Levels of Heavy Metals in some Commercially available Rice on the Liberian Market

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ABSTRACT

Human activities such as agriculture, mining, urbanization and waste disposal can lead to heavy metals contamination of food crops, including rice meant for human consumption. In an effort to ensure quality and safe food consumption, this study determined the levels of toxic heavy metals, Arsenic (As), Cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg) and Nickel (Ni) in rice brands widely consumed in Liberia. Hg was determined by AAS technique using a Lumex RA-915M portable Zeeman Automatic Mercury Analyzer. As, Cd, Cr, Pb and Ni were determined by ICP-MS technique using an Agilent 7900 ICP-MS. The levels of As, Cd, Cr, Pb, Hg and Ni concentrations ranged from 1.1 to 18.1, 4.8 to 117.9, 5.0 to 424.5, 1.1 to 37.1, 1.1 to 9.4 and 15.1 to 655.2 μg/kg respectively. The study revealed no significant statistical variability in the metal concentrations between the locally cultivated and imported rice, except for As (P = 0.002). The levels of As, Cd, Pb and Hg in all brands were below the World Health Organization/Food and Agricultural Organization guideline values. Cr and Ni levels were also below the Chinese Guidelines for all rice brands analyzed. The results imply that although the rice brands analyzed contain low heavy metal concentrations, the levels are unlikely to cause adverse health effects to the consuming populace.

Keywords : Monrovia, Rice, Heavy Metals

I. INTRODUCTION

Food safety remains one of the foremost 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 [1]. Heavy metals contamination of food has become a major concern in the world due to their toxicological effects on human [2]. These metals naturally exist in soil, air, and water and are rapidly dispersed by human activities such as urbanization, waste disposal, agricultural chemicalization, mining, among others. Heavy metals such as Lead, Arsenic Cadmium and Mercury are considered non-essential because they do not have any significance in the biochemical processes that take place in human bodies. On the other hand, some elements such as Chromium and Nickel are considered essential but become toxic at comparatively low concentration [3].

Excessive intakes of dietary heavy metals have been shown to cause serious health problems. For examples, the occurrence of the 1955 Itai Itai disease disaster in Japan resulted from the consumption of rice containing high levels of cadmium [4].

In Liberia, rice is the major staple food for both urban and rural citizens though it is commercially produced

on a small scale. Therefore, many of the rice consumed in Liberia are imported from mostly Asian countries [5,6]. Early studies have revealed the presence of notable levels of heavy metals in rice grains from these countries [7–9]. However, the level of contaminants in the imported brands of rice on the Liberian national market is not reported.

Furthermore, locally cultivated rice is preferred by some members of the population. Aside the use of agrochemicals and other processes leading to rice production, the location of rice farms may also contaminate 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, this study aimed at assessing their levels of contamination in the widely consumed rice sold on the Liberian markets.

II. MATERIAL AND METHODS

Sampling

Sixty-one rice samples of imported and locally cultivated brands were purchased on different occasions from local markets in and around the capital city of Liberia. Samples were collected in freshly purchased and labelled clear clean polyethylene zip lock sampling bags, after which they were packed in solid polyethylene food box, sealed and transported from Liberia to the KNUST Chemistry Department, Kumasi, Ghana for analysis.

Reagents

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 Sulphuric acid (H_2SO_4), Perchloric acid ($HClO_4$),

Potassium permanganate ($KMnO_4$), and Nitric acid (HNO_3). The 98 % H_2SO_4, 70 % $HClO_4$ and 65% HNO_3 concentration 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).

Chemical Analysis
Sample Digestion

Samples were cleaned thoroughly, homogenized and digested by an open tube digestion procedure according to Voegborlo and Akagi [10]. The accuracy of the method has been proven by Certified Reference Materials, such as IAEA-085, IAEA-142 and IAEA-407. In the digestion method, 1 gram of homogenized sample each was weighed in a 50 millimeter graduated Pyrex digestion tube. Added to the tube were 1 milliliter of deionized water, 4 millimeters of 1:1 concentrated Nitric-Perchloric acids (HNO_3 -$HClO_4$) and 5 millimeters of concentrated Sulphuric acid (H_2SO_4). The mixture was swirled for about 1 minute and the tube with contents were then inserted into an aluminum heating block and placed on an electric Aluminum Hotplate set at 200˚C until clear transparent solutions were obtained. The final solutions were shaken thoroughly and filtered through 42 grade Whatman filter papers into top capped polyethylene bottles and kept in fridge until analysis. Digestion blanks were prepared during the digestion process.

Determination of Metals

The concentrations of Hg in the samples were determined by Atomic Absorption Spectroscopy technique using a RA-915M (Lumex Instruments, Canada) portable Zeeman Automatic Mercury Analyzer and the concentrations of As, Cd, Cr, Pb and Ni were determined by an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique using an Agilent 7900 (Agilent Technology, USA)

Inductively Couple Plasma Mass Spectrophotometer. Before the determination of the analytes, the instruments were calibrated to determine their 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.

