

UNIVERSITY OF GHANA
SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
DEPARTMENT OF CHEMISTRY



**AN ASSESSMENT OF POTENTIAL TOXIC ELEMENTS IN SOILS OF SOME
SELECTED FARMING COMMUNITIES IN THE EASTERN REGION OF GHANA.**

BY

CHRISTOPHER ADINKRAH

(10877207)

**A FINAL PROJECT DISSERTATION SUBMITTED TO THE UNIVERSITY OF
GHANA, LEGON IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
AWARD OF MASTER OF PHILOSOPHY (M.PHIL.) DEGREE IN CHEMISTRY**

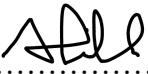


OCTOBER, 2022

DECLARATION

I CHRISTOPHER ADINKRAH, do hereby declare that except for references to other people's work which have been fully referenced, this project work is my own work and that it has neither in whole or part been presented elsewhere.

CHRISTOPHER ADINKRAH

(10877207) 

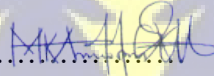
Date: 17/09/2023

PROF. AUGUSTINE DONKOR

Date:

(SUPERVISOR)

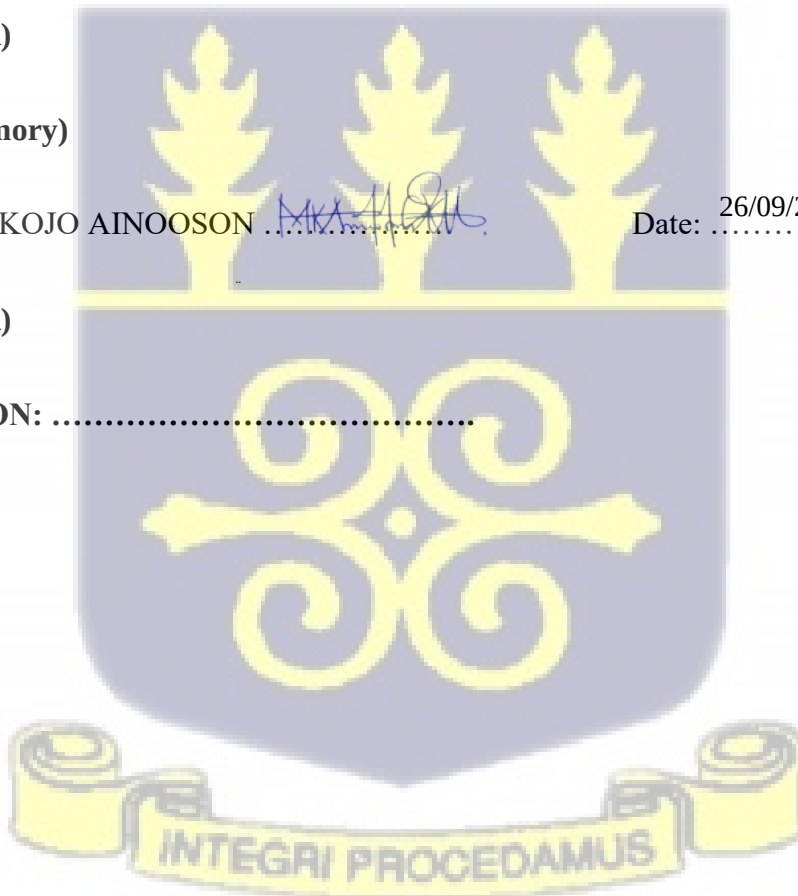
(Of blessed memory)

DR. MICHAEL KOJO AINOOSON 

Date: 26/09/2023

(SUPERVISOR)

SUBMITTED ON:



ABSTRACT

The study investigated the concentration of seven potential toxic elements (PTEs) (As, Cd, Cu, Pb, As Cr and Co) in the farm soil of some selected farming communities (Kwabia, Kwabia Asasehene, Agbom, Aworworso and Asasehene) in the Eastern Region of Ghana using acid digestion and Atomic Absorption Spectrophotometer methods. The mean concentrations of the PTEs recorded from the farms ranged from 3.5mg/kg-0.7mg/kg for Cd, 19.08mg/kg-3.94mg/kg for Cr, 19.24mg/kg-11.42mg/kg for Co, 27.28mg/kg-3.26mg/kg for Pb, 29.62mg/kg-12.42mg/kg for Ni, 30.76mg/kg-14.52mg/kg for Cu and 36.6mg/kg-22.02 mg/kg for As.

The mean concentrations of the PTEs in the studied area decreased in the order As>Cu>Ni>Pb>Co>Cr>Cd for all the five farming communities. The mean concentration for As for all the farms studied exceeded the WHO/FAO limits while that of Cd exceeded the WHO/FAO limits for Aworworso farms. However, the hazard index for children and adult were < 1 which showed that the PTEs posed no Health risk on individual health. The Total Carcinogenic Risk (TCR) was within or below acceptable risk. The study revealed that there was high degree of contamination of the PTEs; Cu, Cr, Pb, As, Co, Ni and Cd shown by the degree of contamination and the pollution load index, PLI. However, enrichment factor, EF showed that the soils of the studied area were much enriched in Cd and As and the PTEs had impact on soil microbial population and vice versa.



DEDICATION

Affectionately dedicated to my mother Hanna Nketiah for her inexhaustible love and modelling the virtue of humility in to me that shaped my life and brought me this far.



ACKNOWLEDGMENT

My gratitude to the person of the Holy Spirit, who is the very reason for my being and made all things possible. I wish to also express my deepest appreciation to my sister (Takyiwaa Charity), for her constant support, care and encouragement and to my lovely friends and family.

Most importantly, to Dr Michael Kojo Ainooson and Prof. Augustine Donkor(of blessed memory) my supervisors, for their time, help and encouragement to get this work done.

To Prof Luis Doamekpor, Prof Dorcas Osei Sarfo the Vice Dean of Graduate School, and the Chemistry Department of University of Ghana for the love, direction and counselling from the very beginning of this dream.

To my beloved, Gracelove Eyi-Mensah for her relentless love and support before, during and after the birth of this dream, I am grateful.

Funding of this project was made possible by the University of Ghana Research Grant (UDRF/11/MDG-019/2018-2019).

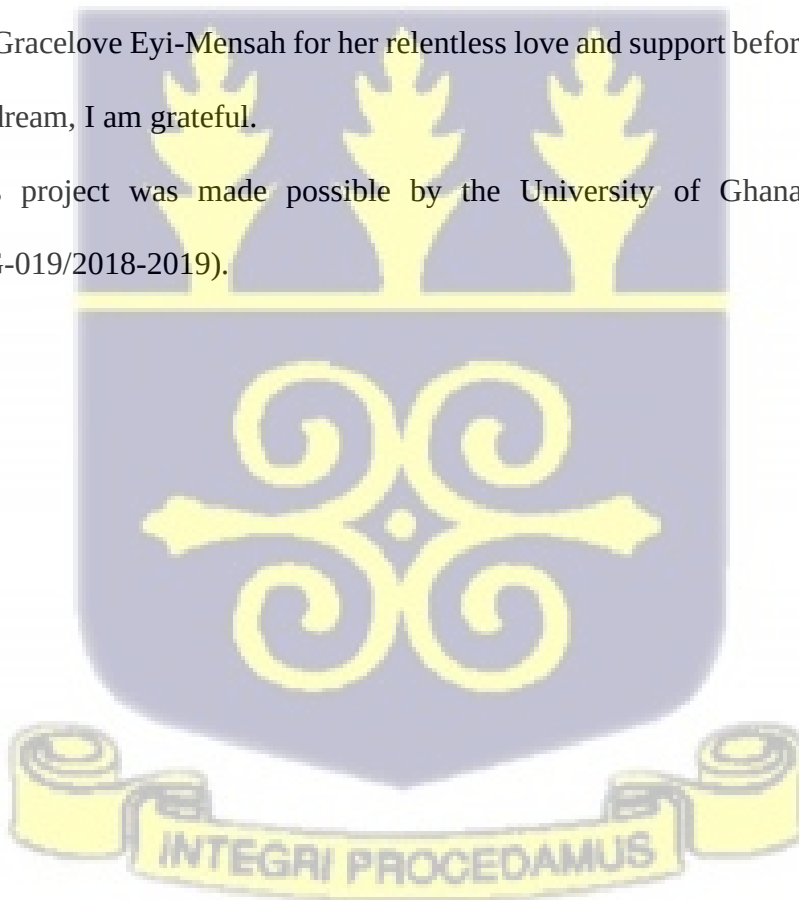


TABLE OF CONTENTS

DECLARATION	ii
ABSTRACT.....	iii
DEDICATION.....	iv
ACKNOWLEDGMENT.....	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES.....	x
LIST OF FIGURES	xii
CHAPTER ONE	1
INTRODUCTION	1
1.1 Background to the study	1
1.2 Problem Statement.....	3
1.3 Justification of the Study	3
1.4 Research Hypothesis.....	4
1.5 Research Questions.....	5
1.6 Main Objectives	5
1.6.1 Specific Objectives	5
1.7 Organization of the Study	5
CHAPTER TWO	7
LITERATURE REVIEW	7
2.1 Background.....	7
2.2 Potential Toxic Elements in soil, distribution, and interaction with soil components.....	7
2.3 Origin, identification, and sources of Potential Toxic Elements (PTEs) in Soils.....	10
2.4 Properties, effects (on fauna, flora, and human) and molecular mechanism of the toxicity of selected PTEs in farms soil	12
2.4.1 Arsenic in Farms Soil.....	12
2.4.2 Lead in farms soil.....	14
2.4.3 Cadmium in farms soil and plants uptake mechanisms	17
2.4.4 Impacts of Copper (Cu) in farms soil, bacteria population, and health	18
2.4.5 Impacts of Nickel (Ni) on farms soil.....	21
2.4.6 Impacts of Chromium (Cr) on farms soil and crop plants.....	23

2.4.7	Effects of Cobalt (Co) on Agriculture soil	25
2.5	Health risks and risk assessment of PTEs in contaminated farm soil.....	28
2.6	PTEs in agricultural soil environments in Ghana	29
2.7	Soil pH	31
2.8	Cation Exchange Capacity (CEC)	33
2.9	Electrical Conductivity (EC) of soil	34
2.10	Soil Organic Matter (SOM)	35
2.11	Soil particle size/texture.....	36
2.12	Soil moisture content	37
2.13	Microbial community and agriculture soil quality.....	37
CHAPTER THREE		39
MATERIALS AND METHODS.....		39
3.1	Study area.....	39
3.2	Sampling	43
3.2.1	Sample collection and treatment	43
3.2.2	Digestion of soil samples	43
3.3	Determination of heavy metals	45
3.4	Data analysis	45
3.5	Contamination Assessment.....	45
3.5.1	Enrichment factor	46
3.5.2	Geoaccumulation index	46
3.5.3	Contamination factor	47
3.5.4	Contamination degree	47
3.5.5	Pollution Load Index.....	48
3.5.5	Potential Ecological Risk	48
3.6	Human health risk assessment	49
3.7	Carcinogenic and Non-Carcinogenic Risks Factor.....	51
3.8	Quality control for the soil samples for the PTEs.....	53
3.9	Determination of the Physicochemical parameters of the soil.....	54
3.9.1	Laboratory analysis for moisture content of soil	54
3.9.2	Soil particle size analysis	55

3.9.2 Soil pH measurement.....	56
3.9.3 Measurement of electrical conductivity.....	56
3.9.4 Extraction of exchangeable bases.....	57
3.9.5 Cation exchange capacity (CEC).....	57
3.9.6 Organic Matter Determination (Weight Loss-On-Ignition at 550°C).....	58
3.10 Biological analysis.....	59
3.11 Preparation of Ringer's solution.....	59
3.12 Preparation of nutrient agar solution.....	59
3.13 Fungal population for ten farms (Kwabia and Kwabia Asasehene).....	60
3.14 Preparation of malt extract agar (MEA) and Dichloran-Glycerol (DG18) agar.....	60
3.15 Preparation of peptone water.....	61
3.16 Isolation and identification of mycoflora population.....	61
3.17 Quality Control/ Quality Assurance for determining the physicochemical properties.....	62
CHAPTER FOUR.....	64
RESULTS AND DISCUSSIONS.....	64
4.1 Concentration of PTEs in the farm soil.....	64
4.2 Sources of PTEs contamination.....	69
4.3 Physicochemical properties of the farms soil.....	71
4.4 Impact of the PTEs on the soil microbial population.....	74
4.5 Effects of the Physicochemical properties of the soil on the PTEs.....	78
4.6 Contamination Indices of the farms soil.....	81
4.6.1 Geoaccumulation Index (I_{geo}) of the Farms Soil.....	81
4.6.2 Contamination factor (CF) of the Farms Soil.....	83
4.6.3 Pollution Load Index (PLI) and Degree of contamination (C_d) of the Farms Soil.....	85
4.6.4 Enrichment Factor (EF) of the Farms Soil.....	86
4.6.5 Potential Ecological Risks (E).....	87
4.7 Human Health Assessment.....	89
4.7.1 Carcinogenic risks of the PTEs in the farms soil.....	90
CHAPTER FIVE.....	92
CONCLUSIONS AND RECOMMENDATIONS.....	92
5.1 Conclusion.....	92
5.2 Recommendation.....	93

REFERENCES	94
APPENDIX.....	111
Appendix A.....	105



LIST OF TABLES

Table 2. 1: Production and reserves of lead (Pb) worldwide (United States Geological Survey, 2011)	15
Table 3. 1: Definition and reference values of some parameters for health risk assessment of heavy metals	50
Table 3. 2: References doses (RfD) and SF values for the PTEs (Chen et al., 2022).....	52
Table 3. 3: Certified and measured concentration of Pb, Cd, and As in ISE sample 999 of moist clay from Liteta/Ivory Coast, WEPAL	54
Table 3. 4: Materials and their quantities for preparing malt extract agar (Oxoid CM167).....	60
Table 3. 5: Materials and their quantities used in the preparation of Dichloran-glycerol (DG18) Agar (Oxoid CM167).....	61
Table 4. 1: Average concentrations of the PTEs present in the farms soil	67
Table 4. 2: Descriptive Statistics of the PTEs in the farm soils (mg/kg).....	68
Table 4. 3: Correlation matrix of the PTEs in the soil	70
Table 4. 4: Physicochemical properties of the farms soil	74
Table 4. 5: Bacteria population for each farm (10^{-4} CFU/g soil) correlated with the PTEs of the soil.....	76
Table 4. 6: Correlation between the physicochemical properties and the PTEs of the farms soil	79
Table 4. 7: Geoaccumulation Index (I_{geo}) for soil quality of the farms	82

Table 4. 8: Soil quality in reference to Geoaccumulation Index (I_{geo}) values	83
Table 4. 9: Contamination factor (CF), Pollution Load Index (PLI) and Degree of contamination (Cd) of the PTEs in the Farms Soil	84
Table 4. 10: Enrichment Factors of the PTEs in the agricultural soils	87
Table 4. 11: The potential ecological risks of the PTEs	88
Table 4. 12: Exposure pathways, hazard index, hazard quotient of the PTEs in soil	89
Table 4. 13: Carcinogenic Risks for children and adult of the PTEs in the farms soil	91



LIST OF FIGURES

Figure 2. 1: The main characteristics, sources, and chemical reactions at various levels of growing rice in As contaminated paddy soil environment (Kumarathilaka et al., 2018).	14
Figure 2. 2: Lead (Pb) uptake mechanism and accumulation in plant parts (Aslam et al., 2021)	17
Figure 2. 3: Illustration of Cu in soil, uptake in plants and contamination of the ecosystem (Shabbir et al., 2020)	20
Figure 2. 4: The transport and update of Cu by plants roots to the shoot cells through different transporters in the farms soil (Reproduced from Shabbir et al., 2020).....	21
Figure 2. 5: The effects of Cobalt (Co) in agriculture soil (Reproduced from Mahey et al., 2020)	27
Figure 2. 6: The mechanism of the oxidation and chelating agents (Mahey et al., 2020)	27
Figure 2. 7: Influences of pH on availability of phosphorus (Barrow, 2017).....	32
Figure 2. 8: Soil pH effects on biogeochemical processes and vice versa	33
Figure 2. 9: Ingestion, detoxification and assimilation of metals by Microbes in the soil (Abdu et al., 2017)	38
Figure 3. 1: Map of study area making up the farming sites within Asesewa in the Upper Manya Krobo District and its surroundings.	42
Figure 4. 1: Regression analysis for strength of correlation between the soil bacteria and As (A), soil bacteria and Pb (B), soil bacteria and Co (C) for Kwabia (K) farms.....	77
Figure 4. 2: Strength of the relationship between clay and nickel concentrations in the farm soils	80

Figure 4. 3: Strength of the relationship between sand and nickel concentrations in the farm soils	80
Figure 4. 4: Strength of the relationship between CEC and lead concentrations in the farm soils	81
Figure 4. 5: Pollution Load Index (PLI) of the PTEs in the farms soil.....	86



CHAPTER ONE

INTRODUCTION

1.1 Background to the study

Worldwide, there is a high dependence on agriculture and related activities for the sustenance of life on earth. Agriculture plays a key role in the economic growth and development of most countries; hence critical attention is given to the sector. Ghana is no exception, as the agricultural sector contributes about 40% to the nation's gross domestic product (GDP) and employs majority of the labour force while providing raw materials for industrial growth and development as well as for the international markets, generating foreign income [1]. With increasing population growth worldwide, the dependence on agriculture for subsistence is even higher with current situation such as poor land usage practices. In sub-Saharan Africa, it is estimated that about 15% of the population currently live in locations that are hit high by food insecurities as a result of soil degradations from unsafe agricultural practices [2].

It is worth noting that the success of the agricultural industry lies on many markers with soil quality among one of the important parameters. Soil quality refers to the capacity of a soil type to function within an ecosystem to sustain plant productivity [3]. Among the soil quality parameters used in assessing soils for agricultural productivity, available nutrients which comprises of the capacity of the soil to support plant growth as well as taking care of elements that present environmental hazard is a key.

Potentially Toxic Elements (PTEs) are usually important class of elements at lower concentrations especially cobalt which mostly serve as source of trace nutrients for plant growth. However, PTEs

presents an important class elements which demands constant monitoring especially due to the increase in anthropogenic activities, as they can cause serious damage to plant growth and production and to the health of consumers [4]. The presence of PTEs in soils have been reported in many literatures with common elements such as Zn, As, Pb, Cu, Cr being studied frequently [4]. In a study conducted [5], it was observed that most of the soils from various sites and areas studied contained PTEs and were in some cases above the permissible limits.

Common sources of PTEs in the soil include mining activities, agrochemical use, fossil fuel consumption, waste disposal and sewage irrigation among others [6]. Accumulation of potentially toxic elements in farmlands and its environs poses a serious threat to various biological (fauna), food safety and human health [7]; [6]. Some of these PTEs such as Cu and Zn are known to perform biological functions in the soil and plants ecosystem but in elevated levels are toxic when ingested. Lead (Pb), mercury (Hg) and Cadmium (Cd) have no biological function but extremely toxic even at low quantities [8]. Contaminated farming soil have been identified by several researchers as a significant causes of soil quality depletion ([9]It affects the activity of microorganism in soil and decreases the expected yield of farm produce [10].

In the Upper Manya Krobo Municipality about 80% of the land support crop production serving as one of the major food baskets of Ghana Ministry of Food and Agriculture [11]. According to [11] the municipality is the leading producer of maize and yam in the Eastern region with an estimate production value of 2886 tonnes of maize and 33034 tonnes of yam annually. Whereas several studies on PTEs have been carried out in the farming communities in Ghana such as Central, Upper West, Ashanti and Western regions, there is paucity of data as regards to potentially toxic elements (PTEs) levels in the Upper Manya Krobo Municipality of Eastern region of Ghana.

Therefore, the primary aim of the study is to determine the physicochemical, microbial properties of the soil and assess the potentially toxic elements levels and their level of contamination in relation to soil quality and soil health within the Municipality while assessing the potential health risks.

1.2 Problem Statement

The major occupation of the residence of Upper Manya Krobo Municipality is crop production. Crops largely cultivated include maize, yam, cassava, cowpea, and plantain. Pest and diseases are among the pressing challenges faced by farmers in Ghana and farmers in the Upper Manya Krobo community are no exception. In the light of this, most farmers resort to the use of pesticides and fungicides to control the prevalence of pest and disease on their farms. These agrochemicals are known to be a major source of PTEs pollution. The pollution of farming soil is a serious environmental problem, as it does not only disturb soil matrix but pose health risk to people who ingest crops grown on these contaminated soils. As a result, it is imperative to assess the levels of potentially toxic elements, (PTEs) in the soils of a major crop production hub in Ghana.

1.3 Justification of the Study

Like other countries in the world, PTEs pose a major problem in Ghana and a danger to human health and other organisms. Most research done on heavy metals and PTEs have been around mining areas used for farming, wastewater for irrigation of crops and levels of PTEs in food crops sold on the market in Ghana. These researches have mostly been in Northern, central, Ashanti, Upper west and Western regions [12]; [1]; [13] This research focused on PTEs in farm soil in Upper Manya Krobo municipality of the Eastern region which is unique. The reported PTEs and heavy

metal levels in various media in Ghana makes this research significant. PTEs contamination is on the increase in most farming soils due to agricultural practices such as application of fertilizers (phosphate fertilizers), pesticides, weedicides, fungicides, and use of contaminated water (wastewater) for irrigation. In addition, urbanization is forcing farming in previously industrial areas, farming close to mining areas and on poorly remediated lands [13]. Soils exposed to PTEs contamination destroys soil quality and have serious health implication to living organisms [14].

Toxicity is also a key problem associated with trace elements in the environment coupled with accumulation through the food chain and their persistence in nature [14]. It is estimated that, 44.7% of people of Upper Manya Krobo municipality rely on income from farming, which is heavily dependent on the use of agrochemicals, fertilizers, and pesticides, thus contributing significant levels of PTEs contamination in soils, which needs to be determined. This will help in policy planning, remediation recommendation approaches and the use of best farming practices which would help remediate potential risk of PTEs to human health.

1.4 Research Hypothesis

The following hypothesis will be tested towards providing answers to the main aim of the study.

H₀: Farm soils within Upper Manya Krobo municipality do not contain Potentially Toxic Elements (PTEs) and pose no risks to health.

H₁: The farm soils/agricultural soils in Upper Manya Krobo municipality have Potentially Toxic Elements (PTEs) and could present health risks.

1.5 Research Questions

To verify the hypothesis listed above, the following questions will be answered;

1. What is the level of PTEs contamination in farm soils in the study area?
2. How can levels PTEs in the studied soils affect human health?
3. How does levels of PTEs in the studied farm soils impact on soil ecology?

1.6 Main Objectives

To assess the levels of Potentially Toxic Elements (PTEs) in the farm soils of Upper Manya Krobo municipality and possible health and ecological implications.

1.6.1 Specific Objectives

1. To determine the presence and level of contamination of PTEs in the farms soil
2. To determine the physicochemical and microbial properties of the soil
3. To assess the implications of the physicochemical properties of the soil on the PTEs and vice versa in relation to soil quality
4. To determine the effects of the PTEs on the soil microorganisms in relation to soil health
5. To perform health risks assessment of the PTEs in the farms soil

1.7 Organization of the Study

The study has been put into five chapters. An introductory chapter provides a background to the study and research problem. The chapter also contribute to scientific knowledge, hypothesis to be tested, research questions and objectives propelling the research. Chapter two evaluates details of

literature that justifies the relevance of the study. Chapter three describes the methodology for achieving the outcomes of the study. Chapter four presents the results and discussion in relation relevant literature. Chapter five provides the concluding remarks. These includes conclusion, recommendation.

PTEs: Potential Toxic Elements.



CHAPTER TWO

LITERATURE REVIEW

2.1 Background

PTEs have various meanings. The term “potential toxic” has been defined differently base on different scholarly views and disciplines. PTE has been given several definitions from biologist to toxicologist thereby pointing no informed footings [15]. [15] admonished that the term PTE is an ill-defined term that means many different things to many different people. Fergusson (1990) added that PTEs are metallic elements that have high density relative to water. [16] admonished PTE is a loose term which is used to show environmentally bad metals. Again, potential toxic elements are naturally occurring ubiquitous substances in the human environment, which typically originated from the weathering of parent’s materials. Examples, Cd, As, Ni, Hg, Pb, and Zn. [17].

2.2 Potential Toxic Elements in soil, distribution, and interaction with soil components

Potentially Toxic Elements (PTEs) are ubiquitous in the environment. They are natural sources largely but human activities such as smelting, mining, application of pesticides and fertilizers, using sewage for irrigations as well as emissions from industries also release PTEs into the soil environment. The PTEs can be toxic to plants, soil organisms and human. These can be metals or metalloids and toxic. It can also be sources of micro-nutrients to plants.

Commonly toxic PTEs are arsenic, cadmium, chromium, mercury, thallium, and lead represented by the abbreviations As, Cd, Cr, Hg, TI, and Pb respectively. PTEs such as copper, zinc molybdenum and nickel are sources of micronutrients in soil to plants at allowable limits of concentrations. However, when these exceed allowable limits, they become toxic in the soil

environment [17]; [18]. The soil usually become sinks for the PTEs because the chemical nature of these compounds make them difficult to degrade in soil therefore when they are released into the soil either accidentally via wet deposition from the atmosphere or intentionally such as discharge of wastewater on the soil presents high possibility if toxic exposure to the organisms of the receiving soils [18]. With an increasing in population, agricultural lands and soils are at huge risks of PTEs contamination. The practice to increase fertility of agricultural land can introduce PTEs into the soil. For example, use of agrochemicals, fertilizers, sewage, on farmlands if not properly treated enrich the soil of PTEs above allowable levels [19].

According to [20], the soil in the Sinop region of Turkey had PTEs above allowable limits that posed health dangers to the children exposed to the risks of the PTEs. In same respect, a study conducted in China, Guangdong region detected volumes of PTEs far above permissible levels and geostatistical analysis identified the sources of the PTEs to be predominantly anthropogenic (industrial wastes, agricultural activities, traffic emissions) and from natural sources [21]. In Italy, the city of Salerno, soil based PTEs study revealed that urban soils had heavy pollutions especially in industrial areas and intense traffic zones of the city [22]. These research outcomes show that in areas where the above activities are profound, the increase in PTEs contamination of soil is high. The anthropogenic activities mentioned above are common among the Krobo Municipality in Ghana.

Several factors influence the availability of PTEs in soil. Temperature is key factor. In high soil temperatures for longer periods, weathering of soil minerals and Organic Matter (OM) decomposition increase resulting in an increase in PTEs in the soil. High temperature from fires such as burning bushes, wildfires, and burning the land in preparation for planting crops when not well controlled and regulated can be sources for emission of PTEs into the soil [23]. However,

there is no evidence of controlled burning contributing to PTEs availability in soils [24]. The practice of burning in preparing farmlands for cultivation is common among farmers in Ghana especially subsistence farmers and are mostly unregulated. To estimate the total amount of PTEs in contaminated soil, the following equation is used:

$$M_{\text{total}} = (M_p + M_a + M_s + M_f + M_{\text{ag}} + M_t + M_{\text{ow}} + M_{\text{ip}}) - (M_{\text{cr}} + M_e + M_l + M_v)$$

The abbreviations p represents parent material, s is the sediments, a is the atmospheric deposition, f represent the sources of fertilizers, ag represents sources of agrochemicals, t represents technological materials, ow, ip, cr, e, v, and l represents wastes sources from organics, wastes from inorganic sources, crop removal, erosion, volatilization and leaching respectively and M_{total} represents the total amount of PTEs in the soil [25].

Some main PTEs in farm soils, the interactions of the PTEs with soil and their sources are reviewed. Chromium (Cr), a main element of the PTEs have an average concentration of 40mg/kg in soil. The main species of Cr are Cr (III) and Cr (IV). Cr (III) is the main form of Cr in soil. It is a bit stable and forms complexes with NH_3 , Cl^- , SO_4^{2-} , F^- and CN^- . Cr (IV) is present in the form of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. They precipitate with metal cations. Sources of contamination are mostly from fertilizers, pesticides, biosolids, manure and electroplating [26]. Vanadium (V) has average concentration of 90mg/kg. V(III) can replace Fe(III) in iron minerals in soil and mainly emanate from phosphate fertilizers, smelting and mining of vanadiferous magnetite and burning of coals and oils [27]. Manganese (Mn) has average concentration of 850mg/kg. The toxicity of Mn (IV) is depended on the sorption or ability to oxidize heavy metals and can be present as insoluble hydroxides. Major sources include discharge from municipal wastewater, mining of alloy and steel [28]. Nickel (Ni) has average concentration of 22mg/kg and normally reported in the range of 0.2-

450mg/kg in soils. Ni (II) forms inner sphere complexes when contact with solid phases and are mostly associated with soil organic matter. It can precipitate as hydroxides at high pH values of the soil. Nickel can come from mining and burning of fossil fuels [29]. The interactions of the PTEs in the soil is important to understand the potential effects on health and how the levels in farms soil could have an impact on agriculture.

2.3 Origin, identification, and sources of Potential Toxic Elements (PTEs) in Soils

Generally, it is practically difficult to pinpoint the origin of different PTEs when found in a contaminated soil. Whether the PTEs originates from anthropogenic sources or from geogenic sources [30]. However, in such instances, three methods help to identify whether the PTEs in a contaminated soil acting together are from anthropogenic or geogenic sources. These are spatial distribution, element speciation and profile distribution [30]. Identification by PTEs speciation is hinged on three assumptions. These assumptions state that lithogenic materials have stronger bonding than the pollutant bonding in polluted materials, ‘interactions between solution and solid phase in polluted systems tend to form more labile associations compared to natural systems’, and finally due to the weaker bonds of pollutants they are more readily mobilized in polluted the soil [31]. The mobile proportions of the PTEs also help to tell whether the pollutants are from anthropogenic or natural sources [32]. To have an approximation of the real PTEs speciation in the soil, extraction methods are often used. This method provides insight into the form of the PTEs present in the soil, the health hazard to the environment, and mobility of the PTE. Factors that affect the extraction methods are temperature, concentration, selectivity, soil/extractant ratio etc [30].

To identify the origin of PTEs in soil by profile distribution, it is much easier. For example, atmospheric deposition is expected to be accumulated in the top soil profile whiles geogenic sources can be found at greater depths of the soil profile [30]. Whiles this method is true in most instances, for historical depositions, the profile distribution for atmospheric deposition at topsoil and geogenic sources at higher depths are untrue [32]. Some authors argue that mobile components of anthropogenic PTEs leach into greater depths especially fluvisols and could be mistaken for geogenic sources of PTEs. Similarly, plants roots can transport PTEs of lithogenic origin and mistaken for anthropogenic sources of PTEs. [32]; [33]. Despite the weaknesses of the profile distribution methods for identifying PTEs origin in soils, it can be a good approach when the shortfalls are carefully considered when performing analysis.

