



Assessment of Heavy Metal Concentration in Fruit Samples from Three Major Markets during the Wet Season in Enugu State

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Authors' contributions

This work was carried out in collaboration between both authors. Author LCO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author GIA managed the analyses of the study and managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

The effect of seasonal changes on heavy metals concentration in three commonly edible fruits in Enugu State was analyzed. Banana, pineapple and watermelon samples were collected during three rainy season months (June, July and August) from three markets in the three districts of Enugu state (Enugu North, Enugu West and Enugu East). Heavy metals evaluated during the study include lead, cadmium, cobalt, nickel, zinc and copper. Metals in the samples were quantified using atomic absorption spectrophotometry (AAS) at specific wave lengths and values reported in mg/kg. The result of the study showed the maximum and minimum values of heavy metals observed in all the samples were; 0.28 – 0.03 mg/kg, 0.22 – 0.01 mg/kg, 0.13 – 0.01 mg/kg, 0.64 – 0.33 mg/kg, 0.69 – 0.01 mg/kg and 13.88 – 1.42 mg/kg for lead, cadmium, nickel, cobalt, copper and zinc respectively. The quantity of metals in all the samples, on average, reduces as the rainy season month progresses. The order of heavy metal concentrations in the fruit samples from the markets were in the following decreasing order; Nsukka market > Ogbete market > Ezeagu market. Banana fruit showed the highest concentration of heavy metals while watermelon showed the least heavy metal concentration. Values obtained were compared to WHO maximum permissible limit for each metal. Environmental pollution should be prevented in market areas to avoid food poisoning from consumption of contaminated food.

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1. INTRODUCTION

Contamination with heavy metals is serious problem, particularly in agricultural production systems and human health. Factors influencing the concentration of heavy metals in plants include climate, environmental pollution, nature of the soil on which the plant is grown, and the degree of maturity of the plant at the time of harvesting. Fertilizers also contain heavy metals, thereby becoming an additional source of metal pollution in vegetables [1]. Toxic metals can accumulate persistently in the body over a lifetime. Lead (Pb) can adversely influence the intelligence development of children, cause excessive lead accumulation in the blood, and induce hypertension, nephropathy and cardiovascular disease [2 and 3]. Some other metals such as zinc, iron, copper, cobalt and chromium are beneficial to the body system, but are dangerous beyond permissible limits. Heavy metal contaminants can result in kidney and liver damage, stomach upset and ulcers, skin rashes, lung cancer, weakened immune system, alteration of genetic material and respiratory problem [4]. Chronic cadmium (Cd) exposure can cause acute toxicity to the liver and lungs, induce nephrotoxicity and osteotoxicity, and impair function of the immune system [5 and 6]. The element arsenic (As) is a metalloid and is associated with angiosarcoma and skin cancer [7]. Other metal elements such as copper (Cu) and zinc (Zn) are important nutrients for humans, but excessive ingestion can also have adverse effects on human health [8].

In some towns and areas in Enugu state, although the agricultural soils are contaminated with heavy metals, the farmers cannot afford to leave the farmland fallow for remediation because the demand and pressure to produce foodstuffs and fruits are so high. While fruits such as banana, pineapple and watermelon are consumed for body nourishment, heavy metals contamination of these food materials remains a challenge. Therefore, the study is aimed at ascertaining the concentration of heavy metals in fruits during rainy seasons from three major markets in Enugu state.

2. MATERIALS AND METHODS

The fruit samples (*Citrullus lanatus*, *Ananas comosus* and *Musa paradisaca*) were collected

from the three senatorial districts of Enugu State. Enugu west senatorial district samples were collected from Ezeagu central market, Enugu north from Nsukka market, while that of Enugu east was collected from Ogbete market. The samples were collected from the same retail store during each collection period (in the month of June, July and August).

Fresh fruit samples were digested according to the method of Food Safety and Standards Authority of India [9]. One gram (1g) of each of the test food sample was weighed into 100 ml beaker. Concentrated hydrochloric acid and nitric acid were added to the weighed samples in the ratio 3:1 volume by volume, that is 30 ml of hydrochloric acid and 10 ml of nitric acid to each sample. Ten (10) drops of hydrogen peroxide were added to each of the samples. Hydrogen peroxide increases the complexing properties of the mineral acids. Each of the preparation was heated on a laboratory hot plate in fume cupboard. Heating was continued until samples digest completely.

