AKENTEN APPIAH MENKA UNIVERSITY OF SKILLS TRAINING AND ENTREPRENEURIAL DEVELOPMENT

FACULTY OF SCIENCE EDUCATION

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HUMAN AND ECOLOGICAL RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS IN SOILS FROM ARTISANAL AND SMALL-SCALE GOLD MINING AREAS

LAWRENCE BRENYAH-KANKAM

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2025

AKENTEN APPIAH MENKA UNIVERSITY OF SKILLS TRAINING AND ENTREPRENEURIAL DEVELOPMENT

FACULTY OF SCIENCE EDUCATION

DEPARTMENT OF CHEMISTRY EDUCATION

HUMAN AND ECOLOGICAL RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS IN SOILS FROM ARTISANAL AND SMALL-SCALE GOLD MINING AREAS

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A Thesis Submitted to the School of Graduate Studies, Department of Chemistry Education, of Faculty of Science Education, Akenten Appiah-Menka University of Skill Training and Entrepreneurial Development in partial fulfilment of the requirements for the award of a Master of Philosophy degree in Chemistry Education

APRIL, 2025

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DECLARATION

Student Declaration

I, BRENNYAH-KANKAM LAWRENCE, declare that this thesis, except quotations and references in published works which have all been identified and duly acknowledged, is entirely my original work, and it has not been submitted, either in part or in whole, for another degree elsewhere.

SIGNATURE ……………………………………….

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Supervisor's Declaration

We, at this moment, declare that the preparation and presentation of this work were supervised by the guidelines for supervision of the thesis as laid down by the Akenten Appiah Menka University of Skills Training and Entrepreneurial Development.

Supervisor: DR. OPOKU GYAMFI

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Supervisor: PROF. KOFI SARPONG

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DATE ………………………………………………………………………..

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DEDICATION

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ABSTRACT

Artisanal and small-scale gold mining (ASGM) plays a significant role in the economies of many developing countries, including Ghana, but it is also associated with serious environmental and health risks due to the release of potentially toxic elements (PTEs) into the ecosystem. This study assessed the concentrations, sources, ecological risks, and human health implications of PTEs in soils from Gbani, a prominent ASGM area in Ghana. Using a Niton XL3t GOLDD+ field portable X-ray fluorescence spectrometer, the levels of key metals such as As, Pb, Cd, Cu, Zn, Cr, Ni, Co, Ti, V, and Mn were quantified. Multivariate statistical methods, including Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF), were employed to identify pollution sources. Pollution indices such as the Geo-accumulation Index (Igeo), Enrichment Factor (EF), and Potential Ecological Risk Index (PERI) indicated moderate to high contamination levels, primarily of anthropogenic origin. Non-carcinogenic and carcinogenic risk assessments were conducted for both children and adults via ingestion, inhalation, and dermal pathways. While most metals remained below regulatory thresholds, elevated concentrations of Cd, Cu, Zn, and V exceeded Dutch intervention values, suggesting a potential ecological threat. However, the Hazard Index (HI) and Hazard Quotient (HQ) values for all exposure pathways were below 1, indicating no immediate health risk. The study highlights the need for regular environmental monitoring and the implementation of mitigation strategies to safeguard human health and ecological integrity in mining communities.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Most emerging economies, including Ghana, have densely populated urban areas that are home to a variety of human activities. The lines separating commercial, residential, and industrial activity are typically blurred in these areas. Lax enforcement of the laws governing human activity and inadequate industrial urban planning and zoning regulations are the main causes of this phenomenon. (Konadu et al., 2023).

The presence of a chemical or material in elevated amounts can be detrimental to humans, animals, and the ecosystem. (FAO, 2015). Consequently, pollution has emerged as a significant ecological issue owing to the non-biodegradable characteristics of Potentially Toxic Elements (PTEs) in the environment and their detrimental effects on soils. (Ajayi et al., 2016). According to Darko et al., (2019), the detrimental health impacts of most elements render elemental pollution in soils a significant concern for researchers and regulatory authorities, and Hanaka et al., (2016), added that with the importance of food safety and human health, there is a growing awareness of PTE contamination of plants, water, and soil in Ghana and around the world.

Sarubbo et al. (2015) emphasized that the world population increased from 500 million to 7.9 billion, and hence, an increase in waste (liquid and solid) generation due to urbanization and industrialization is common (Ahmad et al., 2021)**.** In contrast to organic pollutants, PTE pollution is hidden, persistent, and irreversible. It damages soil, water, the atmosphere, and food crops, and because it builds up in the food chain, it also poses a serious risk to the health and welfare of living things, including humans. (Li et al., 2019).

Eating contaminated meat, vegetables, grains, fruits, fish, and shellfish, breathing in air pollutants, drinking contaminated water, and encountering contaminated soils or industrial waste are just a few of the ways that humans can be exposed to PTEs and trace elements. (Duruibe et al., 2007). Therefore, understanding the distribution pattern and the potential ecological risks of these PTEs is significant to sediment quality evaluation and protection of the terrestrial environment. (Song et al., 2019). These PTEs are typically found in the environment because of either anthropogenic activity like mining, agriculture practices, industrial processes, etc., or natural processes like atmospheric deposition and rock weathering. The distribution of elements is affected by the physicochemical features of the soil, including pH and organic matter concentration, as well as the characteristics of organic matter. (Darko et al., 2019).

Mining significantly affects the environment by releasing mining tailings and contaminated wastewater into the ecosystem. It also has detrimental effects on soil quality. (Kazapoe et al., 2021). Wiafe, et al. (2022). Asserted that surface mining is the predominant technique employed by Artisanal Small-Scale Gold Miners (ASGMs) due to its cost-effectiveness, low-level technical requirements, and low capital investment. In several global places, Artisanal Small-Scale Gold Mining (ASGM) holds equal significance to Large-Scale Mining (LSM), specifically for employment figures. Artisanal and Small-Scale Gold Mining (ASGM) is essential for poverty reduction and rural development among impoverished populations residing in rural mining areas. (Wiafe, et al., 2022).

Restoring soil quality in environments polluted by potentially toxic elements (PTEs) presents significant challenges. Elevated levels of PTEs in soil might adversely affect plant development and diminish agricultural output. Toxic metals, including thallium (Tl), chromium (Cr), mercury (Hg), silver (Ag), lead (Pb), uranium (U), and cadmium (Cd), pose hazards to plants and other creatures at increased concentrations. However, plants require trace amounts of certain PTEs to maintain healthy growth and development. Toxic metals, including thallium (Tl), chromium (Cr), mercury (Hg), silver (Ag), lead (Pb), uranium (U), and cadmium (Cd), pose hazards to plants and other creatures at increased concentrations. By using concentration gradients and selective uptake mechanisms, plants can absorb these vital PTEs from the soil and guarantee that they get the iron, zinc, copper, and manganese they require (Peralta-Videa et al., 2009).

Nevertheless, the release of highly toxic PTEs (i.e., As, Cd, Co, Cr, Cu, Mn, Pb, Ti, V, and Zn) contaminates soil and endangers the health of those nearby through a variety of means. (Zhao et al., 2021), leading to numerous health complications within the local populace due to the increased PTE concentration (Velásquez et al., 2022). Natural sources include sedimentary rocks, volcanic activity, soil development, and the weathering of rocks, while human-related sources consist of mining, industrial activities, agriculture, and household wastewater.

These sources greatly increase the ecosystem's pollution and PTE concentration. Reducing PTE sources is unquestionably a good way to increase the security and safety of food and soil. Numerous remediation approaches are employed to eliminate PTEs and metalloids from soils, including phytoremediation and the application of chelating agents.

1.2 Problem Statement

The artisanal and small-scale gold mining (ASGM) sector, a major contributor to global gold output, is linked to the mobilization of potentially toxic elements (PTEs) from the earth's crust to the surface, raising concerns regarding human health and environmental integrity (Hilson, 2012). This mining produces a lot of waste that contains hazardous metals, with a negative impact on soil quality, soil fertility, and food security (Asare et al., 2021). Concerns about food security are widespread, and studies have revealed that the pollution caused by these metals is resulting in a growing number of health problems. (Bakare & Adeyinka, 2022). The extraction processes, often employing rudimentary techniques, introduce elements such as lead, arsenic, etc. into the environment, creating a potential hazard for both local communities and ecosystems (Nartey et al., 2015; Veiga et al., 2006).

There is a critical gap in our understanding of the extent and consequences of PTEs contamination in soils within and around these mining sites, impeding the development of effective risk management strategies (Bose-O'Reilly et al., 2010; Telmer & Veiga, 2009). The lack of systematic investigations into PTE concentrations, exposure pathways, and associated risks inhibits the formulation of evidence-based policies and regulations to guide sustainable mining practices (Hilson, 2012; Nartey et al., 2015).

Furthermore, the potential long-term consequences of PTEs accumulation, such as soil contamination, biodiversity loss, and impacts on agricultural productivity, remain poorly understood and require immediate attention (Telmer & Veiga, 2009; Yan & Wang, 2017).

Elevated PTE levels in soil can lead to a series of interconnected problems, including cancer, neurological diseases, and developmental problems. These are just a few of the major health hazards that can arise from direct or indirect exposure to PTEs in polluted soil. These risks are particularly felt by vulnerable populations who live close to contaminated areas.

Unknown amounts of dangerous elements may present significant health concerns to users of unlicensed herbal medications. (Sarpong et al, 2013). Addressing this problem requires a multidisciplinary approach that integrates expertise from environmental science, public health, geology, and social sciences. Researchers need to collaboratively develop and implement standardized protocols for assessing PTE concentrations in soils, evaluating exposure pathways, and quantifying the associated risks to both human and ecological receptors (O'Reilly et al., 2010; Wang, 2017). Additionally, understanding community perceptions, practices, and socioeconomic factors influencing the prevalence of Artisanal Small-scale Gold Mining (ASGM) is crucial for the development of context-specific mitigation and management strategies (Hilson, 2012; Telmer & Veiga, 2009). Resolving these difficulties necessitates an in-depth comprehension of the origins, dispersion, and dynamics of PTEs in soil, along with their potential health hazards to human and ecological systems. Developing efficient solutions for monitoring, mitigating, and remediating heavy metal pollution in soil is essential to protecting the environment and public health. Therefore, comprehensive research and effective solutions are essential to evaluate the magnitude of the issue, create risk assessment models, and enforce regulations and practices that can mitigate the detrimental effects of heavy metal pollution in soil. Consequently, it is important to research to measure the degree of elemental pollution in the soil and to increase knowledge regarding the effects of these pollutants on soil quality, food safety, and human health.

1.3 General/Main Objective

This study's main goal is to evaluate the human and ecological risks related to potentially toxic elements found in soils from artisanal and small-scale gold mining regions. This entails analyzing the levels of harmful substances, calculating the health risks to nearby communities via exposure routes, and determining the ecological effects on biodiversity and soil quality in impacted areas.

1.3.1 Specific Objectives

1. Determine the presence and concentration of various PTEs in soil samples from Gbani.
2. Determine probable sources of heavy metal pollution in the soil by Principal Component Analysis and positive matrix factorization.
3. Assess the measured potential toxic elements concentrations in soil against applicable regulatory criteria and recommendations to ascertain if they surpass allowed limits.
4. Establish contaminant status using contamination indices.
5. Evaluate ecological risk.
6. Assess the possible human health risks linked to the detected concentrations of PTEs in the soil, particularly concerning human exposure via several channels (e.g., ingestion, dermal contact, inhalation).

1.4 Research hypothesis

1. The observed PTE concentrations in soil samples from Gbani meet or are below the relevant regulatory standards and guidelines.

2. The level of contamination/pollution in Gbani is within acceptable limits.
3. There is no significant ecological risk associated with the observed heavy metal concentrations in the soil.
4. With different exposure pathways considered, the observed levels of PTEs in the soil do not pose a significant health risk.

1.5 Significance of the Study

In contrast to developed nations, where environmental health policies are either absent or poorly implemented, the use of chemicals in mining, farming, and fishing has not been subject to oversight because the organization in charge of conducting the cross-sectional analysis of soil contamination remains based in offices. The effects that these substances have on the environment are not made public by the Environmental Protection Agency (EPA). The importance of human health, as far as toxic elements are concerned, cannot be overemphasized. The importance of human health concerning hazardous materials is paramount. This study seeks to evaluate the levels of contamination by potentially harmful substances in the soil of artisanal small-scale mining areas. The research aims to identify the health concerns linked to elemental exposure by ingestion, inhalation, and dermal pathways in the soils of the study area. The study will furnish data and demonstrate an effective methodology for risk communication and management.

1.6 Justification of the study

According to Tshibangu et al. (2017), handcrafted gold mining at a small scale (artisanal small-scale gold mining, or ASGM) has been linked to the discharge of potentially hazardous substances into the surroundings, presenting a substantial threat to human well-being. PTEs, such as lead, arsenic, and cadmium, that enter the food chain through soil-plant-human interactions raise alarming health concerns (Li et al., 2018). Therefore, conducting a thorough risk assessment is crucial for understanding the extent of human exposure and devising strategies to safeguard the health of communities residing in and around ASGM areas. ASGM activities have been linked to environmental degradation, including soil and water pollution, with potential repercussions on local ecosystems (Hilson, 2012). The ecological risks associated with PTEs can extend to aquatic environments through the runoff of contaminated water, threatening biodiversity and ecosystem health (Hilson, 2007). Investigating the ecological implications is essential for preserving biodiversity and maintaining the overall ecological balance. The outcomes of this research will provide valuable data to policymakers and regulatory bodies for formulating guidelines and regulations to minimize the environmental and health impacts of ASGM. Evidence-based policy formulation is essential to reconcile economic advancement via mining operations with the safeguarding of environmental integrity and public health.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Artisanal and small-scale gold mining (ASGM) activities substantially impact the environment and endanger human health by introducing potentially toxic elements (PTEs) into the ecosystem. These activities, typically characterized using rudimentary techniques and equipment, are prevalent in many regions worldwide, particularly in developing countries where regulations and oversight may be limited. (Kazapoe et al., 2022). As a result, soils in ASGM areas often demonstrate elevated levels of potentially toxic elements (PTEs), including lead (Pb) and arsenic (As), thereby posing significant risks to human health and ecological systems.

The assessment and management of PTE contamination in ASGM areas are essential for safeguarding human health and environmental integrity. Previous studies have highlighted the need for comprehensive risk assessments to evaluate the extent of contamination, understand exposure pathways, and inform remediation strategies. (Baah et al., 2023). However, conducting risk assessments in ASGM contexts presents numerous challenges, including limited resources, complex geochemical interactions, and socio-economic factors.

This literature review seeks to deliver a thorough overview of the existing information about human and ecological risk assessment of potentially toxic elements in soils from artisanal and small-scale gold mining regions. This study will examine the origins and characteristics of PTEs in soil, their effects on human health and ecosystems, evaluation techniques, and management approaches. This study aims to synthesize existing research findings and identify knowledge gaps to guide future research and enhance effective risk management methods in ASGM-affected areas.

2.2 Agriculture

Agriculture engages 50% of Ghana's economically active populace and constitutes around 37.3% of the country's GDP. Most of it occurs on family-operated, smallholder farms, which constitute around 80% of Ghana's overall agricultural production. Approximately 80% of Ghana's agricultural production is generated by smallholder, family-operated farms, where it is predominantly utilised. (Obasi et al., 2020). Approximately 74 million households own or run farms, and 90% of farm holdings are smaller than two hectares. (Li et al., 2020). Women make up the bulk of the annual crop producers. Additionally, the industry generates an average of 8% of total revenue and 12% of tax revenue overall. (Chang et al., 2014). Therefore, without a major improvement in the agricultural sector, Ghana cannot achieve economic growth and poverty reduction. (Chang et al., 2014).

2.2.1 Land cover

The significant expansion of agricultural land throughout all areas of Ghana is the most prominent alteration in the nation's land cover (Dong et al., 2023). The North-East, East-Central, and South-Western regions have had the most growth (Dash et al., 2021). In Ghana's history, this rapid agricultural expansion has displaced a variety of land cover types, such as forests, woodlands, and savannahs. The percentage of Ghana's land that was used for agriculture increased from 13 – 28% between 1975 and 2000, and by 2013, it had reached 32% (Yuanan et al., 2020). Diverse vegetation and natural habitats are frequently transformed into crop-dominated landscapes as a result of this process.

Ghana's savannas have seen a significant decline, decreasing from 51% to 40% of the nation's total land area between 1975 and 2013 (Rilwan et al., 2020). The once continuous savanna landscapes in the Central Sudan Savanna, Main Transitional Zone, and Central Transitional Zone are now significantly fragmented, with extensive natural ecosystems partitioned into smaller agricultural regions. This fragmentation has greatly reduced habitat suitability for various wildlife species (Chandra et al., 2011).

2.2.2 Farming systems

The vast majority of farms in Ghana are smallholder operations, with most farms being less than two hectares. Larger farms and plantations are significant, especially for crops like rubber, oil palm, and coconut, rice, maize, and pineapples, being of smaller importance (Patil et al., 2023). Traditional farming methods, primarily involving the use of hoes and cutlasses, remain the predominant practice (Appiah-Opong et al., 2021). While bullock farming is prevalent in certain regions, particularly in northern Ghana, mechanized agriculture remains uncommon (Izomor et al., 2019). Agricultural output in the country is significantly influenced by the volume and distribution of precipitation, alongside soil properties such as texture, nutrient composition, and pH levels (Liu et al., 2020). The majority of food crop farms use intercropping systems, while commercial or large-scale farming is more likely to use monoculture. Light-textured surface horizons are typical of Ghanaian soils, and sandy loams and loams are prevalent. The sub-surfaces are a little heavier and include clays and coarse sandy loams (Kumar et al., 2019). Valley bottoms and sections of the Accra plains sometimes include soils with a denser texture. Furthermore, the presence of core materials like gravel, stones, or concretionary materials in many soils affects their physical characteristics (Wang et al., 2020)

2.3 PTEs pollution in Ghana

The poisoning of soils by Potentially Toxic Elements (PTE) poses a considerable environmental issue due to their detrimental impacts on ecosystems and human health. PTEs comprise elements including lead (Pb), arsenic (As), cadmium (Cd), mercury (Hg), among others, which can accumulate in soil by natural processes or human activities (Stirbescu et al., 2019). PTE pollution in soils can be caused by mining operations, industrial emissions, agricultural practices, and inappropriate waste disposal (Liu et al., 2013). PTEs' contamination has been one of the most important threats to the ecosystem, the environment, and human health. (Mohammadi et al., 2020). PTE pollution in soils can be caused by mining operations, industrial emissions, agricultural practices, and inappropriate waste disposal (Ghosh & Singh, 2005). Climate change exposes elements like calcium, iron, aluminium, and silicon to the environment, and soil farming and orogeny processes cause concentrations to vary more across geographic regions. (Liu et al., 2013). Consequently, there may be a fundamental impact on the spatial distribution of components within the soil of the parent material. The spatial variation of PTEs in soils has increased over the past decades of industrialization and urbanization. (Ghosh & Singh, 2005).

PTEs have been extensively utilized in scientific literature on ecotoxicology. Metals and semimetals (metalloids) associated with pollution and potential toxicity or ecotoxicity are collectively termed PTEs (Haghnazar et al., 2023). Soils, water, sediments, and air are the media that transport PTEs into the environment and are of great concern due to the potential long-term effects they have on human health, particularly in developing countries (Dash et al., 2021).

2.3.1 Source of PTES

Potentially Toxic Elements (PTEs) can enter soils from various natural and anthropogenic sources, contributing to soil contamination and posing risks to environmental and human health.

PTEs have their origin either from geogenic or anthropogenic releases (Rilwan et al., 2020; Yuanan et al., 2020). In the environmental system, human emissions constitute a persistent source of pollution, while surface runoff is a seasonal occurrence determined by climatic conditions (Chandra et al., 2011). Significant fluctuations in the total and bioavailable amounts of most elements in soils, including those that are uncontaminated, can arise from the geochemical composition of the parent rock components and differences in the intensity of soil cultivation practices. While this is contingent upon the parameters influencing the bioavailability of elements, pollution from various sources may often lead to significantly elevated concentrations of Potentially Toxic Elements or metalloids, which may be detrimental to vulnerable plants and soil organisms (Izomor et al., 2019).

In Ghana, extensive research on potentially toxic elements (PTEs) has been conducted due to the country's significant mining industry, which encompasses both surface and underground operations. Among these prevalent mining activities, gold mining stands out as one of the most widespread (Izomor et al., 2019). Daily activities like these are accompanied by PTEs like sulfur (S) and arsenic (As), which contaminate soils, ground and surface bodies, and even air pollution, which results in acid rain, environmental degradation, and negative health effects. Scientists divided PTEs' sources into two primary groups: man-made and natural. Anthropogenic sources include activities such as mining, industrial processes, agriculture, and the discharge of residential wastewater, while natural sources originate from sedimentary rocks, volcanic eruptions, soil formation, and the weathering of rocks.

Conversely, pollution indicators serve as an effective instrument for delineating geogenic and anthropogenic contamination in soil (Y. Liu et al., 2020; Schumacher, 2002). PTEs come from a variety of sources, including agrochemicals, raindrops containing heavy metals, and the sedimentation of aerosol particles. Despite reporting a wide variety of metals, the study primarily concentrated on As, Cd, Co, Cr, Cu, Mn, Pb, Ti, V, and Zn, the same PTEs that were examined in this investigation.

