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Determination of heavy metal contamination of street-vended fruits and vegetables in Lagos state, Nigeria

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Abstract

Fruits and vegetables are edible plant products that are good for health. Precise qualitative and quantitative analyses of heavy metals present in them are important for accurate nutritional labeling, determination of compliance with the standard of identification and in ensuring that the products meet manufacturer's specification. Data and information about heavy metal contamination of street-vended fruits and vegetables in many parts of Nigeria are not available in the literature. Therefore, 162 samples consisting of six different fruits and leafy vegetables were purchased from two major markets in Lagos, Nigeria and analyzed for their heavy metal concentrations using Atomic Absorption Spectrometry (AAS). Cadmium (Cd), zinc (Zn), copper (Cu), cobalt (Co) and nickel (Ni) were found in the samples of the three types of fruits (mango, pawpaw and watermelon) and three types of leafy vegetables (smooth amaranth, cabbage and lettuce) studied; but chromium (Cr), arsenic (Ar) and mercury (Hg) were not detected in all. Manganese (Mn) and Lead (Pb) were also absent in mango and smooth amaranth respectively. The results further indicated that the fruits and vegetables collected from the chosen markets have heavy metal concentration within the safe limits prescribed by WHO/FAO except for Pb. The study will bring awareness to consumers of these items about what they are taking and the health implication as well as assist them and the farmers in taking necessary precautions towards proper care of their fruits and vegetables before consumption. This will indeed be a good way of reducing substantial quantity of contaminants from getting to the human body thereby avoiding health problems, with its attendant positive economic implication.

Introduction

Fruits and leafy vegetables are widely used for culinary purposes. They are used to increase the quality of soups (leafy vegetables) and also for their dietary purposes (Sobukola *et al*., 2010). They are made up of chiefly cellulose, hemi-cellulose and pectin that give them their texture and firmness (Sobukola *et al*., 2010). Fresh fruits and vegetables are of great importance in the diet because of the presence of vitamins and mineral salts. In addition, they contain water, calcium, iron, sulphur and potash (Sobukola *et al*., 2010). They constitute an important part of human diet since they contain carbohydrates, proteins, vitamins, minerals and fibers required for human health. They also act as neutralizing agents for acidic substances formed during digestion (Thompson and Kelly, 1990). Therefore, fruits and vegetables are a very important class of food and are very useful for the maintenance of health and as preventive treatment of various diseases (D'Mello, 2003). However, these food items are known to contain both essential and toxic metals over a wide range of concentrations.

As human activities increase, especially with the application of modern technologies, pollution and contamination of human food chain has become inevitable. In particular, human exposure to heavy metals has risen dramatically in the last 50 years as a result of an exponential increase in the use of heavy metals in industrial processes and products. Heavy metals have been reported to have positive and negative roles in human life (Adriano, 1984; Divrikli *et al*., 2003; Dundar and Saglam, 2004; Colak *et al*., 2005). Cadmium, lead and mercury are major contaminants of food supply and may be considered the most important problem to our environment while others like iron, zinc and copper are essential for biochemical reactions in the body (Zaidi *et al*., 2005).

Fruits and vegetables are generally safe for dietary consumption but accumulation of their contaminants in the bodies of the consumers over

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a long period of time is of major concern as it can result to serious health conditions. Large amount of waste substances, effluents, chemicals and energy are introduced into the environment through several sources. Some of these substances contain heavy metals such as cadmium, lead, and mercury, which are known to be toxic to man and wildlife. Generally, most heavy metals are not biodegradable; they have long biological half-lives and have the potential for accumulation in the different body organs leading to unwanted side effects (Jarup, 2003; Sathawara *et al.*, 2004).

