UNIVERSITY OF GHANA

HEAVY METALS IN VEGETABLES SAMPLED FROM FARM AND MARKET SITES IN ACCRA METROPOLIS, GHANA

BY

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DECLARATION

I hereby declare that I have personally, under supervision, undertaken this research herein submitted.

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FORDJOUR LINDA ADDAE   DATE

(STUDENT)

I declare that I have supervised the student in undertaking this project submitted herein and confirm that the student has my permission for presentation and assessment.

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ABSTRACT

This study reports for the first time in Ghana long-term monitoring of heavy metal contamination of vegetables. As reliable residue data analysis resulting from monitoring programs in foods is of great value to the general populace; this could address the possible risk of heavy metal exposure to human health. In this study, monitoring of heavy metals (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in consumable vegetables was assessed for a period of 2 years, 2013-2014. In all, a total of 479 vegetables (cabbage (*Brassica oleracea*), carrot (*Daucus carota*), cucumber (*Cucumis sativus*), green pepper (*Capsicum annuum*) and lettuce (*Lactuca sativa*)) were purchased from farm (production) and market sites within Accra Metropolis, Ghana. Samples were subjected to acid digestion and analyzed with atomic absorption spectrometer (AAS). All the vegetables studied contained at least two (2) or more metals; 18.99% of the samples had metal detections below the European Union (EU) guideline values, whereas 81% were above limits. Vegetables from Mallam Attah market and the Ghana Broadcasting Corporation (GBC) sites registered the highest percentage exceedances (100%) with the largest violation occurring in lettuce (97.41%). Elevated concentrations of these metals were also observed in vegetables from markets compared to the farms except As, Cd, Co and Fe. Ni and Cr were undetected in vegetables from farms, however their maximum concentrations (1.236 and 2.459 mg/kg) were recorded in lettuce at market sites. Additionally, the significant metal increases in vegetables from the markets could be due to atmospheric depositions and mode of handling by both farmers and buyers. On the other hand, studies of the soils from the various farm sites had varying mean concentrations of heavy metals, Fe (189.703), Mn (142.246) and As (9.145 mg/kg). However, all the metal levels in the soil were below EU limits, except As (24.2 mg/kg) found at Dzorwulu site, which exceeded the 20.0 mg/kg limit for As in agricultural soil. The bio-accumulation or transfer factors for the metals in vegetables were highest in leafy and fleshy vegetables than root vegetables. The estimated health risks, average daily intake (ADI) and hazard quotient (HQ) of these metals in the vegetables were far below the FAO/WHO tolerable limits and did not pose any imminent risk to consumers (except As in vegetables from farms). Even so, the calculated risk for children (15 kg) was about 3 times higher than that of adults, indicating that children were prone to metal toxicities.

DEDICATION

This work is dedicated to the Most High God for His mercies.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
ADI	Average Daily Intake
AG	Abogbloshie
APHA	American Public Health Association
AWWA	American Water Works Association
BAF	Bioaccumulation Factor
CSIR	Centre for Scientific and Industrial Research
DM	Dome
EU	European Union
FAO/WHO	Food and Agriculture Organization/World Health Organization
Fig	Figure
GBC	Ghana Broadcasting Co-operation
HDPE	High Density Polyethylene
HQ	Hazard Quotient
IAEA	International Atomic Energy Agency
MA	Mallam Attah
MD	Madina
MK	Makola
NIST	National Institute of Standard and Technology
NRC	National Research Council
SD	Standard Deviation
TDS	Total Dissolved Solids

TSS	Total Suspended Solids
US	EPA United States of America, Environmental Protection Agency
WEF	Water Environment Federation

CHAPTER ONE

1.0 GENERAL INTRODUCTION

1.1 BACKGROUND

Food safety is a worldwide concern because foods are in many cases poisoned and rendered unwholesome with the sources as numerous and varied as the contaminants themselves (US EPA, 2003). Toxins, pesticides and heavy metals are some contaminants that accumulate in foods to cause poisoning. Vegetables, for instance, contain some essential components such as vitamins, carbohydrates, proteins, minerals, trace elements and fibers required by the human body (Itanna, 2002) to fight against diseases.

The essentiality of some heavy metals such as copper (Cu), zinc (Zn), manganese (Mn) and iron (Fe) cannot be overlooked because they help to effectively regulate and maintain the proper functioning and balancing of the human membranes. Their deficiencies may cause immune system breakdown; however, their excessive concentrations could be toxic. Manganese deficiency for instance, causes reproduction impairment with high infant mortality (Burch, 1975) whiles pathological events of iron oxides deposition in Parkinson's disease are credited with the intake of excess trace metal ions (FDA, 2001).

To a large extent, the potential toxicity of heavy metals is crucial because they are widespread and toxic even at low concentrations; though their toxicity may depend on the form in which they exist in the environment (Dube et al., 2001). These metals are not biodegradable, have long biological half-lives and potential for accumulation in the different body organs leading to unwanted side effects (Jarup 2003; Sathawara et al., 2004; Singh et al., 2010; Nabulo et al., 2011). Furthermore, heavy metals disturb important biochemical processes in the human organs of kidney, liver, cardiovascular, nervous and bone causing chronic inflammatory disease and cancer (WHO 1992; Jarup 2003). The biochemical processes of cell and tissue functions are interrupted by these metals through multiple pathways including interactions with proteins and other biomolecules (Varsha et al., 2010). Consequently, their bioaccumulation at higher trophic levels of human occupant in the ecological food chain occurs, creating heavy metal induced problems (Hogarh et al., 2008).

Arsenic (As), lead (Pb) and cadmium (Cd) metals have no beneficial effects in humans, and there is no known homeostasis mechanism for them (Draghici et al., 2010; Morais et al., 2012). Thus, their accumulations in humans only come as threat. Lacatuşu et al. (1996) concluded that the life of humans to death was significantly decreased by an average of 9-10 years in the industrial areas of Baia Mare and Copsa Mica (Romania) when excess palladium (Pd) and cadmium (Cd) pollution of soils and vegetables occurred. Moreover, Heneman (2006) reported that high Pb levels in blood put children at risk for neurobehavioral-cognitive deficits, such as IQ deficiency, behavioral disorders and impaired hearing. Moreover, skin lesions, lung cancer and dermatitis allergies have been linked to chromium (Cr) metal intake (Stoecker, 2001).

Food is the main exposure route for heavy metal ingestion and it is believed that heavy metal contaminants in foods are far higher than any other exposure routes for example air and drinking water. Activities such as urbanization, industrialization, agriculture and mining processes are factors that have greatly accelerated heavy metal concentrations, although these metals are natural occupants in soils (Facchinelli et al., 2001). From their excessive contamination in the environment, vegetables pick them up from the soil, water and air as exposed contaminants.

Fruits and vegetables are very essential to man and necessary attention is being given to them in most nations today. The World Health Organization (WHO) states that food consumption by man should contain at least 30% of fruit and vegetables depending on the weight of the individual (Osei-Fosu et al., 2014 and references therein). Nonetheless, because vegetables are consumed raw or semi-processed, there is the general belief that they would contain elevated levels of heavy metals compared to other foodstuffs. In Ghana, there are limited studies on heavy metal levels in vegetables and other food commodities although some works have been documented (Odai et al., 2008; Bempah et al, 2011; Larbie et al., 2014).

In spite of all these limited studies, the data on metal accumulation in vegetables is still significant as the use of wastewater for irrigation and application of agrochemicals by farmers in their diseases and pest control is on the increase without compliance to good agricultural management practices. This, in the long run may affect both animals and humans who consume them. Thus, measures for heavy metal monitoring in vegetables and the environment, accompanied by continuous regular surveys and monitoring, are very imperative. Nonetheless, such programs are not common or well explored in the Ghanaian environment. All the previous studies monitored metal levels in vegetables for very limited period, between 3 and 12 months (Anim-Gyampo et al., 2012; Akrong et al., 2012; Bempah et al., 2011; Larbie et al., 2014; Odai et al., 2008). Such short term studies do not help in policy and regulatory developments as well as environmental impact assessments. Moreover, there is no coordinated monitoring program that aids to provide database for heavy metals in food at the regional or national levels as indicated by Osei-Fosu et al. (2014) in a recent publication.

The current study for the first time, evaluated the long-term seasonal monitoring of heavy metals such as: arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn) in some popular and widely consumed vegetables- (cabbage (*Brassica oleracea*), carrot (*Daucus carota*), cucumber (*Cucumis sativus*), green pepper (*Capsicum annuum*) and lettuce (*Lactuca sativa*)) from selected farm (production) and markets sites within Accra Metropolis, Ghana.

1.2. PROBLEM STATEMENT AND JUSTIFICATION

Vegetables are rich sources of vitamins, minerals and fibre which provide the required balanced diet of humans, for better health. In the Accra Metropolis, low rainfalls are recorded annually and coupled with the scarcity of lands, limits any agricultural activity in the city. However, vegetable farming is the only significant agricultural activity and is sited along heavily traffic roads, minor streams and major drainage systems (gutters). Upon the WHO (2007) directives, the demand for vegetable consumption has increased, giving rise to numerous producers who use any available space for cultivation. Many producers use nearby untreated wastewaters channeled through main drainages from homes, hospitals and industries while applying a great deal of agrochemicals as well to boost production.

These wastewaters could contain contaminants of heavy metals and coliforms at varying degrees; these are potential toxins for plants and animals. The contributions of these metal depositions may be significantly high to modify their accumulation pattern in the soils and vegetables. Finally, the harvested vegetables are likely to contain heavy metal as contaminants, which eventually end up in the principal markets within the Metropolis. Moreover, the mode of their transfer and handling perhaps could add up heavy metal contaminants. Consequently, there is the fear that these metals could be major contaminants/pollutants in these vegetables and hence on their safety is questionable.

The toxicity and non-biodegradable nature of heavy metals have created the necessity for their control and monitoring in the environment. Accordingly, there is no information available on the dietary intake of heavy metals by the Ghanaian populace. Therefore the only way to assess dietary heavy metal intake of the public is to carry out analysis of the foods that constitute the diet of an average consumer. Therefore, results from this study would provide consumer risk assessment data that could be used to take preventive actions to minimize consumer health risks. It would also serve as baseline upon which annual or other long-term monitoring studies are compared with. More so, with such data the government can be assured of compliance of the principles of good agricultural practices and ease development of regulatory policies as well.

1.3. HYPOTHESIS

H_0: Vegetables produced from and sold at markets sites in Accra Metropolis are contaminated with heavy metals.

H_1: Vegetables produced in Accra Metropolis have tolerable levels of heavy metal contaminations.

1.4. OBJECTIVES OF THE RESEARCH

1.4.1. Aim

To determine the heavy metal concentrations in vegetables sampled from farm (production) and market sites within Accra Metropolis and assess any health implications.

1.4.2. Specific Objectives

The objectives are:

1. To monitor the heavy metal concentrations of As, Cd, Cr, Cu, Co, Fe, Mn, Ni, Pb and Zn in some popularly consumed vegetables grown and marketed in Accra Metropolis.
2. To evaluate heavy metal concentrations of vegetables sampled from production and market sites.
3. To estimate the bioaccumulation factor (BAF) of heavy metal concentrations in the vegetables with respect to their concentration in soils.
4. To assess potential health risks associated with heavy metal via vegetable intake.
5. To provide data that could serve as database for continuous and long-term monitoring as well as comparative studies.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1. INTRODUCTION

The toxicity of heavy metal pollutants in plants and animals and their non-biodegradable nature have raised serious environmental concerns globally (Li et al., 2006; Jang et al., 2006; Zhuang et al., 2009). Several studies have shown varying levels of heavy metals in some fruits and vegetables (Boamponsem et al., 2012; Lui et al., 2013; Sobukola et al., 2010; Zhuang et al., 2009) and it is therefore necessary for the regular monitoring of heavy metal levels in foods.

Fruits and vegetables intake have prevented certain cardiovascular diseases and cancer, which are fatal to the human system. Crawford et al. (1994) emphasized that a diet high in fruits and vegetables could prevent 20% of most types of cancers and this stems from the scientific evidence that the frequent consumption of fruits and vegetables can prevent esophageal, stomach, pancreatic, bladder and cervical cancers. Again, vegetables are considered low in fat and calories and do not contribute to increased blood pressure. For this reason, the World Health Organization (WHO) in their various reports recommends that dietary food intake should contain about 30% of fruits and vegetables (WHO, 2007).

Vegetables contain vitamins, carbohydrates, proteins, minerals, some trace elements and fibers which are essential to the human body (Itanna, 2002). Vitamins and minerals repair damaged cellular and bolster the immune system by producing blood cells and other hormones; carbohydrates release energy; proteins repair worn out tissues and promote growth; fibers prevent constipation and decrease the risk of coronary heart diseases; and some elements like calcium promote strong bone formation. The benefits of these nutrients to enhance the proper functioning of cells and tissues in humans have contributed to the increased consumption of vegetables especially in the urban areas of some developing nations.

However, vegetables have the propensity to pick up heavy metals of environmental concerns. Food chain through the ingestion of contaminated vegetables creates the main route of heavy metal intake and accumulation in humans, although very rarely, the metals could also be inhaled from the environment (Lacatuşu et al., 1996; Jarup, 2003). Heavy metals are natural occupants in soils but anthropogenic activities such as agriculture, urbanization, industrialization and mining have contributed to their upsurge (Facchinelli et al., 2001). The frequent use of fertilizers and pesticides and the continual disposal of waste electronic materials on farms have caused heavy metal elevations in different agricultural soils. Again, other untreated sewages from industries and the release of exhausts from automobiles greatly contribute to contaminate the environment with heavy metals.

Heavy metal toxicity is encountered even at low concentrations. The toxicity has created complex reactions that disrupt cell actions, causing various diseases. US EPA (2000) stated that chromium (Cr), copper (Cu) and zinc (Zn) intake cause non-carcinogenic hazards such as neurologic involvement, headache and liver diseases when they exceed their safe threshold values. Moreover, some heavy metal toxicity reports revealed that children who lived around a former smelter in France had high blood Pb levels (Pruvot et al., 2006) and Brazil (Bosso and Enzweiler, 2008). Also, in a similar report, Park et al. (2004) concluded that the excess lifetime risk of lung cancer deaths resulted from occupational exposure to dusts and mists containing hexavalent chromium in the chromate industry. Due to the numerous risks associated with heavy metal intake, the World Health Organization and Food and Agriculture Organization (Joint FAO/WHO) have provided limits on allowable daily intake of metals in foods.

2.2. ESSENTIALITY OF METALS

Metals are widely found in nature, particularly in various mineral deposits and soils, and are available to be taken up by plants and animals that serve as food sources for humans. In 2002, WHO reported that an element is considered essential to an organism when the reduction of its exposure below certain limit results consistently in the reduction of a physiologically important function, or when the element is an integral part of the organism structure in performing vital function(s) (WHO, 2002). Eleven (11) elements are identified as “trace elements or metals” because of their essentiality; however very limited quantities are available in humans. These metals which include molybdenum (Mo), selenium (Se), arsenic (As), cobalt (Co), chromium (Cr), iron (Fe), vanadium (V), zinc (Zn), copper (Cu), manganese (Mn) and boron (B) belong to the category of micronutrients (generally less than 100 mg/day is required). Some studies have shown also that lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) have no beneficial effects in humans, and there is no known homeostasis mechanism for them (Draghici et al., 2010; Morais et al., 2012).

It is true that these trace metals form some essential components of biological structures, yet, their excessive concentrations can dysfunction biological structures in organisms (Fraga, 2005). Notwithstanding, harmful effects may also arise from the low intake of these metals and it is known as deficiency. This poses a challenge to the basic assumptions of risk assessment where the underlying principle aims at minimizing exposure as far as possible.

2.3. HEAVY METALS

Bioavailability is the key to assess the potential toxicity of metals and their compounds in an organism. Bioavailability depends on both the biological parameters and on the physicochemical properties of metallic elements, their ions and their compounds. Due to the non-biodegradable nature of heavy metals (Zaida et al., 2005) they bio-accumulate and pose numerous health dangers to mankind. The consumption of foods contaminated with heavy metals can seriously deplete some essential nutrients in the body to cause decrease in immunological defences, intrauterine growth retardation, impaired psycho-social behavior, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer (Arora et al., 2008). However, as noted earlier, not all heavy metals are harmful to humans as some are nutritionally essential for a healthy living.

2.3.1. Arsenic, As

Arsenic is a metalloid with some abundance in the Earth’s crust and rocks. The soil, water and air also record considerable amounts through human activities of mining, agricultural pesticide applications and smelting and coal-firing of power plants. Arsenic occurs in different forms and many of its compounds bind to soil and only move short distances when water percolates down through the soil (GreenFacts, 2015).

The inorganic form of As is the most toxic and has emerged as the main cause for most groundwater poisonings. Arsenic exposure is carcinogenic and extreme poisoning may lead to death. With its classification as a toxic element that adversely affect human health, the WHO set standards are 10 ppb in drinking waters and 0.007 mg/kg in vegetables (WHO, 2011). While mild exposure to inorganic arsenic causes various health effects such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin colorings and lung irritation, its high exposure renders infertility and miscarriages in women, declined resistance to infections, heart disruptions and brain damage in both men and women. It is further suggested that, the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development, especially the development of skin cancer, lung cancer, liver cancer and lymphatic cancer. Lastly, inorganic arsenic can damage DNA. However, organic arsenic exposures may only render nerve injury and stomach aches (LENNTECH, 2015).

2.3.2. Cadmium, Cd

Cadmium is an extremely toxic element with very low exposure limits. The application of phosphate fertilizers, the use of Ni-Cd batteries, mining and smelting processes have introduced Cd into the environment which subsequently enter the food chain upon plant uptake from contaminated soils and water. Subsequently, Cd is exposed into the air through the burning of fossil fuel such as coal or oil and other smelting processes (ATSDR, 2013).

Cadmium has no known beneficial effects in humans and its accumulation disrupt cell mechanisms which may lead to death. The average daily intake for Cd is low and range between 0.2 to 0.7 µg/kg for an adult. When Cd is ingested by humans, it is first transported to the liver through the blood. There, it bonds to proteins to form complexes that are transported to the kidneys. Cd then accumulates in the kidneys and damage filtering mechanisms. This causes the excretion of essential proteins and sugars from the body, aside the kidney damage. This effect is strengthened by the fact that Cd stored in the kidneys takes a very long time to be excreted from the human body (LENNTECH, 2015) as its biological half-life is about 10–35 years (WHO, 2008). Cd poisoning leads to diarrhoea, hypertension, lung damage, damaged central nervous system, psychological disorders and infertility in humans.

