

Concentrations and Human Health Risk Assessment of Cd, Co, Cr, Ni, and Pb via Eating White Granulated Garri Produced in Nigeria

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Abstract: White granulated garri, an extensively consumed foodstuff in Nigeria made from fermented cassava tubers has recorded little studies on its heavy metals content. The concentrations of Cd, Co, Cr, Ni and Pb in commercial white granulated garri commonly sold in three major markets in Port Harcourt, Nigeria were established using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) after microwave-assisted acid digestion. The mean concentrations ($\bar{x} \pm SD$, in mg/kg on dry-weight basis) of heavy metals in garri samples were Cd: 0.021 ± 0.005 , Co: 0.027 ± 0.004 , Cr: 2.50 ± 0.047 , Ni: 0.849 ± 0.021 , and Pb: 0.522 ± 0.039 respectively. A food frequency questionnaire-based (FFQ) survey on dietary consumption rates of garri as a source of carbohydrate among consumers and marketers showed that garri accounted for > 97.5% of total carbohydrate consumed in Nigeria. Statistical evaluation of the data by one-way analysis of variance discloses noteworthy differences of metal contents for Cd, Co, Ni and Pb in garri from the study area with the exception of Cr. The mean daily intake of metals (mg/person/day) from garri consumption using dietary modelling was found to be Cd: 1.49×10^{-4} , Co: 1.34×10^{-5} , Cr: 1.24×10^{-2} , Ni: 4.23×10^{-3} and Pb: 2.60×10^{-3} respectively. These values are lower than the upper tolerable daily intake limits for heavy metals in food. The target hazard quotients (THQ), health risk index (HRI) and lifetime cancer risk (CR) for Cd, Co, Cr, Ni, and Pb indicate that, the probable human health risk associated with consumption of garri for the target population is moderately low at the moment. However, modest consumption rate of the product is recommended due to potential bioaccumulation of heavy metals found in garri.

Keywords: Garri, Heavy Metals, Cassava, Health Risk Assessment

1. Introduction

In Nigeria, white granulated garri is served as a daily staple and is consumed by every strata of the society; the rich, the poor and every age group apart from infants within the first three months of birth. It is often consumed as the main meal in the form of a dough which is prepared by mixing dry granulated garri with hot water and served with soup or stew. According to an FAO [1] report, garri may also be consumed as a snack when mixed with coconut, groundnut and sugar and milk. Garri may swell three to four times its volume when mixed with cold water. Garri is made from cassava tubers and

according to Ecocrop [2] and Lebot [3], and it provides major staple food diet for more than a billion people in the world and over 190 million people in Nigeria. Tubers are fleshy underground food-storing plant [4] that have unique and selective uptake capabilities from the soil. Many species of plants can successfully uptake metals which are essential for plant growth, while some metals with unknown biological function may also be accumulated [5]. The capacity to absorb and accumulate heavy metals by tuber crops root systems may lead to contamination of the food products in tuberous plants. Plant may take up and bioaccumulate heavy metals either via the roots, tubers and foliar surfaces [6, 7].

Heavy metals are “Janus-faced” [8], this is because they have important positive and negative roles in human life. They ubiquitous, non-biodegradable and can undergo bio-magnifications in living tissues [9]. Hence, food contamination by heavy metals may occur during the various stages of its production, packaging, transport or holding and as a result of human activities such as farming, industry or car exhausts or from contamination during food processing and storage. Therefore, everyone is exposed to some amount of metals from daily actions such as inhaling dust, eating food, or drinking water. Since contamination generally has a negative impact on the quality of food and may imply a risk to human health, several international legislations lay down maximum allowed limits in foodstuffs (USEPA, Canada, EU, FAO, WHO, Codex,). The ingestion of contaminated plant biomass as foodstuff is a principal factor contributing to human exposure to metals. The objective of this paper is to report the concentrations of Cd, Co, Cr, Ni and Pd in white granulated garri commonly sold in three major markets of Port Harcourt and the associated potential human health risk via eating this form of garri.

2. Materials and Methods

2.1. Study Area

Rivers State with a total land area of 11,077 km² and population of 5,185,400 people (census 2006) is located in the Southern part of Nigeria and is sited between longitude 6°50'E and Latitude 4°45'N. It has 23 local government areas with Port Harcourt as the major capital city. The samples of commercial dry garri were obtained from three different markets in Port Harcourt. The markets were: Choba Market (MKT 1), Rumuokoro Market (MKT 2) and Mile-3 Market (MKT 3).

2.2. Production of Garri from Cassava Tubers

The production of garri from cassava tubers usually takes 2 – 3 days and involves five stages, which include peeling, grating, dewatering/fermentation, pulverization and frying. The most important of these processes is the fermentation stage. The fermentation process of cassava is done in order to remove cyanide and produce the desirable flavors. It is likewise roasted to destroy enzymes and microorganisms, to drive off cyanide gas, and to dry the product. Preservation is achieved by heating during roasting. Low moisture content inhibits recontamination by bacteria. However, white granulated garri is the finished product from cassava tubers.

