KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI

COLLEGE OF SCIENCE

DEPARTMENT OF FOOD SCIENCE AND TECHNOLOGY

ARSENIC, CADMIUM AND LEAD CONTENT OF RICE SOLD IN THE GREATER ACCRA REGION

THESIS SUBMITTED TO THE DEPARTMENT OF FOOD SCIENCE AND TECHNOLOGY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN FOOD QUALITY MANAGEMENT

BY

ABENA AGYEIBEA ASAMOA (MISS)

JULY, 2016

DECLARATION

I declare that I have wholly undertaken the study reported herein under the supervision of Dr Jacob Agbenorhevi and that except portions where references have been duly cited, this dissertation is the outcome of my research.

ABENA AGYEIBEA ASAMOA ______________ ____________________

(PG 2583014) Signature Date

Certified by:

DR JACOB AGBENORHEVI ………………………… …………………

(Supervisor) Signature Date

Certified by:

PROF. (MRS.) I. ODURO ………………………… ……………………..

(Head of Department) Signature Date

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DEDICATION

I dedicate this thesis to the Lord Almighty for His goodness and mercies and to my brother Kwabena Korang Asamoa.

ABSTRACT

Rice is an excellent staple crop which contains vitamins and minerals such as vitamins E & B and potassium needed for human growth and wellbeing. In recent times, majority of Ghanaians consume a lot of rice as compared to other local staple. However, heavy metal contamination of rice and other crops is threatening the quality of these crops and the health of consumers.

Due to industrialization and other human activities, environmental pollution with chemicals is increasing and this has led to the contamination of agricultural produce. Heavy metal contamination has been associated with adverse effects such as damages to the nervous system, kidneys, liver, lungs and other vital organs in humans and animals. With dietary intake as one of the major routes of heavy metal exposure to human, there is the need to investigate the levels of these metals in our foods.

This study intended at determining the concentrations of three heavy metals (arsenic, cadmium and lead) in rice sold on the Ghanaian market. Thirty two samples (16 unpolished rice, 16 polished rice (8 foreign rice and 8 local rice) were purchased from some of the markets in Accra; the capital city of Ghana. Samples were homogenized and digested for analysis using a microwave digester. The concentrations of the 3 elements (As, Cd & Pb) were analysed using Graphite Atomic Absorption Spectrophotometry. The method used was validated using a certified reference material.

Results indicated that, for Arsenic concentration in rice samples, unpolished rice obtained concentrations which ranged from not detected to 0.2370 mg/kg with an average of 0.1212 mg/kg. Concentration of arsenic in polished rice ranged from 0.0531 to 0.1772 mg/kg with an average of 0.1032 mg/kg in foreign rice and 0.0297 to 0.1504 mg/kg with an average of 0.0843 mg/kg in local rice samples. Cadmium concentration ranged from not detected to 0.0628 mg/kg with an average of 0.0179 mg/kg in unpolished rice. Cadmium in polished rice ranged from 0.0012 to 0.0424 mg/kg with an average of 0.0128 mg/kg in foreign rice and 0.0025 to 0.0329 mg/kg with an average of 0.0099 mg/kg in local rice samples. Lead concentration in unpolished rice ranged from 0.0007 mg/kg to 0.1106 mg/kg with an average of 0.0239 mg/kg. Concentration of lead in polished rice samples ranged from 0.0027 to 0.1106 mg/kg with an average of 0.0308 mg/kg in local rice and 0.0007 to 0.0505 mg/kg with an average of 0.0171 mg/kg in foreign rice samples.

It is recommended that agencies or institutions responsible for food regulation need to periodically determine the concentration of metals in both imported and local rice samples sold on our markets to elude the harmful effects of heavy metals on consumers.

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LIST OF ABBREVIATIONS

%	Percentage
AAS	Atomic Absorption Spectrophotometer
As	Arsenic
Cd	Cadmium
CRM	Certified Reference Material
F-AAS	Flame Atomic Absorption Spectrometer
FAO	Food and Agriculture Organisation
g	gram
GF-AAS	Graphite Furnace Atomic Absorption Spectrometer
HCL	Hollow Cathode Lamp
HCl	Hydrochloric acid
ICP- AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
IITA	Institute of International Tropical Agriculture
mg/kg	milligram per kilogram
mg/L	milligram per Litre
^{o}C	Degree Celsius
Pb	Lead
ppb	Parts per billion
ppm	Parts per million
PTFE	Polytetrafluroethylene
SD	Standard deviation
UNESCO	United Nations Educational Scientific and Cultural Organization

WHO	World Health Organisation
UPR	Unpolished rice
PRL	Polished rice- local
PRF	Polished rice - foreign

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Food safety awareness is gaining prevalence in recent years among most developing countries. Safety and quality of foods are of major concern to most individuals and countries. Heavy metal contamination of the environment and food is one the major food safety concerns due to the detrimental effect of these metals on humans and the ecosystem. Heavy metals exists naturally in the soil or occur as a result of anthropogenic activities. These anthropogenic activities include human activities such mining, extraction, indiscriminate waste disposal and some agricultural activities (Ofitoju *et al.*, 2014). In agriculture, activities such as irrigation with contaminated water and the use of metal based agrochemicals (pesticides and fertilizers) introduces these metals into foods (Ghazanfarirad *et al*., 2014). These metals are considered harmful because they are non -degradable, have long half-lives and can accumulate in most animal and plant tissues (Otitoju *et al.*, 2014). Higher concentrations of some heavy metals are known to destroy cell membranes in plants (Payus and Talip, 2014). However, some plants are able to absorb these toxic heavy metals and adapt to their high concentrations in the soil. Farms near industrial areas or irrigated with polluted water stand a higher chance of heavy metal contamination (Faruruwa *et al.,* 2013). Dietary intake is a major route of contact to heavy metals.

Heavy metals such as arsenic, lead and cadmium are of major concern in agriculture particularly in rice farming. They accumulate in the soil and end up contaminating food crops (Payus and Talip, 2014).

Earlier studies have confirmed the presence of significant levels of some of these metals in rice grains. Otitoju *et al.*, (2014), reported that lead content in locally produced rice in Nigeria ranged from 0.311 mg/kg to 0.525 mg/kg. A study by Payus and Talip (2014) also confirms the presence of heavy metals such as lead and cadmium in rice with significant amounts of lead in the roots and grains.

Exposure to these metals is a serious public health issue because these metal contaminants have adverse effects on health. Research has shown long term exposure to arsenic can lead to skin lesion, bronchitis, skin cancer and lung cancer (WHO, 2010). Chronic exposure to lead has been associated with adverse effects in humans causing diseases such as anaemia headache, irritability, lethargy, convulsions, muscle weakness, ataxia, tremors and paralysis (WHO, 2010). Cadmium is also known for its toxic effect on the kidneys, skeletal and respiratory systems. These metals are also noted for their carcinogenic effects on humans and animals (WHO, 2010).

Rice is a key source of energy and protein; it also contains significant amounts of zinc and niacin (FAO, 2006). In Ghana, rice is consumed by majority of the populace and it serves as a major stable for both rural and urban inhabitants. It is mainly cultivated by small farmers in holdings of less than one hectare hence over 80% of the rice consumed in Ghana is imported from most Asian countries (WARDA, 2008). Rice can be classified as polished and unpolished depending on the degree of milling. The process of milling improves sensory attributes of rice, however, it reduces the level of nutrients such as fats, proteins, vitamins and fibre (Abass *et al.*, 2011). Consumption of rice in Ghana has increased tremendously over the last few years and factors such as changes in life style and the relative ease with which it can be cooked based on consumer preference (WARDA, 2008).

The high demand for rice requires that safety measures should be put in place to ensure good health of the public. In our quest to contribute to making rice farming safe from metal contamination, there is the need to determine the levels of heavy metals in rice produced. This will assist in putting in place measures to ensure safety of the rice consumed in Ghana. This study is designed to determine levels of heavy metals such as lead, cadmium and arsenic in foreign and local rice sold on some major markets in Ghana.

1.2 Problem Statement

There has been a rapid increase in consumption levels of rice over the past decade with substantial proportion of consumers moving from consumption of other staples to rice (Tomlins *et al.*, 2005). Rice grains just like most crops is threatened by heavy metal contamination. There is an increase in heavy metal contamination of foods in most countries due to the unregulated increase in urbanization and industrialization and also excessive agrochemical use which leads to environmental pollution (Ghazanfarirad *et al*., 2014). Heavy metal contamination of foods is a major threat to food safety/public health in recent times and this has led to the high demand for quality and safe rice.

There have been reports on heavy metal contamination of rice from some Asian countries such as Iran, China, Japan (Mohammad *et al*, 2008) and these countries happen to be the major sources of rice consumed in Ghana. However, not much is known on the heavy metal levels of these imported rice. Locally, rice farming is also increasing among inhabitants in the rural communities of Ghana. Some of these rice farms are located in communities where mining activities are carried out. Effluent from these mining companies leach into the soil and into water bodies which also serve as irrigation water for these rice farms. Contamination of rice by heavy metals will then lead to consumers ingesting large amounts of these metals on a frequent basis. Unlike contamination by microorganism or physical defects, metal contamination in food is not visible hence likely to be over looked during purchasing of rice. Heavy metals, however, when consumed has damaging effects on human health and can cause cancer (Ghazanfarirad *et al*., 2014).

1.3 Justification

The high yield and nutritional content of rice has made rice farming of much importance in addressing food security issues. The increasing contamination of foods by heavy metals causes adverse effects on plant and human health. Anthropogenic activities such as waste disposal, mining and the use of agricultural chemicals such as weedicides, pesticides and fertilizers have led to the introduction of high quantities of these metals into the environment. These heavy metals accumulate in water bodies and the soil and end up contaminating food crops.

Heavy metal intoxication in humans may cause damage to the gastrointestinal, cardiovascular and central nervous systems as well as other body organs such as the kidneys, lungs, bones and liver. Long term exposure has been associated with the occurrence of some cancers (Ghazanfarirad *et al.*, 2014)

Determining the hazard quotient of heavy metal contaminants in rice, will help address food safety issues. It will provide information which will serve as a basis for determining if consumers are at a risk of metal poisoning and will also assist in the setting of maximum allowable limits by regulatory bodies. This when done will assist in ensuring safety of foods and protecting the health of consumers from the adverse effects of heavy metals.

