

Nigerian Journal of Ecology (2022) 18(1): 17-26  
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ISSN: 1116-753X (Print); E-ISSN: 2955-084X (Online)

**Daily Intake Rates and assessment of concentrations of heavy metals in five food stuffs purchased from Apata market, Ibadan, Oyo state, Nigeria**

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(Accepted June 15, 2022)

**ABSTRACT**

Heavy metals are known environmental toxicants at high concentrations. Their presence in food and intake have been tied to locations of food production, but information is scarce on roles played by market sources. This study assessed the levels of cadmium, chromium, zinc, iron, lead, copper in five selected commonly consumed food samples; rice (*Oryza sativa* L.), beans (*Phaseolus vulgaris*), maize (*Zea mays* L), garri (processed *Manihot esculentus* Crantz) purchased from three randomly selected stores at Apata market, Ibadan, Oyo state, Nigeria. Samples were washed, oven-dried and powdered. Samples were digested with nitric acid and analyzed with Atomic Absorption Spectrophotometer. The concentration of cadmium and lead in the various food stuffs exceeded the WHO permissible level across three stores. Cadmium in rice (0.20mg/kg) and beans(0.20mg/kg) were highest in same store, while Cr(0.74mg/kg) in rice, Ni (0.84mg/kg) in maize and Zn (0.44mg/kg) in beans were exclusively highest same store. Iron (5.10mg/kg) was highest in Zobo drink in one store. Overall 62.5% of the sampled food stuff had levels of metals below the WHO permissible limit, 25% violated the permissible limit and 12.5% were non-detectable. Foodstuffs purchased at Apata market elucidated levels of heavy metals that are of public health importance.

**Keywords:** Heavy metal contamination, urban market, Daily intake rate, contaminated foods, locally processed foods

**INTRODUCTION**

Human health had, will and will forever be a thing of primary concern. Aside poverty, disease, war and famine, pollution has become a topic of great concern. The WHO, FAO, E.U., and many developed countries have hence setup standards and regulation to check levels of pollutions and provide options to avoid the human contribution of this contaminants to the environment. Heavy metals are a major topic of concern under environmental pollution and have both organic and inorganic sources (Gildow, 2004). Anthropogenic activities, such as

mining and industrial processing are the main sources of heavy metal pollution in the environment (Saha and Zaman, 2013). Agrochemicals such as metal-based pesticides and fertilizers, plays an important role in the contamination of foodstuffs by heavy metals (Loutfyet *al.* 2012).

Heavy metals are of great importance due to their hazards in humans via intake through food consumption. Exposure via diet accounts for >90 % compared to other ways of exposure such as inhalation and dermal contact (Loutfyet *al.* 2006). It must be noted that although metals can change their

chemical form, they cannot be degraded or destroyed. Therefore, the risk assessment of these elements via dietary intake is an important issue (Marti-Cid *et al.* 2008). Trace metals such as Fe, Zn and Cu are involved in the function of several enzymes and are essential for maintaining health throughout life (Institute of Medicine, Food and Nutrition Board, 2001). These metals are naturally present in foodstuffs and are nutritionally important to humans, but toxic when consumed in excess. The deficiencies of these metals constitute the largest nutrition and health problem to populations in developed and developing countries (Olivares *et al.*, 2004)

Contaminations from heavy metal can be influenced by factors ranging from environmental conditions during growth to the processing, handling, and storage of food products (Morgan, 1999). There are a number of different factors that can influence a metal's toxicity, but generally the poisonous effect of heavy metals is a function of the concentration level which is attained in a target organ in the human body (Zukowska and Biziuk, 2008). According to Wang (1984) a long-term exposure to low cadmium levels and a short-term exposure to high cadmium level will provide same toxic effect, due to its accumulation and persistence. The kidney, liver and central nervous system appear to be the most affected target organs (Apostoli, 2002). The factors influencing metal toxicity include physical and chemical properties (among others chemical forms of element), element interaction, formation of compounds or complexes among metal and other metalloids, interchange of metal bounds to proteins, sources and sinks, environmental transport, and transformation, influence of concentration and other exposure variables (for example: time, route, pattern of exposure, bioavailability), nutritional status,

taking drugs such as alcohol and nicotine (Nordberg *et al.*, 1978).

