

**ACCUMMULATION AND BIOACCESSIBILITY OF HEAVY METALS IN
SOME ROOT TUBERS AND SOIL IN SELECTED COMMUNITIES IN THE
ASHANTI REGION OF GHANA**

KNUST

BY:

ADJEI SAMUEL

(B.Ed. SCIENCE)

**A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY,
COLLEGE OF SCIENCE, KWAME NKRUMAH UNIVERSITY OF SCIENCE
AND TECHNOLOGY, IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF
PHILOSOPHY IN ANALYTICAL CHEMISTRY**

MAY, 2018

DECLARATION

I hereby declare that this submission is my own work towards the MPhil Degree in Analytical Chemistry and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

Adjei Samuel
PG 4620515

.....
Signature

.....
Date

Certified by:
Dr. Godfred Darko
(Supervisor)

.....
Signature

.....
Date

Certified by:
Dr. Marian Asantewah Nkansah
(Supervisor)

.....
Signature

.....
Date

Certified by:
Dr. Osei Akoto
(Head of Department)

.....
Signature

.....
Date

ABSTRACT

The presence of metal contaminants in agricultural soils or lands and subsequent uptake of heavy metals by food crops pose serious risk to human health. The study assessed the levels of toxic metals -arsenic, chromium, copper, iron, manganese, nickel, and zinc- in soils and some edible root tuber crops in the Ashanti region to evaluate the potential human health risks associated with exposure to these metals. Concentrations of heavy metals in the 154 samples were initially screened using field portable x-ray fluorescence spectrometer prior to confirmation on an inductively coupled plasma-mass spectrometer. The mean metal concentrations analyzed in the various samples were in the order; As < Cu < Ni < Cr < Zn < Mn < Fe for cassava and cocoyam, As < Cu < Zn < Ni < Cr < Mn < Fe, As < Zn < Cu < Ni < Cr < Mn < Fe As < Cu < Ni < Cr < Mn < Fe and Cu < As < Ni < Cr < Zn < Mn < Fe for yam, sweet potato, cassava peels and soil respectively. Soil pH and electrical conductivity ranged between 5.30 to 9.17 and 37.8 $\mu\text{S}/\text{cm}$ to 4020 $\mu\text{S}/\text{cm}$ respectively. The contamination indices indicated low to moderate contamination. The bioaccumulation factor of these heavy metals in foodstuffs from soil indicated that cassava peels had higher capacity to absorb zinc and iron gave the lowest capacity of absorption. Arsenic recorded the highest value in terms of target hazard quotient (THQ) followed by nickel and chromium, the least value. Comparing the THQ values for adults and children, results for children were higher than that of adults which indicates that children are more likely to express the effect than adults.

Key words: Bioaccumulation factor, hyperaccumulator, total hazard quotient, heavy metals

TABLE OF CONTENTS

DECLARATION.....	ii
ABSTRACT.....	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF ABBREVIATIONS	ix
ACKNOWLEDGEMENT.....	xii
DEDICATION.....	xiii
CHAPTER ONE	1
INTRODUCTION.....	1
1.1 Background	1
1.2 Problem Statement	5
1.3 Justification	6
1.4 Objectives	6
1.4.1 General Objective	6
1.4.2 Specific objectives	6
CHAPTER TWO	7
LITERATURE REVIEW	7
2.1 Sources of Metals in the Soil	7
2.2 Rate of Accumulation of Metals in Plants	9
2.3 Toxicity of Metals.....	12
2.4 Biological Importance of Metals	14
2.5 Bioaccessibility and Bioavailability of Heavy Metals.....	16
2.6 Pathways of Heavy Metal Uptake.....	18
CHAPTER THREE	20
MATERIALS AND METHODS	20
3.1 Study Area	20
3.2 Sampling Map	22
3.3 Root Tubers and Soil Sampling	23
3.3.0 Quality Assurance and Quality Control.....	23
3.3.1 Soil and Root Tuber Sampling and Handling.....	23
3.4 Preparation of Samples	24

3.4.1 Drying and Sieving of Soil	24
3.4.2 Treatment of Root Tubers	24
3.4.3 Screening Analysis.....	24
3.5 Analysis for Total Metal Concentration	25
3.6 pH and Electrical Conductivity of Soil	25
3.7 Total Carbon Content.....	25
3.8 Extraction for Bioaccessibility.....	26
3.8.1 Metals Digestion	26
3.8.2 Extraction.....	26
3.8.3 Analysis for Metals in Extracts.....	27
3.8.4 Calculation of Metal Bioaccessibility	27
3.8.3.1 Statistical Analysis.....	27
3.9 Estimation of Contamination	28
3.9.1 Enrichment Factor.....	28
3.9.2 Contamination Factor.....	29
3.9.3 Pollution Load Index.....	29
3.11.4 Modified Degree of Contaminations	30
3.11.5 Bioaccumulation Factor	31
3.11.6 Risk Assessment	31
CHAPTER FOUR.....	34
RESULTS AND DISCUSSION	34
4.1 Soil pH and Conductivity	34
4.2 Heavy Metal Concentration in the Soil analysed using XRF	34
4.2.1 Arsenic	39
4.2.2 Chromium	40
4.2.3 Copper.....	42
4.2.4 Iron.....	44
4.2.5 Manganese	46
4.2.6 Nickel.....	48
4.2.7 Zinc	49
4.3 Total Metal Concentrations from ICP-MS	51
4.4 Estimation Heavy Metal Contamination.....	51
4.5 Metal Bioaccessibility.....	53

CHAPTER FIVE	55
CONCLUSION	55
REFERENCES.....	57
APPENDICES	66
Appendix A1: Sample coordinates	66
Appendix A2: Metal concentrations in root tubers and cassava peels from the different communities	68
Appendix A3: Metal concentrations in soil from the different communities	70
Appendix A5: Enrichment factor of metals	74
Appendix A6: Contamination factor of metals	76
Appendix A7: Pollution load index (PLI) and modified degree of contamination (mCd) of metals	78
Appendix A8: Bioaccumulation factor of metals	80
Appendix A9: Target hazard quotient for root tubers.....	82
Appendix A10: Metal bioaccessibility.....	83



LIST OF TABLES

Table 3.1: Modified degree of contamination and its description	31
Table 4.1: Statistical analysis of data from metal concentrations determined with XRF	35

KNUST



LIST OF FIGURES

Figure 3.1: Map of Ashanti region showing sampling area.....	22
--	----

KNUST



LIST OF ABBREVIATIONS

A2	–	Cocoyam from Amansie Central
AC	–	Cassava from Akomadan
ACP	–	Cassava peel form Akomadan
ACS	–	Soil form Akomadan
ACY	–	Cocoyam from Akomadan
ACYS	–	Soil form Akomadan
AP	–	Sweet potato from Akomadan
APS	–	Soil form Akomadan
AY	–	Yam from Akomadan
AYS	–	Soil form Akomadan
AT	–	Averaging Time
B2	–	Cocoyam from Amansie Central
BF	–	Bioaccumulation Factor
BW	–	Body Weight
C1	–	Cassava from Amansie Central
CF	–	Contamination Factor
D2	–	Cocoyam from Amansie Central
E1	–	Cassava from Amansie Central
EC	–	Electrical Conductivity
ED	–	Exposure Duration
EF	–	Enrichment Factor
EU	–	European Union
F2	–	Cocoyam from Amansie Central
FAO	–	Food Aid Organization

FI	–	Food Ingestion
FPXRF	–	Field Potable X-Ray Fluorescence
FTIR	–	Fourier Transform Infrared
G1	–	Cassava from Amansie Central
G2	–	Cocoyam from Amansie Central
GPS	–	Global Positioning System
GSS	–	Ghana Statistical Service
H1	–	Cassava from Amansie Central
J1	–	Cassava from Amansie Central
J2	–	Cocoyam from Amansie Central
HDPE	–	High Density Polyethylene
ICP-MS	–	Inductively Coupled Plasma Mass Spectroscopy
LOI	–	Loss on Ignition
MCd	–	Modified Degree of Contamination
KN	–	Soil from Konongo
OC	–	Cassava from Offinso
OCP	–	Cassava peel from Offinso
OCS	–	Soil from Offinso
OCY	–	Cocoyam from Offinso
OCYS	–	Soil from Offinso
OY	–	Yam from Offinso
OYS	–	Soil from Offinso
PBET	–	Physiologically Based Extraction Test
PLI	–	Pollution Load Index
QA/QC	–	Quality Assurance and Quality Control

R _f D	–	Reference Dose
ROS	–	Reactive Oxygen Species
THQ	–	Target Hazard Quotient
TOC	–	Total Organic Carbon
TTHQ	–	Total Target Hazard Quotient
USEPA	–	United States Environmental Protection Authority
WHO	–	World Health Organization
XRF	–	X-Ray Fluorescence



ACKNOWLEDGEMENT

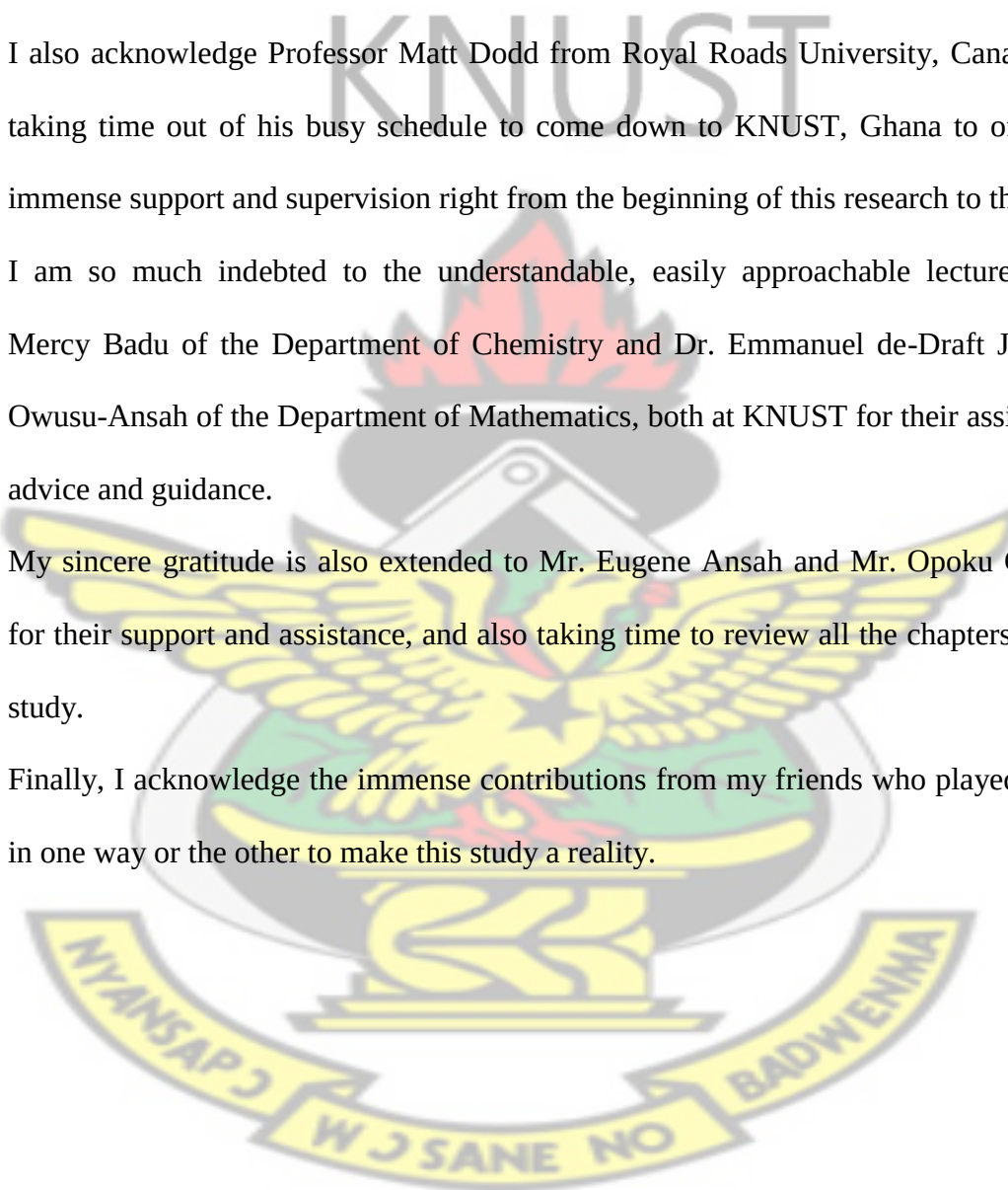
I am very grateful to the Almighty God for letting this research work see light. I am sincerely grateful to my able supervisors, Dr. Godfred Darko and Dr. Marian Asantewaa Nkansah for their guidance, assistance and supervision, and also providing a conducive atmosphere for the smooth sailing of this study.

I also acknowledge Professor Matt Dodd from Royal Roads University, Canada, for taking time out of his busy schedule to come down to KNUST, Ghana to offer his immense support and supervision right from the beginning of this research to the end.

I am so much indebted to the understandable, easily approachable lecturers; Dr. Mercy Badu of the Department of Chemistry and Dr. Emmanuel de-Draft Johnson Owusu-Ansah of the Department of Mathematics, both at KNUST for their assistance, advice and guidance.

My sincere gratitude is also extended to Mr. Eugene Ansah and Mr. Opoku Gyamfi for their support and assistance, and also taking time to review all the chapters in this study.

Finally, I acknowledge the immense contributions from my friends who played a role in one way or the other to make this study a reality.



DEDICATION

This research work is dedicated to my dear mother; Madam Grace Manu, for her great love, care, encouragement and support during the research work.

KNUST



CHAPTER ONE

INTRODUCTION

1.1 Background

Heavy metals occur naturally in the environment usually at low/background concentrations. Human activities such as industrialization, agricultural mechanization, and extraction of precious ores have led to the release, concentration and spreading of heavy metals in the environment (Bak et al., 1997). Environmental pollution by metals is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations (Tchounwou et al., 2012). Metals exist in a number of chemical forms and therefore generally exhibit different physical and chemical properties in terms of chemical interactions, mobility, biological availability and toxicity (Ma et al., 2016). Properties of metals and environmental factors have an impact on metal occurrence in the environment (Caussy et al., 2003).

Metals are highly persistent, ubiquitous and non-biodegradable having very long half-lives (Hosseini Alhashemi et al., 2011). Hence, they can accumulate in soils at environmentally hazardous levels. Most metals form stable compounds, hence they are used to produce variety of products. The application of these metals can therefore cause environmental pollution in diverse ways (Caussy et al., 2003). Exposure to these metal contaminants therefore pose significant public health problems.

Metals are capable of exerting biological characteristics either beneficial or harmful to man. Metals such as Zn, Ni and Cu act as micronutrients to maintain normal body functions. They are needed to maintain certain biological functions in humans. However, excessive intake of the essential metals may also affect human health

negatively (Hu et al., 2013). The essential metals play different roles in metabolic functions, enzymatic activities, sites for receptors, hormonal functions, and protein transport (Khan et al., 2015). Inadequate supply of the essential metals results in a variety of diseases (Tchounwou et al., 2012). For instance, dwarfism and delayed sexual maturation among adolescents is caused by zinc deficiency (Brown et al., 2001). Inadequate supply of iron causes anemia (Lozoff et al., 2000).

Metals such as arsenic, nickel have no beneficial biological function (non-essential elements). They are known to cause deleterious effects on human health (Hu et al. 2013) and are known as toxic metals (Alloway, 1995). Metal ions can cause conditions such as carcinogenesis or apoptosis (Tchounwou et al., 2012)

According to Tchounwou et al. (2012), inorganic arsenic causes toxicity in humans and as such long term exposure can induce carcinogenesis.

Non-essential metals can cause conditions such as diabetes, disorders such as neurobehavioral or neurological disorders or cancer (Tchounwou et al., 2012).

According to Agency for Toxic Substances and Diseases Registry (2015), metal exposures are responsible for specific health conditions. For instance, lead and mercury affect numerous organs in humans from reproductive, renal and cardiovascular.

The main processes through which humans are exposed to toxic metal contaminants are through inhalation, dermal contact and ingestion (Glennon et al., 2014). Food consumption is a major pathway for human exposure to certain environmental

contaminants that accounts for nearly 90% of intake through daily food. Therefore, it is of great importance to determine the oral bioavailability of metals in food stuff, especially, root tubers, to assess human health risk rather than the traditional methods which relies on total metal concentrations (Zhuang et al., 2016).

Agricultural soils can be considered as a sink as they accumulate excessive heavy metals, which can result in elevated heavy metal content over time. Generally, the topsoil accumulate higher concentrations of metals derived from anthropogenic activity more than the other soil strata (Glennon et al., 2014) and soils can be a source of pollution with the capacity to transfer pollutants to the ground-water, food chain and finally, into the human body (Poggio et al., 2009). Humans are therefore likely to experience health risks on getting in contact with contaminated soil through ingestion and dermal contact and also after consuming food crops cultivated on soils which have accumulated excessive heavy metals when there is an uptake of heavy metal into the edible plant part (Zhuang et al., 2009). Heavy metal contamination of food chain needs to be looked at critically as the metal contaminants bioaccumulate and biomagnify in the food chain to cause health-related problems (Khan et al., 2013).

Different plant species bioaccumulate heavy metal at different rates because these plant species show different toxicity to the same pollutant in the same environmental conditions. This is because the processes of metal uptake by plants are not the same for all plant species. Accumulation of heavy metals by plants are classified based on the mode of accumulation, hence, plants are classified as accumulator, hyperaccumulator, and excluders (Khan et al., 2015). This contamination with heavy

metals are said to occur through soil-plant, water-plant, and air-plant interfaces; with soil-plant interface being the major source of plant metal accumulation.

Nonetheless, it has been observed that these contaminant levels do not necessarily indicate actual occurring adverse effects. The accuracy of these predictions is constrained by the ability to determine the fraction of the contaminant that is active in organisms (Peijnenburg et al., 2007). The total metal concentration is not a good indicator of health risk. The risk only exists if the contaminant enters the body through any of the exposure pathways (Cheng et al., 2011). Human risk associated with food contaminants is therefore best accessed by the bioaccessibility of the contaminant. Bioaccessibility refers to the fraction of contaminant that is released from food matrix into the digestive juice chime and becomes available for intestinal absorption, thus, entering the blood stream (Zhuang et al., 2016).

In-vivo examination for the metal concentration is used for risk assessment, however, due to ethical consideration with animal studies, time constraints and cost, physiologically based extraction test (PBET) which involves in-vitro digestion is used (Ruby et al., 1999b; US EPA, 2007a) . PBET measures the fraction of contaminant that is dissolved in the gastro-intestinal tract (Ruby et al., 1999).

In the PBET model, various metal salts, food crops or soils containing metals are incubated in a low-pH solution for a period intended to mimic residence time in the stomach. The pH is then increased to near neutral, and incubation continues for another period intended to mimic residence time in the small intestine. Enzymes and organic acids are then added to simulate gastric and small-intestinal fluids. The

fraction of lead, arsenic, or other metals that dissolve during the stomach and small-intestinal incubations represents the fraction that is bioaccessible (i.e., is soluble and available for absorption). Thus, the model accesses the part of the contaminant which can be absorbed in the intestinal tract (Ruby et al., 1999, Ruby et al., 1996).

1.2 Problem Statement

Food safety is a growing public concern globally due to adverse health effects encountered by humans after consumption of food crops and these food crops are grown in soil, which may be sources of pollution or sinks for metal contaminants in the environment. This concern is further enhanced as increasing population in the world has led to urbanization, mining and industrialization taking a large proportion of the arable land, which could have been used for planting, this leaves behind a small proportion of land to be used for waste disposal from industries and for agricultural practices.

The study areas are major food producing areas in the country. Artisanal mining is also done in especially Konongo and Amansie central which has the potential of releasing heavy metals into the soil (Yao-guo et al., 2010). Agricultural activities also use chemicals containing other forms of heavy metals, which ultimately end in the soil and eventually into the food chain.

The topsoil is the primary receptor of metals from atmospheric deposition and human activities than the rest of the soil strata. Plants, therefore, accumulate the metals in their tissues. In view of this, it is therefore necessary to determine metal concentration

in agricultural soils and root tubers grown on the soil and the bioaccessibility of the metals determined.

1.3 Justification

More than 90% of ingested environmental contaminants are through daily food intake. Essential and non-essential metals, which form part of the environmental contaminants when they exceed the threshold limits, can cause different physiological, morphological, and genetic anomalies including reduced growth, mutagenic effects, and increased mortality. It is therefore necessary to determine heavy metal content in soil and root tubers in order to determine the threats posed to human health and food safety.

1.4 Objectives

1.4.1 General Objective

This work seeks to determine the concentrations and the bioaccessibility of metals in soil and root tubers from Akomadan, Amansie Central, Konongo and Offinso in the Ashanti region of Ghana.

1.4.2 Specific objectives

This research seeks to:

- quantify the levels of concentration of the metals in soil and root tubers.
- examine the metal concentration correlation between soils and root tubers.
- determine the metal bioaccessibility.
- determine the accumulation difference amongst the root tubers.

CHAPTER TWO

LITERATURE REVIEW

2.1 Sources of Metals in the Soil

Metals present in the environment, except those small quantities that have arrived extra terrestrially or have been created in nuclear reactions, have been present in and on the earth since its formation some 4.5 billion years in the past. As part of the natural biogeochemical cycle, metals are released from rocks by weathering processes, are cycled through various environmental compartments by biotic and abiotic processes, and ultimately find their fate in the oceans as sediments (Garrett, 2000).

Soil pollution has become an important environmental issue due to changes in the land use pattern over the last few decades. Considering the different kinds of contaminants, heavy metals are especially dangerous because of their persistence and toxicity. Metals can be transferred from soil to the other ecosystem components, such as underground water or crops, and can affect human health through the water supply and food web (Micó et al., 2006).

The concentration of heavy metals in soil and their impact upon ecosystems can be influenced by many factors, such as parent material, climate and anthropogenic activities. Vehicular emissions, incinerators, industrial waste, atmospheric deposition of dust and aerosols, and other activities have continuously added to the pool of contaminants in the environment for which many research works have been done to quantify levels in different situations and have produced a better understanding of background and anthropogenic sources for metals in soils (Zhang et al., 2009).

There is evidence in literature that metals may be added to surface environments directly by volcanic activity through eruption, gaseous fumaroles and hot spring activity, and through degassing along fractures and faults that provide suitable pathways from depth (Garbisu and Alkorta, 2001). An example is the ejection of 3 to 5 km³ of rock by mountain Pinatubo, equivalent to 104 metric tonnes that contained some 100,000 tonnes of lead and 800 tonnes of mercury. Although most of this mass of material fell within about 100 km radius of mountain Pinatubo, a significant amount reached the stratosphere and circled the globe.

