A COMPARATIVE EVALUATION OF THE HEAVY METALS CONTENT OF SOME CEREALS SOLD IN KADUNA, NORTH WEST NIGERIA

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Abstract- *Heavy Metals (Cd, Fe, Pb and Zn) concentrations of Cereals were investigated using the Atomic Absorption spectroscopic technique (AAS). The mean concentrations of Cd, Fe, Pb and Zn (mg/kg) obtained in Maize ranged from 0.1118 to 0.1155, 0.1846 to 0.5223, 0.1053 to 0.1715 and 0.0394 to 0.1768 respectively while in Sorghum, their concentrations ranged from 0.1110 to 0.1151, 0.1528 to 0.4921, 0.1234 to 0.1763, 0.0539 to 2510 respectively. In Millet, their concentrations however, ranged from 0.1151 to 0.1159, 0.1088 to 0.4819, 0.1026 to 0.1562 and 0.1705 to 0.2988 respectively. These values were found to be below the joint WHO/FAO (2001) safe limit for heavy metals in Cereals but the values obtained in all the samples for Fe and Zn as micro nutrients of great importance in human nutrition were found to be far below the recommended daily allowance for them. Analysis of the variation in the Heavy Metals concentrations at 95 % confidence level showed that their concentrations differed significantly at 95 % confidence level while the correlation coefficients obtained after a comparative evaluation of the heavy metals concentration of the samples showed varying levels of relationship ranging from null, through weak to moderate. Hence, the concentrations of the heavy metals in samples depend to some extent on their nutrient content but to a larger extent could depend on environmental factors.*

Index Terms: *Cancer, Cereals, Chemical analysis, Heavy metals and Toxicity.*

1.0 INTRODUCTION

Cereals, cereal grains or grains are grasses (members of the monocot family-Poaceae or Graminane), cultivated for their edible components or their fruits seeds. The name cereal is derived from Ceres, the name of the Romanian goddess of harvest and agriculture. In FAO, the concept cereals refer to crops harvested for dry grains only while crops harvested for forage, silage or grazing are classified as fodder crops [1].

Cereal crops are mostly grown in temperate and tropical regions of the world and provide more food energy worldwide than any other type of crop. They are therefore staple crops. The principal cereal crops are; Maize (also known as Corn), Rice, Wheat, Barley, Oat, Sorghum, Triticale, Millet and Rye. Cereal grains are the staple food of the people of the tropics providing them with about 75% of their total caloric intake and 67% of their total protein intake [2].

The term “Heavy metal” refers to any chemical element that has a relatively high density and is toxic or poisonous even at low concentration. The Heavy Metals include; Mercury (Hg), Cadmiun(Cd), Lead(Pb), Arsenic(As), Copper(Cu), Nickel(Ni) among others [3].

Heavy metals are natural components of the earth crust. They cannot be degraded or destroyed. To a small extent they enter human bodies via food, drinking water and air [4]. Heavy metal poisoning could result for instance from drinking-water contamination (eg lead pipes), high ambient air circulation near emission sources or intake via the food chain. They are dangerous because they tend to bioaccumulate i.e Their components accumulate in living things anytime they are taken up and stored faster than they are broken down (metabolized) or excreted. [5]

The toxicity of heavy metals most commonly involves the brain and kidney but other manifestations can occur in some other parts of the body for example arsenic is clearly capable of causing cancer, hypertension can result in individuals exposed to lead and renal toxicity in individual exposed to cadmium. [5].

Considering the importance of cereals as staple foods in the tropics, the aim of the research is to compare the Heavy metal of some selected cereals (White maize, yellow maize, red sorghum, white sorghum and millet) sold in Kaduna, Northern Nigeria.

