

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

KUMASI, GHANA

# KNUST

Health Risk from Heavy Metals to the Population of Monrovia, Liberia through the  
Consumption of Rice

BY

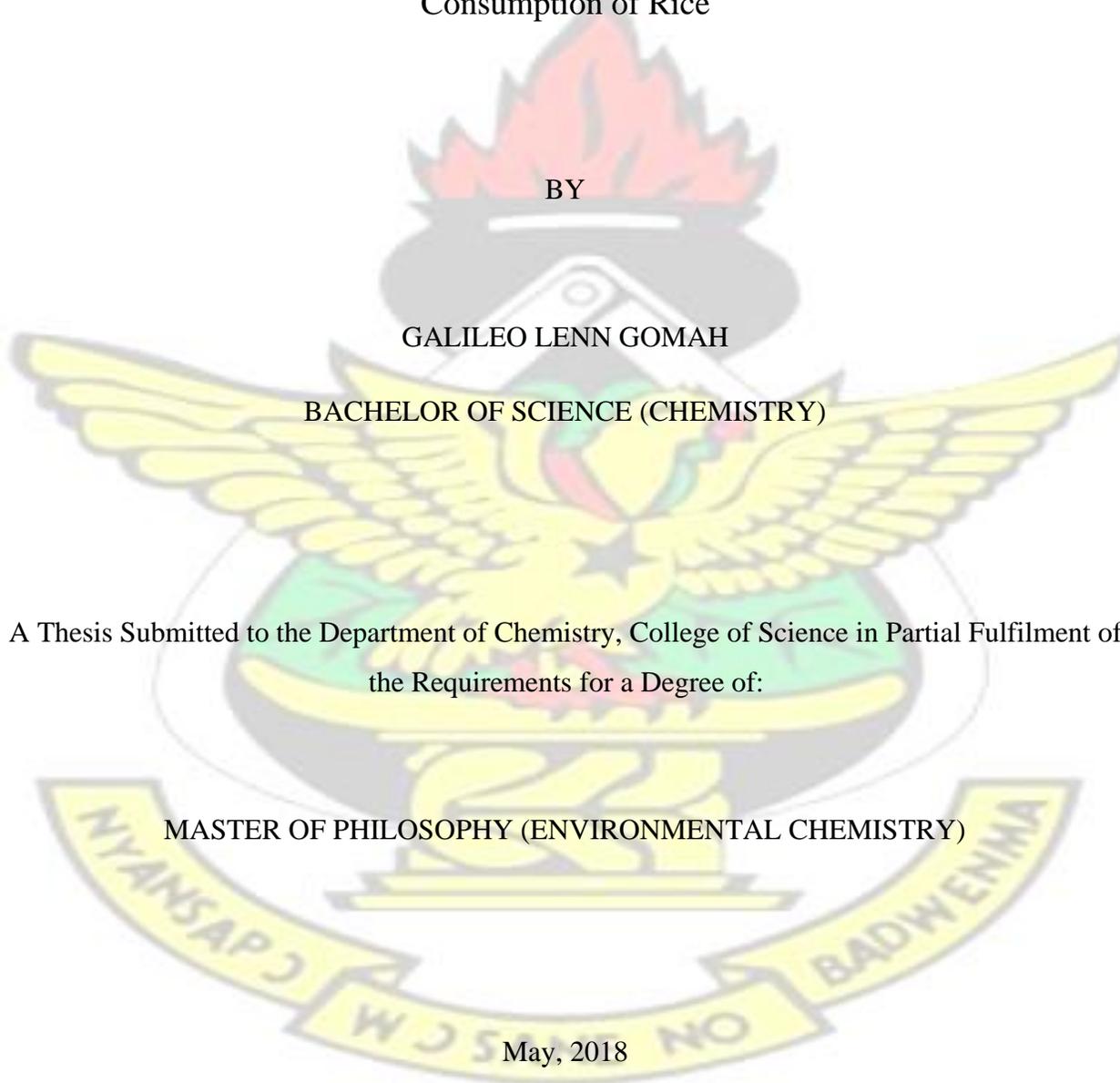
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BACHELOR OF SCIENCE (CHEMISTRY)

A Thesis Submitted to the Department of Chemistry, College of Science in Partial Fulfilment of  
the Requirements for a Degree of:

MASTER OF PHILOSOPHY (ENVIRONMENTAL CHEMISTRY)

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## DECLARATION

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

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## DEDICATION

This work is dedicated to my late father, Mr. Sehgran K. Gomah. You were truly my inspiration. There was not a wasteful day with you. You taught me, by examples, the real meaning of perseverance, dedication, responsibility and hard work. You may be gone, but not forgotten. May your soul rest in perpetual peace. Love you!!!



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## ABSTRACT

Rice is the major component of Liberian diets. It is the most widely consumed crop in Monrovia. Environmental pollution can possibly contaminate the crop with heavy metals. In this study, sixtyone rice samples comprising nine domestic cultivated and twenty imported brands of different batches were obtained from six local markets in Monrovia, Liberia and evaluated for the concentrations of six heavy metals: Arsenic (As), Cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg) and Nickel (Ni). The level of Hg concentrations was determined by AAS using a Lumex RA-915M Portable Zeeman Automatic Mercury Analyzer while the levels of As, Cd, Cr, Pb and Ni concentrations were determined by ICP-MS using an Agilent 7900 Inductively Coupled Plasma Mass Spectrometer. The concentrations of As, Cd, Cr, Pb, Hg and Ni ranged from 0.0011 to 0.0181, 0.0048 to 0.1179, 0.050 to 0.4245, 0.0011 to 0.0371, 0.0011 to 0.0094 and 0.0151 to 0.6552 mg/kg respectively. The study revealed no significant statistical difference in the level of the metal concentrations between the locally cultivated and imported rice samples, except for As ( $P = 0.002$ ). Dietary exposure of the consumers to the metals was assessed by comparing Estimated Daily Intake to the Provisional Tolerable Daily Intake of the metals, and the non-carcinogenic health risk posed was assessed using Hazard Quotients and Hazard Indices. Carcinogenic health risk posed from Arsenic was assessed by using Incremental Lifetime Cancer Risk values. Incremental Lifetime Cancer Risk for As was less than the US EPA threshold value of  $10^{-4}$ . Hazard Quotients and Hazard Indices for all the metals were less than the US EPA permissible value of 1. Therefore, consuming the selected rice samples sold on the local markets in Monrovia at the current consumption rate posed no health risk to the population from As, Cd, Cr, Pb, Hg and Ni alone or when combined. Hence, there is no need for consumption advisory. However, regular monitoring of contaminant levels is highly recommended.

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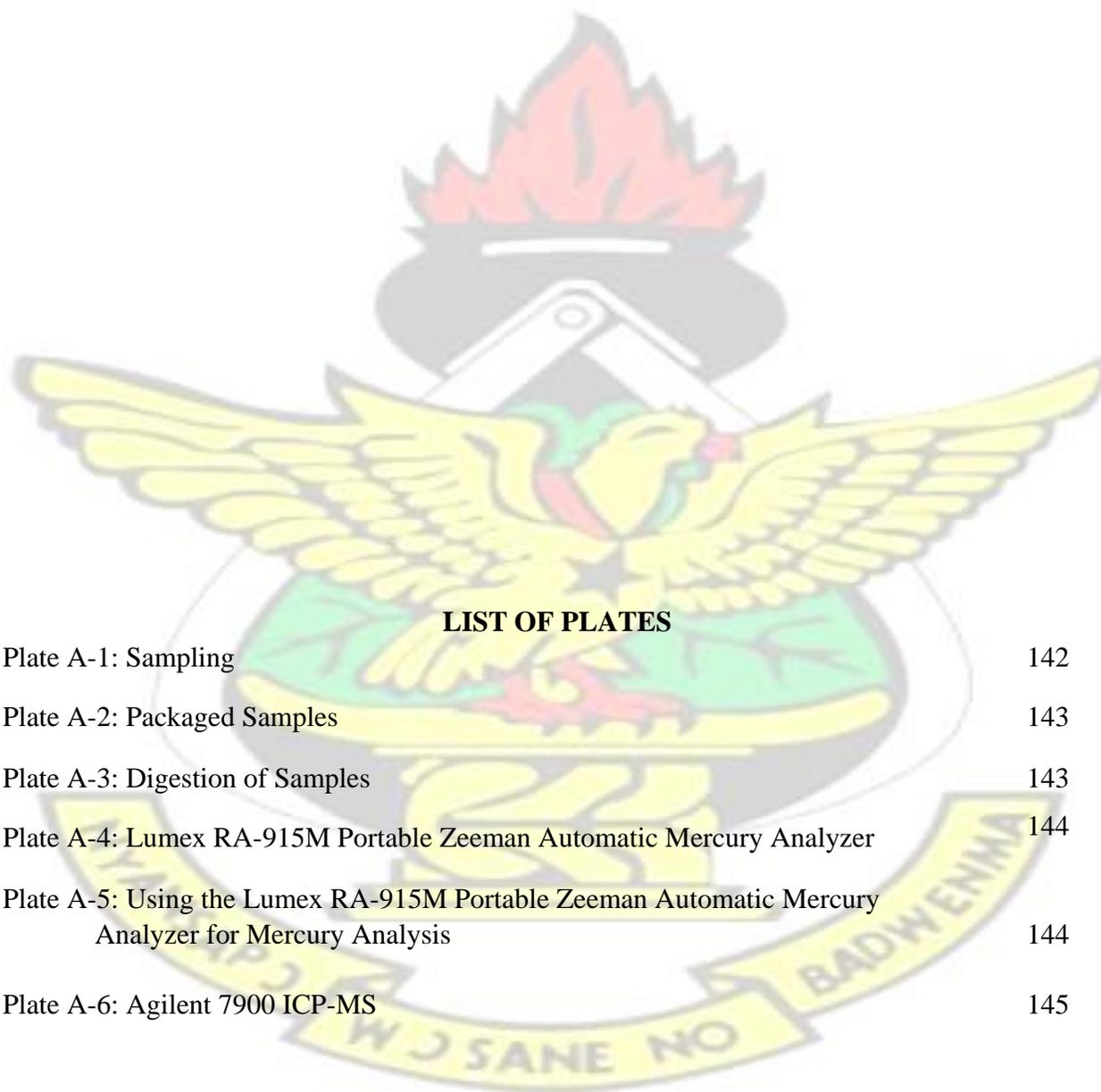
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## **ABBREVIATIONS/INITIALS/ACRONYMS**

ACGIH	American Conference of Government Industrial Hygienists
AOAC	Association of Official Analytical Chemists
APHA	American Public Health Authority
ARC	African Rice Commission
ATSDR	Agency for Toxic Substance and Disease Registry
CDC	Center for Disease Control and Prevention
ECHA	European Chemical Agency
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
EC	European Commission
FAO	Food and Agriculture Organization



FDA	Food and Drugs Authority
GAIN	Global Alliance for Improved Nutrition
GOL	Government of the Republic of Liberia
IARC	International Agency for Research on Cancer
IPCS	International Program on Chemical Safety
IRRI	International Rice Research Institute
JECFA	Joint FAO/WHO Expert Committee on Food Additives
MLME	Ministry of Lands, Minds and Energy (Republic of Liberia)
MOA	Ministry of Agriculture (Republic of Liberia)
MPEA	Ministry of Planning and Economics Affairs (Republic of Liberia)
NERICA	New Rice for Africa
NHANES	National Health and Nutritional Examination Survey
NIOSH	International Institute for Occupational Safety and Health
NJDOH	New Jersey Department of Health
NTP	National Toxicology Program
OEHHA	Office of the Environmental Health Hazard Assessment
OSHA	Occupational Health and Safety Administration
PTDI	Provisional Tolerable Daily Intake
PTWI	Provisional Tolerable Weekly Intake
SPSS	Statistical Package for Service Solution
UNEP	United Nations Environmental Programme
UNICEF	United Nations Children's Fund
USAID	United States Agency for International Development
USDA	United States Department of Agriculture
USDHHS	United States Department of Health and Human Services

USEPA	United States Environmental Protection Agency
USFDA	United States Food and Drugs Authority
USEPA-IRIS	USEPA-Integrated Risk Information System
WARDA	West African Rice Development Authority
WFP	World Food Program
WHO	World Health Organization



## CHAPTER ONE

### 1. INTRODUCTION

#### 1.1. BACKGROUND

Food safety remains one of the major problems faced by the world today. Many of our food items may be loaded with contaminants such as pesticide residues, fertilizers components and heavy metals (Grunert, 2005). Heavy metals contamination of food has become a prominent concern in the world due to their toxicological effects on human (Kalamdhad and Singh, 2011). These metals naturally exist in soil, air, and water and are rapidly dispersed by human activities such as urbanization, waste disposal, agricultural chemicalization, mining, and other activities (Otitoju *et al.*, 2014).

Heavy Metals are described by Duffus (2002) as metalloids and metals with potential toxicity or ecotoxicity. They are non-biodegradable and have the ability to accumulate in plants and animals' tissues. The use of pesticides, weedicides, fertilizers and irrigation with contaminated wastewater in agriculture, initiate the accumulation of these metals in plants (Ghazanfarirad *et al.*, 2014). Like in plants and animals, heavy metals accumulate in human tissues and organs such as livers, bones, and muscles; and pose serious health effects (Castro-González and Méndez-Armenta, 2008).

History had recorded several tragedies of heavy metal poisoning. For example, the Minamata bay poisoning of 1956 recorded nearly 1000 deaths and injuries. The bay was contaminated by discharged mercury containing sewage. This led to the accumulation of mercury in the aquatic biota and its subsequent poisoning of the population which consumed fishes from the bay (Dural, Göksu and Özak, 2007). The contamination of the Jintsu River basin (Toyama, Tsushima and

Nagasaki) in 1955 with cadmium containing effluent led to the occurrence of the Itai Itai disease disaster in Japan. The disease resulted from the consumption of rice whose fields were irrigated with the cadmium contaminated water from the Basin (Yoshida *et al.*, 2009). The Iraqi bread disaster of 1972, the Sandoz chemical spill disaster of 1986 and the Coto de Doñana nature reserve disaster of 1998, are other examples of disasters related to heavy metals poisoning (Chen and Chen, 2001).

Heavy metals such as Lead, Arsenic, Cadmium and Mercury are considered as non-essential because they do not have any significance in the biochemical processes that take place in human bodies (Otitoju *et al.*, 2014). On the other hand, some elements such as Nickel and Chromium are considered as essential but become toxic at comparatively low concentration (Payus *et al.*, 2014).

When these metals are ingested, they alter the shapes and functions of the body's biological molecules such as enzymes and proteins (Duruibe *et al.*, 2007).

Excessive intake of dietary heavy metals has been shown to cause serious health problems. Consumption of food contaminated with heavy metals can cause serious depletion of some important nutrients in the body, which causes immunological deficiencies, psycho-social impediments, malnutrition and other health effects (WHO, 2010a; Kalamdhad and Singh, 2011).

The safety and quality of food is a major global concern, and the accumulation of these metals and other contaminants in the food chain had intensified the need for safety monitoring. To protect the population from the adverse health effects due to the intake of these toxic heavy metals through food, many international organizations have established safety consumption guidelines and tolerable intakes of the toxic heavy metals. For example, the Joint FAO/WHO Experts Committee on Food Additive (JECFA) had established 0.015 mg/kg bodyweight as the Provisional Tolerable

Weekly Intake (PTWI) value for arsenic, and 0.2 mg/kg had also been set as the threshold or maximum limit for the metal in rice. The committee had also established 0.007 mg/kg bodyweight and 0.025 mg/kg bodyweight as the PTWI values for cadmium and lead respectively; and also indicated that the maximum tolerable levels of these metals (Cd and Pb) in rice and other grains or cereals should not exceed 0.4 mg/kg and 0.2 mg/kg respectively (FAO, 2008). Other international authorities such as European Commission Food Safety Authority (EFSA), the United States Food and Drugs Administration (US FDA), Codex Alimentary Commission (CODEX), including health authorities and regulatory bodies of some developed countries like Mainland, China, Australia and Canada, have defined various safety consumption and threshold levels of these metals in some food substances and commodities meant for human consumption (AFFI, 2013).

According to the Food and Agriculture Organization (FAO), rice is the leading dietary energy supplier, providing 30% of dietary energy and 20% of dietary proteins around the world (FAO, 2008). It is a key source of micronutrients such as magnesium, zinc, niacin and other essential minerals for the body. It is the second most cultivated cereal and the third most worldwide produced crop behind maize and wheat, and is levered as the most significant staple food in the world (FAO, 2008). It is classified as either polished or unpolished based on the level of processing. Ordinary milled rice, which appears brown in color, is unpolished rice. This brown rice is further processed by polishing, producing white rice. Polishing improves the storage time. However, the process reduces the level of fats, fibre, lipids, amino acids, and dietary mineral content of the rice (Abbas *et al.*, 2011).

Food assessment for contaminants including heavy metals is being implemented globally to ensure food safety. This is done to minimize the potential hazardous effect on human. In Liberia, rice is

the major staple food for both urban and rural citizens. It is commercially produced on a very small scale, and mostly cultivated in the rural areas by small scale farmers through subsistent farming.

Therefore, many of the rice consumed in Liberia are imported from mostly Asian countries (Balasubramanian *et al.*, 2007; Seck *et al.*, 2010).

Early studies have revealed the presence of notable levels of heavy metals in rice grains (Fu *et al.*, 2008; Orisakwe *et al.*, 2012; Ghazanfarirad *et al.*, 2014; Otitoju *et al.*, 2014).

In southern China, Fu *et al.* (2008) conducted a study to investigate the heavy metals contents in polished rice sold in the region. The result of the study revealed high concentration of lead ( $0.69 \mu\text{g g}^{-1}$ ) as compared to the maximum allowable concentration ( $0.20 \mu\text{g g}^{-1}$ ) set for the safety criteria for milled rice by Codex Alimentary Commission (CODEX).

In Northern Nigeria, Otitoju *et al.* (2014) performed a study to examine the distribution of heavy metals (Pb, Cd, Hg, Cr, As and Ni) in the rice brands sold on the Nigerian markets. Results from the study stated an average concentration of  $0.260 \mu\text{g g}^{-1}$  as the concentration of lead in the rice samples analyzed. According to this study, the estimated weekly consumption of lead in the rice samples analyzed exceeded the  $0.025 \mu\text{g g}^{-1}$  PTWI limit set by WHO/FAO in 2002. Also in Owerri, Nigeria, Orisakwe *et al.* (2012) reported a high Daily Intake value of  $0.3775 \text{ mg/kg}$  bodyweight for lead (Pb) through rice consumption in a study conducted to assess the health risk from heavy metals to the population of the city. The value is high when compared with the Provisional Tolerable Daily Intake (PTDI) value ( $0.00357 \text{ mg/kg}$  bodyweight) set for lead by JECFA.

In 2010, Cao *et al.* (2010) conducted a study to access the health risk of the population of Jiangsu, China through the consumption of rice and vegetables. This study reported a hazard index value of 1.0 for heavy metals (Cu, Zn, Pb, Cr, Hg and Cd) analyzed in locally grown rice sold in the city.

Huang *et al.* (2013) reported a high 97.5 percentile (P97.5) estimated Daily Intake values for Hg (0.37  $\mu\text{g}/\text{kg}\text{-day}$  for adult) and Pb (1.63  $\mu\text{g}/\text{kg}\text{-day}$  for children) in a study conducted to ascertain the health risk from heavy metals to the population of Zhejiang, China through the consumption of rice. These values were greater than the safe values set for Hg (0.14  $\mu\text{g}/\text{kg}\text{-day}$  for adult) and Pb (1.5  $\mu\text{g}/\text{kg}\text{-day}$  for children) by the Chinese's health authorities.

In Korea, Kwon *et al.* (2016) reported levels of Arsenic (0.247 mg/kg) and cadmium (0.174 mg/kg) in rice samples collected from the Korean markets and analyzed. The evaluated daily intake of As and Cd from rice grown in Korea were only 50% and 80% of the respective acceptable daily intake values recommended for the metals by the FAO/WHO Joint Food Additive and Contaminants Committee.

In Sri Lanka, Kariyawasam *et al.* (2016) piloted a study to access the lead, cadmium and arsenic levels in Sri Lanka rice varieties. Results from the study revealed values all below the standard limits set by the Health Division of Sri Lanka; 0.04 ppm, 0.02 ppm, and 0.01 ppm for lead, arsenic and cadmium respectively were reported.

Fu *et al.* (2008); Zazouli *et al.* (2008); Zhuang *et al.* (2008); Naseri *et al.* (2014); Payus *et al.* (2014) have also confirmed the presence of heavy metals in rice consumed in some Asian countries such as China, Iran and Japan.

The proliferation of different brands of rice on the Liberian national market indicates a tremendous demand for the nation's staple food. However, the safety of the population is also relevant, and as far as I am aware, no study has been conducted on the exposure of the population to heavy metal through rice consumption. To ensure the safety of the population through the consumption of rice, it is important to determine the heavy metal contents in these brands of rice sold on the market.

## 1.2. PROBLEM STATEMENT

Rice is the staple food for daily consumption in Liberia, especially in the capital city of Monrovia, though it is produced on a very small scale in the country. The high demand for the staple food increased the proliferation of different brands of imported rice on the Liberian market. Fu *et al.* (2008), Zazouli *et al.* (2008), Zhuang *et al.* (2008), Naseri *et al.* (2014), Payus *et al.* (2014) have reported heavy metal contaminations of rice from some Asian countries such as China, India, Thailand, Iran and Japan. These countries are the major sources of imported rice in Liberia. However, the level of contaminants in these imported brands of rice is not reported. Moreover, these imported brands of rice enter the country without monitoring their contaminations; and there is always a possibility that these rice brands may contain several contaminants, including heavy metals. Heavy metal contaminations of food pose a serious threat to food safety and health risk to the population. This call for the ensuring of safe and quality rice consumption.

Furthermore, locally cultivated rice species are preferred by some urban inhabitants though they are the major source of food for rural inhabitants. Aside the use of agrochemicals and other processes leading to rice production, the location of rice farms may also lead to contamination of the product. Some rice species are grown on farms located near mining areas or wastes disposal sites. After a heavy downpour, effluents from these mining areas and waste deposits percolate into the soil and also into bodies of waters, which may be used by rice producers for irrigation. Considering the toxic nature of heavy metals, it is important to assess their level of contamination in the produce.

### **1.3. OBJECTIVE**

#### **1.3.1. GENERAL OBJECTIVE**

Generally, the objective of the study was to evaluate the potential toxicological health risk from heavy metals to the population of Monrovia through the consumption of the nation's staple food, rice.

#### **1.3.2. SPECIFIC OBJECTIVES**

The specific objectives were:

- To analyze the concentration of toxic elements (As, Cd, Cr, Pb, Hg, Ni) in rice sold on the local markets in Monrovia;
- To compare the levels of heavy metals in imported rice and locally produced rice sold on the local markets;
- To determine the daily dietary exposure of the local population to these heavy metals through rice consumption;
- To assess the risk from these metals to the health of the population through the consumption of rice;
- To evaluate if consumption advisory were needed.

### **1.4. JUSTIFICATION**

Even though many studies have been conducted to assess the concentration of heavy metals in several rice samples in different cities and regions (Zazouli *et al.*, 2008; Orisakwe *et al.*, 2012; Naseri *et al.*, 2014; Otitoju *et al.*, 2014; Payus *et al.*, 2014; Kariyawasam *et al.*, 2016), no study of such has been conducted in Monrovia, Liberia, as far as I am aware.

Heavy metals are very toxic and their increasing contamination of food calls for serious concern. Several studies have documented the toxic effect of heavy metals ( Pb, Hg, Cd, Cr, As, Ni) on the health of human (Lidsky and Schneider, 2003; Duruibe *et al.*, 2007; WHO, 2010a; Kalamdhad and Singh, 2011).

Cadmium contamination has been associated with the Itai-Itai (bone disease) that originated from Japan in the 1960s. Cadmium is very carcinogenic and is noted to cause kidney damage and renal disorder in human (Barakat, 2011). The Joint FAO/WHO Experts Committee on Food Additives had defined maximum exposure limits of 1.0  $\mu\text{g}/\text{kg}$  bodyweight or 0.001  $\text{mg}/\text{kg}$  bodyweight (PTDI) and 7.0  $\mu\text{g}/\text{kg}$  bodyweight or 0.007  $\text{mg}/\text{kg}$  bodyweight (PTWI) for cadmium (JECFA, 2007).

Mercury has the propensity to cause brain damage, gastrointestinal disorder and acrodynia diseases (Kalamdhad and Singh, 2011). Following the 1956 Minamata and 1965 Niigata incidents in Japan, the World Health Organization set the first tolerable exposure limit for Methyl mercury (MeHg) at 0.47  $\mu\text{g}/\text{kg}$  bodyweight or 0.00047  $\text{mg}/\text{kg}$  bodyweight (PTDI) and 3.3  $\mu\text{g}/\text{kg}$  bodyweight or 0.0033  $\text{mg}/\text{kg}$  bodyweight (PTWI), while 0.71  $\mu\text{g}/\text{kg}$  bodyweight or 0.00071  $\text{mg}/\text{kg}$  bodyweight (PTDI) and 5.0  $\mu\text{g}/\text{kg}$  bodyweight or 0.005  $\text{mg}/\text{kg}$  bodyweight (PTWI) were defined for total mercury (Fahmy, 2000). However, studies reveal serious teratogenic effects of mercury at these levels. This led to the revision of the limits to 0.2  $\mu\text{g}/\text{kg}$  bodyweight or 0.0002  $\text{mg}/\text{kg}$  bodyweight (PTDI) and 1.6  $\mu\text{g}/\text{kg}$  bodyweight or 0.0016  $\text{mg}/\text{kg}$  bodyweight (PTWI) for MeHg by the Joint FAO/WHO Experts Committee on Food Additives; and the United States Food and Drugs Administration defined 0.5  $\mu\text{g}/\text{kg}$  bodyweight or 0.0005  $\text{mg}/\text{kg}$  bodyweight (PTDI) and 3.5  $\mu\text{g}/\text{kg}$  bodyweight or 0.0035  $\text{mg}/\text{kg}$  bodyweight (PTWI) as the maximum tolerable levels for total

mercury (JECFA, 2010). Currently, 4.0  $\mu\text{g}/\text{kg}$  bodyweight (0.004  $\text{mg}/\text{kg}$  bodyweight) is the recommended PTWI value set by WHO/FAO for total mercury (JECFA, 2010).

Arsenicosis, melanosis, hepatomegaly, hemolysis, encephalopathy, polyneuropathy, skin manifestation, visceral cancer, vascular diseases and death can be caused by arsenic contaminations; whereas, kidney, nervous and circulatory systems diseases are associated with lead poisoning (Barakat, 2011; Kalamdhad and Singh, 2011). The Joint FAO/WHO Experts Committee on Food Additive had established 15  $\mu\text{g}/\text{kg}$  bodyweight (0.015  $\text{mg}/\text{kg}$  bodyweight) and 25  $\mu\text{g}/\text{kg}$  bodyweight (0.025  $\text{mg}/\text{kg}$  bodyweight) as the PTWI values for arsenic and lead respectively (FAO, 2008), while 2.143  $\mu\text{g}/\text{kg}$  bodyweight (0.002143  $\text{mg}/\text{kg}$  bodyweight) and 3.571  $\mu\text{g}/\text{kg}$  bodyweight (0.003571  $\text{mg}/\text{kg}$  bodyweight) had been defined respectively as the PTDI values for the metals by the committee (JECFA, 2010).

Excessive ingestion of nickel induces mutagenesis, inhibits DNA excision repairs, caused chromosome damage and several allergic reactions (Beveridge, 2008). The Joint FAO/WHO Experts Committee on Food Additive had defined 35  $\mu\text{g}/\text{kg}$  bodyweight or 0.035  $\text{mg}/\text{kg}$  bodyweight as the PTWI and 5  $\mu\text{g}/\text{kg}$  bodyweight or 0.005  $\text{mg}/\text{kg}$  bodyweight as the PTDI value for nickel (JECFA, 2010).

Chromium is very carcinogenic and is noted to cause lungs ailment and liver damages. The PTWI value established for chromium by the Joint FAO/WHO Experts Committee on Food Additive is 23  $\mu\text{g}/\text{kg}$  bodyweight or 0.023  $\text{mg}/\text{kg}$  bodyweight, while 3.286  $\mu\text{g}/\text{kg}$  bodyweight or 0.003286  $\text{mg}/\text{kg}$  bodyweight has been set as the PTDI value for the metal (Yousefi *et al.*, 2016).

One of the major ways humans can be exposed to heavy metals is through the consumption of crops and vegetables as food (Gupta and Gupta, 1998; Järup, 2003). Waste disposal, agricultural

chemicalization, mining, and other activities increase the concentration of these metals in soil (Nan *et al.*, 2000). Soil loaded with heavy metals induces contaminations of these metals in food crops and vegetables (Zarcinas *et al.*, 2004).

The different types of rice consumed by the inhabitants of Monrovia may contain concentration of heavy metals above recommended levels that may cause serious health effect to the population. Determining the concentrations, hazard quotients, hazard indices and Incremental Cancer Risk values of these heavy metals in rice will provide information about the potential health risk of the population through the consumption of this product.

Information from this study will serve as reference or provide baseline data for future research as it relates to heavy metal contamination of rice sold in Liberia.

The information will also assist regulatory bodies in setting up regulations to ensure the protection of the population against the adverse effects of heavy metals, if there may be, through rice consumption.

## **CHAPTER TWO**

### **2. LITERATURE REVIEW**

#### **2.1. RICE**

##### **2.1.1. General Description and Cultivation Methods**

Rice plant is a monocotyledon belonging to the grass family poaceae (Tzvelev, 2017). It is an annual plant that is normally grown and cultivated in wet and warm ecosystems described by the

International Rice Research Institute (IRRI) as lowland, upland, flood-disposed, and irrigated ecosystems (Ajala and Gana, 2015). Nearly 85% of the rice produced in most countries is by irrigated cultivation, where it is grown in flooded rice paddy fields (Tindall *et al.*, 2013). They are rice grown with good water control throughout their growing seasons. Lowland cultivation rely solely on rainfall. Upland rice is usually grown without surface water, and the flood-disposed are rice grown in deep water around river areas. Unlike the irrigated method, the other cultivations methods are capital and labour intensive and usually yield less productivity (Calpe, 2006). According to Savary *et al.* (2000), throughout rice production in south and south east Asia, only 5 % yield losses have been reported using the Irrigated cultivation method.

The germinating plant of rice is normally a bundle made up of 5 to 15 tillers. Each tiller is a branch that consists of roots, stem, and leaves; and may bear about 200 flowers or inflorescence. Hence, thousands of rice grains can be produced from one rice plant. The grain is made up of edible white rice surrounded by a bran and a non-edible protective hull. It also contains an endosperm (germ), that is responsible for majority of its starchy carbohydrate and antioxidant contents (Meng *et al.*, 2005).

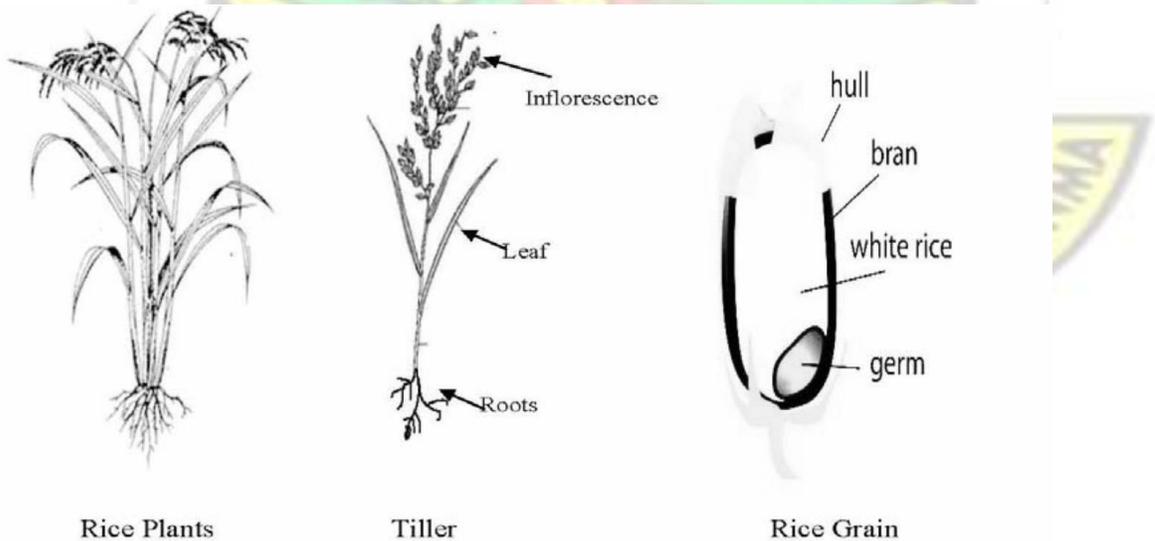


Figure 2.1: Diagram of rice plant and rice grain

The Food and Agriculture Organization (FAO) described rice as the leading dietary energy supplier, providing 30 % of dietary energy and 20% of dietary protein around the world (FAO, 2008). It is the second most cultivated cereal and the third most worldwide produced crop behind maize and wheat. The genus *Oryza* has 22 species but *Oryza glaberrima* (African rice) and *Oryza sativa* (Asian rice) are the two major species globally cultivated, with *Oryza sativa* in high production (Vaughan, 1994).

In the 1990s, the African Rice Center (ARC), formally the West African Rice Development Association (WARDA), made available a hybridized species coined with the acronym “NERICA”, which means “New Rice for Africa”. This species integrated the local African rice (*Oryza glaberrima*) with the Asian rice (*Oryza sativa*). Despite the provision of the genetically modified NERICA by ARC to some farmers of its member countries, *Oryza sativa* still remains the commercially available cultivated rice worldwide (Calpe, 2006). *Oryza sativa* has several varieties that are grouped into two major sub classes depending on their growing environment.

They are the Indica and the Japonica. Japonica is cultivated in temperate and tropical upland climates zones while Indica is characterized by its wide adaptation to different environmental conditions; and accounts for bulk of the world rice production (Roy *et al.*, 2011).

Based on kernel length to width ratio, CODEX classified rice as long grain, medium grain and short grain. Long grain rice has a kernel length greater than 6.0 mm and a length to width ratio greater than 3.0. The kernel length of medium grain rice is between 5.2 mm to 6.0 mm with a length to width ratio less than 3.0, while short grain rice has a kernel length less than 5.2 mm and a length to width ratio of 2.0 (CODEX, 1995).

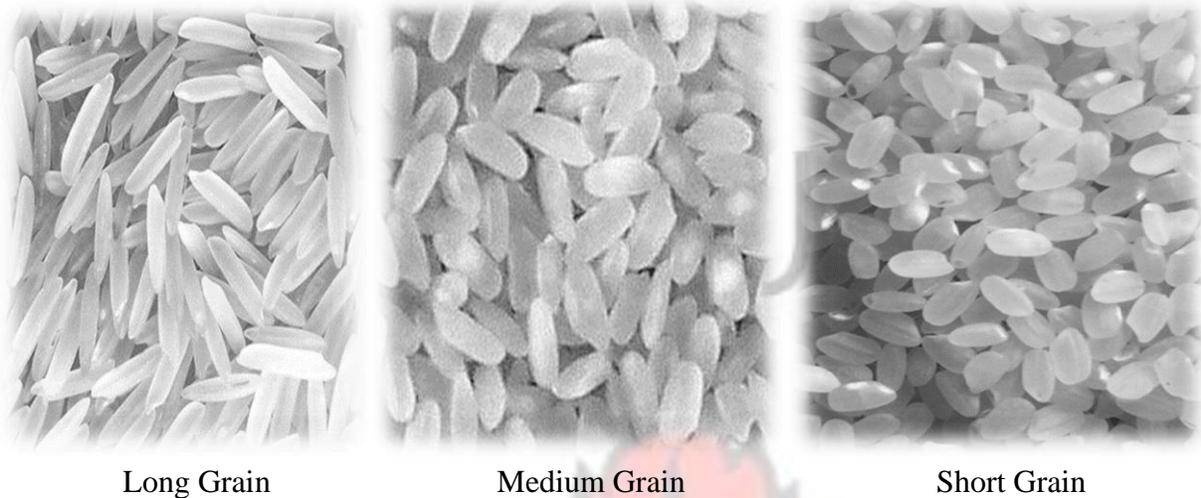


Figure 2.2: Images of the different grains of rice

### 2.1.2. Processing Methods

Rice usually takes minimum three months on the field depending on its variety before harvest. After harvest, it undergoes series of processes to produce the final product suitable for human consumption. These processes include among others drying, de-husking, milling and polishing. The rough harvested rice is dried and de-husked. This is done by passing the rice through a Sheller. A brown rice kernel with bran layers and germs or embryo results from this process. It is milled further to produce a white rice without germ and bran layer (Roy *et al.*, 2011). Depending on the brand, the rice grain can be further processed to produce chalky, red, yellow, or broken kernel rice (Agarwal, 2014). Other processing methods may involve double milling or polishing. Polishing (done by friction or abrasive) improves the physical properties (e.g. Appearance) of rice (Dhankhar, 2004). However, the process decreases the level of fats, fibre, lipids, amino acids, and dietary mineral contents (Abbas *et al.*, 2011).