1.4 Goal

To contribute to making rice farming industry safe from heavy metals (arsenic, cadmium and lead) contamination.

1.5 Objective(s)

The objectives of this work are

I. To determine the levels of arsenic, cadmium and lead in polished and unpolished rice from some markets in the Greater Accra Region.

II. To compare the level of arsenic, cadmium and lead in imported and locally produced polished rice some markets in the Greater Accra Region.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Rice cultivation and classification

Rice (*Oryzae sativa*) is a staple consumed worldwide and cultivated in a wide range of soil lands. Rice is ranked as the second most cultivated cereal. It provides approximately 20% of the per capita energy (Juliano, 1992). Rice is grown in most countries on every continent except the Antarctica. It can be cultivated on a variety of soils such as silts, loams and gravels and can endure acidic as well as alkaline soils. It is cultivated under varying conditions of temperature, water availability and landscape (Roy *et al*. 2011). Rice is mainly cultivated in four broad production ecosystems namely; irrigated land, rain fed land, upland rice and flood-prone land (FAO, 2006). However, rice is mostly cultivated in flooded fields and rain fed lowlands in most countries (Beighley, 2005) .There are several varieties of rice which include traditional varieties and hybrid varieties. Due to the numerous varieties of rice there are several ways of classifying them. Rice can be grouped based on grain length, colour, climate, width, soil conditions, chemical and physical characteristics. Hence there are categories such as short grain, medium grain and long grain (Beighley, 2005). Using the length of kernel to group rice, the CODEX Alimentarius standard requires long grain rice to have a kernel length of 6.6 mm or more, medium grain rice to be 6.2 mm or more but less than 6.6 mm and short grain should have a length of less than 6.2 mm (CODEX, 1995b). Another type of classification per the standard is the use of a grouping based on length and length to width ratio. Per the Codex standard for rice, long grain rice should have kernel length of 6.0 nm or more and a length/width ratio not greater than 2 but less than 3. Medium grain rice is expected to have kernel length of greater than 5.2

mm but not greater than 6.0 mm and a length/width ratio of less than 3 whereas short grain rice should have kernel length of 5.2 mm or less and a length/width ratio below 2 (CODEX, 1995b).

Rice can also be grouped into two main types depending on the environment where they are grown and by their characteristics when cooked. They are namely Japonica which grows best in temperate zones and Indica which grows best in the tropics. Japonica have medium to short kernels and are sticky when cooked. Indica varieties appear as long kernels which are not sticky when cooked (FAO, 2006). The various types of rice can also be categorized into brown rice and white rice depending on the degree of milling. Brown rice is obtained by removing the outermost layer of the rice kernel. The complete milling and polishing of the kernel produces white rice. The dietary composition of rice differs in terms of variety, condition of the soil, environmental factors and fertilizers used (Beighley, 2005).

2.2 Rice Processing

Rice processing involves the use of series of operations to transform paddy rice into well pulverised silky-white rice, which has improved cooking quality attributes (Roy *et al*. 2011). The rough rice kernel obtained after harvesting, undergoes de-husking to remove the hulls from the rice kernel. The de-husked rice which is the brown rice or unpolished rice comprises of the outer layers namely pericarp, seed-coat, the nucleus, the germ or embryo and the endosperm. The pericarp contains a pigment that gives the brown or purplish colour whereas the endosperm contains the starchy component. During milling, factors such as the equipment used, quality of paddy and the skill of the mill technician have an influence on the quality and yield of processed rice (Roy *et al*. 2011). Milling can be done in a one-step milling process where the husk and bran are removed in a single milling process or in a multistage milling process where two or more steps are used to remove the husk first, followed by the other layers before obtaining the white rice (Dhankhar, 2014).The rice grain undergoes a series of cleaning process where all foreign materials such as stones, straw, husk and metals pieces are removed. The grains are further polished using abrasives or by the use of friction to obtain very white grains. Grading is done prior to packaging to obtain small, medium and long grains separately (Dhankhar, 2014).

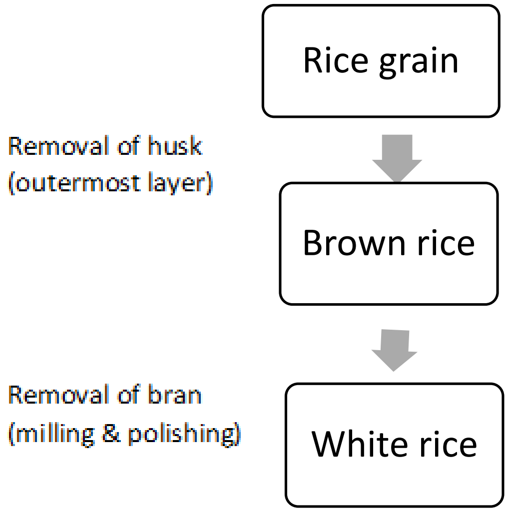

Figure 2.1 Rice polishing process.

Source: http://www.psoriasisselfmanagement.com

2.3 Nutritional Benefits of Rice

2.3.1 Unpolished Rice

Unpolished rice is known as an excellent source of vitamins and fibre and is often brown or purplish in colour (Abbas *et al*., 2011). The various layers of unpolished rice contain different quantities of fat, fibre, proteins and vitamins (Sotelo *et al*., 1990). Since the various layers remain intact, most nutrients are retained hence the unpolished rice is considered to be very nutritious (Abbas *et al*., 2011). A study of the proximate composition of rice by Thomas *et al.*, (2013) shows that unpolished rice has a total fibre content of 8.37% ± 0.1, carbohydrate of 78.21% ± 0.9, fat of 1.74% ± 0.1 and protein of 6.48% ± 0.0. A similar study by Sotelo ,(1990) also reported average fibre of brown rice to be 1.9% ± 0.6, protein to be 9.2% ± 1.3 and carbohydrate to be 84.9% ± 1.6. The high dietary fibre content of brown rice makes it act as a gentle laxative and helps prevent gastro–intestinal diseases (Babu *et al*., 2009). Brown rice is also good for diabetics. It is classified as a low glycemic index food due to its low starch and high complex carbohydrate which helps decrease the possibility of type 2 diabetes. Unpolished rice is also known to be a rich source of some vitamins and minerals such as thiamine, riboflavin, niacin, foliate, iron, selenium and magnesium (Babu *et al*., 2009).

Brown rice is also known to contain phytochemicals such as tocopherol, tocotrienol, oryzanol and ferulic acid (Wichamanee & Teerarat, 2012). It also contains phytic acid which has antioxidant and anti – cancer properties (Babu *et al*., 2009).

2.3.2 Polished Rice

The milling of brown rice to white rice improves the appearance and digestibility of the rice. However, it involves the removal of nutritious components of the grain leading to a loss of some nutrients such as fat, protein, fibre and some vitamins (thiamine, niacin & riboflavin). However, a study by Thomas *et al*., (2013) showed that white rice has a carbohydrate content of 80.14% ±1.1, fat to be 1.24% ± 0.0, fibre to be 7.07% ±0.6 and a protein content of 5.96% ± 0.2. Compared to the proximate values stated for brown rice above by Thomas *et al*. (2013) white rice has a higher carbohydrate content than brown rice. The fat, protein and fibre contents were however lower compared to brown rice. White rice also serves as a source of minerals and vitamins such as niacin, riboflavin, selenium and magnesium (Thomas *et al.,* 2013). White rice is notable for its longer shelf life and good sensory characteristics.

2.4 Trace metals in foods

Trace elements are chemical elements that can be found in humans, plants and animals in minute quantities. They often exist in mg/kg per body weight or less. Trace elements can be categorized as essential and non - essential. Essential heavy metals include micronutrients such as zinc, manganese, iron and copper which are required in small quantities but important for plant and animal growth. Their deficiency in plants can lead to stunted growth and discolouration (Satpathy *et al*., 2014). Non - essential heavy metals are noted for their toxic effects.

2.5 Toxic Heavy metal contamination in food

Heavy metals are termed as elements having a specific density greater than 5g/cm^3 (Järup, 2003). Examples of heavy metals include chromium, arsenic, cobalt, copper, mercury, nickel, iron, lead, selenium, uranium cadmium and zinc. Some heavy metals are toxic metallic contaminants found in the environment. They are toxic contaminants that pose serious threats to life. These toxic metals accumulate in the soil and contaminate food and water bodies hence endangering the safety of the humans and the ecosystem (Payus & Talip, 2014).

Heavy metals exist naturally in the soil or occur as a result of anthropogenic activities of humans. These anthropogenic activities include human activities such mining, extraction, indiscriminate waste disposal and some agricultural activities (Otitoju *et al*,. 2014). In agriculture, activities such as irrigation with contaminated water and the use of metal based pesticides and fertilizers introduce these metals into foods (Ghazanfarirad *et al*., 2014). These metals are considered harmful because they are non -degradable, have long half-lives and can accumulate in most animal and plant tissues (Otitoju *et al.*, 2014). Higher concentrations of some heavy metals are known to destroy cell membranes in plants. However, some plants are able to absorb these toxic heavy metals and adapt to their high concentrations in the soil. Farms near industrial areas or irrigated with polluted water stand a higher chance of heavy metal contamination (Faruruwa *et al*., 2013). Heavy metal contamination leads to the depletion of essential nutrients in the body which causes adverse effect on the immune system. When heavy metals are not effectively excreted in cases of heavy metal poisoning, cancers can occur (Otitoju *et al*., 2014).

2.6. Absorption of heavy metals in plants

Heavy metals exist naturally in the soil from parent materials and from anthropogenic activities such as agricultural activities, industrialisation and extractive activities (mining). The ability of crops to absorb and accumulate these metals differ from species and cultivars (Satpathy *et al*., 2014). Plants are known to absorb heavy metals from the subsurface at a depth of about 25cm where the roots of most cereals are located. Absorption is done by the roots and then translocated to the shoots, the branches and leaves. The higher the amount of heavy metals in the subsoil, the higher the quantity absorbed and eventually consumed by humans and animals (Payus & Talip, 2014).