Each digest was diluted with 50 ml of distilled water and filtered into a 100 ml volumetric flask using Whatman filter paper. The filtrate was made up to the mark with distilled water and used for heavy metal analysis. The sample digestion of the fruits and the metal analysis was carried out in the Chemistry Laboratory of the Projects Development Institute (PRODA) Emene, Enugu.

Five of each fruit (banana, pineapple and watermelon) were purchased from retail stores in three markets in Enugu State. The fruits were processed as stated above and were used as control reference for heavy metals analysis. Table 1 shows the control experimental values and the recommended WHO values. All analysis was done in triplicates. The control samples of the fruits were run in the machine for each element that was being investigated. Their absorbances were read using Atomic Absorption Spectrophotometry (AAS) AA-7000. The mean of each triplicate was calculated and hence the detection limits determined for each element.

2.1 Statistical Analysis

The data obtained from various determinations were subjected to one-way ANOVA, using a

computer program SPSS version 19 and the significance was reported at $P < 0.05$ levels. The mean values were separated using Duncan New Multiple Range Test (DNMRT).

3. RESULTS

3.1 Experimental Control

The results of the experimental control of the three fruit samples (Banana, Pineapple and Watermelon) are shown in Table 1. The result showed minimum concentrations of heavy metals compared to WHO maximum allowed concentration. The concentrations of Pb, Cd, Co, Cu and Zn were 0.09 ± 0.01 mg/kg, 0.03 ± 0.00 mg/kg, 0.30 ± 0.01 mg/kg, 0.20 ± 0.01 and 2.27 ± 0.12 mg/kg respectively with no traces of Ni in banana samples. The concentrations of Pb, Co, Cu, and Zn were 0.02 ± 0.00 mg/kg, 0.18 ± 0.01 mg/kg, 0.01 ± 0.00 mg/kg and 2.00 ± 0.11 mg/kg respectively with no traces of Cd and Ni in the pineapple sample. The concentrations of Pb, Ni, Co, Cu and Zn observed in watermelon sample were 0.05 ± 0.01 mg/kg, 0.01 ± 0.00 mg/kg, 0.20 ± 0.01 mg/kg, 0.05 ± 0.01 mg/kg and 1.12 ± 0.01 mg/kg respectively. Whereas; Cd was not observed in watermelon sample. Thus all the results were in good agreement with the WHO maximum allowed concentration.

3.2 Assessment of Heavy Metal Concentration

The results of the determination of heavy metal concentrations in fruit samples from three markets in Enugu State during wet season are shown in Tables 2, 3 and 4 for June, July and August respectively.

Table 2 indicates that Lead and Cadmium level in all the fruit samples from the three markets were above the WHO maximum allowed concentration (0.1 and 0.05 mg/kg respectively).

Pb level was highest in banana samples for all the three markets, while pineapple samples showed the least level of Pb concentration. Cd level was highest in banana samples from Ezeagu (0.09 mg/kg) and Ogbete markets (0.14 mg/kg) but highest in watermelon samples from Nsukka market (0.13 mg/kg). Ni and Cu levels in all the samples from the three markets were below the WHO maximum allowed concentration (0.8 and 2.0 mg/kg respectively). Similar to Cd, Ni level was highest in banana samples from Ezeagu and Ogbete market (0.10 and 0.11 mg/kg respectively) but highest in watermelon samples from Nsukka market (0.09 mg/kg). Pineapple samples showed the least concentration of Ni in all the three markets. The level of zinc was higher in banana samples compared to the other fruit samples from all the three market locations. Watermelon samples showed the least concentration of Zn.