The Last method, spatial distribution normally tells the sources of enrichment of the PTEs in the soil [30]. Normally point sources of PTEs contamination in soil are easy to tell since it might come from a single identifiable source. Unlike the point sources, the non-point sources of the PTEs contamination in soil are difficult in nature to tell the exact origin since it could be from diverse sources and diffuse as well [30]. However, geostatistical methods are used in spatial distribution analysis of origin of PTEs contamination in soil to give as close as possible, the origin of the PTEs contamination [34]. In using geostatistical methods for spatial distribution of PTEs in soil, geogenic origins should be analysed and interpreted taking the geological conditions of the location into account [34]. Whiles this method is effective, mostly, there are inadequate data to perform the geostatistical method [34]. The three methods outlined above; spatial distribution, element speciation and profile distribution can be used in combination not neglecting known local anthropogenic sources that could release PTEs into the soil for maximum results [30]. These

guided the identification and analysis of PTEs in the farms soil to juxtapose against health impact assessments of the PTEs.

2.4 Properties, effects (on fauna, flora, and human) and molecular mechanism of the toxicity of selected PTEs in farms soil

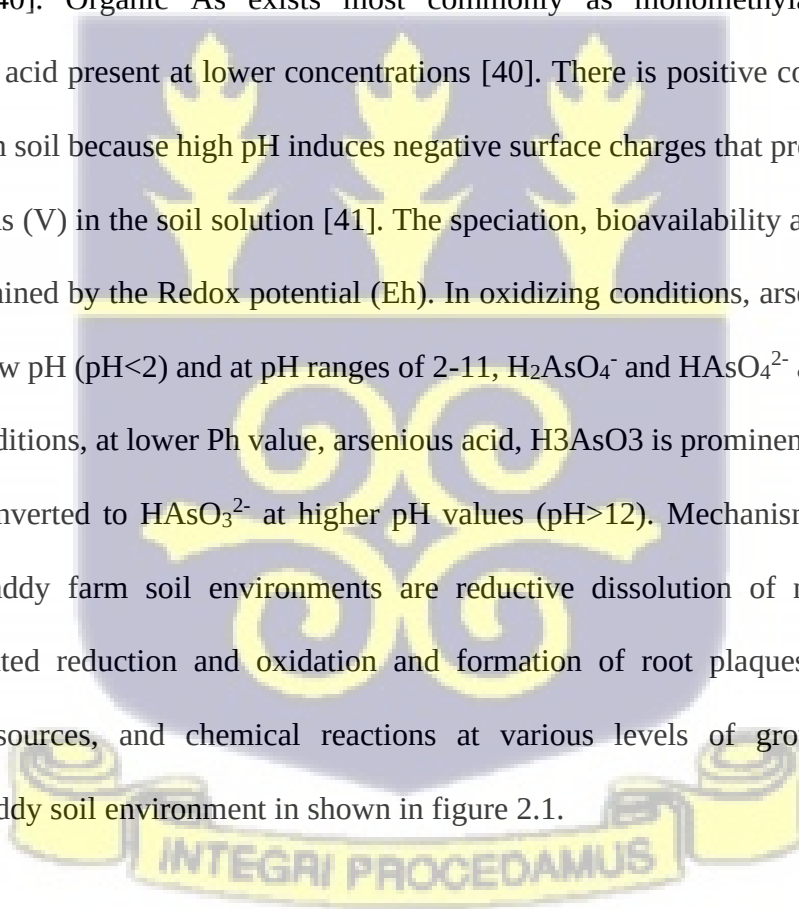
A detailed evaluation of the properties, effects, and the molecular mechanisms of the PTEs under consideration in this study are done. These PTEs are arsenic (As), lead (Pb), cadmium (Cd), copper (Cu), Nickel (Ni), and chromium (Cr). Each of these is evaluated separately below.

2.4.1 Arsenic in Farms Soil

Arsenic is classified as a metalloid and carcinogenic. Arsenic contamination in soils are either from geogenic sources such as weathering of arsenic rich rocks, and natural oxidation [35]. The mining of ores, burning of e-wastes, discharge from landfills and dumpsites also release arsenic into the environment (anthropogenic sources). Groundwater and soil in different countries (>300 million people in 17 countries) have suffered arsenic contamination [35]. Arsenic contamination of soil and other media are reported in Ghana as well. In the Western region of Ghana, arsenic contamination is reported in gold mining areas with repercussions on human health and the soil ecology [35]. Agricultural soils are negatively impacted especially those near these mining areas where mine tailings rich in arsenic are deposited [36]. Rural deprived children who ply and play around these areas ingest these toxic elements and negatively impact on their health [36]. Exposure to Arsenic causes fever, hair losses, weakness, muscle spasms, impaired healing, decreased immune system function including nausea and vomiting [37]. At low levels of arsenic, it has been found to affect soil flora and fauna [37]. The main sources of As that affect farm soils are via

manure applications, biosolids and compost amendments, agrochemicals additions. When the As is in farm soils, it can stop microbial activities, reduce fertility of the soil, prevent seed germination, affects plants nutrient, and reduce farm yields. When the As accumulates in food crops, it gets into the food chain and impacts on human health [37].

Arsenic has different forms of oxidation states in both solid (soil) and liquid phases in the environment, 0, +3, -3 and +5 [38]. But it is rare to find the oxidation state of As(-3) and As(0) in its natural state [39], In farm paddy soils which are normally for rice cultivation, As is often in the form of trivalent arsenite, As(III) or pentavalent arsenate, As (V), in the paddy soil pore water of the farmland [40]. Organic As exists most commonly as monomethylarsonic acid and dimethylarsinic acid present at lower concentrations [40]. There is positive correlation between soil pH and As in soil because high pH induces negative surface charges that promotes desorption of As (III) and As (V) in the soil solution [41]. The speciation, bioavailability and mobility of As species is determined by the Redox potential (Eh). In oxidizing conditions, arsenic acid, H_3AsO_4 is dominant at low pH ($\text{pH} < 2$) and at pH ranges of 2-11, H_2AsO_4^- and HAsO_4^{2-} are dominant [10]. In reduction conditions, at lower Ph value, arsenious acid, H_3AsO_3 is prominent and converted to H_2AsO_3^- and converted to HAsO_3^{2-} at higher pH values ($\text{pH} > 12$). Mechanisms that causes As speciation in paddy farm soil environments are reductive dissolution of metal hydroxides, microbial mediated reduction and oxidation and formation of root plaques [10]. The main characteristics, sources, and chemical reactions at various levels of growing rice in As contaminated paddy soil environment in shown in figure 2.1.



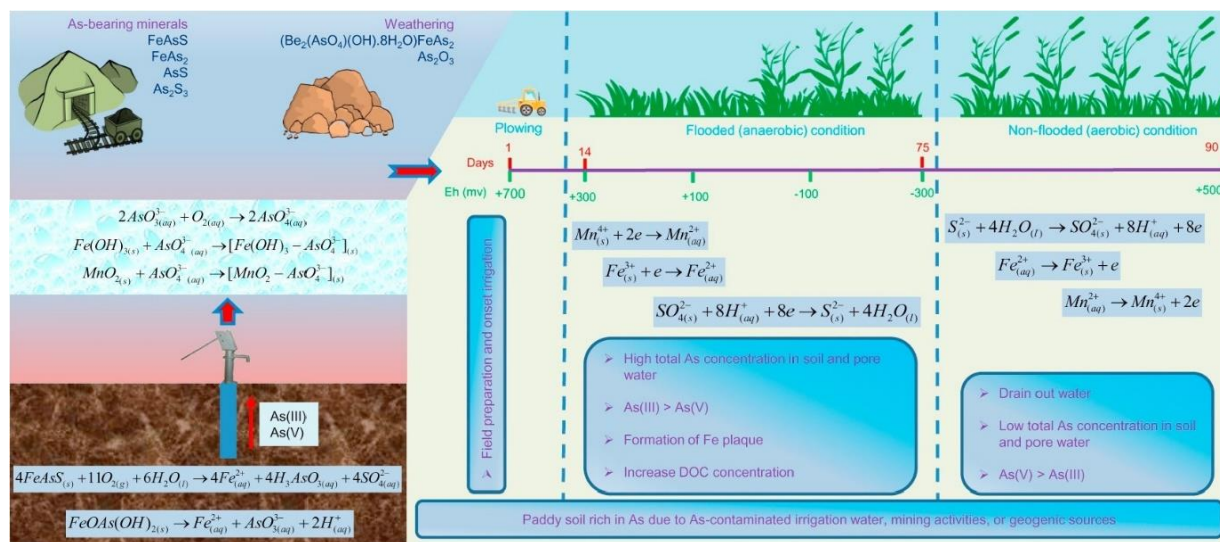


Figure 2. 1: The main characteristics, sources, and chemical reactions at various levels of growing rice in As contaminated paddy soil environment [38].

2.4.2 Lead in farms soil

Lead is a heavy metal classified as PTEs. It is dense, ductile, soft having low electrical conductivity than other metals. Lead can impact negatively on plants metabolic processes since it is non-essential element [42]. Crops grown on Pb contaminated soil show signs of poor growth, poor biomass production and bad root growth [42]. Pb in nature forms minerals by interaction with other elements and arguably does not exist in natural forms. There are however archaeological records that provide evidence that Pb was used for diverse activities in the past. Due to population growth and industrialization, the concentration of lead has increased to about 1000 times over the centuries with most increment witnessed in 1950-2000 [43]. Primarily, Pb are from the mineral deposits together with copper and zinc in the environment. Due to the high application of Pb in the bicycle and automotive industries, Pb concentration in the environment is expected to further

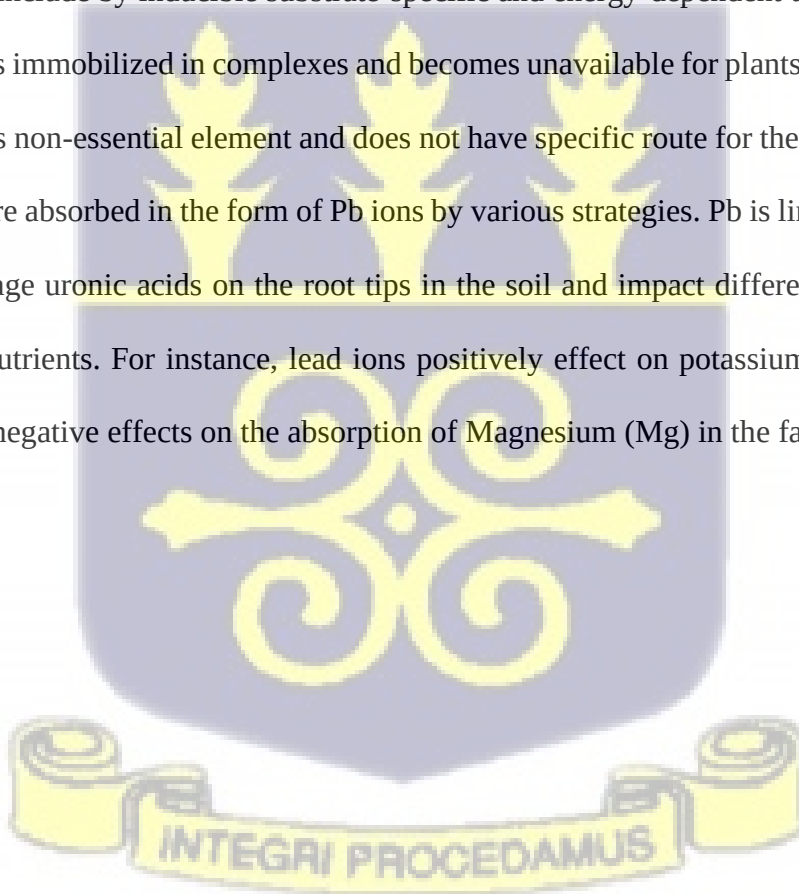
increase. In agriculture production especially cultivation in urban polluted soils close to industries is recording pollution in food crops [44]. Table2.1 is evidence that the production of Pd is increasing across the world and with higher production and reserves, the likelihood of soil contamination is high which can affect crop production.

Table 2. 1: Production and reserves of lead (Pb) worldwide [45]

Country	Production (1000m3 ton)	Reserves
Australia	620	27000
USA	400	7000
Bolivia	90	1600
Canada	65	650
China	1600	13000
Ireland	45	600
India	95	2600
Mexico	185	5600
Peru	280	6000
Russia	90	9200
South Africa	50	300

Sweden	65	1100
Other countries	330	4000
<i>Sum</i>	<i>4065</i>	<i>78500</i>

Lead uptake mechanism in plants on a contaminated farm soil is demonstrated explicitly in figure 2.2. To maintain nutrient homeostasis, plants respond to changes in the soil and within the plant itself to regulate nutrient uptake (Figure 2.2). Soil mineral status, membrane transporters, and mineralization regulate the bioavailability of metals in soil. There are two major routes plants take up metal. These include by inducible substrate-specific and energy-dependent uptake and passive uptake [46]. Pb is immobilized in complexes and becomes unavailable for plants uptake in the soil. This is because is non-essential element and does not have specific route for the plant uptake [44]. However, they are absorbed in the form of Pb ions by various strategies. Pb is linked to carboxylic groups of mucilage uronic acids on the root tips in the soil and impact differently the uptake of other essential nutrients. For instance, lead ions positively effect on potassium (K) and calcium (Ca) uptake but negative effects on the absorption of Magnesium (Mg) in the farms soil [47].



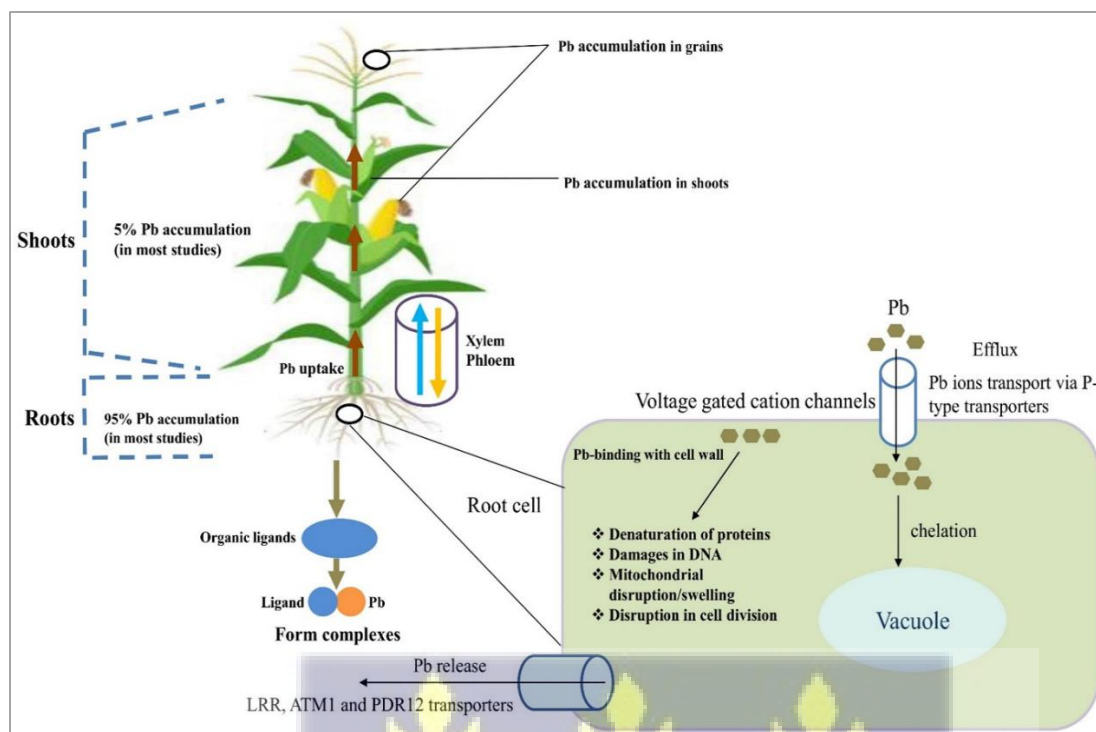


Figure 2. 2: Lead (Pb) uptake mechanism and accumulation in plant parts [43]

2.4.3 Cadmium in farms soil and plants uptake mechanisms

The concentration of Cd in a non-contaminated soil is generally low and reported in the range of (0.01-5)mg/kg [44]. Fertilizer applications, and indiscriminate Cd containing wastes disposals have increased the Cd levels in the soil environment [44]; [48]. An exposure to cadmium concentrations poses various degrees of health implications to human. An acute exposure causes pneumonitis known as oxide fumes, toxic concentrations cause proteinuria and chronic effects are lung cancer, osteomalacia and proteinuria. Kidney, bone damage and risks of cardiovascular mortality are possible when exposed to Cd in soil [49]. The commonest exposure route of Cd is in food and smoking which found to result in penetration of the placenta and absorbed via the alimentary tract [49]. Among the PTEs, cadmium has got more attention on the basis that “ it is

the only metal that might pose human/animal health risks at plant tissue concentrations that are not generally phytotoxic” [49].

The mechanisms of Cd uptake by plants are driven by the electrochemical potential gradient of the plasma membrane within the root cells of the plants. The presence of Fe in soil reduces Cd uptake by plants [50]. According to [51] the presence of barley Fe concentrations (0-10 μ M) reduced cadmium uptake in the studied soils. The uptake of Cd was improved when iron (Fe) deficiency upregulated expression of genes for encoding Fe(II) uptake in *Thlaspi caerulescens* Ganges ecotype [52]. The releases of phytosiderophore were enhanced when maize plants were exposed to Cd. While the Cd transport to the roots symplast of the maize appears unregulated, unknown factors restrict the movement of the Cd into the shoot of the maize in contaminated soil. But it has been reported that Mn enriched medium in soils promoted the Cd uptake with 64% of this compound accumulated in the cell wall of the plant to be transferred potentially to consumers in *Lactuca sativa* plant (Ramos et al., 2002). Cd are found in the root cell vacuoles of wheats by photochelators that influences the symplastic radial cadmium movement. In a rice farm, the soil was found to be contaminated with Cd and 0.73% of Cd uptake by the plants entered the grain of the rice which represented about 1.02mg/kg, about 100 times more than allowable limits by the European Union for concentration of Cd in rice [54].

2.4.4 Impacts of Copper (Cu) in farms soil, bacteria population, and health

Copper is present in fungicides. Farmers use the fungicides to prevent diseases attacking their crops. There have been increasing concerns among farmers that the use of the fungicides can increase copper levels in soil and might be affecting crop yield [55]. Copper is a dietary mineral for animals and can be in animal feed. The animal manure used for crop production may contain

copper added to the soil. At depths of 0-15cm, researchers found that manure application containing factor was critical [56]. However, soil kept at a pH of 6.5 reduces copper availability to crops in the soil. Secondly, > 10% of organic matter content in soil reduces copper availability to plants by sequestering copper ions in the soil [57]. Crops uptake of copper depends on many factors such as kind of crop, soil characteristics and normally absorbed into plant roots not the shoots. Copper to translocate to plant shoots at excessive levels, a level considered toxic which is at $\geq 19\text{mg/kg}$ of copper in farm soils [58]. A study conducted in New Jersey among farming communities on impact of copper on soil bacteria and human health subjected the farm soil environment to copper levels from extremely high level (about 4500mg/kg), high copper levels (about 450mg/kg) and normal exposure levels (about 15mg/kg). The revealed a decline in bacteria population and fungal biomass at higher copper concentrations over time [59]. According to Fagnano et al., (2020) "Copper exerts selection pressure on soil microbiota". However, increased Cu concentration did not relate to diversity indices and microbial richness" [60].

On the contrary, a study conducted in Southern Italy found no correlations between the edible parts of crops and copper levels in the soil. This was conducted at the following parameters: maximum Cu soil content (11.4mg/kg f.w), total maximum value (570mg/kg d.w) and maximum bioavailable value (13.8mg/kg d.w). The range of Cu concentrations found in the foodstuffs were 0.01- 6.2mg/kg and few outside range. Lettuce had concentration of 11.4 mg/kg at soil concentration of 77.2mg/kg , pepper had 8.7 mg/kg at soil concentration of 60.7 mg/kg . The high copper concentrations were not related to copper accumulation in other plants on the soil. Also, the observed high Cu concentrations in plants did not influence high soil values [61]. However [62] also observed a different results. They found positive correlations between the bioavailable and total Cu in the soil and the Cu content in the aerial parts of the plants. With urbanization and

industrialization leading to more industrial sites for agriculture activities, coppers levels in food and health cannot be overlooked.

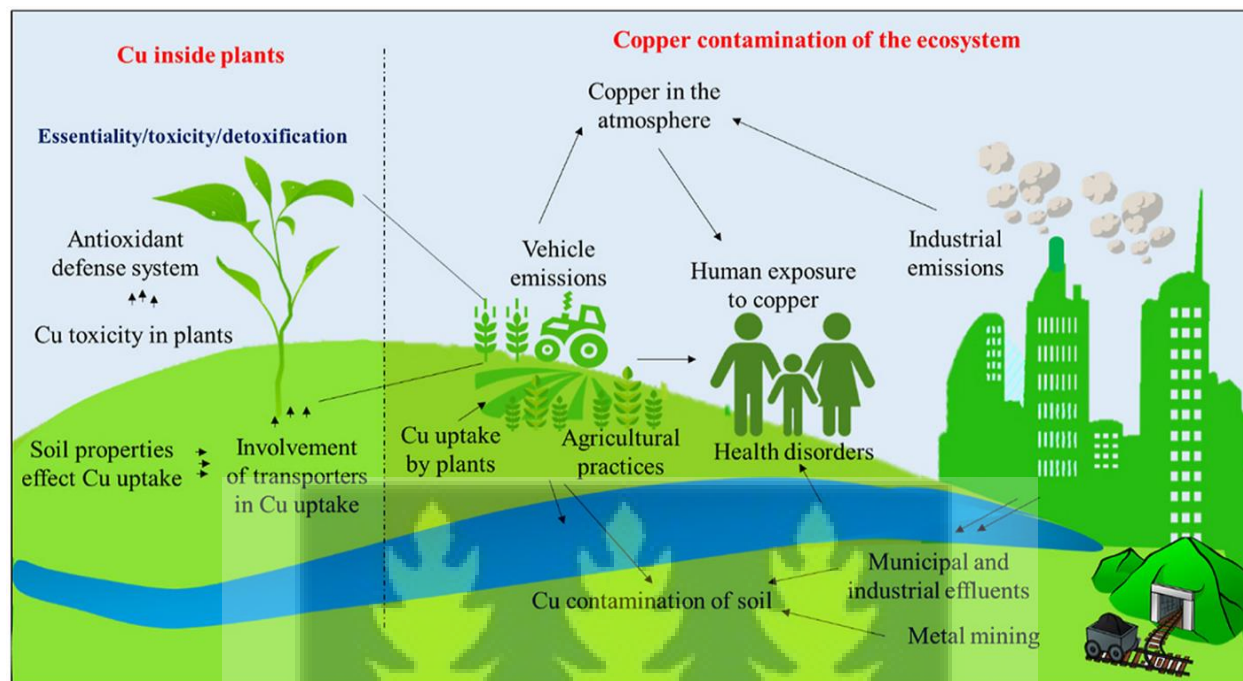


Figure 2. 3: Illustration of Cu in soil, uptake in plants and contamination of the ecosystem [63]

The root to shoot transport of Cu is illustrated in figure 4. Specific metal chelators and transporters transport Cu^{2+} to aerial plant parts in the soil (Figure 4). Initially it was found that Cu translocation was facilitated by amino acids forming stable Cu-complexes in xylem sap [64]. Mineral homeostasis in plants is mediated by Nicotianamine. “The nicotianamine and histidine have highest copper binding capacity making them ideal ligands to chelate Cu and other metals in xylem and translocate to the shoot tissues”[64]. But the concentration of the Cu in the soil determines the nicotianamine activation [63]. It is found that most nicotianamine activation occurred at excess Cu concentration. Recently, it is found that “deoxymugineic acid mediates

copper transporting he xylem sap as specific Cu-chelator and nicotianamine acted as specific Cu-chelator in the phloem sap ‘’ [63].

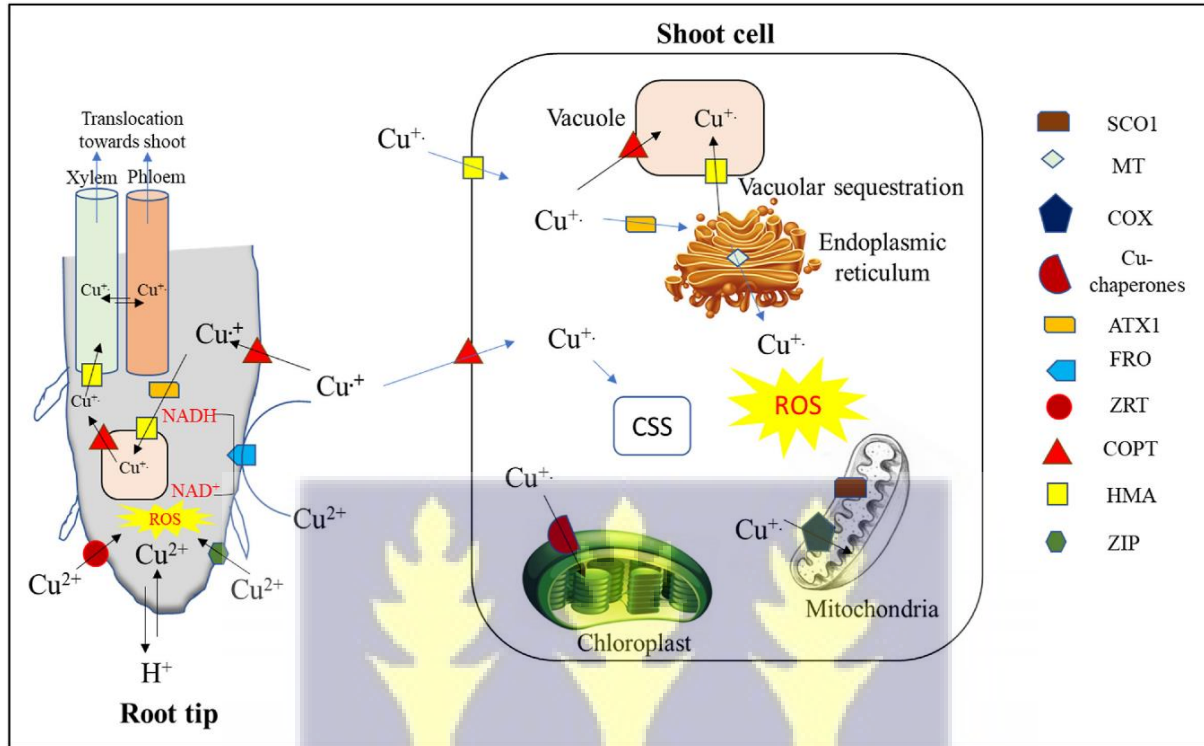


Figure 2. 4: The transport and uptake of Cu by plants roots to the shoot cells through different transporters in the farms soil (Reproduced from [63])

2.4.5 Impacts of Nickel (Ni) on farms soil

Nickel is required by plants in minute quantities and therefore called a micronutrient. Nickel comes from both anthropogenic (application of phosphate fertilizers to soil main source of nickel) and pedogenic processes and its presence in soil much depends on the parent material. It is more present in arid and semi-arid regions [65]. Nickel is a common metal used in electroplating. Due to workers exposure and research confirming the cancerous nature of the metal, the International

Agency for Research on Cancer (IARC) stated that Ni can cause sinonasal and lung cancer. When farming activities are done close to metal industries, or on a former metal industry, the risks of exposure to toxic levels of Ni and the development of cancer is a possibility [66]. High levels of Ni contamination have been found in refinery areas and about 1km away from the refinery. Crop produced on soil about 1km had Ni content exceeding limits. Most of the Ni were found in lettuce, oats and cabbage (Patrick & Bisessar, 2008). Studying the Ni uptake and toxicity in crops on an farmland with Ni content in the range of 2000ppm to 10000ppm revealed inhibition in growth of crops such as potatoes, onions, celery, and cabbage especially at 10000ppm of Ni concentration [67]. Elevated levels of Ni is associated with chlorosis and plant roots growth inhibition [68]. Aerial deposition of contaminants and indiscriminate disposal of industrial wastes could cause high levels of Ni in soil. There was severe toxicity in the crop plants experimented. However, normal growth was found at Ni concentration of 2000-3000ppm (Patrick & Bisessar, 2008).

Ni is one of the transition metals having 1455 °C melting point, boiling point of 1730 °C and high density of 8.9 g/cm³ [29]. The average atomic weight of Ni is 58.69 and a group X element of the periodic table [65]. There are four oxidation states of Ni. These are +4, +3, +2 and +1 oxidation states. The main oxidation state of Ni is +2 which is more toxic in cationic form than its complexes and readily available [69]. Polluted environment with Ni is a concern particularly because it cannot be degraded in the environment [69]. The major sources of Ni in agricultural soil are from smelting operations few distance from farmlands, industrial discharges, insecticides, herbicides, fungicides and fertilizers with high risks of mobility and toxicity in the soil [70]; [69].

Nickel in the farm soils show affinity with metallic iron (Fe) and sulphur (S) therefore Ni-S and Ni-Fe minerals are formed in the soil. Ni moves in the soil and poses risks due to movement to rooting zones for plants uptake as $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ [70]. Decrease in soil pH results in increase Ni

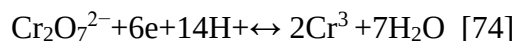
releases into the soil environment which means pH is very critical to control Ni levels in the soil for effective and safe agriculture production and protection of health [69]. The range of allowable Ni in agriculture soils is reported to be 20mg/kg to 60mg/kg and remediation is required at 75-150mg/kg threshold [65].

2.4.6 Impacts of Chromium (Cr) on farms soil and crop plants

Chromium one of the heavy metals exists in different oxidation states and toxicity [71]. The effect from chromium depends on the exposure, intensity, the oxidation state, the exposure time, and the dose exposed to. Chromium exists in 0, +3 and +6 commonly in soil but has oxidation state from 0, +1, +2, +3 +4, +5, and +6. Cr (III) has low toxicity and mobility and absorbed on surface of clay minerals in precipitates. It is important therefor to note factors and conditions that aid the conversion of Cr (III) to Cr (VI) in soil. The speciation of chromium determines its uptake, translocation, and accumulation in plants. It is often imbibed by plants via carriers of essential ions e.g. sulphate [71].

