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A Survey of Heavy Metal (Lead, Cadmium and Copper) Contents of Selected Fruit and Vegetable Crops from Borno State of Nigeria

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Abstract: *The main objective of this study was to determine the concentrations of toxic heavy metals (lead, cadmium and copper) in some fruits (guava and tomato) and vegetables (onion, okra, sorrel, garden egg, potato, cucumber, carrot and spinach) commonly grown and consumed in Borno State.*
The fruits and vegetables were purchased directly from Monday Market Ltd in Maiduguri at their peak seasons. Each sample was subjected to two treatments (washed and unwashed), dry-ashed at 500 - 550^{0}C for 12 – 18 hours to extract the heavy metals (analyte) and each analyte was subsequently quantified using Atomic Absorption Spectrophotometer (AAS).
The results indicate that the concentration of copper was negligible in all the crops; the highest concentrations of the metals were observed in spinach, these were 0.2250 ppm and 0.0325 ppm of lead and cadmium, respectively.
The concentration of lead was higher ($P<0.05$) in the unwashed sample (0.1121 – 0.5010ppm) compared with 0.0132 – 0.2250ppm for the washed samples; that of cadmium were 0.0023 – 0721ppm and 0.0010 – 0.0325 ppm in the unwashed and washed samples, respectively.
Significant difference ($P<0.05$) was observed in the concentration of the metals between and within crop samples indicating the effects of crop types on metal concentration. The leafy vegetables had higher ($P<0.05$) concentrations of the metals than the fruits. The fact that considerable amounts of the metals were removed by washing suggests that the contamination was a surface type.

Key words: *heavy metals, AAS, fruits, vegetables.*

I. Introduction

The definition of food stresses that the basic food ingredients as well as the raw materials used for its production must be wholesome (Igwegbe *et al*., 1992; Reilly, 1980). However, contamination of the environment is fast increasing, especially because of the use of chemicals in agriculture or industry (Demayo *et al*., 1982; Haque and Subramania, 1982; Kabata-Pendius, 1992; Palmer and Moy, 1991). For this reason, certain countries or groups of countries establish limits and recommendations for permissible levels of chemical contaminants, and excess of these contaminants leads to exclusion of such raw material from the production of food for human consumption (Weirsma *et al*., 1986; Wolnik *et al*., 1983). Heavy metals are metallic elements which have a high atomic weight and a density much greater (at least 5 times) than that of water (Reilly, 1980). Toxic heavy metals comprise a group of minerals that have no known function in the body and are harmful to humans (Demayo *et al*., 1982; Robert and Clarkson 2001).

Today mankind is exposed to the highest levels of these metals in recorded history. This is due to their industrial use, the unrestricted burning of coal, natural gas and petroleum, and incineration of waste materials worldwide (Igwegbe, 1990; Ndiokwere, 1984). Toxic metals are now everywhere and affect everyone on planet earth (Goyer, 1991; Kabata-Pendius, 1992; Lisk, 1972). They have become a major cause of illness, aging and even genetic defects (Demayo *et al.*, 1982; Robert and Clarkson 2001).

Some metals are naturally found in the body and are essential to human health. Iron, for example, prevents anemia, and zinc is a cofactor in over 100 enzyme reactions (Mc-Kenna *et al*., 1993). Magnesium and copper are other familiar metals that, in minute amounts, are necessary for proper metabolism to occur (Haque and Subramania, 1982; Lisk, 1972; Goyer, 1997). They normally occur at low concentrations and are known as trace metals.

Heavy or toxic metals are stable elements (they cannot be metabolized by the body) and *bio-accumulative* (passed up the food chain to humans). These include: mercury, nickel, lead, arsenic, cadmium, aluminum, platinum, and copper. If heavy metals enter and accumulate in body tissues faster than the body's detoxification process can handle, a gradual buildup of these toxins will occur. Exposure to high concentrations will not therefore be necessary to produce a state of toxicity in the body, as heavy metals accumulate in body tissues over time, can reach toxic concentration (Palmer and Moy, 1991; Robert and Clarkson, 2001).