2.3. Reagents and Chemicals

All reagents used were of suprapur grade (Merck, Darmstadt, Germany). High-purity water (18 MΩ cm) from a Milli-Q water purification system (Millipore, Bedford, USA) was used for dilution of standards, for preparing samples throughout the chemical process, and for final rinsing of the acid-cleaned vessels, glasses, and plastic utensils. Before use, all glass and plastic utensils were thoroughly acid cleaned and then rinsed with Milli-Q water.

2.4. Sample Preparation

Samples of dried white granulated garri were purchased from the three markets in the study areas. The granulated garri samples were freeze-dried to remove water molecules from the sample by placing the material in a freeze-drying flask and rotating the flask in a shell freezer bath, cooled by liquid nitrogen at 0.0025 millibars at -70 °C where about 95% of the water is sublimated in the material and then powdered by crushing in liquid nitrogen with mortar and pestle. Triplicate analysis was carried out on individual samples (n = 10) for total metal concentrations and the result expressed as mean value (\bar{x}) ± standard deviation (SD).

2.5. Digestion of White Granulated Garri Sample

The acid digestion of the garri samples was performed using a commercial high-pressure laboratory microwave oven (Milestone Ethos 1600 Microwave Labstation, Sorisole, Italy) operating at a frequency of 2450 Hz with an energy output of 900 W. This microwave digestion system was equipped with ten 100 mL tetrafluoromethoxy vessels and a ceramic vessel jacket. The maximum operating temperature and pressure were 300 °C and 100 bar, respectively. The freeze dried garri samples for metal determination were digested following the methods of Amayo [10] with slight modification. About 0.5 g of the freeze dried garri samples from each market were inserted directly into a microwave-closed vessel. One milliliter of 30% (m/m) H₂O₂ and 7.0 mL 7.10 mol/L HNO₃ solution were added to each vessel. The heating program was performed in four successive steps. In the first step, the temperature was increased linearly from 25 to 90 °C in 4 min. In the second step, the temperature was held at 90 °C for 2 min. In the third step, the temperature was increased linearly to 180°C in 6 min, and in the last step, the temperature was held at 180 °C for 10 min. After the digestion procedure and subsequent cooling, the digested samples were diluted to a final volume of 25.0 mL with water. Blanks were prepared in each lot of samples. All experiments were performed in triplicate.

2.6. Heavy Metals Analysis in Garri by ICP-MS

The total heavy metals content was established in the microwave acid digested freeze-dried garri samples using an Agilent 7500c inductively coupled plasma - mass spectrometry (ICP-MS, Agilent Technologies, California, USA).

2.7. Quality Assurance and Quality Control

The analytical procedure was validated by Standard reference materials (SRM) [11]. The heavy metal contents found in the SRMs were in good agreement with the certified values, which established the feasibility of the analytical protocols in the determination of heavy metals in garri (Table 1). The quality control applied to the validation of the analytical method was a DORM-4 certified fish protein in addition to spike recovery. The instrument was recalibrated

after every set of sample has been run. For spike recovery, a known standard of metals was introduced into already analyzed sample and re-analyzed. Acceptable recoveries for the metals were 101.7% for Cd; 111.3% for Co, 108.6% for Cr, 102.6% for Ni and 106.1% for Pb. Blanks were used to correct all instrument reading before statistical calculation. Pearson correlation coefficient was used to determine whether the concentrations of metals varied significantly within and between garri from each markets, with values greater than 0.05 ($p < 0.05$) considered to be statistically significant.

Three batches of these element standard solutions were prepared and digested in the same manner as mentioned for the white granulated garri samples. The average of the three batches was used to build up the calibration curves and the coefficient of

determination (R^2) values were ≥ 0.9986 . The concentrations (mg kg^{-1}) of heavy metals in the white granulated garri samples were calculated from the following equation:

$$M(\text{dry wt. , mg/kg}) = \frac{C \times V \times D}{W} \quad (1)$$

Where M = concentration of metal in white granulated garri sample, C = digest concentration from ICP-MS (mg/l); V = final volume of digest (l); D = dilution factor and W = weight of dried sample (kg)

All the results were expressed on a dry weight basis. All analyses were performed in triplicates using the external calibration method with $R^2 > 0.9992$ for all the metals investigated (Table 1).

Table 1. Quality control protocols applied.

| M | Reference Material | | | Metal calibration curve | |
|----|--------------------|-------|-------|-------------------------|--------|
| | D-4 | CV | % R | RE | R2 |
| Cd | 34.42 | 33.84 | 101.7 | $y = 0.0038x + 0.0393$ | 0.9992 |
| Co | 0.33 | 0.30 | 111.3 | $y = 0.0292x + 0.0109$ | 1.0000 |
| Cr | 3.94 | 3.63 | 108.6 | $y = 0.0231x + 0.0249$ | 1.0000 |
| Ni | 0.99 | 0.97 | 102.6 | $y = 0.001x + 0.0064$ | 0.9992 |
| Pb | 0.62 | 0.58 | 106.1 | $y = 0.005x + 0.0167$ | 0.9999 |

M is metals, D-4 is DOLM-4; CV is Certified Value, % R is % Recovery, RE is Regression equation

2.8. Data Analysis

The aggregate concentrations of Cd, Co, Cr, Ni and Pb found in Nigerian commercial garri investigated were used to approximate the potential human health risk exposure to heavy metals by calculating the Daily Intake of Metals (DIM), Target Hazard Quotient (THQ), Health Risk Index (HRI), Hazard Index (HI) and the life time risk of getting cancer described here as Carcinogenic Risk (CR) as a consequence of eating white granulated garri.