2.7 Arsenic

2.7.1 Chemistry

Arsenic (As) forms part of the fifth group (VA) on the periodic table and considered as a metalloid or semi-metal. It has both metal and non- metal properties. It has a relative atomic mass of 74.92 and atomic number of 33 (WHO, 2001). Arsenic has oxidation states -3,0,+3 and +5 but often occurs in oxidation states of +3 (arsenite) and +5 (arsenate). Arsenic occurs in inorganic and organic forms. Inorganic arsenic is formed when arsenic in the environment combines with compounds such as sulphur, oxygen and chlorine (Maud & Rumsby, 2008) Inorganic arsenic compounds include, sodium arsenite and arsenic, trichloride arsenic, arsenic trioxide pentoxide, arsenic acid and arsenates. Organic arsenic compounds include arsenobetaine, dimethylarsinic acid (cacodylic acid), arsanilic acid and methylarsonic acid (WHO 2001). They are mostly formed when arsenic combines with carbon and hydrogen (Maud & Rumsby, 2008)

2.7.2. Sources of Arsenic

Arsenic occurs naturally in a sulphide form in complex minerals containing silver, copper, cobalt, nickel, lead and iron (Guha Mazumder, 2008). Inorganic arsenic is found in rocks, soils and sediments. Other human activities such as mining and industrial ore smelting also introduce arsenic into the soil and water bodies through the discharge of their effluent (Szymańska-Chabowska *et al*., 2002).

In agriculture, the use of arsenic based pesticides and irrigation of farms with arsenic contaminated water introduces arsenic into crops. Drinking water and foods especially sea foods are the major avenues of arsenic exposure in humans. Arsenic is used industrially in the production of lasers, transistors and semiconductors. It is also used in the manufacture of paper, textiles, metals, pesticides, feed additives, pharmaceuticals among others (WHO, 2001; IARC, 2006). Arsenic is mainly used in the manufacture of copper chromate arsenate which is a wood preservative used to prevent rotting and decay (Maud & Rumsby, 2008)

2.7.3. Dietary Exposure of Arsenic

Ingestion is one of the major routes of arsenic exposure in humans. Some test of food samples have shown positive result for presence of arsenic. The presence or concentration of arsenic in foods is dependent on factors such as type of food, growing conditions, use of arsenic based agro-chemicals and food processing techniques (WHO, 2001). Sea foods are known to have higher arsenic concentrations predominantly organic arsenic and this due to the possible contamination of the water bodies. Other foods such as meats, poultry, cereals, vegetables, fruits and dairy products have recorded some amount of arsenic. Fruits and vegetables just as sea foods have predominant amounts of organic arsenic with cereals, meat and poultry having high amounts of inorganic arsenic (WHO, 2001).

Based on geographical area and which foods are eaten most by a population, arsenic exposure rate differs from place to place. People who consume a lot of seafood might have higher intake of arsenic compared to those who consume less seafood. (WHO, 2001). Arsenic when ingested accumulates in keratin tissues like the hair, nails, blood and urine.

2.7.4. Toxicity to humans

Arsenic is known to cause adverse health effects in humans. The extent of effect often depends on the duration and dose of exposure (Guha Mazumder, 2008). Acute arsenic toxicity leads to symptoms such as vomiting, diarrhoea, nausea, dehydration and shock (Kapaj *et al.*, 2006). Chronic arsenic toxicity has also been implicated in diseases such as skin lesions (melanosis & keratosis), skin cancer and bronchitis. It also has adverse effect on the gastrointestinal, cardiovascular and urinary systems (UNICEF 2008). Other health conditions such as high blood pressure, diabetes, bladder and lung cancer have all been linked to As poisoning.

Studies have suggested that children exposed to arsenic have slower intellectual development. Arsenic poisoning has also been associated to the greater risk of foetal loss and still birth in pregnant women (Guha Mazumder, 2008).

2.8. Lead

2.8.1 Chemistry

Lead is a bluish white metal with an atomic number of 82 and relative mass of 207.2 and belongs to group 14 on the periodic table. Lead is a bad conductor of electricity. It is also described to be malleable, soft and ductile. It exists in oxidation states of +2 and +4. Lead is mostly obtained from galena ores. Lead can be used in the manufacture of lead-acid batteries, plumbing resources and alloys (Abadin *et al*., 2007). It is also used in cable sheathing, paints, glazes and ammunition. Lead in the form of tetra ethyl and tetra methyl lead is used as antiknock and lubricating agents in petrol in some parts of the world (*EFSA*, 2012).

2.8.2. Sources of Lead

At very deep depths of the earth, lead can be found in the form of lead sulphide. Natural activities such as volcanic eruption, weathering of rocks, sea spray emission and human activities such as mining, releases the deeply buried lead to the surface of the earth. Lead can now be found in the environment due to activities such as refining, recycling of lead, usage of gasoline, manufacture of paints, jewellery and its use in water pipes (WHO, 2010).

2.8.3 Dietary Exposure

Lead exposure is mainly via consumption of water, food, soil, air, and dust. Ingestion of lead is mainly attributed to the drinking of lead contaminated water and secondly through contaminated foods (Agency for Toxic Substances and Disease Registry, 2012). Food and water are the major sources of exposure to lead however, children eating soil and dust can also be a significant contributor. A study by (EFSA, 2012) indicated tap water was one of the major contributors to arsenic exposure. Other foods such as grains and grain based products, milk and dairy products, non-alcoholic beverages, wheat bread and bread rolls, regular beer, iodised salt, potatoes, vegetables and tea beverages also contribute to dietary lead exposure in humans.

Lead amasses in the body, predominantly in the skeleton (teeth and bones) hence these body tissues are tested to determine cumulative exposure. Half-life for inorganic lead in the blood is roughly 30 days, while in bone it is amid 10 and 30 years (EFSA, 2012).

2.8.4 Lead Toxicity to humans

Lead poisoning is an intoxication mainly due to the absorption of harmful levels of lead into body tissues (Friend, 1991). Acute lead toxicity may lead to gastrointestinal disorders such as abdominal pain, vomiting, and anorexia. Hypertension, neurological effects and damages to hepatic and renal tissues have also been associated to lead intoxication (IARC, 2006). Chronic exposure to lead has been associated with haematological effects such as anaemia, or neurological disturbances such as paralysis, lethargy, convulsions, muscle weakness, tremors and headache (IPCS, 1995). Studies of lead workers by (Abadin *et al*., 2007) suggests that chronic exposure to lead may be linked to high rates of mortality due to cerebrovascular disease. According to (WHO, 2010), children and pregnant women are the most susceptible to lead poisoning. In children, intellectual and neuro- behavioural disorders are observed in children exposed to lead and this greatly affect their intelligent quotient. Studies propose that an IQ drop of 1– 5 points is associated with an rise in PbB of 10 μg/dL (Abadin *et al*., 2007). Children suffer most from lead exposure because their lead intake per body weight is higher, they ingest and inhale more lead and lead absorption in their gastrointestinal system is high. In the cases of neurological effects, due to their under developed blood–brain barrier, they suffer the most compared to adults (WHO, 2010).

Pregnant women are also adversely affected by lead intoxication. Exposure in pregnant women can lead to miscarriages, stillbirth, premature birth and some malformations.

2.9 Cadmium

2.9.1 Chemistry

Cadmium belongs to group 12 on the periodic table and also on the second row as a transition metal. Cadmium has an atomic mass of 112, atomic number to be 48 and an oxidation state of (+2) and eight naturally occurring isotopes (IARC, 2006).

2.9.2 Sources

Cadmium exist naturally on land and in the sea. Natural activities such as volcanic activity, weathering and erosion and river transport among others releases cadmium into the environment (WHO, 2010). Human activities including manufacture of phosphate fertilizers, recycling of electronic waste, incineration of waste and mining also make cadmium abundant in the environment (WHO, 2010). Lead and zinc mining also introduces cadmium into the environment. By atmospheric transport, cadmium released can be transported and deposited on areas distant from the sources of emission (WHO, 2010). Crops and aquatic organisms uptake cadmium from the soil and sea and this introduces cadmium in the food chain.

2.9.3 Dietary exposure to Cadmium

Exposure to cadmium is mainly through the consumption of cadmium contaminated foods. However inhalation of tobacco smoke can also introduce cadmium to tobacco smokers (Bernard, 2008). Cadmium is mostly found in higher concentrations in molluscs and crustaceans and also in the kidney and liver of mammals fed with cadmium-rich diets. Lower concentrations are found in vegetables, cereals and starchy foods. Rice is also known to sometimes accumulate high concentrations of cadmium (WHO, 2010). In 2010, FAO/WHO Expert Committee on Food

Additives suggested 25 µg/kg body weight as the provisional allowable monthly intake of cadmium (WHO, 2010).

2.9.4 Toxicity to humans

Cadmium is one of the well- known metal toxicants found in humans. Rice is the major source of cadmium for most rice eating countries. Cadmium contamination can cause bone defects and fractures and can lead to kidney damage in humans (Naseri *et al*., 2014). Human renal dysfunction has also been associated with cadmium intoxication and this leads to excretion of high amounts of low molecular weight proteins in the urine (Satpathy *et al*., 2014). High concentrations of cadmium in the body adversely affects calcium metabolism. This leads to softening of the bones leading to occurrence of osteoporosis (Bernard, 2008). Result from some studies have concluded cadmium as a human carcinogen. Studies on workers exposed to cadmium by inhalation has shown that these workers stand the risk of lung cancer (Bernard, 2008).

2.10 Heavy metal determination

Different methods can be used in heavy metal determination. In selecting the type of equipment to use, factors such as cost, limit of detection, availability of instrumentation, sensitivity, physical state of the matrix are considered. Some of the analytical techniques used include; Atomic Absorption Spectroscopy (AAS), Atomic Fluorescence Spectroscopy (AFS), Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X−ray fluorescence (XRF), Electron Microprobe (EM), Flame Photometer (FP) and Instrumental Neutron Activation Analysis (INAA). Depending on the matrix, these instruments accurately measure elements in environmental sample to parts per billion (ppb) concentrations i.e. µg/L and µg/Kg solid samples respectively (de Gennaro *et al*., 2007).

Irrespective of the equipment used, pre-treatment of sample with acidic extraction or with target reagents is required. The significance of pre-treatment is that all elemental species are converted into the inorganic form for easier detection and measurement.

