# HEAVY METALS CONTAMINATION IN IRRIGATION WATER AND SELECTED VEGETABLES GROWN AROUND GOLD MINING AREAS. A CASE STUDY OF GEITA DISTRICT

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**A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN FOOD QUALITY AND SAFETY ASSURANCE OF SOKOINE UNIVERSITY OF AGRICULTURE, MOROGORO, TANZANIA**

**2021**

## ABSTRACT

Humans are exposed to heavy metals mainly through ingestion from different sources such as foods, water, air, and occupational settings. It is estimated that millions of people are exposed to heavy metals in different countries globally. Heavy metals toxicity can result to both carcinogenic and systemic health effects to human body. Artisanal small-scale mining activities are found to be a significant source of heavy metals contamination in crops and environmental. This study aimed to evaluate levels of selected heavy metals (Mercury, Lead and Arsenic) contamination in irrigation water and vegetables grown around small scale mining sites in Geita, Tanzania. The study also evaluated the effects of washing, chopping and cooking on the heavy metal concentrations in the selected vegetables. The study revealed that 10% of irrigation water samples were contaminated above recommended safe limit of 5 mg/L for Lead while 80% were having total Arsenic concentration above recommended safe limit of 0.1 mg/L. For leafy vegetables samples, 23% were contaminated with lead above the recommended safe limit of 0.3 mg/kg and 60% of the samples were contaminated with total Arsenic above the maximum limit of 0.1 mg/kg. Despite the fact that some vegetable samples were contaminated with heavy metal above safe limits, their Non carcinogenic health risk index was found to be below one (1) implying that there will be no immediate obvious health risk upon consumption of these vegetables. None of the samples were found to have cancer risk value ($C_R$) that was categorized as risk or very high risk to cause cancer. Twenty seven percent of the vegetable samples were found to have very low risk while the remaining 73% were found to have moderate carcinogenic risk. Washing, chopping and cooking of the vegetables, following traditional method of cooking significantly reduced the amount of mercury and total arsenic by 84% and 34% of the originally present quantities in the spinach samples; and 70% and 40% for amaranth samples respectively.

## DECLARATION

I, John Philip do hereby declare to the Senate of Sokoine University of Agriculture that this dissertation is my own original work done within the period of registration and that it has neither been submitted nor being concurrently submitted in any other institution for a degree award.

_____ _____

**John Philip** **Date**

**(MSc. Food Quality and Safety Assurance)**

The above declaration is confirmed;

_____ _____

**Prof. B. Chove** **Date**

**(Supervisor)**

## COPYRIGHT

## ACKNOWLEDGEMENTS

I would like to thank my Almighty God for giving me health, strength and keeping me on moving to pursue my studies and conducting this research study.

Second, I wish to extend my sincere appreciation to my supervisor Prof. B Chove for his sincere patient guidance, suggestions, constructive criticisms, and diligent efforts from the research proposal development up to final report of this dissertation.

I am glad to express my gratitude to my employer and sponsor of my study Tanzania Drug and Medical Devices Authority (TMDA) for allowing me to undertake this Master's program and granted me with financial support throughout the period. My appreciation also goes to Mr. Roman M. Fortunatus for his assistance during laboratory analysis and data analysis.

Furthermore, I would like to thank my friends, classmates and Academic Staffs from Department of Food Technology, Nutrition and Consumer Sciences at SUA for their supportive ideas during my study.

Lastly I would like to send my appreciation to my beloved wife Liliani Misango, my children Aloyce, Christine, Kherypatrick and Ernest. May Godless you for the love and support you have shown during my study period.

## DEDICATION

I dedicate this work to my beloved Wife and My parents.

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## LIST OF ABBREVIATION AND ACRONYMS

| | |
|---|---|
| AAS | Atomic Absorption Spectrophotometer |
| AASCG | Atomic absorption spectrophotometer cold vapour generation technique |
| ANOVA | Analysis of Variance |
| AMD | Acidic Mine Drainage |
| As | Arsenic |
| BO | Body Mass |
| CCV | Continuing Calibration Verification |
| CR | Carcinogenic Health Risk |
| DMA | Dimethylarsonic acid |
| EDI | Estimated Dietary Intake |
| EDXRF | Energy Dispersive X-ray Fluorescence spectrometry |
| EU | European Union |
| FAO/WHO | Food and Agriculture Organization/World Health Organization |
| Hg | Mercury |
| HQ | Hazard Quotient |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| ICV | Initial Calibration Verification |
| ILCR | Incremental Lifetime Cancer Risk |
| LMIC | Low and Medium Income Country (LMIC) |
| JECFA | Joint FAO/WHO Expert Committee of Food Additives |
| LOD | Limit of detection |
| TDI | Tolerable Dietary Intake |
| TMDA | Tanzania Medical device and Drug Authority |
| MeHg | Methyl Mercury |
| MMA | Monomethylarsonic acid |

| | |
|---|---|
| MPAES | Microwave Plasma-Atomic Emission Spectrometer |
| MSIS | Multimode sample introduction system |
| PTWI | Provision Total Weekly Intake |
| RfDo | Oral Reference Dose |
| $R^2$ | Coefficient of Correlation |
| USEPA | United States Environmental Protection Agency |
| QA | Quality Assurance |
| QC | Quality Control |
| RfD | Oral reference dose per day |
| RSD | Relative standard deviation |
| SUA | Sokoine University of Agriculture |
| THQ | Target hazard quotient |
| TMDA | Tanzania Drugs and Medical Devices Authority |
| US EPA | United States Environmental Protection Agency |
| WHO | World Health Organization |

# CHAPTER ONE

## 1.0 INTRODUCTION

### 1.1 Background Information

Vegetables are rich sources of vitamins, minerals, and fibers, and have beneficial anti-oxidative effects (Amagloh *et al.,* 2017; Septembre-Malaterre *et al.,* 2018). Eating diet rich in vegetables reduces the risk of the onset of cardiovascular diseases, constipation and cancer (prostate cancer) since vegetables contain antioxidants and phyto nutrients which help in the elimination of damaging free radicals in the body tissues (Sattar *et al.,* 2015). Vegetables also help the human body to maintain the acid- alkaline balance, very good for the human sight and are recommended for bladder and kidney ailment, dropsy and gout (Slavin & Lloyd, 2012).

Heavy metal contamination of the food items is one of the most important aspects of food quality assurance. Consumption of food that is contaminated with heavy metals is the main route of exposure to human beings, accounting for an average intake of 50 µg per day in most of individuals (Tchounwou *et al.,* 2012). Contamination of vegetables with heavy metals is a very big problem and heavy metals may be up-taken through the roots during transpiration or deposited on the plant surfaces and then be absorbed into the tissues of the vegetables. Human beings will get exposed to measurable quantities of heavy metals when they eat the vegetable and/or drink the contaminated water (Gupta *et al.,* 2013).

Recently, concern has been raised about the possibility of heavy metals emanating from mineral processing activities contaminating vegetables and other food crops grown around mining areas. Heavy metals ranks high among the chief contaminants of vegetables and a number of studies have shown heavy metals as important contaminants of the vegetables

(Gupta *et al*., 2013; Sharma *et al*., 2006; Singh & Kumar, 2006). Artisanal small scale mining have been shown to significantly contaminate the environment especially crops since they use heavy metals containing chemicals during amalgamation and amalgam smelting of gold (Afrifa *et al.,* 2019). Vegetables take up heavy metals by absorbing them from contaminated soils, irrigation water, as well as from deposits on different parts of the vegetables exposed to the air from polluted environments (Sobukola *et al.,* 2010). The levels of heavy metal contamination in the soil, air, river, and crops from mining affected areas are reportedly higher than those in non-mining areas in many countries (Yang *et al.,* 2018).

Ingestion of heavy metals can upset the biochemical processes in the body, especially because these metals do not undergo decomposition within the body and have a high affinity for many body systems, which includes nervous systems and excretory system. Evidence indicates that oral exposure is the most important way for heavy metals in the environment to enter the human body. Contaminated soil can result in heavy metal translocation into the food chain. According to Gupta *et al.* (2013), heavy metals accumulation in the body can happen when one consumes vegetables or other food types grown in the contaminated area because plants have ability to accumulate heavy metals and pass them along the food chain. This is extremely dangerous for human health because of the fact that they are non-degradable in nature and they cause extremely serious health problems and chronic diseases, even at very low concentrations when ingested for longer periods of time (Leblebici & Kar, 2018).

## 1.2 Problem Statement and Justification

It has been found that mining and small scale agriculture are the major economic activities in Geita Region (Maliganya & Paul, 2016). Gold mining is the major of mining activity

(both large and small scale) in Geita. Artisanal and small scale gold mining in this region and other parts usually uses mercury for extraction of gold from its ore with little or no skills on protecting the human health and environment (Nyanza *et al.,* 2019). Mining activities pollute the surrounding environment through a range of pathways, including, spilling of mine tailings, emissions of dusts containing heavy metals into atmosphere and generation of large quantity of acidic drainage that contains heavy metals (Ugya *et al.,* 2018).