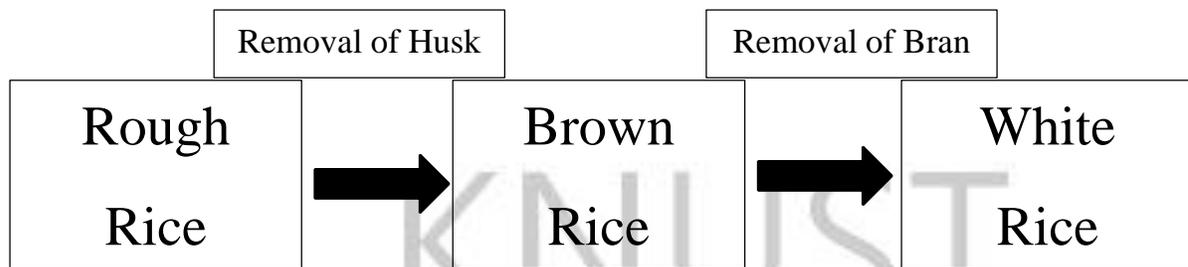


Figure 2.3: Stages of rice processing



Figure 2.4: Images of the types of rice

### 2.1.3. Nutritional Composition

Rice is levered as the most significant staple food in the world because it is a key source of carbohydrates, micronutrients, vitamins and fibers (Calpe, 2006). The amount of nutrients a rice contained depends on its form. Brown rice or unpolished rice are known to contain more nutrients than white or polished rice. This is due to the presence of the bran on the brown rice. Rice bran contains various components such as protein, lipids and fiber. White rice is known to contain mostly starch and 6 to 10 % protein due to the absence of the bran (Sotelo *et al.*, 1990; Ajala and Gana, 2015). The nutritional composition of brown and white rice adapted from the Thai food composition table (1999) is listed in Table 2.1.

Table 2.1: Nutritional composition of brown and white rice (Calpe, 2006; Agarwal, 2014)

Serving per 100g raw rice	Brown rice	White rice
Carbohydrates, g	77.7	82.0
Dietary fibre, g	2.80	0.60
Calories, kcal	362	361
Water (moisture), g	11.2	10.2
Proteins, g	7.40	6.00
Thiamine (Vitamin B1), mg	0.26	0.07
Riboflavin (Vitamin B2), mg	0.04	0.02
Niacin (Vitamin B3), mg	5.50	1.80
Sodium, mg	12.0	31.0
Calcium, mg	12.0	8.00
Potassium, mg	326	111
Phosphorus, mg	255	87.0

Apart from those compositions listed in Table 2.1, brown rice is also composed of phytochemicals such as oryzanols, tocotrienol, ferulic acid and tocopherol (Wichamanee and Teerarat, 2012); and antioxidant such as phytic acid (Dinesh Babu *et al.*, 2009). The composition of rice may show little difference in the varieties (over 100) due to origin and other factors. Some varieties of rice are not popular and are consumed only in areas where they are grown. However, the well-known ones such as Basmati, Jasmine, Kokaho (Shushi), Thailand, Japanese and Indian rice exhibit similar nutritional composition mentioned above.

## 2.2. RICE IN LIBERIA

### 2.2.1. Production and Importation

Liberia ranks among the least rice producing countries in Africa. In 2004, the country had a total of  $1.20 \times 10^5$  hectare of harvested rice area with an irrigated area percentage of 2.0 and an Upland percentage of 98.0 (Balasubramanian *et al.*, 2007; MOA, 2007). In 2014, the country also had a total production of  $1.10 \times 10^5$  Mg, corresponding to 0.92 Mg/ha of un-milled rice, a value that ranks it ahead of Angola (0.80 Mg/ha), DR Congo (0.76 Mg/ha), Congo Republic (0.75 Mg/ha) and Mauritius (0.01 Mg/ha); and behind the likes of Ghana (2.03 Mg/ha), Rwanda (3.55 Mg/ha), Kenya (4.55 Mg/ha) among others (Balasubramanian *et al.*, 2007). Rice is usually harvested between August and October of each year, and upland cultivation is the most preferred cultivation method with 63 percent of farmers using this method as compared to the irrigated method used by only 17 percent of farmers in the country (WFP, 2014).

The low production of rice by the country can be attributed to the technological, social economical and agro-ecological constraints in the country (Thanh and Singh, 2014). Lack of capacity building and suitable rice varieties, low income of farmers, poor infrastructure and agricultural practices, and the presence of rice disease and pest, among others, could also be major contributors to the low production rate in the country (Kuwornu *et al.*, 2012).

According to Sahrawat *et al.* (1996), Iron toxicity to rice is one of the factors that greatly reduces the yield of rice plants. This is normally experienced when Iron (III),  $\text{Fe}^{3+}$  (ferric) is reduced to Iron (II),  $\text{Fe}^{2+}$  (ferrous) in the soil, a condition that inhibits the uptake of other nutrients by the plant (Sahrawat, 2000). Virmani (1979) reported that iron toxicity to rice is a major problem for rice production in Liberia, Burkina Faso and Ivory Coast. This could be due to the mining of iron ore,

the most abundant natural resource in the country. About 65 percent of Liberia is underlain by Archean rocks, the main source of iron ore; and the country was Africa's leading Iron ore producer and the seventh largest exporter of iron ore in the world during the 1970s (Bermudez-Lugo, 2016; MLME, 2016).

The low rice production rate, coupled with increased rate of urbanization and high population growth, have made the country one of the highest importers of rice in West Africa. In 2007, the value of imported rice in the country was estimated at One Hundred Million United States dollars (\$100M USD), equivalent to Six point Five Billion Liberian dollars (\$6.5B LD), a value that had dramatically increased with increased population growth and urbanization (Tsimpo and Wodon, 2008). Currently, rice is imported duty free in Liberia. In response to a spiked increased in food prices in the country in 2008, the Government of Liberia declared a zero tariff for rice import and imposed a government-determined limit on wholesale margins at 1US\$/50kg beg. This 2008 policy remained unchanged, and the office of the president in the exercise of the executive power vested in it by the constitution, had intermediately issued Executive orders (no. 11, 19, 45, 61, 70 and 80), suspending all tariffs on the importation of the nation's staple commodity. In August 2017, the latest executive order (executive order no. 87) was issued by the president, as an extension of executive order no. 80, suspending all tariffs, as defined by the amended Liberian revenue code act of 2000 under tariff no. 1006.30.00 and 1006.40.00, on the importation of rice (Admin, 2017). These policies have fashioned a significant impediment for local rice farmers, evidence from the scarcity of local rice on the national market (USAID, 2015).

Local rice production averaged about 161,000 MT/yr from 2008 to 2013, while rice imports averaged about 280,000 MT/yr, a value that made up about 60 percent of the total rice supply in the country during those years (USAID, 2015). In 2016, import volume recorded 350, 000 MT

while domestic harvest was at 189,000 MT (USDA, 2016). Currently, domestic rice does not have a significant share of the rice market in Liberia, as the imported rice percentage has increased to 80 percent (GAIN, 2016), and is projected to increase to over 85 percent before 2020 if current trend remains unchanged (Hilson and Bockstael, 2012; USAID, 2015). According to GAIN (2016), there are only three functional mills (30 MT/day paddy capacity each) currently in the country; one operated by a private firm and two by the Ministry of Agriculture. As a result, less percentage of domestically grown rice is industrially milled. Subsistent farmers de-husk their rice by hand pounding.

Table 2.2: Liberia rice production and Importation, 2012-2016 (Mega Metric Ton) (USDA, 2016)

Type	2012	2013	2014	2015	2016	Average
Production	0.183	0.170	0.168	0.186	0.189	0.179
Importation	0.325	0.250	0.340	0.300	0.310	0.305

Since 2008, the number of rice importers in the country had tripled, with Supplying West African Traders (SWAT), United Commodity Incorporated (UCI), and Fouta Corporation companies being the highest importers. Even though neighboring African countries such as Nigeria (the highest rice producing country in West Africa), and Senegal are among the world's top 10 leading rice producers (Seck *et al.*, 2010), the imported rice consumed in Liberia are from Asia ( $\approx 90\%$ ) and America ( $\approx 10\%$ ) (Balasubramanian *et al.*, 2007). Most Liberians prefer the Asian rice to the other Africans and locally produced rice because of its relatively low price. Locally produced rice is expensive than imported rice due to its scarcity on the market (USAID, 2009).

### 2.2.2. Consumption Rate of Rice in Monrovia

Household in the capital city of Liberia (Monrovia) are heavily reliance on imported rice (MPEA, 2006). The 2011 Food Fortification Initiative (FFI) report released by GAIN revealed that the total

urban inhabitants in Liberia consumed about 330 grams per day per bodyweight while Monrovia, which constitutes 60 percent of the Urban population was estimated to consume 248 grams per day per bodyweight (GAIN, 2016).

### **2.2.3. Rice and Food Security in Liberia**

The low production rate and the reliance on Asian countries for the supply of the nation's staple food pose a serious threat to food security. For example, in 2008, the value of the population living below the poverty limit in Liberia increased by 3 to 4 percent when rice price increased by 20 percent on the world market (Tsimpo and Wodon, 2008). On April 14, 1979, the country experienced a historic "Rice Riot" when the government through the agricultural ministry announced an increase in the subsidized price of imported rice from \$22/50 kg to \$26/50 kg. The riot, initially planned as a peaceful demonstration by activist, lead to the death of at least 40 civilians and the injury of over 500 persons. Several stores and warehouses of rice were looted and private properties estimated at Forty Million United States dollars (\$40M USD) were damaged (Dennis, 2006).

With global prices of rice projected to increase by 2.5 to 3 percent each year (Seck *et al.*, 2010), availability and access to rice for poor Liberians household are at stake. Since December 2007, the price of rice in Liberia had increased by 60 percent; and with close to 85 percent of the national population surviving on a daily wage below One United States Dollar Twenty Five Cents (\$1.25 USD), only 9 percent of the country's rural population and 51 percent of its urban population is food secure (MPEA, 2006; Hilson and Bockstael, 2012).

Low investment in agricultural sectors hinders the expansion of food production and provisions for the inhabitants of a country (Deininger and Byerlee, 2012). If food security threat, posed by

raising trend and variability in rice prices is to be resolved, there is a need to boost domestic rice production. Access to finance boost the cultivation efficiency of small scale farmers, thus decreases poverty and food insecurity (Omonona *et al.*, 2010).

## **2.3. HEAVY METALS**

### **2.3.1. General Description and Sources**

The term “Heavy Metal” has been in use for over 6 decades now, but has not been precisely defined by any authority or organization. Some writers defined it as metals or metalloids with specific gravities between 4.0 g/cm<sup>3</sup> to 5.0 g/cm<sup>3</sup>. However, in recent studies, the term has been used to describe metalloids and metals with potential toxicity or ecotoxicity (Duffus, 2002).

They are natural components of the environment and can originate from both geochemical and anthropogenic sources. They are emitted to the environment through natural processes and human activities (Tong *et al.*, 2000; Peng *et al.*, 2008). Their emission follows a variety of pathways.

Some of which include emission to the air; followed by deposition on soil and surface water. Hence, into ground waters and plants (Järup, 2003).

On the average, the amount of metals deposited on the Earth surface through natural process is lesser than deposition through anthropogenic activities, such as mining, and wastes or effluents disposal from industries (Phuong *et al.*, 1998), municipal wastewater and wastewater arising from informal settlement (Jackson *et al.*, 2007), and leaches from various landfill sites (Moodley *et al.*, 2007).

Another process is combustion, especially combustion through smelting, incineration, power generators and from internal combustion engines (Nriagu, 1988). Agricultural activities are also known to increase the dispersion of heavy metals (Otitoju *et al.*, 2014). Agricultural activities and

industrious operations have extensively contaminated areas of countries such as China, Japan, and Indonesia by heavy metals such as Copper, Cadmium, and Zinc (Herawati *et al.*, 2000); and North Greece and Albania by Cadmium, Lead and Copper (Zantopoulos, Antoniou and Nikolaidis, 1999). Major contaminations by Copper, Lead, Chromium, Nickel, Zinc and Cadmium had also been reported in England and Wales (Nicholson *et al.*, 2003). The lime, sewage sludge, inorganic and organic fertilizers, irrigation water and pesticide used in agriculture are major sources of heavy metals (Verkleij, 1993).

Industries engaged in mining operations and ore processing, ink manufacturing, metallurgy, petroleum refining, and electroplating release metals of different types and concentrations into the environment. Other industries such as Pottery and Porcelain industries and those engaged in textiles, dyes, pigments and batteries productions also released metals of different types and concentration into the environment (Nagajyoti *et al.*, 2010).

Geological plant materials and rocks are the most significant natural sources of heavy metals. These metals originate in the earth crust and occur in the soil by simple weathering. Igneous rock such as augite, hornblende and olivine contribute significant amount of Mn, Co, Ni, Cu and Zn to the soil. Shale sedimentary rocks has in addition to these metals the highest concentration of Cr, Cd, Sn, Hg, and Pb (Nagajyoti *et al.*, 2010). Below is a table of metal composition in the types of rock.

Table 2.3: Composition of Heavy metals in sedimentary and igneous rocks (Nagajyoti *et al.*, 2010).

Metals (ppm)	Granite igneous	Basaltic igneous	Black shales	Shales and Clays	Sand stone
As	0.2-13.8	0.2-10	-	--	0.6-9.7
Cd	0.003-0.18	0.006-0.6	0.3-8.4	0.0-11	--

Cr	2-90	40-600	26-1,000	30-590	--
Co	1-15	24-90	7-100	5-25	--
Cu	4-30	30-160	20-200	18-120	--
Pb	6-30	2-18	7-150	16-50	> 20
Mo	1-6	0.9-7	1-300	--	--
Ni	2-20	45-410	10-500	20-250	--
Zn	5-140	48-240	34-1,500	18-180	2-41

Apart from weathering, the major natural processes that emit considerable levels of heavy metals is volcanic eruptions. In addition to harmful and toxic gases, this process also emits high concentrations of Zn, Al, Mn, Pb, Ni, Hg and Cu (Seaward and Richardson, 1990). Windblown dust, marine aerosol, fire forest and mist also exert significant impact in the transportation of some heavy metals in the environment (Bech *et al.*, 1997).

Table 2.4 Heavy metals emission from natural sources worldwide (Pacyna, 1986).

Sources	Global production	Annual emission (Kg × 10 <sup>6</sup> )								
		Cr	Cu	Cd	Hg	Mn	Co	Pb	Zn	Ni
Volcanogenic particles	6.5-150	3.9	4.00	0.50	0.030	82.0	1.4	6.4	10	3.8
Windblown dust	6-1,100	5.0	12.0	0.25	0.030	425	4.0	10	25	20
Vegetation	75-1,000	-	2.50	0.20	-	5.00	-	1.6	10	1.6

Sea salt	300-2,000	-	0.10	0.02	0.003	4.00	-	0.1	0.02	0.04
Forest fires	2-200	-	0.30	0.01	0.100	-	-	0.5	0.5	0.6
Total		8.9	18.9	0.96	0.160	516	5.4	18.6	45.52	26

### 2.3.2. Accumulation in Plant

Metals in soil are present as free insoluble particles or are bound to inorganic (clay) soil constituents or organic (humus) soil constituents. Soil has the ability to retain these metals in these forms under normal conditions. However, the retaining capacity of the soil is reduced when the level of metal in the soil is increased extremely. Repeated activities such as runoffs, land spreading (of untreated waste or effluents), industrial discharge (into water bodies) and agricultural activities such as irrigation (with untreated water) and the use of metal based fertilizers and pesticides increased metal concentration in soil. When this occurs, heavy metals leach into ground water or soil solutions available for plant uptake, thus contaminating the soil for crop production (Chary *et al.*, 2008).

Plants are noted to absorb metals from the subsurface of soil at about 25 cm depth, portion where most cereal roots are situated. The metals are transformed into solubilized forms and are taken up by the roots and subsequently transported to the shoots, the leaves and other parts of the plants (Payus *et al.*, 2014). Firstly, the root system of the plant secretes metal chelating molecules (siderophores) to chelate soil bound metals. These siderophores are released in response to the deficiency of essential metals such as zinc and iron, but can mobilize both essential and nonessential elements in the process. Phytosiderophores (nicotinanamine, avenic acid and mugineic acid) and proteins (metallothioneins and  $\gamma$ -glutamylcysteinyl-isopeptide) are examples of plants siderophores. Secondly, the metal ions are reduced by specific plasma membrane bound

metals reductase released by the roots system. This is followed by solubilization of the metals by acidifications with protons extruded from the roots. The solubilized metal ions enter the plant via the root either by the symplastic (intracellular) pathway or by the apoplastic (extracellular) pathway. Metals remaining in complex forms are transported via the plasma membrane by specific carriers (Raskin *et al.*, 1994).

Once the metals enter the roots, they are stored or transported to the shoots and other parts of the plants. The ability of a plant to absorb and accumulate metals vary from species to species and the quantity absorbed depends on the bioavailability (Satpathy *et al.*, 2014).

The bioavailability of a metal is quantified by its transfer quotient. Higher transfer quotient of a metal indicates stronger accumulations of the metal by the plants (Farooq *et al.*, 2009). Research points out that transfer quotient of 0.1 signifies the exclusion of the metal from plant tissues (Farago *et al.*, 1997); and transfer quotient value of  $\geq 0.5$  indicates a greater chance of plants contamination (Sponza and Karaoğlu, 2002).

Under a particular environmental circumstance, a metal uptake by plants can be projected from its Biological Concentration Factor ( $BC_f$ ) in accordance with equation 2.1.

$$BC_f = \frac{M_p}{M_s} \dots\dots\dots 2.1$$

Where “ $M_p$ ” is the metal’s concentration in the plant and “ $M_s$ ” is the metal’s concentration in the soil (Farooq *et al.*, 2009). Interestingly, the uptake of a metal is not directly proportional to the concentration of the metal in the soil. Therefore, several environmental factors such as soil pH, temperature, soil porosity and fertilization, the types and size of the plant, its root system and the bioavailability of the element in the soil influence metal uptake by plant (Wang *et al.*, 2003).

Plants are producers and their absorption of metals introduces the contaminants into the food chain (Orisakwe *et al.*, 2012).

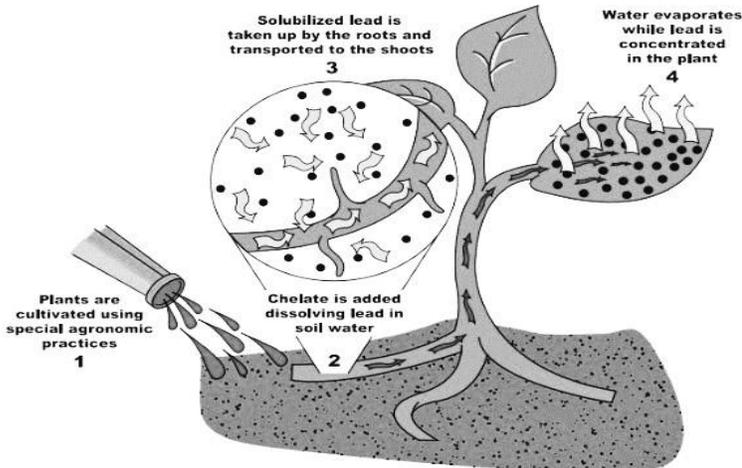


Figure 2.5: Absorption of heavy metals (Pb) by plant

### 2.3.3. Accumulation in Rice Plant

Research has revealed that rice bran, which is responsible for its high nutritional content, accumulates more heavy metals than other parts of the plant. Thus, brown rice contains more heavy metals than white rice. In studying the nutritional content of Indian rice samples, Manjusha *et al.*, (2008) mineralized the organic matrix of the rice by treating the samples with ultraviolet (UV) radiation and digested it with concentrated Nitric acid ( $\text{HNO}_3$ ) and Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), then measured the trace elements by Electro-thermal Atomic Absorption Spectroscopy and Inductive Coupled Plasma Atomic Emission Spectroscopy. The results showed that the white rice contained lower micronutrients than brown rice. For example, the iron content in the white rice varieties was in the range (0.32-4.0) mg/100g while the brown rice recorded a value range (3.04.2) mg/100g. Analysis of broken rice and rice bran conducted by Zoiopoulos and Natskoulis

(2008) in western Greece also indicated a higher level of metals accumulation in the rice bran. However, Mendi *et al.* (2003) had also reported a sufficient accumulation of heavy metals in both straw and paddy rice samples.

The dispersal of heavy metals in rice poses questions about the mechanism of their uptake. Genetic factors had been shown as one of the major factors responsible for the accumulation of heavy metals by rice. Cheng *et al.* (2008) steered a longitudinal study to investigate Cd, Cr, As, and Pd on rice species grown in six locations in china for two years. Their study showed an imperative genotype and environmental interaction on the concentration of five heavy metals in the grains. Cultivation choices revealed that the rice had low heavy metals concentration for certain locations and high concentration for other locations. In a stressful heavy metal environment, rice plants produce metal-binding peptides by phytochelatins, which are small cysteine-rice peptides synthesized from glutathione via metal dependent enzymatic pathways. Purification of phytochelatins synthesized from rice seed by Yan *et al.*, (2000) reported that arsenic and cadmium were the most phytochelatin producing element, followed by lead, copper, silver, cobalt and other divalent cations. Calcium and magnesium had no effect. This indicates that soil composition also influenced the accumulations of heavy metals by rice.

Agricultural activities can increase heavy metals in soil, thus leading to its high uptake by plant. Rahaman *et al.* (2007); Siebers *et al.*, (2013) reported that the application of fertilizers can significantly increase the concentration of heavy metals in rice plant. However, inorganic fertilizers showed a higher influence than organic fertilizers. This is because inorganic fertilizers are composed of chemicals and minerals such as Nitrogen, Phosphate, Potassium, Sulphur and Zinc while organic fertilizers are mainly composed of decayed plants or animal matters. Their studies also proposed that soil pH has a significant impact on rice plant uptake of heavy metals.

Soil with pH between 4.5 and 5.5 tend to accumulate more metal than soil with higher pH.

## 2.4. TOXICITY PROFILE OF SELECTED HEAVY METALS

### 2.4.1. ARSENIC

#### 2.4.1.1. General Descriptions and Sources

Arsenic (As) is an element belonging to group 5A (VA) and column 4 of the modern periodic table. It is a metalloid, thus has properties of both a metal and a non-metal. Its chief usage is in the manufacture of wood preservatives, pesticides, textiles and some pharmaceuticals; and also in the production of electrical conductors, transistors and lasers (Gomez-Caminero *et al.*, 2001).

Arsenic is predominantly distributed in rocks, soil, water and air and occurs naturally (in sulphide forms) in complex silver, cobalt, iron and nickel containing minerals (Guha Mazumder, 2008). It is element number 33 and has a relative atomic mass of 74.92 amu (Gomez-Caminero *et al.*, 2001). It varies in oxidation states such as -3, 0, +3 and +5 but often occurs in the +3 (arsenite) and +5 (arsenate) states. It also occurs in two stable forms; organic and inorganic forms. The organic forms result from the combination of arsenic with hydrocarbons. Compounds such as arsenic acid ( $\text{H}_3\text{AsO}_4$ ), arsenobetaine ( $\text{C}_5\text{H}_{11}\text{AsO}_2$ ), methylarsonic acid [ $\text{CH}_3\text{AsO}(\text{OH})_2$  or  $\text{CH}_5\text{AsO}_3$ ] and dimethylarsenic or cacodylic acid ( $\text{C}_2\text{H}_7\text{AsO}_2$ ) are examples of organic arsenic compounds. Inorganic arsenic compounds result from the reactions of environmental arsenic with elements such as sodium, chloride, Sulphur and oxygen. Noticeable examples include Arsenic trioxide ( $\text{AsO}_3$ ) or Arsenic pentaoxide ( $\text{As}_2\text{O}_5$ ), Sodium arsenide ( $\text{Na}_3\text{As}$ ) and Trichloro arsenine ( $\text{AsCl}_3$ ) (Singh *et al.*, 2007; Wijesekara and Marambe, 2011).

The chief sources of inorganic arsenic compounds are mainly rocks, soil and sediments; and are usually present in ground water used for drinking, while organic compounds such as Arsenobetaine are predominantly found in fishes (Gomez-Caminero *et al.*, 2001). Soil, air and water bodies are contaminated by arsenic and arsenic related compounds through industrial and agricultural processes. The use of fossil fuel for energy production and other activities such as mining and smelting are the three main industrial activities that release arsenic into the environment (Szymańska-Chabowska *et al.*, 2002). The use of arsenic based pesticides and irrigation with contaminated wastewater in agriculture can lead to the contamination of soil by arsenic and thus it subsequent buildup in crops. In its arsenate states, it is an analog of phosphate (P) and competes during the uptake of nutrients by plant root systems (Meharg and Macnair, 1992).

#### **2.4.1.2. Exposure to Arsenic**

Research has shown that intake of food and drinking water are the two major routes of arsenic exposure to human. However, depending on the solubility and particles sizes of arsenic compounds, it can be adsorbed in inhaled airborne particles (FDA, 2016). In human, inorganic arsenic compounds are widely methylated and extracted into the urine while the soluble ones are absorbed from the gastric tract (Gomez-Caminero *et al.*, 2001). The concentration of arsenic metabolites in urine, hair, nails and blood are used as biological indicators of arsenic exposures. Metabolites concentration in hair and nails are used to express past arsenic exposure while those of the blood and urine are useful indicators of recent arsenic doses (UNICEF, 2008).

The Joint FAO/WHO Experts Committee on Food Additive had defined 0.015 mg/kg bodyweight of human as the Provisional Tolerable Weekly Intake value for arsenic (CODEX, 2015).

### 2.4.1.3. Health Effects of Arsenic

Arsenic is one of the elements that have adverse effect on human health. Exposure to arsenic pose excessive risks of lungs, kidney and bladder cancers. It also increases the risk of skin lacerations such as hyperkeratosis and de-coloration. Research shows that smelters, miners, and pesticide manufacturers and applicator exposed to arsenic by inhalation demonstrated considerable levels of risks to lungs cancer (WHO, 2010b). Ingestion of the inorganic forms of arsenic may cause exterior vascular diseases, which in extremes forms lead to decaying changes such as the “Black Foot disease” that is believed to have originated in Taiwan (Gomez-Caminero *et al.*, 2001). Noticeable signs of arsenic poisoning include retching, nausea, dehydration and diarrhea (Kapa *et al.*, 2006).

Organic arsenic is very poisonous and is known to cause several health effect on the cardiovascular, gastrointestinal and central nervous systems of human (Martin and Griswold, 2009). Due to its carcinogenic properties, the World Health Organization (WHO) had established a tolerable maximum of 0.01 mg/L in drinking water (FDA, 2016). High levels of arsenic in drinking water caused arsenic toxicity called arsenicosis (Wijesekara and Marambe, 2011). Ingestion in high amount leads to death. Confirmation incident was the Bangladesh water poisoning in 1970. Before that time, the World Bank reported that most Bangladesh rural population were fetching drinking water from surface ponds and nearly a quarter of a million of children died each year from waterborne diseases. This captivated the construction of tube wells for the provision of clean drinking water in Bangladesh by international agencies headed by the United Nations Children’s Fund (UNICEF). However, it was reported in 1970 that Bangladesh suffered what is described in history as the “mass poisoning ever”, as up to half of the country’s tube wells were poisoned with arsenic, killing thousands of people. Several disorders such as bone marrow depression, melanosis,

hepatomegaly, hemolysis, encephalopathy and polyneuropathy were observed in survivors (UNICEF, 2008; WHO, 2010b).

## **2.4.2. CADMIUM**

### **2.4.2.1. General Description and Sources**

Cadmium (Cd), a transitional metal belonging to group 2B (IIB) and column 5 of the modern periodic table, occurs naturally in ores with copper, lead and zinc. Noticeable ores of cadmium include sphalerite and greenokite. It has an atomic number of 48, a relative atomic mass of 112.4 amu and an oxidation state of +2. The pure form of cadmium is a malleable silvery white metal. It is found in rocks, soil and coal; and ranked 67<sup>th</sup> in abundance among the naturally occurring elements of the earth crust (OSHA, 2004).

Cadmium compounds are used as stabilizers in polyvinyl chloride (PVC) products, several alloys and rechargeable nickel-cadmium batteries. Metallic cadmiums are also used to make colour pigments and anti-corrosion agents. Due to its neutron absorption capacity, cadmium is also used to make control rods in nuclear reactors. It is also a major constituent of agricultural phosphate fertilizers (Järup, 2003).

Cadmium from the Earth crust is released into the environment by natural processes such as weathering, erosion and volcanic eruptions. Human activities such as mining, fertilizers manufacturing, electronic waste recycling, incineration and the burning of coal and household waste also released cadmium into the atmosphere. It has a low settling rate and the particles are deposited distances from the sources of emission (WHO, 2003).

The deposition of cadmium particles on water and soil, and the application of fertilizers and sewage sludge to farm land induced cadmium uptake by crops and vegetables grown for human

consumption. Cadmium is a non-essential element and high level in soil affects plant enzymes systems and contaminates the food chain. Das *et al.*, (1997) suggested that cadmium absorption and accumulation by plants is due to its chemical similarities with essential elements such as Ca and Mg. It inhibits the activities of nitrate reductase, thus reducing the absorption of nitrate by plants (Hernandez *et al.*, 1996). A regulatory limit of 100 mg/kg has been set for agricultural soil by the FAO (Salt *et al.*, 1995).

#### **2.4.2.2. Exposure to Cadmium**

The consumptions of cadmium contaminated food, and the passive and active inhalation of cigarettes smoke are the two major sources of cadmium exposure. The levels of cadmium in food stuff varies, and individual intake also varies due to difference in dietary habits. Cigarette smoking increases the cadmium levels in blood (B-Cd). Research has shown that the concentration of cadmium in the blood of smokers is over 4 times greater than non-smokers (Jarup *et al.*, 1998; Bernard, 2008). Maximum Tolerable Weekly Intake value of 0.007 mg/kg bodyweight of human had been established by the FAO/WHO for cadmium (CDC, 2014).

#### **2.4.2.3. Health Effects of Cadmium**

The adverse effects resulting from human exposure to cadmium were first documented by Friberg (1950), after a test conducted among workers of a cadmium battery factory. This study revealed that workers are occupationally exposed to cadmium by inhalation of dust or fumes, and proposed that workers sampled in the study had already developed decreased glomerular filtration rate due to chronic exposure. This was also confirmed in later studies of occupational exposure by Persson *et al.*, (1995) and Jarup *et al.* (2000). Thus, the major health effect of cadmium is kidney damage, which usually occurs in the form of renal or tubular dysfunction. This condition is the inability of

the kidney to reabsorb substances or adequately filter metabolic wastes from the blood. This leads to glycosuria, proteinuria, hematuria and aminoaciduria.

Increased urine creatinine level is the main indicator of cadmium exposure. The World Health Organization has established that a urinary excretion containing more than 10 nmol/mmol of creatinine (200 mgCd/kg kidney cortex) would be critical to cause kidney damage (WHO, 2010c). Induced kidney damage from cadmium exposure in population having urinary cadmium levels between 2 to 3  $\mu\text{gCd/g}$  creatinine have been reported (Buchet *et al.*, 1990; Jarup *et al.*, 2000).

Long term exposure to cadmium can cause bone damage. The first report of this was the Itai-Itai (Japanese word for “It Hurt! It Hurt!) disease from Japan in the 1950s. The disease is a combination of osteomalacia and osteoporosis, and leads to the softening of bones. It resulted from the consumption of cadmium contaminated rice. It was reported that the Jintsu River basin (Toyama, Tsushima and Nagasaki), the Kakehashi River basin (Ishikawa) and the Chi River basin (Hyogo) were polluted with cadmium containing effluent released by a mining company (Mitsui Mining and Smelting Co.), which was used for irrigation of local rice fields (Yoshida *et al.*, 2009).

Staessen *et al.* (1999); Alfvén *et al.* (2000); and Nordberg *et al.* (2002) also reported that low level of cadmium exposure can cause osteoporosis (low bone mineral density) and fractures in bones. Gastrointestinal disorder and hypertension are also associated with cadmium toxicity (Schoeters *et al.*, 2006).

It has been classified as a human and animal carcinogen by the International Agency of Research on Cancer, and is known to be associated specifically with prostate cancer. Though some studies reported both positive and negative carcinogenic effects, the United States Environmental Protection Agency (USEPA) and the Office of the Environmental Health Hazard Assessment

(OEHHA) in 2000 confirmed that cadmium is carcinogenic to human (US EPA, 2000; NJDOH, 2010).

Pulmonary diseases such as bronchiectasis and emphysema result from long term exposure to cadmium and toxicities are increased by other irritants such as cigarette (ATSDR, 2012a; ECHA, 2013). Epidemiological investigation had shown that prenatal exposure to cadmium caused still or premature birth, reduced birth weight and exerts negative impact on learning and behavior (OEHHA, 1996).

### **2.4.3. CHROMIUM**

#### **2.4.3.1. General Description and Sources**

Chromium (Cr) is the 24<sup>th</sup> element on the periodic table. It is a transitional metal situated between Vanadium and Manganese and belong to group 6B (VIB) along with Molybdenum, Tungsten and Seaborgium. Chromium has a relative atomic mass of 52 amu, four naturally occurring isotopes (<sup>50</sup>Cr, <sup>52</sup>Cr, <sup>53</sup>Cr and <sup>54</sup>Cr) of which <sup>52</sup>Cr is the most abundant with 84% of the total mass. It exists in zero, trivalent and hexavalent oxidation states, and is the 21<sup>st</sup> most abundant element in the Earth crust, with a concentration of about 100 ppm (Barnhart, 1997)

Chromium is naturally found in rocks (Ultramafic, Magnetite and Ilmenite) and minerals (Chromite, Crocoite, Spinel etc), and occurs in soil by natural weathering and other geochemical activities. Its similarities in properties to Al<sup>3+</sup> and Fe<sup>3+</sup> enables it to accumulate greatly in secondary oxides and clays during weathering. However, bulk of the chromium in soil is released by anthropogenic activities. In 1997, about 13,998,872 kilograms of chromium was released to soil by about 3,391 large processing facilities worldwide, a value that amounted to about 94% of total environmental released of chromium (ATSDR, 2011). The activities of Chromium in soil is

governed by pH and organic matters.  $\text{Cr}^{6+}$  adsorption by soil particles decreases with increasing pH, and  $\text{Cr}^{3+}$  adsorption increases with increasing soil pH. The main effect of organic matters is the stimulation of  $\text{Cr}^{6+}$  reduction to  $\text{Cr}^{3+}$ , an effect that increased with increasing soil acidity.  $\text{Cr}^{3+}$  readily substitutes for  $\text{Fe}^{3+}$  in minerals, leading to chromium uptake by plants. Under high concentration, it alters the production of pigments in plants. Chromium in the environment is derived mainly from human activities. About 344,730 kilograms of chromium are discharged to the air annually by point stationary sources. In the atmosphere,  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$  react with dust particles to form other pollutants. Chromium gets to the aquatic environment by discharge from electroplating, leather tanning and textile industries. Improper land filling of chromate containing wastes is a source of ground water contamination. The wearing down of chromium contained asbestos lining and the emission of chromium based automotive catalytic converters are other environmental sources of chromium. Tobacco smoke and some cements also contain chromium (Barnhart, 1997).

The metallic form of chromium is mostly used in metallurgical processes, especially in the manufacturing of steel alloys, in which it makes up about 10-12 percent. It is used in the electroplating and coating of steel. Chromium is the element responsible for the stainless properties of stainless steels. Chromium is also useful in the production of dyes and pigments, leather tanning, wood preservatives and some chromium chemicals (ATSDR, 2011).

#### **2.4.3.2. Exposure to Chromium**

Chromium enters the body through inhalation, ingestion and dermal absorption. Consuming chromium contaminated food and water, and the inhalation of ambient air are the major routes of chromium exposure to the general population. Occupational exposure is mainly through inhalation of contaminated air or direct skin contact. Workers involved in chromium chemical production,

stainless steel production, welding, chrome plating and chrome pigments manufacturing are primarily exposed to  $\text{Cr}^{6+}$  via inhalation of aerosol (ATSDR, 2011). The population residing or working nearby hazardous waste sites are at an increased risk of chromium exposure. Chromates and dichromate containing  $\text{Cr}^{6+}$  are found in effluents released from leather tanning, electroplating and metallurgical industries. These species are readily soluble, leaching into ground water and contaminating drinking water. They may also be exposed through air containing mist or particulate or through skin contact with soil (ATSDR, 2012b). The Provisional Tolerable Weekly Intake value defined for chromium by the Joint FAO/WHO Experts Committee on Food Additive is 0.023 mg/kg bodyweight of human (Yousefi *et al.*, 2016)

#### **2.4.3.3. Health Effects of Chromium**

The toxicity of chromium depends on its valence state and form in the environment.  $\text{Cr}^{3+}$  in soluble form is known to be relatively harmless. It is needed by the body in minute concentration for insulin action and the metabolism of carbohydrates and proteins (Mertz, 1993), however,  $\text{Cr}^{6+}$  is highly toxic. It is on the list of special health hazard substances set by health authorities, thus requires serious attention. The United States EPA had established a maximum tolerable level of 0.1 mg/L for chromium in drinking water. The FDA has also determined that chromium in drinking water and other consumables liquids products should not exceed 0.1 mg/L, and the Occupational Health and Safety Administration (OSHA) has limited worker's exposure to an average of 1.0 mg/m<sup>3</sup> ( $\text{Cr}^0$ ), 0.5 mg/m<sup>3</sup> ( $\text{Cr}^{3+}$ ) and 0.005 mg/m<sup>3</sup> ( $\text{Cr}^{6+}$ ) for an 8-hour workday and 40-hour workweek. Both NIOSH and ACGIH had set 0.5 mg/m<sup>3</sup> as the recommended airborne exposure limit for chromium (NJDOH, 2009; ATSDR, 2012b).

