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# Heavy Metal Contamination of Some Staple Foods across the Agro-ecological Zones of Nigeria

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***ABSTRACT***
*Heavy metals determination in staple food commodity is of vital interest because of their toxic nature and relevance to food safety. In this study, the levels of heavy metals (Cd, Pb Fe, and Zn) in some staple foods collected across the seven (7) agro-ecological zones (AEZ) of Nigeria were investigated using the atomic absorption spectroscopic technique (AAS). The mean concentrations of Cd, Zn, Fe and Pb (mg/Kg) were 0.00 – 9.73, 0.07 – 46.72, 0.00 – 0.05 and 0.00 – 87.50 in garri and cereals samples collected across the agro-ecological zones of Nigeria. These values except for Pb in garri samples obtained from humid forest, were found to be below the joint WHO/FAO (2001) safe limit of 0.2 mg/Kg for Cd and Pb respectively in garri and cereals also, the values obtained in all the samples for Fe and Zn as micro nutrients of great importance in human nutrition were found to be below the recommended daily allowance of 425.5 and 99.4 mg/Kg for Fe and Zn in the samples. Data were analysed using ANOVA at $p<0.05$. Analysis of the variation in levels of heavy metals across the agro-ecological zones showed that their concentrations differed significantly across the AEZ at 95 % confidence. From the results, samples collected from HF had the highest levels of heavy metals analysed and this could be due on environmental factors and crop handling.*

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**INTRODUCTION**

Heavy elements are inherent in the terrestrial crust and are present naturally in agricultural topsoil and are distributed by anthropogenic means (Liu *et al*., 2018). The uptake and accumulation of these heavy metals in crops bring about entry of toxic elements to the food chain, posing a potential threat to human health. Human involvement in the form of use of contaminated water in agriculture, excessive mining, manufacturing and industrial activities leads to heavy metal pollution (Agbaji *et al*., 2015; Kwon *et al*., 2017; Guindo *et al*., 2019). Improper waste disposal activities and excess use of pesticides were among the most significant sources of heavy metal pollution in environment (World Bank Data, 2019). Heavy metals such as Cr, Cd, and Pb are often cited as primary contaminants of concern. Moreover, with about 203, 567, 923 inhabitants (World Bank Data, 2019). Nigeria has become the most populous black nation and one of the aftermaths of the increased human population is environmental pollution. The relationships between overpopulation, poverty and urban air pollution has been well established (FAO/WHO, 2017; World Bank Data, 2019).

Cereals refer to crops harvested for dry their grains only while crops harvested for forage, silage or grazing are classified as fodder crops. They are mostly grown in temperate and tropical regions of the world and provide more food energy worldwide than any other type of crop and are therefore referred to as staple crops. Major cereal crops are; maize (also known as corn), rice, wheat, barley, oat, sorghum, millet and rye. These cereals are the main component of the diet to the Nigerian populations, providing about 75% of the total caloric intake and 67% total protein (FAO/WHO, 2017), and so contamination of cereals will be a public health concern. To avoid health effects when consuming contaminants, international institutions and organizations set levels for the acceptable daily intake (ADI) or provisional weekly tolerable intake (PWTI) (Quedraogo and Amyot, 2013; EFSA CONTAM, 2015)

***Toxicity of Heavy Metals***.

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Heavy metals like Cd and Pb have been known to cause major problem to our environment while the elements like Zn and Fe are essential for biochemical reactions in the body (Agbaji *et al*., 2015). Generally, most of these heavy metals are not biodegradable, having long biological half-lives and the potential for accumulation in the different body organs leading to unwanted side effects.

Lead toxicity in the body can cause – musculoskeletal, renal, ocular, immunological, neurological, reproductive and developmental effects. Cadmium intake is known to result in bone fracture, cancer, diarrhoea, stomach pains, severe vomiting, reproductive failure and damage to the central nervous system. In addition to this cardiovascular, kidney, nervous as well as bone disease (WHO, 2011; Filippini *et al*., 2018). Heavy metals have also been implicated as causing carcinogenesis, mutagenesis and tetra genesis in human. Also, the toxicity of metal ions is correlated to one another; the Copper toxicity induces iron deficiency, lipid peroxidation and destruction of membranes (Salihu *et al*., 2014).