It is recommended that monitoring data from dietary intake studies be compared with standard tolerable daily intake (ADI/TDI) recommended by the Joint FAO/WHO Expert Committee on Food Additives [ECFA]. (Zukowska and Biziuk, 2008). Food contains a wide range of chemicals of fundamental importance to human health. Some are essential minerals and vitamins, while some are hazardous (natural chemicals unintentionally present in foodstuff and intentionally added chemicals to modify food properties) (Zukowska and Biziuk, 2008). Although metals can change their chemical form, they cannot be degraded or destroyed. Therefore, the risk assessment of these elements via dietary intake is an important issue (Marti-cidet *al.*, 2008). This study investigated concentrations of selected heavy metals in selected staple foodstuffs and a locally processed drink (Zobo drink) at Apata Market in Ibadan, Oyo State, Nigeria.

## MATERIALS AND METHODS

### Study area and sampling

Five commonly consumed food samples; rice (*Oryza sativa*), beans (*Phaseolus vulgaris*), maize (*Zea mays*), garri (processed *Manihot esculentus*) were purchased from three different randomly selected stores within Apata market (7.3828<sup>0</sup>Longitude –3.8248<sup>0</sup> Latitude) in Ibadan, Oyo state of Nigeria.

### Sample preparation

All the collected samples of various food crops were washed with de-ionised water to remove airborne pollutants. They were then grounded into fine powders in a ceramic mortar and pestle and passed through a sieve and 1.0g of the powdered samples was weighed using a Mettler weighing balance (P1200) and kept in the already labelled paper and wrapped for further analysis.

### Digestion of the samples

Each weighed sample was poured into a 50ml beaker, 15 ml of HNO<sub>3</sub> was added to the beaker to dissolve the sample (HNO<sub>3</sub> is used as solvent because it dissolves possibly all metals). It was then placed on a hot plate at 350°C in a fume cupboard so as to digest and trap in all possible poisonous gas. After heating, the sample was brought out from the fume cupboard and allowed to cool.

After cooling, it was transferred into a 100ml volumetric flask and diluted with de-ionized water up to the lower meniscus at the mark of 100ml and filtered into a sample bottle using Whattman No.1 filter paper and a funnel, It was then stored for further analysis. All the glass apparatus used throughout the process of this digestion were washed with de-ionized water.

### Determination of heavy metal concentration

The digested samples were carried to the multipurpose laboratory of the Federal College of Animal Health and Production Technology, Moore Plantation, Apata,

Ibadan, Oyo State, Nigeria and was analysed using the atomic absorption spectrophotometer (AAS).

### Daily Intake Rates of Food stuffs

A survey was created on google form and sent to various respondent to carry out indirect assessment method (Kroes *et al.*, 2002), for retrieving data to calculate the daily intake rates of each of the selected commonly consumed food stuffs. The quantity of food and rates were retrieved from the survey.

### Data analysis

Data was analyzed using Microsoft excel 2010 edition.

The daily intake rate of metals (DIR) was calculated using:

$$DIR = C_{\text{metal}} \times D_{\text{food intake}} / B_{\text{average weight}}$$

C<sub>metal</sub>= heavy metal concentration in plants (mg/kg)

D<sub>food intake</sub>= daily intake of food stuff (kg/person)

B<sub>average weight</sub>= average body weight (55.9kg)

## RESULTS AND DISCUSSION

**Table 1: Levels of heavy metals (mg/kg) in various food samples collected from store 1 in Apata market, Ibadan, Nigeria**

Samples	Cd	Cr	Ni	Zn	Fe	Cu	Pb
Zobo	0.11	0.46	0.21	0.27	0.65	0.12	0.26
Maize	0.19	0.42	0.84	0.27	0.41	0.06	0.12
Garri	0.05	0.41	0.07	0.05	0.37	0.04	0.11
Beans	0.10	0.31	0.04	0.44	1.40	0.11	0.06
Rice	ND	0.74	0.08	0.08	0.19	0.07	0.33