The anthropogenic sources of Cr into the soil are from industries such as electroplating, drilling muds, production of chromic acid etc. The tannery and leather industry contaminate the soil environment the most despite efforts to limits their impact on the environment. Until recently, it was used to preserve wood [72]. At a pH less than 4, Cr (III) is insoluble inorganic compounds and rarely mobile or bioavailable. Cr (III) is sparingly soluble and tends to bind to organic substances and at increased pH it presents in hydrolysed forms [73]. The hexavalent form of chromium easily mobilizes in acid and alkaline soils whiles the trivalent forms stable in soil. The trivalent chromium is not easily exchanged with other cations in soil because it is strongly adsorbed on surfaces of soil particles. It is slightly mobile in acid soils [71]. The chemical equation below

shows the expression of balance between Cr (III) and Cr (VI) in the soil phases. The process is same in water bodies:



In a 10nM solution of (KH)₂PO₄ at pH 7.2, if Cr remains oxidized in the soil, cannot be extracted and therefore immobilized since it is adsorbed strongly [74].

In farm soils, the value of chromium varies and can be up to 350 mg/kg. The trivalent forms of chromium are mostly found in soil and complexed with minerals structures in the form of mixed oxides of Fe³⁺ and Cr³⁺. In the presence of high organic matter content in soil, Cr (VI) is reduced to Cr (III). The redox reaction is active in rhizosphere in a different bacterial reductase enzyme released by plant roots [71].

Different factors influence Cr phytoavailability. The most important are the redox potential, pH, organic content of the soil, microbial content, nature of absorbing phase, kind of minerals present in the matrix and the chromium contamination source. Cr (III) is the most stable in low redox potential (Eh) environments. Between 4 -8 Ph range, Cr (III) is in its hydrolysed forms. In high redox potential and between pH interval of 2-14, Cr (VI) is the most stable species thermodynamically. Hexavalent chromium reduces to Cr (III) fast in reducing conditions forming stable solution complexes in acidic condition. Organic complexes of chromium are more mobile and stable in soil [71]. In plants, the biological cell membrane are almost impermeable to Cr(III) which makes it very important to detoxify Cr (VI) to Cr (III) via reduction processes to protect the soil environment [75]. Cr (VI) interferes with plant metabolic processes, negatively affects their growth and are toxic to the plants [75]. Some studies however reports that at higher concentrations of Cr (III) it damages plant/crops tissues in agricultural soils [76]. Chromium inhibits cell division

and reduces root growth and limits absorption of nutrients by plants. It reduces leaf biomass of plants, reducing leaves per plant and yield output. Chromium interferes also with nutrients such as Nitrogen (N), phosphorus (P), potassium (K), Manganese (Mn), Iron (Fe), and boron (B) uptake by plants which puts risks on investment in farming and affects the economic growth of a country including Ghana [71]. This is mostly important since the economic activities of the people in Manya Krobo municipality, the study location are mainly in agriculture. Chromium contamination of the agricultural soil environment will require urgent interventions for remediations to ensure good crop growth, yield and safe farm produce devoid of the consequences of chromium contamination.

2.4.7 Effects of Cobalt (Co) on Agriculture soil

Naturally, cobalt (Co) is found in sedimentary rocks, and igneous rocks. The average abundance of Co is within 25-30mg/kg and the least abundance among the other heavy metals apart from scandium [77]. Anthropogenically, cemented carbide contains about 5-30% of Co. This means the carbide grinding plants and the cement industries release much Co into the environment [78]. E-wastes industries also pollute the soil environment with significant volumes of Co above acceptable thresholds. Co dusts are released into the environment from polishing disc in diamond polishing [79]. Paints and pigments industries are culprits of Co release into soil by using Co as siccative to expedite the paint drying process. Bottom ash from incinerators are sources of anthropogenic Co soil pollution. Mining activities, TVs, mobile batteries are all sources of Co release into the soil which could reach exceedance levels [77].

The chemistry of Co shows that it has atomic mass of 58.93 amu and atomic number of 27. It has different oxidation states but the most common are +2 and +3 [77]. Cobalt is an essential

microelement and important vitamin B12. In leguminous plants, it helps in the plants root nodules development, metabolism, and growth [80]. It can enter the food chain and it is found that human consumption of Co is 5-40µg/day [81]. In soil, the tolerable limit for crop plant growth is 0.2-0.5 ppm. Also, soil concentration of Co in the range of 4000-10000 ppm can support certain plant species growth [77]. In the synthesis of DNA and oxidation of fatty acids, Co acts as coenzyme in such cellular processes. It has been reported that the deficiency of Co in grasses and feedstuffs for ruminants led to diseases such as bone fragility, loss of appetite, and anaemia [82]. However, when it is in excess in soil it becomes deadly to the crop plant growth. When in excess in soil, it causes huge financial loss to farmers by affecting crop biomass and reducing yield. It also becomes toxic to plants in higher concentrations and inhibit the growth of the plants, active transport in the plants. Some of the negative effects of Cobalt in higher concentrations are falling crop plant leaves, discoloured plain veins, reduction in shoot weight, failure of plant greening, and plant leaves closing prematurely [82]. Higher concentrations of Co also affect the function of plant systems. It leads to formation of hydrogen peroxide radicals, reactive oxygen species (ROS), and antioxidant enzyme activities are altered [83]. ROS produced under higher concentration of Co causes disruption in photosystem II including electron transport chain transport disruption [83]. Nitrogen metabolism and photosynthetic pigments are reduced when Co is in excess in agricultural soil. It has been determined that when iron and calcium are inhibited, it easily makes Co toxic in the soil [84]. To produced higher yields in a cost effective and financially sound manner, contaminated Co soil had to be remediated prior to cultivation [84]. The effects of Co in crop plants in soil and the seeming mechanism of action of chelating and oxidizing agents are presented in figure 8 and figure 9 respectively [77].

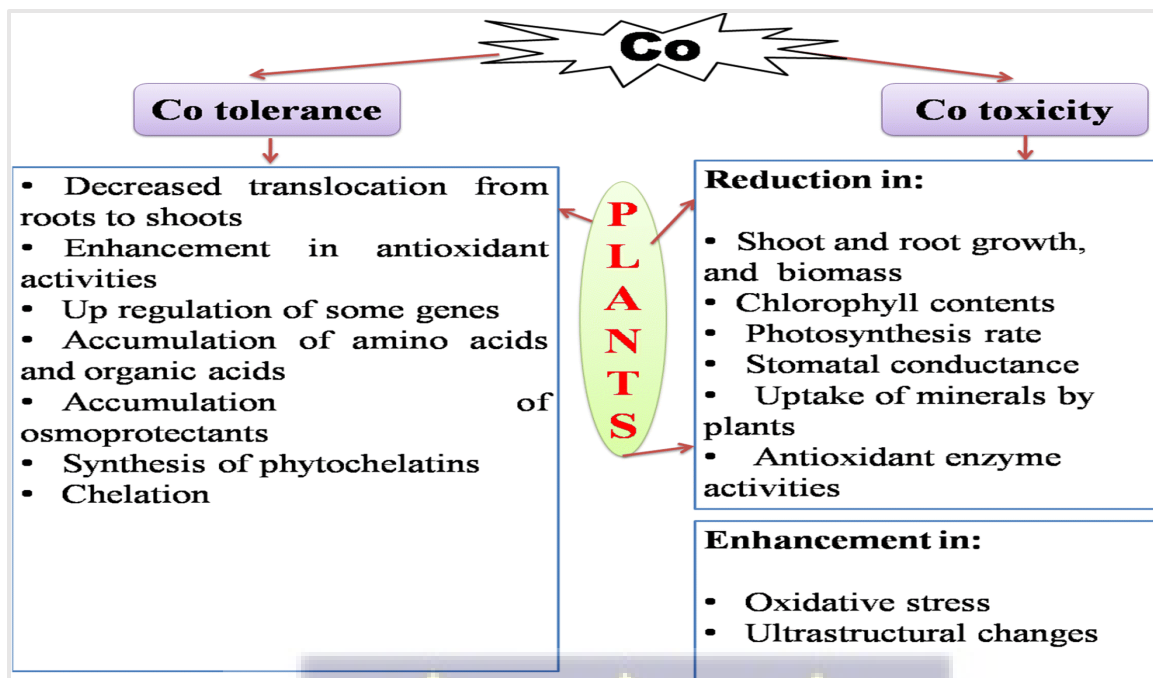


Figure 2. 5: The effects of Cobalt (Co) in agriculture soil (Reproduced from [77])

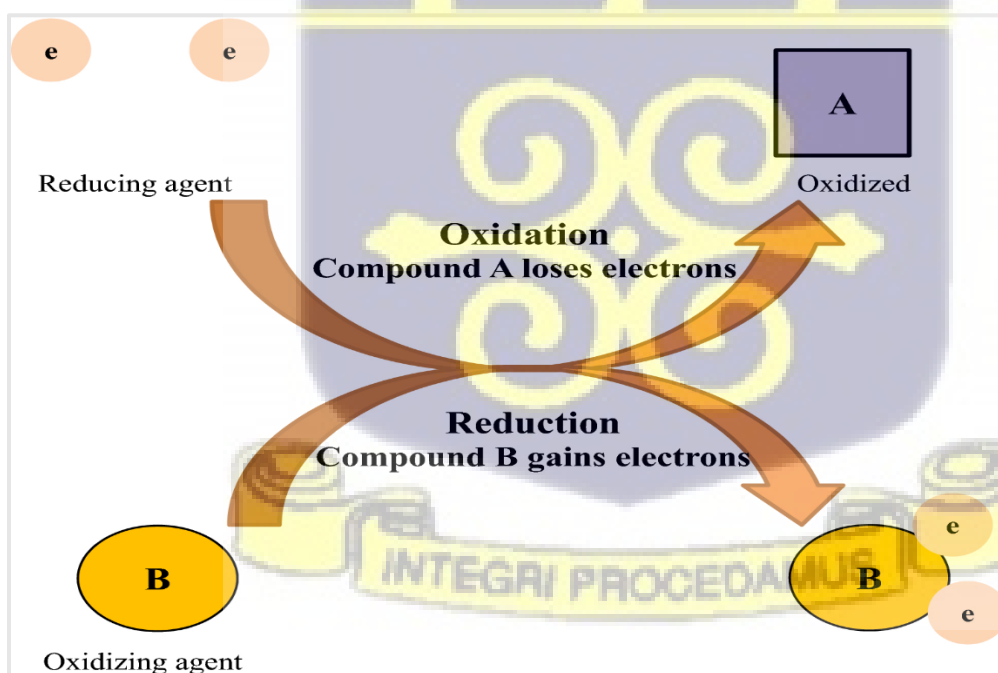


Figure 2. 6: The mechanism of the oxidation and chelating agents [77]

2.5 Health risks and risk assessment of PTEs in contaminated farm soil

PTEs are well known to pose various levels of health risks to human. These risks differs from crop type, soil type and type of the PTEs in the soil [85]. According to [86], the worst case method to understand the health risks of the PTEs when ingested is to plant crops that are able to accumulate these PTEs. These crops may include lettuce, white campion in controlled conditions using pot trials. Lettuce is known to accumulate Zn and Pb in its tissues [87]. White campion is native species in Italy and present in many other countries and the leaves, immature stems are fried, boiled, and cooked to make soup or pasta. The biomass of white campion can accumulate large concentration of PTEs. These biomonitor plants can help to evaluate the PTEs concentration levels and impact on health. Normally the uptake and accumulation in the shoots of the plants/crops are done using the Bioaccumulation coefficient (BAC) method to check the index of the concentrations of the PTEs in the shoots to that of PTEs in the soil of cultivation [88]. When PTEs enters farmlands in high concentrations usually above permissible limits, it affects soil quality, growth of the crop plants, inhibits soil organisms' activity, results in poor yield and enters the food chain affecting animals and humans posing health hazards [89]. Another approach to assess human health risks on exposure to PTEs in soil is to combine data from toxicology, epidemiological research and exposure assessment models to determine the impacts of the PTEs [90]. The most used method worldwide is the soil-human health risks assessment (SHRA) stated the by United States Environmental Protection Agency. The SHRA is viable and effective for application to any commercial, industrial, farming contaminated sites and the results are used to plan initial remediation measures. The limitation with this method is that it does not consider pre-existing

illness and lacks certainty. The limitation should be factored in interpretation of a research outcome. The method is seen to give good outcome of health risks of PTEs in contaminated soil [91]; [92]; [93]

Studies have found that prolong exposure to the PTEs in soil can cause imbalance in cardiovascular systems and result in cancer [94]. Many researchers deduced that human exposure to PTEs in soil can be by skin contact, ingestion, inhalation, dermal absorption leading to accumulation of the toxic elements in the tissues, disruption of cellular metabolism, affect the nervous system, immune system and the endocrine systems [95], [96]. The risks of metal ingestion by children using contaminated soil/land as playground in areas near farmlands have been reported [92]. According to [35], in Ghana, people who walk around abandoned mine areas potentially inhale/ingest PTEs from mine wastes. This applies to farming close to the abandoned mine wastes which endangers health. Consuming food contaminated with Cu leads to Wilson diseases that cause malfunctioning in liver, brain, and other body organ system. Similarly, exposure to PTEs such as Cd, Ni, Cr causes health implications such as abortion, hepatic, development toxicity, reproductive and immunological health defects, birth defects, infertility and malformations in people [97]; [8].

2.6 PTEs in agricultural soil environments in Ghana

In Ghana, common activities that release PTEs into the environment are smelting, mining, automobile exhaust, use of wastewater/contaminated water for irrigation, application of fertilizers, weedicides, fungicides, and pesticides [98].

[12] conducted a study into the accumulation of heavy metals and metalloids in foodstuffs from agricultural soils in Tarkwa, a mining hub in Ghana and found that compared to Codex Alimentarius Commission Standard values, about 30% of cassava had accumulated higher

concentrations of Pb. Ni was found to have the highest capacity of absorption into the foodstuffs. They deduced that cassava consumption among children and adults of the study location (33 communities in Tarkwa) were at higher risks of exposure to health implications.

[1] unearthed the geochemical background of some PTEs in soils in the Upper West region of Ghana of the Nadowli District. They found that Cd and As were higher in soil than background (maximum allowable limits) values. The other PTEs were lower than the background values in the studied soil. The geology of the area and human activities dominated by artisanal mining influenced the detection of the PTEs.

Similarly, a study conducted in Tamale Metropolis of Ghana to assess the health risks of contamination of PTEs in vegetables showed little impact of health. Three main compounds, Cadmium (Cd), chromium (Cr), and lead (Pb) were found in cabbage, carrot, green pepper onion and tomatoes but below World Health Organization (WHO) standards. Children and adults were not at risks to certain of the metals such as Pb since individual hazard index was below 1. Cadmium (Cd) and chromium (Cr) however exceeded 1 of the individual hazard index posing health effect to the population exposed [26].

[99], studied the impact of ‘galamsey’ on the river Pra of Ghana and distribution of Potentially Toxic Metals (PTM) on agricultural soils. He discovered the presence of As, Pb, Zn, Ni, Cu, Co, Cr and Cd in the agricultural soils. As concentrations exceeded allowable levels, represented health risks and a potential chemical of concern on the food chain. The other PTMs did not exceed allowable limits although were present in the agricultural soil. Phosphate fertilizers applications and the use of contaminated water of the river Pra by farmers for their farming activities responsible for the PTMs in the soil.

[13] on a study in the Ashanti region of Ghana about the accumulation and bioaccessibility of toxic metals in root tubers from farming communities in gold mining sites and environs which found the PTEs. Higher concentrations of the PTEs namely As, Ni, Cu, Pb, and Zn found at farm soils closer to the mining sites. The accumulation of the PTEs in the root tubers was established. The soil, and food crops were low to moderately contaminated with PTEs and posed lower risks to consumers.

The literature shows that the PTEs are detected in agricultural soils especially in mining areas in Ghana. Some of these elements impacted negatively on the soil and health upon consumption. Farming dominates Upper Manya Krobo municipality economic activities and evidence from the literature make this study timely.

2.7 Soil pH

Soil pH is described as the “major soil variable” since it affects various chemical reactions in the soil. Either indirectly or directly, soil pH influences availability of essential nutrients to plants, phytotoxic elements and pollutants in the soil [100]. pH management ensures nutrient solubility and accessibility to plants. Before nutrients are available to plants, it has to dissolve and this can be lost via leaching and runoff which makes pH regulation and management very important to ensure maximum plant access to soil nutrients [100]. Nutrients such as phosphate solubility is highly a factor of the soil pH. Formerly, it was reported that a pH of near neutral, plants absorb phosphorus to the maximum, but current research refutes this. According to current findings, at lower pH, plants absorb phosphorus better and there is phosphorus desorption in soil [101]. Figure 5 explains availability of phosphorus to plants based on the soil pH. Soil pH is also significant for the soil fertility and the soil chemistry. The pH of the soil also influences the biogeochemical

processes of the soil. In soil, the leaching of certain cations such as calcium (Ca), sodium (Na), potassium (K), magnesium (Mg) controls the pH more than ions released from weathering in the soil which make ions such as Al^{3+} and H^+ to dominate [102]. The production of carbonic acid via dissolution of CO_2 in soil water releasing H^+ , Nitrification which involves converting NH_4^+ to NO_3^- release H^+ into the soil, nitrogen uptake and acid rain all controls soil pH [102]. The soil pH can control the biological processes of the soil, affect biogeochemical processes of the soil and the biogeochemical processes also affect soil pH is a relationship explained by figure 6. Soil pH determines the distribution and fate of substances in the soil and contribute to nutrient recycling, the removal and translocation of harmful substances, controls soil microbial activities, mineralization of the soil organic matter, enzymatic activities, biodegradation in the soil, and determines nutrient availability for crop production [102].

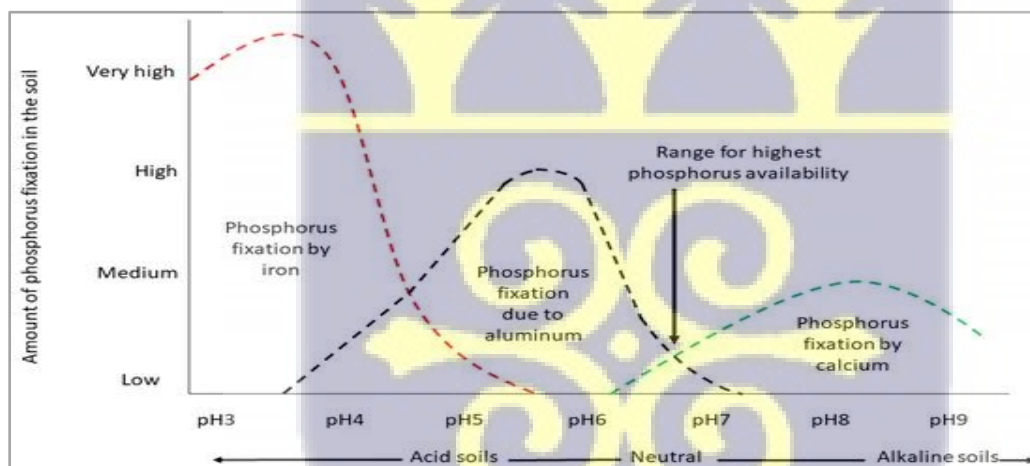


Figure 2. 7: Influences of pH on availability of phosphorus [101]

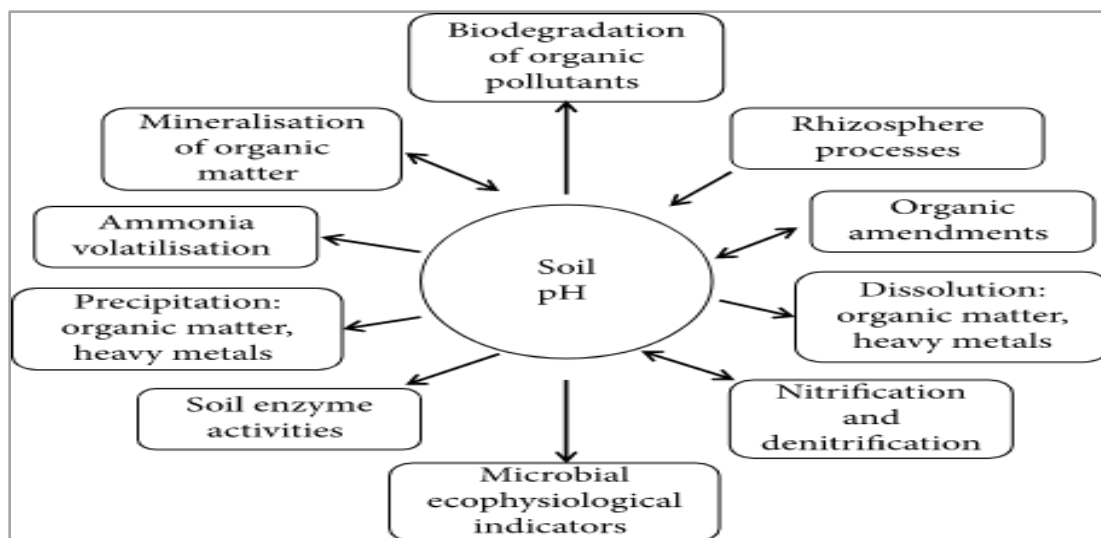


Figure 2. 8: Soil pH effects on biogeochemical processes and vice versa

2.8 Cation Exchange Capacity (CEC)

The CEC is the ability of soil to retain and exchange cations and soils' ability to grip positive charged ions [103]; [104]. To understand soil health and quality, certain soil properties which controls the soil and requires proper management must be determined. The CEC is significant in soil quality assessment and can be influenced by the soil physical, chemical, and biological properties [105]. The correlation between soil colloidal fractions and CEC is very strong. Although determining CEC is very important to understand soil health and quality, the conventional method of analysis is very expensive, cumbersome and time consuming [104]. For soil components, the surface electric charge can be measured using cation exchange capacity. Therefore, the cation exchange capacity has been useful tool to estimate the properties of soil components to understand soil health [103]. It is used to estimate the water properties in clay horizons of soil and done at specific soil pH to avoid variable charges resulting from fluctuation in the soil pH. For lightly acidic/neutral soils, CEC is usually measured at pH=7 what is referred to as the Metson method.

For alkaline soils, the Bower method is used. The CEC is measured at pH =8.2. However, these two methods presents inaccurate results in a soil with different soluble salts and monoionic absorbent on soil material are difficult to make under salinity conditions [103].

2.9 Electrical Conductivity (EC) of soil

The electrical conductivity is a measure of the conductance of the soil. It is indication of the ions (and salts) present in the soil and the sources it might have come from which determines whether crop yield will be better or not based on effects on the crop plants [106]. The wastes (solid wastes and liquid wastes) are disposed onto farmlands, the decomposition releases nutrients, salts and ions influencing the electrical conductivity of the soil [106]. However, this is regulated by many indicators of soil fertility examples phosphorus (P), potassium (K), organic matter (OM), magnesium (Mg), including contents of organic ligand and soluble salts [106]. The EC determination in soil is highly complex but its determination is important. This is because the EC is used to delineate soil fertility index and has direct effect on crop yield/correlated effectively with crop output [106]. Electrical conductivity which measures ions and salts in the farm soils can provide useful information to the farmer. For instance, if salt content is high, it can affect plant growth and productivity. The salt content of soil can be excess naturally due to weathering of rocks and minerals high in salt or mismanagement of the soil by humans. For acceptable salt content for proper crop growth, EC of 0-0.8 dS/m is recommended. When a soil analyzed exceeds 4 dS/m at 25 °C, then such sampled soil is considered saline [107]. The EC is found to impede nutrients availability to plants, inhibit activities of microorganisms, and poor crop yield. When the soil is salty, the plants are unable to extract water/enough nutrients from the soil resulting in the poor yield so the salt become toxic to the crops [108].

2.10 Soil Organic Matter (SOM)

Soil organic matter is a mixture of many biodegradable and non-biodegradable components. It contains about 1-10% of microorganisms and non-degradable plant materials, and a mixture of other biogenic components in evolutionary stages and proportions [107]. The soil organic matter (SOM) can be fast recycling thus relating mainly to the amino acids, carbohydrates, and lipid fractions of the soil (active). This can happen in the soil for either months or decades and represents 10-40% of the SOM [107]. There is the passive SOM called the humic fraction which represents about 40-60% and had remained in the soil for about centuries/millennia [107]. Agricultural soil usually has SOM content of around 0.1-6% and had correlated so well with paramount features of soil physical, chemical, microbial and biological properties [109]. The SOM can influence nutrients availability for both microbial activities and plant growth and also affects the physical and chemical properties of the soil [109]. The SOM do accumulate in the soil over long period of time and current profile in soil could be affected by chemical reactions, tree falls, and microbes reprocessing the soil organic matter. Agriculture activities and practices can in themselves affect soil organic matter content. When this happens, the soil microbes are affected reducing their activities which has direct effect on crop production and yield [109].

The soil organic matter can control soil erosion, but soil erosion increases if there is poor SOM. The addition of manures, composts also adds SOM [110]. The pH of the soil can be lowered if organic matter content is high. Levelling has reduced SOM content from the soil surface to the subsoil. As the weather warms, there is possibility of organic matter decomposition to help plant growth. The organic matter increases water content at field capacity, in sandy soil, it increases available water, and in fine texture soil, the air and water flow rates are increased. Other importance of the SOM in agriculture soil is the supply of nutrients to plants, provide home of

food to microbes in the soil, maintain the soil structure, provides essential nutrients and controls infiltration rate [110].

2.11 Soil particle size/texture

Soil particle size is very important and affects PTEs bioaccessibility [111]. Historically, extraction methods for soil particle sizes had been sieved at <2mm and validated at <250µm for effectiveness [111]. The different particle sizes can have different compositions and characteristics which ultimately affects pollutants distributions in the soil micro-environments [111]. Studies have demonstrated that coarse soil particles accumulate lower PTEs concentrations than fine soil fractions which accumulates higher PTEs concentrations. The fine particles have clay minerals, organic matter content, Fe, Mn, and Al unlike the coarser particles [111]. There are therefore good adsorption sites for the fine soil particles affecting the PTEs bioaccessibility and stability [111]. The soil texture/particle influences soil water penetration, root penetration and aeration as well as the status of nutrients in the soil. It also affects the nutrient supply of the soil. For sandy soil, the nutrient is low, low water retention, low organic matter, very permeable, low cation exchange capacity and low ability to retain moisture in the soil [110]. Therefore, to use sandy soil for agriculture purposes, good management of moisture and nutrient retention should be done. Sandy loam are less resistant to root penetration and could be a problem for deep rooted crops [110]. Clay soils normally have high organic matter, has pH buffering capacity and high cation exchange capacity. The differences in soil particles/texture can directly or indirectly influence soil functions and crop production [110].

2.12 Soil moisture content

The soil moisture content is a significant physical indicator of the soil health and quality [112]. It determines nutrients access to plants/crops [112]. The moisture content of soil is dependent on several factors. These include clay minerals, organic matter, void ratio, groundwater condition and soil particle size. Importantly the water content of soil is dependent on the soil structure and texture which affects soil moisture as well [112]. Porosity determines the wetness of soil. Clayey soil has many pores though small particle sizes than sandy soils which have larger particle sizes. The many micro pore of clayey soil makes clayey soil make more porous and tend to have larger water content compared to sandy soil. However, sandy soil can easily be recharged with soil moisture [113]. Knowledge of this helps the farmers to decide crop type to grow to gain maximum yield. A good physical condition of soil also depends on the excellent water holding capacity of these soil [113]. A plant becomes stressed if there is low moisture of the soil. Organic matter degradation is also slowed when there is low moisture content since microbial activities will be negatively affected. The soil moisture content usually increases in raining seasons and decreases in the dry seasons and therefore for proper agricultural practices, effective planning and management are important [113].

2.13 Microbial community and agriculture soil quality

Potentially toxic elements and heavy metals can affect soil microbes and ultimately the soil quality and health. Heavy metals such as Zn, and Cu which also classed as PTEs in low concentrations are significant plant and animal nutrient [114]. Prokaryotic and eukaryotic microbes have long used these metals for their cell development and structural functions [115]. In the illustration in figure 7, microbes are able to use metals for their metabolism and growth [114] . But in higher

concentrations of the metals, they become very toxic to the microbes. Not all the PTEs have essential functions in the life of microorganisms. For example Cd and Pd have no essential function in living organisms [116]. They destroy enzymatic and cellular functions, DNA structure damage, damage cell membranes and replacement of essential elements and as a result impair living organisms life cycle. The heavy metals can have these destructive characteristics on microbes in soil because of they are not degradable, toxic and have long biological half-life [116]. The microbes are inseparable part of the ecosystem. The soil microbes and the metal contaminants interact in a much complex manner in the soil ecosystem [117]. Soil chemical contaminants (heavy metals and PTEs) can govern the soil microbial biomass activities and dynamic behaviour. It is worth mentioning that some microorganisms such as bacteria, fungi and Protista with the aid of specialized organisms can degrade some heavy metals and transform parts of the heavy metal's products into their metabolism. In this process, the microbes either remove the metal or reduce its toxicity. In the process of biosorption and bioprecipitation, metal mobility and availability can be reduced and bring about immobilization of the metal contaminant in the soil [114].

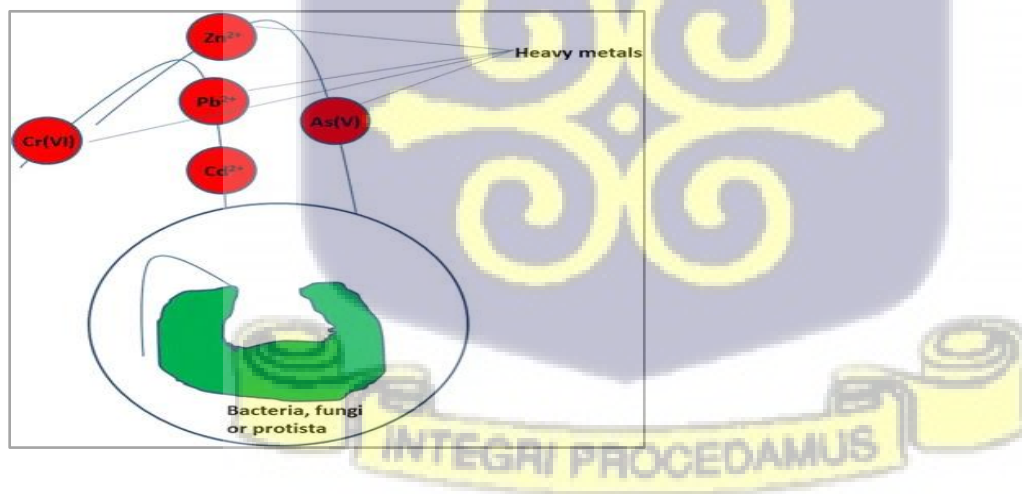


Figure 2. 9: Ingestion, detoxification and assimilation of metals by Microbes in the soil [114]

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study area

The study was conducted within the Asesewa in Upper Manya Krobo District in the Eastern region of Ghana and its surroundings (fig 3.1). The district is located within latitude $6^{\circ} 20''$ North and $6^{\circ} 50''$ North and longitudes $0^{\circ} 30''$ West and $0^{\circ} 00''$ West. The land measures 885sq.km which makes up about 4.8% of the overall geographical area of the region. It shares boundaries with Volta Lake due north and with sister districts such as Fanteakwa due west, Asuogyaman due east, YiloKrobo due south-west and Lower Manya Krobo due south-East. Upper Manya Krobo District (Asesewa being the capital) falls within semi-equatorial climate with two principal seasons being the moist (wet) and arid (dry) seasons. The district is found in the eastern part of Ghana and was chosen for this study because it is one of the major food hubs in Ghana. The crops are produced for local consumption and exportation.