Studies in China, South Korea and USA, have shown that vegetables grown around mining areas are often contaminated with heavy metals, thereby contaminating the food chain and the development of mining industries has generated a big number of risks and hazards that jeopardize ecosystems throughout the world (Chakroun *et al.,* 2010). Irrigation with sewage and industrial waste water have been associated with accumulation of heavy metals in vegetable that leaves different parts of the world with the levels exceeding maximum permissible limits set by WHO (Eissa *et al.,* 2018; Latif *et al.,* 2018; Souri *et al.,* 2018).

The Geita district community has been cultivating vegetables around mining areas and consuming these vegetables without knowing the status of contamination with heavy metals.

Arsenic was found alongside most of gold ores in Tanzania. It can be released into the environment during mining process; therefore, this might increase its potential for exposure to the entire community (Nyanza *et al.,* 2014).

It is known that, heavy metals may accumulate in various locations in the human body, and it is extremely dangerous for human health and heavy metals among many toxic elements, lead, arsenic, and cadmium are considered to be potential carcinogens and are associated with the development of several diseases, especially cardiovascular, kidney, nervous system, blood, and bone diseases (Yang *et al.*, 2018).

Since heavy metals in soil, air, water and other media in mining areas enter plants by absorption through the vegetable roots and dust on leaves and there is a likelihood they can be transferred to human beings and other animals by consuming raw or cooked vegetables and drinking of irrigating water.

It is also of interest to establish whether vegetables and irrigating waters, normally used in these areas contain significant amounts of heavy metals beyond levels set by competent authorities. This situation calls for research on assessment of levels of heavy metals contamination on irrigating water and vegetables cultivated in Geita gold mining areas. The rationale of the study is to generate information on the levels of heavy metals and bring awareness to the vulnerable communities and Tanzanian Government in general on the level of heavy metal contamination on vegetables and irrigating water to the areas where mining operations are taking places. This information is useful for consumers and policy makers so that proper preventive measures can be taken.

## 1.3 Objectives

### 1.3.1 General objective

The general objective of this study was to evaluate the levels of lead, arsenic and mercury in irrigating water and edible portions of selected vegetables grown within the vicinity of the mining sites for assessment of human health risks.

### 1.3.2 Specific objectives

The specific objectives were:-

i. To evaluate the levels of contamination of the heavy metals (lead, arsenic and mercury) in fresh Amaranths and Chinese cabbage grown around gold mining areas;

ii. To evaluate the levels of contamination of the selected heavy metals in irrigating water around gold mining areas;

iii. To evaluate the levels of contamination of the heavy metals in the edible portions of the selected vegetables after washing, chopping and cooking.

iv. To assess human health risks associated with consumption of heavy metals contaminated vegetables from the study areas.

# CHAPTER TWO

## 2.0 LITERATURE REVIEW

### 2.1 Heavy Metals

Heavy metals are generally referred to as those metals which possess a specific density of more than 5 g/cm$^3$ and adversely affect the environment and living organisms. Heavy metals are individual metals and metal compounds that can impact human health and eight common heavy metals are arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver (Tchounwou *et al.,* 2012). Reported sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources and environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations (Bradl, 2005). The presence of toxic metals such as lead (Pb), cadmium (Cd) and mercury (Hg) in the environment is of public health concern when their concentrations are higher than the maximum permissible concentration set by international organization such as WHO/FAO, US EPA and EU in different matrices (Fakhri *et al*., 2015).

Heavy metals such as Zn, Cu, Ni, Co and Cr function as micronutrients and are essential in redox-processes. They are important in the stabilization of molecules through electrostatic interactions, regulation of osmotic pressure and cofactors for numerous enzymes and electron transport chains. Hence, heavy metal ions play an essential role in complex biochemical reactions (Poljšak *et al.,* 2011). The non-essential heavy metal such as Ag, As, Cd, Pb and Hg are of no biological importance to living organisms and are very toxic when found in the ecosystem.

## 2.3 Source of Heavy Metal in Vegetable

Both natural and anthropogenic sources are responsible for increasing the levels of heavy metals in the environment. Natural sources of heavy metals include the parent geologic rock material, volcanic outcropping and spontaneous contribution or forest fires. Whereas anthropogenic sources include sewage sludge, pesticide, organic matter, composite fertilizer supplement (Agrawal *et al.*, 2007), industrial waste, mining, smelting and metallurgical industries (Singh, 2000) and use of untreated or treated industrial and municipal effluents for irrigation purpose (Sharma *et al.*, 2006). Wastewater irrigation is the major contributor of heavy metals contents of the soil (Mapanda *et al*., 2005). High concentrations of heavy metals were reported in vegetables from the untreated wastewater irrigated areas in Lagos Nigeria (Sinha *et al*., 2005; Sharma *et al*., 2006). Use of industrial waste water for raising vegetables is very serious issue in Tanzania because these effluents are heavily loaded with harmful metals and metallic compounds (Singh *et al*., 2004).

The contamination caused by these activities results to increase of heavy metals in the top layer of the soil and consequently in crops via their uptake (Mc Bride, 2003). Lastly aerosols also cause heavy metals contamination of Cd, Pb, Zn, Cr, Ni in soil through atmospheric deposition which are consequently absorbed and accumulated by plant or get adsorbed on aerial surface of the plant (Agrawal *et al.*, 2007). The plant species possess different potential to remove and accumulate different metals and results to serious health complications when such food stuff are consumed.

## 2.4 Heavy metals uptake, transport and accumulation from soil to vegetables

Heavy metals can be transferred from soil pore water into the plants though the roots in the form of dissolved ions (McLaughlin *et al*., 2011). The process of metal uptake and accumulation by different plants depend on different factors such as concentration of

available metal in soils, solubility sequences and the plant species growing on these soils (Andersson, 1977). Plants absorb heavy metals that are present as soluble components in the soil solution and readily available for plant roots hence the bioavailability of metal is the major factor that governs the whole physiological and toxic effects of a metal on biological systems. When plants are exposed to a certain concentrations of heavy metals, plant uptake increase over the whole range of concentrations. The new conceptual framework for plant responses to soil metal with their transporter parameters have been suggested by Guterres *et al*. (2019).

Depending on the external metal ion, four systems have been suggested for metal uptake and transport. These systems are Constitutive High Affinity Transport Systems (CHATS), Inducible High Affinity Transport Systems (IHATS), Constitutive Low Affinity Transport Systems (CLATS) and Inducible Low Affinity Transport Systems (ILATS) (Dechorgnat *et al*., 2011; Nikolic *et al*., 2012; Sorgonà *et al*., 2011). CHATS and IHATS are involved when plant is exposed to high concentration of the metal ion while CLATS and ILATS are involved at lower concentration. Generally the uptake of ion for plants and animals high affinity transport systems follow the Michaelis-Menten kinetics (Ritchie & Prvan, 1996).

Also according to Agrawal *et al*. (2007) accumulation and uptake of heavy metals by different plants and parts depends on the concentration of available heavy metals in the soil and form of metal. Positively charged metal ions are attracted by negative charge like hydroxyl groups and electron pairs of oxygen in the structure of clay mineral and the carboxyl and phenolic group of organic substance. Whereas negatively charged metal ions are attracted to positive charged hydrous oxide of Iron (Fe) and Aluminum (Al), the rate of solubilisation of metals and differences in plant species also affects the availability of heavy metals due to differences in their genotype and transport properties (Agrawal *et al*.,

2007). Difference in root uptake of heavy metals that affect cutical formation by forming epicuticula lipid which are shorter and have high polarity resulting in higher permeability and increased uptake of heavy metals by the plant leaves. Leafy vegetable were found to have more translocation to above ground level that results to higher level of heavy metals compared to non-leafy vegetable due to that there is higher transpiration of leafy vegetable to maintain growth and moisture content (Sinha *et al*., 2006)

Singh and Kumar (2006) found that the differences in accumulation of heavy metals is ascribed to the physiology and morphology of plants such as variation in root interception of metals ions, variation in entry of the metal ions through mass flow, diffusion and translocation of metal ions from the root to shoot, their accumulation tendency and retention capacity.

A study done by Sharma *et al*. (2006) in suburban area of Varanas, India showed that Zn, Cr and Mn concentration in plants are influenced by seasonal variation (Summer and Winter) where in summer heavy metals concentration was higher compared to winter due to higher rate of decomposition of organic matter during summer season thus more release of heavy metals in the soil solution for plant uptake. Also a the study by Dermirezen and Aksoy (2006) found that the levels of heavy metals in vegetables differ depending on location grown (urban or Rural), vegetables from urban area have high levels of heavy metals like Cd, Pb, Cu compared to rural as they are more affected by municipal discharge, traffic and industrial discharge where in rural are affected by traffic and industrial activities. Lastly atmospheric deposition also contributes to elevating the level of heavy metals in vegetables.

