UNIVERSITY OF EDUCATION, WINNEBA

LEVELS AND HEALTH RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS IN RICE (*ORYZA SATIVA*) AND SOIL FROM ASHANTI REGION

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DECLARATION

STUDENT'S DECLARATION

I, Portia Asare declare that this thesis, with the exception of quotations and references contained in published works which have all been identified and duly acknowledged, is entirely my own original work, and it has not been submitted, either in part or whole, for another degree elsewhere.

SIGNATURE:………………………………..

DATE:………………………………………...

SUPERVISOR'S DECLARATION

We hereby declare that the preparation and presentation of this work was supervised in accordance with the guidelines for supervision of thesis as laid down by the University of Education, Winneba.

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DEDICATION

I dedicate this work to my lovely children, Janice Ofori Kuragu and Harrison Ofori Gyekye.

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ABBREVIATIONS

ADI:	Acceptable Daily Intake
ATSDR:	Agency for Toxic Substances and Disease Registry
BDH:	British Drug House
BCF:	Bioconcentration factor
EDI:	Estimated Daily Intake
EPA:	Environmental Protection Agency
FAO:	Food and Agriculture Organization
HQ:	Hazard quotient
IARC:	International Agency for Research on Cancer
JECFA:	Joint FAO/WHO Expert Committee on Food Additives
LOD:	Limits of Detection
MAC:	Maximum allowable concentrations
NTP:	National Toxicology Program
pH:	Hydrogen Ion Concentration
PTDI:	Provisional Tolerable Daily Intake
TF:	Translocation factor
USEPA:	United State Environmental Protection Agency
WHO:	World Health Organization

ABSTRACT

Anthropogenic activities release potentially toxic elements into the environment, which contaminate the food chain. The main objective of this research was to evaluate heavy metal exposure and potential health risk of consuming heavy metals in rice cultivated in the Asante Akim area. The levels of potentially toxic elements; As, Cd, Cr, Hg and Pb, in soil and rice samples were assayed using Agilent 7700 Series Inductively Coupled Plasma-Mass Spectrophotometer and compared with that of the WHO/FAO recommended levels. The mean heavy metal content in soil was 7.5 mg/kg, 0.52 mg/kg, 0.47 mg/kg, 1.30 mg/kg and 8.69 mg/kg for As, Cd, Cr, Hg and Pb, respectively. Mean levels of the elements in rice were 0.082 mg/kg, 0.27 mg/kg, 0.48 mg/kg, 0.028 mg/kg and 0.14 mg/kg for As, Cd, Cr, Hg and Pb, respectively. Soil pollution indices showed that the soils are unpolluted with the potentially toxic elements studied. The concentrations of the potentially toxic elements in rice were below the Maximum Allowable Concentration (MAC) recommended by Codex Alimentary Commission except Cd which was marginally higher than the MAC. Dietary exposure of the elements to consumers was assessed by comparing the estimated daily intake (EDI) to the Provisional Tolerable Daily Intake (PTDI). The estimated daily intake values for As, Cd, Cr, Hg and Pb were 1.45×10^{-4}, 4.8×10^{-4}, 8.5×10^{-4}, 4.95×10^{-5} and 2.4×10^{-4} respectively. The non-carcinogenic health risk was assessed using Hazard Quotients (HQ). The HQ for all the potentially toxic elements were less than the USEPA permissible value of 1, suggesting that the consumption of rice from the study area constitutes no potential health risk to the population. Although the current levels of the potentially toxic elements in rice is low, it is recommended that, regular monitoring studies be conducted to ascertain the levels of

heavy metals in rice cultivated in the area, since heavy metals can accumulate and the concentrations could go up with time.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Minerals extracted through mining activities are of immense importance to a country since it contributes greatly to socio-economic development in the nation. However, the exploitation of minerals such as gold puts immense stress on air, water, soil and vegetation and also poses hazards to human health. This is due to the production of wastes. Mining activities and many industrialized processes give rise to contamination of agricultural soils, water and air by heavy metals such as cadmium, arsenic, zinc and lead. These contaminants can be accumulated and transferred into plants and crops such as rice (Huang *et al.*, 2013).

The high concentrations of heavy metals in agricultural soils may also result from anthropogenic activities such as wastewater irrigation, improper fertilizer application, metal smelting and fossil fuel combustion which lead to the deposition of airborne metals (Guo *et al*., 2020).

Pollution within mining communities of Ghana by heavy metals has been extensively studied by some researchers, (Armah *et al.*,2010; Owusu-Donkor, 2011; Zango *et al.*, 2013; Anane-Acheampong, *et al*., 2013; Kyeremateng, 2013). It is a fact that the problem of soil contamination by heavy metals actually exist in some parts of the Ashanti Region.

Heavy metals present in soils include Zn, Cu, Fe, Cd, Pb and Mn of which high levels above permissible limits set by FAO/WHO have been reported for Cd and Pb in soils from Asante Akim North District (Owusu-Donkor, 2011).

Chemicals such as mercury used for mining may pollute water bodies and food crops like rice which is cultivated mostly by flooding farmlands. This will adversely affect the health of consumers when they are taken in. Upon consumption, it may affect the central nervous system, reproductive system, skeletal system and even may cause death. Pollution caused by these mining activities may bring about decrease in biodiversity (Anane-Acheampong *et al.*, 2013).

A number of studies eventually (Guo *et al.*, 2020; Otitoju *et al.*, 2014; Huang *et al*, 2013; Owusu-Donkor, 2011) have already shown that mining activities can emit appreciable quantities of heavy metals into the atmosphere, and the deposition of emitted metals can result in increased metals concentrations in surface soils in farmlands nearby the mines and thus enters the food chain.

Rice (*Oryza sativa*) is a major commodity in world trade, and provides about 20% of the world's dietary energy supply (Dube, 2022). It is utilized mostly at the household level, where it is consumed as boiled or fried with stew. Rice is a rich source of minerals such as sodium, potassium, calcium and phosphorus, as well as vitamins and fibre (CREA, 2021). Rice also provides high dietary energy since carbohydrate and starch constitutes about 80% of grain dry matter (Carcea, 2021).

Aside the minerals, traces of iron, copper, zinc and manganese are also present in rice, but an increase in the level of the heavy metals that are required in trace amounts could be hazardous to health (Udedi, 2003; Ogwuegbu and Muhanga, 2005). Heavy metals reach rice soils through water runoff and atmospheric deposits from sources such as mining activities, industries, rock weathering, wastewater and agriculture (Mandi and Muedi, 2018).

Consequently, heavy metals may pose health risk to the inhabitants living closer to the mining areas since accumulation of these potentially toxic elements affects the nervous and digestive systems and can cause kidney diseases, cancer. In this study, heavy metal content of rice which is caused by artisanal mining, human and other commercial activities within the catchment of the Asante Akim area is being investigated and the potential health risk of heavy metals to the indigenes of the area in relation to the consumption of local rice, evaluated.

1.2 Statement of Problem

Rice is one of the most widely consumed foods in the world and also one of nature's great scavengers of metallic compounds (Didi Kirsten, 2014). In Ghana, contamination of sediments and surface water bodies has particularly been encountered in communities where gold is mined (Kuma and Young, 2004).

According to Tatlow (2014), heavy metal intake through food is a long term intoxication process by small amounts, and this means that it is a very slow accumulation process, and the excretion is even slower. About a third of the heavy metals absorbed by the human body will concentrate in the kidneys and a quarter in the liver (Didi Kirsten, 2014).

Heavy metals such as As, Cd, Cr, Hg and Pb are toxic even at low levels of exposure, and that the levels can build up in the body through consistent exposures and the effects are irreversible (ATSDR, 2012).

Food chain contamination by heavy metals has become an issue of concern in recent times because of their potential accumulation in biosystems through contaminated water, air and soil. Growth media for crops (soil, nutrient solutions, air) serve as their main source of these heavy metals from which the heavy metals are taken up by the roots or the foliage (Lokoshwad and Chandrappa, 2006).

Currently, concerns are being raised about possible contamination of food crops by heavy metals as a result of pollutants that are produced from the mining sector. There is also increasing concern that, the mining activities are causing significant heavy metal contamination to the environment and plants eventually act as a channel through which pollutants are transferred into the food chain (Bridgen *et al*, 2014).

The common methods of growing rice often involves flooding the field, and this increases the formation of soluble metallic compounds that can easily be absorbed by the rice plant (Abedi and Mojiri, 2020). Higher concentrations of heavy metals can potentially be toxic to humans and animals. In view of this, a study on the level of pollution of these metals; cadmium, arsenic, chromium, lead and mercury is deemed important, especially in communities where heavy metal contaminated water is used for agricultural purposes.

Moreover, concerns have also been raised recently over levels of heavy metals in the environment where scientists suggest that foodstuff from mining communities may contain toxic amounts of these heavy metals (Anane-Acheampong *et al.*, 2013). Thus the urgent need to evaluate the potential health risk of heavy metals to the local inhabitants of these mining sites in relation to the consumption of local rice and make necessary recommendations for sustainable rice production in Ghana.

1.3 Significance of the Study

The importance of the food safety as far as hazardous elements are concerned cannot be overemphasized. The purpose of this research is to ascertain the contamination levels of potentially toxic elements in the soils and the rice cultivated on such soils. The research also hopes to determine the health risk associated with elemental consumption through rice cultivated on soils in the study area. Thus, the research would determine whether the consumers of locally cultivated rice in the Asante Akim Central municipality would be likely to experience major toxicological effects of the potentially toxic elements under study. The study would provide data and also illustrate a useful approach in risk communication and management.

1.4 Main Objective

- To evaluate heavy metal exposure and potential health risk of consuming locally cultivated rice in the Asante Akim area.

Specific objectives:

- To determine the levels of Arsenic, Cadmium, Chromium, Mercury and Lead in soil and rice cultivated within the Asante Akim Central Municipality.
- To assess the magnitude of exposure to Arsenic, Cadmium, Chromium, Mercury and Lead through the consumption of locally cultivated rice in the area.
- To estimate the risk of adverse health effect to the population through the consumption of rice cultivated in the Asante Akim Central Municipality.

1.5 Justification of the Research

According to Bridgen *et al.* (2014), a study that was conducted to investigate surface soils for metal contamination also sought to determine metal concentrations in water and in rice crops, all in an area where an industrial complex is situated in Hunan Province, China. The industrial complex consisted of facilities that undertake smelting and processing of non-ferrous metals. It was noted that rice that was cultivated in locations closer to the mining complex had high concentrations of lead, cadmium and arsenic. It was also observed that rice that was collected from two control areas farther away from the mining complex contained lower levels of lead and cadmium. They attributed the results to the fact that the two control areas are located a bit farther away from the mining complex, hence the lower levels of lead and cadmium as compared to the test areas that were closer to the complex.

Bridgen *et al*. (2014) again pointed out that, metals such as lead and cadmium are very toxic and are able to bioaccumulate. As a result, exposure to even low levels of these metals can lead to build up in the body. Therefore, rice that contains lead and cadmium at higher concentrations poses health risk to consumers, especially in cases where the concentrations are above the maximum permitted level for human consumption (Bridgen *et al.*, 2014).

Huang *et al.* (2013) frankly stated that, adverse effects of exposure of heavy metals like lead and cadmium to human health had been confirmed. It was also indicated that, heavy metals such as Pb was also shown to be associated with damage to the central nervous system, which may lead to reduced intelligence quotients in children**.** Another observation was that, the main exposure pathway to the whole population was through intake of food**.**

This study therefore seeks to answer the following research questions.

- Do the study soils contain higher amounts of heavy metals which are above permissible limits?
- Have the rice plants cultivated on such soil accumulated heavy metals at levels that is harmful to consumers?
- Does the presence of these heavy metals in rice pose non-carcinogenic health risk to consumers?

It was therefore found to be important to state the hypothesis as; rice cultivated near mining sites has high concentrations of heavy metals and therefore has the potential to pose health risk to consumers. However, only a couple of studies have been done on the levels of heavy metals in rice, and exposure assessment in the Asante Akim area which have been reported.

It is therefore imperative to determine the levels of heavy metals in rice cultivated in areas near mining impacted soils and to do ecological and human health risk assessment of consumption of heavy metal-contaminated rice cultivated locally.

1.6 Limitations of the Study

The short duration of the study coupled with limited resources forced the research to be conducted in only five (5) out of the eighteen (18) communities in the Asante Akim Central municipality. Thus, the result may not provide a representative data for the whole municipality. Regardless, this limitation does not affect the credibility or the validity of the findings of this study in any way.

CHAPTER TWO

LITERATURE REVIEW

2.1 Background

This chapter reviews some related theoretical and empirical literature regarding the heavy metal exposure and potential health risk of consuming rice produced locally. The main concern will also be in relation to the measure of the levels of heavy metals such as As, Cd, Cr, Hg and Pb in rice cultivated within the Asante Akim Central Area. It also concentrates on the estimation of the magnitude of exposure to these heavy metals to humans through the consumption of rice cultivated near the mining sites in the area. Moreover, it uses this information to assess the potential health risks of As, Cd, Cr, Hg and Pb on consumers of the locally cultivated rice.

2.2 Potentially Toxic Elements

These elements are considered very toxic to life forms (humans, plants and animals) and the general environment due to their accumulative and non-biodegradable nature (Wang & Cheng, 2009). Heavy metals persist in the environment as deposits on soil, plant parts, in water bodies; and as airborne particles (Olawoyin e*t al.*, 2012). Examples of heavy metals are Pb, Cd, Hg, Cr and Ni. These are critically toxic and carcinogenic to biological systems (Morais *et al.*, 2012; Bánfalvi, 2011).

Mineral elements are very important for physiological, structural, catalytic and regulatory functions in humans and animals (Underwoood and Suttle, 2001). There are 92 naturally occurring elements, Be, B, Li, Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, W, Pt, Au, Hg, Pb, and Bi; out of which about

30 metals and metalloids are considered toxic to human health (Morais *et al.*, 2012). Pb, Cd, Hg and As are generally considered the most toxic and carcinogenic to humans and animals (Morais *et al.*, 2012; Bánfalvi, 2011).

While heavy metals are even in minor quantities (IARC, 2012), other metals (trace minerals) such as Co, Cu, Ca, Na, K, Mg, Fe, Mn, Mo and Zn are considered essential to biological growth and development (Aziz *et al*., 2015). Deficiency signs and symptoms may occur in both plants and animals if required amounts of particular essential metals are not met. For instance, white muscle disease is a nutritional muscular dystrophy associated with selenium deficiency in beef calf (Butarbush and Radoatits, 2003). Trace minerals can be found naturally in fruits (tomato), vegetables (spinach, onion), cereals (paddy rice, wheat, oats), tuber crops (potato) milk; and commercially in drugs and food supplements.

Naturally, heavy metals occur in organic and inorganic forms (Hite, 2013).Unlike inorganic forms of heavy metals, heavy metals in organic forms can degrade to less harmful components through chemical or biological processes (Ayangbenro and Babalola, 2017; Cao and Hu, 2000). This is why inorganic forms of heavy metals persist in the environment for very long time (Zhao *et al*., 2015; Duruibe *et al.,* 2007). The presence and mobility of heavy metals in agricultural soils from possible pollution sources presents considerable concerns to the various pathways and fate of heavy metals accumulated within the environment. Natural and anthropogenic sources, such as weathering of parent materials, volcanic eruptions, mining operations, discharge from industrial waste, waste from landfills, agricultural chemicals and transport (Zogaj, 2016; Duruibe *et al*., 2007).