It experiences both forest and savannah climatic conditions. It is a relatively warm climatic zone with mean monthly temperature of 21 to 30° C; annual rainfall levels of 1200 to 1500 mm and relative humidity of 90% in the rainy season and 55% in the dry season [11].

At Asesewa, 80% of the land supports crop production and majority of the people are farmers who mostly and annually rely on bushfire and ploughing for clearing their lands before growing of crops. Ploughing, slashing, burning, application of fertilizer and pesticide are inevitable farming practices amongst the farmers.

The major occupations for inhabitants are crop production and livestock production. Some of the crops produced include maize, yam, cassava, cowpea, groundnut, plantain, rice and vegetables like okro, tomatoes, garden, eggs and pepper. Livestock production includes the production of cattle, goat, sheep and poultry. The Municipality is noted as the leading producer of maize and yam in the Eastern Region with estimated production values of 28,861 tonnes of maize and 33,034 tonnes of yams annually [11].



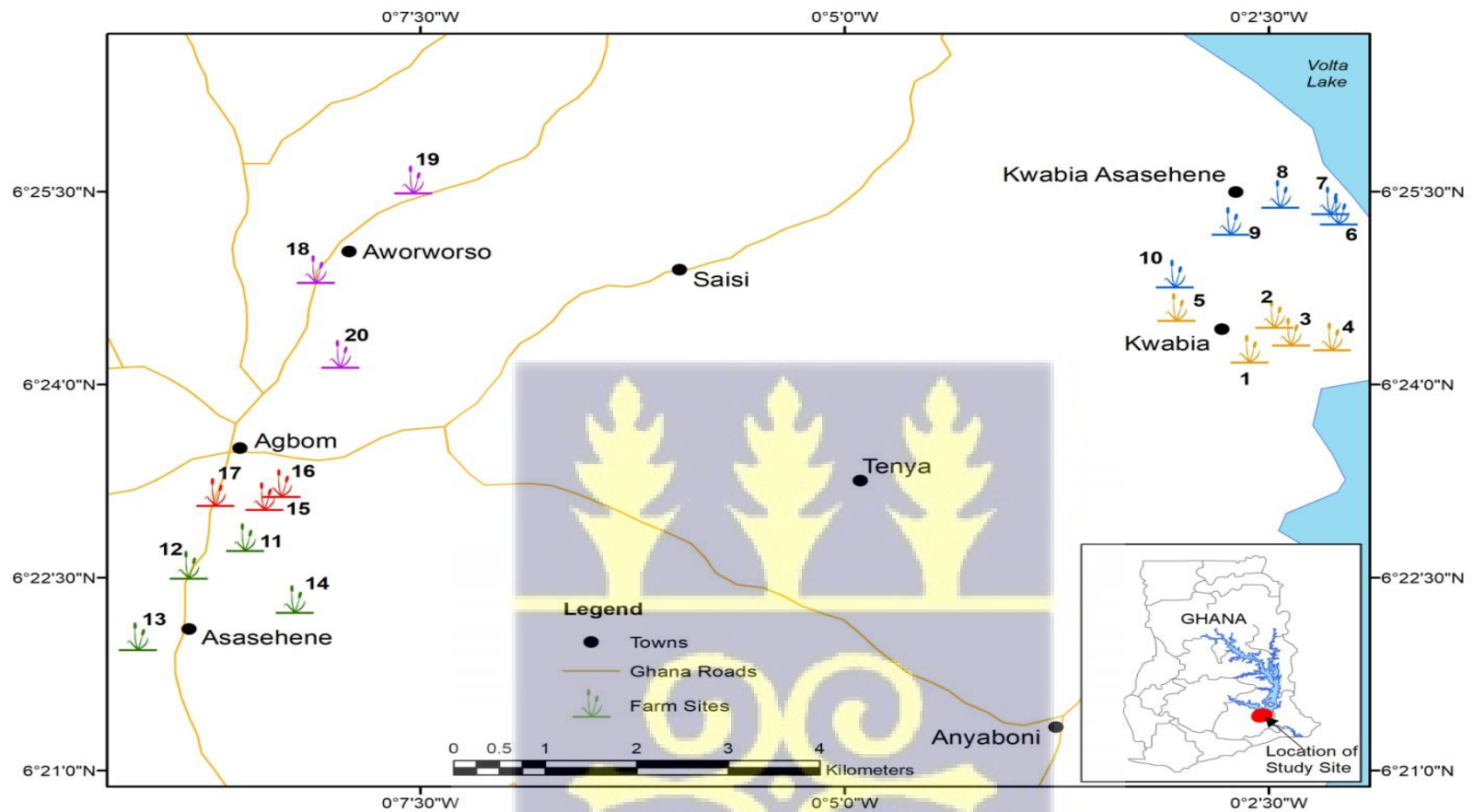


Figure 3. 1: Map of study area making up the farming sites within Asesewa in the Upper Manya Krobo District and its surroundings.



3.2 Sampling

3.2.1 Sample collection and treatment

Fresh soil samples were taken from five randomly selected farms in the farming communities of Asesewa namely, Kwabia, Kwabia Asasehene, Asasehene, Agbom and Aworworso in December, 2021. In each farming community, soil samples from five random farms were sampled by dividing each farm by four parts where four soil samples were taken from each quarter and one was sampled from the centre at a depth 30cm and were placed in zip-lock bags and appropriately labelled with a unique identity and then put in an ice chest containing ice and then transported to the analytical chemistry laboratory of the University of Ghana. The samples were then stored in the fridge. In all, total of 25 soil samples (from five different farms) were taken from the five farming communities. The soil samples were ground using porcelain pestle and mortar and passed through a 2 mm sieve to remove plant roots, debris, stones, and other materials to obtain soil fraction (sand, silt, and clay). The sieved soil samples were stored in a well labelled zip polyethylene bags for later analysis.

3.2.2 Digestion of soil samples

Approximately, 1.0 g of soil sample was weighed into the digestion tube, digested with 10 mL $\text{HClO}_4\text{:HNO}_3$ (1:2) mixture and placed on an electric hot plate at 95 °C for 1-2 hours under fume chamber until the solution was reduced to near dryness. The samples were then removed from the hot plate and allowed to cool to room temperature. Deionised (20ml) water was added to the digested samples and filtered through Whatman No. 42 filter paper into a 100 mL volumetric flask and the volume adjusted.



3.3 Determination of heavy metals

The concentration of heavy metals was measured using PINAAcle 900T Perkin Elmer Atomic Absorption Spectrophotometer for (Cd, Pb, Cr, Cu, and Ni). As was determined using Flow Injection Analysis System – Atomic Absorption Spectrophotometer (FIAS-AAS) (Hydride Generation Technique). Air-acetylene gas was used as the source of fuel for Cd, Pb, Cr, Cu, and Ni while argon gas was used for As.

3.4 Data analysis

The statistical analysis was performed using SPSS 26.0 (SPSS Inc., USA) software and Microsoft Office Excel 2019. The values of minimum, maximum, mean, standard deviation ($\pm$ SD), standard error (SE), and coefficient of variation of the data were calculated. The results were subjected to one-way analysis of variance (ANOVA) at 0.05 significance level. To identify the relationship between the heavy metals in the soil and their possible sources, Pearson's correlation coefficient analysis was used. The correlation coefficient measures the strength of the interrelationship between the heavy metals.

3.5 Contamination Assessment

A number of mathematical models have been used to quantify the degree of metal enrichment or pollution in soils, [118];[29]. In this study enrichment factor (EF), geoaccumulation index (*I_{geo}*), contamination factor (C_f), contamination degree (Cd), and pollution load index (PLI) were employed. To assess pollution status of the soil, the following defines each of the factors used:

3.5.1 Enrichment factor

The enrichment factor is used to assess the degree of contamination by individual elements in the soil [78]. It is based on the assumption that under natural conditions, there is a linear relationship between a reference element and other element constituent of the soils. A reference element was based on the standardization of a measured element against the reference element. A reference element is often the one commonly used element elements: Al, Fe, Ti, Si Sr, K etc. [9],[119]. Iron (Fe) was chosen as a conservative tracer to differentiate natural from anthropogenic component because it is a major sorbent phase for trace element [98]. It was calculated using the following equation [21];[8].

$$EF = \frac{C_n/C_{ref}}{B_n/B_{ref}} \text{-----[1]}$$

where C_n is the concentration of the element of interest and C_{ref} is the concentration of reference element for normalization. Enrichment factor is placed in five categories: $EF < 2$ as deficiency to minimal enrichment, EF 2-5 as moderate enrichment, $EF = 5-20$ as significant enrichment, $EF = 20-40$ very high enrichment and $EF > 40$ as extremely high enrichment [18].

2.5.2 Geoaccumulation index

The geoaccumulation index (I_{geo}) is a geochemical criterion used to assess heavy metal accumulation in soils to measure the degree of metal pollution [120].

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right] \text{-----[2]}$$

where C_n represent the measured concentration of the element and B_n denoted the concentration of element in the earth's crust [93]. The metal content accepted as background was multiplied each time by the constant 1.5 in order to take into account natural fluctuations of a given

substance in the environment as well as very small anthropogenic influence. The following classification is given for geoaccumulation index: < 0 = practically unpolluted, $0-1$ = unpolluted to moderately polluted, $1-2$ = moderately polluted, $2-3$ = moderately to strongly polluted, $3-4$ = strongly polluted, $4-5$ = strongly to extreme polluted and >5 =extremely polluted [21].

3.5.3 Contamination factor

[120]proposed an overall indicator of contamination by integrating data for several heavy metals under study. The contamination factor is an index used to estimate the contamination or pollution range of a certain metal set as;

$$C_f = \frac{C_x \text{ sample}}{C_n \text{ background}} \text{-----[3]}$$

where C_x is the mean content of metals from the study area, and C_n is the background values of individual metals [37]. [120]categorized contaminated soils into four classes based on contamination factor values as follows: $C_f < 1$ as low contamination, $1 < C_f \leq 3$ as moderate contamination, $3 \leq C_f < 6$ as high contamination, and $6 \leq C_f$ as very high contamination.

3.5.4 Contamination degree

The degree of contamination (C_d) is the sum of contamination factors for all of the elements. The degree of contamination by the heavy metal in the soil was determined as follows ([60]).

$$C_d = \sum_{i=1}^n C_f \text{-----[4]}$$

In this study, four categories of C_d were used to evaluate metal contamination levels as follow; $C_d < 8$ as low degree of contamination, $8 \leq C_d < 16$ as moderate degree of contamination, $16 \leq$

$C_d < 32$ as considerable degree of contamination and $32 \leq C_d$ as very high degree of contamination.

3.5.5 Pollution Load Index

The Pollution Load Index (PLI) is commonly used to assess the quality of the environment. [48]The pollution load index is defined as the ratio of element concentration in the study area to the background content of the corresponding element, it is also the geometric mean of CFs of the heavy metals under study. The PLI is calculated as follows;

$$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_n)^{\frac{1}{n}} \text{-----} [5]$$

The PLI was classified as either low ($PLI \leq 1$), moderate ($1 < PLI \leq 3$), and high ($PLI > 3$) ([48]

3.5.5 Potential Ecological Risk

The potential ecological risk index, proposed by [120]was used to investigate the ecological risk of the potential toxic elements in the study area. The potential ecological risk (PER) was calculated using the following formula;

$$CF = \frac{C_x \text{ sample}}{C_n \text{ background}} \text{-----} [6]$$

$$E = CF \times T \text{-----} [7]$$

where C_x is the measured concentration of the heavy metal, C_n is the background value of heavy metal, C_f is the contamination factor of the heavy metal, E is the potential ecological risk factor of each heavy metal, and T is the toxic response factor of heavy metals. The toxic response factor for As, Hg, Pb, Cd, Cr, Cu, and Ni are 10, 40, 5, 30, 2, 5, and 5 respectively. The categories for ecological risk classification were presented as follow: $E < 40$ as low ecological

risk, $40 \leq E < 80$ as moderate ecological risk, $80 \leq E < 160$ as considerable ecological risk, $160 \leq E < 320$ as high ecological risk, and $E \geq 320$ very high ecological risk [120].

3.6 Human health risk assessment

Health risk assessment of the studied soils was widely used to obtain both carcinogenic and non – carcinogenic risks to human via three exposure pathways: ingestion, dermal contact and inhalation. The methodology used for the health risk assessment was based on the guidelines and Exposure Factors Handbook of US Environmental Protection Agency [121]. The average daily doses (ADDs) (mg/kg/day) of potentially toxic metals via ingestion (ADD_{ing}), inhalation (ADD_{inh}), and dermal contact (ADD_{der}) for both adults and children were estimated using the following:

$$ADD_{ing} = \frac{C_{soil} \times IngR \times EF \times ED \times 10^{-6}}{BW \times AT} \text{ --- [8]}$$

$$ADD_{inh} = \frac{C_{soil} \times IngR \times EF \times ED}{PEF \times BW \times AT} \text{ --- [9]}$$

$$ADD_{der} = \frac{C_{soil} \times SA \times AF \times ABS \times EF \times ED \times 10^{-6}}{BW \times AT} \text{ --- [10]}$$

where ADD_{ing} , ADD_{inh} , and ADD_{der} are the daily amount of exposure to metals (mg/kg/day) via ingestion, inhalation, and dermal contact respectively. The other exposure factors and values used to estimate the intake value and risk are listed in Table 3.1

Table 3. 1: Definition and reference values of some parameters for health risk assessment of heavy metals.

Factor	Definition	Units	Value		Reference
			Children	Adult	
C_{soil}	Heavy metal conc. in soil	mg/kg			This study
IngR	Ingestion rate of soil	mg/day	200	100	[121]
EF	Exposure frequency	days/year	350	350	Environmental site assessment guideline [121]
ED	Exposure duration	Years	6	24	[91]
BW	Body weight	Kg	15	55.9	Environmental site assessment guideline [45]
AT	Average time	Days	365ED	365ED	[91]

InhR	Inhalation rate	m ³ /day	7.63	12.8	[122]
	of soil				
PEF	Particle	m ³ /kg	1.36×10 ⁹	1.36×10 ⁹	[91]
	emission factor				
SA	Exposed skin	cm ²	1600	4350	[121]
	surface area				
AF	Skin adherence factor	mg/cm day	0.2	0.7	[91]
ABF	Dermal absorption factor	Unit	0.0001	0.0001	[121]

3.7 Carcinogenic and Non-Carcinogenic Risks Factor

The carcinogenic risks determine the possibility of cancer development in the lifetime of an individual exposed to carcinogenic hazards and in this case the PTEs [123]. The equations below were used to estimate the carcinogenic risks (CR) and the total carcinogenic risks (TCRs) of the PTEs of the farm soils

$$CR = ADD \times SF \text{ ----- [11]}$$

$$TCR = \sum CR = CR_{oral} + CR_{dermal} + CR_{Inh} \text{ ----- [12]}$$

Where CR is the carcinogenic risks, ADD is the average daily exposure dose (mg/kg/day) of the PTEs, and SF is the carcinogenic slope factor under three exposure routes of the PTEs

measured in mg/kg/day. Acceptable risks range are considered in the range of 1×10^{-6} and 1×10^{-4} . Significant risks to humans considered at $TCR > 1 \times 10^{-4}$

Table 3. 2: References doses (RfD) and SF values for the PTEs [123]

Metal	SF ing	SF Inh	SF derm
Cu	1.7	-	42.5
Cd	6.1	6.3	6.1
Zn	-	-	-
Co	-	-	-
Pb	-	-	-
Ni	-	-	-
Cr	0.5	42	20
As	1.5	15.1	3.66

In this study, non-carcinogenic and carcinogenic effects of heavy metals were assessed using the hazard quotient (HQ), hazard index (HI) and carcinogenic risk (RI) methods [124]; [8]. The HQ is the ratio of the ADD (Average Daily Dose), of a heavy metal to its reference dose (RfD) for the same exposure pathways [91]. The reference dose (RfD) (mg/kg/day) is the maximum daily dose of a metal from specific exposure pathway for both adult and children, that is believed not to lead to an appreciable risk of deleterious effects to sensitive individuals during a lifetime. If the ADD is less than the RfD, $HQ \leq 1$, it is considered that there will be no adverse health effects, whereas if the ADD exceeds the RfD, $HQ > 1$, it is likely that there will be adverse health effects (USEPA, 1989, 2001).

The hazard index (HI) is the sum of HQ and means of the total risk of non-carcinogenic element via three exposure pathways for single element. If the value of $HI < 1$, no risk of non-carcinogenic effects is believed to occur, whereas $HI > 1$ indicated a probability of an adverse health effects, and probability increases with the increase of HI values. Carcinogenic risk is regarded as the probability of an individual developing any type of cancer in the whole life time due to exposure to carcinogenic hazards [84]. The HI and carcinogenic risk are calculated as follows:

$$HI = \sum HQ = \sum \frac{ADD}{RfD} \text{-----} [11]$$

$$\text{Risk (RI)} = \sum ADD \times SF \text{-----} [12]$$

The value of SF represents the probability of developing cancer per unit exposure level of mg/kg/day. The values for RfD, SF and other calculated parameters are given in Table 3.1. If $RI < 10^{-6}$, the carcinogenic risk to health from the soil can be negligible and an RI above 1×10^{-4} is likely to be high risk of developing cancer in human beings. An RI value within a range from 1×10^{-6} to 1×10^{-4} indicate an acceptable or tolerable risk to social stability and to human health [48].

3.8 Quality control for the soil samples for the PTEs

All the reagents used were of analytical grade. A blank was run for each digestion procedure to correct the measurement. Each sample was analyzed in triplicates and two standards were tested after every 10 samples to check for interference and cross contamination. The percent recoveries of the metals analyzed were also calculated (Table 3.3). ISE Sample 999 of moist clay from Liteta/Ivory Coast, WEPAL (Wageningen Evaluating Programs for Analytical

Laboratories were included in every batch of the sample digestion and analysis as part of the quality control protocol.

Table 3. 3: Certified and measured concentration of Pb, Cd, and As in ISE sample 999 of moist clay from Liteta/Ivory Coast, WEPAL

Analyte	Certified value (mg/kg)	Measured value (mg/kg)	% Recoveries
Pb	4.710 ± 1.157	4.907 ± 0.235	99.8
Cd	0.040 ± 0.020	0.048 ± 0.031	95.7
As	0.772 ± 0.344	0.852 ± 0.223	101.4
Cr	221.0 ± 32.0	215 ± 29.2	98.7
Cu	12.5 ± 1.61	13.2 ± 2.52	104.2
Ni	74.1 ± 13.83	76.3 ± 14.51	98.3

3.9 Determination of the Physicochemical parameters of the soil

3.9.1 Laboratory analysis for moisture content of soil

50g each of wet soil sample was weighed into moisture cans and dried at 105°C and oven dried for 24 hours. The hot sample was placed in desiccators and allowed to cool at room temperature and reweighed. The percentage water content at field capacity of the samples was measured by the difference in mass between wet soil and oven-dried soil per oven dried soil expressed as a percentage. Mathematically,

$$\% \text{ Water content} = \frac{\text{weight of wet soil} - \text{weight of oven dried soil}}{\text{weight of oven dried soil}} \times 100\%$$

3.9.2 Soil particle size analysis

Bouyoucos (1962) method as modified by Day (1965) was employed for the measurement of particle size analysis for each of the twenty-five representative soil sample. 40g each air-dried homogeneous sample was weighed into dispersion bottles and pre-treated with hydrogen peroxide 1:1 (soil: solution) for the destruction of organic matter. 100ml of 5% calgon (sodium hexametaphosphate) solution was added as a dispersion agent to form a suspension. The suspensions were shaken thoroughly on a mechanical shaker for two hours (2hrs) in order to disperse each sample into sand, silt and clay. The suspensions were then transferred into 1L sedimentation cylinder and topped up with distilled water to the mark.

After this, a plunger was dipped into the suspensions in and out vigorously and left to equilibrate. After five minutes a hydrometer was immersed and the first hydrometer reading was taken and recorded. The first density reading was for both silt and clay in the suspensions. The second hydrometer reading was taken and recorded after five hours (density of clay only in the suspension). The content of sand was determined by pouring the suspension directly into a 47 μ m sieve. The content (sand) on the sieve was properly washed with tap water to wash off all clay and silt particles on the sieve and then transferred into moisture cans, preweighed and dried in the oven at 105°C for 24 hours. After this the weight of the oven dried sand was determined. Hydrometer readings in a blank that contains only 5% calgon were taken at five minutes and five hours' time intervals. The percentage clay, silt and sand were calculated mathematically as follows:

$$\%(\text{clay and silt}) = \frac{(\text{5 minutes hydrometer reading})}{\text{mass of sample (g)}} \times 100$$

$$\% \text{Clay} = \frac{(5 \text{ hours hydrometer reading})}{\text{mass of sample (g)}} \times 100$$

$$\% \text{Silt} = \%(\text{clay and silt}) - \% \text{Clay}$$

$$\% \text{Sand} = \frac{(\text{oven dry weight of particles retained on the } 47\mu\text{m sieve})}{\text{mass of sample (g)}} \times 100$$

The USDA textural triangle was used to determine the textural classes of the soil samples.

3.9.2 Soil pH measurement

The soil samples were air dried at 25°C and sieved with less than 2mm sieve. Soil pH was determined in distilled water to soil mass (1:1) with a pH meter (ACCSEN, EL150 pH electrode). 20g of each soil sample was weighed on an electronic balance into a beaker of 100ml capacity followed by addition of 20ml distilled water to form a soil-liquid suspension. The suspension was stirred for thirty minutes (30mins) and was allowed to equilibrate for a period of one hour to equilibrate. The pH meter was calibrated at buffers 4.01, 7 and 10.01 (triple point calibration). The pH of the soil samples was measured by immersing the probes gently into the suspension.

3.9.3 Measurement of electrical conductivity

The Soil samples under study were air dried at 25°C and sieved with less than 2mm sieve. The soil electrical conductivity was measured in distilled water of 1:5 mass to water ratio with the conductivity electrode using the pH meter (ACCSEN, EL150). Electrical conductivity probe was use to measure the soil's electrical conductivity. A 10g soil sample was weighed into 100ml beaker and then 50ml of distilled water was added to form a suspension. The resulting suspension was stirred for thirty minutes (30mins) and left undisturbed for one hour to equilibrate. The conductivity meter was calibrated at buffers 1413µs/cm, 12.88ms/cm and

84 μ S/cm (triple point calibration). The electrical conductivity probe was gently immersed into the soil-liquid suspension to measure the electrical conductivity.

3.9.4 Extraction of exchangeable bases

5 g sample of the soil (fine) was weighed into a 200 ml extraction bottles for each sample. Fifty milliliters (50ml) of 1M NH₄OAc solution at pH 7 was transferred to the content of the extraction bottles. The bottles were covered tightly and shaken on a reciprocating mechanical shaker for 1hr and it was filtered with filter paper (Whatman No.42 filter paper). Using Atomic Absorption Spectrophotometric techniques (AAS) (A Analyst 800), the Ca, Mg, K and Na was measured. Appropriate standards were used for the calibration of the AAS instrument for calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) respectively to determine their absorbance. Concentrations of the basic cations in the filtrates were determined on the AAS device. Exchangeable bases were calculated as follow:

$$X(\text{cmol}_c\text{Kg}^{-1}) = \frac{R \times \text{volume of extract} \times 10^3 (\text{g}) \times 100 (\text{cmol}) \times E}{\text{Weight of soil} \times 10^6 (\mu\text{g}) \times M}$$

Where X = Basic cation,

R = Absorbance measured in mgL^{-1}

E = Represents charge of cation

M= Basic cation's atomic mass

3.9.5 Cation exchange capacity (CEC)

5 g sample of the soil (fine) was weighed into a 200ml extraction bottles. Fifty milliliters (50ml) of 1M NH₄OAc solution at pH 7 was transferred to the content of the extraction bottles. The bottles were covered tightly and shaken on a reciprocating mechanical shaker for 1hr. The

suspension was filtered with filter paper (Whatman No.42 filter paper). After filtration, the residues were immediately washed four times with 50ml portions of ethanol (in order to get rid of excess ammonium ion) into empty plastic bottles. The residues were again washed four times with 50ml portions of acidified KCl (1M). Each portion was added at a time and allowed to drain through the residue before adding the next portion. Ten milliliters (10ml) of the filtrate were transferred into a Kjeldahl flask and 10ml solution of forty percent sodium hydroxide (40% NaOH) portions were added and distilled into 5ml 2% boric acid. The solutions were back titrated against 0.01M HCl solution. The ammonium ion concentrations in the various samples were determined as the CEC of the soil.

$$\text{CEC (cmol}_c\text{/kg soil)} = \frac{V(\text{HCl}) \times M(\text{HCl}) \times 0.001 \times \text{vol.of extract} \times 1000 \times 100}{\text{vol.of the aliquot} \times \text{weight of soil}}$$

3.9.6 Organic Matter Determination (Weight Loss-On-Ignition at 550°C)

50g each of the wet soil sample was weighed into clean and well dried moisture cans. It was then dried in the oven for one day (24hrs) at 105°C. The hot sample was quickly placed in desiccator and allowed to cool at room temperature. Two grams (2g) of each soil sample that was oven dried was measured into clean dry and already weighed heating crucible. The heating crucibles were arranged in a pattern that followed their labels and were placed in the VECSTAR muffle furnace at a temperature 550°C for four hours. Thereafter, samples were allowed to cool and placed into the desiccators to further induce cooling without absorbing moisture and the contents reweighed to determine weight loss after ignition.

Percent organic matter is calculated as follows:

$$\% \text{ Organic Matter} = \frac{\text{Weight of sample at } 105^\circ\text{C} - \text{Weight of sample at } 550^\circ\text{C}}{\text{Weight of sample at } 105^\circ\text{C}} \times 100$$

3.10 Biological analysis

3.11 Preparation of Ringer's solution

2g sodium chloride (NaCl), 0.07g potassium chloride (KCl), 0.12g calcium chloride (CaCl_2) and 0.5g hydrated sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) were weighed and dissolved in distilled and topped up to the 1L mark.

3.12 Preparation of nutrient agar solution

28g of nutrient agar was dissolved in distilled water and made up to the 1L mark and autoclaved at 121°C for 15 minutes.

10g sample of fine soil was transferred into ninety millilitres (90ml) sterilized Ringer's solution followed by shaking in sterilized medicinal bottle. Using aseptic technique, the cap of the test tube was removed from the 9ml dilution blank (Ringer's solution) and the mouth was flamed. 100 microlitres ($100\mu\text{L}$) of the suspension was pipetted into 9ml Ringer's solution (blank) in a screw cap test tube with sterile micropipette for each subsequent transfer. Using aseptic technique, 1ml of the diluents from the 10 to the negative 1 dilution was transferred to the 10 to the negative 2 dilution blank which followed in that order to 10 to the negative 5 dilution blank (serial dilution of 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} and 10^{-5}) and recapped and shaken for about 1min in each case. The micropipette tips were changed in each case. $100\mu\text{l}$ of serial diluents 10^{-4} and 10^{-5} (duplicate of each) were pipetted into a sterile petri dish followed by pouring 12ml to 15ml of melted nutrient agar (pour plate method) solution. It was then covered and gently shaken and allowed to set. The petri dish and its content were placed in the incubator at 37°C for 3 days when growth was observed. The number of microorganisms was estimated using marker on the Colony Forming Units (CFU). Plates with too numerous colony-forming units to count

(TNTC above 300) and plates with colony forming units too few to count (TFTC below 30) were ignored. The number of microorganisms was estimated as follows:

$$\text{Microbial population} = \frac{\text{CFU}}{\text{Dilution factor per gram of sample}}$$

3.13 Fungal population for ten farms (Kwabia and Kwabia Asasehene)

The five soil samples each from the five farms were homogenized. Ten (10g ± 0.1g) of each was analyzed in the Department of Botany for soil mycoflora profile and population analysis. The analysis was done in malt extra media and DG18 media.

3.14 Preparation of malt extract agar (MEA) and Dichloran-Glycerol (DG18) agar

50g of MEA or 31.8g of DG-18 powder were weighed and dissolved in 1L distilled water after which the mixture was heated in a water bath for about 10 minutes for complete dissolution. The solution was transferred into medicinal bottles and was sterilized at 121°C and 1.1Kg/cm³ pressure for 15mins in an autoclave.

Table 3. 4: Materials and their quantities for preparing malt extract agar (Oxoid CM167)

Material	Quantity
Malt extract	30.0g
Mycological Peptone	5.0g
Agar	15.0g
Distilled Water	1000mL
Ph	5.4±0.2
Temperature	25°C

Table 3. 5: Materials and their quantities used in the preparation of Dichloran-glycerol (DG18) Agar (Oxoid CM167).

Material	Quantity
Peptone	5.0g
Glucose	10.0g
Potassium dihydrogen phosphate	1.0g
Magnesium Sulphate	0.5g
Dichloran	0.002g
Agar	15g
pH	5.6±0.2
Temperature	25°C

3.15 Preparation of peptone water

1% peptone water was prepared by dissolving 1g in 99ml of distilled water. Exactly 10ml aliquots were dispensed into McCartney tubes and autoclaved at 121°C (1.1kg/stem pressure) for 15 minutes. These were used for the various serial dilution preparations.

3.16 Isolation and identification of mycoflora population

One percent (1%) peptone water was used for serial dilution preparations of a stock solution of 10g sample/100ml of peptone water of each sample into a McCartney tube filled with 9ml of

the aliquot (peptone water) and a serial dilution up to $1:10^3$. Each tube was shaken at 140 rev/min for 2-3 mins on an orbital shaker (Gallenkamp, England). Serial dilution up to $1:10^3$ aliquot was made and 1 ml aliquot was plated on 20 ml of either MEA or DG18 and incubated at room temperature (26°C) for 7 days. Colonies of mycoflora appeared were counted and calculated as $\log_{10}$ CFU/g sample. Fungi isolated were identified by their cultural, colour morphological characteristics (microscopic and macroscopic) according to [127]; [128]; [129] as well as other relevant identification manuals.