2.8.1. Estimation of Daily Intake of Metals (DIM) from Garri

The daily intake of metals (DIM) from consumption of white granulated garri by adults was estimated using the formula in equation 2.

$$\text{DIM}(\text{mg/kg} - \text{bw/day}) = \frac{C_M \times D_{FI}}{BW} \quad (2)$$

Where C_M = concentration of each metal in white granulated garri (mg/kg); D_{FI} = mean mass of daily intake of garri (0.299 kg/person) and BW = average body weight (60 kg of an adult).

The average white granulated garri intake in the study area was calculated by conducting a food frequency questionnaire (FFQ) survey of 300 people (150 males and 150 females) having an average body weight of 60 kg. Each respondent was politely asked for their daily intake of garri from the sampling sites using the standard garri measuring gauge commonly used at the local markets.

2.8.2. Estimation of Target Hazard Quotient (THQ)

The target hazard quotient (THQ) was calculated by the formulation established by the United States Environmental Protection Agency [12].

$$\text{THQ} = 10^{-3} \times \frac{\text{EF} \times \text{ED} \times C_M \times D_{FI}}{\text{RfD}_{inj} \times \text{BW} \times \text{AT}} \quad (3)$$

Where: EF = Exposure frequency (365 days / year); ED is the exposure duration (51.86 years) [13] which corresponded to average life expectancy of a Nigerian; AT = averaging exposure time for non-carcinogens (365 days/year \times ED); RfD_{inj} = is the ingestion reference dose. RfD_{inj} is an estimate of daily exposure to human population (including sensitive sub-group) that is likely to be without an appreciable risk of deleterious effect during life time. 10^{-3} is the unit conversion factor. The ingestion reference dose. RfD_{inj} (mg /kg/day) used are presented in Table 2. [12].

2.8.3. Estimation of Health Risk Index (HRI)

The procedure to estimate risk in terms of HRI was provided in the USEPA Region III risk-based concentration table [12]. This technique of risk evaluation has been used by several researchers including Osakwe [13], Mamood [14], Shin [15], Divya [16] and Chauhan [17] and proved to be valid and useful. HRI is expressed using equation 4:

$$\text{HRI} = \frac{\text{DIM}}{\text{RfD}_{inj}} \quad (4)$$

2.8.4. Estimation of Total Hazard Index (HI)

The hazard index (HI) for residents of Port Harcourt, Nigeria who consumes Garri as their major source of carbohydrate was obtained using the equation 4 given below

$$\text{HI} = \sum_i \text{HRI} = \text{HRI}_{Cd} + \text{HRI}_{Co} + \text{HRI}_{Cr} + \text{HRI}_{Ni} + \text{HRI}_{Pb} \quad (5)$$

Where i is the distinct heavy metals tested. $\text{HI} < 1$ indicate that chronic risks are unlikely, whereas, $\text{HI} > 1$ indicate that non-cancerous risks are likely to occur.

2.8.5. Estimation of Carcinogenic Risk (CR)

The carcinogenic risks (CR) was estimated using equation 6.

$$CR = DIM \times CSF_{inj} \quad (6)$$

Where DIM = estimated daily intake of each heavy metal (mg/kg/person) and CSF_{inj} = injection cancer slope factor (mg/kg/day). The USEPA [18] and FAO/WHO [19] has provided some toxicological characteristics of heavy metals for computation of carcinogenic and non-cancer risks (table 2).

Table 2. Some toxicological characteristics of metals used for estimation in Garri.

| Metals | Ingestion reference dose (RfD_{inj}), mg/kg/day | Ingestion carcinogenic slope factor (CSF_{inj}), mg/kg/day |
|----------|---|--|
| Cadmium | 0.001 | 0.38 |
| Cobalt | 0.003 | 0.02 |
| Chromium | 1.5 | 0.5 |
| Nickel | 0.02 | 1.7 |
| Lead | 0.0035 | 0.0085 |

2.9. Statistical Analysis

Ten samples were randomly taken in each market place and measured individually. Each sample was measured with three main acquisition runs during the experiment, providing mean values and standard deviation. Results reported in this work are the mean value and standard deviation of the replicates. The documented data were subjected to one-way analysis of variance (ANOVA) without replication to assess the influence of market variables on the concentration of heavy metals in garri. Statistical significance of means was computed using F-test with significance level of $P < 0.05$.

