cancer risk followed by the dermal pathway and the primary pollutants posing the greatest cancer risk are Cr and As.

23.3 Recommendations

It is advised that additional research focus on the following areas and the recommendations implemented:

1. Conduct regular health screenings for workers and residents to identify symptoms of PTE exposure.
2. Research is needed to evaluate the socioeconomic impact of artisanal mining on affected communities.
3. To lessen the risks that PTEs in the soil in the study area pose, environmental governance and oversight measures are of vital importance.
4. Environmentalists and civil society organizations need to educate and raise awareness among people of the dangers of coming into contact with PTEs.
5. Instituting more stringent rules and regulations to control artisanal mining activities, especially in these vulnerable communities.

6. Mining regulations must be implemented immediately to safeguard locals, particularly children, from the environmental contamination caused by these hazardous substances.
7. Proper monitoring and treatment of PTEs in soil, especially As, Cd, and Co, must be carried out to protect the health of residents, particularly children.
8. This research has the possibility of reducing soil pollution and providing a baseline for future research in similar areas.

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APPENDIX

	Coordinates for Sampling	
Sample ID	**Latitude**	**Longitutude**
Dan 1	10° 0'15.00"N	2°13'57.02"W
Dan 2	10° 0'10.02"N	2°13'50.12"W
Dan 3	10° 0'10.12"N	2°13'59.38"W
Dan 4	10° 0'15.64"N	2°13'48.82"W
Dan 5	10° 0'10.21"N	2°13'54.42"W
Dan 6	10° 0'16.52"N	2°13'53.36"W
Dan 7	10° 0'13.68"N	2°13'50.24"W
Jan-08	10° 0'10.62"N	2°16'3.17"W
Jan-09	10° 0'20.58"N	2°16'23.97"W
Jan-10	10° 0'22.65"N	2°16'5.51"W
Jan-11	10° 0'26.84"N	2°16'17.75"W
Jan-12	10° 0'22.04"N	2°16'11.71"W
Jan-13	10° 0'14.98"N	2°16'2.84"W
Jan-14	10° 0'19.71"N	2°16'15.52"W
Jon 15	10° 2'13.53"N	2°15'40.84"W
Jon 16	10° 2'10.93"N	2°15'51.20"W
Jon 17	10° 2'7.91"N	2°15'31.13"W
Jon 18	10° 2'20.22"N	2°15'41.28"W
Jon 19	10° 2'37.92"N	2°15'32.22"W
Jon 20	10° 2'29.46"N	2°15'35.81"W
Jon 21	10° 2'39.32"N	2°15'41.25"W
Jon 22	10° 2'32.55"N	2°15'43.30"W
Via 23	10° 0'26.00"N	2°17'24.07"W
Via 24	10° 0'41.26"N	2°17'10.64"W
Via 25	10° 0'37.26"N	2°17'25.53"W

Via 26	10° 0'43.79"N	2°17'21.49"W
Via 27	10° 0'35.96"N	2°17'13.16"W
Via 28	10° 0'49.85"N	2°17'13.83"W
Via 29	10° 0'29.84"N	2°17'15.82"W
Via 30	10° 0'51.98"N	2°17'21.48"W
Duu 31	10°22'26.36"N	1°46'49.54"W
Duu 32	10°22'20.72"N	1°46'49.43"W
Duu 33	10°22'26.03"N	1°46'55.20"W
Duu 34	10°22'23.47"N	1°46'53.03"W
Duu 35	10°22'21.15"N	1°46'52.95"W
Duu 36	10°22'33.11"N	1°46'56.42"W
Duu 37	10°22'28.05"N	1°46'50.26"W
Duu 38	10°22'23.81"N	1°46'48.14"W
Gor 39	9°58'6.10"N	2°16'7.14"W
Gor 40	9°58'2.67"N	2°15'57.38"W
Gor 41	9°58'19.18"N	2°15'58.75"W
Gor 42	9°58'18.60"N	2°16'5.23"W
Gor 43	9°58'27.54"N	2°16'6.71"W
Gor 44	9°58'28.94"N	2°16'21.15"W
Gor 45	9°58'16.87"N	2°16'29.59"W
Gor 46	9°58'0.65"N	2°16'16.76"W
Gor 47	9°58'6.86"N	2°16'27.66"W
Bul 48	9°56'16.88"N	2°11'52.77"W
Bul 49	9°56'13.42"N	2°11'44.81"W
Bul 50	9°56'13.97"N	2°11'38.97"W
Bul 51	9°56'7.66"N	2°11'40.82"W
Bul 52	9°55'58.02"N	

		2°11'44.09"W
Bul 53	9°56'17.26"N	2°11'58.30"W
Bul 54	9°56'12.79"N	2°12'3.93"W
Bul 55	9°55'59.30"N	2°11'51.37"W
Bul 56	9°56'0.50"N	2°11'57.76"W
Man 57	9°58'40.90"N	2°19'26.94"W
Man 58	9°58'32.87"N	2°18'46.48"W
Man 59	9°59'0.55"N	2°19'2.13"W
Man 60	9°58'58.00"N	2°19'13.53"W
Man 61	9°58'31.78"N	2°19'3.03"W
Man 62	9°58'35.04"N	2°19'21.96"W
Man 63	9°58'37.19"N	2°18'55.58"W
Man 64	9°58'50.38"N	2°18'54.44"W
Man 65	9°58'44.57"N	2°18'44.90"W