3.17 Quality Control/ Quality Assurance for determining the physicochemical properties

For the study, samples were carefully handled during sample collection, transporting, preparation, analysis to avoid any external influences that could interfere with the integrity of the sample and hence contaminate it; protocols were carefully followed for each analytical parameter alongside careful tracking of samples for error minimization. Also, results and data entry including reporting were carefully done to avoid statistical errors. To minimize chemical (photochemical and microbiological degradation) and physical (volatilization, adsorption, diffusion, and precipitation) changes between collection and analysis sample bags were well sealed and the cooler which contained samples with ice was airtight. Samples were kept in the refrigerator until all chemical and biological analyses were carried out. Extractions were carried out within one week after sampling. Quality assurance measures applied in the laboratory included rigorous contamination control procedures (strict washing and cleaning procedures), analysis of procedural blanks, monitoring of detector response and linearity. During extraction, blanks duplicates were included in the analysis and re-calibration standards run frequently to check the linearity of the determination. For validation of the analytical procedure, repeated analysis of the samples against internationally certified/standard reference material was used. Except for the temperature, multi-probe meters were calibrated together using the same

standard and procedures. Electrical conductivity was calibrated against 0.005, 0.05, and 0.5M standard potassium chloride solution; pH was calibrated with standard buffer at pH of 4, 7 and 10. The temperature was checked against standard mercury thermometer for consistency.

All reagents used during the analysis were of high quality and exposed to the same extraction procedures and subsequently run to check for interfering substances. Sample of each series was analysed in duplicates.



CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Concentration of PTEs in the farm soil

The mean concentrations of the PTEs ranged from 3.5mg/kg-0.7mg/kg for Cd, 19.08mg/kg-3.94mg/kg for Cr, 19.24mg/kg-11.42mg/kg for Co, 27.28mg/kg-3.26mg/kg for Pb, 29.62mg/kg-12.42mg/kg for Ni, 30.76mg/kg-14.52mg/kg for Cu and 36.6mg/kg-22.02 mg/kg for As. Therefore, the concentrations of the PTEs decreased in the order As>Cu>Ni>Pb>Co>Cr>Cd in the farms soil studied (Table 4.1). Analysis of variance (ANOVA) between the metals concentrations and the farms was used to unearth the variations in level of the PTEs' concentrations among the five farms (Appendix A, Table 10, Table 11, Table 12, Table 13, Table 14, Table 15, and Table 16). The mean concentration of Cu decreased among the farms as follows: KA>K>Aw>AS>Ag. There was no significant difference between the concentration of copper (Cu) for all the five farms ($p>0.05$). For Cd concentration, there was significant difference between all the farms ($p<0.05$) and the Cd concentration decreased among the farms in the order; Aw>AS>KA>Ag>K (Table 4.1). Also, there was significant variations in the concentrations of Cr among the five farms especially between Kwabia and Aworworso as well as Kwabia Asasehene and Agbom farms ($p<0.05$) (Table 12 appendix A). The concentration of Cr decreased in the order; Ag>Aw>AS>KA>K for the farms. The concentration of Co decreased among the farms in the order KA>K>Ag>AS>Aw (Table 4.1). The Tukey HSD tests revealed that the concentration of Co was not significantly different between the farms ($p>0.05$). In decreasing order, the concentration of Pb among the farms were Ag>Aw> AS> K>KA and the concentration of Ni were Ag>Aw>KA>AS>K for the farms. Also, the concentration of Pb and Ni were significantly different among all the farms ($p<0.05$)

but As concentration were not significantly different between the farms ($p>0.05$). The variation degrees of concentrations among the farms could represent different activities that releases different kinds of PTEs into the farms soil. Several studies had indicated also that the presence and content of PTEs in soils in varying concentrations depends on the location, activities at/around the agricultural site and sources of the pollutants [130]; [13]; [9]; [131]. The maximum allowable concentrations of the PTEs established by the World Health Organization and the Food and Agriculture Organization (WHO/FAO) were above the mean concentrations of the PTEs in all the farms soil except for As similarly reported elsewhere [130]. The mean concentration for As for all the farms exceeded the WHO/FAO limits and Cd exceeded the WHO/FAO limits for Aworworso farms (Table 4.1). Descriptive statistics revealed that the maximum values for Cu, Cr, Co, Pb, and Ni for the five farms were below WHO/FAO maximum limits (Table 4.2). The maximum values for As exceeded WHO/FAO limits for all the five farming communities. The maximum concentration for Cd for Aworworso, Kwabia Asasehene and Asasehene farms exceeded the WHO/FAO allowable limits. The As and Cd exceeding allowable concentrations could endanger soil health for agriculture production [37]. It also means that the farms soil had arsenic rich rocks coupled with natural oxidation. Discharges from landfills, dumpsites and burning of e-wastes near the farming locations accounts for increased arsenic concentrations [35]. Also, excess fertilizer applications by farmers, and indiscriminate Cd containing wastes disposals increased the Cd levels in the soil environment [44]; [132].

From table 4.1, the coefficient of variation (CV) of the metals was further used to infer the sources of contamination of the metals in the soil. Heavy metal pollution with low CV represents natural sources and high CV is mostly caused by human activities [124]). The coefficient of variation of PTEs in the soils were in the following decreasing order: Pb (69.94%) > Cr (55.55%) > Cd (55.54%) > Ni (42.25%) > Cu (30.94%) > Co (20.83%) > As (19.20%)

(Table 4.1). The CV and the Pearson correlation both confirmed Pb and Cd in the farms soil to emanate from human activities (Table 4.1 and Table 4 .3). The coefficient of variation of the PTEs analysed indicated moderate degree of variability. The greater the coefficient of variation the greater the likelihood that heavy metals concentrations were affected by human activities [13]. Anthropogenic activities such as fertilizer applications, discharge of effluents, etc contribute significantly to the concentration of PTEs in the soils. Natural sources of PTEs may originate from parent materials and lithogenic sources [35].



Table 4. 1: Average concentrations of the PTEs present in the farm soils

Farms	Mean concentrations of the PTEs in the farm soil (mg/kg)												
	Cu	Cd		Cr		Co		Pb	Ni	As			
K	26.00 ± 9.4	0.7± 0.04	3.94	±	17.02	±	5.1 ± 1.16	12.42	±	35.6 ± 8.37			
			1.57		6.19			3.32					
KA	30.76 ± 7.90	1.6	±	6.24	±	19.24	±	3.26 ± 0.45	14.68	±	26.96	±	
		1.59		4.34		6.98			8.08		7.63		
AS	16.00 ± 3.20	2.42	±	13.42	±	12.74	±	22.28	±	14.62	±	24.86	±
		1.34		8.71		1.86		5.33		8.51		9.88	
Ag	14.52 ± 2.71	1.42	±	19.08	±	15.68	±	27.22± 6.34	29.62	±	22.02	±	
		0.71		5.90		2.72			6.94		7.07		
Aw	24.34 ± 7.18	3.5 ± 1.31	17.14	±	11.42	±	27.14±		28.94	±	25.12	±	
			7.32		3.55		12.72		1.59		8.91		
C	2.58 ± 0.51	0.12	3.08	±	7.76	±	2.30 ± 0.81	0.52	±	1.36 ± 0.04			
		±0.06	0.21		0.45			0.19					
CV (%)	30.94	55.54	55.55		20.83		69.94	42.25		19.20			
^b WHO/FAO	100.00	3.00	100.00		50.00		100.00	50.00		20.00			

K=Kwabia farming community, KA=Kwabia Asasehene, A=Asasehene, Ag=Agbom, Aw=Aworworso, C=Control; CV=Coefficient of Variation; WHO/FAO=World Health Organization/Food and Agriculture Organization

Table 4. 2: Descriptive Statistics of the PTEs in the farm soils (mg/kg)

Farming Communities	Cu	Cd	Cr	Co	Pb	Ni	As
Kwabia							
Minimum	12.1	0.3	0.2	6.3	3.4	9.1	10.7
Maximum	56.4	1.5	8.3	20.8	8.4	16.8	60.6
Median	17.3	0.5	5.2	20.5	3.9	12.2	41.7
Skewness	1.47	1.51	-0.09	-1.92	1.13	0.34	-0.09
Kurtosis	1.64	2.07	-2.26	3.64	-0.23	-1.89	-0.83
Kwabia Asasehene							
Minimum	21.30	0.2	1.1	9.8	0.1	1.5	14.6
Maximum	41.20	3.7	12.1	29.2	12.4	23.7	41.5
Median	31.1	0.8	7.3	19.2	1.1	16	24.5
Skewness	0.16	0.67	0.17	0.17	2.12	-1.22	0.42
Kurtosis	-1.16	-2.43	-0.95	1.37	4.59	2.81	-1.01
Asasehene							
Minimum	13.2	0.4	2.7	10.2	17.2	1.5	10.5
Maximum	21.4	3.6	23.1	14.7	31.2	24.3	59.6
Median	15.1	2.8	12.2	12.5	21.3	14	16.1
Skewness	1.63	-0.96	-0.01	-0.32	1.54	-0.84	1.99
Kurtosis	2.95	-0.17	-2.18	-1.24	2.93	1.29	4.10
Agbom							
Minimum	11.3	0.5	11.1	11.8	11.2	19.2	8.5
Maximum	17.1	2.5	27.6	17.7	42.1	34.4	50.6

Median	15.1	1.4	18.8	17.5	34.2	34.4	19
Skewness	-0.31	0.55	0.22	-0.90	-0.42	-1.08	1.58
Kurtosis	-2.80	2.10	1.65	-1.63	-2.96	-0.66	2.67
Aworworso							
Minimum	12.1	2.3	11.2	9	12.1	26.7	11.5
Maximum	41	4.9	26.1	17.6	45.1	30.9	61.5
Median	21.3	3	12.7	9.7	23.1	28.8	16.2
Skewness	0.41	0.43	0.63	1.97	0.49	-0.31	1.95
Kurtosis	-2.48	-3.15	-3.05	3.93	-0.42	0.03	3.88
Control							
Minimum	0.2	0.05	1.1	7.1	1.2	0.3	0.6
Maximum	4.1	0.2	8.6	8.3	3.1	0.8	2.5
Median	3.1	0.1	1.3	7.8	2.1	0.5	0.6
Skewness	-1.13	0.40	1.87	-0.55	-0.27	0.59	0.61
Kurtosis	1.08	-0.18	3.44	0.46	-1.32	-0.02	-3.33
^b WHO/FAO	100.00	3.00	100.00	50.00	100.00	50.00	20.00

4.2 Sources of PTEs contamination

To further identify the sources of contamination, correlation coefficient analysis was carried out. The correlation matrix was carried out to examine the relationship between the metals enable inference to the sources of pollution (Table 4.3). Pearson's correlation analysis showed strong negative correlation between Cr and Cu ($r = -0.89$), Co and Cd ($r = -0.81$), Pb and Cu ($r = -0.78$), As and Cr ($r = -0.80$), Pb and Co ($r = -0.82$), As and Pb ($r = -0.74$) and As and Ni ($r = -0.67$) (Table 4.3). Also, there was strong positive correlation between Pb and Cd ($r = 0.64$), Pb and Cr ($r = 0.71$), Ni and Pb ($r = 0.80$) and moderate correlation between Co and Cu ($r = 0.52$),

As and Cu ($r=0.58$), As and Cd ($r= -0.54$), Ni and Cr ($r= 0.54$). However, significant correlation was established between the following: Cd/Cu ($r= -0.12$, $p<0.05$), Cd/Co ($r= -0.81$, $p<0.05$), Ni/Cd ($r= 0.48$, $p<0.05$), As/Cd ($r= -0.54$, $p<0.05$), Ni/Cr ($r=0.54$, $p<0.05$), As/Cr ($r= -0.80$, $p<0.05$), and As/Co ($r=0.39$, $p<0.05$). Again, strongest positive significant correlation was found for Pb/Cd ($r= 0.64$, $p<0.05$) which meant a possible common source of the PTEs in the farms soil. This corroborates with findings by [37], that a strong positive significant correlation between the metals was indication of possible sources of contamination of the elements in the agricultural soil. Similarly, according to [37], strong positive correlation suggests that the PTEs may come from the similar sources mainly originating from anthropogenic activities and while negative correlation indicates different sources. In Table 4.3, there was more significantly negative correlation between the metals which implied that majority of the PTEs had different sources of contamination in the soil [37]. High correlation of PTEs could be influenced by human activities in addition to natural sources.

Table 4. 3: Correlation matrix of the PTEs in the soil

PTEs	Cu	Cd	Cr	Co	Pb	Ni	As
Cu	1.00						
Cd	-0.12*	1.00					

Cr	-0.89	0.08	1.00				
Co	0.52	-0.81*	-0.26	1.00			
Pb	-0.78	0.64*	0.71	-0.82	1.00		
Ni	-0.42	0.48*	0.54*	-0.48	0.80	1.00	
As	0.58	-0.54*	-0.80*	0.39*	-0.74	-0.67	1.00

*Correlation is significant at $p < 0.05$ level (2-tailed)

4.3 Physicochemical properties of the farms soil

The pH of the soils were weakly acidic for all farms and ranged from 5.50 ± 0.26 (AW farms)- 6.69 ± 0.98 (A farms). The pH for **Agbom** was significantly different from **Aworworso** ($p < 0.05$) (Table 4.4). The pH reflects the kinds of anthropogenic activities, rock, and mineral properties of the farm soils. Each crop plant has unique pH range for optimal performances. The acidic pH possibly comes from the application of ammonium-based nitrogen (N) fertilizers. Also from Table 4.4, there is high amount of sand which could decrease the buffering capacity of the soil. High precipitation washes away base cations to make pH acidic. This agrees with observations made from the studies [133]. When the Ph of the soil is within the pH of 6.5-8.0, macronutrients are more available in the soil [133]. Therefore, Aworworso farms were in pH that favoured availability of macronutrients. At pH ranges between 5.0-7.0, micronutrients become predominant in the soil which was expected for KA, A and AW (Table 4.4). On the other hand, other studies have found much lower pH in agricultural soils as opposed to the current study. According to [101], a lower pH of 3.0-3.5 determined from agricultural soil promoted better absorption of phosphorus by plants better and enhanced phosphorus desorption in the soil which influenced nutrients availability for crop production and promotion of soil health. Also, pH affects CEC of the soil [133]. The CEC determined for the five farms were not significantly different ($p > 0.05$). The CEC gives an indication of the

soil's ability to retain and release nutrients to the plants. The low pH (5.5-6.9) of the farms soil meant that more H^+ ions available in the soil to exchange with the cations which are basic. This will remove them from the exchangeable sites of the soil to the soil water (solution) which makes nutrients available to plants or lost via erosion.

The soil moisture is a key indicator of soil health and quality [112]. The soil moisture ranged from 4.12-8.28% among the farms. Significant differences existed in the percentage soil moisture between Kwabia Asasehene farms and Asasehene farms ($p < 0.05$). From Table 4.4, the percentage of sand was higher than the percentage of clay and silt. The pores of sand are larger than for clay and silt which allows for less water holding capacity of the soil which accounted for the low percentage of soil moisture observed. While rainfall and irrigation influence the moisture content of soil, exposure to high temperature and evaporation as well as the soil structure determines the amount accessible to soil organisms and for plant growth. A moderate soil moisture promotes microbial functions and improves crop production while high moisture obstruct oxygen penetration in soil which affects microbial activities [112]. It is noteworthy to mention that, different crop plants require varying amounts of soil moisture and the percentage of moisture recorded in this study effects on crop plants is dependent on the kind of crop plants that are grown on the farms [134].

In addition, the percentage of the soil textural classes were of the farms were assessed. The percentage of clay for Kwabia (K) farming community was significantly different from Kwabia Asasehene (AS) farming community ($K = 33.4 \pm 7\%$, $KA = 18.2 \pm 4\%$, $p < 0.05$). Similarly, significant difference was observed between K and KA farming communities for percentage of sand ($K = 55.8 \pm 10\%$, $KA = 73.6 \pm 5\%$, $p < 0.05$) while there was no significant difference between silt among all the farming communities ($p > 0.05$). The soil textural class therefore was sandy clay loam (Table 4.4). According to [135] and [110], fine soil particles have good

adsorption sites which affects the PTEs bioaccessibility and stability. The differences in soil particles/texture can directly or indirectly influence soil functions and crop production [110].

The Electrical Conductivity (EC) is an indication of ions and salts present in the soil. The EC for the farms were Kwabia (0.1 ± 0.04) dS/m, Kwabia Asasehene (0.1 ± 0.04) dS/m, A (0.1 ± 0.05) dS/m, Agbom (0.10 ± 0.12) dS/m and Aworworso (0.06 ± 0.01) dS/m (Table 4.4). There was no significant difference in EC among the farms ($p > 0.05$) (Table 4.4). The ions and salts could be from wastes dumped on/around the farm, rocks, and minerals of the soil. If salt content is high, it can affect plant growth and productivity. For acceptable salt content for proper crop growth, EC of 0-0.8 dS/m is recommended. When a soil analyzed exceeds 4 dS/m at 25 °C, then such sampled soil is considered saline [107]. The recorded EC was between 0.07-0.1 dS/m which were within acceptable recommendations and hence represented no impediment to nutrients availability to plants, microorganisms, and crop yield as opposed to observations made elsewhere [108].

In Table 4.4, the soil organic matter (OM) contents were all within commonly reported range of soil organic matter content of 0.1-6% agreeing with other existing studies [109]. The soil OM originates from the biodegradation of organic materials, addition of fertilizers and the decay of plant leaves. This influences nutrients availability for crop plant growth [109]. Significant differences ($p < 0.05$) were observed among the following farming communities for the exchangeable bases: K and KA, Ag and Aw for Ca and Mg respectively; K and KA for potassium (K) (Table 4.4).



Parameters	Farming communities				
	K	KA	A	AG	AW

Moisture (%)	8.28 ±2.24 ^a	4.12 ±1.73 ^a	7.32± 0.77 ^b	7.15 ±0.45 ^b	5.95± 1.24 ^b
Clay (%)	33.4±7.23 ^c	18.2±4.38 ^d	42.6±30.33 ^d	20.2±3.96 ^d	16.4±0.89 ^d
Silt (%)	10.8±5.17 ^e	6.6±2.07 ^e	8.2±4.50 ^e	5.2±1.48 ^e	7.8±3.42 ^e
Sand (%)	55.8±9.65 ^b	73.6±4.51 ^a	49.2±33.55 ^a	74.6±2.61 ^a	75.00±3.08 ^a
pH	5.87±0.87 ^d	6.03±0.68 ^d	6.69±0.98 ^d	6.13±0.47 ^d	5.40±0.26 ^c
EC (dS/m)	0.07±0.04 ^e	0.1±0.04 ^e	0.07±0.05 ^e	0.10±0.12 ^e	0.06±0.01 ^e
% Organic matter	4.41±2.88 ^a	3.06±1.61 ^a	3.04±0.49 ^a	3.52±0.24 ^a	3.74±0.51 ^a
CEC (cmol(+)/Kg soil	22.22±7.72 ^b	14.01±1.79 ^b	19.03±7.20 ^b	24.70±7.33 ^b	27.82±6.28 ^b
Exchangeable bases (cmol(+)/Kg)					
Ca	8.75±1.85 ^c	4.91±1.23 ^d	5.62±2.89 ^d	5.22±0.46 ^d	3.47±0.16 ^c
Mg	2.65±0.46 ^e	1.10±0.18 ^a	1.53±0.71 ^a	1.49±0.24 ^a	0.74±0.18 ^b
K	0.88±0.12 ^c	0.77±0.10 ^d	0.97±0.32 ^d	1.06±0.46 ^d	0.62±0.11 ^d
Na	0.33±0.05 ^e	0.34±0.02 ^e	0.37±0.07 ^e	0.39±0.12 ^e	0.34±0.07 ^e

Table 4. 4: Physicochemical properties of the farms soil

The mean values of the farms in rows with different letters are significantly different at $p < 0.05$

K=Kwabia, KA=Kwabia Asasehene, AS= Asasehene, Ag= Agbom and Aw= Aworworso

4.4 Impact of the PTEs on the soil microbial population

The number of microorganisms (bacteria) detected in the soil was comparatively small. In the five farms analysed from each farming community, most of the samples had bacteria too few to count (TFTC) especially for 10^{-5} cfu/gsoil (Table 8 Appendix A). When a correlation was performed between the mean total bacteria counts (10^{-4} cfu/gsoil) and the PTEs, it showed

mixed effects at $p=0.05$ at 95% confidence interval. There was strong negative correlation between the bacteria in the soil for Kwabia farms and Co ($r=-0.86$), Pb ($r=-0.77$) and As ($r=-0.54$) in the soil (Table 4.5 and Figure 4.1 a, b, c). Also, the bacteria isolated for Kwabia Asasehene (KA) farms correlated strongly positively with Co ($r=0.95$) and Cu ($r=0.74$) signifying serious impacts of these PTEs on the soil bacteria (Nunes et al., 2016). But Cd, Cr, Pb, Ni and As had no effect on the bacteria for KA farms (Table 4.5). For Asasehene (A) farms, Cd ($r=-0.57$), Cr ($r=-0.62$), Ni ($r=0.57$), As ($r=0.58$) and Cu ($r=0.73$) correlated strongly with the soil bacteria (Table 4.5). Again, there was strong negative correlation between the bacteria in the soil for Agbom (Ag) farms and Cd ($r=-0.74$), Co ($r=-0.72$), Ni ($r=-0.66$) and As ($r=-0.78$) in the soil (Table 4.5). There was strong correlation between the bacteria in the soil for Aworworso (Aw) farms and Cd ($r=-0.77$), and Co ($r=0.57$) in the soil (Table 4.5). This means that some of the PTEs impacted on the soil bacteria in the farms soil. This corroborates with other studies that have found effect of PTEs on the soil microbial population. A study conducted in New Jersey among farming communities on impact of copper on soil bacteria and human health subjected the farm soil environment to copper levels from extremely high level (about 4500mg/kg), high copper levels (about 450mg/kg) and normal exposure levels (about 15mg/kg). This revealed a decline in bacteria population and fungal biomass at higher copper concentrations over time [59]. According to [60] "Copper exerts selection pressure on soil microbiota". The impact of the PTEs on the bacteria in this study could be evident for the few numbers of bacteria detected at 10^{-5} cfu/gsoil that was significantly too few to count. This could have led to death of some of the bacteria due to high concentrations and degree of contamination (Table 4.9). This can have effect on the nutrient circulation and availability in the soil.

Table 4. 5: Bacteria population for each farm (10^{-4} CFU/g soil) correlated with the PTEs of the soil

Farms	PTEs						
	Cd	Cr	Co	Pb	Ni	As	Cu
Kwabia	-0.04	0.43	-0.86	-0.77	-0.21	-0.54	-0.05
Kwabia Asasehene	-0.38	-0.36	0.95	0.30	0.09	-0.28	0.74
Asasehene	-0.57	-0.62	-0.28	0.30	0.57	0.58	0.73
Agbom	-0.74	0.05	-0.72	-0.35	-0.66	0.40	-0.78
Aworworso	-0.77	0.23	0.57	-0.35	0.24	-0.37	-0.06



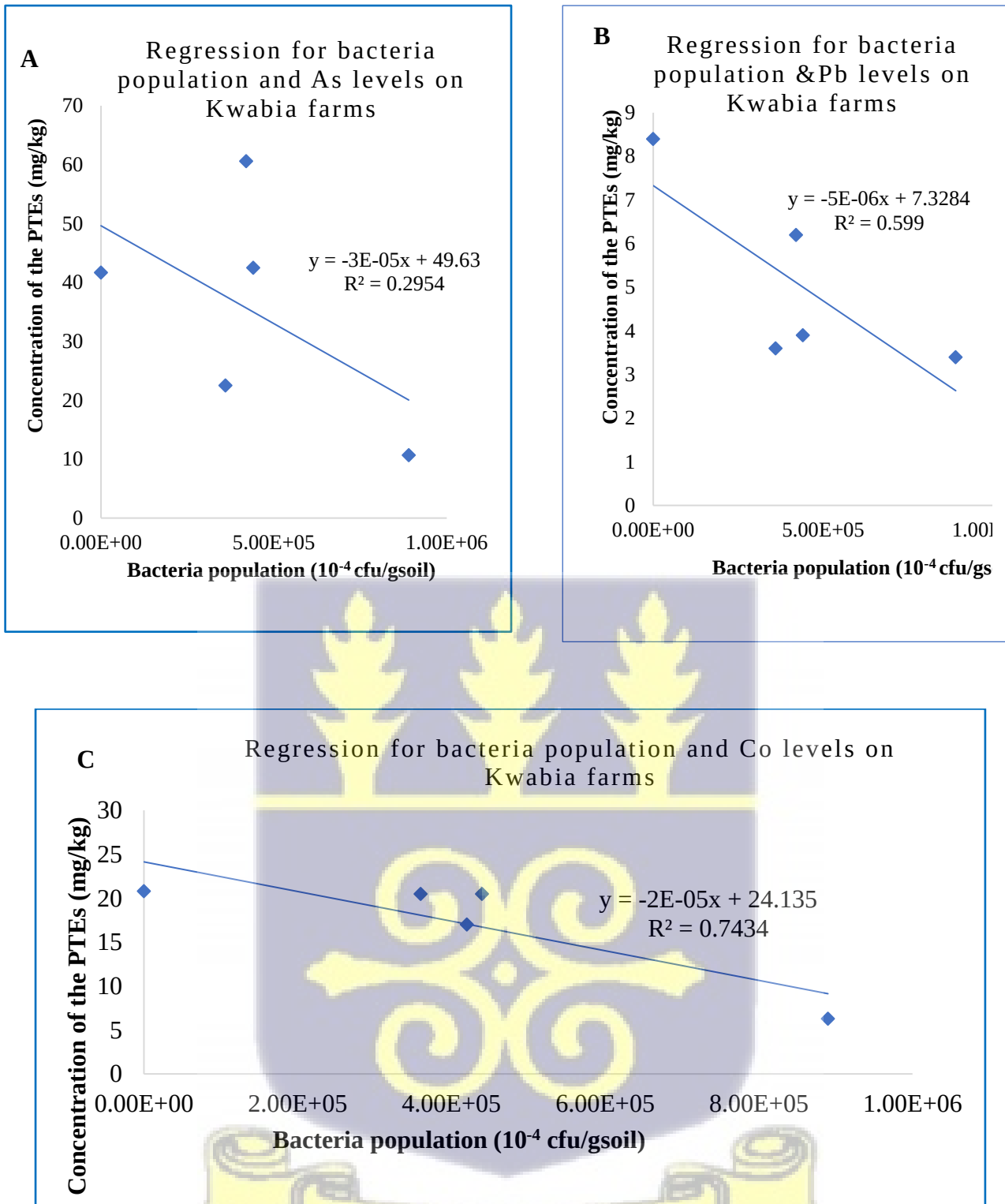


Figure 4. 1: Regression analysis for strength of correlation between the soil bacteria and As (A), soil bacteria and Pb (B), soil bacteria and Co (C) for Kwabia (K) farms

4.5 Effects of the Physicochemical properties of the soil on the PTEs

The impacts of the physical and chemical properties of the soil on the PTEs and vice versa was determined using correlation at $\alpha=5\%$. A correlation of 0.00-0.49 was classified as no correlation to poorly correlated. From 0.50-1.0 was classified moderate to strong correlation. Correlation between the mean concentrations of PTEs for all farms and the physicochemical properties of soil for all farms were performed. There was moderate negative correlation between clay and Ni concentration of the farms soil ($r=-0.54$) (Table 4.6). Regression analysis depicted a weak strength of the relationship between clay and Ni ($R^2=0.30$). This implies that the clay content impacted on the nickel concentration in the soils (Table 4.6 and Figure 4.2). Moderately positive correlation was found between sand and Ni ($r=0.57$). The pore sizes of the sand and grain arrangement impacted on Ni infiltration in the soil (Figure 4.3). The CEC affected the concentration of Pb in the soil ($r=0.51$) (Figure 4.4). The CEC therefore possibly affected the release of Pb ions which is found to affect exchangeable bases such as potassium (K) and calcium (Ca) uptake but negative effects on the absorption of Magnesium (Mg) in agricultural soil [47]. Organic matter (OM) content did not correlate with the mean concentrations of the PTEs of the five farms similar to findings of other studies [9].

Correlations between concentrations of PTEs for each farming community and each physicochemical parameter of the soil revealed mixed results. The moisture content had strong correlation with Co ($r=-0.90$) and As ($r=-0.75$) for Kwabia farms; Cr ($r=0.78$), Pb ($r=-0.56$) for Asasehene farms; Ni ($r=0.70$), As ($r=0.73$), Cu ($r=-0.72$) for Agbom farms; Cr ($r=-0.56$), As ($r=0.93$), Cu ($r=0.77$) for Aworworso farms (Table 1, Appendix A). The details of the correlation between each farm site and the physicochemical properties of the soil are presented in Table 1 appendix A. The pH correlated with the metals for the individual farms (Table 1 Appendix A). This means that the pH influenced the adsorption, retention, migration and

transfer of the PTEs [9]. Decrease in soil pH results in increase Ni releases into the soil environment which means pH is very critical to control Ni levels in the soil for effective and safe agriculture production [69]. In the present study, pH correlated with Ni for Asasehene (A) farms, Ni ($r=-0.54$). Also, pH correlated with Kwabia (K), Kwabia Asasehene (KA) and Agbom (AG) farms at $r=0.50$, $r=-0.62$ and $r=0.75$ respectively (Table 1 Appendix A).