Acute exposure to chromium can irritate and burn the skin and eyes, and in some cases, lead to eye damage. Inhalation of chromium can cause irritation of the nose and throat, and exposure to its

fumes can cause metal fume fever. Acute symptoms include headaches, chills, coughing, fever and metallic taste in the mouth (NJDOH, 2009). Chronic health effect associated with chromium include skin allergies, ulcers and anemia. Prolonged skin contact can cause blisters and ingestion of chromium results into deep ulcers of the stomach and small intestine. Allergic reactions cause severe redness and swelling of the skin (ATSDR, 2012b). Chromium has been tested to cause sperm damage in males, and the International Agency of Research on Cancer, along with the United States Department of Health and Human Service and the EPA have confirmed that  $\text{Cr}^{6+}$  compounds are human and animal carcinogens. Workers continuously exposed to  $\text{Cr}^{6+}$  have been diagnosed of lung cancer, heart disease, emphysema and liver damage, conditions that were seen worse in smokers. Increased stomach tumors have also been observed in human and animals exposed to  $\text{Cr}^{6+}$  through drinking water (Martin and Griswold, 2009).

#### **2.4.4. LEAD**

##### **2.4.4.1. General Description and Sources**

Lead (Pb) is a blueish white metal that exist in minute quantities in the earth crust. It belongs to group 4A (IVA) and column 6 of the modern periodic table. Lead has an atomic number of 82 and a relative atomic mass of 207.7 amu. It is malleable, ductile and a bad conductor of electricity. The major oxidation states of lead are +2 and +4. It occurs in both organic and inorganic forms. Galena, Lead (II) sulfide; Anglesite, Lead (II) sulfate and Minium, Lead (II or IV) oxide are the element's main ore; and are found deep into the earth crust (Abadin *et al.*, 2007). Lead can be released unto the earth surface through natural processes such as weathering of rocks or ores, emission of sea spray and eruption of volcanoes. However, the major source of environmental lead pollution is exhaust of vehicles (Pattee and Pain, 2007).

During the last decades, Lead was widely used in the form of tetraethyl lead (TEL) or tetra methyl lead (TML) as anti-knocking and lubricating agents in petrol. During that time, many developed countries suffered the adverse effect of lead. In 1924, it was reported that at least 17 workers at the Standard and DuPont refineries died and several injured as a result of the lead poisoning (EFSA, 2012). This initiated series of research to investigate the danger of organic lead to public health. After several years of research, the US clean air act banned the sale of leaded petrol in 1996; and in 2000, the European Union banned the sale of leaded gasoline on its markets. However, lead (TEL and TML) are still used in some parts of the world as anti-knocking and lubricating agents in petrol (EFSA, 2012). Lead is also used to produce plumbing materials, lead acid batteries, jewels, paints and some alloys (WHO, 2010d).

#### **2.4.4.2. Exposure to Lead**

The primary exposure to lead is through the inhalation of ambient air and the consumption of contaminated food. Lead acetate (used as sweetener) and many kitchen utensils (e.g. pots) are the major sources of lead in food stuff (Järup, 2003).

Work-related exposure to the inorganic forms of lead usually take place in mining, smelting and welding industries, and also in batteries plants workers. The deposition of airborne lead on soil and water can introduce lead into the food chain (ATSDR, 2015). The human lungs can absorb up to 50% of inhaled lead which can subsequently accumulate in the skeleton (half-life of 20-30 years) and the blood (half-life of 1 month) of humans. Unlike in adults, the inorganic forms of lead can penetrate the blood brain barrier in children. This happens because the barrier is permeable or less developed at early ages. Children also absorb inorganic lead via the gastrointestinal tract. This high gastric uptake, together with porous blood brain barrier, make children highly predisposed to lead

exposure. The organic compounds of lead such as TEL or TML are able to penetrate the skin and the blood brain barrier of both children and adults, which can lead to lead encephalopathy (Järup, 2003; Kielhorn *et al.*, 2006). Due to its acute toxicity, the Joint FAO/WHO Expert's Committee on Food and Additives had defined 0.025 mg/kg bodyweight as the Provisional Tolerable Weekly Intake value of lead (WHO, 2010d).

#### **2.4.4.3. Health Effects of Lead**

Lead toxicity affects the kidney, heart, lungs, brain and reproductive organs (EC, 2013). The main indicators of lead poisoning are irritability, abdominal pains and headache. In less serious cases, lead poisoning disturbed hemoglobin synthesis; and long term exposure can lead to neurological effects such as lethargy, weakness of muscles, tremors, convulsions, paralysis and hematological disturbance such as anemia (UNEP/IPCS, 1995; Sharma and Agrawal, 2014). According to Järup (2003), individuals with mean blood levels of 3  $\mu\text{mol/L}$  concentration of lead may experience reduced nerve transmission and dermal sensitivity. Exposure can also affect intelligent functions, cause kidney damage and hypertension (Kielhorn *et al.*, 2006).

Research had indicated that children exposed to lead suffer reduced Intelligent Quotient (IQ) and other neuro-behavioral disorders. Some studies proposed that every increase of 10  $\mu\text{g/dL}$  in blood lead levels decreases the Intelligent Quotient of exposed children by 1 to 5 points (Abadin *et al.*, 2007; EFSA, 2012). Delinquency, aggressiveness, hyperactive disorder and attention deficit have also been associated with lead exposure mainly in children (Males) in their late childhood (UNEP/IPCS, 1995; Abadin *et al.*, 2007).

Intoxications of pregnant women through acute exposure can lead to miscarriages, premature or still birth, and other abnormalities. Males are known to experience low sperm counts and reduced

semen quality (Telisman *et al.*, 2000). Intoxication mainly results from the absorption of high levels into the body tissues (UNEP/IPCS, 1995; Kielhorn *et al.*, 2006).

Lead toxicity also has adverse effect on plant. Apart from its accumulation in plants, high levels of lead in soil can cause radial thickening in some roots and lignification of cortical parenchyma of plants. It also inhibits plants enzymes activities. For example, it hinders the activities of carboxylation enzymes thereby affecting photosynthesis. The stimulation of Indol-3-acetic acid oxidation by lead primarily prevents plant cell growth (Sharma and Dubey, 2005); and the reaction of lead with sulfhydryl groups induces oxidative stress in plants (Reddy *et al.*, 2005). The USEPA had generally classified lead and its compounds as group 2B carcinogens (probable human carcinogens) while the IARC had classified inorganic lead compounds as carcinogenic to humans (group 2A carcinogens) and organic lead compounds as nonhuman carcinogens (group 3 carcinogens) (US EPA, 2014a).

## **2.4.5. MERCURY**

### **2.4.5.1. General Description and Sources**

Mercury (Hg), a metal of column 6 and group 2B (IIB) of the modern periodic table, is one of the only two elements (Bromine being the second) that is liquid at room temperature. It has an atomic number of 80, a relative atomic mass of 201 amu, two stable oxidation states (+1 and +2) and seven stable isotopes.  $^{202}\text{Hg}$  is the most abundant of the isotopes, occupying 29.6% of the total mass. It is followed by  $^{200}\text{Hg}$  (23.3%) and  $^{199}\text{Hg}$  (17.0%) respectively (UNEP, 2008).

Sedimentary rocks and volcanic hot springs are the main sources of mercury mineralization, with the principal mineral being cinnabar ( $\text{HgS}$ ). Igneous rocks, basalts and gabbro have relatively

lower contents of Hg than granites. Coal and crude oil also contain some levels of mercury (UNEP, 2013).

Mercury exist in three interchangeable forms, elemental (metallic) mercury, inorganic mercury and organic mercury. Elemental mercury (liquid at room temperature) is used in barometers, thermometers, dental amalgams, some electrical appliances, fluorescent light bulbs and some blood pressure measuring instruments. It is also used in some geochemical prospecting apparatus as pathfinder element for mercury deposits. Inorganic mercury is mainly used for industrial processes such as cosmetics skin creams manufacturing. Organic mercury compounds such as Thimerosal and Phenylmercuric acetate are used as preservatives (GreenFacts, 2006; CDC, 2009).

Mercury is released from the earth crust through volcanic eruption and other activities. Anthropogenic mercury are released to the atmosphere by smelting, coal burning and chloro alkali production plants (Hansen and Danscher, 1997). Zhang *et al.*, (2002) estimated that the emission of mercury to the environment by anthropogenic influence will steadily increase at the rate of 5 % yearly. Municipal waste combustion, hazardous and medical waste incineration and stationary internal combustion engines also contribute to mercury level in the environment (Murray and Holmes, 2004).

#### **2.4.5.2. Exposure to Mercury**

Specific occupational groups such as dental care staff, smelters and some chemical industry staff are exposed to elemental mercury vapor. Inhalation is the major occupational route of exposure. Apart from occupational exposure, the general public is exposed to mercury through inhalation by natural diffusion of mercury vapor from the crust of the earth or by evaporation from the surfaces of the sea to the atmosphere (Gårdfeldt *et al.*, 2003). The Mediterranean Sea has been reported to

release mercury vapor into the atmosphere (Hedgecock *et al.*, 2006). Vapor mercury is readily converted to inorganic mercury in the body. The general public is also exposed to mercury through dental amalgam and food. Research had revealed that mercury is released from dental amalgam, and the release rate is increased by chewing after filling (Sällsten *et al.*, 1996). Food (fish) is the chief source of mercury exposure. When mercury is emitted into the atmosphere (usually in the form of metallic vapor), they can eventually fall on water bodies. Inorganic mercury in the aquatic environment is converted to methyl mercury (MeHg) by activities of microorganisms. This transformation introduces mercury into the food chain. Methyl mercury can be taken up by aquatic organisms and can be concentrated by fish, shellfish and other higher members in the food chain. Consequently, the population with high consumption rate of fish or other aquatic organisms are exposed to mercury (CDC, 2009). Mercury can also be released into soil. Ionic mercury ( $\text{Hg}^{2+}$ ) is also predominant in agricultural soil (Han *et al.*, 2006); and can remain in solid state by adsorbing unto clay particles, sulfides and organic substances. However, they can be solubilized by chelation and hydration and eventually be taken up by plants. Research showed that ( $\text{Hg}^{2+}$ ) can readily accumulate in higher and aquatic plants (Wang and Greger, 2004; Israr *et al.*, 2006; Kamal, 2006). Other sources of mercury exposure include broken devices or apparatus such mercury containing batteries, electrical appliances, thermometer, and barometer, among others.

The concentration of mercury in blood is used to identify exposure to methylmercury whereas mercury in urine is used as exposure indicator to inorganic mercury compounds. It also indicates recent exposure to mercury, while mercury content in hair is used to approximate long term exposure. Mercury is released from the body at a slower rate than the rate of intake into the body, thus leading to its high bio-magnification ability along the food chain (Van Walleghem *et al.*, 2007). The World Health Organization and the United Nations Food and Agricultural organization

had defined 0.004 mg/kg bodyweight of human as the Provisional Tolerable Weekly Intake of mercury (WHO, 2010a).

### **2.4.5.3. Health Effect of Mercury**

Psychological and neurological disorder such as tremor, restiveness, nervousness, sleep depression and instabilities result from chronic mercury poisoning. Acute exposure to mercury give rise to lung damages. Metallic mercury is an allergen that causes eczema. It also causes kidney damage while inorganic mercury is known to cause nervous related effects due to its ability to penetrate the blood brain barrier (Rice and Barone, 2000).

Mercury in dental amalgams caused amalgam disease, and those released from the dental amalgam as a result of chewing, can also cause oral lichen planus in the mouth (Lindh *et al.*, 2002).

Exposure to the organic forms of mercury is of crucial concern because of its ability to cause death, usually two to four weeks after onset of symptoms. Symptoms are related to nervous systems damage, and the latency of poisoning is three to four weeks after acute exposure. The Minamata catastrophe of 1956 in Japan, which lead to the death of over 52 people, resulted from the consumption of fish contaminated by methylmercury. In 1972, over 10,000 persons were poisoned and several died in Iraq as a result of eating bread baked from mercury contaminated wheat (Järup, 2003).

Mercury is transferred from mother to fetus and infants. Research reported that offspring of pregnant survivals in both the Japanese and Iraqi mercury poisoning incidents suffered psychomotor retardations (Grandjean *et al.*, 1999). The transfer of the toxicant from mother to fetus (via the placenta) and mother to infants (via breast milk) is reported to be due to maternal consumptions of diets containing mercury, especially contaminated fishes (Murata *et al.*, 2004).

High dietary intake of mercury increases the risk of coronary health disease in adults and autism in children (Lee *et al.*, 2003; Johnson, 2004). Children also suffer neuronal ectopies, cerebral palsy, cerebellar cortexes dysplasia and several other developmental abnormalities (Geelen *et al.*, 1990). The 2003/2004 National Health and Nutritional Examination Survey (NHANES) conducted by the Center for Disease Control and Prevention in the United States revealed that both blood and urine mercury levels increase with age (CDC, 2009).

## **2.4.6. NICKEL**

### **2.4.6.1. General Description and Sources**

Nickel (Ni), a hard silvery-white glossy transition metal, is the 28<sup>th</sup> element (with a relative atomic mass of 58.69 amu), that belong to group 8B (VIII B) and column 4 of the modern periodic table. Though the -1, +1 and +4 oxidation states are known, it exists in two major oxidation states (+2 and +3) and occurred naturally in five isotopes (<sup>58</sup>Ni, <sup>60</sup>Ni, <sup>61</sup>Ni, <sup>62</sup>Ni, and <sup>64</sup>Ni), of which <sup>58</sup>Ni occupies about 68.3% of the total mass as the most abundant isotope (Cempel and Nickel, 2006). It is malleable and ductile, a fair conductor of heat and electricity, and exhibits strong resistance to corrosion. Nickel is the 7<sup>th</sup> most abundant transitional metal and the 24<sup>th</sup> most abundant element in the earth crust; and exists naturally in two basic groups of ores, the laterites (garnierite or meteorites) and the sulfides (Pentlandites) (Kerfoot, 2000).

The occurrence of nickel and nickel related compounds in the atmosphere is through emission from the earth crust via natural processes, such as volcanic eruptions, windblown dust, and forest fires, as well as from human activities, such as mining, refining, smelting, wastes incineration, fossil fuel combustion and in the production and manufacture of stainless steel and other nickel-containing alloys (Filipek, 2015). Natural and anthropogenic processes and sources such as

commercial wastes, metal manufacturing wastes, bottom ash, coal fly ash, urban refuse and sewage sludge, atmospheric fallouts and deposition, chemical weathering and dissolution of nickel containing rocks, land fill leachates and domestic or industrial wastewater and effluents are major contributors to the presence of nickel in both the terrestrial and aquatic environments (NTP, 2000; ATSDR, 2005; WHO, 2007).

The metal exists in soil as free ions or inorganic crystalline precipitates or as chelated metal ion in complexes and soil solutions (Cempel and Nikel, 2006). Its bioavailability in minute concentration (10-50 mg/kg) in agricultural soil is essential for plant growth (Llamas *et al.*, 2008). It serves as a cofactor (Ni-metalloenzyme) of urease (Urea amidohydrolase) in the conversion of urea to ammonium ion, the source of plants' nitrogen (Liu *et al.*, 2017). The uptake of Nickel by plant is similar to the uptake of zinc and copper, therefore, high bioavailability of Nickel in agricultural soil suppresses the uptake of these elements and also leads to its accumulation in various part of the plant, causing serious physiological alterations to the plant, and also affecting the food chain (Pandey and Sharma, 2002; Rahman *et al.*, 2005). Plants have high affinity for nickel, and up to 70 percent of the absorbed nickel can be transported to the ovary of the plant, the part that bears its fruit (Brown, 2006). According to Kerfoot (2000), areas affected by industrial activities show high level of soil nickel ion, but the concentration of nickel in soil generally increases with decreasing soil pH. Apart from other chemical processes, the reduced use of soil lime in agriculture and an increase in acid rain can decrease the pH of the soil, thus increasing the capacity of the soil to accumulate nickel.

The major use of pure nickel metal is in the manufacturing of alloys. Many chemical and hospital equipment, domestic utensils, and engine components, made from stainless steel, alloy steel and cast irons, are produced by alloying nickel with iron (Antonsen and Meshri, 2004). Alloys made

from nickel and copper are usually used for industrial plumbing and coinage purposes. Others are used as thermocouples, heat exchangers, condensing tubes, pumps and electrodes in instruments. Nickel can also be alloyed with chromium, molybdenum and other metals for specific purposes (ATSDR, 2005).

The salts of nickel are used as pigments or catalysts (Nickel carbonates) and dye mordants (Nickel ammonium sulfates). Others are used in electroplating and in the manufacturing of nickel-cadmium batteries. Nickel sulfides are used in petrochemical hydrogenation while the oxides and hydroxides are used in ceramics (Kerfoot, 2000; Antonsen and Meshri, 2004).

#### **2.4.6.2. Exposure to Nickel**

Ingestion of contaminated food and water, inhalation of ambient air, and absorption through the skin are the major routes of nickel exposure. The ingestion of nickel in food and drinking water is the major exposure route for the general population of non-smokers (ATSDR, 2005; Dolara, 2014). Nickel is an essential plant nutrient, and thus can be found naturally in most vegetables, fruits, nuts and crops, and in food products derived from them; and are usually in the range from 0.01 mg/kg to 0.1 mg/kg. It is considered to be a normal constituent of the diet, and levels in consumables below 0.2 mg/kg are said to be safe (WHO, 2007). The occurrence of nickel in food is a natural process, but leaching from nickel-containing alloys in food processing equipment or machines, or the catalytic dehydrogenation of triglycerides (fats and oils) by the use of nickel catalysts may apparently increase the level of nickel already present in foodstuffs (Beveridge, 2008). Despite these processes, the WHO had reported, from concordance data, that diet contributes less than 0.2 mg of nickel consumed by an individual on a daily basis (WHO, 2007).

Inhalation of nickel from ambient air is considered as a minor exposure route to the general population. However, it is the major route for occupational exposure. Workers of nickel producing industries such as mining, milling, smelting, and refining; as well as nickel using industries such as alloys and stainless steel manufacture, welding, cutting, grinding, electro-winning and electroplating are exposed to nickel through inhalation and dermal absorption (Buekers *et al.*, 2015). Coins and jewelry plated with nickel and smoke of tobacco made of nickel are other common sources of nickel exposure. Nickel in the serum and urine are used as indicator to environmental, occupational and iatrogenic exposure to nickel and nickel compounds. Nickel in the serum have short half-life and are used to indicate recent exposure; while those present in the urine reflect chronic exposure (Cempel and Nickel, 2006; Schaumlöffel, 2012). The concentration of 1-3 µg/L (in urine) and 0.2 µg/L (in serum) are the reference values for nickel in a healthy adult. Any values above these limits are said to induce nickel toxicity. The USEPA had set an enforceable limit of 0.1 mg/L for nickel in drinking water, while the OSHA had defined a maximum exposure limit of 1.0 mg/m<sup>3</sup> for metallic nickel and nickel compounds over an eight hours working day and forty hours working week in workplace environments (ATSDR, 2005). Health authorities, JECFA, had defined 0.035 mg/kg bodyweight as the Provisional Tolerable Weekly Intake value for nickel (Yousefi *et al.*, 2016)

#### **2.4.6.3. Health Effect of Nickel**

Research had shown that nickel caused chromosome damage, induce mutagenesis and inhibits DNA excision repairs (Beveridge, 2008). Nickel compounds are very carcinogenic, and they are known to cause a number of human cancers and different types of tumors in occupational exposed workers (NTP, 2000; ATSDR, 2005; Beveridge, 2008; Schaumlöffel, 2012). Nickel can also cause oxidative stress through nickel-induced lipid peroxidation (LPO). This condition leads to cell

death, lungs inflammation, and damages to the kidney, liver, bone marrow, and the nasal cavity (Saedi *et al.*, 2013).

Nickel is also one of the elements responsible for most allergic skin reaction or dermatitis. About 10-20 % (mostly women) of the general population is sensitive to nickel. Sensitization occurred from coins, jewelry (chains, bracelets, wrist watches, earring) and other materials plated with nickel (Dolara, 2014). Sensitization to nickel results from both dermal contact and ingestion of the metal. Skin rashes, eczema and erythema are common dermatitis that result from nickel sensitivity to exposure to nickel (ATSDR, 2005; Cempel and Nikel, 2006). Extreme sensitivity leads to asthma and conjunctivitis. It also caused some systematic reactions to nickel containing fluids and medications, which may lead to serious medical complication (NTP, 2000; Schaumlöffel, 2012; Saedi *et al.*, 2013; Dolara, 2014).

## **2.5. HEAVY METAL DETERMINATION**

Several methods have been utilized in determining heavy metals in environmental and biological samples. Some of the commonly used analytical techniques include Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), X-Ray Fluorescent (XRF) Spectroscopy, Neutron Activation Analysis (NAA), Flame Photometry (FP), Atomic Fluorescent Spectroscopy (AFS), and Anodic Striping Voltammetry (ASV). Methods are selected primarily based on the availability of the instrument, its detection limits and sensitivity, cost of analysis and the matrix of the sample (Helaluddin *et al.*, 2016).

ICP-AES, also known as ICP-OES, Optical Emission Spectroscopy, generates excited atoms through an intense electromagnetic field, which emit detectable amount of light at specific

wavelengths, with intensities proportional to the concentration of the atoms. The technique measured and analyzed spectra by an atomic emission spectrometer (AES), using correlations of concentration-intensity that are similar to how the Beer Lambert law applies to AAS. However, the technique is considered more sensitive than F-AAS due to its low detection limits (as low as 0.1 µg/L). It is also preferred over AAS because of its invaluable ability to simultaneously record spectra of multiple trace elements (Melville *et al.*, 2014).

Neutron Activation Analysis (NAA) is based on excitation by neutrons. The sample is bombarded with neutrons, causing the elements to form radioactive isotopes with specific emission and decay pathways. The technique is non-destructive, very sensitive and provides multi-elemental analysis at once, but requires long time for analysis (IPCS/IOMC/WHO, 2001).

X-Ray Fluorescence (XRF) spectroscopy is also a non-destructive analytical technique that measures emitted characteristic fluorescent or X-ray emitted by elements in a sample. Sample is stricken with X-ray of high energy that dislodges tightly held core electrons from the inner shell of an atoms of an element in the sample, causing vacuums in the shell that needed to be filled by the element in order to attain original configuration or stability. This caused a prompt transfer of electrons from the outer shell to the inner shell of the element, releasing a characteristic secondary fluorescence X-ray, which is measured (Lagoida and Trushin, 2016). One unique type, the Energy Dispersive XRF (ED-XRF) is a portable analyzer used for the analysis of dried or powdered samples with better precision than AAS (Nielson *et al.*, 1991).

Flame Photometry provides high atomization of elements but is not suitable for many elements. The alkaline metals and the alkaline earth metals such as calcium, potassium, sodium, among others, provide better sensitivities to Flame Photometry due to their low excitation energies.

Customarily, Atomic Emission Spectrometry, Atomic Fluorescent Spectrometry, Anodic Stripping Voltammetry and Electron Microprobe are also widely used for elemental analysis (Pesavento *et al.*, 2009). Despite their availabilities, the ICP-MS and the AAS, due to their high sensitivity and low detection limits are the most preferred and commonly used methods. These methods were therefore used in this study.

### **2.5.1. ICP-MS: Theory and Instrument Description**

Amongst the methods currently available for metal determination, ICP-MS is the most preferred techniques because of its low detection limits (as low as 0.001 µg/L), and high sensitivity. As its name implied, the technique joins a viable ionization source of an Inductively Coupled Plasma (ICP) with a sensitive Mass Spectrometer (MS) together to accomplish multi-element analysis. The principle is based on the production, separation, and detection of ions formed from atoms of elements in a sample, and the subsequent measurement of electric signals produced from those ions (Batsala *et al.*, 2012). The ICP-MS instrumentation is made up of six basic components: a sample introduction system that provides a way of getting the sample into the instrument, an ionization chamber that produces and converts the atoms of analytes into ions, an interface that couple the ICP to the MS, a filter that sort ions by their mass to charge ( $m/z$ ) ratio, a detector that counts individual ions and measures electric signal, and a readout that displays processed signal reading of the instrument (Van de Wiel, 2003).

Depending on the sample matrix, different sample introduction systems are used. Liquids or slurries are usually introduced into the instrument by a nebulization system. In this system, the sample is aspirated into a nebulizer that converts it into an aerosol mist, which is then carried into the ionization chamber by a flowing argon gas. The Electro Thermal Vaporization (ETV) or Ablation systems are used to introduce solid samples into the instrument. Both systems use

different means to generate aerosols of samples. The ETV system uses electric current while the Ablation system uses laser. The aerosol generated is then swept into the ionization chamber by a flowing argon gas (Batsala *et al.*, 2012).

The ionization chamber is made of an ICP torch and a Radio Frequency (RF) coil. The torch contains a flowing argon gas and the RF coil is connected to an RF generator. When power is supplied from the generator, an oscillating electric and magnetic fields are created at the end of the torch. Argon ions formed by spiked argon gas flowing through the torch are caught in the oscillating fields, colliding with other argon ions to produce plasma (argon discharge) with temperature ranging from 6,000 K to 10,000 K along the torch. The temperature range of the plasma makes it an excellent atomization and ionization source. When the aerosol enters the ionization unit, it is first atomized. The atoms absorb energies as they moved along the plasma until they become ionized (release energy).

After ionization, the ions then travel out of the torch to the filter via the interface. There, they are separated based on their mass-to-charge ( $m/z$ ) ratio. The most common type of filter used is the quadrupole mass filter. It has four rods, and an alternating AC and DC voltages are applied to opposite pairs of the rods. This filter is selective. Only ions of certain  $m/z$  ratios can pass through the rods at a given time. It separates ions by scanning the voltages, switched along with an RF field (Cawley and Flenker, 2008).

Once the ions have been filtered based on their  $m/z$  ratios, they moved to the detector, which multiplies or amplifies the number of ions striking it dynodes and translates the result into an electric signal that can be measured. ICP-MS detectors are usually electron multiplier devices with high sensitivity and background correction characteristics. The number of analyte ion present in the sample is proportional to the magnitude of the electric signal. With preset calibration curves,

the concentrations of the analytes are determined from the magnitudes of the electric signals (Cawley and Flenker, 2008).

The ICP-MS technique is very sensitive and can also be coupled with separate techniques such as Liquid Chromatography (LC) and Gas Chromatography (GC), using a capillary electrophoresis as an element selective detector for further analysis of samples. ICP-MS major disadvantage is its lack of availability (Van de Wiel, 2003).

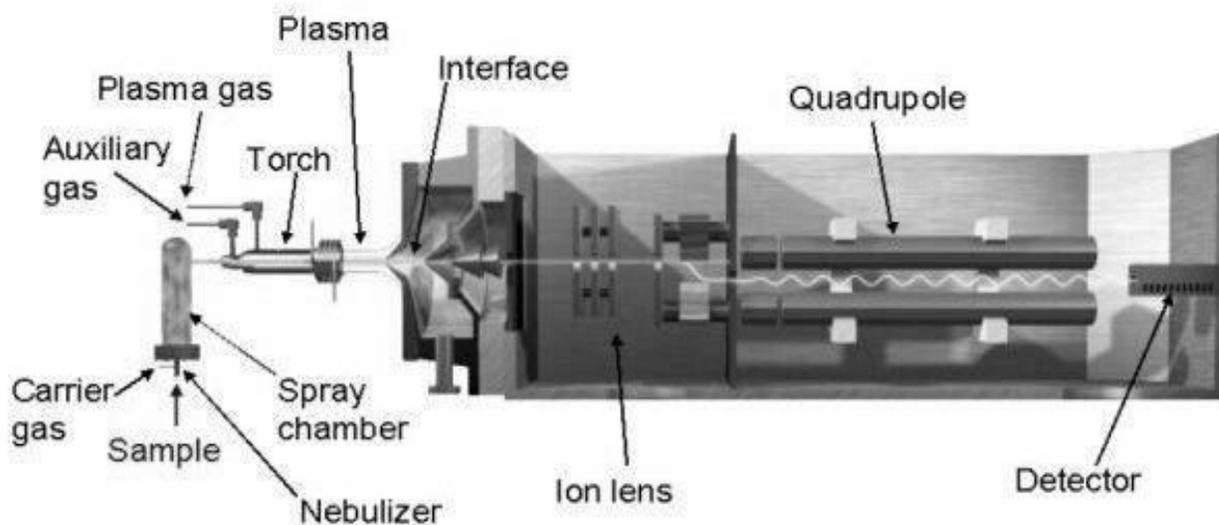


Figure 2.6: Schematic Diagram of ICP-MS (Cawley and Flenker, 2008)

### 2.5.2. AAS: Theory and Instrument Description

Atomic Absorption Spectrophotometry (AAS) is an analytical technique based on measuring radiation absorbed at a specific wavelength by atoms of elements in a sample. The elements are atomized in a flame or other thermal devices and get excited by absorbing portion of a beam of light provided by a light source. The AAS instrument consist of five basic components: a radiation source that produces the radiation of the element of interest, an absorbing cell or atomizer in which

atomization of the element in the samples occurred, a monochromator that dispersed lights, a detector that quantifies the intensity of the radiation and amplifies the signal, and a readout that displays the processed signal reading of the instrument's electronics (Helaluddin *et al.*, 2016).

Based on atomization techniques, different methods of AAS can be mentioned. Examples are the Flame AAS (F-AAS), Electro-thermal or Graphite Furnace AAS (ET/GF-AAS), Hydride Generation AAS (HG-AAS), Cold Vapour AAS (CV-AAS) amongst others. The Flame AAS technique is referred to as direct aspiration technique. Samples (in liquid form) are aspirated into a nebulizer system, which forms an aerosol mist and transport it to the flame for atomization. The flame is generated by a Burner system through the combination of oxidant-fuel gases. Two commonly used oxidant-fuel gases are the Air-Acetylene (2300°C maximum) and the Nitrous Oxide-Acetylene (2900°C maximum). Flame can be selected based on the element to be analyzed. Of the elements determined by atomic absorption, approximately 36 of them can be determined using the Air-Acetylene flame. The Nitrous Oxide-Acetylene is used for the determination of elements which form refractories oxides. The flame sprouts from the head of the Burner system. The burner head (usually 10 cm or 5 cm) are mostly made of solid corrosion resistance titanium that is freed of elements normally determined by atomic absorption spectroscopy. The sample aerosol undergoes processes such as desolvation, vaporation or volatization and then atomization (PEC, 1996; AOAC, 2002). Flame method is fast (about 10-15 seconds per sample analysis), and provides good precision. However, the method offers low sensitivity and high detection limits (as high as 1.0 µg/L). This is because a large percentage of the sample is left in trench, and the residence time of individual atoms on the optical path in the flame is very short (approximately 10<sup>-4</sup> seconds) (Helaluddin *et al.*, 2016)

Graphite Furnace AAS uses an electro-thermal graphite furnace to heat sample progressively (up to 3000°C) for atomization. Samples are injected into a graphite tube and directly positioned into the graphite furnace, and the furnace is electrically heated in a gradual manner for atomization. GF-AAS offers better atomizer, sensitivity and detection limits (as low as 0.01 µg/L) than Flame AAS, and most Graphite Furnace AAS can accept solutions, slurries or solid samples, and usually in extremely trivial quantities, (about 20 µl) for liquids (Bush, 2006).

For low level determination of volatile elements such as Se, Sb, As, and Ge, Hydride Generation AAS provides lower detection limits (as low as 0.01 µg/L). This is achieved through reaction of the element with Sodium Borohydride (NaBH<sub>4</sub>) reducing agent in a reaction vessel before atomization. This generates a volatile hydride of the element, and the hydrides are subsequently converted to gaseous analytes, which are atomized in a specialized cell (Helaluddin *et al.*, 2016).

Mercury is also a volatile element, but the traditional Hydride Generation AAS methods and other methods such as Atomic Fluorescence Spectroscopy and Inductively Coupled Plasma-Atomic Emission Spectroscopy exhibit poor sensitivity to its analysis. This is due to the much higher vapour pressure of the element at ambient temperature (Habashi, 2013). The Cold Vapour-AAS technique has proven to be the best method of mercury analysis in liquid samples. This method generates a hydride of Hg from an acidified mercury containing solution through treatment with Stannous Chloride (SnCl<sub>2</sub>) or Sodium Borohydride (NaBH<sub>4</sub>) in a peripheral reaction vessel before atomization in a specialized Mercury-Hydride System (MHS) cell. The reaction reduces combined mercury to its metallic form and then to its subsequent vapour states before they are atomized.

This enhances the detection limits (0.01 µg/L) and reduces the chances for matrix interferences (Baughman, 2005). Specialized instruments designed for mercury determination may use other

AAS methods for mercury atomization and subsequent determination in dried and powdered samples.

The concentration of analytes in AAS is determined by the principle of the Beer Lambert's law. This is done by passing a beam of light from an appropriate light source through the atoms. The light source is usually a Hollow Cathode Lamp (HCL) or an Electrodeless Discharge Lamp (EDL) whose cathode is made of the element being determined. Part of this light is absorbed (Absorbance) by the created atom for excitation and the rest is transmitted to a photomultiplier tube (Detector).

The concentration of the analyte is directly proportional to the absorbance as followed by the Beer Lambert's law (Tüzen, 2003).

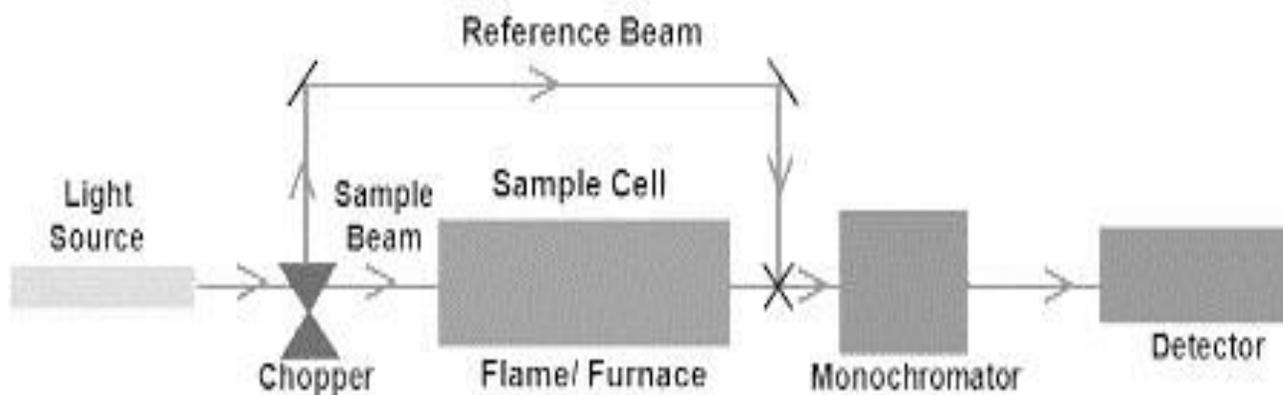


Figure 2.7: Schematic diagram of AAS (De Lloyd, 2000)

## 2.6. Human Health Risk Assessment

Human Health Risk Assessment (HHRA) is the term that describe the processes leading to the determination of risk a particular chemical poses to human health. The process seeks to address whether a current or future exposure to a chemical will pose any health risk to a population (Choudhury *et al.*, 2000; IPCS/FAO/WHO, 2009). Despite the variety of chemicals, human health

risk assessment for any chemical follows a general four step process developed by the US-EPA. The steps include hazard identification, exposure assessment, dose-response assessment, and risk characterization. Hazard identification is the process in which research is conducted to identify the potential health effect that may be caused by a chemical; exposure assessment is where pattern of exposure to the chemical is determined; dose-response assessment establishes the quantity or level of the chemical that may cause a particular carcinogenic or non-carcinogenic health effect to an exposed population, and risk characterization describes the expected health risk of the chemical to the exposed population (US EPA, 2012).

## **CHAPTER THREE**

### **3. METHODOLOGY**

#### **3.1. Study Area**

Monrovia is the official capital city of Liberia. It is located along the coast of the Atlantic Ocean in Cape Mesurado (Montserrado), and houses the country's political, cultural and financial centers. It constitutes 29 percent of the country's population with a population of 1.011 million (Hadden, 2006; GOL, 2008).