Agricultural soils can be long-term sinks for heavy metals. Intensification of agriculture has resulted in the incorporation of several types of pollutants to soil, such as heavy metals, due to excessive use of agrochemicals. These soils have also been influenced by other activities such as the use of manures, sewage sludge disposal or aerial fallout from industrial activities. It has also been found that heterogeneous lithology can affect heavy metal contents. For example, organic matter, clay and carbonates play a relevant role in the distribution and availability of heavy metals in calcareous soils (Micó et al., 2006).

Literature has shown that there has been a conscious effort to formulate methods for distinguishing between anthropogenic and geogenic sources of the potential toxic elements which include element speciation, profile distribution, spatial distribution, information such as parent rock composition, and known anthropogenic loads (Yalcin et al., 2010)

There have been several attempts to quantify the amount of some heavy metals released into the environment through various activities within a particular time. For example, the annual worldwide release of heavy metals reached 22,000 t (metric ton) for cadmium, 939,000 t for copper, 783,000 t for lead and 1,350,000 t for zinc for which some of the sources included metalliferous mining and smelting, metallurgical industries, sewage sludge treatment, warfare and military training, waste disposal sites, and electronic industries (Padmavathiamma and Li, 2007). They further claimed that ground transportation also causes metal contamination. Tread wear, brake abrasion, and corrosion are well-documented heavy metal sources associated with highway traffic. Heavy metal contaminants in roadside soils originate from engine and brake pad wear.

2.2 Rate of Accumulation of Metals in Plants

The assertion that the elemental composition of plant is very different from that of the soil in which they grow is sometimes misunderstood. Most of these differences can be attributed to the ability of the plant to fix carbon from the air and to absorb essential macronutrients and micronutrients from the soil. In other words, living plants can be compared to a solar driven pump that can concentrate certain elements from the environment (Raskin et al., 1994).

The rates of accumulation of metals are necessarily governed by physiological requirements rather than toxicity; however, some of the metals are accumulated while others are not. Generally, accumulation of a given metal is a function of uptake capacity and intracellular binding sites. The processes that are assumed to be influencing metal accumulation rates in plants include: mobilization and uptake from

the soil, compartmentalization and sequestration within the root, efficiency of xylem loading and transport, distribution between metal sinks in the aerial parts, sequestration and storage in leaf cells. At every level, concentration and affinities of chelating molecules, as well as the presence and selectivity of transport activities, affect metal accumulation rates (Clemens et al., 2002). However, metal accumulation in tree tissues can vary hugely according to the source of metal contamination and site conditions (Pulford and Watson, 2003). Heavy metals such as Cd and Pb generally intrude into plant cells at the expense of essential inorganic ions on account of similar properties, such as ionic radii (Sharma and Dietz, 2009).

The transfer of potentially toxic heavy metals from soils into shoots of higher terrestrial plants is said to be typically low compared to those of macronutrients. Therefore, those species that accumulate exceptionally large concentrations of heavy metals in their tissues have attracted scientists to study evolutionary, ecological and physiological concepts involved in the process (Wenzel and Jockwer, 1999). Absorption, accumulation and tolerance to heavy metals may vary between different crops. Crop plants may develop adaptive response to tolerate the heavy metal stress (Singh and Agrawal, 2010). However, some plants which grow on metalliferous soils have developed the ability to accumulate higher amounts of indigenous metals in their tissues without symptoms of toxicity (Padmavathiamma and Li, 2007). Essentially, the ability to accumulate heavy metals varies significantly among species and among cultivars within individual species. For instance, *Thlaspi* (*Brassicaceae*), can accumulate more than 3% Zn, 0.5% Pb and 0.1% Cd in their shoots, and *Alyssum* (*Brassicaceae*), can accumulate over 1% Ni, 3% Pb and 0.5% Cd (Pulford and Watson, 2003)

Clemens et al. (2002) have pointed out that, root-colonizing bacteria, as well as mycorrhiza, have a large influence on heavy metal availability for plant uptake. They further gave the assertion that soil microorganisms significantly enhance Zn accumulation in the shoot of the hyperaccumulator *Thlaspi caerulescens*.

The uptake or accumulation of certain heavy metals is dependent on the presence of other substances or pollutants. The metal-metal interaction influence the uptake of some metals as compared to others. For example, Cd suppress the manganese uptake by plants resulting in iron deficiency in plants. Similarly, Cd suppresses the uptake of calcium, magnesium, and nitrogen (Sajwan et al., 2002).

According to Baker (1981) the prolonged presence of a specie or a race on metal-contaminated soil implies that, it is tolerant of the metal's toxicity. Either such edaphic adaptation necessitates a specialized physiology resulting from a constitutional tolerance within the species or from ecotypic differentiation of the species into metal-tolerant races, which are specifically adapted physiologically. The same writer asserts that there is much evidence in literature to suggest that plants growing on toxic metalliferous soils cannot prevent metal uptake but only restrict it and hence accumulate metals in their tissues to varying degrees. Therefore, the strategies of survival adopted by plants are that of tolerance and not avoidance of metal toxicity. Species therefore differ considerably in their metal uptake characteristics and for any species, these characteristics may vary for different metals. Typically, some metals are accumulated in roots especially, Pb, probably due to some physiological barriers against metal transport to aerial parts, while others are easily transported in plants, for

example, Cd (Garbisu and Alkorta, 2001). Nickel is the metal most frequently hyperaccumulated.

Based on these and other examples, three types of plant- soil relationships are proposed (Baker 1981):

1. Accumulators, where metals are concentrated in above ground plant parts from low or high soil levels.
2. Indicators, where uptake and transport of metals to the shoot are regulated so that internal concentration reflects external levels.
3. Excluders, where metal concentrations in the shoot are maintained constant and low over a wide range of soil concentration up to a critical soil value above which the mechanism breaks down and unrestricted transport results.

2.3 Toxicity of Metals

Heavy metals, such as cadmium, copper, lead, chromium and mercury, are important environmental pollutants, particularly in areas with high anthropogenic pressure. Their presence in the atmosphere, soil and water, even in traces, can cause serious problems to all organisms. Heavy metal accumulation in agricultural soil can have negative impact on food quality. For instance, cumulative poisons such as copper, mercury and cadmium (Islam et al., 2007) can compromise food quality.

Heavy metals availability is high in soil and aquatic ecosystems and exists in particulate matter or vapors in the atmosphere. Plants can have varying degrees of metal toxicity with respect to plant species (Sharma & Agrawal, 2005).

A number of heavy metals are known to have a strong impact on the stability of ecosystems and may have adverse effects on humans. It is a known fact that heavy metals cause acute toxic effects and cancer in mammals particularly owing to damage of DNA (Steinkellner et al., 1998). Heavy metals are therefore considered carcinogenic (Sharma and Agrawal, 2005). Molecular genetic studies have shown that certain metals ions cause DNA damage (Laird et al., 2015). In view of that, efforts have been made to limit metal emission.

Hall (2002) points to the fact that a range of interactions at the cellular or molecular level can induce toxicity symptoms in the presence of excessive amounts of heavy metals. Toxicity may result from the binding of metals to sulphydryl groups in proteins leading to an inhibition of activity, disruption of structure or from displacement of an essential element resulting in deficiency effects. Heavy metal excess may stimulate the formation of free radicals and reactive oxygen species perhaps resulting in oxidative stress.

According to Sharma & Dietz (2008) metal toxicity is ascribed to three main reasons:

1. Direct interaction with proteins due to their affinities for thioyl-, histidyl- and carboxyl-groups, causing the metals to target structural, catalytic and transport sites of the cell.
2. Stimulated generation of reactive oxygen species (ROS) that modify the antioxidant defense and elicit oxidative stress.
3. Displacement of essential cations from specific binding sites, causing functions to collapse. For example, Cd^{2+} replaces Ca^{2+} in the photosystem II reaction centre, causing the inhibition of PSII photoactivation.

The ions of copper and zinc are essential for a vast number of metabolic processes yet are potentially dangerous; hence, they pose a specific dilemma to organisms. Cu (I) and Cu(II) ions show an extremely high affinity to various organic molecules. The redox-activity of Cu, which is exploited in many electron transfer reactions, for example, in photosynthesis, can lead to the generation of oxygen radicals. Zinc ions are key structural or catalytic components in DNA binding proteins and hydrolytic enzymes. However, uncontrolled binding can result in the inactivation of proteins (Clemens et al., 2002).

The ability of heavy metals to generate Reactive Oxygen Species (ROS), thereby inducing a cellular pro-inflammatory response have been observed both in vitro and in vivo. Metals are therefore said to have potential involvement in respiratory health issues. For example, oxidized forms of manganese as Mn^{3+} are involved in the formation of ROS and may compromise biological functions. Zn concentration in airborne particulates have been clearly associated to the lung toxicity in mouse, and the water-extractable fraction of Fe, V and Ni has been reported to be the primary cause of acute inflammatory infection in humans (Julien et al., 2011)

2.4 Biological Importance of Metals

Generally, heavy metals are seen as environmental pollutants due to their direct negative effects on organisms. These direct effects stem from the general toxicity of heavy metals to a variety of biological processes. The effects are dose-dependent, but some heavy metals are required in relatively small amounts as micronutrients for many organisms, so that low doses can have positive direct effects (Boyd, 2010). Caussy et al., (2003) reports that metals can cause biological effects either harmful or

beneficial; therefore, for exposure beyond a particular threshold, toxicity begins to mount. For example, metals such as Fe, Cu, Co, Mn, Zn, and Cr are essential for humans, and deficiency states with clinical abnormalities with accompanying symptoms have been identified. Goiter results from the deficiency of iodine and iron. Through biotechnology, Zn is engineered into plants that are able to accumulate metals in their edible parts to prevent Zn deficiency in diets (Boyd, 2010).

Metals have several other application from the industrial front. Metal plating, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and the maintenance of storage batteries all employ metals (Kadirvelu et al., 2001). The agricultural setting also uses metals. An instance is the production of biocides and fertilizers (Caussy et al., 2003). Health care facilities also employ the services of mercury in its functions.

There are still in use mercury containing instruments in hospitals even though it has been banned in some countries. Dentists use mercury amalgam in their operation. Some drugs are manufactured with Hg (Thimerosal) as a preservative. Some high level Hg-containing antiaging and skin lightening creams, lotions, and soaps are products also in use (Liang et al., 2013).

Another example is the use of arsenic. Arsenic compounds have also been used for at least a century in the treatment of syphilis, yaws, amoebic dysentery, and trypanosomiasis (Tchounwou et al., 2012). Because of its therapeutic properties, arsenic-based drugs are used in both humans and animals: treatment of African sleeping sickness in humans and filariasis in dogs.

Metals are effective against parasites. Boyd, (2010) puts it that snails in a heavy metal-polluted lake were less sensitive to the metals than their internal parasites, such that parasite loads were markedly reduced in the polluted lake and this resulted in greater abundance of the snail. Ecological structure can be altered in polluted locations by both direct and indirect effects induced by metals.

2.5 Bioaccessibility and Bioavailability of Heavy Metals

Diet is assumed to be the most important route through which toxic substances such as metals get into the human system. Sharma & Dietz (2008) found that, heavy metals intrude into plant cells mostly through the soil. However, a wide range of soil properties such as pH, organic matter content, clay content, iron oxide content and redox conditions all alter the effects of given metal loadings on soil. Among these properties, soil pH is often found to have the largest influence, due to its high influence on solubility and speciation of metals both in the soil as a whole and soil solution, particularly (Giller et al., 1998). Other factors that can hinder heavy metals bioavailability is limited solubility in oxygenated water and strong binding to soil particles (Clemens et al., 2002). Not only do binding forms affect bioaccessibility of heavy metals but the properties of the food, (such as source and type) (Hu et al., 2013) also contribute to bioaccessibility.

Accessibility of metals to some extent is restricted by certain plants from moving from the soil into the plant. For instance, plants reduce the mobility and bioavailability of pollutants in the environment either by immobilisation or by prevention of migration (Pulford and Watson, 2003). Hence, trees or plants differ in their ability to translocate heavy metals. Lead may be immobilised by the formation

of the lead phosphate mineral chloropyromorphite in soils and within roots. This phenomenon is promoted in soils by *Agrostis capillaris* growing on lead/zinc mining wastes.

The bioavailability of trace metals, (including their toxicity) relates to the metal's ability to cross biological barriers, for instance, plasma membrane which depends on the concentration or flux of internalized metal. The uptake process depends not only on the internalization pathways and their specificity but also on the physicochemistry of the medium and the size and nature of the organism (Worms et al., 2006).

Exposure and bioavailability influences metal effects on the environment (Caussy et al., 2003). However, metals vary greatly in their bioavailability or ability to enter organisms and cause toxicity. For example, absorption of Na and K is greater than 90%, while absorption of Cr is less than 1% in the gastrointestinal tract of humans. Copper is, for example, more strongly bound to dissolved organic carbon than zinc, and hence copper is in general less available for uptake by aquatic organisms (Peijnenburg and Jager, 2003).

Bioavailability is essential in ascertaining the potential health effects associated with ingestion of metal contaminants. Dodd et al. (2013) defined bioavailability as the fraction of an ingested dose that crosses the gastrointestinal epithelium and becomes available for distribution to internal target tissues and organs. This fraction induces the toxic effects. The unabsorbed part may be embedded in the un-absorbable fraction and excreted or changed in chemical form through a speciation process (Cano-Sancho et al., 2015). The determination of bioavailability and bioaccessibility

of the metal helps identify if the accumulated concentration can have an effect on organisms. Therefore, it is not out of place to determine the oral bioavailability of metals, which is the absorbed dose by human body in reality to assess human health risk rather than the traditional methods based on total concentrations of metals (Zhuang et al., 2016)

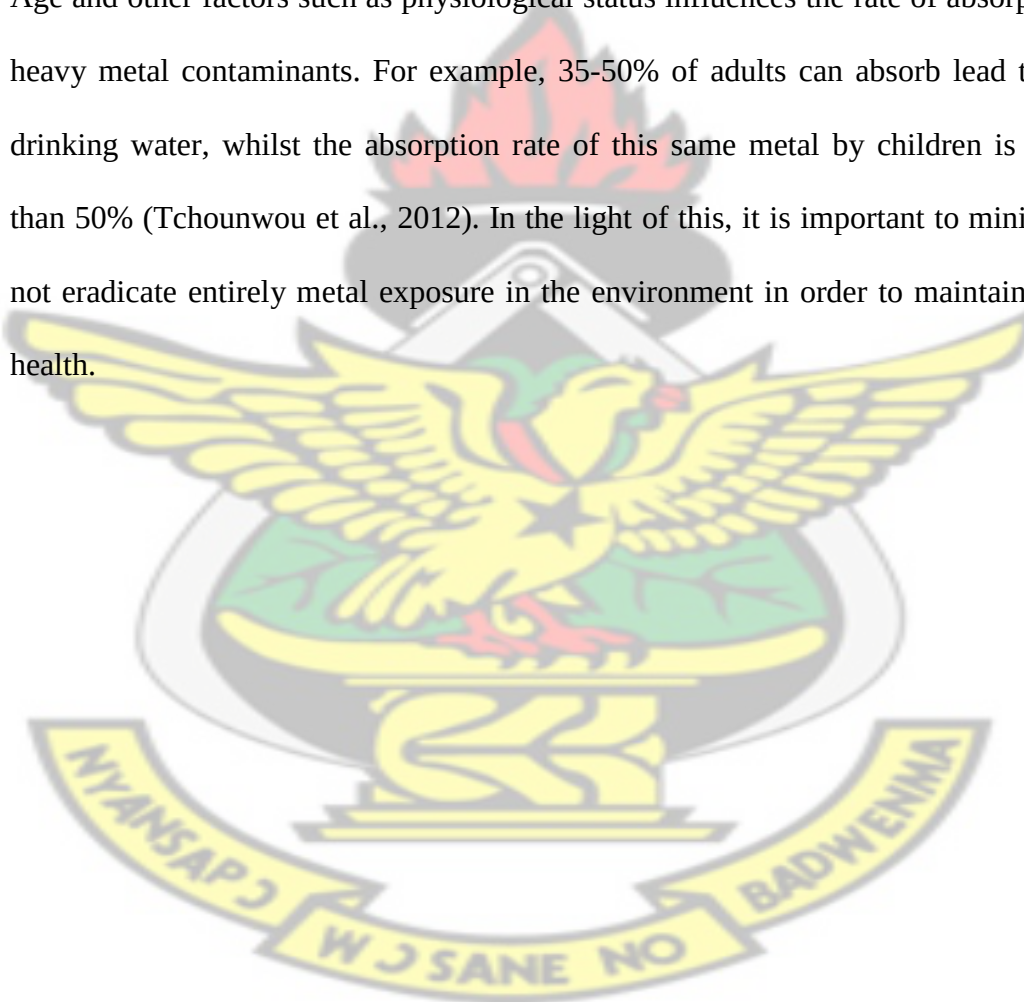
2.6 Pathways of Heavy Metal Uptake

Conscious efforts have been made to identify the various route of exposure of toxic contaminants into the environment. Plumlee et al. (2006) identify some of the major pathways by which humans are exposed to these potential toxicants. The effect a given toxicant or pathogen can exert, depends upon the exposure route due to the differences in physical processes, physiological processes, and chemical conditions to which it is subjected along each of the pathways.

These pathways as described by many researchers include: ingestion by the gastrointestinal tract, inhalation by the respiratory tract, direct contact through unbroken skin, thus, through the percutaneous, eyes, through the ocular or wounds (Plumlee et al., 2006, Reeder and Schoonen, 2015). The form in which the metal exist influences the type of exposure. It is possible for a particular metal to exist in either solid, liquid or gas. For example, arsenic that is from iron oxide coated sand in an aquifer will enter groundwater that may be a source of drinking water for other people or organisms. However, inhalation would be the primary exposure pathway for arsenic associated with airborne particles in mineral dust. Cigarette smoking has been linked to be one of the exposure pathways of Cd (Tchounwou et al., 2012.).

Zhuang et al. (2016) points to the fact that the major pathway for human exposure to certain environmental contaminants, accounting for 90% of intake is through daily food. They further assert that a certain group of the population is at a higher risk due to the type of food they consume. Tchounwou et al. (2012) also point to the fact that one's occupation can be a potential source of heavy metal exposure; deteriorating household paint can also be a source of heavy metal exposure e.g. lead paint.

Age and other factors such as physiological status influences the rate of absorption of heavy metal contaminants. For example, 35-50% of adults can absorb lead through drinking water, whilst the absorption rate of this same metal by children is greater than 50% (Tchounwou et al., 2012). In the light of this, it is important to minimize if not eradicate entirely metal exposure in the environment in order to maintain public health.



CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The study was carried out in some selected communities in the Ashanti Region of Ghana. The region lies within the boundaries of 6.7470° N, 1.5209° W of the southern half of the country and occupies an area of 24, 389 km² with a population density of 196.01 inhabitants/km². It is the third largest region after the Northern and Brong Ahafo regions, respectively. Its location makes it strategic for some economic activities in the country. The southwestern part is found in the semi-equatorial forest zone and a smaller northeastern part lies in the savanna zone. The annual average rainfall is about 1270 mm and this spans for two rainy seasons. The main rainy season starts from April to mid-August whilst the minor season starts from September to November. Averagely, the daily temperature is about 27 °C (GSS, 2013). The communities selected were Akumadan, Amansie Central, Offinso and Konongo.

Akumadan is a community noted for its farming activities especially, cultivation of vegetables such as tomatoes (*Solanum lycopersicum*), eggplant (*Solanum melongena*), okro (*Abelmoschus esculantus*), and other food crops which include; maize (*Zea mays*), cassava (*Manihot esculenta*), plantain (*Musa paradisiaca*), yam (*Dioscorea sp*) among others. The vegetation is predominantly semi-deciduous forest for which a large portion has been lost due to excessive logging (Quansah et al., 2016). The major rainfall season starts from April and ends in June and the minor period is ushered in from September to October with an annual mean rainfall of 125-180 cm (GSS, 2013).

Amansie Central District Assembly is one of the thirty Administrative Districts in the Ashanti Region, which was created from Bekwai Municipality in 2004. Amansie Central is located between latitude 6°00N and 6°30N and longitudes 1°00W and 2°00W (GSS, 2014). The vegetation of the area is predominantly semi-deciduous with trees such as Odum (*Iroko*), Wawa (*Obeche*), Mahogany (*Mahogany*) and Cedar (*Sapele*). Meanwhile, excessive logging activities, poor farming activities and bush fires are affecting the vegetation. Rivers such as Oda, Offin and Fena are the main rivers draining the area. These rivers especially, river Offin dry up due to activities such as gold mining and poor farming practices along the river's catchment area. The annual mean rainfall is between 1,600–1800 mm from the two main rainfall patterns. The major rainy season starts from March to July whilst the minor season starts from September to November while temperature ranges from 20 °C to 32 °C.

Offinso is one of the municipal assemblies in Ashanti region located in the extreme northwestern part of the Ashanti Region. The neighboring assemblies are Offinso North to the North, Ejura-Sekyedumase Municipal to the East, Sekyere South to the Southeast, Atwima Nwabiagya and Ahafo Ano South Municipals to the West (GSS, 2014). The municipality is drained by four main rivers namely, Offin, Anyinasu, Ode and the Pro. The area is covered with moist semi-deciduous vegetation with patches of thick green cover. The rainfall seasons are of two categories, a major season (April to June) and a minor season (September and October). The soil is formed from three main rocks; Voltain, Birimian and the Granite. Wide range of crops are cultivated in the area which include, plantain, cocoyam, cassava, maize and vegetables as well as cash crops such as cocoa, oil palm and citrus.

Konongo is the capital town of Asante Akim Central municipality which was created from the then Asante Akim District Council in 1988. It is located at the eastern part of Ashanti Region. The municipality is enclosed by the following assemblies, Asante Akim North District at the North, Ejisu-Juaben and Sekyere East at the West, Asante Akim South at the East and South whilst the South – Western corner borders with Bosome-Freho District (GSS, 2014). Semi-deciduous forest with open and closed forests characterizes the area's vegetation. There are two rainfall patterns; May to July and the second from September to November. The annual temperature is usually around 26 °C. The soil is mostly forest ochrosol, which is good for the production of cash and food crops such as oil palm, cereals, cassava, plantain, cocoa and vegetables. The topography is highly undulating and the prominent rivers that drain the area include the Annum, Owerri and Bomire rivers (Boadi et al., 2013).