2.3.2 Natural Sources of PTEs

Igneous and sedimentary rocks are regarded as the main natural origins of potentially toxic elements (PTEs) (Kumar et al., 2019). It has been discovered that the proportion of various elements varies from one type of rock to another, as do the elements that are present in a particular type of rock (Palin et al., 2016). The PTE concentration may be determined based on the kind of rocks and the surrounding ecological conditions. Natural weathering processes, such as chemical and physical weathering, can release PTEs from rocks and minerals into the soil environment (Wang et al., 2020). This release transpires when minerals decompose over time, liberating elemental constituents, including potentially toxic elements (PTEs). In conjunction with river sediments, soil formation is regarded as a primary factor in PTE accumulation (Darko et al., 2017). Certain geological formations naturally contain elevated concentrations of PTEs due to their mineralogical composition (Yang et al., 2021). Because of geological processes like sedimentation, hydrothermal alteration, and volcanic activity, PTEs can be concentrated in areas and end up in soils.

2.3.3 Anthropogenic Sources of PTEs

Anthropogenic sources of PTEs include mining, wastewater, industries, and agriculture. These sources considerably increase the concentration of PTEs and cause pollution in the environment. The combustion of fossil fuels emits mercury, the smelting process releases copper, zinc, and lead, and the application of pesticides results in lead contamination (Fu et al., 2021). These industrial activities, such as mining, smelting, manufacturing, and combustion of fossil fuels, release PTEs into the atmosphere (Bhuiyan et al., 2021). Mining operations, particularly those involving the extraction and processing of metal ores, are major sources of PTE contamination in soils (Qin et al., 2021). The disposal of mining waste, including tailings and mine effluents, can lead to the discharge of potentially toxic elements (PTEs) into the surrounding environment, particularly soils. Urbanization and construction activities contribute to PTE pollution in soils through activities such as demolition, road construction, and improper waste disposal (Proshad et al., 2021). These activities, as shown in Figure 2.1, can disturb soil layers and release PTEs previously sequestered in the soil matrix. Daily human endeavours like farming and manufacturing also disrupt the biosphere's equilibrium (Roseline et al., 2016).

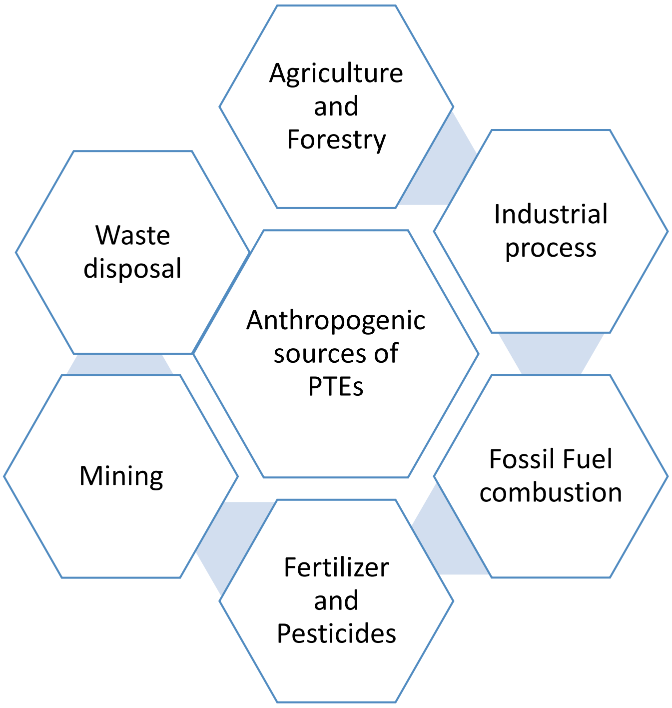

Figure 2.1 illustrates the principal anthropogenic sources of PTEs

2.3.3 Agriculture as a source of PTEs

The application of PTE-laden fertilizers, herbicides, and sewage sludge in agriculture can significantly elevate PTE levels in soils (Qaswar et al., 2020). Repeated use of these inputs over time can result in the buildup of potentially toxic elements (PTEs) in soil, particularly in intensively managed agricultural regions (Patil et al., 2023).

Agroecosystems are frequently affected by many contaminants, including biotic and abiotic waste resulting from agricultural operations. These pollutants frequently result in the pollution and deterioration of adjacent agroecosystems. Fertilizers, insecticides, and sewage sludge are the principal agricultural sources of potentially toxic elements (PTEs).

The nature of these toxic PTEs and their accumulation patterns, whether in soil or plants, vary significantly (Kayode et al., 2022).

2.4 Bioaccumulation

Bioaccumulation denotes the process by which persistent toxic elements (PTEs) amass in the tissues of animals over time, frequently attaining quantities that exceed those present in the surrounding environment. This condition transpires as organisms absorb PTEs from their surroundings via many channels and accumulate them in their tissues due to inadequate elimination systems.

A limited number of plants readily assimilate elevated concentrations of metals from the adjacent soil. These organisms are referred to as hyperaccumulators (Hassan et al., 2019). Harvesting these plants for human consumption may result in exposure to detrimental quantities of metals. This danger often arises only when plants are harvested from regions with elevated metal concentrations in the soil. The absorption of metals by plants is contingent upon soil acidity (pH). Increased acidity enhances the solubility and mobility of metals, hence increasing their likelihood of being absorbed and stored by plants (Obiri-Yeboah et al.,2021).

Generally, individuals are more susceptible to metal exposure via soil adhering to plants than from bioaccumulation. This is due to the considerable challenge of removing all soil particles from plant materials before preparation and consumption (Gyamfi et al., 2019). Root vegetables (such as potatoes and carrots), leafy greens (such as spinach and lettuce), and plant parts that develop close to the ground (such as strawberries) are more susceptible to metal contamination than the upper sections of plants, such as fruits or berries. Stressed plants may indicate metal pollution (Hadzi et al., 2019). Seeking a typical alteration in the pigmentation or development patterns of plants as indicators of a stressful growing environment, such as drought, in conjunction with elevated metal concentrations in the soil. Plants may absorb PTEs from soil and water via their roots, leading to accumulation in various plant components, such as leaves, stems, and roots (Bello et al., 2019). This process is affected by variables like soil pH, organic matter level, and plant type. Such circumstances increase the likelihood of plants bioaccumulating metals. Deficiencies in plants, such as insufficient zinc levels, might affect their propensity to accumulate metals (Hadzi et al., 2018)

PTEs accumulated in plants can be transferred to higher trophic levels through consumption by herbivores and subsequent predators. This process, known as biomagnification, can lead to the bioaccumulation of PTEs in the tissues of animals at higher trophic levels, including humans (Rezapour et al., 2014). Animals can accumulate metals by consuming vegetation, seafood, or drinking water with high metal concentrations. These metals are not eliminated by the animals; instead, they predominantly concentrate in the organs, skin, hair, and bones. Fish amass metals from their aquatic environment and their prey. Bottom feeders are especially vulnerable to metal bioaccumulation due to their ingestion of metal-contaminated sediments, regarding fish consumption advisories (Peters et al., 2018). Seaweed absorbs metals from both the surrounding water and the sediments in which it proliferates. Besides consuming metals through food, there are other avenues for exposure to metal contamination through the use of plants. They comprise:

- absorbing pollutants from the combustion of botanical substances (such as smudging),
- absorbing pollutants from the combustion of botanical substances (such as tobacco or Jimson marijuana),

- volatilization of pollutants in plant materials inside confined spaces (such as sweat lodges or workplaces),
- ingestion, inhalation, or dermal exposure from artisanal activities using flora, and
- daily use of botanical substances as tonics to enhance health (such as ginseng or sage) (Mohammadi et al., 2019)

2.5 Wastewater and PTES

Wastewater can significantly contribute to environmental pollution by Potentially Toxic Elements (PTEs), since it may include high amounts of these elements resulting from diverse human activities. Wastewater significantly contributes to the accumulation of heavy metals in crops and soils (Mohammadi et al., 2019). The contamination of agricultural soils and crops with heavy metals is particularly severe in developing industrialized nations like China and India, owing to the widespread utilization of untreated industrial wastewater (Okereke, 2016).

Rail wastewater often contains high concentrations of PTEs due to the discharge of process waters from manufacturing, mining, and metal-processing industries (Mohammadi et al., 2019). These industries may use PTEs in their processes or generate wastewater contaminated with PTEs as byproducts. Despite Ghana's little industrialization, untreated yet diluted wastewater mixed with stream or stormwater is extensively utilized for urban vegetable cultivation. In Ghana's capital, Accra, it is believed that there are between 800 and 1,000 urban vegetable producers. In metropolitan regions, almost 200,000 individuals purchase vegetables cultivated for street food components daily (Koptsik & Koptsik, 2022)

Agricultural practices, including the use of fertilizers and pesticides containing potentially toxic elements (PTEs), can lead to the buildup of PTEs in soils. When rainfall or irrigation water washes these PTE-laden soils, they can enter surface water bodies or groundwater, contributing to wastewater contamination (Omeje et al., 2024). Crops may absorb PTEs from polluted soils via their roots or by deposition on leaf surfaces. The absorption of PTEs through roots is influenced by several parameters, including the soluble concentration of PTEs in the soil, soil pH, plant growth phases, and the types of crops, fertilizers, and soil (Siaw et al., 2020).

These PTEs accumulate in the consumable parts of plants, including the leaves and roots. Heavy metals like cadmium, copper, arsenic, chromium, lead, zinc, cobalt, and nickel are commonly found in vegetables. Certain substances are classified as micronutrients when found in minimal quantities. Nonetheless, they can be profoundly detrimental to human health and induce many chronic diseases, particularly when ingested in substantial amounts or over prolonged durations (Peng et al., 2019). Excessive PTE not only presents a safety hazard but also contaminates soils, therefore impairing agricultural quality and development (Ahmad et al., 2021).

Routine monitoring of heavy metal concentrations in soils and crops is essential to ascertain levels and formulate strategies to mitigate contamination and reduce risks to human health (Izomor et al., 2019) McBride (1994) noted that urban runoff, encompassing stormwater runoff from urban areas, can transport potentially toxic elements (PTEs) from roads, roofs, and other urban surfaces into water bodies and wastewater treatment systems. Road salts, vehicular pollutants, and air deposition may contribute to the pollution of potentially toxic elements in urban runoff.

Microbiological pollution has been the primary emphasis of research about the health dangers linked to wastewater irrigation in Ghana. The use of untreated urban wastewater for irrigation has been a longstanding practice, mostly motivated by water shortage, accessibility, minimal or no cost, and the perception that wastewater provides essential plant nutrients (Ashraf et al., 2021).

In several semi-arid and dry regions globally, fresh surface water is often accessible in sufficient quantities just during the rainy seasons. The long day season necessitates water for irrigation. Because of low water tables, which result in high expenses for well drilling and water pumping, groundwater may be costly to access (Akoto & Anning, 2021). The irrigation of crops with untreated wastewater is a prevalent practice in several underdeveloped nations globally (Akoto et al., 2015).

These customs are typically seen in Ghana's peri-urban regions, including Accra, Kumasi, and Tamale, from a general survey conducted in 2002 among vegetable farmers. It was discovered that nearly all 700 farmers in Tamal and approximately 84% of the nearly 800 farmers in Accra and the surrounding area irrigated their fields with untreated wastewater during the dry season (Asante et al., 2023; Bortey-Sam, Nakayama, Akoto, Ikenaka, Baidoo, et al., 2015).

It is impossible to overstate how important vegetables are to our diet. The significance of vegetables in our diet cannot be overstated. The erratic rainfall pattern and insufficient irrigation infrastructure hinder farmers' capacity to supply the requisite number of veggies to the ever-growing population. Because it is easily accessible, farmers thus turn to using untreated wastewater for produce cultivation. Many contaminants, including

PTEs, are known to be present in untreated wastewaters (Akoto & Anning, 2021). The application of untreated wastewater frequently introduces pollutants into the soil, rendering them bioavailable for plant absorption (Akoto et al., 2015). While certain metals are essential for human health in trace quantities, the levels typically introduced through irrigation with untreated wastewater exceed acceptable limits, thereby contaminating crops (Asante et al., 2023).

The PTEs may spread through wastewater irrigation of vegetables and fodder in the human food chain. Such crops can pose several health risks when consumed, and frequent irrigation with wastewater raises the soil's heavy metal content, which increases plant uptake and contaminates groundwater through heavy metal leaching (Bortey-Sam, Nakayama, Akoto, Ikenaka, Baidoo, et al., 2015).

2.6 Fertilizers

Fertilizers are soil nutrient augmentations applied to stimulate plant development. The primary chemical constituents of fertilizers are nitrogen, phosphorus, and potassium. They are the most efficient method for enhancing crop yield and elevating the quality of food and fodder. The continuous application of fertilizers to soils is known to elevate heavy metal concentrations to levels that may ultimately surpass natural soil levels (Bortey-Sam, Nakayama, Akoto, Ikenaka, Fobil, et al., 2015).

These components are crucial for plant growth, and the use of fertilizers often leads to enhanced crop yields. Nevertheless, additional elements, mostly PTEs, which either lack recognized applications or may be harmful to humans and plants, are frequently present in trace amounts in these fertilizers, many of which contribute to various detrimental health impacts (Neina, 2019).

A diverse array of hazardous elements may be present in fertilizers, including Arsenic, Lead, Cadmium, and Mercury (Haghnazar et al., 2023). The Environmental Protection Agency of the United States identifies these metals as potentially harmful to humans, leading to cancer, developmental issues, birth abnormalities, reproductive complications, and damage to the liver and kidneys. Children are more vulnerable to the harmful effects of fertilizers due to their increased time spent on the ground and their tendency to place unwashed hands in their mouths (Collin et al., 2022).

Adults may be exposed to PTEs by inhalation and dermal contact when fertilizers are administered with bare hands (Shan et al., 2013). Ghana is known for producing well-fermented cocoa beans that command a premium price and must sustain, if not enhance, buyer confidence and trust. A significant difficulty is maintaining consistency in the quality of maintaining consistency in the quality of the cocoa provided. To enhance the nation's cocoa output while preserving high-quality standards, the Ghana Cocoa Board has initiated a project called “Cocoa Hi-Tech,” which strongly advocates the use of fertilizers among cocoa growers. Currently, the government of Ghana is the primary source of fertilizers to cocoa growers at minimal or no expense to them (Wiafe, Awuah Yeboah, et al., 2022). The continual application of fertilizers to soil can elevate heavy metal concentrations beyond their normal levels, facilitating their entry into the human food chain, even though these potentially toxic elements may exist in negligible amounts inside fertilizers (Zinn et al., 2020). Therefore, the necessity to evaluate the concentration of PTEs in these fertilizers and their accumulation in agricultural soils and food products is paramount.

The accumulation of potentially toxic elements (PTEs) in agricultural soils is attributed to the use of fertilizers and plant nutrients. These inputs play a vital role in providing essential nutrients to support plant growth and productivity while also contributing to the organic matter content of the soil. Consequently, fertilizers enhance soil fertility Gyurits et al., (2020)

Fertilizers are broadly categorized into organic (natural) and inorganic (synthetic) types. Organic fertilizers, also referred to as biofertilizers, such as ammonium fertilizers (sulfate and nitrate), are produced through anaerobic digestion (AD) processes (Kamunda & Madhuku, 2017). Inorganic fertilizers, referred to as chemically synthesized fertilizers, consist of a combination of inorganic compounds and chemical components (Khatun et al., 2022). Fertilizers, comprising organic and inorganic components, contribute to the generation of PTEs in the soil. The table below compares the global and European Union (EU) data about the variation of PTEs in different fertilizer types by region. Phosphorus is extensively utilized in fertilizer production and concurrently contributes to the buildup of potentially toxic elements (PTE) by its application to soil (Uzarowicz et al., 2024)
Water-insoluble phosphorus fertilizers have been found to facilitate the formation of phosphate rocks, which contribute significantly to the immobilization of metals by causing them to precipitate as metal phosphates in the soil (Brugge et al., 2005). Agricultural soils accumulate potentially hazardous elements (PTE) as a result of prolonged, excessive fertilizer use, which reduces soil fertility and impedes plant growth and yield (Kacholi & Sahu, 2018).

Water-insoluble phosphorus fertilizers have been demonstrated to facilitate the formation of phosphate rocks, which are crucial in the immobilization of metals by precipitating them as metal phosphates in the soil (Wang et al., 2020). In agricultural soil, phosphate fertilizers, liming agents, and bio-fertilizers are the main types of inorganic fertilizers that allow potentially hazardous elements (PTEs) to be released and then absorbed by plants (Darko et al., 2022). They enter the food chain and eventually have an impact on both humans and animals (Wang & Wang, 2016).

2.7 Composting and PTEs

The three primary stages of composting include chilling (the compost stabilization phase), mesophilic and thermophilic stages, and the treatment of organic waste by aerobic microbes (Dang et al., 2022) The process can reduce solid waste volume by 40–50% (Chen et al., 2015). The metabolic heat generated during the thermophilic phase eradicates pathogens, degrades numerous hazardous organic pollutants, and yields a final product suitable for use as fertilizer or soil amendment (Xiao et al., 2017). However, elevated concentrations of potentially toxic elements (PTEs) in the final product may pose risks to plants, soil, and human health. Human health and the environment are jeopardized by the absorption of PTEs by plants, their accumulation in human tissues, and biomagnification within the food chain (Lu et al., 2012).

2.7.1 Effects on composting

The impacts of PTE extend beyond soil, plants, and human health, influencing the composting process by altering microbial diversity. Microorganisms facilitate the decomposition of organic matter, detoxify some organic and inorganic contaminants, and alter the mobility and bioavailability of potentially toxic elements in plants. PTEs can influence microbial proliferation and induce morphological and physiological alterations. The biodegradation processes may be affected by environmentally harmful PTEs. Microbial enzymes may be influenced by PTEs, potentially inhibiting enzymatic reactions and intricate metabolic processes (Antoniadis et al., 2022). During the composting process, PTEs reduce the synthesis of phosphatase (Luo et al., 2015). Microorganisms must deal with toxic Pb while growing in Pb-contaminated substrates, and metal exposure always prevents microorganisms from growing and functioning (Mensah et al., 2020).

2.8 Pesticides and PTES

The rapid advancement of technology has recently exposed the environment and humankind to a wide range of chemical toxicants, particularly pesticides (herbicides, insecticides, and fungicides) (Liu et al., 2021) Pesticides, according to scientists, are synthetic chemical compounds that are used to control pests in a variety of settings, including agriculture (Liu et al., 2019). Therefore, in integrated pest management systems (IPMs), pesticides are considered effective, inexpensive, and efficient tools Wang et al., 2019). Unregulated pesticide application endangers animals and other non-target species due to the bioaccumulation of pesticides within food chains (Liu et al., 2012). Furthermore, pesticides' direct or indirect effects on non-target animals upset the balance of the environment (Xu et al., 2023). Plant parts, soil, and air all contain pesticide residues, and some of them can even leak into the water (Zhang et al., 2015). These residues, which may last in the environment for extended periods and possess carcinogenic properties, are considered one of the most detrimental dangers to the ecosystem (Shi et al., 2022).

Pesticides are either naturally occurring or chemically synthesized toxic substances or mixtures of substances. These are commonly employed in agricultural settings to manage insect infestations (insecticides), bacterial infections (bactericides), fungal growth (fungicides), and detrimental weeds (herbicides) (Liu et al., 2017). Additionally, they can be used across the ecosystem to combat a variety of pests and disease-carrying insects, including ticks, rats, mosquitoes, and lice (Meng et al., 2016). The largest consumer, accounting for around 85% of the world's pesticide production, is the agricultural sector. Additionally, these can aid in the suppression and prevention of bacterial, fungal, and insect infestation outbreaks in moist areas (Kong et al., 2014).

2.9 Effects of PTEs toxicity on agricultural soils and plants

It is widely established that elevated levels of heavy metals affect plants and soil. The World Health Organization (2015) has established the maximum residue limits (MRL) for their concentrations ($mg \cdot kg^{-1}$) in soil and plants. Metals with elevated permitted limits are considered safe. Metals with elevated permitted limits are considered safe. Metals with elevated permitted limits are considered safe. The maximum permissible concentrations of Pb, Zn, and Cu in soil are established; however, the minimum concentrations of Cd are strictly forbidden. According to these limit values, the accumulation of Cd in the soil is more perilous than that of Cu, Zn, and Pb, even at lower concentrations. Copper has the greatest concentration threshold in plants, succeeded by lead, zinc, and cadmium. The highest concentration of cadmium (Cd) in plants is typically associated with its presence in soil, while copper (Cu) has the highest permissible limits, followed by lead (Pb) and zinc (Zn). Although considered a soil component, PTEs may significantly damage plants and soil when present in elevated amounts. Consequently, they are regarded as toxicants; (Li et al., 2020) conducted a study to delineate the relationship between pollution sources and contaminated soils in the vicinity of a mining area in Gbani. The study focused on both forest and agricultural soils. Their findings indicated that both soils are affected by the smelting operations, albeit to varying extents. The concentrations of Cd, Pb, and Zn in the PTEs were 200, 25, and 20 mgkg^{-1}, respectively. Research conducted by Dash et al. (2021) examined the accumulation and variations in PTE concentrations near the Tisza River and its tributaries, reporting concentration ranges of 1.3–21 mgkg^{-1} for Cd, 38–3630 mgkg^{-1} for Pb, 54–4850 mgkg^{-1} for Cu, and 200–770 mgkg^{-1} for Zn at the studied sites.