## 2.5 Toxicity of heavy metals in vegetables

Heavy metals that contaminate vegetable are present in air, water as well in soil and sediments. Plants are able to take up heavy metals from all those media depending on their concentrations. Heavy metals are first absorbed by the apoplast of roots and transported further into other parts of the cells. Heavy metals are trans-located to different parts through various pathways and results into reduction in growth by altering the physiological, biochemical and metabolic activities of the plant (Sharma & Dubey, 2005). For example, cadmium toxicity induces changes in plant- water relations and oxidative metabolism of *Brassica juncea* (L). In a study done by Singh and Tiwari (2003) where the effect in vegetable was reduction in plant height, fresh and dry matters, and reduction in chlorophyll. Also According to Singh and Agrawal (2007), heavy metal toxicity in vegetables cause adverse effects on physiological, biochemical and morphological characteristic, photosynthetic rate also decreased and lipid peroxidation increased significantly.

## 2.6 Heavy metal toxicity to human (As, Hg and Pb)

The toxicity of these heavy metals has two main aspects:

(a) The fact that they have no known metabolic function, but when present in the body they disrupt normal cellular processes, leading to toxicity in a number of organs;

(b) The potential, particularly of the so-called heavy metals Pb, Hg and As, to accumulate in biological tissues, a process known as bioaccumulation (Jaishankar *et al*., 2014).

This occurs because the metal, once taken up into the body, is stored in particular organs, for example the liver or the kidney, and is excreted at a slow rate compared with its uptake. This process of bioaccumulation of metals occurs in all animals, including food

animals such as fish and cattle as well as humans. It is therefore necessary to control the levels of these toxic metals in foodstuffs in order to protect human health (Briffa *et al*., 2020).

Heavy metal contamination has become a global issue, degrading the environment and causing a serious threat to human health (Afonne & Ifediba, 2020). Because of their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance (Tchounwou *et al*., 2012).

Arsenic is a ubiquitous element that is detected at low concentrations in virtually all environmental matrices (ATSDR, 2007). Contamination with high levels of arsenic is of concern because arsenic can cause a number of human health effects that include, increased risks of both carcinogenic and systemic health effects cardiovascular and peripheral vascular disease, developmental anomalies, neurologic, diabetes, hearing loss, portal fibrosis, hematologic disorders and carcinoma (Tchounwou *et al.,* 2012).

Lead is a naturally occurring bluish-gray metal present in small amounts in the earth's crust occurs naturally in the environment, anthropogenic activities such as fossil fuels burning, mining and manufacturing contribute to the release of high concentrations. Once lead is consumed it is introduced into the bloodstream some is excreted in urine and bile at a clearance rate of 1 to 3 mL/min while the remained bind to red blood cells, distributed to other soft tissues and some bind to the bone (Mason *et al.,* 2014). it is further quickly absorbed in the blood stream and is believed to have adverse effects on different organ systems such as the central nervous system, the cardiovascular system, kidneys, and the immune system (Wani *et al.,* 2015). Very high doses of lead can results to development of irritability, headache, mental dullness and attention difficulty, memory loss, tremor, and

hallucinations within weeks of exposure. Symptoms abruptly worsen to paralysis, convulsions, delirium, coma, or death (Mason *et al.,* 2014). Due to high solubility of organic lead in lipids, it has found to be more toxic hence rapid consequences than inorganic lead (Mason *et al.,* 2014).

Mercury is a heavy metal belonging to the transition element series of the periodic table. It is unique in that it exists in nature in three forms (elemental, inorganic, and organic), with each having its own profile of toxicity. Human toxicity varies with the form of mercury, the dose and the rate of exposure, brain being the target organ (Bernhoft, 2012). All forms of mercury are toxic and their effects include gastrointestinal toxicity, neurotoxicity and nephrotoxicity (Tchounwou *et al.,* 2012). Mercury ions produce toxic effects by protein precipitation, enzyme inhibition and generalized corrosive action (Broussard *et al.*, 2002). Occupational exposure to mercury vapor also causes mercury toxicity. WHO experts have determined that a 24-h urine mercury level over 50 µg is indicative of excessive exposure to mercury (Dasgupta & Wahed, 2014).

## 2.7 Heavy Metal Contaminations in Vegetables in Tanzania

There are few studies on evaluation of lead, total arsenic and total mercury contamination in vegetables in Tanzania, the results of these studies are summarized in Table 1. The levels of heavy metals found in these studies were ranging from non-detected to 5900, 225 and 795 µg/kg for lead, arsenic and mercury respectively. The main sources of contamination suggested by these studies were anthropogenic activities such as mining, industrial activities and road traffic.

**Table 1: Summary of studies on heavy metal contamination in different vegetables in Tanzania**

| Type of vegetable | Instrument used | Concentration of heavy metal (µg/kg) | | | Study location | Suggested main source | Reference |
|---|---|---|---|---|---|---|---|
| | | Lead | Mercury | Arsenic | | | |
| Tomato | AASCG | NM | <20 | NM | Mugusu, Mwanza | Mining | Tungaraza *et al*., (2011) |
| Cabbage | AASCG | NM | 123 | NM | Mugusu, Mwanza | Mining | |
| Amaranth | AASCG | NM | <20 | NM | Mugusu, Mwanza | Mining | |
| Amaranth | AAS | 56 | 795 | 0.777 | Morogoro and Dar es Salaam | Mining and Industries | Saria(2016) |
| *Ipomoea batatas* | AAS | 2460 | NM | NM | Chang'ombe, Dar es Salaam | Road traffic | Kacholi & Sahu (2018) |
| *Amaranthus hybridus* | AAS | 1390 | NM | NM | Chang'ombe, Dar es Salaam | Road traffic | |
| *Abelmoschusesculentus* | AAS | 330 | NM | NM | Chang'ombe, Dar es Salaam | Road traffic | |
| *Solunum molongena* | AAS | 320 | NM | NM | Chang'ombe, Dar es Salaam | Road traffic | |
| Cassava leaves | ICP-MS | NM | 61.4 | 225 | Rwamagasa, Geita | Mining | Nyanza *et al*., (2014) |
| African spinach | AAS | 5900 | NM | NM | Rwamagasa, Geita | Mining | |
| Chinese cabbage | AAS | 3000 | NM | NM | Sinza and Msimbazi, Dar es Salaam | Domestic and Industrial effluents | Bahemuka & Mubofu (1999) |
| Cabbage | EDXRF | 1300 | NM | NM | Unguja, Zanzibar | Road traffic | Najat K. & Fatma O.(2012) |
| Chinese cabbage | AAS | 500-3150 | NM | NM | Mazimbu, Kihonda and Towelo, Morogoro | Domestic and Industrial effluents | Chove *et al*., (2006) |

*NM means not measured
EDXRF = Energy Dispersive X-ray Fluorescence spectrometry
AAS = Atomic Absorption Spectrophotometer
ICP-MS = Inductively coupled plasma mass spectrometry
AASCG = Atomic absorption spectrophotometer cold vapour generation technique

# CHAPTER THREE

## 3.0 MATERIALS AND METHODOLOGY

### 3.1 Sample collection and handling

Thirty frequently consumed vegetable samples of two different crops and 30 irrigation water samples were collected in Geita district along mining areas of five different wards/village/namely; Kaseme/Nyamatondo, Magenge/Nyamalimbe, Nyarugusu/Nyarugusu, Rwamgasa/Rwamgasa, Nyakagwe/Nyakagwe as shown in Figure 1. Vegetable samples were packed in aluminum coated zipper bags while water samples were packed in 1 L bottles. The samples were kept in a cool box with ice-blocks then transported to Tanzania Drugs and Medical Devices Authority (TMDA) quality control laboratory for analysis. The samples were kept frozen at a temperature of (-18 ºC) till further analysis.

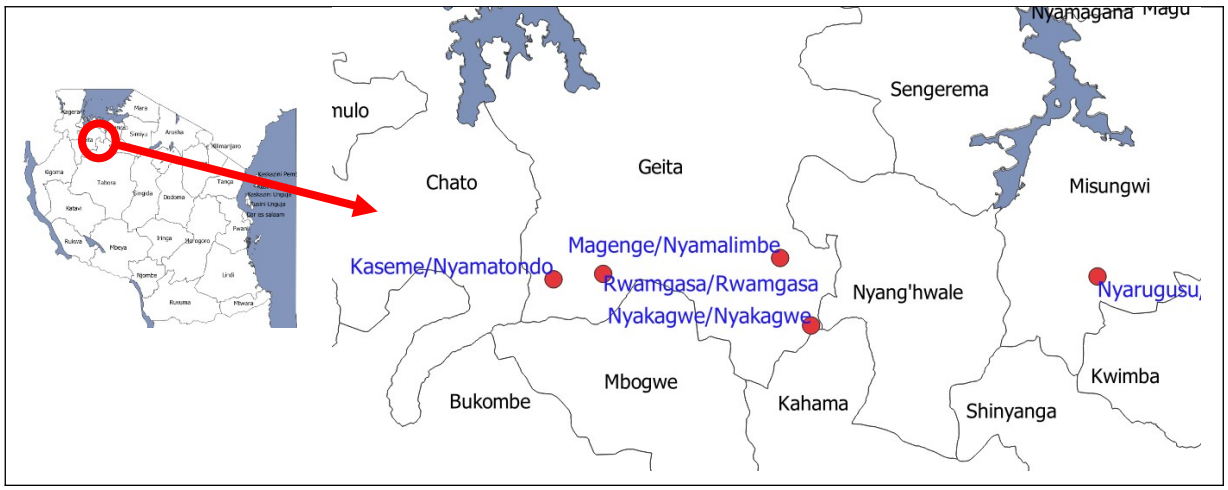


**Figure 1: A map of Tanzania (left) locating the sampling sites (right) in Geita districts**

### 3.2 Sample analysis

Samples were analyzed by Microwave Plasma Atomic Emission Spectrometry (MP-AES 4210), Agilent technologies Australia, equipped with MP Expert software (Version 1.6.0.9255) with hydride generation (HG) for analysis of Total Arsenic and Mercury. MP-AES is a novel atomic emission spectroscopy method that is operated based on

magnetic coupling microwave energy to generate self-sustained atmospheric pressure nitrogen plasma. Samples are typically nebulized prior to interaction with the plasma in MP-AES measurements. The atomized sample passes through the plasma then electrons are promoted to the excited state. The light emitted electrons during return to the ground state light are separated into a spectrum and the intensity of each emission line is measured at the detector.