Quality Assurance

A Standard Certified Reference Material (IAEA-359) obtained from the analytical quality control services unit of the International Atomic Energy Agency (Vienna, Austria) was used to ascertain the accuracy of the digestion and analytical measurement processes.

Statistical Analysis

Microsoft Excel (v2016) and IBM-SPSS (v23.0) tools were employed for statistical analysis. All P-Values ≤ 0.05 were considered significant.
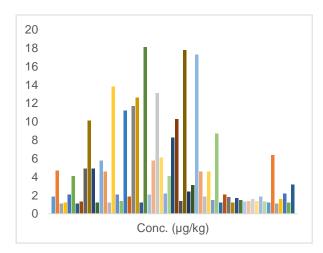
III. RESULTS

A total of 61 rice samples collected from local markets in Liberia were analyzed for the levels of Arsenic (As), Cadmium (Cd), Chromium (Cr), Mercury (Hg), Lead (Pb) and Nickel (Ni). The accuracy of the analytical procedure used in this study was validated by a Certified Reference Material (IAEA-359). Result of the CRM is summarized in Table 1. Recovery percentage were in the range of 90.00 to 107.2 %, indicating accuracy of the analytical techniques.

The results for the tested metals in the analyzed samples are presented in figures 1 to 6. The result indicates that the selected metals were all present in all the tested rice samples, and a wide range of contamination values was observed. The levels of

contamination ranked in the order of Ni > Cr > Cd > Pb > Hg > As. The concentrations of the metals ranged from 1.1 to 18.1 µg/kg for As, 4.8 to 117.9 µg/kg for Cd, 5.0 to 424.5 µg/kg for Cr, 1.1 to 37.1 µg/kg for Pb, 1.1 to 9.4 µg/kg for Hg and 15.1 to 655.2 µg/kg for Ni. Student T-test performed at 95 % confidence interval produced P-Values of 0.002 for As, 0.195 for Cd, 0.96 for Cr, 0.113 for Pb, 0.254 for Hg and 0.081 for Ni. This showed no significant statistical difference in the level of metal concentrations between the imported and the locally cultivated rice samples, except for As. The difference in As concentration could be attributed to regional difference in the cultivation of the rice samples. Zavala and Duxbury [11] reported that geographic location is the key factor to arsenic variability in rice grains.

Table 1 : Results (µg/kg) of CRM (IAEA-359) showing certified values, measured values and percent recoveries.

Element	Certified Value	n	Mean Value	% Recovery
As	100.0	3	90.00	90. 00
Cd	120.0	3	110.0	91.67
Cr	1300	3	1283	98.69
Hg	13.00	3	13.94	107.2
Ni	1050	3	1067	101.6

Figure 1 : Concentration (μg/kg) of As in the rice samples
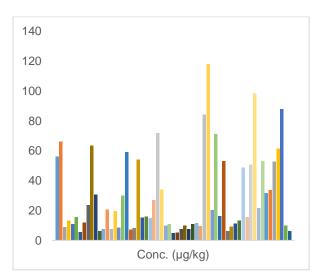

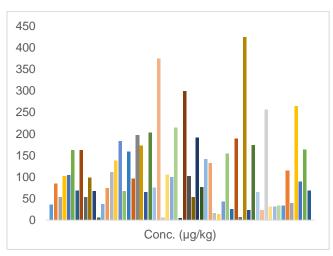**Figure 2 :** Concentration (μg/kg) of Cd in the rice samples

Figure 3 : Concentration (μg/kg) of Cr in the rice samples
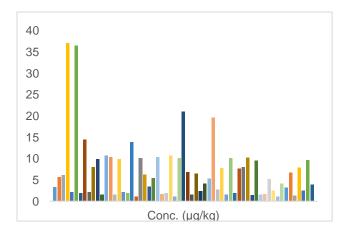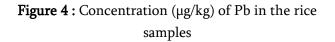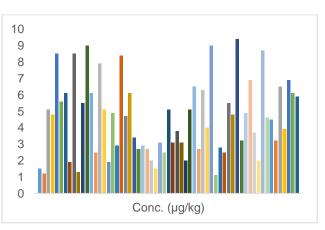

Figure 4 : Concentration (μg/kg) of Pb in the rice samples

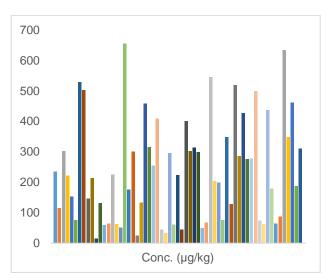**Figure 5 :** Concentration (μg/kg) of Hg in the rice samples

Figure 6 : Concentration (μg/kg) of Ni in the rice samples

IV. DISCUSSION

Rice is the second most cultivated cereal and the third most worldwide produced crop, that provides about 30 % dietary energy and 20 % dietary proteins to consumers [12]. It has been implicated as the major source of dietary exposure to Heavy metals, such as As, Cd, Cr, Pb, Hg and Ni [13].