The findings indicated that the studied metals exhibited quantities above permissible limits, signifying their toxicity. Soil acidity and the restricted availability of macronutrients are two primary concerns associated with cumulative PTE toxicity. The effective rehabilitation of polluted soils via phytostabilization necessitates the resolution of these difficulties. Yuanan et al. (2020), carried out a comprehensive investigation evaluating the PTEs' composition and the sources in Southern Poland's Upper Silesia industrial zone.

To determine the PTE concentration in various soil strata, they utilized a range of established contamination markers. Their findings indicate that the concentration of heavy metals in the superficial layers was ranked as follows: Pb > Cd > Zn. On the other hand, Zn > Cd > Pb was the order observed in the deep strata. Every metal concentration was higher than the geological background limits, suggesting that the area under study was extremely dangerous.

2.9.1 Effect of cadmium toxicity on agricultural soil

Due to the economic revolution, swift industrial advancement, and sophisticated agricultural techniques, cadmium deposition in the soil is a prevalent concern among PTEs. The primary factors often affected by cadmium accumulation are soil pH and organic matter concentration. An anomaly in the soil characteristics was evidenced by the rise in Cd bioavailability when the soil pH diminished. In 2023, Patil et al. investigated the accumulation of PTEs in Hunan Province, China's three agronomic regions. The research examined the content of PTEs in each location. The results indicated that in the three examined regions, Cd and Ni exhibited the highest mean concentrations (1.40 and 14.9 mg/kg, respectively), above the Chinese environmental quality criteria for soil. Mohammadi et al. (2020), on the other hand, examined the Cd isotope composition of Olkusz as an example from a Western country. The study focused on three forest soil profiles and two meadows impacted by various sources of pollution. The investigation indicated that the lightest Cd isotope compositions were in the deeper humus layer of the soil, whilst the heaviest were identified in the upper soils of the forest soil profile. Liao et al. (2005) conducted a thorough investigation on the detrimental impacts of cadmium on the properties of paddy soil. To ascertain ecological doses of Cd, they employed various kinetic and sigmoid dose-response models. According to their findings, Cd inhibited the growth, metabolic processes, and activities of soil microorganisms. Ghosh & Singh, (2005), examined the combined effects of salinity and Cd on soil microorganisms and enzymatic activity

Salinity and Cd had a synergistic detrimental impact on soil properties, according to their findings. Additionally, the amount of microbial biomass in the soil and microbial respiration decreased as a result of their combined action. Haghnazar et al. (2023) Using a GIS-based methodology, the PTE contamination in agricultural soil was measured. The findings indicated that the concentrations exceeded the thresholds set by WHO (2010), confirming the high mobility of cadmium (Cd) in soil. Consequently, this resulted in significant toxicity, which altered the soil's physicochemical properties, affected essential microorganisms, inhibited microbial activity, and absorbed the soil's organic matter.

2.9.2 Effect of lead toxicity on lead toxicity on agricultural soil

Lead's significant toxicity has resulted in its classification as a hazardous heavy metal pollution (X. Li et al., 2020). Prolonged exposure to low concentrations of lead elevates dangerous levels. Lead pollution in soil is mostly attributed to its geogenic sources, which diminish soil microbial activity. Pb affects soil in a number of ways, including decreasing soil fertility, microbial diversity, and nutrients. (Chang et al., 2014)). Earthworm mortality may also result from Pb toxicity, which typically affects earthworms (Eisenia fetida).

Using phytoremediation or phytostabilization techniques to lower the bioavailability of lead in the soil is a significant problem that needs attention (Zhao et al., 2021). Numerous investigations into the impact of lead on agricultural soil have been conducted in various geographic locations. Tabelin et al. (2020) addressed how soil characteristics impact Pb absorption and retention. The results showed that the main parameters with Pb accumulation were soil pH and cation exchange capacity. Also, corroborating the former, Obiri et al. (2016) stated that there is a negative relationship between Pb solubility and soil pH, which accounts for the disruption of the soil absorption mechanism of the plant by Pb accumulation. As a result, Pb further affects the concentration of hemic acid and the sorption capacity of soil. Grynberg et al. (2022) examined the individual and joint effects of Pb and Cd on soil microbes and their enzymatic activity. The results suggested that the microbial populations were severely distressed due to pollution, which lowered the levels of enzyme activity. Moreover, the prevalence of Pb and Cd in synergetic toxicity was manifested in the marked depletion of bacterial and actinomycete populations. It is worth noting that the mobility and bioavailability of lead in soil are controlled by key soil characteristics such as pH, organic matter, cation exchange capacity, and texture. These characteristics are, in turn, influenced by the deposition of Pb in the soil.

2.9.3 Effect of copper toxicity on agricultural soil

One micronutrient that is crucial for plants is copper. Furthermore, it is an important component of the soil. A form of poisoning known as Cu toxicity results in a malfunction in any system where the levels are higher than ideal. (Kawakami et al., 2019). In agricultural soil, the availability of Cu is often influenced by many variables, including soil pH, since it is generally more accessible in acidic soils compared to alkaline ones, and organic matter (Arhin et al., 2016). There is often a correlation between the presence of copper-based fungicides or other agricultural practices and the high level of copper soil concentration. According to Yin et al. (2015), the amount of Cu present in agricultural soils varies between 5 to 30 $mgkg^{-1}$ depending on the type of soil and the area where it is located. A European nation, as reported by, Ondayo et al., (2023), examined the toxicity of copper in Portuguese natural soil; the ecotoxicological assessment revealed an inverse correlation between urease activity and Cu content. Urease is an extracellular enzyme that decomposes soil organic materials (Affum et al., 2016). The findings correspond with the research done by Cudjoe et al. (2023). Numerous investigations have indicated that Cu toxicity significantly diminishes soil microbial activity. Copper toxicity can denature microbial proteins and damage cell membranes.

Wang et al. (2019) examined the detrimental effects of copper on microbial biomass and soil microorganisms. The microorganisms most affected by the toxicity were identified in the following hierarchy: bacteria > actinomycetes > fungi. A study conducted by Tabelin et al. (2020) illustrated the detrimental effects of nanoscale copper, namely copper oxide (CuO), on soil microbial groups such as Rhizobiales. Despite only being 1 per cent, the applied CuO concentration altered the formation of the community and significantly reduced the oxidation potential. investigated how Cu affects agricultural soil functions over the long term. The results confirmed the significant toxicity of Cu values over 200 mgkg^{-1} in agricultural soil.

2.9.4 Effect of zinc toxicity on agricultural soil

Zinc is an essential element that facilitates protein synthesis and promotes plant growth hormones (Ondayo et al., 2023). It plays an active function in the metabolic and physiological processes of plants by participating in sugar utilization. Nonetheless, the threat of zinc toxicity is demonstrated by its detrimental effects on soil microorganisms that play a crucial role in improving soil fertility and structure (Affum et al., 2016).The active sites of soil enzymes are significantly impacted by zinc toxicity, which replaces some cations that are essential for cell function (Yoshimura et al., 2021). Moreover, Cudjoe et al. (2023) indicated that zinc shortage influences soil properties, including pH, organic matter content, and bicarbonate levels, while also hindering the functions of magnesium and iron in the soil. Mensah et al. (2021) examined the zinc concentration in contaminated soil in southern Poland. The zinc content was 10638 mg·kg^{-1}, beyond permissible limits and indicating the considerable detrimental effects this soil type poses to both humans and plants. These findings align with Akoto & Anning (2021), who demonstrated that elevated zinc concentrations in the examined soil impede the function of soil enzymes. Velásquez et al. (2022) investigated the adverse impacts of PTE toxicity on the characteristics of Polish soil, microorganisms, and enzymes. According to their research, a high pH in the soil enhanced zinc's bioavailability. Soil homeostasis is upset by excessive zinc and other metal concentrations. Additionally, it was observed that microbial enzymatic activities were inhibited.

2.9.5 Effect of PTES toxicity on plants

For the plant to thrive, specific ingredients are essential. Exposure to PTEs can significantly damage plants, even though these trace elements are essential. PTE effects on plants begin in the rhizosphere, where root exudates interact with metalliferous minerals and substances (Qi et al., 2022) investigated the characteristics of Zn–Pb mining-contaminated rhizosphere soils and their adverse impacts on plant roots. The carbonate deposits occurring on plant roots signify significant mineral oxidation and dissolution in the rhizosphere. It has been discovered that these procedures raise the concentrations of metal ions in rhizosphere solutions. Mineral deficiencies in plants are a result of cadmium toxicity (Nakazawa et al., 2021). Elevated lead levels can contribute to several physiological and metabolic abnormalities (Olujimi et al., 2015).

Cu and Zn have an interaction that impacts the soil's nutrient bioavailability. The figure depicts the PTEs' pathway and mode of action, which begins with soil accumulation and continues through plant uptake to various plant sections. Free radicals generated by PTEs elevate intracellular reactive oxygen species (ROS) levels, resulting in oxidative stress and consequent damage to biological molecules (e.g., lipids, proteins, enzymes, and nucleic acids). All these biological molecules possess deficiencies that lead to various physiological complications, including DNA damage, cellular impairment, and the suppression of enzymatic activity, which can ultimately result in plant mortality (Chavez, 2021; Gyamfi, et al., 2020).

2.9.6 Effect of cadmium toxicity on the plant

Despite many industries using cadmium in their processes and products, it is a superfluous and toxic heavy metal that poses risks to the environment and the ecosystem as it exists around us as a part of the anthropogenic activities (Wiafe et al, 2022). Plants absorb most cadmium ions through their roots owing to the mobility, concentration, and bioavailability of the ions, and the remaining amount is taken in directly from the vicinity (Ajayi et al, 2016). Alternative transporters such as the dominant calcium (Ca) channels move cadmium (Cd) into the cells of the plant, where its deposition occurs in the roots, shoots, and edible parts (Obiri et al., 2016). Many physiological and biochemical changes result from a plant containing high amounts of cadmium, for example, more than a given concentration (Olujimi et al, 2015). Also, concentrating cadmium in plants brings about adverse effects that include inhibition of several activities like photosynthesis, transport of minerals, and absorption of nutrients.

Moreover, it might also deter the movement of Fe into the shoots of plants (Basu et al., 2015). It has been reported that cadmium causes phenotypic losses in plants which include reduction in biomass production as well as in root and shoot elongation, cytotoxicity which alters the chlorophyll concentration and photosynthetic efficiency, and impairment of metabolic processes such as destruction of cellular structures or chlorosis as noted by Song et al., (2019) who showed that xylem parenchyma facilitated the movement of PTEs into vascular tissues while very little of Cd was moved through the xylem. Souza & Teixeira (2017) claimed that cadmium poisoning might reduce the dry bulk of the root and its length. Wang et al (2019), in a more recent study, investigated the effect of Cd ions on environmental parameters using seeds of Lactuca sativa together with seedlings of *Pichia sp* and *Aztobacter chroococcum*. Results suggest that exposure to Cd (II) reduced biomass, suppressed growth and further development of the root system and restricted.

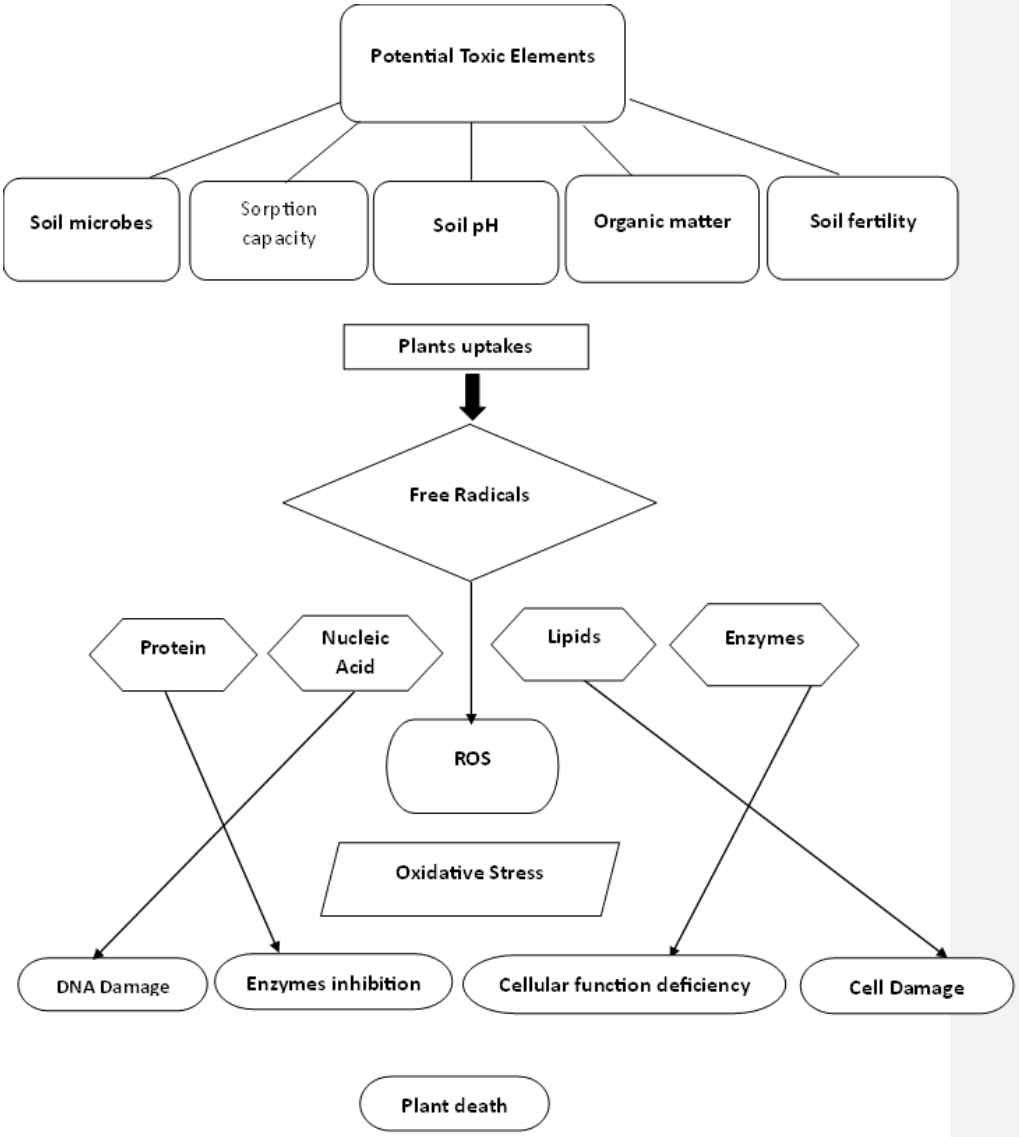

Figure 2.2: Mechanism of action and pathway of PTEs toxicity in soil and plants

(Kazapoe et al., 2022; Rajaee et al., 2015)

2.9.7 Effect of lead toxicity on plants

Similar to cadmium (Cd) and mercury (Hg), lead (Pb) is not requisite for plant development. (Bortey-Samet al., 2015). Pb is regarded as a metal that is both toxic and useful (Owusu-Prempeh et al., 2022). The high toxicity of this substance has led to its classification as a major pollutant (Bonah & Belford, 2022). Typically, the xylem of the roots carries Pb ions from the soil to the plant. (Odukoya et al., 2018). Lead poisoning impedes healthy plant growth and diminishes agricultural output and productivity, posing a threat to plants even at minimal doses (Kimijima et al., 2023). Inhibition of cell membrane permeability and reduction of nutrient absorption are two definitive indicators of Pb toxicity in plants (Sako & Nimi, 2018). Lead buildup in plants induces physiological issues, including DNA damage and the degradation of root and shoot systems (Hadzi et al., 2019). influences enzymatic activity (Bempah & Ewusi, 2016). The impact of lead poisoning on plants was investigated by Addai-Arhin et al. 2022. The results indicated that increased Pb concentrations affected fresh biomass and plant growth. The outcomes aligned with the earlier research conducted by (Asante et al., 2023). A study by Odukoya et al. (2022) on soybean crops investigated the harmful effects of lead on crop growth; the findings showed that the plant's chlorophyll content had decreased. Chen et al. (2022) shown that Pb reduced the protein content and prevented seed germination. They said that morphological and physiological processes would be adversely affected if the Pb level exceeded the critical threshold.

2.9.8 Effect of copper toxicity on plants

After steel and aluminium, copper comes in third place in terms of global consumption. A minimal quantity of copper is essential for plant nutrition and seed development. Cu is considered an extremely hazardous metal in elevated quantities, nevertheless. (Ma et al., 2022; Owusu-Prempeh et al., 2022) . In addition, since the root system takes up Cu ions from the soil, the concentration of Cu in the roots is greater than that of the shoots. The highest concentration of copper was in the root epidermis according to Kazapoe et al. (2022). The review article (Rajaee et al., 2015) noted that copper poisoning impaired photosynthesis and assimilation of nutrients, hence reducing the production of crops; synthesis of chlorophyll, and the productivity of plants in general. Copper concentration of 5 $mg \cdot kg^{-1}$ may prove harmful to the plant; it may lead to reduced growth and production. Barbosa et al. (2013) explored the effect of high concentrations of copper on the productivity and morphological characteristics of maize plants. They established that the effect of copper at higher doses was a reduction in plant height (Mensah et al., 2020). The negative effects of the increase in the concentration on maize plants were investigated. The results further showed that there was significant shoot length reduction among the plants treated with Cu, indicating its negative effects are felt throughout the plant, the germination of seeds (Ma et al., 2022). The development of bacteria was hindered in the presence of Cd (II).

2.9.9 Effect of zinc toxicity on plants

For plants and all other living things, zinc is an essential micronutrient. (Baah et al., 2023). After iron, zinc is thought to be the second most accessible transition metal in living things. It is closely linked to all enzymatic processes. Typically, zinc enters plants through their roots and is transferred from the soil as Zn^{2+} (Rajaee et al., 2015). Zinc is essential in photosynthetic redox processes (Souza & Teixeira, 2017). Severe harm results from zinc buildup in plant roots or shoots. Excessive zinc in plant cells induces significant turbulence in physiological processes, ultimately leading to plant mortality

(Basu et al., 2015). Prior research conducted by Song et al., (2019) argued that the first incidence of zinc toxicity led to younger leaves turning chlorotic before spreading to the older leaves. A study conducted by Obiri et al. (2016) examined the toxicity of zinc in the young peach tree. The elements were unable to reach the leaves due to the buildup of zinc in the root system, as the results showed. Furthermore, there was also a negative impact on dry matter productivity. Song et al., (2019) noted considerable loss of root length and photosynthesis level after zinc exposure. provided an overview regarding the phytoextraction of zinc by plants, but the majority of the plant physiological characteristics were also negatively affected, showing the toxic impact of zinc accumulation in plants. Placement of copper and phosphorus as contaminants in the soil and vegetation toxicity indicates their order, with phosphorus being the most toxic, followed by copper, and advancing the adverse effects of PTEs.

Table 2.1: Forms of Heavy Metal Toxicity and Their Adverse Effects on Soil and Vegetation

PTEs	Toxicity form	Soil	Plant
Cd	Cd^{2+}	Kills microorganisms, absorbs organic matter, and changes soil physicochemical characteristics.	Reduce biomass and root length, inhibit seed germination, and reduce stem conductivity.
Pb	Pb^{2+}	Changes soil PH, affects soil sorption capacity, and reduces soil fertility.	DNA damage decreases chlorophyll content, decreases protein content, and causes stunted foliage.
Cu	Cu salt	Change urease activity, affect microbial communities, and decrease oxidation potential.	Root deformation, decreased shoot length, reduced polypeptides, and a change in lipid content.
Zn	Zn^{2+}	Change bicarbonate and organic matter content, inhibit enzymatic activity, and affect soil pH.	Variation in enzymatic activity, obstruction of element transmission, and interveinal chlorosis

(Darko et al., 2022; Xu et al., 2023)

2.10 Pollution indices assessment

The growing concern over the adverse effects of pollution has spurred the development of pollution indices as tools to quantify and assess pollution levels in diverse settings. Pollution indices aggregate data from multiple sources, providing a holistic view of environmental quality. This research aims to explore the different aspects of pollution indices, ranging from their historical development to contemporary applications. An impartial way to evaluate the true enrichment of soils with trace elements is through pollution indices. The impact and toxicity of PTE contamination must be assessed by examining the productive soil quality of agricultural land. Various pollution indicators, such as the pollution index (PI), risk index (RI), and comprehensive ecological risk (ER), were employed to assess the pollution levels at the research site. According to your thesis, indices may properly quantify soil pollution and the extent of human impact on the soil environment (Xu et al., 2019). These metrics are commonly utilized when assessing the extent of PTE contamination in agricultural soils.

2.10.1 Effect of PTES toxicity on human health

The composition of metallic elements, naturally occurring components in the earth's crust, varies based on their origins and geographical location (Tabelin et al., 2020). Their existence is deemed unusual because of the difficulty of entirely eradicating them from the ecosystem once established (Grynberg et al., 2022). Heavy metal contamination, even at minimal concentrations, has attracted significant interest due to its hazardous effects, persistent accumulation, and bio-magnification characteristics. Among the many different types of environmental and soil pollutants, PTEs are regarded as one of the most dangerous (Arhin et al., 2016). Because of their presence in the environment, PTEs have a greater chance of being consumed by living things and building up in various body organs, such as the kidneys, liver, bones, etc. Additionally, these metals build up and negatively impact several bodily systems, including the circulatory, immune, endocrine, skeletal, and neurological systems (Taux et al., 2022).