2.10.1 Atomic absorption spectroscopy (AAS)

It is based on absorption of monochromatic light by a cloud of atoms of the analyte metal. During the analysis, liquid sample is aspirated into a nebulizer system. The sample then mixes with an oxidant gas under pressure into a burner to form an aerosol. The flame which uses either air-acetylene or nitrous-oxide acetylene operates at a temperature of 2400^oC and 2800^oC respectively. Within the flame, the aerosol undergoes processes such as evaporation of the solvent and excitation of the gaseous metallic element. To determine the concentration of the analyte, a light beam from a lamp usually a Hollow Cathode Lamp (HCL) whose cathode is made of the element being determined is passed through the flame. A photomultiplier tube then detects the amount of reduction of the light intensity due to absorption (absorbance) by the analyte. The absorption is proportional to the concentration of the metal ions following the Beer-Lambert Law (de Gennaro *et al*., 2007)

2.11 Heavy metal presence in rice

There have been several reported cases of heavy metal contamination of rice and some studies have also confirmed this. One of such studies is the work by (Naseri *et al*., 2014) on the effect of cooking on some heavy metal content of some rice sold on the Iranian market. In that study, the presence of some heavy metals such as Pb, Ni, Cd, Cr were confirmed. In their analysis, they had lead ranging from 0.363 – 1.617 ug/g and cadmium ranged from 0.346-2.000 ug/g in three different types of raw rice sold on Iranian market. These values according to them, exceeded the maximum allowable contents as permitted by the standards institute in Iran.

In a study by (Otitoju *et al*., 2014) to quantify heavy metals in some locally produced rice from northern Nigeria, lead concentration in samples ranged from 0.311 to 0.525 mg/kg with a mean lead value of 0.260 mg/kg. Their result also showed that the concentrations of other heavy metals such as chromium, arsenic, cadmium and mercury could not be detected at less than 0.001mg/kg in any of the samples.

The occurrence of cadmium in rice, was also studied by Mohammad *et al.*, (2008) and the results showed that cadmium concentration ranged from 0.12 to 0.83 µg/g with an average concentration 0.40 ± 0.16 µg/g.

These works confirm that heavy metal contamination of rice is a serious public health issue and hence measures should be put in place to address it. Although some studies have been done to confirm heavy metals in rice in other countries, not much has been done in this area in Ghana. There is the need to continually test for the presence of these heavy metals so as to monitor their concentrations and ensure that they do not exceed the allowable intake concentrations. This will help curb the risk of heavy metal contamination and its associated adverse effect on human health.

2.12 WHO/ FAO (CODEX) standards for metallic contaminants in rice.

Due to the harmful nature of heavy metals, it is appropriate that standards clearly states the permissible amount of these metals in foods. In view of this, there are standards which state the maximum limits (ML) for metallic contaminants. One of such standards is the Codex General Standard for Contaminants and Toxins in Food and Feed (CODEX STAN 193-1995). In this standard, ML's for cadmium in polished rice is 0.4mg/kg which is the highest among all the foods listed in that standard (CODEX, 1995a) . The standard however has no clearly stated ML for arsenic and lead in rice. It however states an ML of 0.2mg/kg for lead in cereal grains, except buckwheat, cañihua and quinoa.

The codex standard for rice (i.e CODEX STAN 198-1995) under section 4.1 states that the products (rice) as per the requirement of this standard shall be free from heavy metals in levels which may pose as a hazard to human health. It however does not state any allowable or maximum limits (CODEX, 1995b).

CODEX (2012), which gives a list of maximum levels for contaminants and toxins in foods, also states an ML of 0.4 mg/kg for cadmium in rice and an ML of 0.2 mg/kg for lead in cereal grains except buckwheat, cañihua and quinoa (CODEX, 2012).

The 5th Session of the Codex Committee on Contaminants in Foods (CCCF) has however proposed an ML of 0.3 mg/kg for arsenic (whether inorganic or total arsenic) in rice (CODEX, 2012). The CODEX committee is also putting measures in place to set maximum limits for arsenic in unpolished rice.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study Area

Accra, the capital city of Ghana was selected for this study. Accra as a capital city and its proximity to the ports has made it one of the prepared destination for rice trading. The increasing population of Accra has also resulted in a high demand for rice making rice trading prominent. Some major markets in Accra were randomly selected for the study. These markets were the Madina market, Makola market, Mallam Atta market, Nima market, Agboboloshie market and Kanashie market. These are major markets where most commodities are sold including rice. Rice sold in these markets include both foreign and local rice which are either polished or unpolished. However, the polished imported rice out-number the local rice samples as well as the unpolished rice.

3.2 Sample acquisition

Samples were purchased from different rice traders in these markets within the month of July 2015. Random sampling method was used in purchasing samples based on the origin of the rice. Samples were obtained in duplicates of 500g each.

Figure 3.1. Rice displayed on the market for sale

Figure 3.2 Purchased rice sample

3.3 Sample Preparation

Rice samples were homogenized and pulverized using a stainless steel homogenizer (Warring Commercial blender). The samples were then microwave digested before further analysis (using AOAC 999.11 (2002).

Figure 3.3. Milling of rice samples

Figure 3.4. Milled rice samples

3.3.1 Digestion procedure (AOAC 999.11)

Each sample was weighed in duplicates (0.5g each) into Teflon PTFE vessel. Deionised water (1ml) was added to the powdered rice samples followed by 5mL of HNO_3 (65 % v/v) and 3mL of H_2O_2 (30% v/v). The samples were digested in a microwave (Ethos 900, Tokyo, Japan) at a temperature of 200^{o}C, pressure of 50 bars, and power of 1000 watts for 50 minutes. Upon cooling to room temperature, the digested samples were poured into 50 mL polypropylene tubes and topped up to 20 mL with deionized-water. The digested sample was then used to determine the concentrations of cadmium, lead and arsenic.

Figure3.5. Microwave digester

3.4 Analysis of Cadmium, Lead and Arsenic

Lead, cadmium and arsenic were determined using graphite furnace atomic absorption spectrometer (GFASVarian SpectrAA model 240FS, Tokyo, Japan) since they are present at very low concentrations that are usually not detected by F-AAS. In the GF-AAS (Varian GTA 120) technique, a pyrolytically coated tube with platform was used for the analysis and a programmed autosampler delivered a volume of 25uL that gave an absorbance within the linear range. The atomization temperatures of Pb, Cd and As were 2100^{o}C, 1800^{o}C and 2600^{0}C and were determined at wavelength of 283.3nm, 228.8nm and 193.7nm with lamp currents of 9.0mA, 4.0mA and 9 mA respectively using acetylene as the fuel and air as the support gas. The digest were aspirated into the spectrometer according to the manufacturer's guidelines for each element in the cookbook of the atomic absorption spectrometer.

3.5 Detection limits

The analytical detection limits (DL) for heavy metals in the digest were calculated as DL = x+3std; where x is the mean and std is the standard deviation of blank reading ($n \geq 20$). The calculated DL for the digest was approximately 0.001mgCd/kg, 0.03mgAs/kg and 0.01mgPb/kg. A DL is not static and will need re-evaluation from time to time in accordance with changes in the blank levels.

3.6 Quality control and assurance

Quality assurance techniques were conducted during the analysis to validate the accuracy and reliability of the analytical results obtained. Reagent blanks were analysed with each batch of samples as a guide to correct sample readings in case of any form of contamination of heavy metal in reagents or water used. Certified reference materials (CRM Dorm 4, and Fapas proficiency material) with assigned concentrations were analyzed with every batch of analyses. The certified reference materials (Dorm 4) and PT (powdered rice) were obtained from the National Research Council, Canada and FAPAS respectively. Standard solutions used as calibration checks were also analyzed at intervals (1 in every 8 samples) during analyses to monitor and control readings of the atomic absorption spectrometer. To ensure reproducibility of test results, samples were independently analyzed in triplicates.

3.7 Data analysis

Minitab 16 software was used for the statistical analysis of data. Differences between samples were determined using two sample t- test and significance was accepted at $p < 0.05$.

CHAPTER FOUR

4.0 Results and Discussion

4.1 Arsenic concentration

Contamination of rice by arsenic continue to be a threat to food safety and human health (Zavala & Duxbury, 2008). Research has shown that rice accumulate arsenic in different forms such as arsenite, arsenate, methylarsenic acid and dimethyl- arsenic acid from the soil and water used for farming (Shraim, 2014). Studies have also shown that the wide variability of total arsenic concentrations in rice can be attributed to the region of growth (Zavala & Duxbury, 2008). According to WHO, (2010) the utmost risk to public health from arsenic is mainly found in contaminated groundwater, which may be attributed to natural geochemical processes or anthropogenic pollution.

Results from this study, indicated that the concentration of arsenic in all of the rice samples analysed were within allowable limits of 0.2 mg/kg as stated in the Codex General Standard for Contaminants and Toxins in Food and Feed (Codex Stan 193-1995). The level of arsenic in locally polished rice ranged from 0.0297 mg/kg to 0.1504 mg/kg with a mean value of 0.0843mg/kg whiles the levels in foreign polished rice ranged from 0.0531mg/kg to 0.1772 mg/kg with an average value of 0.1032 mg/kg (Fig.4.1). Though the mean values of arsenic detected in foreign rice was higher than the local rice, there was however no statistically significant difference ($p>0.05$) between the means of local and foreign polished rice. The concentration of As obtained in this study were lower than 0.11- 0.65 mg/kg reported by Rintala *et al.*, (2014) and 0.005– 0.710 mg/kg reported by Zavala & Duxbury, (2008).