2.3.3. Chromium, Cr

Cr element is required in trace amounts in humans, although its mechanisms of action in the body and the amounts needed for optimal health are not well defined (NIH, 2013). Cr occurs naturally in rocks, however, through mining and industrial activities, Cr is released into the environment contaminating sources of air, water and soil. Vegetables pick up Cr from the soil as an essential nutrient which is transferred to man upon consumption. Two (2) forms of Cr are primarily found: Cr^{3+}, which is biologically active and found in foods, and the hexavalent Cr^{6+}, a toxic form which is released from industrial pollutions (NIH, 2013).

The transport mechanism for Cr is unknown in humans. Some findings have reported that Cr enhances the action of insulin, the hormone critical to the metabolism and storage of carbohydrate, fat and protein in the body (Emsley, 2001). In 1957, a compound in brewers' yeast was found to prevent an age-related decline in the ability of rats to maintain normal levels of sugar (glucose) in their blood (Mertz, 1988), and in 1959, Cr was identified as the active ingredient in "glucose tolerance factor" (Schwarz, 1959). However, numerous vitro studies have indicated that excessive Cr^{3}+ in the cell can cause DNA damage (Eastmond, 2008). Also, the carcinogenity of chromate dust is known for a long time, and in 1890 the first publication described the elevated cancer risk of workers in a chromate dye company (Newman, 1890; Langard, 1990).

2.3.4. Cobalt, Co

Cobalt is a hard, silvery grey metal which is naturally found in rocks, soil, water and meteorites. It is usually found in the environment combined with other elements such as oxygen, sulphur, and arsenic. Co is used in alloy making of aircraft engines, magnets, and grinding and cutting tools (ATSDR, 2004).

The biological activity of Co is vitamin B-12, which is essential for producing red blood cells and maintaining the nervous system. It can also replace Mn and Zn to activate several enzyme functions in the body. Cobalt also participates in the biotin-dependent Krebs-cycle, the process of sugar breakdown into energy. However, Co entering the body in some other form can be very toxic. Excessive intake of cobalt may cause heart muscle failure, goiter and hyperglycemia (increased blood sugar) (Eskenazi Health, 2015).

2.3.5. Copper, Cu

Copper is a commonly encountered substance in the environment. When in soil, Cu strongly attaches itself to organic matter and soil minerals and is picked up by plants. Through food, organisms are able to ingest Cu which initiates many biological activities. In humans, the essentiality of copper arises from its incorporation into a large number of proteins. Copper has the ability to cycle between stable oxidised Cu^{2+} and unstable reduced Cu^{+} (EBRC, 2007). Cu is carried by the protein ceruloplasmin and acts as a reductant in the enzymes superoxide dismutase, cytochrome oxidase, lysil oxidase, dopamine hydroxylase, and several other oxidases that reduce molecular oxygen in the organism (Fraga et al., 2005). Cu forms an essential structural component of many macromolecules, ensuring normal activity for a large number of enzymes and other proteins. Cu essentiality is known in its physiological effects where it is critical to foetal/infant development and growth, immune function, brain development and function, bone and collagen strength, haematopoiesis, iron metabolism, cholesterol and glucose metabolism, myocardial contractility, maintenance of hair and skin, and pigment formation. Cu also participates in both iron and energy metabolism.

Adverse health effects due to copper excess are focused on the liver which is the target organ for copper-related toxicity. With a damaged liver (cirrhosis); a high amount of zinc may produce adverse nutrient interactions with Cu and reduces immune function and the levels of high density lipoproteins (FDA, 2001). Again, emphasizes is made that true absorption rates are intake-dependent, decreasing with increasing daily intakes. From the intake mechanisms, systemic absorption of 63-65% occurred at an intake of 1mg/day, whereas at an intake of 8 mg/day, the systemic absorption dropped to 29-32% (EBRC, 2007).

2.3.6. Iron, Fe

Rocks are the natural deposit for iron; however, certain anthropogenic activities such as mining, agriculture and the rusting of iron containing metal machines increase the iron contents in the environment. Plants pick up Fe primarily from the soil which is subsequently transferred to humans upon consumption. Iron is a good candidate for redox reactions due to its ability to exist as either Fe^{2+} or Fe^{3+}, and thus plays a central part in many biological metabolisms.

In mammals, Fe is also central to oxygen transport and forms the central part of the haeme moiety of haemoglobin. The metabolism of haeme also facilitates other metabolic processes, with the haemeoxygenase enzymes underpinning important cell signaling and cell differentiation roles. Haeme is found in meat and in other products of animal origin and when it transports to the body; it is absorbed and processed in the same way as Fe from other sources. Iron is reduced to $Fe^{2+}$from diets and transported into cells where it can be stored in ferritin as FeOH complexes (EBRC, 2007).

There is no known excretion of iron from within the human body. Inside the cell, iron is complexed in the haeme or found in iron-sulphur clusters. Fe deficiency greatly results in anaemia but this only occurs when Fe stored is very low, so that many other processes are likely to have been adversely affected before the anaemia develops. Fe deficiency may include weakness, hair loss, depression and a decreased ability to concentrate. Chronic Fe intoxication may frequently occur and it is associated with genetic and metabolic diseases, repeated blood transfusions, or with excessive Fe intake (Fraga and Oteiza, 2002). Liver failure, loss of appetite, fatigue, weight loss, headache, vomiting, nausea and dizziness are however associated with large Fe intake.

2.3.7. Manganese, Mn

Manganese is released into the environment through its discharge from the mining and stainless steel industries and it is naturally found bonded to iron in nature. Mn is an essential element which is required by the human body, however, in trace amounts because its toxicity arises from high concentrations. The highest concentration of Mn is about 20 mg in the body. Mn is found in the tissues of kidney, pancreas, liver and bones. Mn promotes normal brain functioning and activity of the nervous system in the body (Organic Facts, 2015).

Mn^{2+} is the reduced form of manganese and often competes with Mg^{2+} in biological systems. Mn promotes different enzyme activities like the mitochondrial, Mn superoxide dismutase, glutamine synthetase, arginase, and activates several hydrolases, transferases and carboxylases (Fraga, 2005). High blood pressure, heart ailments, muscular contraction, bone malformation, high cholesterol, poor eyesight, hearing trouble, severe memory loss, shivers and tremors are some deficiency associated with low Mn intake. Even though some medical experts argue that Mn deficiency is quite rare, more than 35% of the world population is thought to be deficient (Organic Facts, 2015). Nevertheless, excessive exposure may cause a condition known as manganism, a neurodegenerative disorder that causes dopaminergic neuronal death and parkinsonian- like symptoms (Avila et al., 2013; Emsley, 2001).

2.3.8. Nickel, Ni

Most Ni is inaccessible because it is locked away in the earth's iron-nickel molten core, which is 10% nickel. The element is mostly used to make alloys in the steel and coal industries and it is also released as waste from vehicles. Organic matter absorbs Ni at a higher rate and that is why coal and oil contain considerable amounts. The nickel content in soil varies from 0.2-450 ppm in some clay and loamy soils. Vegetables particularly take up Ni during their growth on contaminated soils, thereby boosting Ni uptake in humans at vegetables consumption (LENNTECH, 2015).

Ni oxidation states range from −1 to +4 with the +2 oxidation state as the most prevalent form in bio-systems (Denkhau and Salnikow, 2002). Nickel is believed to play a role in physiological processes acting as a co-factor in the absorption of iron from the intestine (Das et al., 2008). However, epidemiological studies have clearly implicated Ni compounds as human carcinogens based upon a higher incidence of lung and nasal cancer among nickel mining, smelting and refinery workers (Denkhau and Salnikow, 2002). Skin rash, dermatitis, nausea and weakness may be associated additionally with Ni toxicity.

2.3.9. Lead, Pb

Lead is classified as a potent occupational toxin and its toxicological manifestations are well known. Because of its non-biodegradable nature, Pb persists long enough in the environment. Human exposure to lead occurs from leaded gasoline use, lead smelting and coal combustion industries, agriculture, lead-based paints, lead containing pipes or lead-based solder in water supply systems, battery recycling and grids and bearings (Flora et al., 2012). Food chain and inhalation are the major routes of Pb exposure to humans. Vegetables pick up Pb primarily from the soils which become contaminated through industrial Pb discharge, vehicular deposits and the dumping of Pb containing materials like batteries, pipes and paints onto soils.

$Pb^{2+}$is the ionic form of lead and can replace Ca^{2+} and Zn^{2+} in body mechanisms and contributes principally to neurological deficits as it crosses the blood-brain barrier (BBB) at an appreciable rate (Flora et al., 2012). Again, Na^{+} ions activities like the generation of action potentials in the excitatory tissues for the purpose of cell to cell communication, uptake of neurotransmitters (choline and dopamine) and regulation of uptake and retention of calcium by synaptosomes are disrupted by the Pb interaction (Bressler et al., 1999).

Some animal studies have shown that liver, lungs, and kidneys have the greatest soft-tissue lead concentrations immediately after acute exposure. The developing tissues of children make them vulnerable to retain more lead in soft tissue than adults with an approximate half-life of 40 days accumulation (Holstege, 2013). US EPA has made conclusions that exposure to environmental Pb for the general population, and in particular, pre-school children are a national health concern (US EPA, 1986). The observable signs and symptoms in children are loss of appetite, abdominal pain, vomiting, weight loss, constipation, anemia, kidney failure, irritability, lethargy, learning disabilities, and behavioral problems (disassociation) (Landrigan, 2012). Generally, Pb toxicity leads to high blood pressure, cardiovascular diseases, kidney damage, nervous system damage (brain damage), and psychological disorder and subsequently to death.

2.3.10. Zinc, Zn

Zinc has high uptake by plants and its ions are strongly adsorbed to soils at pH 5 or greater and are expected to have low mobility in most soils (Christensen et al., 1996; Gao et al., 1997). It interacts electrostatically with anions (carbonate, hydroxide, oxalate, phytate) and negatively charged moieties on macromolecules such as proteins. It can also form soluble chelation complexes with amino acids and multidentate organic acids such as EDTA (US EPA, 2005). Zn is released from the mining, coal and steel processing companies into water bodies contaminating the environment.

As an essential element, Zn is highly needed by humans to promote biochemical functioning of cells and tissues. Zn possesses antioxidant effects and it is a recommended dietary supplement. Zn is mainly transported by ceruloplasmin and its activity affects about 100 enzymes, e.g. RNA polymerase, carbonic anhydrase, Cu–Zn superoxide dismutase, angiotensin I converting enzyme and present in Zn-fingers associated with DNA (Fraga, 2005). Zn deficiency results in diseases such as diarrhea, alopecia, mental disturbances, and impaired cell-mediated immunity resulting in intercurrent infections. Again, symptoms with moderate zinc deficiency include: growth retardation, male hypogonadism, skin changes, poor appetite, mental lethargy, abnormal dark adaptation, and delayed wound healing (US EPA, 2005). However, Zn toxicity can disrupt Cu and Fe absorption and create large amounts of toxic free radicals.

2.4. ROUTES OF HEAVY METAL UPTAKE IN VEGETABLES

Naturally, plants are able to take up metals which are essential and some few others (Hg, Cd, Ni and Pb) which are toxic to them (Singh et al., 2003; Chen et al., 2005, Anim-Gyampo et al., 2012). Many different paths account for the deposit of heavy metals in vegetables. Potentially harmful heavy metals in soils may not come solely from the soil (bedrock), but also from human activities such as solid or liquid waste deposits, agricultural inputs, and fallout of industrial and urban emissions (Wilson and Pyatt, 2007). To an extent, the farmer’s practices also contribute a great percentage of heavy metal uptakes by vegetables. The main routes of heavy metal entry in vegetables are through soil, water and atmospheric depositions.

2.4.1. Soil

Soil has the ability to immobilise introduced chemicals like heavy metal ions. The natural processes of weathering and/ or mining release heavy metals in the soil. The transport of these metals depend on their physicochemical properties (density, conductivity, reactivity) and also on the physicochemical properties of the soil such as pH, organic matter content, clay fraction content, mineralogical composition all of which collectively determine the binding ability of soil (Dube et al., 2001).

Soil has an ability to adsorb, exchange, oxidise, reduce, catalyse and precipitate chemicals and metal ions in particular (Weber, 1991). The metals introduced exist in soil solutions as either free (uncomplexed) metal ions (e.g. $Cd^{2+,}$ $Zn^{2+,}$ Cr^{3+}) in various soluble complexes with inorganic or organic ligands (e.g. $CdSO_4$, $ZnCl^+$, $CdCl^{3-}$) or associated with mobile inorganic and organic colloidal material (McLean et al., 1992). The metals become readily mobile based on their solubility and exchangeable forms or they could be bound within the crystalline lattice structure of clay minerals. Again, the metals are mobile at lower pH but tend to be immobilized at higher pH rates (Wright et al., 2012). The heavy metal levels generally decrease from clay to coarse slit and to rich organic matter soils due to the high surface area of clay minerals and weak pH dependence of cation exchange capacity (Shulten, 2000).

Moreover, agriculture lands have witnessed several residue depositions from the atmosphere and industries especially the mining companies either directly or indirectly. These depositions have caused the elevation of contaminants like heavy metals to increase in the soils. And as much as agricultural organic soils accumulate these heavy metals, a significant correlation is produced in the transfer of these metals from soils to vegetables. Numerous remedies to produce safer and quality vegetables have involved the use of greenhouse vegetable production houses, and even now on soilless greenhouse vegetable productions. This management mode is to limit the excessive application of chemicals like fertilizer and pesticides that would increase plant growth. Coupled to these benefits is the fact that less water (clean water) is used for the crops irrigation purposes. However, this mode of production systems is not found in Ghana, where most vegetables farms are sited near gutters, refuse and other dumping areas owing to the huge cost involved in setting up the greenhouse farms. As such, many vegetables produced have been reported to contain some metals as poisons which pose a health threat to humans (Bempah et al., 2011; Anim-Gyampo et al., 2012).

In a study conducted in the northwest of Thessaloniki, North Greece, Kasassi et al. (2008) found low concentrations of heavy metals in the studied soils samples. The soils were taken from a closed unlined landfill site in heavy industrial area where metal-processing, chemicals, cement, food and wood industries were located. From the drilling depths of 2.5–17.5 m, the sample analyzed using atomic absorption spectrophotometry showed varying results from 0.50–356.25 mg/kg for Cd, Cr, Cu, Ni, Pb and Zn metals. Angelova et al. (2004) also reported that the heavy metal concentrations in the leaves and seeds of fibre crops grown in heavily polluted soils were found lower than those concentrations that were present in the soil. Also, in Romania, from the strongly polluted areas of Copşa Mica, Zlatna and Baia Mare with heavy metals caused by nonferrous ores extraction and processing industry, reports indicated that the heavy metal total contents in the soil had Cd (2.3 times), Cu (1.7 times) and Zn (2.1 times) the maximum allowable limits. It was also clear that the metal levels found in the root vegetables had high Cd (2.5 times) and Pb (11 times), the leafy vegetables had Cd (7 times) and Pb (17 times) above the maximum allowable limits (Lacatuşu et al., 2008).

2.4.2. Water

It is believed that an estimated twenty million hectares in 50 countries worldwide are irrigated with raw or partially treated wastewater and this is likely to increase markedly during the next few decades as water stress intensifies (Hussein et al., 2001; Scott et al., 2004; Hamilton et al., 2007). Wastewaters contain fewer amounts of essential metals and substantial amounts of toxic heavy metals. Heavy metals are transported through wastewaters either as dissolved and/ or as adsorbed substances to suspended solids. The metal levels in these waters increase with a decrease in pH and an increase in salinity because of the competition created between metal and hydrogen ions, and metal and cations respectively, for binding sites (Connell et al., 1984). Therefore free metal ions become released into the water column exhibiting significant effects on wildlife and humans as they cycle in the food chain system.

Accra, has long experienced water shortage for its domestic use and to the large extent, for its agricultural purposes, therefore it is a common practice that majority of vegetable growers use wastewater for irrigation. The effluent from hospitals and other industrial companies containing toxic chemicals and pathogens are channeled through closed gutters untreated. From a survey conducted in Accra Metropolis on this research, it was found that only few vegetable growers used tap water and bore-hole waters, but the majority relied on rainfall, streams, rivers and wastewater from gutters to irrigate their crops. Obuobie et al. (2006) found out that the various irrigation technologies adopted by these farmers for vegetable irrigation included the use of watering cans, buckets, motorized pump and hosepipe, surface and sprinkler systems, with the watering cans commonly used by farmers who cultivate in the valley bottoms of urban Kumasi.

In a study conducted by Arora et al. (2008), it was found out that there was a substantial build-up of heavy metals among vegetables irrigated with water from different sources. Results of his study also highlighted that both adults and children consuming vegetables grown in wastewater-irrigated soils ingest significant amount of these metals although the metal values analyzed were below the tolerable levels. He however requested for the regular monitoring of heavy metals levels from effluents and sewage, in vegetables and in other food materials to prevent excessive build-up of these metals in food produce. As a remedy to curb heavy metal pollution, recent studies have employed the use of microalgae in irrigation waters to remove free metals ions from the water due to their high affinity to sequester (biosorbents) heavy metals (Kumar et al., 2015). Some farmers are being aware of the risks involved in using wastewater for crop production and the application of this microalgae technology could promote safer vegetable production as wastewater treatment is cost effective.

2.4.3. Atmospheric Depositions

Urban growth has brought about an increase in industrial activities which have stirred up atmospheric pollutions concern. Many volatile metals such as Hg, As and Se are released as unwanted gases into the immediate environment from industries. Demirezen and Aksoy (2006) reported higher concentrations for Pb, Cd and Cu in *Abelmoschus esculentus*, which was collected from the urban areas of Kayseri in Turkey as compared those from its rural areas. It is a recommended effort that the EPA agencies have faced out Pb which was previously used in gasoline and contributed to atmospheric metal pollutions. Nonetheless, many farms are sited near highways and are constantly being exposed to atmospheric depositions of metal-aerosols. More so, Accra records heavy vehicular traffic daily, which has increased the rate of poisonous release of gases into the environment and subsequently unto agricultural produce.

Sharma et al. (2008) reported high accumulation of Zn, Cu, Cd and Pb in some selected vegetables in urban India. The report showed that atmospheric deposition contributed to the increased levels of heavy metals in the vegetables with Cu, Cd and Pb posing great health risk to local population via test vegetables consumption. Finally, they concluded that atmospheric depositions elevated the heavy metals levels in vegetables during the marketing processes. Agrawal (2003) also has reports that air pollution may pose a threat to post-harvest vegetables during transportation and marketing, causing elevated levels of heavy metals in vegetables.