Plants also take up small amount of contaminant heavy metal compounds together with essential nutrients and can translocate them through their various organs and tissues and to the food chain (Alva *et al*., 2004; Crump and Barlow, 1982; Kabata-Pendius, 1992; Peterson, 1979; Rodriguez-Flores and Rodriguez-Castellon, 1982; Wang, 2011).

Different methods have been applied in many countries to assess the extent of exposure of their population to lead, cadmium, and other toxic trace elements such as copper. Continuous surveillance of exposure to toxic heavy metals is essential for identifying and targeting high-risk groups, evaluating intervention measures, tracking exposure over time, and monitoring exposures during emergency situations. The literature available on the extent of exposure of Nigerian population to heavy metals such as lead and cadmium, and trace element such as copper, is scanty, particularly for commonly consumed fruits and vegetables.

The main objective of this study was to determine the concentrations of the toxic heavy metals (lead and cadmium) and a trace element (copper) in randomly selected fruit and vegetable crops commonly grown in Borno State, Nigeria, using Atomic Absorption Spectrophotometer (AAS) after dry ashing.

II. Materials and Methods

The Maiduguri Central Market (Monday Market Ltd) was chosen for this study because it accommodates crops from all parts of the State. The purpose was to study the concentration and effect of washing on lead, cadmium and copper contents in randomly selected fruits and vegetables sold and consumed within the state. The samples were purchased directly from 8 – 10 different distributors within the market, for each crop, the results were pooled.

The samples were prepared for the analysis according to the method described by Igwegbe *et al*. (1992) and following the procedures outlined in JAOAC, 2000 and in Rouessac and Rouessac, 2005. Only the edible parts of the crops were used for the analysis. Each crop sample was divided into two equal parts for washed and unwashed treatments. The washed samples were prepared as though for consumption, and were rinsed several times with distilled water to ensure that wash water did not serve as a possible source of contamination; while the unwashed samples were simply cleaned of sand and inedible plant materials using stainless steal knives. Special care was taken to prevent metal contamination of the samples by the laboratory equipments {all equipment and materials that contacted the samples during handling and preparation procedures were either of stainless steel or non-metallic (plastic wares)}. All samples were prepared identically in triplicates (using ten (10) grams of dried samples) and in the following sequences: sorting, washing (for the washed treatments only), manual cutting and/or mashing, drying (at 110 – 120^{0}C for 2 – 3 hours in a drying oven), weighing, pre-ashing (charring at low temperature, using a controllable hot plate at 200^{0}C for 30 minutes), ashing (in a muffle furnace at 500 – 550^{0}C for 12 – 18 hrs.

At the end of the ashing process, the crucibles containing the ash were removed from the muffle furnace and allowed to cool to room temperature in desiccators before dissolving in concentrated HCl (35 -37%) and distilled water, filtered into 100 ml volumetric flasks, ready for analyte determination with the AAS. The blank was prepared exactly in the same manner as the samples, including the ashing process (crucibles with the reagents used in the ashing process were dry-ashed without the samples).

The analytes, (lead, cadmium and copper) were quantified in ppm using the atomic absorption spectrophotometer (AAS, Model AA-6800 SHIM) provided by the National Agency for Food and Drug Administration and Control (NAFDAC). The calibration of the instrument and subsequent determination of the three analytes in the samples were carried out in triplicates.

Statistical Analysis

The data was subjected to statistical analysis. Analysis of variance was used to determine the difference between the effects of washing and crop types on the concentration of the heavy metals in the crops, at 5% levels of significance (Montgomery, 1975).

Results and Discussion

Toxic heavy metals can be taken into the body via inhalation, ingestion with plant or animal food, and skin absorption (Goyer, 1991; Palmer and Moy, 1991). They can contribute to any imaginable illness. For example, lead that replaces calcium in the bones can contribute to weakened bones and osteoporosis. Cadmium that replaces zinc in the arteries causes inflammation and hardening of the arteries. Iron that replaces zinc and other minerals in the pancreas, adrenals and elsewhere can contribute to impaired blood sugar tolerance and diabetes (Goyer, 1997). Also copper that replaces zinc in the brain is associated with migraine headaches, premenstrual syndrome, depression, anxiety, panic attacks and much more. Mercury and copper that replace selenium in various tissues impairs the conversion of T4 to T3, contributing to thyroid imbalances (Robert and Clarkson, 2001).