Accumulation of lead in edible aquatic plants and in animals has been reported (He *et al.*, 2003). Lead has been found to be toxic to the red blood cell, kidney, nervous and reproductive systems. Excess of cadmium has been reported to cause renal tubular dysfunction accompanied by osteomalacia (bone softening) and other complications, which can lead to death (Itanna, 2002). Lead and cadmium poisoning has also been reported in Japan in which many lives were lost and many more developed bodily abnormalities (Onianwa *et al.*, 2000; Karavoltsos *et al.*, 2002, Parveen *et al.*, 2003). High concentration of zinc can result to damage of the pancreas, disruption of protein metabolism and arteriosclerosis while elevated levels of copper have been reported to cause brain damage (Parveen *et al.*, 2003). Mercury has been reported to target the liver, the immune system and the pituitary gland. A number of studies have associated chronic mercury exposure with elevated risks for autism, mental impairment and neurodegenerative disorders such as Alzheimer's disease (Jarup, 2003). Lead poisoning is a global reality, and fortunately is not a very common clinical diagnosis yet in Nigeria except for few occupational exposures. The national campaign for the promotion of a green environment is therefore a very timely one.

There is a strong association between micronutrient nutrition of plants, animals and humans and the uptake and impact of contaminants in these organisms (De Leonardis *et al.*, 2000; Yuzbasi *et al.*, 2003; Yaman *et al.*, 2005). The content of essential elements in plants is conditional, the content being affected by the characteristics of the soil and the ability of plants to selectively accumulate some metals (Divrikli *et al.*, 2006). In addition to the soil, other sources of heavy metals for plants are: rainfall in atmospheric-polluted areas, traffic density, use of oil or fossil fuels for heating, atmospheric dusts, plant protection agents and fertilizers, which could be absorbed through aerial parts such as the fruits and leaves (Kovacheva *et al.*, 2000; Lozak *et al.*, 2002; Atrouse *et al.*, 2004). These plant materials could also be contaminated by various substances including trace metals as farmers wash them with unhygienic water before bringing them into the market (Divrikli *et al.*, 2006).

Some of these elements are toxic to humans even at a very low level. Excessive content of Pb and Cd metals in food is associated with etiology of a number of diseases especially with cardiovascular, kidney, nervous as well as bone diseases (WHO, 1992, 1995; Steenland and Boffetta, 2000; Jarup, 2003). They have also been implicated in causing carcinogenesis, mutagenesis and teratogenesis (IARC, 1993; Pitot and Dragan, 1996). Copper toxicity induces iron deficiency, lipid peroxidation and destruction of membranes (Zaidi *et al.*, 2005). High level of Nickel may also result in Zn or Fe deficiency as well as enzymic malfunctioning (Jarup, 2003).

Heavy metal contamination of food items is one of the most important considerations in food quality assurance (Marshall, 2004; Wang *et al.*, 2005; Khan *et al.*, 2008). Heavy metal contamination in vegetables cannot be underestimated as these food items are highly nutritious, largely consumed and form important components of human diet. International and national regulations on food quality have lowered the maximum permissible levels of toxic metals in food items due to an increased awareness of the risk, these metals pose to food chain contamination. Based on persistent nature and cumulative behavior as well as the probability of potential toxicity effects of heavy metals as a result of consumption of leafy vegetables and fruits, there is need to test and analyze these food items to ensure that the levels of these trace elements meet the agreed international requirements.

This study is particularly important for farm products from this part of the world where only limited data on heavy metal contents of such highly consumed agricultural produce are available. The study therefore sought to qualitatively and quantitatively establish possible heavy metal contamination of some street-vended fruits and vegetables in West Africa's most popular mega city, Lagos, Nigeria with a view to comparing the results with those available in the literature and the tolerable limits of WHO/FAO recommendations.

Materials and Methods

Sample collection

The plant materials used for this study were three types of fruits namely, pawpaw (*Carica papaya* L.), watermelon (*Citrullus lanatus* Thunb.), mango (*Mangifera indica* L.) and three of vegetables namely, cabbage (*Brassica oleoracea* L.), lettuce (*Lactuca sativa* L.) and smooth amaranth/tete (*Amaranthus hybridus* L.). In February 2013, the Ketu and Ikorodu popular fruits and vegetable markets in Lagos were visited. In each market, three vendors were identified and samples purchased thrice from each at different times. About 10 to 15 fruits and/or vegetables of each type were randomly procured each time from each vendor making a total of 162 samples. Only ripe fruits and vegetables were purchased. These were properly washed after the bruised and rotten parts were removed, labeled, kept in plastic bags and then refrigerated.