Individuals globally are exposed to PTEs by ingestion (consuming food or beverages) or inhalation (breathing). Proximity to sites of unauthorized metal discharge poses a significant risk to individuals, as does employment at or near facilities using these metals and their compounds. Hunting and fishing activities may elevate the hazards of exposure and health repercussions for subsistence lifestyles. The widespread exposure to these hazardous compounds has generated significant worry over their effects on human health. The increasing utilization of various metals in contemporary applications and production has resulted in substantial escalations in the issues associated with the release of harmful metals into the environment (Wang et al., 2019).

2.10.2 Effect of heavy metal toxicity on children's health

Certain penetrating mechanisms of toxic PTEs, such as inhalation, dermal absorption, and swallowing, result in adverse health effects after PTE exposure. PTEs are now having a more detrimental impact on children's health than on adults. Given their high toxicity risk, widespread use, and prevalence, PTEs deserve more attention. Arhin et al., (2016), emphasizing that damage to the proximal convoluted tubule, along with mitochondrial dysfunction, might arise from Cd poisoning and lead to renal impairment. Moreover, exposure to cadmium (Cd) has been associated with osteoporosis (Yoshimura et al., 2021), as well as pediatric cancer, and delayed development in children. (Velásquez et al., 2022). Kinimo et al. (2018) noticed a link between neotenic cadmium exposure, via smoking and a mother's, and a child's weight and height. Common lead exposure is the most common cause of early childhood morbidity. Lead poisoning is a condition with peak incidence in preschool children, other than in the womb, where it is disastrous as it paralyses a child's brain and their behavioural and learning process (Nakazawa et al, 2021). From one product to another, lead has been shown to exist in baby food, which can damage a baby's multiple organ systems in a very deleterious way (Olujimi et al., 2015). It was further observed that other children with extreme lead exposure have an overactive, dull central nervous system full of attention followers as opposed to leaders.

The result includes persistent serious headaches, epileptic episodes, comas, and occasionally even death (Wiafe, Yeboah, et al., 2022).

While copper is necessary for brain performance, it can become detrimental if there is an excess of what is needed for cellular functioning and metabolism (Xu et al., 2021). Higher serum cu levels have been connected to lower levels of working and functional memory in Kids. Determining the correlation was Zhou et al (2020), who did a working memory test and concluded their hypothesis that working memory is affected by Cu concentration levels.

Wilson's disease (WD) is a genetic disorder that arises from the defective functionality of Wilson ATPase, a P1B-ATPase protein, which causes the mutation of the Cu degrading ATP7B..Children and adolescents mostly suffer from hepatic illnesses, but WD may have mental, neurological and haematological manifestations. Younger children may have a clinical form of accompanying liver disease in the form of Wilson's disease (Tuo et al., 2020). Isolated instances of zinc poisoning in youngsters have also been recorded. Severe acute ingestion was associated with headaches, vomiting, diarrhoea and loss of appetite. In a 2003 study of preschool children by Arsenault and Brown, in about 36% of children's meals, zinc ingestion level surpassed the tolerable upper intake limit, and thus their intake above the usual recommended dietary allowance. As suggested by Wei et al., (2022) due to a greater dependency on supplements and easier availability of zinc fortification, children may overconsume zinc in the USA (2015). Additionally, it was demonstrated that Cu competition at the same absorption site caused Zn-induced Cu deficiency state in the body system (Odukoya et al., 2018). It has been determined that excessive oral consumption of Zinc results in an increase of metallothionein in circulation, which in turn captures oral copper and promotes its excretion from the body (Kimijima et al., 2023). It has been reported that over-consuming zinc supplements has resulted in a negative impact on immune functioning (Bempah & Ewusi, 2016; Hadzi et al., 2019).

2.10.3 Effect of heavy metal toxicity on adults

Specific PTEs can influence almost all cells and tissues inside the human body. Cadmium and its constituents can adversely affect lung cancer, osteoporosis, bone diseases, renal tubular failure, and calcium metabolism (Addai-Arhin et al., 2022). Cadmium poisoning has been connected in some cases to diabetes, neurodegenerative illnesses, and prostate and breast cancers (Karungamye et al., 2023). Exposure to Cd has been linked to an increased risk of developing musculoskeletal disorders, including osteoporosis, osteoarthritis, and rheumatoid arthritis, according to epidemiological research (Asante et al., 2023). Exposure to Cd impacts spermatogenesis, specifically sperm motility and hormonal synthesis/release, as well as male reproductive systems and semen quality. Furthermore, clinical and human studies have demonstrated that cadmium interferes with menstrual cycles, reproductive hormonal equilibrium, and fertility (Asamoah et al., 2024). Scientists indicate that pregnant women may be susceptible to cadmium exposure. Cadmium may adversely affect the placenta and result in reduced birth weight, as indicated by research (Chen et al., (2022). Cadmium inhalation has the potential to cause fatalities as well as severe lung damage (Akoto & Anning, 2021). There are numerous detrimental effects of lead on bodily systems. Predominantly non-specific symptoms include behavioural abnormalities in children, infertility in men, miscarriage in women, and declining cognitive function in adults. Common symptoms also include anaemia, renal failure, hypertension, and abdominal colic (Baah et al., 2023).

Additionally, because Pb crosses the placenta, it poses a serious risk to the fetus and can result in adverse birth outcomes like preterm birth (Zhao et al., 2021). Overall growth trajectories may be impacted by the decrease in maternal thyroid hormone levels that may result from it. In addition to affecting heme synthesis, lead causes neurotoxicity and nephrotoxicity disorders (Tabelin et al., 2020). Extreme Pb intoxication has been reported for several neurological syndromes, including palsy and Pb encephalopathy. It can cause cancer, and excessive exposure can be fatal (Tabelin et al., 2020). Elevated levels of the hazardous element copper are present in the brain, liver, and kidneys (Kawakami et al., 2019).

Gastrointestinal (GI) side symptoms of copper poisoning include abdominal discomfort, hematemesis, melena, jaundice, anorexia, vomiting, and erosive gastropathy (Zhao et al., 2021). In addition to renal symptoms, GI side effects have also been reported to be accompanied sometimes by headache, tachycardia, coma, and altered mental status (Grynberg et al. 2022). Some individuals who are intravascularly toxic due to copper (that is, due to faulty infusion of hemodialysis fluid) may display signs and symptoms of intravascular hemolysis, and patients with glucose-6-phosphate dehydrogenase deficiency are more prone to copper hemolytic adverse effects. Some other psychological illnesses, such as Cu, cause the same side effects as well, i.e. fatigue, depression, agitation, irritability and difficulty in concentration. It is known that Cu toxicity rapidly deteriorates into methemoglobinemia, then intravascular hemolysis, hepatic necrosis, encephalopathy, progressively affecting cardiac and renal functions and eventual death in most acute forms (Arhin et al., 2016; Ogbeide et al., 2016). Cu ions in high amounts have a dual effect: they inhibit cellular multiplication, and together, they induce oxidative stress and DNA breakage (Taux et al., 2021). It is well-documented that zinc, especially in its oral form, is relatively less toxic. This inadequacy will eventually give rise to toxicity signs, including, but not limited to, nausea and vomiting, tiredness, and upper abdominal discomfort. Even though it has been required that larger amounts of zinc intake are required to exhibit clear signs of toxicity, it has been found that zinc supplementation can be detrimental in some cases, yes it is true that in fact, the auxiliary neurodegenerative processes linked to head trauma, stroke, and seizure have been demonstrated to include neuronal death as well as zinc induced neurotoxic reaction Vaporized and released free zinc ions perspective of ‘zincergic and other) neurons firing,' this sort of activity disengages a multitude of post-synaptic neuronal receptors scattered out and about the synaptic cleft. But in case of diseases occurring or injury has taken place, traction that occurs, excess zinc is released. As a matter of fact, amyloid plaques on Alzheimer's patients' neurons tissues are mainly caused by zinc accumulation and increased oxidative conditions. Otherwise, the refusal of heavy metals concentration presence would go up with plague presence and insulin metabolic syndrome, which will finally lead to cardiac and numerous other syndromes, including diabetes, to occur.

CHAPTER THREE

METHODOLOGY

3.1 Description of the Study Area

Gbani is one of the budding communities in the Talensi district of the Upper East Region of Ghana, and a small-scale mining community in the district. It has a population of 1028, comprising 652 males and 376 females who live in 316 households in the community. (Gyamfi et al 2020), where there are widespread artisanal gold mining activities as the mainstay of the community.

As shown in Figure 3.1, Gbani is located between latitudes $10^{0}15$ and $10^{0}60$ North and longitudes $0^{0}31$ and $1^{0}05$ West. The district covers an area of 838.4 km^2. The geographical setting of Gbani varies from hills to valleys down to plains. The topography is made up of hills, valleys, and plains of different sizes, making it attractive and interesting. These features contribute to adding beauty not only to the region but also to the daily livelihood of the inhabitants within it, as noted by Dodd et al. (2023). The vegetation of the area features Guinea Savannah woodlands composed of scanty short deciduous trees and a ground flora of grass. The climate of the area is tropical with two distinct seasons, which are a rainy season (erratic runoff from May to October) and a dry season stretching from October to April. The mean annual rainfall for the area stands at 95 mm and oscillates between 88 and 110 mm. The area experiences a maximum temperature of 45 ^{o}C in March and April and a minimum of 12 ^{o}C in December (Gyamfi et al., 2020). The topography of the town features scattered rock outcrops and upland slopes with relatively undulating lowlands with gentle slopes ranging from 10 to 50 gradients. The soil in the study area developed mainly from granitic rocks. It is shallow and low in soil fertility, weak with low organic matter content and predominantly coarse in texture.

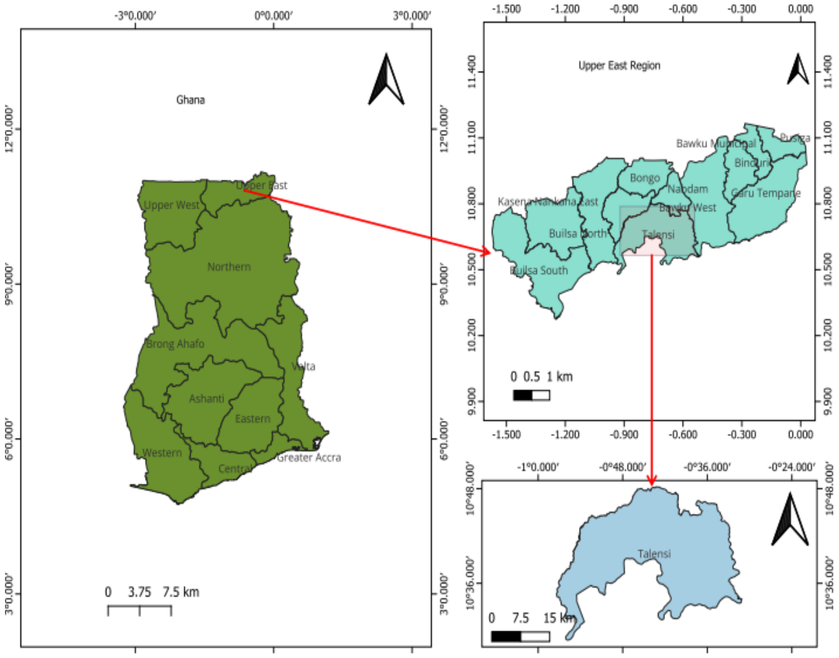

Figure 3.1: Map of the study area

3.2 Sampling

A total of 147 top-soil samples were collected from various locations, including mining activity hotspots (n = 12), two transects running through the community (Transect: n = 110), and two heaps of cyanide-treated mine waste tailings (n = 25). The transect method involved systematically placing linear sample lines across the study area, with samples collected at 5 m intervals along each line. This method facilitates the collection of representative data by establishing linear pathways across the study area, aiding in the analysis of spatial patterns and variations (Darko et al., 2019). Additionally, the entire community was mapped on a 100 x 100 m grid, and samples (n = 15) were taken at the intersections of the coordinates, extending to the surrounding areas. Where sampling was not possible due to obstructions such as tarred roads, rivers, or houses, sampling locations were adjusted by moving 2 m to either the left or right of the intended point.

Approximately 500 g of soil samples were collected from the top 0-10 cm depth at all locations using a plastic trowel. To avoid cross-contamination, the digging equipment was cleaned with deionized water and detergents after each sample was collected. The soil samples were then placed into sealed, labelled Ziploc bags and transported to the laboratory for analysis.

3.2.1 Sample collection, preparation, and storage

A dried, clean plastic trowel was used for the collection of surface soil, roughly 500 g, down to a depth of 15 cm, and packaged into a zip-lock bag. This is the depth believed to be in contact with people during daily activities, which enhances the assessment of human risk (Dodd et al., 2017). To minimize cross-contamination while sampling, the digging tools were washed with detergents and then rinsed with deionized water after each sample had been taken. The samples were all transported to the laboratory, where they were allowed to dry air at room temperature in a fume hood. Then the dried samples were carefully cleared of any debris, stones, and pebbles before they were ground into powder and sieved.

3.3 Instrumental Analysis

The quantitative determination of concentrations of the possibly toxic elements Pb, As, Zn, Cu, Fe, Mn, Cr, V, Ti, Ni, and Cd was made with a Thermo Scientific Niton XL3 field portable X-ray fluorescence-spectrometer (XRF). The concentration of PTEs in the samples was analysed through a Niton XL3t GOLDD FP-XRF spectrometer (Rweyemamu et al., 2020). A part of the quality checks that were done during XRF runs included NIST 2711a standard reference materials (SRM) procedure blanks, and recovery tests. Satisfactory recoveries were obtained for Pb, As, Zn, Ni, Co, Cu, Cr, Cd, Fe, Mn, Ni, Ti, and V. Using five replicates of standard reference material the repeatability of the analysis, variability of the measurement system was assessed to be 4-5 % which indicated a high reliability (Xu. et al., 2023). After which, two-thirds of the shrouded XRF were loaded with the sample holder. The XRF analysis produces metal concentration data, with a sample resolution of 180 seconds. The samples were then wrapped in a Mylar film after being analyzed in triplicate, and the mean calculated (Darko et al. 2022).

The cup-shaped sample was inserted into the XRF shroud with the same treatment applied to all other samples and scanned for about 180 seconds. The average of the findings was calculated after each XRF analysis, which was repeated three times, had been performed. The instrument was calibrated using certified standard reference material before being employed for the analysis of the concentration of potentially toxic elements. For the XRF assay, the sample was put into the device after being coned.

3.3.1 Total Organic Carbon (TOC) Content

The total organic carbon in the soil samples was determined using the loss on ignition (LOI) method, a semi-quantitative technique that estimates organic matter by measuring the weight loss of a sample after heating (Schumacher, 2002). To estimate TOC, conversion factors were applied to reflect the proportion of carbon in the organic matter. The analysis followed the procedure by Heiri et. al. (2001), which states that organic carbon is combusted at 550 °C. Approximately 1 gram of soil was placed into a crucible and heated in an oven at 105 °C for two hours. After cooling to room temperature in a desiccator, the sample was weighed and then transferred to a muffle furnace set at 550 °C for four hours. After combustion, the samples were left to cool overnight in a desiccator before the final weighing. Replicate measurements were conducted to ensure result consistency and reliability.

3.3.2 Soil pH and Electrical Conductivity

The pH and electrical conductivity (EC) of the soil samples were measured using a PC 700 Eutech Instruments Multi-Parameter meter equipped with a probe. For analysis, 20 grams of dried soil was mixed with 40 mL of distilled water in a 1:2 ratio. To maintain accuracy, the meter was regularly calibrated using standard buffer solutions with known pH values (4.01, 7.00, and 10.01). The instrument, capable of calibrating with up to five buffer solutions, retained calibration data even after shutdown due to its non-volatile memory. It automatically recognized calibration buffers from both the USA and NIST standard groups. To minimize errors due to temperature fluctuations, an automatic temperature compensation (ATC) probe was used, as pH readings become less accurate when samples deviate from 25 °C and neutral pH.

3.4 Quality Assurance and Quality Control

In this work, a lot of quality assurance and control procedures were adopted to ensure the validity, reliability, and accuracy of the data. The handling of the soil samples was done with utmost care both on the site and in the laboratory to avoid sample contamination. Samples were put in a zip-lock polyethylene bag, which was sealed very tightly and labelled with permanent ink for the purpose of avoiding sample contamination and muddling. The sampling and sieving tools, such as soil pan, brush, test sieve, mortar, and pestle, were washed thoroughly after each use to reduce the sample's chances of cross-contamination. The polyethylene container and cap were cleaned by washing with tap water followed by another rinse with distilled water and drying at room temperature before reusing during analysis with XRF. Duplicate analysis was carried out after every ten samples to calculate the repeatability of the data obtained. NIST 2711a is a certified standard reference material which was analyzed as a sample to check the validity of the results obtained from XRF. NIST 2711a soil reference material was analyzed with XRF to check method accuracy, giving recoveries between 83% and 101%, within the acceptable ±15% range. LOD values were <2 mg/kg (As), <3 mg/kg (Cd), 10 mg/kg (Cr), <6 mg/kg (Cu), <10 mg/kg (Ni), 2 mg/kg (Pb), and <3 mg/kg (Zn). LODs were determined from blank/low-level measurements using LOD=3σblankLOD = 3\sigma_{\text{blank}}LOD=3σblank, and LOQs were derived as LOQ=10σblankLOQ = 10\sigma_{\text{blank}}LOQ=10σblank, ensuring reported values above the LOQ are reliable.

Table 3.1: showing QA/QC measurements

Elements	**Recoveries**	**LOD**
As	96%	<2 mg/kg
Cd	89%	<3 mg/kg
Cr	89%	10 mg/kg
Cu	83%	<6 mg/kg
Ni	101%	<10 mg/kg
Pb	93%	2 mg/kg
Zn	91%	<3 mg/kg

3.5 Statistical Analysis

In this study, all the computations of descriptive statistics, that is, mean, standard deviation, skewness, kurtosis, and minimum and maximum concentrations, were performed using Minitab version 21. Microsoft Excel (version 2021) was used to calculate the pollutant indices, risk assessments, and Pearson's correlation analyses, whereas JASP (version 0.17.2.1) was used to determine the principal component analysis. Kurtosis and skewness values were used to examine the results of the normalcy tests. According to the contributions of the works of Hair et al. (2010) and Bryne (2010), where skewness and kurtosis all fall between the limits of -2 to +2 and -7 to +7, respectively, the data is normally distributed. The data set for statistical analysis was excluded from the results that were reported as being below the detection limit.

3.6 Source apportionment of potentially toxic elements

Researchers can better understand the origins and distribution patterns of potentially toxic elements like lead, cadmium, arsenic, and chromium by using source apportionment, a technique for identifying and attributing sources of pollutants in environmental matrices like soil, air, water, and biological tissues

3.6.1 Principal component analysis

Principal Component Analysis (PCA) is a statistical tool widely employed to reduce the dimensionality of complex datasets by transforming correlated variables into uncorrelated principal components (PCs). These PCs are ranked according to the variance they explain, enabling researchers to uncover dominant factors and relationships in datasets (Liu et al., 2023). PCA is particularly valuable in environmental studies, where it is used to identify key sources and correlations among variables, such as pollutants in soils.

As recommended by the Kaiser criterion, only principal components with eigenvalues greater than 1.0 were retained (Braeken & Van Assen, 2017). PCA was performed on the varimax-rotated data using Minitab version 21 to assess relationships and variance among potentially toxic elements in soil samples. The PCA results revealed correlations between elements, aiding in the interpretation of environmental risks and pollutant sources. An inter-elemental correlation analysis was also conducted to further ascertain the degree of association between elements at various sampling points.

3.6.2 Positive matrix factorization (PMF) model

A sophisticated receptor modelling method called Positive Matrix Factorization (PMF) is frequently used to assign sources of environmental pollutants, such as heavy metals, particulate matter, and toxic metals in soils, water, and air. PMF excels in analyzing complex environmental datasets by decomposing observed concentration matrices into two components: source profiles and their contributions. Its non-negative constraint ensures physically meaningful solutions, making it a robust tool even in cases of missing or uncertain data. PMF operates on the principle of minimizing the objective function Q, which is defined as indicated in Equation 3.1.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right)^2 = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{u_{ij}} \right)^2 \text{.................eqn 3.1}$$

where xij represents the observed concentration of the j-th species in the i-th sample, gik and fkj denote the contributions and profiles of the k-th source, respectively, and u_{ij} is the uncertainty associated with x_{ij}. The PMF model aims to identify the number of sources

(p) and derive their respective contributions and profiles while minimizing the residual eij, as defined in Equation 3.2.

$\mathrm{X_{ij}} = \sum_{\mathrm{k=1}}^{\mathrm{p}} \mathrm{g_{ikf_{kj}}}\, _{+\mathrm{e_{ij}}}$ ………………………………….. Equation 3.2

This study applied PMF to apportion sources of potentially toxic metal pollution in Ghani mining soils in the Talensi District, the northern part of Ghana.

Core PMF Equations and uncertainty calculation

PMF estimates uncertainty u_{ij} using the following formula in Equations 3.3 and 3.4:

$\mathrm{u_{ij}} = \frac{5}{6} \times \mathrm{MDL} \qquad \mathrm{C} \leq \mathrm{MDL}$………………….. Eqn 3.3

$\mathrm{u_{ij}} = \sqrt{(\delta \times C)^2 + (0.5 \times MDL)^2} \qquad \mathrm{C} > \mathrm{MDL}$……………………… Eqn 3.4

C is the chemical species concentration, MDL is the method detection limit, and δ error fraction in the chemical species analysis. This research work conducted the soil pollutant source apportionment using the PMF receptor model since this receptor model has been suggested by the United States Environmental Protection Agency (Hernández-López et al., 2021). After inputting the data into EPA PMF 5.0, the software was executed by setting the number of factors. The random seeds may lead to different levels of errors in the analysis results. Hence, PMF with different factors from 3 to 7 and random seeds verified the data 20 times. Using a different number of factors in the trial, the algorithm contrasted Q/Qexp, whereas Qexp is computed by (number of non-weak data values in X)- (number of elements in G plus those of F). Four factors, for instance, matched 463 samples. An excess of appropriate factors is indicated when Q/Qexp varies more slowly as factors increase. The ideal number of factors in this research was 2, which was discovered by figuring out the Q/Qexp inflection point.