Earlier researchers (Bridgen *et al*., 2013; Guo *et al*., 2020) have reported that mining operations are major cause of heavy metal emission and movement to agricultural soils. Large quantities of tailing and waste containing heavy metals scattered in the open and pits are carried through wind and runoff to the agricultural fields close to the mining sites, within 0 – 1.5 km from the mining sites (Escarré *et al*., 2011). So, heavy metal levels reaching agricultural soils decrease as the distance from the mining sites increases (Escarré *et al* 2011; Duruibe *et al*., 2007).

Depending on the exposure and content of heavy metals in the environment several health threats are posed to humans, animals and plants. In Japan, cadmium consumption through contaminated rice was reported to reduce renal tubular functions in the rice farmers (Horiguchi, 2012; Aoeshima, 2012). Consumers also suffered spinal and leg pains in consuming cadmium contaminated rice (Aoeshima, 2012).

Significant levels of cadmium were found in six selected poultry feed in Nigeria (Bakar and Sa'id, 2014). This confirms an earlier study by Carobs *et al*., (1997), on quails fed a diet containing 1 ppm radio-cadmium. They found cadmium accumulated in the liver, kidney and intestinal tract of the quails, suggesting subsequent human-heavy metal exposure when contaminated animal products are consumed.

2.2.1 Arsenic

2.2.1.1 Description and sources

Arsenic is a metalloid and it is under Group 5 on the periodic table. As is part of the first 20 elements on the Agency for Toxic Substances & Disease Registry’s (ATSDR) table of hazardous substances. Arsenic is used in the production of pharmaceuticals, pesticides, insecticides and wood preservatives as an additive (WHO, 2018). It is also used as an alloying agent in electronics for making conductors, transistors and lasers (Gomez-Caminero *et al*., 2001).

Arsenic is predominantly found in the Earth's crust; rocks, soil and mineral sediments (Mazumder, 2008; Gomez *et al*., 2001). Some disruptions such as volcanic eruptions and mineral ore mining result in the release of arsenic into the environment (WHO, 2018). Industrial activities such as energy production from fossil fuels and smelting of minerals are other sources of arsenic in the environment (Szymanska-Chabowska *et al*., 2002).

Arsenic can occur in two stable forms in the environment, organic and inorganic forms. Organic arsenic compounds form from reaction of arsenic with carbon and hydrogen. These compounds are mostly present in fishes, fish products, sea plants and supplemented minerals (NRC, 2005). Examples of organic arsenic are dimethylarsenic acid ($C_2H_7AsO_2$), arsenic acid (H_3AsO_4), arsenobetaine ($C_5H_{11}AsO_2$), methylarsonic acid [$CH_3AsO(OH)_2$] (Gomah, 2018). Inorganic arsenic forms are more toxic than the organic forms, and are considered as type 1 carcinogen (IAAC, 2014).Inorganic arsenic compounds in the environment are formed from the reaction of arsenic with elements such as Oxygen, Sulphur, Sodium and Chlorine. Major inorganic arsenic sources include rocks soil and sediments. Some inorganic compounds include Arsenic trioxide (AsO_3) or Arsenic pentaoxide (As_2O_5), Trichloro arsenine ($AsCl_3$) and Sodium arsenide (Na_3As) (Wijesekara and Marambe, 2011; Singh *et al*., 2007).

2.2.1.2 Arsenic exposure

Arsenic forms released from parent sources are deposited in the atmosphere, aquatic and terrestrial environments. This means that humans are primarily exposed to arsenic toxicity through air, water and food (Martin, 2020; WHO, 2018; WHO, 2010). Arsenic exposure through water is generally regarded as the most important route for people in most parts of the world (WHO, 2018). Arsenic contamination, particularly inorganic arsenic, is prevalent in both surface water and underground water systems as a result of arsenic droplets from the atmosphere, erosion and leaching from contaminated soils and arsenic mining localities. As a result, most people of all ages are exposed to elevated levels of inorganic arsenic through drinking and cooking with water from arsenic contaminated municipal water supplies or dug-out wells, as well as irrigating food crops with arsenic contaminated irrigation water (WHO, 2010). Moreover, aquatic animals such as fish, shellfish, cod, and haddock have been found to expose sea food consumers to adverse health consequences (WHO, 2018).

Direct skin contact with Arsenic and its associated dermal effects may also result through deposition from Arsenic contaminated soils, air and water (Dadzie, 2012).Arsenic is also used as components or ingredients in daily life and industrial products such as pigments, textiles, wood preservatives, metal adhesives, pesticides, fungicides, feed additives, cosmetics and paints (WHO, 2018; ATSDR, 2011).

2.2.1.3 Effects of arsenic

Arsenic contamination in food is fairly high because plants absorption and accumulation of arsenic from soil medium is relatively high (Dadzie, 2012).Arsenic contamination is even high in water bodies such as lagoon, streams and rivers (Clottey, 2018).

Arsenic interferes with respiration in humans. During cellular respiration Arsenic readily substitutes phosphorous during ATP production. This activity promotes cell death and delayed growth, especially in infants and children with high arsenic toxicity (Garden *et al.*, 2013).

Arsenic toxicity, arsenicosis, can even cause death. A fatal incident occurred in Bangladesh in the 1970.Thousands of inhabitants suffered death from drinking contaminated water. It was reported that about half of the country's tube well were heavily contaminated with arsenic which led to the tragic mass poisoning (WHO, 2010; UNICEF, 2006).

Although inorganic arsenic is more toxic than organic arsenic, both forms are associated with life threatening health issues. Exposure to inorganic arsenic can lead to bladder and kidney cancers, tumors including vascular diseases and genetic alterations (Dadzie, 2012). Organic arsenic is also associated with gastrointestinal, cardiovascular and neurological diseases in humans (Martin & Griswold, 2018).

2.2.2 Cadmium

2.2.2.1 General Description and Sources

Cadmium is the 48th atomic element on the modern periodic table. Cadmium is a rare element in the Earth’s crust. Naturally, cadmium does not occur in its pure state, it occurs naturally in ores with other elements (zinc, lead and copper). Some of these ores include zinc sulphide, greenolate spalerite and wurtzite (Gomah, 2018; Kosek-Hoehne *et al.*, 2017). Among the naturally occurring elements in the Earth's crust, cadmium is ranked 67th in abundance (OSHA, 2004). It has an average concentration of 0.1 to 0.2 mg/kg in the Earth's crust (Rizwan, 2012).

Cadmium is released in the environment through natural and anthropogenic sources. Natural release of cadmium in the environment occurs through volcanic eruption, rock weathering, and erosion. Volcanic eruption is the major source of cadmium in the Earth's crust. Volcanic eruption alone releases about 100-500 tons of cadmium into the atmosphere (Kosek-Hoehne *et al.*,2017).Cadmium is also released through phosphate fertilizer application, mining of minerals, burning of coal, municipal waste, metallurgy and electronic waste recycling (Kosek-Hoehne *et al.*, 2017).

2.2.2.2 Cadmium exposure

Cadmium exposure occurs mainly through food for most people, especially for nonsmokers. In humans, food contributes to about 1μg of cadmium per day (WHO/FAO, 1993). Both plant and animal food sources are high cadmium exposure pathways. For instance, the concentration of cadmium in the world's staple foods such as rice, potato and wheat is in the range of 10 – 300 μg/kg and up to about 1000μg/kg in aquatic animals such as oysters and mussels (WHO, 2007).

However, with high cadmium deposit in agricultural soils, cadmium accumulation in food crops (especially staple foods) increase human-cadmium exposure risk. Plants accumulate cadmium through root uptake from cadmium contaminated soil, and through foliar absorption from atmospheric deposits (Wong *et al.*, 2003). The food chain sequence then acts as a major cadmium pathway from plants to animals through direct feeding of animals on plants or through feed formulation in farm animals. Up to 50µg/kg of cadmium can be present in meat, and over 100 µg/kg in liver and kidney of mammals (WHO, 2000). Significant levels of cadmium were found in six selected poultry feed in Nigeria (Bakar and Sa'id, 2014). A similar earlier study by Carobs *et al*., (1997) was done on quails fed a diet containing 1 ppm radio-cadmium. They found cadmium accumulated in the liver, kidney and intestinal tract of the quails, suggesting subsequent human-heavy metal exposure when such contaminated animal products are consumed.

Cadmium exposure can also occur through cigarette smoking. Cigarette made from tobacco in Europe contains 0.5 – 2µg/g cadmium (Friberg *et al.*, 1986). This mean cigarette smokers can accumulate relatively high concentration of cadmium up to about four times higher than nonsmokers (Bernard, 2008), and the resulting health effects in the smoking group may be highly detrimental.

2.2.2.3 Effects of Cadmium

Cadmium is a non-essential dietary element for both human and animal health. Cadmium uptake accumulates in the kidney, liver, bones and lungs (WHO, 2000). Due to the long half life of cadmium, its accumulation in organs can spread through several body tissues leading to serious physiological dysfunctions and health conditions. Studies have shown that high cadmium levels can lead to diseases like; Chronic Obstructive Pulmonary Disease (COPD) (WHO, 2000), chronic bronchitis, irritation in digestive system (ATSDR, 2012), kidney diseases (Naseri *et al.*, 2014), osteoporosis (Ljung *et al.*, 2011; Schoeters,*et al.*, 2006), cancers (Chunhabundit, 2016) and neurological disturbances (OEHHA, 1996).

Studies on health risk assessment of dietary cadmium intake revealed that cadmium level > 16µg/day was associated with the development of breast cancer (Satarug *et al.*, 2017; Ponce, 2013; Julin *et al.*, 2012).

Hyder *et al.* (2013) reported in a longitudinal study that adverse exposure to cadmium was associated with increased mortality resulting from cadmium toxicity-liver related diseases.

In a research conducted by Frieberg, (1950) in a cadmium battery industry, report from a clinical test showed that 32 workers from the sample had developed progressive glomerular filtration problem from inhalation of fumes containing cadmium at the industry.

Even low cadmium levels in bones have been reported to cause bone fracture and low bone density (Norberg *et al.*, 2002; Alfvén *et al.*, 2000). The United States Environmental Protection Agency (USEPA) and International Agency of Research Council have stated that cadmium is very carcinogenic to human and animal lives.

2.2.4 Mercury

2.4.4.1 General description and sources

Mercury is a silver-white, volatile liquid metallic element with symbol Hg. Mercury is the 80th chemical element on the modern periodic table with atomic weight 200.59, boiling point 356.58°C, melting point -38.87°C and two main oxidation states: I and II.

Mercury occurs naturally in the mineral cinnabar (HgS) and combines with other metals such as zinc and chlorine to form amalgams (Barnhart, 1986). Volcanic eruption is the main natural process that releases mercury into the biosphere in the form of Hg^{2+} (Alan & Rthats, 1996). Due to the prevalence of sulphides in volcanic gases, over time an insoluble red sulphide ore (HgS) called cinnabar, is formed through hydrothermal mineralization (Steinnes, 1995). Mercury is deposited in sulphide ores from which it is commercially mined.

Anthropogenic activities contribute greatly to the global mercury emissions, accounting for approximately 2,220 metric tons annually. Artisanal and small-scale gold mining is estimated as the largest anthropogenic mercury emission source (37.7%), (USEPA, 2018).Some other anthropogenic mercury sources are stationary combustion of coal, non-ferrous metals production, cement production, Chloe-alkali production, waste from mercury containing products and their incineration, biomass burning, oil refining, and cremation (USEPA, 2018).A list of major anthropogenic sources of mercury estimated under Global Mercury Assessment programme by the United States Environmental Protection Agency(USEPA) in 2018 is presented in table 2.1.

Table 2.1: Four Major Global Sources of Mercury Emission

Source	**Amount**	
	Kilogram (kg)	Percentage(%)
Artisanal and small-scale gold mining	837,658	37.7
Stationary combustion of coal	473,777	21
Non-ferrous metals production	326,657	15
Cement Production	233,168	11

Source: Global Mercury Assessment, 2018.

2.2.4.2 Mercury exposure

Acute exposure to elemental mercury progresses severely in regions with high environmental mercury release, especially in mining communities. Around the world, Artisanal Small-Scale Gold Mining (ASGM) is the largest mercury releasing activity in the atmosphere due to its important use in gold mining (UNEP, 2013, Mensah, 2012). Mercury particles released from ASGM may travel across nearby non-mining communities. Meanwhile, within the mining areas, workers are first exposed to this heavy metal through inhalation, accidental oral ingestion and skin deposits from tiny mercury droplets. An epidemiological study for occupational mercury exposure at Prestea, an ASGM locality in Ghana, reported the development of numbness in some gold mining workers (Mensah, 2012).Hair, nail, blood and urine analysis are major biological markers that reflect mercury exposure in people (Wranová *et al.*, 2008; Clarkson & Magos, 2006).

Additionally, inorganic mercury exposure may also occur through but not limited to dental amalgams, thermometer, barometer, fluorescent lamps, ultra violet lamps, food, paints, batteries, household bleach, detergents and cleaners, pesticides, drugs, paper coatings, ink and textiles (Dadzie, 2012).

Human exposure to certain forms or organic mercury has been observed through ingestion of fishes and sea foods (UNEP, 2013). Some forms of inorganic mercury may be methylated into toxic organic forms, notably methylmercury (MeHg), and biomagnified in aquatic organisms (UNEP, 2013; USEPA, 1997). Thus, consumption of mercury contaminated fish and sea food products is the primary exposure route for methylmercury in mining communities and even non-mining dwellers with higher diet of fish (Rajaee *et al.*, 2015; Mensah, 2012).

2.2.4.3 Effects of mercury

Studies have well established that chronic exposure to mercury mainly affects the nervous system in humans (Rasaee *et al.*, 2005; Alan and Rand, 1996).In aquatic environments, inorganic mercury deposits undergo methylation by microorganism and bio-magnification process to form the organic toxic form methyl mercury (MeHg) (Li *et al.*, 2010; Fact Sheet, 2007; Clarkson, 2006; WHO, 1990). Bio-accumulative MeHg is accumulated in tissues of fish and other aquatic meat products. Individuals who consume more fish and seafood products are at risk of serious neurological effects.

An alarming effect of MeHg has been reported in fetal tissues in pregnant women who consumed more fish and seafood products. Their offspring suffered adverse neuro-developmental effects (National Research Council, 2000; Grandejea *et al.*, 1999).

In children, high dietary mercury intake is associated with increased autism (Johnson, 2004; Lee *et al.*, 2003); cerebral palsy, cerebellar cortex dysplasia, neuronal ectopic expression (Geelen *et al.*, 1990) and even death (Järup, 2003).

2.2.5 Lead

2.4.5.1 Description and sources

Lead is the 82nd chemical element which belongs to group 14 on the modern periodic table. Lead is a soft, blueish-grey metallic element which has a relative atomic mass of 207.7 amu, melting point of 327.5°C and two major oxidation states; +2 and +4. Lead is present in organic and inorganic forms of which both can pose serious threats to humans, plants and animals.

However, lead is an important metal in some manufacturing industries. Lead is highly malleable and resistant to corrosion. It is used to make lead plates and other alloy materials (solder, abrasion and bearing) for shipbuilding and machinery building. Lead is preferred to other materials such as glass and plastic in providing effective sound barrier. Lead has a high surface density and good insulating characteristics which is used to reduce sound transmission through vibration and resonance in soundproofing (pedia.asianmetal.com). Lead sheet is also popular in medical radiology as it is used to make aprons to protect patient's vital organs from x-ray effects during medical imaging (Maghrabi, 2017).