2.5. HEAVY METAL TOXICITY

Metal toxicity is classified under toxicology, dose-response relationship and related risk assessments. Also, according to the National Research Council (NRC), four assessment steps are specified for toxicity; hazard identification, exposure assessment, dose/response assessment, and risk characterization (NRC, 1983).

2.5.1. Toxicology

Toxicology is the study of poisons and their effect on biological systems. The target of a toxicant refers to a particular macromolecule, cell, organ, or biochemical process that the toxicant disrupts. A toxicant may not be lethal but may lead to disease, tissue damage, genetic alterations, and cancer. The pathway for the toxicant disruption process is called its mechanism of action (SOT, 2015).

Trace metals toxicology is gathered most easily by determining its acute toxicity, which is the rapid onset of symptoms including death at the extreme limit following the intake of a dose of the substance. Although the acute toxicity of a substance is of interest when one is exposed accidently to pure chemicals, in environmental toxicology one is usually more concerned about chronic (continuous, long-term) exposures at relatively low individual doses of a toxic chemical that is present in the air, water, or the food we eat. The same chemical exposure may lead to acute or chronic effects in the same organism, although usually by different physiological mechanisms. For example, a symptom of acute toxicity in human exposure to methyl mercury could eventually lead to death (Hughes, 1996; Baird and Cann, 2005). US EPA reports have shown that environmental exposure to low levels of Pb cause metabolic disorders and neuropsychological deficits (US EPA, 1986).

2.5.2. Dose – Response Relationship

Dose talks about how much (quantity) of a chemical an organism has been exposed to and the resultant biological effect encountered is called the response. The dose of the substance administered in toxicity tests is usually expressed as the mass of the chemical, usually in milligrams per unit of the test animal's body weight expressed in kilograms, thus giving units of milligrams per kilogram (mg/kg). Also, division by body weight is necessary because the toxicity of a given amount of a substance usually decreases as the size of the individual increases (Hughes, 1996; Baird and Cann, 2005). In most cases, the greater the dose, the greater the response, but this is not always true as dose-response curves take many different shapes. A study in China revealed that the producers of vegetables under different management modes in different facilities had their children at greater health risks due to their exposure to heavy metal contamination than the other residents' children (Chen et al., 2013).

Individuals differ significantly in their susceptibility to a given chemical: some respond to it even at very low doses whereas others require a much higher dose before they respond. For this reason scientists have created dose-response relationships for toxic substances, including environmental agents (Hughes, 1996; Baird and Cann, 2005).

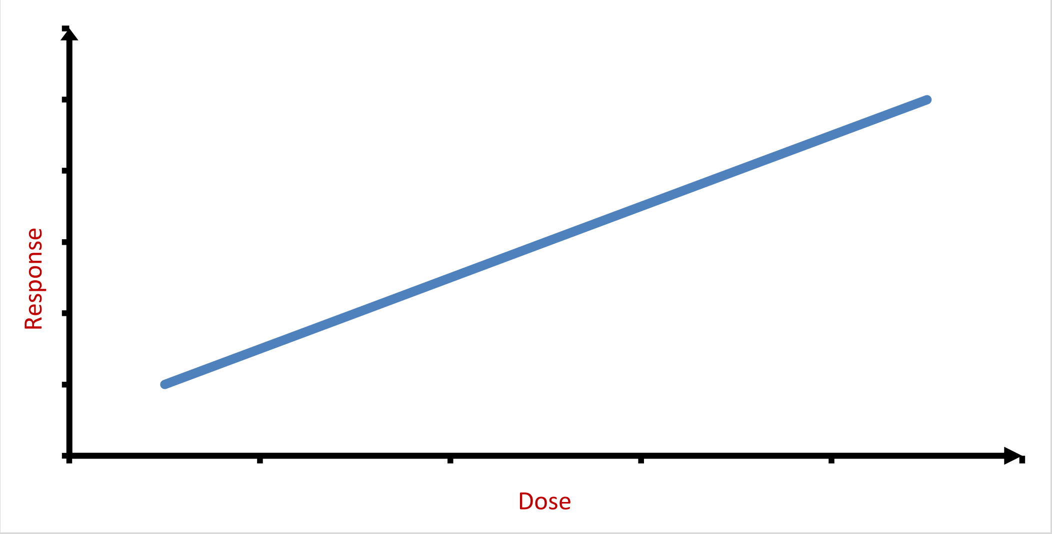

Fig. 2.1. Linear relationship curve between dose and response.

Most often, the response effect on the test animals that is used to construct dose – response curve is death. The dose that proves to be lethal to 50% of the population of the test animals is called the LD_{50} value of the substance under the curve, though it differs among species. The smaller the value of LD_{50}, the more potent (more toxic) the chemical, since less of it is required to affect the animal (Hughes, 1996; Baird and Cann, 2005).

2.5.6. Risk Assessment

This category looks at the impact of contaminants on ecosystem health and it is further implied that a large segment of the "well population" could be suffering from metal poisoning without even realizing it (Nriagu, 1988). General exposure equations are used to calculate for recommended heavy metals levels in humans. The assessment calculations are based on an average daily intake, ADI (mg/kg/day) and hazard quotients (HQ) of individual vegetable consumption (HC, Health Canada, 2004; US EPA, 2007; Mahmood and Malik, 2014; Zhuang et al., 2009).

2.6. ANALYTICAL METHODS FOR HEAVY METAL ANALYSES

Elements in water, soils and vegetables can be determined in the laboratory using the following fixed laboratory assays: the Atomic Absorption Spectroscopy (AAS), Atomic Fluorescence Spectroscopy (AFS), Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Inductively Coupled Plasma-Emission Spectrometry (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X−ray fluorescence (XRF), Electron Microprobe (EM) Flame Photometer (FP) and Instrumental Neutron Activation Analysis (INAA). These instruments accurately measure elements in environmental sample to parts per billion (ppb) concentrations i.e. µg/L and µg/kg samples respectively (Melamed, 2005). Before any element is determined with any of these instruments, pre-treatment with acidic extraction or acidic oxidation digestion of the sample is required. The significance of pre-treatment is that all elemental species is converted into the inorganic form for easier detection and measurement.

2.7. HEAVY METAL STUDIES IN VEGETABLES, GHANA

Studies that ascertain heavy metal contaminations in vegetables have been conducted in the different regions of Ghana. Boamponsem et al. (2012) analyzed for heavy metal contents in vegetables from the mining area of Nagodi, northern Ghana. The work compared heavy metal accumulation in the stems, leaves and roots of lettuce, cabbage and carrot which were irrigated with wastewater (harvested 90 days maximum after planting) from the Nagodi mining site. Using AAS as the analytical tool, Mn was found highest in the stem of lettuce, Fe and Zn were highest in cabbage roots and Cu was highest in carrot roots. Pb was found below detection limit in all the analyzed samples and Cd amounts also below detection limit in cabbage. They concluded that although the vegetables had accumulated some heavy metals, their concentrations were below WHO/FAO recommended limits issuing that it may be safe to consume vegetables cultivated with such wastewater. Another work conducted by Larbie et al. (2014) revealed high levels of Pb and Hg in the mid and outer sections of cabbage as compared to their inner sections from different vegetable farms in Ghana.

Different studies show varying results for heavy metal accumulation in water used for vegetable irrigations. Akrong et al. (2012) analyzed for the quality of irrigation water from different sources used by urban farmers in the Accra Metropolis. Their results showed that the heavy metal concentrations in the water samples were within the FAO/WHO recommended values for irrigation. Lente et al. (2012) also established that the levels of Cd detected in wastewater irrigated vegetables were below their maximum residue limits (MRLs). Pb had high concentrations detection in all samples, with a mean range of 5.6-10.5 mg/kg. However, all the other heavy metals analyzed were stated to be within the recommendations of FAO/WHO values and did not pose any health risks to consumers.

Nonetheless, comparison with similar work done by Odai et al. (2008) in Kumasi had high Pb values ranging from 2.42-13.50 mg/kg. Affum et al. (2008) whose work was referenced by Lente et al. (2012) reported that the high Pb levels detected in Ghana could probably be more attributable to vehicular exhaust fumes (Affum et al. 2008) than to irrigation water or contaminated soils. However, Anim-Gyampo et al. (2012) assessment for heavy metal accumulation in lettuce irrigated with wastewater showed low levels of metal accumulation in the samples. The low level detected for Pb (0.038 mg/kg) was concluded to be due to the low traffic intensity and the less discharge of industrial waste in the Tamale Metropolis than in Kumasi or Accra environs.

Following the review information on heavy metals accumulation in vegetables and their adverse health impacts that may result, it is imperative that this long-term monitoring study of heavy metals in vegetables within Accra Municipality be done, and this dissertation is structured as follows:

- ✓ **Chapter 3** describes the methodology of the study. Captures the site of study, the digestion process, the heavy metal analysis and the assessment tools used for risk analysis.
- ✓ **Chapter 4** presents result of analysis; evaluates results using the statistical tools and discusses these results to expose the effects that may be posed to the consumer whiles presenting a long-term data for comparative and further studies.
- ✓ **Chapter 5** provides a general conclusion and emphasizes the major findings of this study, as well as recommendations for further studies.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 INTRODUCTION

In the Accra Metropolis, vegetable farms are sighted along heavily traffic roads, minor streams and major drainage systems (gutters). The gross industrial activities in many of the suburbs of the Metropolis produce lots of untreated wastewater which are channeled through various drains. The effluents are mostly used for irrigation purposes on the vegetable farms. These farms sites supply bulk of the vegetables in most markets of the Metropolis where consumers obtain their commodities.

3.2. DESCRIPTION OF THE STUDY SITES

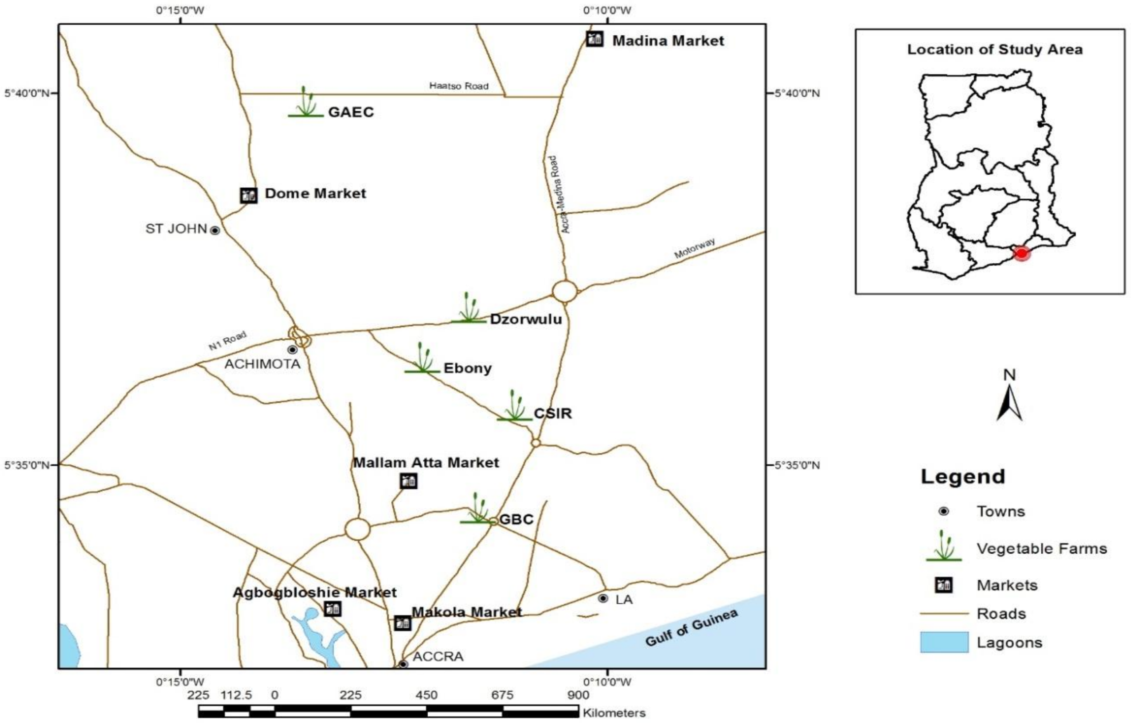

Fig. 3.1. Map showing the geographic areas of the sampling sites within Accra Metropolis.

Accra Metropolis is located in the Greater Accra Region (with total land size of 1.4% of Ghana), and serves as the capital city of Ghana, Fig. 3.1. The Metropolis is located along the southern coast of the region and has an estimated population of 2.27 million as at 2012. It also records two (2) main rainfall patterns, major rainfall from March to June and minor rainfall from September to October. The mean annual rainfall is about 730 mm (Obuobie et al., 2006; Akrong et al., 2012).

The names of the farms are operationally defined and identified with major landmarks within the Metropolis. Ebony site is a medium scale farm located off the Olusegun Obasanjo Road, Fig. 3.1. Vegetable farms are cultivated along the Onyasia stream that flows through the Metropolis. However, this stream contaminated with other effluents from nearby industries, hotels and homes is used for irrigation by the vegetable growers. The soil in this site is black and compact.

The Centre for Scientific and Industrial Research (CSIR) farm is situated close to Alliance Francaise, and off the Kanda Highway. The vegetable farm also stretches along the ends of the Onyasia stream. The farm is a medium scale and soil is loamy.

The third vegetable farm is at Dzorwulu, off the N1 Highway and close to the Royal Fiesta Hotel, all in Accra. The farm is very close to traffic. The agricultural soil is sandy brown and tap water is used for irrigation. This location has no industrial activity.

The Ghana Atomic Energy Commission (GAEC) farm is a large scale one which is located on the Haatso-Kwabenya road. The soil is sandy brown and somewhat laterite in nature. The irrigation source is from a main wastewater drain emanating from various industries and homes around.

The last farm is the Ghana Broadcasting Cooperation (GBC) which is carried out on small scale basis. This farm is located along the 37 Military Hospital to Kwame Nkrumah Circle road. The soil is wet, black and compact. Hand-dug well is used for irrigation.

The markets, Agbogbloshie, Makola, Madina, Dome and Mallam Atta are well-known and very close to these farms which supply bulk of their produce to them in the Metropolis. These markets are the locations where people purchase their vegetables. It is noteworthy to indicate that some supermarkets or restaurants within the Metropolis obtain the vegetables from these farm sites, sometimes also called production sites. Individuals can also buy from these farms.

3.3. QUALITATIVE ASSESSMENT ON VEGETABLE CONSUMPTION

Formal interview and structured questionnaires which were not age and gender biased was used to gather information from vegetable consumers (at study sites and elsewhere). The questionnaire survey presented focus on the consumers' perception of vegetable intake, and or any health benefits or effects associated with their consumption. Information covered was: (1) personal (2) lifestyle (i.e. nutrition) and (3) perception on vegetable production and its safety.

Table 3.1. Overview of the investigative questionnaire covered in and around study sites.

Data Classification	Description
Personal data	Sex; age; marital status; education
Lifestyle	Consumers’ reason for vegetable consumption based either on nutritional or aesthetics; choice of vegetables; how often they are consumed; how long they have been consumed; where the vegetables are bought from; the quantity; knowledge on the benefits or adverse health effects on vegetable consumption
Cultivation, treatment, storage and handling of vegetables	Knowledge about how vegetables are cultivated, its handling and display at the markets, how vegetables are treated prior to eating, and also, about possible contaminants that could render the vegetables unwholesome.

The questionnaires were administered at various locations within the sampling areas as well as places outside the study sites but within the study area. The study objectives were explained to the respondents in the identified areas, and their consent to participate in the study was obtained prior to administration of the questionnaire. The questionnaires and interviews were conducted in English and or translated into local languages easily understood by the respondents with assistance from colleagues. In all a total of 180 people were interviewed cutting across all age groups about their knowledge on vegetable consumption.

3.4. SAMPLE COLLECTION

Vegetables, soil, manure, fertilizer and water were sampled between 2013 and 2014.

3.4.1. Vegetable Sampling

A total of 479 vegetables were sampled from the farm (production) and market sites within the Metropolis. Each vegetable commodity was collected into previously acid-cleaned polypropylene sampling bags and labeled. The samples were thoroughly washed with deionized water (DI) to remove dust and extraneous matter. The edible portion of each vegetable was blended and stored in zip-polyethylene bags and frozen until digestion and analysis.

3.4.2. Soil Sampling

Composite soils (about 1 kg) each was taken from the different agricultural plots within a site. Prior to sampling, the area was cleared to remove surface weed, straws and gravels. The soil was scooped out at a depth of 0-15 cm, using polypropylene spoon into acid-cleaned polypropylene sampling bags and labeled. Fertilizer used and chicken manure from some sites were also taken at 10 cm depth in the piles. The samples were then air-dried, pulverized and sieved to <200 mm and bagged into polyethylene containers.

3.4.3. Water Sampling

Irrigation waters at or along the production sites were collected into acid-cleaned 5 L high density polyethylene (HDPE) bottles. Each bottle was submerged into the water, filled and cupped under the water. This was labeled and brought to the laboratory in cold condition and analyzed within 48 hours.

3.5. SAMPLE PREPARATION AND ANALYSIS

3.5.1. Vegetable Digestion

1 g of each vegetable was digested with 10 ml aqua-regia/$HClO_4$ (1:1 mixture) until the transparent solution appeared. The solutions were then diluted to a 100 ml volume, filtered and analyzed for total metal concentrations using Atomic Absorption Spectrophotometer (AAS).

3.5.2. Digestion of Soil, Fertilizer and Manure

0.5 g each of the soils, manure and fertilizer samples was digested with aqua-regia/$HClO_4$ (1:1 mixture) on a hot plate at 90ºC overnight until the solutions turned pale/light yellow. This was then diluted to a 100 ml volume, filtered and analyzed for total metal concentrations.

3.5.3. Water Samples

3.5.3.1. Water digestion

50 ml each of the water samples were digested with 1 ml acid mixture of HNO_3/$HClO_4$ (2:1 mixture). The solutions were shaken and allowed to stand overnight, filtered and analyzed by Atomic Absorption Spectrophotometer (AAS).

3.5.3.2. Physicochemical parameters of water

Standard methods by American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF), (1998) were used to examine the physicochemical parameters of the different irrigation waters.

a. Physical Parameters

pH and Electrical Conductivity (EC)

Water pH and EC were measured by the Mettler Toledo (MP 220) pH meter and the PHYWE (13701.93) conductivity meter respectively. Each instrument was calibrated prior to usage.