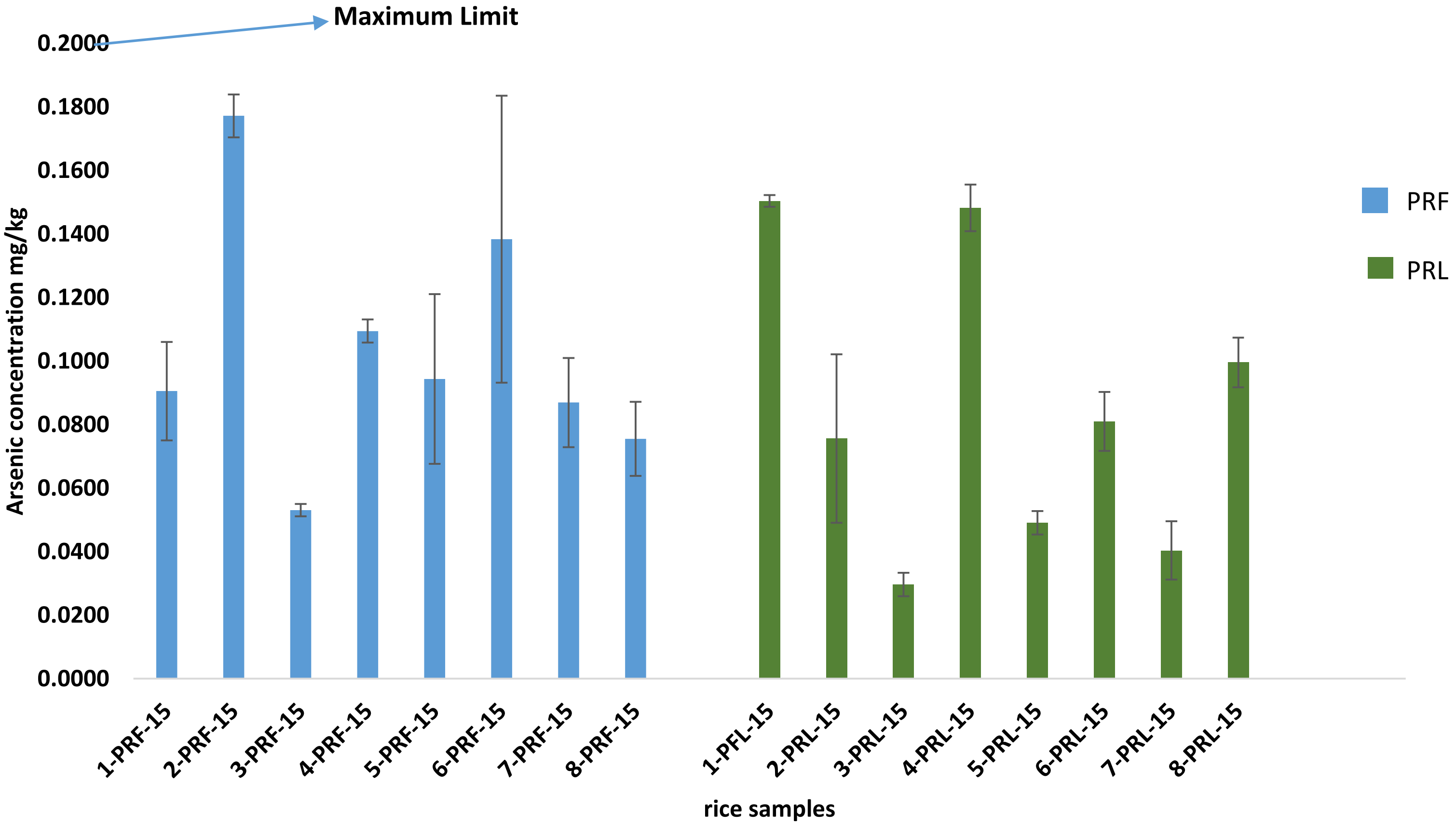

Figure 4.1. Concentration of arsenic in foreign and local polished rice.

Figure 4.2 indicates that concentration of arsenic in unpolished rice were below the highest maximum limit of 0.4 mg/kg proposed by the eWG establishing ML's for arsenic in unpolished rice (CODEX 2015). The levels of As varied widely from not detected (N/D) to 0.2370 mg/kg with an average value of 0.1212 mg/kg. The average As concentrations for unpolished rice in this study was lower than that of Narukawa, *et al.* (2014) who had an average of 0.239 mg/kg. Comparing arsenic concentrations in unpolished rice to polished rice showed no significant difference ($p > 0.05$) in the means. However, Zavala & Duxbury, (2008) observed significant difference in rice based on color or type. Brown rice had a high As concentration of 0.196 mg kg^{-1} followed by white rice with 0.127 mg kg^{-1} and other colors with 0.070 mg kg^{-1}.

The greater concentration of As in brown rice is credited to the fact that it still contains its outer layers which are detached in white rice after milling (Zavala & Duxbury, 2008).

Lower levels of arsenic in rice were observed by Otitoju *et al.* (2014), in Nigeria who did not detect arsenic at LOD of 0.001 mg/kg. In a similar study, Shraim (2014), reported a mean arsenic concentration of 0.136 ± 0.086 mg /kg and a concentration range of 0.026 – 0.464 mg /kg. The results of their study indicated that arsenic concentrations varied widely with the country of origin.

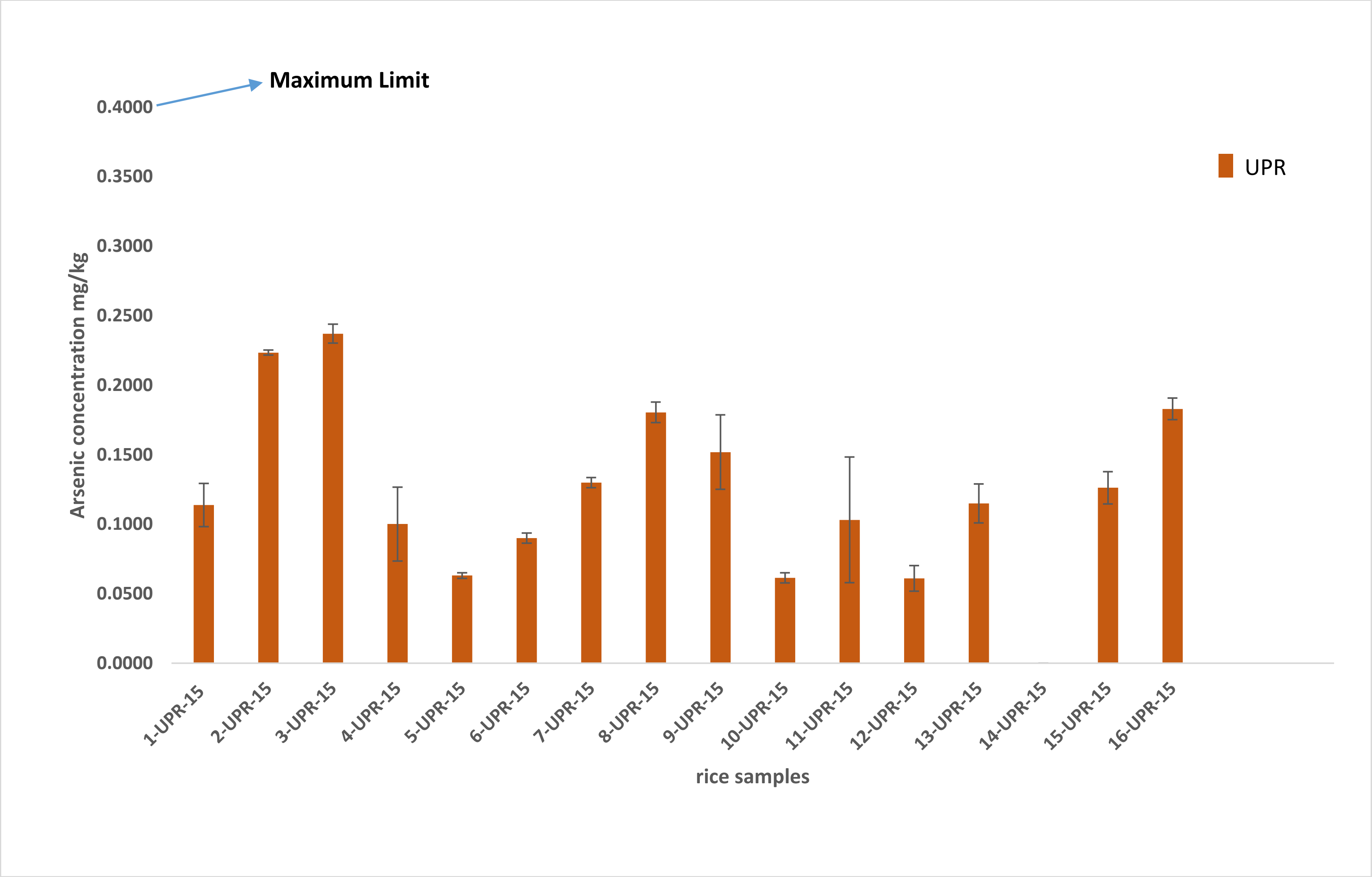

Figure4.2. Concentration of Arsenic in unpolished rice

It is recognized that many factors contribute to the uptake of As by the rice plant. Arsenic concentration in rice may be influenced by the following but not limited to the level of As in water used for irrigation and soil, the chemical and physical properties of the soil, agrochemical application, management practices as well as genetic differences (Zavala & Duxbury, 2008).

Since As is obtained through natural sources such as volcanic action or anthropogenic activities, the concentration of As in crops may depend on the degree of these activities within a particular environment hence the reason for variability in results obtained in this study as compared to earlier works.

4.2 Cadmium concentration

Cadmium exposure in humans has been linked with several adverse effects leading to illnesses notably amongst them being cancer (Ji *et al.,* 2012). Foods such as cereals, vegetables and starchy root tubers are known to contain lower cadmium concentrations. Rice is known to accumulate high concentration of cadmium if grown on cadmium polluted soils, thus considered as one of the major sources of cadmium in humans (WHO, 2010)

In this study, the cadmium content of both polished and unpolished rice were far below the maximum limit of 0.4 mg/kg permitted by CODEX standard (FAO/WHO, 2012). The content of Cadmium in all of the samples analysed were below 0.1 mg/kg (Fig.4.3).