#### **3.2. Sampling**

A total of 61 samples comprising of 29 different rice brands (20 Foreign and 9 Local) of different batches were purchased on different occasions from six markets in Monrovia from March to April and August to September, 2017. The markets are the ELWA market in Paynesville, Junkpent Town market in Sinkor, Redlight Market in Redlight, Duala Market in Duala (Bushrod Island), Duport Road market in Duport Road and the Rally Town Market in Rally Town (UN Drive). Samples

were collected based on their popularity among local consumers and availability at the time of sampling. They were also collected based on production dates within each brand. This was done to obtain samples that reflect all commercially available types of rice brands on the local markets. Moreover, it is possible that samples of the same brand produced on different dates may not have the same source or were not grown under the same conditions. Samples were obtained in about 150 g each, and were collected in clear clean polyethylene zip lock sampling bags (200×140 mm), after which were tightly zipped and then labelled. Table 3.1 summarized the kinds of rice brands sampled in this study.

Table 3.1: List of rice brands sampled in this study

No.	Sample Brand	Origin (Country)	Batch(es)
1.	Americanna	China	2
2.	Bellaluna 1 (Bella 1)	India	2
3.	Bellaluna 2 (Bella 2)	India	2
4.	Bitter International (Butter Rice)	China	2
5.	Bong Rice*	Liberia	2
6.	Crown	Japan	2
7.	Firestone Parboil (Puusawa Rice)	America	1
8.	Horse	India	2
9.	Indo-Lion	India	1
10.	IR-64	Japan	3
11.	Kissi Rice*	Liberia	2
12.	Kpelleh Rice*	Liberia	3
13.	Lady Norah (Fenfen)	Pakistan	2
14.	Lion	Iran	2
15.	Lofa Rice*	Liberia	3
16.	Nimba Rice*	Liberia	3
17.	Nobel Express	USA	1
18.	Old Lady*	Liberia	1
19.	Pure White*	Liberia	2
20.	Red Rice*	Liberia	2
21.	Red Star (Pink bag)	India	3
22.	Royal Elephant	India	3
23.	Royal Parboil	Thailand	2
24.	Savanna (New Butter Rice)	Thailand	2

25.	Six Months*	Liberia	1
26.	UCI (Blue Bag)	China	3
27.	Uncle Mario	India	3
28.	Uncle Sam (Fender Rice)	Thailand	2
29.	USA Parboil	USA	2

\*Local Rice

All rice brands sampled were rice that are widely consumed in the country. Samples were packed in solid polyethylene food box (66×46×15 cm), sealed and transported from Monrovia, Liberia to Kumasi, Ghana for analysis.

### 3.3. Stock Reagents and Standards

All stock standard solutions, chemicals and reagents used in this study were of analytical grade unless otherwise stated. All dilutions were made with deionized water. Reagents used in this study include Sulfuric acid ( $H_2SO_4$ ), Per-chloric acid ( $HClO_4$ ), Potassium permanganate ( $KMnO_4$ ), and Nitric acid ( $HNO_3$ ).

The 98 %  $H_2SO_4$ , 70 %  $HClO_4$  and 65 %  $HNO_3$  concentrated acids used were obtained from Merck, Darmstadt (Germany). Various concentrated stock standard solutions for each metal were products of Agilent Technology, California (USA). Potassium permanganate ( $KMnO_4$ ) was from Breckland Scientific, Stafford (UK).

### 3.4. Preparation of Working Reagents

#### 3.4.1. Metal Reagents and standard solutions

Reagents and standard solutions used in this study were prepared from salts and stock standard solutions by diluting an appropriate amount of these salts and stocks standard solutions through intermediate solutions. The volumes of stock solutions and masses of salts required to prepare appropriate working standard solutions and reagents for each metal were computed, and standard

solutions and reagents preparation procedures were followed. Blanks to be used as diluents were also prepared alongside the procedures. 0.5 % (w/v) Potassium permanganate ( $\text{KMnO}_4$ ) solution was prepared by weighing 10 grams of Potassium permanganate ( $\text{KMnO}_4$ ) salt and then dissolving it in deionized water to obtain solution of 2 L. 0.5 L of the concentrated Nitric acid ( $\text{HNO}_3$ ) solution was diluted with 4.5 L of deionized water to prepare a 10 % (v/v) Nitric acid solution. These solutions were used for washing glassware. Other standard solutions were prepared in similar way.

### **3.5.2. Blanks**

Generally, two types of blank solutions (Calibration and Method) were used in this study. The calibration blanks were used to establish calibration curves for each of the analytes. Calibration blanks were prepared alongside the preparation of the metal standards used in the calibration of the instrument. Method blanks, such as reagent and digestion blanks, were used to ascertain any possible contaminations resulting from reagents used during the study. Reagent blanks were prepared alongside the preparation of standards and reagents.

## **3.5. Preparation of Samples**

### **3.5.1. Homogenization of samples**

Samples were thoroughly washed with deionized water and air dried at room temperature for one week. This was followed by homogenization. Samples were pulverized and powdered using a high speed two-in-one BLG-600S Binatone blender (Binatone Company, UK). After grinding of one sample, the Blender was thoroughly washed with tap water and rinsed twice with deionized water then allowed to air dry before the grinding of the next sample.

### 3.5.2. Digestion of samples

All glassware, digestion tubes and PET bottles used for digestion and storage of samples were prewashed, soaked in detergent water for two hours, washed properly and rinsed with distilled water and then soaked in Nitric acid ( $\text{HNO}_3$ ) for about 20 hours. Thereafter, they were rinsed with deionized water followed by Potassium permanganate ( $\text{KMnO}_4$ ) solution and finally rinsed with deionized water and then allowed to air dry before use. Modified open tube digestion procedure according to Voegborlo and Akagi (2007) was used to digest the samples. The accuracy of the method has been proven by Certified Reference Materials, such as IAEA-085, IAEA-142 and IAEA-407.

In the digestion procedure, 1 gram of pulverized sample each was weighed, using a Sartorius CPA623S Analytical balance (Sartorius Group, Germany), in to a 50 mL graduated Pyrex digestion tube. 1 mL of deionized water, 4 mL of 1:1 concentrated Nitric acid-Perchloric acid ( $\text{HNO}_3$  -  $\text{HClO}_4$ ) and 5 mL of concentrated Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were added in turns to the sample in the tube. The mixture was swirled for about 2 minutes to mix well in the tube. The digestion tubes with contents were then inserted into an aluminum heating block and placed on an electric VWR-97042-662 Aluminum Chauffant Hotplate (VWR International, USA) for heating. The heating block contains 6 holes each and the hot plate can accommodate 10 heating blocks at a time, enabling 60 samples to be digested at once. The hotplate was set at  $200^\circ\text{C}$ , and the mixture heated until clear transparent solutions were obtained. The tubes containing the digestates were removed from the hot plate, allowed to cool and diluted to the 50 mL mark with deionized water. The final solutions were shaken thoroughly and transferred into top capped PET bottles and kept in freezer at  $10^\circ\text{C}$  until analysis.

Digestion blanks were prepared during the digestion procedures. In the preparation procedure, 1 mL of deionized water was measured into a 50 mL graduated Pyrex digestion tube and 4 mL Nitric and Perchloric acids mixture (HNO<sub>3</sub>-HClO<sub>4</sub>) in a ratio of 1:1 was gradually added to the tube. Added to the tube also was 5 mL Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). The mixture was swirled for about 2 minutes and then placed in digestion block on the hot plate, VWR 97042-662 Aluminum Chauffant Hotplate (VWR International, USA) set at 200°C for heating. Heating was done for 30 minutes and the solution was removed, allowed to cool and then diluted with deionized water to the 50 mL mark.

### 3.6. Determinations of Selected Metals

#### 3.6.1. Determination of As, Cd, Cr, Pb and Ni

The concentrations of these metals (As, Cd, Cr, Pb and Ni) were determined by an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) technique, using a compact benchtop designed Agilent 7900 (Agilent Technology, USA) Inductively Coupled Plasma Mass Spectrophotometer. In the determination procedure, samples were loaded in the sampling tray and a programmed Agilent SPS-4 Auto-sampler auto injected and delivered 20 µL of each sample into the instrument's ionization section via the sample introduction system. Prior to that, the instrument was calibrated to determine its response to calibration standards of known concentrations. The stock solutions of the analytes were used to prepare calibration standards with varying concentrations and their signals were measured to obtain calibration curves, which were used to determine the concentration of the analytes in the digests. Since no dilution was done in the analysis of the samples, the final concentrations of the analytes were computed by the following formula:

$$C \text{ (mg/kg)} = \frac{R}{1000} \times \frac{V}{W} \dots\dots\dots 3.1$$

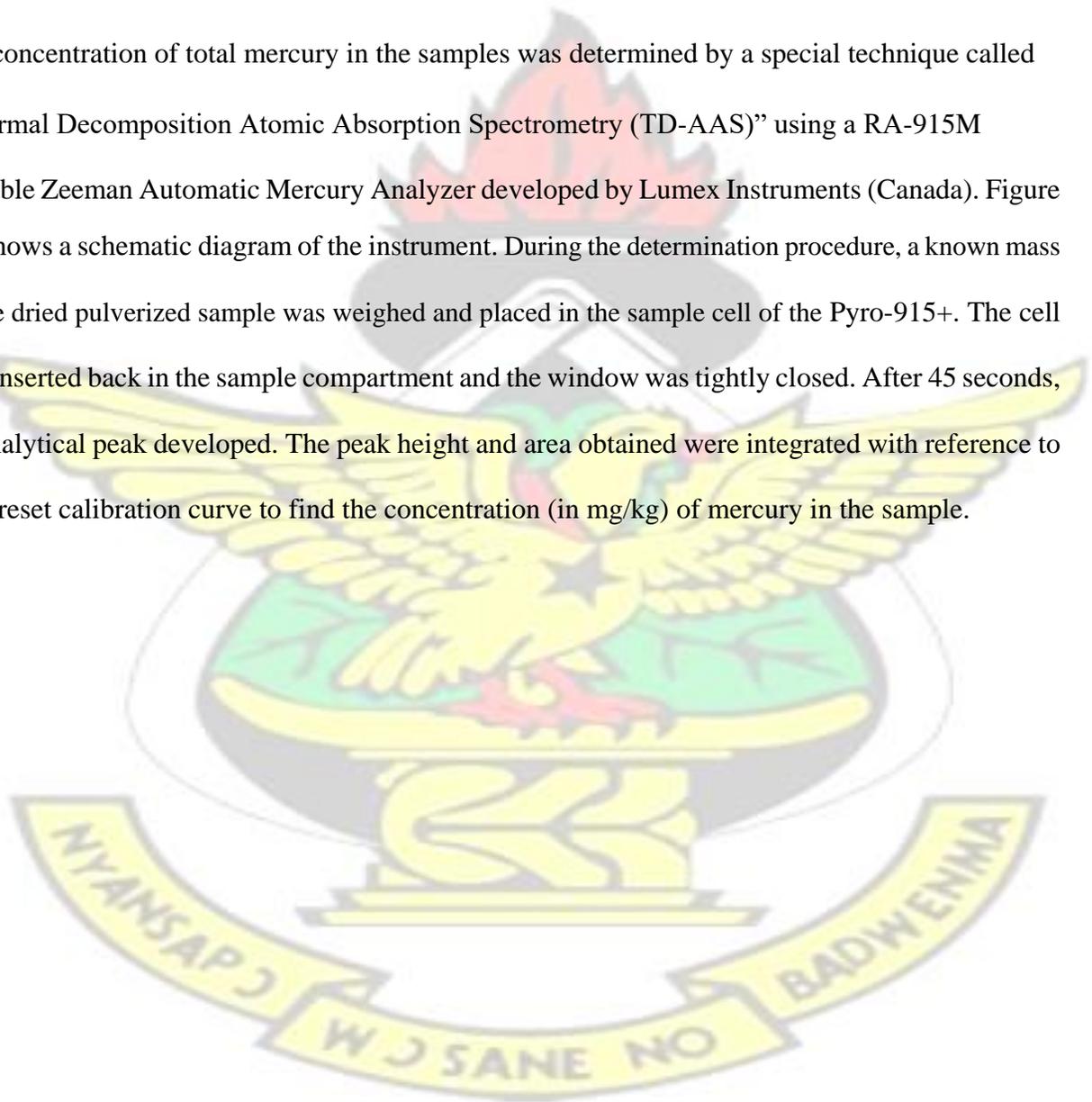
Where “R” is the Concentration obtained from the calibration curve in micrograms per liter.

“V” is the Final Volume of the processed sample in liters.

“W” is the Weight of the sample in kilograms.

### 3.6.3. Determination of Hg

The concentration of total mercury in the samples was determined by a special technique called “Thermal Decomposition Atomic Absorption Spectrometry (TD-AAS)” using a RA-915M Portable Zeeman Automatic Mercury Analyzer developed by Lumex Instruments (Canada). Figure 3.1 shows a schematic diagram of the instrument. During the determination procedure, a known mass of the dried pulverized sample was weighed and placed in the sample cell of the Pyro-915+. The cell was inserted back in the sample compartment and the window was tightly closed. After 45 seconds, an analytical peak developed. The peak height and area obtained were integrated with reference to the preset calibration curve to find the concentration (in mg/kg) of mercury in the sample.



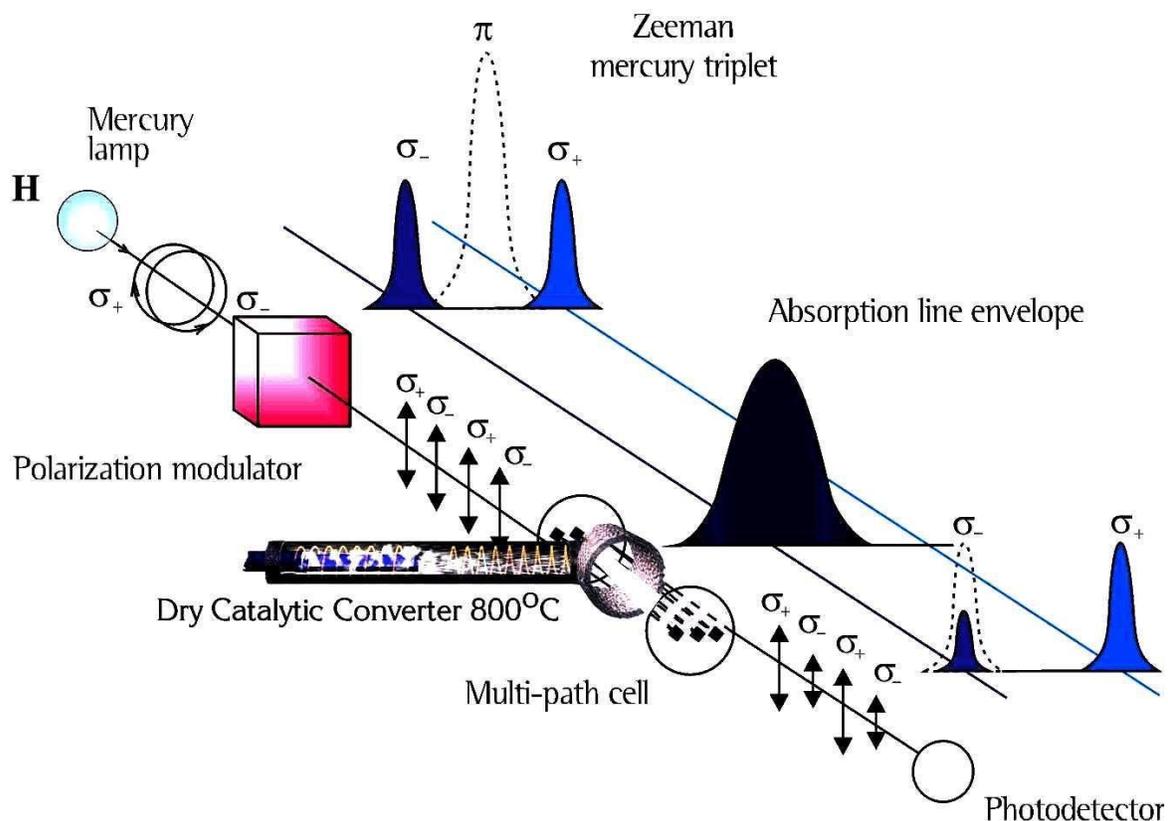


Figure 3.1: Schematic diagram of the Lumex RA-915M Portable Automatic Mercury Analyzer

### 3.7. Quality Assurance

Various quality control measures were employed in this study to ensure the reliability, validity and accuracy of the results obtained. Samples were handled with care to avoid contamination. All wares were properly cleaned and all reagents used were of analytical grade. In the ICP-MS analysis procedure, calibration verification standards measurements were performed following every ten samples, and also at the end of the total samples run, to ensure accuracy of the procedures. The samples were divided into six batches, thus a total of seven measurements of the calibration verification standard measurements were performed during the analysis process. Analysis of

reagent blanks was also performed with each batch of the samples to correct any error introduced into the result due to the reagents or deionized water used in the study.

To assess the repeatability of the results obtained, triplicate analysis of each of the sample was conducted in each analytical process. Precision analysis was also conducted to further assess the repeatability of the results obtained. This was done by selecting ten subsamples each from two randomly selected samples. The subsamples were treated and analyzed under similar conditions.

Recovery analysis was also performed to confirm the accuracy of the overall method. This was done by spiking three replicates of one sample with known and increasing amount of the standard solutions of the metals. The spiked samples were treated and analyzed under the same conditions to determine the percent recoveries. A certified standard reference material (IAEA-359) obtained from the analytical quality control services unit of the International Atomic Energy Agency (Vienna, Austria) was also included in the digestion and analytical measurement processes.

### **3.8. Health Risk Determination**

In this study, the health risk effects, both carcinogenic and non-carcinogenic, posed to the population of Monrovia from the consumption of contaminated rice with heavy metals was conducted according to the US EPA integrated metal risk assessment guideline (US EPA, 2007; Koki *et al.*, 2015; Kingsley and Nganwuchu, 2017; Sultana *et al.*, 2017).

#### **3.8.1. Non-Carcinogenic Health Risk**

The non-carcinogenic health risk posed to the population of Monrovia from heavy metals contaminations of rice was assessed by using Hazard Quotients and Hazard Indices. Dietary Exposure of the population to these metals was assessed by computing estimates of daily metal

intake. Dietary exposure, in the form of Estimated Daily Intake (EDI), was computed by using the formula:

$$EDI \text{ (mg/kg/day)} = \frac{C_m \times DCR}{B_w} \dots\dots\dots 3.2$$

Where “Cm” is the Measured Concentration of the metal in rice samples in milligrams per kilogram.

“DCR” is the rice Daily Consumption Rate (in grams per day) of the inhabitants of Monrovia.

“Bw” is the average Body Weight of adult in kilograms.

Hazard Quotient is the ratio of the EDI or potential exposure to the maximum daily oral exposure or reference dose, and HI is the combination of Hazard Quotients (US EPA, 2007). Hazard Quotients and Hazard Indices were calculated from the following formula:

$$HQ = \frac{EDI}{RfD} \dots\dots\dots 3.3$$

$$HI = HQ_1 + HQ_2 + HQ_3 + \dots HQ_n \dots\dots\dots 3.4$$

Where “EDI” is the Estimated Daily Intake in milligrams per kilogram day. “RfD”

is the Reference Dose in milligrams per kilogram day

**3.8.2. Carcinogenic Health Risk**

Carcinogenic health risk posed to the population of Monrovia from heavy metals contamination of rice was assessed by computing Incremental Lifetime Cancer Risk (ILCR) of the carcinogenic

metals in this study (Gillespie *et al.*, 2011; US EPA, 2014a; US EPA, 2016). Incremental Lifetime Cancer Risk can be computed from the formula:

$$ILCR = CD_i \times CS_F \dots\dots\dots 3.5$$

Where “CD<sub>i</sub>” is the Chronic Daily Intake in milligrams per kilogram per day.

“CS<sub>F</sub>” is the Cancer Slope Factor in (milligrams per kilogram per day)<sup>-1</sup>.

Chronic Daily Intake (CD<sub>i</sub>) was computed from the formula:

$$CD_i \text{ (mg/kg/day)} = \frac{EDI \times EFr \times ED_{tot}}{AT} \dots\dots\dots 3.6$$

Where “EDI” is the Estimated Daily Intake in milligrams per kilogram per day.

“EFr” is the Exposure Frequency in days per year.

“ED<sub>tot</sub>” is the Total Exposure Duration in year.

“AT” is the Period of Exposure in days.

The US EPA-IRIS has recommended 365 days per year as Exposure Frequency and 70 years as Exposure Period for carcinogenic health risk assessment (US EPA, 2015), and the WHO has reported 61.50 years as the average life expectancy of a Liberian (WHO, 2017). These values were used to compute the Chronic Daily Intake values for the metals.

### 3.9. Statistical Analysis

Microsoft Excel (v2016) tools were employed in this study for statistical analysis. Data were imported into IBM Statistical Package for Service Solution (v23.0) for further analysis. Student t-test (P @ 0.05) was conducted using IBM-SPSS.

## CHAPTER FOUR

### 4. RESULTS AND DISCUSSION

A total of 61 rice samples were analyzed in this study. All results obtained from analysis are computed in mg/kg unless otherwise stated; and are also presented in tables and figures. Precision analysis, recovery analysis (through spiking) and the use of Certified Reference Material (CRM), amongst others quality control procedures were conducted to ensure the authenticity and reliability of the results obtained. Though samples were analyzed in triplicate, precision analysis was conducted to further assess the repeatability of the results obtained. This was done by randomly selecting two samples and obtaining ten subsamples from each. The subsamples were treated and analyzed under similar conditions. Results from the precision analysis is summarized in Table 4.1. The Standard Deviations and Relative Standard Deviations from the data sets show little dispersion within the results, hence, signifying better precision.

Table 4.1: Precision analysis showing concentration of metals in subsamples of rice.

Subsamples	Belleluna 2a	Crown 2				
	Hg (mg/kg)	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Pb (mg/kg)
A	0.0085	0.0101	0.0634	0.0986	0.2142	0.0080
B	0.0068	0.0105	0.0782	0.0827	0.1892	0.0068
C	0.0076	0.0114	0.0547	0.0884	0.2533	0.0081
D	0.0088	0.0091	0.0670	0.0975	0.2464	0.0083
E	0.0078	0.0116	0.0601	0.0790	0.1934	0.0072
F	0.0094	0.0110	0.0614	0.0911	0.2311	0.0087
G	0.0083	0.0111	0.0797	0.1018	0.2271	0.0071
H	0.0081	0.0092	0.0660	0.1047	0.2047	0.0077
I	0.0072	0.0106	0.0714	0.0873	0.2123	0.0093
J	0.0079	0.0117	0.0747	0.0805	0.2119	0.0075
Mean	0.0081	0.0106	0.0677	0.0912	0.2184	0.0079
Std. Dev.	0.0007	0.0009	0.0082	0.0091	0.0211	0.0008
RSD (%)	9.4760	8.8870	12.121	9.9980	9.6560	9.7880

A certified standard reference material (IAEA-359) obtained from the analytical quality control services unit of the International Atomic Energy Agency (Vienna, Austria) was used to validate the accuracy of the analytical procedures. The closeness of the measured values to the certified values of the reference material proves accuracy of the analytical methods. Recovery percentages were in the range of 90.0 to 107 %, indicating accuracy of the analytical technique employed in this study (Table 4.2).

Table 4.2: Results (mg/kg) of CRM (IAEA-359) showing certified values, measured values and percent recoveries.

Element	Certified value	n	Measured value			Mean	Percent recovery (%)
			1	2	3		
Arsenic (As)	0.100	3	0.100	0.080	0.090	0.090	90.0
Cadmium (Cd)	0.120	3	0.130	0.110	0.100	0.110	91.6
Chromium (Cr)	1.300	3	1.290	1.250	1.310	1.280	98.7
Mercury (Hg)	0.013	3	0.014	0.013	0.014	0.014	107
Nickel (Ni)	1.050	3	1.160	0.990	1.050	1.070	102

To further confirm the accuracy of the overall method, three replicates of one sample were spiked with known and increasing amounts of standard solutions of the metals. The spiked samples were digested using the same digestion procedure as the other samples, and analyzed to determine the metal concentration. Recovery percentages, summarized in Table 4.3, were in the range of 87 % to 107 %, which shows the accuracy of the analytical procedure used in this study.

Table 4.3: Results of spiked rice samples showing recovery amounts and percentages

Samples	Metals			
	Nobel Express (1.0 g)	As Added ( $\mu\text{g}$ )	As Found ( $\mu\text{g}$ )	As Recovered ( $\mu\text{g}$ )
None		0.0126	None	None
0.010		0.0215	0.0089	89
0.025		0.0388	0.0262	105
0.040		0.0551	0.0425	106
Nobel Express (1.0 g)	Cd Added ( $\mu\text{g}$ )	Cd Found ( $\mu\text{g}$ )	Cd Recovered ( $\mu\text{g}$ )	Percent Recovery (%)
	None	0.0539	None	None
	0.010	0.0631	0.0092	92
	0.025	0.0775	0.0236	94
	0.040	0.0949	0.041	103
Nobel Express (1.0 g)	Cr Added	Cr Found ( $\mu\text{g}$ )	Cr Recovered ( $\mu\text{g}$ )	Percent Recovery (%)
	None	0.1734	None	None
	0.010	0.1822	0.0088	88
	0.025	0.1951	0.0217	87
	0.040	0.2097	0.0363	91
Nobel Express (1.0 g)	Pb Added	Pb Found ( $\mu\text{g}$ )	Pb Recovered ( $\mu\text{g}$ )	Percent Recovery (%)
	None	0.0062	None	None
	0.010	0.0166	0.0104	104
	0.025	0.0279	0.0217	87
	0.040	0.0435	0.0373	93
Nobel Express (1.0 g)	Ni Added	Ni Found ( $\mu\text{g}$ )	Ni Recovered ( $\mu\text{g}$ )	Percent Recovery (%)
	None	0.1341	None	None
	0.010	0.143	0.0089	89
	0.025	0.1598	0.0257	103
	0.040	0.1769	0.0428	107

#### 4.1. Arsenic Concentration

The intake of food and drinking water is the major path of human exposure to arsenic, thus leading to its adverse effects (FDA, 2016). The levels of Arsenic (in mg/kg) in the rice sold on the local markets in Monrovia, Liberia (2017), are presented in Figure 4.1. The concentrations of Arsenic in the rice samples analyzed ranged from 0.0011 mg/kg to 0.0181 mg/kg. Foreign rice brands recorded concentration values in the range of 0.0011 mg/kg to 0.0181 mg/kg. The concentrations of As recorded in the locally cultivated rice ranged from 0.0011 mg/kg to 0.0064 mg/kg. Student

T-test performed at 95 % confidence interval using IBM-SPSS data analysis tool pack was used to compare the concentration values obtained for both the local and foreign rice brands. The comparative analysis produced a p-value of 0.002, which indicated a significant statistical difference in As concentration between the rice samples. The p-value ( $0.002 < 0.05$ ) showed that As concentrations in the imported rice samples were statistically higher than in the local rice samples. The difference in the results could be attributed to regional differences in the cultivation of the rice samples. Zavala and Duxbury (2008) reported that geographic location is the key factor to arsenic variability in rice grains. Overall, Red Star 2 recorded the highest value (0.0181 mg/kg) followed by UCI 2 (0.0178 mg/kg) and Uncle Mario 2 (0.0173 mg/kg). Pure White 1, Belleluna 1a and Bitter International 1 reported the least value 0.0011 mg/kg.

The concentrations of As in all the tested rice samples were less than 0.02 mg/kg, which is lower than 0.2 mg/kg, the threshold limit recommended by the National Food Standard Authority of China (Bugang and Woolsey, 2010) and the Codex Alimentary Commission (CODEX, 2015). The highest concentration (0.0181 mg/kg), which was found in Red Star 2, is about 0.182 folds or 91 % lesser than the Codex Alimentary Commission and the Chinese guideline (Figure 4.1). This showed low As Contamination of the rice products.

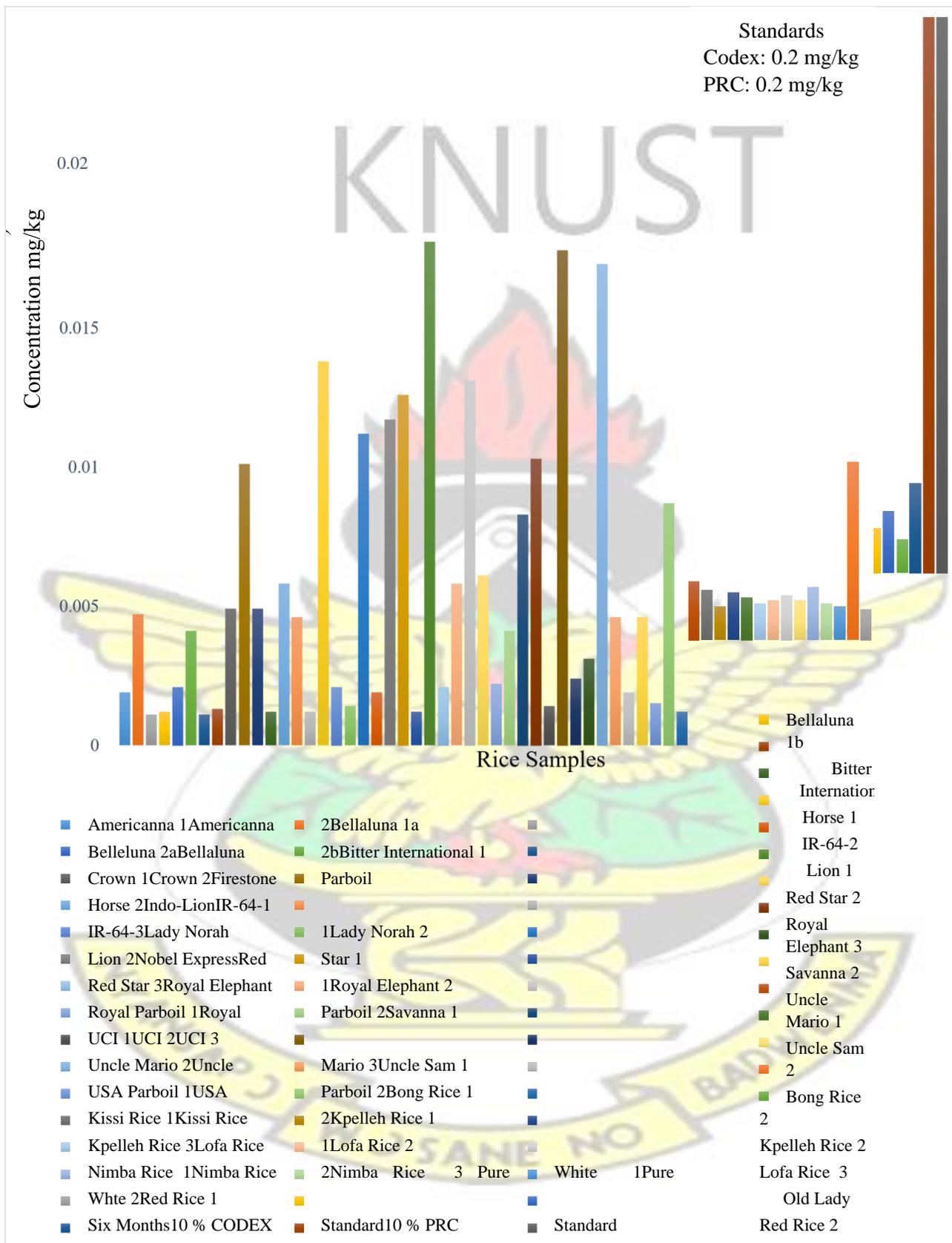


Figure 4.1: Concentration (mg/kg) of Arsenic (As) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

The processes that account for the presence of As in rice grains was examined by Meharg (2004). Though not clearly described, the author asserted that rice grown under continuous flood tends to have considerable amount of As in their edible part. This is due to the formation of iron oxyhydroxide plaque, which releases substantial amount of As in the plant. The formation of iron oxyhydroxide plaque results from the oxygenation of the plant's rhizosphere under anaerobic conditions, and the plaque formation rate increases under low phosphorus condition. According to the author, As is also transported to the grains via the root system of the plant by a phosphate cotransporter. This has been confirmed by other authors (Ma *et al.*, 2008). In another study by Ma *et al.* (2014), they explained that As behaves as an analog of water at neutral pH. It is transported to the plant's plasma membrane, and subsequently to the grains via the root system by an aquaporins transporters. In summary, conditions such as flood, that supports anaerobic activities in the soil promotes the accumulation of As in rice grain. Rice cultivated in region with continues flood may contain higher level of arsenic in their grains than those cultivated under different conditions.

The concentrations of As reported in this study are relatively low when compared to As levels in rice grain reported in other studies around the world. For example, As concentration reported in rice grains from Jharkhand, India were in the range 0.008 to 0.162 mg/kg (Giri and Singh, 2017). Song *et al.* (2015) determined the levels of As in rice samples from Suxian, China. The author reported As in the range of 0.02 to 1.48 mg/kg. The range is higher than those recorded in this study and far above the Chinese and Codex Alimentary Commission guideline of 0.2 mg/kg. The concentration of As reported in rice grains sampled from four districts (Manikgani, Camilla,

Brahmanbaria and Mushiganj) in Bangladesh were in the range 0.002 to 0.557 mg/kg (Rahman *et al.*, 2009). Zavala and Duxbury (2008) reported As concentration in the range of 0.005 to 0.710 mg/kg in rice samples purchased from retail stores in New York, USA. The range is high when compared to those reported in this study. The authors also combined their data set with other data sets reported in literature from several countries across the world, and reported global normal values of As contamination of rice in the range of 0.08 to 0.20 mg/kg, below which this study As values fall. The variation in these studies mentioned, confirms the statement that geographic factor plays key role in the levels of As in rice grains.

#### **4.1.1. Non Carcinogenic Health Risk to Arsenic**

Estimated Daily Intake and Hazard Quotients of As obtained in this study are presented in Figures 4.2 and 4.3 respectively. Hazard Quotients were obtained from the Estimated Daily intake and the Reference Dose of the metal. The Reference Dose of 0.0003 mg/kg/day obtained from the US EPA Integrated Risk Information System for As was used (US EPA, 2015). Estimated Daily Intake values for As were computed using the average 248 grams per day per bodyweight rice consumption rate of the inhabitants of Monrovia (GAIN, 2016), the US EPA recommended 70 kg bodyweight for adult in health risk assessment (US EPA, 2012), and the concentrations of As obtained in this study.