### 3.3 Analysis of Lead (Pb)

#### 3.3.1 Sample extraction/digestion

Sample was digested following a method by Karlsson, Sjöberg, and Ogar(2015) with modifications. Exactly 0.5g of thawed vegetable sample or 1 mL of water was weighed in analytical balance (Mettler Toledo - XP205, Switzerland). Five milliliter of 32% Nitric acid (LobaChemiePvt, India) was added followed by 1 mL of 30% hydrogen peroxide (Scharlau, Spain). The mixture was then digested with advanced microwave digestion system (EthosEasy - Millstone, Italy). The temperature was risen from room to 150 $^{o}$C for 15 minutes, held at 150 $^{o}$C for 30 minutes then cooled for 20 minutes. Finally, the mixture was transferred to 50 mL volumetric flask then filled to the mark with ultra-pure water (Evoque Water Technologies Farrernberg, USA).

#### 3.3.2 Instrument conditions

Single pass cyclonic spray chamber was used as shown in Figure 2 for sample introduction from auto-sample (SPS 4) to MP-AES. The wavelength was 405.781 nm Replicate = 3, pump speed = 15, sample uptake time = 60 sec, rinse time = 30 sec, stabilization time = 15 sec, read time = 20 sec, sample uptake by fast pump ON, Rinse time with fast pump ON, Quality Control enabled was initial calibration verification (1.5 mg/L) and continues calibration verification (2.0 mg/L). Background correction was set to

Automatic, correlation coefficient = 0.999 in rational mode, % error = 10%, read time = 30 sec. The rinsing solution was 2% nitric acid.

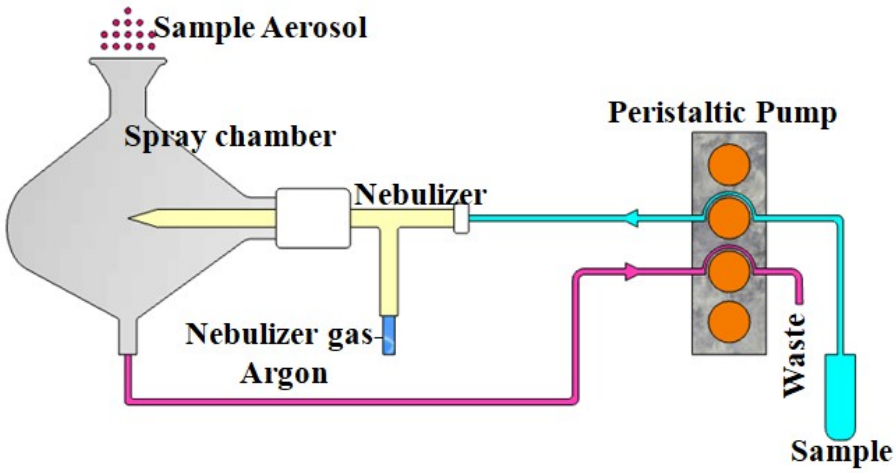


**Figure *2*: Sample introduction system to MP-AES for measurement of lead content in digested irrigation water and vegetables**

### 3.3.3 Preparation of lead standards

Lead reference standard (10000 ± 20 µg/mL), Agilent technologies, USA was diluted with 2% nitric acid to get a stock/working solution of 100 mg/L. This solution was used to create a concentration of 0.5, 1.0, 1.5, 2.0 and 2.5 mg/L that was used to create linear relationship between intensity and concentration.

## 3.4 Analysis of Mercury (Hg) and Total arsenic (As)

### 3.4.1 Sample extraction/Digestion

Sample was digested following procedure as the digestion of lead but for mercury analysis the sample was acidified with 10 mL of 10 % hydrochloric acid (Fisher Chemicals, UK) then filled to 50 mL mark with ultra-pure water. For Total arsenic, the sample was digested and acidified as in mercury analysis but 5 mL of 10% potassium iodide (Sigma Aldrich, Germany) then left for 3 hours to allow for reduction of arsenic (V) to total arsenic (III) (Tanabe *et al*., 2016).

### 3.4.2 Preparation of mercury and total arsenic standards

Mercury reference standard (10100 ± 60 µg/mL) Agilent technologies- USA was diluted with 2% nitric acid to get 100 mg/L stock solution. Stock solution was further diluted to 1000 µg/L to get working solution. This solution was further diluted to 10, 20, 30, 50 and 100 µg/L with 10 mL of 10% hydrochloric acid then filled to 50 mL by using 2% nitric acid.

Total arsenic reference standard (10000 ± 20 µg/mL) Agilent technologies- USA was diluted with 2% to get stock solution of 100 mg/L. This solution was further diluted to 1000 µg/mL with 2% nitric acid. The standards for calibration curve was made by diluting the stock solution to get 20, 40, 60, 80 and 100 µg/mL with 10 mL of 10% hydrochloric acid and 5 mL potassium iodide and finally filled to the 50 mL mark with 2% nitric acid. This solution was also left for 3 hours before analysis.

### 3.4.3 Instrument conditions

Multimode sample introduction system (MSIS) spray chamber was used as shown in Figure 3 to create mercury hydride/ Total arsenic hydride and introduce them to MP-AES from auto-sample (SPS 4).1.5% of sodium borohydrade (Alfa Aesar, England) in 0.1% Sodium hydroxide solution was used as reductant for both mercury and total arsenic analysis. The wavelength was 253.652 and 193.695 nm for mercury and total arsenic respectively. Replicate = 3, pump speed = 15, sample uptake time = 60 sec, rinse time = 30 sec, stabilization time = 15 sec, read time = 30 sec, sample uptake by fast pump ON, Rinse time with fast pump ON, Quality Control enabled was initial calibration verification (40 µg/L and 60µg/L) and continues calibration verification (50 µg/L and 80µg/L) for mercury and total arsenic respectively. Background correction was set to

Automatic, correlation coefficient = 0.999 in rational mode, % error = 10%, read time = 30 sec. The rinsing solution was 2 % nitric acid.

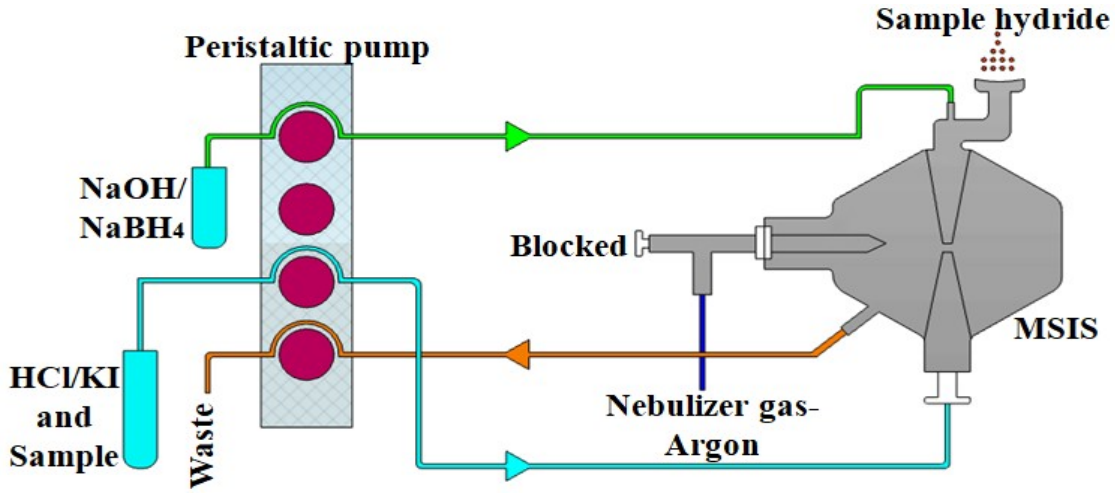


**Figure 3: Sample introduction system for mercury and total arsenic analysis in Microwave plasma Atomic Emission Spectrometry**

