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Heavy Metals in Some Fruits and Cereals in Minna Markets, Nigeria

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Abstract: Food production and safety can be used as a measure of a nation's economic growth and stability as well as the responsiveness of government to the need of its people. In Nigeria, fruits and cereals are grown and distributed to all parts of the country through retails. They are a source of energy and minerals to humans in particular. Trace elements do not provide calorie but play an important role in the metabolic regulations of the human body systems if present in required amounts. They are co-enzymes and co-factors in human system which play different roles in growth, metabolism and immune system development. They can however bio-accumulate over a period of time in vital human organs-lungs, kidney, heart, liver and the brain causing serious damages and death. Worldwide food quality is monitored through metal analysis. This study was carried out in Minna, Nigeria, located 9°36' 50N; 6°33'25E with nearly 300,000 inhabitants. The trace metals Fe, Pb, Cr, Mn, Cu and Zn were analysed from Rice (*Oryza sativa*), Maize (*Zea maize*), Guinea corn (*Sorghum bicolor*) and Millet (*Panicum miliaceum*) and edible parts of Banana (*Musa* spp), Orange (*Citrus auratium*), Pineapple (*Ananas comossus*), Watermelon (*Citrullus lanatus*) and Apple (*Malus domestica*). Fe was 18.400-252.160 and 1.120-20.800 mg/kg in fruits. In cereals, Cr was not detectable while Pb (1.154 mg/kg) was found only in maize. Fe content was considerably low in cereals compare to fruits. Compare to research elsewhere, similarities and dis-similarities in metals concentration were observed.

Key words: Metals, fruits, cereals, absorption spectroscopy, minna and markets

INTRODUCTION

There is an increasing concern about the quality of foods and fruits globally. According to WHO (1998), "Food safety" implies absence or presence of acceptable and safe levels of contaminants, adulterants, naturally-occurring toxins or any other substance that may make food injurious to health on an acute or chronic basis. Food quality can be considered as a complex characteristic of food that determines its value or acceptability by consumers. Quality attributes include nutritional value, organoleptic properties such as appearance, colour, texture, taste and functional properties, (WHO, 1998). Metals uptake by plants may pose risks to human when such plants are grown on or near contaminated areas. Metal accumulation in plant depends on plant species, genetics, types of soil and metal, soil conditions, weather and environment. Other factors are stage of maturity and supply route to the market, (Chang *et al*., 1984; Zahir *et al*., 2009; Ismail *et al*., 2011; Inoti *et al*., 2012).

Fruits are rich sources of vitamins, minerals and fibres and also have beneficial anti-oxidative effects. While cereals, in addition to providing some minerals are a source of energy needs for humans' daily activities and form a major part of diet. Trace elements do not provide any calorie but they play an important role in the metabolic regulations of the human body if present in required amounts. For example, they are co-enzymes and co-factors in human system which play different roles in growth, metabolism and immune system development, (Ismail *et al*., 2011).

However, it is known that metals bio-accumulate in the vital organs of human system-lungs, kidney, heart, liver and the brain, over a long period due largely to the consumption of contaminated foods and fruits. The intake of heavy metal-contaminated fruits and cereal crops may pose a risk to human health; hence the heavy metal contamination of food is one of the most important when such plants are grown on or near contaminated areas. Metal analysis of foods and fruits is an important aspects of food quality assurance, (Elbagermi *et al*., 2012; Ismail *et al*., 2011).

Due to the importance and attendant danger posed by metal to humans coupled with an increase in environmental pollution, it is important to assess the quality food items periodically through metal analysis. The assessment will give an insight on the level of metal contamination and by extension the impact on food safety standard and risk to consumers, this is the basic objective of this study.

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MATERIALS AND METHODS

Sampling: Samples were collected in three major markets within Minna metropolis, Nigeria (Fig. 1). These markets include Tunga, Bosso and A.A Kure markets. Minna is the capital city of Niger State, Nigeria. Located 9°36' 50N; 6°33'25E and 229 m above sea level. It is home to nearly 300,000 people, from the 1991 census, (Tiptopglobe.com). Samples collected and analysed were the seeds of four cereal crops including Rice (*Oryza sativa*), Maize (*Zea maize*), Guinea corn (*Sorghum bicolor*) and Millet (*Panicum miliaceum*) and edible parts of five fruit species which are, Banana (*Musa* spp), Orange (*Citrus auratium*), Pineapple (*Ananas comossus*), Watermelon (*Citrullus lanatus*) and Apple (*Malus domestica*). The samples were chosen due to their wide acceptability and consumption by the inhabitants. They were collected consecutively for three months. The fruits were bought fresh while the cereals were already dry at the time of purchase. All samples were picked at random into polythene bags. Peeling of the fruits was done with the aid of a cake knife (made of polymer material) and by hand. Samples were sun dried until properly dry. A porcelain pestle and mortar was used to micronize the soft samples while a wooden pestle and mortar was employed in the milling of the hard samples. A suitable sieve made of high density polyethylene (HDPE) was used for sieving the samples. A composite sample was obtained from a combination of each sample type before micronizing. The powdered samples were stored in HDPE sample bottles prior to wet digestion.