Total Suspended Solids (TSS)

TSS was determined by gravimetry. Water samples (250 ml) were vacuum filtered with 0.45 µm pore size filter paper. The filter paper with the solids was dried in an electrical oven at a temperature of 104ºC and cooled. TSS was reported as mg/L.

Total Dissolved Solids (TDS)

The HACH DR 2800 ultra-violet (UV) spectrophotometer was calibrated and used to measure the total dissolved solids. The required Permachem Reagents pillows were used for the analysis. TDS was reported as mg/L.

b. Determination of Anions (mg/L)

Sulphates, Phosphates and Nitrates (mg/L)

The HACH DR 2800 ultra-violet (UV) spectrophotometer was calibrated and used to measure sulphates (SO_4^{2-}), phosphates (PO_4^{3-}) and nitrates (NO_3^-).

Chloride ions (mg/L)

The Mohr Method which uses silver nitrate (AgNO3) for titration (0.02M) was used to determine chloride (Cl^-) in each sample.

Total Alkalinity (mg/L)

The total alkalinity and bicarbonate ions (HCO_3^-) were measured by volumetric titration (25 ml) employing a standard 0.2 M H_2SO_4 and expressed as mg/L $CaCO_3$.

c. Cations Analysis

Water Hardness (mg/L)

Total hardness, calcium (Ca^{2+}) and magnesium (Mg^{2+}) hardness were estimated titrimetrically using 0.01M ethylenediaminetetraacetic acid (EDTA) and ammonium buffer (pH 10.0) for each water sample (25 ml).

3.6. QUALITY ASSURANCE AND QUALITY CONTROL

Appropriate procedures and precautions were taken to ensure reliability of the results. Deionized water was used throughout the study. 20% HNO_3 was used to clean glassware and HDPE bottles and the reagents were of analytical grade. Standards were prepared for each metal from their stock solution to calibrate the AAS instrument. Replicate analyses were done with reagent blanks and standards after every ten (10) sample measurement to ensure precision and accuracy of the analytical results. For validation of the analytical procedure, standard reference materials (SRM) were obtained from the International Atomic Energy Agency (IAEA) for soil (IAEA/SL3) and the National Institute of Standard and Technology (NIST) for plant (SRM-1570). The recovery rates ranged from 80-110% for all elements.

3.7. DATA ANALYSIS

3.7.1. Bio-accumulation Factor (BAF)

Heavy metal concentrations of soils and crops were calculated on fresh weight basis. The bio-accumulation factor or transfer factor (TF) expressed the ability of the vegetable to accumulate a particular heavy metal with respect to its concentration in the soil. The factor was calculated as,

$$BAF = \frac{C_{veg}}{C_{soil}}$$

where,

C_{veg} is the heavy metal concentration in vegetables and C_{soil} is the heavy metal concentration in soils (Zhuang et al., 2009).

3.7.2. Risk Assessment on Heavy Metal Intake

Average Daily Intake (ADI)

The average daily intake (ADI) estimated how much of the metal was consumed daily and depended on both the metal concentration in vegetable and the quantity consumed of the respective vegetable. ADI was calculated in (mg/kg/day) as:

$$ADI = \frac{C_{veg} \times IR_{veg}}{BW}$$

where,

C_{veg} is the heavy metal concentration in vegetables (mg/kg, on fresh weight basis), IR_{veg} is the ingestion rate or the daily average consumption of vegetables (kg/day) and BW is the body weight of the exposed individual (kg) (Zhuang et al., 2009). Table 3.2 gives the different ingestion rates of the vegetables consumed in Ghana. However, the ingestion rates of cabbage and lettuce were adopted from India and Uganda respectively. The BW of an adult Ghanaian was estimated as 60 kg (above 18 years), 30 kg (7-13 years) and 15 kg (0-6 years).

Table 3.2. Ingestion rates of vegetables.

Vegetables	**Adult (kg/day)**	**Children (kg/day)**	**References**
Cabbage	0.345	0.232	Arora et al., 2008
Carrot	0.1373	0.1373	Ruel et al., 2005
Cucumber	0.1373	0.1373	Ruel et al., 2005
Green pepper	0.1373	0.1373	Ruel et al., 2005
Lettuce	0.182	0.118	Nabulo et al., 2012

Hazard Quotient (HQ)

The health risks from consumption of vegetables by the consumers were assessed based on the hazard quotient (HQ). The HQ is a ratio of determined dose of a pollutant to a reference dose level. The HQ expressed the non-carcinogenic risks or the level of human exposure associated with the consumption of contaminated vegetables. If the HQ value was less than 1, the exposed population was unlikely to experience obvious adverse effects during life time (Mahmood and Malik, 2014; Zhuang et al., 2009).

$$HQ = \frac{ADI}{RfD}$$

where,

ADI (mg/kg) is the average daily intake of heavy metals and RfD is the oral reference dose(mg/kg); which is regarded as an estimation of a daily exposure of the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA, 2007, Hu et al. 2013).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

The consumption of vegetables has increased lately among the Ghanaian population because they contain some essential nutrients needed by man to fight against certain diseases. However, there is a global concern for their consumption as the vegetables could be contaminated with some heavy metals which are a threat to human life. Accordingly there is the need for continuous and regular monitoring programmes that would ensure that the levels of these metals in vegetables do comply with existing regulations and present appropriate measures to safeguard the health of the consuming populace. The combination of monitoring data with food consumption data provides exposure estimate that can be used in toxicological appreciation.

In this study, a total of 479 vegetables were purchased from the listed production and market sites and analyzed. The highest number of samples (12.53%) each was obtained from Makola, Madina, Dome and Mallam Attah, Table 4.1. The least was from GBC (3.55%).

Table 4.1. Vegetable distribution between farm and market sites.

Sites		Cabbage	Carrot	Cucumber	Green pepper	Lettuce	Total	%
Farm	**Ebony**	6	10	12	12	11	51	**10.65**
	CSIR	12	6	6	8	12	44	**9.19**
	Dzorwulu	6	6	6	12	11	41	**8.56**
	GAEC	12	6	0	12	10	40	**8.35**
	GBC	0	0	0	5	12	17	**3.55**
Market	**Agbogbloshie**	12	12	6	4	12	46	**9.60**
	Makola	12	12	12	12	12	60	**12.53**
	Madina	12	12	12	12	12	60	**12.53**
	Dome	12	12	12	12	12	60	**12.53**
	Mallam Atta	12	12	12	12	12	60	**12.53**
	Total	**96**	**88**	**78**	**101**	**116**	**479**	**100.0**

4.1. STATISTICAL DISTRIBUTION OF HEAVY METALS IN VEGETABLES

4.1.1. Percent of vegetables with heavy metals

Table 4.2 presents the overall statistical distribution of heavy metals levels in vegetables during the monitoring program between 2013 and 2014. The Table also summarizes the number of vegetables analyzed for each year as well as the percent of vegetables that contained heavy metal contaminants and the percent that were higher than EU limits. The results revealed that more vegetables exceeded the EU limits in 2013 (84.62%) than 2014 (75.65%). All the vegetables gave at least one positive metal detections with 18.99% below the EU limits. Likewise, 388 vegetables contained metal levels above the EU safe values.

Table 4.2. Summary of vegetables analyzed in this study from 2013 to 2014 as percent of positive detection.

Year	No. of samples analyzed	No. of samples with no metal detection	%	No. of samples with detection ≤ EU limits	%	No. of samples with detection ≥ EU limits	%
2013	286	0	**0**	44	**15.38**	242	**84.62**
2014	193	0	**0**	47	**24.35**	146	**75.65**
Total	**479**	**0**	**0**	**91**	**18.99**	**388**	**81.0**

Table 4.3 on the other hand, gives the number of vegetables analyzed from each site with metal detections either above or below the EU recommendations. The contaminants at or below the safe limits were found in 91 vegetables (18.99%) for all the sites. Among the production sites, 42 (82.35%) and 35 (79.55%) samples from Ebony and CSIR respectively, contained at least one trace metal above the EU guidelines. The GBC site had the least number of commodities with all its 17 (100%) samples having two (2) or more heavy metals above EU recommendations. On the

contrary, vegetables from the market sites contained the highest number of metal contaminants exceeding their EU safe limits. Vegetables from Mallam Attah recorded the highest metal contamination (100%) whereas Dome and Makola had 86.67% and 90.0% greater than EU limits accordingly.

Table 4.3. Summary of number of detections from the selected production and market sites in the Municipality between 2013 and 2014.

Sites	**No. of samples analyzed**	**No. of samples with no metal detection**	**%**	**No. of samples with detection ≤ EU limits**	**%**	**No. of samples with detection ≥ EU limits**	**%**
Ebony	51	0	0	9	17.65	42	**82.35**
CSIR	44	0	0	9	20.45	35	**79.55**
Dzorwulu	41	0	0	17	41.46	24	**58.54**
GAEC	40	0	0	12	30.0	28	**70.0**
GBC	17	0	0	0	0	17	**100.0**
Agbogbloshie	46	0	0	13	28.26	33	**71.74**
Makola	60	0	0	6	10.0	54	**90.0**
Madina	60	0	0	17	28.33	43	**71.67**
Dome	60	0	0	8	13.33	52	**86.67**
Mallam Atta	60	0	0	0	0	60	**100.0**
Total	**479**	**0**	**0**	**91**	**18.99**	**388**	**81.0**

These exceedances in most cases were observed in market products due to contaminations which might occur between harvesting, conveyance and selling of these commodities at the market centers. Likewise, the numbers of vegetables with metal detection below EU values were few, suggesting that bad agricultural practices could be in place in some of the production areas.

Table 4.4 presents the percent violation of each vegetable studied. The largest percent of violations occurred in lettuce (97.41%) while cucumber had the least percent (67.95%). The violation for lettuce could arise from its high transpiration rate and large surface area that enhance its continuous metal intake from the soil/environment (Mahmood and Malik, 2014). Besides, many of these farmers have little or no education and receive limited technical support, thus do not read the chemical labels or understand their contents. More so, there could be non-compliance by farmers in the application of agrochemicals before crop maturity. Likewise carrot and green pepper had over 70% of metal violation(s) with 25.74% (green pepper) lower than EU limits.

Table 4.4. Number of vegetable samples analyzed and percentage of detection and violation.

Vegetables	**No. of samples analyzed**	**Detection ≤ EU recommendations**		**Violation against EU recommendations**	
		No. of samples	**%**	**No. of samples**	**%**
Cabbage	96	13	**13.54**	83	**86.46**
Carrot	88	24	**27.27**	64	**72.73**
Cucumber	78	25	**32.05**	53	**67.95**
Green pepper	101	26	**25.74**	75	**74.26**
Lettuce	116	3	**2.59**	113	**97.41**

The overall percentage exceedance for all the vegetables between 2013 and 2014 was 81.0%, Table 4.5. The highest percentage exceedance was from GBC and Mallam Attah (100%)

whereas Dzorwulu recorded the lowest (58.54%). However, Mallam Attah showed higher levels of percentage exceedance of all vegetables samples. Cucumber which had the least percent violation was not found in GBC and GAEC sites. Obviously, vegetables from the markets sites contributed the largest percentage exceedances.

Table 4.5. Percentage exceedance of vegetables among the various sites between 2013 and 2014.

Sites	Vegetables						
	Cabbage	Carrot	Cucumber	Green pepper	Lettuce	Total	%
Ebony	5	7	6	12	12	42	**82.35**
CSIR	6	6	4	7	12	35	**79.55**
Dzorwulu	6	6	3	0	9	24	**58.54**
GAEC	6	4	0	6	12	28	**70.0**
GBC	0	0	0	5	12	17	**100.0**
Agbogbloshie	12	0	9	0	12	33	**71.74**
Makola	12	12	6	12	12	54	**90.0**
Madina	12	6	6	9	10	43	**71.67**
Dome	12	11	7	12	10	52	**86.67**
Mallam Atta	12	12	12	12	12	60	**100.0**
Total	83	64	53	75	113	**388**	**81.0**
%	**86.46**	**72.73**	**67.95**	**74.26**	**97.41**	**81.0**	

4.1.2. Multiple metal detections in vegetables

With regard to this, several vegetables were found to contain many metal contaminants. In all a total of 2,298 heavy metals were found in 479 samples, Table 4.6. A maximum of ten (10) metals were obtained in lettuce from Mallam Attah. Samples registering only (5) heavy metals (21.29%) in 102 samples were the most predominant. As many as 36 samples had only two (2) different metals present. Most of the vegetables analyzed contained at least two (2) or more metals, however carrot had the greatest multiple detection in thirty (30) samples.

Table 4.6. Number of heavy metals detected in each vegetable.

Vegetables	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Total**
Cabbage	0	12	24	6	18	6	12	18	0	0	**96**
Carrot	0	0	10	24	30	18	0	6	0	0	**88**
Cucumber	0	6	24	18	18	12	0	0	0	0	**78**
Green pepper	0	6	30	32	12	15	0	6	0	0	**101**
Lettuce	0	12	24	0	24	12	12	20	6	6	**116**
Total	0	36	112	80	102	63	24	50	6	6	**479**
%	**0**	**7.52**	**23.38**	**16.70**	**21.29**	**13.15**	**5.01**	**10.44**	**1.25**	**1.25**	

Heavy metal levels were detected in all 479 vegetables analyzed and each vegetable had more than one (1) metal present. The results also demonstrated that leafy and fleshy vegetables registered more metal contaminations than the others.

4.2. CONCENTRATION OF HEAVY METALS IN SOIL

The concentrations of heavy metals (mg/kg) in agricultural soil sampled from the different farm sites are presented in Table 4.7. In general, the metal concentrations decreased from Mn>Fe>As>Cr>Zn>Co>Cu>Pb>Cd and GAEC>CSIR>Ebony>Dzorwulu>GBC among the farm sites. The concentrations ranged from a minimum of 0.78 at GBC to a maximum of 24.2 at Dzorwulu for As, 0.1 at Ebony to 2.86 at GAEC for Cd, 0.2 at Ebony to 8.43 at CSIR for Co, 1.4 at Ebony to 11.57 at GAEC for Cr, 0.11 to 8.5 both at GAEC for Cu, 94.28 at GBC to 230.1 at GAEC for Fe, 22.75 at GBC to 648.37 at CSIR for Mn, 0.4 at CSIR to 3.8 at GAEC for Pb and 1.96 at GBC to 8.16 at GAEC for Zn. All the metal concentrations measured (except As 24.2 mg/kg at Dzorwulu site) were below the EU recommendations for heavy metals in agricultural soils.

From the study, Pb was measured in irrigation water (0.18 mg/kg) at GAEC during the dry season. This indicated that the Pb level in the soil (2.75 mg/kg) was probably increased by the addition of the irrigation water. Likewise, the highest values of Cd, Cr and Fe (2.86, 11.57 and 230.1 mg/kg respectively) were also measured at this site. This increase could be due to abandoned old batteries, radios and other electronic gadgets found lying haphazardly on the farm.

CSIR and Ebony farms are located along the Onyasia stream in Accra Metropolis, Ghana. This stream serves as a source of irrigation water for the vegetables grown in these sites. The farms here are again exposed to vehicular emissions and other atmospheric depositions from the surroundings. Ebony farm is close to an abandoned railway station which is now a working site

Table 4.7. Concentrations of heavy metals (mean ±SD, mg/kg) in the agricultural soils.

Sites	Seasons	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ebony	Wet	3.8±0.0	0.19±0.0	0.2±0.0	5.0±0.0	2.1±0.10	210.72±0.0	145.6±0	ND	3.6±0.0	5.4±0.0
	Dry	0.8±0.0	0.1±0.1	ND	1.4±0.0	0.16±0.1	192.5±0.1	116.0±0.0	ND	2.3±0.0	3.0±0.0
CSIR	Wet	2.04±0.0	1.7±0.1	8.43±0.0	2.86±0.0	1.0±0.0	195.41±0.0	648.37±0.0	ND	1.0±0.0	4.49±0.0
	Dry	20.0±0.0	0.4±0.1	1.6±0.1	2.94±0.0	0.73±0.02	200.77±0.0	70.19±0.0	ND	0.4±0.1	4.12±0.0
Dzorwulu	Wet	24.2±0.0	0.98±0.0	1.23±0.2	5.2±0.1	12.62±0	204.24±0.0	63.0±0	ND	2.3±0.1	2.4±0.1
	Dry	13.67±0.0	ND	ND	5.1±0.0	3.7±0.0	210.12±0.0	74.08±0.0	ND	2.1±0.0	8.16±0.0
GAEC	Wet	2.75±0.0	2.86±0	5.03±0.0	11.57±0.0	8.5±0.0	230.1±0.0	123.53±0.3	ND	3.8±0.0	2.16±0.0
	Dry	9.61±0.0	0.76±0.0	2.0±0.2	4.51±0.0	0.11±0.0	209.41±0.0	133.14±0.0	ND	2.75±0.0	3.14±0.0
GBC	Wet	0.78±0.0	1.2±0.0	ND	ND	0.4±0.0	94.28±0.0	22.75±0.0	ND	0.5±0.2	1.96±0.0
	Dry	13.8±0.0	1.0±0.0	ND	ND	0.2±0.2	149.48±0.0	25.8±0.0	ND	ND	3.2±0.0
EU, 2002		**20.0**	**3.0**	**50.0**	**100.0**	**100.0**	**50000.0**	**2000.0**	**50.0**	**100.0**	**300.0**

for metallic waste and scrap dealers. The metal analysis of the Onyasia stream revealed the presence of some metals that might have added to the already existing levels in the soils. In accordance, relatively high concentrations of As (0.8-20.0), Cd (0.1-1.7), Co (0.2-8.43), Cr (1.4-5.0), Cu (0.16-2.1) and Pb (0.4-3.6 mg/kg) were measured in the soils from these sites. However, all the concentrations were below the EU guideline values for metals in soil, except As (20.0 mg/kg) at CSIR, which was similar to the specifications.

On the contrary, Dzorwulu and GBC used tap water and hand dug-well respectively for irrigation. Consequently, it was not surprising that these sites recorded the least metal contaminations in the agricultural soils except As at Dzorwulu (24.2 mg/kg). Moreover, the sources of metal contaminations in the soils other than being natural deposits were recognized from the high use of agrochemicals. Furthermore, the elevated As concentrations (0.78-24.2 mg/kg) at these sites arose from the irrigation waters employed, where As is a known cause of underground water poisoning (WHO, 2007). However, in a similar study, Akrong et al. (2012) reported higher values of Fe (17200-32400), Mn (202-836) and Zn (41.3-107.0 mg/kg) compared to Fe (210.12-204.24), Mn (74.08-63) and Zn (2.4-8.16 mg/kg) observed in this study.