Lead and cadmium were detected in all the fruits and vegetable samples analyzed in this study, while copper was not detected in any of the crop samples (probably due to fact that the copper concentration may be less than the detection limit of the instrument used in this study or it may not be a major contaminant in the production areas). The mean concentrations of lead and cadmium are presented in Tables 1 and 2. Spinach was observed to have higher concentrations of lead and cadmium in washed and unwashed treatments when compared to other crops (Tables 1 and 2). Also, the lowest concentration of lead, 0.0132ppm and 0.0981ppm was observed in washed and unwashed samples of cucumber, respectively. The values of cadmium obtained in unwashed cucumber and guava were 0.0981 and 0.1121ppm, respectively. Following washing, the values decreased significantly ($P<0.05$) to 0.0132 and 0.0911ppm for cucumber and guava, respectively. Cadmium accumulates in many agricultural crops mainly as a result of the use of sewage sludge or phosphate fertilizers. Humans consuming high level of products from grazing animals such as offal products could face significant health risk as a result of hyper-accumulation of cadmium in such products (Wilkinson, *et al.,* 2003). In New Zealand, the maximum residue limit for cadmium in kidney used for human consumption is 2.5mg/kg while in European Union, a maximum of 1mg/kg is tolerated (Phillips and Tudoreanu, 2010). The low level of cadmium reported in these crops suggests that they were neither cultivated with phosphate fertilizers nor sewage sludge. Cadmium has also been reported to damage biomembranes and cause uncontrolled uptake or translocation of the metal in plants (Sarwar, *et al.,* 2010). The low level of cadmium reported in this study indicates that biomembranes may not have been damaged in these crops.

Results indicate that washing the samples significantly reduced ($P <0.05$) the level of metals from all the crops investigated. This is also in agreement with the findings of Igwegbe *et al*. (1992); indicating that the sizable amounts of the metal may be present on the crops as surface contaminants, leading to their removal by washing. In their investigation of the effects of highway's traffic on the level of lead and cadmium in fruits and vegetables grown along the roadsides in Libya, they observed that washing decreased the concentration of the two metals by more than 50% from tomato, potato, onion and spinach. Washing resulted in decrease of lead concentrations by 73, 89, 27, 48 percent and cadmium concentrations by 6, 60, 76, 21percent in unwashed and washed samples of tomato, potato, onion and spinach, respectively. In this study, the concentration of cadmium was lower than that of lead in onion, okro and sorrel or the fruits and vegetable crops investigated (Tables 1 and 2). This does not agree with the report of Karami *et al.,* (2009) who observed that compounds of lead were less soluble than cadmium, and therefore less readily available or taken up by plant and plant parts. The discrepancy could be due to the fact that soils in the arid area are generally characterized by high content of carbonate, low concentration of organic matter, low cation exchange capcity, and basic pH value which can affect the uptake and accumulation of heavy metals in growing crops from arid area (McLaughlin *et al.,*1999).

Also, comparing the results of this study to a proposed maximum acceptable levels of lead and cadmium in similar crops in the Netherlands (Wiersma *et al*., 1986), it was observed that the concentrations of lead (0.1061, 0.1051, 0.1051 and 0.2250ppm) and that of cadmium (0.0069, 0.0029, 0.0150, and 0.0325ppm) in tomato, potato, onion, spinach, respectively, were much lower — even when unwashed, than the proposed maximum acceptable levels of lead (0.30, 0.20, 0.30, and 0.50ppm) and cadmium (0.10, 0.10, 0.10 and 0.20ppm) in tomato, potato, onion, spinach, respectively.

Finally, this study indicates that the leafy vegetables such as spinach and sorrel have more tendency to absorb metals than the fruit crops such as guava and cucumber. The reason may be as result of their different botanical structures.