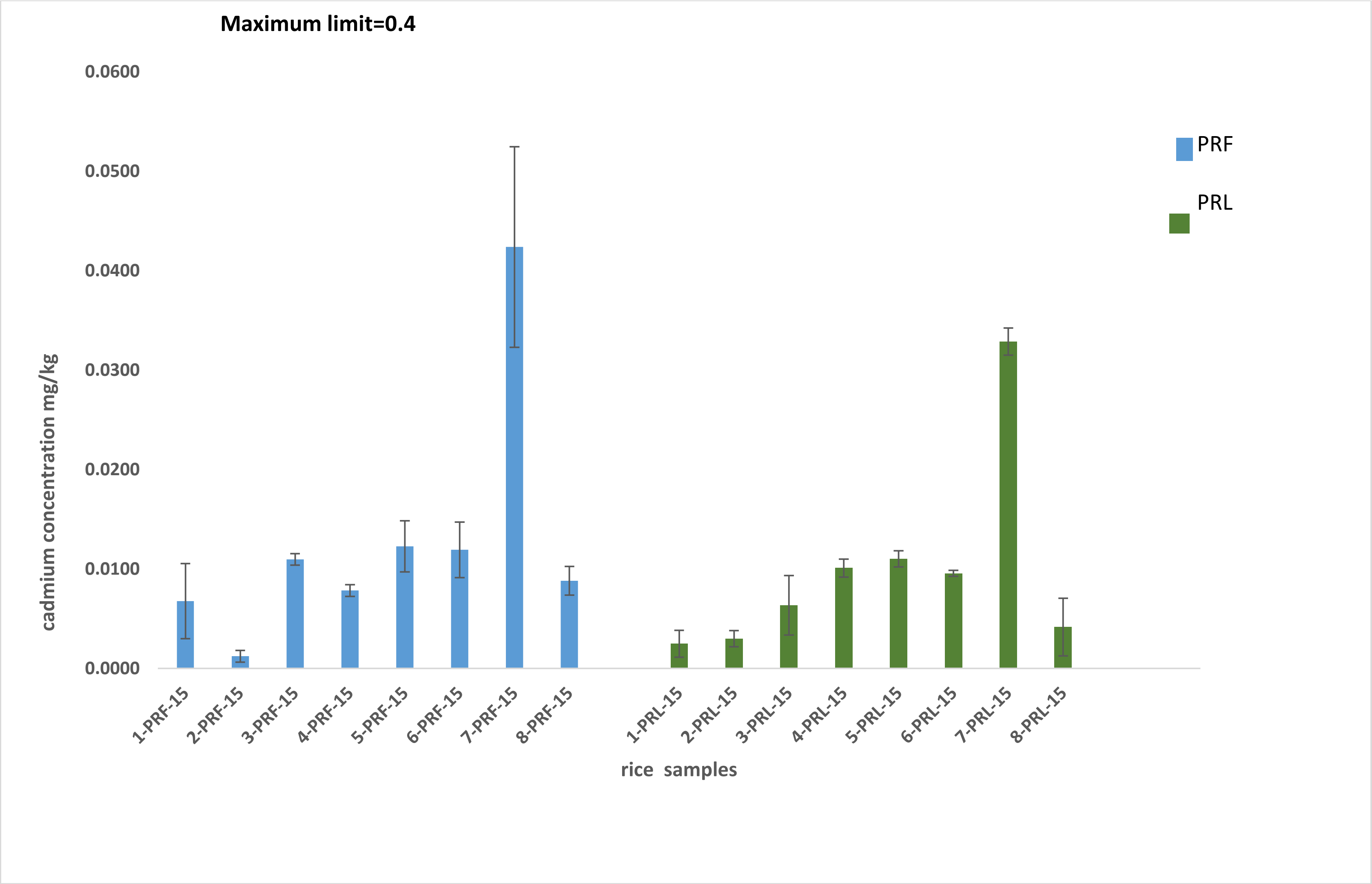

Figure 4.3. Concentration of Cadmium in foreign and local polished rice

The level of Cd in foreign polished rice ranged from 0.0012mg/kg to 0.0424 mg/kg with a mean of 0.0128 mg/kg whiles locally produced polished rice reported a mean cadmium content of 0.0099 mg/kg with a maximum value of 0.0329 mg/kg and a minimum value of 0.0025 mg/kg (Fig 4.3). Results indicated no significant difference (p>0.05) in the means of cadmium between the locally produced and foreign polished rice.

Shraim, (2014) reported lower cadmium concentration in rice with an average Cd of 0.017 mg/kg and a range of 0.003 mg/kg to 0.046 mg/kg. A study in Nigeria by Ghazanfarirad *et al.,* (2014) reported cadmium in rice to have an average mean of 0.022 ± 0.027 mg/kg. However, Otitoju *et a*l., (2014) in their study on rice samples imported to Nigeria had no detected values for cadmium.

Results for cadmium in unpolished rice ranged from not detected to 0.0628 mg/kg with a mean value of 0.0179 mg/kg. In a study by Ji *et al*., (2012), cadmium concentration in brown rice ranged from 0.03 mg/kg to 0.96 mg/kg, with an average as 0.15±0.17 mg/kg. In their study, they reported that about 15.6% of the total samples analyzed exceeded the maximum limit for cadmium.

The results of this study compares favorably with that of Payus & Talip, (2014) who reported mean concentration of 0.13 ± 0.08 mg/kg for cadmium. According to Payus & Talip, (2014) the rice grain concentrated the highest cadmium levels as compared to other part of the rice plant such as the root, stem and shoot.

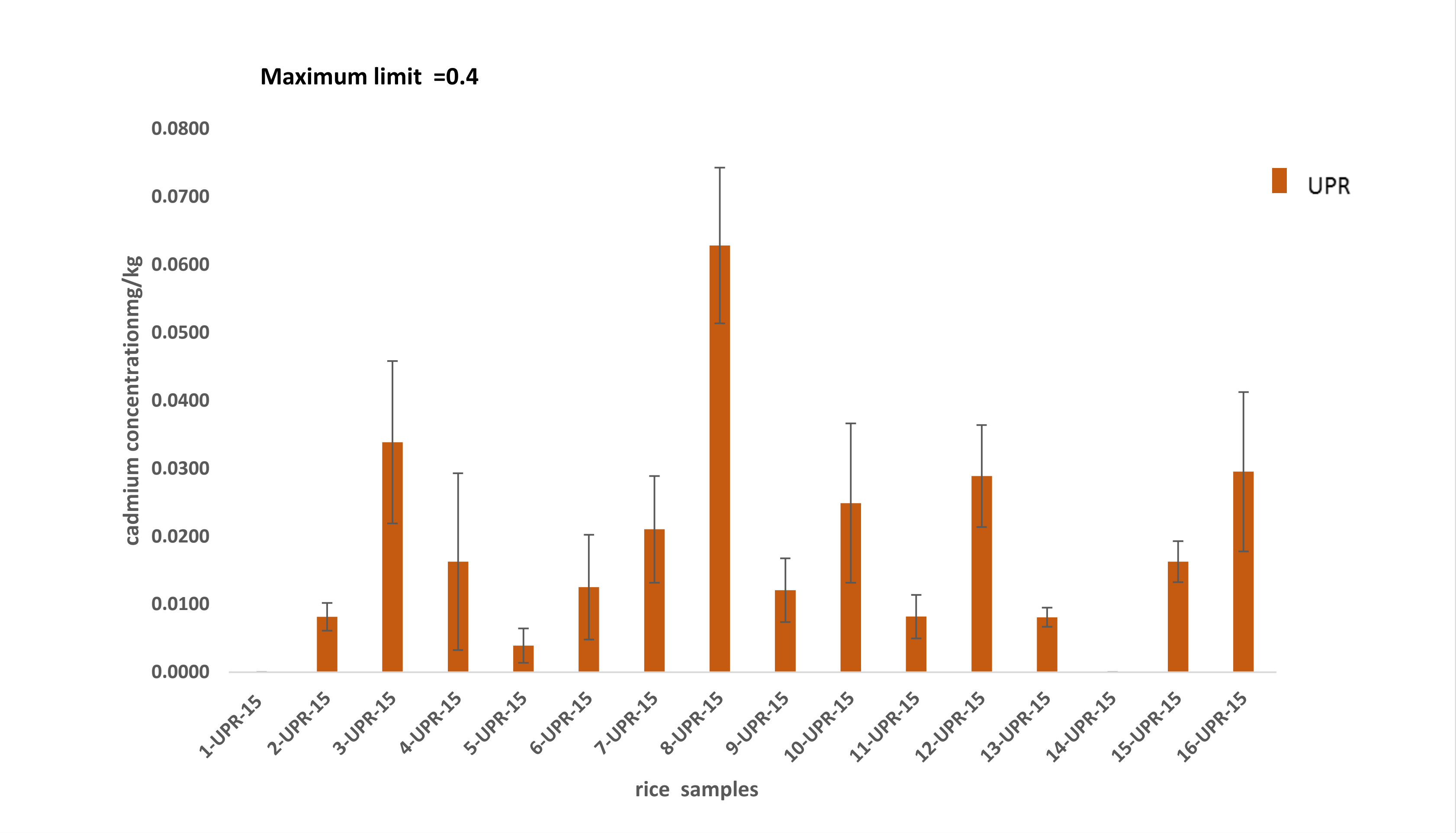

Figure 4.4. Cadmium concentration of unpolished rice.

Similar to arsenic, cadmium has been categorized by International Agency on Research into Cancer (IARC) as a human carcinogen. According to Shraim, (2014) exposure to high levels of Cd causes severe irritations in the digestive system leading to vomiting and diarrhea.

4.3 Lead concentration

In this study, the concentrations of lead in rice were below the maximum allowable limit of 0.2 mg/kg permitted for cereal grains by CODEX Standard (CODEX STAN 193-1995). For polished rice, concentration of lead in foreign rice ranged from to 0.0007 mg/kg to 0.0505 mg/kg with an average of 0.0171 mg/kg whiles polished local rice reported an average concentration of 0.0308 mg/kg with a minimum of 0.0027 mg/kg and a maximum value of 0.1106 mg/kg (fig 4.5).