3.2 Sampling Map

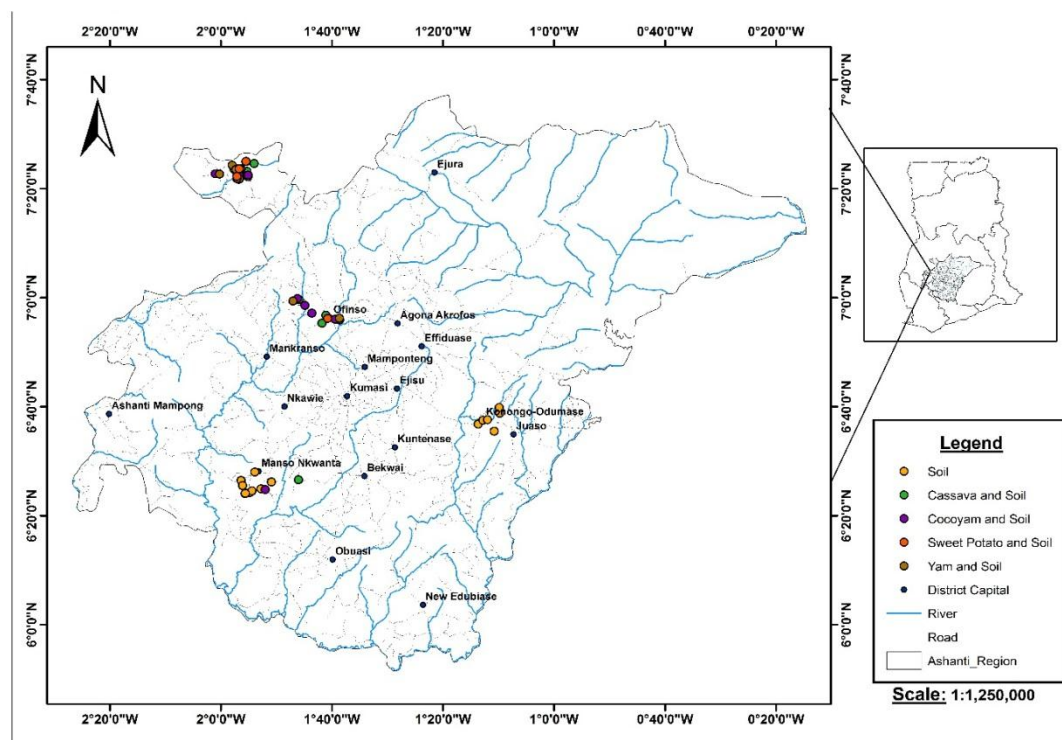


Figure 3.1: Map of Ashanti region showing sampling area

3.3 Root Tubers and Soil Sampling

The samples for the study were taken from sixty-nine (69) sampling sites. Convenience sampling approach was employed by the researcher who located various farms where root tubers are cultivated with the help of indigenes or inhabitants. Root tubers, such as, cassava, cocoyam, sweet potato and yam were removed from the ground and soil samples underneath these root tubers were sampled as well. The soil samples underneath the root tubers were sampled due to their close proximity to the tubers. Moreover, the top soil is assumed the area where human beings are exposed to and is likely to provide better human risk estimates. The soil samples were sampled with a plastic trowel to avoid metal contamination from the trowel. After each sampling, the plastic trowel was cleaned with tissue paper and subsequently rinsed with distilled water. The samples were placed in plastic bags and was identified with unique codes. Hand-held global positioning system (GPS) device indicated the precise location of sampling points. Sampling started in 25th November, 2016 and ended on 7th December, 2016.

3.3.0 Quality Assurance and Quality Control

3.3.1 Soil and Root Tuber Sampling and Handling

The following quality assurance (QA) and quality control (QC) procedures were adopted:

- Sampling containers were obtained from the laboratory and treated such that contamination could be minimized.
- Samples were placed in containers supplied from the laboratory and coded.
- The plastic trowel were thoroughly cleaned after each sample to avoid sample cross contamination.

- New gloves were used for each sampling
- Analysis included duplicates to ensure consistency in results.

3.4 Preparation of Samples

3.4.1 Drying and Sieving of Soil

The soil samples were dried in air at room temperature to take away moisture from the soil. Subsequently, USA Standard Testing Sieve ASTM E11 was used to sieve all the dried soil samples to $< 250 \mu\text{m}$. The sieved samples were put in a container with codes for easier identification for further analysis.

3.4.2 Treatment of Root Tubers

The root tubers were washed severally with distilled water then later peeled and sliced into smaller units. The smaller units of edible portion and the peels of the cassava were air dried at room temperature to take away moisture. The dried samples were then milled in a stainless steel blender and subsequently sieved to take away coarse particle.

3.4.3 Screening Analysis

About 500g of the soil sample was taken and approximately 20% of the soil and roots tuber samples were selected for detailed laboratory analysis including physiologically base extraction test (PBET). The sieved samples were divided. Determination of total metal concentration using Niton field portable x-ray fluorescence analyzer (FPXRF) as well as inductively coupled plasma mass spectrometry (ICP-MS) on one part and the other part was used for bioaccessibility determination method (Dodd et al., 2013; Koch et al., 2013).

Procedural blanks, standard reference materials and replicates (10%), were used to ensure that laboratory quality assurance/quality control were complied with. The XRF was calibrated to generate useable data.

3.5 Analysis for Total Metal Concentration

Niton XL3t GOLDD+X-ray fluorescence analyzer was used to screen dried soil and milled root tuber samples.

The XRF analysis uses United States Environmental Protection Agency (US EPA) method 6200 for determination of metals in soils and sediments (US EPA, 2007b). A portion of the sieved sample was placed in a small (~30 mm) polyethylene container to about three-quarters full. A Mylar film was used to keep sample in place and sealed before the analysis. The sample was analysed in the XRF shroud for 180 seconds.

3.6 pH and Electrical Conductivity of Soil

Electrical conductivity and soil pH were determined using Jenway pH and conductivity meter probe (model 3540). The determination was done with 1:2 dry soil to distilled water ratio.

3.7 Total Carbon Content

Total organic carbon (TOC) was determined for soil samples and the technique used was loss on ignition (LOI). Loss on ignition (LOI) is one of the semi – quantitative methods used for the determination of organic matter in soil. This involves destroying the organic matter in the soil through heating (Schumacher, 2014). The difference between the final and initial sample weight gives the total organic content (carbon). The difference is then expressed as a fraction over the initial sample weight.

One (1) gram of soil sample was put into a crucible and heated in an oven at 105 °C for 2 hours. The sample was then cooled in a desiccator and weighed again. The sample was then heated in a pre – heated muffle furnace that had been heated for about four hours at 550 °C. The sample was then cooled to room temperature overnight and weighed.

3.8 Extraction for Bioaccessibility

3.8.1 Metals Digestion

A 0.5 g of sieved sample was added to a 3 mL 1:1:1 HCl-HNO₃-H₂O. The digestion was carried out at 95 °C for 1 hour in a heating block. The sample was made up to volume with dilute HCl. Subsequently, ICP-MS was used for total metal analysis (US EPA 2015).

3.8.2 Extraction

The extraction protocol was based on EPA Method 9200.2-86 (US EPA, 2007). Procedure blank and a laboratory control sample were used to observe quality assurance and quality control (QA/QC). 1 g of the sieved sample was put in a 125 mL high-density polyethylene (HDPE) bottle which had been cleaned with acid. A 100±0.5 mL of extraction fluid was added to the bottle to yield sample mass to fluid ratio of 1:100. pH was measured.

The pH of the sample/extraction fluid mixture was measured. 30 g/L of glycine (Calbiochem, Massachusetts) was the extraction solution used whose pH was regulated to 1.5 with concentrated HCl (Fisher Scientific, trace metal grade). The sealed bottles were placed in an extractor in groups of eight (8) and rotated for 1 hour

in a water bath at 37 ± 2 °C. The bottles were removed after the extraction and a 20 mL plastic syringe with a luer slip (National Scientific) was used to take each of the extract. The extracts were filtered into a 20 mL polyethylene scintillation vial (Wheaton) by using a 0.45 µm cellulose acetate filter (25 mm diameter, Cole Palmer). The filtered extract was stored at 4 °C before analysis for metals by ICP-MS (US EPA 2015).

3.8.3 Analysis for Metals in Extracts

Agilent Model 7500ce Collision Cell ICP-MS which operates on the United States Environmental Protection Agency (US EPA) SW846 Method 6020A was used for the metal analysis (USEPA 2007a)..

3.8.4 Calculation of Metal Bioaccessibility

Bioaccessibility of metals were determined using the formula adapted from the US EPA standard operating method for accessing in-vitro extraction test as follows:

$$\text{Bioaccessibility, \%} = \frac{(\text{concentration in extract, } \mu\text{g/L}) \times (\text{volume of extract, L})}{(\text{concentration in soil, mg/kg}) \times (\text{mass of soil used, g})} \times 100$$

3.8.3.1 Statistical Analysis

Statistical methods were used to ascertain the minimum, maximum, mean and standard deviation of the concentrations of metals in the samples. XRF results for total metals were compared with ICP-MS total metals. Results from either method which was below detection was discarded.

3.9 Estimation of Contamination

The level of pollution of a particular heavy metal can be ascertained if there is reference, i.e. a point upon which comparisons of the said pollution can be made. Pollution indices then become a useful tool in characterizing the source of the contaminants and transforming the raw data into a meaningful language for better understanding and interpretation. There are numerous approaches suggested by researchers in the quantification of metal pollution in the soil (Chen et al., 2015; Likuku et al., 2013; Reli et al., 2017). The pollution intensities have been placed in a continuum ranging from 'low' to 'high', which helps in the ranking of pollution levels. Pollution indices such as enrichment factor (EF), contamination factor (CF), pollution load index (PLI), modified degree of contamination (mCd), and bioaccumulation factor (BF) (Chen et al., 2015; Likuku et al., 2013; Reli et al., 2017) were used to assess the degree of contamination.

3.9.1 Enrichment Factor

Enrichment factor (EF) is applied to differentiate between metal pollution originating from human activities and those from natural ancestry, and to assess the degree of anthropogenic influence (Chen et al., 2015; Likuku et al., 2013; Reli et al., 2017). Aluminum, iron and manganese are mostly used as background elements due to their abundance in the soil. The EF can be obtained by using the formula in equation (1) below,

$$EF = \frac{(C_n/C_{ref})_{sample}}{(B_n/B_{ref})_{background}} \quad (1)$$

where C_n (sample) is the concentration of the examined chemical element in the examined environment, C_{ref} (sample) is the concentration of the examined chemical

element in the reference environment, B_n is the concentration of the reference chemical element in the examined environment and B_{ref} is the concentration of the reference element in the reference environment. Enrichment factor can be grouped as deficiency to minimal enrichment ($EF < 2$), moderate enrichment ($2 \leq EF < 5$), significant enrichment ($5 \leq EF < 20$), very high enrichment ($20 \leq EF < 40$) or extremely high enrichment ($EF \geq 40$). For the determination of source of pollution, EF values between 0.05 and 1.5 indicate the metal originates from some natural source and values higher than 1.5 indicates anthropogenic sources.

3.9.2 Contamination Factor

Contamination factor (CF) is the ratio between pollutant concentration and the concentration of the initial concentration of that metal in the soil (Milićević et al., 2017). Concentration factor is calculated from the equation (equation 2)

$$CF = \frac{C_n}{B_n} \quad (2)$$

Where C_n is a pollutant's (element's) concentration and B_n is the initial concentration of that metal in the soil. Concentration factor (CF) can be seen as either ($CF \leq 1$) interpreted as low, (1-3) for moderate contamination, considerably contaminated (3-6), or very high contamination ($CF \geq 6$) (Chen et al., 2015; Hakanson, 1980; Wu et al., 2015)

3.9.3 Pollution Load Index

The pollution load index (PLI) gives an assessment of the overall pollution status for a sample (Chen et al., 2015; Milićević et al., 2017). The PLI can be calculated from the CF of each samples according to the relation (equation 3)

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_N)^{1/N} \quad (3)$$

Where N is the number of metals studied and CF is the contamination factor. The PLI has seven levels from none to high pollution. It is classified as either background concentration ($PLI = 0$), unpolluted ($0 < PLI \leq 1$), unpolluted to moderately polluted ($1 < PLI \leq 2$), moderately polluted ($2 < PLI \leq 3$), moderately to highly polluted ($3 < PLI \leq 4$), highly polluted ($4 \leq PLI \leq 5$), or very highly polluted ($PLI > 5$).

3.11.4 Modified Degree of Contaminations

Degree of contamination (Cd) and modified degree of contamination (mCd) describe the toxicity of a metal. This can be arrived at by calculating the contamination factor (CF) for each pollutant (Reli et al., 2017; Swarnalatha et al., 2015). The relation in equation 4 is therefore used to calculate the degree of contamination

$$Cd = \sum_{i=1}^n CF \quad (4)$$

Where: ' n ' stand for number of elements and ' i ' is i^{th} element, CF is contamination factor.

Modified degree of contamination (mCd) is the ratio of the sum of all the contamination factors to the number of contaminants determined. It is calculated from the relation in equation 5

$$mCd = \frac{Cd}{n} \quad (5)$$

Where: Cd is the degree of contamination

n is the number of metals analysed.

The mCd is classified as shown in Table 3.1 (Swarnalatha et al., 2015)

Table 3.1: Modified degree of contamination and its description

mCd values	Contamination description
mCd < 1.5	Nil to very low
1.5 ≤ mCd < 2	Low
2 ≤ mCd < 4	Moderate
4 ≤ mCd < 8	High
8 ≤ mCd < 16	Very
16 ≤ mCd < 32	Extremely high
mCd ≥ 32	Ultra-high

3.11.5 Bioaccumulation Factor

The bioaccumulation factor (BF) indicates the ratio of the concentration of metal between the plant part and the soil (Milićević et al., 2017; Zhuang et al., 2009). This factor was calculated from the relation in equation (6)

$$BF = \frac{C_p}{C_s} \quad (6)$$

Where C_p is the major or trace element concentration in different plant parts and C_s is the concentration of the same element in the soil from where the plant part was taken. $BF > 1$ indicates that the plants could be accumulators; $BF = 1$ indicates no influences of the soil and $BF < 1$ means that the plant can be an excluder.

3.11.6 Risk Assessment

Metal contaminants in agricultural soils or lands causing heavy metal uptake by food crops pose serious risk to human health. Consumption of these food crops produced in contaminated soils as well as ingestion or inhalation of contaminated particles are among the three major pathways which principally contribute to human exposure to metals (Zhuang et al., 2009). The metal contaminant can either be carcinogenic and or non-carcinogenic. This has resulted in food security threat in terms of food quality among the general populace. It is therefore necessary to characterise the risk assessment of these food crops. The characterization is based on a model of USEPA

(US EPA, 1989). This model gives human health risk as a numeric quantity that is easily understood.

The determination of non-carcinogenic hazard involved the estimation of the value of target hazard quotient (THQ.) The THQ was estimated by taking the ratio of the estimated daily intake (EDI) to the oral reference dose (RfD). The resultant was used to evaluate potential health risks associated with long-term exposure to chemical pollutants in foodstuffs (Pan et al., 2015; Zhu ang et al., 2008). The relation in equation (7) was therefore used.

$$THQ = \frac{EFr \times ED \times FI \times MC \times 10^{-3}}{RfDo \times BW \times AT} \quad (7)$$

The THQ was further adjusted taking into account the relative bioavailability by using the equation;

$$THQ = \frac{EFr \times ED \times FI \times MC \times RBA \times 10^{-6}}{RfDo \times BW \times AT} \quad (8)$$

Where THQ = target hazard quotient, EFr = exposure frequency, ED = exposure duration, FI = food ingestion (g person⁻¹ d⁻¹), MC = metal concentration in food (mg kg⁻¹, on fresh weight basis), RfDo = the oral reference dose (mg kg⁻¹ d⁻¹), BW= the average body weight, AT = averaging time for non-carcinogens (Chang et al., 2014), RBA = relative bioavailability. The averaging time for non – carcinogens (AT) were 8760 and 2190 for adults and children respectively, exposure frequency (EFr) was 350 days, and exposure duration (ED) been 24 years and 6 years for adults and children respectively (Bortey-Sam et al., 2015, Darko and Dodd, 2017), the ingestion rates for the root tubers were, cassava: 421.9 and 281.27, cocoyam:104.1 and 69.4 and yam: 137 and 91.33 for adults and children respectively (Ministry of Food and Agriculture, 2011), however, the ingestion rate for children was assumed. The

ingestion rate for soil was 50 and 20 for children and adults respectively (Darko and Dodd, 2017). The average weight was 15 and 24 for children and adults respectively (Darko and Dodd 2017), RfDo As – $3\text{E}-04$, Cr – $1.5\text{ E}-00$, Cu – $4\text{E}-02$, Fe – $7\text{E}-01$, Mn – $1.4\text{ E}-01$, Ni – $2\text{ E}-02$ and Zn – $3\text{ E}-01$ (Hu et al., 2013; Hu et al., 2011). If $\text{THQ} > 1$, indicate a potential risk associated with this pollutant whereas $\text{THQ} < 1$, indicate no obvious potential risk associated with the pollutants.



CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Soil pH and Conductivity

The pH of soil samples ranged from 5.30 to 9.17 in deionized water. Most of the soil pH ranged from 7.02 – 9.17 which is roughly neutral to alkaline, which can be linked to the presence of carbonates in the soil (Imperato et al., 2003). A few of the soil samples had pH “between” 5.30 – 6.98 which is considered as being slightly acidic according to the United States Department of Agriculture (Candeias et al., 2014). The sites that showed the acidic nature include: ACS2, ACS3, ACS7, ACYS3, ACYS7, APS3, AYS1, AYS3, AYS5, AYS7, KCS1, KN2, KN4, KS1, KSS2, OCS1, OCS2, OCS4, OCS6, OCS7, OCS8, OCYS1 and OYS1 (See Appendix 3 on pages 77 & 78). The acidic soil can be attributed to acidic deposition of strong acids or acid-forming substances from the atmosphere onto the earth surface (Driscoll et al., 2001). pH plays a major role in the mobility and persistence of metals in the soil. This feature enhances the ability of heavy metals ending up in the food chain (Sadick et al., 2015). Similarly, pH influences organic matter decomposition on agricultural soils (Candeias et al., 2014). The electrical conductivity (EC) had a minimum value of 37.8 $\mu\text{S}/\text{cm}$ and a maximum value of 4020 $\mu\text{S}/\text{cm}$. The mean value stood at 296.52 $\mu\text{S}/\text{cm}$.

4.2 Heavy Metal Concentration in the Soil analysed using XRF

Table 4.1 shows the mean, minimum, maximum and standard deviations of the total metals determined in the root tubers, cassava peels and soil samples from the study area. The average concentration of metals analysed in the various samples were in the order;

As < Cu < Ni < Cr < Zn < Mn < Fe for cassava and cocoyam, As < Cu < Zn < Ni < Cr < Mn < Fe, As < Zn < Cu < Ni < Cr < Mn < Fe and As < Cu < Ni < Cr < Mn and Cu < As < Ni < Cr < Zn < Mn < Fe for yam, sweet potato, cassava peels and soil respectively.

Table 4.1: Statistical analysis of data from metal concentrations determined with XRF

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
AKOMADAN							
N=10							
CASSAVA							
MINIMUM	1.17	11.05	5.54	36.81	15.46	9.06	2.98
MAXIMUM	1.25	12.86	5.99	442.60	17.07	9.49	21.07
AVERAGE	1.22	12.11	5.84	180.52	15.97	9.31	8.88
STD	0.03	0.51	0.16	135.52	0.49	0.15	6.18
CASSAVA PEEL							
N=9							
MINIMUM	1.17	10.65	5.53	269.84	17.02	9.15	12.56
MAXIMUM	1.43	12.76	6.29	2926.25	20.97	10.17	75.88
AVERAGE	1.29	11.90	5.93	1210.96	18.86	9.58	31.73
STD	0.08	0.71	0.26	884.85	1.49	0.30	19.01
SOIL UNDER CASSAVA							
N=9							
MINIMUM	2.56	8.24	9.28	4070.45	148.48	16.53	6.47
MAXIMUM	6.10	68.03	24.93	39556.35	788.09	36.83	79.20
AVERAGE	3.58	34.04	15.82	19368.84	438.67	21.94	22.50
STD	1.29	25.25	5.72	11940.57	193.65	7.04	22.48
COCOYAM							
N=10							
MINIMUM	1.16	11.17	5.58	14.32	15.29	8.97	3.22
MAXIMUM	1.23	12.92	8.48	117.88	16.53	9.31	25.79
AVERAGE	1.20	12.13	6.06	34.23	15.94	9.20	9.47
STD	0.02	0.50	0.86	36.51	0.44	0.11	7.36
SOIL UNDER COCOYAM							
N=10							
Minimum	2.34	7.43	8.86	2794.53	61.07	15.87	6.04
Maximum	11.22	103.43	29.50	86996.66	742.15	32.31	282.24
Average	4.09	33.59	13.88	21544.19	414.33	19.51	42.30
STD	2.75	32.05	7.07	25999.86	201.60	5.29	84.65

Con't Table 4.1: Statistical analysis of metal concentrations from XRF

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
YAM							
N=7							
Minimum	1.17	12.39	5.35	13.87	15.57	8.87	3.19
Maximum	1.24	13.54	5.92	98.92	16.68	9.28	5.26
Average	1.19	12.98	5.59	26.67	15.96	9.00	3.81
Std	0.02	0.45	0.18	31.86	0.39	0.15	0.96
SOIL UNDER YAM							
N=7							
Minimum	2.45	8.11	8.99	3335.33	166.85	16.31	7.16
Maximum	4.86	51.68	13.96	24665.35	560.04	41.16	19.75
Average	3.52	29.52	10.13	16454.39	394.91	21.70	13.17
STD	0.84	15.90	1.76	7049.55	122.69	8.87	3.95
POTATO							
N=4							
Minimum	1.17	10.84	5.61	15.26	16.00	9.04	3.15
Maximum	1.22	11.98	5.99	135.15	16.91	9.33	3.24
Average	1.19	11.62	5.76	65.20	16.46	9.23	3.21
STD	0.02	0.53	0.16	50.30	0.37	0.13	0.04
SOIL UNDER POTATO							
N=4							
MINIMUM	2.33	7.97	9.18	4004.70	33.53	15.40	5.19
MAXIMUM	6.17	44.49	20.68	28699.03	392.53	21.03	126.91
AVERAGE	3.79	26.27	13.97	14291.12	244.48	17.62	42.75
STD	1.82	20.96	5.73	12197.55	151.00	2.43	56.73
OFFINSO							
CASSAVA							
N=10							
MINIMUM	1.17	11.73	5.54	14.50	15.35	8.93	3.18
MAXIMUM	1.23	12.97	5.98	82.46	16.10	9.36	17.22
AVERAGE	1.21	12.22	5.74	31.41	15.68	9.21	9.47
STD	0.02	0.44	0.16	28.70	0.23	0.16	6.10
CASSAVA PEEL							
N=6							
MINIMUM	1.24	10.03	5.64	339.61	17.19	9.46	16.58
MAXIMUM	1.37	12.50	5.96	2051.88	20.43	9.82	50.38
AVERAGE	1.31	11.54	5.78	1417.01	18.79	9.65	28.94
STD	0.05	0.89	0.12	636.10	1.23	0.15	11.35