Data presented in Table 3, shows heavy metal Pb concentration below the WHO maximum allowed concentration (0.1 mg/kg) in pineapple samples from the three markets viz; Ezeagu, Ogbete and Nsukka market (0.06 , 0.07 and 0.09 mg/kg). In watermelon, samples from ogbete market shows low Pb (0.09 mg/kg) whereas, samples from Ezeagu and Nsukka market shows 0.10 and 0.11 mg/kg Pb, which was above the WHO maximum allowed concentration. All banana samples from all the three markets were above the WHO maximum allowed concentration (0.1 mg/kg). Cd concentration in all samples was above WHO maximum allowed concentration except pineapple samples from Nsukka and Ezeagu markets (0.02 mg/kg). All the samples analyzed for Ni, Co and Cu in all the three markets were below the WHO maximum allowed concentration (0.8 , 2.0 and 4.5 mg/kg respectively). Co, Cu and Zn concentrations were highest in banana samples from all the three markets whereas; watermelon samples

Table 1. Experimental sample value and WHO maximum allowed concentration

Parameters	Banana mg/kg	Pineapple mg/kg	Watermelon mg/kg	MAC [16] mg/kg
Lead (Pb)	0.09 ± 0.01	0.02 ± 0.00	0.05 ± 0.01	0.1
Cadmium (Cd)	0.03 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.05
Nickel (Ni)	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.8
Cobalt (Co)	0.30 ± 0.01	0.18 ± 0.01	0.20 ± 0.01	2.0
Copper (Cu)	0.20 ± 0.01	0.01 ± 0.00	0.05 ± 0.01	4.5
Zinc (Zn)	2.27 ± 0.12	2.00 ± 0.11	1.12 ± 0.01	-

MAC-Maximum allowed concentration. Results are in mean \pm SE

Table 2. Heavy metal concentration in fruit samples from three market locations in Enugu state for the month of June

Location	Samples	Heavy metals (mg/kg)					
		Pb	Cd	Ni	Co	Cu	Zn
Nsukka market	Banana	0.23±0.01 ^a	0.11±0.01 ^{ac}	0.06±0.00 ^{ab}	0.63±0.13 ^a	0.44±0.01 ^a	8.74±0.40 ^a
	Pineapple	0.15±0.01 ^b	0.07±0.01 ^b	0.04±0.00 ^{ab}	0.43±0.03 ^b	0.09±0.01 ^b	4.83±0.15 ^{bc}
	Watermelon	0.19±0.01 ^c	0.13±0.01 ^{ac}	0.09±0.01 ^{ac}	0.51±0.11 ^c	0.22±0.01 ^c	3.07±0.13 ^{bc}
Ezeagu market	Banana	0.15±0.01 ^a	0.09±0.01 ^{ac}	0.10±0.01 ^{ac}	0.50±0.11 ^{ac}	0.61±0.13 ^a	11.52±0.62 ^a
	Pineapple	0.10±0.01 ^{bc}	0.04±0.00 ^{bc}	0.05±0.01 ^{bc}	0.44±0.01 ^b	0.07±0.01 ^b	2.91±0.13 ^{bc}
	Watermelon	0.13±0.00 ^{bc}	0.07±0.00 ^{ac}	0.07±0.01 ^{bc}	0.50±0.12 ^{ac}	0.21±0.01 ^c	2.43±0.14 ^{bc}
Ogbete market	Banana	0.17±0.01 ^a	0.14±0.01 ^{ac}	0.11±0.01 ^{ac}	0.56±0.13 ^a	0.52±0.12 ^a	7.22±0.40 ^a
	Pineapple	0.11±0.01 ^{bc}	0.09±0.00 ^{bc}	0.05±0.00 ^b	0.42±0.03 ^b	0.06±0.01 ^b	3.71±0.13 ^{bc}
	Watermelon	0.12±0.01 ^{bc}	0.12±0.01 ^{ac}	0.10±0.01 ^{ac}	0.49±0.03 ^c	0.19±0.01 ^c	2.35±0.15 ^{bc}
MAC [16]		0.1	0.05	0.8	2.0	4.5	

MAC-Maximum allowed concentration. Results are in mean±SE. Similar alphabets in a column are not significantly different ($p < 0.05$)

Table 3. Heavy metal concentration in fruit samples from three market locations in Enugu state for the month of July