\*ND = Not Detected

Table 1 elucidates the levels (mg/kg) of cadmium, chromium, nickel, zinc, iron, copper and lead present in commonly consumed food stuffs purchased at Apata market from store 1. Nickel has the highest occurrence of 0.84mg/kg in maize. The range of metals were 0.05 – 0.19, 0.31 – 0.74, 0.04 – 0.84, 0.05 – 0.44, 0.19 – 1.40,

0.04 – 0.12 and 0.06 – 0.33mg/kg for cadmium (Cd), chromium (Cr), nickel (Ni), zinc (Zn), iron (Fe), copper (Cu) and lead (Pb) respectively. The highest levels of Cd, Ni and Zn were found in maize; Cr and Pb in rice; Zn and Cu in Zobo leaf and Fe in rice. Cd level was not detectable in rice.

**Table 2: Levels of heavy metals (mg/kg) in various food samples collected from store 2 in Apata market, Ibadan, Nigeria**

Samples	Cd	Cr	Ni	Zn	Fe	Cu
Zobo	0.16	0.31	0.09	0.29	4.97	0.08
Maize	0.16	0.24	0.04	0.28	0.47	0.03
Garri	0.10	0.08	ND	0.04	0.30	ND
Beans	0.20	0.13	0.04	0.29	0.69	0.14
Rice	0.20	ND	ND	0.09	0.24	0.06

\*ND = Not Detected

Table 2 elucidates the levels (mg/kg) of Cd, Cr, Ni, Zn, Fe and Cu present in commonly consumed food stuffs purchased at Apata market from store 2. Fe having the highest occurrence of 4.97mg/kg in Zobo leaf. The range of metals were 0.10 – 0.20, ND – 0.31, ND – 0.09, 0.04 – 0.29, 0.24 – 4.97 and 0.03 – 0.14 for Cd, Cr, Ni, Zn, Fe and Cu respectively. The highest levels of Cd, Cu and Zn in store 2, were in Beans, while Cr, Ni, Zn and Fe in Zobo leaf. Cr and Ni levels were not detectable in rice, Ni not detectable in Garri and rice and Cu not detectable in Garri. Cd and Ni levels were generally lower in store 2 compared to store 1, Zn and Cu were within same range, but Fe and Cr were higher in store 2 than in store 1.

Table 3 elucidates the concentration levels (mg/kg) of Cd, Cr, Ni, Zn, Fe and Cu present in commonly consumed food stuffs purchased at Apata market from store 3. Fe having the highest occurrence of 5.10mg/kg in Zobo leaf. The range of metals were ND – 0.14, 0.15 – 0.62, ND – 0.13, 0.08 – 0.37, 0.29 – 5.10 and ND – 0.11 for Cd, Cr, Ni, Zn, Fe and Cu respectively. The highest levels of Cd, Ni and Zn were found in maize; Cr and Pb in rice; Zn and Cu in Zobo leaf and Fe in rice. Cadmium level was not detectable in rice. Cadmium concentration levels range was similar to that of store 1 but below store 2; Cr concentration levels range

was similar to that of store 1 and above store 2; Ni concentration levels was similar to that of store 2 and below store 1; Zn concentration levels were uniform in all the stores; Fe concentration level was similar to that of store 2 and higher than in store 1. Copper concentration level was similar to that of store 2 and below store 1.

Ranges of the selected heavy metal contaminant levels in table 4 appear to vary within the 3 stores, when compared. Zn showed consistency across the 3 stores (0.08mg/kg – 0.37 mg/kg), however Cd (ND – 0.14 mg/kg) and Cr (0.31 mg/kg – 0.74 mg/kg) levels were similar in store 1 and 3, but different from store 2 (0.10 mg/kg – 0.20 mg/kg) and (ND – 0.31 mg/kg) respectively. This might be due to more specific activities within or around the stores. There is also the possibility of contamination from other sources, aside the immediate environment.