The level of As concentrations documented in this study were low when compared to the 200 μg/kg

threshold limit recommended by the Codex Alimentary Commission [14]. The highest concentration of As in the samples was 181.9 folds lower than the Codex Standard. This showed low As contamination of the rice products. According to Meharg [15], rice cultivated on dry land or under moderate sunny conditions may contain low concentration of As compared to rice cultivated in region with continues flood. The low concentration of As recorded for the tested samples may be influenced by their cultivation conditions. Though this study recorded low levels of As in rice, others studies have reported high levels of As concentration in rice samples analyzed in China and India respectively [16,17].

The presence of Cadmium in rice grains is due to its similarities to essential elements such as Calcium and Magnesium. 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 [18]. However, it uptake can be inhibited by the presence of silicon (Si) in the plant's cell wall. Therefore, in a cadmium contaminated soil, silicate fertilizers are usually applied during rice cultivation. The application of this fertilizer inhibits the uptake of the element, and therefore account for it low level in rice grain. Cadmium concentrations reported in all the rice samples analyzed were less than the 400 µg/kg threshold limit recommended by the Codex Alimentary Commission. The values were also less than the 200 µg/kg limit recommended by the European Commission [19]. This indicates low contamination of the tested rice samples by Cd. The levels also indicated that the samples might have been cultivated on soils rich in Calcium or Magnesium, or silicate fertilizers might have been used during the cultivation periods. Cd concentration reported for rice consumed in Sindh, Pakistan, were in agreement with the values recorded in this study [20].

The concentrations of Pb in all the analyzed rice samples were less than 50 µg/kg, which is less than the 200 µg/kg threshold limit recommended by the European Commission and adopted by the Codex Alimentary Commission. The level of Hg concentrations found in all the rice tested were less than 10 µg/kg, which is significantly below the 200 µg/kg threshold limit set by the European Commission, an indication of low contamination of the tested products by the metals. Soil pH and redox potential are the basic factors responsible for the presence of Pb and Hg in rice grains. Under low pH and redox potential, these metals are bioavailable in high concentrations to the plant [21]. However, their accumulation in the grain is not positively correlated to the amount of the metals absorbed by the plant [22]. Hg levels obtained in this study showed little disparities when compared to other studies published in literature [23–25]. For Pb, the range reported by Huang et al. [26] was in agreement with this study but below the range documented in these articles [27,28].

Nickel and Chromium had the highest concentrations in the tested samples. This can be traceable to their essentiality to many plants and animals. For example, in most plants, including rice, nickel served as urease cofactor, aiding in the production of plants nitrogen or ammonium ions [29], while chromium is needed in minute concentration for growth stimulation [30]. Under normal soil condition, rice is known to absorb and utilize minute concentrations of these metals. Their uptake process is similar to the uptake of iron. Therefore, in excess amount, they suppressed the uptake of iron, leading to the absorption of more soluble and exchangeable amounts of the elements by the plant. However, their tolerance is also enhanced by the application of exogenous silicon fertilizer [31]. Nickel and Chromium levels in this study were similar to other studies from Ethiopia, India and Iran [9,32,33]. The European Commission and the Codex

Alimentary Commission had not established a threshold for nickel and chromium in rice, but the Food Safety Authorities of the Peoples' Republic of China recognized 1000 μg/kg and 1500 μg/kg as a threshold for the metals in grains and other cereals respectively [34]. Though the two metals recorded the highest values in the hierarchy order of contamination of the samples, their values were less than their respective threshold limits recommended by the Food Safety Authorities of the Peoples' Republic of China. The highest concentrations of Cr and Ni concentrations in all the analyzed rice samples were about 58 % and 56 % lesser than their respective permissible limits. This showed very low dietary contamination of the tested rice products by the metals.

V. CONCLUSION

The study assessed the levels of heavy metals (As, Cd, Cr, Pb, Hg and Ni) in commercially available rice on the local markets in Liberia. The selected heavy metals were all present in all the rice samples analyzed. There was no significant statistical variability in the level of metal concentrations between the imported and the locally cultivated rice samples, except for As. 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. This showed low contamination of the selected rice brands by the metals, and therefore safe for human consumption. However, high level of heavy metals contamination is possible. Therefore, the level of heavy metals in these rice brands must be regularly monitored to ensure the safety of consumers.

VI. REFERENCES

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