Based on persistent nature, accumulation behaviour and the probability of potential toxic effects of heavy metals as a result of consumption of food grains, there is need to assess their presence in food grains and considering the importance of cereals as staple foods in the across Nigeria, this study sets to compare the heavy metal level of some selected cereals across the agro-ecological zones of Nigeria and providing their toxicological profiles.

**MATERIAL AND METHODS**

***Sampling:*** A total of 225 samples of rice (n = 42), garri (n = 43), maize (n= 41), sorghum (n= 32), millet (n = 39) and wheat (n = 28) samples were collected for heavy metals profiling across 31 states and 7 agro-ecological zones of Nigeria.

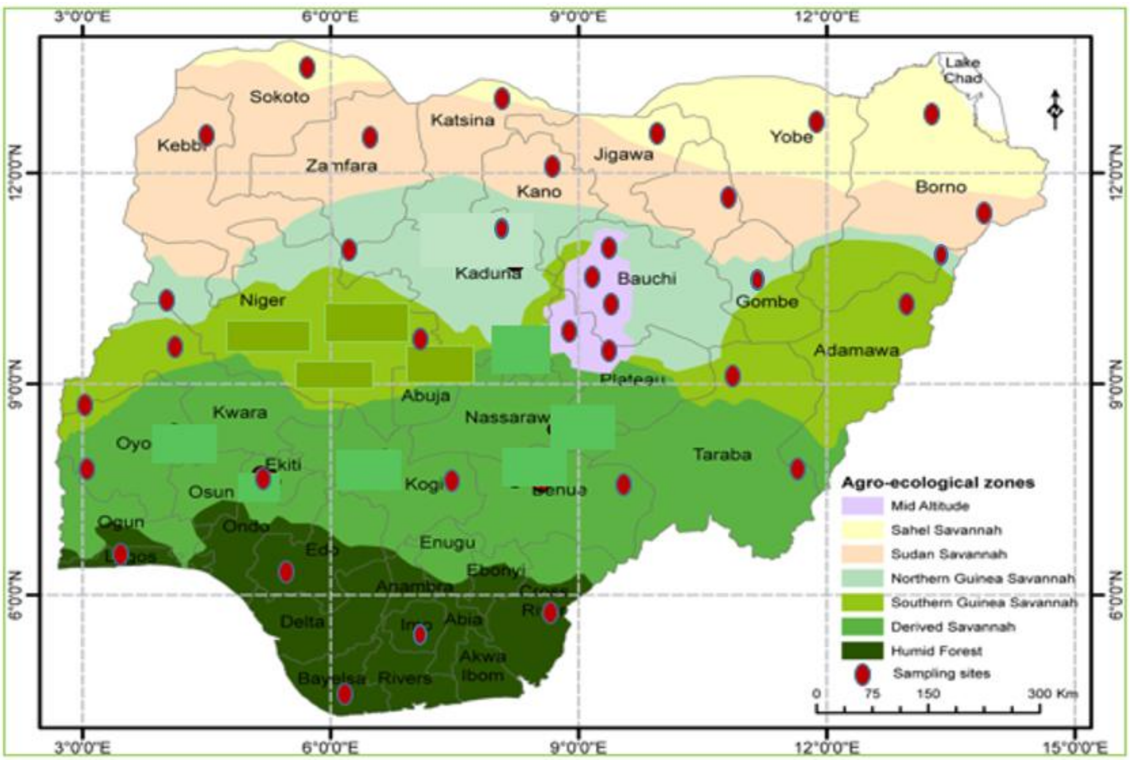


**Figure 1.** Map of Nigeria showing districts in seven agro-ecological zones from which garri and other cereals were sampled according to protocol to by Atehnkeng *et al*. (2008).

The samples were sun dried until properly dry, pulverized and then a suitable sieve was used to sieve the samples. Four two (42) composite samples (seven (7) sample type per AEZ) were obtained from a combination of each sample type after grinding. The powdered samples were stored in HDPE sample bottles prior to wet digestion. The samples were chosen due to their wide acceptability and consumption across the country.

***Reagents:*** All chemicals and reagents used for the study of analar grade unless otherwise specified and were purchased from Sigma-Aldrich (Germany).

