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Determination of Heavy Metals in Four Mango Fruit Varieties Sold in Minna Modern Market, Niger State, Nigeria

Dangana Mohammed Chata[1], Auta Yohanna Iliya[1], Mailafiya Simon Chidawa[2], Moses Bali Emmanuel[2], Oluwafemi Oghenekevwe Juliana[1], Ebyna Kofi Chibuzor[1]

[1]Department of Biological Sciences, Federal University of Technology, Minna, Nigeria
[2]Department of Biochemistry, Federal University of Technology, Minna, Nigeria

Email address

danganachata@gmail.com (D. M. Chata)

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Abstract: This study explored heavy metals contamination in four varieties of mango fruits from Minna main market, Niger State, Nigeria. The contents of lead (Pb), copper (Cu), Iron (Fe), and manganese (Mn) in the selected fruits were measured using atomic absorption spectrophotometer (AAS) Shimadzu 7000 F. Digestion of the Mango fruit juice was conducted using wet acid digestion methods of [28, 27]. The results of this study showed that the average concentrations detected ranged from 0.10 - 1.30, 0.59 - 1.84, 0.03 - 0.16 and 0.50 - 0.80 mg/L for Mn, Fe, Cu, and Pb, respectively. The highest mean levels of Mn, Fe, Cu, and Pb were detected in *Binta* Sugar mango, Kerosene mango, Kerosene mango and Kerosene mango fruits respectively for late February. The average concentration detected ranged from 0.30 - 1.30, 0.80 - 1.60, 0.09 - 0.20 and 0.33 - 0.50 mg/L for Mn, Fe, Cu and Pb respectively for late April. The highest mean levels of Mn, Fe, Cu and Pb were detected in *Binta* Sugar mango, Julie mango, *Binta* Sugar and Kerosene mango varieties, and Sherry and Binta Sugar mango varieties respectively. The levels of these metals from the four mango varieties studied were compared with recommended limits established by WHO/FAO in 2011. The values obtained for Mn, Fe, and Cu were below the recommended values but the values of Pb were higher than the established limit. It is essential to ascertain the safety levels of heavy metals in the foods we consume for good nutrition which will further enhance healthy living.

Keywords: Heavy Metals, Determination, Mango Fruits, Varieties, Safety

1. Introduction

Mango *(Magnifera indica* L.) is also known as the 'king of fruit' due to its consummation in most parts of the world and its numerous health benefits [1-4]. It has so many uses with every part of the plant being utilized in some way or the other. Mango is native to south Asia, from where it has been taken to become one of the most widely cultivated fruits in the tropics. It is the national fruit of both Pakistan and India [2] with India having the highest production in the world [3]. There are different varieties of mango in Nigeria which are given common names based on the characteristics of their fruits [5]. There are various varieties of mango trees in Nigeria which are usually differentiated by their fruit characteristics and therefore given common names [5]. Eight varieties of mangoes are found in Nigeria: Sheri also known as Cherie, Sherry and Cherry mango; Kerosene mango; Normal mango also known as Ogbomosho, Enugu (Eastern), Calabar, Abuja and Yellow mango; Julie mango; Benue mango; Binta also known as Peter and Jane mango; German mango/Opion; and Contonou mango [6].

Consumption of fruits on a regular basis is critical in providing nutrients to the human body. Vital components in fresh fruits such as vitamin C, carotenoids, minerals and dietary fiber are vital requisites to body's optimum immune functions. These protective functions derived from fresh fruits necessitates that every human meal serving be accompanied with fresh fruit intake in providing a balanced diet and boosting of the body's immune system [7-9]. Its valuable antioxidant activity decreases the risk of cardiac disease alongside its anticancer and antiviral activities [8, 3].

Other important nutrients in foods are macro and micro elements which have been found to occur in foods and play vital roles in human health [1, 10]. Heavy metals are those that have atomic weights from 63.546 to 200.590 and specific weight greater than 4 [11-13]. Although heavy metals are naturally occurring elements that are found throughout the earth crust, most environmental contamination and human exposure results from anthropogenic activities such as mining and smelting operations, industrial production and usage, domestic and agricultural use of metals and metal containing compounds [14-17].

Among the major contaminants in food supplies are heavy metals which endanger the products of plants being used as foods and feeds. This problem of heavy metals contamination has been on the increase globally especially in developing countries [29] An aspect to consider in food quality assurance is contamination of food items by heavy metals [17] due to their effects on human health [18, 16, 9]. In general, various heavy metals are not degraded by living systems; they however have long biological half-lives and the potential to accumulate in different body organs resulting to unnecessary harmful effects [17, 9, 13, 32].