Sample preparation and treatment

Sample of fruits and vegetables collected were processed on the same day. The fruits were rinsed with distilled water, peeled, sliced to obtain the edible portion for analysis. Vegetables were also rinsed with distilled water and cut to simulate the human intake conditions. Samples for analysis were dried using the oven dry method at 105^{o}C for 24 hrs (AOAC, 1990); and processed for analysis by the dry-ashing method. The dried samples were then powdered manually in a mixer grinder.

Powdered samples (14 g each), with three replicates taken from each food item, were accurately weighed and placed each in a silica crucible, and few drops of concentrated nitric acid was added to aid ashing. The dry-ashing process was carried out in a muffle furnace by stepwise increase of the temperature up to 550°C and the samples left to ash at this temperature for 6 hrs. The ash was kept in desiccators and then rinsed with 3M hydrochloric acid. The ash suspension was filtered into a 50 mL volumetric flask through Whatman No. 1 filter paper, and the volume was made up to the mark with 3N hydrochloric acid.

Qualitative analytical methods

In this study, the qualitative procedure adopted for the determination of heavy metals of interest in the selected fruits and vegetables made use of the Osumex's Heavy metal Test Kit. The kit contains a colour chart for test results against which the presence of the metals, were detected or determined. The digested samples (5 ml of each) was taken into glass tube, exactly 2 drops of liquid reagent of the kit (containing complexes of cupferon solution, Potassium bromide, hydrazine solution, chloroform, Ammonium molybdate solution etc) was added to the samples. After a little while, there were different colour developments depending on each metal concentration in the samples.

Standards

Standard solutions of the heavy metals, namely, lead (Pb), cadmium (Cd), copper (Cu), cobalt (Co), nickel (Ni), and zinc (Zn), were purchased from Merck (Darmstadt, Germany). The standards were prepared from the individual 1000 mg/L standards (Merck) supplied in 0.1 N HNO_3. A series of working standards were prepared from these standard stock solutions.

Quantitative analytical methods

Analysis of the heavy metals of interest was carried out using Atomic Absorption Spectrophotometer, RAYLEIGH WFX-110B. Measurements were made using standard hollow cathode lamps for Pb, Cd, Zn, Cu, Co, and Ni. The limit of detection (LOD) of the analytical method for each metal was calculated as being triple the standard deviation of a series of measurements for each solution, the concentration of which is distinctly detectable above the background level. These values were 0.001, 0.001, 0.001, 0.003, 0.001, and 0.002 mg/kg for Pb, Cd, Zn, Cu, Co and Ni, respectively. Also, the limit of quantification (LOQ) of the element was determined; these were calculated as 0.003, 0.003, 0.003, 0.01, 0.003, and 0.007 mg/kg for Pb, Cd, Zn, Cu, Co, and Ni, respectively.

Quality assurance

Appropriate quality assurance procedures and precautions were taken to ensure the reliability of the results. Samples were carefully handled to avoid cross-contamination. Glassware was properly cleaned, and reagents used were of analytical grades. Deionized water was used throughout the study. Reagent blank determinations were used to apply corrections to the instrument readings. For validation of the analytical procedure, repeated analyses of the samples against internationally certified plant standard reference material (SRM) of the National Institute of Standard and Technology were used, and the results were found to lie within ±1% of the certified values.

Statistical analyses

Two types of statistical analyses were carried out on the replicated values of the quantitative results using the computer-based SPSS (statistical) software version 17.0. Firstly, one-way analysis of variance was conducted along with Duncan's multiple range tests (at P = 0.01) to compare the means of each heavy metal across the six food items; and secondly, for each heavy metal, the mean for each food item was compared with the WHO/FAO permissible level as test value using a one-sample student-t test at 99% confidence interval of the difference.

Results and Discussion

The qualitative and quantitative results of heavy metals in the selected fruits and vegetables obtained in this study are as shown in Tables 1 to 3. Heavy metals have been widely acknowledged to adversely affect the nutritive values of agricultural produce on account of their deleterious effect on human beings. Therefore, national and international regulations on food quality have set the maximum permissible levels of toxic metals in human food. As such, an increasingly important aspect of food quality assurance has been to control the concentrations of heavy metals in food (Sobukola *et al.*, 2010).