3. Results and Discussion

3.1. Concentrations of Cd, Co, Cr, Ni and Pb in Garri

The aggregate concentrations (mg/kg) of heavy metals in garri were (range, mean \pm standard deviation on dry-weight basis are Cd: (0.09 – 0.05, 0.03 ± 0.05), Co: (0.01 – 0.05, 0.03 ± 0.01), Cr: (2.26 – 3.19, 2.59 ± 0.33), Ni: (0.66 – 0.91, 0.82 ± 0.08), Pb: (0.47 – 0.72, 0.60 ± 0.07) for market 1, Cd: (0.008 – 0.02, 0.01 ± 0.005), Co: (0.01 – 0.03, 0.02 ± 0.006), Cr: (2.37 – 2.56, 2.43 ± 0.6), Ni: (0.82 – 0.92, 0.89 ± 0.03), Pb: (0.43 – 0.56, 0.50 ± 0.05) for market 2 and Cd: (0.017 – 0.022, 0.02 ± 0.02), Co: (0.02 – 0.04, 0.03 ± 0.009), Cr: (2.39 – 2.54, 2.47 ± 0.05), Ni: (0.79 – 0.90, 0.84 ± 0.04), Pb: (0.41 – 0.52, 0.47 ± 0.03) for market 3 respectively. The results

showed that, the levels of heavy metals (Cd, Co, Cr, Ni and Pb) tested in the commercial garri samples were not consistent throughout the three markets investigated. This inconsistency is an indication that garri reaching the markets are from diverse cassava cultivating areas. Due to paucity of published research information on the contents of heavy metals in garri and other tuberous foodstuffs in Nigeria, the average concentrations of Cd, Co, Cr, Ni and Pb in commercial garri samples collected from the three markets in the study areas was compared with levels in commercial yam (a similar tuberous crop) powder commonly sold in South Korea [20, 21] and the CODEX standard for food [22] as shown in Table 3. The levels of Cd and Ni in commercial garri from the three major markets of the study area in Nigeria was lower than the average value of Cd in commercial yam powder of South Korea, while Cr levels in Nigerian commercial garri was higher than the South Korean commercial yam powder (Table 3). Further comparison reveals that, Pb levels in Nigerian commercial garri product was within the range of Pb content in South Korean commercial yam powder product. The metal contents in commercial garri from the three markets in Nigeria were not within similar concentration ranges. This is an indication of diverse sources of garri in the market places as a result of different cultivation areas. Cobalt level in Nigerian commercial garri could not be compared to the South Korean yam powder because of absence of data on cobalt for yam product (Table 3).

Table 3. Comparison of heavy metal levels (mg/kg) in commercial garri and commercial yam powder; cassava with international standards.

| M | MKT 1 | | MKT 2 | | MKT 3 | | Comparison | | |
|----|--------------|------------------|------------|------------------|-------------|------------------|-----------------|-----|--------|
| | w | $\bar{x} \pm SD$ | w | $\bar{x} \pm SD$ | w | $\bar{x} \pm SD$ | CYP | EU | *Codex |
| Cd | 0.009 – 0.05 | 0.03 ± 0.02 | 0.008-0.02 | 0.01 ± 0.005 | 0.017-0.022 | 0.02 ± 0.002 | 40.9 ± 7.9 | 0.1 | 0.1 |
| Co | 0.01-0.05 | 0.03 ± 0.01 | 0.01-0.03 | 0.02 ± 0.006 | 0.02-0.04 | 0.03 ± 0.009 | - | 0.1 | 0.1 |
| Cr | 2.26-3.19 | 2.59 ± 0.33 | 2.37-2.56 | 2.43 ± 0.06 | 2.39-2.54 | 2.47 ± 0.05 | 1.27 ± 0.21 | 0.1 | 0.1 |
| Ni | 0.66-0.91 | 0.82 ± 0.08 | 0.82-0.92 | 0.89 ± 0.03 | 0.79-0.90 | 0.84 ± 0.04 | 1.00 | 0.1 | 0.1 |
| Pb | 0.47-0.72 | 0.60 ± 0.07 | 0.43-0.56 | 0.50 ± 0.05 | 0.41-0.52 | 0.47 ± 0.03 | 0.46 ± 0.14 | 0.1 | 0.1 |

Where w is the range, x is the mean, SD is the standard deviation, M is metal, MKT is market and CYP is Commercial yam powder

The levels of heavy metal (Cd, Co, Cr, Ni and Pb) in Nigerian white granular garri were also compared to the international food standard levels (Tables 3). The data revealed that the concentration (mg/kg) of Cr (2.50 ± 0.005), Ni (0.85 ± 0.021) and Pb (0.52 ± 0.04) in Nigerian commercial garri products were higher than both European Commission

(EU) and CODEX food standards levels (0.1 mg/kg), while Cd (0.021 ± 0.005) and Co (0.027 ± 0.004) contents in Nigerian garri product were lower than the EU and CODEX food standards levels (0.1 mg/kg). The inconsistency of heavy metal (Cd, Co, Cr, Ni and Pb) levels in Nigerian commercial garri products from the three markets presented in table 3 were

tested with one-way analysis of variance (ANOVA) without replication (Table 4). The data indicated significant differences in heavy metals content of Cd, Co, Ni and Pb except Cr, suggestive of the availability of commercial garri

products to the exposed population in the three markets investigated ($p < 0.05$) came from different cassava cultivating areas.