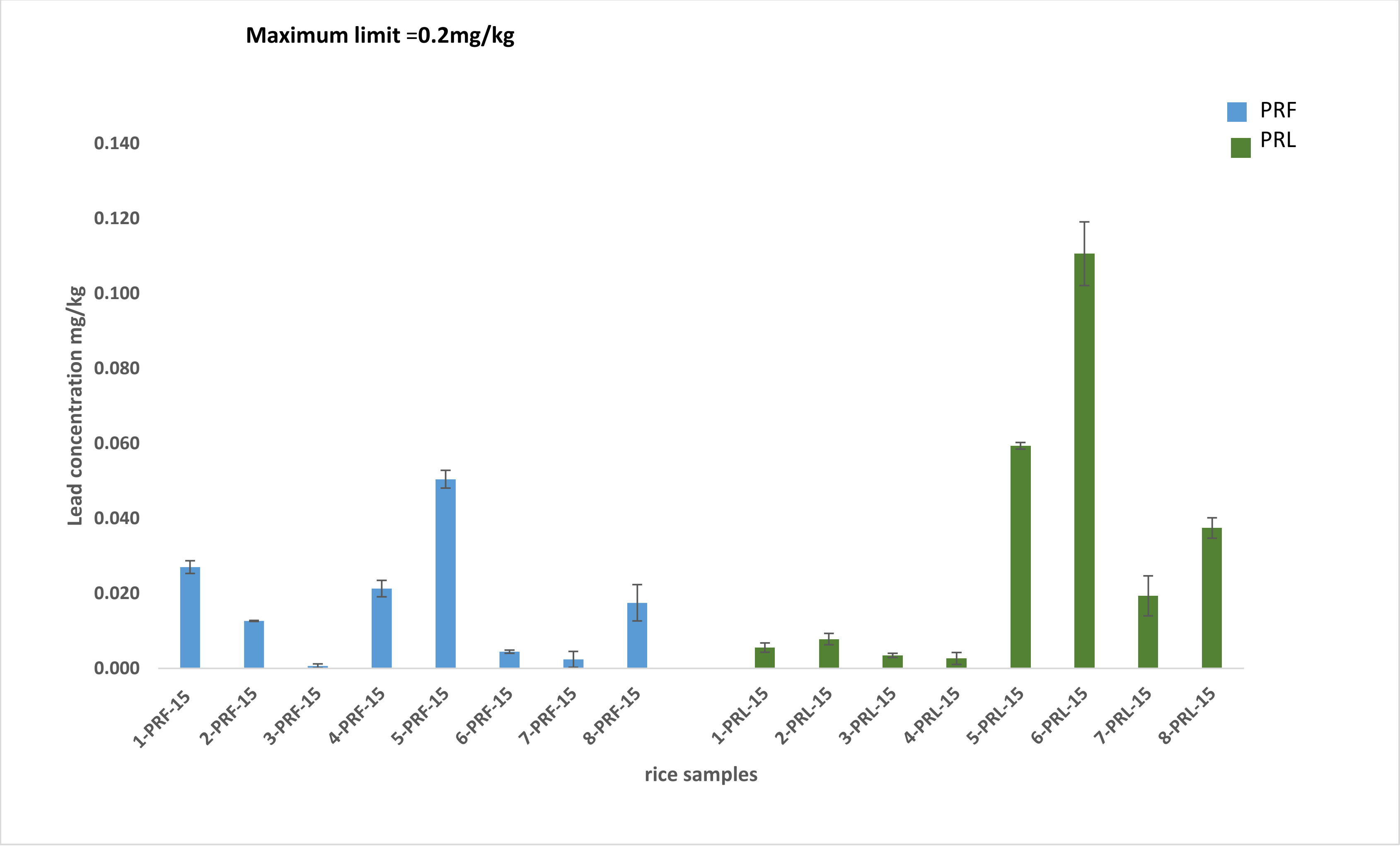

Figure 4.5. Lead concentration of foreign and local polished rice samples

These concentrations are similar to the values obtained by Ghazanfarirad *et al*, (2014) who conducted a similar study in the Northwest of Iran. They obtained an average lead concentration of 0.037 ± 0.9 mg/kg. Results for lead concentration for unpolished rice in this study ranged from a minimum of 0.0007 mg/kg to a maximum of 0.1106 mg/kg with an average concentration of 0.0239 mg/kg (Fig 4.6).

A study by Batista (2012), on rice samples consisting of white polished rice, white parboiled and brown parboiled showed much lower concentration of lead in the samples. Lead concentration ranged from 0.4 to 14.5 ng·g^{-1} with parboiled brown rice having the highest concentration of 7.8 ng·g^{-1} followed by white rice with 5.3 ng·g^{-1} and parboiled white rice having lowest of 3.1 ng·g^{-1}. On the other hand, Naseri *et al*. (2014) had a higher average lead concentration of 1.75 µg/g in raw rice samples obtained from Iranian market in their study.

Results from this study showed there is no significant difference in concentration of lead between local and foreign polished rice samples. Unpolished rice samples recorded the highest lead concentrations compared to the polished rice samples. Statistical analysis showed no significant difference between the lead concentrations of unpolished and polished samples.

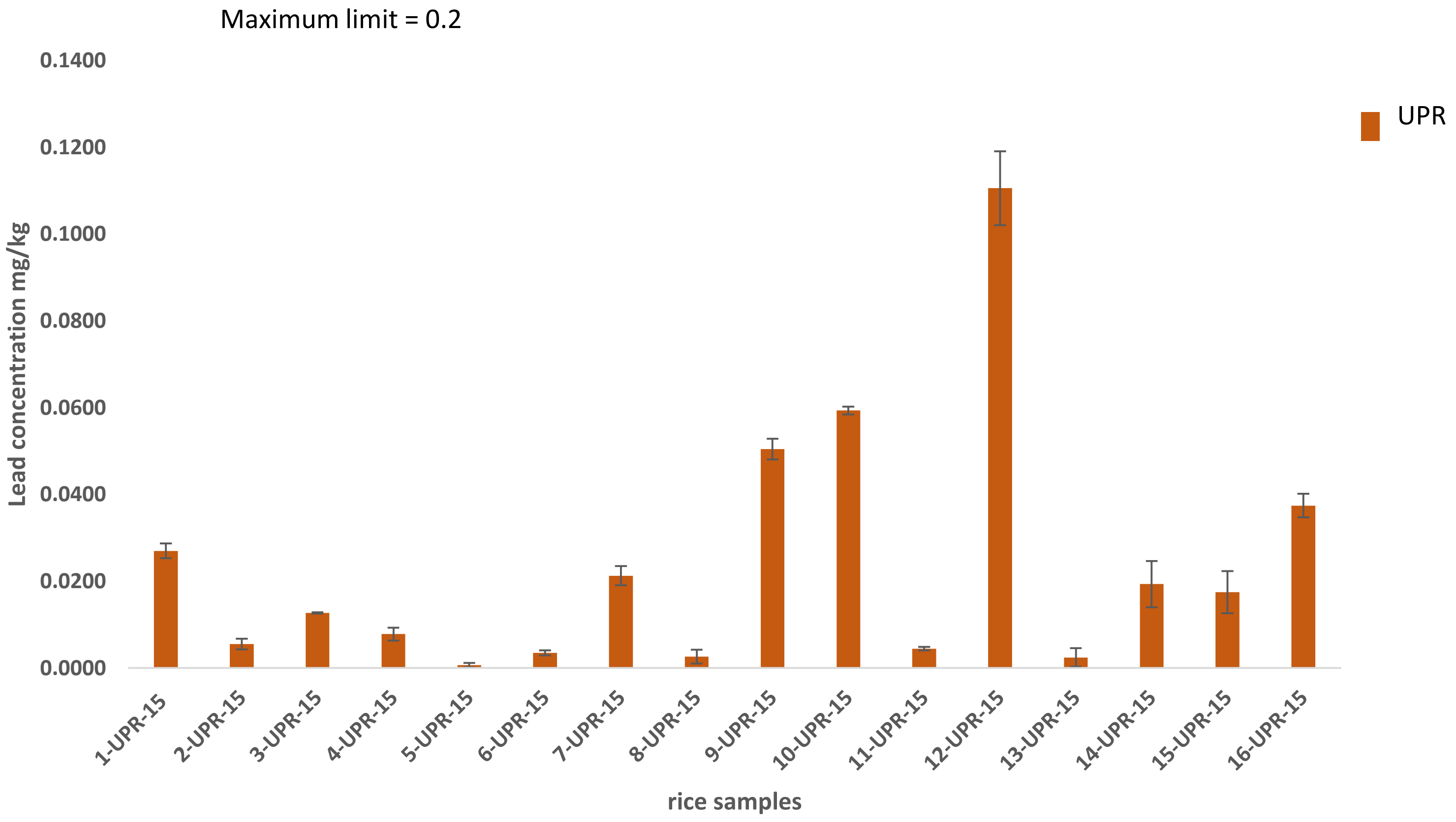

Figure 4.6. Lead concentration of unpolished rice samples

Lead contamination in rice samples continue to be a threat to food safety and health of consumers since other studies have also reported higher concentration of lead in rice. A study by (Otitoju *et al.*, 2014) in Northern part of Nigeria reported higher concentrations of lead in rice. They recorded an average lead concentration of 0.152 mg/kg with maximum and minimum concentration of 0.383 mg/kg and 0.014 mg/kg respectively. Some rice samples in their study had concentrations exceeding the maximum limit allowed by WHO/CODEX. Lead has toxic effects on neurobehavioral development and on the brain cell function.

CHAPTER FIVE

5.0 Conclusion and Recommendation

5.1 Conclusion

The concentrations of As, Cd and Pb in unpolished and polished rice samples investigated in this study were lower than their allowed limits in rice set by CODEX . Also concentrations of As, Cd and Pb in both imported and local rice purchased for this study were within the available recommended limits and are thus, generally safe from heavy metal contamination. Concentrations of lead in rice were significantly higher compared to the concentrations of arsenic and cadmium obtained. Agencies or institutions responsible for food regulation need to periodically determine the concentration of metals in both imported and local rice samples sold on our markets to elude the harmful effects of heavy metals on consumers.

5.2 Recommendation

Based on the outcomes from this study, the following recommendations are being suggested;

i. Although currents levels suggest rice on the Ghanaian market is safe, there is a possibility of heavy metal contamination if levels are not monitored

ii. Further studies should be carried out to conduct exposure assessment on the dietary levels of these heavy metals to provide consumer advice.

iii. Further studies should be conducted to investigate the levels of heavy metals in the soils of rice farms to ascertain the correlation between soil and grain concentration.

iv. Environmental protection managers and other relevant stakeholders should use the findings obtained to regulate the rate of agrochemical application and formulate policies to safeguard the safety of rice produced in Ghana as well as the environment.

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APPENDIX

APPENDIX A.