Con't Table 4.1: Statistical analysis of metal concentrations from XRF

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
SOIL UNDER							
N=7							
MINIMUM	2.76	8.89	8.83	6747.47	179.92	15.96	23.87
MAXIMUM	6.64	68.13	34.35	34513.52	1055.48	23.79	45.12
AVERAGE	4.55	37.25	16.51	20451.87	438.25	17.86	33.02
STD	1.36	18.45	9.60	8874.84	314.02	2.70	7.06
COCOYAM							
N=7							
OCY7	1.22	10.34	5.37	15.66	16.11	9.21	8.65
MINIMUM	1.18	7.43	5.37	14.60	15.80	9.07	5.91
MAXIMUM	1.25	12.33	6.06	48.98	16.65	9.85	22.83
AVERAGE	1.21	11.00	5.78	24.20	16.26	9.29	14.37
STD	0.03	1.75	0.22	14.70	0.29	0.26	6.90
SOIL UNDER							
N=7							
MINIMUM	2.60	9.70	8.63	8397.84	136.48	15.64	24.55
MAXIMUM	11.76	97.35	23.55	48518.42	697.26	43.20	99.01
AVERAGE	5.28	51.54	14.92	25295.15	349.67	21.83	42.90
STD	3.25	37.63	6.32	15417.04	225.37	9.79	25.52
YAM							
N=4							
MINIMUM	1.18	8.70	5.72	36.05	15.44	9.11	3.07
MAXIMUM	1.24	12.26	6.38	156.67	16.54	9.98	19.30
AVERAGE	1.21	11.19	5.96	90.36	16.01	9.37	13.23
STD	0.03	1.68	0.29	53.22	0.45	0.41	7.22
SOIL UNDER							
N=4							
MINIMUM	4.18	19.01	9.14	9722.72	109.59	16.23	44.37
MAXIMUM	9.05	47.70	34.43	26968.54	844.20	35.20	117.59
AVERAGE	5.82	33.87	17.99	18533.17	368.67	23.41	76.02
STD	2.21	12.72	11.25	8024.48	345.38	8.98	35.15
AMANSIE CENTRAL							
CASSAVA							
N=8							
MINIMUM	1.19	8.24	5.62	14.91	15.55	9.10	3.35
MAXIMUM	1.32	12.91	6.51	487.67	17.17	10.38	66.02
AVERAGE	1.24	10.74	6.06	107.37	16.19	9.65	18.96
STD	0.05	1.76	0.36	162.53	0.66	0.52	20.13

Con't Table 4.1: Statistical analysis of metal concentrations from XRF

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
CASSAVA PEEL							
N=7							
MINIMUM	1.22	9.49	5.59	409.26	17.55	9.11	27.71
MAXIMUM	1.45	13.14	6.59	3244.40	19.92	10.19	147.88
AVERAGE	1.34	11.61	5.86	1210.71	18.32	9.59	52.05
STD	0.07	1.22	0.33	1042.66	1.02	0.34	43.11
SOIL CASSAVA							
N=8							
MINIMUM	7.64	9.42	8.53	8675.75	83.71	15.58	11.28
MAXIMUM	87.07	91.04	23.33	41499.13	519.87	25.58	389.69
AVERAGE	27.25	45.34	14.22	22384.43	260.47	18.25	76.29
STD	25.03	28.35	5.74	10520.40	123.59	2.94	123.23
COCOYAM							
N=5							
MINIMUM	1.18	11.29	5.87	15.97	15.65	9.06	11.56
MAXIMUM	1.36	12.18	10.71	877.00	17.14	9.76	37.80
AVERAGE	1.25	11.71	7.01	284.42	16.17	9.33	21.68
STD	0.07	0.45	2.08	381.83	0.57	0.27	10.31
SOIL UNDER COCOYAM							
N=5							
MINIMUM	7.20	11.65	8.84	9064.02	94.41	16.12	11.12
MAXIMUM	183.17	372.69	32.71	37212.27	551.67	26.26	85.91
AVERAGE	46.46	139.66	14.99	23443.26	278.04	19.29	57.37
STD	67.29	160.80	9.17	12255.83	161.01	3.86	32.74
KONONGO SOIL							
N=7							
MINIMUM	1.18	9.70	5.67	60.59	15.95	9.01	11.82
MAXIMUM	325.88	124.94	30.82	30995.27	380.04	41.99	155.17
AVERAGE	80.76	41.75	13.35	11522.16	191.19	18.99	69.90
STD	131.17	47.78	10.11	10916.43	153.96	11.48	56.57

4.2.1 Arsenic

The range of values of arsenic content in tubers from Akomadan were in the ranges cassava 1.17-1.25 mg/kg with a mean of 1.22 mg/kg, cassava peels 1.17-1.43 mg/kg with 1.29 mg/kg mean, soil underneath cassava 2.56-6.1 mg/kg and 3.58 mg/kg mean respectively. Cocoyam had arsenic content range of 1.16-1.23 mg/kg with 1.19 mg/kg mean and soil underneath the cocoyam been 2.34-11.22 mg/kg and a mean of 4.09 mg/kg. That of yam ranged from 1.17-1.24 mg/kg, mean of 1.19 mg/kg and soil underneath been 2.45-4.86 mg/kg and a mean of 3.52 mg/kg. Sweet potato had the ranges from 1.17-1.22 mg/kg, mean of 1.19 mg/kg and soil underneath been 2.33-6.17 mg/kg and 3.79 mg/kg mean.

Tubers from Offinso had the following arsenic contents; cassava 1.17-1.23 mg/kg with a mean of 1.21 mg/kg, cassava peels 1.24-1.37 mg/kg, mean of 1.31 mg/kg whilst soil underneath cassava was 2.76-6.64 mg/kg with 4.55 mg/kg. The range of cocoyam was 1.18-1.25 mg/kg, 1.21 mg/kg as the mean whilst the soil underneath saw a range of 2.6-11.76 mg/kg and mean of 5.28 mg/kg. Yam samples had the ranges of 1.18-1.24 mg/kg, 1.21 mg/kg mean whilst the soil underneath had the range of 4.18 – 9.05 mg/kg and mean 5.82 mg/kg.

Amansie Central tubers had the arsenic content ranging from; cassava 1.19-1.32 mg/kg with mean 1.24 mg/kg, cassava peels 1.22-1.45 mg/kg with mean 1.34 mg/kg whilst the soil underneath the cassava had 7.16-87.07 mg/kg and mean of 27.25 mg/kg. Cocoyam 1.18-1.36 mg/kg with mean of 1.25 mg/kg whilst the soil underneath the cocoyam was 7.2-183.17 mg/kg and 46.46 mg/kg. Soil samples from Konongo had arsenic content that ranged from 1.18-325.88 mg/kg with mean 80.76 mg/kg.

The findings of this work was lower than what was recorded by Yaney et al. (2007) from Tarkwa with respect to arsenic concentration in cocoyam and yam in all the sampling communities. However, values obtained were higher than the WHO permissible limits. Comparing the results by Bortey-sam et al. (2015) for arsenic in cassava, their finding was lower (0.0090 mg/kg). However, Ahiamadjie et al. (2011) in a similar research with respect to cassava and cocoyam, had higher values compared to the current work.

In the case of soil samples, Akumadan and Offinso were similar to the findings of Ahiamadjie et al. (2011) with the exception of those from Amansie central and Konongo which were on the high side. Nonetheless, arsenic concentration in soil from Akomadan and Offinso were lower than the acceptable limit set by Ontario Soils Quality Guidelines (Ministry of the Environment, 2011) (11 mg/kg) but the soil from Amansie central and Konongo were higher. Similarly, results from Akomadan, Offinso and Amansie central were lower than the reference set by (US EPA, 2005) (75 mg/kg). However, samples from Konongo recorded higher values.

One of the likely sources of arsenic in food is as a result of arsenic compounds usage in herbicides and fungicides (Antoine et al., 2012). Arsenic content in foods are mainly non-toxic arsenobetaine and arsenocholine, which are removed from the body unaltered.

4.2.2 Chromium

The chromium content of tubers from Akomadan were in the range of 11.05-12.86 mg/kg, 10.65-12.76 mg/kg, and 8.24-68.03 mg/kg for cassava, cassava peels, soil

underneath cassava respectively. The corresponding mean concentrations were also 12.11 mg/kg, 11.90 mg/kg and 12.13 mg/kg respectively for cassava, cassava peels and soil underneath the cassava respectively. Cocoyam and soil underneath cocoyam had chromium concentration ranging from 11.17-12.92 mg/kg and 7.43-103.43 mg/kg respectively, with mean concentration of 12.13 mg/kg and 33.59 mg/kg respectively. That of yam and soil underneath the yam were 12.39-13.54 mg/kg and 8.11-51.68 mg/kg respectively with mean concentration of 12.98 mg/kg and 11.62 mg/kg respectively. Sweet potato ranged from 10.84-11.98 mg/kg and soil underneath the sweet potato been 7.97-44.49 mg/kg. The mean concentrations were 11.62 mg/kg and 26.27 mg/kg respectively.

Root tubers from Offinso had chromium content ranging from; cassava, cassava peels, soil underneath cassava, cocoyam, soil underneath cocoyam, yam and soil underneath yam been 11.73-12.97 mg/kg, 10.03-12.50 mg/kg, 8.89-68.13 mg/kg, 7.43-12.33 mg/kg, 9.7-97.35 mg/kg, 8.7-12.26 mg/kg and 19.01-47.70 mg/kg respectively. The mean concentrations were found to be 12.22 mg/kg, 11.54 mg/kg, 37.25 mg/kg, 10.99 mg/kg, 51.54 mg/kg, 11.19 mg/kg and 33.87 mg/kg respectively. Amansie central had the chromium content ranging from; 8.24-12.91 mg/kg, 9.49-13.14 mg/kg, 9.42-91.04 mg/kg, 11.29-12.18 mg/kg, 11.65-372.69 mg/kg for cassava, cassava peel, soil underneath cassava, cocoyam and soil underneath cocoyam respectively. The mean concentrations were found to be 10.74 mg/kg, 11.61 mg/kg, 45.34 mg/kg, 11.71 mg/kg and 139.66 mg/kg respectively. Soil samples from Konongo had the range of 9.70-124.94 mg/kg and a mean value of 41.75 mg/kg.

Other studies undertaken to ascertain the level of toxic metals in food stuff recorded chromium concentration in cassava and cocoyam been lower than the current study (Bortey-sam et al., 2015; Ahiamadjie et al., 2011). However, the findings of the current study exceeded the allowable limit for chromium in plant (codex alimentarius commission, 2001).

With regard to the concentration of chromium in soil, the results of the current study is comparable to the findings of Ahiamadjie et al. (2011) except that of Ankam and Agroyesum which recorded higher values. Nonetheless, the result were within the limits set by some international organisations (codex alimentarius commission, 2001; US EPA, 2005). Similar study in other parts of the world recorded results which the current study fall within (Abollino et al., 2002; Huang et al., 2007).

Chromium is an essential nutrient required in human diet. Inadequate intake of chromium are associated with some symptoms of particular diseases (Anderson, 1997). It is known to play a role in sugar and fat metabolism in humans. Chromium supplement improves blood glucose, insulin, and lipid variables. However, excessive intake can be toxic. Other research conclude that it mainly originates from parent rock (Micó et al., 2006).

4.2.3 Copper

Concentration of Cu in the root tubers from Akomadan ranged from 5.54-5.99 mg/kg, 5.53-6.29 mg/kg, 9.28-24.93 mg/kg, 5.58-8.48 mg/kg, 8.86-29.5 mg/kg, 5.35-5.92 mg/kg, 8.99-13.96 mg/kg, 5.61-5.99 mg/kg, 9.18-20.68 mg/kg for cassava, cassava peel, soil underneath cassava, cocoyam, soil underneath cocoyam, yam, soil

underneath yam, sweet potato and soil underneath sweet potato respectively. The corresponding mean concentrations were found to be 5.84 mg/kg, 5.93 mg/kg, 15.82 mg/kg, 6.06 mg/kg, 13.88 mg/kg, 5.59 mg/kg, 10.13 mg/kg, 5.76 mg/kg and 13.97 mg/kg respectively. Those from Offinso ranged from 5.54-5.98 mg/kg, 5.64-5.96 mg/kg, 8.83 – 34.35 mg/kg, 5.37-6.06 mg/kg, 8.63-23.55 mg/kg, 5.72-6.38 mg/kg and 9.14-34.43 mg/kg for cassava, cassava peel, soil underneath cassava, cocoyam, soil underneath cocoyam, yam, and soil underneath yam respectively. The corresponding mean concentrations were found to be 5.74 mg/kg, 5.78 mg/kg, 16.51 mg/kg, 5.78 mg/kg, 14.92 mg/kg, 5.96 mg/kg and 17.99 mg/kg respectively. The copper concentration from Amansie Central ranged from 5.62 – 6.51 mg/kg for cassava, 5.59-6.59 mg/kg for cassava peel and 8.53-23.33 mg/kg for soil underneath cassava, 5.87-10.71 mg/kg, 8.84-32.71 mg/kg. The corresponding mean concentration was found to be 6.06 mg/kg, 5.86 mg/kg, 14.22 mg/kg, 7.01 mg/kg and 14.99 mg/kg respectively. Soil samples from Konongo recorded a range of 5.67 -30.82 mg/kg with a mean of 13.35 mg/kg.

Comparing the current study to previous studies done within the same territory, the findings by Bortey-sam et al. (2015) with regard to concentration of copper in cassava was lower than the current study, likewise Boadi et al.(2009). However, Ahiamadjie et al. (2011) recorded a higher copper concentration in cassava. Similarly, the concentration of copper found in cassava, cocoyam, sweet potato and yam in a study done in Kumasi were lower than the current study (Acheampong et al., 2014). The findings from this current study was below the international standards set for different heavy metals in plants (codex alimentarius commission, 2001; US EPA, 2005).

With the concentration of copper in the soil samples, previous studies recorded varying concentrations. Some of them recorded higher copper concentration (Ahiamadjie et al., 2011 ; Boadi et al., 2009) whilst Zango et al. (2013) and Bortey-sam et al. (2015) recorded concentrations lower than the current study. In Netherlands the acceptable limit of copper is 36 mg/kg which the current study was below (Pietrzak and Mcphail, 2004). However, the findings of the current study were below acceptable threshold of copper in agricultural soils (Ministry of the Environment, 2011; codex alimentarius commission, 2001)

Copper is an essential element that has several functions in humans. It plays critical role in oxidative metabolism and a cofactor in enzymes among other functions (Scheiber et al., 2014). Copper in the soil can come from parental rock, fungicidal, bactericidal sprays, fertilisers and stimulants of animal growth (Pietrzak and Mcphail, 2004).

4.2.4 Iron

The range of values of iron content in tubers from Akomadan were in the ranges of; cassava 36.81-442.6 mg/kg with a mean of 180.52 mg/kg, cassava peels 269.84-2926.25 mg /kg with 1210.96 mg/kg mean, soil underneath cassava 4070.45-39556.35 mg/kg and 19368.84 mg/kg mean. Cocoyam had iron content range of 14.32-117.88 mg/kg with 34.23 mg/kg mean and soil underneath the cocoyam been 2794.53-86996.66 mg/kg and a mean of 21544.19 mg/kg. That of yam ranged from 13.87-98.92 mg/kg, mean of 26.67 mg/kg and soil underneath been 3335.33-24665.35 mg/kg and a mean of 16454.39 mg/kg. Sweet potato had the ranges from 15.26-

135.15 mg/kg, mean of 65.15 mg/kg and soil underneath been 4004.7-28699.03 mg/kg and 14291.12 mg/kg mean.

Tubers from Offinso had the following iron contents; cassava 14.50-82.46 mg/kg with a mean of 31.41 mg/kg, cassava peels 339.61-2051.88 mg/kg, mean of 1417.01 mg/kg whilst soil underneath cassava was 6747.47-34513.52 mg/kg with 20451.87 mg/kg. The range of cocoyam was 14.60-48.98 mg/kg, with 14.19 mg/kg mean whilst the soil underneath saw a range of 8397.84-48518.42 mg/kg and mean of 25295.15 mg/kg. Yam samples had the ranges of 36.05-156.67 mg/kg, 90.36 mg/kg mean whilst the soil underneath had the range of 9722.72-26968.54 mg/kg and mean 18533.17 mg/kg.

Amansie Central tubers had the iron content ranging from; cassava 14.91-487.67 mg/kg with mean 107.37 mg/kg, cassava peels 409.26-3244.40 mg/kg with mean 1210.71 mg/kg whilst the soil underneath the cassava had 8675.75-41499.13 mg/kg and mean of 22384.43 mg/kg. Cocoyam samples had the ranges of 15.98-877.00 mg/kg and mean of 284.42 mg/kg whilst the soil underneath the cocoyam was 9064.02-37212.27 mg/kg and 23443.26 mg/kg. Soil samples from Konongo had iron content that ranged from 60.59-30995.27 mg/kg with mean 11522.16 mg/kg.

Cassava from Akomadan recorded the highest iron concentration followed by Amansie central and Offinso the least. For cocoyam, Amansie central recorded the highest concentration, followed by Akomadan, and Offinso the least. For yam, Offinso recorded the highest concentration.

Acheampong et al. (2014) reported varying values, thus, their value for cassava was lower than the current study in all the towns. For cocoyam, their findings were lower than the current study in Akomadan and Amansie central except Offinso. For yam, the current study recorded a higher value in Offinso. Akomadan was lower when compared to their findings. The value however, for the current study for sweet potato was higher. Cassava from Akomadan and cocoyam from Amansie central recorded values which fell outside the range in many literature (140 mg/kg) (Sreekanth et al., 2010). Variations of heavy metal concentration in foodstuffs can be linked to differences in origin, cultivar and cultivation practices (Jorhem and Sundstrom, 1993).

For the soil, Micó et al. (2006) reported a value lower than all the towns in the current study except Konongo but Romic and Romic 2003 reported higher values than the current study. However, the values reported in the current study were within the typical range of iron concentration in agricultural soils (70000-42000 mg/kg) (Abollino et al., 2002).

4.2.5 Manganese

The manganese content in tubers from Akomadan ranged from 15.46-17.07 mg/kg, 17.02-20.97 mg/kg, and 148.48-788.09 mg/kg for cassava, cassava peels, and soil underneath cassava respectively. The corresponding mean concentrations were also 15.97 mg/kg, 18.86 mg/kg and 438.67 mg/kg respectively for cassava, cassava peels and soil underneath the cassava respectively. Cocoyam and soil underneath cocoyam manganese concentration ranged from 15.29-16.53 mg/kg and 61.07-742.15 mg/kg respectively, with mean concentration of 15.94 mg/kg and 414.33 mg/kg respectively. That of yam and soil underneath the yam were 15.57-16.68 mg/kg and 166.85-560.05

mg/kg respectively with mean concentration of 15.96 mg/kg and 394.91 mg/kg respectively. Sweet potato ranged from 16.00-16.91 mg/kg and soil underneath the sweet potato been 33.53-392.53 mg/kg. The mean concentrations were 16.46 mg/kg and 244.48 mg/kg respectively.

Root tubers from Offinso had manganese content ranging from; cassava, cassava peels, soil underneath cassava, cocoyam, soil underneath cocoyam, yam and soil underneath yam been 15.35 – 16.10 mg/kg, 17.19 – 20.43 mg/kg, 179.92 – 1055.48 mg/kg, 15.80 – 16.65 mg/kg, 136.48 – 697.26 mg/kg, 15.44 – 16.54 mg/kg and 109.59 – 844.20 mg/kg respectively. The mean concentrations were found to be 15.68 mg/kg, 18.79 mg/kg, 438.25 mg/kg, 16.26 mg/kg, 349.67 mg/kg, 16.01 mg/kg and 368.67 mg/kg respectively. Amansie central had the manganese content ranging from; 15.55 – 17.17 mg/kg, 17.55 – 19.92 mg/kg, 83.71 – 519.87 mg/kg, 15.65 – 17.14 mg/kg, 94.41 – 551.67 mg/kg for cassava, cassava peel, soil underneath cassava, cocoyam and soil underneath cocoyam respectively. The mean concentrations were found to be 16.18 mg/kg, 18.32 mg/kg, 260.47 mg/kg, 16.17 mg/kg and 278.04 mg/kg respectively. Konongo soil sample had the range of 15.95 – 380.04 mg/kg and a mean value of 191.19 mg/kg.

The concentration of manganese for root tubers in all the towns did not show any significant variation. The values, however, fell within the range found in other literature (15–100) (Sreekanth et al., 2010).

With regard to manganese in the soil, Offinso recorded the highest value followed by Akomadan and Amansie central respectively. The least was obtained at Konongo.

However, reports from other studies were higher than the current study (Romic and Romic, 2003; Abollino et al., 2002).

4.2.6 Nickel

The nickel concentration in the root tubers from Akomadan ranged from 9.06-9.49 mg/kg, 9.15-10.19 mg/kg, 16.53-36.83 mg/kg, 8.97-9.31 mg/kg, 15.87-32.31 mg/kg, 8.87-9.28 mg/kg, 16.31-41.16 mg/kg, 9.04-9.33 mg/kg, 15.4-21.03 mg/kg for cassava, cassava peel, soil underneath cassava, cocoyam, soil underneath cocoyam, yam, soil underneath yam, sweet potato and soil underneath sweet potato respectively. The corresponding mean concentrations were found to be 9.31 mg/kg, 9.58 mg/kg, 21.94 mg/kg, and 9.20 mg/kg, 19.51 mg/kg 8.99 mg/kg, 21.69 mg/kg, 9.22 mg/kg and 17.62 mg/kg respectively. Those from Offinso ranged from 8.93-9.36 mg/kg, 9.46-9.82 mg/kg, 15.96-23.79 mg/kg, 9.07-9.85 mg/kg 15.64-43.20 mg/kg and 9.11-9.98 mg/kg, 16.23 – 35.20 mg/kg for cassava, cassava peel, soil underneath cassava, cocoyam, soil underneath cocoyam, yam, and soil underneath yam respectively. The corresponding mean concentrations were found to be 9.21 mg/kg, 9.65 mg/kg, 17.86 mg/kg, 9.29 mg/kg, 21.83 mg/kg, 9.37 mg/kg and 23.41 mg/kg respectively. The nickel concentration from Amansie Central ranged from 9.10-10.38 mg/kg for cassava, 9.11-10.19 mg/kg for cassava peel and 15.58-25.58 mg/kg for soil underneath cassava, 9.06-9.76 mg/kg for cocoyam, 16.12-26.26 mg/kg for soil underneath cocoyam. The corresponding mean concentration was found to be 9.65 mg/kg, 9.59 mg/kg, 18.23 mg/kg, 9.33 mg/kg and 19.29 mg/kg respectively. Soil samples from Konongo recorded a range of 9.01-41.99 mg/kg with a mean of 18.99 mg/kg.