Table 4. One-way analysis of variance without replication of heavy metals in dry garri between the three markets with $n = 10$, $df = 2$, $27 \alpha = 0.05$.

| Source of Variation | SS | df | MS | F | P-value | F crit |
|---------------------|--------|----|--------|------|---------|--------|
| Cd between Markets | 0.0015 | 2 | 0.0008 | 9.09 | 0.00096 | 3.35 |
| Co between Markets | 0.0007 | 2 | 0.0004 | 4.24 | 0.02510 | |
| Cr between Markets | 0.0691 | 2 | 0.0345 | 0.83 | 0.44506 | |
| Ni between Markets | 0.0301 | 2 | 0.0151 | 5.83 | 0.00785 | |
| Pb between Markets | 0.0631 | 2 | 0.0315 | 8.92 | 0.00106 | |

In order to identify potential correlation between metals (Cd, Co, Cr, Ni and Pb) investigated in commercial garri from the three markets, a critical correlation matrix was obtained (Table 5). Ni demonstrated negative correlations with all other metals, Pb showed no correlation with any of the investigated metals, however, Cd showed strong correlation with Co and Cr. Hence, the presence of Cr and Co in the soil may exacerbate the levels of Cd. This indicated that soil quantitative and qualitative evaluation for heavy metals levels before planting season is very important for tuberous crops. A comparative analysis of percent (%) metals content using the aggregate concentrations in commercial Nigerian garri from the three markets was obtained (Figure 1) to identify potential differences in heavy metals.

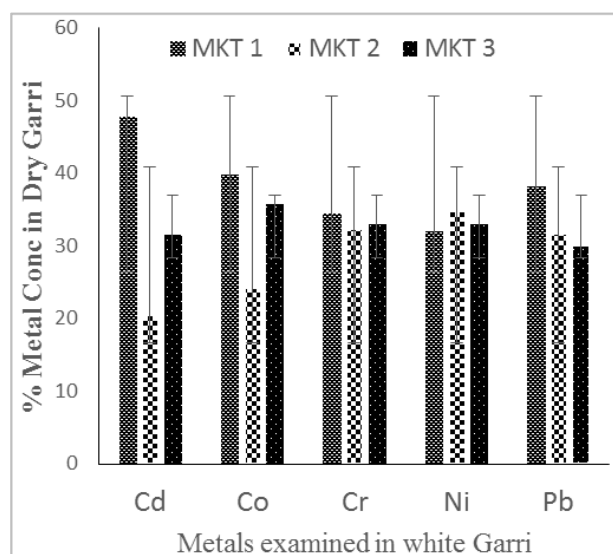


Figure 1. Comparative analysis of metal concentrations in white granular garri from the three markets investigated.

The data revealed that on a scale of 100: 47.85% Cd, 39.84% Co, 34.53% Cr, 32.11% Ni and 38.20% Pb are attributable to market 1, 20.63% Cd, 24.1% Co, 32.44% Cr, 34.46% Ni and 31.75% Pb to market 2, while 31.53% Cd, 35.85% Co, 33.03% Cr, 33.03% Ni and 30.55% Pb was attributable to market 3. The geometric order of percent (%) heavy metal (Cd, Co, Cr, Ni and Pb) level amongst the markets investigated are market 1 > market 3 > market 2 except for Ni and Pb where the order is market 1 > market 2 > market 3.

Table 5. Correlation matrix for heavy metals in white granular garri from the three markets.

| | Cd | Co | Cr | Ni | Pb |
|----|--------|--------|--------|--------|----|
| Cd | 1 | | | | |
| Co | 0.925 | 1 | | | |
| Cr | 0.991 | 0.867 | 1 | | |
| Ni | -0.954 | -0.997 | -0.905 | 1 | |
| Pb | 0.820 | 0.543 | 0.889 | -0.610 | 1 |

3.2. Potential Human Health Risk Assessment of Cd, Co, Cr, Ni and Pb in Garri

Dietary modelling was used to estimate the exposure to heavy metals through the consumption of commercial garri from the study areas. A food frequency questionnaire (FFQ) survey of 300 people (150 males and 150 females) having an average body weight of 60 kg revealed that on the average over 96.5 - 98.7% of respondents ingest garri at least once as a major source of carbohydrate for a number of age-gender groups of the Nigerian population. Consequently, one can say that the rate of consumption of garri and garri products in Nigeria is very high. Hence, applying the notion of daily intake of metal (DIM) to assess the potential health risk of poisonous substances is authoritative.

3.3. Evaluation of Daily Intake of Metals (Cd, Co, Cr, Ni and Pb) in Garri

The application of daily intake of metals (DIM) in assessing potential human health risk from poisonous substances is based on the differences in the average rate of garri consumption in the study area. The DIM values calculated for adult Nigeria population of average weight of 60 kg consuming commercial garri were compared with the upper tolerable daily intake limit (UL) of heavy metals as presented in table 6. The tolerable Upper Intake Level (UL) (USEPA, 2013) [23] is the highest level of daily nutrient intake that is likely to pose no risk of adverse health effects for almost all individuals. The probable DIM (mg/person/day) values for Cd in the three markets investigated were 1.49×10^{-4} , 6.42×10^{-5} , and 9.82×10^{-5} for market 1, 2 and 3 respectively. The DIM value for Cd was highest in market 1 compared to the other two markets. However, the results show that these values are less than the upper tolerable daily intake limit of cadmium (6.40×10^{-2} mg/person/day). For cobalt, the DIM values were 1.61×10^{-4} for market 1, 9.80×10^{-5} for market 2 and 1.45×10^{-4} for market 3.