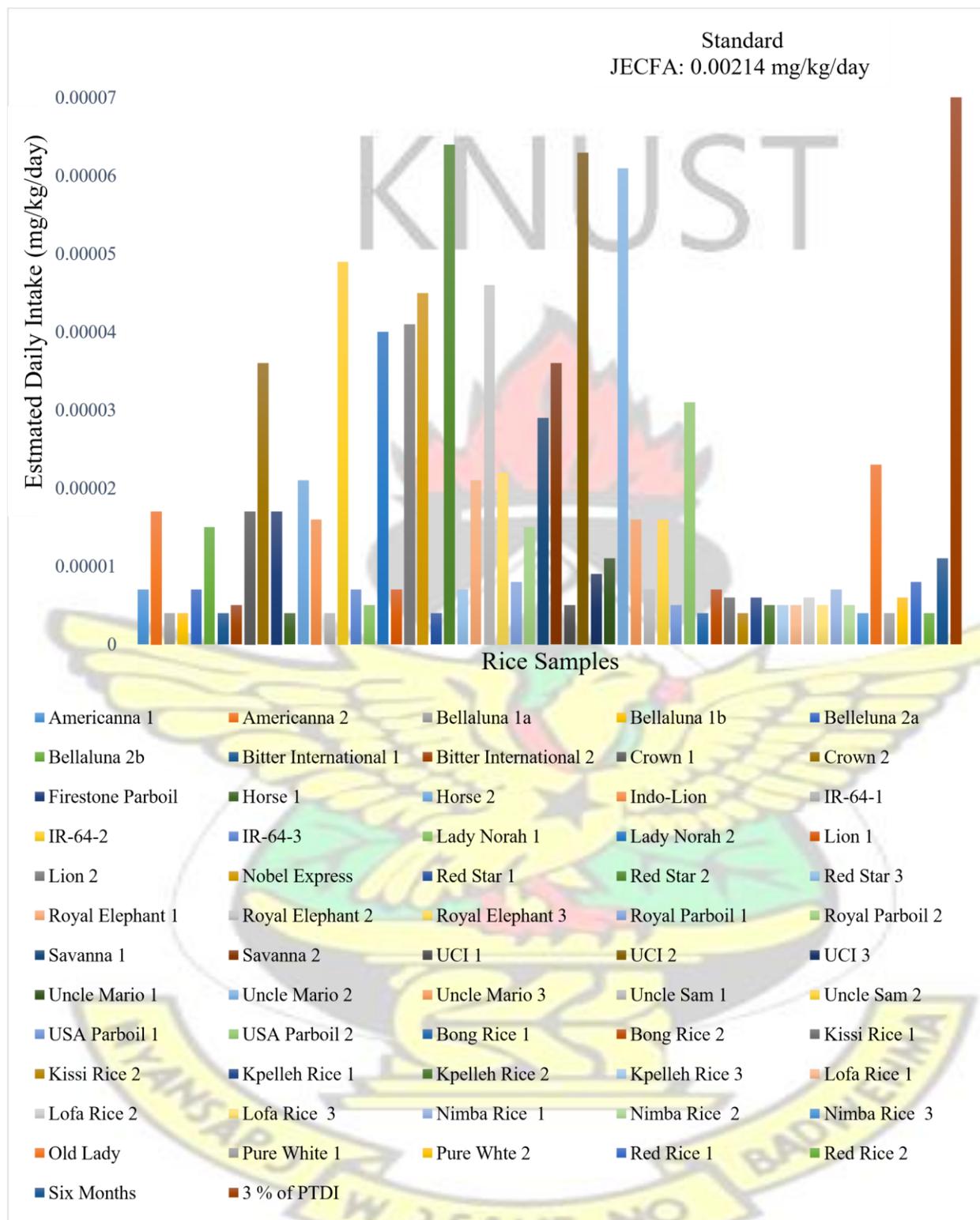


Figure 4.2: Dietary Intake (mg/kg/day) of Arsenic (As) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

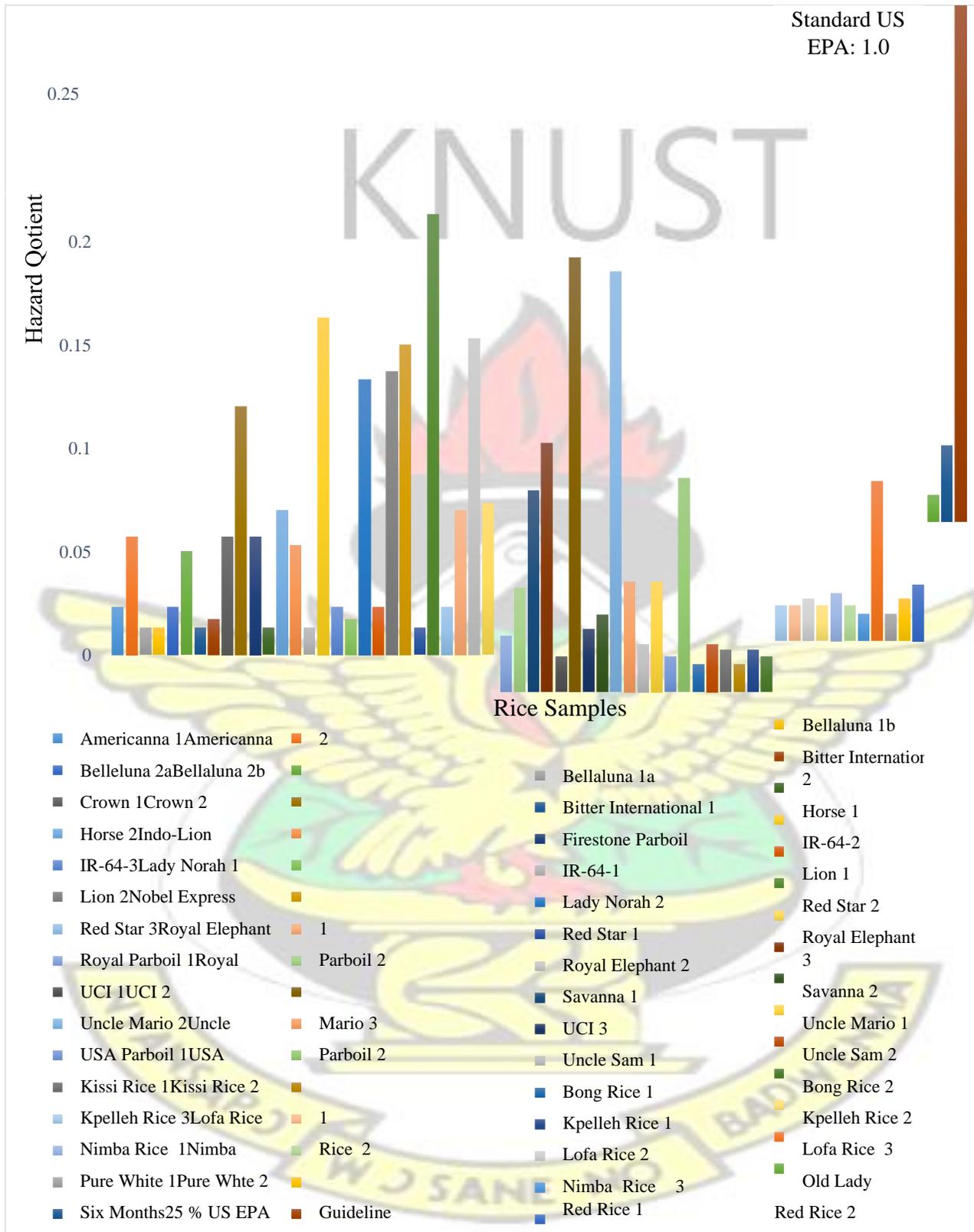


Figure 4.3: Hazard Quotients of Arsenic (As) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

The Estimated Daily Intake values, which quantified the amount of As ingested per day through the consumption of the rice samples evaluated in this study, were less than 0.00007 mg/kg/day, which is lower than the PTDI value of 0.00214 mg/kg/day recommended for As by JECFA (JECFA, 2010). This showed low dietary exposure of consumers to As. The Hazard Quotient values recorded for As in this study ranged from 0.013 to 0.213. The US EPA integrated metal risk assessment framework suggested that Hazard Quotient value equal to or less than one ( $\leq 1$ ) posed no expected non carcinogenic health risk to a population or an individual of that population (US EPA, 2007). All the studied rice samples recorded Hazard Quotient values less than 0.5, which indicates no potential non carcinogenic health risk from As toxicity to individuals who consumed the studied products. Therefore, no non carcinogenic health threat from As toxicity to the population of Monrovia through the consumption of the studied rice products is expected. The highest Hazard Quotient value for As was recorded in Red Star 2 (0.213). If an average individual consumed Red Star 2 at the regular consumption rate of 248 g per day, he/she consumed approximately 0.000064 mg of As, which is far below the daily consumption limit set by JECFA. To exceed the daily threshold, he/she would have to consume over 8.27 Kg of Red Star 2 per day. The range of the Hazard Quotient values reported in this study is far below the (0.258 to 1.076) reported by Song *et al.* (2015) for Chinese population in Suxian and the (0 to 14.183) range reported by Jolly, Huque and Islam (2014) for Bangladeshi population in northern Bangladesh.

#### **4.1.2. Carcinogenic Health Risk to Arsenic**

Arsenic is classified by IARC as a group one carcinogen, meaning, there is sufficient evidence that it is carcinogenic to human. Dietary exposure to the chemical posed excess risk to lungs, kidney and bladder cancers (Mulware, 2013). In this study, carcinogenic health risk posed to the population of Monrovia from As contaminated rice was assessed by using Incremental Lifetime

Cancer Risk values (US EPA, 2014b). For arsenic, the ingestion cancer slope factor of 1.5 (mg/kg/day)<sup>-1</sup> recommended by the US EPA was used in this study (US EPA, 2015) to compute the Incremental Lifetime Cancer Risk. Chronic Daily Intake and Incremental Lifetime Cancer Risk of As obtained in this study are presented in Figures 4.4 and 4.5 respectively.



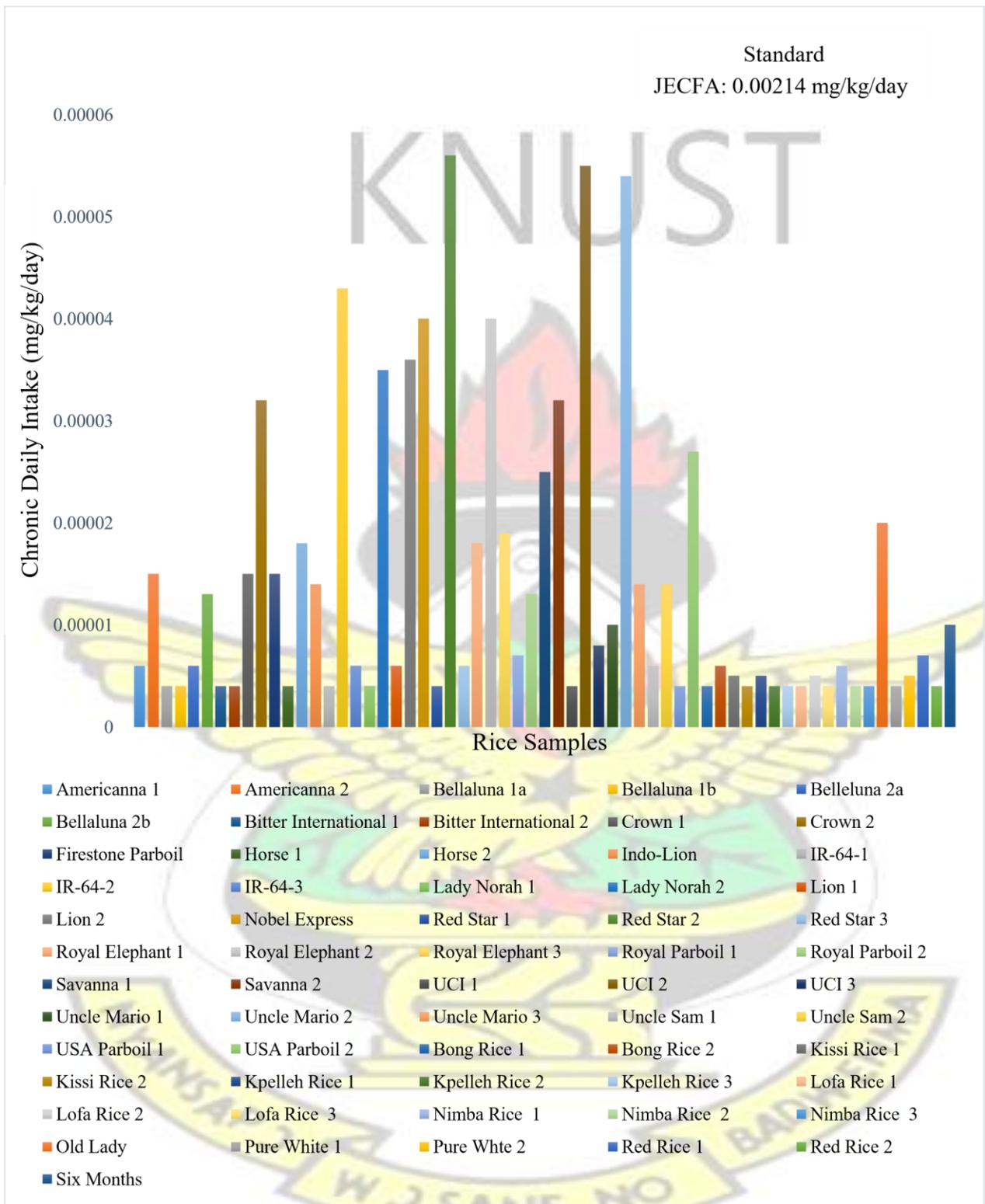
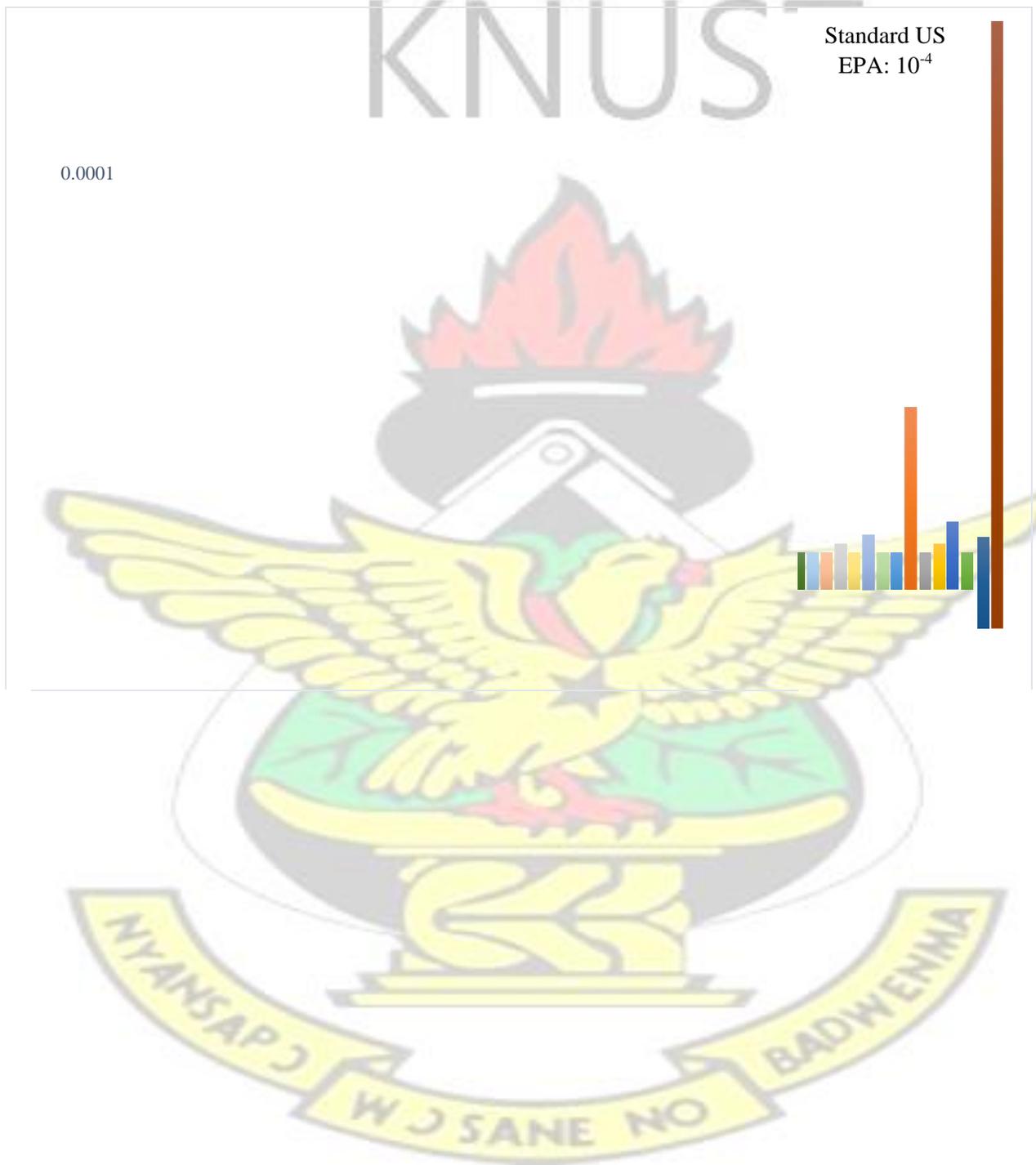


Figure 4.4: Chronic Daily Intake (mg/kg/day) of Arsenic (As) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).



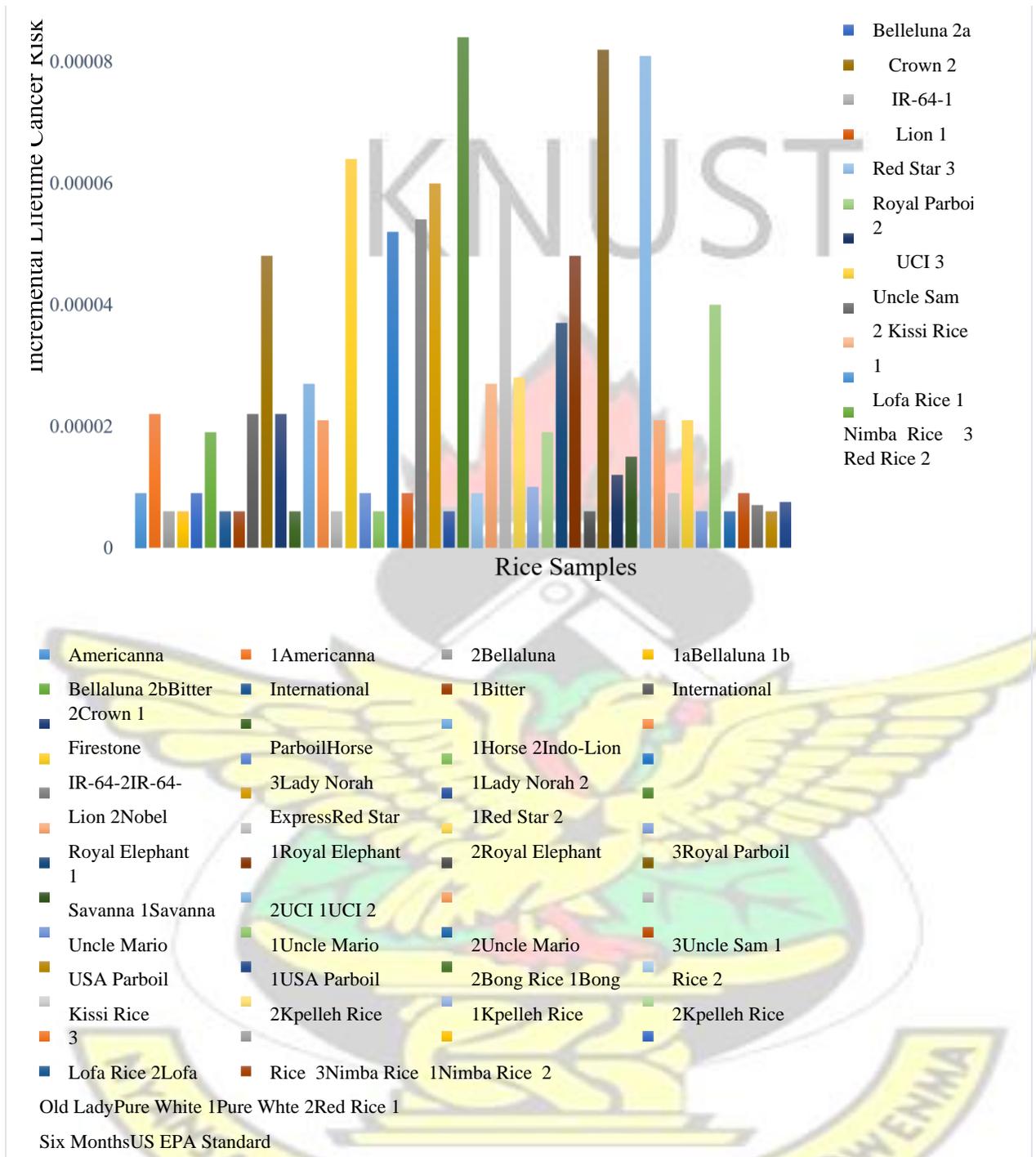


Figure 4.5: Incremental Lifetime Cancer Risk of Arsenic (As) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

The values obtained for the Incremental Lifetime Cancer Risks for As through the consumption of rice samples analyzed in this study ranged from  $6.0 \times 10^{-6}$  to  $8.4 \times 10^{-5}$ . According to the US EPA metal risk guideline, Incremental Lifetime Cancer Risk value equal to or greater than  $1.0 \times 10^{-3}$  ( $\geq 1.0 \times 10^{-3}$ ) is considered unsafe and requires public health concern (US EPA, 2015). Any Incremental Lifetime Cancer Risk value equal to or less than  $10^{-4}$  is labelled safe and posed no considerable expected carcinogenic health risk to a population (US EPA, 2007). This value shows the incremental probability of one individual in a population of ten thousand (1 in 10,000) to develop cancer from long term exposure to a carcinogen. Among the 61 rice sampled in this study, none recorded Incremental Lifetime Cancer Risk value above the threshold limit, thus calls for no public health concern. The highest Chronic Daily Intake value for As (0.000056 mg/kg/day) in the tested rice samples was found in Red Star 2. However, significantly low to produce chronic effect from long term consumption of the product, as revealed from the Incremental Lifetime Cancer Risk value ( $8.4 \times 10^{-5}$ ) obtained.

The range of Incremental Lifetime Cancer Risk values reported in this study is not high when compared with other studies. For example, Fan *et al.* (2017) determined Incremental Lifetime Cancer Risks values for As in rice consumed in major cities in China. The authors reported an average value of  $3.0 \times 10^{-4}$ , higher than the values recorded in this study. In a study performed by Fakhri *et al.* (2018) on 21 studies conducted between 2008 and 2017 in Iran to ascertain the carcinogenic health risk posed to population of different cities, the authors found Incremental Lifetime Cancer Risk values for As in the range of  $4.53 \times 10^{-2}$  to  $5.50 \times 10^{-2}$ , which is far above this study values and also the threshold value.

#### 4.2. Cadmium Concentration

The concentrations (in mg/kg per) of Cadmium in the rice sold on the local markets in Monrovia, Liberia (2017), are presented in Figure 4.6. The concentrations of Cadmium in the rice samples analyzed ranged from 0.0048 mg/kg to 0.1179 mg/kg. The concentrations of Cd recorded in the locally cultivated rice samples ranged from 0.0061 mg/kg to 0.0982 mg/kg. Foreign rice samples documented Cd concentration values in the range of 0.0048 mg/kg to 0.1179 mg/kg. The data were subjected to Student T-test performed at 95 % confidence interval using IBM-SPSS data analysis tool pack to compare the concentration levels obtained for the locally cultivated rice brands to the foreign rice brands. A p-value of 0.195, which is greater than 0.05, was obtained from the comparative analysis. This indicates no significant statistical difference in the concentrations of Cd between the locally cultivated and the foreign rice brands. In general, Uncle Sam 2 gave the highest value (0.1179 mg/kg) followed by Lofa Rice 3 (0.0982 mg/kg) and Red Rice 1 (0.0819 mg/kg). Savanna 1 reported the least value (0.0048 mg/kg), followed by Savanna 2 (0.0052 mg/kg) and Bitter International 1 (0.0057 mg/kg).

Cd concentrations reported in all the rice samples analyzed in this study were less than 0.20 mg/kg, which is less than the 0.40 mg/kg threshold limit recommended by the Codex Alimentary Commission (CODEX, 2015). The values were also less than the 0.2 mg/kg limit recommended by the European Commission (EC, 2006), and adopted by the Republic of Ireland (FSAI, 2009) and China (Bugang and Woolsey, 2010). The Codex Standard is 0.2821 folds higher than the highest Cd concentration found in the samples. This showed low cantamination of the samples by Cd.

0.2	Standards
	Codex: 0.4 mg/kg EC: 0.2 mg/kg

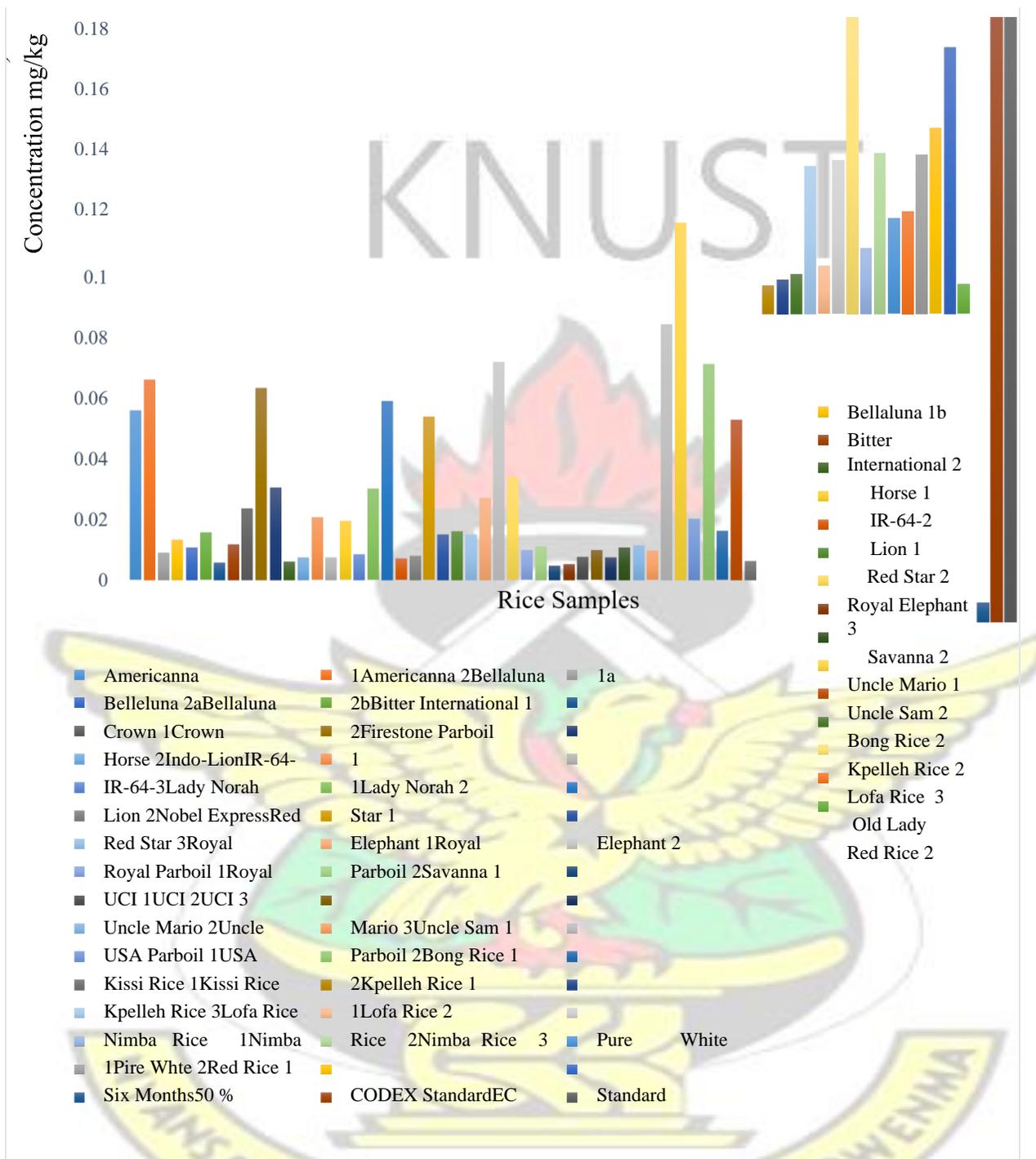


Figure 4.6: Concentration (mg/kg) of Cadmium (Cd) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

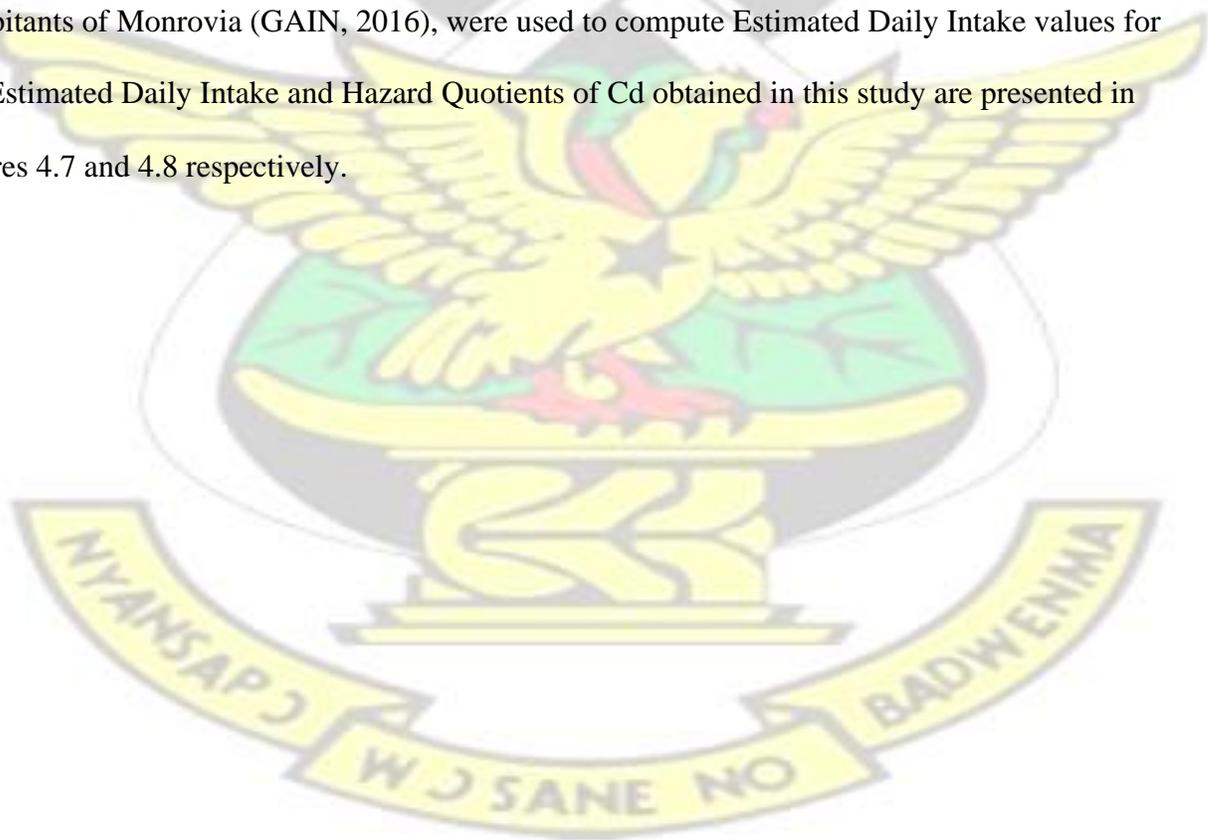
Cadmium is phytotoxic to plant, however, rice is one of the plants that highly accumulates bioavailable cadmium in soil (Liu *et al.*, 2007). The mechanism for its uptake and accumulation in

the grain was elucidated by Das *et al.*, (1997). According to the authors, the similarities of Cd to essential elements such as Ca and Mg are the major reasons for its presence in rice grains. It is highly mobile, soluble and persist in the soil. Even in minute concentration, and under low conditions of these elements (Ca and Mg), it is passively or actively absorbed by the root system and translocated to other parts of the plants. Nramp5 transporter is responsible for the transportation of the element to the plant's root cells (Ma *et al.*, 2015). In the root cells, xylem tissues collect and transport Cd to the shoots and directly to the developing grains. Cd transported to the shoots are stored and later transported by the phloem to the panicle, which bears the fruits (Li *et al.*, 2017). Despite these processes, Ma *et al.* (2015) noted that the level of cadmium in rice can be reduced by the presence of silicon (Si) in the plant's cell wall. According to the authors, Si is able to displace Cd from the plant's cells. Though silicon is predominant in soil, it is not in a bioavailable form for uptake by rice plants. Therefore, silicate fertilizers are usually employed in rice production. The application of this fertilizer inhibits the uptake of the element, contributing to its low level in the grain of the plant.

The levels of Cd concentration reported in this study were either low or in agreement with the levels of Cd in rice grains reported in other studies around the world. For example, Cd concentration in rice grains reported by Jalbani *et al.* (2014) in a study conducted to find out the level of Cd in rice consumed in Sindh, Pakistan, were in the range 0.001 to 0.129 mg/kg, which is in agreement with this study values. Cd level in rice grains from Ghaemshahr, Iran, were in the range 0.12 to 0.83 mg/kg (Zazouli *et al.*, 2008), below which this study values fall. Locally grown rice consumed in Taegu, South Korea, were reported to contain Cd in the range 0.01 to 0.98 mg/kg (Kwon *et al.*, 2016), below which values from this study fall.

#### 4.2.1. Non Carcinogenic Health Risk to Cadmium

In this study, dietary exposure of consumers to Cd in the analyzed rice samples was assessed by comparing the Estimated Daily Intake of Cd to the Joint FAO/WHO Expert Committee on Food Additives recommended Provisional Tolerable Daily Intake of the metal; and the non-carcinogenic health risk posed to the population of Monrovia from the Cd contaminated rice was assessed using Hazard Quotient values obtained from the Estimated Daily intake and the reference dose of the metal. The Reference Dose for Cd (0.001 mg/kg/day) obtained from the US EPA Integrated Risk Information System was used in this study (US EPA, 2015). The concentrations of Cd found in this study, the US EPA recommended 70 kg body weight for adult in health risk assessment (US EPA, 2012), and the average 248 grams per day per bodyweight rice consumption rate of the inhabitants of Monrovia (GAIN, 2016), were used to compute Estimated Daily Intake values for Cd. Estimated Daily Intake and Hazard Quotients of Cd obtained in this study are presented in Figures 4.7 and 4.8 respectively.



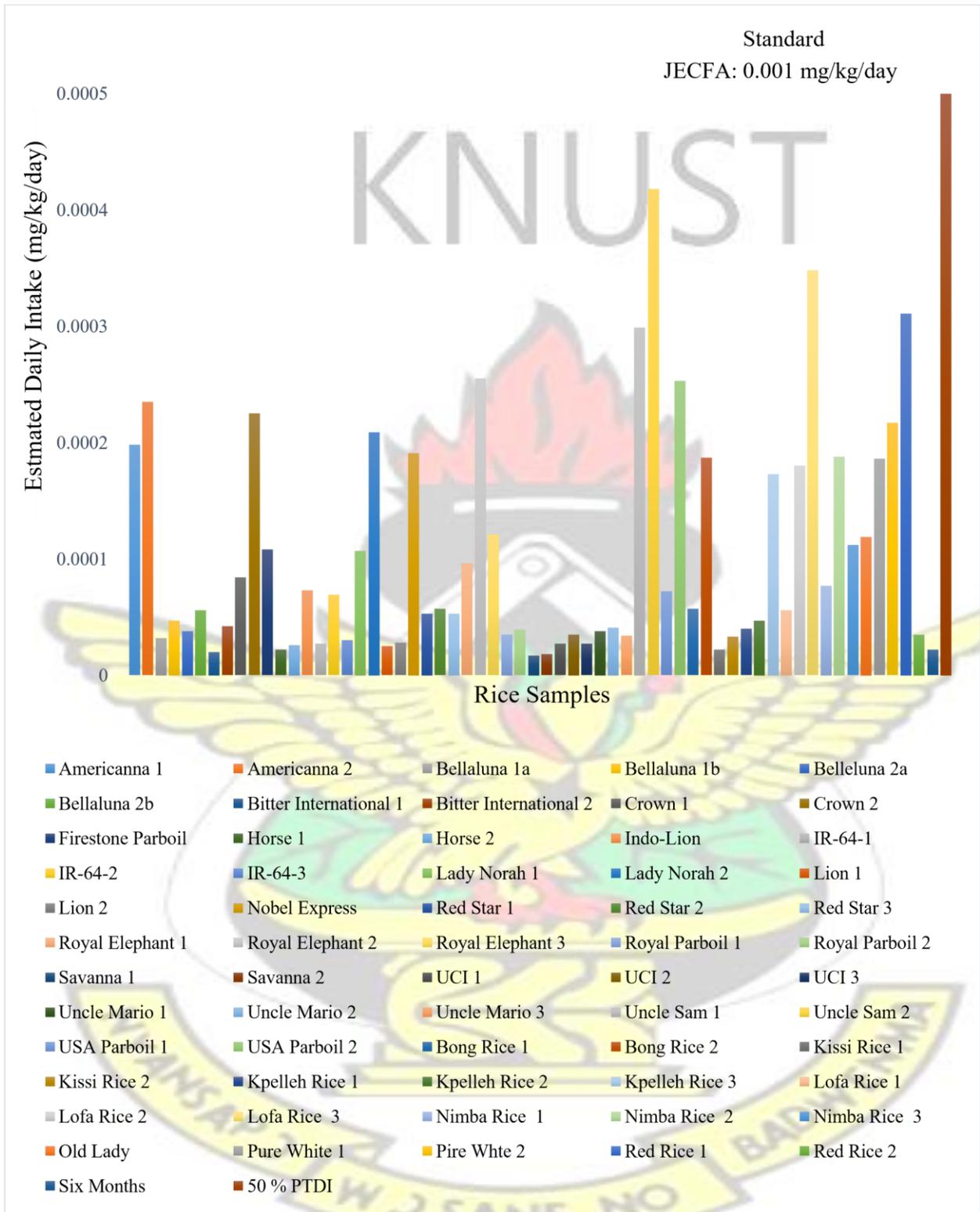
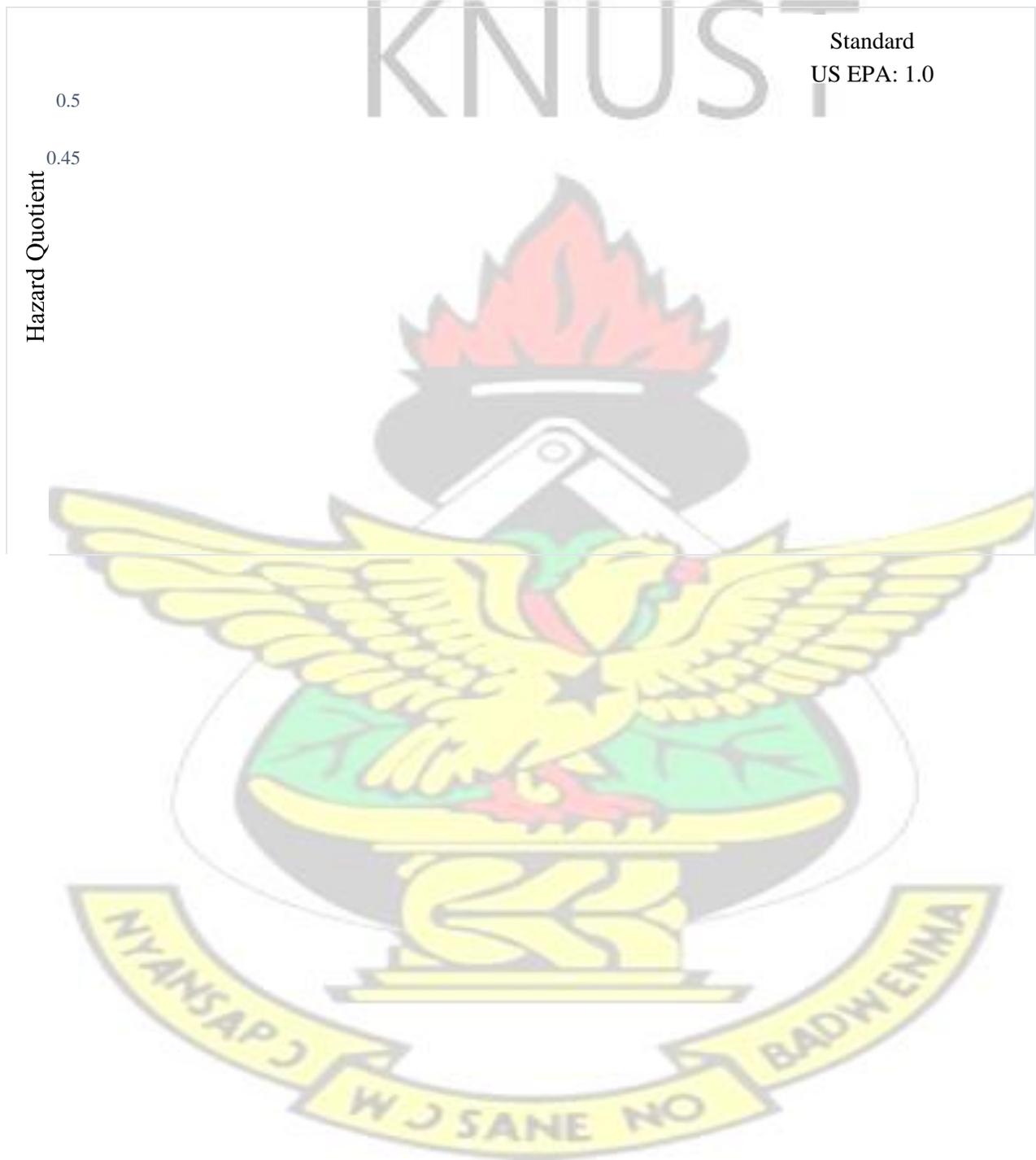


Figure 4.7: Dietary Intake (mg/kg/day) of Cadmium (Cd) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).