***Digestion:*** Ground samples weighing 2.5 g each, taken from previously dried to constant weight samples were placed in 100 mL reflux flask. 15 mL

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of concentrated $HNO_3$ and 5 mL of concentrated $H_2O_2$ were mixed with the samples. The mixture was allowed to stand for about 48 hrs at room temperature. It was then refluxed on a heating mantle at 90°C until brown fumes ceased to evolve, 4-6 hrs and allowed to cool. 5 mL of 60% (v/v) $HClO_4$ was added to the mixture and further refluxed for 30 min. The digest was allowed to cool to room temperature. It was filtered into a 100 mL volumetric flask with a Whatman's No. 42 filter paper and made to the mark with de-ionized water. This was repeated for all the samples in triplicate. A blank was also prepared similarly (Brizio *et al*., 2016).

***Analysis***: The digests were analysed for their content of Cr, Pb, Fe and Zn with the aid of an Atomic Absorption Spectrophotometer at the Multi User Research Laboratory, Ahmadu Bello University Zaria, Nigeria.

**STATISTICAL ANALYSIS**

The data collected were subjected to two-way analysis of variance (ANOVA) to compare treatments in triplicates, the Duncan multiple range test (DMRT) was used to test the variations in mean concentrations of heavy metals in the cereals and garri samples collected across the seven agro-ecological zones and the statistical significance was set at $P \leq 0.05$. All statistical analyses were computed with SPSS software version 20.