Lead occurs naturally in the Earth's crust within various rock minerals and compounds such as galena ore (PbS, major natural lead source), anglesite ($PbSO_4$) and cerussite ($PbCO_3$) (Dorleku, 2018). Lead is about 0.0013% of the Earth's crust with an average of 0.2 mg/kg and 15 mg/kg available in surface waters and ground respectively (Kosek-Hoehne, 2017). Lead may be released into the environment mainly through natural as well as human activities. Natural activities such as volcanic eruptions, rock weathering and sea spray emissions. Human activities, notably mining, also contribute to lead mobilization in the environment (WHO, 2010).

2.2.5.2 Lead exposure

Lead exposure occurs mainly through water, food, soil and atmosphere. Lead is released from the Earth's crust from both natural and anthropogenic processes and deposited into the environment (atmosphere, water bodies and soil).

In the atmosphere, Lead exists as particulate matter as a result of deposits from lead ore mining and refining as well as indiscriminate burning and disposal of lead waste and effluent from metallurgical, Lead-acid battery and petroleum industries (Mondol *et al.*, 2019; Ferguson, 1990).Once Lead is in the atmosphere, particulate Lead transport may proceed from local to intercontinental scale depending on factors like particle size, height of the emission outlet and meteorology. Inhalation of lead particles in the air is therefore a major exposure route in humans and a growing global concern especially for inhabitants and workers at lead-based industries (United Nations Environment Programme, 2010).

Lead deposits in agricultural soils accumulate mostly in the topsoil from the various sources, usually up to about 20cm depth (Kosek-Hoehne *et al.*, 2017). Within the soil profile lead absorbs to solid phases and forms complex compounds particularly with soil organic matter (Bradl, 2004). Lead activity in soil becomes very low achieving minimum mobility (Solberg, 2009). Lead becomes available for uptake by vegetation, hence the risk of human-lead dietary exposure through lead contaminated food crops. Heavy metals distribution and concentrations in soils and some food crops in Ghana have been established, (Owusu-Donkor, 2011; Amonoo-Neizer, 1993). The Lead concentrations in soils from some selected Municipalities in Ghana are presented in Table 2.2.

Table 2.2: Mean Lead Concentrations in Soils in Selected Municipalities in the Ashanti Region of Ghana

Location	Lead (mg/kg)
Obuasi	3.00
Asante-Akyim North	2.70
Ejisu-Juaben	2.00
Sekyere West	2.03

Source: (Owusu-Donkor, 2011)

2.2.5.3 Effects of lead

Lead is of special concern with issues of heavy metal toxicity especially in human health. Among heavy metals, Lead is described as the most significant toxin as it is associated with many adverse health and environmental effects (Grubinger and Ross, 2011; Sipitey, 2007).The target organs of lead in the human body include bones, teeth, brain, kidney and thyroid gland (Owusu-Donkor, 2011).

According to the World Health Organization (WHO), children mostly suffer lead poisoning than adults (WHO, 2010).Lead excretion in children appears to be slow in children than adults. Up to about 38% of Lead ingested by children can be excreted from the body within two weeks but adults may excrete up to about 99% of ingested lead from their bodies (ATSDR, 1999b). Lead is reported to mimic the role of calcium in bones and muscle tissues (Fisher, 2009). Therefore, in children where growth rate and metabolism are high, a significant fraction of ingested lead can be stored in bones and muscle tissues during processes like mineralization which causes reduced bone growth, density, weak joints and muscles (LeCoultre,2001).Lead toxicity is also associated with anaemia, tremors, convulsions (PCS, 1995), neurological disorders and hypertension (IARC, 2006).

Adverse effects resulting from increased lead in agricultural soils have also been documented. In lead contaminated agricultural soils, Lead is first taken up through plants root system, transferred to the different plant parts where it is accumulated (Hadif *et al*., 2015). Elevated levels of accumulated lead in plants causes oxidative stress, enzyme inactivation (Zeng *at al*,. 2007), limits metabolic functions and reduces plant growth (Seregin & Ivanov, 2001). Shattered and Dube (2004), reported that increased lead phyto-toxicity in rice fried reduced rice germination rate, chlorophyll content, dry weight and overall grain yield. In humans, chronic lead toxicity is associated with hemoglobin synthesis disturbances (Jarup, 2003).

Addae (2013) examined heavy metal accumulation in vegetation around Korle lagoon Reclamation Site in Ghana. Among the list of heavy metals examined (Pb, Hg, Cd, As, Zn, Sn, Ni, Cu and Cr), only Cu (0.16 – 95.56), Pb (< 0.09) and Cd (0.10 – 1.64) exceeded the international permissible limit for heavy metals in plants. This can pose health risk to humans and livestock living around the site.

Clottey (2018), conducted a study on the physicochemical parameters and heavy metal contamination in Korle and Kpeshie Lagoons in Ghana. Analysis from the pollution indices showed that sediments from both lagoons were heavily polluted with lead and cadmium. For this reason, further heavy metal analysis on two aquatic animals; big fisted swim crab (*Callinectes amnicola*) and tilapia (*Sarotherodon melanotheron*), indicated very high levels of lead (10.902 ± 12.95 and 1.227 ± 5.77respectively) in both lagoons exceeding the permissible limit provided by FAO/WHO.

2.3 Soil Pollution

In the course of the exploitation of heavy metal mining, a mining area and its surrounding environment may become affected by serious pollution from heavy metals. Undoubtedly, the heavy emissions of metals can contaminate groundwater and surface water, agricultural soils, and food crops which in turn also pose a health risk to residents near mining areas. Since 1970, mining activities entered a period of rapid development worldwide. Numerous reports indicate that water, soil, vegetables and dust have been heavily polluted by lead (Pb), arsenic (As), copper (Cu), chromium (Cr), zinc (Zn) and cadmium (Cd) near the mining areas (Liu *et al*., 2005). According to the World Health Organisation (WHO, 1993) study of the evaluation of food additives and contaminants, Pb, As, Cu, Cr and Cd are important toxic heavy metals, and have been identified as health risks in several countries. For instance, South China has encountered serious environmental problems posed by these heavy metals in recent years. This emanates from the work of Liu *et al.*, (2005) which noted that the mean concentrations of Pb, As and Cd in the soils of Chenzhou city in South China were 751.98 mg/kg, 459.02 mg/kg, and 6.77 mg/kg, respectively. Other subsequent studies such as Zhuang *et al.*(2009) concluded that the heavy metal concentrations in vegetables (mg/kg, dry weight basis) ranged from 5.0 to 14.3 for Cu, 34.7 to 170 for Zn, 0.90 to 2.23 for Pb, and 0.45 to 4.1 for Cd around Dabaoshan mine in Guangdong, South China.

Moreover, many researchers and authors are of the view that mining, industrial processing, pesticide and chemical fertilizer, and automobile exhaust are the major sources of heavy metal contamination in the environment. Such studies like Sipter *et al*. (2008) and Wang *et al*. (2005) have consented that these metals may accumulate to a toxic concentration level which can lead to impairment in the quality of human life. Also, these threats to human health from heavy metals are associated with exposure to Pb, Cd and Hg. For instance, exposure to Cd may pose adverse health effects, including kidney damage and possibly also bone effects and fractures (WHO, 1993). Similarly, Pb is highly neurotoxic and its adverse effects can be expressed in multiple organ systems throughout the lifespan (WHO, 1990). Long-term exposure to Pb may lead to memory deterioration, prolonged reaction times and reduced ability to understand. According to J¨arup (2003), children may be affected by behavioral disturbances and learning and concentration difficulties. The dangers and hazards of exposure to Cr, Cu and Zn also have revealed by the United States' Environmental Protection Agency in their studies in the year 2000. According that study, Cr, Zn and Cu have non-carcinogenic hazardous effects to human health when exposures exceed the tolerable reference dose.

The other significant source of heavy metal contamination of the soil is disposal of electronic waste. The disposal of electronic and electric waste (E-waste) has caused a serious environmental problem, including the pollution of the soil for the cultivation of crops like rice. For instance in China, rapidly increasing amount of E-waste from both domestic generation and illegal imports has been cited by United Nation Environmental Programme (UNEP, 2005) as a serious hazard for the development of the country's agriculture. According to Hicks *et al.*(2005), a large amount of E-waste have been dismantled in Taizhou, Zhejiang Province since the 1990s, which is a well known E-waste recycling centre in southeast China. In fact, hundreds of small and open specialized E-waste recycling shelters or yards appear in this area and it is believed that many toxic ingredients such as lead, cadmium, beryllium, mercury, polychlorinated biphenyls and brominated flame retardants contained in these E-wastes are deposited in the soil (Schmidt, 2002).

The study by many others reveals that E-waste dismantling sites are usually situated in rural areas, and crops are grown around these areas. In recent times, studies in other jurisdictions have shown that contamination of persistent organic pollutants such as polychlorinated biphenyls and organochlorine pesticides in local food such as rice seeds, hen eggs, and silver carp muscle is worrisome. In the view of many authors, very few studies have investigated the heavy metal contents in crops collected from E-waste dismantling areas and conducted the corresponding risk assessment. According to statistical data from the Food and Agriculture Organization (FAO) (2004), rice nearly provides 30% of the dietary energy supply and 20% of the dietary protein intake around the world. As rice is a staple food for daily consumption in China and other parts of the world, especially in the studied region, heavy metals in rice may contribute a major part to the FAO total daily intake. Therefore, there is an increasing requirement for the study of heavy metal levels in rice sampled from E-waste areas.

As jointly revealed by Gupta and Attreja (1998) and Ja¨rup (2003), soils that have been contaminated by heavy metals from either aerial depositions or irrigation are likely to induce a corresponding contamination in harvested crops. Moreover, their studies have proven that crops in or close to contaminated sites can uptake and accumulate these metals, and then exert potential risk to humans and animals. Malfunction of organs and chronic syndromes may be caused by ingestion of relatively low doses of toxic heavy metals over a long period. The major route for heavy metals exposure to humans is mainly through soil–crop–food pathway. The residual plant components, including hull, straw and the root are partly returned to the soil and partly used as an ingredient in food for livestock, which is also a possible pathway for heavy metals to enter the human body by ingesting contaminated food.

The main route of exposure to these heavy metals into the human body is dietary intake. The other channel is inhalation which can also play an important role in very contaminated sites. This explains why Zhuang *et al*.(2009) asserted that heavy metal concentrations in food products and their dietary intake is very important for assessing their risk to human health. Most research works have focused on the assessment of potential health risks for inhabitants in the vicinity of hazardous sites, such as mines and smelters, because of their exposure to environmental heavy metals via consumption of farm crops which include Zhuang *et al*. (2009), Sipter *et al*.(2008), Cui *et al*.(2004) and Zheng *et al*. (2007), at least in the last decade. Some researchers have assessed the risk of heavy metals from consuming food grown on soils irrigated with sewage and food chain transfer.

In Ghana, Owusu-Donkor (2011) also conducted a study in some selected districts in Ashanti region on heavy metal contents of soil and citrus grown in the areas. The study area included the Asante Akim North (now Central) municipality, in Ghana where it was realized that, there have been recent concerns raised on the levels of heavy metals in the environment and scientists suggested that foodstuff from mining communities may contain toxic amounts of these heavy metals. Thus, there was an urgent need to characterize the heavy metal contents of mining and non-mining sites and correlate these with the heavy metal content of fruits grown in these sites and make the necessary recommendations for sustainable citrus production in Ghana. The aim of the research work was to characterize mining sites as against non –mining sites in terms of heavy metal content.

Mining activities, use of agrochemicals in agriculture production and vehicle exhaust fumes were proposed as the main sources of heavy metals. The accumulation of these metals in these municipalities were in the order Obuasi>Sekyere West > Asante Akim North >Ejisu-Juaben. There were significant differences in the selected metals contents in citrus fruits and soils from the four districts.

It was observed that, though the heavy metal load of soils from all the four municipalities were below the permissible limit set by the Dutch standards for soil contamination assessment, the levels of citrus fruit Zn and Pb of all the four districts were above the permissible limits set by FAO/WHO while Cd in citrus fruit from

Obuasi, Asante Akim North and Sekyere West were above the permissible limit. This could be due to the low pH of the soils in the Asante Akim study area, and as a result, the citrus fruits with high acid contents absorb more of the heavy metals than the soil could retain. It was therefore concluded that consumption of citrus fruit from the selected districts could pose health hazards to humans as at the time of the study. The assertion that Cadmium, Lead and other metals other than calcium is readily taken up by plants in soils of low pH is emphasized in another study by Chamannejadian *et al.* (2013). It was noted that, lead solubility and plant availability decreased in calcareous soils of higher pH. This was attributed to metal carbonate precipitation and calcium competition with other metal cations for plant uptake. This means that, the other metal cations would rather be taken up readily in soils of low pH since the competition with calcium is reduced under such conditions.

2.4 Rice Production in Ghana

Rice has become a major food crop along with wheat serving as a staple food for over 70% of the world's population (Takele, 2010). Rice represents the first major staple food in Ghana, providing high caloric value to its consumers both urban and rural dwellers.

Rice is an annual monocot cereal belonging to the *Gramineae* family. Two main species of rice are cultivated in Ghana including *Oryza sativa Linus* and *Oryza glaberrima Stead*. *Oryza glaberrima* is native to West Africa where its domestication occurred around 1300BC.*Oryza sativa* originated from Asia but has been distributed throughout the regions of the world including West Africa where it is gradually replacing the native *Oryza glaberrima* species.

Rice grows vigorously in wet and warm environments however; it can adapt to diverse conditions. Rice is extensively cultivated in all regions of Ghana, among all the ecological zones. Rice cultivation is done once in a year, usually during the rainy season. Rice farmers in the Ashanti, Eastern and Volta regions begin planting in April/May and harvest produce in June/July. Rice farmers in the Northern part of Ghana plant rice in July/August and harvest produce in October/November. However, farmers with secured irrigation facilities and water source succeed in a second cropping cycle. Majority of rice cultivated in Ghana comes from the Volta, Eastern, Ashanti, Upper East and Northern Regions (GAIN, 2018). Rice is cultivated under three main production systems in Ghana including; rain-fed lowland, rain-fed upland and irrigated systems (IRRI, 2013c).

Rain-fed lowland system is the most common system in Ghana accounting for 78.8% of the total rice farm area and 534,903 tons in production (FAO, 2021). Rain-fed lowland fields are managed in bunded forms that allows for flooding and conservation of rainwater and underground water during production. This system relies on continuous rainfall but there are problems of drought and uncontrolled flooding as a result of uncertainty in timing, duration and intensity of rainfall (Makafui, 2013). Rice yield under Rain-fed lowland system is marginally higher than in other farming systems. It is reported to account for 20% of rice produced in the world (Makafui, 2013).

Rain-fed upland system also depends on sufficient and continuous rainfall. It accounts for 36,399 tons of Ghana’s rice production and covers 6.1% in land area (MOFA, 2021). Rain-fed upland system is characterized by well-draining soils with water table below rice roots zone. Drought tolerant and short duration rice varieties such as varieties of *Oryza glaberrima* are suitable for this system. Although rice varieties for this type of system are low-yielding and tolerant types, weeds competition, low soil fertility level, pest damage, changing climate and low mechanization have been reported to account for very poor rice yield (Takele, 2010).