Table 4. 6: Correlation between the physicochemical properties and the PTEs of the farms soil

Parameters	PTEs						
	Cd	Cr	Co	Pb	Ni	As	Cu
Moisture (%)	-0.29	0.06	-0.26	0.09	-0.04	0.08	-0.21
Clay (%)	0.17	-0.04	0.12	0.05	-0.54	0.03	-0.03
Silt (%)	-0.01	-0.43	0.16	-0.18	-0.39	0.09	0.09
Sand (%)	-0.14	0.14	-0.15	0.01	0.57	-0.02	0.01
pH	0.03	0.11	-0.06	-0.01	-0.25	0.06	-0.21
EC (dS/m)	-0.22	-0.07	0.21	-0.21	0.03	0.14	0.06
Organic matter (%)	-0.24	0.00	-0.15	-0.01	0.05	-0.18	0.11
CEC (cmol(+)/Kg soil)	0.23	0.31	-0.17	0.51	0.37	-0.13	0.07
Exchangeable bases (cmol (+)/Kg)							
Ca	-0.48	-0.47	0.08	-0.37	-0.31	0.21	0.08
Mg	-0.47	-0.32	0.18	-0.28	-0.44	0.28	0.08
K	-0.10	0.30	0.06	-0.06	-0.11	-0.21	-0.28

Na	-0.12	0.04	-0.16	-0.05	0.00	-0.07	-0.21
Control	0.21	0.11	0.30	0.10	-0.16	-0.03	0.27

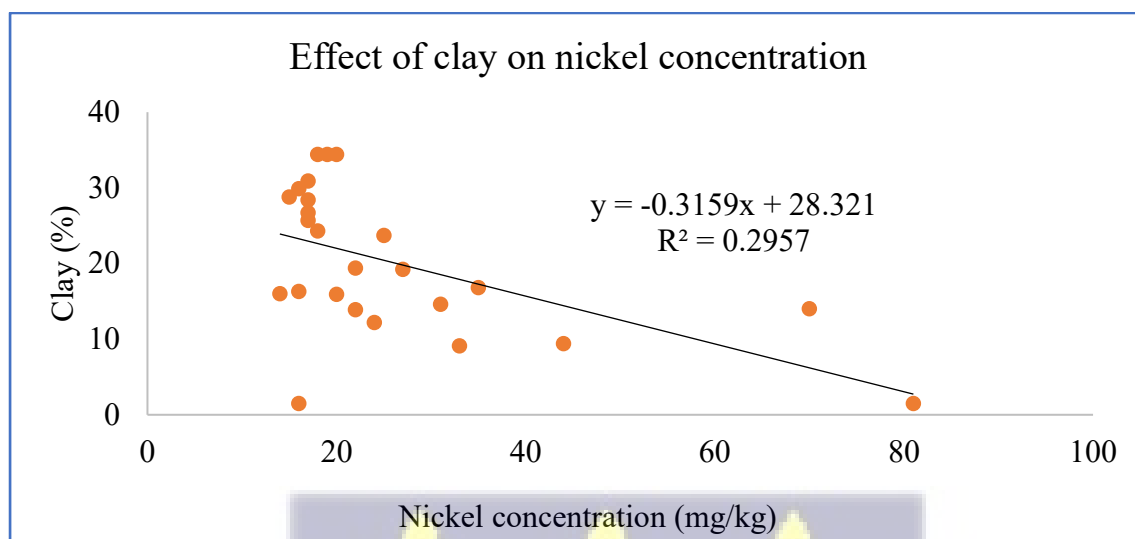


Figure 4. 2: Strength of the relationship between clay and nickel concentrations in the farm soils

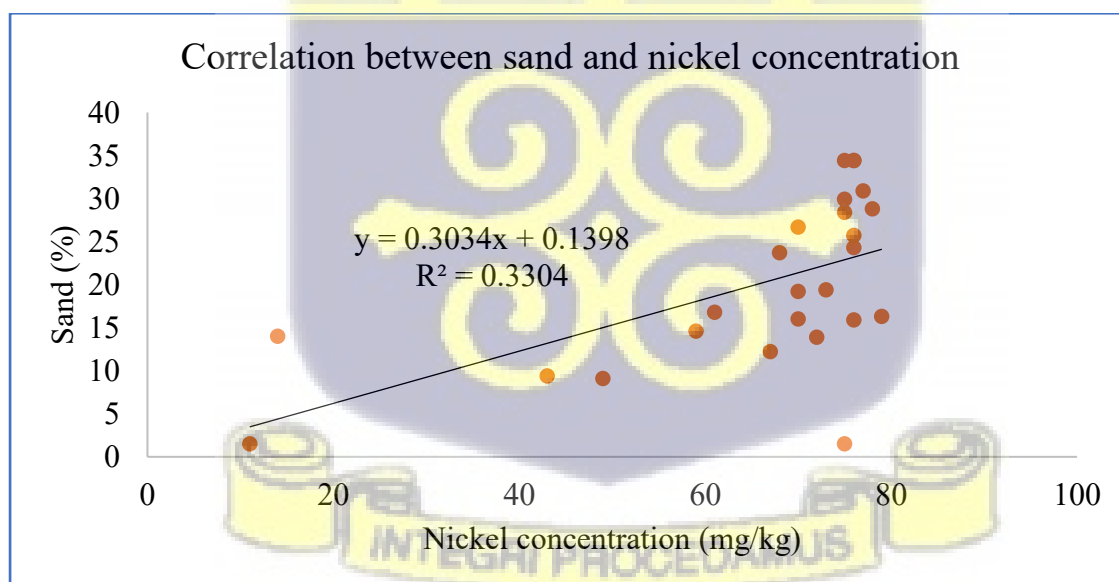


Figure 4. 3: Strength of the relationship between sand and nickel concentrations in the farm soils

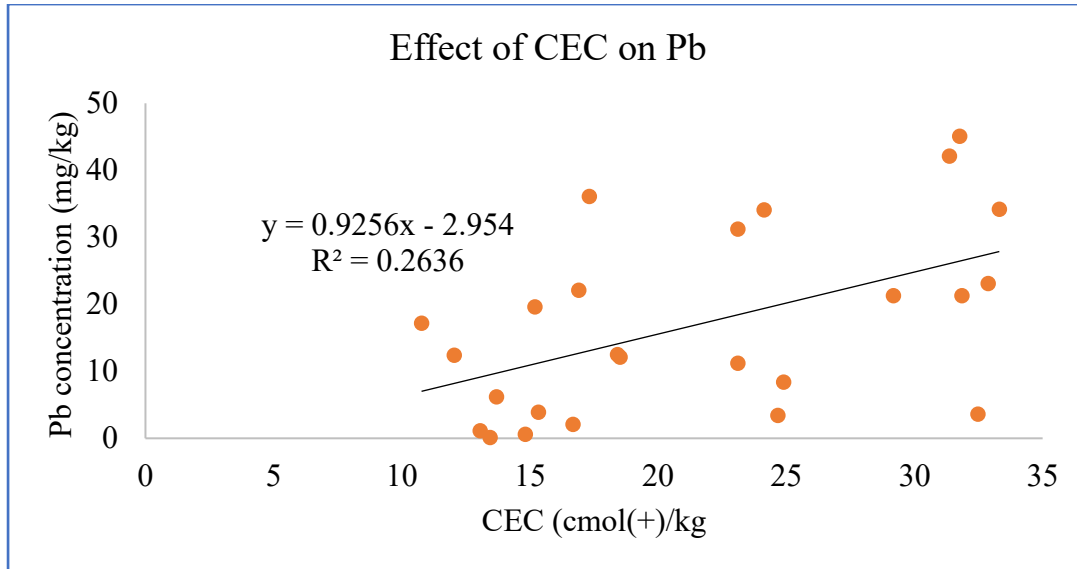


Figure 4. 4: Strength of the relationship between CEC and lead concentrations in the farm soils

4.6 Contamination Indices of the farms soil

4.6.1 Geoaccumulation Index (I_{geo}) of the Farms Soil

The degree of PTEs and the metals enrichment of the farms soil are determined by the I_{geo} [123]. The I_{geo} takes into account the human factors, the effect of diagenesis on soil background values, and geochemical background values [132]. Table 4.8 represented the soil quality classification with reference to the geoaccumulation index estimated from the farms soil. The mean geoaccumulation index values of the PTEs were in the increasing order $Cr < Ni < As < Cu < Cd < Co < Pb$ (Table 4.7). The mean values of the PTEs (Cu, Cr, Co, Pb, Ni and As) were within $I_{geo} \leq 0$ implying that the soils were not contaminated for Cu, Cr, Co, Pb, Ni and As (Table 4.7). There was moderate pollution of Cd in the soil depicted by the mean values (Table 4.7). The absence of contamination of these PTEs are also recorded by Sun and Chen, (2018) that after I_{geo} analysis for contamination of PTEs in soil, Cr and Cu did not pollute the soil ($I_{geo} \leq 0$). For the individual farms, the soil for Kwabia farms (K) was moderately polluted

with Cd whiles there was no contamination of Cu, Cr, Co, Pb, Ni and As in the K farm soil (Table 4.7). For Kwabia Asasehene (KA) farms, there was no pollution of Cu, Cr, Co, Pb, Ni and As similarly reported in other studies [37]. However, moderate to high Cd pollution of the KA farms was found (Table 4.7 and Table 4.8). For Asasehene farms (A), the soil was highly polluted with Cd and slightly polluted for Pb. For Agbom farms (AG), the soil quality was in class 3 of Igeo classification representing moderate to high pollution of Cd. There was moderate pollution of Pb in the Agbom farms. For Aworworso farms (Aw), the soils were unpolluted for Cu, Cr, Co, Ni and As. It is however highly polluted for Cd and moderately polluted for Pb (Table 4.7 and Table 4.8). The farms were more polluted for Cd translating that the distribution of Cd in the farms soil is high from sources of electronic wastes disposals, indiscriminate disposal of used batteries and possible erosion of Cd containing substances from Auto repair shops from the farming communities. It can therefore be reasoned that the levels of the seven PTEs contamination in the five farms are in the order $Pb > Co > Cd > Cu > As > Ni > Cr$ (Table 4.7) and the PTEs that polluted the farms soil were within the classes of 1-4 of I_{geo} values of 0-1 to 3-4. This compromise soil quality whiles the majority of the PTEs fall within the 0 ($I_{geo} \leq 0$) indicating absence of pollution for those metals (Table 4.7 and Table 4.8).

Table 4. 7: Geoaccumulation Index (I_{geo}) for soil quality of the farms

Farming communities	Cu	Cd	Cr	Co	Pb	Ni	As
Kwabra	-1.21	1.22	-5.47	-1.14	-1.88	-3.18	-3.18
kwabia Asasehene	-1.61	2.42	-4.59	-0.96	-2.52	-2.94	-2.94
Asasehene	-1.73	3.01	-3.48	-1.56	0.25	-2.94	-2.94
Agbom	-1.91	2.24	-2.97	-1.26	0.54	-1.93	-1.93
Aworworso	-1.72	3.54	-4.36	-1.72	0.53	-1.96	-1.96
Control	-5.92	-1.32	-5.55	-2.27	-3.03	-7.76	-7.76

Min	-5.92	-1.32	-5.55	-2.27	-3.03	-7.76	-7.76
Max	-1.21	3.54	-2.97	-0.96	0.54	-1.93	-1.93
mean	-2.35	1.85	-4.40	-1.48	-1.02	-3.45	-3.45
SD	1.765	1.741	1.036	0.474	1.642	2.177	2.177
CV (%)	-75.12	93.97	-23.52	-31.92	-161.24	-63.09	-63.09

Table 4. 8: Soil quality in reference to Geoaccumulation Index (I_{geo}) values

Class	Values of I_{geo}	Soil quality
0	$I \leq 0$	Unpolluted
1	0-1	unpolluted to moderately polluted
2	1-2	moderately polluted
3	2-3	moderately to highly polluted
4	3-4	highly polluted
5	4-5	highly to extremely high polluted
6	5-6	extremely high polluted

4.6.2 Contamination factor (CF) of the Farms Soil

The classification of soil contamination based on the contamination factor criteria $CF < 1$ represents low contamination, $CF (1-3)$ represents moderate contamination, $CF (3-6)$ considerable contamination, $CF \geq 6$ represents high contamination [35]; [92]. The mean value for the CF showed that there was low Cr contamination in the soil (Table 4.9). Moderate contamination of Cu in the soil, considerable contamination of Pb and high contamination of Cd, Ni and As in the farms soil. Farms at Kwabia were highly contaminated for Ni and As

(CF=12.42 and 11.87 respectively). This was similar to contamination factor values determined in farms soils near mine site in Ghana [8]. There was low contamination for Cr and Pb (CF<1). Cu and Cd were moderate to considerate contamination respectively (Table 4.9). Kwabia Asasehene farms soil were highly contaminated with Cd, Ni and As. There was high contamination of Cd, Pb, Ni and As for the Asasehene farm soils. Similarly, Cd, Ni and As highly contamination found in the soils of Agbom and Aworworso farms. The results shows that Cd, Ni, and As predominantly highly contaminated the farms soils with CF values above one (1) (Table 4.9). The source contributions of the PTEs could be from either anthropogenic or geogenic sources [8]. The average contamination factor calculated increase in the order of Cr<Cu<Pb<As<Cd<Ni. The coefficient of variation (CV) of the metals further confirmed that Pb, Cd, Cr, Ni with high CV emanated from human activities [136].

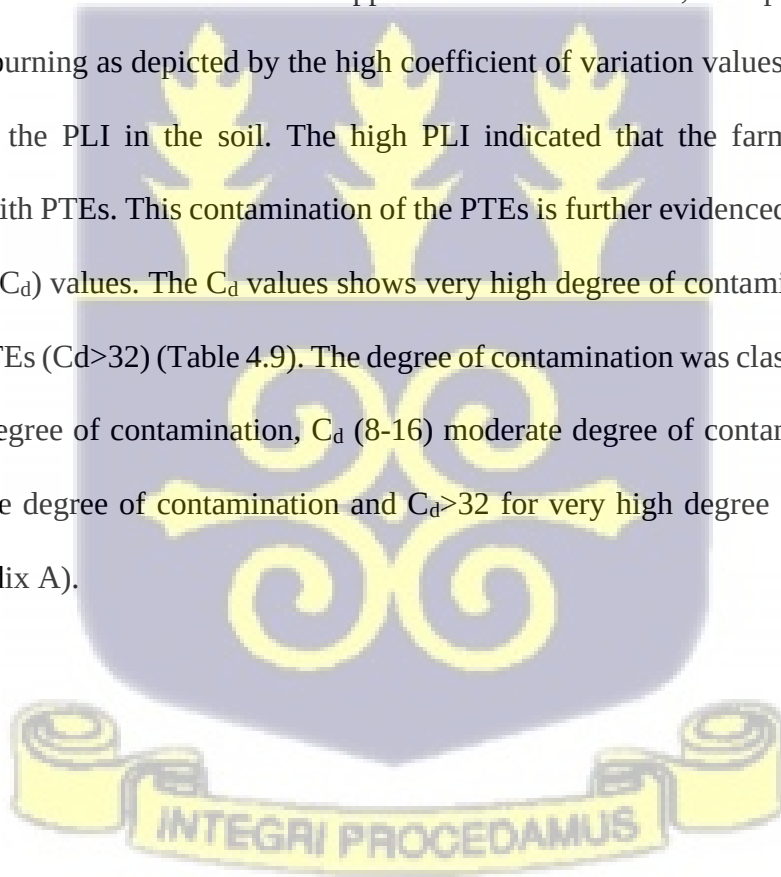
Table 4. 9: Contamination factor (CF), Pollution Load Index (PLI) and Degree of contamination (Cd) of the PTEs in the Farms Soil

Farming	CF							
Communities	PTEs							
	Cu	Cd	Cr	Pb	Ni	As	PLI	Cd
Kwabra	2.51	3.50	0.22	0.36	12.42	11.87	1.94	30.88
kwabia Asasehene	3.08	8.00	0.35	0.23	14.68	8.99	2.22	35.32
Asasehene	1.60	12.10	0.75	22.28	14.62	8.29	4.53	59.63
Agbom	1.45	7.10	1.06	1.94	29.62	7.34	3.34	48.52
Aworworso	2.43	17.50	0.95	1.94	28.94	8.37	4.09	60.14
Minimum	1.45	3.50	0.22	0.23	12.42	7.34	1.94	30.88
Maximum	3.08	17.50	1.06	22.28	29.62	11.87	4.53	60.14
Mean	2.21	9.64	0.66	5.35	20.06	8.97	3.22	46.90

SD	0.68	1.35	0.37	1.50	8.47	1.72	1.13	11.52
CV (%)	30.59	55.54	55.55	177.48	42.25	19.20	35.13	28.82

4.6.3 Pollution Load Index (PLI) and Degree of contamination (C_d) of the Farms Soil

The PLI is an index that assesses the pollution collectively caused by the PTEs found in the farms soils. The PLI for all the farms were above unity (Table 4.9 and Figure 4.5). This implies a deterioration of soil quality for all the farms in the five farming communities. Similar observations have been made in other studies of PTEs in soil [137]. This could be due to anthropogenic activities such as overapplication of fertilizers, rampant tilling, and indiscriminate burning as depicted by the high coefficient of variation values (Table 4.9). The CF determined the PLI in the soil. The high PLI indicated that the farms soil had been contaminated with PTEs. This contamination of the PTEs is further evidenced by the degree of contamination (C_d) values. The C_d values shows very high degree of contamination for all the farms soil by PTEs ($C_d > 32$) (Table 4.9). The degree of contamination was classified as follows: $C_d < 8$ for low degree of contamination, C_d (8-16) moderate degree of contamination, C_d (16-32) considerable degree of contamination and $C_d > 32$ for very high degree of contamination (Table 7 appendix A).



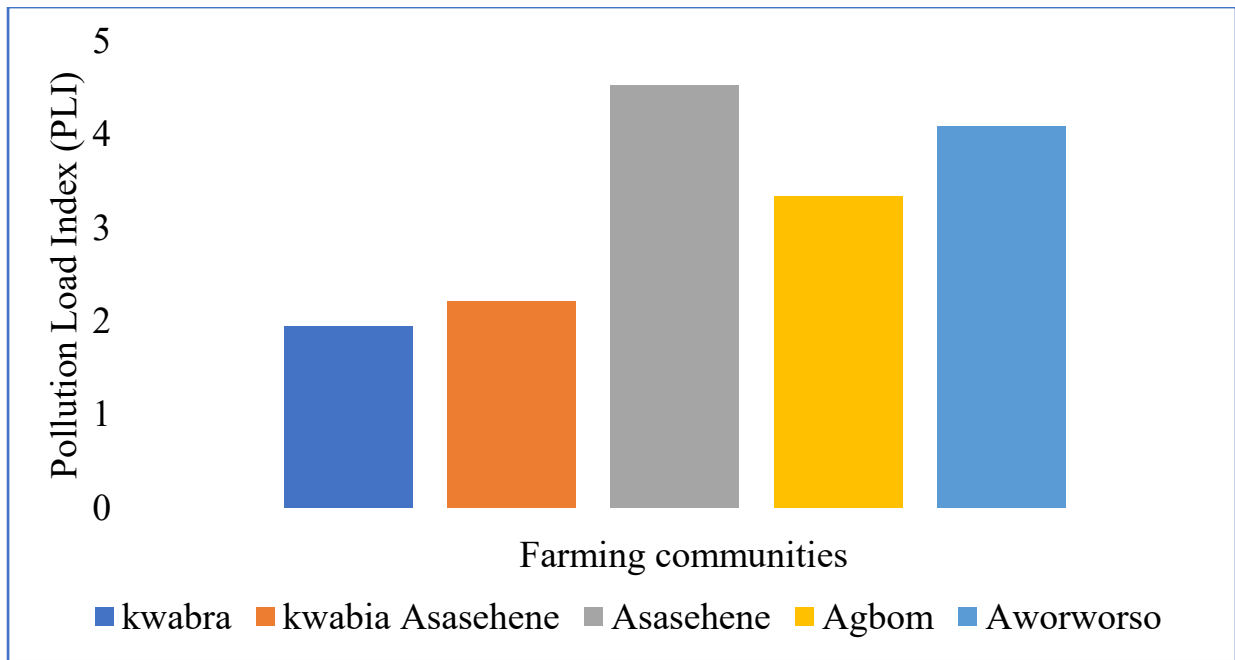


Figure 4. 5: Pollution Load Index (PLI) of the PTEs in the farms soil

4.6.4 Enrichment Factor (EF) of the Farms Soil

The enrichment factors for the PTEs showed little to minimal enrichment of Cu, Cr, Pb, Ni and Co for all farms (Table 4.10, Appendix A Table 2). According to deductions by Mensah et al. (2021), $EF > 1.5$ represented anthropogenic contamination sources. From table 4.10, on the average, there was highly extreme enrichment of As ($EF = 57.54$) and Cd ($EF = 334.69$) which might have arisen from anthropogenic pollution sources in the soil similar to EF for heavy metals in soils reported in other works [92]. Each farm had extremely high enrichment of Cd and As ($EF > 40$) such that Kwabia farms had $EF = 144.03$, Kwabia Asasehene(KA) farms ($EF = 329.20$), A farms ($EF = 497.92$), Agbom farms ($EF = 292.17$), and Aworworso farms ($EF = 720.13$) for Cd. Arsenic (As) enrichment due to the EF values were Kwabia farms ($EF = 90.43$), KA farms ($EF = 68.48$), A farms ($EF = 63.15$), AG farms ($EF = 55.93$) and

Aworworso farms (EF=63.81) representing extremely high enrichment of the metal in the farm soils of anthropogenic origins.

Table 4. 10: Enrichment Factors of the PTEs in the agricultural soils

Farming communities	PTEs						
	Cu	Cd	Cr	Pb	Ni	As	Co
Kwabra	0.072	144.025	0.003	0.269	0.018	90.428	0.224
kwabia Asasehene	0.084	329.200	0.005	0.172	0.021	68.482	0.253
Asasehene	0.044	497.915	0.011	1.174	0.021	63.147	0.168
Agbom	0.040	292.165	0.016	1.434	0.043	55.934	0.206
Aworworso	0.066	720.125	0.006	1.430	0.042	63.808	0.150
Control	0.007	24.690	0.003	0.121	0.001	3.455	0.102
Min	0.007	24.690	0.003	0.121	0.001	3.455	0.102
Max	0.084	720.125	0.016	1.434	0.043	90.428	0.253
mean	0.052	334.687	0.007	0.766	0.025	57.542	0.184
SD	0.018	148.795	0.001	0.043	0.006	20.982	0.005
CV (%)	53.375	74.337	71.388	83.929	65.487	50.367	29.773

4.6.5 Potential Ecological Risks (E)

The potential ecological risks of the contamination of the PTEs in the farm soils indicated Cd as strong ecological risks. This similar to other studies [123]. The mean values of the PTEs showed Cd has a very strong ecological risk (Table 11). The PTEs per farm indicated that Cd and As had moderate potential ecological risks for Kwabia farms; strong ecological risks of Cd for Kwabia Asasehene farms, for Asasehene farms, there was strong potential ecological risks

for Cd and moderate potential ecological risks for Pb; for Agbom farms, Cd had strong potential ecological risks and Ni moderate ecological risks; Aworworso farms showed very strong and moderate potential ecological risks for Cd and Ni respectively (Table 4.11 and Appendix A Table 3). As observed, there was low potential ecological risks (Risk Index (RI)<90) on all the farms for Cr and Cu in the studied soils (Table 4.13). Unlike this current study (low potential ecological risks to strong potential ecological risks found among the soils for the PTEs), an assessment of potential toxic metals (PTM) in farmland soil samples found low potential ecological risks for all the metals [99]. The mean potential ecological risk index calculated increased in order Cr<Cu<Pb<As<Ni<Cd.

Table 4. 11: The potential ecological risks of the PTEs

Farms	Cu	Cd	Cr	Pb	Ni	As
Kwabia	12.53	105.00	0.44	1.82	62.10	118.67
kwabia	15.38	240.00	0.69	1.16	73.40	89.87
Asasehene						
Asasehene	8.00	363.00	1.49	111.40	73.10	82.87
Agbom	7.26	213.00	2.12	9.72	148.10	73.40
Aworworso	12.17	525.00	1.90	9.69	144.70	83.73
Control	12.90	3.60	6.42	11.50	2.60	13.60
Minimum	7.26	3.60	0.44	1.16	2.60	13.60
Maximum	15.38	525.00	6.42	111.40	148.10	118.67
mean	11.37	241.60	2.18	24.22	84.00	77.02
SD	3.12	185.03	2.18	42.93	55.01	34.68

4.7 Human Health Assessment

The exposure of the PTEs from soil to human occurs through three main pathways; ingestion (oral), inhalation and dermal contact. The Human Health Assessment were determined for children and adults. The results showed that all the daily exposure via ingestion, inhalation and dermal contact for children and adult for all the PTEs investigated were <1 , similar to work observed by [132]. Similarly, the non-carcinogenic hazard quotient (HQ) for ingestion, inhalation, and dermal contact as well as the hazard index were also <1 . This means that the contaminants (PTEs) in the farms soil did not represent a potential health risk to children and adult upon exposure (Table 4.12). According to the United States Environmental Protection Agency (USEPA), when the $HQ < 1$, detrimental health impacts are unlikely [121]. $HQ > 1$ represents risks. It is important to mention that the health risks determination method does not consider existing health issues. It puts certain and rigid assumptions such as exposure duration etc and is unable to indicate certainty of the risks but a possibility. Despite these inherent shortfalls, it is the most used method for reporting health risks exposure to the PTEs in soil [138]. In this study, Cu, Cd, Cr, Co, Pb, Ni and As did not pose health risks upon exposure via inhalation, ingestion and dermal contact for children and adult (Table 4.12). Other studies found As to pose health impacts to children and adults [138]. Cd has also been noted for health impacts in soil [132].

Table 4. 12: Exposure pathways, hazard index, hazard quotient of the PTEs in soil

Metal/exposure	Cu	Cd	Cr	Co	Pb	Ni	As
^a ADD _{ing} Child	2.44E-04	2.81E-05	1.15E-04	1.79E-04	1.91E-04	2.15E-04	2.90E-04
Adult	3.27E-05	2.74E-06	1.51E-05	2.4E-05	2.5E-05	2.88E-05	3.89E-05
^a ADD _{inh} Child	6.84E-09	5.73E-10	3.15E-09	5.01E-09	5.22E-09	6.03E-09	8.12E-09

	Adult	3.10E-09	2.60E-10	1.43E-09	2.27E-09	2.37E-09	2.73E-09	3.68E-09
^a ADD _{der}	Child	3.90E-07	3.27E-08	1.80E-07	2.86E-07	2.98E-07	3.44E-07	4.63E-07
	Adult	9.97E-07	8.34E-08	4.58E-07	7.3E-07	7.6E-07	8.78E-07	1.18E-06
^b HQ _{ing}	Child	6.10E-03	0.0281174	-	-	5.45E-02	0.01074	0.965439
	Adult	9.35E-03	7.83E-04	-	-	1.21E-04	0.008234	0.011103
^b HQ _{inh}	Child	1.70E-07	5.72643E-07	-	-	1.47E-06	2.92E-07	2.62E-06
	Adult	8.82E-07	7.37753E-08	-	-	6.72E-07	7.76E-07	1.05E-06
^b HQ _{der}	Child	7.44E-04	6.22141E-05	0.000342	0.000545	0.000567	0.000655	0.000883
	Adult	1.90E-03	1.59E-04	8.73E-04	1.39E-03	1.45E-03	0.001671	0.002254
^c HI	Child	0.006843448	0.028180187	-	-	0.055063	0.011395	0.966324
	Adult	0.01125251	0.000941476	0.000873	0.001391	0.001569	0.009906	0.013358

^a Daily amount of exposure (ADD) to metals through ingestion, inhalation, and dermal contact pathways

^b non-carcinogenic hazard quotient (HQ) for ingestion, inhalation, and dermal contact

^c Hazard index (HI) of the metals upon child and adult exposure in the farms soil

4.7.1 Carcinogenic risks of the PTEs in the farms soil

Acceptable risks range are considered in the range of 1×10^{-6} - 1×10^{-4} . Significant risks to humans considered at Total Carcinogenic Risks (TCR) $> 1 \times 10^{-4}$. The PTEs assessed were all within or below the acceptable risks range indicating the absence of carcinogenic risks to children and adults (Table 4.13). Although the EF, degree of contamination, PLI and the CF showed the contamination of As and Cd for most of the farms, these did not represent

carcinogenic risks whether exposed through inhalation, ingestion or derma contact for children and adult.

Table 4. 13: Carcinogenic Risks for children and adult of the PTEs in the farms soil

Parameter	Metal	Cu	Cd	Cr	Co	Pb	Ni	As
CR (oral)	Child	4.15E-04	1.72E-04	5.75E-05	-	-	-	4.34E-04
	Adult	5.57E-05	1.67E-05	7.53E-06	-	-	-	5.83E-05
CR (inhalation)	Child	-	3.61E-09	1.32E-07	-	-	-	1.23E-07
	Adult	-	1.64E-09	6.00E-08	-	-	-	5.56E-08
CR (dermal)	Child	1.66E-05	1.99E-07	3.59E-06	-	-	-	1.70E-06
	Adult	4.24E-05	5.09E-07	9.17E-06	-	-	-	4.33E-06
TCR	Child	-	1.72E-04	6.12E-05	-	-	-	4.36E-04
	Adult	-	1.72E-05	1.68E-05	-	-	-	6.27E-05

CR: Carcinogenic risks; TCR: Total carcinogenic risks

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The study found the presence of seven potentially toxic elements (PTEs) in the farm soils in five farming communities in Upper Manya Krobo namely; Kwabia, Kwabia Asasehene, Asasehene, Agbom and Aworworso. The mean concentration of all the PTEs in all studied soil were below WHO/AFO permissible levels except for As. There was high degree of contamination of the PTEs; Cu, Cr, Pb, As, Co, Ni and Cd shown by the degree of contamination and the pollution load index (PLI) in the studied soils. However, enrichment factor (EF) showed that the soils were much enriched in Cd and As. The mean potential ecological risk index of the PTEs calculated were low to moderate for all the studied soils except for Cd which recorded high values indicating very high ecological risk.

The physicochemical properties of the soil influenced soil health and impacted on the PTEs. Especially, clay, and sand affected Ni concentration in the soil and CEC also impacted on Pb concentration. The pH, soil organic matter and soil moisture varied on individual farms. In addition, PTEs influence nutrient availability and bioaccessibility, retention and microorganisms' activity.

The microorganism population isolated in the soil correlated with most of PTEs in the soils. This implies the impact of PTEs on soil microorganisms and vice versa were found in this study.

All the PTEs had hazard quotient (HQ), Hazard index $HI < 1$ which meant the PTEs for the farms posed no health risks to human both children and adult when exposed via ingestion, inhalation, and dermal contact. The possibility of contracting cancer through the PTEs in the

soil was assessed. The carcinogenic risk (CR) and total carcinogenic risk (TCR) via inhalation, ingestion and dermal contact were within acceptable range and represented no risks of cancer.

5.2 Recommendation

Further work should focus on the possibility of health risks of Arsenic and Cadmium via food consumption from crops cultivated on Aworworso farm soils via the food chain.

Although the PTEs in the soils did not pose health risks both carcinogenic and non-carcinogenic risks but the concentration of the PTEs warrants attention to training on fertilizer applications, insecticides usage, and soil remediation using indigenous plants.