**RESULTS**

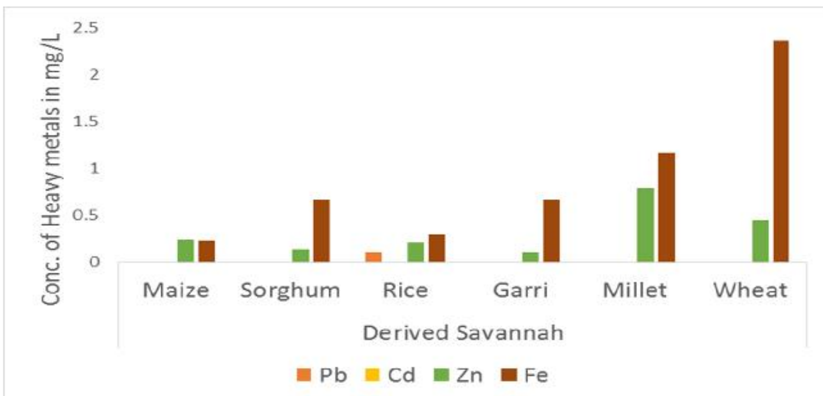


**Figure 1:** Concentrations (mg/L) of heavy metals in samples collected from Derived Savannah

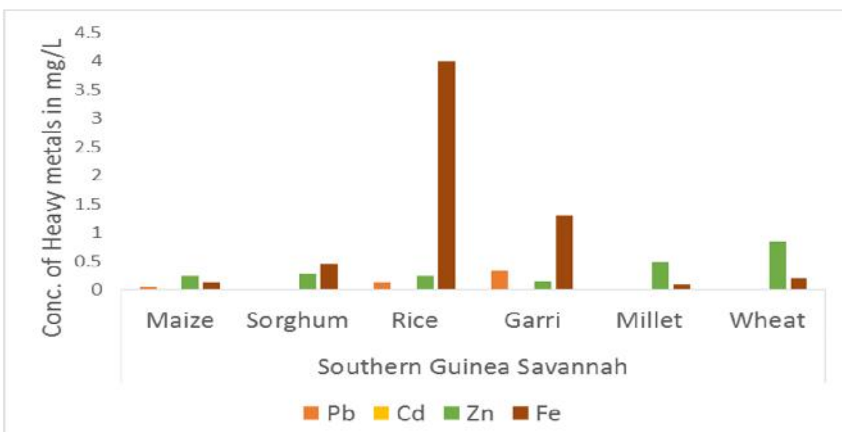


**Figure 2:** Concentrations (mg/L) of heavy metals in samples collected from southern Guinea Savannah.

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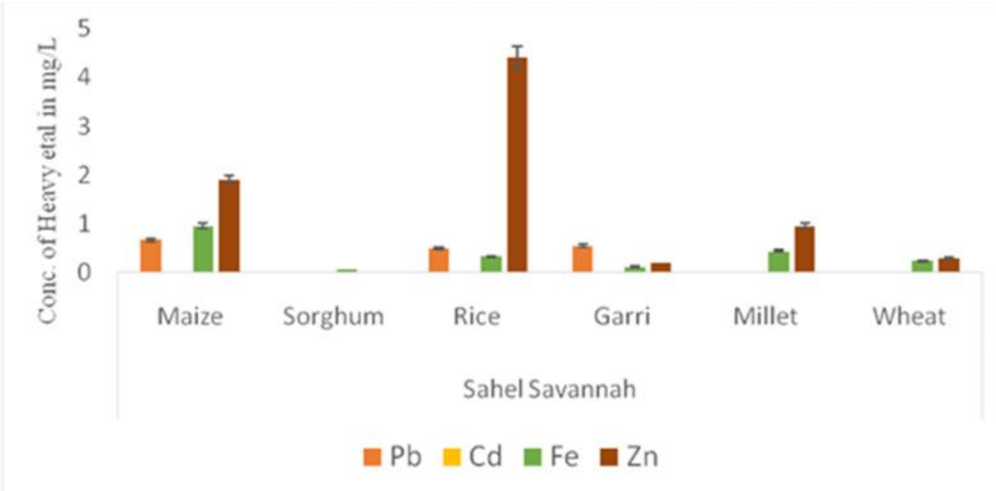