Irrigated rice system involves high cropping intensity, intensive inputs and high level of technological use. Irrigation channels are constructed and distributed across the field for watering. Improved rice varieties are dominantly cultivated under this system. Land preparation, weeds, diseases, pests and fertilizer application are well managed for maximum rice yield. Irrigated rice system covers 10.1% of rice total land area providing 110,977 tons of rice (MOFA, 2021) and 75% of rice produced in the world (Makafui, 2013).

2.3.1 Nutritional and health importance of rice

Rice is an important cereal crop that provides high dietary energy. Carbohydrate and starch constitute about 80% of rice grain dry matter (Carcea, 2021). Carbohydrate is broken down to glucose which provides rice consumers with energy for body activities. According to Qi *et al*. (2010), consuming brown rice is associated with lower risk of diabetes. Dolson *et al*. (2009), explained in a study that brown rice has a low glycemic index and a slow starch digestibility. For this reason, some of the starch is never turned into sugar. There is high proportion of protein which makes about 7% of rice grain. According to Acquistucci *et al.* (2009)**,** the amino acid proportion in rice grain shows significant amounts of lysine (Prabha *et* al., 2018)**,** glutamic acid and aspartic acid which represents the major amino acids in rice. Both white and brown rice are rich sources of minerals (sodium, potassium, calcium, phosphorus and iron), vitamins (thiamine, riboflavin, niacin and vitamin E) fat and fiber (CREA, 2021). Bioactive compounds such as flavonoids, phenols, antioxidants and anthocyanins have been found in brown and unmilled rice (Ma *et al.,* 2020). These compounds are associated with some health benefits such as antioxidation, anti-inflammation, lipid and cholesterol lowering effects (Prabha *et* al., 2018).

2.5 Heavy Metal in Rice Food Chain

It is apparent that heavy metals have become a major environmental issue with concerns from almost all regions of the world. Heavy metals reach rice soils through water runoff and atmospheric deposits from sources such as mining activities, industries, rock weathering, wastewater and agriculture (Mandi and Muedi, 2018). Rice plant generally exhibits considerable tolerance to heavy metal toxicity but different degrees of these metal toxicants are able to accumulate in different parts of the plant (Arunakumara et al., 2013).

As paddy soils and irrigation water become contaminated with heavy metals, rice plants absorb these metals in addition to essential nutrients. The metals accumulate first in the roots and subsequently to the stem, leaves and grains (Liu *et al*., 2009).Once the metals get accumulated in rice grains, they are in turn transferred through to higher trophic levels along rice food chain.

Heavy metal contaminated rice grains are fed to farm animals where they accumulate in tissues (Marçal et al., 2005; Swarup et al., 2005; Rumbeiha et al., 2002) and milk (Xhou, 2019; Strojan and Phillips, 2002) or directly consumed by humans (Horiguchi, 2012). Humans may again be vulnerable when they consume contaminated animal products.

2.6 Heavy Metals Mobility and Uptake

Accumulation of heavy metals in variable concentrations does not necessarily present a risk of damage to plants and animals including humans. These metals can be available in stable forms (Solberg, 2009), or strongly held within rock minerals, clay minerals, or complex organic constituents within the soil profile (Ivezic, 2012; Shuman, 1991). The transfer of heavy metals into solution makes them available for uptake by plants and a potential threat through the food chain. Therefore, in defining the toxicity of heavy metals in the soil, heavy metals concentration and mobility factors may be well considered. Also, the sorption of heavy metals to various soil constituents is necessary for mobility control (Fergusson, 1990). Even in low concentrations, heavy metals bioaccumulation by organisms that cannot effectively metabolize and excrete the accumulated heavy metals may be at a high risk (Otitoloju and Don-Pedro, 2002).

In fact, soil characteristics including organic matter content, clay content, nutrient balance, metallic oxides, cation exchange capacity, pH and redox potentials influence the mobility, uptake and to some extent, assimilation of heavy metals in the environment (Kabata-Pendias, 2011, 2004; Kadovic *et al*., 2011; Solberg, 2009; Chuangchum *et al*., 2008). Soil pH and clay content are among major soil properties influencing the total and relative uptake of heavy metals, especially cadmium.

Soil pH has important effect on heavy metals concentration and mobility in soil solution (Kong *et al*., 2018) as well as plant tissues (Sipitey, 2007). Heavy metals tend to be more mobile under acid conditions than under neutral to alkaline conditions. For instance, an earlier study by Darland and Inskeep (1997) indicated a positive interaction between pH and arsenate movement through sand with iron oxides. Their study revealed that, a pH 8.5 facilitated arsenate transport more than pH levels below 6.5. Akeel et al., (2013), reported that cadmium solubility is affected by the acidity of soil medium and a higher acidity enhances dissolution of sediment-bound cadmium.

Clay fractions of soils have large surface area with large number of ionic binding sites. As a result, heavy metals ions, such as lead, arsenic and chromium are adsorbed unto the clay surfaces of the soil through strong ionic bonds (LeCoultre, 2001; Li and Wu 1999; Lee *et al*., 1997). Adsorption of heavy metals indicates that the heavy metals are immobile for uptake by plants. Moreover, this action limits heavy metal contamination in underground water systems through dissolution, erosion and leaching from topsoil (Kong *et al.*, 2018).

The presence of other plant nutrients or trace metals in agricultural soils significantly influences heavy metals uptake, and to some extent assimilation (Kong *et al*., 2018; Khan and Frankland, 1983). High nutrient levels in soil inhibit heavy metal uptake due to complex formation between the nutrients and heavy metal ions (Göthberg *et al*., 2004; Haglund *et al*., 1996). Göthberg *et al*., (2004) described an inverse relationship between plant nutrients and heavy metals accumulation in fresh water. With higher nutrient levels, the uptake of mercury, cadmium and lead decreased. In an earlier study on oats, John *et al*., (1972) declared that addition of phosphorous to soil contaminated with cadmium significantly reduced cadmium accumulation in oats roots. Larlson, (2001) reported that, cadmium and calcium ions are almost indistinguishable, due to their similar ionic size (Ochiai, 1995). Larlson, (2001) concluded that, higher affinity for calcium results in higher calcium uptake and assimilation by plants.

In addition, the level of metal toxicity in paddy soil or irrigation water may correlate to exposure, that is, the amount of a substance (heavy metal) in contact, over time and space with the outer boundary of a body (plant root) (Morai *et* al., 2012; Mamboya, 2007; WHO, 2000). Therefore, the higher the levels of heavy metals available in these media, the higher the quantity potentially free for uptake by rice plants and eventually consumed by humans and animals (Payus & Talip, 2014). For instance, arsenic content could exceed 10 mg/kg in heavily contaminated soils (Williams *et al*., 2006) but ranges from 0.08 mg/kg to 0.20 mg/kg in not heavily contaminated soils (Zavala and Duxbury, 2008). A positive correlation of arsenic content in paddy soil and rice grains was recorded near a coal mining site in Bangladesh (Zhang *et al.*, 2013). The study showed that an average arsenic content of 20.58 mg/kg accumulated in rice roots, 3.76 mg/kg accumulated in straw and 0.83mg/kg accumulated in grain. Adomako *et al.*, (2014) assessed the concentrations of iron and arsenic in paddy soils and rice grains in a gold mining site in the Anum Valley of Ghana. They reported that soils of paddy field near the gold mining site were heavily contaminated with arsenic at a mean of 41.1 mg/kg when compared to the permissible limits for paddy rice according to the Environmental Quality Standards. But the iron levels within the soil samples were below considerable limits. Consequently, the arsenic content accumulated in the rice grains was considerably great.

According to Bridgen *et al.* (2014), a study was conducted to investigate surface soils for metal contamination. The study also sought to determine metal concentrations in water and in rice crops, all in an area where an industrial complex is situated in Hunan Province, China. The industrial complex consisted of facilities that undertake smelting and processing of non-ferrous metals. In order to determine the concentrations of metals in surface soil, two different soils were used. Soil from regularly cultivated land and what was referred to as uncultivated land; which actually meant soil that was both uncultivated and undisturbed artificially. These lands were found in the neighbourhood of the industrial complex with metal smelters and processing facilities. In determining the significance of water as a carrier of metal contaminants, samples of discharged water from industrial origin, and surface water used for irrigation were analyzed.

In their study, soils from the uncultivated land in areas closer to the complex were found to have higher concentrations of some metals such as Pb, Cd and As among others, compared to the concentrations of metals typically expected in soils from uncultivated areas away from the complex. It was observed that the areas located to the south of the industrial complex and to a lesser extent, the location to the west of the complex had very significant increase in metal concentrations (Bridgen *et al.*, 2004).

It was noted that, the distribution pattern of increased metal concentrations is consistent with atmospheric emissions from the complex. This makes a significant contribution to higher levels of most metals in soils in the areas close to the complex, which includes lead. The results however indicated that there could be other contributing sources of metals to the uncultivated soil in some locations which have not yet been identified.

For the following metals; arsenic, cadmium, lead, manganese and zinc, it was observed that, strong correlations of concentrations in uncultivated soils showed a common source. This suggests that, the discharge from the industrial complex may be a major contributory factor to increased concentrations of the metals that were mentioned in uncultivated land in the study area**.** There were similarities observed in the results of soil samples from the fields where rice were cultivated and soil samples from the uncultivated land. There were high concentrations of some metals, especially cadmium as well as lead and zinc. Arsenic and nickel were also found in soils at some locations in some of the rice fields in the neighbourhood of the industrial complex. These were considerably higher than the levels that were found in soils samples that were taken from the rice fields in the two control areas which were situated farther away from the complex (Bridgen *et al.,* 2004).

The results also showed that for all the rice field soil samples, which include the ones from the two control areas located approximately 11 km to the southeast and northwest of the complex, the concentrations of the metals were high. Since the concentrations of the metals were high in the soil samples, it could imply that crops including rice that may be cultivated in the areas could also contain high levels of the metals.

In another study by Otitoju *et al.* (2014), the researchers determined the levels of some metals such as cadmium, chromium, arsenic, lead and mercury in locally produced rice samples from the northern region of Nigeria. Ten rice samples were obtained from various locations in Benue, Borno, Kaduna and Nasarawa states. The results showed that the concentrations of lead ranged from 0.311 mg/kg to 0.525 mg/kg in the samples. Average Pb concentration was 0.260 mg/kg. However, Cd, Cr, As and Hg were not detectable at 0.001 mg/kg. A calculation of weekly intake of rice by an average Nigerian revealed that weekly consumption of Pb in this locally produced rice exceeded the 0.025 mg/kg WHO/FAO (2002; 2001) provisional tolerable weekly intake of Pb. This is of public health importance as individuals who consume this locally produced rice are at greater risk of Pb toxicity.

Zazouli *et al.* (2010), in an investigation, surveyed lead and cadmium concentrations of Iranian local rice in the northern part of Iran. In their study, a total of 72 samples were collected from rice farms in Babol region of Mazandaran Province. The rice samples were collected during harvesting of rice in the farms. Two methods were used for cooking; which are Kateh and Pilaw. The grains of raw polished and cooked rice were digested by acid digestion method and then analyzed for Pb and Cd by atomic absorption spectrometry. The results show that average content of Pb in raw polished rice was 11.5 ± 6.4 μg/g dry wt. the minimum and maximum Pb content in raw polished rice was 2.92 ± 0.8 and 20.26 ± 7.8 μg/g for Tarom Hashemi from Boleh Kola and Fajer from Meson Abad, respectively.

The analysis showed that cadmium was not detectable in all rice samples. The average content of Pb in Pilaw was lower than Kateh in all samples. It was noted that the average content of Pb was above the FAO/WHO guidelines. This could be attributed to the fact that some amount of Pb was retained in the water that was used to par-boil the rice samples in the pilaw method, and since the water was drained, this could lead to the reduction of Pb content in the rice. In order to assess the safety of dietary intake, weekly intake of lead (Pb) by rice was calculated based on daily consumption of rice, and dietary in (PTWI) established by the JECFA (WHO/FAO). The results showed that the weekly intake Pb was less than the maximum weekly intake recommended by WHO/FAO. Since the contents of Pb were low, it was expected for the weekly intake to be low as was observed.

In China, some prior studies have shown that residents eating various vegetables will potentially incur major risks to their health through the intake of Pb and Cd contained in the vegetables; the risk to the health of children is higher than that for adults, and the risk for residents of mining areas is much higher than that for residents of a control area (Sun *et al.*, 2013). Other studies have shown that for residents in Japan and Korea, exposure to Cd primarily from a diet that is heavy in rice accounts for 40% and 23% of their total intake of Cd, respectively (Nakadaira and Nishi, 2003). This indicates that arable land near mining areas is easily affected by mining; the surrounding soil can be polluted by sewage irrigation and falling dust.

Data from the United States Integrated Risk Information Database (US IRIS) and WHO show that Pb can damage the brain and nervous system, causing neurological disorders and high blood pressure, and can lead to a slowing of growth in children, hearing impairment, headaches, reduction in learning ability, and abnormal behaviour (USEPA, 2004). The intake of Arsenic can cause cancer in internal organs (such as liver, kidney, lung, bladder), and can increase the risk for skin cancer (USEPA, 1993). With regard to the eating habits of residents in the study area, rice is the main cereal crop in Suxian County, and residents treat it as their staple food. The vast majority of local residents grow their own crops as a source of food in the study area, greatly increasing their health risks. However, because heavy metals have the characteristic that they tend to accumulate and persistent in an environment, the risk of other heavy metal contamination still exists. Related departments should pay increased attention to the situation, and they should take appropriate measures to address the problem of soil contamination and industrial dust emissions in Suxian County to reduce the harmful effects of heavy metals on people in the area, especially children.

2.7 Bio-accumulation of Heavy Metals in Plants

Plants have evolved highly specific and efficient mechanisms to absorb essential nutrients from the environment. In fact, at very low nutrient concentrations and in nearly insoluble precipitates, plants are able to develop special adaptive mechanisms, including plant-produced chelating agents, plant-produced pH changes and redox reactions; to obtain nutrients for development (Zulkafflee *et al.*, 2020). Furthermore, the accumulation rate of heavy metals from various pollution sources is controlled by mechanisms such as mobilization, soil mobilization and uptake, compartmentalization and sequestration within the root, xylem loading efficiency and transport, aerial distribution between metal sinks, and sequestration and leaf cell storage (Vymazal *et al*, 2007).

Plants and individual plant mineral elements including heavy metals interact in a specific way. This interaction depends on factors including soil type, plant type and specie, growth conditions, presence of other ions, organic matter content (Zulkafflee *et al.*,2020), growth stage, plant age, or plant genotype (Naser *et al.*, 2011; Oyedele *et* *al*., 2008). The major Heavy metal accumulation pathways by plants are through uptake by root systems and adsorption due to deposition of particulate matter on leaves (Wong *et al*., 2003). In a study on heavy metal accumulation and translocation, Zarcinas *et al*., (2004) and Zehras, (2009) reported that, plant species and crop type influence heavy metal uptake from the contaminated soil. Other authors have also revealed that diffusion due to concentration gradient, ions exchange (Lippard *et a*l., 1994; Lyngby *et al*.,1982), root system (Wong *et al*., 2003), uptake capacity and intracellular binding sites (Park, 2015).