It is gratifying to note that arsenic (Ar), chromium (Cr) and mercury (Hg) were not detected in these commonly consumed fruits and leafy vegetables (Table 1). These three are highly toxic heavy metals, their presence in foods should be very negligible or trace amount. Arsenic is an element found in nature, and in man-made products, including some pesticides. Low levels of arsenic are found in soil, water and air. The element is taken up by plants as they grow, meaning that the metal makes its way into our food. Long term exposure to low doses of arsenic may change the way cells communicate, and reduce their ability to function. It could, in fact, play a role in the development of diabetes, cancer, vascular disease and lung disease (Jarup, 2003).

People can be exposed to Chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water are generally low. Chromium (III) occurs naturally in fruits and vegetables, meat, yeast and grains and is an essential nutrient for humans, shortages of which may cause heart conditions disruptions of metabolisms and diabetes. Excess uptake of chromium may however cause skin rashes. Chromium VI is a danger to human health like stomach upset, kidney and liver damage, lung cancer and ultimately death.

Mercury is a global pollutant which comes from local industrial sources, such as smelters or coal-fired power plants. Some quantity also falls out of the atmosphere from distant polluters and there are natural sources, such as erupting volcanoes (Selin and Selin, 2006). This heavy metal targets the liver, the immune system and the pituitary gland, causing untold damage that may sometimes result into death. Several researchers have reported some appreciable amount of Hg, Ar and Cr in fruits and vegetables. (Giri *et al.*, 1990) reported between 1.25 – 9.5 ug/100 g of Cr for fruits and 3.0 – 8.2 ug/100 g for fleshly vegetables. Pentanika (2000), reported high mercury content 0.16 and 0.77 mg/kg in mango and pawpaw, respectively all of which are contrary to the results of this study.

Table 1. Qualitative results of heavy metals in some fruits and vegetables from Lagos, Nigeria

Fruit Vegetable	Heavy metals									
	Ar	Pb	Cd	Cr	Zn	Cu	Co	Mn	Ni	Hg
Mango	-	+	+	-	+	+	+	-	+	-
Pawpaw	-	+	+	-	+	+	+	+	+	-
Watermelon	-	+	+	-	+	+	+	+	+	-
Smooth amaranth (Tete)	-	-	+	-	+	+	+	+	+	-
Cabbage	-	+	+	-	+	+	+	+	+	-
Lettuce	-	+	+	-	+	+	+	+	+	-

Positive (+) Detected, Negative (-) Not Detected

Table 2. Means of heavy metal concentration (mg/kg) in some fruits and vegetables from Lagos, Nigeria

	Fruit / vegetable samples					
Heavy metals	Mango	Pawpaw	Watermelon	Smooth amaranth	Cabbage	Lettuce
Ar	ND	ND	ND	ND	ND	ND
Pb	1.620^{b}	0.074^{a}	1.760^{b}	ND	1.840^{b}	1.930^{b}
Cd	0.091^{b}	0.077^{b}	0.004^{a}	0.078^{b}	0.061^{b}	0.089^{b}
Cr	ND	ND	ND	ND	ND	ND
Zn	0.033^{a}	0.056^{bc}	0.049^{ab}	0.073^{c}	0.064^{bc}	0.132^{d}
Cu	0.005^{a}	0.004^{a}	0.006^{a}	0.019^{b}	0.070^{c}	0.002^{a}
Co	0.029^{ab}	0.023^{a}	0.015^{a}	0.042^{bc}	0.046^{c}	0.045^{bc}
Mn	ND	1.610^{b}	0.340^{a}	1.670^{b}	0.417^{a}	0.160^{a}
Ni	0.050^{a}	0.113^{a}	0.139^{a}	0.190^{ab}	0.137^{a}	0.290^{b}
Hg	ND	ND	ND	ND	ND	ND

ND = Not detected. In each row, means with the same superscript(s) are not significantly different while those with different superscript(s) are significantly different (P = 0.01).