**Figure 3:** Concentrations (mg/L) of heavy metals in samples collected from Sahel Savannah.


**Figure 4:** Concentrations of heavy metals (mg/L) in samples collected from Northern Guinea

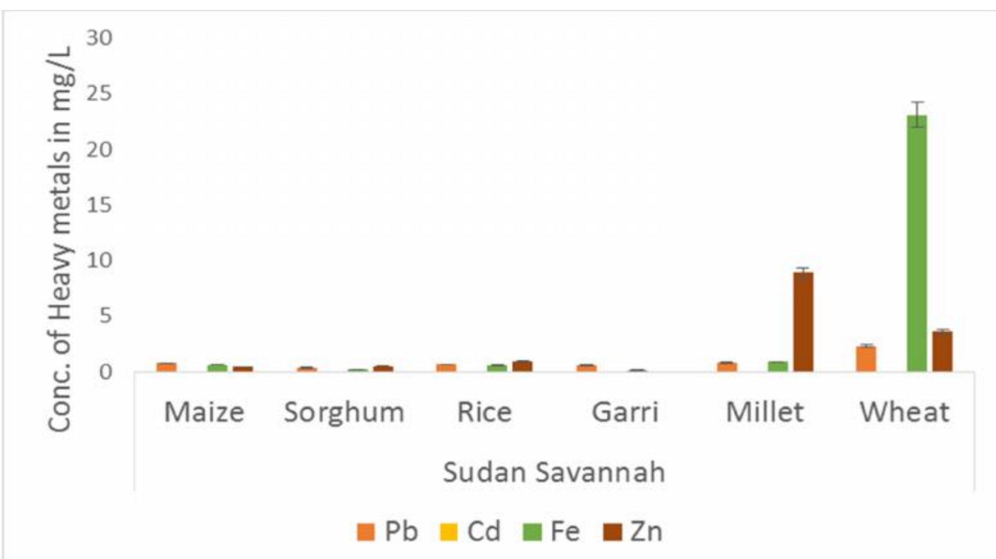


**Figure 5:** Concentrations of heavy metals (mg/L) in samples collected from Sudan Savannah.

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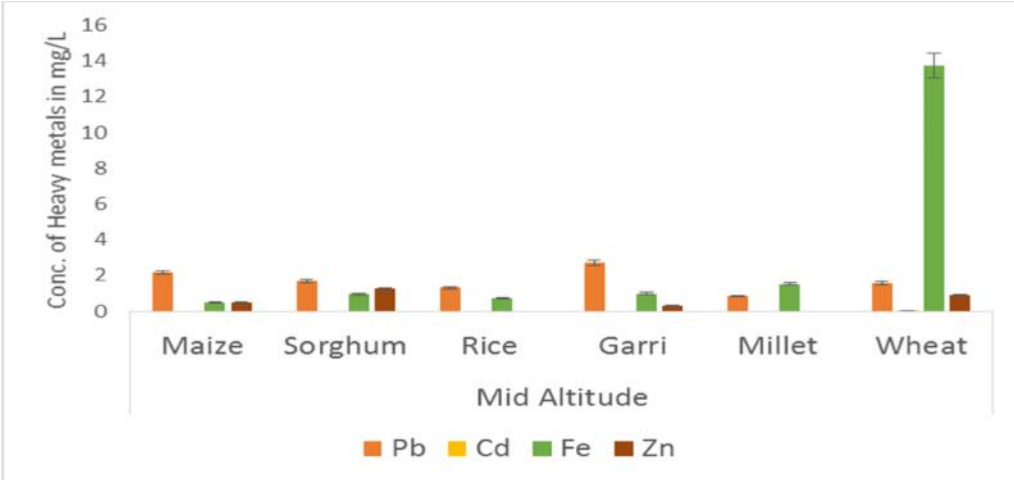


**Figure 6:** Concentrations of heavy metals (mg/L) in samples collected from Mid Altitude.

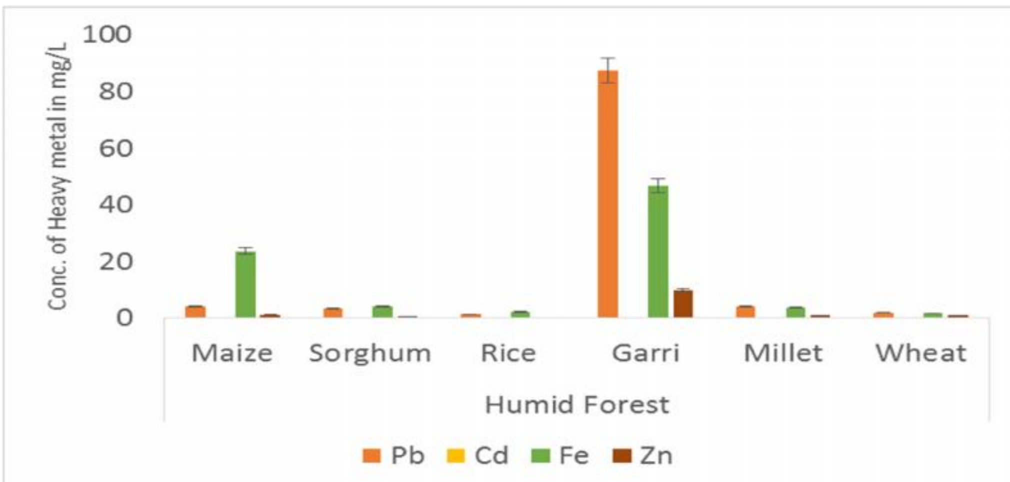


**Figure 7:** Concentrations of heavy metals (mg/L) in samples collected from Humid Forest.

**Table 1:** Distribution of heavy metal (Mean ± SEM) in garri and cereals samples across Nigeria

| ELEMENT | SAMPLE | Mean ± SEM | Min | Max | Perm. L. |
|---|---|---|---|---|---|
| **Pb** | Maize | $1.1107 \pm 0.386^{b}$ | BDL | 4.06 | 0.2 |
| | Sorghum | $0.8097 \pm 0.339^{b}$ | BDL | 3.47 | |
| | Rice | $0.5974 \pm 0.137^{b}$ | 0.11 | 1.32 | |
| | Garri | $13.1517 \pm 8.421^{a}$ | BDL | 87.5 | |
| | Millet | $0.8596 \pm 0.391^{b}$ | BDL | 4.21 | |
| | Wheat | $0.8627 \pm 0.267^{b}$ | BDL | 2.29 | |
| **Cd** | Sorghum | $0.001 \pm 0.000^{b}$ | BDL | 0.01 | 0.2 |
| | Rice | $0.001 \pm 0.000^{b}$ | BDL | 0.01 | |
| | Garri | $0.0074 \pm 0.004^{b}$ | BDL | 0.05 | |
| | Millet | $0.0031 \pm 0.001^{b}$ | BDL | 0.02 | |
| | Wheat | $0.0036 \pm 0.001^{b}$ | BDL | 0.01 | |
| | Maize | $3.795 \pm 2.246^{a}$ | 0.24 | 23.63 | |
| **Zn** | Sorghum | $0.8561 \pm 0.372^{c}$ | 0.07 | 4.08 | |
| | Rice | $0.6454 \pm 0.185^{c}$ | 0.21 | 2.21 | |