Plants respond to the bio-available and bio-accessible fraction of heavy metals only, not the total heavy metal concentration in an environment (Park, 2015). The concept of bio-accumulation shows an increase in the concentration of a chemical in an organism over time compared to the concentration of the chemical in the environment (LENTECH.com). Bio-accumulation factor (BAF) analyses the ability of a plant to absorb a specific metal from soil substrate (Kong *et al*., 2018; AIP, 2015; Otitoloju, 2002). BAF is a dimensionless value expressed as the ratio of a chemical's concentration in plant to that chemical's concentration in the corresponding soil (Rahimi *et al*., 2017; Kong *et al*., 2015). As a quantitative indicator, when BAF is less than or equal to 1, it indicates that the plant only absorbs a heavy metal, and when the BAF is greater than 1, it indicates that the plant absorbs and stores the metal (Singh *et al*., 2011).

2.8 Heavy Metal Translocation to Rice Grain

Unlike organic pollutants, heavy metals do not degrade but stay longer in the environment. They are transported from one environment to the next, adding to the problems of containment, treatment, removal, and disposal (Long *et al*., 1995; Ho and El-Khaiary, 2009). Roots of most cereal crops do not extend very deep within the soil, but are usually found within the soil subsurface where heavy metals are absorbed (Mico *et al*., 2007). Living organisms only respond to the bio-accessible and bioavailable metal content, not to the overall concentration. The bio-accessibility of toxicants and their bioavailability depend on the chemical properties of the contaminant, the various exposure pathways and the temporal variability of these factors for use by the organism (Park, 2015). Also crops absorb and accumulate metals differently in different parts of the plant, and there is a wide variation in metal uptake and translocation between plant species and even cultivars that belong to the same species (Kurz *et al*., 1999; Arao and Ac, 2003; Yu *et al*., 2006).

When adsorption of heavy metals in the soil has been saturated, more heavy metals will be dispersed in the aqueous phase, increasing their bioavailability (Sridhara *et al*., 2008). Heavy metals at high concentrations in soil will have a greater chance of being taken up by plants. These pollutants will subsequently be transferred from roots to shoots, and ultimately to grains, which are ingested by humans (Payus and Talip, 2014).

2.8.1 Translocation factor

One of the most important components of human exposure to heavy metals through the food chain is the Translocation factor (TF) (Singh *et al*., 2011). TF is described as the ratio of metal concentration in aerial parts of any plant to the concentration of that metal in the plant root (Tiwari *et al*., 2011; Singh *et al*., 2011; Boularbah, 2006). High translocation factor values for some heavy metals from the roots to the shoots of

Oryza sativa was reported from a paddy field near a quarry site in Malaysia (Payus and Talip, 2014). The results showed that only Zinc (3.14) and Chromium (3.41) had the translocation factor value greater than 1, which means that *O. sativa* was able to hyper accumulate only Zinc and Chromium from roots to the shoots in rice plants.

Moreover, with rice crops being extensively cultivated in wetlands under submerged conditions, the degree of exposure of rice crops to both soil and water heavy metal sources can be great, making it more vulnerable to heavy metal poisoning than other food crops. Hence, many of rice consumers may be exposed to the risk of heavy metals. Rahimi *et al.*, (2017) reported significant translocation of cadmium (TF = 1.52) from the paddy soil to rice roots. A significant translocation of zinc (TF = 1.228) was further recorded from roots to straw. Copper and lead metals were transferred to rice grains more than leaves and stem. Wheat plants irrigated with contaminated wastewater in Pakistan retained high quantities of chromium, nickel and iron metals in the grains, which were found to exceed the permissible dietary limits (Hassan *et al*., 2012).

2.9 Risk Assessment

Risk assessment as part of risk analysis, is the scientific evaluation of the probability of occurrence of a known or potential adverse health effect. It is a science- based task of measuring and describing the nature of the risk being analyzed and is performed during the risk assessment phase. Risk assessment should then be carried out to ensure the Health and Safety of humans. Risk assessment consists of four main steps which include Hazard Identification, Hazard Characterization, Exposure Assessment and Risk characterization.

2.9.1 Hazard identification

This involves the determination of whether a particular chemical or biological agent is capable of causing a particular adverse health effect which may be present in a particular food or a group of foods. In the case of chemical agent, the process examines the available scientific data for a given chemical or group of chemicals and develops a weight of evidence to characterize the link between the negative effects and chemical agent. Exposure to an agent may lead to different adverse health effects such as diseases, reproductive defects, formation of tumors, death and other effects (Huang *et al*., 2013).

Sources of data could be clinical studies on humans (statistically controlled), epidemiological studies or data from animal studies. Epidemiological studies are thus appropriate for the research since it involves a statistical evaluation of human populations to examine there is association between exposure to Pb and a human health effect.

2.9.2 Hazard characterization

This is the second step in risk assessment, and can be defined as qualitative and/or quantitative evaluation of the nature of the adverse health effect associated with the biological, physical or chemical agent that may be present in a particular food or groups of foods. Questions asked at this stage include, what are the health problems at different exposures. Dose response is usually performed at this stage. Dose response relationship describes how the likelihood and severity of adverse health effects are related to the amount and condition of exposure to an agent.

The shape of dose response relationship depends on the agent, the kind of response whether tumor, disease etc, and the experimental subject. Generally it is expected that as the dose increases, the measured response also increases. However there may be no response at low doses.

2.9.3 Exposure assessment

Exposure Assessment which is the third step involves qualitative and/or quantitative evaluation of the nature of the likelihood of intake of biological, chemical or physical agents, either through food or other sources. This stage answers the question, how much of the pollutant are people exposed to during a specific time period, and how many people are exposed. Exposure assessment is the process of measuring or estimating the magnitude, frequency and duration of human exposure to an agent in the environment, or estimating future exposures for an agent that has not yet been released. Some discussions that may be included in exposure assessment are nature, size and types of human populations exposed to the agent and also the uncertainties in them. Although exposure can be measured directly, it is mostly estimated indirectly by considering the measured concentrations in the environment, considering models of chemical transport and the fate in the environment, and also by considering the estimates of human intake over time. Exposure assessment also considers the exposure pathway as well as the exposure route (Sipter *et al*., 2008).

2.9.4 Risk characterization

The final stage in risk assessment is Risk characterization whereby the potential chemical/agent intake is compared with the toxicologically acceptable intake limit (Ofosu, 2014). Risk characterization conveys the risk assessor’s judgment as to the nature and presence or absence of risks. Information on how the risk was assessed, where assumptions and uncertainties still exist and also where policy choices may be made are all provided. This final stage answers the question, what is the extra risk of health problems in the exposed population.

Risks to a population are determined by either direct observation or by the use of mathematical models and a series of assumptions to predictor guess correctly the potential risk to humans. Whatever ways risks are defined or quantified, they are precisely expressed as a probability of effects associated with a particular activity. Risk or probability is expressed as a fraction without units from 0 to 1. A probability of 1 is an indication of an absolute certainty that an event or outcome will occur.

CHAPTER THREE

METHODOLOGY

3.1 Description of Study Area

The study was conducted in five different communities; Odumase, Ohene Nkwanta, Nyaboo, Agyareago and the Konongo Mines vicinity of the Asante Akim Central Municipality. The Asante Akim Central municipal assembly is one of the 43 districts in the Ashanti Region of Ghana. Konongo, the Capital of the Asante Akim Central Municipal is a known artisanal and small scale gold mining hub. The municipality is located in the eastern part of Ashanti Region and is about 45 km east of Kumasi with coordinates 6°37’5"N 1°12’36"W. The municipality covers a land area of 1,462 square kilometers with a population of 91,673 in the 2021 population census, (Ghana Statistical Service, 2021). The municipality shares boundaries with Asante Akim North District on the north, Asante Akim South on the east and south and Sekyere East and Juaben on the west.At the south-western corner, it shares boundary with Bosome-Freho district.

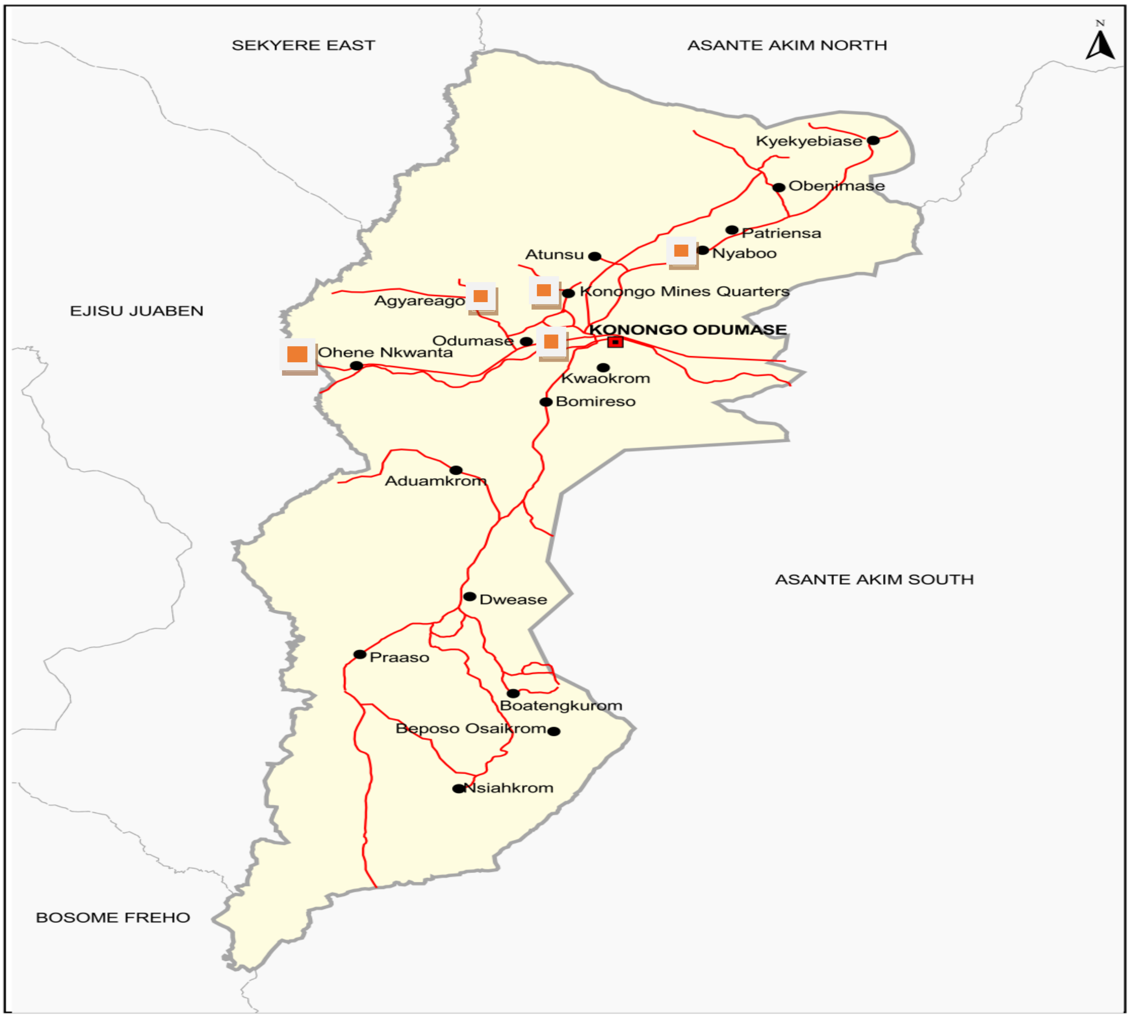

Figure 1: Map of Asante Akim Central Municipality, the study area.

*Samples were picked from the communities with the block icons; Odumase, Ohene Nkwanta, Nyaboo, Agyareago and the Konongo Mines area.

3.2 Sampling Design

A total of ten farms from five farming communities in the Asante Akim Central municipality were selected in this study. The communities from which soil and rice samples were taken are Odumase, Ohene Nkwanta, Nyaboo, Agyareago and the Konongo Mines vicinity with coordinates 6° 37' 19"N 1° 13' 47"W, 6° 36' 42"N 1° 14' 36"W, 6° 38' 21"N 1° 12' 32"W, 6° 38'N 1° 14'W, 6° 37' 23"N 1° 12' 53"W respectively.

The varieties of rice mostly grown by farmers in this locality are the Jasmine-85 and the Agra varieties. Ten farms were selected from the 5 communities, that is, two farms from each community in Asante Akim Central municipality.

Two farms were randomly selected from each farming community and a total of 10 locally cultivated rice samples (polished) were collected (one composite sample per farm). The Jasmine-85 and Agra varieties of rice, which are the predominant varieties grown in the communities in the Asante Akim Central municipality, were used for this study. Samples were collected during harvesting period of rice in the farms (between July and September). About 20 g of polished rice was collected from each farm and put in plastic bags stored in refrigerator until further analysis.

Soil samples from the ten selected farms were also taken at 5cm from the surface to analyse the heavy metal content in them. Samples of rice were collected from the same location as samples of soil from farmed lands. This was done to ascertain whether and to what extent the metal contents in the rice samples correlated with the metal levels in the soils in which rice was cultivated.

3.3 Metal Analysis

3.3.1 Glassware and equipment

All glassware, digestion and filter flasks as well as polypropylene tubes used for digestion and storage of samples were washed with detergent and soaked in HNO_3 overnight. They were then rinsed with distilled water and dried in an oven before use.

Digestion of samples was done using microwave digester (Ethos 900, Tokyo, Japan).Varian AA 240 Fast Sequential Hydride Generation AAS (Melbourne, Australia) was used for arsenic analysis. Automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho Co., Ltd, Japan) was used for mercury determinations. Agilent 7700 Series Inductively Coupled Plasma-Mass Spectrometer (Germany) was used for all other metal determinations. All reagents were of analytical grade (BDH chemical limited, Poole, England). Standards solutions were from Park Scientific Limited, UK.

3.3.2 Preparation of solutions

Preparation of Standard Solutions for Recovery Analysis

Stock Standard Solutions (1000 ppm) were serially diluted. 10 ppm, 15 ppm, 20 ppm and 25 ppm solutions were prepared by diluting 1.0 mL, 1.5 mL, 2.0 mL and 2.5 mL each of the standard solutions to 100 mL Aqua-Regia of HCl and HNO_3 (3:1) – 200 ml concentrated HCl and 100 mL HNO_3 was transferred into 1L conical flask. The mixture was then shaken, allowed to cool and stored.

Results accuracy was verified by analysis of appropriate certified reference elemental standard solutions (Park Scientific, UK). 10, 15, 20 and 25 ppm were prepared by dilution of 1000 mg/L stock solutions of the certified reference materials (Park Scientific, UK). Approximately 40 mL of each standard was taken through the dilution described above and their concentrations measured.

3.3.3 Digestion of samples

Digestion of Rice samples

Digestion of rice samples was done in accordance to the procedure by the AOAC (2015). Rice samples were homogenized and milled using blender. 1g of each sample was weighed into 250 mL digestion flask. 2 mL of distilled water was added to the powdered rice samples followed by 10 mL of HNO_3 (65 % v/v) and 6 mL of H_2O_2 (30% v/v). The samples were digested in a microwave (Ethos 900, Tokyo, Japan) at a temperature of 150 ^{O}C, pressure of 50 bars, and power of 1000 watts for an hour. Upon cooling to room temperature, the digested samples were poured into 50 mL polypropylene tubes and topped up to 20 mL with deionized-water. The digested samples were then sent for instrumental determination of the concentrations of the metals (AOAC, 2015).

Soil Treatment

The samples were dried and ground into fine powder. About 4.0 g of oven-dried lump-free soil was placed in a 10 mL test-tube. It was wet-ashed with 10 mL aqua-regia and heated on a hot plate until no brown fumes were seen. The solution was cooled, filtered and topped to the 10 mL mark with distilled water. It was then sent for metal analyses. Blanks were prepared likewise (AOAC, 2015).