There was no significant variation in nickel concentration in the root tubers from all the towns in the current study. Report from similar studies conducted showed concentration in cassava being lower than the current study (Addo et al., 2010 ; Bortey-sam et al., 2015) but Zango et al. (2013) reported higher nickel concentration in cassava than the current study. The report from the current study exceeded the allowable limit of nickel concentration in foodstuffs (Allaway, 1968).

Nickel concentration in the soil did not show any significant variation amongst the towns. Studies conducted in other parts of the country showed varying nickel concentration from the current study. Bortey-sam et al. (2015) reported concentration lower than the current study whilst Addo et al. (2010) reported higher values than the current study. Similarly, studies from other part of the globe gave higher nickel concentration than the current study (Romic and Romic, 2003; Rodrı et al., 2006; Huang et al., 2007; Cai et al., 2012; Abollino et al., 2002). However, the results of the study did not exceed the allowable limit set for agricultural soils (Ministry of the Environment, 2011).

4.2.7 Zinc

The zinc concentration in tubers from Akomadan were found to be; cassava 2.98-21.07 mg/kg with a mean of 8.88 mg/kg, cassava peels 12.56-75.88 mg /kg with 31.73 mg/kg mean, soil underneath cassava 6.47-79.20 mg/kg and 22.50 mg/kg mean. Cocoyam had zinc content range of 3.22-25.79 mg/kg with 9.47 mg/kg mean and soil underneath the cocoyam been 6.04 -282.24 mg/kg and a mean of 42.30 mg/kg. That of yam ranged from 3.19-5.26 mg/kg, mean of 3.81 mg/kg and soil underneath been 7.16-19.75 mg/kg and a mean of 13.17 mg/kg. Sweet potato had the ranges from 3.15-

3.24 mg/kg, mean of 3.21 mg/kg and soil underneath been 5.19-126.91 mg/kg and 42.75 mg/kg mean.

Zinc concentration in tubers from Offinso were in the ranges; 3.18-17.22 mg/kg, 16.58-50.38 mg/kg, 23.87-45.12 mg/kg, 5.91-22.83 mg/kg, 24.55-99.01 mg/kg, 3.07-19.30 mg/kg and 44.37-117.59 mg/kg for cassava, cassava peels, soil underneath cassava, cocoyam, soil underneath cocoyam, yam and soil underneath yam, respectively. The mean concentrations were found to be 9.47 mg/kg, 28.94 mg/kg, 33.02 mg/kg, 14.37 mg/kg, 42.89 mg/kg, 13.23 mg/kg and 76.02 mg/kg respectively.

Zinc concentrations for tubers from Amansie Central ranged from; cassava 3.35-66.02 mg/kg with mean 20.13 mg/kg, cassava peels 27.71-147.88 mg/kg with mean 52.05 mg/kg whilst the soil underneath the cassava had 11.28-389.69 mg/kg and mean of 76.29 mg/kg. Cocoyam samples had the ranges of 11.56-37.80 mg/kg and mean of 21.68 mg/kg whilst the soil underneath the cocoyam was 11.12-85.91 mg/kg and 57.37 mg/kg. Soil samples from Konongo had zinc content that ranged from 11.82-155.17 mg/kg with mean 69.90 mg/kg.

Amansie central recorded the highest concentration of zinc in cassava followed by Offinso and Akomadan recorded the least. The same trend was observed in cocoyam. In yam, Offinso recorded a higher value than Akomadan. Bortey-sam et al. (2015) reported lower concentration with regard to zinc in cassava in a similar study but Zango et al. (2013) reported a higher zinc concentration in that same foodstuff. Similarly, a study by Acheampong et al. (2015) reported higher concentrations in cassava, yam and sweet potato whilst the value reported for cocoyam was lower than the current study. However, the results of the current study was within the limit for

zinc in foodstuffs (Sreekanth et al., 2010). Similarly, the corresponding soil from their study showed varying concentrations from the current study (Zango et al., 2013). Reports from other part of the globe indicated different values. For example, soil from Akomadan and Offinso gave lower values, whilst, Amansie central and Konongo soils had higher values when compared to other studies (Cai et al., 2012; Martin et al., 2006; Micó et al., 2006 and Sun et al., 2013). Similarly, other studies reported higher values than the current study (Abollino et al., 2002; Huang et al., 2007 Romic & Romic, 2003; Wong et al., 2002).

4.3 Total Metal Concentrations from ICP-MS

The ICP-MS was used to validate the results from the XRF for the soil samples.

4.4 Estimation Heavy Metal Contamination

A number of assessment tools were employed to assess the level of contamination of the study area. Enrichment factor was used as one of those pollution indices, which also indicates the source of contamination from either human or natural source. A number of researchers use iron to normalize heavy metal contaminants in the soil (Likuku et al., 2013; Swarnalatha et al., 2013), therefore, iron was used as normalizer in this study. Iron occurs in abundance and therefore anthropogenic effect does not alter its concentration. EF value indicates the source of contamination; values between 0.05 and 1.5 indicate the metal originates from some natural source and values higher than 1.5 indicates human activities. From the study, soils from Akomadan indicated that the contamination of heavy metal is from natural or crustal source except Ni (1.53), for Offinso, Zn gave a value of 2.32, which indicates that the contamination may be coming from human influences and the rest seem to occur naturally. In

Amansie central, the contamination of As (5.35) and Zn (2.06) may come from human activities whilst the rest seem to come from natural source. Konongo soils gave values, which suggest that all the heavy metal contamination come from human activities except Fe (1.0). The heavy metals that were enriched spanned from minimal enrichment to severely high enrichment especially Zn (88.14) from Konongo.

The contamination factor (CF) gives an indication of metal in the soil. The CF is placed on a scale of 1 to 6, which indicates the level of contamination. From the study, the level of contamination of the heavy metals ranged from low to moderate contamination from all the study areas except from Amansie central where As (7.58) and Zn(3.45) and Konongo As(14.23) and Zn(3.63) were considerably or very highly contaminated.

The pollution load index (PLI) was one of the indices used. The average PLI values from Akomadan (0.97) and Konongo (0.73) indicated that the soil is unpolluted. However, soil samples from Offinso (1.21) and Amansie central (1.51) indicated that the soils are moderately polluted.

The degree of contamination was also analysed by using modified degree of contamination. The average mCd from the study areas indicated that samples from Akomadan and Offinso indicated that the contaminated ranged from nil to very low degree of contamination ($mCd < 1.5$) whilst those from Amansie central and Konongo showed moderate degree of contamination ($2 \leq mCd < 4$).

Bioaccumulation factor (BF) was also used to assess the level of contamination of heavy metals in the foodstuff. From the current study, the bioaccumulation of all the heavy metals were lower than 1 except zinc concentration in cassava peels from

Akomadan and Amansie central which gave 2.070 and 1.251 respectively. This indicates that cassava peels had a greater degree of accumulating zinc than the food. Iron gave the least bioaccumulation factor in all the root tubers from all the study sites.

The potential health risk was assessed using target hazard quotient (THQ) for the residents from the study areas. The values recorded for all the root tubers in all the study sites were below one (1) for both children and adults. This gives an indication of no or minimal risk for both adults and children. Although, the hazard quotient for all the root tubers from all the study sites were below one (1), the values recorded for children were all slightly higher than adults which gives an indication that children are risk receptors than adults. The values recorded for As were higher in all the root tubers from all the study sites, especially, cassava. However, Cr recorded the least value in all the root tubers.

For soils from the study sites, the THQ for all the samples were lower than one (1) for both adults and children. This was based on the assumption of 100% bioaccessibility. However, with incorporation of relative bioaccessibility (RBA), the THQ values reduced further. This indicates that the use of relative bioaccessibility gives a better assessment of risk characterization. Arsenic recorded the highest value of soils from Konongo followed by Amasie Central for both receptors whereas Ni gave the least values from all the study areas.

4.5 Metal Bioaccessibility

The bioaccessibility of the metals under study were determined to ascertain the fraction that reaches the target organs. The determination was done for As, Cr, Cu, Fe,

Mn and Ni. Copper bioaccessibility in one sample exceeded 100%; which can be attributed to analytical constraints and sample heterogeneity (Darko et al., 2017). The bioaccessibility of Zn was not calculated since concentrations in most of the extracts were below detection. The mean bioaccessibility for all the elements were below 100%. This indicates that the use of bioaccessibility data in estimating the risk of ingestion of chemicals gives a better risk estimation. Values obtained for the bioaccessibility for the following metals were 15.6 ± 10.2 , 8.7 ± 8.1 , 60.7 ± 35.7 , 1.7 ± 2.2 , 62.3 ± 11.0 and 48.4 ± 52.7 for As, Cr, Cu, Fe, Mn and Ni respectively. The high bioaccessibility can therefore be due to non – stability of metals from anthropogenic sources (Darko et al., 2017).



CHAPTER FIVE

CONCLUSION

This study has indicated the presence of heavy metals (As, Cr, Cu, Fe, Ni, Mn, and Zn) in root tubers and soil. It has also enabled comparison of pollution load assessment and its associated health and environmental effects of these metals. The concentration of heavy metals in root tubers and soil sample were in the order of: As < Cu < Ni < Cr < Zn < Mn < Fe for cassava and cocoyam, As < Cu < Zn < Ni < Cr < Mn < Fe, As < Zn < Cu < Ni < Cr < Mn < Fe and As < Cu < Ni < Cr < Mn < Fe and Cu < As < Ni < Cr < Zn < Mn < Fe for yam, potato, cassava peels and soil respectively. The contamination factor indicated that all the metals analysed for soils in Konongo were enriched except iron whilst Ni, Zn and As were the metals enriched for soils from Akomadan, Offinso and Amansie Central respectively. Contamination factor of the heavy metals ranged from low to moderate contamination except for Amansie Central and Konongo where As and Zn were considerably or very highly contaminated. Pollution load index for Akomadan and Konongo indicated the sites were unpolluted but Offinso and Amansie Central PLI indicated that the sites are moderately polluted. Modified degrees of contamination (mCd) for Akomadan and Offinso indicated nil to very low contamination whilst Amansie Central and Konongo indicated moderate degree of contamination. The bioaccumulation factor of these heavy metals in foodstuffs from soil indicated that cassava peels had higher capacity to absorb zinc and iron gave the lowest capacity of absorption. With respect to target hazard quotient (THQ), all the root tubers and soils in all the study sites recorded values below one (1) for both children and adults. However, values recorded for children were slightly higher than adults. This shows that children are a higher risk

than adults. The mean bioaccessibility were below 100%, however, Zn bioaccessibility was not calculated most of the extracts were below detection.

KNUST



REFERENCES

- Abollino, O., Aceto, M., Mentasi, E., Sarzanini, E., Petrella, F., 2002. "Heavy Metals in Agricultural Soils from Piedmont, Italy. Distribution, Speciation and Chemometric Data Treatment." *Chemosphere* 49(6): 545–57.
- Acheampong, A., Appiah, J.A., Ansong, E., and Apau, J., 2015. "Levels and Health Risk Assessment of Heavy Metals in Tubers from Markets in the Kumasi Levels and Health Risk Assessment of Heavy Metals in Tubers from Markets in the Kumasi Metropolis , Ghana." (September).
- Addo, M. A., Darko, E. O., Nyarko, B. J. B., 2013. "Heavy Metal Contaminations in Soil and Cassava Harvested near a Cement Processing Facility in the Volta Region , Ghana : Implications of Health Risk for the Population Living in the Vicinity." *e-Journal of Science & Technology* 3(8): 71–83.
- Ahiamadjie, H., Tandoh, J. B., Gyampo, O., Ofosu, F. G., Dampare, S. B., Adotey, D. K., Nyarko, B. J. B., 2011. "Evaluation of Trace Elements Contents in Staple Foodstuffs from the Gold Mining Areas in Southwestern Part of Ghana Using Neutron Activation Analysis." *Journal of Radioanalytical and Nuclear Chemistry* 288(3): 653–61.
- Ali, H., Ezzat, K., Muhammad, Anwar, S., 2013. "Phytoremediation of Heavy Metals- Concepts and Applications." *Chemosphere* 91(7): 869–81. [http://dx.doi.org/ 10.1016/j.chemosphere.2013.01.075](http://dx.doi.org/10.1016/j.chemosphere.2013.01.075).
- Allaway, W. H., 1968. "Agronomic Controls Over the Environmental Cycling of Trace Elements." *Advances in Agronomy* 20(C): 235–74.
- Alloway, B. J., 1995. 'Soil Pollution and Land Contamination ', in Pollution: Causes, Effects and Control, Ed. R. M. Harrison. Cambridge." *The Royal Society of Chemistry*: 318.
- Anderson, R. A., 1997. "Chromium as an Essential Nutrient for Humans." *Regulatory Toxicology and Pharmacology* 26(26): s35--s41.
- Antoine, J. M. R., Hoo Fung, L. A., Grant, C. N., Dennis, H. T., Lalor, G. C., 2012. "Dietary Intake of Minerals and Trace Elements in Rice on the Jamaican Market." *Journal of Food Composition and Analysis* 26(1–2): 111–21. [http:// dx.doi.org/10.1016/j.jfca.2012.01.003](http://dx.doi.org/10.1016/j.jfca.2012.01.003).
- Antonio, R., Lo, M., Grau Corbi, M., 2006. "Heavy Metals Contents in Agricultural Topsoils in the Ebro Basin (Spain). Application of the Multivariate Geoestatistical Methods to Study Spatial Variations." 144.
- Bak, J., Jensen, J., Larsen, M. M., Pritzl, G., Scott - Fordsmand, J., 1997. "A Heavy Metal Monitoring-Programme in Denmark." *Science of the Total Environment* 207(2–3): 179–86.

- Baker, A. J. M., 1981. "Accumulators and Excluders – Strategies in the Response of Plants to Heavy Metals." *Journal of Plant Nutrition* 3(1–4): 643–54. <http://www.tandfonline.com/doi/abs/10.1080/01904168.199362867>.
- Boadi, B., Wemegah, D. D., Preko, K., 2013. "Geological and Structural Interpretation of the Konongo Area of the Ashanti Gold Belt of Ghana from Aero- Magnetic and Radiometric Data." *International Research Journal of Geology and Mining* 3(3)(April): 124–35.
- Bortey-Sam, N., Nakayama, S. M. M., Akoto, O., Ikenaka, Y., Fobil, J. N., Baidoo, F., Mizukawa, H., Ishizuka, M., 2015. "Accumulation of Heavy Metals and Metalloid in Foodstuffs from Agricultural Soils around Tarkwa Area in Ghana, and Associated Human Health Risks." *International Journal of Environmental Research and Public Health* 12(8): 8811–27.
- Boyd, R. S., 2010. "Heavy Metal Pollutants and Chemical Ecology: Exploring New Frontiers." *Journal of Chemical Ecology* 36(1): 46–58.
- Brown, K. H., Wuehler, S. E., Peerson, J. M., 2001. "The Importance of Zinc in Human Nutrition and Estimation of the Global Prevalence of Zinc Deficiency." *Food and Nutrition Bulletin* 22(2): 113–25.
- Candeias, C., Melo, R., Avila, P. F., Ferreira da Silva, E., Salgueiro, A. R., Teixeira, J. P., 2014. "Heavy Metal Pollution in Mine-Soil-Plant System in S. Francisco de Assis - Panasqueira Mine (Portugal)." *Applied Geochemistry* 44: 12–26. <http://dx.doi.org/10.1016/j.apgeochem.2013.07.009>.
- Cano-Sancho, G., Perelló, G., Maulvault, A.L., Marques, A., Nadal, M., Domingo, J.L., 2015. Oral bioaccessibility of arsenic, mercury and methylmercury in marine species commercialized in Catalonia (Spain) and health risks for the consumers. *Food Chem. Toxicol.* 86, 34–40. doi:10.1016/j.fct.2015.09.012
- Caussy, D., Gochfeld, M., Gurzau, E., Neagu, C., Ruedel, H., 2003. Lessons from case studies of metals: Investigating exposure, bioavailability, and risk. *Ecotoxicol. Environ. Saf.* 56, 45–51. Doi: 10.1016/S0147-6513(03)00049-6
- Chang, C Y, Yu, H. Y., Chen, J. J., Li, F. B., 2014. "Accumulation of Heavy Metals in Leaf Vegetables from Agricultural Soils and Associated Potential Health Risks in the Pearl River Delta, South China." 1547–60.
- Chen, H., Teng, Y., Lu, S., Wang, Y., Wang, J., 2015. Contamination features and health risk of soil heavy metals in China. *Sci. Total Environ.* 512–513, 143–153. doi:10.1016/j.scitotenv.2015.01.025
- Cheng, Z., Lee, L., Dayan, S., Grinshtein, M., Shaw, R., 2011. Speciation of heavy metals in garden soils: Evidences from selective and sequential chemical leaching. *J. Soils Sediments* 11, 628–638. Doi: 10.1007/s11368-011-0351-6

- Clemens, S., Palmgren, M. G., Krämer, U., 2002. "A Long Way Ahead: Understanding and Engineering Plant Metal Accumulation." *Trends in Plant Science* 7(7): 309–15.
- Corapci, F., Radan, A. E., Lozoff, B., 2000. "After Treatment for Iron Deficiency in Infancy." *Pediatrics* 105(4): E51.
- Darko, G., Dodd, M., Nkansah, A. M., Ansah, E., Aduse-Poku, Y., 2017. "Distribution and Bioaccessibility of Metals in Urban Soils." *Environ Monit Assess* (2017) 189:260 DOI 10.1007/s10661-017-5972-9
- Dodd, M., Rasmussen, P., Chénier, M., 2012. "Comparison of Two In Vitro Extraction Protocols for Assessing Metals' Bioaccessibility Using Dust and Soil Reference Materials." *Human and Ecological Risk Assessment: An International Journal* 19(4): 120919072309002.
- Dodd, M., Rasmussen, P., Chénier, M., 2013. "Comparison of Two In Vitro Extraction Protocols for Assessing Metals' Bioaccessibility Using Dust and Soil Reference Materials." *Human and Ecological Risk Assessment: An International Journal* 19(4):1014–27. <http://www.tandfonline.com/doi/abs/10.1080/10807039.2012.719381> http://www.tandfonline.com/doi/abs/10.1080/10807039.2012.719381#.Um_m-BAR5ec.
- Driscoll, C.T., Lawrence, G. B., Bulger, A. J., Butler, T. J., Cronan, C. S., Eagar, C., Lambert, K. F., Likens, G. E., Stoddard, J. L., Weathers, K. C., 2001. "Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies." *BioScience* 51(3): 180.
- Ejaz ul, I., Yang, X., Zhen-li, H., Qaisar, M., 2007. "Assessing Potential Dietary Toxicity of Heavy Metals in Selected Vegetables and Food Crops." *Journal of Zhejiang University. Science. B* 8(1): 1–13. <http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=1764924&tool=pmcentrez&rendertype=abstract>.
- EPA. 1989. "Reference Dose (RfD): Description and Use in Health Risk Assessments. Background Document 1A. Integrated Risk Information System (IRIS). United States Environmental Protection Agency." 2001. "Baseline Human Health Risk Assessment. Vasquez Boulevard and 1-70 Superfund Site Denver, Denver (Co). United States Environmental Protection Agency."
- Flora, S. J. S., Megha, M., Mehta, A., 2008. "Heavy Metal Induced Oxidative Stress & Its Possible Reversal by Chelation Therapy." *Indian Journal of Medical Research* 128(4): 501–23.
- Food, Ministry of Food and Agriculture 2011. "Facts and Figures (2010)." *Agriculture in Ghana* (2010).
- Garbisu, C., Alkorta, I., 2001. "Phytoextraction: A Cost-Effective Plant-Based Technology for the Removal of Metals from the Environment." *Bioresource Technology* 77(3): 229–36.
- Ghana Statistical Service. 2014. "Amansie Central." 1–67. [http://www.statsghana.gov.gh/docfiles/2010_District_Report/Ashanti/AMANSIE CENTRAL.pdf](http://www.statsghana.gov.gh/docfiles/2010_District_Report/Ashanti/AMANSIE%20CENTRAL.pdf).

