Heavy Metal Concentration in Fruit Samples During the Dry Season From three Major Markets in Enugu, Nigeria

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ABSTRACT

The dynamics of seasonal changes of heavy metals composition in three common edible fruits in Enugu State, Nigeria were analyzed. Banana, pineapple and watermelon samples were collected during the three dry season months (December, January and February) from the three markets in the three senatorial districts of the state (Nsukka market, Ezeagu market, and Ogbete market). Heavy metals evaluated during the study include lead, cadmium, cobalt, nickel, zinc and copper. Samples digestion was done using wet digestion method which comprises a mixture of acids and hydrogen peroxide. Metals in the samples were quantified using atomic absorption spectrophotometry (AAS) at specific wave lengths and values reported in mg/kg. Among the three samples for all metals studied, maximum and minimum values are; 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 quantities of metals in all the samples in average increased with progression in dry season. The heavy metals analyzed were more in banana and least in watermelon samples. Values obtained were compared to WHO maximum permissible limit for each metal.

Keywords: *Heavy metals, Fruit samples, Atomic absorption spectrophotometry, Seasonal change.*

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Highlights of this paper

- There were presence of heavy metals in the three fuits (Banana, Pineapple and Water melon) examined.
- The quantities of heavy metals increased with progression of the dry season.
- The heavy metals were more in banana and least in water melon.

1. INTRODUCTION

Food safety is a major public health concern worldwide. As a result of the increasing risk of contamination of food by pesticides, heavy metals, and/or toxins, the food safety issues have attracted the attention of researchers recently [1]. 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 [2].

Heavy metals have been reported to have positive and negative roles in human life [3, 4]. Heavy metal elements, such as lead (Pb), cadmium (Cd), arsenic (As), etc., have toxic effects on human health. Toxic metals can accumulate persistently in the body over a lifetime. Pb can adversely influence the intelligence development of children, cause excessive lead in the blood, and induce hypertension, nephropathy and cardiovascular disease [5]. 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 [6]. Chronic Cd exposure can cause acute toxicity to the liver and lungs, induce nephrotoxicity and osteotoxicity, and impair function of the immune system [7, 8]. 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 [9] For example, a Cu surplus can cause acute stomach and intestine aches, and liver damage [9, 10] and Zn can reduce immune function and levels of high-density lipoproteins [11]. Compared with inhalation of soil particles, drinking water, and dermal contact, food consumption has been identified as the major pathway for human exposure to toxic metals [12, 13].

There are elevated levels of heavy metal in fruits in many areas of Nigeria, especially in developing states and regions like Enugu [14]. 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. In Enugu state, some researchers have reported the composition of some heavy metals in fruit samples and products [14]. Despite the economic and nutritional value of fruits, there is little information on heavy metal contamination of most fruits. It is therefore important to ascertain the concentration of heavy metals in watermelon, banana and pineapple, from major markets in the three senatorial zones of Enugu state.

2. MATERIALS AND METHODS

The fruit samples (*Citrulluslanatus*, *Ananascomosus* and *Musa paradisaca*) were collected from the three senatorial districts of Enugu state. Enugu West senatorial district samples were collected from Ezeagu central market, that of Enugu North was collected from Nsukka market, while that of Enugu East was collected from Ogbete market. The samples were collected from retail stores during each collection period (in the month of December, January and February).

Fresh fruit samples were digested according to the method of Food Safety and Standards Authority of India (FSSAI) [15]. 1g of each of the test food sample was weighed into 100ml beaker. Concentrated hydrochloric acid and nitric acid were added to the weighed samples in the ratio 3:1 volume by volume, that is 30ml of hydrochloric acid and 10ml of nitric acid to each sample. 10 drops of hydrogen peroxide were added to each of the sample. 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 digests completely. Each digest was diluted with 50ml of distilled water and filtered into a 100ml volumetric flask using whatman filter paper. The filtrate was made up to the mark with distilled water and used for heavy metal analysis (using AAS). 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, Nigeria.

Five of each fruits (banana, pineapple and watermelon) were collected from an organic farm. 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 for each element that was being investigated and their absorbance were read. The mean of each triplicate was calculated and hence the detection limits determined for each element.