The potential of the PTEs mobilization in the topsoil and levels of concentration in the soil should be investigated with respect to potential health impacts



REFERENCES

- [1] E. Arhin, S. Zango, and B. Berdie, "Geochemical Background of Some Potentially Toxic and Essential Trace Elements in Soils at the Nadowli District of the Upper West Region of Ghana," *J. Earth, Environ. Heal. Sci.*, vol. 2, no. 2, p. 56, 2016, doi: 10.4103/2423-7752.191402.
- [2] J. Bremner, "By Jason Bremner Population and Food Security ;," no. February, 2012.
- [3] D. L. Karlen, M. J. Mausbach, J. W. Doran, R. G. Cline, R. F. Harris, and G. E. Schuman, "Soil Quality: A Concept, Definition, and Framework for Evaluation (A Guest Editorial)," 1984.
- [4] E. A. Oluyemi, A. S. Adekunle, A. A. Adenuga, and W. O. Makinde, "Physico-chemical properties and heavy metal content of water sources in Ife North Local Government Area of Osun State , Nigeria," vol. 4, no. October, pp. 691–697, 2010.
- [5] C. Kanellopoulos, "Influence of ultramafic rocks and hot springs with travertine depositions on geochemical composition and baseline of soils. Application to eastern central Greece," *Geoderma*, vol. 380, 2020, doi: 10.1016/j.geoderma.2020.114649.
- [6] T. Moghtaderi, A. Shakeri, and A. Rodríguez-Seijo, "Potentially toxic element content in arid agricultural soils in South Iran," *Agronomy*, vol. 10, no. 4, pp. 1–15, 2020, doi: 10.3390/agronomy10040564.
- [7] Z. Zhuang *et al.*, "Accumulation of potentially toxic elements in agricultural soil and

- scenario analysis of cadmium inputs by fertilization : A case study in Quzhou county,” *J. Environ. Manage.*, vol. 269, no. February, p. 110797, 2020, doi: 10.1016/j.jenvman.2020.110797.
- [8] A. K. Mensah, B. Marschner, V. Antoniadis, E. Stemn, S. M. Shaheen, and J. Rinklebe, “Human health risk via soil ingestion of potentially toxic elements and remediation potential of native plants near an abandoned mine spoil in Ghana,” *Sci. Total Environ.*, vol. 798, p. 149272, 2021, doi: 10.1016/j.scitotenv.2021.149272.
- [9] O. Akoto *et al.*, “Contamination Levels and Sources of Heavy Metals and a Metalloid in Surface Soils in the Kumasi Metropolis, Ghana,” *J. Heal. Pollut.*, vol. 7, no. 15, pp. 28–39, 2017, doi: 10.5696/2156-9614-8.15.28.
- [10] M. O. Arnous and M. A. A. Hassan, “Heavy metals risk assessment in water and bottom sediments of the eastern part of Lake Manzala, Egypt, based on remote sensing and GIS,” *Arab. J. Geosci.*, vol. 8, no. 10, pp. 7899–7918, 2015, doi: 10.1007/s12517-014-1763-6.
- [11] Ministry of Food and Agriculture, “Ejura-Sekyeredumase,” 2019.
- [12] N. Bortey-Sam *et al.*, “Accumulation of heavy metals and metalloid in foodstuffs from agricultural soils around Tarkwa area in Ghana, and associated human health risks,” *Int. J. Environ. Res. Public Health*, vol. 12, no. 8, pp. 8811–8827, 2015, doi: 10.3390/ijerph120808811.
- [13] G. Darko, S. Adjei, M. A. Nkansah, L. S. Borquaye, K. O. Boakye, and M. Dodd, “Accumulation and bioaccessibility of toxic metals in root tubers and soils from gold mining and farming communities in the Ashanti region of Ghana,” *Int. J. Environ. Health Res.*, vol. 32, no. 2, pp. 426–436, 2022, doi: 10.1080/09603123.2020.1772203.
- [14] M. Mng, S. Comber, L. K. Munishi, P. A. Ndakidemi, W. Blake, and T. H. Hutchinson, “Chemosphere Land use patterns influence the distribution of potentially

- toxic elements in soils of the Usangu Basin , Tanzania,” *Chemosphere*, vol. 284, no. June, p. 131410, 2021, doi: 10.1016/j.chemosphere.2021.131410.
- [15] I. Union *et al.*, “‘ HEAVY METALS ’— A MEANINGLESS TERM ? (IUPAC Technical Report) (IUPAC Technical Report),” vol. 74, no. 5, pp. 793–807, 2002.
- [16] S. L. Houghton and A. Osborn, “Extraction and analysis of arsenic in soils and sediments,” vol. 23, no. 10, 2004, doi: 10.1016/j.trac.2004.07.010.
- [17] L. Pan, Y. Wang, J. Ma, Y. Hu, B. Su, and G. Fang, “A review of heavy metal pollution levels and health risk assessment of urban soils in Chinese cities,” 2017.
- [18] R. Terzano *et al.*, “Fire effects on the distribution and bioavailability of potentially toxic elements (PTEs) in agricultural soils,” *Chemosphere*, vol. 281, no. May, p. 130752, 2021, doi: 10.1016/j.chemosphere.2021.130752.
- [19] C. E. Gattullo, I. Allegretta, C. Porfido, I. Rascio, M. Spagnuolo, and R. Terzano, “Assessing chromium pollution and natural stabilization processes in agricultural soils by bulk and micro X-ray analyses,” no. Vi, 2020.
- [20] A. E. Baltas, H., Sirin, M., Gokbayrak, E., Ozcelik, “A case study on pollution and a human health risk assessment of heavy metals in agricultural soils around Sinop province, Turkey,” *Chemosphere*, vol. 241, no. February 2020, p. 125015, 2020.
- [21] J. Jiang, H.-H., Cai, L.-M., Wen, H.-H., Hu, G.-C., Chen, L.-G., Luo, “An integrated approach to quantifying ecological and human health risks from different sources of soil heavy metals,” *Sci. Total Environ.*, vol. 701, no. 20, p. 134466, 2020.
- [22] D. Cicchella *et al.*, “Urban soil contamination in Salerno (Italy): Concentrations and patterns of major, minor, trace and ultra-trace elements in soils,” *J. Geochemical Explor.*, vol. 213, no. October 2019, p. 106519, 2020, doi: 10.1016/j.gexplo.2020.106519.
- [23] E. D. Burton, G. Choppala, N. Karimian, and S. G. Johnston, “A new pathway for

- hexavalent chromium formation in soil: Fire-induced alteration of iron oxides,” *Environ. Pollut.*, vol. 247, no. 2019, pp. 618–625, 2019, doi: 10.1016/j.envpol.2019.01.094.
- [24] J. Abraham, K. Dowling, and S. Florentine, “Controlled burn and immediate mobilization of potentially toxic elements in soil, from a legacy mine site in Central Victoria, Australia,” *Sci. Total Environ.*, vol. 616–617, no. 2018, pp. 1022–1034, 2018, doi: 10.1016/j.scitotenv.2017.10.216.
- [25] L. S. Keith and O. M. Faroon, “Heavy metals in soils,” in *Handbook on the Toxicology of Metals: Fifth Edition*, 2021, pp. 885–936. doi: 10.1016/B978-0-12-822946-0.00032-5.
- [26] S. T. Ametepey, S. J. Cobbina, F. J. Akpabey, A. B. Duwiejuah, and Z. N. Abuntori, “Health risk assessment and heavy metal contamination levels in vegetables from tamale metropolis, Ghana,” *Int. J. Food Contam.*, vol. 5, no. 1, p. 5, 2018, doi: 10.1186/s40550-018-0067-0.
- [27] P. Madejon, *Vanadium*. In: Alloway, B.J. (Ed.), *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability*. 2013. doi: https://doi.org/10.1007/978-94-007-4470-7_27.
- [28] N. C. Uren, *Cobalt and manganese*. In: Alloway, B.J. (Ed.), *Heavy Metals in Soils, Environmental Pollution*. Dordrecht, Netherlands: Springer Netherlands, 2013. doi: https://doi.org/10.1007/978-94-007-4470-7_12.
- [29] G. Gonnelli, C., and Renella, “Chromium and nickel. In: Alloway, B.J. (Ed.), *Heavy Metals in Soils*,” Netherlands: Springer, 2013, pp. 313–333. doi: https://doi.org/10.1007/978-94-007-4470-7_11.
- [30] L. Borůvka, O. Vacek, and J. Jehlička, “Principal component analysis as a tool to indicate the origin of potentially toxic elements in soils,” in *Geoderma*, 2005, pp. 289–

300. doi: 10.1016/j.geoderma.2005.04.010.
- [31] U. Forstner, “Metal speciation in solid wastes—factors affecting mobility. In: Landner, L. (Ed.), Speciation of Metals in Water, Sediment and Soil Systems.,” *Springer, Berlin*, pp. 13 – 41, 1987.
- [32] E. Va’cha, R., Ne’mec’ek, J., Podles’a’kova’, “Geochemical and anthropogenic soil loads by potentially risky elements.,” *Rostlinna’ Vy’roba*, vol. 48, pp. 441 – 447, 2002.
- [33] H. Borgegard, S.O., and Rydin, “Biomass, root penetration and heavy metal uptake in birch in a soil cover over copper tailings.,” *J. Appl. Ecol.*, vol. 26, no. 2, pp. 585 – 595, 1989.
- [34] A. B. Markus, J.A., McBratney, “An urban soil study: heavy metals in Glebe, Australia.,” *Aust. J. Soil Res.*, vol. 34, pp. 453 – 465, 1996.
- [35] A. K. Mensah, B. Marschner, S. M. Shaheen, J. Wang, S. L. Wang, and J. Rinklebe, “Arsenic contamination in abandoned and active gold mine spoils in Ghana: Geochemical fractionation, speciation, and assessment of the potential human health risk,” *Environ. Pollut.*, vol. 261, 2020, doi: 10.1016/j.envpol.2020.114116.
- [36] K. J. Bansah, N. K. Dumakor-Dupey, E. Stemn, and G. Galecki, “Mutualism, commensalism or parasitism? Perspectives on tailings trade between large-scale and artisanal and small-scale gold mining in Ghana,” *Resour. Policy*, vol. 57, no. March, pp. 246–254, 2018, doi: 10.1016/j.resourpol.2018.03.010.
- [37] P. Sabet Aghlidi, M. Cheraghi, B. Lorestani, S. Sobhanardakani, and H. Merrikhpour, “Analysis, spatial distribution and ecological risk assessment of arsenic and some heavy metals of agricultural soils, case study: South of Iran,” *J. Environ. Heal. Sci. Eng.*, vol. 18, no. 2, pp. 665–676, 2020, doi: 10.1007/s40201-020-00492-x.
- [38] P. Kumarathilaka, S. Seneweera, A. Meharg, and J. Bundschuh, “Arsenic speciation

- dynamics in paddy rice soil-water environment: sources, physico-chemical, and biological factors - A review,” *Water Res.*, vol. 140, pp. 403–414, 2018, doi: 10.1016/j.watres.2018.04.034.
- [39] S. Wang and C. N. Mulligan, “Occurrence of arsenic contamination in Canada: Sources, behavior and distribution,” *Sci. Total Environ.*, vol. 366, no. 2–3, pp. 701–721, 2006, doi: 10.1016/j.scitotenv.2005.09.005.
- [40] N. S. Keller, A. Stefánsson, and B. Sigfússon, “Arsenic speciation in natural sulfidic geothermal waters,” *Geochim. Cosmochim. Acta*, vol. 142, pp. 15–26, 2014, doi: 10.1016/j.gca.2014.08.007.
- [41] Z. U. Ahmed *et al.*, “Genotype and environment effects on rice (*Oryza sativa* L.) grain arsenic concentration in Bangladesh,” *Plant Soil*, vol. 338, no. 1, pp. 367–382, 2011, doi: 10.1007/s11104-010-0551-7.
- [42] B. Ali *et al.*, “Hydrogen sulfide alleviates lead-induced photosynthetic and ultrastructural changes in oilseed rape,” *Ecotoxicol. Environ. Saf.*, vol. 102, no. 1, pp. 25–33, 2014, doi: 10.1016/j.ecoenv.2014.01.013.
- [43] M. Aslam *et al.*, “Lead Toxicity in Cereals: Mechanistic Insight Into Toxicity, Mode of Action, and Management,” *Front. Plant Sci.*, vol. 11, no. February, 2021, doi: 10.3389/fpls.2020.587785.
- [44] J. R. Peralta-Videa, M. L. Lopez, M. Narayan, G. Saupe, and J. Gardea-Torresdey, “The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain,” *Int. J. Biochem. Cell Biol.*, vol. 41, no. 8–9, pp. 1665–1677, 2009, doi: 10.1016/j.biocel.2009.03.005.
- [45] United States Geological Survey, “Uses of Lead,” *Geoscience News and Information*, 2011.
- [46] L. E. Williams, J. K. Pittman, and J. L. Hall, “Emerging mechanisms for heavy metal

- transport in plants,” *Biochim. Biophys. Acta - Biomembr.*, vol. 1465, no. 1–2, pp. 104–126, 2000, doi: 10.1016/S0005-2736(00)00133-4.
- [47] P. Sharma, “Lead toxicity in plants,” *Brazilian J. plant Physiol.*, vol. 17, pp. 35–52, 2005.
- [48] W. Chen, A. C. Chang, and L. Wu, “Assessing long-term environmental risks of trace elements in phosphate fertilizers,” *Ecotoxicol. Environ. Saf.*, vol. 67, no. 1, pp. 48–58, 2007, doi: 10.1016/j.ecoenv.2006.12.013.
- [49] W. Peijnenburg *et al.*, “Quantification of metal bioavailability for lettuce (*Lactuca sativa* L.) in field soils,” *Arch. Environ. Contam. Toxicol.*, vol. 39, no. 4, pp. 420–430, 2000, doi: 10.1007/s002440010123.
- [50] J. W. Blaylock, M.J. Huang, “Phytoextraction of metals. In: Raskin I, Ensley BD, editors. *Phytoremediation of toxic metals: using plants to clean up the environment.*,” in *John Wiley*, New York: John Wiley, 2000, pp. 53–71.
- [51] S. S. Sharma, S. Kaul, A. Metwally, K. C. Goyal, I. Finkemeier, and K. J. Dietz, “Cadmium toxicity to barley (*Hordeum vulgare*) as affected by varying Fe nutritional status,” *Plant Sci.*, vol. 166, no. 5, pp. 1287–1295, 2004, doi: 10.1016/j.plantsci.2004.01.006.
- [52] E. Lombi, K. L. Tearall, J. R. Howarth, F. J. Zhao, M. J. Hawkesford, and S. P. McGrath, “Influence of iron status on cadmium and zinc uptake by different ecotypes of the hyperaccumulator *Thlaspi caerulescens*,” *Plant Physiol.*, vol. 128, no. 4, pp. 1359–1367, 2002, doi: 10.1104/pp.010731.
- [53] A. Ramos, I. Esteban, E. Lucena, J.J. Garate, “Cadmium uptake and subcellular distribution in plants of *Lactuca* sp. Cd–Mn interaction,” *Plant Sci.*, vol. 162, pp. 761–7, 2002.
- [54] G. K. Oskarsson A, Widell A, Olsson IM, “Cadmium in food chain and health effects

- in sensitive population groups.,” *Biometals*, vol. 17, no. 5, pp. 531–4., 2004, doi: doi: 10.1023/b:biom.0000045733.38583.8e. PMID: 15688858.
- [55] M. V Melendez, J. R. Heckman, S. Murphy, and F. D’amico, “New Jersey farm soil copper levels resulting from copper fungicide applications,” *Horttechnology*, vol. 30, no. 2, pp. 268–272, 2020, doi: 10.21273/HORTTECH04494-19.
- [56] Z. He, D. M. Endale, H. H. Schomberg, and M. B. Jenkins, “Total phosphorus, zinc, copper, and manganese concentrations in cecil soil through 10 years of poultry litter application,” *Soil Sci.*, vol. 174, no. 12, pp. 687–695, 2009, doi: 10.1097/SS.0b013e3181c30821.
- [57] U.S. Department of Agriculture, “Soil quality—urban technical note number 3: Heavy metal soil contamination.,” 2000.
- [58] H. T. BECKETT and R. D. DAVIS, “Upper Critical Levels of Toxic Elements in Plants,” *New Phytol.*, vol. 79, no. 1, pp. 95–106, 1977, doi: 10.1111/j.1469-8137.1977.tb02185.x.
- [59] I. Nunes *et al.*, “Coping with copper: legacy effect of copper on potential activity of soil bacteria following a century of exposure,” *FEMS Microbiol. Ecol.*, vol. 92, no. 11, p. fiw175, 2016, doi: 10.1093/femsec/fiw175.
- [60] M. Fagnano *et al.*, “Copper accumulation in agricultural soils: Risks for the food chain and soil microbial populations,” *Sci. Total Environ.*, vol. 734, no. 2020, p. 139434, 2020, doi: 10.1016/j.scitotenv.2020.139434.
- [61] M. Agrelli, D., Adamo, P., Cirillo, T., Duri, L. G., Duro, I., Fasano, E. and Fagnano, “Soil versus plant as indicators of agroecosystem pollution by potentially toxic elements.,” *J. Plant Nutr. Soil Sci.*, vol. 180, no. 6, pp. 705–719, 2017.
- [62] M. Beygi and M. Jalali, “Assessment of trace elements (Cd, Cu, Ni, Zn) fractionation and bioavailability in vineyard soils from the Hamedan, Iran,” *Geoderma*, vol. 337, no.

- May 2018, pp. 1009–1020, 2019, doi: 10.1016/j.geoderma.2018.11.009.
- [63] Z. Shabbir *et al.*, “Copper uptake, essentiality, toxicity, detoxification and risk assessment in soil-plant environment,” *Chemosphere*, vol. 259, no. 2020, p. 127436, 2020, doi: 10.1016/j.chemosphere.2020.127436.
- [64] B. Irtelli, W. A. Petrucci, and F. Navari-Izzo, “Nicotianamine and histidine/proline are, respectively, the most important copper chelators in xylem sap of *Brassica carinata* under conditions of copper deficiency and excess,” *J. Exp. Bot.*, vol. 60, no. 1, pp. 269–277, 2009, doi: 10.1093/jxb/ern286.
- [65] H. Kabata-Pendias, A., Pendias, *Trace Elements in Soils and Plants*, 4th ed. Florida, USA: CRC Press, 2011. doi: <https://doi.org/10.1201/b10158>.
- [66] International Agency for Research on Cancer (IARC)., “Chromium, nickel and welding. IARC monographs on the evaluation of carcinogenic risks to humans / World Health Organization,” *Int. Agency Res. Cancer*, vol. 49, no. 1, p. 648., 1990.
- [67] S. Patrick J. T. & Bisessar, “Uptake and toxicity of nickel and other metals in crops grown on soil contaminated by a nickel refinery,” *J. Plant Nutr.*, vol. 3, no. 1–4, pp. 473–482, 2008.
- [68] O. T. Kayode, E. F. Ogunyemi, A. M. Odukoya, and A. P. Aizebeokhai, “Assessment of chromium and nickel in agricultural soil: implications for sustainable agriculture,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 993, no. 1, p. 012014, 2022, doi: 10.1088/1755-1315/993/1/012014.
- [69] A. El-naggar *et al.*, “Nickel in soil and water : Sources , biogeochemistry , and remediation using biochar,” *J. Hazard. Mater.*, vol. 419, no. June, p. 126421, 2021, doi: 10.1016/j.jhazmat.2021.126421.
- [70] K. N. Palansooriya *et al.*, “Soil amendments for immobilization of potentially toxic elements in contaminated soils: A critical review,” *Environ. Int.*, vol. 134, no. April

- 2019, p. 105046, 2020, doi: 10.1016/j.envint.2019.105046.
- [71] A. Ertani, A. Mietto, M. Borin, and S. Nardi, “Chromium in Agricultural Soils and Crops: A Review,” *Water. Air. Soil Pollut.*, vol. 228, no. 5, p. 190, 2017, doi: 10.1007/s11270-017-3356-y.
- [72] A. K. Shanker, C. Cervantes, H. Loza-Tavera, and S. Avudainayagam, “Chromium toxicity in plants,” *Environ. Int.*, vol. 31, no. 5, pp. 739–753, 2005, doi: 10.1016/j.envint.2005.02.003.
- [73] A. Salmani Abyaneh and M. H. Fazelipour, “Evaluation of rhamnolipid (RL) as a biosurfactant for the removal of chromium from aqueous solutions by precipitate flotation,” *J. Environ. Manage.*, vol. 165, no. 2016, pp. 184–187, 2016, doi: 10.1016/j.jenvman.2015.09.034.
- [74] R. J. Bartlett, “Chromium cycling in soils and water: Links, gaps, and methods,” *Environ. Health Perspect.*, vol. 92, pp. 17–24, 1991, doi: 10.1289/ehp.919217.
- [75] S. K. Panda, “Chromium-mediated oxidative stress and ultrastructural changes in root cells of developing rice seedlings,” *J. Plant Physiol.*, vol. 164, no. 11, pp. 1419–1428, 2007, doi: 10.1016/j.jplph.2007.01.012.
- [76] and C.-G. Cervantes, C., “Reduction and efflux of chromate by bacteria,” *Microbiol. Monogr.*, vol. 6, pp. 407–419, 2007.
- [77] S. Mahey, R. Kumar, M. Sharma, V. Kumar, and R. Bhardwaj, “A critical review on toxicity of cobalt and its bioremediation strategies,” *SN Appl. Sci.*, vol. 2, no. 7, pp. 1–12, 2020, doi: 10.1007/s42452-020-3020-9.
- [78] H. Lu, F. Wei, J. Tang, and J. P. Giesy, “Leaching of metals from cement under simulated environmental conditions,” *J. Environ. Manage.*, vol. 169, pp. 319–327, 2016, doi: 10.1016/j.jenvman.2015.12.008.
- [79] L. Leyssens, B. Vinck, C. Van Der Straeten, F. Wuyts, and L. Maes, “Cobalt toxicity

- in humans—A review of the potential sources and systemic health effects,” *Toxicology*, vol. 387, pp. 43–56, 2017, doi: 10.1016/j.tox.2017.05.015.
- [80] I. A. Tsyganov, V. E., Tsyganova, A. V., Gorshkov, A. P., Seliverstova, E. V., Kim, V. E., Chizhevskaya, E. P., ... & Tikhonovich, “Efficacy of a Plant-Microbe System: *Pisum sativum* (L.) Cadmium-Tolerant Mutant and *Rhizobium leguminosarum* Strains, Expressing Pea Metallothionein Genes PsMT1,” *Microb. Control Nitrogen Cycle*, vol. 11, no. 15, 2020.
- [81] B. E. Tvermoes, K. M. Unice, D. J. Paustenbach, B. L. Finley, J. M. Otani, and D. A. Galbraith, “Effects and blood concentrations of cobalt after ingestion of 1 mg/d by human volunteers for 90 d1-3,” *Am. J. Clin. Nutr.*, vol. 99, no. 3, pp. 632–646, 2014, doi: 10.3945/ajcn.113.071449.
- [82] L. Begović *et al.*, “Response of *Lemna minor* L. to short-term cobalt exposure: The effect on photosynthetic electron transport chain and induction of oxidative damage,” *Aquat. Toxicol.*, vol. 175, pp. 117–126, 2016, doi: 10.1016/j.aquatox.2016.03.009.
- [83] M. R. Azarakhsh, Z. Asrar, and H. Mansouri, “Effects of seed and vegetative stage cysteine treatments on oxidative stress response molecules and enzymes in *Ocimum basilicum* L. under cobalt stress,” *J. Soil Sci. Plant Nutr.*, vol. 15, no. 3, pp. 651–662, 2015, doi: 10.4067/S0718-95162015005000044.
- [84] B. Ali, S. Hayat, Q. Hayat, and A. Ahmad, “Cobalt stress affects nitrogen metabolism, photosynthesis and antioxidant system in chickpea (*Cicer arietinum* L.),” *J. Plant Interact.*, vol. 5, no. 3, pp. 223–231, 2010, doi: 10.1080/17429140903370584.
- [85] L. G. Duri, D. Visconti, N. Fiorentino, P. Adamo, M. Fagnano, and A. G. Caporale, “Health risk assessment in agricultural soil potentially contaminated by geogenic thallium: Influence of plant species on metal mobility in soil-plant system,” *Agronomy*, vol. 10, no. 6, 2020, doi: 10.3390/agronomy10060890.

- [86] G. Zampogna, E. Alessandri, and M. Cutolo, “Bioassays for evaluation of sanitary risks from food crops cultivated in potentially contaminated sites,” vol. 65, no. 4, pp. 186–191, 2013.
- [87] C. LaCoste, B. Robinson, and R. Brooks, “Uptake of thallium by vegetables: Its significance for human health, phytoremediation, and phytomining,” *J. Plant Nutr.*, vol. 24, no. 8, pp. 1205–1215, 2001, doi: 10.1081/PLN-100106976.
- [88] D. Visconti *et al.*, “Analysis of native vegetation for detailed characterization of a soil contaminated by tannery waste,” *Environ. Pollut.*, vol. 252, no. 2019, pp. 1599–1608, 2019, doi: 10.1016/j.envpol.2019.06.125.
- [89] L. Xiao *et al.*, “Application of geostatistical analysis and random forest for source analysis and human health risk assessment of potentially toxic elements (PTEs) in arable land soil,” *Int. J. Environ. Res. Public Health*, vol. 17, no. 24, pp. 1–19, 2020, doi: 10.3390/ijerph17249296.
- [90] Y. Deng, W.B.; Li, X.X.; An, Z.S.; Yang, L.; Hou, K.; Zhang, “Identification of sources of metal in the agricultural soils of the Guanzhong Plain, northwest China,” *Environ. Toxicol. Chem.*, vol. 36, pp. 1510–1516, 2017.
- [91] US EPA, “Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites,” 2002.
- [92] S. M. Shaheen *et al.*, “Soil contamination by potentially toxic elements and the associated human health risk in geo- and anthropogenic contaminated soils: A case study from the temperate region (Germany) and the arid region (Egypt),” *Environ. Pollut.*, vol. 262, no. 2020, pp. 1–10, 2020, doi: 10.1016/j.envpol.2020.114312.
- [93] A. A. Taylor *et al.*, “Critical Review of Exposure and Effects: Implications for Setting Regulatory Health Criteria for Ingested Copper,” *Environ. Manage.*, vol. 65, no. 1, pp. 131–159, 2020, doi: 10.1007/s00267-019-01234-y.

- [94] Y. Yousefi, N. Karballaezadeh, D. Moazami, A. S. Zahed, S. Danial Mohammadzadeh, and A. Mosavi, “Improving aviation safety through modeling accident risk assessment of runway,” *Int. J. Environ. Res. Public Health*, vol. 17, no. 17, pp. 1–36, 2020, doi: 10.3390/ijerph17176085.
- [95] I. Turkdogan, M.K., Kilicel, F., Kara, K., Tuncer, I., Uygan, “Heavy metals in soil, vegetables and fruits in the endemic upper gastrointestinal cancer region of Turkey,” *Environ. Toxicol. Pharmacol.*, vol. 13, no. 3, pp. 175–179, 2003.
- [96] R. J. Kim, K.H., Jahan, S.A., Kabir, E., Brown, “A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects,” *Environ. Int.*, vol. 60, pp. 71–80, 2013.
- [97] J. M. Mulligan, C., Bronstein, “Wilson disease: an overview and approach to management,” *Neurol. Clin.*, vol. 38, no. 2, pp. 417–432, 2020, doi: <https://doi.org/10.1016/j.ncl.2020.01.005>.
- [98] O. Akoto *et al.*, “Distribution of Heavy Metals in Organs of Sheep and Goat Reared in Obuasi: A Gold Mining Town in Ghana,” *Int. J. Environ. Sci. Toxicol.*, vol. 2, no. 4, pp. 2315–9927, 2014.
- [99] E. A. Asare, “Impact of the Illegal Gold Mining Activities on Pra River of Ghana on the Distribution of Potentially Toxic Metals and Naturally Occurring Radioactive Elements in Agricultural Land Soils,” *Chem. Africa*, vol. 4, no. 4, pp. 1051–1068, 2021, doi: 10.1007/s42250-021-00285-1.
- [100] C. J. Penn and J. J. Camberato, “A critical review on soil chemical processes that control how soil ph affects phosphorus availability to plants,” *Agric.*, vol. 9, no. 6, pp. 1–18, 2019, doi: 10.3390/agriculture9060120.
- [101] N. J. Barrow, “The effects of pH on phosphate uptake from the soil,” *Plant Soil*, vol. 410, no. 1–2, pp. 401–410, 2017, doi: 10.1007/s11104-016-3008-9.

- [102] D. Neina, “The Role of Soil pH in Plant Nutrition and Soil Remediation,” *Appl. Environ. Soil Sci.*, vol. 2019, no. 3, pp. 1–10, 2019, doi: 10.1155/2019/5794869.
- [103] D. Saidi, “Importance and role of cation exchange capacity on the physical properties of the Cheliff saline soils (Algeria),” *Procedia Eng.*, vol. 33, no. 2011, pp. 435–449, 2012, doi: 10.1016/j.proeng.2012.01.1223.
- [104] Y. Khaledian, E. C. Brevik, P. Pereira, A. Cerdà, M. A. Fattah, and H. Tazikeh, “Modeling soil cation exchange capacity in multiple countries,” *Catena*, vol. 158, no. May, pp. 194–200, 2017, doi: 10.1016/j.catena.2017.07.002.
- [105] A. Mukherjee and A. R. Zimmerman, “Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar-soil mixtures,” *Geoderma*, vol. 193–194, pp. 122–130, 2013, doi: 10.1016/j.geoderma.2012.10.002.
- [106] D. L. do Carmo, L. B. de Lima, and C. A. Silva, “Soil fertility and electrical conductivity affected by organic waste rates and nutrient inputs,” *Rev. Bras. Cienc. do Solo*, vol. 40, pp. 1–17, 2016, doi: 10.1590/18069657rbcs20150152.
- [107] F. J. González-vila and A. S. Ball, “Soil health — a new challenge for microbiologists and chemists,” *Int. Microbiol.*, vol. 8, pp. 13–21, 2013.
- [108] B. Takoutsing *et al.*, “Assessment of soil health indicators for sustainable production of maize in smallholder farming systems in the highlands of Cameroon,” *Geoderma*, vol. 276, pp. 64–73, 2016, doi: 10.1016/j.geoderma.2016.04.027.
- [109] I. Kögel-Knabner, “Analytical approaches for characterizing soil organic matter,” *Org. Geochem.*, vol. 31, no. 7–8, pp. 609–625, 2000, doi: 10.1016/S0146-6380(00)00042-5.
- [110] K. Smita Tale and S. Ingole, “A Review on Role of Physico-Chemical Properties in Soil Quality,” *Chem Sci Rev Lett*, vol. 4, no. 13, pp. 57–66, 2015.
- [111] Y. Li, E. Padoan, and F. Ajmone-Marsan, “Soil particle size fraction and potentially toxic elements bioaccessibility: A review,” *Ecotoxicol. Environ. Saf.*, vol. 209, p.