2.0 MATERIAL AND METHODS

Description of Sampling Sites

The sites (Markets) where the samples were collected are located in the heart of Kaduna. They are the major markets in Kaduna metropolis-North West, Nigeria. They are; the Kaduna Central Market located on Ibrahim Taiwo road, Monday market located in Kakuri and Sabo Market, located in Sabon Tasha, all indicated on the Map. (Fig 1.0)

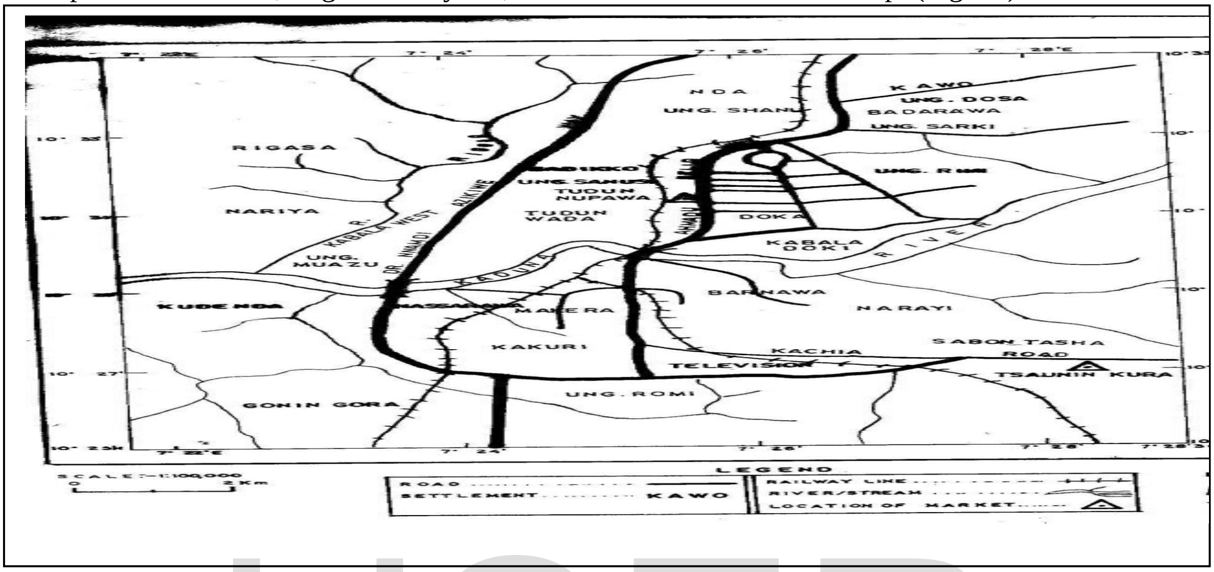

Fig 1.0 Map of Kaduna Metropolis showing the three sampling sites

Sample Collection

A bulk of each of the samples-yellow maize, white maize, white sorghum, red sorghum, and millet was collected by combining the little fractions (Grab) obtained from ten different sellers in the three major markets in Kaduna to make up one Bulk sample (composite) per cereal from each market and labeled.

Sample Preparation and Preservation

The samples were cleaned by sieving and hand separation to remove extraneous materials and then they were ground using the laboratory mortar and pestle. For the determination of moisture total protein and ash, ground samples were passed through 20-mesh (opening per linear inch) so as to avoid loss of materials. For analysis involving extraction e.g lipids, samples were ground to pass a 40-mesh sieve [6].

The bulk samples for each grain were thoroughly mixed, ground and representative samples drawn from them. The samples were stored dry in polyethylene bags in preparation for analysis.

Zinc Stock Solution

Zinc metals dust (1.00 g) was dissolved in 60 cm^3 of 5 mol/dm^3 HCl. The solution was diluted to 1000 cm^3 in a 1 liter volumetric flask with deionized water and stored in a polypropylene bottle giving a concentration of 1000 mg/L. Serial dilutions were made from the stock to give various desired concentrations with respect to the concentration range of zinc-using the dilution factor.

Lead Stock Solution

About 1.5980 g of Lead Nitrate [$Pb(NO_3)_2$] (BDH Analar 99.99%) was dissolved in 100 cm^3 of deionized water. The solution was then diluted to 1000 cm^3 in a 1 litre volumetric flask with deionized water to give a 1000 mg/L Lead solution. Serial dilutions were made from the stock to give concentrations with respect to the working concentration of lead.

Cadmium Stock Solution

About 2.1031 g Cadmium nitrate [$Cd(NO_3)_2$] (BDH Analar 99.99%) was dissolved in 100 cm^3 and then diluted to the mark in a 1 litre volumetric flask with deionized water to give 1000 mg/L Cd solution. Serial dilutions were made with deionized water to give concentrations with respect to the working concentration of cadmium.