Additionally, the application of fertilizer and manure on soil and vegetables by farmers in their bid to increase crop yield and control diseases and pest could elevate some metal levels in the soil and vegetables. Table 4.8 expresses the metal concentrations of fertilizer and chicken manure samples studied from the sites. The components of many fertilizer products contain phosphate linked metals such as As, Cd and Pb at varying concentrations. All the same, only As, Cu, Fe, Mn and Zn metals were evaluated in these agrochemicals which possibly influenced their levels in the soils. The fertilizer contained As (9.2), Fe (37.66), Mn (40.8) and Zn (32.2 mg/kg) whereas the manure had relatively lower quantities of As (2.04) and Zn (26.94 mg/kg) and higher values for Cu (7.94), Fe (118.57) and Mn (118.57 mg/kg).

More so, the geographical environs of a particular land could influence its metal concentrations. Anim-Gyampo et al. (2012) measured lower levels of Cd (0.030-0.036), Cu (0.030-0.036), Fe (170-196), Mn (5.24-12.76), Pb (0.020-0.106) and Zn (0.154-0.205 mg/kg) in soil sampled from the Tamale Municipality. However, in this work, the metal concentrations studied had ranges shown: Cd (0.10-2.86), Cu (0.11-8.50), Fe (94.28-230.1), Mn (22.75-648.37), Pb (0.40-3.80) and Zn (1.96-5.4 mg/kg). This could be so because the farmers in this Metropolis employ copious amounts of agrochemicals on the farms than those from northern Ghana. Besides, the city records high industrial and vehicular discharges, possibly of high metal content that could have deposited in the environment, hence contaminate soils.

The levels of Ni were undetected in all the soil analyzed. Although heavy metals are natural deposits in soil, significant contributions in these soils could arise from the irrigation wastewaters, agrochemicals and some metal deposits from the atmosphere. In general, the metal levels evaluated in wet season (except As, Fe and Zn) were higher than dry period. The reason could be that during the wet period, the rains and its runoffs contained some metals that added up to the existing ones. Besides, these farms witness the dumping of refuse and other old electronic gadgets of metal parts which could sink into soil to influence its levels.

Table 4.8. Concentrations of heavy metals (mg/kg, mean ±SD) in fertilizer and manure.

Samples	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Fertilizer	9.2±0.0	ND	ND	ND	ND	37.66±0.0	40.8±0.1	ND	ND	32.2±0.1
Manure	2.04±0.0	ND	ND	ND	7.96±0.0	118.57±0.0	118.57±0.0	ND	ND	26.94±0.0

4.3. CONCENTRATIONS OF HEAVY METALS IN VEGETABLES FROM FARMS

The concentrations of heavy metals (on fresh weight basis) in vegetables were measured at the farm sites for the wet and dry seasons. The metal levels present in the vegetables varied among different vegetables, sites and seasons.

Within the farm sites, the metal concentration decreased from Ebony>CSIR>Dzorwulu>GAEC>GBC and Fe>Cu>Mn>Pb>Zn>Co>Cd>As during the wet season, Table 4.9. The concentration of Fe in the vegetables varied from 0.6-84.6, 0.6-7.4 for Cu, 1.1-6.2 for Mn, 0.2-3.8 for Pb, 0.3-3.1 for Zn, 0.9-2.3 for Co, 0.3-1.7 for Cd and 0.1-0.4 mg/kg for As. The mean concentrations of the metals in cabbage, carrot, cucumber, green pepper and lettuce respectively, ranged from a minimum of 0.6 at Dzorwulu to a maximum of 2.5 at CSIR, 0.1 to 13.6 both at Ebony, 0.4 to 5.4 at Ebony, 0.2 at GAEC to 2.5 at Ebony and 0.2 at GBC to 84.6 mg/kg at Ebony. Cr and Ni were undetected in all the vegetables, however, the levels of Cd and Pb (except in green pepper at GAEC) exceeded the EU safe limits.

In the dry season, these metals decreased from GAEC>CSIR>Dorwulu>Ebony>GBC among the different locations, Table 4.10. However, only four (4) metals were detected in the vegetables and decreased from As>Mn>Fe>Zn. The concentration of As ranged from 1.1-7.23, 0.8-3.3 for Fe, 0.3-4.0 for Mn and 0.7-1.77 mg/kg for Zn. The metal levels in cabbage, carrot, cucumber, green pepper and lettuce respectively, ranged from a minimum of 0.5 at CSIR to a maximum of 6.53 Ebony, 0.4 at Ebony to 7.13 at GAEC, 0.3 at CSIR to 4.12 at Dzorwulu, 0.3 at GAEC to 7.23 at CSIR and 0.98 at CSIR to 6.6 mg/kg at GBC.

Table 4.9. Heavy metal concentrations in vegetables (mean ±SD, mg/kg, on fresh weight basis) from farm sites, wet season.

Sites	Vegetables	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
	Cabbage	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ebony	Carrot	0.1±0.0	0.5±0.0	ND	ND	ND	13.6±0	ND	ND	1.8±0.1	1.1±0.0
	Cucumber	ND	ND	ND	ND	ND	5.4±0.0	ND	ND	3.8±0.0	0.4±0.0
	Green Pepper	ND	1.7±0.0	ND	ND	0.6±0.0	2.0±0.1	ND	ND	2.5±0.0	1.5±0.0
	Lettuce	0.4±0.1	0.3±0.1	ND	ND	ND	84.6±0.0	1.4±0.141	ND	ND	1.4±0.3
	Cabbage	ND	ND	1.9±0.0	ND	ND	2.5±0.0	ND	ND	ND	ND
CSIR	Carrot	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Cucumber	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Green Pepper	ND	0.8±0.0	0.9±0.0	ND	0.6±0.0	1.4±0.0	ND	ND	ND	0.9±0.0
	Lettuce	0.3±0.0	0.5±0.1	1.2±0.0	ND	0.7±0.0	72.6±0.1	3.9±0.1	ND	0.6±0.0	0.6±0.1
	Cabbage	ND	1.0±0.0	ND	ND	ND	0.6±0.0	ND	ND	ND	1.0±0.0
Dzorwulu	Carrot	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Cucumber	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Green Pepper	ND	ND	ND	ND	1.6±0.0	1.3±0.0	ND	ND	ND	0.8±0.1
	Lettuce	0.3±0.1	ND	1.6±0.0	ND	7.4±0.0	66.0±1.4	2.2±0.1	ND	1.6±0.1	3.1±0.1
	Cabbage	ND	ND	ND	ND	ND	1.3±0.141	ND	ND	1.1±0.0	0.9±0.0
GAEC	Carrot	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Cucumber	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Green Pepper	ND	ND	ND	ND	1.0±0.0	ND	ND	ND	0.2±0.1	0.3±0.1
	Lettuce	0.3±0.0	1.1±0.1	2.3±0.3	ND	0.9±0.0	40.3±0.2	6.2±0.3	ND	ND	1.0±0.0
	Cabbage	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

GBC	Carrot	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Cucumber	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Green Pepper	ND	ND	ND	ND	ND	2.0±0.1	ND	ND	1.2±0.1	0.6±0.1
	Lettuce	0.2±0.0	0.8±0.1	ND	ND	ND	17.0±0.2	1.1±0.0	ND	1.2±0.1	2.0±0.0
EU, 2007		**0.2**	**0.2**	**50.0**	**1.0**	**20.0**	**500.0**	**500.0**	**50.0**	**0.4**	**50.0**

Table 4.10. Heavy metal concentrations in vegetables (mean ±SD, mg/kg, on fresh weight basis) from farm sites, dry season.

Sites	Vegetables	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ebony	Cabbage	6.53±0.0	ND	ND	ND	ND	ND	0.60±0.0	ND	ND	1.20±0.0
	Carrot	1.10±0.0	ND	ND	ND	ND	1.40±0.3	0.40±0.0	ND	ND	1.40±0.1
	Cucumber	ND	ND	ND	ND	ND	ND	0.50±0.0	ND	ND	0.90±0.0
	Green Pepper	2.94±0.0	ND	ND	ND	ND	1.30±0.0	1.30±0.0	ND	ND	0.98±0.0
	Lettuce	1.88±0.0	ND	ND	ND	ND	ND	0.30±0.0	ND	ND	0.99±0.0
CSIR	Cabbage	2.48±0.0	ND	ND	ND	ND	ND	0.50±0.0	ND	ND	1.10±0.0
	Carrot	4.55±0.0	ND	ND	ND	ND	ND	1.50±0.0	ND	ND	1.09±0.0
	Cucumber	3.86±0.0	ND	ND	ND	ND	ND	0.30±0.0	ND	ND	0.70±0.0
	Green Pepper	7.23±0.0	ND	ND	ND	ND	ND	0.40±0.0	ND	ND	1.50±0.0
	Lettuce	4.22±0.0	ND	ND	ND	ND	ND	1.60±0.0	ND	ND	0.98±0.0
Dzorwulu	Cabbage	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Carrot	3.90±0.0	ND	ND	ND	ND	0.80±0.0	0.70±0.0	ND	ND	0.80±0.0
	Cucumber	4.12±0.0	ND	ND	ND	ND	ND	0.40±0.0	ND	ND	0.98±0.0
	Green Pepper	ND	ND	ND	ND	ND	ND	0.60±0.1	ND	ND	1.30±0.0
	Lettuce	ND	ND	ND	ND	ND	ND	2.50±0.0	ND	ND	1.28±0.0
GAEC	Cabbage	ND	ND	ND	ND	ND	ND	0.80±0.0	ND	ND	1.40±0.0
	Carrot	7.13±0.0	ND	ND	ND	ND	ND	0.60±0.0	ND	ND	1.39±0.0

	Cucumber	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Green Pepper	4.02±0.0	ND	ND	ND	ND	3.30±0.0	0.30±0.0	ND	ND	0.59±0.0
	Lettuce	5.00±0.0	ND	ND	ND	ND	ND	4.00±0.0	ND	ND	1.77±0.0
GBC	Cabbage	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Carrot	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Cucumber	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Green Pepper	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Lettuce	6.60±0.0	ND	ND	ND	ND	ND	ND	ND	ND	1.70±0.0
EU, 2007		**0.2**	**0.2**	**50.0**	**1.0**	**20.0**	**500.0**	**500.0**	**50.0**	**0.4**	**50.0**

However, in another work, Amoah et al., (2014), reported high levels of these metals in cabbage, green pepper and lettuce (Zn recorded 5.1-10.6, 2.6-8.1 for Cu, 5.6-10.5 for Pb, 0.01-0.5 for Cd, 0.2-1.5 for Co and 1.1 mg/kg for Cr). Documentation has it that, the concentrations of toxic elements vary amongst locations and are affected by various factors of the environment and human interactions (WHO, 2006; Anim-Gyampo et al., 2012). Therefore, the low metal concentrations recorded in this study may pertain to the different study locations and sampling periods. Cd, Co, Cr, Cu, Ni and Pb were however below detection limits in the samples measured.

Although the metal levels in the irrigation waters and soils were relatively high during the dry season, the vegetables proved otherwise except for As (6.53 mg/kg in cabbage in the dry season and 0.4 mg/kg in lettuce in the wet season). This observed trend may be related to the continuous and excessive applications of fertilizers and organic manures on plantations during this season. For agricultural benefits, vegetables need to be fertilized. All the same the practical thing is to apply agrochemicals three (3) weeks before maturity, some farmers do the application only as late as a week to maturity, in their bid to fight diseases and enhance growth. Also, the observations gathered during sampling revealed that the labourers carelessly sprayed or dropped these chemicals on the vegetables directly instead of being applied at a distance, subsequently enhancing the uptake and/ accumulation of any present metal in the agrochemicals.

The concentrations of heavy metals were generally higher in vegetables from Ebony, GAEC and CSIR, which are located in areas of industrial activities, where effluents from these industries are used for irrigation. Again, all production sites were close to roads of heavy traffics which emit gases of toxic metals like Pb and Cd. The levels of Pb and Cd measured in all the vegetables were above the EU safe limits. Pb was high in cucumber, then lettuce and lastly in carrot; Cd was high in green pepper, followed by lettuce and then carrot; Zn was also high in lettuce, followed by green pepper and then cabbage. The highest Pb (3.8 mg/kg) was measured in cucumber and Cd (1.7 mg/kg) in green pepper at Ebony. This elevation can be attributed to the high use of fertilizer; excessive contamination of the wastewater for irrigation; and the sites closeness to a metal scrap yard where there could be possible wash off of metals onto the farms. However, essential metals such as Fe, Mn and Zn measured were far below their recommendations in vegetables.

Variably, Anim-Gyampo et al. (2012) however measured very low levels of Pb (0.002-0.038 mg/kg) in lettuce in the Tamale Municipality than in this location, where the Pb ranged from 0.2 to 3.8 mg/kg. This could be ascribed to the existence of few industries and low traffic emissions in the municipality. The heavy metal concentrations were higher in lettuce and green pepper than in carrots and cucumber.

4.4. CONCENTRATIONS OF HEAVY METALS IN VEGETABLES FROM MARKETS.

Within the market sites, the metal concentrations decreased from MA>DM>AG>MK>MD, as defined in Table 4.11 and Fe>Zn>Mn>Cu>Pb>As>Co>Cd>Cr>Ni for the wet season. The concentration of Fe ranged from 1.04 in cucumber at MK to 93.46 in lettuce at MA, 0.63 in carrot at AG to 15.42 in cabbage at MA for Zn, 0.12 in green pepper at AG to 5.14 in cabbage at MA for Pb, 0.27 in carrot at DM to 0.54 in green pepper at MD for Ni, 1.04 in green pepper at MD to 13.46 in green pepper at AG for Cu, 0.12 in lettuce at MA to 2.99 in lettuce at MD for Cr, 0.13 in lettuce to 1.83 in cabbage at DM for Co, 0.11 in lettuce and cabbage to 0.63 in cucumber at MA for Cd and 0.07 in lettuce at MA to 1.95 mg/kg in lettuce at MD.

Also, the concentrations decreased from MK>AG>DM>MA>MD and Pb>Fe>Mn>Co>Zn>Cd>Cu>As>Cr in the dry season, Table 4.12. The range in concentrations were from 0.1-0.3 for As, 0.3-1.9 for Cd, 0.9-2.2 for Co, 0.2-0.3 for Cr, 1.0-4.8 for Fe, 0.2-3.7 for Mn, 1.7-15.7 for Pb, 0.2-1.7 for Zn and 1.1 for Cu in lettuce only. These carcinogenic metals; Pb and Cd exceeded the EU safe limits of heavy metals in all the vegetables. The highest value of Pb (15.7 mg/kg) was measured in green pepper at MA.

In general, the metal concentrations in the vegetables were higher in the wet than the dry periods. The reason could be that there were more runoffs of high metal contents that were used in vegetable irrigation. Moreover, some humid conditions from industrial and market activities during the season could cause most metals to be suspended in the air, which later drop on these vegetables to increase their levels.

Table 4.11. Heavy metal concentrations in vegetables (mean ±SD, mg/kg, on fresh weight basis) from market sites, wet season.

Sites	Vegetables	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Agbogbloshie (AG)	Cabbage	0.30±0.0	ND	ND	ND	ND	3.36±0.1	1.21±0.1	ND	0.64±0.1	1.62±0.
	Carrot	0.10±0.0	ND	ND	ND	1.10±0.0	1.24±0.0	1.00±0.0	ND	ND	0.63±0.1
	Cucumber	ND	ND	0.19±0.1	ND	1.66±0.2	4.45±0.0	0.92±0.1	1.53±0.0	ND	2.35±0.2
	Green Pepper	ND	ND	ND	2.03±0.1	13.46±0.3	2.51±0.1	1.81±0.0	ND	0.12±0.1	3.54±0.0
	Lettuce	0.13±0.0	0.43±0.0	0.70±0.0	ND	ND	6.88±0.0	1.42±0.0	ND	0.79±0.1	2.33±9.0
Makola (MK)	Cabbage	0.11±0.1	ND	ND	ND	ND	5.26±0.1	1.1±0.1	ND	0.65±0.2	2.17±0.1
	Carrot	0.30±0.1	ND	0.13±0.0	ND	ND	4.49±0.0	1.32±0.1	ND	0.28±0.0	2.46±0.1
	Cucumber	ND	ND	ND	ND	ND	1.04±0.1	1.15±0.0	ND	0.40±0.0	0.98±0.0
	Green Pepper	0.54±0.0	ND	0.41±0.0	0.29±0.1	ND	3.52±0.0	0.15±0.0	ND	0.38±0.0	2.42±0.1
	Lettuce	1.09±0.1	ND	0.66±0.0	0.60±0.1	2.89±0.0	6.4±0.0	0.32±0.0	ND	0.28±0.0	2.76±0.0
Madina (MD)	Cabbage	ND	ND	ND	ND	ND	3.56±0.5	1.25±0.0	ND	0.83±0.1	1.70±0.0
	Carrot	0.20±.6	ND	ND	ND	ND	2.28±0.0	1.17±0.1	ND	0.39±0.01	1.44±0.2
	Cucumber	ND	ND	ND	ND	ND	1.18±0.0	1.10±0.1	ND	0.31±0.3	0.77±0.0
	Green Pepper	ND	ND	0.39±0.1	ND	1.04±0.1	14.69±0.1	4.27±0.0	0.54±0.0	ND	6.40±0.0
	Lettuce	1.95±0.0	0.13±0.0	ND	2.99±0.0	1.19±0.0	74.25±0.0	8.54±0.0	ND	0.77±0.1	5.29±0.0

Dome (DM)	Cabbage	0.17±0.0	ND	1.83±0.0	ND	ND	1.58±0.0	2.0±0.0	ND	ND	1.93±0.0
	Carrot	0.20±0.1	ND	0.64±0.0	ND	2.29±0.1	23.05±0.1	11.59±0.0	0.27±0.0	0.45±0.0	9.18±0.0
	Cucumber	ND	ND	0.20±0.1	ND	ND	1.10±0.2	1.18±0.0	ND	0.69±0.0	0.95±0.0
	Green Pepper	ND	0.11±0.0	ND	ND	2.99±0.1	14.05±0.0	2.78±0.0	ND	1.33±0.0	4.22±0.0
	Lettuce	0.84±0.0	ND	0.13±0	ND	2.20±0.0	15.35±0.0	13.0	ND	0.21±0.0	6.91±0.0
Mallam Atta (MA)	Cabbage	ND	ND	0.79±0.0	ND	1.11±0.0	20.68±0.028	7.99±0.0	ND	5.14±0.1	15.42±0
	Carrot	ND	ND	1.00±0.1	ND	1.47±0.1	14.48±0.134	7.94±0.1	ND	0.50±0.0	8.08±0.1
	Cucumber	ND	0.63±0.1	1.06±0.0	ND	ND	5.32±0.071	0.84±0.1	ND	1.32±0.0	5.44±0.0
	Green Pepper	ND	ND	0.17±0.1	ND	ND	1.04±0.004	0.22±0.0	ND	0.7±0.0	2.24±0.0
	Lettuce	0.07±0.0	0.11±0.0	1.79±0.0	0.12±0.0	1.24±0.0	93.46±0.001	3.33±0.0	2.46±0.1	1.97±0.0	9.37±0.0

Table 4.12. Heavy metal concentrations in vegetables (mean ±SD, mg/kg, on fresh weight basis) from market sites, dry season.