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| | | | | | |
|---|---|---|---|---|---|
| | Garri | 6.8997 ± 4.508[a] | 0.09 | 46.72 | 99.4 |
| | Millet | 1.2394 ± 0.307[b] | 0.44 | 3.83 | |
| | Wheat | 5.7841 ± 2.324[a] | 0.24 | 23.09 | |
| | Maize | 0.6161 ± 0.173[c] | BDL | 1.89 | |
| **Fe** | Sorghum | 0.499 ± 0.110[b] | BDL | 1.26 | 425.5 |
| | Rice | 1.382 ± 0.504[a] | BDL | 4.41 | |
| | Garri | 1.745 ± 0.912[a] | BDL | 9.73 | |
| | Millet | 1.804 ± 0.809[a] | BDL | 8.88 | |
| | Wheat | 0.231±0.213[b] | BDL | 7.35 | |
| | Maize | 0.011 ± 0.000[c] | BDL | 0.01 | |

Key: SEM = Standard Error of Mean: P-value is significant at <0.05, Values with different alphabets are statistically significantly different, with alphabet "a" been the highest, Min = Minimum, Max = Maximum, Perm. L. = Permissible Limits.

The result of the analysis of heavy metals in garri and some selected cereals (namely maize, millet, rice, sorghum and wheat) collected from the seven AEZs in Nigeria are presented in Figure 1-7 respectively. These results showed a variation in the concentration of metals analysed in all samples across the AEZ. Fe and Zn had higher concentration over other metals. Cadmium (Cd) was not detected in any of the samples while wheat and millet had more of these elements. The garri and cereal samples from all the AEZ were found to be below the permissible limit set by Joint FAO/WHO Food Programme (FAO/WHO, 2017).

Iron, a nutritional element was detected in 80.95 % of the samples with a concentration range of 0.0 – 9.73 mg/kg and mean concentration of 0.4991±0.110, 1.382±0.504, 1.745±0.912, 1.8044±0.809, 0.231±0.213 and 0.011±0.0.00 $mgkg^{-1}$ for sorghum, rice, garri, millet, wheat and maize respectively (Table 1). The levels of Fe found in the garri and cereals collected were generally comparable with reported values for cereals and their products (Shimbo *et al*., 2001; Hermandez-Martinez and Navarro, 2012; Norton *et al*., 2014). It should be noted that, garri collected from the HF had the highest amount of Fe (9.73 mg/Kg) followed by millet from SuS (8.88 mg/Kg) while rice from SaS and SGS had 4.41 mg/Kg and 4.0 mg/kg respectively. The higher levels of Fe in the garri and rice samples could be as a result of processing and milling which is relatively higher in the HF agro ecological zone. Also, in some of these zones, agricultural practices are been carried out near industrial areas, roads with heavy traffics and areas like this, have been shown to cause significant increase and wide variation (p<0.05) heavy metals in cereals (Fangmin *et al*., 2006; Xie *et al*., 2017; Shobba & Kalshetty, 2017). The elevated levels of Iron in these samples compared to others does not pose any concern as Fe concentrations in the samples collected across the AEZ were found to be below the limit set by WHO (425.5 mg/kg) but, were similar to reports from similar works (Xie *et al*., 2017; Shobba & Kalshetty, 2017) .