Table 1 Microwave program for digesting rice sample

Step	**Time (mins)**	**Power (watts)**	**Pressure (Bar)**	**Temp °C**
1	00:20:00	1000	50	200
2	00:20:00	1000	50	200
Vent: 00:10:00		Rotorctrl on		Twist on

Ref: Milestone Operator Manual MA127 (2009)

APPENDIX B

Table 2 Working conditions for Atomic Absorption Spectrometer

Optimization parameters for Graphite furnace Atomic Absorption spectrometer (GTA-AAS)

Elements	Pb	Cd	As
Background correction	Deuterium	Deuterium	Deuterium
Conc. Unit	ug/L	ug/L	ug/L
Instrument mode	Absorbance	absorbance	Absorbance
Sampling mode	Automix	Automix	Automix
Calibration mode	Concentration	Concentration	Concentration
Measurement mode	Peak height	Peak height	Peak height
Replicate standards	3	3	3
Replicate samples	3	3	3
Wavelength	283.3nm	228.8nm	193.5nm
Slit width	0.5	0.5nm	0.5%
Gain	42%	50%	80
Lamp current	9.0mA	4.0mA	4.0mA
Atomization temperature	2100^{o}C	1800^{o}C	2600^{o}C
Total volume	25uL	25uL	25Ul
Calibration Algorithm	Linear	Linear	Linear

APPENDIX C

Table 3. Samples collected from the various markets

TYPE	SOURCE	SAMPLE NUMBER/ID
Unpolished Rice		
Brown rice	Madina	1/UPR/15
Brown rice	Madina	2/UPR/15
Brown rice	Kanashie	3/UPR/15
Brown rice	Kanashie	4/UPR/15
Brown rice	Kanashie	5/UPR/15
Brown rice	Makola	6/UPR/15
Brown rice	Makola	7/UPR/15
Brown rice	Makola	8/UPR/15
Brown rice	Nima	9/UPR/15
Brown rice	Nima	10/UPR/15
Brown rice	Nima	11/UPR/15
Brown rice	Mallam Atta	12/UPR/15
Brown rice	Mallam Atta	13/UPR/15
Brown rice	Agbobloshie	14/UPR/15
Brown rice	Agbobloshie	15/UPR/15
Brown rice	Agbobloshie	16/UPR/15

TYPE	SOURCE	SAMPLE NUMBER/ID
Polished Rice (Foreign)		
Indian long grain	Madina	1/PRF/15
Salna	Madina	2/PRF/15
Royal feast	Kanashie	3/PRF/15
Millicent	Kanashie	4/PRF/15
Bella	Makola	5/PRF/15
My dear	Makola	6/PRF/15
Cindy	Agbobloshie	7/PRF/15
Jasmine	Agbobloshie	8/PRF/15
Polished Rice (Local)		
White Rice	Madina	1/PRL/15
White Rice	Madina	2/PRL/15
White Rice	Kanashie	3/PRL/15
White Rice	Kanashie	4/PRL/15
White Rice	Makola	5/PRL/15
White Rice	Makola	6/PRL/15
White Rice	Agbobloshie	7/PRL/15
White Rice	Agbobloshie	8/PRL/15

APPENDIX D. Concentrations of heavy metals in rice sample

Table 4. Concentrations of arsenic in rice samples

Rice	Mean	SD(±)
1-PRF-15	0.0906	0.0155
2-PRF-15	0.1772	0.0068
3-PRF-15	0.0531	0.0020
4-PRF-15	0.1095	0.0037
5-PRF-15	0.0944	0.0267
6-PRF-15	0.1384	0.0452
7-PRF-15	0.0870	0.0141
8-PRF-15	0.0755	0.0116
1-PFL-15	0.1504	0.0018
2-PRL-15	0.0756	0.0265
3-PRL-15	0.0297	0.0036
4-PRL-15	0.1483	0.0074
5-PRL-15	0.0491	0.0037
6-PRL-15	0.0810	0.0092
7-PRL-15	0.0404	0.0092
8-PRL-15	0.0996	0.0078

Rice	Mean	SD(±)
1-UPR-15	0.1138	0.0155
2-UPR-15	0.2234	0.0018
3-UPR-15	0.2370	0.0068
4-UPR-15	0.1001	0.0265
5-UPR-15	0.0631	0.0020
6-UPR-15	0.0900	0.0036
7-UPR-15	0.1299	0.0037
8-UPR-15	0.1804	0.0074
9-UPR-15	0.1519	0.0267
10-UPR-15	0.0615	0.0037
11-UPR-15	0.1031	0.0452
12-UPR-15	0.0610	0.0092
13-UPR-15	0.1150	0.0141
14-UPR-15	0.0000	0.0000
15-UPR-15	0.1262	0.0116
16-UPR-15	0.1829	0.0078

Table 5. Concentrations of cadmium in rice samples

Rice	Mean	SD(±)
1-PRF-15	0.0068	0.0038
2-PRF-15	0.0012	0.0006
3-PRF-15	0.0110	0.0006
4-PRF-15	0.0078	0.0006
5-PRF-15	0.0123	0.0026
6-PRF-15	0.0119	0.0028
7-PRF-15	0.0424	0.0101
8-PRF-15	0.0088	0.0014
1-PRL-15	0.0025	0.0014
2-PRL-15	0.0030	0.0008
3-PRL-15	0.0064	0.0030
4-PRL-15	0.0101	0.0009
5-PRL-15	0.0110	0.0008
6-PRL-15	0.0096	0.0003
7-PRL-15	0.0329	0.0014
8-PRL-15	0.0042	0.0029

Rice	Mean	SD(±)
1-UPR-15	0.0000	0.0000
2-UPR-15	0.0082	0.0021
3-UPR-15	0.0339	0.0120
4-UPR-15	0.0163	0.0130
5-UPR-15	0.0039	0.0025
6-UPR-15	0.0125	0.0077
7-UPR-15	0.0210	0.0078
8-UPR-15	0.0628	0.0115
9-UPR-15	0.0121	0.0047
10-UPR-15	0.0249	0.0117
11-UPR-15	0.0082	0.0032
12-UPR-15	0.0289	0.0075
13-UPR-15	0.0081	0.0014
14-UPR-15	0.0000	0.0000
15-UPR-15	0.0163	0.0030
16-UPR-15	0.0295	0.0117

Table 6. Concentrations of lead in rice samples

Rice	Mean (x)	SD
1-PRF-15	0.0270	0.0017
2-PRF-15	0.0127	0.0001
3-PRF-15	0.0007	0.0005
4-PRF-15	0.0213	0.0022
5-PRF-15	0.0505	0.0024
6-PRF-15	0.0045	0.0004
7-PRF-15	0.0024	0.0021
8-PRF-15	0.0175	0.0049
1-PRL-15	0.0055	0.0012
2-PRL-15	0.0078	0.0015
3-PRL-15	0.0035	0.0006
4-PRL-15	0.0027	0.0016
5-PRL-15	0.0594	0.0009
6-PRL-15	0.1106	0.0085
7-PRL-15	0.0194	0.0053
8-PRL-15	0.0374	0.0027

Rice	Mean	SD(±)
1-UPR-15	0.0270	0.0017
2-UPR-15	0.0055	0.0012
3-UPR-15	0.0127	0.0001
4-UPR-15	0.0078	0.0015
5-UPR-15	0.0007	0.0005
6-UPR-15	0.0035	0.0006
7-UPR-15	0.0213	0.0022
8-UPR-15	0.0027	0.0016
9-UPR-15	0.0505	0.0024
10-UPR-15	0.0594	0.0009
11-UPR-15	0.0045	0.0004
12-UPR-15	0.1106	0.0085
13-UPR-15	0.0024	0.0021
14-UPR-15	0.0194	0.0053
15-UPR-15	0.0175	0.0049
16-UPR-15	0.0374	0.0027

Appendix E

<u>Arsenic concentration</u>

Polished rice foreign vs polished rice local

Two-Sample T-Test and CI: Mean (x), mean

```
Two-sample T for Mean (x) vs mean

          N    Mean   StDev  SE Mean
Mean (x)  8  0.1032  0.0388    0.014
mean      8  0.0843  0.0462    0.016


Difference = mu (Mean (x)) - mu (mean)
Estimate for difference:  0.0189
95% CI for difference:  (-0.0268, 0.0647)
T-Test of difference = 0 (vs not =): T-Value = 0.89  P-Value = 0.390  DF = 14
Both use Pooled StDev = 0.0427
```

Polished rice versus unpolished rice

Two-Sample T-Test and CI: Mean (xp), Mean (xup)

```
Two-sample T for Mean (xp) vs Mean (xup)

             N    Mean   StDev  SE Mean
Mean (xp)   16  0.0937  0.0423    0.011
Mean (xup)  16  0.1212  0.0629    0.016


Difference = mu (Mean (xp)) - mu (Mean (xup))
Estimate for difference:  -0.027469
95% CI for difference:  (-0.066425, 0.011488)
T-Test of difference = 0 (vs not =): T-Value = -1.45  P-Value = 0.159  DF = 26
```

<u>Cadmium concentration</u>

Polished rice foreign versus polished rice local

Two-Sample T-Test and CI: Mean (x), mean x L

```
Two-sample T for Mean (x) vs mean x L

          N     Mean    StDev  SE Mean
Mean (x)  8   0.0128   0.0125   0.0044
mean x L  8  0.00996  0.00984   0.0035
```

```
Difference = mu (Mean (x)) - mu (mean x L)
Estimate for difference:  0.002813
95% CI for difference:  (-0.009331, 0.014956)
T-Test of difference = 0 (vs not =): T-Value = 0.50  P-Value = 0.625  DF = 13
```

Polished rice versus unpolished rice

Two-Sample T-Test and CI: Mean (x), mean xup

```
Two-sample T for Mean (x) vs mean xup

           N    Mean   StDev  SE Mean
Mean (x)  16  0.0114  0.0110   0.0027
mean xup  16  0.0179  0.0159   0.0040


Difference = mu (Mean (x)) - mu (mean xup)
Estimate for difference:  -0.006544
95% CI for difference:  (-0.016452, 0.003364)
T-Test of difference = 0 (vs not =): T-Value = -1.36  P-Value = 0.186  DF = 26
```

Lead concentration

Polished rice foreign versus polished rice local

Two-Sample T-Test and CI: Mean (x), mean x L

```
Two-sample T for Mean (x) vs mean x L

          N    Mean   StDev  SE Mean
Mean (x)  8  0.0171  0.0165   0.0058
mean x L  8  0.0308  0.0379    0.013


Difference = mu (Mean (x)) - mu (mean x L)
Estimate for difference:  -0.013713
95% CI for difference:  (-0.046769, 0.019344)
T-Test of difference = 0 (vs not =): T-Value = -0.94  P-Value = 0.373  DF = 9
```

Polished rice versus unpolished rice

Two-Sample T-Test and CI: Mean (x), mean x up

```
Two-sample T for Mean (x) vs mean x up

            N    Mean   StDev  SE Mean
Mean (x)   16  0.0239  0.0291   0.0073
mean x up  16  0.0239  0.0291   0.0073


Difference = mu (Mean (x)) - mu (mean x up)
Estimate for difference:  0.000000
95% CI for difference:  (-0.021018, 0.021018)
T-Test of difference = 0 (vs not =): T-Value = 0.00  P-Value = 1.000  DF = 30
```