Sites	Vegetables	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Agbogbloshie (AG)	Cabbage	0.3±0.0	1.6±0.3	1.6±0.0	0.3±0.1	ND	4.0±0.1	1.5±0.1	ND	ND	1.1±0.0
	Carrot	0.2±0.0	ND	ND	ND	ND	3.2±0.0	0.6±0.1	ND	ND	1.4±0.0
	Cucumber	0.3±0.0	1.9±0.1	ND	ND	ND	4.1±0.0	ND	ND	2.1±0.1	1.0±0.0
	Green Pepper	NA	NA	NA	NA	NA	NA	NA	ND	NA	NA
	Lettuce	ND	0.3±0.0	1.2±0.3	ND	ND	2.0±0.0	ND	ND	3.6±0.1	0.2±0.0
Makola (MK)	Cabbage	0.1±0.0	0.7±0.0	2.1±0.0	0.2±0.0	ND	2.4±0.0	2.3±.00	ND	3.8±0.1	ND
	Carrot	0.2±0.0	0.6±0.0	ND	ND	ND	3.1±0.0	1.4±0.3	ND	2.7±0.1	1.4±0.1
	Cucumber	0.1±0.6	ND	ND	ND	ND	2.4±0.1	ND	ND	12.1±0.1	1.0±0.0
	Green Pepper	ND	0.6±0.1	0.9 ±0.0	ND	ND	1.2±0.3	ND	ND	3.0±0.1	0.8±0.1
	Lettuce	ND	0.8±0.0	2.2±0.1	ND	ND	3.0±0.0	ND	ND	7.4±0.1	0.6±0.0
Madina (MD)	Cabbage	0.1±0.0	0.7±0.0	1.0±0.0	0.3±0.0	ND	1.7±0.1	0.2±0.0	ND	6.2±0.0	1.0±0.0
	Carrot	ND	0.8±0.0	ND	ND	ND	1.0±0	ND	ND	2.9±0.0	1.4±0.1
	Cucumber	ND	0.7±0.0	ND	ND	ND	ND	ND	ND	15.3±0.0	0.5±0.1
	Green Pepper	ND	ND	ND	ND	ND	1.8±0.2	ND	ND	3.0±0.0	0.4±0.0
	Lettuce	ND	1.9±0.1	2.1±0.0	ND	1.1±0.1	4.8±0.0	ND	ND	2.5±0.1	0.8±0.0
Dome (DM)	Cabbage	0.1±0.6	1.1±0.1	1.2±0.0	ND	ND	1.9±0.1	1.0±0.0	ND	13.6±0.1	0.9±0.0
	Carrot	0.3±0.0	0.5±0.1	ND	ND	ND	4.1±0.1	0.9±0.0	ND	ND	0.9±0.0

	Cucumber	ND	0.3±0.1	2.2±0.0	ND	ND	1.3±0.0	ND	ND	13.2±0.1	0.2±0.0
	Green Pepper	0.2±0.0	ND	1.5±0.1	ND	ND	3.0±0.1	ND	ND	2.8±0.0	0.8±0.1
	Lettuce	ND	ND	2.0±0.1	ND	ND	2.6±0.1	3.7±0.1	ND	7.6±0.1	1.2±0.0
Mallam Atta (MA)	Cabbage	0.2±0.0	0.5±0.0	1.7±0.0	0.2±0.0	ND	3.0±0.0	1.1±0.0	ND	9.5±0.0	1.0±0.0
	Carrot	0.2±0.0	0.9±0.1	ND	ND	ND	3.4±0.1	1.5±0.0	ND	ND	1.5±0.0
	Cucumber	ND	0.4±0.1	ND	ND	ND	2.0±0.0	ND	ND	1.7±0.1	1.7±0.0
	Green Pepper	0.2±0.0	1.9±0.0	ND	ND	ND	3.0±0.0	ND	ND	15.7±0.1	1.0±0.0
	Lettuce	ND	ND	ND	ND	ND	3.1±0.1	ND	ND	2.5±0.3	0.9±0.1

4.5. LEVELS OF HEAVY METALS IN VEGETABLES FROM FARM AND MARKET SITES.

Generally, vegetables from the markets were more contaminated with heavy metals than those from the farms, except As, Cd, Co and Fe, Table 4.13. The mean metal levels decreased from Fe>As>Cu>Pb>Co>Zn>Mn>Cd for farm and Fe>Pb>As>Cu>Mn>Zn>Ni>Co>Cr>Cd for market samples. The highest metal concentration of Fe was 14.023 and 7.852 mg/kg for farm and markets samples respectively.

The levels of carcinogenic Pb, Ni and Cr were estimated as 3.526, 1.302 and 0.99 mg/kg for market samples while Ni and Cr were not detected in farm samples. The observed metal contaminations in the market samples could arise from certain unhygienic activities at these centers which create room for contaminations of all sorts in food products. In the selected markets, many sellers sold their vegetables in open places on the floor, sometimes near refuse or a burning site or close to traffic emissions. It is believed that the result of these deeds could cause various contaminations in the commodities (atmospheric depositions), thereby increasing metal levels in vegetables.

Even so the concentrations of As, Cd, Co and Fe found in vegetables from farms were higher than those from markets. The reason could come from various dilutions by rains and or washings that could take away most of these metal deposits on the vegetables displayed at the various markets hence reduce their original concentrations. However, each of the metal level(s) in the vegetables could vary greatly from their general mean. The metal uptakes (especially Co, Pb and Fe) were higher in leafy and fleshy vegetables than by root vegetables. Lacatuşu et al. (1996) also reported high Pb in lettuce than carrots suggesting that the uptake of metals depended on the physiological properties of the vegetable.

Table 4.13. Mean metal concentrations in vegetables (mg/kg, on fresh weight basis) in vegetables from farm and market sites.

	Vegetables	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Farm	Cabbage	4.505	1.000	1.900	ND	ND	1.467	0.633	ND	1.100	0.933
	Carrot	3.356	0.500	NA	ND	ND	5.267	0.800	ND	1.800	1.156
	Cucumber	3.990	ND	NA	ND	ND	5.400	0.400	ND	3.800	0.745
	Green pepper	4.730	1.250	0.900	ND	0.950	1.883	0.650	ND	1.730	0.852
	Lettuce	2.133	0.675	1.700	ND	3.000	56.100	2.578	ND	1.133	1.477
	Total	**3.743**	**0.838**	**1.500**	**NA**	**1.975**	**14.023**	**1.012**	**NA**	**1.913**	**1.033**
Market	Cabbage	0.184	0.780	1.459	0.250	1.109	4.696	1.913	ND	5.043	2.956
	Carrot	0.213	0.699	0.559	ND	1.621	6.119	3.046	0.677	1.202	2.836
	Cucumber	0.200	0.786	0.913	ND	1.655	2.540	1.040	1.529	5.244	1.490
	Green pepper	0.313	0.677	0.673	1.158	5.812	4.807	1.844	0.542	3.378	1.612
	Lettuce	0.818	0.635	1.348	1.236	3.029	21.099	4.495	2.459	2.763	3.036
	Total	**0.346**	**0.714**	**0.990**	**0.881**	**2.645**	**7.852**	**2.468**	**1.302**	**3.526**	**2.386**

ND - Not detected.

NA - Not available or applicable.

4.6. BIOACCUMULATION FACTOR (BAF) OF METALS FROM SOILS TO VEGETABLES AT THE FARMS

The bioaccumulation factor (BAF) was calculated for heavy metal transfer from soils to vegetables in the wet and dry season, Table 4.14 and Table 4.15 respectively. BAF estimates the human risks to heavy metal intake (Mahmood and Malik, 2014) and largely evaluates metal contamination in the environment (Huang et al., 2008).

BAF depends on several factors such as the soil pH, organic matter, metal availability, soil particle size and vegetable species (Gebrekidan et al., 2013). BAF was calculated for As, Cd, Co, Cu, Fe, Mn, Pb and Zn while Cr metal in the soil showed no corresponding transfer in the vegetables. The BAF trend was Pb>Zn>Fe>Cu>Cd>Co>As>Mn for the wet season and As>Zn>Mn>Fe for the dry season. The BAF results indicated that green pepper and lettuce bio-accumulated higher amounts of Pb, Cd, Co, Cu, Fe, Zn and As; cabbage and carrot bio-accumulated As, Co, Cd, Fe, Mn and Zn in relatively moderate amounts and cucumber bio-accumulated As, Pb and Zn in low amounts. The highest value of As (8.16), Cu (0.7), Pb (2.4), Zn (0.56), Fe (0.37) and Mn (5.17) suggested that these metals were more mobile in nature than the other metals.

As recorded the highest BAF factor (8.16) in the dry season and this could result from its high mobility rate and abundance in underground water. During the drought periods, the vegetables may reach deep into the soil for water, thereby increasing their metal uptake, particularly As and Pb. Notwithstanding, Zn, Fe and Mn are essential micronutrients required by plants in the functioning and build-up of structures, thus their uptake was also significant by the vegetables.

Table 4.14. Bioaccumulation factor (BAF) of heavy metals in vegetables at the farm sites, wet season.

Sites	Vegetables	As	Cd	Co	Cu	Fe	Mn	Pb	Zn
Ebony	Carrot	0.026	0.026	NA	NA	0.065	NA	0.500	0.204
	Cucumber	NA	NA	NA	NA	0.026	NA	1.056	0.074
	Green Pepper	NA	NA	NA	0.286	0.0095	NA	0.694	0.278
	Lettuce	0.105	0.105	NA	NA	0.402	0.0096	NA	0.259
CSIR	Cabbage	NA	NA	0.0225	NA	0.013	NA	NA	NA
	Green Pepper	NA	0.471	0.107	0.600	0.0072	NA	NA	0.20
	Lettuce	NA	0.294	0.142	0.700	0.372	0.006	0.6	0.134
Dzorwulu	Cabbage	NA	1.020	NA	NA	NA	NA	NA	0.417
	Green Pepper	NA	NA	NA	0.128	0.006	NA	NA	0.330
	Lettuce	NA	NA	1.301	0.586	0.323	0.035	0.696	1.291
GAEC	Cabbage	NA	NA	NA	NA	0.0056	NA	0.289	0.417
	Green Pepper	NA	NA	NA	0.118	NA	NA	0.053	0.139
	Lettuce	0.109	0.385	0.457	0.106	0.175	0.502	NA	0.464
GBC	Green Pepper	NA	NA	NA	NA	0.021	NA	2.400	0.306
	Lettuce	0.255	0.667	NA	NA	0.180	0.048	2.400	1.020

NA- Not available.

Table 4.15. Bioaccumulation factor (BAF) of heavy metals in vegetables at the farm sites, dry season.

Sites	Vegetables	As	Fe	Mn	Zn
Ebony	Cabbage	8.163	NA	5.172	0.4000
	Carrot	1.375	0.0073	0.003	0.467
	Cucumber	NA	NA	0.004	0.300
	Green Pepper	3.680	0.007	0.011	0.327
	Lettuce	2.350	NA	0.003	0.330
CSIR	Cabbage	0.124	NA	0.007	0.267
	Carrot	0.228	NA	0.021	0.264
	Cucumber	0.193	NA	0.004	0.170
	Green Pepper	0.361	NA	0.006	0.364
	Lettuce	0.211	NA	0.023	0.238
Dzorwulu	Cabbage	NA	NA	NA	NA
	Carrot	0.285	0.004	0.009	0.098
	Cucumber	0.300	NA	0.005	0.116
	Green Pepper	NA	NA	0.008	0.159
	Lettuce	NA	NA	0.034	0.156
GAEC	Cabbage	NA	NA	0.006	0.446
	Carrot	0.742	NA	0.005	0.442
	Cucumber	NA	NA	NA	NA
	Green Pepper	0.418	0.0158	0.002	0.187
	Lettuce	0.520	NA	0.030	0.563
GBC	Lettuce	0.478	NA	NA	3.200

NA- Not available.

The BAF values differed significantly among the sampling locations and vegetable species. The variations probably arose from the different metal concentrations in the soil and their uptake by the different vegetable species. The BAF was maximum for leafy and fleshy vegetables than root vegetables. Leafy vegetables have high transpiration rates and in order to sustain their growth and moisture content, they mostly become susceptible to uptake these metal deposits from the soil and water. Lettuce had BAF value of 2.35 for As at Ebony, 0.66 for Cd at GBC, 2.4 for Pb at GBC and 3.2 for Zn at GBC. However, carrot ranged from 0.004 for Fe at Dzorwulu to 1.375 for As at Ebony.

BAF values which were also calculated for the fertilizer and manure samples had As, Cu, Fe, Mn and Zn metals present, Table 4.16. BAF values were absent for Cr and Ni. Although Cr was present in soil at some sites, its accumulation in the vegetables was either absent or below detection limits. Therefore, the levels of Cr and Ni in the vegetables might have been greatly influenced by fertilizer applications, use of irrigation wastewaters and atmospheric depositions on vegetables rather than the soils. It could also be explained that these metals were greatly adhered to soil and limited their uptake by the plants.

The BAF values suggested that heavy metals are transported and accumulated in vegetables from soils and this could increase the health risk of humans to toxic metal intakes via vegetable consumption.

Table 4.16. Bioaccumulation factor (BAF) of heavy metals in fertilizer and manure.

Fertilizer and manure	As	Cu	Fe	Mn	Zn
Wet season	0.837	1.617	0.417	0.397	9.009
Dry season	0.485	8.120	0.406	0.950	6.839

4.7. QUALITATIVE ASSESSMENTS FOR VEGETABLE CONSUMERS

4.7.1. Demographic Characteristic

Table 4.17. Demographic characteristics of respondents.

Variable	**Mean (%)**
Sex	46.3
Male	53.3
Female	
Age	
Below 6 years	1.7
6-18 years	16.7
Above 18 years	81.7
Marital status	28.3
Married	68.3
Single	3.3
Divorced	
Educational level	
Diploma/Degree	56.7
Secondary	30.0
JHS	10.0
None	3.3

Table 4.17 expresses the mean values (%) of the demographic characteristics of vegetable consumers. From the 180 volunteer interviewed, 46.5% were male and 53.3% were female. The maximum age for the highest respondents was above 18 years (81.7%) and only 56.7% of the respondents had diploma/degree. All the respondents had reason(s) for consuming vegetables although the rate of consumption was low.

4.7.2. Consumers Response to Vegetable Intake and Why?

Vegetables were identified as food commodities which could be bought and eaten at any time. Table 4.18 provides the perception of consumers on vegetable intake.

Table 4.18. Responses of vegetable consumers under study.

Variable	**Response**	**No of respondents**	**Mean (%)**
Do you consume vegetables?	Yes	180	100
Reasons for consuming vegetables?	Nutritional	153	85
	Aesthetic Value	27	15
	Total	180	100
What kind of vegetable do you often consume?	Cabbage	102	56.7
	Carrot	30	16.7
	Cucumber	15	8.3
	Green pepper	3	1.7
	Lettuce	30	16.7
	Total	180	100
Where do you get these commodities?	Market	162	90
	Hawkers	6	3.3
	Home	6	3.3
	Stall	3	1.7
	Mall/Supermarkets	3	1.7
	Total	180	100
How often do you consume them?	Everyday	27	15
	3 times weekly	48	26.7
	Weekly	90	50
	Monthly	12	6.7
	Hardly	3	1.7
	Total	180	100
Period of vegetable consumption (years)?	1	9	5
	3	27	15
	4	3	1.7
	5	12	6.7
	6	9	5
	10	30	16.7
	15	6	3.3
	17	3	1.7
	18	6	3.3
	20	48	26.7
	21	3	1.7
	24	3	1.7

	25	3	1.7
	26	3	1.7
	27	3	1.7
	28	3	1.7
	30	9	5
	Total	180	100
How do you eat the vegetables?	Raw	78	43.3
	Semi-cooked	75	41.7
	Fully-cooked	27	15
	Total	180	100
What quantity do you eat a day?	Small	93	51.7
	Medium	81	45
	Large	6	3.3
	Total	180	100
What are the benefits of consuming vegetables?	Vitamins, minerals	60	33.3
	Boost immune system	108	60
	Prevents constipation	12	6.7
	Total	180	100
Do you react when you eat the vegetables?	**Yes**	**15**	
	No	**165**	
	Total	**180**	

Most respondents consumed vegetables based on their nutritional value (85%) other than their aesthetic qualities (15%), Table 4.18. The commonly consumed vegetable was cabbage (56.7%), followed by carrot and lettuce (16.7%), then cucumber (8.3%). The least patronized was green pepper (1.7%). The reason for the choice of cabbage was due to its size and cheaper price for the households. However, lettuce and carrot came second because the respondents (especially men) ate them in foods purchased from restaurants and other food vendors.

Majority of the respondents (90%) bought their vegetables from neighboring markets, with 3.3% purchase from hawkers or home stores and 1.7% from the mall or supermarkets, Table 4.18. Furthermore, 50% of the respondents consumed vegetables weekly as a special food prepared on weekends, whereas 1.7% hardly consumed vegetables. The highest period of consumption was found to be 20 years (26.7%) and the least was 1 year (5%).

Moreover, 43.3% respondents ate their vegetables raw, 41.7% ate them semi-cooked while 15% eat them fully-cooked. As a statement issued by the WHO (WHO, 2007), food consumption should contain at least 30% of fruits and vegetables. However, Ruel et al. (2005) reported a daily vegetable intake of 0.137 kg/day for every Ghanaian. The amounts of vegetables consumed by the respondents were 51.7% for small quantities, 45% for medium quantities and 3.3 % for large quantities. Additionally, 60% said that the vegetables boosted their immune system whereas 6.7% indicated that they prevented constipation. 91.7% consumers confirmed to having no reaction such as nausea, irritation etc. after consumption.