### 3.5 Quality control parameters

The method for detection and quantification of heavy metal was semi-validated by using selected method validation parameters such as detection limit, quantification limit, precision, accuracy and calibration verifications. Precision and accuracy of the results were assessed by determining recovery and repeatability of the analysis of matrix spiked sample. Precision was expressed as relative standard deviation (RSD) of seven replicates of spiked sample results and calculated as shown in Equation 1.

$$RSD(\%) = \frac{Standarddeviation}{Meanvalue} * 100\% \qquad \text{.....Equation 1}$$

The percentage recoveries of the analyte were calculated to evaluate the accuracy of the analytical method and were expressed as shown in Equation 2;

$$Recovery(\%) = \frac{Concentration\ of\ the\ spiked\ sample - Concentration\ of\ unspiked\ sample}{Expected\ spiked\ c\ oncentration} * 100\%$$

**…..Equation *2***

Initial calibration verification was done after the instrument reading the standards and it was assessed if pass or fail if it was within 100±10%. Continuers calibration verification was done after every 20 samples and it was assessed the same as initial calibration verification. In each of heavy metal analysis the third standard and fourth standard was used for initial calibration verification and continuing calibration verification respectively.

$$Calibration\ verification = \frac{Measured\ concentration}{Defined\ concentration} * 100\%$$

**……Equation 3**

### 3.6 Sample preparation for assessing effect of washing, chopping and cooking on heavy metal concentration

Five amaranth and spinach cabbage samples were taken from remaining portion of raw samples that were tested and found to have high heavy metal concentration (total) for evaluation of effect of washing and cooking on heavy metals. Vegetables were prepared and cooked according to the method by (Traoré *et al.,* 2017) with minor modifications. In summary about 50 g of fresh thawed vegetables were added in a cooking port with 200 mL ultra-pure water after washing, sorting and chopping. The mixture was boiled at approximately 98 ±3 ºC for 15 minutes. The water that was used to cook these vegetables was discarded. The sample was cooled to room temperature for lead, total arsenic and total mercury analysis.

### 3.7 Risk Assessment

Expected health risks associated with ingestion of heavy metals in the vegetables in this study was assessed using hazard quotient (HQ) ratio. This ratio was determined using Equation (4) below.

$$HQ = \frac{¿ * C_{metal}}{R_{fd} * Bo} \text{.....Equation } \textit{4}$$

Where; Div is the daily intake of vegetables ((kg/person)/day), $C_{metal}$ is the concentration of specific metal (mg/kg), RfD is the oral reference dose for the metal (mg/kg per day) and Bo is the human body mass (kg). The RfD is an estimate of a daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime ( US EPA, 2014).

Cumulative non cariogenic health risks were assessed by summing up the HQs for each element analysed as shown in $i=1\,n\,HQ_i$…….. Equation 5 bellow

$$HI = \sum_{i=1}^{n} HQ_i \text{..... Equation 5}$$

Average intake of amaranth and Chines cabbage were obtained from the study in Mugusu village in Tanzania by Tungaraza, Chibunda, and Pereka (2011) that was 17 g and 19 g respectively. This study also found that an average African man weighs 55 kg. When HQ is < 1, there is no obvious risk from the substance over a lifetime of exposure, while HQ is > 1, the toxicant may produce an adverse effect to the human over lifetime.

Potential non carcinogenic health risk for long exposure to Geita residents through selected vegetables (spinach and amaranth) consumption were assessed using target hazard quotient (THQ) that was proposed by the United States Environmental Protection

Agency (US EPA) for assessing the potential health risks of pollutant exposure to human health (US EPA, 2002) as shown in ……Equation 6.

$$THQ = \frac{C_{metal} * ¿ * EF * ED}{AT * R_{fd} * Bo}$$

**……Equation 6**

Where Div is the daily intake of vegetables ((kg/person)/day), Cmetal is the concentration of specific metal (mg/kg), RfD is the oral reference dose for the metal (mg/kg per day), Bo is the human body mass (kg), EF is the exposure frequency (exposure days per year = 365 days per Annum), ED is the exposure duration = 60 annums, AT is the average exposure time for non-carcinogens (exposure days within whole lifetime =21900days) (Chang *et al.*, 2014).

For carcinogenic health risk (CR) assessment upon consumption of these vegetables was evaluated based US EPA, (2001, 2002) Incremental Lifetime Cancer Risk (ILCR) as incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen.

$$C_R = \left[ \frac{C_{metal} * ¿ * EF * ED}{AT * Bo} \right] * SF$$ ……Equation 7

Where by SF is carcinogenic slope factor that was approximated to be 1.5 mg/kg/day obtained from US EPA. Slope Factor have been defined as the risk generated by a lifetime average amount of one mg/kg/day of carcinogen chemical and is contaminant specific (Mohammadi *et al*., 2019). Qualitative descriptions of lifetime cancer risks were based on ATSDR standards as follows; very low when the estimated value is low or equal to $10^{-6}$, low when ranges from greater than $10^{-6}$ to less or equal to $10^{-4}$, moderate when ranges from greater than $10^{-4}$ to less than or equal to $10^{-3}$, high when ranges from greater than $10^{-3}$

to less than or equal to $10^{-1}$, and very high when the estimated value is greater or equal to $10^{-1}$ (ATSDR, 1995; Rapant *et al*., 2011; Tepanosyan *et al.*, 2017).

### 3.8 Data Analysis

All data analysis and visualization was done by R software (4.0.2 of 2020) (R Core Team, 2013). Data was subjected to two-way analysis of variance (ANOVA). ANOVA assumption was checked on normality, homogeneity and independence. Shapiro's test, histograms and quartile-quartile plots were used for checking normality; Bartlett's test was used for checking homogeneity of variance and standardized residual plots for independence.

Since all the data was not obeying ANOVA assumption and the groups (location and sample types) was unbalanced, the Skillings–Mack's test (Chatfield & Mander, 2009) by using 'Skillings. Mack' package in R was used for testing the significance variation between location and sample types. Kruskal-Wallis test was used for testing effect of each treatment (location or sample type) while it's pairwise comparisons was done by using Wilcoxon rank sum test with continuity correction. Data on effect of cooking on heavy metal was done by unpaired student's t test. Alpha level less than 0.05 was considered significant.

# CHAPTER FOUR

## 4.1 RESULTS AND DISCUSSIONS

## 4.2 Method Validation

Perfect linear relationships ($r^2 > 0.99$) between concentrations (µg/kg) of the standards with the intensities were observed as shown in Figure 4. This indicates that there were a good linear relationship between concentration and intensities (c/s), also all correlation coefficient were greater than acceptable limit of 0.998 for linearity of regression line (Christian, 2007). Method detection limits, quantification limits and precision are shown in Table 2. The recoveries were in the range of 93—99 %. All the recovery values were within the acceptable range of 80—120% for metal analysis (Harvey, 1999).

The method for detection and quantification of heavy metals by using MP-AES was observed to be robust since all the semi- validation parameters were in the range that is requested by ISO.

**Table 2: Method semi validation parameters used for heavy metal analysis by HG-MP-AES**

| Quality control parameters | Hg | As | Pb |
|---|---|---|---|
| Detection limits (µg/L) | 1.00 | 1.50 | 2.5 |
| Quantification limits (µg/L) | 10.0 | 15.0 | 30 |
| Precision (% n=7) | 3.4±0.40 | 7.2±1.54 | 0.3±0.04 |
| Accuracy (Recovery (%)) | 97.56 | 93.67 | 98.25 |
| Initial calibration verifications (%) | 101.43 | 99.48 | 100.8 |
| Continuing calibration verifications (%) | 97.82 | 95.45 | 98.75 |