3.7 Extent of contamination

Contamination levels are typically assessed by comparing site-specific data with background data or through the application of calculated pollution indices. In this study, the degree of contamination was evaluated using contamination indices.

3.7.1 Index of geo-accumulation (I_{geo})

The geo-accumulation index allows the estimation of metal contamination by comparing preindustrial and recent metal concentrations. The geo-accumulation index (I_{geo}) was used to analyse and evaluate the PTEs contamination levels in the soil of Gbani, which can provide information for monitoring the soil environment in this area. The Index of Geo-accumulation was first proposed by Müller in 1969 as a method of measuring the level of metal pollution in sediments. It has since gained wide application in the environmental sciences to provide an indication of the impact of human activities on soil and sediment quality as expressed in Equation 3.5 (Kazapoe et al., 2022b).

$$\mathrm{I_{geo}} = \log_2\left(\frac{\mathrm{C_n}}{1.5\times\mathrm{B_n}}\right) \text{ .... Eqn 3.5}$$

Where C_n, is the measured concentration of the metal in question, B_n is the geochemical background concentration of the metal. The mean elemental concentration in 11 control samples taken from the Wa Botanical Gardens (pristine environment in the study area) was used to estimate the Bn for this investigation (As =11.9, Cd = 0.3, Co = 19.2, Cr = 90, Cu = 45.1, Mn = 859, Ni = 66.9, Pb = 20, Ti = 4690, V = 128.6, Zn = 17.8). According to the I_{geo} value, there are seven classes, which are described in Table 3.1.

Table 3.1 Classification of the index of Geo-accumulation

Ranges	Classification
<0	Unsaturated

0 -1	Unsaturated to moderately contaminated
1 – 2	Moderately contaminated
2 – 3	Moderately to heavily contaminated
3 – 4	Heavily contaminated
4 – 5	Heavily to extremely contaminated
>5	Extremely contaminated.

3.7.2 Enrichment factor

The enrichment factor (EF) was used to assess the degree of heavy metal pollution sourced from the anthropogenic contribution and to specify anthropogenic and natural causes, Equation 3.7 (Kazapoe et al., 2022; Mensah et al., 2020). In this work, iron (Fe) was used as the normalizing element (Abrahim & Parker, 2008). Iron is used as a normalizing element because it is abundant, lithogenic, stable, and easy to analyze. It helps researchers distinguish between natural and anthropogenic sources of metals in environmental samples, which is essential for pollution assessment and risk evaluation.

$$\mathrm{EF} = \frac{(\mathrm{C_n/Cref})\mathrm{sample}}{(\mathrm{B_n/Bref})\mathrm{background}} \quad \text{…………………………..Eqn 3.7}$$

Where C_n sample is the concentration of the analyzed chemical element in the analyzed Environment. C_{ref} sample is the concentration of the analyzed chemical element in the Reference environment, B_n and B_{ref} are the concentrations of the reference element in the studies and referenced environment, respectively, as elucidated in Table 3.3 (Darko et al., 2022).

Table 3.2 Range and classification of enrichment factor

Range	Classification
EF > 1	This indicates the metal concentration in the soil sample is enriched relative to the average continental crust and surface soil values and the source of the metal in the topsoil is likely to be anthropogenic.
EF < 1	shows that the concentration of metal is not enriched and might have a natural origin.
EF = 1	shows that the reference value and the metal concentration are identical.

3.7.3 Contamination Factor (CF)

The level of metal pollution was assessed by the contamination factor, which is the ratio of the concentration of a metal under study in the soil sample to that in the background (Hakason, 1980). To calculate the CF, Equation 3.8 was used.

$$\mathrm{CF} = \frac{\mathrm{Mz}}{\mathrm{Mr}} \quad \text{...Eqn 3.8}$$

Where M_χ and M_r are the mean concentrations of the metal contaminants in the soil samples and background reference material, respectively (Chen, Teng, Lu, Wang, 2015) The degree of contamination (C_d), which is based on the CF of the pollutant, was used to describe the extent of contamination of a metal contaminant (Bakare & Adeyinka, 2022) using Equation 3.9.

$$C_d = \sum_{I=1}^{n} \mathrm{CF} \quad \text{.. Equation 3.9}$$

Where n is the number of analyzed elements, and I is the element, CF is the contamination factor and is explained using Table 3.4.

Table 3.3: Scales of contamination factors (levels)

Contamination factor	Contamination level
$CF<1$	Low contamination
$1 \leq CF< 2$	Low to moderate contamination
$2 \leq CF<3$	Moderate contamination
$3 \leq CF< 4$	Moderate to high contamination
$4 \leq CF< 5$	High contamination
$5 \leq CF<6$	High to very high contamination
$CF>6$	Extreme contamination

3.7.4 Pollution Load Index

It is defined as the ratio between a metal's concentration in the sample collected and its concentration in the ambient environment. Hence, the contamination factor was calculated as a measure of the extent of metal pollution by Hakanson, 1980. The Pollution load index was calculated by using the following formula (cheng et al., 2015; Qing et al., 2015)

$$PLI = (CF_1 \times CF_2 \times CF_3 \ldots\ldots\ldots\ldots CF_n)^{1/n} \ldots\ldots\ldots\ldots \text{Equation 3.10}$$

where CF is the contamination factor of any metal, and n is the number of metals analyzed. The PLI values classify the samples into the following classes, which are given in Table 3.4 (Qing et al., 2015).

Table 3.4: Scales of pollution load index (levels)

Range	Classification
$PLI <1$	Unpolluted
$PLI = 1\text{-}3$	Moderately polluted
$PLI = 3\text{-}5$	Highly polluted
$PLI > 5$	Very highly polluted

3.7.5 Potential Ecological Risk Index (PERI)

The potential ecological risk index (PERI) was adopted to calculate the degree of pollution of heavy metals in soils. This was based on the contamination factor of PTEs and the ecological response to the pollutants. The PERI was computed as the summation of individual RIs.

Hakanson 1980, using the Equation 3.11 below.

$\mathbf{PERI} \quad = \sum_{\mathbf{i}}^{\mathbf{n}} \mathbf{TrF} \ \times \mathbf{CF}$ **……………………………Eqn 3.11**

The degree of ecological risk can be classified in Table 3.6 below:

Table 3.5: Scales of pollution ecological risk index (levels)

Ranges	Classification
PERI < 40	Low risk
40 < PERI < 80	Moderate risk
80 < PERI < 160	Considerable risk
160 < PERI<320	High risk
PER > 320	Very high risk

3.8 Human health risk assessment

Risk assessment is meant to be the appraisal of the degree of exposure, expressed as an expected daily intake (Nkansah et al., 2017). Intake of the potentially toxic elements from soil samples via ingestion, inhalation, and skin absorption are computed through four diverse types of parameters which are contact rate, exposure frequency, exposure duration and body weight of the population that might get exposed (Aguilera et al., 2021).

In this work, the USEPA's model was adopted to assess the risk of exposure to heavy metals on human health (Aguilera et al., 2021; Mmaduakor et al., 2022) This model may be used to characterize soil samples on the following assumptions: Humans are exposed to heavy metal in the soil via three main pathways: through ingestion, inhalation, and dermal contact. Relevant exposure parameters of children and adults in the study areas are equal to those of the reference populations. The total non-carcinogenic and carcinogenic risk for every potentially toxic element may be obtained by summing the individual risks from the study areas (Aguilera et al., 2021).

3.8.1 Exposure Assessment

To calculate EDI in mg/kg per day through ingestion (EDIing), inhalation (EDIinh), and dermal contact (EDIdermal), and LADD, the following equations are widely adopted (Huang et al., 2022; Liu et al., 2021; Mihankhah et al., 2020):

$$\mathrm{EDI}_{\mathrm{ing}} = \frac{\mathrm{C \; x \; IngR \; x \; EF \; x \; ED \; x \; CF}}{\mathrm{BW \; x \; AT}} \quad \text{...Eqn. 12}$$

$$\mathrm{EDI}_{\mathrm{inh}} = \frac{\mathrm{C \; x \; InhR \; x \; EF \; x \; ED}}{\mathrm{PEF \; x \; BW \; x \; AT}} \quad \text{..Eqn. 13}$$

$$\mathrm{EDI}_{\mathrm{derma}}\mathrm{l} = \frac{\mathrm{C \; x \; SA \; x \; AF \; x \; ABS \; x \; EF \; x \; ED \; x \; CF}}{\mathrm{BW \; x \; AT}} \quad \text{................................Eqn. 14}$$

$$\mathrm{EDI}_{\mathrm{LADD}} = \frac{\mathrm{C}}{\mathrm{PEF \; x \; ATcan}} \; \mathrm{x} \; \left(\frac{\mathrm{CRchld \; x \; EFchild \; x \; EDchild}}{\mathrm{BWchild}} + \frac{\mathrm{CRadult \; x \; EFadult \; x \; EDadult}}{\mathrm{BWadult}}\right) \quad \text{... Eqn 15}$$

Table 3.6: Scales for calculating exposure assessment (levels)

Factor [units]	**Value** **Child**	 **Adult**
Ingestion rate (IngR) [mg/day]	200	100
Inhalation rate (InhR) [m^3 /day]	7.6	20
Particle emission factor (PEF)	1.36E+09	1.36E+09

Surface of exposed skin area (SA) [cm^2]	2800	5700
Dermal absorption factor (ABS)	0.001	0.001
Skin adherence factor (AF) [mg/cm^2]	0.2	0.07
Duration of exposure (ED) [years]	6	24
Frequency of exposure (EF) [days/year]	350(180)	350(180)
Average time non-carcinogens (AT) [days]	ED*365	ED*365
Average time for carcinogens (At_{can}) [days]	70*365	70*365
Body weight (BW) [kg]	15	70
Heavy metal concentration (C) [mg/kg]	95 percent	95 percent
Conversion factor (CF)	1×10^{-6}	1×10^{-6}

(Odukoya et al., 2018)

In soil samples, C is the concentration of PTE; IngR and InhR are the ingestion and inhalation rates, respectively; EF is the exposure frequency; ED is the exposure duration; BW is the body weight; and $AT_{non-can}$ is the average time for non-carcinogens. Particle emission factor is denoted as PEF; exposed skin area, SA; skin adherence factor, SF; and dermal absorption factor, ABS (Aguilera et al., 2021).

The contact or absorption rate is denoted as CR. For ingestion, CR = IngR; for inhalation, CR = InhR; and for cutaneous contact, CR = SA x AF x ABS. (Aguilera et al., (2021) and Fabiana Meijon Fadul, (2019).

UCL: upper confidence limit.

3.8.2 Non-Carcinogenic Risk Assessment

Hazard Quotient (HQ)

Ingestion, inhalation, and dermal contact hazard quotients (HQing/inh/derm) are calculated by dividing the EDI by the reference dose (RfD) (Nkansah et al., 2017; Tawabini et al., 2023), as shown in Equation 16:

$$HQ_{ing/inh/derm} = \frac{EDI\ ing\ /\ inh\ /\ derm}{RfD} \text{ .... Eqn. 16}$$

Table 3. 7: Reference doses for Oral, dermal, and inhalation for potentially toxic elements

Potentially Toxic Element	Oral RfD	Dermal RfD	Inhalation RfD	CSF
As	3.00E-04	1.23E-04	3.01E-04	1.51E+00
Cd	1.00E-03	1.00E-05	1.00E-03	6.30E+00
Co	2.00E-02	1.60E-02	5.71E-06	
Cr	3.00E-03	6.00E-05	2.86E-05	4.20E+01
Cu	4.00E-02	1.20E-02	4.02E-02	
Fe	8.40E+00	7.00E-02	2.20E-04	
Ni	3.00E-04	2.10E-05	8.57E-05	
Mn	4.60E-02	1.85E-03	1.43E-05	
Ni	2.00E-02	5.40E-03	2.06E-02	8.40E-01
Pb	3.50E-03	5.25E-04	3.52E-03	
V	7.00E-03	7.00E-05	7.00E-03	
Zn	3.00E-01	6.00E-02	3.00E-01	

The most popular RfD is shown in Table 5. when HQ ≤ 1 denotes the absence of any negative health impacts and HQ > 1 denotes the likelihood of negative health consequences. Because it is believed that, after inhalation, the absorption of the particle-bound toxicants will cause similar health consequences to when the particles had been consumed, the inhalation reference dose values are occasionally replaced by oral reference doses (Aguilera et al., 2021).

3.8.3 Hazard Index (HI)

The hazard index is the summation of the HQ for the three exposure routes, e.g., skin contact, inhalation, and ingestion. Based on the HI, it is possible to assess the risks to human health that exceed the value of 1 may develop non-carcinogenic consequences while less than 1 may expect the opposite, (Aguilera et al., 2021; Rabin et al., 2023).

$HI = \sum HQ$ ……………………………………………..Eqn. 17

3.8.3 Carcinogenic Risk Assessment

Equation 18 is generally used to estimate incremental lifetime cancer risk for the carcinogens, e.g., As, Cd, Cr, Ni and Pb.

$ILCR = LADD \times CSF$ …………………………………………..Eqn. 18

The acceptable or tolerable risk is between 10^{-6} and 10^{-4}. If the number of risks is 10^{-6}, then there exists no carcinogenic risk to health due to the soil, but risk values more significant than 10^{-4} signify a high chance of getting cancer (Kabir & Rashid, 2022; Rabin et al., 2023). From the numbers, it can be clearly seen that one additional case in a population of 1,000,000 to 10,000 is acceptable (Aguilera et al., 2021). The CSF refers to the cancer slope factor.

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter presents the findings of the study, focusing on the potentially toxic elements identified in the mining soil samples. It includes a discussion of the descriptive statistics of these elements and their contribution to soil pollution, with comparisons made to the threshold values set by the WHO, FAO, and CCME. A total of 147 soil samples were collected from the mining site in the Gbani community, situated in the Talensi District of the Upper East Region of Ghana.

The results were compared to CCME limits to determine whether there were statistically significant differences between the values obtained at $p<0.05$ using the independent samples t-test and one-way ANOVA. From the elemental analysis, concentrations of the eleven PTEs i.e., Pb, As, Zn, Cu, Ni, Co, Cr, Cd, Mn, Ti, and V, were identified and quantified.

Table 4.1 statistical summary of transect, waste, and hotspot of potentially toxic element

	As	Zn	Cu	Ni	Co	Cr	Cd	Mn	Ti	V	Pb
						Transet					
Mean	76.76	137.30	35.21	46.47	99.13	72.02	6.85	1704.78	4051.16	39.20	6.89
Std. Deviation	73.93	159.30	54.44	84.76	112.30	57.58	7.94	4180.21	911.73	24.67	9.39
Variance	5466.28	25375.58	2963.26	7183.70	12610.90	3315.05	63.00	$1.747\times10^{+7}$	831249.70	608.48	88.12
Range	382.01	930.85	565.78	874.88	1171.86	304.77	82.66	43529.19	6261.25	107.64	61.05
Minimum	6.89	2.93	9.06	15.89	44.57	8.82	5.18	145.55	273.47	15.89	2.82
Maximum	388.90	933.78	574.84	890.77	1216.43	313.59	87.84	43674.74	6534.72	123.53	63.87
25th percentile	18.99	43.14	16.61	18.28	61.53	25.55	5.57	485.15	3551.15	18.28	3.23
50th percentile	62.65	72.71	29.28	30.24	83.84	56.72	5.87	1101.19	4055.29	30.24	3.72
75th percentile	110.60	168.70	40.51	53.72	110.28	107.10	6.32	1897.74	4642.56	53.72	5.02
				Waste Soil							
Mean	29.05	43.23	30.61	18.28	37.37	64.39	20.15	166.01	9927.02	222.13	1488.16
Std. Deviation	75.56	76.64	30.71	15.16	27.33	65.64	16.22	237.95	7513.12	199.35	1342.83
Variance	5709.91	5873.71	943.18	229.88	746.65	4308.39	263.04	56622.12	5.645×10+7	39738.66	1.803×10+6
Range	279.38	279.38	130.07	60.45	90.12	347.88	63.53	798.33	24257.46	585.05	3517.60
Minimum	1.36	1.36	6.34	6.34	9.76	11.29	2.61	2.61	316.80	9.76	1.69
Maximum	280.74	280.74	136.41	66.79	99.88	359.17	66.14	800.94	24574.26	594.81	3519.29
25th percentile	2.97	11.45	9.56	9.47	16.69	35.32	6.17	5.68	2358.00	17.04	3.46
50th percentile	3.18	13.98	17.46	13.25	19.28	59.04	15.74	6.23	12805.52	249.58	1558.44
75th percentile	13.09	22.67	38.99	17.01	59.39	63.51	30.73	312.13	15062.33	331.08	2679.10

Table 4.1 statistical summary of transect, waste, and hotspot of potentially toxic element (con't)

	Hotspot										
Mean	93.09	336.31	107.63	47.69	77.87	103.92	66.96	831.56	27167.38	1103.71	1760.49
Std. Deviation	84.64	554.40	75.99	15.20	39.17	37.73	77.55	1168.22	28000.43	1257.54	1751.42
Variance	7164.13	307358.30	5774.60	231.09	1534.14	1423.25	6014.47	$1.365\times10^{+6}$	$7.840\times10^{+8}$	$1.581\times10^{+6}$	$3.067\times10^{+6}$
Range	195.12	1887.18	269.45	54.70	110.92	125.26	232.71	3364.25	76071.24	3344.18	4330.18
Minimum	3.79	112.51	37.72	25.91	25.91	29.68	5.84	5.84	1936.72	25.91	3.79
Maximum	198.91	1999.69	307.17	80.61	136.83	154.94	238.55	3370.09	78007.96	3370.09	4333.97
25th percentile	8.69	135.85	52.78	39.34	46.61	79.62	6.11	6.11	3241.60	46.61	28.90
50th percentile	57.48	181.00	110.35	47.88	74.69	106.15	29.68	6.59	20972.57	745.89	1936.72
75th percentile	181.97	195.26	125.04	52.78	112.84	127.34	105.95	1260.23	46522.80	1941.74	3241.60
CCME	12	200	63	50	40	64	10	NA	NA	130	140
VROM	29	140	36	35	9	100	0.8	NA	NA	42	85

The descriptive analysis of hotspot, waste soil, and transect data underscores substantial variability in the concentrations of potentially toxic elements, revealing patterns of contamination with profound environmental and health implications. In hotspot data (samples are collected from mining activity sites, which are scattered in the community mostly near or at homes), mean concentrations exhibit a range from 66.96 mg/kg and 27,167.38 mg/kg, for Cd and Ti respectively, with considerable dispersion indicated by standard deviations of 554.399 mg/kg (Zn) and 28000.428 mg/kg (Ti). This heterogeneity is reinforced by variance values 7.840×10^8 $(mg/kg)^2$ (Ti) and 3.067×10^6 $(mg/kg)^2$ (Pb). Similarly, waste soil data (collected from two heaps of mine waste tailings that have been treated with cyanide) showcases wide-ranging means from 18.278 mg/kg for Ni to 9927.022 mg/kg of Ti, with high standard deviations (e.g., 7513.124 mg/kg) and variance (5.645×10^7 mg/kg) illustrating pronounced inconsistencies in contaminant levels. In transect data (perpendicular lines that run through the community), elevated mean values for Mn (1704.777 mg/kg) and Ti (4051.159 mg/kg), paired with high standard deviations (4180.209 mg/kg for Mn), signal substantial variability across samples, as evidenced by variance calculations such as 1.747×10^7 mg/kg for Mn. The range of values across all datasets highlights significant disparities. Hotspot concentrations span from 3.79 mg/kg to a staggering 78007.96 mg/kg, while waste soil ranges from 1.36 mg/kg (As) to 24574.26 mg/kg (Ti), and transect data shows minimum values like 2.93 mg/kg (Zn) and maximums of 43 mg/kg, 674.74 mg/kg (Mn). Percentile analyses further reveal skewed distributions, with higher concentrations clustered in the 75th percentiles. For instance, hotspot data exhibits 75th percentiles of 181.965 mg/kg for As and 46522.8 mg/kg (Ti), while waste soil shows 13.09 mg/kg (As) and 15,062.325 mg/kg (Ti), and transect data reveals As (110.595 mg/kg) and Mn (1897.735 mg/kg), indicating localized hotspots.

Comparing these results with international World Health Organization (WHO), Canadian Council of Ministers of the Environment CCME, and Dutch Target and Intervention Values (VROM) guidelines reveals widespread exceedances across datasets. In hotspot data, elements like Cd surpassed VROM’s limit of 0.8 mg/kg, while in waste soil, mean values such as 166.013 mg/kg exceed WHO's threshold of 20. For transect data, Mn (1704.777 mg/kg) approaches WHO's permissible limit of 2000, and Cd (6.854 mg/kg) significantly exceeds VROM's strict guideline of 0.8 mg/kg. Highly exceedances draw awareness to the possible hazards to human health and the environment that come with extended exposure to extremely high concentrations (Ondayo et al., 2023). The comparative analysis demonstrates that all three datasets, hotspot, waste soil, and transect, exhibit substantial contamination and variability, necessitating urgent interventions. Hotspot data reflect the most extreme concentrations, indicating severe localized contamination, whereas waste soil and transect data suggest more dispersed but still significant contamination levels. Comprehensive monitoring and targeted remediation strategies are essential to mitigate the environmental and health risks of these elevated concentrations of potentially toxic elements.