The concentration of heavy metals; Cadmium, Chromium and Lead in digested rice and soil samples were analyzed by Agilent 7700 Series Inductively Coupled Plasma-Mass Spectrometer from Germany. Arsenic (As) in rice and soil samples was analyzed with Varian AA 240 Fast Sequential Hydride Generation AAS (Melbourne, Australia).

Automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho Co., Ltd, Japan) was used for determining mercury levels in rice and soil samples.

3.3.4 Quality assurance

The accuracy of the analytical procedures was verified by the analysis of appropriate certified reference materials (Appendix A) using the same digestion and analytical methods. Standards were obtained from Park Scientific Limited, UK. Results accuracy was checked using certified reference elemental standard solutions. 10, 15, 20 and 25 ppm were prepared by dilution of 1000 mg/L stock solutions of the CRMs. Approximately 40 ml of each standard was taken through the treatment process described above and their concentrations measured. The mean metals recoveries were ranged between 99.858- 100.001%.

The sample flow rate for the instruments used are 5 L/min for the Agilent 7700 series ICP-MS, 6.5 ml/min for the Shimadzu automatic mercury analyzer model HG-5000 and 1 ml/min for the Varian AA 240 Fast sequential hydride generation AAS. Detection limit of 0.001 ppm was obtained by multiplying the standard deviation of the calibration curve by 3. Limit of quantification was set at 0.003 ppm which was obtained by multiplying the standard deviation of the calibration curve by 10.

3.4 Heavy Metal Pollution Analysis of Soil

3.4.1 Bioaccumulation Factor (BAF)

The Bioaccumulation factor (BAF) has been used as a form of transfer factor which indicate plant uptake of metals in soil, water and sediments. The BAF is defined as the ratio of the concentration of a particular metal in plant to the concentration of that metal in soil. The BAF was calculated using Equation 1.

$BAF = C_p/C_{so}$.....(1) (Bu-Olayan and Thomas, 2009)

Where C_p and C_s are metal concentrations in rice grains and soil respectively.

3.4.2 Translocation factor (TF)

Translocation Factor is described as the ratio of metal concentration aerial parts of any plant to the concentration of that metal in the plant root (Singh et al, 2011). The TF was calculated using Equation 2.

$$TF = C_s/C_r \ldots\ldots(2)$$

Where C_s and C_r represent metal concentrations in the shoot and root respectively, (Bu-Olayan and Thomas, 2009).

3.4.3 Enrichment factor

This measures the abundance of a chemical element relative to the background reference or the native uncontaminated element. The mathematical representation of enrichment factor (EF) as given in Equation 3 (Yan *et al*, 2021).

$$EF = \frac{(Me/Fe)_{sample}}{(Me/Fe)_{crust}} \ldots\ldots\ldots.(3)$$

Where Fe (iron) is chosen as a natural element of reference;

$(Me/Fe)_{\text{sample}}$ is the ratio between concentration of the element X and that of Fe in the sediment sample;

$(Me/Fe)_{\text{crust}}$ is the ratio between the concentration of the element X and that of Fe in unpolluted reference baseline value of 12.3 (Turekian and Wedepohl, 1961).

3.4.4 Index of geoaccumulation (Igeo)

This determines the contamination in sediments by metals by comparing current concentrations to pre-industrial levels as in equation 4.

$$\text{I geo} = log_2[Cn/1.5Bn] \ \ldots..(4)$$

Where Cn is the measured concentration in the sediment for the metal n, Bn is the background value for the metal n and the factor 1.5 is used because of possible variations of the background data due to lithological variations, (Mohsen and Alireza, 2014). The description of the geo-accumulation index is presented in Table 3.1.

Table 3.1 Geo-accumulation and Enrichment Factor Categories

Geo-accumulation	Description	Enrichment Factor	Description Enrichment
$Igeo \leq 0$	Practically uncontaminated	$EF < 2$	Depletion to minimal
$0 < Igeo \leq 1$	Uncontaminated to moderately contaminated	$2 \leq EF < 5$	Moderate
$1 < Igeo \leq 2$	Moderately contaminated	$5 \leq EF < 20$	Significant
$2 < Igeo \leq 3$	Moderately to heavily contaminated	$20 \leq EF < 40$	Very high
$3 < Igeo \leq 4$	Heavily contaminated	$EF \geq 40$	Extremely high
$4 < Igeo \leq 5$	Heavily contaminated		
$Igeo > 5$	Extremely contaminated		

3.4.4 Contamination Factor and Pollution Load Index

Contamination factor (CF) describes the contamination of any given toxic substance in an environment (Hakanson, 1980). The mathematical representation of contamination factor CF is:

$$CF = C_0/C_n \ldots.(5)$$

Where C_0 is the average content of a particular metal in at least 5 samples, C_n is the pre-industrial reference level of the substance, CF is the contamination factor and n is the number of contamination factors in a specific site (Hakanson, 1980). The description of contamination factor and pollution load index is presented in table 3.2.

Table 3.2 Contamination Factor and Pollution Load Index Categories

Contamination Factor	Description	PLI	Implication
$CF < 1$	Low contamination	$PLI < 1$	Unpolluted
$1 \leq CF < 3$	Moderate contamination	$1 \leq PLI < 2$	Moderately polluted
$3 \leq CF < 6$	Considerably contaminated	$2 \leq PLI < 3$	Strongly polluted
$CF \geq 6$	Highly contaminated	$PLI \geq 3$	Extremely polluted

3.5 Rice Consumption Data

The rice consumption data was extracted from the food consumption survey (Appendix B) that was conducted in Asante Akim Central municipality, Ghana. The representative sample of participants included 300 people, who were interviewed by the use of questionnaires about their rice consumption per day, and also per week in order to obtain a rice consumption profile that represents the population. The socio-demographic characteristics of respondents were included in the questionnaire. The body weights of individual participants were also taken.

3.6 Dietary Exposure

The exposure of the heavy metals from rice was obtained using the consumption data and concentrations of heavy metals in rice samples and then dividing by the average body weight. The mean of the daily exposure levels was used to represent the dietary exposure for average consumers.

In order to assess the safety of dietary intake, daily intake of the heavy metals through rice was estimated based on daily consumption of rice obtained from the rice consumption survey (Appendix B).

Whenever possible, monitoring data from dietary intake studies are to be compared with acceptable or tolerable levels recommended by the Joint FAO/WHO Expert committee on food additives. Hence the total dietary exposure levels of As, Cd, Cr, Hg and Pb from rice determined in this study compared with the Allowable Daily intakes (ADIs) proposed by the JECFA to assess potential health risks faced by consumers (Mohammad *et al.*, 2008).

The estimated daily intake (EDI) was calculated based on the formula;

$EDI = \frac{Cm \times DCR}{BW} \ldots .(6)$(Gomah *et al*, 2019)

EDI is estimated daily intake.

Cm is the metal concentration in rice (mg/kg)

DCR is rice daily consumption rate, which was considered to be 118 g/person/day.

Bw is average body weight (67 kg)

3.7 Health Risk

The non-carcinogenic health risk index, which is indicated by the Hazard Quotient, HQ was calculated as given in Equation 7.

$$HQ = \frac{EDI}{RfD} \ldots\ldots(7)$$

Rf D is Oral reference Dose (WHO, 2006). The RfD for As, Cd, Cr, Hg and Pb was 3×10^{-4}, 1×10^{-3}, 3×10^{-3}, 3×10^{-4} and 3.5×10^{-3}mg/kg/day respectively (USEPA IRIS, 2011).

HQ less than 1 means the exposed population is unlikely to experience obvious adverse effects, while HQ above 1 means that there is a chance of non-carcinogenic effects to consumers upon consumption of locally cultivated rice, (Gomah *et al*, 2019, Alsafran *et al*, 2021).

Carcinogenic health risk

The carcinogenic health risk to human by individual potential carcinogenic metal was calculated from Equation 8:

$$CR = EDI \times C_{SF} \ldots(8)$$

Where CR is the cancer risk over a lifetime by individual metal ingestion

EDI is estimated daily metal intake (mg/kg bw/day)

C_{SF} is oral cancer slope factor (mg/kg/day) (Alsafran *et al*, 2021).

The permissible limit for carcinogenic metals is set at10^{-4} (US EPA). Therefore CR equal to or less than 10^{-4} is considered safe and pose no considerable carcinogenic health risk.

3.4 Statistical Analysis

The mean and standard deviation of concentrations of heavy metals in rice and soil were determined using IBM SPSS Version 20. The mean of the daily exposure levels from rice were used to represent the dietary exposure for average consumers. Microsoft Office Excel 2017 was used to determine the correlation between soil heavy metal content and rice heavy metal levels. A Pearson correlation was run to determine relationships between heavy metals in soil and rice samples. The level of significance was set to $p<0.05$.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results

Table 4.1: Age group and Sex Distribution of Respondents

	Respondents % (n=300)	
Sex	Percentage of respondents	Number of respondents
Male	58	173
Female	42	127
Age Group(yrs)		
10-17	11	33
18-30	32	96
31-44	31	93
45-64	24	72
65-80	2	6

As shown in Table 4.1, out of the 300 respondents, 42%were females. The percentage of males was 58 and that is 173 out of the 300 respondents. About 74% of the total respondents were youth while only 26% of the respondents belonged to the older age group (above 44yrs).

Table 4.2: Elemental concentrations of the soil samples (mg/kg).

	Mean ±SD (mg/kg)				
Soil samples	As	Cd	Hg	Pb	Cr
SS1	8.09±0.05	BDL	1.01±0.02	5.02±0.05	BDL
SS2	7.27±0.13	0.30±0.01	1.23±0.01	5.44±0.03	0.19±0.02
SS3	6.45±0.17	0.59±0.03	2.01±0.06	9.26±0.11	0.47±0.05
SS4	7.60±0.19	BDL	BDL	7.68±0.05	0.75±0.18
SS5	7.80±0.10	0.95±0.05	1.47±0.08	8.50±0.05	0.93±0.10
SS6	8.09±0.02	0.63±0.01	1.09±0.03	9.15±0.10	0.11±0.02
SS7	9.07±0.04	BDL	1.50±0.05	12.35±0.18	0.25±0.05
SS8	8.55±0.06	0.25±0.05	1.12±0.17	9.71±0.16	0.40±0.04
SS9	5.53±0.18	0.40±0.01	BDL	11.37±0.14	BDL
SS10	6.51±0.10	BDL	0.96±0.09	8.45±0.02	0.68±0.16

The results are presented as the mean of three replicates ± SD. SS represents soil samples from the different farms. BDL represents below detection limit of heavy metal.

Table 4.3: Elemental concentrations of the rice samples (mg/kg).

		Mean±SD (mg/kg)			
Rice sample	As	Cd	Hg	Pb	Cr
RS1	0.07±0.01	0.35±0.02	0.02±0.01	BDL	0.29±0.01
RS2	0.23±0.08	BDL	BDL	BDL	0.46±0.01
RS3	0.04±0.01	0.21±0.01	0.04±0.01	0.10±0.01	0.64±0.02
RS4	0.08±0.02	0.33±0.01	BDL	0.13±0.01	0.82±0.02
RS5	BDL	0.29±0.01	0.03±0.01	BDL	0.95±0.03
RS6	0.05±0.01	0.24±0.01	0.02±0.01	0.14±0.01	0.05±0.01
RS7	0.05±0.01	0.14±0.01	BDL	0.16±0.02	0.50±0.01
RS8	0.06±0.01	0.25±0.01	0.04±0.01	BDL	0.59±0.02
RS9	0.11±0.03	0.24±0.01	BDL	BDL	0.17±0.01
RS10	0.05±0.01	0.35±0.03	0.02±0.01	0.15±0.01	0.35±0.01

The results are presented as the mean of three replicates ± SD. RS represents rice samples from the different rice farms. BDL represents below detection limit of heavy metal.

Heavy metal concentration in soil samples

The heavy metal content in soil from the ten farms is presented in Table 4.2.

The mean concentrations (mg/kg) of arsenic in soil ranged between 5.53 to 9.07 mg/kg with mean of 7.50 mg/kg. Soil arsenic content was highest in SS7 and lowest in SS9.

The mean concentrations (mg/kg) of cadmium in soil ranged between 0.25 mg/kg to 0.95 mg/kg with mean of 0.52 mg/kg. Soil Cd content was highest in SS5 (0.95 mg/kg). Cadmium content was below detection limit in four of the soil samples; SS1, SS4, SS7 and SS10.

Chromium was below detection limit in two out of the ten soil samples that were analysed for chromium; SS1 and SS9. The highest chromium concentration was recorded in SS5 (0.93 mg/kg). The mean chromium concentration in soil was determined to be 0.47 mg/kg.

In two of the soil samples; SS4 and SS9, mercury (Hg) was below detection limit. The highest Hg level was found in SS3 (2.01 mg/kg) with the mean concentration of Hg in soil samples to be 1.30 mg/kg.

The concentrations (mg/kg) of lead (Pb) in soil ranged between 5.02 to12.35 mg/kg with average mean of 8.69 mg/kg. Soil lead content was highest in SS7 and lowest in SS1.

Soil Pollution Indices

Table 4.4 Enrichment Factor and Index of Geoaccumulation values for tested soils.

Heavy metals	EF	Description	Igeo	Pollution level
As	2.62	Moderate enrichment	-1.38	<0, practically uncontaminated
Cd	2.62	Moderate enrichment	0.21	Uncontaminated to moderately contaminated
Cr	2.61	Moderate enrichment	-8.17	Practically uncontaminated
Hg	2.59	Moderate enrichment	1.12	Moderately uncontaminated
Pb	2.60	Moderate enrichment	-1.79	Practically uncontaminated

Heavy metals in rice

Arsenic was below detection limit in RS5. The highest As content in rice was found in RS2 (0.23 mg/kg). The mean As content in rice was determined to be 0.082 mg/kg. The mean concentration of Cadmium was determined to be 0.27 mg/kg with RS1 and RS10 containing the highest Cd levels (0.35 mg/kg) in rice. Cadmium was below detection limit in RS2.

Out of the ten rice samples analysed, Hg was below detection limit in RS2, RS4, RS7 and RS9. The mean concentration of Hg in rice was 0.028 mg/kg. Rice samples RS3 and RS8 contained the highest levels of Hg (0.04 mg/kg). The Chromium (Cr) content in rice samples ranged from 0.05 to 0.95 mg/kg with a mean of 0.48 mg/kg. The least Cr concentration was recorded in RS6 (0.05 mg/kg) with RS5 recording the highest rice Cr concentration of 0.93 mg/kg. Pb was below detection limit in 50% of the rice samples. RS7 recorded the highest Pb concentration of 0.16 mg/kg. The mean Pb concentration was 0.14 mg/kg. All samples that were analyzed had lead content lower than the maximum permitted level of 0.2 mg/kg proposed by the JECFA.