- Giller, K. E., Witter, E., McGrath, S. P., 1998. "Toxicity of Heavy Metals to Microorganisms and Microbial Processes in Agricultural Soils: A Review." *Soil Biol. Biochem.* 30(10/11): 1389–1414.
- Glennon, M. M., Harris, P., Ottesen, R. T., Scanlon, R. P., O'Connor, P. J., 2014. "The Dublin SURGE Project: Geochemical Baseline for Heavy Metals in Topsoils and Spatial Correlation with Historical Industry in Dublin, Ireland." *Environmental Geochemistry and Health* 36(2): 235–54.
- Hague, The. 2001. "Codex Alimentarius Commission." (July): 2–7.
- Hakanson, L. 1980, "An Ecological Risk Index for Aquatic Pollution Control. A Sedimentological Approach." *Water Research* 14(8): 975–1001.
- Hall, J. L., 2002. "Cellular Mechanisms for Heavy Metal Detoxification and Tolerance." *Journal of experimental botany* 53(366): 1–11.
- Hosseini Alhashemi, A. S., Karbassi, A. R., Kiabi, B. H., Monavari, S. M., Nabavi, S. M. B., Sekhavatjou, M. S. 2011. "Bioaccumulation of Trace Elements in Trophic Levels of Wetland Plants and Waterfowl Birds." *Biological Trace Element Research* 142(3): 500–516.
- Hu, J., Wu, F., Wu, S., Cao, Z., Lin, X., Hung, M., 2013. "Bioaccessibility, Dietary Exposure and Human Risk Assessment of Heavy Metals from Market Vegetables in Hong Kong Revealed with an in Vitro Gastrointestinal Model." *Chemosphere* 91(4):455–61 <http://dx.doi.org/10.1016/j.chemosphere.2012.11.066>.
- Huang, S. S., Liao, Q. L., Hua, M., Wu, X. M., Bi, K. S., Yan, C. Y., Chen, B., Zhang, X.Y., 2007. Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China 67, 2148–2155. doi:10.1016/j.chemosphere.2006.12.043
- Ilya, R., Nanda Kumar, P. B. A., Dushenkov, S., Salt, D. E., 1994. "Bioconcentration of Heavy Metals by Plants." *Current Opinion in Biotechnology* 5(3): 285–90.
- Imperato, M., Adamo, P., Naimo, D., Arienzo, M., Stanzione, D., Violante, P., 2003 "Spatial Distribution of Heavy Metals in Urban Soils of Naples City (Italy)." *Environmental Pollution* 124(2): 247–56.
- Julien, C., Esperanza, P., Bruno, M., Alleman, L. Y., 2011. "Development of an in Vitro Method to Estimate Lung Bioaccessibility of Metals from Atmospheric Particles." *Journal of environmental monitoring: JEM* 13(3): 621–30.
- Kadirvelu, K., Thamaraiselvi, K., Namasivayam, C., 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresour. Technol.* 76, 63–65. doi:10.1016/S0960-8524(00)00072-9
- Khan, A., Khan, S., Khan, M. A., Qamar, Z., Waqas, M., 2015. The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: a review. *Environ. Sci. Pollut. Res.* 22, 13772–13799. Doi: 10.1007/s11356-015-4881-0

- Koch, I., Reimer, K. J., Bakker, M. I., Basta, N. T., Cave, M. R., Denys, S., Dodd, M., 2013. "Variability of Bioaccessibility Results Using Seventeen Different Methods on a Standard Reference Material, NIST 2710." *Journal of Environmental Science and Health Part a-Toxic*, 48(6), p. 641-655. 48(6): 641–55.
- Koch, I., Reimer, K. J., Bakker, M. I., Basta, N. T., Cave, M. R., Denys, S., Dodd, M., 2013. "Variability of Bioaccessibility Results Using Seventeen Different Methods on a Standard Reference Material, NIST 2710." *Journal of Environmental Science and Health, Part A* 48(6): 641–55.
- Laird, B. D., Weiseth, B., Packull-McCormick, S. R., Peak, D., Dodd, M., Siciliano, S.D., 2015. "Solid-Liquid Separation Method Governs the in Vitro Bioaccessibility of Metals in Contaminated Soil-like Test Materials." *Chemosphere* 134:544–49. <http://dx.doi.org/10.1016/j.chemosphere.2014.12.019>.
- Liang, L., Gilkeson, J., Swain, E., Bennett, E., Li, M., Deng, M., Pang, P., 2013. "A Pilot Survey of Mercury in Drugs, Cosmetics and Household Products Using Reliable Analytical Methods." 2013(December): 256–62.
- Ma, X., Zuo, H., Tian, M., Zhang, L., Meng, J., Zhou, X., Min, N., Chang, X., Liu, Y., 2016. "Assessment of Heavy Metals Contamination in Sediments from Three Adjacent Regions of the Yellow River Using Metal Chemical Fractions and Multivariate Analysis Techniques." *Chemosphere* 144: 264–72. <http://dx.doi.org/10.1016/j.chemosphere.2015.08.026>.
- Marija, R., Romic, D., 2003. "Heavy Metals Distribution in Agricultural Topsoils in Urban Area.": 795–805.
- Micó, C., Recatalá, L., Peris, M., Sánchez, J., 2006. "Assessing Heavy Metal Sources in Agricultural Soils of an European Mediterranean Area by Multivariate Analysis." *Chemosphere* 65(5): 863–72.
- Mielke, H. W., Gonzales, C. R., Smith, M. K., Mielke, P. W., 1999. "The Urban Environment and Children's Health: Soils as an Integrator of Lead, Zinc, and Cadmium in New Orleans, Louisiana, U.S.A." *Environmental research* 81: 117–29.
- Milicevic, T., Relic, D., Skrivanj, S., Tesic, Z., Popovic, A., 2017. "Assessment of Major and Trace Element Bioavailability in Vineyard Soil Applying Different Single Extraction Procedures and Pseudo-Total Digestion." *Chemosphere* 171: 284–93.
- Ministry of the Environment. 2011. "Soil, Ground Water and Sediment Standards for Use under Part XV. 1 of the Ontario Protection Act. Ministry of the Environment, Canada.": 32.
- Nganje, T. N., Adamu, C. I., Ukpog, E. E., 2010. "Heavy Metal Concentrations in Soils and Plants in the Vicinity of Arufu Lead-Zinc Mine, Middle Benue Trough, Nigeria." *Chinese Journal of Geochemistry* 29(2): 167–74.

- Oswer. 2007. "Guidance for Developing Ecological Soil Screening Levels (Eco-SSLs)." (April): 111.
- Padmavathiamma, P. K., Li, L. Y., 2007. "Phytoremediation Technology: Hyper-Accumulation Metals in Plants." *Water, Air, and Soil Pollution* 184(1–4): 105–26.
- Pan, W., Kang, Y., Li, N., Zeng, L., Zhang, Q., Wu, J., 2015. "Bioaccessibility of Heavy Metals in Vegetables and Its Association with the Physicochemical Characteristics."
- Peijnenburg, W. J. G. M., Jager, T., 2003. "Monitoring Approaches to Assess Bioaccessibility and Bioavailability of Metals: Matrix Issues." *Ecotoxicology and Environmental Safety* 56(1): 63–77.
- Peijnenburg, W. J. G. M., Zablotskaja, M., Vijver, M. G., 2007. "Monitoring Metals in Terrestrial Environments within a Bioavailability Framework and a Focus on Soil Extraction." *Ecotoxicology and Environmental Safety* 67(2): 163–79.
- Plumlee, G. S., S. a. Morman, and T. L. Ziegler. 2006. "The Toxicological Geochemistry of Earth Materials: An Overview of Processes and the Interdisciplinary Methods Used to Understand Them." *Reviews in Mineralogy and Geochemistry* 64: 5–57.
- Poggio, L., Vrscaj, B., Schulin, R., Hepperle, E., Ajmone Marsan, F., 2009. "Metals Pollution and Human Bioaccessibility of Topsoils in Grugliasco (Italy)." *Environmental Pollution* 157(2): 680–89.
- Province, G., Cai, L., Xu, Z., Ren, M., Guo, Q., Hu, X., Hu, G., 2012. "Ecotoxicology and Environmental Safety Source Identification of Eight Hazardous Heavy Metals in Agricultural Soils of." *Ecotoxicology and Environmental Safety* 78: 2–8.
- Pulford, I. D., Watson, C. 2003. "Phytoremediation of Heavy Metal-Contaminated Land by Trees - A Review." *Environment International* 29(4): 529–40.
- Quansah, R., Bend, J.R., Abdul-Rahaman, A., Armah, F. A., Luginaah, I., Essumang, D.K., Iddi, S., Chevrier, J., Cobbina, S.J., Nketiah-Amponsah, E., Adu-Kumi, S., Darko, G., Afful, S., 2016. "Associations between Pesticide Use and Respiratory Symptoms: A Cross-Sectional Study in Southern Ghana." *Environmental Research* 150: 245–54.
- Reeder, R. J., Schoonen, M. A. A., Lanzirotti, A., 2006. "Metal Speciation and Its Role in Bioaccessibility and Bioavailability." *Reviews in Mineralogy and Geochemistry* 64(1): 59–113.
- Robert, G. G., 2000. "Human and Ecological Risk Assessment: An International Journal Natural Sources of Metals to the Environment Natural Sources of Metals to the Environment." *Human and Ecological Risk Assessment* 6(6): 945–63. <http://www.tandfonline.com/loi/bher20%5Cnhttp://dx.doi.org/10.1080/10807030091124383%5Cnhttp://%5Cnwww.tandfonline.com/page/terms-and-conditions>.

- Ruby, M. V, Schoof, R., Brattin, W., Goldade, M., Post, G., Harnois, M., MOsby, E., Casteel, S.W., Berti, W., Carpenter, M., Edwards, D., Cragin, D., Chappell, W., 1996. "Estimation of Lead and Arsenic Bioavailability Using a Physiologically Based Extraction Test." *Environmental Science and Technology* 30(2): 422–30.
- Ruby, M. V. Davis, A., Schoof, R., Eberle, S., Sellstone, C. M., 1999. "Advances in Evaluating the Oral Bioavailability of Inorganics in Soil for Use in Human Health Risk Assessment." *Environmental Science and Technology* 33(21): 3697–3705.
- Sajwan, K. S., Paramasivam, S., Richardson, J. P., Alva, A. K., 2002. "Phosphorus Alleviation of Cadmium Phytotoxicity." *Journal of Plant Nutrition* 25(9): 2027–34.
- Scheiber, I. F., Mercer, J. F. B., Dringen, R., 2014. "Ac Ce P Te D Us Cr T." *Progress in Neurobiology*.
- Schumacher, B. A., 2014. "Methods for the Determination of Total Organic Carbon (TOC) In Soils and Sediments." (September).
- Sello, L. A., Mmolawa, K. B., Gaboutloeloe, G. K., 2013. "Assessment of Heavy Metal Enrichment and Degree of Contamination Around the Copper-Nickel Mine in the Selebi Phikwe Region , Eastern Botswana." 1(2): 32–40.
- Sharma, R. K., Agrawal, M., 2005. "Biological Effects of Heavy Metals: An Overview." 26(2): 313.
- Sharma, S. S., K. J., Dietz, K. J., 2009. "The Relationship between Metal Toxicity and Cellular Redox Imbalance." *Trends in Plant Science* 14(1): 43–50.
- Singh, R. P., Agrawal, M., 2010. "Variations in Heavy Metal Accumulation, Growth and Yield of Rice Plants Grown at Different Sewage Sludge Amendment Rates." *Ecotoxicology and Environmental Safety* 73(4): 632–41. [http://dx.doi.org/ 10 .1016/j.ecoenv.2010.01.020](http://dx.doi.org/10.1016/j.ecoenv.2010.01.020).
- Sreekanth, P. C., Nagajyoti, K. D., Lee, T. V. M., 2010. "Heavy Metals , Occurrence and Toxicity for Plants : A Review." : 199–216.
- Steinkellner, H., Mun-Sik, K., Helma, C., Ecker, S., Ma, T. H., Horak, O., Kundi, M., Knasmüller, S., 1998. "Genotoxic Effects of Heavy Metals: Comparative Investigation with Plant Bioassays." *Environmental and molecular mutagenesis* 31(2): 183–91. <http://www.ncbi.nlm.nih.gov/pubmed/9544197>.
- Sun, C., Liu, J., Wang, Y., Sun, L., Yu, H., 2013. "Multivariate and Geostatistical Analyses of the Spatial Distribution and Sources of Heavy Metals in Agricultural Soil in Dehui, Northeast China." *Chemosphere* 92(5): 517–23. <http://dx.doi.org/10.1016/j.chemosphere.2013.02.063>.
- Swarnalatha, K., J. Letha, and S. Ayoob. 2013. "An Investigation into the Heavy Metal Burden of Akkulam-Veli Lake in South India." *Environmental Earth Sciences* 68(3): 795–806.

- Swarnalatha, K., Letha, J., Ayoob, S., Ajith, G. N., 2015. "Risk Assessment of Heavy Metal Contamination in Sediments of a Tropical Lake." *Environmental monitoring and assessment* 187(6): 322.
- Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., Sutton, D. J., 2012. 101 *Molecular, Clinical and Environmental Toxicology*. <http://link.springer.com/10.1007/978-3-7643-8340-4> *Heavy Metal Toxicity and the Environment*.
- Ursula, P., Mcphail, D. C., 2004. "Copper Accumulation , Distribution and Fractionation in Vineyard Soils of Victoria , Australia." 122: 151–66.
- US EPA., 2007. "Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry - Method 7473 - Total Mercury." *SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (February): 1–17, 2009. "Exposure Factors Handbook."
- USEPA., 2007a. "EPA SW846 Method 6020A, Inductively Coupled Plasma - Mass Spectrometry." *United States Environmental Protection Agency* 2007b. "Method 6200 - Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment." : 32.
- Wenzel, W. W., Jockwer, F., 1999. "Accumulation of Heavy Metals in Plants Grown on Mineralised Soils of the Austrian Alps." *Environmental Pollution* 104(1): 145–55.
- Wonga, S. C., Lia, X. D., Zhangb, G., Qib, S. H., Minb, Y. S., 2002. "Heavy Metals in Agricultural Soils of the Pearl River Delta, South China." *Environmental pollution (Barking, Essex : 1987)* 119(1): 33–44.
- Worms, I., Simon, D. F., Hassler, C. S., Wilkinson, K. J., 2006. "Bioavailability of Trace Metals to Aquatic Microorganisms: Importance of Chemical, Biological and Physical Processes on Biouptake." *Biochimie* 88(11): 1721–31. <http://linkinghub.elsevier.com/retrieve/pii/S0300908406002045>.
- Wu, Q., Leung, Y. S. J, Geng, X, Chen, S. Huang, X, Li., H., Huang, Z., Zhu, L., Chen, J., and Lu, Y. 2015. "Heavy Metal Contamination of Soil and Water in the Vicinity of an Abandoned E-Waste Recycling Site: Implications for Dissemination of Heavy Metals." *Science of the Total Environment* 506–507: 217–25. <http://dx.doi.org/10.1016/j.scitotenv.2014.10.121>.
- Yalcin, M. G., Tumuklu, A., Sonmez, M., Erdag, D. S., 2010. "Application of Multivariate Statistical Approach to Identify Heavy Metal Sources in Bottom Soil of the Seyhan River (Adana), Turkey." *Environmental Monitoring and Assessment* 164(1–4): 311–22.
- Yaney, J. Y., Essumang, D. K., Dodoo, D. K., Obiri, S., 2007. "Arsenic , Cadmium , and Mercury in Cocoyam (Xanthosoma Sagittolium) and Watercocoyam (Colocasia Esculenta) in Tarkwa a Mining Community." : 377–79.
- Yao-guo, W. U., You-ning, X. U., Jiang-hua, Z., Si-hai, H. U., 2010. "Evaluation of Ecological Risk and Primary Empirical Research on Heavy Metals in Polluted

Soil over Xiaoqinling Gold Mining Region , Shaanxi , China.” *Transactions of Nonferrous Metals Society of China* 20(4): 688–94. [http://dx.doi.org/10.1016/S1003-6326\(09\)60199-0](http://dx.doi.org/10.1016/S1003-6326(09)60199-0).

Zango, M. S., Anim-gyampo, M., Ampadu, B., 2013. “Health Risks of Heavy Metals in Selected Food Crops Cultivated in Small-Scale Gold-Mining Areas in Wassa-Amenfi-West District of.” 3(5): 96–106.

Zhang, X. Y., Lin, F. F., Wong, M. T. F., Feng, X. L., Wang, K. 2009. “Identification of Soil Heavy Metal Sources from Anthropogenic Activities and Pollution Assessment of Fuyang County, China.” *Environmental Monitoring and Assessment* 154(1–4): 439–49.

Zhuang, P., Li, Y., Zou, B., Su, F., Zhang, C., Mo, H., 2016. “Oral Bioaccessibility and Human Exposure Assessment of Cadmium and Lead in Market Vegetables in the Pearl River.” *Environmental Science and Pollution Research*. [http:// dx.doi.org/10.1007/s11356-016-7801-z](http://dx.doi.org/10.1007/s11356-016-7801-z).

Zhuang, P., McBride, M. B., Xia, H., Li, N., Li, Z., 2009. “Health Risk from Heavy Metals via Consumption of Food Crops in the Vicinity of Dabaoshan Mine, South China.” *Science of the Total Environment* 407(5): 1551–61. [http:// dx.doi.org/10.1016/j.scitotenv.2008.10.061](http://dx.doi.org/10.1016/j.scitotenv.2008.10.061).



APPENDICES

Appendix A1: Sample coordinates

Sample	Code	Latitude	Longitude	Community
Cassava	OC1	6.93161	-1.6433	Offinso
Cassava	OC2	6.93399	-1.65704	Offinso
Cassava	OC3	6.92174	-1.69644	Offinso
Cassava	OC4	6.98945	-1.78349	Offinso
Cassava	OC5	6.99419	-1.76506	Offinso
Cassava	OC6	6.97631	1.74777	Offinso
Cassava	OC7	6.95261	-1.72666	Offinso
Cassava	OC8	6.94608	-1.6848	Offinso
Cocoyam	OCY1	6.93162	-1.64329	Offinso
Cocoyam	OCY2	6.93399	-1.65704	Offinso
Cocoyam	OCY3	6.93625	-1.67961	Offinso
Cocoyam	OCY4	6.98945	-1.78349	Offinso
Cocoyam	OCY5	6.9971	-1.77005	Offinso
Cocoyam	OCY6	6.97631	-1.74777	Offinso
Cocoyam	OCY7	6.95261	-1.72666	Offinso
Yam	OY1	6.93699	-1.64433	Offinso
Yam	OY2	6.93625	-1.67961	Offinso
Yam	OY3	6.98945	-1.78349	Offinso
Sweet potato	OP1	6.93625	-1.67961	Offinso
Cassava	AC1	7.37899	-2.01669	Akomadan
Cassava	AC2	7.39352	-1.94321	Akomadan
Cassava	AC3	7.38644	-1.92202	Akomadan
Cassava	AC4	7.39372	-1.93929	Akomadan
Cassava	AC5	7.36991	-1.91909	Akomadan
Cassava	AC6	7.41001	-1.90031	Akomadan
Cassava	AC7	7.3641	-1.95208	Akomadan
Cassava	AC8	7.39185	-1.95212	Akomadan
Cassava	AC9	7.41603	-1.92508	Akomadan
Cassava	AC10	7.39185	-1.96007	Akomadan
Cocoyam	ACY1	7.40528	-1.96625	Akomadan
Cocoyam	ACY2	7.37899	-2.01669	Akomadan
Cocoyam	ACY3	7.39352	-1.95164	Akomadan
Cocoyam	ACY4	7.37483	-1.91845	Akomadan
Cocoyam	ACY5	7.39463	-1.9409	Akomadan
Cocoyam	ACY6	7.37548	-1.9455	Akomadan
Cocoyam	ACY7	7.37187	-1.95224	Akomadan
Cocoyam	ACY8	7.3641	-1.95208	Akomadan
Cocoyam	ACY9	7.41604	-1.92455	Akomadan
Cocoyam	ACY10	7.36329	-1.94618	Akomadan

Yam	AY1	7.4163	-1.92442	Akomadan
Yam	AY2	7.40528	-1.96625	Akomadan
Yam	AY3	7.39185	-1.95522	Akomadan
Yam	AY4	7.3616	-1.94637	Akomadan
Yam	AY5	7.36329	-1.9444	Akomadan
Yam	AY6	7.3646	-1.95144	Akomadan
Yam	AY7	7.3776	-2.00403	Akomadan
Sweet potato	AP1	7.39463	-1.94089	Akomadan
Sweet potato	AP2	7.37105	-1.95205	Akomadan
Sweet potato	AP3	7.39425	-1.94527	Akomadan
Sweet potato	AP4	7.41672	-1.92452	Akomadan
Cocoyam	A2	6.440815	-1.93948	Amansie Central
Cocoyam	B2	6.403416	-1.9139	Amansie Central
Cassava	C1	6.42519	-1.93482	Amansie Central
Cassava	D2	6.409322	-1.90623	Amansie Central
Cassava	E1	6.400752	-1.9273	Amansie Central
Cocoyam	F2	6.40159	-1.9266	Amansie Central
Cocoyam	G2	6.415545	-1.87987	Amansie Central
Cassava	G1	6.413229	-1.8666	Amansie Central
Cassava	H1	6.4363	-1.84799	Amansie Central
Cocoyam	I2	6.443	-1.7672	Amansie Central
Cassava	J1	6.466904	-1.89818	Amansie Central
Cassava	E1	6.40159	-1.9266	Amansie Central

Appendix A2: Metal concentrations in root tubers and cassava peels from the different communities

AKOMADAN

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
AC1	1.18	12.31	5.94	258.17	16.07	9.44	4.77
AC2	1.25	12.31	5.99	312.52	15.88	9.42	15.6
AC3	1.17	12.26	5.54	92.03	15.77	9.06	3.1
AC4	1.21	12.04	5.83	101.56	15.53	9.22	6.34
AC5	1.23	12.18	5.66	135.49	15.57	9.25	11.77
AC6	1.25	12.29	5.99	287.55	16.45	9.38	7
AC7	1.23	11.42	5.87	36.81	15.46	9.41	3.35
AC8	1.24	11.05	5.93	442.6	17.07	9.49	21.07
AC9	1.25	12.36	5.97	78.8	15.99	9.29	12.85
AC10	1.21	12.86	5.67	59.7	15.86	9.09	2.98
AC1P	1.17	12.31	5.75	725.37	18.01	9.3	30.79
AC2P	1.28	12.02	5.85	1761.58	18.69	9.6	75.88
AC3P	1.22	12.18	5.78	728.96	17.21	9.36	22.12
AC4P	1.43	11.83	6.15	2926.25	20.97	10.17	21.09
AC6P	1.21	12.76	5.53	269.84	17.02	9.15	12.56
AC7P	1.35	10.65	6.05	461.36	17.96	9.57	32.51
AC8P	1.3	12.62	6.22	1503.92	20.5	9.61	32.53
AC9P	1.31	11.81	5.76	549.4	18.76	9.62	15.77
AC10P	1.37	10.95	6.29	1971.94	20.58	9.84	42.3
ACY1	1.23	11.88	5.83	14.76	15.3	9.28	6.92
ACY2	1.2	12.92	5.62	14.32	16	8.97	3.22
ACY3	1.19	12.46	5.8	15.06	16.34	9.23	12.25
ACY4	1.19	12.39	5.91	84.47	15.66	9.1	5.87
ACY5	1.18	11.17	5.83	117.88	15.75	9.31	25.79
ACY6	1.16	12.16	5.62	18.24	16.47	9.2	5.24
ACY7	1.21	12.04	5.58	15.85	16.09	9.21	8.44
ACY8	1.21	12.33	6.04	14.75	15.29	9.25	3.31
ACY9	1.19	12.44	8.48	31.56	16	9.14	18.42
ACY10	1.19	11.53	5.88	15.39	16.53	9.31	5.19
AY1	1.18	13.02	5.65	13.87	15.57	9.04	3.23
AY2	1.17	13.09	5.57	15.26	16.01	8.89	3.19
AY3	1.19	12.39	5.92	15.05	15.68	9.09	3.28
AY4	1.19	13.54	5.43	13.87	16.12	8.92	3.19
AY5	1.17	13.52	5.35	14.8	15.61	8.87	3.36
AY6	1.24	12.61	5.53	14.91	16.68	9.28	5.26
AY7	1.18	12.67	5.66	98.92	16.08	8.9	5.15
AP1	1.22	11.95	5.61	135.15	16.91	9.33	3.24
AP2	1.18	11.72	5.73	15.26	16.45	9.04	3.15
AP3	1.19	10.84	5.71	54.42	16.46	9.21	3.22
AP4	1.17	11.98	5.99	55.95	16	9.32	3.24