Location	Samples	Heavy metals (mg/kg)					
		Pb	Cd	Ni	Co	Cu	Zn
Nsukka market	Banana	0.14±0.01 ^{ac}	0.08±0.01 ^{ac}	0.05±0.01 ^{ac}	0.57±0.13 ^a	0.40±0.01 ^a	6.18±0.13 ^a
	Pineapple	0.09±0.01 ^{bc}	0.02±0.01 ^b	0.02±0.00 ^b	0.42±0.01 ^{bc}	0.04±0.00 ^b	4.10±0.13 ^b
	Watermelon	0.11±0.01 ^{bc}	0.10±0.01 ^{ac}	0.06±0.00 ^{ac}	0.48±0.13 ^{bc}	0.16±0.01 ^c	2.47±0.01 ^c
Ezeagu market	Banana	0.12±0.01 ^{ac}	0.06±0.01 ^{ac}	0.07±0.01 ^{abc}	0.49±0.11 ^{abc}	0.54±0.13 ^a	7.26±0.12 ^a
	Pineapple	0.06±0.01 ^b	0.02±0.00 ^b	0.04±0.00 ^{abc}	0.41±0.01 ^{abc}	0.05±0.01 ^b	2.41±0.11 ^{bc}
	Watermelon	0.10±0.01 ^{ac}	0.04±0.00 ^{ac}	0.05±0.01 ^{abc}	0.46±0.11 ^{abc}	0.14±0.01 ^c	2.16±0.11 ^{bc}
Ogbete market	Banana	0.14±0.01 ^a	0.11±0.01 ^{ac}	0.06±0.01 ^{ac}	0.52±0.11 ^a	0.45±0.01 ^a	6.18±0.14 ^a
	Pineapple	0.07±0.01 ^{bc}	0.07±0.01 ^{ab}	0.03±0.00 ^{ab}	0.37±0.02 ^b	0.04±0.00 ^b	3.42±0.13 ^b
	Watermelon	0.09±0.00 ^{bc}	0.09±0.01 ^{ac}	0.08±0.01 ^{ac}	0.45±0.12 ^c	0.15±0.01 ^c	1.93±0.11 ^c
MAC [16]		0.1	0.05	0.8	2.0	4.5	

MAC-Maximum allowed concentration. Results are in mean±SE. Similar alphabets in a column are not significantly different ($p < 0.05$)

Table 4. Heavy metal concentration in fruit samples from three market locations in Enugu state for the month of August

Location	Samples	Heavy metals (mg/kg)					
		Pb	Cd	Ni	Co	Cu	Zn
Nsukka market	Banana	0.13±0.01 ^a	0.07±0.01 ^{abc}	0.03±0.00 ^{ac}	0.53±0.11 ^a	0.39±0.01 ^a	5.28±0.13 ^a
	Pineapple	0.05±0.01 ^{bc}	0.05±0.01 ^{abc}	0.01±0.00 ^b	0.40±0.01 ^{bc}	0.03±0.00 ^b	3.36±0.12 ^b
	Watermelon	0.08±0.01 ^{bc}	0.08±0.01 ^{abc}	0.05±0.01 ^{ac}	0.44±0.01 ^{bc}	0.11±0.01 ^c	1.97±0.11 ^c
Ezeagu market	Banana	0.11±0.01 ^{ac}	0.04±0.00 ^{abc}	0.03±0.00 ^{abc}	0.42±0.01 ^{ac}	0.51±0.11 ^a	5.44±0.14 ^a
	Pineapple	0.03±0.00 ^b	0.01±0.00 ^{abc}	0.02±0.00 ^{abc}	0.38±0.02 ^b	0.03±0.00 ^{bc}	2.27±0.11 ^b
	Watermelon	0.09±0.01 ^{ac}	0.02±0.00 ^{abc}	0.02±0.00 ^{abc}	0.44±0.01 ^{ac}	0.07±0.01 ^{bc}	1.81±0.11 ^c
Ogbete market	Banana	0.11±0.01 ^{ac}	0.08±0.01 ^{abc}	0.05±0.01 ^{ac}	0.51±0.11 ^a	0.38±0.01 ^a	5.77±0.13 ^a
	Pineapple	0.06±0.01 ^{bc}	0.04±0.00 ^{abc}	0.02±0.00 ^b	0.33±0.01 ^b	0.01±0.00 ^b	3.29±0.11 ^b
	Watermelon	0.08±0.01 ^{ac}	0.05±0.01 ^{abc}	0.05±0.01 ^{ac}	0.41±0.01 ^c	0.13±0.01 ^c	1.43±0.01 ^c
MAC [16]		0.1	0.05	0.8	2.0	4.5	

MAC-Maximum allowed concentration. Results are in mean±SE. Similar alphabets in a column are not significantly different ($p < 0.05$)

showed the highest Ni concentration with least level of Zn and Cu for all the three markets.