Reagents: Reagents were purchased from Bristol Scientific Company Limited Lagos, Nigeria. A supplier for Sigma-Aldrich Company, U.S.A. All reagents were of analytical grade. A multi-element stock solution containing 1000 ppm of each element of interest was prepared from the following salts; Fe (4.965 g $FeSO_4$); Cr (3.735 g K_2CrO_4); Zn (2.085 g $ZnCl_2$); Cu (2.512 g $CuSO_4$) and Mn (3.602 g $MnCl_2.4H_2O$). The stock solution of lead was prepared separately with 1.598 g $Pb(NO_3)_2$ in 1000 mL solution. The salts were dissolved in 100 mL, 2M HNO_3 in a HDPE beaker and transferred into a 1L volumetric flask before diluting to the mark. Deionized (DI) water was used for the dilutions. Calibration standards containing 3, 6, 8 and 10 ppm where prepared from the stock solutions in 50 mL volumetric flasks for the determination of all elements except Fe. For the determination of Fe, standards containing 5, 10, 12 and 15 ppm were prepared.

Procedure

Digestion: 2.5 g of the sample, previously dried to constant weight was placed in 100 mL reflux flask. 15 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2 were mixed with the sample. The mixture was allowed to stand for about 48 h at room temperature. It was then refluxed on a heating mantle at 90°C until brown fumes ceased to evolve, 4-6 h 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 No. 42 filter paper and made to the mark with de-ionized (DI) water. This was repeated for all the samples in triplicate. A blank was also prepared similarly.

Analysis: The digests were analysis for their content of Fe, Pb, Cr, Mn, Cu and Zn with the aid of an Atomic Absorption Spectrophotometer, (Model: PG990), manufactured by PG Instruments Limited, Beijing, China. The acetylene gas pressure and flow rate as well as burner positioning were automated. The instrument was allowed to warm for 30 min before analysis. Determinations were made at the following

Fig. 1: Map of Nigeria showing Minna and the sampling areas. A: Bosso market; B: A.A. Kure market and C: Tunga market

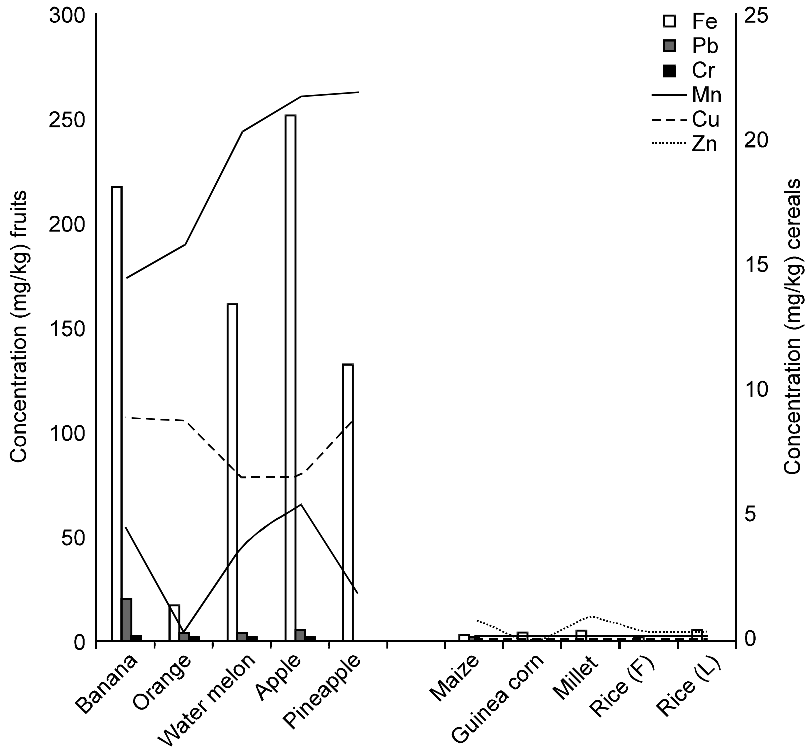

Fig. 2: Concentration (mg/kg) of some heavy metals in some fruits and cereals from minna markets, nigeria