In conclusion, the definition of food stresses that the basic food ingredients as well as the raw materials used for its production must be wholesome. However, contamination of the environment is fast increasing, especially through the use of chemicals in agriculture or in industry. For that reason, certain countries or groups of countries establish limits and recommendations for permissible levels of heavy metal contaminants the excess of which leads to exclusion of such raw materials from the production of food for human consumption. Although the results of this study indicate the presence of the heavy metals at concentrations far below the permissible limits in other countries, the periodic monitoring of heavy metal concentrations in all the agricultural produce is essential and highly recommended, to asses the temporal trends in human exposure to these metals. This is also necessary due to increasing uses of fertilizers, pesticides and veterinary chemicals in our food production. It is hoped that the result of this study would prompt further investigation of heavy metal contents of other food items widely consumed in Borno State. When thoroughly washed, these fruits and vegetables are not likely to contribute significantly to the body burden of the heavy metals.

Table 1: Mean Concentration of Lead (ppm) in Washed (w) and Unwashed (uw) Samples of Fruit and Vegetable Crops[1, 2]

	Lead (ppm)	
Type of Crop	**Washed**	**Unwashed**
Onion	0.1051[e]	0.1145[f]
Okro	0.1191[c]	0.1261[e]
Sorrel	0.0771[h]	0.3331[c]
Garden egg	0.1261[b]	0.1401[d]
Potato	0.1051[e]	0.1124[fg]
Cucumber	0.0132[j]	0.0981[h]
Guava	0.0911[h]	0.1121[g]
Carrot	0.0981[f]	0.1121[g]
Tomato	0.1061[d]	0.1332[i]
Spinach	0.2250[a]	0.5010[b]
Standard Error	0.001561	0.001058

[1] Each value is a mean of three determinations;
[2] In a column, means bearing the same superscript are not significantly different, and in a row, means bearing different superscript are significantly different at 5% level of significance.

Table 2: Mean Concentration of Cadmium (ppm) in Washed (w) and Unwashed (uw) Samples of Fruit and Vegetable Crops[1, 2]

	Cadmium (ppm)	
Type of Crop	**Washed***	**Unwashed***
Onion	0.0150[b]	0.0214[e]
Okro	0.0092[d]	0.0110[h]
Sorrel	0.0098[c]	0.0347[d]
Garden egg	0.1261[b]	0.1401[d]
Potato	0.1051[e]	0.1124[fg]
Cucumber	0.0132[j]	0.0981[h]
Guava	0.0911[h]	0.1121[g]
Carrot	0.0981[f]	0.1121[g]
Tomato	0.1061[d]	0.1332[i]
Spinach	0.2250[a]	0.5010[b]
Standard Error	0.001561	0.001058

[1] Each value is a mean of three determinations;
[2] In a column, means bearing the same superscript are not significantly different, and in a row, means bearing different superscript are significantly different at 5% level of significance.

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References

[1]. Alva, A.K; Baugh, T.J., Sajwan, K.S. and Paramasivam, S. (2004). Soil pH and anion abundance: effects on copper adsorption. J. Environ. Sci. Health, 39: 903 – 910.

[2]. Crump, D.R. and Barlow, P.J. (1982). Factors controlling the lead content of pasture grass. Environ. Pollut. Ser. B., 3(3): 181 – 192.

[3]. Demayo, A; Taylor M.C., Taylor, K.W. and Hodson, P.V. (1982). Toxic effects of lead and lead compounds on human health, aquatic life, wildlife, plants and live stocks. Crit. Rev. Environ. Cont., 12(4): 257 – 305.

[4]. Goyer, R.A. (1991). Heavy metals: sources and specific effect.

[5]. http://www.etremehealthusa.com/source.html

[6]. Goyer, R.A. (1997). Toxic and essential metal interactions. Annu. Rev. Nutr., 17: 37 – 50.

[7]. Haque, A. and Subramania, V. (1982). Copper, lead and zinc pollution of soil environment. Crit. Rev. Environ. Cont., 12(1):13 - 70.

[8]. Igwegbe, A.O. (1990). Effects of Oil Refinery, Highway Traffic, and Treated Sewage Water on the Level of Lead and Cadmium in Fruits and Vegetables grown within these Locations, M.Sc. Thesis, Al-Fateh University, Tripoli, Libya.

[9]. Igwegbe, A.O; Belhaj, H.M, Hassan, T.M. and Gibali, A.S. (1992). Effects of highway's traffic on the level of lead and cadmium in fruits and vegetables grown along the roadsides. J. Food Safety, 13: 7 – 18.

[10]. J.A.O.A.C. (2000). Determination of metals in foods by atomic absorption spectrometry after dry-ashing. NKML Collaborative study. 83(5):1204 – 1211.