4.7.3. Knowledge on Possible Contaminants and Vegetable Treatments

Table 4.19. Contaminants, treatment and handling of vegetables.

Variable	**Response**	**No of respondents**	**Mean (%)**
Are you satisfied with the cultivation, storage and handling of vegetables?	Yes	63	35
	No	117	65
	Total	180	100
Do you know of any possible contaminants of vegetables?	Yes	96	53.3
	No	84	46.7
	Total	180	100
How do you treat and store your vegetables before consumption?	**Water**	**66**	**36.7**
	Brine	**96**	**53.3**
	Vinegar	**18**	**10**
	Total	**180**	**100**

From Table 4.19 the mode of satisfaction to vegetable cultivation, their storage and handling prior to purchase revealed that 65% respondents were not satisfied while the 35% were satisfied. Similarly, 53.3% responded to having knowledge of possible contaminants such as heavy metals, pesticides, microbes etc. in vegetables. Finally, in treatment (cleaning) of vegetables before consumption, 53.3% of participants agreed to using brine solution, 36.7% used water while 10% employed vinegar.

4.8. HEALTH RISK ASSESSMENT

Human health risk assessments associated with heavy metal contamination of vegetables sampled from Accra Metropolis were estimated on their average daily intake (ADI) and hazard quotient (HQ). The ADI was calculated according to the average concentration of each heavy metal present in each vegetable and their respective ingestion rates for adults (60 kg) and children (30 and 15 kg), Table 3.2. The HQ, which evaluated the effect of heavy metal consumption over the individual's lifetime, was calculated using reference dose, RfD values from the Joint FAO/WHO. The RfD values were 0.007, 0.2, 0.5, 2.3, 3.0, 60.0, 2.0, 0.2, 0.3 and 15.0 for As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively (Joint WHO/FAO, 2010, 2011).

The ADI of metals from farms decreased from Fe>As>Mn>Pb>Co=Cu>Zn>Cd, Table 4.20. This trend was calculated based on the percent intake of these metals in the vegetables, Fig. 4.1. The highest values expressed for Fe, As, Mn and Pb were because these metals are more mobile in nature as well as having low retention abilities in soil. However, the ADI value for each metal was far below recommendation except As, which exceeded its limit in all the vegetable types, Fig 4.2. The HQ values of As for children; 15 and 30 kg and adults (60 kg) were 9.95, 4.9 and 3.7 respectively. These estimated values put these children (15 and 30 kg) to higher risk of metal toxicity than adults, approximately 2.7 and 1.32 times higher than adults respectively for As intake. Therefore, certain toxicities associated with As intake such as heart and brain damage and in some cases death are more likely to be faced by children than adults. Generally, the risks of metal intake for each vegetable decreased from cabbage>green pepper>cucumber>carrot>lettuce.

Table 4.20. Health risk assessment of heavy metals in vegetables from the farm sites.

	Vegetables	Reference dose (mg/kg/day), (Joint WHO/FAO, 2010, 2011)	Adults (above 18 years)			Children (7-13 years)			Children (0-6 years)		
			Average daily dose (mg/kg/day)	Hazard quotient, HQ	Health Risk	Average daily dose (mg/kg/day)	Hazard quotient, HQ	Health Risk	Average daily dose (mg/kg/day)	Hazard quotient, HQ	Health Risk
Arsenic	Cabbage	0.007	0.0256	3.70	Yes	0.0348	4.98	Yes	0.0696	9.95	Yes
	Carrot		0.0077	1.09	Yes	0.0154	2.19	Yes	0.0307	4.39	Yes
	Cucumber		0.0091	1.30	Yes	0.0183	2.61	Yes	0.0365	5.22	Yes
	Green Pep		0.0108	1.55	Yes	0.0216	3.09	Yes	0.0433	6.19	Yes
	Lettuce		0.0065	0.92	No	0.0084	1.19	Yes	0.0168	2.40	Yes
Cadmium	Cabbage	0.2	0.0058	0.029	No	0.0077	0.39	No	0.0155	0.08	No
	Carrot		0.0011	6×10^{-3}	No	0.0023	0.011	No	0.0046	0.02	No
	Green Pep		0.0029	0.01	No	0.0057	0.029	No	0.0114	0.06	No
	Lettuce		0.0020	0.01	No	0.0027	0.013	No	0.0053	0.03	No
Cobalt	Cabbage	0.5	0.0109	0.02	No	0.0147	0.029	No	0.029	0.06	No
	Green Pep		0.0021	4×10^{-3}	No	0.004	0.008	No	0.008	0.02	No
	Lettuce		0.0052	0.01	No	0.0067	0.013	No	0.0133	0.03	No
Copper	Green Pep	3.0	0.0022	7.25×10^{-4}	No	0.0043	0.001	No	0.0089	3×10^{-3}	No
	Lettuce		0.0091	3×10^{-3}	No	0.0118	0.004	No	0.024	8×10^{-3}	No
Iron	Cabbage	60.0	0.0084	1.41×10^{-4}	No	0.0113	1.89×10^{-4}	No	0.0227	3.78×10^{-4}	No
	Carrot		0.0121	2.01×10^{-4}	No	0.0241	4.02×10^{-4}	No	0.0482	8.04×10^{-4}	No
	Cucumber		0.0124	2.06×10^{-4}	No	0.0247	4.12×10^{-4}	No	0.0494	8.24×10^{-4}	No
	Green Pep		0.0043	7.18×10^{-5}	No	0.0086	1.44×10^{-4}	No	0.0172	2.87×10^{-4}	No
	Lettuce		0.1702	2.84×10^{-4}	No	0.2206	3.68×10^{-3}	No	0.4413	7.36×10^{-3}	No
Manganese	Cabbage	2.0	0.0036	1.82×10^{-3}	No	0.0049	2.45×10^{-3}	No	0.0098	4.89×10^{-3}	No
	Carrot		0.0018	9.15×10^{-4}	No	0.0037	1.83×10^{-3}	No	0.0073	3.66×10^{-3}	No
	Cucumber		9.15×10^{-4}	4.58×10^{-4}	No	0.0018	9.15×10^{-4}	No	0.0037	1.83×10^{-3}	No
	Green Pep		0.0015	7.44×10^{-4}	No	0.0029	1.49×10^{-3}	No	0.0059	2.97×10^{-3}	No
	Lettuce		0.0078	3.91×10^{-3}	No	0.0101	5.07×10^{-3}	No	0.0203	0.01	No
Lead	Cabbage	0.3	0.0063	0.02	No	0.0085	0.03	No	0.0170	0.06	No
	Carrot		0.0041	0.01	No	0.0082	0.03	No	0.0165	0.05	No
	Cucumber		0.0087	0.03	No	0.0174	0.06	No	0.0348	0.12	No
	Green Pep		0.0039	0.01	No	0.0079	0.03	No	0.0158	0.05	No
	Lettuce		0.0034	0.01	No	0.0046	0.01	No	0.0089	0.03	No
Zinc	Cabbage	15.0	0.0054	3.57×10^{-4}	No	0.0072	4.81×10^{-4}	No	0.0144	9.62×10^{-4}	No
	Carrot		0.0064	1.76×10^{-4}	No	0.0053	3.53×10^{-4}	No	0.0106	7.05×10^{-4}	No
	Cucumber		0.0017	1.14×10^{-4}	No	0.0034	2.27×10^{-4}	No	0.0068	4.55×10^{-4}	No
	Green Pep		0.0019	1.29×10^{-4}	No	0.0039	2.59×10^{-4}	No	0.0078	5.19×10^{-4}	No

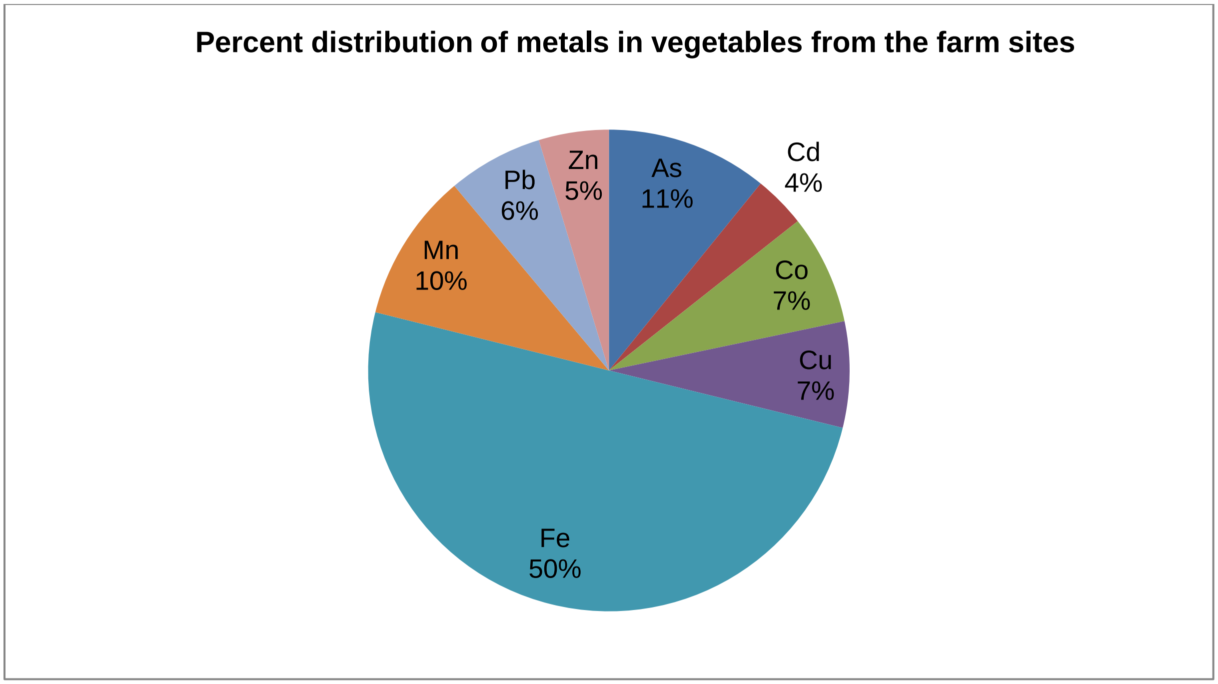

Fig. 4.1. % distribution of the metals (daily intake) in vegetables.

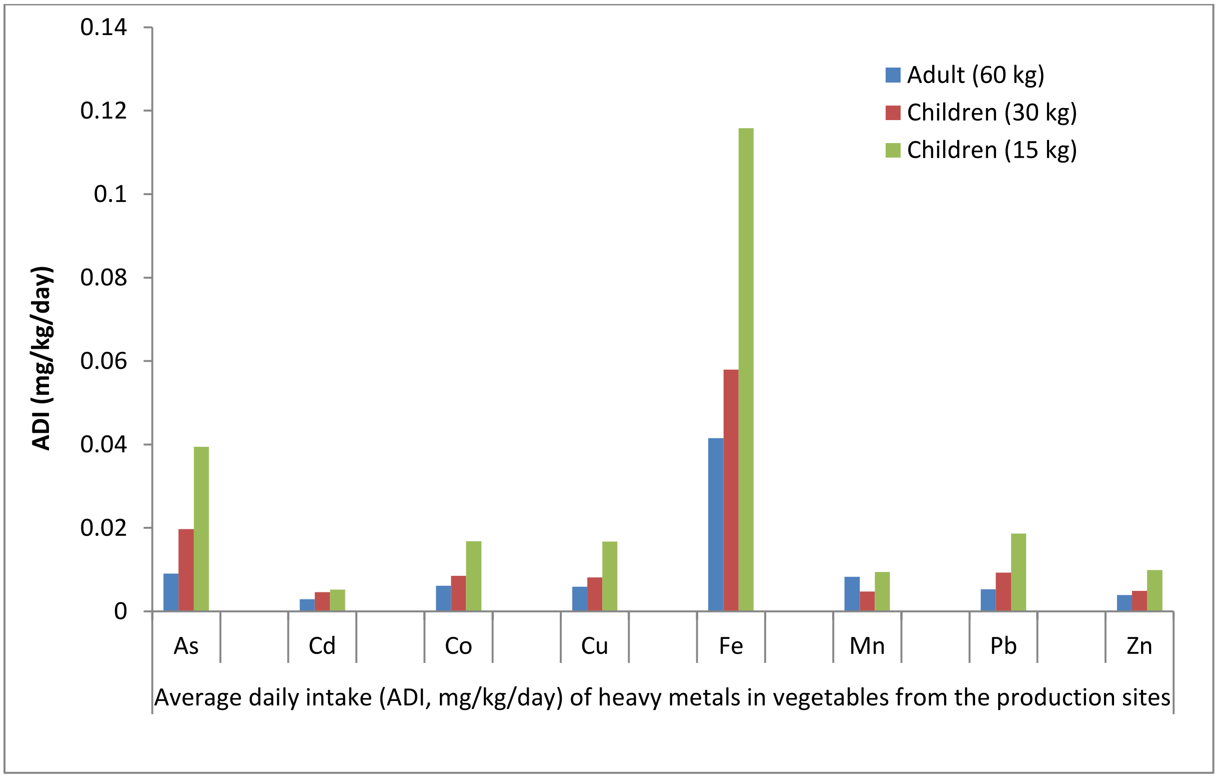

Fig. 4.2. ADI (mg/kg/day) of heavy metals in vegetables.

The risk assessments of vegetables sampled from the selected markets were below their recommendation and did not pose any health risk to consumers. The ADI for the metal consumption in vegetables decreased from Fe>Pb>Cu>Ni>Cr>Mn>Cd>Zn>As>Co, Table 2.21. The highest HQ value for Pb was in cabbage; 0.26 and 0.13 and 0.097 for 15 and 30 kg children and adults respectively. Moreover, the estimated HQ for Ni was 0.097 and 0.048 and 0.037 for children (15 and 30 kg) and adults respectively. The HQ value of Ni for children (15 and 30 kg) was about 2.62 and 1.29 times respectively, and renders children more prone to metal toxicities. The risk of these metals expressed in the vegetables was highest for lettuce (27), cabbage (24), green pepper (19), carrot (16) and cucumber (14%), Fig. 4.3.

Comparatively, the calculated ADI and HQ of heavy metals in vegetables were relatively high for market samples than production ones, except for Fe, As and Co. These results are in agreement with previous studies in Ghana, who stated zero risk of metal consumption in vegetables and fruits (Bempah et al., 2011; Lente et al., 2012). Bempah et al. (2011) also reported ADI values of Pb (0.214), Cd (0.06), Cu (3.0), Cr (0.15) and Zn (60) in fruits and vegetables sampled from Ghanaian markets, and concluded that there were no apparent risks associated with their intake in these commodities.

More so, Nabulo et al. (2010) stated that the proper washing of vegetables before consumption minimized the risk of some metal transfer in human diet. Therefore, it was important that a number of the respondents washed their vegetables with water (36.7), brine (53.3) and vinegar (10%), to reduce the levels of possible contaminants such as heavy metals before consumption.

Table 4.21. Health risk assessment of heavy metals in vegetables from the market sites.

			Adults (above 18 years)			Children (7-13 years)			Children (4-6 years)		
	Vegetables	**Reference dose (mg/kg/day), (Joint WHO/FAO, 2010, 2011)**	**Average daily dose (mg/kg/day)**	**Hazard quotient, HQ**	**Health Risk**	**Average daily dose (mg/kg/day)**	**Hazard quotient, HQ**	**Health Risk**	**Average daily dose (mg/kg/day)**	**Hazard quotient, HQ**	**Health Risk**
Arsenic	Cabbage	0.007	1.06×10^{-3}	0.152	No	1.43×10^{-3}	0.204	No	2.86×10^{-3}	0.408	No
	Carrot		4.87×10^{-4}	0.069	No	9.75×10^{-4}	0.139	No	1.95×10^{-3}	0.279	No
	Cucumber		4.58×10^{-4}	0.065	No	9.15×10^{-4}	0.131	No	1.83×10^{-3}	0.262	No
	Green Pep		7.162×10^{-4}	0.102	No	1.43×10^{-3}	0.205	No	2.86×10^{-3}	0.409	No
	Lettuce		2.48×10^{-3}	0.353	No	1.46×10^{-3}	0.209	No	6.419×10^{-3}	0.917	No
Cadmium	Cabbage	0.2	5.29×10^{-3}	0.026	No	0.014	0.071	No	0.014	0.071	No
	Carrot		1.60×10^{-3}	0.083	No	3.30×10^{-3}	0.017	No	6.41×10^{-3}	0.032	No
	Cucumber		2.25×10^{-3}	0.011	No	4.49×10^{-3}	0.022	No	8.99×10^{-3}	0.045	No
	Green Pep		1.55×10^{-3}	7.76×10^{-3}	No	3.11×10^{-3}	0.016	No	6.22×10^{-3}	0.031	No
	Lettuce		2.24×10^{-3}	0.011	No	2.91×10^{-3}	0.015	No	5.82×10^{-3}	0.029	No
Cobalt	Cabbage	0.5	8.39×10^{-3}	0.018	No	0.011	0.023	No	0.023	0.045	No
	Carrot		1.28×10^{-3}	2.56×10^{-3}	No	2.56×10^{-3}	5.13×10^{-3}	No	5.13×10^{-3}	0.010	No
	Cucumber		2.09×10^{-3}	4.18×10^{-3}	No	4.18×10^{-3}	8.36×10^{-3}	No	8.36×10^{-3}	0.017	No
	Green Pep		1.54×10^{-3}	3.08×10^{-3}	No	3.08×10^{-3}	6.16×10^{-3}	No	6.17×10^{-3}	0.012	No
	Lettuce		4.09×10^{-3}	8.18×10^{-3}	No	5.30×10^{-3}	0.011	No	0.011	0.021	No
Chromium	Cabbage	2.3	1.44×10^{-3}	6.25×10^{-4}	No	1.93×10^{-3}	8.41×10^{-3}	No	3.87×10^{-3}	1.68×10^{-3}	No
	Green Pep		2.65×10^{-3}	1.15×10^{-3}	No	5.31×10^{-3}	2.31×10^{-3}	No	0.0134	5.82×10^{-3}	No
	Lettuce		3.75×10^{-3}	1.63×10^{-3}	No	4.85×10^{-3}	2.12×10^{-3}	No	9.73×10^{-3}	4.23×10^{-3}	No
Copper	Cabbage	3.0	6.38×10^{-3}	2.13×10^{-3}	No	8.58×10^{-3}	2.86×10^{-3}	No	0.017	5.72×10^{-3}	No
	Carrot		3.71×10^{-3}	1.24×10^{-3}	No	7.41×10^{-3}	2.47×10^{-3}	No	0.015	4.94×10^{-3}	No
	Cucumber		3.79×10^{-3}	1.27×10^{-3}	No	7.59×10^{-3}	2.53×10^{-3}	No	0.015	5.06×10^{-3}	No
	Green Pep		0.0133	4.45×10^{-3}	No	0.027	8.89×10^{-3}	No	0.053	0.018	No
	Lettuce		9.19×10^{-3}	3.06×10^{-3}	No	0.012	3.97×10^{-3}	No	0.024	7.95×10^{-3}	No
Iron	Cabbage	60.0	0.027	4.55×10^{-4}	No	0.037	6.11×10^{-4}	No	0.073	1.22×10^{-3}	No
	Carrot		0.014	2.301	No	0.027	4.60×10^{-4}	No	0.055	9.205	No
	Cucumber		5.82×10^{-3}	9.69×10^{-5}	No	0.012	1.94×10^{-4}	No	0.023	3.88×10^{-4}	No
	Green Pep		0.011	1.89×10^{-4}	No	0.023	3.79×10^{-4}	No	0.046	7.59×10^{-4}	No