These values are all < 1.4 mg/person/day UL for Co. The DIM values for Cr for markets 1 (1.29×10^{-2}) and 3 (1.23×10^{-2}) were slightly higher than market 2 (1.21×10^{-3}). These values are virtually on the same range with the upper tolerable daily intake limit of Cr which is pegged at 1.05×10^{-2} mg/person/day. The estimated DIM (mg/person/day) values for Ni and Pb for the three markets were Ni: 4.08×10^{-3} , 4.42×10^{-3} , and 4.19×10^{-3} and Pb: 2.98×10^{-3} , 2.48×10^{-3} , and 2.35×10^{-3} for markets 1, 2 and 3 respectively. These values are lower than the upper tolerable daily intake limit of Ni (1.00 mg/person/day) and Pb

(2.40×10^{-1} mg/person/day) respectively. In general, the DIM observed values for all the metals investigated were lower than the upper tolerable daily limits for Cd, Co, Cr, Ni and Pb respectively (Table 6). According to Orisakwe and co-workers [7], large variations exist in the toxicity of heavy metals to humans which depend on their dietary daily intake through consumption of various kind of food stuffs grown and sold in Southeastern Nigeria. The estimated daily intake rate for Cd, Co, Cr, Ni and Pb were marginally lower than the upper tolerable intake rates for food stuffs.

Table 6. Mean Daily intake of metals (mg/person/day) in commercial garri obtained from the three markets compared with the upper tolerable daily intake of heavy metals.

| Heavy Metals | MKT 1 mg/person/day | MKT 2 | MKT 3 | *Upper tolerable daily intake limit of heavy metals (mg/person/day) | Orisakwe <i>et al.</i> (2012) cassava |
|--------------|------------------------|-----------------------|-----------------------|--|--|
| Cd | 1.49×10^{-4} | 6.42×10^{-5} | 9.82×10^{-5} | 6.40×10^{-2} | 0.0006 |
| Co | 1.61×10^{-4} | 9.80×10^{-5} | 1.45×10^{-4} | 1.40 | NA |
| Cr | 1.29×10^{-2} | 1.21×10^{-3} | 1.23×10^{-2} | 1.05×10^{-2} | NA |
| Ni | 4.08×10^{-3} | 4.42×10^{-3} | 4.19×10^{-3} | 1.00 | 0.0019 |
| Pb | 2.98×10^{-3} | 2.48×10^{-3} | 2.35×10^{-3} | 2.40×10^{-1} | 0.002 |

*Source: USEPA, 2000a [24]

According to Orisakwe and co-workers [7], large variations exist in the toxicity of heavy metals to humans which depend on their dietary daily intake through consumption of various kind of food stuffs grown and sold in Southeastern Nigeria. The estimated daily intake rate for Cd, Co, Cr, Ni and Pb were marginally lower than the upper tolerable intake rates for food stuffs.

3.4. Evaluation of Total Hazard Quotient and Health Risk Indices of Heavy Metals (Cd, Co, Cr, Ni and Pb) in Garri

3.4.1. Total Hazard Quotient (THQ)

The probable health risks resultant from ingesting commercial garri as a chief source of carbohydrate by millions of people inhabiting Port Harcourt was evaluated based on target hazard quotient (THQ). The THQ is a ratio of determined dose of a pollutant to a reference ingestion dose (RfD_{inj}). THQ is used in expressing the hazard of non-carcinogenic effects. The interpretation of the THQ value is binary: THQ is either ≥ 1 or < 1 , where $THQ > 1$ indicates a reason for health concern because an exposed population is likely to experience health hazards. It is essential to point out that THQ is not applied to quantify hazard but indicates a level of concern. Also, THQ values are additive, but not

multiplicative [25, 26]. In this investigation, the THQ values were computed by means of the measured concentrations of the five heavy metals (Cd, Co, Cr, Ni and Pb) from commercial garri as exposure route. The computed values of THQ for the three major markets of Port Harcourt are shown in table 7. The THQ for Cd ranged from 3.9×10^{-4} to 9.1×10^{-4} with market 1 recording the highest value and market 2 the lowest. THQ values for Co from the three markets were 3.26×10^{-5} , 1.99×10^{-5} and 2.93×10^{-5} for markets 1, 2 and 3 respectively. The THQ values for Cr were within the range of 4.91×10^{-5} to 5.23×10^{-5} for the three markets with market 2 having the lowest value. In the case of Ni, the THQ values computed for the three markets were market 1 (1.2×10^{-3}), market 2 (1.38×10^{-3}), and market 3 (3.57×10^{-3}) with marking 2 recording the highest value. THQ values for Pb ranged from 3.77×10^{-3} to 4.54×10^{-3} with market 1 recoding the highest THQ value. The geometric behaviour of the THQ values of heavy metals (Cd, Co, Cr, Ni and Pb) amongst the three markets were: Market 1 $>$ Market 3 $>$ Market 2 for Cd, Co, Cr and Pb, except for Ni where the order is Market 2 $>$ Market 3 $>$ Market 1. Computed THQ values for all the metals in the three investigated markets in Port Harcourt reveals that THQ is < 1 , indicating no immediate health concern for the exposed population.