4.1 The levels of Potentially Toxic Elements in the study area

Table 4.2. Statistical summary of potentially toxic elements

	As	**Zn**	**Cu**	**Ni**	**Co**	**Cr**	**Cd**	**Mn**	**Ti**	**V**	**Pb**
Mean	97.64	133.37	35.56	45	97.12	71.89	6.74	1622.08	3871.99	38.6	7.57
Std. Deviation	154.78	152.97	51.9	79.94	105.97	56.03	7.45	3938.63	1039.3	24.45	10.73
Variance	23956.5	23399.9	2693.77	6390.99	11228.6	3138.82	55.58	1.55×10^{7}	1.08×10^{6}	597.79	115.19
Range	1346.43	930.85	568.5	881.01	1202.31	304.77	85.23	43657.6	6261.25	113.77	62.18
Minimum	1.36	2.93	6.34	9.76	14.12	8.82	2.61	17.14	273.47	9.76	1.69
Maximum	1347.79	933.78	574.84	890.77	1216.43	313.59	87.84	43674.7	6534.72	123.53	63.87
25th percentile	18.68	42.23	15.61	17.78	61.35	29.68	5.59	483.47	3362.62	17.78	3.21
50th percentile	63.12	75.1	29.75	29.26	82.67	56.99	5.91	1090.64	3919.45	29.26	3.73
75th percentile	118.27	152.85	41.49	53.12	111.01	106.15	6.32	1876.25	4515.13	53.12	5.73
CCME	12	200	63	50	40	64	10	NA	NA	130	140
VROM	29	140	36	35	9	100	0.8	NA	NA	42	85

(CCME, 2007; VROM, 2000; World Health Organisation, 2015). P-value 6.37836E-30

4.1.1 Arsenic

The arsenic concentration in the soil from the Gbani mining area ranges from 1.36 mg/kg to 1346.43 mg/kg, with a mean concentration of 97.64 mg/kg, which is three (3) times higher than the Dutch Intervention value of 29 mg/kg (VROM, 2000), and also exceeded the CCME soil quality guidelines of 12 mg/kg (CCME, 2007). A previous study in the same study area Darko et al. (2019) recorded, As concentrations of 59.66 mg/kg which is almost twice the value of this study. As concentrations of 3.8 mg/kg and 5.1 mg/kg from agricultural soils in Akumadan and Offinso were recorded, respectively. The following anthropogenic activities, such as the combustion of fossil fuel in vehicles, and the use of food antibacterial, fungicides, herbicides, pesticides, and paint, are leading to elevated Arsenic in the study area (Rahaman et al., 2021). Arsenic is not a vital element, and excessive exposure can result in various adverse effects to human beings, such as circulatory diseases, lung diseases, hypertension, nervous system diseases, peripheral and skin lesions (Mohammed Abdul et al., 2015).

4.1.2 Zinc

Statistically, the concentrations of zinc range from 2.93 mg/kg to 933.76 mg/kg with a mean of 133.37 mg/kg which is 4.97% below the Dutch Intervention value of 140 mg/kg (VROM, 2000) and 33.32 % lower than the CCME soil quality guidelines of 12 mg/kg (CCME, 2007). An earlier study by Darko et al. (2022) recorded maximum values of 389.7 mg/kg and 155.2 mg/kg, and a mean value of 67.8 mg/kg and 69.9 mg/kg for Amansie and Konongo, respectively, which fall within the range of zinc of this study. Another study by Gyamfi et al. (2019) recorded concentrations ranging from 16.4 mg/kg to 95.8 mg/kg in the Kototeasua study area. Being deficient in zinc can negatively affect our health, and being overly exposed to it can also be hazardous (Akoto & Anning, 2021) since Zinc is an essential micronutrient crucial for human health, plant growth, and animal development. In humans, it supports immune function, wound healing, and growth, acting as a cofactor for enzymes involved in various metabolic processes (Qi et al., 2022). Plants rely on zinc for enzyme activation, protein synthesis, and root development, influencing nutrient uptake and overall growth (Kazapoe et al., 2021). Similarly, animals require zinc for growth, enzyme function, reproduction, and maintaining skin and coat health (Zhao et al., 2021). Zinc deficiency can lead to impaired growth, a weakened immune system, and other health issues across all three domains (Chasapis et al., 2020).

4.1.3 Copper

Copper is a necessary element for plants and animals, but high concentrations can be hazardous. The possible effects of copper contamination on the environment and human health are reasons for increasing concern. The minimum, maximum, and mean values from the table above for copper range from 6.34 mg/kg to 574.84 mg/kg, and a mean of 35.56 mg/kg, respectively, which is below the CCME and VROM values of 63.0 mg/kg and 36.0 mg/kg, respectively (CCME, 2007; VROM, 2000). The mean value, 35.56 mg/kg, is well below these standards, indicating that the Cu level is probably safe. Darko et al. (2019) recorded concentrations ranging from 9.7 mg/kg to 140.1 mg/kg with a mean value of 41.3 mg/kg, which is similar to the current study’s trend. As a result, the high levels of Cu found may have been caused by the distribution of engine exhausts, wear and tear on brake linings and tires, and corrosion of vehicle components from the miners and application of fungicide from the farmers.

4.1.4 Nickel

At high concentrations, the naturally occurring element nickel can be harmful to people, animals, and plants. Soil contamination with nickel is a growing concern due to its potential impact on human health and the environment. The nickel levels in soil ranged from 9.76 mg/kg to 890.77 mg/kg, with a mean of 45.00 mg/kg. The Dutch Soil Quality Standard (VROM, 2000) sets a maximum permissible value of 210 mg/kg for nickel in soil. Our maximum value (890.77 mg/kg) exceeds this threshold, indicating potentially harmful levels of nickel contamination. However, our mean value (45.00 mg/kg) is significantly lower than this threshold (210 mg/kg), suggesting relatively safe levels. Compared to a study conducted by Darko et al. (2019), which recorded a mean value of 38.7 mg/kg, and minimum and maximum values ranged from 8.0 mg/kg to 118.1 mg/kg, which fall within the range of this study. Descriptive analysis from a study by Odukoya et al. (2018) recorded a range of 4.10 mg/kg to 73.80 mg/kg with a mean of 28.29 mg/kg. Nickel toxicity in animals can cause a range of health problems, including gastrointestinal disturbances, anaemia, and liver damage (WHO, 1998). Since mining is predominant in the studied area, Ni enters the soil mainly through anthropogenic activities such as mining (Rizwan et al., 2024).

4.1.5 Cobalt

Soil contaminated with cobalt is a growing concern due to its potential impact on human health and the environment. This study presents a dataset on cobalt levels in soil, ranging from 14.12 mg/kg to 1226.43 mg/kg, with a mean of 35.56 mg/kg. The Dutch Soil Quality Standard and Canadian Soil Quality Guidelines for Environmental and Human Health (CCME, 2007; VROM, 2000) set a maximum permissible value of 240 mg/kg and 300 mg/kg for cobalt in soil, respectively. Our maximum value (1226.43 mg/kg) exceeds these thresholds, indicating potentially harmful levels of cobalt contamination. However, our mean value (35.56 mg/kg) is significantly lower than those thresholds, suggesting relatively safe levels. This discussion also compares these findings to similar work conducted by Odukoya et al. (2018), with a minimum value of 3.50 mg/kg, and a maximum of 32.80 mg/kg, which, together with the mean of 14.41 mg/kg, are within the range of the study. Cobalt enters the soil as a result of the burning of fossil fuels and sewage sludge, phosphate fertilizers, mining and smelting during ore processing. Cobalt toxicity in humans can cause a range of health problems, including gastrointestinal disturbances, anaemia, and liver damage (FAO/WHO, 2008). Prolonged exposure to high levels of cobalt can lead to chronic health effects, including reproductive problems and cancer(USEPA, 2003, 2017) and plant growth inhibition, chlorosis, and root damage can also lead to reduced crop yields and decreased plant productivity (Lotfy & Mostafa, 2014).

4.1.6 Chromium

Excessive amounts of chromium can be hazardous to humans, though chromium is necessary for plants, animals, and humans (Putra et al., 2024). Soil contamination with chromium is a growing concern due to its potential impact on human health and the environment (Balali-Mood et al., 2021). Chromium levels in soil ranged from 8.82 mg/kg to 313.59 mg/kg, with a mean of 71.89 mg/kg. The Dutch Soil Quality Standard (VROM, 2000) sets a maximum permissible value of 380 mg/kg for chromium in soil. The study recorded a maximum value of 313.59 mg/kg below this permissible limit, indicating no potentially harmful levels of chromium contamination. Moreover, our mean value (71.89 mg/kg) was also significantly lower than this threshold, suggesting relatively safe levels. The mean value of the Cr (71.89 mg/kg) as recorded in the study was lower than the

CCME (2007) target value of 87 mg/kg for chromium in soil. This was comparable to the results of Darko et al. (2022), where the maximum and the mean levels of chromium were, (maximum = 103, mean = 30.5) mg/kg, (maximum = 97.4, mean = 41.3) mg/kg, (maximum = 372.7, mean = 82.8) mg/kg and, (maximum = 124.9, mean = 41.8) mg/kg for Akomadan, Offinso, Gbani, and Konongo study areas respectively in which the chromium content found in this study was within the range of the values obtained in Gbani. The chromium content in the soil of the study area may have come from the mining activities and fertilizer application in farming going on in the study area.

4.1.7 Cadmium

Cadmium is a toxic element that can pose serious health risks to the ecosystem (Haider et al., 2021). Soil contaminated with cadmium is a major concern due to its potential impact on human health and the environment (Charkiewicz et al., 2023). Table 4.1 presents cadmium levels in soil, ranging from 2.61 mg/kg to 87.84 mg/kg, with a mean of 6.74 mg/kg. This debate compares these findings to international standards, CCME, (2007); VROM, (2000), with values of (0.8 and 12) mg/kg respectively, the mean concentration for cadmium was higher than the CCME permissible limit but lower than the VROM permissible limit, suggesting relatively safe levels. A study by Mensah et al. (2021)recorded cadmium concentration ranging from 0.2 mg/kg to 1.6 mg/kg, which is lower than the findings of cadmium in this study. Though cadmium concentration has not exceeded the VROM standard, the concentrations present resulted from the use of phosphate fertilizer for farming.

4.1.8 Manganese

Manganese is essential for humans, animals, and plants, but excessive levels can be toxic (Kong et al., 2014). Soil polluted with manganese is a growing concern due to its potential adverse impact on human health and the environment (Affum et al., 2016; Appenroth, 2010). The manganese levels in soil ranged from 17.14 mg/kg to 43674.74 mg/kg, with a mean of 1622.08 mg/kg, and associating these manganese levels in this study with those of a study by Darko et al. (2019), which recorded manganese levels with a mean of 1195.49 mg/kg for Gbani. Another study recorded a maximum of 1055.5 mg/kg and a mean of 373.7mg/kg for Offinso, and a maximum of 380.0 mg/kg and a mean of 191.2 mg/kg for Konongo of which the maximum and the mean concentrations of this study is above these findings, and it was introduced into the soil by the mining activities (Kong et al., 2014).

4.1.9 Titanium

Elevated concentrations of titanium can become a significant health and environmental concern, particularly in nanoparticle form, posing significant health and environmental risks due to their potential toxicity, persistence, and bioaccumulation (Baranowska-Wójcik et al., 2020; Zheng et al., 2021). The potential risks associated with soil contamination raise concerns about its impact on human health and ecosystems. In this study, the mean concentration of titanium in soil was measured at 3871.99 mg/kg, with a range of 273.47 mg/kg to 6534.72 mg/kg. Various studies in Ghana have reported differing levels of titanium in the soil. For instance, research by Mensah et al. (2021) found concentrations between 4.5 mg/kg and 170.4 mg/kg which is below the findings of this study, while another by Arhin et al. (2016), reported 0.1 mg/kg and 0.5 mg/kg as minimum and maximum respectively which were all below the findings of this study. These studies suggested that the titanium levels in the present study area reflected significant contamination when compared to these findings. Exposure to elevated levels of titanium poses various health risks to animals, including anaemia, gastrointestinal problems, and liver damage (WHO, 2015). Long-term exposure can lead to more severe health effects, such as cancer and reproductive disorders (Xu et al., 2021). For plants, titanium is not essential, and excessive concentration can be harmful. Elevated titanium levels can cause root damage, chlorosis, and stunted growth, negatively affecting plant health and development in contaminated soils (Mensah et al., 2021).

4.1.10 Vanadium

High concentrations of the naturally occurring metal vanadium in soil can be dangerous (Chen et al., 2021). Vanadium contamination of soil is a developing concern because of its possible effects on the environment and human health. The vanadium levels in soil from Table 4.1 range from 9.76 mg/kg to 123.53 mg/kg, with a mean of 38.60 mg/kg. Compared to the international standard, CCME (2007) reported a permissible level for vanadium to be 130 mg/kg, which is above the findings of this study. (VROM, 2000). The maximum value for vanadium in this study was dissimilar to the findings reported by Darko et al. (2022) with 788.1mg/kg and 387.1 as maximum and mean values, respectively. Though the vanadium level in the soil was below the permissible limit since it is a naturally occurring metal, they were brought to the surface soil by the mining activities and combustion of fuel used by the trucks used for mining.

4.1.11 Lead

Lead, a toxic element, poses considerable health and environmental risks, impacting humans, animals, and plants (Lei et al., 2016). The potential adverse effects of lead contamination have become an increasing concern. In this study, the lead concentrations in soil are reported with a mean value of 7.57 mg/kg and a range of 1.69 mg/kg to 63.87 mg/kg. According to the VROM (2000), the permissible maximum concentration of lead in soil is 70 mg/kg. While our maximum observed value of 63.87 mg/kg is below this threshold, it is still close, suggesting levels of lead contamination that may pose a risk. Pb can accumulate; therefore, levels can increase with time to toxic levels. According to the CCME (2007), the target value for lead in soil is 140 mg/kg, and our mean value of 7.57 mg/kg falls below this limit, indicating that lead levels in the study area are generally within acceptable standards. Comparatively, a study by Gyamfi et al. (2019) obtained values for Pb ranging from 6.5 mg/kg to 42.5 mg/kg, which falls within the range of this study. A similar study by Kazapoe et al. (2022) recorded values of 3.6 mg/kg and 63.20 mg/kg for minimum and maximum, respectively, which were similar to the concentration of lead in this study. This Pb may be introduced into the soil as a result of mining activities and the smelting of other metals in the study area by the miners and vehicular emissions.

4.1.12 Soil pH and Electrical Conductivity

The pH levels of the soil samples collected from the study area ranged between 6.00 and 13.92. This variation, from slightly acidic to highly alkaline, may be attributed to the presence of alkaline substances in the atmosphere that eventually settle on the ground and alter soil pH (Al Obaidy & Al Mashhadi, 2013). Soil pH plays a crucial role in determining the level of acidity or alkalinity, which in turn affects the stability and movement of metals within the soil (Sadick et al., 2015). Consequently, it influences the mobility of heavy metals in the area. The electrical conductivity (EC) of the soils analyzed ranged from 80 µS/cm to 909 µS/cm, with an average value of 387.50 µS/cm. A correlation analysis revealed that total organic content (TOC) had a weak positive relationship with chromium (Cr) and iron (Fe) (ranging from 0.34 to 0.50, $p<0.05$), and a very weak positive correlation with copper (Cu) (0.26, $p<0.05$). Additionally, TOC showed a strong positive correlation with manganese (Mn) and nickel (Ni) (ranging from 0.50 to 0.57, $p<0.05$), indicating that TOC may significantly affect the concentration of these metals in the soil.

4.2 Pearson's Correlation Analysis of Potentially Toxic Elements in the Mining Site.

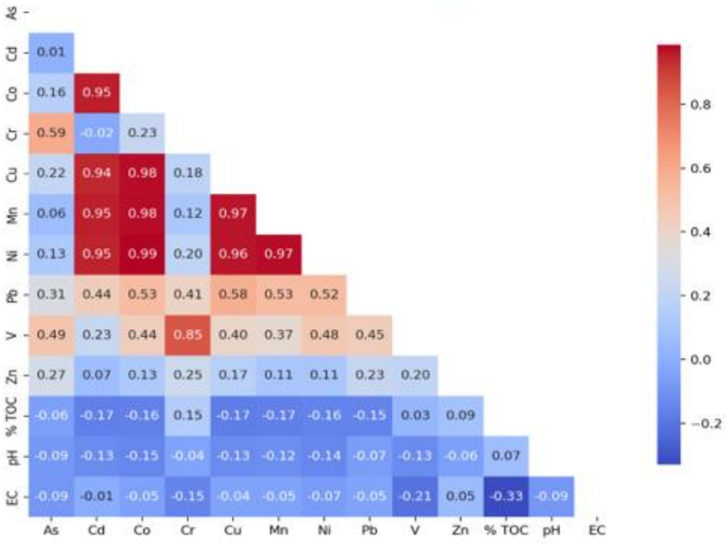

Figure 4.1 Correlation matrix of potentially toxic elements

4.2.1 Correlation Analysis of Potentially Toxic Elements and Soil Parameters

The Pearson correlation matrix was employed to assess the linear relationships among potentially toxic elements (PTEs) and selected soil parameters. The analysis revealed several statistically significant positive correlations among metals, indicating the likelihood of common sources or similar geochemical behavior within the studied area. Notably, cadmium (Cd) exhibited strong positive correlations with cobalt (Co) (r = 0.951), manganese (Mn) (r = 0.951), copper (Cu) (r = 0.941), and nickel (Ni) (r = 0.948). Similarly, Co showed very strong correlations with Cu (r = 0.975), Mn (r = 0.975), and Ni (r = 0.986). These relationships suggest that these elements may originate from a shared anthropogenic source, most likely related to artisanal and small-scale gold mining (ASGM) operations prevalent in the study region. The strength of these associations further implies that these metals may be mobilized and distributed together in the environment, potentially through similar geochemical pathways.

Furthermore, Cu demonstrated strong correlations with Mn (r = 0.965) and Ni (r = 0.965), reinforcing the hypothesis of a shared source and comparable environmental behavior. The clustering of Cd, Co, Cu, Mn, and Ni may reflect contamination from sulfide-bearing ores or associated waste products frequently encountered in ASGM sites. The correlation between arsenic (As) and chromium (Cr) was moderately positive (r = 0.591), suggesting a possible partial overlap in their sources or geochemical associations. A particularly strong correlation was observed between Cr and vanadium (V) (r = 0.845), indicating that these elements may coexist within certain mineral phases or be concurrently released during mining and processing activities. Such associations may also be indicative of lithogenic inputs or the weathering of Cr-V-rich minerals in the geological substrate.

Lead (Pb) showed moderate correlations with Cu (r = 0.581), Cr (r = 0.413), and Co (r = 0.533), which may point to contributions from both geogenic and anthropogenic sources, including lead-acid battery disposal, fuel combustion, and mining tailings. Conversely, As demonstrated weak correlations with Cd (r = 0.012), Mn (r = 0.057), and Ni (r = 0.126), suggesting that its distribution may be influenced by different mechanisms or sources, such as the oxidation of arsenopyrite minerals or localized application of arsenical pesticides, independent of other trace metals. In relation to soil physicochemical properties, the metals generally exhibited weak to moderate negative correlations with total organic carbon (% TOC), indicating limited complexation or adsorption onto organic matter. For instance, Cd (r = -0.167), Co (r = -0.160), Cu (r = -0.170), and Ni (r = -0.159) all had inverse relationships with TOC. This may imply that organic matter is not the dominant factor controlling metal retention in the soil, or that degradation of organic matter reduces its capacity to bind metal ions. An exception was observed with Cr, which showed a slight positive correlation with % TOC (r = 0.151), possibly suggesting some affinity for organic ligands or complexation under specific conditions.

Soil pH showed consistent weak negative correlations with the majority of the PTEs, including Co (r = -0.146), Cu (r = -0.131), and Ni (r = -0.144), which is consistent with established principles of soil chemistry. As soil pH decreases, the solubility of metal ions tends to increase, enhancing their mobility and potential bioavailability. This trend suggests that slightly acidic conditions within the study area may promote the mobilization of PTEs, thereby increasing the risk of ecological and human exposure.
Electrical conductivity (EC), which reflects the ionic strength of the soil solution, also displayed negative correlations with several metals, including Cr (r = -0.151) and V (r = -0.206). This may be indicative of ionic competition in the soil solution or leaching processes that reduce the overall metal concentrations in highly conductive soils. Additionally, the strong negative correlation between EC and % TOC (r = -0.328) implies that increased salinity or ion concentration may be associated with lower organic matter

content, potentially due to microbial degradation or reduced organic input in disturbed or erosion-prone areas.

4.3 Source Apportionment of Potentially Toxic Elements

Source apportionment was utilized to unravel the complex mixture of potential sources contributing to PTE contamination within the study area. Advanced analytical techniques, such as Positive Matrix Factorization (PMF) and Principal Component Analysis (PCA), were employed to distinguish between sources associated with mining activities and those from background origins. This approach identifies the primary contributors to contamination and quantifies their relative impact on soil quality, allowing for a more nuanced understanding of risk factors in this region.