Table 4.5: **Correlations Analysis for Five Heavy Metals Between Paddy Soil and Rice Grain Samples.**

	As	**Cd**	**Cr**	**Hg**	**Pb**	**As**	**Cd**	**Cr**	**Hg**	**Pb**
As	1									
Cd	-0.1702	1								
Cr	0.0114	0.2142	1							
Hg	0.3143	0.3612	0.1162	1						
Pb	-0.0057	0.1153	-0.0126	0.0026	1					
As	-0.2312	-0.2599	-0.4497	-0.2584	-0.4043	1				
Cd	-0.0770	-0.1242	0.3444	-0.3367	-0.0557	-0.6789	1			
Cr	0.1961	0.1928	0.8143	0.2110	-0.0675	-0.2585	0.0664	1		
Hg	0.0852	0.4442	0.2972	0.5821	-0.0343	-0.5702	0.3230	0.2312	1	
Pb	0.1355	-0.2974	0.2090	0.0749	0.3554	-0.3297	0.1301	-0.0953	-0.1630	1

Correlation is significant at α = 0.05

The Pearson's correlation analysis was used to identify the relationship between soil metal levels and the rice metal concentration.

Table 4.6: Estimated daily intake (mg/kg bw/day) of metals for the population due to consumption of tested rice samples

Metal	EDI	ADI
As	1.45×10^{-4}	2.0×10^{-3}
Cd	4.8×10^{-4}	1.0×10^{-3}
Cr	8.5×10^{-4}	3.4×10^{-3}
Hg	4.95×10^{-5}	5.7×10^{-2}
Pb	2.4×10^{-4}	3.6×10^{-3}

4.2 Discussion

Soil Pollution Indices

Table 4.4 shows that the Enrichment Factor for all the soils studied fall under the second category (2≤EF<5) which indicates that, the soils are moderately polluted by all the heavy metals; As, Cd, Cr, Hg and Pb. This result suggests that anthropogenic activities also contribute to soil pollution by these metals since EF value greater than 1.5 indicate anthropogenic contribution (Zhang and Liu, 2002). Similar EF value for Pb has been reported by Odat (2015) where the result was attributed to anthropogenic activities.

The Igeo values indicate that the soils studied are practically uncontaminated with respect to As, Cr and Pb with Igeo values -1.38, -8.17 and -1.79 respectively, (Table 4.4). The soils were moderately contaminated with Hg (Igeo=1.12) and uncontaminated to moderately contaminated with Cd (Igeo=0.21). These results could be attributed to the use of mercury by artisanal and small-scale miners in their activities as well as other anthropogenic activities such the production of cement since there is a cement production plant situated at the study area (Odat, 2015). The calculated contamination factor (CF) for the sampled soils from the study area indicate that there was low As contamination in the soil (CF=0.58), Cr (CF=0.01) and Pb (CF=0.43). However the soils were seen to be very highly contaminated by Hg (CF=7.2) and moderately contaminated by Cd (CF=1.73). The PLI value for the metals indicate that the soils are unpolluted by the heavy metals since the PLI is less than 1 (PLI=0.50). Moderate contamination of soils in the study area by heavy metals has been reported (Sarpong, 2021).

4.2.1 Heavy metal contamination of soil and rice

Arsenic

Arsenic is potentially carcinogenic and high exposure causes arsenicosis (WHO 2010, UNICEF, 2006). It can also form complexes with organic compounds to form methylarsonic acid and dimethylarsinic acid among others (WHO, 2000). These complexes may hinder the production of adenosine triphosphates (ATP) during respiration, (Gomah *et al*, 2019).

The results indicate the presence of Arsenic in all the soil samples. The mean arsenic concentration was estimated to be 7.50 mg/kg. Adomako (2010) reported up to 103 mg/kg arsenic in soil in the study area, Konongo, where samples were picked from the Anum Valley Irrigation Project Sitewhich is located close to the old Konongo Gold

Mine. High arsenic concentration in soil was attributed to the nearness of the location where samples were picked to the gold mine.

Arsenic was present in all the rice samples but one, (RS5) with an average arsenic concentration in rice as 0.082 mg/kg which is lower than the maximum allowable concentration of arsenic of 0.2 mg/kg (Fig. 2) proposed by the Joint FAO/WHO Experts Standards Program Codex Alimentation Commission (JECFA, 2014). The result is consistent with Arsenic content of 0.0843 mg/kg in locally cultivated rice reported by Asamoa (2016). However higher levels of arsenic (0.59 mg/kg) in rice was reported by Adomako (2010).

Arsenic translocation in rice

The Bioconcentration factor (BCF) is an index for evaluating the transfer potential of a metal from soil to rice grains (Takarina and Pin, 2017). The Pearson's correlation analysis (Table 4.4) was used to identify the relationship between soil metal levels and the rice metal concentration. Results from the correlation analysis shows that, there is a negative relationship (correlation coefficient, $r = -0.23$, $p<0.05$) between soil arsenic and rice arsenic levels. The lower levels of arsenic in rice could be due to the poor absorption of soil arsenic by the rice plants since the soil is able to retain more arsenic. This can further be explained by the low BCF (0.011) for arsenic through rice grains, since low enrichment factor or BCF suggests high retention of arsenic in soil and low transfer potential of As in rice. Gomah *et al*, (2019) have also reported lower levels (0.018 mg/kg) of arsenic in rice and attributed their results to soil pH and redox potential as the major factors that accounted for the presence of heavy metals in rice grains.

The low content of arsenic in rice could also be attributed to the long distance (about 10 km) from the location where samples were collected and the gold mine in the study area, indicating the gold mine as the source of arsenic contamination. In his study, Adomako (2010), reported high levels (0.59 mg/kg) of arsenic in soil as well as in rice and indicated that gold mining contributed to soil contamination by arsenic since samples were collected from an area close to a gold mine. This assertion was further emphasized by the fact that samples from non-gold mining areas contained significantly lower arsenic levels than gold mining communities, suggesting the gold mine as the source of arsenic contamination. Furthermore, it has been stated that, there have been many reports that the extent of heavy metal contamination in agricultural soils is influenced by their closeness to mining or industrial areas, (Simon *et al*, 2016).

Table 4.7 Mean soil and rice metal concentrations (mg/kg) and their respective BCF

	As	**Cd**	**Cr**	**Hg**	**Pb**
Soil	7.50	0.52	0.47	1.30	8.69
Rice	0.08	0.27	0.48	0.03	0.14
BCF	0.01	0.52	1.02	0.02	0.02

BCF: Bioconcentration factor

Cadmium

Cd is one of the most toxic and mobile soil elements (WHO, 2000). Health risks of consuming rice that is contaminated with cadmium were of particular concern since rice consumption accounts for the majority of calories consumed (Dube, 2022). Exposure to Cd has adverse health effects on the pulmonary, cardiovascular, and musculoskeletal systems as well (Guo *et al*, 2020). Cadmium affects the bone and can also cause kidney and renal disorder in human.

Cadmium was not detected in 40% of the soil samples. However, 90% of the rice samples contained Cd. The mean Cd concentration in rice was estimated to be 0.27 mg/kg which is below the 0.3 mg/kg proposed by the FAO/WHO Joint Expert Committee on Food Additives, JECFA. Lower levels of cadmium in locally cultivated rice had been reported in Ghana by Asamoa (2016), where the mean level of cadmium in rice was estimated at 0.01 mg/kg. However, Valentine and Dawda (2013) reported high cadmium content (2.4 mg/kg) which was above the maximum permissible limit in locally cultivated rice in Kassena-Nankana district in Ghana. Naseri *et al* (2014) have also reported higher cadmium concentration (0.33 µg/g)in raw rice in Iran.

The correlation between Cd content measured in soil and rice samples was found to be insignificant ($r = -0.12$, $p<0.05$). As shown in Table 4.7 above, Bioconcentration factor of 0.52 suggests Cd has low capacity to be absorbed by the rice plants from the soil and translocated to the grains. Singh *et al*, (2010) have reported lower levels of Cd in cereals (wheat and rice), but high enrichment factor or high translocation in rice (TF=0.68), which means poor soil retention for Cd. This could explain the ‘no detection’ at 0.001 mg/L Limit of Detection in about 40% of the soil samples for Cd. This is consistent with results obtained by Rahimi *et al*, (2017), whereby the low levels of Cd were attributed to Cd being highly mobile and its easy absorption properties in rice plants. Guo *et al* (2020) however reported significantly positive correlation between soil cadmium and rice cadmium levels and stated that, cadmium uptake by rice root and the subsequent accumulation in the grains was affected by many soil factors which include soil acidity, organic matter, clay minerals and other metal oxides.

Chromium

High chromium exposure causes skin cancer, lungs ailment and liver damages (UNEP, 2010). Chromium was detected in eight out of the ten soil samples but was detected in all the ten rice samples. The mean chromium content in rice was estimated to be 0.48 mg/kg which is below the level (1.0 mg/kg) proposed by the JECFA (Fig. 3). Otitoju *et al* (2014) reported far lower chromium levels (0.06 mg/kg) in locally cultivated rice in some parts of Nigeria. The correlation analysis showed a strong positive correlation between soil chromium and rice chromium ($r = 0.814$, $p<0.05$), which means that high Cr content in soil may likely result in high Cr rice levels. This assertion is further confirmed by the high BCF of 1.02 which suggests high transfer potential of Cr from soil and high uptake of Cr by the rice plant. The results could be attributed to lower pH of the soil since lower soil pH increases plant availability for metals. Thus, the higher the metal content in a soil with low pH, the higher the metal levels in food crops since metal uptake is increased due to plant availability which is increased under such conditions, (Owusu-Donkor, 2011). Again chromium might be introduced through atmospheric deposition during mining activities since the study area is noted for mining and ‘galamsey’ operations.

Higher levels of chromium in rice have also been reported by Singh et al (2010), in which high enrichment factor for Cr in rice was recorded. The high enrichment factor was attributed to bioavailability of metals which also depends on metal concentration in soil, chemical form of the metal, difference in uptake capabilities and growth rate of different plant species. High enrichment factor of chromium has also been reported for rice, (Singh *et al*, 2010).

Mercury

Mercury is known to cause gastrointestinal disorder, acrodynia diseases, brain and central nervous system damages, (Guo *et al*, 2020). Mercury was below the LOD of 0.001 mg/L in two of the soil samples that was analysed. The mean mercury content in rice was estimated to be 0.028 mg/kg which is above the level (0.02 mg/kg) proposed by the JECFA (Fig3). This result could be attributed to the nearness of the farms to the mining sites in the area since “galamsey” operators in personal communications with the researcher claim to use heavy metals such as mercury in their mining operations.

However, different results were obtained by Ugochukwu *et al* (2017), where the mean mercury concentration of rice was reported to be 0.270 mg/kg in Awka, Nigeria. It was stated that the high level of mercury in rice could be attributed to the different farming methods employed since mercury contamination increases with the use of inorganic fertilizers in rice farming. Huang *et al* (2013) also reported a lower mean mercury concentration of 0.05 mg/kg in Zheijiang Province of China.

There was a positive correlation ($r=0.58$, $p<0.05$) between soil mercury and rice mercury levels (Table 4.5). A lower BCF of 0.022 (Table 4.7) indicates high retention of metal in soil and thus low translocation in rice grains. The second highest mercury content was recorded in soil sample SS7, however mercury was not detected in rice sample obtained from the SS7 soil sample. This confirms the low BCF value which indicates lower translocation or uptake of mercury from soil into rice grains.

Lead

Lead is toxic even at low levels of exposure, which is able to enter the food chain, and that the levels can build up in the body through consistent exposures and the effects are irreversible (ATSDR, 2012). Lead has the ability to cause anaemia, weakness in muscles, lethargy and paralysis (Sharma and Agrawal, 2014).

All the soil samples contained lead ranging from 5.02 mg/kg to 12.35 mg/kg with average lead level of 8.69 mg/kg. However, lead was below detection limit of 0.001 mg/L in 50% of the rice samples. The mean lead content in rice was estimated to be 0.14 mg/kg which is below the 0.2 mg/kg level proposed by the JECFA (Fig 3).Similar results were found by Guo *et al*, (2020) where rice lead concentration was reported as 0.148 mg/kg. A much lower concentration (0.0308 mg/kg) of lead in locally cultivated rice has been reported in Ghana by Asamoa, (2016). In contrast, Valentine and Dawda (2013) reported high lead content (0.24 mg/kg) which was above the maximum permissible limit in locally cultivated rice in Kassena-Nankana district in Ghana. Otitoju *et al* (2017) also reported higher lead levels in locally cultivated rice in the northern part of Nigeria with the least concentration of lead being 0.311 mg/kg. The results was attributed to the differences in the species of the rice that were considered, the total heavy metal content of soil, and also soil chemical and physical properties; which affect bioavailability of heavy metals in plants, (Otitoju *et al*, 2014).

As shown in Table 4.4, the correlation between soil lead and rice lead content was a weak positive correlation (r=0.36, p<0.05). A lower BCF of 0.016 further confirms the low uptake of lead by rice plants which accounts for lower levels of lead in rice in this study.

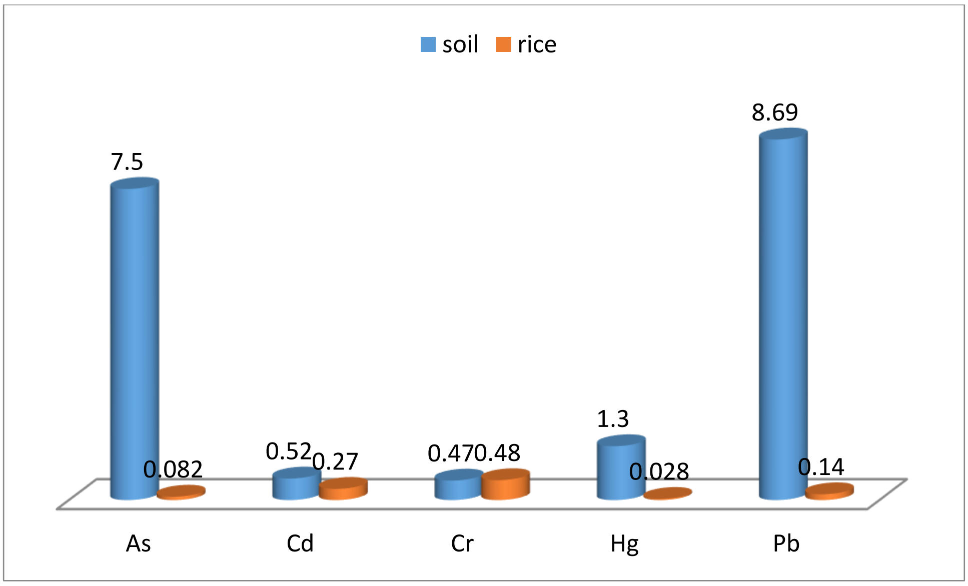

Figure 2: Mean concentration of the elements (mg/kg) in tested soil and rice samples.

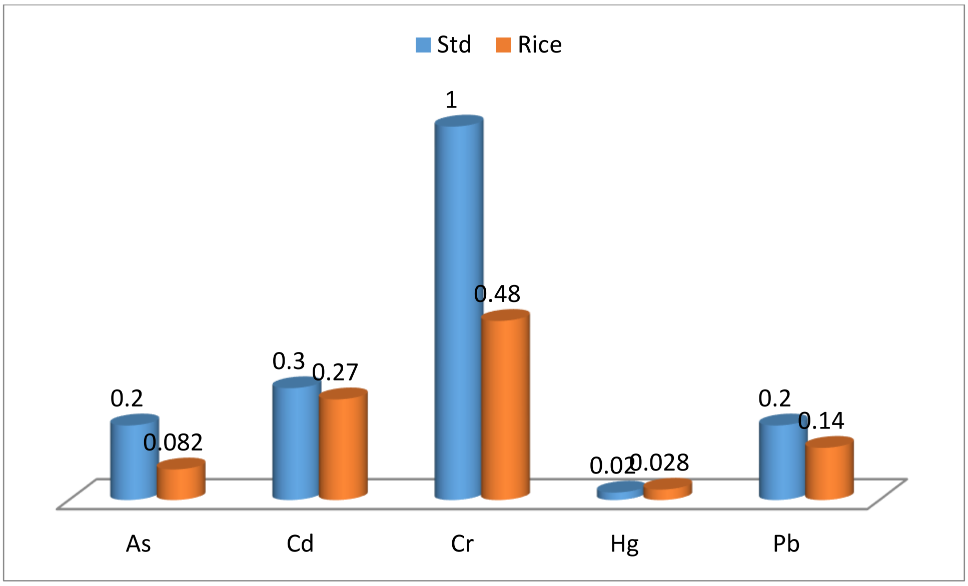

Figure 3: Concentration of the elements in rice samples compared to CODEX Standards (mg/kg).