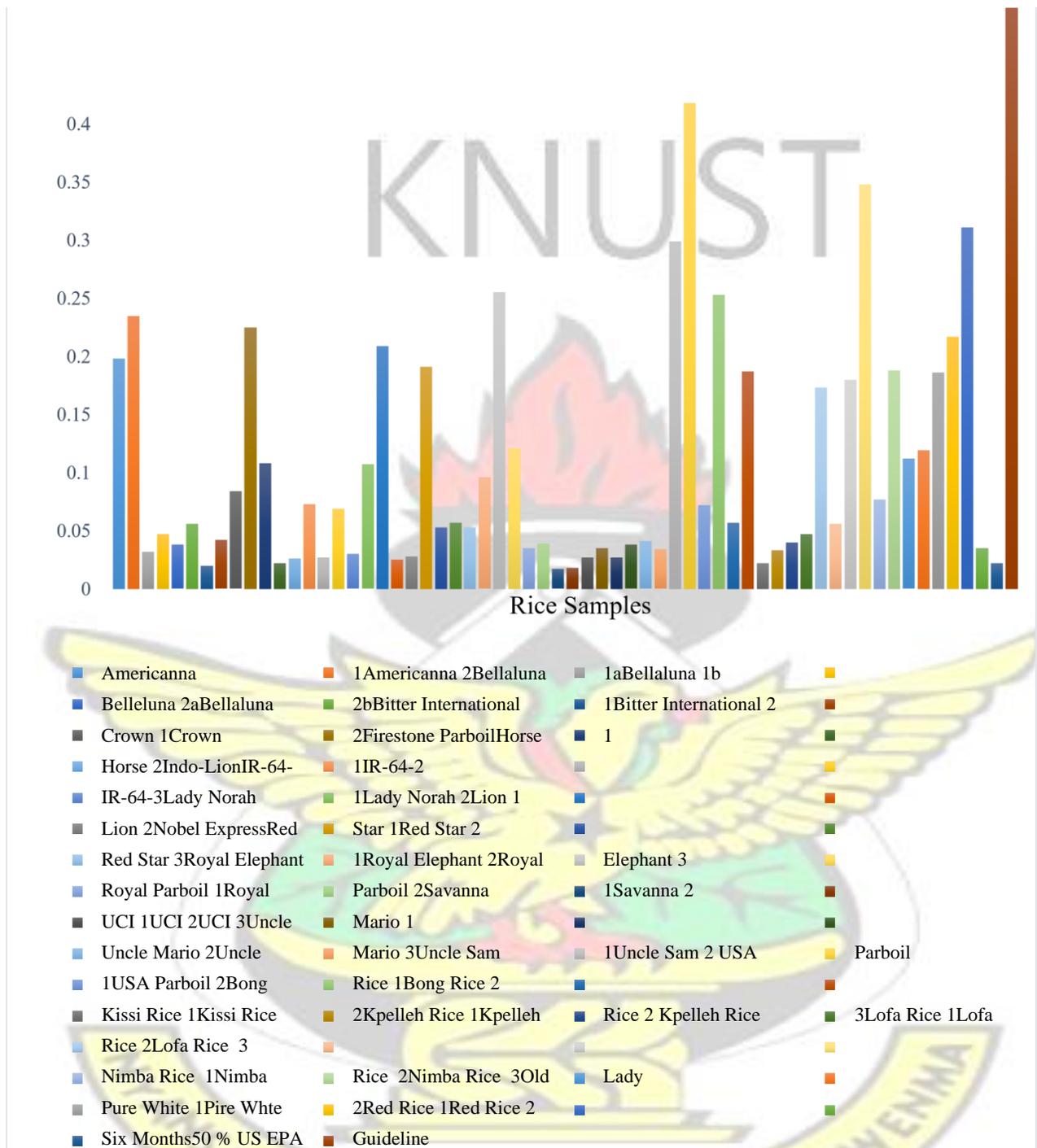


Figure 4.8: Hazard Quotients of Cadmium (Cd) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

All the Estimated Daily Ingestion values obtained for Cd through the consumption of the rice samples tested in this study were less than 0.0005 mg/kg/day, which is lower than the 0.001

mg/kg/day PTDI value recommended for Cd by JECFA (JECFA, 2010). Therefore, the amount of Cd ingested per day from the consumption of the rice products sampled in the study is significantly low, and poses no potential non carcinogenic health risk to consumers. The highest concentration of Cd recorded in this study was found in Uncle Sam 2 (0.1179 mg/kg). If an average person consumes 248 g of Uncle Sam 2 per day, he/she would consume approximately 0.000418 mg of Cd, which is significantly below the permissible consumption amount per day. To exceed the recommended daily threshold, he/she would have to consume over 345.7 g of Uncle Sam 2, in addition to the normal 248 g consumption rate per day. Hazard Quotient values recorded for Cd in this study ranged from 0.017 to 0.418, lower than the range 1.797 to 2.353 reported by Song *et al.* (2015). From the observed Hazard Quotient values, and based on the US EPA guideline, the rice brands analyzed in this study posed no non carcinogenic health risk from Cd toxicity to the population of Monrovia through their consumption.

#### **4.2.2. Carcinogenic Health Risk to Cadmium**

Cadmium is classified by the IARC as a human carcinogen, and its carcinogenic activities reported in several studies have been documented (Mulware, 2013). However, the US EPA is yet to establish the ingestion cancer slope factor for cadmium. Therefore, carcinogenic health risk posed to the population of Monrovia from Cd contaminated rice in the form of Incremental Lifetime Cancer Risk was not assessed in this study.

#### **4.3. Chromium Concentration**

Chromium (Cr) is an essential element for both plant and animal, but becomes toxic at considerable high level. It is carcinogenic and its accumulation in the human body can lead to anemia and ulcer (Martin and Griswold, 2009). The levels of Chromium (in mg/kg) in the rice sold on the local

markets in Monrovia, Liberia (2017) are presented in Figure 4.9. The concentrations of Chromium in the rice samples analyzed ranged from 0.0050 mg/kg to 0.4245 mg/kg. The concentrations of Cr recorded in the locally cultivated rice and the foreign rice brands ranged from 0.0069 mg/kg to 0.4245 mg/kg and 0.0050 mg/kg to 0.3750 mg/kg respectively. Student T-test at 95 % confidence interval performed on the data using IBM-SPSS data analysis tool pack produces a p-value of 0.960, which indicates no significant statistical difference in the concentration of Cr between the local cultivated and the foreign rice samples. The highest concentration of Cr was found in Kissi Rice 2 (0.4245 mg/kg), followed by Royal Elephant 1 (0.3750 mg/kg) and Savanna 2 (0.2987 mg/kg). Savanna 1 reported the least Cr concentration (0.0050 mg/kg), followed by Royal Elephant 2 (0.0058 mg/kg) and Horse 1 (0.0062 mg/kg).

Codex Alimentary Commission is yet to define a threshold limit for chromium in rice and other grains or cereals (CODEX, 2015). However, the National Food Safety Committee of the Chinese Health Ministry had established 1.5 mg/kg as the threshold for Cr in rice and other cereals (Bugang and Woolsey, 2010). Cr concentrations in all the rice samples analyzed in this study were less than 0.5 mg/kg, which is less than that permissible limit. The difference between the Codex Standard and the highest value of Cr found is about 1.076 mg/kg, which is about 72 % of the standard value. This indicates that the level of contamination is not significant.



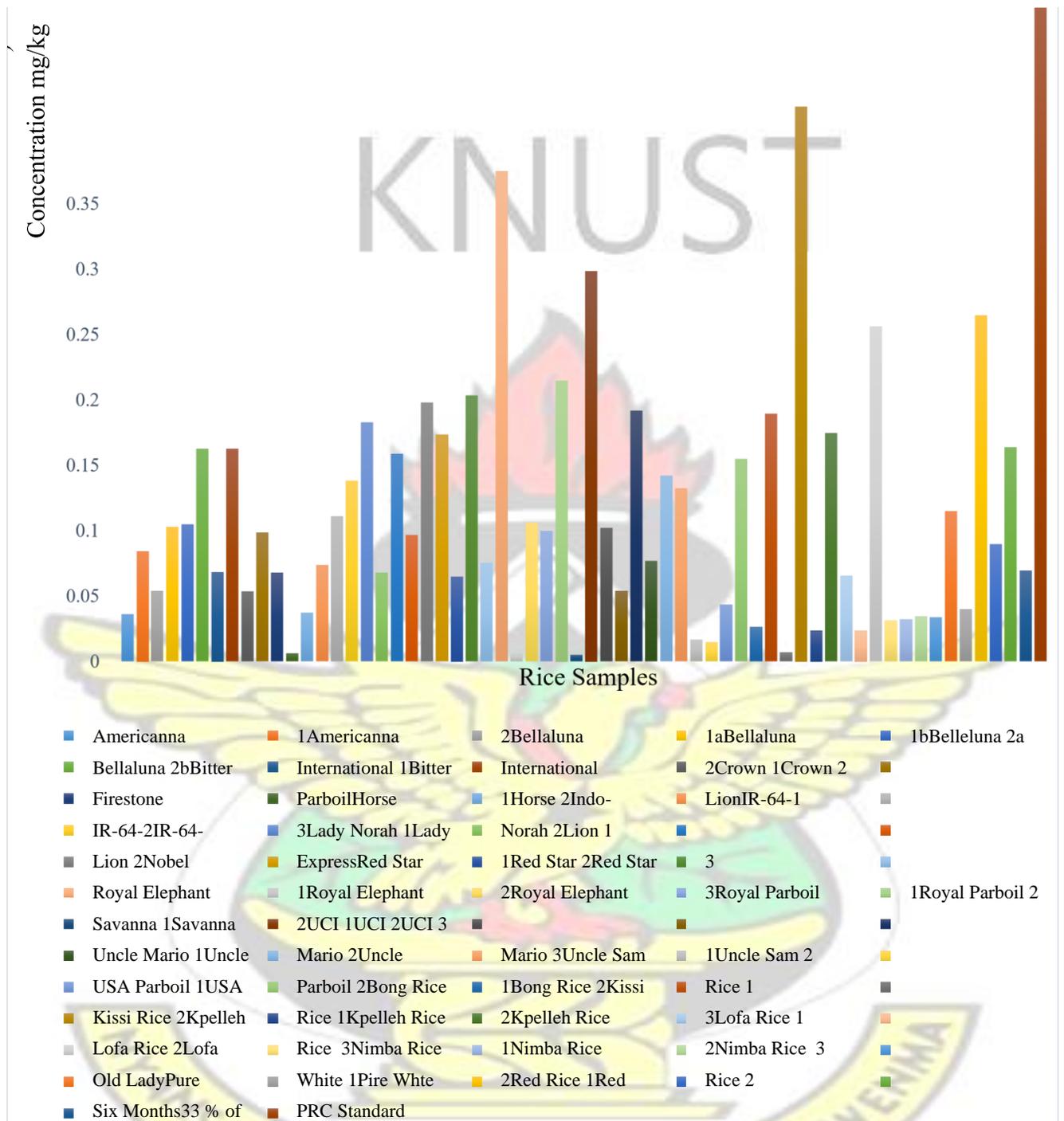


Figure 4.9: Concentration (mg/kg) of Chromium in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

Chromium is naturally present in rice grain. It is needed in minute concentration for growth stimulation (Tripathi *et al.*, 2012). Under normal soil condition, rice is known to absorb and utilize

minute concentration of chromium. The uptake process is similar to the uptake of iron. Therefore, in excess amount, chromium suppresses the uptake of iron, leading to the absorption of more soluble and exchangeable chromium by the plant (Bhattacharyya *et al.*, 2005). In a hydroponic experiment conducted by Tripathi *et al.* (2012), the authors explained that the application of exogenous silicon fertilizer, that is usually practiced in rice production, decreased chromium rootshoot-grain transport and enhanced its tolerance.

The level of Chromium concentrations reported in this study is not high when compared with other studies in literature. For example, this study values are below the concentration range (1.37 to 2.82 mg/kg) reported in a study conducted in Northern Wisconsin, USA (Bennett *et al.*, 2000). FerréHuguet *et al.* (2008) determined the level of Cr in rice samples from Catalonia, Spain. The author reported Cr concentration in the range of 0.02 to 0.90 mg/kg, below which this study values also fall. Values reported from Zhejiang, China (0.1186 to 0.4983 mg/kg) and Shiraz, Iran (0.33 to 0.44 mg/kg) are in agreement with the values recorded in this study (Fu *et al.*, 2008; Naseri *et al.*, 2014). **4.3.1. Non Carcinogenic Health Risk to Chromium**

Several studies have documented the adverse effects of chromium to human health (Martin and Griswold, 2009; NJDOH, 2009; ATSDR, 2011). In this study, dietary exposure of consumers to Cr in the analyzed rice samples was assessed by comparing the Estimated Daily Intake of Cr to its recommended Provisional Tolerable Daily Intake set by the Joint FAO/WHO Expert Committee on Food Additives; and the non-carcinogenic health risk posed to the population of Monrovia from the Cr contaminated rice was assessed by using Hazard Quotient values obtained from the Estimated Daily intake and the reference dose of the metal. The Reference Dose of 0.003 mg/kg/day obtained from the US EPA Integrated Risk Information System for Cr was used in this study (US EPA, 2015). The concentrations of Cr obtained in this study, the US EPA recommended

70 kg body weight for adult in health risk assessment (US EPA, 2012), and the average rice consumption rate (248 grams per day per bodyweight) of the inhabitants of Monrovia (GAIN, 2016), were used to compute Estimated Daily Intake values for Cr. Estimated Daily Intake and Hazard Quotient of Cr obtained in this study are presented in Figures 4.10 and 4.11 respectively.



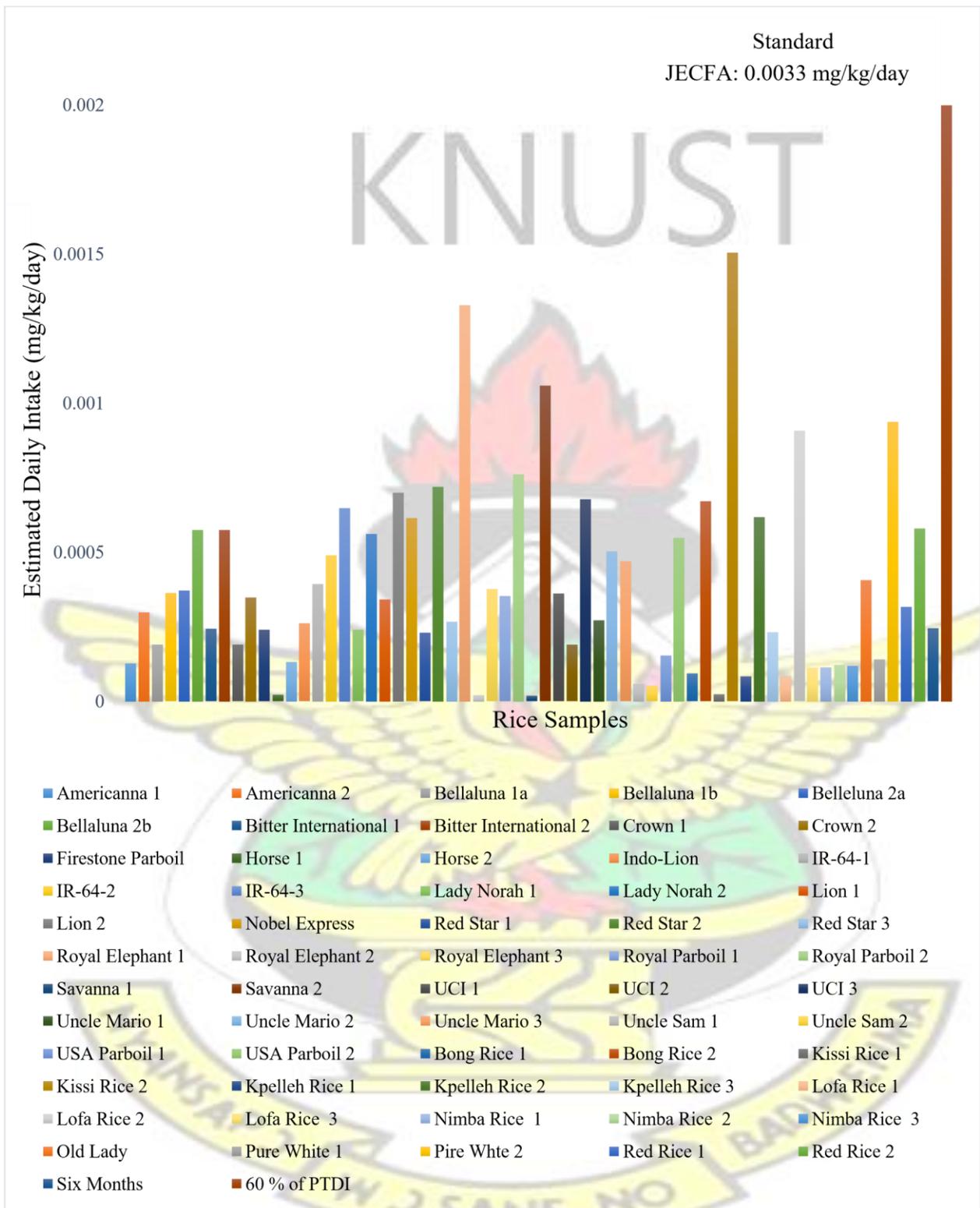
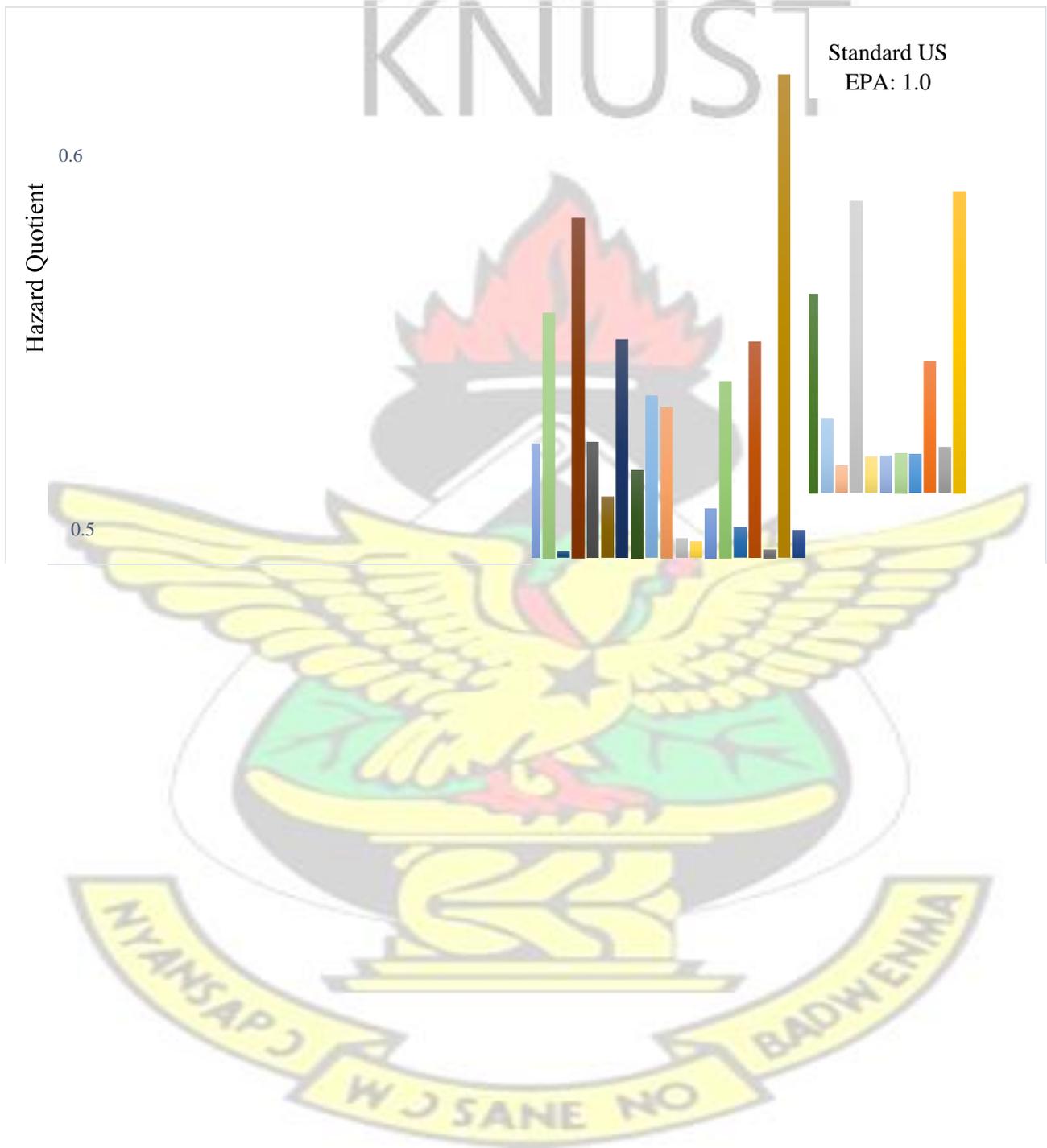


Figure 4.10: Dietary Intake (mg/kg/day) of Chromium (Cr) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).



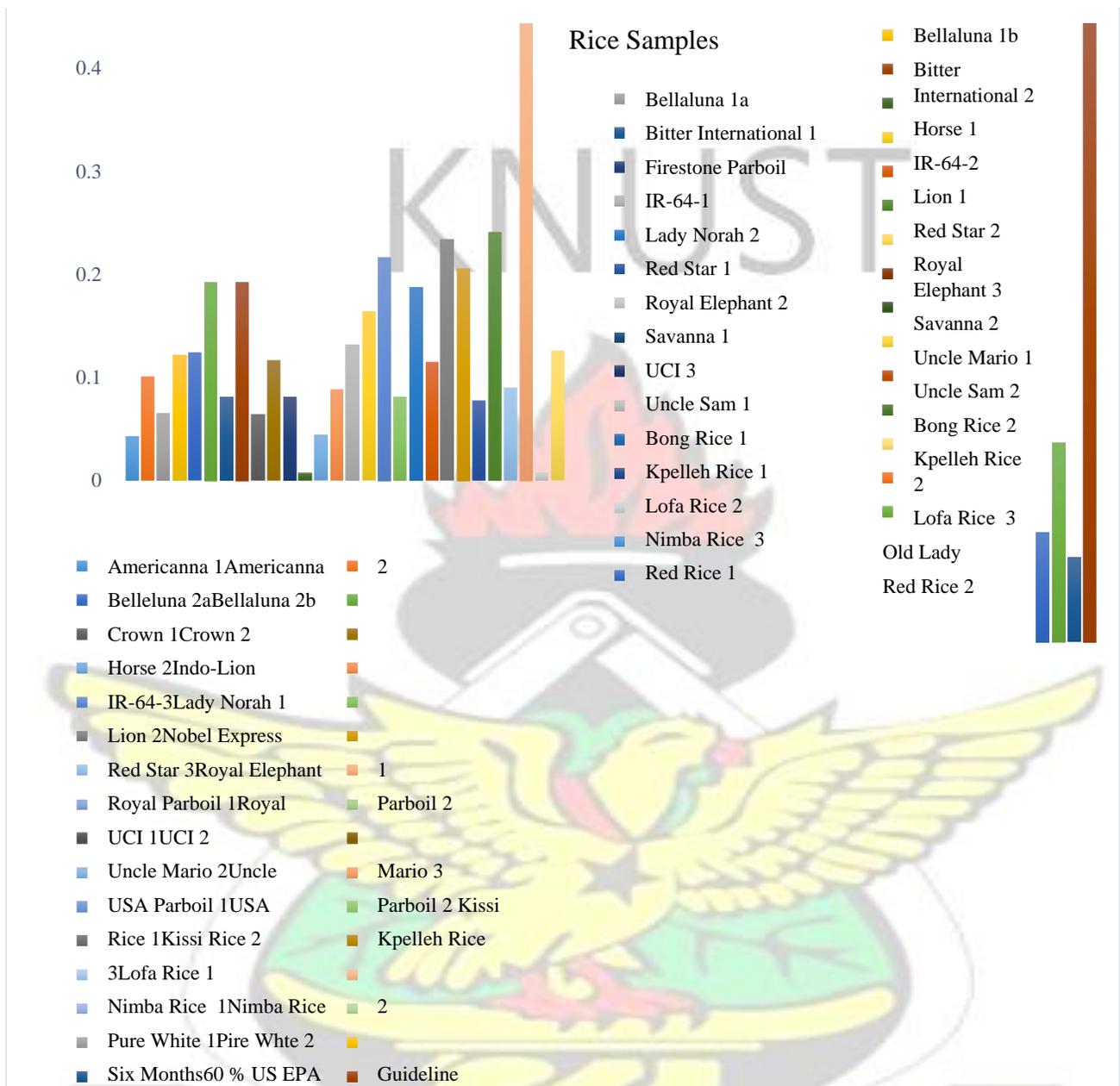


Figure 4.11: Hazard Quotient of Chromium (Cr) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

All the daily ingestion values estimated for Cr through the consumption of the rice brands sampled in this study were less than 0.002 mg/kg/day, which is lower than the 0.0033 mg/kg/day PTDI value recommended for Cr by JECFA (JECFA, 2010). This indicates that the amount of Cr exposed

to or consumed per day from the consumptions of the rice products sampled in the study is significantly too low to pose a considerable potential carcinogenic health threat to consumers.

The highest concentration of Cr recorded in this study was found in Kissi Rice 2 (0.4245 mg/kg). If an average person consumes 248 g of Kissi Rice 2 per day, he/she would consume approximately 0.001504 mg of Cr, which is considerably below the maximum consumption amount per day. To exceed the daily recommended threshold, he/she would have to consume over 544.2 g of Kissi Rice 2, which is nearly three times the usual consumption rate. Hazard Quotient range recorded for Cr in this study (0.006 to 0.501) were lower than the range (0.003 to 1.67) reported in literature (Giri and Singh, 2017). Based on the US EPA guideline and the observed Hazard Quotients values, no non carcinogenic health threat from Cr toxicity to the population of Monrovia through the consumption of the rice products analyzed in this study is expected.

#### **4.3.2. Carcinogenic Health risk to Chromium**

Chromium is classified by the IARC as a group one carcinogen, and its carcinogenic activities described in several studies have been documented (Mulware, 2013). However, the US EPA is yet to establish the ingestion cancer slope factor for chromium. Therefore, carcinogenic health risk posed to the population of Monrovia from Cd contamination of rice in the form of Incremental Lifetime Cancer Risk was not assessed in this study.

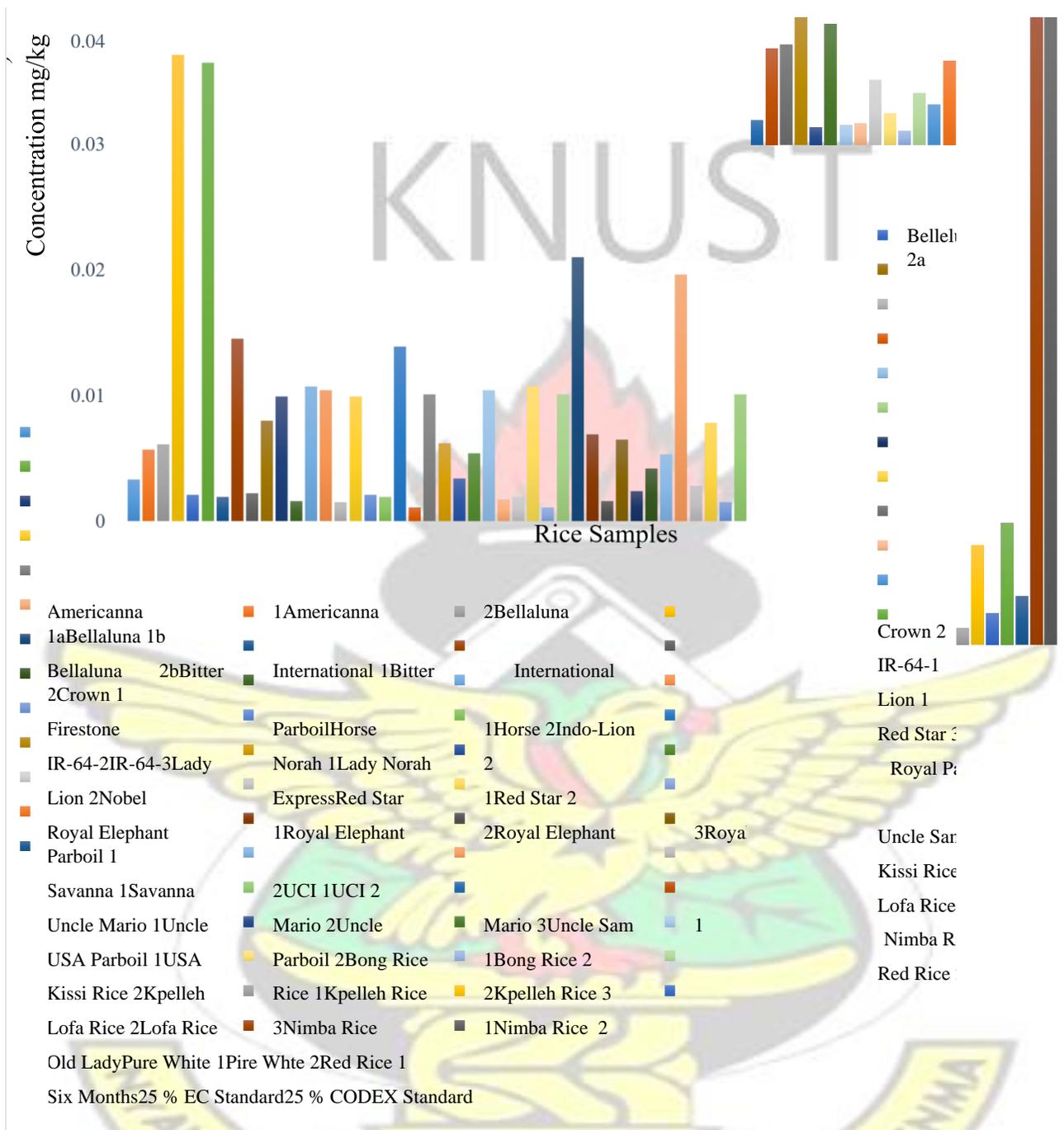
#### **4.4. Lead Concentration**

Lead (Pb) is a non-essential element and has no biological significance to human (Kielhorn *et al.*, 2006). The levels of Pb (in mg/kg) in the rice sold on the local markets in Monrovia, Liberia (2017) are presented in Figure 4.12. The concentrations of Lead in the rice samples analyzed ranged from 0.0011 mg/kg to 0.0371 mg/kg. The locally cultivated studied rice samples recorded Pb

concentrations in range from 0.0011 mg/kg to 0.0102 mg/kg while the foreign rice samples documented Pb concentrations in the range of 0.0011 mg/kg to 0.0371 mg/kg. After subjecting the data to Student T-test performed at 95 % confidence interval using IBM-SPSS data analysis tool pack, a p-value of 0.113 was generated, which indicates no statistical difference in Pb concentrations between the rice products. Generally, Belleluna 1b reported the highest concentration (0.0371 mg/kg), followed by Belleluna 2b (0.0365 mg/kg) and Savanna 1 (0.0210 mg/kg). The least Pb concentration (0.0011 mg/kg) was recorded in Lion 1, Nimba Rice 1 and Royal Elephant 1.

The concentration of Pb in all the rice samples analyzed in this study were less than 0.05 mg/kg, which is less than the 0.20 mg/kg threshold limit recommended by the European Commission (EC, 2006) and the Codex Alimentary Commission (CODEX, 2015), and adopted by health authorities in the Republic of Ireland (FSAI, 2009), China (Bugang and Woolsey, 2010), New Zealand (FSANZ, 2016) and Hong Kong (CFS, 2017). The standand value is about 5 times the highest concentration value obtained for Pb in this study, indicating very low contamination of the products by Pb.





of the metal absorbed by the plant. According to Liu *et al.* (2003), the accumulation of Pb in rice greatly decreased from root to shoots and to grain. In a pot experiment conducted by the authors, they observed less concentration of the metal in grain than other parts of the plants; and only 32.88 % of accumulated Pb in the grain was recovered after polishing. Under normal soil condition, rice is known to contain low level of Pb in its grains (Zeng *et al.*, 2008).

The level of Pb concentrations found in the rice samples examined in this study are either in agreement or much lower when compared to Pb concentration reported in rice by some published studies around the world. For example, the levels of Pb concentration reported in rice purchased from markets in four regions of northern Nigeria (Kaduna, Nasarawa, Bomo and Taraba) were in the range 0.311 to 0.525 mg/kg (Otitoju *et al.*, 2014), below which the values obtained for this study fall. Also in Sydney, Australia, Rahman *et al.* (2014) piloted a study to examine the levels of Pb in rice sold in the region. The authors reported Pb concentration in the range 0.016 to 1.248 mg/kg, which is above the range recorded in this study. This study values were also lower than the concentration range (0.0231 to 1.529 mg/kg) of Pb found in rice from Riyadh, Saudi Arabia (AlSaleh and Shinwari, 2001), but in agreement with the range 0.005 to 0.220 mg/kg reported from Zhejiang, China (Huang *et al.*, 2013).

#### **4.4.1. Non Carcinogenic Health Risk to Lead**

Lead has several adverse health effects on human. For example, its toxicity caused damage to the kidney, heart, lungs and reproductive organs (Kielhorn *et al.*, 2006). In this study, dietary exposure of consumers to Pb in the analyzed rice samples was assessed by comparing the Estimated Daily Intake of Pb to its Provisional Tolerable Daily Intake recommended by the Joint FAO/WHO Expert Committee on Food Additives; and the non-carcinogenic health risk posed to the population of

Monrovia from the Pb contaminated rice was assessed by using Hazard Quotient values that were obtained from the Estimated Daily intake and the reference dose of the metal. The US EPA had not established a reference dose for Pb (US EPA, 2015) due to improbability about its health effects. According to the agency, some of its effects occur at level so low as to be basically without threshold. Thus, found it inappropriate to develop reference dose for the metal. However, the World Health Organization established 0.0036 mg/kg-day as the maximum daily permissible dose of the metal (Fan *et al.*, 2017). This value was therefore used in this study. The US EPA recommended 70 kg body weight for adult in health risk assessment (US EPA, 2012), the average rice consumption rate (248 grams per day per bodyweight) of the inhabitants of Monrovia (GAIN, 2016), and the concentrations of Pb obtained in this study were used to compute Estimated Daily Intake values for the metal. Estimated Daily Intake and Hazard Quotients obtained for Pb in this study are presented in Figures 4.13 and 4.14 respectively.