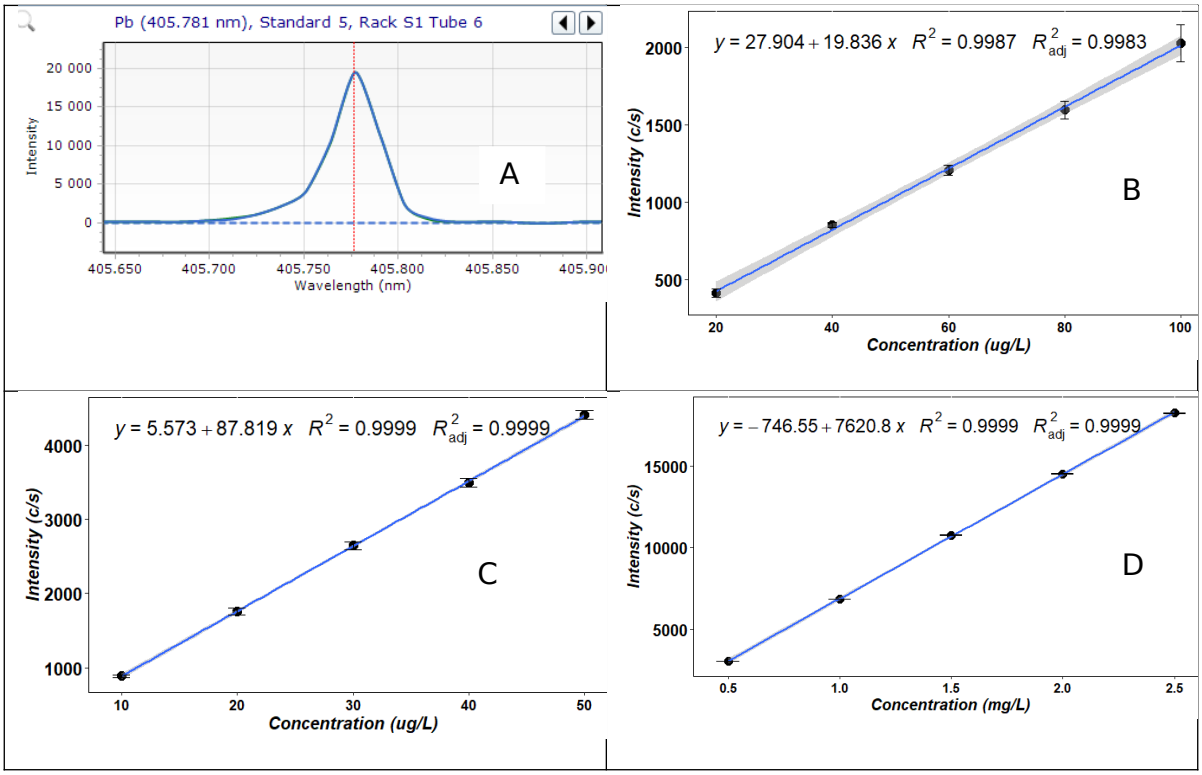


**Figure 4: Sample chromatogram for Lead standard (A), calibration curves (±SE, n= 3 replication) for Total arsenic (B), Mercury (C), lead (D).**

### 4.3 Heavy metal contamination in general

The results showed a great variation in heavy metal contamination (As, Hg and Lead) in amaranth, spinach and irrigation water from different wards as shown in Figure 5. Water samples had concentration of heavy metals ranging from 0.39-8.97, 0.035-1.089, 0-0.35 mg/L for lead, total arsenic and mercury respectively. For leafy vegetables the concentration of heavy metals ranged from 0-1.18, 0.03-0.36, 0-0.16 mg/kg for lead, total arsenic and mercury respectively. Out of 30 irrigation water samples, 10% of the samples were contaminated above safe limit of 5 mg/L for lead while 80% of the samples were having total arsenic concentration above safe limit of 0.1 mg/L. For leafy vegetables, out of 30 leafy vegetable samples, 23% of the samples were contaminated with lead above safe limit of 0.3 mg/kg while 60% samples were contaminated with total arsenic above maximum limit of 0.1 mg/kg. Based in our knowledge the maximum limits are not established internationally for total mercury in irrigation water or leafy vegetables even

during the conduct of this study. However, different countries such as China have established maximum limit as 10 µg/kg (CSEPA, 2014).

Lead content was high in all samples followed by total arsenic then mercury. The high levels of all heavy metal concentration in vegetables and water samples might be attributed to the reason that, there was an ongoing processing of gold ores and reprocessing of tailing to get gold using poor technology by small scale miners and amalgamation technology which involves use of mercury and waste water are discharged to nearby river/water stream and open ground used for cultivation of vegetable. Contamination of the wetland, ponds and river by sluicing these waste and AMD could provide a pathway for heavy metals into vegetables grown around the mining areas. The findings of the current study are in agreement with the results from the work done by Zhuang *et al.* (2014) at Dabaoshan mine in southern China where vegetables and water samples were found to contain high concentration of heavy metals due to effects of mining activities.

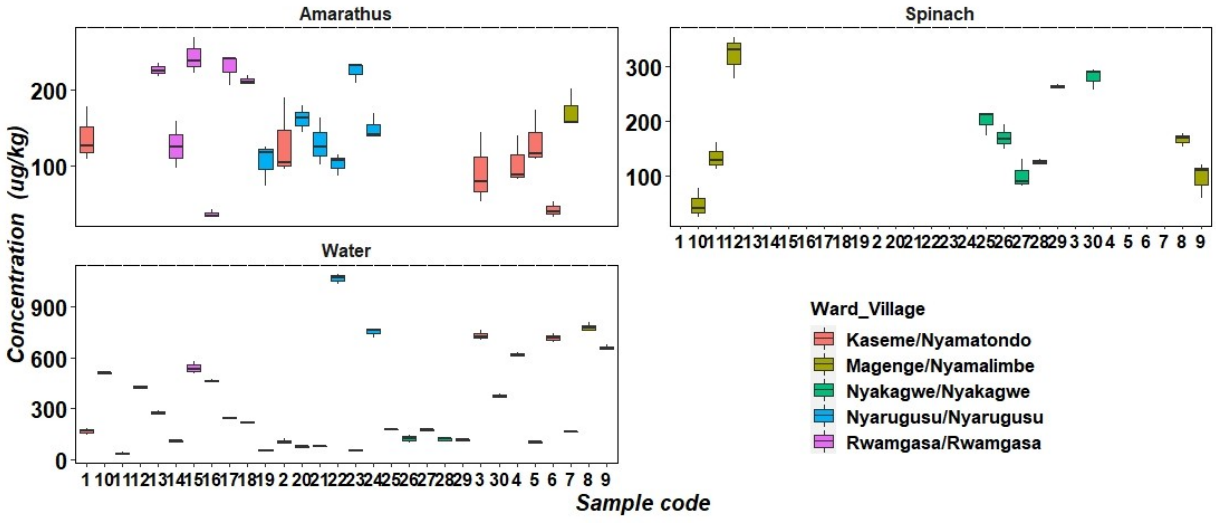


**Figure 5: Boxplot showing total arsenic concentration (± SE in µg/kg, n=3 replications, fresh basis) in samples collected at different wards along mining areas in Geita.**

### 4.4 Effect of sample type

The results showed that the type of the sample had a significant difference ($p<0.05$) in concentration of lead ($p=2.2e-16$) and total arsenic ($p=0.0015$). Irrigation water and spinach were found to contain a significantly high total arsenic content (334.67±29.228 and 173.76±14.820 µg/kg respectively) than amaranth (145.33±8.388). Tungaraza *et al.* (2011) reported lower values of mercury content (<20 µg/kg) in amaranth leaves around artisan mining in Mugusu, Tanzania. Irrigation water was also reported to have high lead concentration (1794.05±155.546 µg/kg) than spinach and amaranth (158.84±30.062 and 162.03±27.486 µg/kg respectively) as shown in Figure 6. Presence of heavy metals in vegetables might be a result of contamination from the water that was used for irrigation or translocated from contaminated soil (Eissa *et al.,* 2018) since there is a possibility that the soil was also contaminated. Most environmental contamination and human exposure to heavy metals are due to anthropogenic activities such as mining, smelting operations, and various uses of metals and metal-containing compounds in different human activities (Tchounwou *et al.,* 2012).

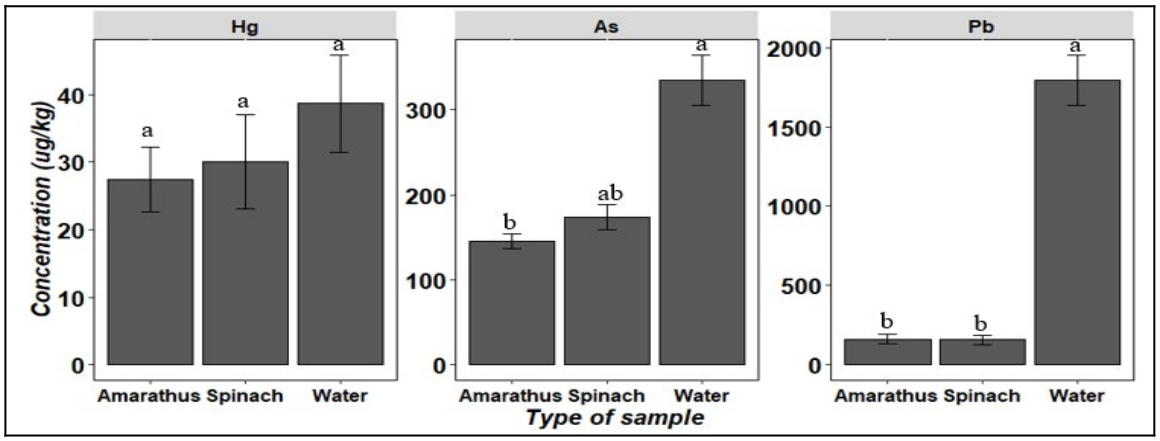


**Figure 6: Heavy metal contamination (±SE in µg/kg fresh basis) in irrigation water (n=90) and two leafy vegetables (n=33 for spinach and 57 for Amaranth) samples collected along small-medium scale mining areas in Geita. Bar graph of the same metal with different letters shows a statistical difference according to pairwise comparisons using Wilcoxon rank sum test with continuity correction.**

## 4.5 Effect of location

In general, the result shows that there was a statistical difference on mercury and total arsenic concentration between all locations ($p<0.05$) Nyakangwe village was observed to have high heavy metal contamination (µg/kg) in all the sample types as shown in Figure 7 which may be caused by huge contamination of water and soil due to gold processing operations by huge number of small scale miner processors where amalgamation was used as mining is still new and active. For As concentration being high may be due to the inherent mineralogy of the ores which contain the mineral arsenopyrite $FeAsS_2$ also application of phosphate fertilizers produced in Tanzania consist of Hg, Cd, As, Pb, Cu, and Ni, these may increase the levels of these metals as reported by Jama & Van Straaten, (2006)

The trend of amount of heavy metal between locations was similar in which Lead content was high followed by total Arsenic then Mercury. The results of total Arsenic in this study is similar to the study done in vegetables grown in urban areas of coastal of Tanzania; that study found the samples to range from 1 µg/kg Kigogo ward in Dar es Salaam city to 1533 µg/kg at Mji Mpya Morogoro Region (Saria, 2016).