Table 5 elucidates Cd, Fe and Pb levels in Zobo leaf to be above the WHO permissible level across all stores conversely, Cr, Ni, Zn and Cu were below the permissible concentration levels.

Zn with range of 0.35 – 0.71 mg/kg in a similar study on Zobo drink in Gombe state, Nigeria (Maigari *et al.*, 2016) was higher than Zn levels 0.27 – 0.37 mg/kg in this study, all other heavy metals were lower than values recorded in this study.

**Table 3: Levels of heavy metals (mg/kg) in various food samples collected from store 3 in Apata market, Ibadan, Nigeria**

Samples	Cd	Cr	Ni	Zn	Fe	Cu
Zobo	0.06	0.22	0.01	0.37	5.10	0.11
Maize	0.14	0.15	0.01	0.37	0.97	0.06
Garri	0.01	0.52	ND	0.08	0.31	ND
Beans	ND	0.61	0.13	0.30	0.71	0.11
Rice	ND	0.62	ND	0.10	0.29	0.04

\*ND = Not Detected

**Table 4: S Comparisons among the heavy metals in the food stuffs purchased from different stores in Apata market, Ibadan, Oyo state**

Samples	Store 1	Store 2	Store 3
Cd	0	+	0
Cr	0	-	0
Ni	+	0	0
Zn	0	0	0
Fe	-	0	0
Cu	+	0	0

\* 0 = similar range, + = above others, - = below others

**Table 5: Levels of heavy metals (mg/kg) in Zobo leaf collected from various stores at Apata market, Ibadan in relation to the WHO standard**

ZOBO							
Samples	Cd	Cr	Ni	Zn	Fe	Cu	Pb
Store 1	0.11	0.22	0.01	0.37	5.10	0.12	0.26
Store 2	0.16	0.31	0.09	0.29	4.97	0.08	-
Store 3	0.06	0.46	0.21	0.27	0.65	0.11	-
WHO	0.05	2.3	0.67	0.99	0.43	0.74	0.1

In Table 6, Cr, Zn, Cu and Ni (in stores 1 and 2), their concentration levels in maize across the stores were lower than the WHO safe limits for each of the heavy metals. Cd and Pb were above the limits. Fe in store 1 was also lower. The mean Cr, Ni, Zn, Fe and Cu levels in maize (0.27, 0.02, 0.31, 0.62 and 0.05) mg/kg respectively were similar to the results (0.52, 0.07, 0.66, 0.40 and 0.13) mg/kg respectively obtained from a study carried out in local markets of Ambo city, Ethiopia (Tegegne *et al.*, 2015).

Conversly, Pb and Cd concentration levels were not detected in the study.

Garri was generally safe except for Pb concentration level in store 1 that was slightly higher than the permissible limit (Table 7). This is appreciable considering that garri is mostly consumed without been cooked. The mean value of Fe (0.33 mg/kg), Cu (0.04mg/kg) and Zn (0.06mg/kg) in this study is far lower than the mean values reported for Fe (29.16mg/kg), Cu (2.6 mg/kg) and Zn (4.55mg/kg) in a study carried out in Nigeria in assessing chemical and trace metal of dried cassava products (Abass *et al.*, 2019). Generally, the processing of cassava to garri increase the possibilities of contamination with heavy metals (Bolade, 2016).

Cadmium was at safe levels in beans except for store 2. Cr, Ni, Zn, Cu and Pb were within the safe limit (Table 8). Conversely, Fe was above the permissible level across the 3 stores. Cr concentration levels (0.13mg/kg – 0.61mg/kg) were corroborative to Cr levels (0.189mg/kg – 0.586mg/kg) as reported Yaradua *et al.* (2017) in a study carried out in selected markets in Katsina state on unprocessed beans. Conversely, concentration levels of heavy metals in the processed bean porridge had lower levels (ND – 0.16mg/kg) in same

study, suggesting that processing reduced the concentration of Cd, Mn, Ni and Cr. This contradicts Watzke (1998) and Ersoy *et al.* (2006) who reported that toxic elements are sensitive to processing effects. Peeling, washing, cooking, frying, and other culinary activities can have a significant influence on the content of heavy metals in foodstuffs. Pb concentration levels were lower than the permissible limit which is corroborates with that reported for market sold beans in eastern Nigeria (Okoye *et al.*, 2009) and Katsina State (Yaradua *et al.*, 2017).