Standard JECFA: 0.00357 mg/kg/day
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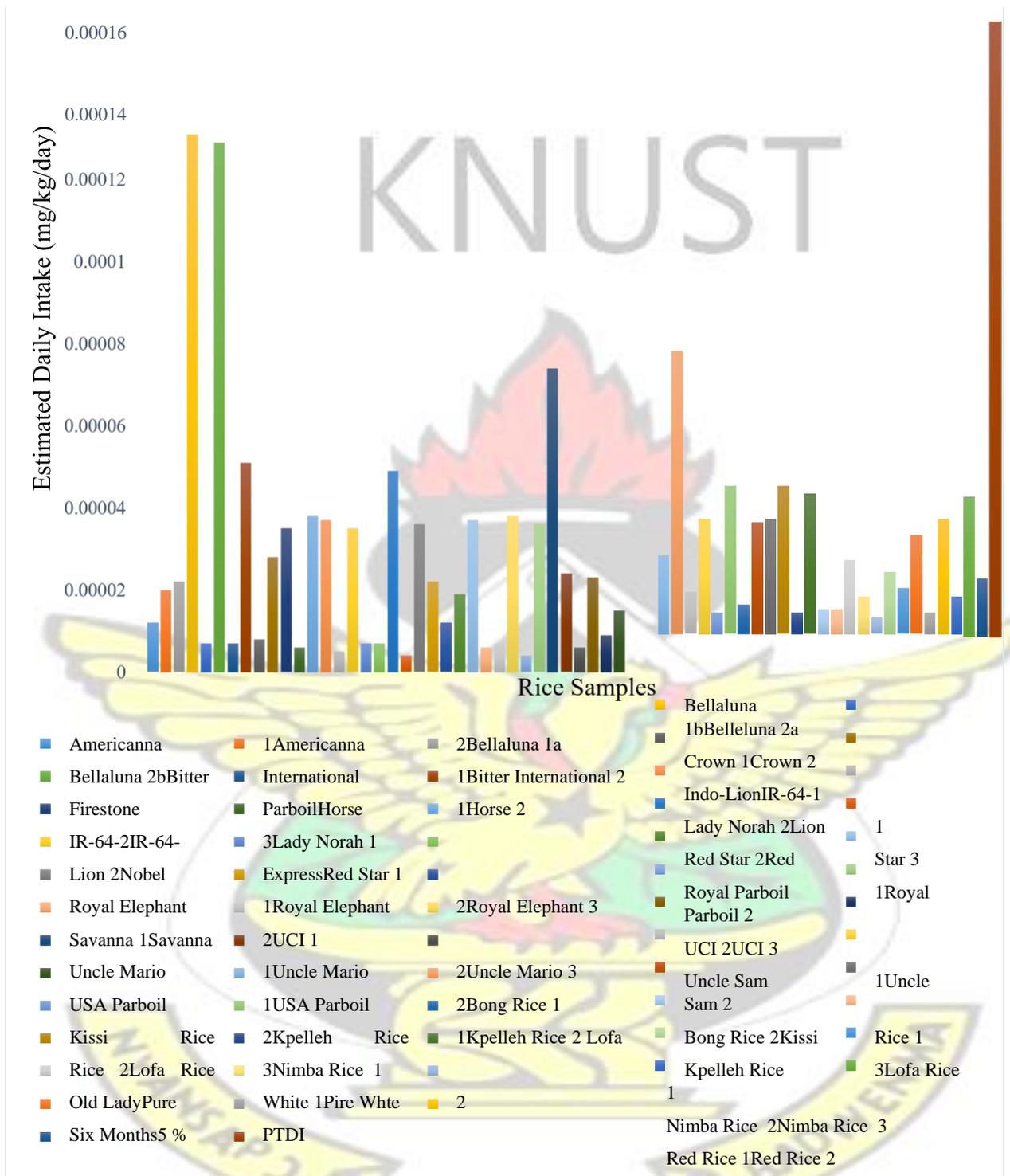


Figure 4.13: Dietary Intake (mg/kg/day) of Lead (Pb) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

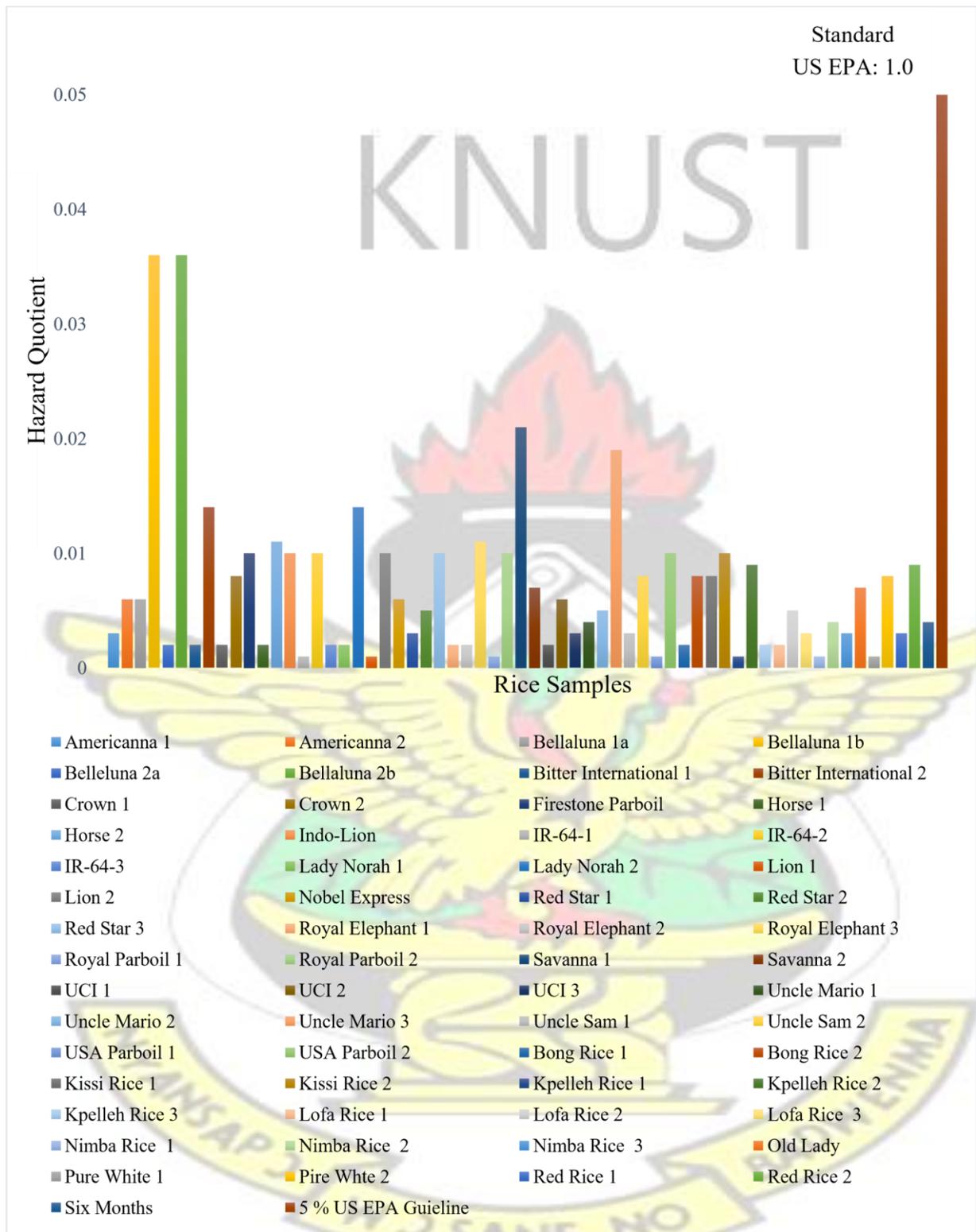


Figure 4.14: Hazard Quotients of Lead (Pb) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

The amount of Pb ingested per day from the consumptions of the rice products sampled in the study is significantly low as revealed by the observed EDI values. The EDI values for Pb obtained for the rice brands sampled in this study were all less than 0.00015 mg/kg/day, which is lower than the 0.00357 mg/kg/day PTDI value recommended for the metal by JECFA (JECFA, 2010). This indicates low dietary exposure of consumers to Pb. The highest concentration of Pb recorded in this study was found in Belleluna 1b (0.0371 mg/kg). If an average person in Monrovia consumed Belleluna 1b at the regular 248 g per day, he/she consumed approximately 0.000131 mg of Pb, which is significantly below the daily consumption threshold. To exceed the daily threshold, he/she would have to consume over 6.735 kg of Belleluna 1b, which is highly unlikely. Hazard Quotient values recorded in this study for Pb ranged from 0.001 to 0.036, lower than (1.43 to 1.99) reported by Zhuang *et al.* (2008). Based on the US EPA integrated metal risk assessment framework and the observed Hazard Quotient values, no non carcinogenic health risk from Pb toxicity to the population of Monrovia through their consumption of the rice brands analyzed in this study is expected.

#### **4.4.2. Carcinogenic Health Risk to Lead**

Despite the classification of Lead and its compounds by the US EPA and the IARC as carcinogens (US EPA, 2014a), the US EPA had not established the ingestion cancer slope factor for lead. Therefore, carcinogenic health risk posed to the population of Monrovia from Pb contamination of rice in the form of Incremental Lifetime Cancer Risk was not assessed in this study.

#### 4.5. Mercury Concentration

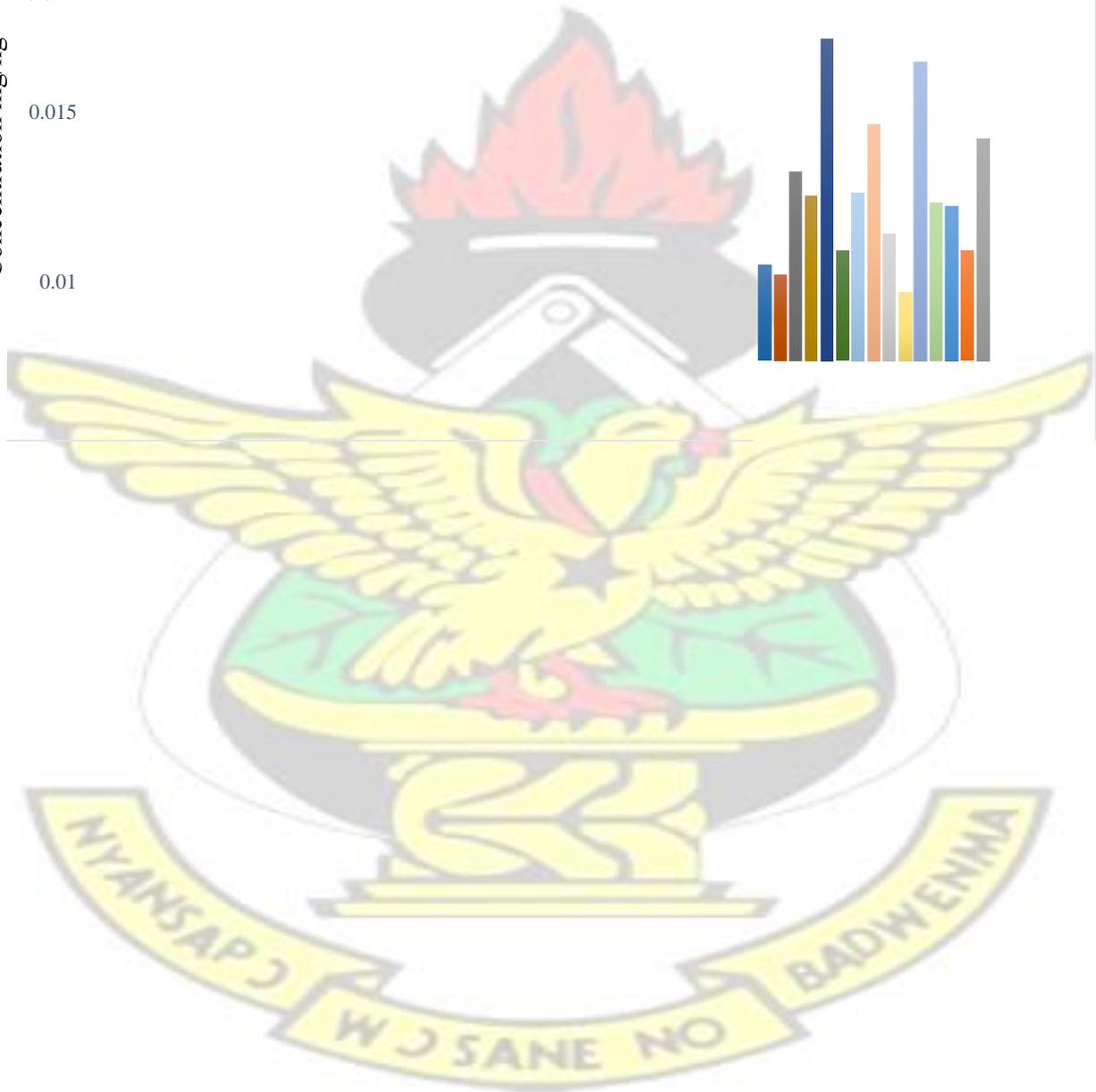
The consumption of mercury (Hg) contaminated rice causes accumulation of free radical and yields oxidative stress; and its long term dietary consumption leads to DNA strain damage (Jie *et al.*, 2007). The levels of mercury (in mg/kg per) in the rice sold on the local markets in Monrovia, Liberia (2017) are presented in Figure 4.15. The concentrations of Hg ranged from 0.0011 mg/kg to 0.0094 mg/kg. The concentrations of Hg in the locally cultivated rice samples ranged from 0.0020 mg/kg to 0.0094 mg/kg. The imported rice samples recorded values in the range from 0.0011 mg/kg to 0.0090 mg/kg. Student's T-Test was performed at 95 % confidence interval on the data, and a p-value of 0.254 was obtained. The value, which is greater than 0.05, indicates no significant statistical difference in Hg concentrations between the imported and the locally cultivated rice brand samples. Overall, Kpelleh Rice 1 reported the highest Hg concentration (0.0094 mg/kg), followed by USA Parboil 1 (0.0090 mg/kg) and Nimba Rice 1 (0.0087 mg/kg). USA Parboil 2, Americanna 2 and Crown 2 documented 0.0011 mg/kg, 0.0012 mg/kg and 0.0013 mg/kg as the least concentrations respectively.

The level of Hg concentrations found in all the rice tested were less than 0.01 mg/kg, which is significantly below the 0.20 mg/kg threshold limit set by the European Commission (EC, 2006), and the Food Safety Authority of Ireland (FSAI, 2009). The values were also lower than the 0.5 mg/kg threshold established by the Food Safety Authority of Hong Kong (CFS, 2017), and the 0.020 mg/kg recommended value issued by the National Food Safety Agency of China (Bugang and Woolsey, 2010). The highest concentration of Hg obtained is about 4.7 % of the threshold value, indicating very low level of contamination.

# KNUS

Standards  
PRC: 0.02 mg/kg  
EC: 0.2 mg/kg

Concentration mg/kg



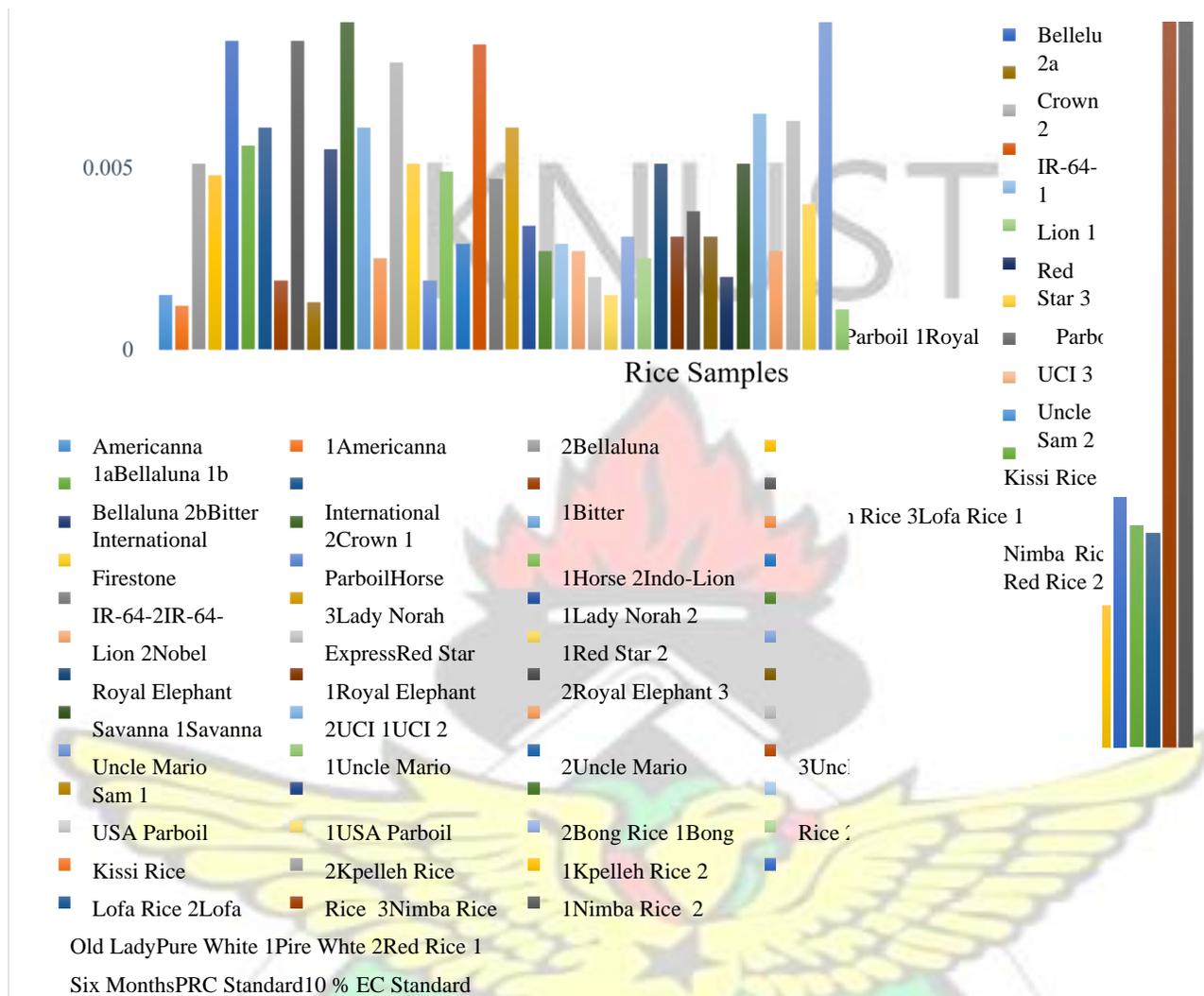


Figure 4.15: Concentration (mg/kg) of Total Mercury in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

The processes that account for the presence of Hg in rice grain was described by Rothenberg *et al.* (2012). Even though not clearly elucidated, the authors revealed that low soil pH plays significant role in the bioavailability of mercury to rice plant. Hang *et al.* (2017) reported that bioavailable mercury in soil accumulate higher in the grain than the stalk and the root. Environmental condition under which the rice is grown also contribute to the presence of Hg in the grains. For example, the submergence of rice paddy field during its growing season aids in the growth of Sulfur Reducing Bacteria (SRB), which can convert other forms of mercury to methyl mercury (MeHg). MeHg

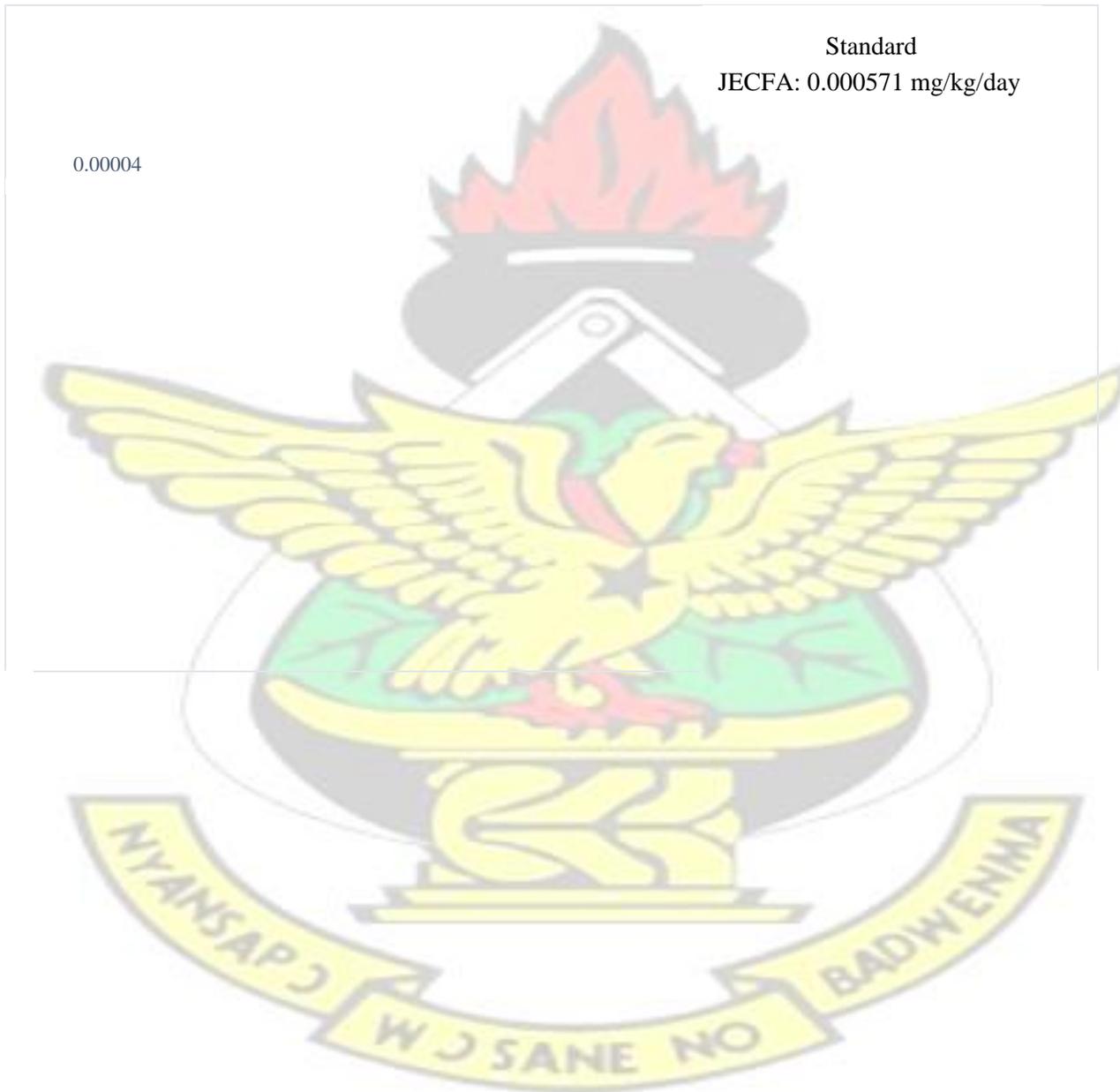
from all other parts of the plant (roots, stalk, and leaves) can be translocated to the grain, thereby increasing the total concentration of mercury in the edible portion (Qiu *et al.*, 2008). Rice grown under non-flooded condition usually have low level of Hg in their grains. Meng *et al.* (2010, 2012) established that under non-flooded conditions, only bioavailable mercury in the soil can be translocated to the grain of the rice plant. Accumulated mercury in the above ground parts of the plant cannot be translocated to the grain.

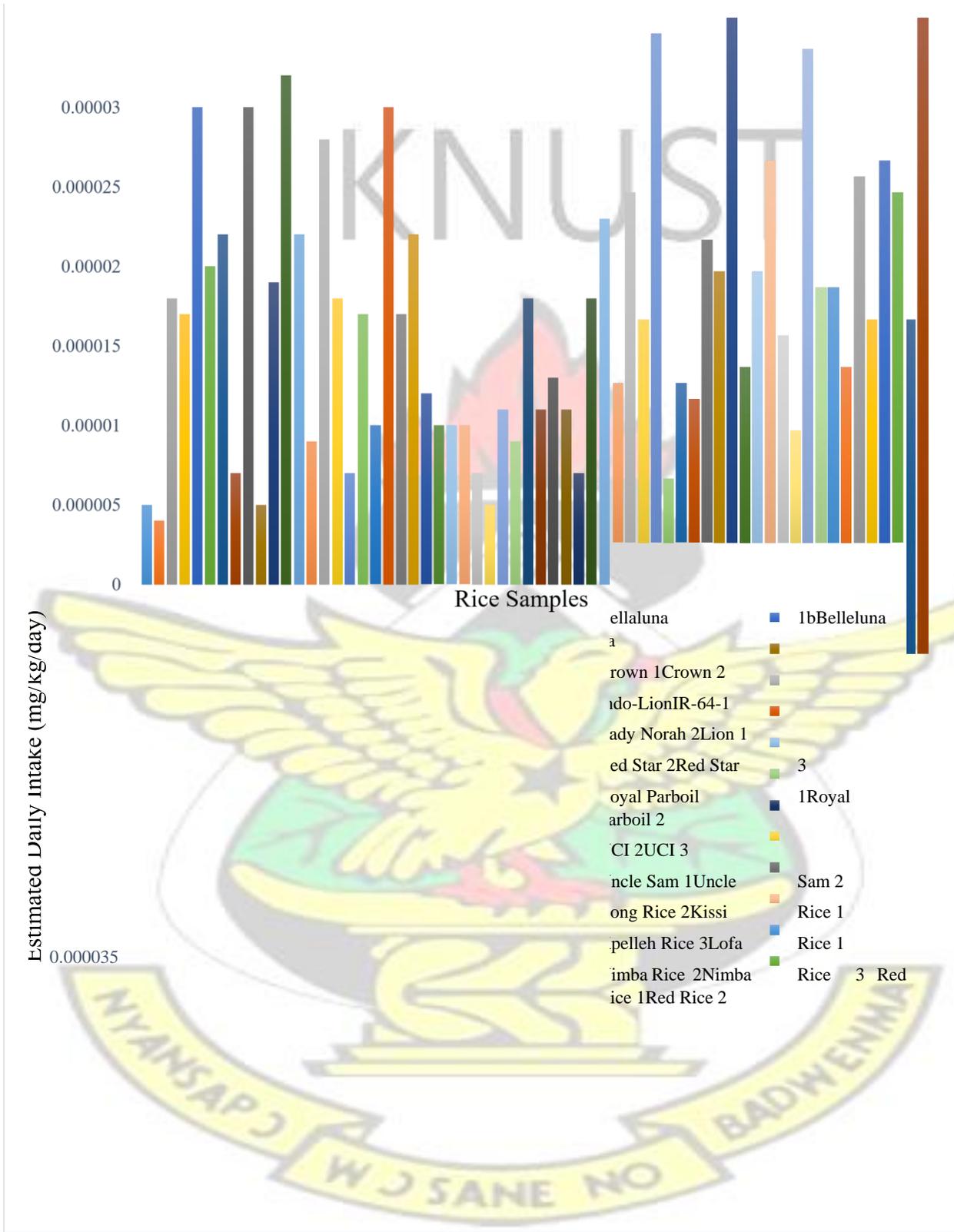
The level of Hg concentrations obtained in this study show little disparities when compared to other studies published in literature from some regions around the world. For example, Hg concentration reported by Da Silva *et al.* (2010) in both local and imported rice brands sold on the Brazilian market were in the range 0.0013 to 0.0078 mg/kg, slightly lower than the ones recorded in this study. In Palma de Mallorca, Spain, rice products sold on the Markets recorded Hg concentration in the range 0.0022 to 0.0073 mg/kg (Da Silva *et al.*, 2013), above which Hg values in this study fall. Hg concentrations in rice reported from Jiangsu, China were in the range 0.001 to 0.013 mg/kg (Cao *et al.*, 2010), below which this study values also fall.

#### **4.5.1. Non Carcinogenic Health risk to Mercury**

Several adverse effects of mercury (Hg) to human health have been well documented (Rice and Barone, 2000; Lee *et al.*, 2003; Johnson, 2004). In this study, non-carcinogenic health risk posed to the population of Monrovia from the Hg contaminated rice was assessed by using Hazard Quotient values, and the dietary exposure of consumers to Hg in the contaminated rice samples was assessed by comparing the Estimated Daily Intake of Hg to its Provisional Tolerable Daily Intake recommended by the Joint FAO/WHO Expert Committee on Food Additives. For Hg, the reference dose of 0.0001 mg/kg/day obtained from the US EPA Integrated Risk Information System was used in this study (US EPA, 2015). Daily rice consumption rate of 248 grams per day

per bodyweight of the inhabitants of Monrovia (GAIN, 2016), standard bodyweight of 70 kg for adult in health risk assessment recommended by the US EPA (US EPA, 2012), and the concentrations of Hg obtained in this study were used to compute the Estimated Daily Intake for Hg. Estimated Daily Intake and Hazard Quotients of Hg obtained in this study are presented in Figures 4.16 and 4.17 respectively.





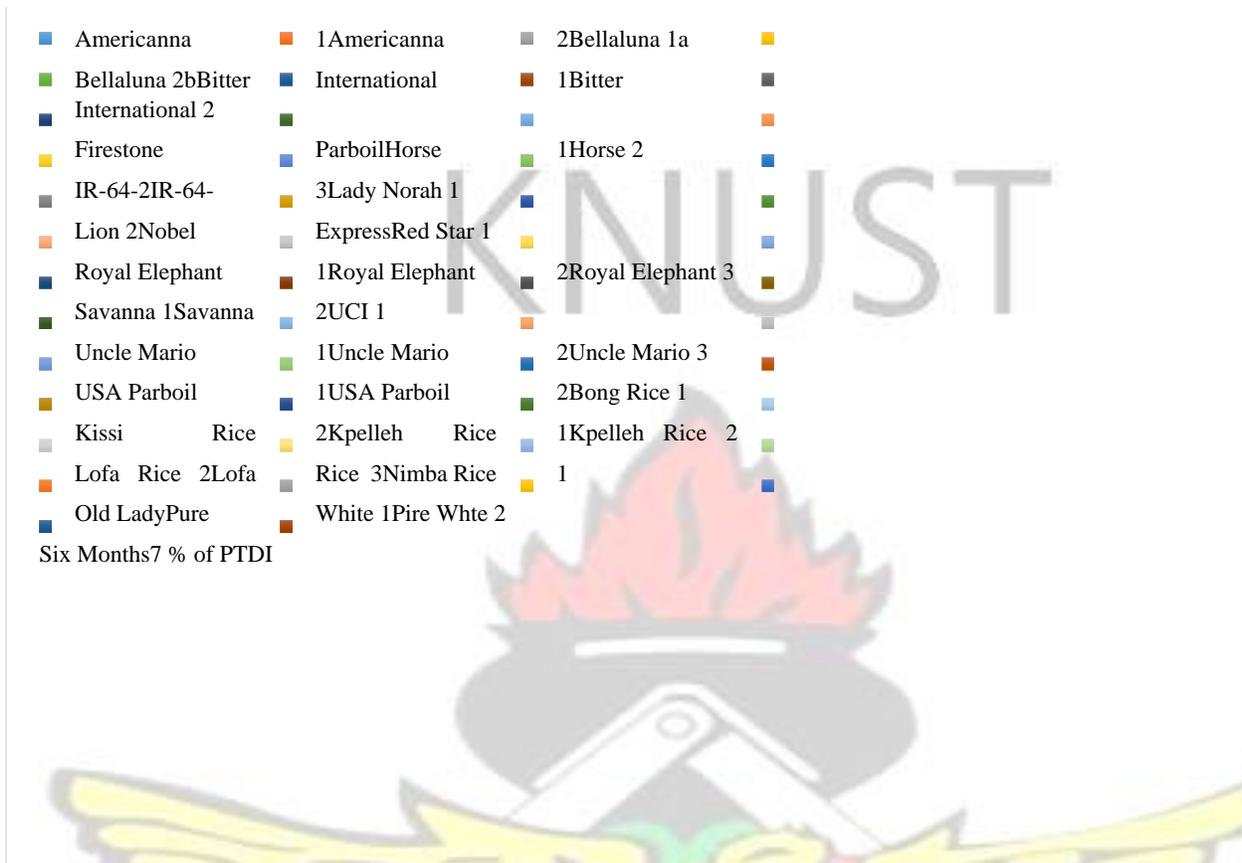


Figure 4.16: Dietary Intake (mg/kg/day) of Mercury (Hg) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).