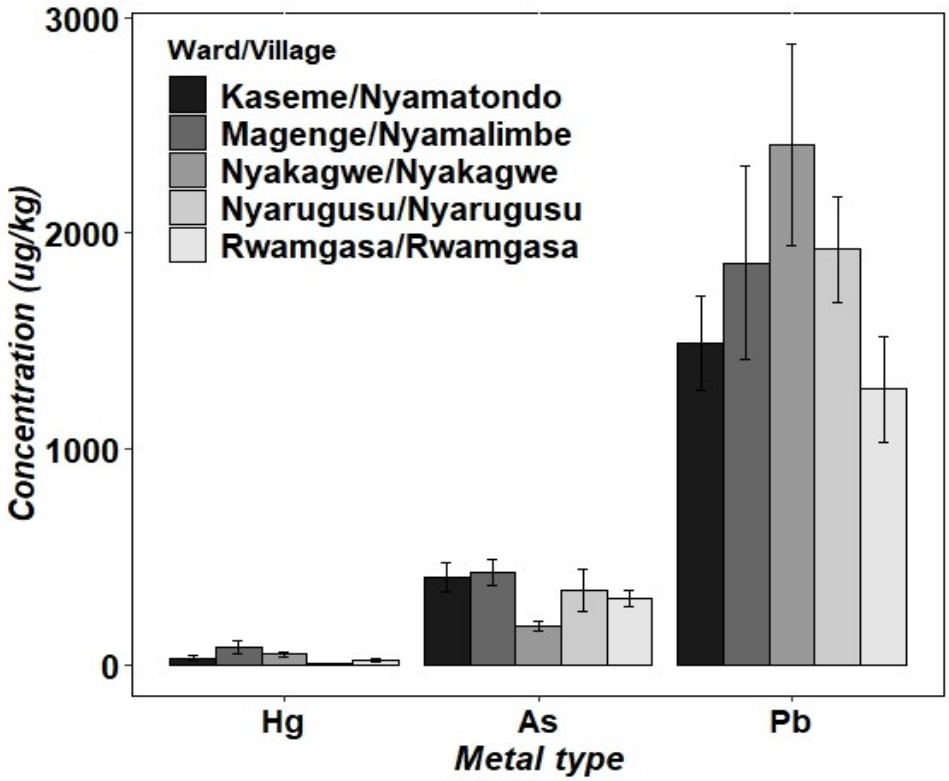
Ward/Village
Kaseme/Nyamatondo
Magenge/Nyamalimbe
Nyakagwe/Nyakagwe
Nyarugusu/Nyarugusu
Rwamgasa/Rwamgasa
Concentration (ug/kg)
3000
2000
1000
0
Hg
As
Pb
Metal type

**Figure 7: Metal concentration (µg/kg fresh basis) ± SE (n=18) in irrigation water along mining areas in Geita.**

### 4.8 Interaction effect on location and sample type

Location and type of sample were combined as randomized block research design and the influence of the interaction was analyzed. The results showed that location and type of the sample do not have a significant difference ($p<0.05$, according to sci.mack test) in heavy metals contamination in any metal determined. This observation might be due to high variation in heavy metals concentration in the samples. Table 3 shows concentration of heavy metals in only leafy vegetables in different locations. On average, both amaranths and spinach from all locations were contaminated with total arsenic above the safe limit.

**Table 3: Heavy metal concentration (± SE in µg/kg fresh basis) in selected leafy vegetables irrigated with water along mining areas in Geita, Tanzania**

| Ward/Village | Produce | N | Hg | As | Pb |
|---|---|---|---|---|---|
| Kaseme/Nyamatondo | Amaranth | 18 | 32.17±11.36 | 106.69±10.90 | 208.10±58.87 |
| Magenge/Nyamalimbe | Amaranth | 3 | 52.21±2.78 | 172.19±14.77 | 86.75±5.31 |
| Nyarugusu/Nyarugusu | Amaranth | 18 | 36.37±9.08 | 145.73±10.79 | 165.11±60.74 |
| Rwamgasa/Rwamgasa | Amaranth | 18 | 9.61±2.05 | 179.10±18.24 | 125.42±21.57 |
| Magenge/Nyamalimbe | Spinach | 15 | 6.24±0.58 | 153.54±25.61 | 119.59±12.30 |
| Nyakagwe/Nyakagwe | Spinach | 18 | 50.01±10.77 | 190.60±16.47 | 191.55±53.63 |

### 4.9 Health risk assessment

Mercury, Arsenic and Lead have been ranked among the five priority metals that are of great public health significance because of their high degree of toxicity, others are

Cadmium and Chromium (Tchounwou *et al.*, 2012). The results show that the average HQ of both amaranth and spinach in Mercury, total Arsenic and Lead were below one (1) (Table 4); this implies that consumption of these vegetables will not pose any risk to health throughout the life time. Lower value of HQ is caused by lower amount of vegetables that was estimated to be consumed per person per day, if the exposure is summed up from other food products that are consumed in large quantities in this region the HQ might have been greater than one (1). Falandysz and Drewnowska (2015) observed similar findings in which the daily intake of mushroom was below the established RfD for total mercury.

**Table 4: The oral reference dose and Hazard Quotient (HQ), Target Hazard Quotient (THQ) ±SE for total Arsenic, Mercury and Lead in vegetables studied**

| | **Arsenic** | **Lead** | **Mercury** |
|---|---|---|---|
| RfD mg/kg-day | $3 \times 10^{-4}$ | $3.5 \times 10^{-3}$ | $3 \times 10^{-4}$ |
| Amaranths (HQ) | $0.000167 \pm 1.09 \times 10^{-5}$ | $5.1 \times 10^{-5} \pm 2.89 \times 10^{-6}$ | $2.83 \times 10^{-5} \pm 5.64 \times 10^{-6}$ |
| Spinach (HQ) | $0.0002 \pm 1.46 \times 10^{-5}$ | $1.4x\ 10^{-5} \pm 2.41 \times 10^{-6}$ | $3.10 \times 10^{-5} \pm 6.15 \times 10^{-6}$ |
| Amaranths (THQ) | 0.150±0.01 | 0.014±0.00 | 0.028±0.01 |
| Spinach (THQ) | 0.179±0.01 | 0.014±0.00 | 0.031±0.01 |

RfD is Reference Dose for Oral exposure in mg/kg-day obtained from integrated risk information system (US EPA, 1987a, 1987b).

The results also showed that none of the vegetable were found to have non carcinogenic health impact due to low cumulative health risk (HI) being less than one ( 1); implying that the vegetables were not having a significant amount of heavy metal to pose a

significant health effect upon consumption. On the other have none of the sample found to have cancer risk value ($C_R$) that was categorized as risk or very high risk to cause cancer. Twenty seven percent of the samples were found to have very low risk while 73% were found to have moderate carcinogenic risk. In general all samples in each vegetable were having the $C_R$ value in the range of moderate carcinogenic health risk as shown in Table 5. Studies in other region of the world such as in Iran have shown high cancer risk upon consumption of contaminated vegetables (Zafarzadeh *et al*., 2018). In Bangladesh it was found that the cumulative carcinogenic health risk upon consumption of selected fruit vegetables, root vegetables, leafy vegetables, and fruits were greater than $10^{-4}$ at 22, 15, 59, and 4%, respectively (Sultana *et al.*, 2017), while the US EPA recommended the safe limit for cancer risk to be below about 1 chance in 1,000,000 lifetime exposure ($< 10^{-6}$) (US EPA, 2001).