	Lettuce		0.064	1.07×10^{-3}	No	0.083	1.39×10^{-3}	No	0.167	2.77×10^{-3}	No
Manganese	Cabbage	2.0	0.011	5.65×10^{-3}	No	0.015	7.59×10^{-3}	No	0.030	0.015	No
	Carrot		6.97×10^{-3}	3.49×10^{-3}	No	0.014	6.97×10^{-3}	No	0.028	0.014	No
	Cucumber		2.38×10^{-3}	1.19×10^{-3}	No	4.75×10^{-3}	2.38×10^{-3}	No	9.50×10^{-3}	4.75×10^{-3}	No
	Green Pep		4.22×10^{-3}	2.11×10^{-3}	No	8.45×10^{-3}	4.22×10^{-3}	No	0.017	8.45×10^{-3}	No
	Lettuce		0.015	7.68×10^{-3}	No	0.019	9.97×10^{-3}	No	0.039	0.019	No
Nickel	Carrot	0.2	1.55×10^{-3}	7.76×10^{-3}	No	2.09×10^{-3}	0.010	No	4.18×10^{-3}	0.021	No
	Cucumber		3.50×10^{-3}	0.018	No	7.00×10^{-3}	0.035	No	0.014	0.070	No
	Green Pep		1.24×10^{-3}	6.18×10^{-3}	No	2.47×10^{-3}	0.012	No	4.94×10^{-3}	0.025	No
	Lettuce		7.46×10^{-3}	0.037	No	9.78×10^{-3}	0.048	No	0.019	0.097	No
Lead	Cabbage	0.3	0.029	0.097	No	0.039	0.130	No	0.078	0.260	No
	Carrot		2.75×10^{-3}	9.18×10^{-3}	No	5.51×10^{-3}	0.018	No	0.011	0.037	No
	Cucumber		0.012	0.039	No	0.023	0.079	No	0.048	0.159	No
	Green Pep		7.73×10^{-3}	0.026	No	0.015	0.051	No	0.031	0.103	No
	Lettuce		8.38×10^{-3}	0.028	No	0.011	0.036	No	0.022	0.072	No
Zinc	Cabbage	15.0	0.017	1.14×10^{-3}	No	0.023	1.54×10^{-3}	No	0.046	3.07×10^{-3}	No
	Carrot		6.49×10^{-3}	4.33×10^{-4}	No	0.013	8.66×10^{-4}	No	0.026	1.73×10^{-3}	No
	Cucumber		3.41×10^{-3}	2.27×10^{-4}	No	6.81×10^{-3}	4.54×10^{-3}	No	0.014	9.09×10^{-3}	No
	Green Pep		5.55×10^{-3}	3.69×10^{-3}	No	0.011	7.38×10^{-3}	No	0.022	1.48×10^{-3}	No
	Lettuce		9.21×10^{-3}	6.14×10^{-4}	No	0.012	7.96×10^{-4}	No	0.024	1.59×10^{-3}	No

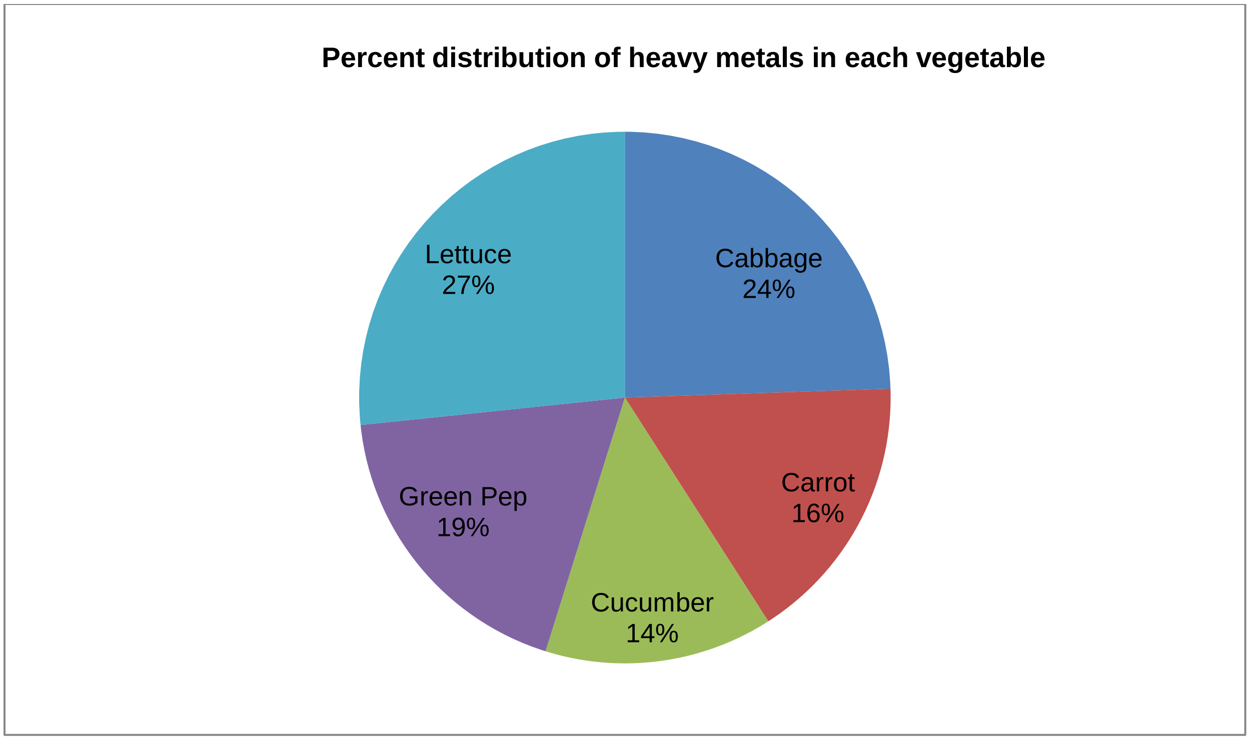

Fig 4.3. % distribution of heavy metals in each vegetable.

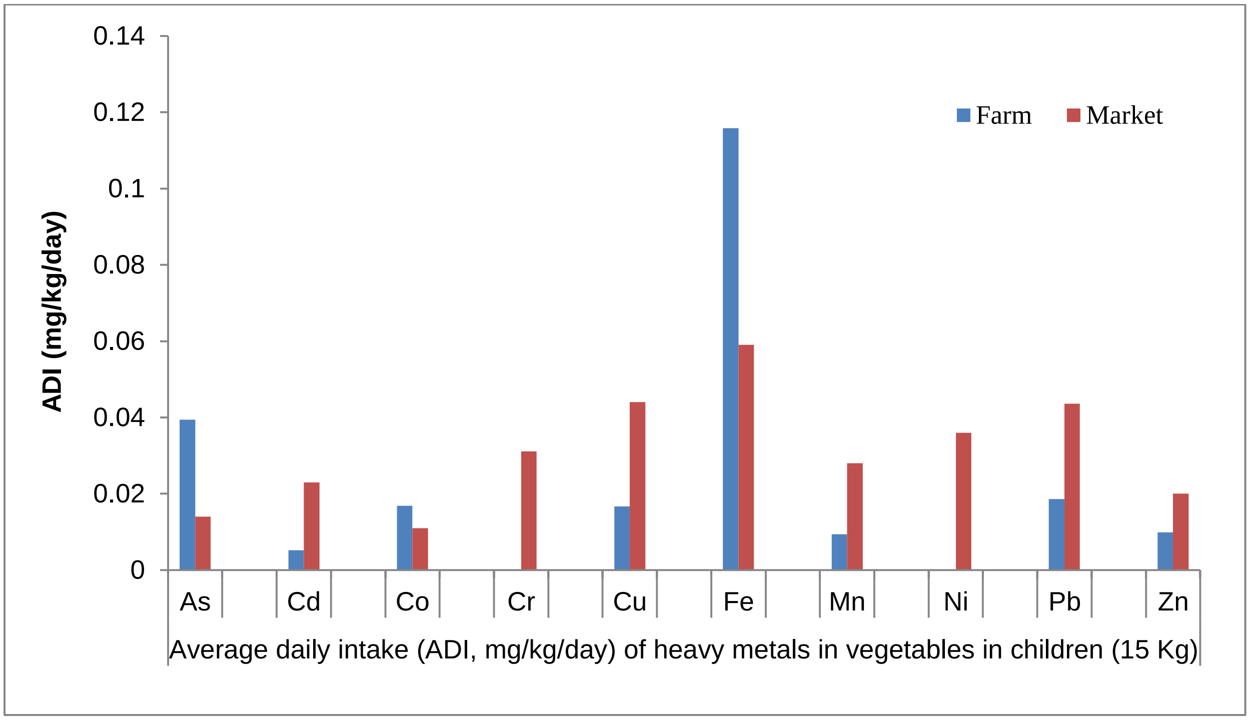

Fig 4.4. ADI of children (15 kg) from farm and market sites.

Although the estimated risks of heavy metals in vegetables were low and proved no obvious adverse effect in humans (except As in vegetables from production sites), the risks of children recorded was approximately 3 times higher than adults. This information could be used by regulators to set precautionary measures that would limit the risks of consumers towards metal intake in vegetables.

CHAPTER FIVE

5.1. CONCLUSION

The following conclusions are drawn from this research investigation:

- Out of 479 vegetables sampled from farm and market sites in Accra Metropolis, 91 (18.99%) were below EU limits for heavy metals in vegetables whereas 388 (81%) exceeded the limits. Mallam Attah and GBC recorded the highest metal concentrations (100%). All the vegetables gave at least one positive metal detection.
- The concentrations of heavy metals in soil suggested some metal accumulation(s) in vegetables. This was evident by the BAF values which demonstrated that some heavy metals were transferred from the soil into the vegetables. The metal levels in the soil decreased from Mn>Fe>As>Cr>Zn>Co>Cu>Pb>Cd and from GAEC>CSIR>Ebony>Dzorwulu>GBC. The highest concentration of Fe and Pb were 648.37 mg/kg at CSIR and 3.8 mg/kg accordingly in wet season. All the metal levels were below the EU recommendations, except As (24.2 mg/kg at Dzorwulu site).
- The estimated heavy metal concentrations in the vegetables sampled from markets were higher than farms. Vegetables from markets were more contaminated with heavy metals than those from farms, except As, Cd, Co and Fe. The metal levels were maximum in leafy and fleshy vegetables than root vegetables and differed significantly among the sampling locations and vegetable and metal specie(s).
- From the study, the human health risks associated with the consumption of vegetables from markets were higher than those from farms. The estimated assessments showed that children (15 kg) were more prone (about 3 times higher) to metal toxicities than adults (60 kg).

5.2. RECOMMENDATIONS

The following recommendations are made to further the extent of knowledge of heavy metals in vegetables:

- Heavy metal levels were found in vegetables sampled from Accra Metropolis. Continuous and regular monitoring programmes for heavy metals in food commodities in the other regions are done in order to safeguard the health of consumers against metal toxicities.
- It is imperative that vegetables are thoroughly washed with clean water before their consumption in order to reduce the initial metal levels.
- Additionally, the government should ensure that some educational and management programmes are organized for the farmers to ensure compliance of good agricultural practices.

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APPENDIX

A. Physiochemical parameters of irrigation waters in (mg/L) except Elect. Conductivity (µs/cm) and pH (pH units), farm sites.

Sites	Seasons	pH	EC	TSS	TDS	Cl^-	SO_4^{2-}	PO_4^{3-}	NO_3^-	Total Hardness	Ca^{2+}	Mg^{2+}	Total Alkalinity	HCO_3^-
Ebony	Wet	8.02±0.04	1298±4.20	576±4.24	733±2.82	361.59±0.09	75±0.14	0.86±0.02	1.3±0.01	30±0.78	13±0.856	17±0.05	300±0.21	180±0
	Dry	7.86±0.04	524±1.41	10±0.28	288±0.21	73±0.14	30.9±0.0	1.52±0.02	0.11±0.03	563±0.49	61.3±0.28	502±0.02	136±0.01	112±0.04
CSIR	Wet	8.31±0.02	883±1.41	407±4.24	49±2.83	120±0.42	87±0.02	2.35±0.04	6.8±0.02	25±0.35	13±0	12±0.01	500±0.01	300±0.02
	Dry	7.83±0.03	1271±3.53	137±4.31	699±0.21	144±0	74.4±0.14	0.45±0.08	1.29±0.03	133±0.07	42±0.21	26±0.14	464±0.02	386±0.01
Dzorwulu	Wet	8.07±0.03	81.8±0.21	32±1.41	43±0.21	10.64±0.01	21±0.21	0.91±0.01	1.4±0	10±0.141	7±0.21	3±0.14	100±0.28	60±0.04
	Dry	7.38±0.11	103±2.83	61±1.41	56±0.70	6±0.28	12.3±0.04	0.18±0	0.14±0.02	34±0.21	27.3±0.07	6.5±0.04	56.4±0.49	46.2±0.28
GAEC	Wet	8.26±0.01	366±1.41	300±2.12	186±1.41	106.35±0.09	33±0.01	0.96±0.04	2.8±0.10	20±1.49	18±0.01	2±0.64	200±0.01	120±0.01
	Dry	8.03±0.01	1446±4.95	2±0.06	795±1.41	28±0.28	28.1±0.01	0.13±0.03	0.39±0.03	375±0.07	168±0.01	207±0.01	398±0.16	326±0.14
GBC	Wet	7.18±0.01	483±4.24	54±0.49	295±5.66	99.26±0.30	21±0.05	0.43±0.04	1.4±0.05	20±0.07	13±0.01	7±0.07	20±0.24	12±0.49
	Dry	7.23±0.05	167±1.41	6±0.04	92±0.14	14±0.04	6.9±0.28	0.45±0.01	0.20±0	47±0.35	35.3±0.03	12±0.18	71±0.01	58±0.02
WHO		**6.5-8.5**	**1500**	**-**	**1000**	**250**	**250**	**-**	**10**	**400**	**200**	**150**	**500**	**120**

B. Heavy metal concentrations (mean, mg/L) in irrigation waters.

Sites	Seasons	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ebony	Wet	Nd	<0.002	<0.005	<0.006	Nd	Nd	0.420	Nd	<0.010	0.010
	Dry	0.02	Nd	Nd	Nd	Nd	3.424	0.376	Nd	Nd	0.012
CSIR	Wet	Nd	Nd	Nd	Nd	Nd	0.380	2.115	Nd	Nd	0.105
	Dry	0.032	Nd	Nd	Nd	Nd	3.256	0.104	Nd	Nd	0.024
Dzorwulu	Wet	Nd	Nd	Nd	Nd	Nd	13.97	0.035	Nd	Nd	0.050
	Dry	0.036	Nd	Nd	Nd	Nd	1.208	0.152	Nd	Nd	0.004
GAEC	Wet	Nd	Nd	Nd	Nd	Nd	0.605	0.350	Nd	Nd	0.070
	Dry	0.012	Nd	Nd	Nd	Nd	Nd	0.192	Nd	0.180	Nd
GBC	Wet	Nd	Nd	Nd	Nd	Nd	2.735	0.295	Nd	Nd	0.125
	Dry	0.024	Nd	Nd	Nd	Nd	1.588	0.100	Nd	Nd	0.008
FAO		**-**	**0.01**		**0.1**	**0.2**		**0.2**	**0.2**	**5.0**	**2.0**

FAO (1985) - Water quality for Agriculture.

C. QUALITATIVE ASSESSMENT ON VEGETABLE CONSUMPTION

Questionnaire administered to inquire the perceptions of people on vegetable intake; its health and or effects.

Vegetables include: **Cabbage, Carrot, Cucumber, Green Pepper and Lettuce.**

(Please either fill in the blank space provided or tick where applicable)

a. Personal Info.

1. Sex: Male [ ] Female [ ]

2. Marital Status: Married [ ] Single [ ] Divorced [ ]

3. Age: Below 6 yrs [ ] 6-18 yrs [ ] Above 18 yrs [ ]

4. Education: Diploma/Degree [ ] Sec [ ] JSS [ ] None [ ]

b. Lifestyle

5. Do you consume vegetables? Yes [ ] No [ ]

6. If yes, what is the reason for vegetable consumption?

....

....

7. What kinds of vegetables do you consume?

....

8. Where do you get these commodities? Farm [ ] Market [ ] Hawkers [ ] Home

Stall [ ] Mall/ supermarket [ ]

9. How often do you consume them? Everyday [ ] 3 times weekly [ ] Weekly [ ] Monthly [ ] Hardly [ ]

10. How long have you been taking these vegetables?

……………………………………………………………………………………………………

11. How do you eat the vegetables? Raw [ ] Semi-cooked [ ] Fully-cooked [ ]

12. What quantity do you eat a day? ……………………………………………………………

……………………………………………………………………………………………………

14. Do you perceive any benefits from consuming vegetables?

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

15. Do you react to the vegetables when you eat?

……………………………………………………………………………………………………

……………………………………………………………………………………………………

c. Treatment, storage and handling

16. Are you satisfied with the cultivation, storage and handling of these commodities at the farms and markets?

……

……

17. Do you know of any possible contaminants that could raid the vegetables unwholesome?

……

……

18. How do you treat and store your vegetables before consumption?

……