Iron Stock Solution

Iron metal (1.00 g) was dissolved in 20 cm^3 of 5 mol/dm^3 hydrochloric acid and 5 cm^3 of 6 mol/dm^3 nitric acid and diluted to 1 litre to obtain 1000 mg/L Fe solution. Serial dilutions were then made from the stock to give concentrations with respect to working concentrations of iron.

Preparation of Working Solution

From all the stock solutions above, a working solution of 50 mg/L was prepared, each, for the metals by measuring 12.5 cm^3 of the stock and dissolving in deionized water (DW) in a 250 cm^3 volumetric flask and the flask made up to volume with DW. This working standard was thereafter used in preparation of the calibration standards in 100 cm^3 volumetric flasks. Both the working solutions and the calibration standards were prepared using the serial diltution ratio: $C_1V_1 = C_2V_2$.

Sample Digestion

The wet oxidation method was employed in the digestion of the samples. 5 g of the sample and 100 cm^3 Conc. Nitric acids was placed in a 400 cm^3 beaker, swirled and allowed to react for 10 min, then evaporated on a hot plate and allowed to cool. 50 cm^3 conc. nitric acid and 10 cm^3 of perchloric acid ($HClO_4$) was added and evaporation continued till the sample was completely ashed (grey in colour). The digest was then transferred to 100 cm^3 volumetric flask and diluted to the mark with deionised water and filtered. A blank was also prepared in the same way but without the sample. Using Atomic Absorption Spectrometer, Cd, Pb, Zn and Fe were determined with aliquots of the digest. The concentrations of the metals were determined from calibration curves of the various metals.

Calibration Curve

A calibration curve of absorbance against standard concentration of each metal ion analyzed (Cd, Fe, Pb and Zn) was prepared so as to yield a good linearity. The calibration curve was used to determine the metal concentrations in the Samples.

3.0 RESULTS AND DISCUSSION

Heavy Metals Concentration in the Samples

Table 3.1 shows the concentrations (mg/kg) of the metals (Cd, Fe, Pd and Zn) in different Cereals analysed using the calibration curve obtained from Atomic absorption spectrometre (AAS).

Table 3.1: HEAVY METALS IN MAIZE, SORGHUM, AND MILLET

	SAMPLES	Cd (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
MAIZE	YM_1	0.1118	0.3613	0.1291	0.0394
	YM_2	0.1214	0.3224	0.1053	0.1079
	YM_3	0.1151	0.5223	0.1212	0.1141
	WM_1	0.1145	0.2426	0.1715	0.0519
	WM_2	0.1146	0.2456	0.1175	0.1560
	WM_3	0.1155	0.1847	0.1238	0.1768
SORGUM	RS_1	0.1151	0.3815	0.1763	0.0539
	RS_2	0.1144	0.1528	0.1241	0.1539
	RS_3	0.1140	0.4921	0.1249	0.1017
	WS_1	0.1155	0.2831	0.1367	0.2510
	WS_2	0.1150	0.2819	0.1357	0.1726
	WS_3	0.1110	0.2011	0.1234	0.2021
MILLET	M_1	0.1159	0.3917	0.1562	0.1705
	M_2	0.1158	0.4819	0.1072	0.1871
	M_3	0.1151	0.1088	0.1026	0.2988

key; YM- Yellow Maize, WM-White Maize, RS-Red Sorghum, WS-White Sorghum, M-Millet. Subscript; 1- Samples from Sabo Market, 2- Samples from Monday Market, 3- Samples from Central Market

Table 3.1 contains the concentrations of these metals (mg/kg dry weight) in the samples (Maize, Sorghum and Millet) obtained from the three major markets in Kaduna.