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4.3.1 Source Apportionment by Principal Component Analysis

Table 4.3 Component Loadings of Potentially Toxic Elements

	PC1	PC2	PC3	Uniqueness
Mn	0.98			0.02
Cd	0.98			0.03
Ni	0.97			0.02
Co	0.97			0.02
Cu	0.96			0.03
Pb	0.51	0.47		0.49
Cr		0.95		0.10
V		0.88		0.13
As		0.64	0.58	0.25
Ti			-0.84	0.18
Zn			0.48	0.67

Note. The applied rotation method is varimax

Table 4.4 Component Characteristics of Potentially Toxic Elements

	Unrotated solution			Rotated solution		
	Eigenvalue	Proportion var.	Cumulative	SumSq. Loadings	Proportion var.	Cumulative
Component 1	5.66	0.51	0.51	5.16	0.47	0.47
Component 2	2.26	0.21	0.72	2.55	0.23	0.70
Component 3	1.15	0.10	0.82	1.36	0.12	0.82

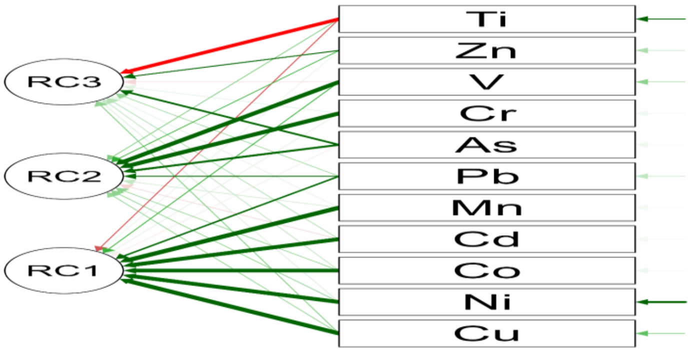

Figure 4.2: Component loadings of potentially toxic elements

The variables were condensed into three models, which accounted for 82 % of the total variance, and three principal components (PCs) whose eigenvalues were greater than one was extracted. The outcomes of the main component analysis are presented in Tables 4.2 and 4.3, and Figure 4.2.

PCA 1 with a total eigenvalue of 5.665, which is loaded with Mn, Cd, Co, Cr, Ni, Cu, and Pb, accounted for 51.5% of the total variability of the source of the metals, with coefficients of 0.984, 0.977, 0.973, 0.970, 0.957, and 0.515, respectively. Since Cd and Cr are associated with the production of fertilizer and pesticides, elements in PCA 1 may be coming from anthropogenic activities such as fertilizer and pesticide application in farming, which is prevalent in the study area.

PCA 2 was constituted with Pb, Cr, V, and, As with an eigenvalue of 2.256, explained 20.5% of the total variability of the source of the metals, which have coefficients of 0.0.476, 0.946, 0.882, and 0.643, respectively. Meanwhile, Cr, which has a correlation value of 0.946, and chromium naturally occurs in minerals such as chromite ($FeCr_2O_4$). Therefore, elements in PCA 2 may come from anthropogenic activities such as mining and farming, which are predominant in the study area.

PCA 3, having a total eigenvalue of 1.152, is full of As, Ti, and Zn, and explained 10% of the total variability of the source of the metals. Since Ti was predominant, the source of the metals may be coming from the geogenic source.

4.3.2 Source Apportionment by Positive Matrix Factorization

The Positive Matrix Factorization (PMF) receptor model was used to compute the contribution and source of pollutants in the environment (Yang et al., 2022). To verify accuracy, the residual matrix E was controlled by minimizing the value of the critical parameter (Q). The model was employed to establish the lowest critical parameter (Q) value where the residue between -1 and +1 for (3-6) was 20 times for the best solution to be obtained. The correlation coefficient (r^2) values for As, Cd, Cr, Cu, Ni, Pb, and Zn between the observed and the predicted values were greater than 0.96, indicating a strong correlation. The strong correlation between the observed and the predicted value signifies that the analysed heavy metals were well apportioned by the PMF model, and the results are accurate, reliable, and applicable.

In the Gbani soil samples, the source profiles and their contributions to heavy metals are shown in Figures 4.3 and 4.4. The sum of the heavy metals' contributions decreased as follows: Factor 4 (24%), Factor 5 (23%), Factor 1 (20%), Factor 2 (18%), and Factor 3 (15%). In this study, Factor 1 was heavily loaded with Cr (59.99%) and moderately loaded with Cd, Cu, Ni, Pb, and As with loadings of 20.07%, 16.42%, 13.61%, 13.59%, and 13.56%, respectively. Cr dominated Factor 1. According to research, the accumulation of Cr in soil may be caused by industrial processes, agricultural practices, and parent material pedogenesis (Amir et al., 2021). In the current study, it can be observed from the results that the total Cr concentration in the Gbani soils was significantly lower than background values and even below the environmental quality criteria. Moreover, the EF and Igeo values of Cr show minimal enrichment of the metal in the soils of the studied area. (Figures 4.3 and 4.4). Furthermore, Cu and Pb could originate from the atmospheric deposition; thus, the species loadings indicate a significant geogenic process. Factor 2 was described by As (25.93%), Cr (21.82%), Pb (26.85%), Ni (23.27%) and Zn (23.84%). Earlier studies indicate that As, Pb, and Ni in soils are associated with human-induced activities such as mining and farming. (Gworek et al., 2020; Haghnazar et al., 2023; Madhav et al., 2024). The field observation revealed unregulated mining and farming activities in this area, which could be a source of As, Pb, and Cr in soils. Consequently, Factor 2 was considered as a result of anthropogenic impacts such as mining and farming.

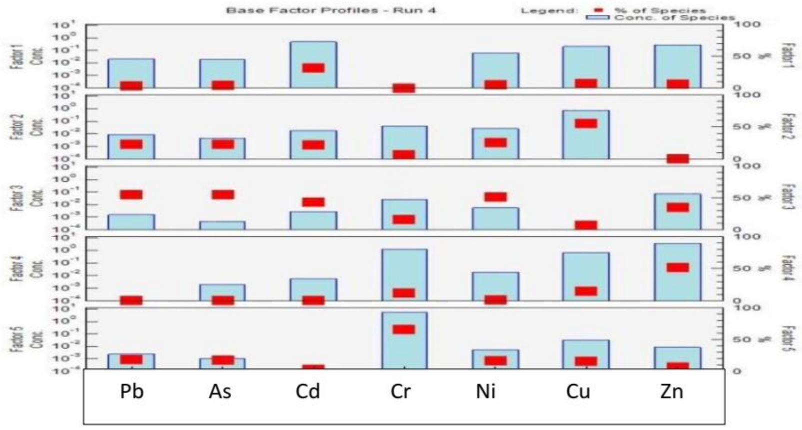

Figure 4.3: Source profiles and source contributions of soil heavy metals at Gbani

Factor 3 was loaded significantly on Zn (58.52%), moderately on Cr (10.29%), and Cd (8.48%) low weight for Pb (3.43%), As (3.91%), and Ni (5.01%). Fertilizers are important Zn and Cd sources for agricultural soils in Ghana. A study by (Nartey et al., 2012), highlighted that the use of chemical fertilizers increases heavy metal (Cd, Cu, Pb, and Zn) content in soil. Considering this, Factor 3 was regarded as an agricultural source. Factor 4 was dominated by Cu (65.17%), which was recognized as the source of air pollution and fuel combustion, vehicular bodies containing metals, and the application of fertilizers and pesticides. The EF value of Cu indicates no enrichment of soil in the study area (Figure 4.4). This suggests that Cu may enter the soil from natural sources such as pedogenic processes. (Uzarowicz et al., 2024). Factor 5 was characterized by Cd (39.65%), Pb (36.73%), As (36.58%), Ni (34.64%), and Zn (11.09%). Soil contamination with Cd, Pb, and As could be attributed to agricultural practices such as the use of phosphate fertilizers, organic manure, and pesticides. Field observations suggest a huge quantity of chemical fertilizers being applied in agricultural areas in Gbani. Based on EF and Igeo values, Gbani soils have a moderate to significant enrichment of As, Cd, and Pb

(Figures 6A and 7A). Again, Gbani soils could be contaminated with As, Pb, and Ni through mining Activities. Field studies revealed that mining activities are unregulated throughout the study area. Considering the significant contributions of As, Cd, Ni, and Pb in this factor, it can be attributed to anthropogenic activities such as mining and agriculture.

4.4 Contamination Assessment of Potentially Toxic Elements in Soil

An important issue for the environment and human health is the contamination assessment of potentially hazardous elements in mining areas. The degree of potentially toxic element contamination in the soil samples from the mining area was determined using pollution indices.

4.4.1 Contamination Factor

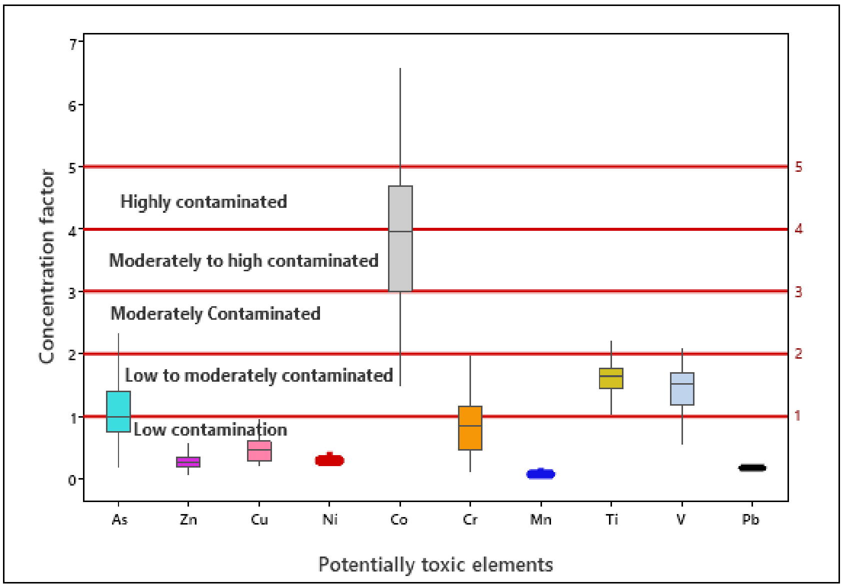

Figure 4.4: Contamination factor of potentially toxic elements

In this investigation, the contamination factor was employed as a contamination estimation method. The soil's metal enrichment is indicated by the contamination factor. Figure 4.5 displays the CF values. CF is evaluated on a scale of 1 to 6, representing little to very high contamination, depending on the extent of contamination. According to this study, the levels of As, Co, Ti, and V contamination factors were all greater than 1, indicating a moderate level of contamination in the study area. The values indicated low contamination for Zn, Cu, Ni, Cr, Mn, and Pb, but very high contamination for Cd, with a CF value of 19.33.

4.4.2 Geo-accumulation index (Igeo)

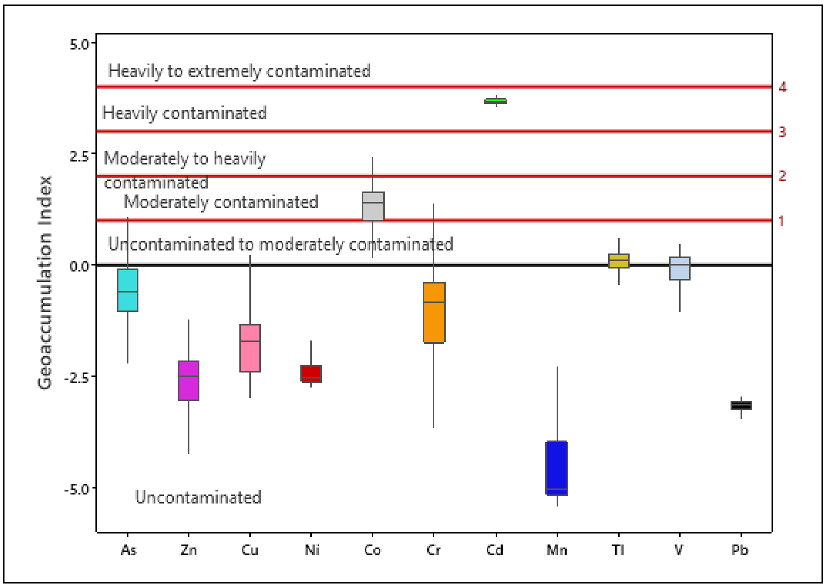

Figure 4.5: Geo-accumulation index (Igeo) of potentially toxic elements

The Geo-accumulation Index (Igeo) is a valuable tool for assessing metal contamination in sediments and soils, providing insights into the degree of enrichment and potential environmental risks. From Figure 4.6, the average values of Igeo decreased in the order of Ti>Cu>Co>Ni>Cd>Pb>Zn>V>Cr>Mn. Upon calculating the Igeo values for the provided mean concentrations of Zn (-0.59), Cu (-2.64), Ni (-1.72), Co (-2.36), Cr (1.32), Cd (-1.19), Mn (3.68), Ti (-4.55), V (0.03), and Pb (-0.12), a suggested understanding of the contamination levels emerges. Manganese (Mn) stands out as heavily contaminated with an Igeo value of 3.68, indicating significant enrichment and potential ecological harm. These elevated levels warrant immediate attention and remediation efforts to mitigate adverse effects on the environment and human health. Chromium (Cr), with an Igeo value of 1.32, falls within the moderately contaminated range, suggesting some enrichment. While chromium contamination is less critical compared to manganese, it still necessitates consistent monitoring and potential mitigation measures to prevent further accumulation in the environment. The remaining elements, zinc (Zn), nickel (Ni), cadmium (Cd), and lead (Pb), exhibit Igeo (Index of Geoaccumulation) values within the range of unsaturated to moderately contaminated. In contrast, copper (Cu), cobalt (Co), and titanium (Ti) fall within the unsaturated range, indicating minimal enrichment. Notably, vanadium (V), with an Igeo value of 0.03, lies near the threshold between unsaturated and moderately contaminated, highlighting the need for careful observation to prevent future environmental risks.

4.4.2 Pollution Load Index and Modified Degree of Contamination

The Pollution Load Index (PLI) is a widely used metric for assessing soil contamination. The range of PLI values varies depending on the location and type of pollutants present. Based on the analysis provided, the mean PLI value is 8.191198, with a minimum value of 3.06E-14 and a maximum value of 1122.165. In comparison to international standards, the World Health Organization (WHO) and the Food and Agriculture Organization (FAO) recommend a maximum PLI value of 1 for soil (WHO/FAO, 2016). The Dutch Ministry of Housing, Spatial Planning, and the Environment (VROM) set a maximum PLI value of 10 for soil (VROM, 2017). The Dutch standards are generally considered more stringent than WHO/FAO guidelines. In Ghana, West Africa, and Africa, there are limited studies on PLI values in soil. However, a study in Ghana found PLI values ranging from 0.02 to 14.1 (Boateng et al., 2019). Another study in West Africa reported PLI values between 0.1 and 10.5 (Sagna et al., 2020). A review of African studies found PLI values ranging from 0.01 to 100 (Kumar et al., 2020). Globally, PLI values vary widely depending on the location and type of pollutants present. A study in China reported PLI values ranging from 0.1 to 100 (Liu et al., 2019). Another study in India found PLI values between 0.01 and 10 (Singh et al., 2020). The high PLI values observed in this analysis (up to 1122.165) indicate severe soil contamination, which can have significant environmental and human health impacts. Soil pollution can lead to the accumulation of toxic substances in the food chain, contaminating crops and water sources (Chen et al., 2018). Human exposure to polluted soil can cause a range of health problems, including cancer, neurological damage, and reproductive issues (WHO, 2018).

4.4.4 Enrichment Factor (EF)

Quantifying heavy metal pollution from geogenic and lithogenic sources as well as anthropogenic activities is made easier by evaluating the degree of enrichment in the soil (Kazapoe et al., 2022). It is worth mentioning that EF-standardised metals with reference elements such as Fe (Gyimah et al., 2022). The boxplot illustrates the distribution of EF values for arsenic (As), zinc (Zn), copper (Cu), nickel (Ni), cobalt (Co), chromium (Cr), manganese (Mn), titanium (Ti), vanadium (V), and lead (Pb). The red reference line at EF = 1 represents the baseline level, indicating elements that are predominantly of natural origin, whereas values greater than 1 suggest enrichment due to human activities. Among the analyzed elements, cobalt (Co) exhibits the highest enrichment factor, with a median EF value significantly above 6 and an upper range exceeding 14. This indicates a considerable level of anthropogenic input, likely linked to mining activities, industrial effluents, or other anthropogenic sources prevalent in the study area. Similarly, titanium (Ti) and vanadium (V) show notable enrichment, with their EF distributions suggesting moderate to high contamination levels. These elements could be associated with mineral processing, vehicular emissions, or industrial discharges. Arsenic (As) presents moderate enrichment, with EF values mostly above 1, suggesting a mixed origin from both natural geochemical processes and anthropogenic inputs, possibly related to mining and agricultural activities. The boxplot reveals that Zn, Cu, and Pb have relatively low EF values, clustering around the baseline, indicating minimal anthropogenic influence on these metals in comparison to other elements. However, slight deviations above EF = 1 suggest localized contamination, which could be attributed to the disposal of metal-containing waste or atmospheric deposition from industrial sources. Nickel (Ni) and chromium (Cr) demonstrate relatively low EF values, indicating their predominantly lithogenic origin with minimal anthropogenic enrichment. Manganese (Mn) appears to have the lowest EF among the analyzed elements, remaining close to the baseline level, suggesting it is primarily sourced from natural geological formations rather than anthropogenic activities. The observed variations in EF across different metals highlight the complex interplay between natural and anthropogenic factors influencing metal contamination in the study area. Elements such as Co, Ti, and V, which exhibit significant enrichment, warrant further investigation to ascertain their primary sources and potential environmental and human health implications. Moreover, the presence of even moderate enrichment in As suggests the need for continuous monitoring and potential remediation strategies to mitigate associated risks. Overall, this EF assessment provides a valuable framework for understanding contamination patterns and guiding environmental management efforts in areas impacted by potentially toxic elements.

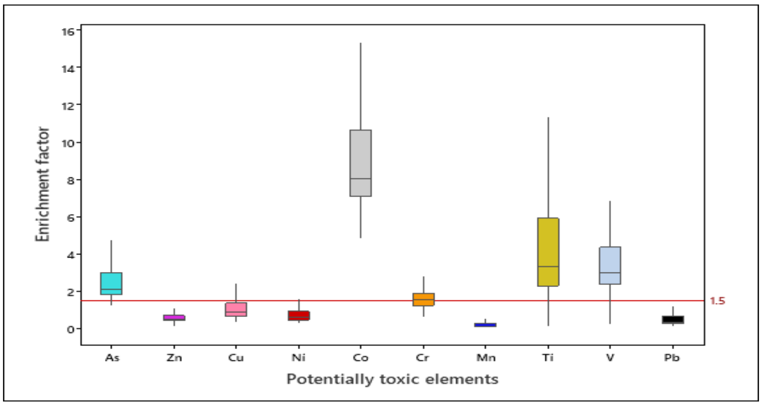

Figure 4.6: Enrichment factor of potentially toxic elements

4.5 Potential Ecological Risk (PER) and Potential Ecological Risk Index (PERI)

Table 4.5: Potential Ecological Risk (PER) and Potential Ecological Risk Index (PERI)

Variable	Mean	StDev	Variance	Minimum	Maximum	Range	Skewness	Kurtosis
As	12.44	9.82	96.34	1.69	55.02	53.32	2.62	7.92
Zn	0.28	0.14	0.02	0.05	0.85	0.81	1.16	2.99
Cu	2.92	2.91	8.45	0.93	26.27	25.33	4.61	30.92
Ni	1.62	1.69	2.87	1.11	20.67	19.56	10.64	120.03
Co	20.37	11.78	138.71	7.32	134.58	127.26	6.82	65.23
Cr	1.71	1.06	1.11	0.18	7.69	7.50	1.34	6.31
Cd	579.85	101.32	10266.20	524.00	1707.00	1183.00	10.29	114.67
Mn	0.08	0.09	0.01	0.03	0.65	0.61	3.33	13.41
Ti	1.57	0.30	0.09	0.12	2.31	2.18	-1.26	3.99
V	2.86	0.71	0.51	0.45	4.18	3.73	-0.69	0.05

Pb	0.96	0.57	0.33	0.67	5.70	5.04	5.64	37.99
PERI	624.7	119.1	14190.3	540.1	1914.6	1374.5	9.49	102.67

The analysis of Potential Ecological Risk (PER) and Potential Ecological Risk Index (PERI) based on the data in Table 4.4 reveals a varied level of risk posed by different metals to the environment. For most metals, including arsenic, zinc, copper, nickel, cobalt, chromium, manganese, titanium, vanadium, and lead, the mean PER values are classified as low risk (PER < 40). However, certain metals like arsenic, cobalt, and lead exhibit skewness and kurtosis values that suggest occasional spikes at risk levels, with some locations experiencing moderate or considerable risk. For instance, arsenic has a mean PER of 12.437, indicating low risk overall, but a skewness of 2.62 suggests some areas might have moderate risks. Similarly, cobalt, while having a low mean PER of 20.37, has a maximum value of 134.58, indicating that certain areas could fall into the considerable risk category. In contrast, cadmium (Cd) poses a very high ecological risk with a mean PER of 579.85, far exceeding the 320 thresholds for very high risk. The high skewness (10.29) and kurtosis (114.67) associated with cadmium indicate significant outliers, with some areas showing extreme contamination levels, as highlighted by a maximum PER of 1707.00. This suggests that cadmium is a major contributor to the overall ecological threat in the study area. Other metals such as zinc, copper, nickel, and lead show generally low risk, though skewness values suggest occasional high-risk occurrences, particularly for lead, which has a skewness of 5.64 and a maximum PER of 5.7025. The PERI, which aggregates the risks from all metals, is calculated to be 624.7, classifying the overall ecological risk as very high (PERI ≥ 600). The high standard deviation (119.1) and the large range (1374.5) suggest significant variability in risk levels across different locations. Metals like cadmium, with their exceptionally high-risk values, heavily influence the PERI. The skewness (9.49) and kurtosis (102.67) further emphasize the presence of extreme outliers, indicating that some areas face disproportionately higher ecological risks. The very high PERI underscores the need for urgent environmental management strategies, particularly targeting the mitigation of cadmium contamination, to reduce potential harm to ecosystems and prevent further degradation.