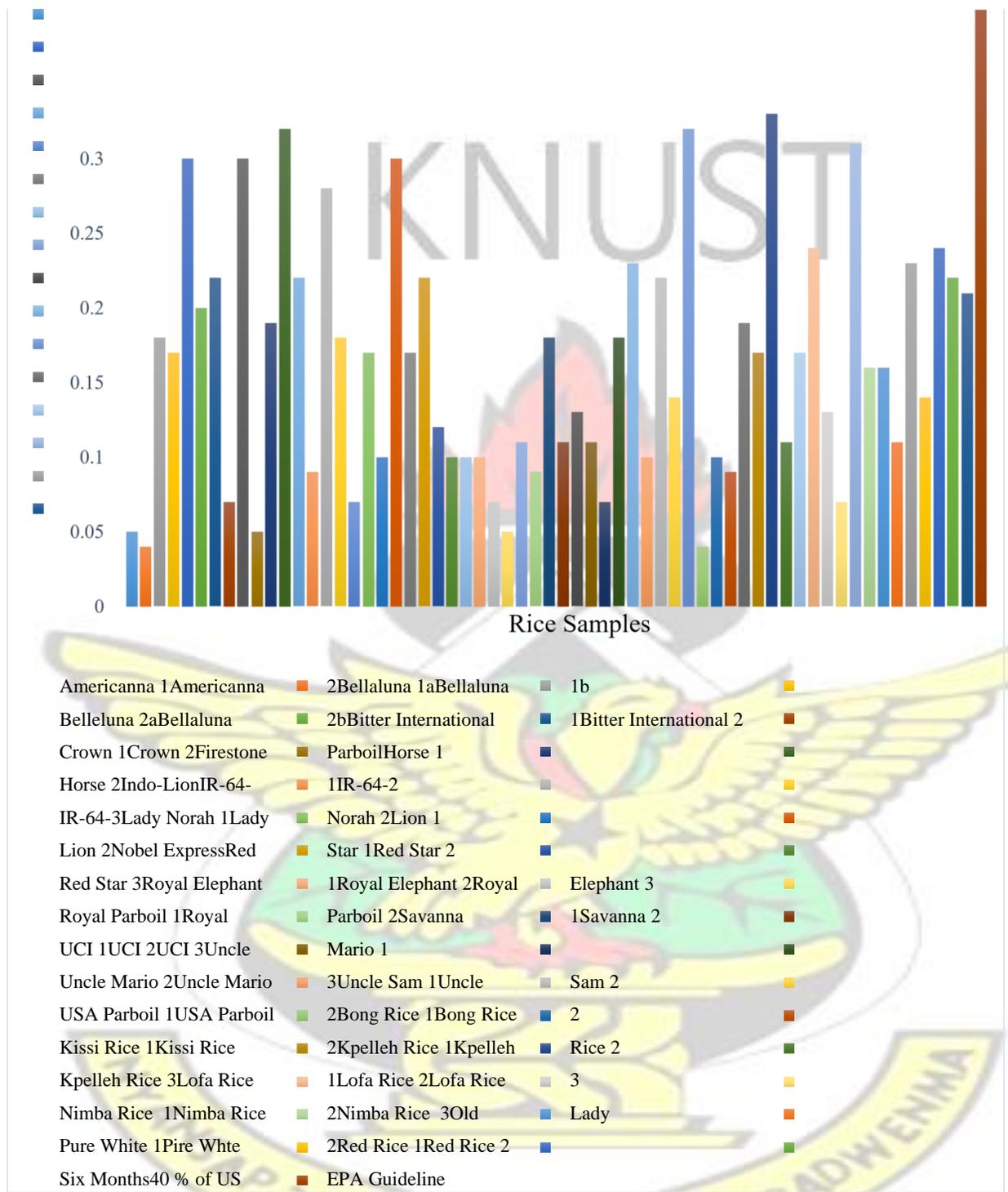


Figure 4.17: Hazard Quotient of Mercury (Hg) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

The amount of Hg taken in per day as represented by the Estimated Daily Intake values obtained for the rice sampled in this study were less than 0.00004 mg/kg/day, which is significantly below

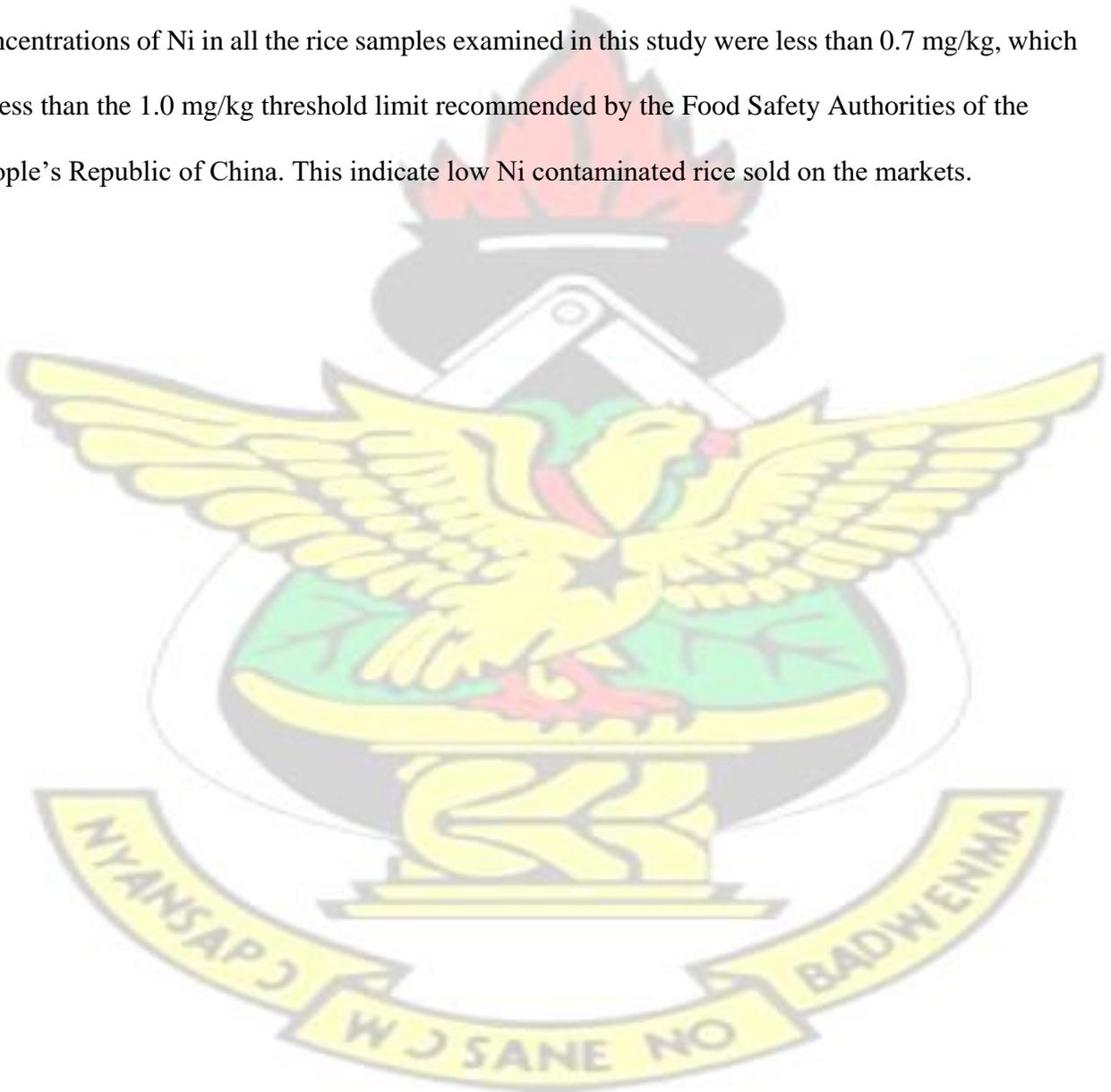
the PTDI value of 0.000571 mg/kg/day recommended for Hg by JECFA (JECFA, 2010). This indicates low dietary exposure of consumers to Hg. At the consumption rate of 248 g per day, Kpelleh Rice 1 reported the highest Estimated Daily Intake value (0.000033 mg/kg/day), but far below the recommended daily intake value set by JECFA. To exceed the recommended daily threshold value, an adult will have to consume over 4.25 kg of Kpelleh Rice 1 per day, which is extremely improbable. The Hazard Quotients obtained for Hg in all the tested samples ranged from 0.04 to 0.33, slightly higher than the range (0.001 to 0.013) reported by Cao *et al.* (2010). From the observed Hazard Quotient values and based on the US EPA guideline, there is no expected non carcinogenic health risk from Hg toxicity to the population of Monrovia through the consumption of the rice products tested in this study.

#### **4.6. Nickel Concentration**

Nickel (Ni) is an essential element for plants and animals biological systems but becomes toxic at high levels (Llamas *et al.*, 2008). The levels of Ni (in mg/kg) in the rice sold on the local markets in Monrovia, Liberia (2017), are presented in Figure 4.18. Nickel concentrations in the rice samples analyzed ranged from 0.0151 mg/kg to 0.6552 mg/kg. The locally cultivated rice samples recorded Ni concentration in the range of 0.0631 mg/kg to 0.6348 mg/kg. Foreign rice brands documented Ni concentration values in the range of 0.0151 mg/kg to 0.6552 mg/kg. A p-value of 0.081 was generated after subjecting the data to Student T-test performed at 95 % confidence interval using IBM-SPSS data analysis tool pack. The value is greater than 0.05, which indicates no significant statistical difference in Ni concentration between the locally cultivated and the foreign rice samples. Lady Norah 1 documented the highest Ni concentration (0.6552 mg/kg), followed by Pure White 1 (0.6348 mg/kg) and Uncle Sam 1 (0.5454 mg/kg). The least Ni

concentration was found in Firestone Parboil (0.0151 mg/kg), followed by Lion 2 (0.0246 mg/kg) and Savanna 2 (0.0447 mg/kg).

The European Commission and the Codex Alimentary Commission had not established a threshold for nickel in rice (EC, 2006; CODEX, 2015), but the Republic of China recognized 1.0 mg/kg as a threshold for Ni in grains and other cereals (Bugang and Woolsey, 2010). The concentrations of Ni in all the rice samples examined in this study were less than 0.7 mg/kg, which is less than the 1.0 mg/kg threshold limit recommended by the Food Safety Authorities of the People's Republic of China. This indicate low Ni contaminated rice sold on the markets.



Standard  
PRC: 1.0 mg/kg

# KNUST

Concentration mg/kg



Rice Samples

- Americanna
- Bellaluna 2bBitter
- Firestone
- IR-64-2IR-64-3Lady
- Lion 2Nobel
- Royal Elephant
- Savanna 1Savanna
- Uncle Mario 1Uncle
- 1USA Parboil 2Bong
- Kissi Rice 2Kpelleh
- Lofa Rice 2Lofa Rice
- Old LadyPure White
- 1Americanna
- International
- ParboilHorse
- Norah 1Lady
- ExpressRed Star
- 1Royal Elephant
- 2UCI 1UCI 2UCI 3
- Mario 2Uncle
- Rice 1Bong Rice
- Rice 1Kpelleh Rice
- 3Nimba Rice
- 1Pire White 2Red Rice 1Red Rice 2
- 2Bellaluna
- 1Bitter
- International
- 1Horse 2Indo-
- Norah 2Lion 1
- 1Red Star 2Red
- 2Royal Elephant
- Mario 3Uncle Sam
- 2Kissi Rice 1
- 2Kpelleh Rice
- 1Nimba Rice
- 2Nimba Rice 3
- 1aBellaluna
- LionIR-64-1
- Star 3
- 3Royal Parboil
- 1Uncle Sam 2 USA
- 1Belleluna 2a
- 2Crown 1Crown
- Parboil

# KNUST

Figure 4.18: Concentration (mg/kg) of Nickel in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

Due to the essentiality of nickel to many plants, it is normally present in their biological systems. For example, in most plants, including rice, it served as urease cofactor, aiding in the production of plants nitrogen or ammonium ions (Liu *et al.*, 2017). Just like Zinc and Iron, the absorption of Ni by rice is through diffusion or passive transport (Seregin and Kozhevnikova, 2006). However, nickel absorbed by the root system is predominantly concentrated in the shoots. In a study conducted to understand the distribution of Ni in rice plant, it was found that 81 % of the absorbed metal was translocated to the plant's shoot and less than 10 % accumulated in the grain (Rubio *et al.*, 2004).

Nickel levels reported in this study are either high or low when compared with other studies reported in literature from some regions around the world. For example, values recorded in this

study are slightly above the concentration range (0.379 to 0.455 mg/kg) reported in a study conducted in Gondar, Ethiopia (Belayneh *et al.*, 2015), and the range (0.054 to 0.44 mg/kg) reported in rice consumed on the Indian Markets (Yousefi *et al.*, 2016). However, study conducted in six districts (Khagrachari, Joypurhat, Rangamati, Naogaon, Jessore, Shatkhira, Savar and Bandarban) in Bangladesh, documented Ni concentration in the range 1.45 to 5.83 mg/kg (Jolly *et al.*, 2014), below which this study values fall.

#### **4.6.1. Non-Carcinogenic Health effect of Nickel**

Several health effects of nickel had been reported in literature (Beveridge, 2008; Schaumlöffel, 2012; Saedi *et al.*, 2013). In this study, dietary exposure of consumers to Ni in the tested rice samples was assessed by comparing the Estimated Daily Intake of Pb to its Provisional Tolerable Daily Intake recommended by the Joint FAO/WHO Expert Committee on Food Additives; and the non-carcinogenic health risk posed to the population of Monrovia from the Ni contaminated rice was assessed by using Hazard Quotient values. Hazard Quotients values were obtained from the Estimated Daily intake and the reference dose of the metal. The reference dose for Ni recommended by the US EPA is 0.02 mg/kg/day (US EPA, 2015). The Estimated Daily Intake values for Ni was computed by using the US EPA recommended 70 kg body weight for adult in health risk assessment (US EPA, 2012), the average rice consumption rate (248 grams per day per bodyweight) of the inhabitants of Monrovia (GAIN, 2016) and the concentrations of Ni obtained in this study. Estimated Daily Intake and Hazard Quotient values of Ni obtained in this study are presented in Figures 4.19 and 4.20 respectively.

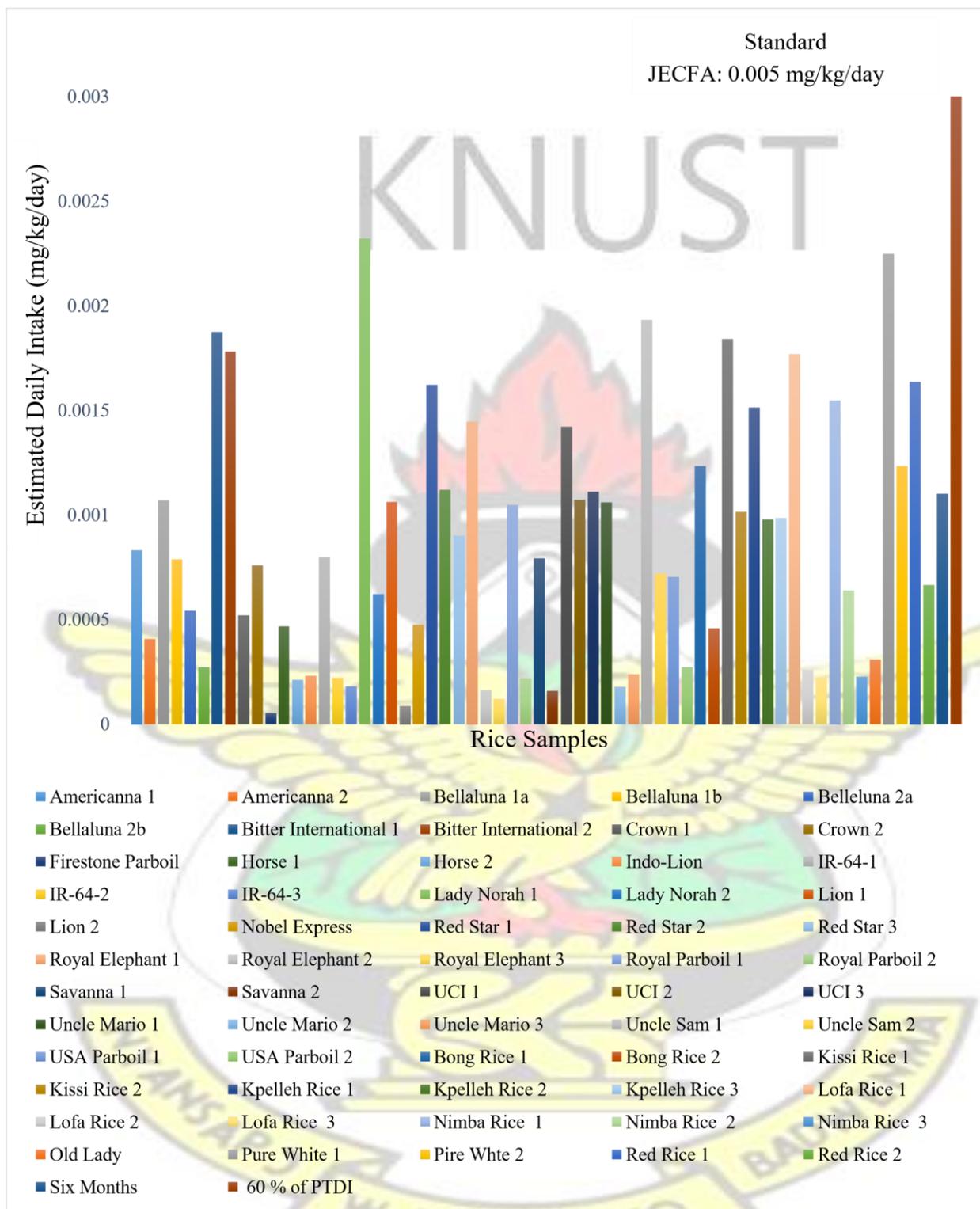


Figure 4.19: Dietary Intake (mg/kg/day) of Nickel (Ni) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

# KNUST

Standard  
US EPA: 1.0

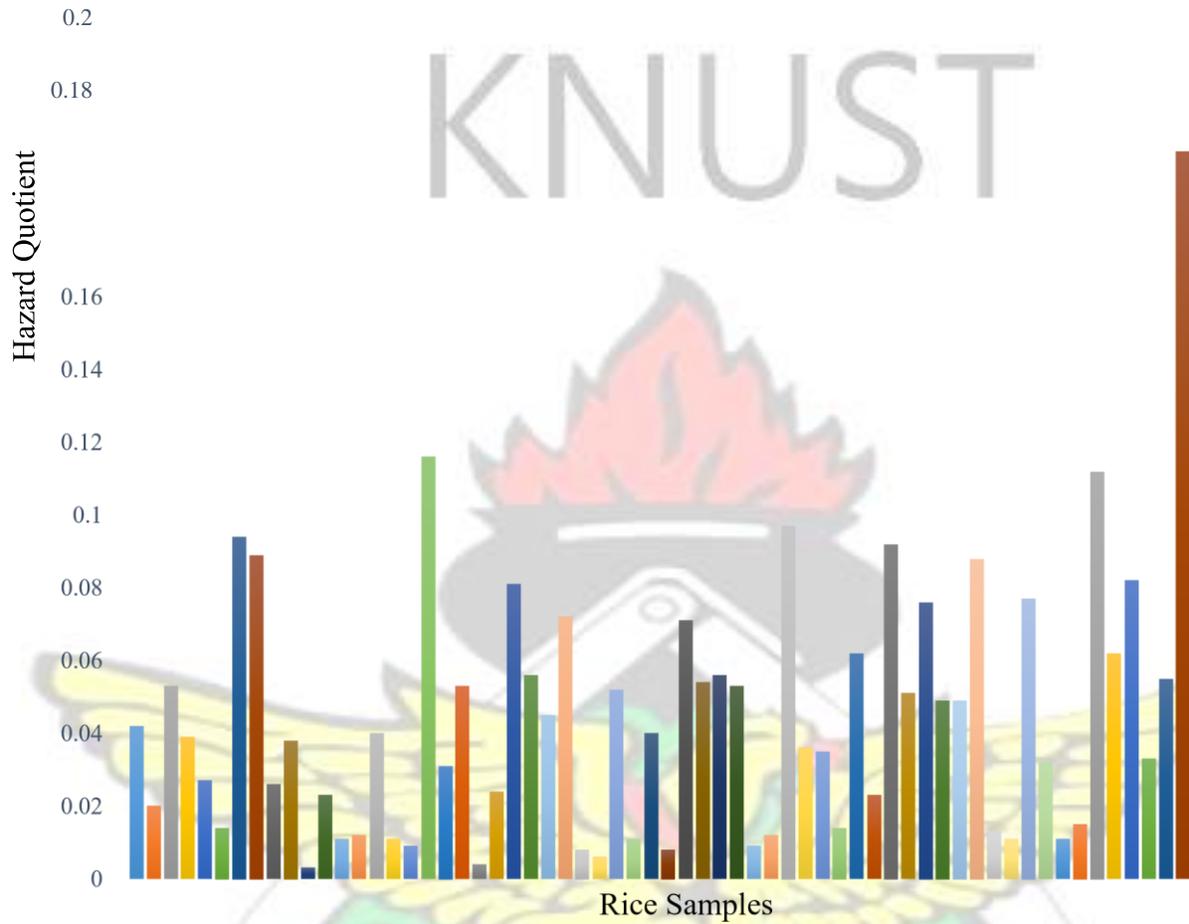


Figure 4.20: Hazard Quotients of Nickel (Ni) in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

The amount of Ni taken in per day from the consumptions of the rice products sampled in the study were significantly low as revealed by the observed Estimated Daily Intake values. All the Estimated Daily Intake values for Ni obtained from the rice brands sampled in this study were all less than 0.003 mg/kg/day, which is lower than the 0.005 mg/kg/day PTDI value recommended for Ni by JECFA (JECFA, 2010). This indicates low dietary exposure and potentially no carcinogenic health risk to consumers. The highest concentration of Ni recorded in this study was found in Lady Norah 1 (0.6552 mg/kg). If an average person consumed 248 g of Lady Norah 1 per day, he/she ingested approximately 0.002321 mg of Ni, which is significantly below the permissible consumption amount per day. To exceed the recommended daily threshold, he/she would have to consume over 534.2 g of Lady Norah 1, which is nearly three times the regular consumption rate. Hazard Quotient values recorded for Ni in this study ranged from 0.003 to 0.116, lower than 0.607 to 1.674 reported in literature (Jolly *et al.*, 2014). From the observed Hazard Quotient values and based on the US EPA guideline, consumption of the selected rice samples analyzed in this study posed no non carcinogenic health risk from Ni toxicity to the population of Monrovia.

#### **4.6.2. Carcinogenic Health Risk to Nickel**

Nickel and its compounds are labelled as human carcinogen by the US EPA and the IARC (Mulware, 2013). However, the ingestion cancer slope factor for nickel is yet to be established by the US EPA. Therefore, carcinogenic health risk posed to the population of Monrovia from Ni contamination of rice in the form of Incremental Lifetime Cancer Risk was not assessed in this study.

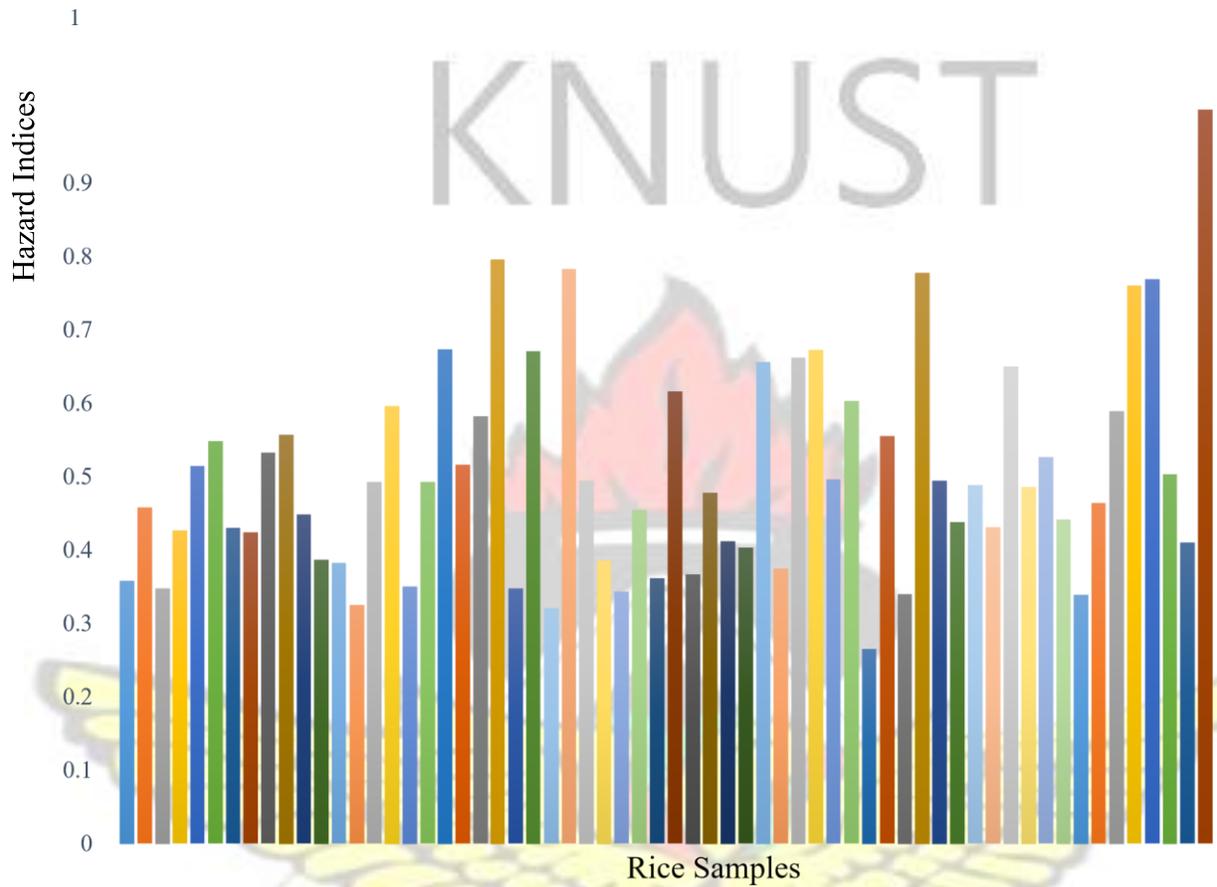
#### 4.7. Hazard Indices

The Hazard Index values or total carcinogenic health risk posed from exposure to the tested metals (As, Cd, Cr, Pb, Hg and Ni) to the population of Monrovia through the consumption of the studied rice brands are presented in Figure 4.21. The Hazard Index values ranged from 0.265 to 0.796.

According to the US EPA, any Hazard Index value equal to or greater than one ( $\geq 1$ ) posed potential health effect. Among the 61 rice sampled studied, none recorded Hazard Index value above the acceptable safety limit. Nobel Express recorded the highest Hazard Index value (0.796), however, below the US EPA guideline. The range of Hazard Indices obtained indicates low dietary exposure to As, Cd, Cr, Pb, Hg and Ni in combination to each other. With regards to the US EPA guideline, the range of Hazard Indices also indicates that consumption of the studied rice samples at the current rate posed no carcinogenic health risk from the combination of As, Cd, Cr, Pb, Hg and Ni to the population of Monrovia.

The cumulative ingestion of metals through the intake of rice represented in this study as hazard indices are either in agreement, high or low when compared to other studies in literature. For example, values for this study were high when compared to Hazard Index values reported for the Korean population in Taegu (Kwon *et al.*, 2016) and the Chinese population in Jiangsu (Cao *et al.*, 2010). Hazard Index values reported from Changshu (Hang *et al.*, 2009) and Suxian (Song *et al.*, 2015), China were in agreement with this study values. However, those documented in studies from Zheijiang (Huang *et al.*, 2013), Hunan Province (Fan *et al.*, 2017), China and Singhbhum (Giri and Singh, 2017), India were higher than those recorded in this study.

Standard  
US EPA: 1.0



- |                      |                     |                   |                     |                    |
|----------------------|---------------------|-------------------|---------------------|--------------------|
| ■ Americanna         | ■ 1Americanna       | ■ 2Bellaluna      | ■ 1aBellaluna       | ■ 1bBelleluna 2a   |
| ■ Bellaluna 2bBitter | ■ International     | ■ 1Bitter         | ■ International     | ■ 2Crown 1Crown 2  |
| ■ Firestone          | ■ ParboilHorse      | ■ 1Horse 2Indo-   | ■ LionIR-64-1       |                    |
| ■ IR-64-2IR-64-      | ■ 3Lady Norah       | ■ 1Lady Norah     | ■ 2Lion 1           |                    |
| ■ Lion 2Nobel        | ■ ExpressRed Star   | ■ 1Red Star 2Red  | ■ Star 3            |                    |
| ■ Royal Elephant     | ■ 1Royal Elephant   | ■ 2Royal Elephant | ■ 3Royal Parboil    | ■ 1Royal Parboil 2 |
| ■ Savanna            | ■ 1Savanna 2UCI     | ■ 1UCI 2UCI 3     |                     |                    |
| ■ Uncle Mario        | ■ 1Uncle Mario      | ■ 2Uncle Mario    | ■ 3Uncle Sam        | ■ 1Uncle Sam 2     |
| ■ USA Parboil        | ■ 1USA Parboil      | ■ 2Bong Rice      | ■ 1Bong Rice 2Kissi | ■ Rice 1           |
| ■ Kissi Rice         | ■ 2Kpelleh Rice     | ■ 1Kpelleh Rice   | ■ 2Kpelleh Rice     | ■ 3Lofa Rice 1     |
| ■ Lofa Rice 2Lofa    | ■ Rice 3Nimba       | ■ Rice 1Nimba     | ■ Rice 2Nimba       | ■ Rice 3           |
| ■ Old LadyPure       | ■ White 1Pire White | ■ 2Red Rice 1Red  | ■ Rice 2            |                    |
| ■ Six MonthsUS       | ■ EPA Guideline     |                   |                     |                    |

Figure 4.21: Hazard Indices of the selected metals in Foreign and Local rice samples from local markets in Monrovia, Liberia (2017).

## CHAPTER FIVE

### 5. CONCLUSION AND RECOMMENDATION

#### 5.1. CONCLUSION

The study sought to assess the level of heavy metals (As, Cd, Cr, Pb, Hg and Ni) in rice brands sold on the local markets in Monrovia, and the health risk posed to the population through their consumption. The outcome revealed that:

The selected heavy metals were all present in all the rice samples analyzed. The concentrations of As, Cd, Pb and Hg in the studied samples were generally below the Codex and European Commission threshold limits. Cr and Ni were also below the Chinese permissible limit.

The level of As in the tested rice brands ranged from 0.0011 mg/kg to 0.0181 mg/kg. Red Star 2 recorded the highest As concentration while Pure white1, Belleluna 1a and Bitter International 1 recorded the least. Student T-test showed a significant statistical difference in As concentration between the locally cultivated and imported rice samples ( $P = 0.002$ ). Hazard Quotients for As in the tested samples ranged from 0.013 to 0.213. Incremental Lifetime Cancer Risk documented values in the range from  $6.0 \times 10^{-6}$  to  $8.4 \times 10^{-5}$ .

The level of Cd in the tested rice brands ranged from 0.0048 mg/kg to 0.1179 mg/kg. Uncle Sam 2 recorded the highest Cd concentration while Savanna 1 recorded the least. Student T-test showed no significant statistical difference in Cd concentration between the locally cultivated and imported rice samples ( $P = 0.107$ ). Hazard Quotients for Cd in the tested samples ranged from 0.017 to

0.418.

The level of Cr in the tested rice brands ranged from 0.005 mg/kg to 0.4245 mg/kg. Kissi Rice 2 recorded the highest Cr concentration while Savanna 1 recorded the least. Student T-test showed no significant statistical difference in Cr concentration between the locally cultivated and imported rice samples ( $P = 0.96$ ). Hazard Quotients for Cr in the tested samples ranged from 0.006 to 0.501.

The level of Pb in the tested rice brands ranged from 0.0011 mg/kg to 0.0371 mg/kg. Belleluna 1b recorded the highest Pb concentration while Lion 1, Nimba Rice 1 and Royal Elephant 1 recorded the least. Student T-test showed no significant statistical difference in Pb concentration between the locally cultivated and imported rice samples ( $P = 0.113$ ). Hazard Quotients for Pb in the tested samples ranged from 0.001 to 0.036.

The level of Hg in the tested rice brands ranged from 0.0011 mg/kg to 0.0094 mg/kg. Kpelleh Rice 1 recorded the highest Hg concentration while USA Parboil 2 recorded the least. Student T-test showed no significant statistical difference in Hg concentration between the locally cultivated and imported rice samples ( $P = 0.254$ ). Hazard Quotients for Hg in the tested samples ranged from 0.04 to 0.33.

The level of Ni in the tested rice brands ranged from 0.0151 mg/kg to 0.6552 mg/kg. Lady Norah 1 recorded the highest Ni concentration while Firestone Parboil recorded the least. Student T-test showed no significant statistical difference in Ni concentration between the locally cultivated and imported rice samples ( $P = 0.081$ ). Hazard Quotients for Ni in the tested samples ranged from 0.003 to 0.116.

The observed level of Hazard Quotients and Hazard Indices in all the rice samples tested were less than the US EPA permissible safety limit. Therefore, consuming the selected rice samples sold on

the local markets in Monrovia at the current consumption rate posed no health risk to the population from As, Cd, Cr, Pb, Hg and Ni alone or when combined. Hence, do not call for any safety concern.

The study also revealed that the observed dietary intake values of each of the metals were less than JECFA permissible safety limits. Therefore, the population is not at any significant health risk to As, Cd, Cr, Pb, Hg and Ni exposure through the consumption of the selected rice brands.

From the results obtained, no consumption advisory is needed for any of the tested rice samples.

## **5.2. RECOMMENDATION**

The study recommends the following:

Future research with large sample size be piloted to better disclose the level of heavy metals in the rice brands sold on the local markets in Monrovia. The number of rice brands sampled in this study was limited due to resource and brands availability during the time of sampling.

Other metals like zinc and copper can also be toxic at high concentrations. They were not included in this study due to resource limitation. Therefore, it is recommended that subsequent research should include these metals in addition to the ones evaluated in this study.

Rice is randomly produced and imported to Liberia during the year. The brands tested were the ones available at the time of sampling. Since random production and importation is expected annually, it is further recommended that subsequent research should include new brands.

Though all of the rice brands sampled from the local markets in Monrovia (2017) proved to be safe for human consumption, high level of heavy metals contamination is possible. Therefore, the level of heavy metals in these rice brands must be regularly monitored to ensure safety.

Responsible regulatory agencies must ensure that the rice (local and imported) sold on the local markets in Monrovia remain safe for human consumption.

# KNUST



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## APPENDICES

### Appendix A: List of Plates

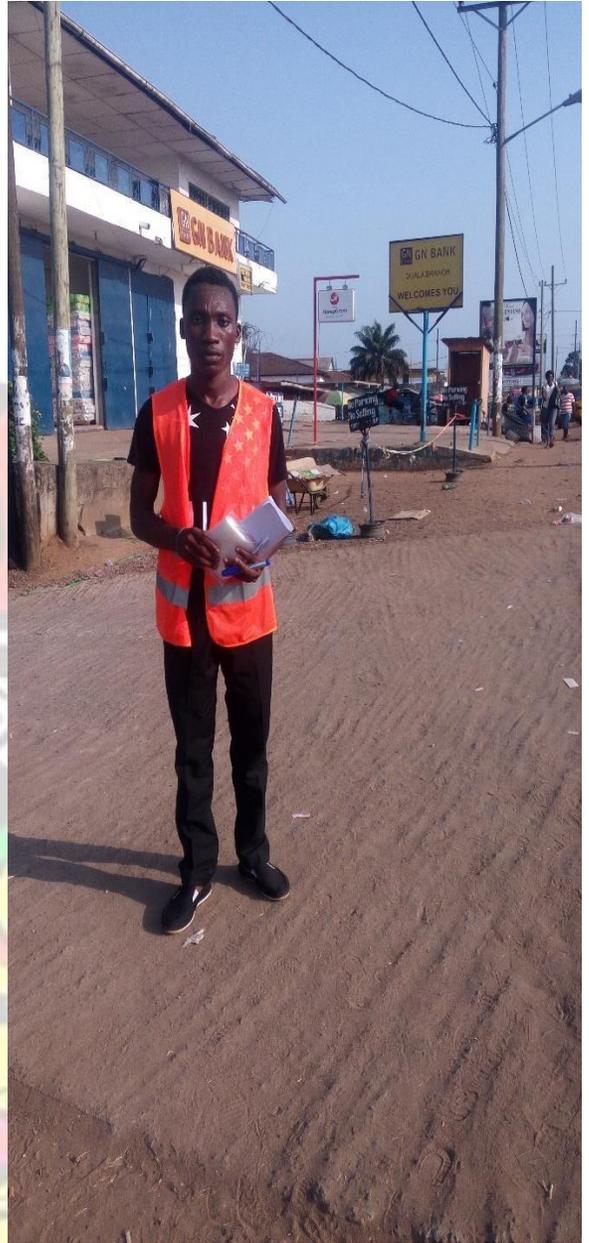


Plate A-1: Sampling





Plate A-2: Packaged Samples



Plate A-3: Digestion of Samples



Plate A-4: Lumex RA-915M Portable Zeeman Automatic Mercury Analyzer



Plate A-5: Using the Lumex RA-915M Zeeman Automatic Mercury Analyzer for Mercury Analysis

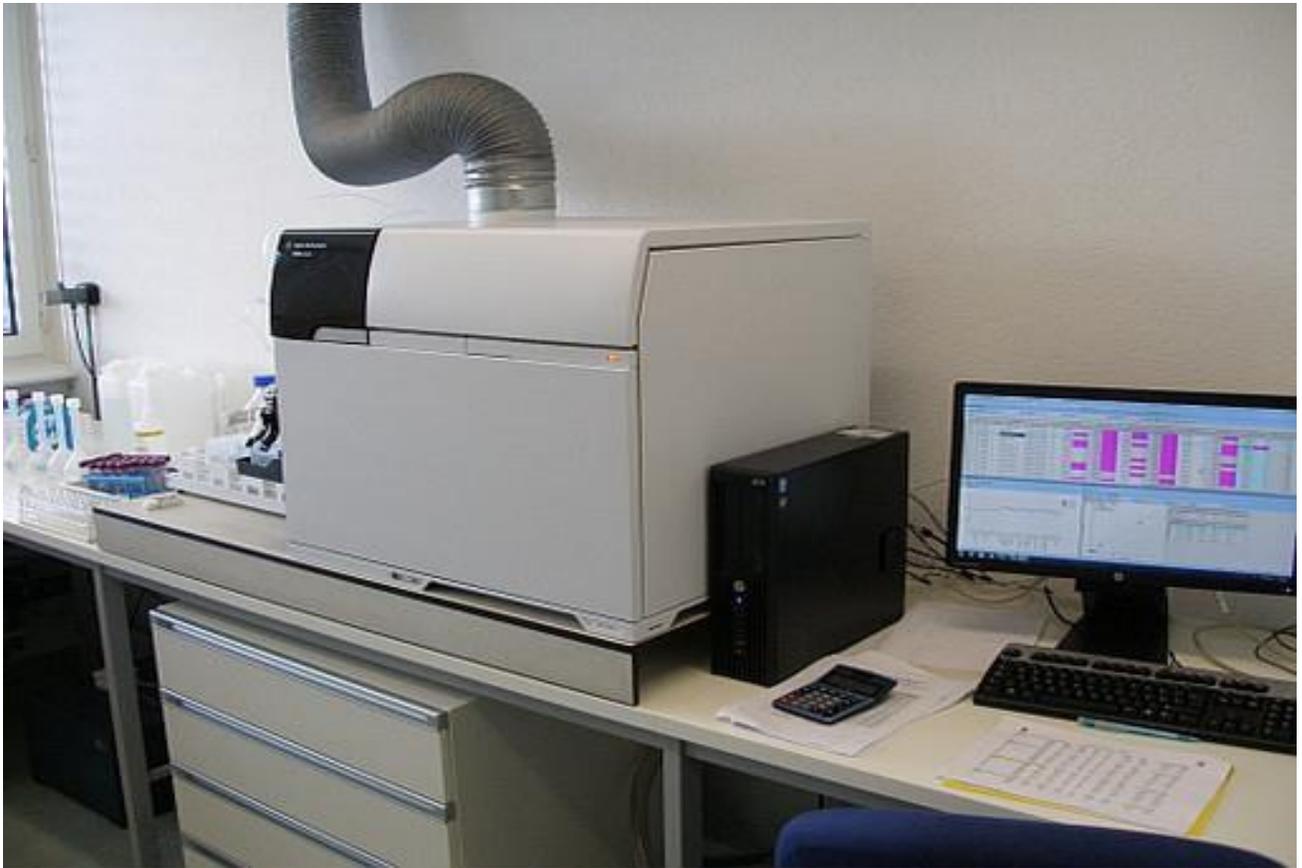


Plate A-6: Agilent 7900 ICP-MS