(a) Cd; The concentration of Cd (mg/kg) range from 0.1118 to 0.1214 in Maize, 0.1110 to 0.1155 in Sorghum and 0.1151 to 0.1159 in Millet. These values are higher than the range (0.002 to 0.004 mg/kg) reported by Edem *et al.*, in Wheat flours in 2009 [7]. The values obtained by Okoye *et al.*, in Cereals in South eastern Nigeria (0.007 to 0.23mg/kg) in 2009 [8], Ahmed and Mohammed in Cereal products (0.091-0.143mg/kg) in 2005 [9], Orisakwe *et al.*,in Owerre (0.00 to 0.24mg/kg) in 2012 [10], and Dahiru *et al.*, in Kano (0.11 to 0.28mg/kg) in 2013 were however within the range of values obtained in this research work. These differences could be due to differences in the concentration of the metal in the soils where these Cereals were grown. These values are however, below the WHO safe limit for Cd in Cereals as reported by Dahiru *et al*., in 2013 and Orisakwe et al., in 2012 [11][10].

(Fe); The values obtained for Fe (mg/kg dry weight) ranged from 0.1847 to 0.5223 in Maize, 0.1528 to 0.4921 in Sorghum and 0.1088 to 0.4819 in Millet. These values are higher than the range reported by Edem *et al.*, in Calabar (0.002 to 0.004mg/kg) in 2009 but much lower than those reported by Okoye *et al.*, in south east (59.00 to 102.40) in 2009 and far below the joint FAO/WHO (2001) permissible limit (40.7 mg/kg) for Fe in Cereals. These values are also too low to provide for the Recommended Daily allowance for Fe in both adult male (10mg/day) and female (15mg/day) from a nutritional point of view.

© Pb; Pb Concentrations obtained for Maize (0.1053 to 0.1715 mg/kg), Sorghum (0.1234 to 0.1763 mg/kg) and Millet (0.1026 to 0.1562 mg/kg) were within the range (0.116 to 0.390) reported by Ahmed and Mohammed in Egypt (0.116 to 0.390) in 2005 [9] but higher than the range (0.007 to 0.032 mg/kg) reported by Okoye *et al.*, the South east in 2009 [8]. This could be due to differences in anthropogenic activities that introduce metals into the soil in the areas where these Cereals were grown or even deposition of Pb on the surface of these grains during production, transport and Marketing or by emissions from Vehicles and industries. Gottipolu *et al.*, (2012) [5]. These values are also below the WHO safe limit for Pb in Cereals as reported by Ahmed and Mohammed, in 2005 [9].

(d) Zn; For Zn, values (mg/kg dry weight) obtained range from 0.0394 to 0.1768 in Maize, 0.0539 to 0.2510 in Sorghum and 0.1705 to 0.2988 in Millet samples. These values are higher than the range (0.04 to 0.19mg/kg) reported by Edem *et al.*, in 2009 [7] but far below the range reported by Ahmed and Mohammed in 2005 [9] (4.893 to 15.450 mg/kg). These values are lower than WHO permissible limit for Zn as reported by Umar *et al*., 2012 [12] and can also not provide for the required daily allowance for Zn which is 11mg/day for men and 8mg/day for women.

Cd and Pb are carcinogens with no known nutritional benefits, hence the lower their concentration in food samples, the safer the food for consumption. However, since Fe and Zn are micro nutrients of great importance in human nutrition, their deficiency cause severe health complications including impairment in the immune system, physical growth, mental and cognitive development and increase in Anaemia, Morbidity and Mortality [13]. This is an important factor to be considered for a population depending so much on these Cereals for their nutrition.

CONCLUSION

After carrying out a chemical analysis of the nutrients and Heavy metals (Cd, Fe, Pb and Zn) composition of some cereals (Maize, Sorghum and Millet) that are commonly sold in the major markets in Kaduna, we observed (from the two sample t – test) that there were significant differences in the concentrations of these metals in the samples.

The Heavy Metals content of these grains were however, below the FAO/WHO (2001) permissible limit for them in Cereals. This implies that the grains are safe for consumption from a toxicological point of view although the concentration of Fe and Zn which are micro nutrients were too low to provide for the WHO (2001) daily recommended allowance for a population depending so much on these grains for their nutrition. Therefore, these grains need to be consumed by complementation with foods that are rich in Fe and Zn [1].

A comparative analyses of the heavy metals and the nutrients revealed varied levels of relationship between them ranging from null through weak to moderate correlation. This suggests that the heavy metal content of the grains depends to some extent on the level of nutrients but more on environmental factors as earlier on stated.

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