Table 7. Target hazard quotients (THQ) computed the Heavy Metals (Cd, Co, Cr, Ni and Pb) in Garri.

| Markets | THQ | | | | | Σ THQ HQ |
|---------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | Cd | Co | Cr | Ni | Pb | |
| MKT 1 | 9.06×10^{-4} | 3.26×10^{-5} | 5.23×10^{-5} | 1.24×10^{-3} | 4.54×10^{-3} | 6.77×10^{-3} |
| MKT 2 | 3.91×10^{-4} | 1.99×10^{-5} | 4.91×10^{-5} | 1.35×10^{-3} | 3.77×10^{-3} | 5.58×10^{-3} |
| MKT 3 | 5.97×10^{-4} | 2.93×10^{-5} | 5.05×10^{-5} | 1.28×10^{-3} | 3.57×10^{-3} | 5.52×10^{-3} |

The hazard quotient (HQ) which is the summation of individual heavy metals in each market was also computed and known as the total non-carcinogenic hazard index. The market toxicological order in terms of HQ values based on garri consumption rates with respect to the five heavy metals

(Cd, Co, Cr, Ni and Pb) decreased in the following order: Market 1 ($HQ = 6.77 \times 10^{-3}$) $>$ Market 2 \approx Market 3. The hazard values for the metals decreased in the order of Pb $>$ Ni $>$ Cd $>$ Cr $>$ Co, and their risk values were 0.012, 0.004, 0.002, 0.0002 and 0.00008 respectively. The total non-carcinogenic

hazard indices for various heavy metals (Cd, Co, Cr, Ni and Pb) and for the single exposure pathway is 0.018 indicative that the hazards from commercial garri consumption in the study area is about 98% less than the threshold value of observable toxicological effect. Hence, heavy metals (Cd, Co, Cr, Ni and Pb) in commercial garri may not present likely health hazards in the study area for now and the exposed population could continue to consume the product. However, it was observed that Pb alone contributed 66.49% to the combined or total hazard quotient, Ni contributed 21.60% while Cd contributed 10.60% through this primary pathway of consuming commercial garri. Amongst the heavy metals (Cd, Co, Cr, Ni and Pb) analyzed in the commercial garri samples obtained from the study area, the most toxic metals (Pb, Ni and Cd) contributed over 97% to the combined THQ which however could be a source of concern because these three metals (Pb, Ni and Cd) are potential bioaccumulating metals and are classified as possibly carcinogenic substances to humans [27].

3.4.2. Evaluation of Health Risk Index (HRI)

The human health risks from consumption of garri by the local residents were assessed based on the health risk index (HRI). HRI characterizes the health risk of non-carcinogenic adverse effects due to exposure to contaminants. This index is calculated as the ratio of daily intake of heavy metals (DIM) in garri and an oral reference dose (RfD). If the HRI value computed is less than 0.1, it implies that the exposed population is said to be safe and is unlikely to experience

obvious adverse effects. However, if HRI is greater than 1.0, it is assumed to indicate potential non-carcinogenic effects.

Consequent upon the contribution (97.60%) of the three heavy metals (Cd, Ni, Pb) found in commercial garri to the overall THQ, we characterized the health risk index (HRI) of the three heavy metals from the daily intake of metals (DIM) in commercial garri and the ingestion reference dose (RfD_{inj}). The RfD_{inj} values for Cd, Ni and Pb are 0.001, 0.02 and 0.004 mg/kg/day respectively. The health risk index as a consequence of consuming garri at the rate evaluated by the FFQ, DIM and the RfD_{inj} from the study area is presented in table 8 for the five heavy metals investigated. Based on the three heavy metals of concern (Cd, Ni and Pb) in garri, the HRI for the three markets were Cd: 0.14, Ni: 0.20 and Pb: 0.75 for market 1, Cd: 0.064, Ni: 0.22 and Pb: 0.62 for market 2 and Cd: 0.098, Ni: 0.21 and Pb: 0.59 for market 3 respectively. The maximum HRI values were found in Pb in all three markets. Further observation of the data show that HRI values computed for Cd, Ni and Pb for commercial garri samples from the three markets under investigation are greater than 0.1 which indicates some level of concern that the exposed population may be at risk of toxicity due to these three metals. Hence, there could be potential health hazard to the population consuming commercial garri from these markets. The HRI of the study area suggest that commercial garri is slightly unsafe for consumption and may pose potential health risk with regard to the levels of Cd, Ni and Pb respectively.