4.2.2 Heavy metal risk assessment to human health through rice consumption

Dietary consumption has been identified as a major pathway through which humans are exposed to heavy metals. The risk of exposures to humans and the associated health effects depend on the extent of heavy metal contamination in rice and the amount of rice consumed by the individual, Simon *et al*, (2016). From the food consumption survey, it was estimated that an individual consumed 472.5 g of rice in a week with an average of four (4) days in the week. The consumption rate was estimated at 118 g/person/day. The average body weight of respondents was 67 kg. The estimated daily intakes (EDI) of the heavy metals understudy are presented in Table 4.5.

Dietary Exposure to Arsenic

The estimated daily intake (EDI) of arsenic was estimated at 0.000145 mg/kg/day, equivalent to 0.001 mg/kg/wk. According to the JECFA, the Tolerable Daily Intake (TDI) for As is 0.002 µg/kg Bw/day. This is an indication that the amount of Arsenic ingested is low considering the current rice consumption rate. An individual must consume higher amount of locally cultivated rice per day in order to exceed the recommended daily threshold limit. For example the mean concentration of Arsenic in the rice samples was 0.082 mg/kg, if a consumer of locally cultivated rice in the Asante Akim Central Municipality consumes 118g of the rice per day, the person consumes approximately 0.000145 mg of arsenic per day. This is below the 0.002 – 0.007 mg/kg body weight per day limit set by the JECFA, (Guo *et al*, 2020). In an unlikely situation will a consumer consume 1.74 kg of locally cultivated rice per day to exceed the threshold limit. Similar results were obtained by Huang *et al*, (2013), where the EDI for arsenic in rice was estimated at 0.49 µg/kg bw/day. Lower EDI value for arsenic which was estimated at 0.000064 mg/kg/day has been reported and it was far below the limit set by JECFA, (Gomah *et al*, 2010).

The non-carcinogenic health risk associated with the consumption of arsenic contaminated rice is indicated by the hazard quotient of 0.48 which is lower than the value 1. This therefore suggests that rice consumption does not pose serious health risk to the consumers of locally cultivated rice. The low level of risk might be due to the low exposure rate of the population to arsenic. Reports by both Huang *et al* (2013) and Gomah *et al* (2019) also showed that the non-carcinogenic health risk associated with arsenic through the consumption of rice was very low.

Dietary exposure to Cadmium

The estimated daily intake (EDI) of cadmium was calculated as 0.00048 mg/kg/day (0.48 µg/kg/day) (Table 4.5) which is lower than 1.0µg/kg Bw/day proposed by JECFA. In consideration of the current rice consumption rate, the amount of cadmium ingested through consumption of locally cultivated rice is lower. In comparison with the EDI obtained, higher EDI values for cadmium have been reported by Guo *et al*. (2020) and Naseri *et al*, (2014) as 0.92 µg/kg/day and 0.612 µg/kg/day respectively. However, Huang *et al*, (2013) and Gomah *et al* (2019) reported low EDI values below the 1.0 µg/kg Bw/day. Lower dietary intake of cadmium has also been reported by Othman (2011).

The non carcinogenic health risk associated with the consumption of cadmium contaminated rice from the study area was estimated at 0.48 which is lower than 1. This is an indication that rice consumption is not expected to pose serious health risk to consumers of locally cultivated rice. The low rate of consumption of locally cultivated rice could account for the low level of risk. Huang *et al*, (2013) and Gomah *et al* (2019) estimated health risk index values for cadmium below 1, which is an indication of the absence of health risks associated with cadmium through the consumption of rice. Guo *et al*, (2020) however reported a hazard quotient of 0.918 which is close to 1, and indicates that the population might be exposed to serious health risk through the consumption of rice.

Since cadmium is a potential carcinogen, the carcinogenic health risk through the consumption of cadmium contaminated rice was estimated. The cancer risk for cadmium was estimated at 4.8×10^{-6} which is lower than the threshold value of 10^{-4}. This indicates that the population in the study area are not at any cancer risk due to cadmium exposure from rice.

Dietary Exposure to Chromium

The EDI of chromium was estimated at 8.5×10^{-4} mg/kg bw/day which is lower than the maximum limit for chromium intake, (FAO/WHO, 2021). Comparing the EDI value for chromium obtained for this study, a higher value of 1.5 µg/kg bw/day has been reported by Guo *et al*, (2020). However a lower EDI value (0.698 µg/kg bw/day) for chromium has been reported by Naseri et al (2014). Gomah *et al*, (2019) have also reported EDI value below the maximum limit of 0.003 mg/kg/day in Monrovia.

Hazard Quotient for chromium was estimated at 0.28, an indication of absence of non-carcinogenic health risk to the consumers of locally cultivated rice. Similarly, Guo *et al* (2020) reported hazard quotient of 0.001, while Gomah *et al* (2019) reported a Hazard Quotient of 0.4, all of which are below 1, suggesting that consumption of rice does not pose serious health risk from chromium to the consumers.

Dietary exposure to Mercury

The EDI of mercury was estimated at 0.0495 µg/kg bw/day (Table 4.5), which is lower than the 0.57 µg/kg bw/day value proposed by the JECFA. This result indicates that the exposure of consumers to Hg is low. A comparatively lower EDI value of 0.03 µg/kg bw/day has been reported by Huang *et al* (2013). Gomah *et al* (2019) have also reported a very low EDI for Mercury through rice in Monrovia.

The hazard quotient was estimated at 0.165, which indicates that the non-carcinogenic health risk associated with the consumption of mercury contaminated rice is very low. This suggests that consumption of locally cultivated rice does not pose serious health risk. However, a long term large consumption if rice will result in high exposure to Hg. A lower hazard quotient was also obtained by Gomah *et al* (2019) which indicate that the consumption of rice in Monrovia does not pose serious health risk to consumers as far as mercury is concerned.

Dietary exposure to Lead

The estimated daily intake (EDI) of Pb by the population was estimated to be 0.24 µg/kg bw/day (Table 4.5).Huang *et al* (2013) have reported 0.37 µg/kg bw/day in a study in Zhejiang, China. In contrast, Naseri *et al* (2014) reported 3.2 µg/kg bw/day while Guo *et al* (2020) reported the EDI in a research conducted in Monrovia as 1.38 µg/kg bw/day. A lower EDI value has also been reported in a research by Gomah *et al*

(2019). Dietary intake of lead through cereals including rice was also reported by Othman (2011) to be low in Dar es Salaam.

The hazard quotient for Pb in this research was calculated to be 0.069 and this indicates that the consumers of locally cultivated rice are at no risk of non-carcinogenic effects that might be posed by consumption of lead in rice. This result is consistent with the findings by Huang *et al* (2013), Gomah *et al* (2019) and Guo *et al* (2020), in which hazard quotients were reported as 0.11, 0.394 and 0.02 respectively, which are all below 1 indicating the absence of non-carcinogenic health risk to the consumers of rice in the study area.

The carcinogenic health risk associated with consumption of locally cultivated rice was estimated at 9.12×10^{-5} which is lower than the threshold value of 10^{-4}. This is an indication that, the population in the study area is not at any expected carcinogenic health risk due to Pb through intake of locally cultivated rice.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The study determined the levels of As, Cd, Cr, Hg and Pb in soils and locally cultivated rice in the Asante Akim Central municipality. It was observed that, the levels of the elements in the soil samples were generally low, with the highest soil heavy metal content being 8.69 mg/kg recorded for Pb. The metal concentrations in rice samples were also found to be lower, below the levels permitted by the JECFA. However, Hg levels were found to be narrowly higher than the maximum permitted level.

The lower levels of the metalloid and heavy metals in both soil and rice samples were further confirmed by the translocation factors for each of the metals which were lower with the exception of Cr whose translocation factor exceeded one. Rice Cr content was however below the maximum permitted level despite the high translocation factor which indicates the low level of Cr in the soil.

The enrichment factor values indicate that the soils in this study are moderately enriched. The index of geo-accumulation values also suggest that, the soils are unpolluted by As, Cr and Pb while there exist moderate pollution by Cd and Hg. The contamination factor (CF) values indicate low contamination of soils by As, Cr and Pb while there exist very high contamination by Hg and moderate contamination by Cd. Soil pollution index indicate that the soils are uncontaminated.

The Pearson's correlation analysis that was used to identify the relationship between soil metal levels and the rice metal concentration showed that, at $p<0.05$, the correlation between soil and rice As and Cd was poor. However, there was positive correlation between soil and rice Cr, Hg as well as Pb. It can therefore be concluded that the level of contamination is low.

Dietary exposure of consumers to heavy metals was generally low. The observed dietary intake values for each of the metals were below the permissible limits set by the JECFA. The hazard quotients were also lower than the US EPA permissible safety limit. This shows that the population is not at significant health risk to the exposure of As, Cd, Cr, Hg and Pb through the consumption of locally cultivated rice in the Asante Akim area. The cancer risk values for Cd and Lead were found to be less than the threshold value of 10^{-4}, which is an indication that the population in the study area is not at any cancer risk due to Cd and Pb exposure to rice.

5.2 Recommendation

Considering the increasing industrial activities as well as the existing artisanal mining activities in the municipality, there is the possibility of an increase in the levels of heavy metals in food crops in the near future which may pose serious health risk to the population. It is therefore recommended that, Government agencies such as EPA should conduct regular monitoring and studies to check the levels of heavy metals in soil in the study area.

Regular monitoring of food crops such as rice cultivated in the area must be conducted by the Ministry of Food and Agriculture to ascertain the safety of food crops over time since an increase in the levels of heavy metals is possible and may pose adverse health effects to consumers.

The risk associated with consuming the locally cultivated rice may be lower but the estimated intake is just for rice consumption. Other media for exposure to heavy metal contamination also exist. It is therefore recommended that, Departments in related fields of academic institutions should do more research into other food crops to determine their levels of contamination by heavy metals in the area. This might help determine the actual risk posed by heavy metals through food consumption in the area.

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APPENDICES

APPENDIX A

APPENDIX A1: Results obtained for Elemental Recoveries

Conc/ppm	As	Cd	Cr	Hg	Pb
10.000	10.002	10.004	9.992	10.004	9.992
15.000	15.001	14.990	15.002	14.982	15.002
20.000	20.003	19.995	19.997	19.902	20.002
25.000	24.999	25.007	24.993	25.000	24.994
Average recovery	%100.001	99.994	99.973	99.858	99.980

APPENDIX A2: OPERATING CONDITIONS OF INSTRUMENTS

AGILENT 7700 SERIES ICP-MS

Minimum dwell time: 100 µs

Standards: Certified Elements

Concentration range: 0.001- 500 ppm

Spray Chamber: Teflon

Gas: 99.99% pure argon at 20 L/min

Nebulizer: 7700 PFA micro-flow

Flow rate: 5 L/min

Operating Temperature: 27°C

Electrical Power: 240 V, 30A, 50 Hz

Operating Humidity: 30%

APPENDIX A3: SHIMADZU Automatic Mercury Analyzer Model HG-5000

Sample 1D: Rice samples	Wavelength: 253 nm
Blank: Distilled Water	Detection limit: 0.001 ppm
Standards: Certified Metals	Lamp Current: 4 mA
Sample flow rate: 6.5 ml/min	Gas: Argon
Support: Air	

APPENDIX A4: VARIAN HYDRIDE GENERATION AAS

PARAMETER	VARIAN AA 240FS
Lamp Current	10 mA (Arsenic hollow cathode)
Wavelength	193.7 nm
Slit	0.5 nm
HCl	6 M at 1 ml/min flow rate
NaOH	0.5%
Detection limit	0.001 mg/L
$NaBH_4$	0.6% at 1.5 ml/min
Fuel	Acetylene
Support	Air

APPENDIX A5: Calibrations

Certified reference elemental standard solutions.

10, 15, 20 and 25 ppm were prepared by dilution of 1000 mg/L stock solutions of the CRMs. Approximately 20 ml of each standard was analysed for their metal levels and the degree of accuracy determined. Blanks were run intermittently and the expected metal levels of 0 ppm were ensured.

APPENDIX A6: Certified Reference Materials and Codes

ELEMENT	SERIAL NUMBER
As	AW 2454
Cd	AW 2662
Cr	AW 9441
Hg	AW 20059
Pb	AW 7202

APPENDIX B

Interview Questionnaire

AKENTEN APPIAH-MENKA UNIVERSITY OF SKILLS TRAINING AND ENTERPRENEURIAL DEVELOPMENT

DEPARTMENT OF CHEMISTRY EDUCATION

STUDY ON RISK ASSESSMENT OF HEAVY METALS IN RICE

INTERVIEW SCHEDULE FOR LOCAL RICE CONSUMERS

Identification

Investigator: ________________ Date: _____________ Tel:____________________

Location of the bussiness____

Interviewer's Declaration

I am an MPhil Chemistry Education student in the above mentioned institution. I am carrying out an academic research on risk assessment of heavy metals in rice. I need your response to some few questions to enable me complete my thesis.

Information provided will be treated as confidential and the data will only be used for academic purposes. If you don't want to give an answer to any particular question please mention it along the conduction of the survey.

Personal Profile

Questions

1. Age

i. 12 – 17
ii. 18 – 30
iii. 31 – 60
iv. 61 – 70
v. Above 70

2. Gender

i. Male
ii. Female

3. Weight ....

4. Religious affiliation

i. Christian ☐
ii. Muslim
iii. Traditionalist
iv. Others(Specify) ………………………………………..

5. Educational level?

i. Tertiary
ii. Training college
iii. Tech/voc
iv. Secondary
v. Middle School/ Basic school
vi. g. None

6. Ethnic group

i. Ewe

ii. Akan

iii. Hausa

iv. Ga/Adangbe

v. Guan

vi. other (specify)……………………………………….

7**. Do you eat rice**?

i. Yes

ii. No

8**. If yes, Which type of rice do you prefer**?

i. Locally cultivated rice

ii. Imported rice

9. **Why do you prefer either type of rice**?

10. **Source of rice**

i. farmers

ii. market

iii. tenders

iv. others (specify)

11. **Have you eaten rice in the past four weeks?**

i. Yes

ii. No

12. **How many days in an average week do you eat rice?**

i. One day
ii. Two days
iii. Three days
iv. Four days
v. Five days
vi. Six days
vii. Daily

13. **On average how many servings of rice do you eat per day**? (1/4 cup of dry rice equates to 1 cup of rice When cooked. 1cup of rice equates to two servings of grains)

i. 1 serving
ii. 2 servings
iii. 3 servings
iv. 4 or more servings
v. Don't know

THANK YOU.