**Table 6: Levels of heavy metals (mg/kg) in Maize collected from various stores at Apata market in relation to the WHO standard**

MAIZE							
Samples	Cd	Cr	Ni	Zn	Fe	Cu	Pb
Store 1	0.19	0.42	0.84	0.27	0.41	0.06	0.12
Store 2	0.16	0.24	0.04	0.28	0.47	0.03	-
Store 3	0.14	0.15	0.01	0.37	0.97	0.06	-
WHO	0.05	2.3	0.67	0.99	0.43	0.74	0.05

**Table 7: Levels of heavy metals (mg/kg) in Garri collected from various stores at Apata market in relation to the WHO standard**

GARRI							
Samples	Cd	Cr	Ni	Zn	Fe	Cu	Pb
Store 1	0.05	0.41	0.07	0.05	0.37	0.04	0.11
Store 2	0.10	0.08	ND	0.04	0.30	ND	-
Store 3	0.01	0.52	ND	0.08	0.31	ND	-
WHO	0.10	2.3	0.67	0.99	0.43	0.74	0.1

\*ND = Not Detected

**Table 8: Levels of heavy metals (mg/kg) in Beans collected from various stores at Apata market, Ibadan in relation to the WHO standard**

BEANS							
Samples	Cd	Cr	Ni	Zn	Fe	Cu	Pb
Store 1	0.10	0.31	0.04	0.44	1.40	0.11	0.06
Store 2	0.20	0.13	0.04	0.29	0.69	0.14	-
Store 3	ND	0.61	0.13	0.30	0.71	0.11	-
WHO	0.10	2.3	0.67	0.99	0.43	0.74	0.1

\*ND = Not Detected

Generally, concentration levels of the selected heavy metals in rice were within safe limits for all the 3 stores except for Pb (0.33mg/kg) which was higher than the WHO safe level of 0.2mg/kg for rice (Table 9).

Levels of Cd, Cr and Pb which were 0.20mg/kg, 0.074mg/kg, 0.33mg/kg respectively in this study were lower than levels reported in various rice samples for Cd (1.12 – 1.30) mg/kg, Cr (0.86 – 0.93) mg/kg and Pb (0.89 – 0.98)mg/kg purchased from Ofada, Ogun state, Nigeria (Olalekan *et al.*, 2019).

In general, highest levels of Cd, Cr, Ni, Zn, Fe, Cu and Pb were detected in beans and rice in store 2; rice in store 1; maize in store 1; beans in store 1; zobo in store 3; beans in store 2 and rice in store 1 respectively. Rice and beans appear to be the most contaminated (Table 10). Overall 62.5% of the sampled food stuffs had concentration levels of heavy metals below the WHO permissible limit, which varied based on food stuffs, 25% violated the permissible limit and 12.5% were non-detectable. Beans had the highest DIR of 0.0347, 0.025, 0.1215 and 0.0436 for Cd, Ni, Zn and Cu respectively. Rice had the highest DIR of 0.1907 and 0.1371 for Cr and Pb respectively while Zobo leaf had the highest DIR of 0.6873 for Fe (Table 11).

According to this study the levels of cadmium was high in most foodstuff sampled, across all the three randomly selected stores within the market. This might be due to other activities such as processing, handling and so forth. Studies have shown cereals and potatoes as the major sources contributing to dietary cadmium intake, in almost all countries (Peterson, 1995). Cadmium is listed as endocrine-disturbing

substance and may lead to the development of prostate cancer and breast cancer (Pan *et al.* 2010). High levels of which are hazardous to the population, since they can't bio-degrade, but rather bio-accumulate.