[11]. Kabata-Pendius, A.H. (1992). Trace elements in soils and plants, CRC Press Inc., Florida, USA.

[12]. Karami, M.; Afyuni, M., Rezainejad, Y., and Schulin, R. (2009). Heavy metal uptake by wheat from a sewage sludge-amended calcareous soil. Nutr Cycl. Agroecosyst., 83:51- 61.

[13]. Lisk, O.J. (1972). Trace Metals in Soil, Plants and Animals. Adv. Environ. Sci. Technol., 3: 1 - 111

[14]. Mc-Kenna, I.M.; Chaney, R.L. and Williams, F.M. (1993). The effect of cadmium and zinc interactions on the accumulation and tissue distribution of zinc and cadmium in lettuce and spinach. Environ. Pollut., 79: 113 – 120.

[15]. McLaughlin, M.J.; Parker, D.R. and Clarke, J.M. (1999). Metals and micronutrients — safety issues. Field Crop Res., 60:143 – 163.

[16]. Montgomery, D.C. (1976). Design and Analysis of Experiments. John Wiley and Sons, Inc., USA.

[17]. Ndiokwere, C.L. (1984). A study of heavy metal pollution from motor vehicle emissions and its effect on road side soil, vegetation and crops in Nigeria. Environ. Pollut. Ser. B, 7(1): 35 – 42.

[18]. Palmer, S. and Moy, G. (1991). Environmental pollution, food contamination and public health. Euro. J. Clinic. Nutr., 45: 144 – 146.

[19]. Peterson, O. (1979). Heavy metal ion uptake by plants from nutrient solution with metal ion, plant species and growth period variations. Plant Soil, 45(8): 445 – 459.

[20]. Phillips, C.J.C and Tudreanu, L. (2010). A model of cadmium accumulation in the liver and kidney of sheep derived from soil and dietary characteristics. J. Sci. Food Agric., 91:370 - 376

[21]. Reilly, C. (1980). Metal Contamination of Food. Applied Science Publishers Ltd., London.

[22]. Robert, A.G. and Clarkson T.W. (2001). Toxic effects of Metals. In "Casaraec and Doull's Toxicology: The Basic Science of Poison. 6th Ed" C.D. Klaassen, (Ed). McGraw-Hill Medical Pub. Division New York pp 811 – 868.

[23]. Rodriguez-Flores, M. and Rodriguez-Castellon, E. (1982). Lead and cadmium levels in soil and plants near highways and their correlation with traffic density. Environ. Pollut. Ser. B, 4(4): 281 – 290.

[24]. Rouessac, F. and Rouessac, A. (2005). Chemical Analysis : Modern Instrumentation Methods and Techniques. John Wiley and Sons Ltd., New York.

[25]. Sarwar, N.; Saifullah, M., Malhi, S.S. Zia. M.H., Naeem, A. and Bibi, S. (2010). Role of mineral nutrition in minimizing calcium accumulation by plants. J.Sci. Food Agric., 90:925 – 937.

[26]. Wang, Z.; Nan, Z., Wang, S and Zhao, Z. (2011). Accumulation and distribution of cadmium and lead in wheat (*Triticum aestivum L.)* grown in contaminated soils from the oasis, north-west China. J. Sci. Food Agric., 91:377 – 384.

[27]. Wiersma, D.; Vangoor, B.J. and Vandernveem, N.G. (1986). Cadmium, lead, mercury, and arsenic concentrations in crops and corresponding soils in Netherlands. J. Agric. Food. Chem., 34(6):1057 – 1074.

[28]. Wilkinson, J.M., Hill, J and Phillips, C.J.C. (2003) The accumulation of potentially toxic metals by grazing ruminants. Proc. Nutr. Soc., 62:267 – 277.

[29]. Wolnik, K.A.; Fricko, S.L., Copper, S.G., Braude, G.L, mayer, M.W., Satzger, R.D. and Bonnon, E. (1983). Elements in major agricultural crops in the United States, 1: cadmium and lead in lettuce, peanuts potatoes, soyabeans, sweet corn and wheat. J. Agric. Edu. Chem., 31(6):1240 – 1244.