OFFINSO

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
OC1	1.22	12.14	5.98	20.31	15.67	9.23	4.66
OC2	1.17	12.79	5.55	15.14	15.46	9	4.26
OC3	1.2	11.88	5.76	15.4	15.88	9.31	17.22
OC4	1.2	12.08	5.69	15.23	15.65	9.28	7.6
OC5	1.23	11.91	5.81	72.78	16.1	9.32	16.2
OC6	1.2	11.73	5.94	82.46	15.62	9.36	16.55
OC7	1.22	12.22	5.66	14.5	15.7	9.23	6.08
OC8	1.21	12.97	5.54	15.45	15.35	8.93	3.18
OC3P	1.28	11.17	5.96	1284.46	17.52	9.7	50.38
OC4P	1.28	10.03	5.69	1138.64	18.98	9.49	16.58
OC5P	1.34	12.14	5.72	1841.35	20.43	9.82	24.76
OC6P	1.36	11.35	5.82	2051.88	19.12	9.64	26.37
OC7P	1.24	12.05	5.64	339.61	17.19	9.46	26.29
OC8P	1.37	12.5	5.85	1846.13	19.52	9.8	29.25
OCY1	1.25	7.43	6.06	16.28	16.48	9.85	7.97
OCY2	1.21	12.02	5.66	14.6	15.8	9.07	5.91
OCY3	1.2	11.93	5.8	16	16.65	9.2	22.83
OCY4	1.19	10.73	5.83	48.98	16.24	9.12	21.9
OCY5	1.24	12.2	5.8	15.84	16.06	9.21	15.7
OCY6	1.18	12.33	5.93	42.02	16.46	9.34	17.6
OCY7	1.22	10.34	5.37	15.66	16.11	9.21	8.65
OY1	1.18	12.26	5.83	107.58	15.94	9.19	13.24
OY2	1.18	12.12	5.91	36.05	15.44	9.11	19.3
OY3	1.22	8.7	6.38	61.14	16.54	9.98	17.29
OY4	1.24	11.68	5.72	156.67	16.11	9.21	3.07

AMANSIE CENTRAL

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
F2	1.18	12.18	5.87	15.97	15.98	9.06	11.56
I2	1.23	11.29	6.21	25.17	15.65	9.42	17.98
D2	1.25	11.6	10.71	39.09	16.06	9.23	37.8
E2	1.36	11.29	6.34	877	17.14	9.76	25.35
A2	1.23	12.18	5.92	464.89	16.01	9.17	15.72
F1	1.19	12.91	5.7	52.49	15.72	9.1	8.47
A1	1.32	8.4	6.28	17.16	17.17	10.24	19.55
I1	1.3	8.24	6.51	17.14	17.01	10.38	3.35
G1	1.25	9.83	6.3	59	16.36	10.07	14.11
C1	1.19	12.14	5.62	34.26	15.63	9.23	18.13
E1	1.19	12.28	5.73	14.91	15.61	9.2	18.67
KC1	1.28	11.06	6.44	487.67	16.46	9.72	66.02
J1	1.22	11.05	5.9	176.33	15.55	9.27	3.35
KC1P	1.41	11.55	6.59	3244.4	19.57	10.19	147.88
A1P	1.45	12.43	5.74	599.1	17.55	9.44	52.15
J1P	1.32	10.56	5.79	1003.15	18.35	9.4	29.59
E1P	1.22	13.14	5.59	409.26	17.65	9.11	30.29
I1P	1.3	9.49	5.76	411.6	17.63	9.67	27.71
G1P	1.32	12.08	5.78	1958	17.57	9.49	35.2
C1P	1.34	12.01	5.79	849.45	19.92	9.8	41.52

Appendix A3: Metal concentrations in soil from the different communities

AKOMADAN

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
ACS4	2.8	16.8	22.26	16601.73	345.19	17.42	32.1
ACS5	2.62	10.04	12.06	10146.73	499.83	16.75	12.98
ACS6	3.91	39.72	10.37	17163.27	494.53	18.98	13.53
ACS7	2.65	8.69	24.93	6639.4	148.48	16.53	6.47
ACS9	2.56	8.24	9.28	4070.45	298.01	16.8	8.5
ACS10	5.3	28.95	21.44	19523.32	788.09	21.13	18.29
ACYS1	2.34	8.9	8.86	6295.13	224.73	15.87	30.27
ACYS2	2.95	75	23.99	45364	616.7	25.33	24.16
ACYS3	2.78	20.07	14.36	16422.65	296.39	17.47	19.49
ACYS4	6.24	32.05	9.93	15746.36	498.08	16.9	19.13
ACYS5	11.22	103.43	29.5	86996.66	742.15	32.31	282.24
ACYS6	4.00	26.16	10.49	16270.76	465.11	16.83	10.96
ACYS7	2.75	7.43	11.28	2794.53	61.07	20.07	6.04
ACYS8	3.01	41.38	11.44	14115.57	511.82	17.03	11.75
ACYS9	2.52	8.47	9.18	4189.6	267.47	16.39	8.15
ACYS10	3.11	12.98	9.77	7246.63	459.75	16.93	10.84
AYS1	2.45	8.11	8.99	3335.33	166.85	16.31	7.16
AYS2	3.82	25.27	9.45	15692.36	445.03	17.16	13.93
AYS3	4.86	51.68	10.44	24665.35	435.56	41.16	13.34
AYS4	3.89	35.77	9.36	20234.09	424.35	17.62	10.43
AYS5	3.83	44.57	9.65	20792.16	560.04	22.36	12.16
AYS6	2.55	12.68	9.05	11916.36	319.52	16.59	19.75
AYS7	3.26	28.54	13.96	18545.06	412.99	20.69	15.43
APS1	6.17	44.34	16.8	28699.03	392.53	21.03	126.91
APS2	4.26	44.49	20.68	20118.63	277.33	17.44	25.53
APS3	2.33	7.97	9.18	4004.7	33.53	15.4	5.19
APS4	2.4	8.27	9.23	4342.13	274.54	16.59	13.37

OFFINSO

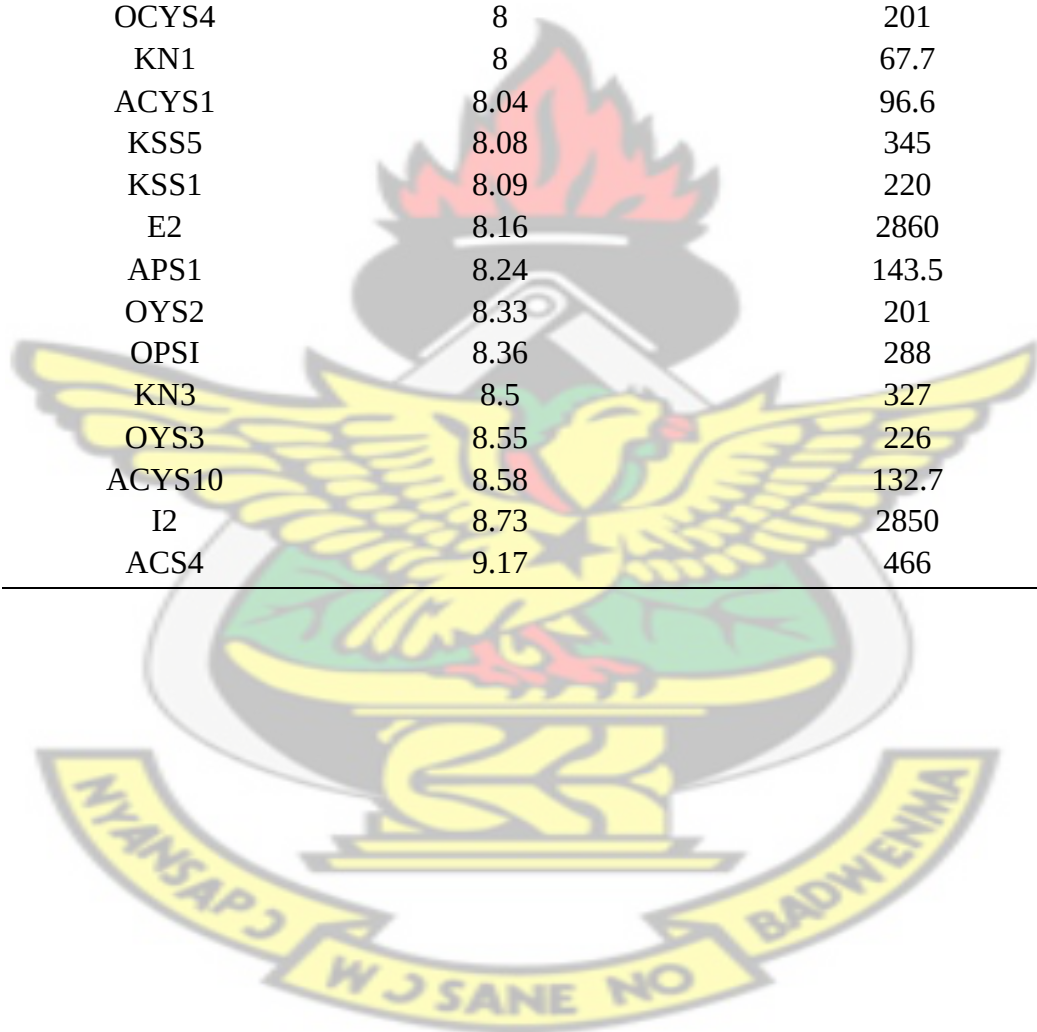
SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
OCS1	4.6	36.27	11.04	22400.74	401.46	17.16	39.08
OCS2	3.84	23.08	9.03	12705.24	200.19	15.99	33.12
OCS3	6.64	38.09	34.35	24038.83	1055.48	17.86	45.12
OCS4	3.29	8.89	8.83	6747.47	179.92	15.96	31.04
OCS5	5.08	40.64	10.87	23457.54	639.43	17.3	28.23
OCS6	2.76	68.13	24.09	34513.52	344.49	23.79	23.87
OCS8	5.62	45.64	17.38	19299.74	246.77	16.99	30.67
OCYS1	4.8	57.15	19.59	24713.67	508.82	23.32	43.58
OCYS2	5.1	13.24	8.94	10510.5	155.35	16.41	27.54
OCYS3	2.69	19.68	8.95	12956.8	136.48	16.4	99.01
OCYS4	6.91	69.6	23.55	36876.55	697.26	43.2	34.93
OCYS5	11.76	94.07	20.55	48518.42	535.82	19.9	37.18
OCYS6	2.6	97.35	14.23	35092.29	203.57	17.96	24.55

OCYS7	3.13	9.7	8.63	8397.84	210.36	15.64	33.48
OPS1	4.18	28.35	13.08	14012.88	109.59	16.6	117.59
OYS1	4.18	28.35	13.08	14012.88	109.59	16.6	117.59
OYS2	5.35	47.7	15.31	23428.52	403.94	35.2	44.37
OYS3	9.05	19.01	9.14	9722.72	116.93	16.23	92.59
OYS4	4.7	40.4	34.43	26968.54	844.2	25.6	49.52
KONONGO							
SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
KN1	1.3	11.58	5.95	375.53	16.62	9.19	155.17
KN2	10.97	17.31	8.77	9470.51	77.41	16.05	27.89
KN3	205.83	22.26	8.88	10549.41	261.39	15.85	27.22
KN4	9.16	9.7	8.58	9307.13	380.04	15.75	135.46
KN5	1.18	10.8	5.67	60.59	15.95	9.01	11.82
KCS1	10.97	95.66	30.82	30995.27	236.11	41.99	83.72
KS1	325.88	124.94	24.77	19896.65	350.82	25.08	48.04
AMANSIE CENTRAL							
SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
F13	7.64	9.42	8.73	9520.97	83.71	16.24	13.21
D13	18.72	74.56	23.33	29139.55	519.87	18.43	389.69
I13	21.04	51.39	11.18	18118.57	176.12	16.76	26.53
E13	87.07	21.55	16.58	17029.92	271.5	25.58	132.04
G13	46.87	91.04	20.9	41499.13	237.15	18.72	43.09
C13	16.36	41.26	10.03	21358.11	222.15	16.98	20.66
A13	11.48	11.63	8.53	8675.75	213.3	15.58	11.28
J13	15.42	41.2	18.87	25972.26	250.03	17.69	28.97
H13	20.64	65.98	9.82	30145.63	370.36	18.3	21.16
A23	7.2	11.65	8.84	9064.02	94.41	16.12	11.12
F23	19.35	35.99	9.09	15684.75	337.52	16.73	24.58
E23	22.47	17.47	9.2	12790.38	277.03	16.67	56.43
B23	20.04	372.69	14.63	37212.27	260.7	19.12	85.09
G23	26.5	313.23	15.48	32742.18	551.67	26.26	85.91

Appendix A4: Soil pH and conductivity

Sample	pH	Conductivity/($\mu\text{S}/\text{cm}$)
KN2	5.3	284
AYS1	5.77	94.6
OCS2	6.03	81.9
AYS7	6.05	85.8
AYS3	6.45	86
ACS7	6.49	37.8
ACYS3	6.52	94.7
OCS8	6.52	121
APS3	6.54	93.3
KN4	6.62	308
ACS2	6.66	127.9
ACYS7	6.66	120.2
OCS7	6.66	143.3
KS1	6.68	961
OCS6	6.74	130.8
ACS3	6.76	111.6
AYS5	6.87	79.3
OCS4	6.9	109.7
OCS1	6.91	46.3
OYS1	6.91	95.2
KCS1	6.92	61.9
OCYS1	6.98	83.1
KSS2	6.98	119.7
E2	7.02	3240
ACS8	7.05	86.4
A2	7.06	4020
KSS4	7.12	107.8
ACS1	7.13	124.3
AYS2	7.14	75.5
OCYS6	7.18	103.3
ACYS8	7.19	88.7
ACYS2	7.22	84.4
ACYS6	7.23	83.4
ACS5	7.24	50.9
APS2	7.28	125.3
ACYS9	7.29	53.9
ACS9	7.3	46.6
ACS6	7.31	95.7
OCYS2	7.32	128.5
OCYS7	7.32	175.7
AYS4	7.35	133.8

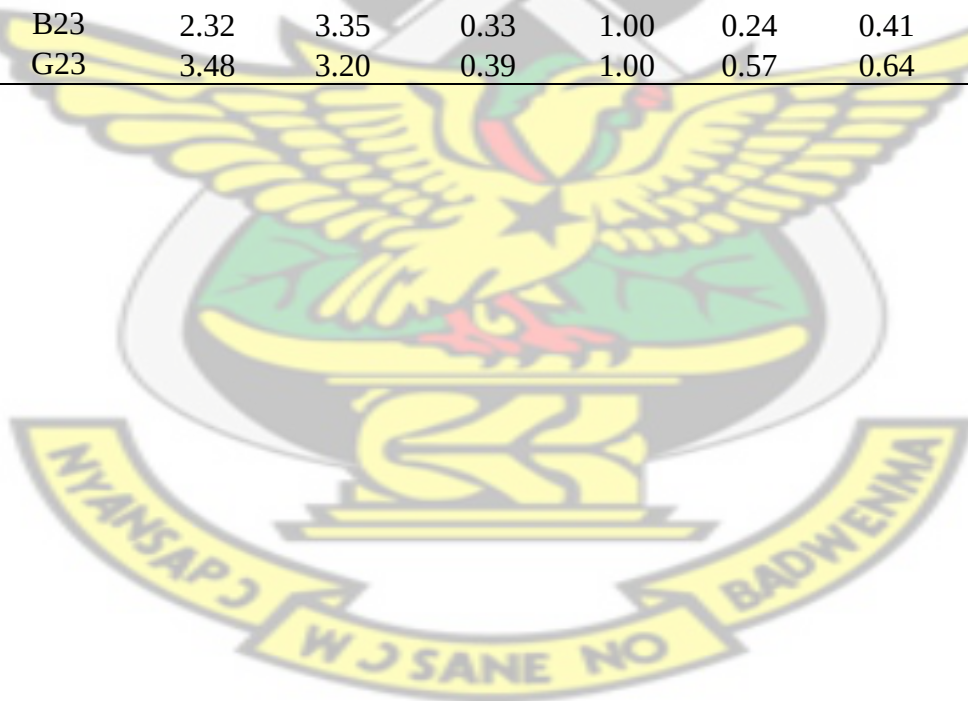
ACYS5	7.5	232
ACS10	7.55	83.7
OCYS5	7.68	131.6
J2	7.7	437
KSS3	7.72	80.9
ACYS4	7.74	151.5
OCS5	7.74	162.7
KN5	7.79	170.3
AYS6	7.87	101.6
OCS3	7.88	123.3
APS4	7.94	116.4
OCYS3	7.99	199.8
OCYS4	8	201
KN1	8	67.7
ACYS1	8.04	96.6
KSS5	8.08	345
KSS1	8.09	220
E2	8.16	2860
APS1	8.24	143.5
OYS2	8.33	201
OPSI	8.36	288
KN3	8.5	327
OYS3	8.55	226
ACYS10	8.58	132.7
I2	8.73	2850
ACS4	9.17	466



Appendix A5: Enrichment factor of metals

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
ACS10	1.17	0.50	0.91	1.00	1.36	0.86	0.66
ACS2	0.86	0.65	0.36	1.00	0.54	0.96	1.83
ACS3	0.46	0.74	0.34	1.00	0.31	0.61	0.35
ACS4	0.73	0.34	1.11	1.00	0.70	0.83	1.36
ACS5	1.11	0.33	0.99	1.00	1.65	1.31	0.90
ACS6	0.98	0.77	0.50	1.00	0.97	0.88	0.55
ACS7	1.72	0.44	3.12	1.00	0.75	1.97	0.68
ACS9	2.71	0.68	1.89	1.00	2.46	3.27	1.46
ACYS1	1.60	0.47	1.17	1.00	1.20	2.00	3.37
ACYS10	1.85	0.60	1.12	1.00	2.13	1.85	1.05
ACYS2	0.28	0.55	0.44	1.00	0.46	0.44	0.37
ACYS3	0.73	0.41	0.73	1.00	0.61	0.84	0.83
ACYS4	1.70	0.68	0.52	1.00	1.06	0.85	0.85
ACYS5	0.55	0.40	0.28	1.00	0.29	0.29	2.28
ACYS6	1.06	0.54	0.54	1.00	0.96	0.82	0.47
ACYS7	4.23	0.89	3.35	1.00	0.73	5.69	1.52
ACYS8	0.92	0.98	0.67	1.00	1.22	0.96	0.58
ACYS9	2.59	0.68	1.82	1.00	2.14	3.10	1.36
APS1	0.92	0.52	0.49	1.00	0.46	0.58	3.10
APS2	0.91	0.74	0.85	1.00	0.46	0.69	0.89
APS3	2.50	0.67	1.90	1.00	0.28	3.05	0.91
APS4	2.38	0.64	1.76	1.00	2.12	3.03	2.16
AYS1	3.16	0.81	2.24	1.00	1.68	3.87	1.51
AYS2	1.05	0.54	0.50	1.00	0.95	0.87	0.62
AYS3	0.85	0.70	0.35	1.00	0.59	1.32	0.38
AYS4	0.83	0.59	0.38	1.00	0.70	0.69	0.36
AYS5	0.79	0.72	0.39	1.00	0.90	0.85	0.41
AYS6	0.92	0.36	0.63	1.00	0.90	1.10	1.16
AYS7	0.76	0.51	0.62	1.00	0.75	0.88	0.58
OYS1	1.28	0.68	0.77	1.00	0.26	0.94	5.89
OYS2	0.98	0.68	0.54	1.00	0.58	1.19	1.33
OYS3	4.00	0.65	0.78	1.00	0.40	1.32	6.68
OYS4	0.75	0.50	1.06	1.00	1.05	0.75	1.29
OCS2	1.30	0.61	0.59	1.00	0.53	1.00	1.83
OCS3	1.19	0.53	1.19	1.00	1.47	0.59	1.32
OCS4	2.10	0.44	1.09	1.00	0.90	1.87	3.23
OCS5	0.93	0.58	0.38	1.00	0.92	0.58	0.84
OCS6	0.34	0.66	0.58	1.00	0.34	0.55	0.49
OCS8	1.25	0.79	0.75	1.00	0.43	0.70	1.11
OCYS1	0.84	0.77	0.66	1.00	0.69	0.75	1.24
OCYS2	2.09	0.42	0.71	1.00	0.50	1.24	1.84
OCYS3	0.89	0.51	0.57	1.00	0.35	1.00	5.36
OCYS4	0.81	0.63	0.53	1.00	0.64	0.93	0.66

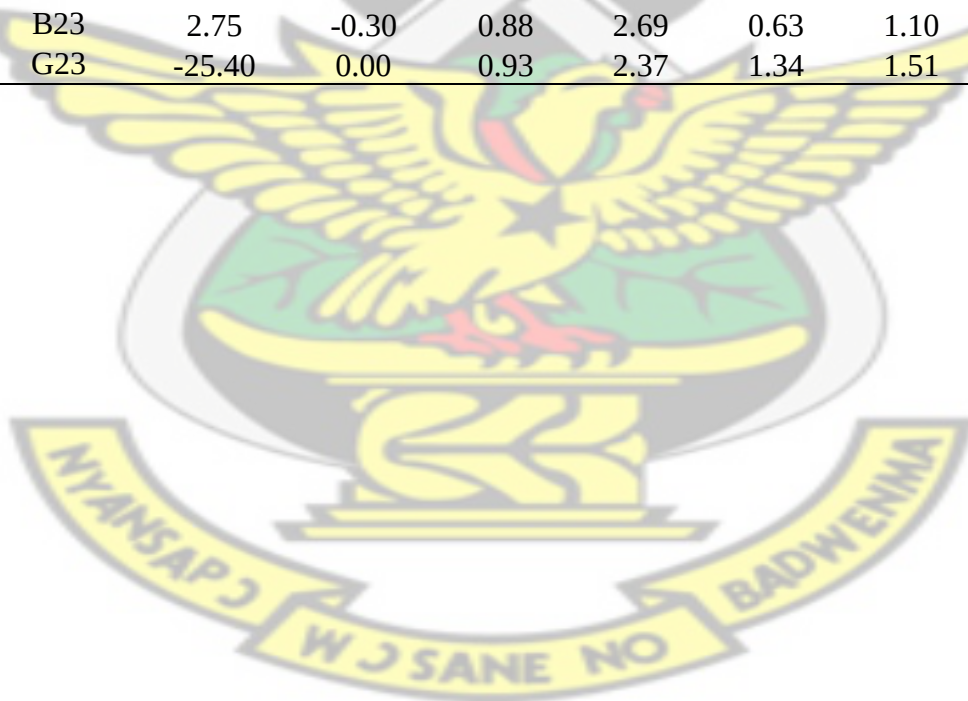
OCYS5	1.04	0.65	0.35	1.00	0.37	0.32	0.54
OCYS6	0.32	0.93	0.34	1.00	0.19	0.41	0.49
OCYS7	1.60	0.39	0.85	1.00	0.84	1.48	2.80
OPS1	1.28	0.68	0.77	1.00	0.26	0.94	5.89
KN1	14.89	10.32	13.15	1.00	1.49	19.39	289.80
KN2	4.98	0.61	0.77	1.00	0.27	1.34	2.07
KN3	83.94	0.71	0.70	1.00	0.83	1.19	1.81
KN4	4.23	0.35	0.77	1.00	1.37	1.34	10.21
KN5	83.78	59.63	77.66	1.00	8.84	117.81	136.82
F13	3.45	0.33	0.76	1.00	0.30	1.35	0.97
D13	2.76	0.86	0.66	1.00	0.60	0.50	9.38
I13	5.00	0.95	0.51	1.00	0.33	0.73	1.03
E13	22.00	0.42	0.81	1.00	0.54	1.19	5.44
G13	4.86	0.73	0.42	1.00	0.19	0.36	0.73
C13	3.30	0.65	0.39	1.00	0.35	0.63	0.68
A13	5.69	0.45	0.82	1.00	0.83	1.42	0.91
J13	2.55	0.53	0.60	1.00	0.32	0.54	0.78
H13	2.95	0.73	0.27	1.00	0.41	0.48	0.49
A23	3.42	0.43	0.81	1.00	0.35	1.41	0.86
F23	5.31	0.77	0.48	1.00	0.72	0.85	1.10
E23	7.56	0.46	0.60	1.00	0.73	1.03	3.09
B23	2.32	3.35	0.33	1.00	0.24	0.41	1.60
G23	3.48	3.20	0.39	1.00	0.57	0.64	1.84