Data presented in Table 4, shows heavy metal Pb concentration below the WHO maximum allowed concentration (0.1mg/kg) in pineapple (0.03, 0.05 and 0.06mg/kg) and watermelon samples (0.09, 0.08 and 0.08mg/kg) from the three markets viz; Ezeagu, Nsukka and Ogbete market respectively. All banana samples from all the three markets were above the WHO maximum allowed concentration (0.1mg/kg). Cd concentration in all samples was below WHO maximum allowed concentration in Ezeagu market. Further, all other samples from Nsukka and Ogbete market were above the WHO level. All the samples analyzed for Ni, Co and Cu in all the three markets for banana, pineapple and watermelon samples were below the WHO maximum allowed concentration (0.8, 2.0 and 4.5 mg/kg respectively). Zn concentrations were highest in banana samples from all the three markets followed by pineapple samples whereas; watermelon samples showed the least level of Zn for all the three markets.

4. DISCUSSION

The present study investigated the concentrations of heavy metals (Cd, Co, Cu, Ni, Pb and Zn) in fruit samples (banana, pineapple and watermelon) from three markets in Enugu state (Nsukka market, Ezeagu market and Ogbete market) during the wet season (June, July and August). These study areas were characterized by high anthropogenic activities that cause environmental pollution, which are sources of trace metals pollution to the environment. The sources of anthropogenic metal contamination include industrial effluents, fuel production, mining, smelting processes, military operations, utilization of agricultural chemicals, small-scale industries (including battery production, metal products, metal smelting and cable coating industries), brick kilns and coal combustion [10]. The rate of heavy metal concentrations in the fruit samples was in the order; Banana>Watermelon>Pineapple, which is in line with reports by Zheng et al., [11] who reported that vegetable species differ widely in their ability to take up and accumulate heavy metals, even among cultivars and varieties within the same species.

The results from the present study revealed heavy metals to be present in the fruit samples (banana, pineapple and watermelon) investigated. The concentrations of Pb and Cd were observed to be above WHO maximum allowable concentrations (0.1 mg/kg and 0.05 mg/kg respectively) while the concentrations of Ni, Co, Cu and Zn were below WHO maximum allowable concentration (Ni 0.8mg/kg, Co 2.0mg/kg, Cu 4.5mg/kg). There were differences in the mean concentrations of these heavy metals in the fruit samples. Banana samples showed highest concentrations of the heavy metals investigated while pineapple samples showed the lowest concentrations of the heavy metals investigated. The rate of heavy metal concentrations in the fruit samples was in the order; Banana>Watermelon>Pineapple. This is in line with Zheng et al. [11] who reported that vegetable species differ widely in their ability to take up and accumulate heavy metals, even among cultivars and varieties within the same species. Alexander *et al.* [12] reported that Cu accumulated to the greatest extent in spinach and lettuce. According to Yang et al. [13] Cd accumulation in vegetable species decreased in the order of leafy vegetables > solanaceous vegetables > root vegetables > allium vegetables > melon vegetables > legumes vegetables.

Heavy metals are toxic because they react with body's biomolecules, clog up receptor sites, break and bend sulfur bonds in important enzymes such as insulin, and damage the DNA [14 and 15]. Vegetables and Fruits take up heavy metals and accumulate them in their edible and non-edible parts at quantities high enough to cause clinical problems to both animals and human beings.

5. CONCLUSION

The result of the present study revealed the presence of heavy metals in the fruit samples analyzed. Some of the heavy metals (Pb and Cd) investigated were above the WHO maximum allowable concentration while some (Ni, Co, Cu and Zn) were below the WHO maximum allowable concentration. The concentration of heavy metals in the fruit samples decreased progressively from the month of June to August. Banana fruit samples were observed to contain higher concentrations of heavy metals compared to the other fruit samples investigated.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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