- 111806, 2021, doi: 10.1016/j.ecoenv.2020.111806.
- [112] A. B. B. and K. P. Yannawar V.B., “Soil analysis and its environmental Impact on Nanded city, Maharashtra,” vol. 1, no. 1, pp. 73–78, 2013.
- [113] O. A. Oseni, M. M. Ekperigin, A. A. Akindahunsi, and G. Oboh, “Studies of physiochemical and microbial properties of soils from rainforest and plantation in Ondo state, Nigeria,” *African J. Agric. Res.*, vol. 2, no. 11, pp. 605–609, 2007.
- [114] N. Abdu, A. A. Abdullahi, and A. Abdulkadir, “Heavy metals and soil microbes,” *Environ. Chem. Lett.*, vol. 15, no. 1, pp. 65–84, 2017, doi: 10.1007/s10311-016-0587-x.
- [115] Y. E. Navarro-Noya, J. Jan-Roblero, D. C. González-Chávez, R. Hernández-Gama, and C. Hernández-Rodríguez, “Bacterial communities associated with the rhizosphere of pioneer plants (*Bahia xylopoda* and *Viguiera linearis*) growing on heavy metals-contaminated soils,” *Antonie van Leeuwenhoek, Int. J. Gen. Mol. Microbiol.*, vol. 97, no. 4, pp. 335–349, 2010, doi: 10.1007/s10482-010-9413-9.
- [116] V. Göhre and U. Paszkowski, “Contribution of the arbuscular mycorrhizal symbiosis to heavy metal phytoremediation,” *Planta*, vol. 223, no. 6, pp. 1115–1122, 2006, doi: 10.1007/s00425-006-0225-0.
- [117] S. T. Berlin, H. New, L. Paris, and H. Kong, *Trace Elements in soils and plants*. Boca, Raton Florida: CRC Press, 1989.
- [118] A. González-Martínez, M. de Simón-Martín, R. López, R. Táboas-Fernández, and A. Bernardo-Sánchez, “Remediation of potential toxic elements from wastes and soils: Analysis and energy prospects,” *Sustain.*, vol. 11, no. 12, 2019, doi: 10.3390/SU11123307.
- [119] W. Jiao, W. Chen, A. C. Chang, and A. L. Page, “Environmental risks of trace elements associated with long-term phosphate fertilizers applications : A review,”

- Environ. Pollut.*, vol. 168, pp. 44–53, 2012, doi: 10.1016/j.envpol.2012.03.052.
- [120] A. I. M. Of and T. H. E. Work, “An ecological risk index for aquatic pollution control. a sedimentological approach,” vol. 14, 1980.
- [121] United States Environmental Protection Agency, “Risk Assessment Guidance for Superfund: Volume III e Part A, Process for Conducting probabilistic Risk Assessment. Office of Emergency and Remedial Response. U.S. Environmental Protection Agency,” *Washington, DC*, 2001.
- [122] H. Qi, B. Zhao, L. Li, and X. Chen, “Heavy metal contamination and ecological risk assessment of the agricultural soil in Shanxi Province , China,” 2020.
- [123] L. Chen, J. Wang, J. Beiyuan, X. Guo, H. Wu, and L. Fang, “Environmental and health risk assessment of potentially toxic trace elements in soils near uranium (U) mines: A global meta-analysis,” *Sci. Total Environ.*, vol. 816, p. 151556, 2022, doi: 10.1016/j.scitotenv.2021.151556.
- [124] Y. Xie *et al.*, “Effect of Heavy Metals Pollution on Soil Microbial Diversity and Bermudagrass Genetic Variation,” vol. 7, no. May, pp. 1–12, 2016, doi: 10.3389/fpls.2016.00755.
- [125] G. J. Bouyoucos, “54(5,” *Hydrom. method Improv. Mak. Part. size Anal. soils 1. Agron. journal*, vol. 54, no. 5, pp. 464–465, 1962.
- [126] P. R. Day, “,” *Part. fractionation Part. Anal. Methods Soil Anal. Part 1 Phys. Mineral. Prop. Incl. Stat. Meas. Sampl.*, pp. 9, 545–567, 1965.
- [127] H. B. Barnett HL, “Illustrated genera of imperfect fungi. 4th ed. Minnesota, USA: American Phytopathological Society Press,” *Illus. genera imperfect fungi. 4th ed. Minnesota, USA Am. Phytopathol. Soc. Press*, 2006.
- [128] E. S. Samson, R. A. and van Reenen-Hoekstra, “Introduction to food-borne fungi. 3rd edn. Baarn, Netherlands, Centraalbureau voor Schimmelcul- tures.,” *Introd. to food-*

- borne fungi. 3rd edn. Baarn, Netherlands, Centraalbureau voor Schimmelcul- tures., 1988.
- [129] J. A. Von Arx, . “T,” *genera fungi sporulating pure Cult.*, 1970.
- [130] Chiroma T. M, Ebewe R. O, and Hymore F.K, “Comparative Assesment Of Heavy Metal Levels In Soil, Vegetables And Urban Grey Waste Water Used For Irrigation In Yola And Kano,” *Int. Ref. J. Eng. Sci.*, vol. 3, no. 2, pp. 1–09, 2014.
- [131] K. K. Pobi, S. Satpati, S. Dutta, S. Nayek, R. N. Saha, and S. Gupta, “Sources evaluation and ecological risk assessment of heavy metals accumulated within a natural stream of Durgapur industrial zone, India, by using multivariate analysis and pollution indices,” *Appl. Water Sci.*, vol. 9, no. 3, pp. 1–16, 2019, doi: 10.1007/s13201-019-0946-4.
- [132] Z. Sun and J. Chen, “Risk assessment of potentially toxic elements (PTEs) pollution at a rural industrial wasteland in an abandoned metallurgy factory in north China,” *Int. J. Environ. Res. Public Health*, vol. 15, no. 1, 2018, doi: 10.3390/ijerph15010085.
- [133] A. McCauley, C. Jones, and J. Jacobsen, “Soil pH and Organic Matter,” *Nutr. Manag. Modul. No. 8*, no. 8, pp. 1–12, 2009.
- [134] L. Rossato *et al.*, “Impact of soil moisture on crop yields over Brazilian semiarid,” *Front. Environ. Sci.*, vol. 5, no. NOV, pp. 1–16, 2017, doi: 10.3389/fenvs.2017.00073.
- [135] L. Huang *et al.*, “Risk Assessment in Huixian Wetland , South China,” no. Cd, pp. 1–14.
- [136] U. Okerefor, M. Makhatha, and L. Mekuto, “Toxic Metal Implications on Agricultural Soils , Plants , Animals , Aquatic life and Human Health,” pp. 1–24, 2006.
- [137] R. Wennrich, V. Antoniadis, S. M. Shaheen, H. St, E. Levizou, and I. Merbach, “Phytoremediation potential of twelve wild plant species for toxic elements in a

contaminated soil,” *Environ. Int.*, vol. 146, no. October 2020, 2021, doi:
10.1016/j.envint.2020.106233.

- [138] J. Rinklebe, V. Antoniadis, S. M. Shaheen, O. Rosche, and M. Altermann, “Health risk assessment of potentially toxic elements in soils along the Central Elbe River, Germany,” *Environ. Int.*, vol. 126, no. October 2018, pp. 76–88, 2019, doi:
10.1016/j.envint.2019.02.011.

APPENDIX

Table 1: Correlation between PTEs and Physicochemical properties of the farm soil

Physicochemical Properties	PTEs						
	Cd	Cr	Co	Pb	Ni	As	Cu
Moisture (%)							
K	-0.19	0.14	-0.90	-0.24	0.06	-0.75	-0.24
KA	-0.42	0.34	0.42	0.28	-0.05	0.08	-0.01
A	-0.44	0.78	0.09	-0.56	0.49	0.13	-0.17
AG	0.10	-0.31	-0.73	0.04	-0.70	0.73	-0.72
AW	-0.27	-0.56	0.02	-0.42	-0.43	0.93	0.77
pH							
K	-0.30	0.50	-0.68	-0.36	0.28	0.10	-0.28
KA	0.63	-0.62	0.21	-0.28	0.42	-0.17	0.57

A	0.13	0.33	0.76	0.58	-0.55	0.47	0.55
AG	-0.13	0.75	-0.32	-0.42	-0.31	-0.01	-0.45
AW	0.38	-0.15	-0.51	0.14	0.13	-0.38	-0.73
EC (dS/m)							
K	-0.01	0.44	0.25	0.51	0.76	0.90	0.05
KA	0.43	-0.46	0.77	0.07	0.39	-0.03	0.94
A	-0.37	-0.45	0.13	0.60	0.33	0.59	0.79
AG	-0.77	0.03	-0.30	-0.55	-0.23	-0.06	-0.40
AW	-0.36	0.52	0.01	-0.16	-0.04	-0.50	-0.58
Organic matter							
K	0.10	0.32	-0.66	0.13	0.38	-0.54	0.17
KA	-0.91	0.09	0.43	0.35	-0.29	-0.26	-0.02
A	-0.48	0.39	-0.29	-0.65	0.77	-0.07	-0.33
AG	0.10	0.69	0.22	-0.17	0.20	-0.35	0.15
AW	0.74	-0.49	-0.04	0.48	0.53	-0.13	0.06
CEC							
K	0.59	0.00	-0.02	-0.18	-0.39	-0.73	0.58
KA	0.46	-0.85	0.62	-0.52	0.84	-0.56	0.56
A	-0.37	-0.32	0.14	0.52	-0.01	0.78	0.95
AG	0.63	0.16	-0.17	0.50	-0.23	0.23	-0.04
AW	0.14	0.55	0.55	0.44	0.61	-0.74	-0.10
Exchangeable bases (cmol(+)/Kg)							
Ca							
K	0.00	0.23	-0.80	-0.85	-0.46	-0.77	-0.04

KA	0.67	-0.78	0.07	-0.61	0.66	-0.42	0.32
A	-0.53	-0.36	0.04	0.44	0.30	0.78	0.92
AG	-0.13	0.75	-0.32	-0.42	-0.31	-0.01	-0.45
AW	-0.78	-0.05	0.29	-0.64	-0.54	0.72	0.68
Mg							
K	0.34	0.85	-0.71	-0.60	0.10	-0.27	0.36
KA	0.42	-0.52	0.83	-0.11	0.60	-0.19	0.81
A	-0.20	0.30	0.30	0.13	-0.53	0.72	0.70
AG	0.75	-0.70	0.06	0.93	-0.01	0.36	0.32
AW	-0.40	-0.11	0.79	-0.28	0.61	-0.43	0.10
K							
K	-0.49	-0.06	-0.89	-0.23	0.03	-0.63	-0.47
KA	0.42	-0.67	-0.15	-0.47	0.35	-0.39	0.16
A	0.55	0.33	0.92	0.71	-0.70	0.02	0.13
AG	-0.06	0.94	0.05	-0.67	0.07	-0.19	-0.21
AW	0.19	0.35	0.51	0.38	0.78	-0.89	-0.31
Na							
K	-0.36	-0.31	-0.68	-0.31	-0.31	-0.83	-0.37
KA	-0.16	-0.79	0.40	-0.21	0.25	-0.63	0.43
A	0.41	-0.42	0.49	0.89	0.09	-0.26	0.02
AG	-0.34	0.37	-0.63	-0.41	-0.59	0.24	-0.72
AW	-0.76	-0.60	0.00	-0.94	-0.43	0.61	0.21

Table 2: Categories of Enrichment Factor (*EF*) (Chen et al., 2022)

<i>EF</i> Value	Enrichment of soil
< 2	deficiency to minimal enrichment
2-5	moderate enrichment
5-20	significant enrichment
20-40	very high enrichment
> 40	extremely high enrichment

Table 3. Classification of Potential Ecological Risk (Chen et al., 2022)

<i>RI</i>	Potential Ecological Risk
< 90	low
90-180	moderate
180-360	strong
360-720	very strong
≥ 720	highly strong



Table 4: Ingestion exposure route of the PTEs for children and adult per farm

Parameter	^a ADD _{Ing} (Child)						
Farms	Cu	Cd	Cr	Co	Pb	Ni	As
Kwabra	3.36E-04	1.23E-05	4.44E-05	2.18E-04	6.69E-05	1.59E-04	4.55E-04
kwabia	3.93E-04	2.82E-05	8.18E-05	2.46E-04	4.27E-05	1.88E-04	3.45E-04
Asasehene							
Asasehene	2.05E-04	3.94E-05	1.76E-04	1.63E-04	2.92E-04	1.87E-04	3.18E-04
Agbom	1.86E-04	2.50E-05	2.50E-04	2.00E-04	3.57E-04	3.79E-04	2.82E-04
Aworworso	3.11E-04	6.16E-05	9.60E-05	1.46E-04	3.56E-04	3.70E-04	3.21E-04
Control	3.30E-05	2.11E-06	4.21E-05	9.92E-05	3.01E-05	6.65E-06	1.74E-05
^a ADD _{Inges} (Adult)							
Kwabra	4.51E-05	1.20E-06	5.82E-06	2.92E-05	8.75E-06	2.13E-05	6.11E-05
kwabia	5.28E-05	2.74E-06	1.07E-05	3.30E-05	5.59E-06	2.52E-05	4.62E-05
Asasehene							
Asasehene	2.74E-05	3.84E-06	2.30E-05	2.19E-05	3.82E-05	2.51E-05	4.26E-05
Agbom	2.49E-05	2.44E-06	3.27E-05	2.69E-05	4.67E-05	5.08E-05	3.78E-05
Aworworso	4.18E-05	6.00E-06	1.26E-05	1.96E-05	4.66E-05	4.96E-05	4.31E-05
Control	4.43E-06	2.06E-07	5.51E-06	1.33E-05	3.95E-06	8.92E-07	2.33E-06
^a Daily amount of exposure (ADD) to metals through ingestion							

Table 5: Inhalation exposure route of the PTEs for children and adult per farm

Parameter	ADD _{Inh} (Child)						
	Cu	Cd	Cr	Co	Pb	Ni	As
Kwabra	9.43E-09	2.51E-10	1.22E-09	6.10E-09	1.83E-09	4.45E-09	1.28E-08

kwabia	1.10E-08	5.74E-10	2.24E-09	6.90E-09	1.17E-09	5.26E-09	9.67E-09
Asasehene							
Asasehene	5.74E-09	8.03E-10	4.81E-09	4.57E-09	7.99E-09	5.24E-09	8.92E-09
Agbom	5.21E-09	5.09E-10	6.84E-09	5.62E-09	9.76E-09	1.06E-08	7.90E-09
Aworworso	8.73E-09	1.26E-09	2.63E-09	4.10E-09	9.73E-09	1.04E-08	9.01E-09
Control	9.25E-10	4.30E-11	1.15E-09	2.78E-09	8.25E-10	1.86E-10	4.88E-10
ADDInh (Adult)							
Kwabra	4.28E-09	1.14E-10	5.51E-10	2.77E-09	8.29E-10	2.02E-09	5.79E-09
kwabia	5.00E-09	2.60E-10	1.01E-09	3.13E-09	5.30E-10	2.39E-09	4.38E-09
Asasehene							
Asasehene	2.60E-09	3.64E-10	2.18E-09	2.07E-09	3.62E-09	2.38E-09	4.04E-09
Agbom	2.36E-09	2.31E-10	3.10E-09	2.55E-09	4.43E-09	4.82E-09	3.58E-09
Aworworso	3.96E-09	5.69E-10	1.19E-09	1.86E-09	4.41E-09	4.71E-09	4.09E-09
Control	4.20E-10	1.95E-11	5.22E-10	1.26E-09	3.74E-10	8.46E-11	2.21E-10

^a Daily amount of exposure (ADD) to metals through inhalation pathway

Table 6: Dermal exposure route of the PTEs for children and adult per farm

Parameter	^a ADD _{der} (Child)						
	Cu	Cd	Cr	Co	Pb	Ni	As
Kwabra	5.38E-07	1.43E-08	6.93E-08	3.48E-07	1.04E-07	2.54E-07	7.28E-07
kwabia	6.29E-07	3.27E-08	1.28E-07	3.94E-07	6.67E-08	3.00E-07	5.52E-07
Asasehene							

Asasehene	3.27E-07	4.58E-08	2.75E-07	2.61E-07	4.56E-07	2.99E-07	5.09E-07
Agbom	2.97E-07	2.90E-08	3.90E-07	3.21E-07	5.57E-07	6.06E-07	4.50E-07
Aworworso	4.98E-07	7.16E-08	1.50E-07	2.34E-07	5.55E-07	5.92E-07	5.14E-07
Control	5.28E-08	2.45E-09	6.57E-08	1.59E-07	4.71E-08	1.06E-08	2.78E-08
^a ADDder (Adult)							
Kwabra	1.37E-06	3.66E-08	1.77E-07	8.89E-07	2.66E-07	6.49E-07	1.86E-06
kwabia	1.61E-06	8.36E-08	3.26E-07	1.00E-06	1.70E-07	7.67E-07	1.41E-06
Asasehene							
Asasehene	8.36E-07	1.17E-07	7.01E-07	6.65E-07	1.16E-06	7.64E-07	1.30E-06
Agbom	7.58E-07	7.42E-08	9.97E-07	8.19E-07	1.42E-06	1.55E-06	1.15E-06
Aworworso	1.27E-06	1.83E-07	3.82E-07	5.97E-07	1.42E-06	1.51E-06	1.31E-06
Control	1.35E-07	6.27E-09	1.68E-07	4.05E-07	1.20E-07	2.72E-08	7.10E-08

^a Daily amount of exposure (ADD) to metals through dermal contact pathways

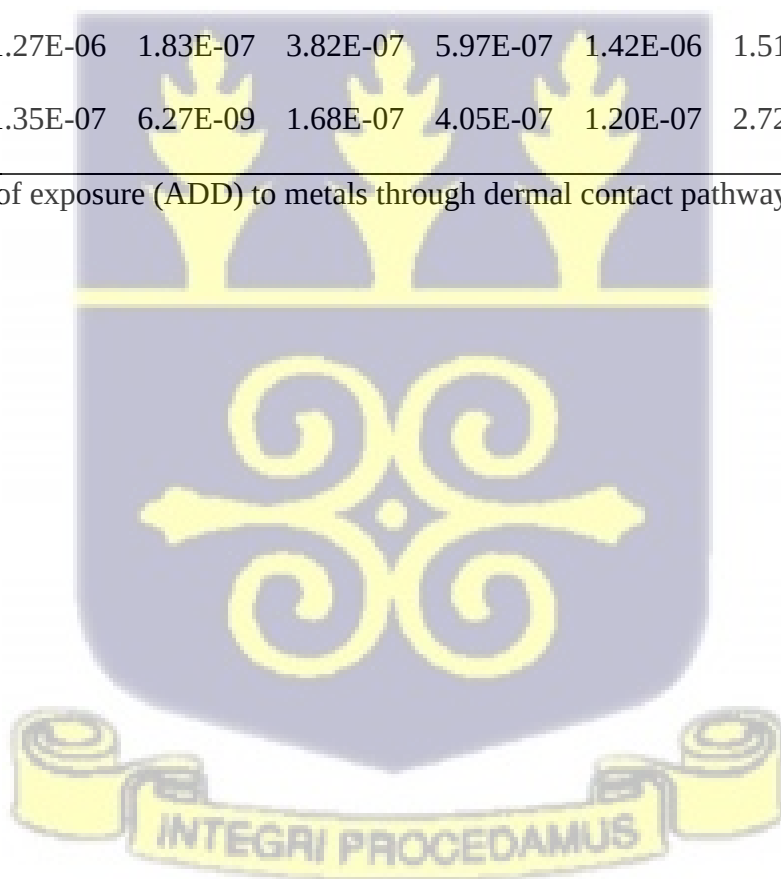
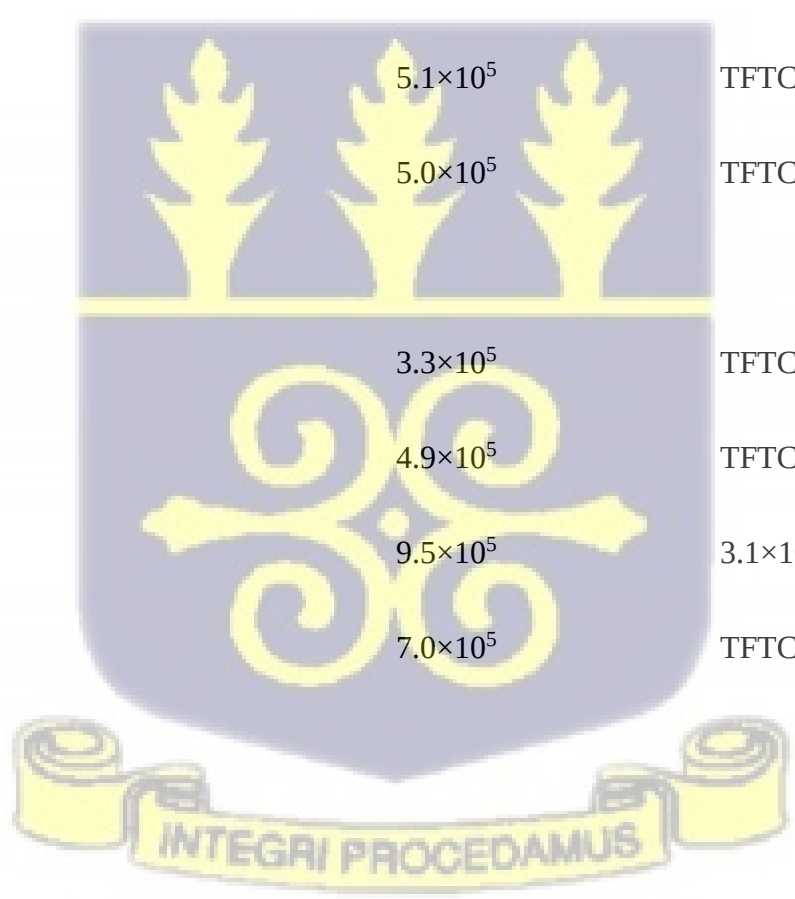


Table 7: Contamination Factor (C_f) and Degree of Contamination (C_{deg}) interpretation (Chen et al., 2022)

C_f value	Contamination	C_{deg} value	Contamination
< 1	low contamination	< 8	low degree of contamination
1-3	moderate contamination	8-16	moderate degree of contamination
3-6	considerable contamination	16-32	considerable degree of contamination
> 6	very high contamination	> 32	very high degree of contamination

Table 8: Mean total microbial (bacterial) population with serial dilutions of 10^{-4} and 10^{-5}

S/N	10^{-4} CFU/g soil	10^{-5} CFU/g soil
KWABIA		
1	4.2×10^5	TFTC

2	4.4×10^5	TFTC
3	8.9×10^5	4.3×10^6
4	TFTC	TFTC
5	3.6×10^5	TFTC
KWABIA ASASEHENE		
6	3.7×10^5	TFTC
7	6.9×10^5	TFTC
8	TFTC	TFTC
9	5.1×10^5	TFTC
10	5.0×10^5	TFTC
ASASEHENE		
11	3.3×10^5	TFTC
12	4.9×10^5	TFTC
13	9.5×10^5	3.1×10^6
14	7.0×10^5	TFTC
15		
AGBOM		
16	13.1×10^5	TFTC
17	TFTC	TFTC

18	5.2×10^5	TFTC
19	3.6×10^5	TFTC
20	5.3×10^5	TFTC
AWORWORSO		
21	6.2×10^5	TFTC
22	TFTC	TFTC
23	4.0×10^5	TFTC
24	5.3×10^5	TFTC
25	3.4×10^5	TFTC

Table 9: Significance difference between the correlation matrix of the metals (p-values @ $\alpha=0.05$)

PTEs	Cu	Cd	Cr	Co	Pb	Ni	As
Cu	na						
Cd	0.00	na					
Cr	0.10	0.05	na				
Co	0.05	0.00	0.20	na			
Pb	0.54	0.04	0.14	0.80	na		
Ni	0.71	0.01	0.04	0.36	0.39	na	
As	0.15	0.00	0.03	0.01	0.24	0.29	na

Table 10: Tukey HSD results between the five farms for Copper (Cu)

Farms pair	Tukey Q statistic	HSD	Tukey p-value	HSD	Tukey inference	HSD
Kwabia vs Kwabia Asasehene	0.9154		0.8999947		insignificant	
Kwabia vs Asasehene	2.1141		0.5694144		insignificant	
Kwabra vs Agbom	2.4178		0.4521038		insignificant	
Kwabia vs Aworworso	0.4023		0.8999947		insignificant	
Kwabia Asasehene vs Asasehene	3.0295		0.2417066		insignificant	
Kwabia Asasehene vs Agbom	3.3332		0.1686318		insignificant	
Kwabia Asasehene vs Aworworso	1.3177		0.8730550		insignificant	
Asasehene vs Agbom	0.3038		0.8999947		insignificant	
Asasehene vs Aworworso	1.7118		0.7228003		insignificant	
Agbom vs Aworworso	2.0155		0.6069785		insignificant	

Table 11: Tukey HSD results between the five farms for Cadmium (Cd)

Farms pair	Tukey HSD Q statistic	Tukey HSD p-value	Tukey HSD inference
Kwabia vs Kwabia Asasehene	1.7290	0.7162398	insignificant
Kwabia vs Asasehene	3.3043	0.1747760	insignificant
Kwabia vs Agbom	1.3832	0.8480838	insignificant
Kwabia vs Aworworso	5.3790	0.0087448	** p<0.01
Kwabia Asasehene vs Asasehene	1.5753	0.7748379	insignificant
Kwabia Asasehene vs Agbom	0.3458	0.8999947	insignificant
Kwabia Asasehene vs Aworworso	3.6501	0.1123554	insignificant
Asasehene vs Agbom	1.9211	0.6429930	insignificant
Asasehene vs Aworworso	2.0748	0.5843931	insignificant
Agbom vs Aworworso	3.9959	0.0701114	insignificant

Table 12: Tukey tests post-hoc HSD results for Chromium (Cr) between the farms

Farms pair	Tukey HSD Q statistic	Tukey HSD p-value	Tukey HSD inference
Kwabia vs Kwabia Asasehene	0.8216	0.8999947	insignificant
Kwabia vs Asasehene	3.3865	0.1577514	insignificant
Kwabia vs Agbom	5.4084	0.0083502	** p<0.01
Kwabia vs Aworworso	4.7154	0.0244133	* p<0.05
Kwabia Asasehene vs Asasehene	2.5649	0.3948306	insignificant

Kwabia Asasehene vs Agbom	4.5868	0.0296411	* p<0.05
Kwabia Asasehene vs Aworworso	3.8938	0.0808310	insignificant
Asasehene vs Agbom	2.0219	0.6045538	insignificant
Asasehene vs Aworworso	1.3289	0.8687889	insignificant
Agbom vs Aworworso	0.6930	0.8999947	insignificant

Table 13: Tukey HSD results between the five farms for Cobalt

Farms	Tukey	HSD	Tukey	HSD	Tukey	HSD
pair	Q statistic		p-value		inference	
Kwabia vs Kwabia Asasehene	1.0557		0.8999947		insignificant	
Kwabia vs Asasehene	2.0354		0.5994226		insignificant	
Kwabia vs Agbom	0.6372		0.8999947		insignificant	
Kwabia vs Aworworso	2.6631		0.3581840		insignificant	
Kwabia Asasehene vs Asasehene	3.0911		0.2253298		insignificant	
Kwabia Asasehene vs Agbom	1.6930		0.7299734		insignificant	
Kwabia Asasehene vs Aworworso	3.7188		0.1024365		insignificant	
Asasehene vs Agbom	1.3981		0.8423902		insignificant	
Asasehene vs Aworworso	0.6277		0.8999947		insignificant	
Agbom vs Aworworso	2.0258		0.6030483		insignificant	

Table 14: Tukey HSD results between the five farms for Lead (Pb)

Farms	Tukey	HSD	Tukey	HSD	Tukey	HSD
pair	Q statistic		p-value		inference	
Kwabia vs Kwabia Asasehene	0.4451		0.8999947		insignificant	
Kwabia vs Asasehene	4.1560		0.0558183		insignificant	
Kwabia vs Agbom	5.3511		0.0091390		** p<0.01	
Kwabia vs Aworworso	5.3317		0.0094192		** p<0.01	
Kwabia Asasehene vs Asasehene	4.6012		0.0290092		* p<0.05	
Kwabia Asasehene vs Agbom	5.7962		0.0045189		** p<0.01	
Kwabia Asasehene vs Aworworso	5.7769		0.0046626		** p<0.01	
Asasehene vs Agbom	1.1950		0.8999947		insignificant	
Asasehene vs Aworworso	1.1757		0.8999947		insignificant	
Agbom vs Aworworso	0.0194		0.8999947		insignificant	

Table 15: Tukey HSD results between the five farms for nickel (Ni)

Farms	Tukey	HSD	Tukey	HSD	Tukey	HSD
pair	Q statistic		p-value		inference	
Kwabia vs Kwabia Asasehene	0.8004		0.8999947		insignificant	

Kwabia vs Asasehene	0.7792	0.8999947	insignificant
Kwabia vs Agbom	6.0917	0.0028225	** p<0.01
Kwabia vs Aworworso	5.8509	0.0041422	** p<0.01
Kwabia Asasehene vs Asasehene	0.0213	0.8999947	insignificant
Kwabia Asasehene vs Agbom	5.2913	0.0100379	* p<0.05
Kwabia Asasehene vs Aworworso	5.0504	0.0146097	* p<0.05
Asasehene vs Agbom	5.3125	0.0097082	** p<0.01
Asasehene vs Aworworso	5.0717	0.0141354	* p<0.05
Agbom vs Aworworso	0.2408	0.8999947	insignificant

Table 16: Tukey HSD results between the five farms for Arsenic (As)

Farms pair	Tukey HSD Q statistic	Tukey HSD p-value	Tukey HSD inference
Kwabia vs Kwabia Asasehene	1.0758	0.8999947	insignificant
Kwabia vs Asasehene	1.3373	0.8655772	insignificant
Kwabia vs Agbom	1.6909	0.7307458	insignificant
Kwabia vs Aworworso	1.3049	0.8779202	insignificant
Kwabia Asasehene vs Asasehene	0.2615	0.8999947	insignificant
Kwabia Asasehene vs Agbom	0.6151	0.8999947	insignificant

Kwabia Asasehene vs Aworworso	0.2291	0.8999947	insignificant
Asasehene vs Agbom	0.3536	0.8999947	insignificant
Asasehene vs Aworworso	0.0324	0.8999947	insignificant
Agbom vs Aworworso	0.3860	0.8999947	insignificant