**Table 5: Carcinogenic health risk assessment (CR) and Non carcinogenic health risk assessment ±SE for total Arsenic, Mercury and Lead in vegetables studied**

| Type of vegetable | HI | Metal | N | $C_R$ |
|---|---|---|---|---|
| Amaranths | 3.0 x 10-3±5.01 x $10^{-4}$ | Arsenic | 57 | 6.7 x $10^{-5}$ ±3.89 x $10^{-6}$ |
| | | Lead | 57 | 7.5 x $10^{-5}$ ±1.27 x $10^{-5}$ |
| | | Mercury | 57 | 1.3 x $10^{-5}$ ±2.25 x $10^{-6}$ |
| Spinach | 3.3 x 10-3±7.19 x $10^{-4}$ | Arsenic | 33 | 8.1 x $10^{-5}$ ±6.87 x $10^{-6}$ |
| | | Lead | 33 | 7.4 x $10^{-5}$ ±1.39 x $10^{-5}$ |
| | | Mercury | 33 | 1.4 x $10^{-5}$ ±3.23 x $10^{-6}$ |

### 4.10 Effect of washing, chopping and cooking on heavy metal concentration

Studies on the effect of cooking vegetables on heavy metals are very rare. The results show that washing, chopping and cooking the vegetables significantly reduces the amount of heavy metals originally present in the samples (except lead content) as shown in Table

6. Cooking vegetables in distilled water have been shown to reduce total arsenic in vegetables for about 60% in spinach in Chile (Díaz *et al.,* 2004). Other studies show that roasting can significantly reduce mercury content up to 67% (Morgan, 1999). Also it was observed that precooking activities such as sorting, peeling, washing and chopping can significantly reduce heavy metal in vegetables (Rahman *et al*., 2019).

Cooking have been shown to reduce significantly Lead (Pb) content in different vegetables (Sadeghi *et al*., 2017). Cooking also have shown to significantly reduce lead content in potatoes while cooking didn't result to significant effect on amount of mercury (Perelló *et al.,* 2008). Ionic (II) mercury and organic mercury are partially soluble in water (AMAP/UNEP, 2013) while elemental mercury evaporates easily at higher/elevated temperatures (Falandysz *et al.,* 2019); therefore, washing and cooking might result to reduction of total mercury levels. Reduction of heavy metal during cooking might be also accounted retention of water in vegetables after cooking since ultra-pure water was used for cooking. Leaching of metal from leaves folia to water during processing/cooking might also be the reason of reduction in heavy metal in cooked vegetables (Falandysz & Drewnowska, 2015). Cooking resulted to reduction though not significant in lead content that was also observed by another study on rice (Naseri *et al.,* 2018). It was observed that major vegetables available in Tanzania are eaten while washed, chopped and cooked *(*Mamiro *et al*., 2016) hence dietary exposure through vegetable might slightly be reduced.

**Table 6: Effect of cooking vegetables in heavy metal concentration (µg/kg ± SE, n=5, fresh basis)**

| Produce | Processing | Mercury | Total Arsenic | Lead |
|---|---|---|---|---|
| Amaranth | Raw | 38.10±13.94 [a] | 165.82±26.38 [a] | 695.32±170.12 [a] |
| Amaranth | Cooked | 11.50±5.39 [b] | 99.81±28.75 [b] | 496.52±174.73 [a] |
| Amaranth | % Reduction | 69.8 | 39.8 | 28.6 |

| | | | | |
|---|---|---|---|---|
| Spinach | Raw | 33.96±17.01 [a] | 235.16±36.69 [a] | 422.70±144.13 [a] |
| Spinach | Cooked | 5.31±3.25 [b] | 154.19±18.53 [b] | 272.70±152.15 [a] |
| Spinach | % Reduction | 84.4 | 34.4 | 35.5 |

Rows with different letters in different processing methods indicates significance different in processing according to t-test $p<0.05$. % Reduction due to cooking was calculated as the ratio of reduced concentration (initial – final) of the metal to initial concentration before cooking times 100%.

# CHAPTER FIVE

## 5.0 CONCLUSION AND RECOMMENDATIONS

Improper management of miner's waste water that contains Hg used in amalgamation and AMD, that comes into contact with soil near the mining areas cause elevated level of heavy metals in soil finally. Plants can also accumulate these heavy metals from soil and may consequence an adverse health effect on human beings after consumption of these vegetables.

In this study, the levels of Mercury, total Arsenic and Lead were determined in irrigation water and frequently consumed vegetables around artisanal mining sites in Geita. Few samples were contaminated with heavy metals above the maximum levels. This poses a risk not only to consumption of vegetables but also on all varieties of food crops grown around mining sites in Geita.

The Hazard Quotient Index (HQ), Target hazard Quotient (THQ) and non-carcinogenic health risk (HI) was found below one that means there will be no immediately obvious risk on consumption of these vegetables. None of the sample found to have cancer risk value ($C_R$) that was categorized as risk or very high risk to cause cancer. Twenty seven percent of the samples were found to have very low risk while 73% were found to have moderate carcinogenic risk. However, accumulation of these heavy metals especially from other much/frequently consumed food crops might be of alarming levels. More studies on the exposure to heavy metals from artisanal mining in developing countries need to be done since little is known on levels of heavy metals in people around mining sites especially small to medium scale sites and the general public needs to be educated on handling of heavy metals that are used in the mining sites not to contaminate soil, irrigation water or crops grown in general.

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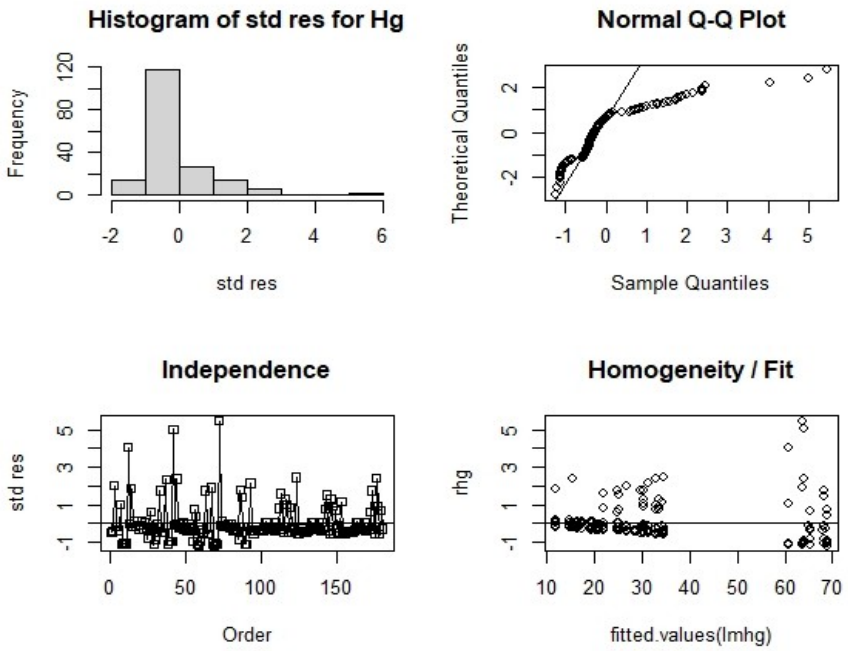
# APPENDICES

## Appendix 1: Checking the ANOVA assumptions



## Appendix 2: Selected data analysis outputs

```
        Kruskal-Wallis rank sum test

data:  Hg by Ward_Village
Kruskal-Wallis chi-squared = 16.694, df = 4, p-value = 0.002217
```

```
        Pairwise comparisons using Wilcoxon rank sum test with continuity correction

data:  data$Hg and data$Ward_Village
```

| | Kaseme/Nyamatondo | Magenge/Nyamalimbe | Nyakagwe/Nyakagwe | Nyarugusu/Nyarugusu |
|---|---|---|---|---|
| Magenge/Nyamalimbe | 0.3959 | - | - | - |
| Nyakagwe/Nyakagwe | 0.1068 | 0.0492 | - | - |
| Nyarugusu/Nyarugusu | 0.2812 | 0.5097 | 0.0047 | - |
| Rwamgasa/Rwamgasa | 0.1802 | 0.5586 | 0.0021 | 0.8969 |

```
        Kruskal-Wallis rank sum test

data:  As by Ward_Village
Kruskal-Wallis chi-squared = 10.431, df = 4, p-value = 0.03376
```

```
Skillings-Mack Statistic =  0.400000 , p-value =  0.818731
Note: the p-value is based on the chi-squared distribution with d.f. =  2

$Nblocks
[1] 5

$Ntreatments
[1] 3

$rawdata
            [,1]         [,2]         [,3]         [,4]         [,5]
[1,] 32.16748664  6.236924476 49.878076697  9.611421377 30.144988662
[2,] 30.14498866 83.018964467 36.368069340 22.892413516 52.206944183
[3,] 52.20694418 50.010560586  7.237185306 32.167486643  6.236924476

$rankdata
     [,1] [,2] [,3] [,4] [,5]
[1,]    2    1    3    1    2
[2,]    1    3    2    2    3
[3,]    3    2    1    3    1

$varCovarMatrix
     [,1] [,2] [,3]
[1,]   10   -5   -5
[2,]   -5   10   -5
[3,]   -5   -5   10

$adjustedSum
             [,1]        [,2] [,3]
[1,] -1.732050808 1.732050808    0
```

```
           Df   Sum Sq   Mean Sq F value   Pr(>F)
Processing  1 27000.67 27000.668 7.11571 0.016238 *
Produce     1 19132.79 19132.790 5.04223 0.038324 *
Residuals  17 64506.71  3794.513
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```