Poisoning as a result of lead (Pb) is due to the interaction of the metal with biological electron-donor groups, specifically the sulfhydryl groups that affect so many enzymatic processes. Clinical indications of Pb toxicity consist of symptoms related to the central nervous system, the peripheral nervous system, the hematopoietic system, the renal system, the gastrointestinal systems and the reproductive system [19, 20, 10, 17]. Iron (Fe) is a constituent of hemoglobin, myoglobin, some enzymes and approximately 30% of Fe in the body is present in storage forms such as ferritin and hemosiderin in the spleen, liver, bone marrow and a trivial amount is associated with the blood transport protein transferrin [31]. While excess of iron (Fe) has been reported to cause colorectal cancer, its deficiency causes anaemia with one third of the world being affected [20, 10]. Copper is one of the vital elements necessary for important biochemical functions and the maintenance of well-being [21, 10]. An adult body weight has around 1.5 - 2.0 ppm of copper (Cu) that is an important component of a number of metal enzymes necessary for hemoglobin synthesis and in the catalysis of metabolic oxidation [10]. Cu is also necessary for the maintenance of a healthy nervous system, body pigmentation in addition to iron and is interrelated with the function of zinc and iron in the body [30]. Cu deficiency may give rise to gastro-intestinal disturbances, bone demineralization and depressed growth, whereas, excess may cause dermatitis, liver cirrhosis, neurological disorders [10]; iron deficiency, lipid peroxidation and destruction of membranes [19, 17]; kidney damage and even death [22]. Manganese is a vital trace element which performs important biochemical functions and is important for the maintenance of health throughout life. It is required for the development of connective tissues and bone, growth, carbohydrate and lipid metabolism, embryonic development of the inner ear and reproductive function [23-25]. In recent times, Mn has been identified as a mineral that plays important role in the genes and progression of several diseases related in certain manner to oxidative stress [8]. Manganese deficiency resulting from poor diet alcoholism and mal-absorption, causes dwarfism, hypogonadism and dermatitis. Its presence in environment and consequent up take by humans causes pulmonary manifestation, fever, chills and gastroenteritis [8].

Publicity concerning the concentration of heavy metals in fruits and vegetables particularly mango which is widely distributed, cheap and consumed extensively will create fear in the public as per the presence of heavy metal residues in their daily foods, bearing in mind the potential toxicity and persistent nature of heavy metals and the frequent consumption of vegetables and fruits; it is necessary to analyze these food items to ensure the levels of these contaminants meet agreed international requirements [26, 24].

This study therefore sought to determine the concentration of heavy metals in four mango fruit varieties sold in Minna Modern Market, Niger State in order to determine their health statuses and implications where present.

2. Materials and Methods

2.1. Sample Collection

Forty mango fruits were collected between the months of late February and early April from the Minna main market in Niger State and four varieties of the mango fruits were selected - the Cherry, Julie, Binta Sugar and Kerosene mangoes. Minna main market is one the major mango selling markets in Niger State. The samples were taken to the laboratory of the Department of Biological Sciences, Federal University of Technology, Minna, Niger State for identification and analysis.

2.2. Morphology of the Mango Fruit Varieties

2.2.1. Binta Sugar Mango

Other names include Peter and Jane mango, skin color is green, flesh colour is orange and size is large. It is sour when unripe, sweet, like sugar when ripe, texture is firm and ripening cue is yellow/ red blush. Peak availability is from March to April.

2.2.2. Kerosene Mango

Skin color is pale peach, flesh colour is yellow to orange, shape is ellipse-shaped and flavor is aftertaste of kerosene. Texture varies from firm to soft and juicy; fibrous flesh ripening cue is green, overtones diminish and peachy-tan colour prevails. Peak availability is between February and April.

2.2.3. Julie Mango

Skin colour is green, flesh colour is dark yellow to orange, and shape is ovate and flat. Flavour is rich, texture is juicy flesh, and ripening cue is yellow at the base. Peak availability is between February and May.

2.2.4. Sheri Mango

Other names are Cherie, Cherry and Sherry. It is believed to be the same as the most beloved Alphonso mango of India, of which love letters and gifts to kings have been made. Skin colour is green, flesh colour is dark yellow to orange, and shape is ellipse-shaped. The flavour is sweet, rich and spicy, with aftertaste of 'turpentine'. Texture is firm flesh and holds shape when cut. Ripening cue is green. Overtones diminish and yellow becomes dominant. Peak availability is between February and May.