Table 1: Mean concentration (mg/kg), of metals in fruits from Minna markets, Nigeria

Sample	Concentration of metals (mg/kg)					
Fruits	Fe	Pb	Cr	Mn	Cu	Zn
Banana	218.000±0.925	20.800±0.002	1.680±0.002	14.520±0.003	8.960±0.035	4.600±0.012
orange	18.400±0.925	5.400±0250	2.280±0.000	15.880±0.007	8.840±0.005	0.400±7.032
Water melon	161.840±0.925	3.760±0.005	1.320±0.015	20.320±0.005	6.520±0.002	4.000±0.003
Apple	252.160±0.008	7.200±0.009	1.200±0.009	21.720±0.009	6.640±0.000	5.480±0.02
Pineapple	132.600±0.012	1.120±0.031	0.200±0.007	21.880±0.008	9.080±0.002	1.840±0.003
Maximum	252.160±0.008	20.800±0.002	2.280±0.000	21.880±0.008	9.080±0.002	5.480±0.02
Minimum	18.400±0.925	1.120±0.031	0.200±0.007	14.520±0.003	6.520±0.002	0.400±7.032
Cereals						
Maize	3.444±0.051	1.154±0.017	-	0.250±0.004	0.227±0.004	0.889±0.014
Guinea corn	4.778±0.072	-	-	0.350±0.006	0.102±0.002	0.02±0.015
Millet	6.110±0.092	-	-	0.325±0.005	0.102±0.002	1.047±0.016
Rice (F)	2.667±0.040	-	-	0.200±0.003	0.133±0.002	0.45±0.007
Rice (L)	6.334±0.493	-	-	0.300±0.005	0.078±0.001	0.456±0.007
Maximum	6.334±0.493	1.154±0.017	-	0.350±0.006	0.266±0.004	1.047±0.016
Minimum	2.667±0.040	-	-	0.200±0.003	0.078±0.001	0.02±0.015

Key: -: not detectable F: Foreign L: Local

Table 2: Recommended daily allowance (RDA), daily intake (DI), (mg/day) and acceptable levels (AL) of some metals in foods (mg)

Metals	RDA/DI/AL	Reference
Fe	8.0-15.0 mg	(NSF International USA, 2003)
Pb	0.0038-0.0081 mg	(Korfali *et al*., 2013)
Cr	0.05 and 0.20 mg/day	(National Research Council, 1989)
Mn	2.0-5.0 mg	
Cu	2.0-2.6 mg	
Zn	8-26 mg	(NSF International USA, 2003)

wavelengths, Fe (248.3 nm), Pb (283.3 nm), Cr (357.9 nm) and Mn (279.5 nm). Others are Cu (324.8) and Zn (213.9 nm). The result obtained was converted from mg/L to mg/kg using the USEPA method 3060A Eq. 1, (USEPA, 1996). Analysis of Variance (ANOVA) was done using MINITAB 14 at 95% confidence level:

$$\text{Conc. (mg/kg)} = \frac{\text{Conc. obt. (mg/L)} \times \text{DF} \times \text{FV (L)}}{(\%\ \text{DM}/100) \times \text{MS (kg)}} \quad (1)$$

Conc. Obt.: Concentration obtained, DF: Dilution Factor, FV: Final volume of digest, DM: Dry matter, MS: Mass of sample, where, the samples were dried to constant weight before analysis. Therefore ("% dry matter/100") in the equation is negligible. In Eq. 1 becomes:

$$\text{Conc. (mg/kg)} = \frac{\text{Conc. obt. (mg/L)} \times \text{DF} \times \text{FV (L)}}{\text{MS (kg)}} \quad (2)$$

Table 3: Some ranges and levels of metals in fruits and cereals from other authors (mg/kg)