Appendix A6: Contamination factor of metals

SAMPLE	As	Cr	Cu	Fe	Mn	Ni	Zn
AYS3	5.50	0.30	0.86	1.19	0.72	1.00	0.00
AYS2	2.02	-20.31	0.84	1.34	1.00	1.19	0.25
AYS4	1.78	0.57	0.58	1.51	1.36	1.28	0.36
ACYS4	2.77	0.33	0.69	1.02	1.24	0.98	-0.03
ACYS5	1.79	0.36	1.77	6.30	1.81	1.85	0.89
ACS9	1.45	1.13	0.54	0.24	0.41	0.94	-0.10
AYS6	1.64	0.36	0.56	1.47	1.03	1.01	0.02
APS1	0.47	0.54	0.80	2.20	1.19	2.11	1.08
APS4	3.11	0.30	0.63	1.79	1.06	2.36	1.24
ACYS6	8.74	0.17	0.68	0.20	0.15	1.15	0.20
APS3	1.82	0.97	0.55	0.29	0.08	0.88	-0.18
ACYS9	1.43	-4.88	0.56	0.29	0.72	0.96	-0.05
AYS7	0.00	0.16	1.50	0.48	0.36	0.95	-0.08
APS2	0.43	0.47	1.24	1.46	0.67	1.00	0.00
ACYS3	0.68	0.43	0.62	1.24	1.20	1.09	0.12
ACS6	6.88	0.17	0.55	0.31	0.67	0.95	-0.07
ACS7	1.71	0.36	0.74	2.19	0.67	1.33	0.42
ACYS8	0.77	0.56	1.01	2.08	0.95	1.21	0.27
ACS3	0.62	0.18	0.57	1.14	1.08	0.98	-0.02
ACS5	0.95	0.38	0.72	0.73	1.22	0.96	-0.06
ACYS2	0.69	0.41	1.44	3.29	1.50	1.45	0.54
AYS1	0.64	0.44	1.34	1.20	0.84	1.00	0.00
ACS2	1.97	2.78	0.60	1.14	1.21	0.97	-0.04
AYS5	-0.77	-0.57	0.59	0.52	1.12	0.97	-0.04
ACS4	-1.15	0.44	0.55	0.30	0.65	0.94	-0.09
ACYS1	-0.67	0.35	1.29	1.41	1.92	1.21	0.28
ACS10	2.08	-0.15	0.63	1.18	1.13	0.97	-0.05
ACYS7	0.49	1.00	0.53	0.46	0.55	0.91	-0.14
ACYS10	0.87	0.09	0.54	0.86	0.78	0.95	-0.07
OYS1	3.80	-0.33	0.79	1.01	0.27	0.95	-0.07
OYS2	-1.42	0.73	0.92	1.70	0.98	2.02	1.01
OYS3	3.49	-0.42	0.55	0.70	0.28	0.93	-0.10
OYS4	-14.90	-0.04	2.07	1.95	2.05	1.47	0.55
OCS2	2.29	-4.29	0.54	0.92	0.49	0.92	-0.12
OCS3	-1.41	-0.90	2.06	1.74	2.57	1.02	0.04
OCS4	2.50	-9.93	0.53	0.49	0.44	0.92	-0.13
OCS5	-0.09	9.14	0.65	1.70	1.56	0.99	-0.01
OCS6	6.17	0.44	1.45	2.50	0.84	1.36	0.45
OCS8	2.13	-11.43	1.04	1.40	0.60	0.97	-0.04
OCYS1	1.68	-0.29	1.18	1.79	1.24	1.34	0.42
OCYS2	2.96	6.66	0.54	0.76	0.38	0.94	-0.09
OCYS3	3.23	-0.39	0.54	0.94	0.33	0.94	-0.09
OCYS4	0.24	2.99	1.42	2.67	1.70	2.48	1.31

OCYS5	0.52	-1.19	1.23	3.51	1.30	1.14	0.19
OCYS6	2.95	2.03	0.86	2.54	0.50	1.03	0.04
OCYS7	2.09	-4.10	0.52	0.61	0.51	0.90	-0.16
OPS1	3.80	-0.33	0.79	1.01	0.27	0.95	-0.07
KN1	3.46	-0.63	0.36	0.03	0.04	0.53	-0.92
KN2	4.25	8.51	0.53	0.69	0.19	0.92	-0.12
KN3	1.72	6.13	0.53	0.76	0.64	0.91	-0.14
KN4	0.96	-0.33	0.52	0.67	0.92	0.90	-0.15
KN5	3.43	1.16	0.34	0.00	0.04	0.52	-0.95
F13	4.19	0.59	0.52	0.69	0.20	0.93	-0.10
D13	0.49	-0.14	1.40	2.11	1.26	1.06	0.08
I13	2.82	4.14	0.67	1.31	0.43	0.96	-0.06
E13	37.56	-0.01	1.00	1.23	0.66	1.47	0.55
G13	2.86	-0.88	1.26	3.01	0.58	1.07	0.10
C13	2.37	1.21	0.60	1.55	0.54	0.97	-0.04
A13	2.05	0.54	0.51	0.63	0.52	0.89	-0.16
J13	2.31	20.23	1.13	1.88	0.61	1.01	0.02
H13	1.43	1.07	0.59	2.18	0.90	1.05	0.07
A23	3.88	0.50	0.53	0.66	0.23	0.92	-0.11
F23	1.35	2.43	0.55	1.14	0.82	0.96	-0.06
E23	1.78	-0.70	0.55	0.93	0.67	0.96	-0.06
B23	2.75	-0.30	0.88	2.69	0.63	1.10	0.13
G23	-25.40	0.00	0.93	2.37	1.34	1.51	0.59

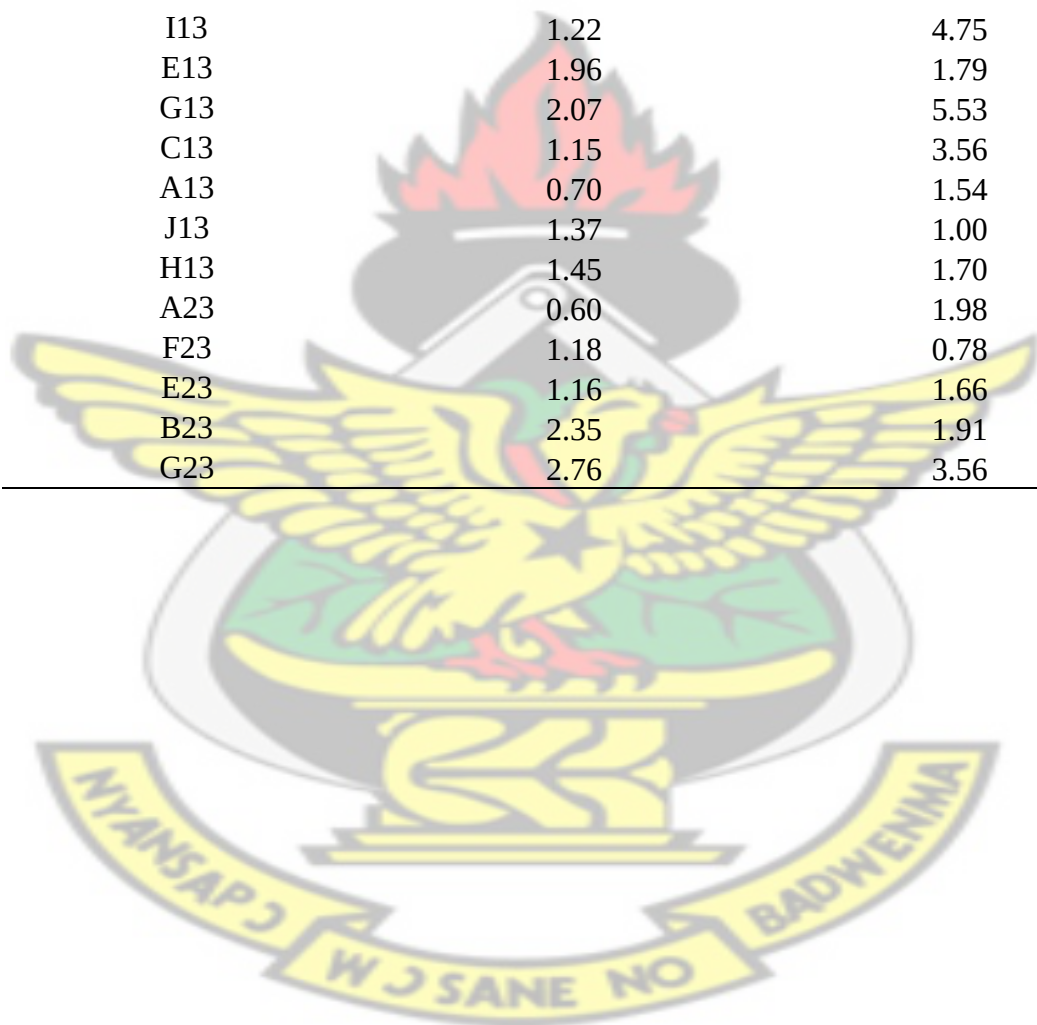


Appendix A7: Pollution load index (PLI) and modified degree of contamination

(mCd) of metals

SAMPLE	PLI	mCd
ACS10	1.24	0.57
ACS2	1.74	1.79
ACS3	1.09	1.95
ACS4	0.97	1.19
ACS5	0.70	1.04
ACS6	0.97	0.76
ACS7	0.54	1.00
ACS9	0.50	0.66
ACYS1	0.60	1.30
ACYS10	0.66	0.55
ACYS2	1.55	0.70
ACYS3	0.85	1.66
ACYS4	1.02	0.87
ACYS5	3.35	1.09
ACYS6	0.86	4.58
ACYS7	0.38	0.91
ACYS8	0.90	0.50
ACYS9	0.49	0.92
APS1	1.64	0.98
APS2	1.12	2.10
APS3	0.33	1.15
APS4	0.53	0.43
AYS1	0.43	0.72
AYS2	0.86	0.49
AYS3	1.20	0.90
AYS4	0.90	1.33
AYS5	1.03	0.95
AYS6	0.70	1.09
AYS7	0.96	0.75
OYS1	1.01	1.57
OYS2	1.45	1.57
OYS3	0.94	1.53
OYS4	1.72	1.49
OCS2	0.82	1.22
OCS3	1.70	0.90
OCS4	0.62	1.81
OCS5	1.21	0.74
OCS6	1.32	1.27
OCS8	1.14	1.41
OCYS1	1.49	1.20
OCYS2	0.72	1.52

OCYS3	0.85	0.85
OCYS4	1.94	1.30
OCYS5	1.94	1.98
OCYS6	1.15	2.15
OCYS7	0.66	1.33
OPS1	1.01	0.78
KN1	0.29	1.57
KN2	0.74	1.36
KN3	1.41	1.08
KN4	1.04	9.84
KN5	0.15	1.86
F13	0.59	0.30
D13	2.61	0.80
I13	1.22	4.75
E13	1.96	1.79
G13	2.07	5.53
C13	1.15	3.56
A13	0.70	1.54
J13	1.37	1.00
H13	1.45	1.70
A23	0.60	1.98
F23	1.18	0.78
E23	1.16	1.66
B23	2.35	1.91
G23	2.76	3.56



Appendix A8: Bioaccumulation factor of metals**Akomadan**

Sample	Cassava						
	As	Cr	Cu	Fe	Mn	Ni	Zn
AC2	0.20	0.21	0.45	0.01	0.03	0.26	0.20
AC3	0.36	0.18	0.45	0.00	0.06	0.39	0.21
AC4	0.43	0.72	0.26	0.01	0.04	0.53	0.20
AC5	0.47	1.21	0.47	0.01	0.03	0.55	0.91
AC6	0.32	0.31	0.58	0.02	0.03	0.49	0.52
AC7	0.46	1.31	0.24	0.01	0.10	0.57	0.52
AC9	0.49	1.50	0.64	0.02	0.05	0.55	1.51
AC10	0.23	0.44	0.26	0.00	0.02	0.43	0.16
Cassava peels							
AC1P	0.19	0.21	0.35	0.02	0.03	0.31	1.87
AC2P	0.40	0.18	0.48	0.06	0.04	0.26	0.96
AC3P	0.44	0.73	0.26	0.04	0.06	0.40	1.48
AC4P	0.55	1.18	0.51	0.18	0.06	0.58	0.66
AC6P	0.31	0.32	0.53	0.03	0.03	0.48	2.40
AC7P	0.51	1.23	0.24	0.23	0.12	0.58	5.03
AC9P	0.51	1.43	0.62	0.13	0.06	0.57	1.86
AC10P	0.26	0.38	0.29	0.10	0.03	0.47	2.31
Cocoyam							
ACY1	0.53	1.33	0.66	0.00	0.07	0.58	0.23
ACY2	0.41	0.17	0.23	0.00	0.03	0.35	0.13
ACY3	0.43	0.62	0.40	0.00	0.06	0.53	0.63
ACY4	0.19	0.39	0.60	0.01	0.03	0.54	0.31
ACY5	0.11	0.11	0.20	0.00	0.02	0.29	0.09
ACY6	0.29	0.46	0.54	0.00	0.04	0.55	0.48
ACY7	0.44	1.62	0.49	0.01	0.26	0.46	1.40
ACY8	0.40	0.30	0.53	0.00	0.03	0.54	0.28
ACY9	0.47	1.47	0.92	0.01	0.06	0.56	2.26
ACY10	0.38	0.89	0.60	0.00	0.04	0.55	0.48
Yam							
AY1	0.48	1.61	0.63	0.00	0.09	0.55	0.45
AY2	0.31	0.52	0.59	0.00	0.04	0.52	0.23
AY3	0.24	0.24	0.57	0.00	0.04	0.22	0.25
AY4	0.31	0.38	0.58	0.00	0.04	0.51	0.31
AY5	0.31	0.30	0.55	0.00	0.03	0.40	0.28
AY6	0.49	0.99	0.61	0.00	0.05	0.56	0.27
AY7	0.36	0.44	0.41	0.01	0.04	0.43	0.33
Sweet potato							
AP1	0.20	0.27	0.33	0.00	0.04	0.44	0.03
AP2	0.28	0.26	0.28	0.00	0.06	0.52	0.12
AP3	0.51	1.36	0.62	0.01	0.49	0.60	0.62
AP4	0.49	1.45	0.65	0.01	0.06	0.56	0.24

Offinso

Cassava							
OC1	0.27	0.33	0.54	0.00	0.04	0.54	0.12
OC2	0.30	0.55	0.61	0.00	0.08	0.56	0.13

OC3	0.18	0.31	0.17	0.00	0.02	0.52	0.38
OC4	0.36	1.36	0.64	0.00	0.09	0.58	0.24
OC5	0.24	0.29	0.53	0.00	0.03	0.54	0.57
OC6	0.43	0.17	0.25	0.00	0.05	0.39	0.69
OC8	0.22	0.28	0.33	0.00	0.06	0.53	0.10
Cassava peels							
OC3P	0.19	0.29	0.17	0.05	0.02	0.54	1.12
OC4P	0.39	1.13	0.64	0.17	0.11	0.59	0.53
OC5P	0.26	0.30	0.53	0.08	0.03	0.57	0.88
OC6P	0.49	0.17	0.24	0.06	0.06	0.41	1.10
OC8P	0.24	0.27	0.34	0.10	0.08	0.58	0.95
Cocoyam							
OCY1	0.26	0.13	0.31	0.00	0.03	0.42	0.18
OCY2	0.24	0.91	0.63	0.00	0.10	0.55	0.21
OCY3	0.45	0.61	0.65	0.00	0.12	0.56	0.23
OCY4	0.17	0.15	0.25	0.00	0.02	0.21	0.63
OCY5	0.11	0.13	0.28	0.00	0.03	0.46	0.42
OCY6	0.45	0.13	0.42	0.00	0.08	0.52	0.72
OCY7	0.39	1.07	0.62	0.00	0.08	0.59	0.26
Yam							
OY1	0.28	0.43	0.45	0.01	0.15	0.55	0.11
OY2	0.22	0.25	0.39	0.00	0.04	0.26	0.43
OY3	0.13	0.46	0.70	0.01	0.14	0.61	0.19
OY4	0.26	0.29	0.17	0.01	0.02	0.36	0.06
Amansie central							
Cocoyam							
F2	0.16	1.05	0.66	0.00	0.17	0.56	1.04
I2	0.06	0.31	0.68	0.00	0.05	0.56	0.73
D2	0.06	0.66	1.16	0.00	0.06	0.55	0.67
E2	0.07	0.03	0.43	0.02	0.07	0.51	0.30
A2	0.05	0.04	0.38	0.01	0.03	0.35	0.18
Cassava							
F1	0.16	1.37	0.65	0.01	0.19	0.56	0.64
A1	0.07	0.11	0.27	0.00	0.03	0.56	0.05
I1	0.06	0.16	0.58	0.00	0.10	0.62	0.13
G1	0.01	0.46	0.38	0.00	0.06	0.39	0.11
C1	0.03	0.13	0.27	0.00	0.07	0.49	0.42
E1	0.07	0.30	0.57	0.00	0.07	0.54	0.90
J1	0.11	0.95	0.69	0.02	0.07	0.59	0.30
Cassava peels							
A1P	0.19	0.17	0.25	0.02	0.03	0.51	0.13
J1P	0.07	0.21	0.52	0.06	0.10	0.56	1.12
E1P	0.06	0.61	0.34	0.02	0.07	0.36	0.23
I1P	0.01	0.10	0.28	0.01	0.07	0.52	0.64
G1P	0.03	0.29	0.58	0.09	0.08	0.56	1.70
C1P	0.08	1.03	0.68	0.10	0.09	0.63	3.68

Appendix A9: Target hazard quotient for root tubers

ADULT		As	Cr	Cu	Fe	Mn	Ni	Zn
CASSAVA	AKUMADAN	0.02895	0.00006	0.01004	0.00187	0.00083	0.00337	0.00021
	OFFINSO	0.02895	0.00006	0.00987	0.00032	0.00081	0.00333	0.00023
	AMANSIE CENTRAL	0.02895	0.00005	0.01056	0.00111	0.00084	0.00351	0.00046
COCOYAM	AKUMADAN	0.00714	0.00001	0.00027	0.00009	0.00020	0.00082	0.00006
	OFFINSO	0.00714	0.00001	0.00026	0.00006	0.00021	0.00083	0.00009
	AMANSIE CENTRAL	0.00774	0.00001	0.00031	0.00073	0.00021	0.00083	0.00013
		0.00734	0.00001	0.00028	0.00029	0.00021	0.00083	0.00009
YAM		As	Cr	Cu	Fe	Mn	Ni	Zn
	AKUMADAN	0.00940	0.00002	0.00033	0.00009	0.00027	0.00106	0.00003
	OFFINSO	0.00940	0.00002	0.00035	0.00030	0.00027	0.00110	0.00010
		0.00940	0.00002	0.00034	0.00020	0.00027	0.00108	0.00007

CHILDREN	AKUMADAN	HQ	0.07192	0.00015	0.00261	0.00464	0.05480	0.00836	0.00053
CASSAVA	OFFINSO	HQ	0.07192	0.00015	0.00256	0.00081	0.05377	0.00827	0.00057
	AMANSIE CENTRAL	HQ	0.07192	0.00013	0.00274	0.00276	0.05548	0.00872	0.00114
COCOYAM		Mean	0.07192	0.00014	0.00264	0.00273	0.05468	0.00845	0.00075
			As	Cr	Cu	Fe	Mn	Ni	Zn
	AKUMADAN	HQ	0.01775	0.00004	0.00068	0.00023	0.00051	0.00204	0.00014
	OFFINSO	HQ	0.01775	0.00004	0.00068	0.00023	0.00051	0.00204	0.00014
	AMANSIE CENTRAL	HQ	0.01775	0.00003	0.00078	0.00180	0.00051	0.00206	0.00032
		Mean	0.01775	0.00004	0.00071	0.00075	0.00051	0.00205	0.00020
YAM			As	Cr	Cu	Fe	Mn	Ni	Zn
	AKUMADAN	HQ	0.01775	0.00003	0.00078	0.00180	0.00051	0.00206	0.00032
	OFFINSO	HQ	0.02335	0.00004	0.00088	0.00075	0.00067	0.00271	0.00026

Appendix A10: Metal bioaccessibility

Sample ID	As	Cr	Cu	Fe	Mn	Ni
J2	35.9	NC	106.8	5.4	NC	79.7
KN1	18.9	15.2	NC	6.1	61.4	17.6
KN3	9.8	1.2	NC	2.0	49.4	34.4
ACYS4	21.6	NC	NC	0.1	79.4	52.7
ACS8	22.3	NC	55.6	NC	70.5	65.7
APS4	25.1	NC	NC	0.2	67.5	66.6
AYS3	20.1	18.2	19.8	0.2	50.3	38.9
OYS1	5.3	NC	NC	NC	68.8	53.2
OCS2	5.8	NC	NC	0.6	68.7	64.1
OCYS5	2.5	NC	NC	0.1	NC	46.3
OPS1	4.4	0.1	NC	0.8	44.9	13.4

Figure 1: Metal concentrations in soils from XRF from sampling locations