Figure 1. *Morphology of Cherry Mango.*

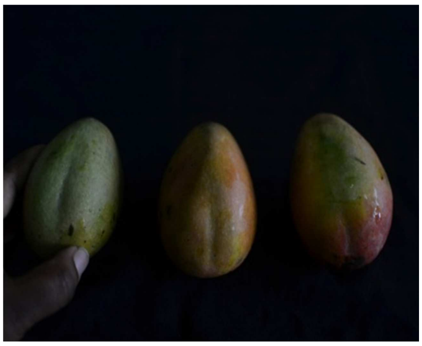

Figure 2. *Morphology of Kerosene Mango.*

Figure 3. *Morphology of Julie Mango.*

Figure 4. *Morphology of Binta Sugar Mango.*

2.3. Sample Treatment

The fruits were washed with distilled water to remove any contaminants, pesticide residues, dirt and dust on the surface.

2.4. Pulp Extraction

Five fruits from each variety were collected and sampled out for digestion. The steel knife was used as a mango pulpier to separate pulp from the seed and skin. The pulps were obtained and packed in labeled polyethylene bags. These bags were stored in a refrigerator at 4 ºC for digestion.

2.5. Digestion of the Mango Juice Samples

Mango juice samples were extracted using acid digestion method [27, 28]. Four aliquots of 30 ml each and two replicates for each fruit were accurately measured and placed in a 200 ml volumetric flask to which 30 ml of 10% concentrated HNO_3 was added and left to settle for 15 minutes. Wet acid digestion followed in 10 ml of 1:3 mixtures of concentrated 65% HCl: HNO_3 (Merck) using a hotplate, until a clear solution was obtained. Digested samples were allowed to cool off at room temperature. Digested samples were then acidified with 10 ml of 1:1 mixture of HCl: H_2O and filtered through 0.45-micron filter paper and the final volume made up to 50 ml with distilled water. The resultant filtrate was transferred to cleaned dried plastic bottles for heavy metal level analysis.

2.6. Heavy Metals Determination

Atomic Absorption Spectrophotometer (AAS) Shimadzu 7000 F was used for elemental detection in juice samples. Four heavy metals - copper (Cu), manganese (Mn), lead (Pb) and iron (Fe) were analyzed. For each sample, four standard solutions of different concentrations (0.5ppm, 1ppm, 2ppm and 4ppm) were prepared. The absorbances of the four standard solutions were measured and a calibration curve prepared from these values; then the absorbance of the sample solutions measured to determine the concentration of the samples.

2.7. Statistical Analysis

This was carried out by the use of Statistical Package for Social Science (SPSS) for Windows version 16.0 and results obtained are reported as mean values ± standard deviation (SD). The significant differences between mean values were analyzed by Duncan multiple range test at a significance level of $p < 0.05$.

3. Results

3.1. Mango Fruit Varieties Juice Extract in Late February

The data in Table 1 show the comparison of heavy metals in four mango fruit varieties with that of WHO/FAO, (2011) guideline and standard respectively. The heavy metals were obtained at part per million levels and reported as mg/L for all the mango fruit varieties.

Table 1. *Comparative analysis of mango fruit juice extracts in late February.*

Parameters (mg/L)	Sample A	Sample B	Sample C	Sample D	
	Sherry Mango	**Julie Mango**	**Binta Sugar Mango**	**Kerosene Mango**	**WHO/FAO, Standard (mg/L)**
Manganese (Mn)	0.37±0.012a	0.10±0.029a	1.30±0.231a	0.38±0.012a	2.03
Iron (Fe)	1.31±0.173bc	1.07±0.116ab	0.59±0.012a	1.84±0.035d	8.0
Copper (Cu)	0.13±0.023a	0.03±0.006a	0.15±0.006a	0.16±0.012a	3.5
Lead (Pb)	0.60±0.056a	0.50±0.006ab	0.70±0.116bc	0.80±0.116bc	0.3

Values are expressed in mean ± Standard error for three replicates (n=3).

3.2. Mango Fruit Varieties Juice Extract in Early April

The data in Table 2 show the comparison of heavy metals in four mango fruit varieties with that of WHO/FAO, (2011) guideline and standard respectively. The heavy metals were obtained at part per million levels and reported as mg/L for all the mango fruit varieties.