Nickel deficiency results in decreased growth in rats, sheep, cows, goats and minipigs. It also causes depressed hematopoiesis in rats, sheep, cows, and goats (Nielsen, 1988). Nickel is reported to be associated with eczema. According to (Peltonen, 1978) hand eczema co-existing with nickel allergy occurred in 0.9% of a tested population. The author further stated that 45.5% (20/44) of the nickel sensitive individuals in the total tested population reported a present or previous case of hand eczema.

Lead and iron levels were high. The activities of 2 petrol (Premium Motor Spirit) stations few meters from the store, exhausts from the exhaust of generators and heavy traffic is a presumable cause. Lead toxicity has been noted to be neurotoxic, carcinogenic, cause hypertension and lower immune systems of animals (Gidlow, 2004). According to (CDC, 1999), the most common route of exposure to lead, in countries where leaded gasoline has been banned, is through food. The amounts of Pb in foodstuffs originating from plants are found to be higher than those from animals (Krizova *et al.*, 2004; Munoz *et al.*, 2005). High blood lead levels are poisonous to human health. At very high blood lead levels, lead is a powerful abortifacient, produce renal tubular damage with glycosuria and aminoaciduria (saturnine gout), (Gidlow, 2003; Nordstrom *et al.*, 1979). At lower levels, it has been associated with miscarriages and low birth weights of infants (Nordstrom *et al.*, 1979).

**Table 9: Levels of heavy metals (mg/kg) in Rice collected from various stores at Apata market in relation to the WHO standard**

Samples	RICE						
	Cd	Cr	Ni	Zn	Fe	Cu	Pb
Store 1	ND	0.74	0.08	0.08	0.19	0.07	0.33
Store 2	0.20	ND	ND	0.09	0.24	0.06	-
Store 3	ND	0.62	ND	0.10	0.29	0.04	-
WHO	0.40	2.3	0.67	0.99	0.43	0.74	0.2

\*ND = Not Detected

**Table 10: Stores with the highest occurrence of each heavy metal based on the sampled food stuffs and the percentage of samples that had no detectable trace of the heavy metals**

Samples	Cd	Cr	Ni	Zn	Fe	Cu	Pb
Highest occurrence	Store 2 (rice, beans)	store (rice)	1 Store 1 (maize)	1 Store 1 (beans)	1 Store 3 (Zobo)	2 Store (beans)	1 Store (rice)
ND levels (%)	20.00	6.67	26.67	0.00	0.00	13.33	0.00

\*ND = Not detected

**Table 11: Average Daily intake rate (g person<sup>-1</sup> day<sup>-1</sup>) of heavy metals (DIR) through consumption of contaminated food stuffs in Apata market, Ibadan, Nigeria**

Samples	Cd	Cr	Ni	Zn	Fe	Cu	Pb
ZOBO	0.0208 ±0.01	0.0635 ±0.024	0.0197 ±0.02	0.0598 ±0.01	0.6873 ±0.486	0.0198 ±0.004	0.0493 ±0.000
MAIZE	0.0329 ±0.005	0.055 ±0.028	0.0596 ±0.095	0.0622 ±0.011	0.1247 ±0.062	0.0097 ±0.003	0.0248 ±0.000
GARRI	0.0184 ±0.015	0.1191 ±0.082	0.0083 ±0.013	0.0198 ±0.007	0.115 ±0.013	0.0046 ±0.007	0.0377 ±0.000
BEANS	0.0347 ±0.034	0.123 ±0.085	0.025 ±0.018	0.1215 ±0.03	0.3295 ±0.143	0.0436 ±0.006	0.0212 ±0.000
RICE	0.0287 ±0.05	0.1907 ±0.167	0.0118 ±0.02	0.0381 ±0.004	0.1022 ±0.022	0.0257 ±0.007	0.1371 ±0.000

## CONCLUSION

Heavy metals contamination remains a threat to humanity especially because of their bio accumulative potential. This study has elucidated high levels of Cadmium and varying levels of Lead and other essential metals when compared to the recommended WHO permissible level.

It is recommended that the market should be relocated to an environment with less industrial activities or the gas stations be relocated. Further studies need to be carried out on levels of heavy metals in other

markets and animal protein sources to assess and monitor the levels of heavy metals.

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