Garri, maize, millet, rice, sorghum and wheat are staple food for most Nigerians suggesting that, these staples could also serve a source of micronutrient like Zn. In the study, Zinc was detected in all the samples (0.07 – 46.72 mg/kg) collected across the AEZ with mean concentration of 0.8561±0.372, 0.6454±0.185, 6.8997±4.508, 1.2394±0.307, 5.7841±2.324 and 0.6161±0.173 $mgkg^{-1}$ for sorghum, rice, garri, millet, wheat and maize respectively (Table 1) which is similar to the average value of 2.72 $mgkg^{-1}$ reported in literature (Norton *et al*., 2014). The result showed a significant variation (p<0.05) across the AEZ of Nigeria. Garri samples collected for the HF had 46.72 mg/Kg followed by maize from MA with 23.63 mg/Kg and then wheat from SuS with 23.09 mg/Kg. The consistent higher levels of Fe and now Zn in samples obtained from HF indicates the higher industrial activities and also because, most of these cereals (i.e maize, millet, sorghum and wheat) are not cultivated in the region but transported over long distances therefore, exposing them to pollution due to poor handling during transit (Cabrera *et al.,* 2003). Also, higher levels of zinc in the samples compared to other metals may be due to natural occurrence of zinc in soil and environment with about 70 mg $kg^{-1}$ in crustal rocks (Onianwa *et al*., 2000). Very high concentrations of this metal occurring in the Humid Forest could be due to several transportation and local industrial activities and wares and tears from tyres and lubricant oil from high vehicular traffic along these locations.

The levels of Cd in this study ranged from <0.01 mg/Kg to 0.05 in cereals samples. Only samples (13.04 %) obtained from the HF AEZ had Cd

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in them. The levels of Cd were 0.05, 0.02 and 0.01 for garri, millet and other cereals respectively collected from same AEZ. Cd levels of 0.06 – 0.28 mg/Kg slightly higher than values obtained in this study have been report in cereals (Cabrera *et al.,* 2003). All samples analysed had Cd within range reported in literature. Just like Fe and Zn, the samples collected from humid forest AEZ were the once found to be contaminated with Cd between 0.01 to 0.05 mg/Kg, these values were slightly above the permissible limits of 0.2 mg/Kg set by FAO/WHO. Therefore, commercial phosphate containing fertilizers which are heavily used in this region, should be limited as they contain amounts of Cd < 20 mg/Kg and could bio-accumulate in the food chain and cause toxicity (Awata *et al.,* 2017).

There have been a concern that, the consumption of foods such as cereals can contribute significantly to the intakes of Pb if these foods are contaminated with the element (Llobet *et al*., 2003; Satarug *et al*., 2017). In this current study, Pb was detected in 71.24% of the samples (at 0.0 – 87.50 mg/kg) collected across the AEZ with mean concentration of 1.1107±0.386, 0.8097±0.339, 0.5974±0.137, 13.1517±8.421, 0.85961±0.391 and 0.8627±0.267 $mgkg^{-1}$ for maize, sorghum, rice, garri, millet and wheat respectively (Table 1). All the values were below the permissible limits set by WHO (0.2 mg/Kg) except for the sample of garri which had an outrageous level of 87.50 mg/Kg. Maize, millet and sorghum also had values above the permissible limits of 0.2 mg/Kg. The unexpected high levels of Pb in garri and other samples obtained from the HF could be as a result of geographical differences, most of these cereals are transported to this zone, farmlands are also situated in and around industrialized areas which are prone to pollution by the release of chemicals into them leading to contamination of plant crop with Pb. The levels of Pb in samples obtained from the HF is of major concern because, a long term exposure to Pb is a major health concern as this metal has been classified by the International Agency for Research on Cancer as a Type 1 carcinogen (Anjula, 2017; Satarug *et al*., 2017).

## CONCLUSION

From this study, the selected cereals collected across the seven (7) agro-ecological zones of Nigeria were found to contain heavy metals (cadmium (Cu), zinc (Zn), lead (Pb) and iron (Fe)) at varied levels (p<0.05). Cadmium (Cd) was not present in all the cereals across the AEZ except for those collected from Humid Forest. However, the levels Fe and Zn in the garri and cereals samples analysed were below the safe limit set by FAO/WHO. Except for Pb in garri and other cereals collected from humid forest which were found to be above the permissible limit of 0.2 mg/Kg set by FAO/WHO and should therefore be placed under proper surveillance. These cereal sampled across the seven agro-ecological zones of Nigeria should be considered safe for human consumption and may as well serve as sources of trace metals.

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