Table 8. Health risk index for heavy metals (Cd, Co, Cr, Ni and Pb) in commercial garri.

| Markets | HRI (mg/kg/day) | | | | | ΣHRI |
|------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-------|
| | Cd | Co | Cr | Ni | Pb | |
| MKT 1 | 1.49×10^{-1} | 5.35×10^{-3} | 8.59×10^{-3} | 2.04×10^{-1} | 7.46×10^{-1} | |
| MKT 2 | 6.42×10^{-2} | 3.27×10^{-3} | 8.07×10^{-3} | 2.21×10^{-1} | 6.20×10^{-1} | |
| MKT 3 | 9.81×10^{-2} | 4.82×10^{-3} | 8.22×10^{-3} | 2.10×10^{-1} | 5.87×10^{-1} | |
| TOTAL (all MKT) | 0.3113 | 0.01344 | 0.02488 | 0.635 | 1.953 | |
| Mean | 0.103767 | 0.00448 | 0.008293 | 0.211667 | 0.651 | 0.979 |
| % contribution of each metal | 10.60 | 0.46 | 0.85 | 21.62 | 66.48 | |

3.4.3. Evaluation of Hazard Index (HI)

In order to access the potential risk of adverse health effects from a mixture of chemical elements in commercial garri and the low level of concern observed in HRI computations due to Cd, Ni and Pb, we went forward to evaluate the hazard index arising from the sum of HRIs to confirm the contribution of the individual elements. The total non-carcinogenic hazard index (HI) for the various heavy metals and for the single exposure pathway is 0.979 (Table 8). The HI values obtained due to this primary exposure route for all heavy metals investigated was all less than 1 but very closed to the threshold value of 1. This high HI value and indicates that uncontrolled consumption of commercial garri may pose a health problem. Therefore, the exposed population could reduce the rate and amount of garri consumption. The contribution of individual HRI values to the HI was evaluated and the results showed that Pb was a major contributor to the HRI value accounting up to 66.48% of the total HRI value. This could be pose treat to the consumers considering the fact that, Ph has no biological role in human body.

3.4.4. Evaluation of Carcinogenic Risk of Metals (Cd, Co, Cr, Ni and Pb) in Garri

Carcinogenic risks (CR) are estimated as the incremental probability of an individual developing cancer over a lifetime. The lifetime risk of the exposed populations on getting cancer due to consumption of garri as a source of carbohydrate was evaluated using the ingestion cancer slope factor and the results presented in Table 9. The ingestion cancer slope factor evaluates the probability of an individual developing cancer from oral exposure to contaminants levels over a lifetime. This approach is based on the assumption that there are no absolutely "safe" toxicity values for carcinogens. USEPA has developed cancer slope factors for many carcinogens. A slope factor is an estimate of a chemical's carcinogenic potency, or potential, for causing cancer. If adequate information about the level of exposure, frequency of exposure, and length of exposure to a particular carcinogen is available, an estimate of excess cancer risk associated with the exposure can be calculated using the slope factor for that carcinogen.

Specifically, to obtain risk estimates, the estimated chronic exposure dose (which is averaged over a lifetime or 70 years) is multiplied by the slope factor for that carcinogen. In the factual biosphere, CR estimation should consider the effects of multiple carcinogenic elements. Thus, the sum of CRs from all carcinogens was obtained and reported as total cancer risks CR_t using equation 8.

$$CR_t = \sum CR \quad (8)$$

The USEPA [28] position is that 10^{-6} (i.e 1 in 1,000,000) represent a range of permissible predicted lifetime risks for

carcinogens. Chemical for which the risk factor falls below 10^{-6} may be eliminated from further consideration as a chemical of concern. The risk associated with the carcinogenic effect of target metal is expressed as the excess probability of getting cancer over a lifetime of 70 years. A CR of 1×10^{-4} indicates the probability that 1 person in 10,000 individuals will develop cancer [28].

In this investigation, the total cancer risk for the individual heavy metals (Cd, Co, Cr, Ni and Pb) in commercial garri from the three major markets in Port Harcourt are presented in Table 9.

Table 9. Cancer risks (CR) of heavy metals in commercial garri from the study area in Nigeria.

| Heavy metals | CR | | | USEPA permissible predicted lifetime risks for carcinogens. |
|--------------|-----------------------|-----------------------|-----------------------|---|
| | MKT 1 | MKT 2 | MKT 3 | |
| Cd | 5.66×10^{-5} | 5.66×10^{-5} | 3.73×10^{-5} | 1×10^{-4} |
| Co | 3.21×10^{-6} | 3.21×10^{-6} | 2.89×10^{-6} | |
| Cr | 6.45×10^{-6} | 6.45×10^{-6} | 6.16×10^{-6} | |
| Ni | 6.92×10^{-5} | 6.93×10^{-5} | 7.12×10^{-5} | |
| Pb | 2.54×10^{-5} | 2.54×10^{-5} | 1.99×10^{-5} | |

4. Conclusion

The investigation of five priority heavy metals in garri showed different concentrations of Cd, Co, Cr, Ni and Pb in garri consumed by the population as a primary carbohydrate source at the investigated locations in Nigeria. The observed variation in metal concentrations in the garri products could be attributed to different cassava cultivating areas, bioaccumulation and mobility of metals to cassava plant. Potential human health risk assessments of Cd, Co, Cr, Ni and Pb in garri by computation of DIM, THQ, HRI and CR show that observable health concern at the moment may be moderately low, however, garri consumption should be reduced to its lowest minimum by the exposed population in the study area.

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