4.6 Human Health Risk Assessment

Assessment of human health risks associated with environmental contaminants is a critical aspect of environmental health research (Dash et al., 2021). This section presents a thorough analysis of this risk assessment using Hazard Quotient (HQ) values for ingestion, inhalation, and dermal exposure pathways in both children and adults. Human health risk assessment is a key process to evaluate the potential adverse health effects of exposure to hazardous substances (Appiah-Opong et al., 2021). This process involves assessing both non-carcinogenic and carcinogenic risks for different population groups, such as children and adults, across various exposure routes, including ingestion, inhalation, and dermal contact. The data provided on Hazard Quotients (HQ) across these exposure routes offers important insights

into the associated health risks.

4.6.1 Non-Carcinogenic Risk Assessment

Table 4.6: Non-Carcinogenic Risk Assessment of some PTEs

	HQing		HQinh		HQ derm		HI	
PTEs	Children	Adults	Children	Adult	Children	Adult	Children	Adult
As	3.88E-01	1.50E+00	1.00E-04	2.84E-04	5.79E-03	1.18E-02	3.93E-01	1.51E+00

Cd	1.93E-02	1.50E+01	3.53E-01	7.09E-06	7.91E+02	7.95E+02	7.91E+02	8.10E+02
Co	4.31E+00	4.62E-01	6.29E-03	1.78E-02	6.89E-03	1.41E-02	4.32E+00	4.93E-01
Cr	3.39E-01	5.00E-01	9.21E-04	2.61E-03	1.52E-03	3.09E-03	3.41E-01	5.06E-01
Cu	2.34E-02	2.51E-03	3.23E-07	9.17E-07	1.87E-05	3.82E-05	2.34E-02	2.55E-03
Mn	1.55E+00	1.66E-01	4.22E-02	1.20E-01	1.74E-03	3.54E-03	1.59E+00	2.89E-01
Ni	3.18E-03	9.10E-01	8.01E-07	2.27E-06	3.88E-04	9.10E-01	3.57E-03	1.82E+00
Pb	2.94E-03	8.50E-03	7.79E-07	2.21E-06	1.58E-04	3.22E-04	3.10E-03	8.82E-03
V	1.69E-03	1.81E-04	2.01E-06	5.70E-06	8.11E-04	1.65E-03	2.50E-03	1.84E-03
Zn	5.90E-03	7.91E-02	1.64E-07	4.65E-07	9.44E-06	1.92E-05	5.91E-03	7.91E-02

The non-carcinogenic health risk assessment based on hazard quotients (HQ) and hazard index (HI) for different exposure routes (ingestion, inhalation, and dermal contact) revealed significant variations in potential risks among the studied potentially toxic elements (PTEs), with notable differences between children and adults.

Arsenic presented a significant non-carcinogenic risk through ingestion in adults, with an HQ_ing of 1.50, exceeding the safety threshold value of 1. For children, although the ingestion pathway HQ_ing was lower (3.88E-01), the cumulative exposure (HI) reached 3.93E-01 in children and 1.51 in adults. This suggests that adults are at a higher risk of arsenic toxicity, potentially due to prolonged exposure or bioaccumulation. While dermal and inhalation pathways contributed minimally to the total hazard for As, ingestion remained the dominant route of exposure.

Cadmium presented the most alarming non-carcinogenic risk, particularly through dermal exposure. For children and adults, HQ_derm values were 791 and 795, respectively, which are extremely high and suggest severe exposure risks through skin contact with contaminated soil. Interestingly, the ingestion HQ_ing for adults was also exceptionally high (15.0), exceeding safety thresholds by a wide margin. The total hazard index (HI) for Cd was 7.91E+02 (children) and 8.10E+02 (adults), indicating a critical health threat for both groups. These findings strongly suggest that cadmium contamination in the area is a significant environmental and public health concern.

Cobalt also exceeded the safety threshold, particularly in children, with an HQ_ing of 4.31, far above the acceptable limit. The adult ingestion $HQ_{\_ing}$ was 0.462, still below the threshold but notably higher than most other metals. The overall hazard index was 4.32 (children) and 0.493 (adults), indicating children are disproportionately affected by cobalt exposure. Dermal and inhalation pathways contributed less significantly, though their combined effect in children still warrants attention.

Chromium, while generally within acceptable limits, approached the risk threshold for ingestion, especially in adults ($HQ_{\_ing}$ = 0.5). Children exhibited a total HI of 0.341, indicating moderate risk. These results suggest that chromium exposure might become a concern if concentrations increase or if exposure duration extends, particularly in adult populations.

Copper, manganese, and vanadium exhibited relatively low non-carcinogenic risks across all pathways. However, manganese showed a higher hazard index in children (1.59) due to elevated ingestion exposure (HQ_ing = 1.55), indicating potential health implications for children living in the contaminated area. This underscores the vulnerability of children to environmental manganese exposure, likely due to their higher intake-to-body-weight ratio and frequent hand-to-mouth behavior.

Nickel demonstrated a unique exposure profile where the adult hazard index was significantly higher (1.82) compared to children (0.00357), largely due to the dermal and ingestion pathways. This suggests that adults, perhaps due to occupational or environmental behaviors, face higher nickel-related risks in the study area.

Lead, a well-documented neurotoxin, exhibited HQs below 1 across all pathways for both children and adults. However, because of the element's cumulative and irreversible health impacts, even low HQs (e.g., 0.00882 in adults) remain concerning, especially in vulnerable populations like children. Continuous monitoring is therefore necessary to avoid long-term exposure and associated neurodevelopmental effects.

Vanadium and zinc posed minimal non-carcinogenic risks, with hazard indices well below 1 for both populations. Nonetheless, the presence of these elements in trace amounts indicates persistent environmental contamination, and although they may not cause immediate health concerns, chronic exposure over time could amplify risks, especially when combined with other elements.

The cumulative hazard index (HI) results emphasize that children are generally more at risk from PTE exposure than adults, particularly for cobalt, manganese, and cadmium. However, adults demonstrated greater vulnerability to arsenic, cadmium (through ingestion), and nickel, suggesting age-specific risk dynamics in the study area. The most concerning findings relate to cadmium and cobalt, both of which presented critical hazard levels across multiple exposure routes, thus requiring urgent public health interventions.

These results underline the need for effective soil remediation strategies, stricter environmental regulations, and routine health monitoring in communities affected by artisanal and small-scale mining (ASM). Furthermore, public health awareness campaigns should be initiated to educate local populations, especially children and women of reproductive age, about potential exposure risks and safety measures. Finally, the findings provide important insights into the ecological and health impacts of PTEs, which could influence hypertension prevalence indirectly, as chronic exposure to heavy metals like lead, arsenic, and cadmium has been linked to elevated blood pressure and renal dysfunction in other studies. Hence, mitigating PTE exposure may also contribute to improved hypertension control and prevention in the Asante Mampong area.

4.6.2 Carcinogenic Risk Assessment

Table 4.6: Carcinogenic Risk Assessment of some PTEs

		Carcinogenic				
		As	**Cd**	**Cr**	**Ni**	**Pb**
CRing	Children	**1.63E-03**	**1.35E-03**	**4.74E-04**	**5.41E-04**	8.39E-07
	Adults	**1.74E-04**	**1.45E-04**	5.08E-05	5.79E-05	8.99E-08
CRinh	Children	4.55E-07	1.57E-08	3.93E-11	5.63E-14	1.15E-09
	Adult	1.29E-06	4.47E-05	3.14E-06	3.93E-08	3.27E-09
CRderm	Children	6.36E-06	2.16E-06	3.03E-05	8.65E-07	6.64E-09
	Adult	1.30E-05	4.40E-06	6.19E-05	1.76E-06	1.35E-08

From Table 4.6, the carcinogenic risks associated with five potentially toxic elements (PTEs), arsenic, cadmium, chromium, nickel, and lead were evaluated for both children and adults through three main exposure pathways: ingestion (CRing), inhalation (CRinh), and dermal contact (CRderm). The assessment aims to determine whether the cumulative risk exceeds the acceptable threshold established by the United States Environmental Protection Agency (USEPA), which is between 1E-06 and 1E-04 (Baah et al., 2021).

The ingestion pathway is typically the most significant route of exposure, especially in contaminated environments. The calculated CRing values for children were consistently higher than those for adults across all the metals assessed, indicating that children face a greater carcinogenic risk from direct ingestion of contaminated soil or dust. Arsenic presented the highest ingestion risk for children at 1.63E-03, which is significantly higher than the value for adults (1.74E-04). This suggests that children are more vulnerable to arsenic exposure due to their increased hand-to-mouth activity and higher soil ingestion rates relative to body weight. Similarly, cadmium showed a higher ingestion risk for children (1.35E-03) compared to adults (1.45E-04), highlighting the potential for bioaccumulation and long-term health consequences. Chromium ingestion risk for children (4.74E-04) was nearly ten times higher than for adults (5.08E-05), reflecting children's increased sensitivity to chromium toxicity. Nickel ingestion risk values were 5.41E-04 for children and 5.79E-05 for adults, showing a similar trend of higher risk in children. Lead ingestion posed a relatively lower carcinogenic risk compared to the other metals, with values of 8.39E-07 for children and 8.99E-08 for adults. However, lead remains a significant neurotoxicant, warranting attention even at low exposure levels.

Inhalation risk tends to be lower compared to ingestion and dermal contact, but it remains an important pathway in areas with high levels of airborne contaminants. The inhalation risk for arsenic was higher for adults (1.29E-06) than for children (4.55E-07), indicating that adults may be more exposed to arsenic through inhalation due to higher breathing rates and increased occupational exposure. Cadmium inhalation risk for children (1.57E-08) was substantially lower than for adults (4.47E-05), reflecting differences in exposure patterns and metabolic capacity. Chromium inhalation risk for children (3.93E-11) was negligible compared to adults (3.14E-06), suggesting that inhalation is not a significant pathway for chromium-related cancer risk in children. Nickel inhalation risk was minimal for children (5.63E-14) but more pronounced for adults (3.93E-08), consistent with adult occupational exposure scenarios. Lead inhalation risk was higher in adults (3.27E-09) compared to children (1.15E-09), but the overall value remained low.

Dermal absorption represents another key exposure pathway, particularly in contaminated environments where direct skin contact with soil or dust is likely. Arsenic dermal risk for children (6.36E-06) was nearly half that for adults (1.30E-05), reflecting differences in skin permeability and exposure duration. Cadmium dermal risk for children (2.16E-06) was lower than for adults (4.40E-06), though both values were below the threshold for significant carcinogenic concerns. Chromium dermal risk for children (3.03E-05) was about half the value for adults (6.19E-05), suggesting a higher absorption potential in adults due to increased body surface area. Nickel dermal risk was higher for adults (1.76E-06) than for children (8.65E-07), but the values remained within acceptable limits. Lead dermal risk was very low for both children (6.64E-09) and adults (1.35E-08), indicating limited percutaneous absorption and a lower carcinogenic threat through skin contact.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The study identified and quantified the concentrations of eleven PTEs (Pb, As, Zn, Cu, Ni, Co, Cr, Cd, Mn, Ti, and V) in soil samples from the Gbani mining area. The results revealed elevated levels of several PTEs, with some exceeding the permissible limits set by international regulatory agencies such as WHO, CCME, and VROM. For instance, arsenic (As) and cadmium (Cd) concentrations were significantly higher than the recommended thresholds, indicating severe contamination.

The concentrations of PTEs were compared with international regulatory standards, revealing widespread exceedances. For example, cadmium (Cd) levels were significantly higher than the VROM intervention value, while manganese (Mn) approached the WHO permissible limit. These exceedances underscore the potential environmental and health risks associated with prolonged exposure to these contaminants.

Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) were employed to identify the probable sources of heavy metal pollution. The analysis revealed that anthropogenic activities, particularly mining and agricultural practices (e.g., the use of fertilizers and pesticides), were the primary contributors to soil contamination. Geogenic sources also played a role, especially for elements like titanium (Ti).

The contamination status was assessed using various indices, including the Contamination Factor (CF), Pollution Load Index (PLI), Geo-accumulation Index (Igeo), and Enrichment Factor (EF). The results indicated moderate to high levels of contamination for several elements, with cadmium (Cd) showing the highest contamination factor. The PLI values further confirmed severe soil contamination, with PTEs, in some areas exhibiting extremely high pollution levels.

The Potential Ecological Risk Index (PERI) revealed a very high ecological risk, primarily driven by cadmium (Cd) contamination. Other metals, such as arsenic (As) and cobalt (Co), also contributed to the overall ecological risk, albeit to a lesser extent. The findings highlight the urgent need for environmental management strategies to mitigate these risks.

The human health risk assessment, conducted for both children and adults, indicated significant non-carcinogenic and carcinogenic risks. Ingestion was identified as the primary exposure pathway, with titanium (Ti) and lead (Pb) posing the highest risks. Children were found to be more vulnerable to the carcinogenic effects of PTEs, particularly through ingestion and dermal exposure. The Hazard Index (HI) for adults was notably high, driven by lead (Pb) exposure through dermal contact.

5.2 Recommendations

To reduce the risks of PTE contamination in the study area, the following suggestions are put forth, considering the research's findings:

There is a need for stricter monitoring of soil in artisanal mining areas to ensure adherence to environmental standards. Regular assessments will help identify emerging contamination zones and facilitate timely interventions. Additionally, regulatory frameworks governing small-scale mining should be strengthened to enforce stricter limits on the release of toxic substances into the environment by the EPA.

Initiating soil remediation projects, such as phytoremediation, can help reduce heavy metal concentrations in affected areas. The use of hyperaccumulator plant species could assist in either removing or immobilizing harmful metals within the soil. In areas where immediate remediation is not feasible, protective measures, such as covering contaminated soil with clean soil or barriers, should be implemented to reduce direct human exposure.

Educational campaigns should be launched to raise awareness among residents, particularly those in high-risk areas, about the dangers of PTE exposure and practical steps to minimize contact with contaminated soil. Health screening programs targeting children and adults living near mining sites should be implemented, with a focus on early detection of health issues associated with heavy metal exposure, such as lead poisoning and respiratory problems, by the WHO (FAO/WHO, 2008).

The adoption of environmentally friendly mining techniques that minimize soil disruption and the release of hazardous materials should be promoted. Training programs for artisanal could help foster safer and more sustainable mining practices. Additionally, collaboration with local authorities and mining cooperatives to provide access to technologies that reduce environmental contamination, such as improved ore processing methods, would limit the generation of hazardous waste by the EPA (Hadzi et al., 2019; Sako & Nimi, 2018).

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APPENDICES

Appendix A1: Table showing pH and electrical conductivity

SAMPLE	Mass (g)	pH	Electrical Conductivity *(µS/cm)*
C7	20	7.18	131.7
C9	20	8.5	145
E2	20	10.51	790
H19	20	7.46	170.2
HS2	20	6.93	184.7
HS20	20	6.74	342
HS5	20	7.39	85.1
HS-9	20	7.53	472
RB4	20	7.35	592
RB5	20	8.01	388
RB6	20	6.78	273
RB7	20	6.73	276
SA19	20	13.95	481
SA 18	20	9.64	84.5
T6	20	7.14	358
TS_23	20	6.98	637
TS1	20	13.4	203
TS10	20	8.12	146
TS-11	20	6.41	353
TS-12	20	7.07	314
TS13	20	8.28	460
TS13	20	7.18	88.3
TS-14	20	8.35	118.3
TS15	20	9.38	151.8
TS16	20	8.31	348
TS-17	20	8.79	755
TS18	20	7.4	159.2
TS-19	20	9.1	362
TS-2	20	7.58	248
TS20	20	8.34	218
TS21	20	9.11	293
TS22	20	7.82	137
TS22L	20	7.6	200
TS23	20	6.9	231
TS24	20	9.68	690
TS25	20	7.42	737
TS-25	20	8.38	85
TS-26	20	8.92	90.5
TS29	20	7.63	236

TS-3.1R	20	7.99	883
TS30	20	7.8	240
TS30	20	7.46	205
TS-31	20	8.44	420
TS31 L	20	9.44	300
TS32	20	7.25	629
TS-33	20	7.76	482
TS34	20	7.24	219
TS35	20	7.88	457
TS36	20	13.92	337
TS37	20	6	857
TS38	20	8	840
TS39	20	7.8	180
TS4	20	7.73	156.2
TS40	20	6.88	282
TS41	20	7.87	370
TS42	20	7.46	173.5
TS-43	20	6.96	163
TS44	20	7.61	619
TS45	20	7.4	600
TS-46	20	7.2	170
TS47	20	7.14	196.2
TS48	20	8.92	326
TS-49	20	6.85	340
TS5	20	6.9	430
TS56	20	6.55	447
TS-7	20	7.85	540
TS7-13R	20	8.33	680
TS-8	20	9.05	133.8
TS-9	20	11.22	211
TSS-1	20	10.22	110
TSS-10	20	8.03	264
TSS-11	20	7.95	255
TSS-13	20	8.48	490
TSS-14	20	7.74	82.5
TSS-15	20	7.66	119.4
TSS-16	20	7.55	620
TSS-17	20	8.25	790
TSS-18	20	8.31	541
TSS-19	20	8.1	355
TSS-2	20	8.33	235
TSS-20	20	8.07	331
TSS-21	20	7.56	690
TSS-22	20	7.16	296

TSS-23	20	7.2	559
TSS-24	20	6.98	797
TSS-25	20	6.88	680
TSS-26	20	7.29	843
TSS-27	20	7.12	909
TSS-28	20	7.78	354
TSS-29	20	7.48	187
TSS-3	20	7.39	116.1
TSS-30	20	7.56	178
TSS-31	20	8.22	200
TSS-32	20	8	230
TSS-33	20	7.29	277
TSS-34	20	7.44	819
TSS-35	20	7.92	405
TSS-36	20	7.64	643
TSS-37	20	7.6	550
TSS-38	20	7.66	586
TSS-39	20	7.19	577
TSS-4	20	8.17	95.5
TSS-40	20	7.09	612
TSS-41	20	9.33	703
TSS-42	20	9.5	498
TSS-43	20	8.4	153.6
TSS-44	20	8.3	80
TSS-45	20	8.27	694
TSS-46	20	7.29	756
TSS-47	20	7.76	777
TSS-48	20	7.71	633
G reference	20	7.06	204
Average		8.01	387.5

APPENDIX A2. Table showing Total Organic Carbon (TOC)

Code	Crucible weight/g	Sample weight/g	Dried sample+crucible weight/g	Ashed sample+crucible weight/g	% TOC
RB4	42.8215	1.0543	43.8578	43.8024	5.25
RB5	47.6605	1.0434	48.6867	48.6521	3.32
RB6	50.0135	1.0528	51.0616	51.0356	2.47
RB7	41.4849	1.0446	42.5226	42.4882	3.29
SA19	48.8773	1.0373	49.9046	49.8599	4.31
SA 18	48.749	1.0384	49.7789	49.7434	3.42
T6	50.1595	1.0312	51.1736	51.1273	4.49
TS_23	52.6273	1.0486	53.6604	53.5938	6.35
TS1	43.9134	1.031	44.9374	44.9103	2.63
TS10	48.6973	1.0311	49.7174	49.6674	4.85
TS-11	21.3279	1.0478	22.3524	22.2826	6.66
TS-12	48.7389	1.0078	49.7451	49.734	1.1
TS13	50.0031	1.0109	51.0023	50.9808	2.13
TS13	48.6727	1.0151	49.677	49.4847	18.94
TS-14	41.4859	1.0192	42.4765	42.4204	5.5
TS15	50.1497	1.0114	51.1544	51.0905	6.32
TS16	47.654	1.0131	48.6552	48.6036	5.09
TS-17	48.8435	1.0145	49.8292	49.769	5.93
TS18	52.6034	1.0187	53.617	53.5942	2.24
TS-19	49.4608	1.0161	50.4552	50.3818	7.22

APPENDIX A11: REPLICATES SAMPLES

Code	Crucible weight/g	Sample weight/g	Dried sample+crucible weight/g	Ashed sample+crucible weight/g	% TOC
TS30	41.4859	1.0072	42.4813	42.4502	3.09
TS-31	53.6028	1.0079	54.6089	54.5847	2.40
TS31 L	48.7431	1.0078	49.7439	49.7099	3.37
TS32	50.1535	1.0076	51.1567	51.1161	4.03
TS-33	49.4641	1.0065	50.4668	50.4341	3.25
TS34	48.6745	1.008	49.6722	49.6265	4.53
TS35	52.607	1.0074	53.6041	53.541	6.26
TS36	48.8484	1.0065	49.8513	49.8261	2.50
TS37	47.6559	1.0069	48.6553	48.6101	4.49
TS38	50.0052	1.0071	50.9933	50.9259	6.69