	Concentration of metals (mg/kg)						
Sample fruits	Fe	Pb	Cr	Mn	Cu	Zn	Authors
Apple	286.55, 121.15	19.04, 23.48	8.75	43.17, 8.75	3.00	28.05, 35.88	(Mahdavian and Somashekar, 2008)
	24.676	1.818	3.930	0.019	0.543	21.496	(Zahir *et al*., 2009)
	-	0.20	-	-	1.50	2.34	(Elbagermi *et al*., 2012)
	-	0.078	-	-	0.607	1.723	(Krejpcio *et al*., 2005)
Banana	163.00	-	-	1.159	1.100	1.100	(Ismail *et al*., 2011)
	-	1.106	-	-	0.002	0.046	(Sobukola *et al*., 2010)
	-	0.10	-	-	3.21	6.34	(Elbagermi *et al*., 2012)
	84.53, 190.99	195.18, 7.46	37.87, 88.32	12.99, 417.39	0.88, 14.19	32.01, 45.64	(Mahdavian and Somashekar, 2008)
	16.508	3.152	4.343	0.037	1.606	0.785	(Zahir *et al*., 2009)
Orange	220.47, 114.04	70.49	32.82, 61.25	59.63, 17.51	15.10, 12.78	35.43, 22.01	(Mahdavian and Somashekar, 2008)
	-	0.22	-	-	1.25	2.15	(Elbagermi *et al*., 2012)
	-	0.106	-	-	0.002	0.039	(Sobukola *et al*., 2010)
Pineapple	-	0.128	-	-	0.015	0.050	(Sobukola *et al*., 2010)
Watermelon	-	0.52	-	-	1.19	5.11	(Elbagermi *et al*., 2012)
	-	0.108	-	-	0.004	0.047	(Sobukola *et al*., 2010)
Cereals							
Guinea corn	7.50-70.00	10.00-21.00		3.10-20.00	6.00-20.00	20.00-102.00	(Aremu *et al*., 2006)
Maize	-	0.116	-	-	0.458	15.45	(Ahmed and Mohamed, 2005)
	4.40-10.73	-	-	3.59-9.33	1.09-1.91	16.26-31.16	(Shar *et al*., 2011)
	-	-	3.30	-	-	-	(Hokin *et al*., 2004)
Millet	6.50-12.90	-	356.00	-	-	-	(Hokin *et al*., 2004)
	-	-	-	-	-	4.90-6.60	(Musa *et al*., 2012)
Rice	-	0.239	-	-	0.241	4.893	(Ahmed and Mohamed, 2005)
	-	-	8.00	-	-	-	(Hokin *et al*., 2004)
	3.00-15.10	-	-	-	-	-	(Musa *et al*., 2012)

RESULTS AND DISCUSSION

The result of the analysis of some fruits and cereals is presented in Table 1. A bird-eye-view of this result showed a variation in the concentration of metals analysed in all samples. The fruits recorded higher levels of the metals. Compare to other metals, Fe was higher in concentration in all samples. Only Maize recorded the presence of Pb among the cereals. While Cr was not detected in all cereals analysed it concentration was least, except for orange, among the fruits studied.

Table 1 and Fig. 2, revealed the range of Fe Content in fruits and cereals, 18.400 mg/kg in Orange to 252.160 mg/kg in Apple and 2.667 to 6.336 mg/kg in foreign and local rice, respectively.

The Pb content fruit is higher in banana and least in pineapple with concentration of 20.800 and 1.120 mg/kg, respectively while only Maize recorded the presence of Pb (1.154 mg/kg).

On the other hand, Cr was not detectable in cereals. However, its concentration range from 0.200 to 2.280 mg/kg in the fruits analysed. The value being higher in orange.

Cu and Zn ranged from 6.520 to 9.080 mg/kg and 0.400 to 5.480 mg/kg, respectively in fruits. While the cereals had 0.078 to 0.266 mg/kg and 0.020 to 1.047 mg/kg as ranges of Cu and Zn respectively. Pineapple recorded the highest amount of Cu and Apple, Zn.

Comparing the result in this study with those in Table 3 from other researchers, some differences and similarities can be observed. For example, the Fe content is higher compare to other elements determined in both cases. Lead content is observed more in fruits from other researchers and in this research with some variation within the tables. Chromium was not detectable in the cereals used in this research but was found in cereals from other places. Such differences could be as a result of soil and water compositions and pollution, storage containers contamination as well as contamination due to human activities among other factors.

The Recommended Daily Allowance (RDA), Daily Intake (DI) and Acceptable Levels (AL) are given in Table 2. From this Table, it can be suggested that, deficiency of any metal determined in this study may not result from the consumption of cereals and fruits analysed except the case of chromium in cereals. Conversely, toxicity may result overtime.

As for Mn, 21.88 and 14.520 mg/kg were recorded as highest and lowest value in Pineapple and Banana respectively, while the cereals has Guinea corn with the highest value of 0.350 mg/kg and foreign rice recorded the lowest amount of 0.200 mg/kg.

Conclusion: Result in this research showed varied concentration of metals in some fruits and cereals. Metal concentration are higher in fruits generally. This observation is true with results from other researchers except in few cases from Hokin *et al*. (2004).

Although metal accumulation in the body system depend greatly on concentration, bioavailability, physiological importance as well as specie or form of the metals' existence, the result in this study is scary especially with regards to Pb concentration in fruits when compared to RDA/DI/AL. However, the consumption of the fruits and cereals analysed in this research may not lead to deficiency of essential minerals determined.

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