Table 2. *Comparative analysis of mango fruit juice extracts in Early April.*

Parameters (mg/L)	Sample A	Sample B	Sample C	Sample D	
	Sherry Mango	**Julie Mango**	**Binta Sugar Mango**	**Kerosene Mango**	**WHO/FAO, Standard (mg/L)**
Manganese (Mn)	0.40±0.00a	0.30±0.058a	1.30±0.231a	0.37±0.033a	2.03
Iron (Fe)	1.30±0.116ab	1.60±0.058bc	0.80± 0.116a	1.50b± 0.173c	8.0
Copper (Cu)	0.13±0.033a	0.09± 0.007a	0.20± 0.058a	0.20± 0.058a	3.5
Lead (Pb)	0.50±0.058a	0.40± 0.116a	0.50± 0.058a	0.33± 0.088a	0.3

Values are expressed in mean ± Standard error for three replicates (n=3).

4. Discussions

A comparative analysis of mango fruit juice extracts in late February and early April was carried out. The heavy metals investigated in the four mango fruit varieties (the Binta Sugar, Sherry, Kerosene, and Julie mangoes) were iron (Fe), manganese (Mn), copper (Cu), and lead (Pb). The quantitative results of heavy metals of the selected fruits in this study are as shown in Tables 1 and 2. Heavy metals have been widely acknowledged to adversely affect the nutritive values of agricultural produce on account of their deleterious effects on living systems [18, 24, 16, 23, 17, 9, 13]. Therefore, national and international regulations on food quality have set the maximum permissible levels of toxic metals in foods. As such, an increasingly important aspect of food quality assurance has been to control the concentrations of heavy metals in foods.. In the present study, the concentrations of Cu, Mn and Fe were within the tolerable intake levels set by the [24] for the four mango fruit varieties for late February and early April making them safe for consumption. However, Pb concentration on the other hand was found to be above the tolerable intake level for the four mango fruit varieties for late February and early April. The concentration of Mn was found to be highest in Binta mango (1.30 mg/L) for late February and Early April, and lowest in Julie mango variety for both late February and early April (0.10 mg/L and 0.30 mg/L respectively). The level of Mn in all the mango fruit varieties was within the range of 0.10 - 1.30 mg/L for late February and 0.30 – 1.30 for early April making the presence of this metal far below its acceptable limit. Fe content was highest in kerosene mango (1.84 mg/L) and it was found to be lowest in Binta mango (0.59 mg/L) for late February. For early April, it was determined to be highest in Julie mango (1.60 mg/L) and lowest in Binta Sugar mango (0.80 mg/L). The Fe content ranged from 0.59 to 1.84 mg/L for late February and 0.80 to 1.60 mg/L in Early April. The concentration of Cu was found to be highest in Kerosene mango (0.16 mg/L) and least in Julie mango (0.03 mg/L) for late February, while it was highest in kerosene and Binta Sugar mango varieties (0.20 mg/L respectively) and least in Julie mango (0.09 mg/L) for early April. The level of Cu in all the mango fruit varieties were within the range of 0.03 - 0.20 mg/L for both months. The presence of this metal in the mango fruit varieties was far below its acceptable limit. Pb is a non-essential element for living organism and it is highly toxic to man and animal. The concentration of Pb was highest in Kerosene mango (0.80 mg/L) and least in Julie mango (0.60) for early February, whereas, it was highest in both Sherry and Binta Sugar mango varieties (0.50 mg/L respectively) and lowest in Kerosene mango (0.33 mg/L). Pb content in the four mango fruit varieties analyzed in this study ranged from 0.33 – 0.80 mg/L for both late February and early April which were above the established limit. Based on the foregoing, the four mango fruit varieties can be consumed without consequent negative health effects with respect to the levels of Mn, Fe and Cu determined whereas, some certain negative effects may present following consumption of the four mango fruit varieties due the fact that Pb levels determined were above the safety limit.

5. Conclusion

The results of this study confirmed that the four mango fruit varieties collected from Minna main Market of Niger State contained measured levels of non - essential toxic metal (Pb) and essential metals (Mn, Fe and Cu) which were below the recommended safety limits for the essential metals and slightly above the recommended limit for the non-essential toxic metal. Continuous biomonitoring of heavy metals in fleshy fruits is vital as these serve as sources of food for humans in many parts of the world.

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