Table 3. Results of comparison of heavy metal concentrations in some fruits and vegetables with WHO/FAO permissible values

		Fruit / vegetable samples					
Heavy metals	WHO/FAO Permissible values(mg/kg)*	Mango	Pawpaw	Watermelon	Smooth amaranth	Cabbage	Lettuce
Ar	0.1	ND	ND	ND	ND	ND	ND
Pb	0.5	1.620*	0.074*	1.760*	ND	1.840*	1.930*
Cd	0.2	0.091*	0.077*	0.004*	0.078*	0.061*	0.089*
Cr	1.2	ND	ND	ND	ND	ND	ND
Zn	1.5	0.033*	0.056*	0.049*	0.073*	0.064*	0.132*
Cu	2.0	0.005*	0.004*	0.006*	0.019*	0.070*	0.002*
Co	2.0	0.029*	0.023*	0.015*	0.042*	0.046*	0.045*
Mn	5.0	ND	1.610*	0.034*	1.670*	0.084*	0.160*
Ni	<1.0(0.5)	0.050*	0.113*	0.139*	0.190*	0.137*	0.290^{ns}
Hg	0.05	ND	ND	ND	ND	ND	ND

ND = Not detected. In each row, mean value with asterisk is significantly different from the corresponding WHO/FAO permissible value; ns = not significant (P = 0.01); underlined means are critical values for necessary intervention.
*(WHO, 1999).

Arising from this study, Pb was absent in the most populous vegetable in southwest Nigeria i.e smooth amaranth while manganese (Mn) was not detected in mango. In a similar study, Yuzbasi *et al*. (2003) did not detect Pb in amaranth, and this could be due to the way these vegetables are packaged in sacks, in such a way that they are not ordinarily exposed to atmospheric contaminants. Moreover, it is likely that amaranth is not a good candidate when it comes to phyto-extraction of Pb from soil (Yuzbasi *et al.*, 2003; Mepha *et al.*, 2007). In contrary, heavy concentrations of Pb were detected in the other food items studied except pawpaw (Table 2), and statistically speaking, the quantity of this serious cumulative body poison far surpasses the permissible level (Table 3).

The level of Pb observed in this study is comparable to those reported by Sobukola *et al*. (2010) for pawpaw (i.e 0.072 mg/kg) and Pentanika (2000) for mango (i.e 1.64 mg/kg), with the implication that pawpaw generally accumulates lesser quantity of this dreaded heavy metal. In Nigeria, mango and watermelon are among the highly consumed fruits by the common people, while cabbage and lettuce are preferred by the elites (Turan *et al*., 2003). These four food items were observed to accumulate Pb beyond tolerable limits for human consumption (Table 3). The high levels of Pb in these plants may probably be attributed to pollutants in irrigation water, farm soil or due to pollution from the highways traffic (Ladipo and Doherty, 2011). Lead is a serious cumulative body poison which enters into the body system through air, water and food and cannot be removed by washing fruits and vegetables (Divrikli *et al*., 2003). Accumulation of Pb in these food items beyond tolerable levels calls for some intervention.

The concentration of cadmium (Cd), zinc (Zn), copper (Cu), cobalt (Co), manganese (Mn) and nickel (Ni) observed in the fruits and vegetables were substantially lower than the maximum permissible values (Table 3; WHO, 1999). The implication of these results is that the food items purchased in Lagos, Nigeria are safe for human consumption with respect to the fear of contamination by the heavy metals enumerated. A cursory look at the results of this study points to the general trend that fruits accumulate lesser amounts of heavy metals than do vegetables. However, evidence from statistical point of view does not indicate a significant difference between the two (Table 2).

Conclusion

From the results obtained in this study, it can be concluded as follows : Firstly, arsenic, chromium and mercury, which have been acknowledged as serious human poisons were absent in the fruits and vegetable samples procured from Ketu and Ikorodu markets of Lagos in Nigeria; secondly, the samples of mango, watermelon, cabbage and lettuce contained heavy concentrations of Lead (1.620, 1.670, 1.840 and 1.930 mg/kg, respectively) that are significantly higher than the maximum WHO/FAO permissible level; thirdly, Pb was not detected in the analyzed sample of the smooth amaranth vegetable popularly consumed in south western Nigeria; and finally, the concentrations of Cd, Zn, Cu, Co, Mn and Ni in the studied fruits (mango, pawpaw, watermelon) and leafy vegetables (amaranth, cabbage , lettuce) significantly fall below the maximum value recommended by WHO. Thus, these farm produce may be taken by man with a substantial level of safety.

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