3. RESULTS

3.1. Experimental Control

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	-

Note: MAC-Maximum allowed concentration. Results are in mean±SE.

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, Ni, Co, Cu and Zn were 0.09±0.01mg/kg, 0.03±0.00mg/kg, 0.00±0.00mg/kg, 0.30±0.01mg/kg, 0.20±0.01 and 2.27±0.12mg/kg respectively. The concentration Ni was below the detection level for Banana sample. The concentrations of Pb, Co, Cu, and Zn in pineapple samples were 0.02±0.00mg/kg, 0.18±0.01mg/kg, 0.01±0.00mg/kg and 2.00±0.11mg/kg respectively. Cd and Ni were not observed in the pineapple sample. The concentrations of Pb, Ni, Co, Cu and Zn observed in watermelon sample were 0.05±0.01mg/kg, 0.01±0.00mg/kg, 0.20±0.01mg/kg, 0.05±0.01mg/kg and 1.12±0.01mg/kg respectively, Cd was not observed in watermelon sample. The results of the control experiment were lesser than the WHO maximum allowed concentration for all the heavy metals investigated (Pb 0.1mg/kg, Cd 0.05mg/kg, Ni 0.8mg/kg, Co 2.0mg/kg, Zn 4.5mg/kg). Thus the results are in good agreement with the WHO maximum allowed concentration.

3.2. Heavy Metals Concentrations in Fruit Samples from Three Markets in Enugu State during Dry Season

The results of the determination of heavy metal concentrations in fruit samples from three markets in Enugu State during dry season were shown in Table 2, 3 and 4 for December, January and February respectively.

Table-2. Heavy metal concentration in fruit samples from three market locations in Enugu State for the month of December.

Location	Samples	Heavy metals (mg/kg)					
		Pb	Cd	Ni	Co	Cu	Zn
Nsukka market	Banana	0.24±0.02[a]	0.13±0.01[ac]	0.06±0.00[abc]	0.56±0.13[a]	0.47±0.01[a]	7.33±0.31[a]
	Pineapple	0.16±0.01[bc]	0.05±0.01[b]	0.04±0.00[abc]	0.43±0.01[bc]	0.08±0.01[b]	3.92±0.13[b]
	Watermelon	0.19±0.01[bc]	0.15±0.01[ac]	0.05±0.01[abc]	0.48±0.02[bc]	0.18±0.00[c]	2.81±0.15[c]
Ezeagu market	Banana	0.21±0.01[a]	0.11±0.01[ac]	0.07±0.00[ac]	0.47±0.01[ac]	0.62±0.04[a]	9.47±0.62[a]
	Pineapple	0.13±0.00[bc]	0.07±0.00[b]	0.02±0.00[b]	0.41±0.01[b]	0.06±0.00[bc]	5.03±0.55[b]
	Watermelon	0.15±0.01[bc]	0.10±0.01[ac]	0.05±0.01[ac]	0.49±0.03[ac]	0.11±0.00[bc]	2.10±0.15[c]
Ogbete market	Banana	0.18±0.00[ac]	0.15±0.00[ac]	0.09±0.01[ac]	0.54±0.13[a]	0.41±0.01[a]	6.19±0.56[a]
	Pineapple	0.12±0.01[b]	0.08±0.01[b]	0.04±0.00[b]	0.41±0.01[bc]	0.05±0.01[b]	3.36±0.13[b]
	Watermelon	0.17±0.01[ac]	0.12±0.01[ac]	0.07±0.00[ac]	0.46±0.01[bc]	0.16±0.00[c]	1.83±0.08[c]
MAC [16]		0.1	0.05	0.8	2.0	4.5	

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

The Table 2 above shows the mean concentration of heavy metals in all the samples (Banana, Pineapple and Watermelon) from the three markets (Nsukka, Ezeagu and Ogbete markets). The concentrations of Lead (Pb) were slightly above the WHO maximum allowed concentration (0.1mg/kg). Banana sample from the three markets showed the highest concentrations of Pb (0.24mg/kg Nsukka market, 0.21mg/kg Ezeagu market and 0.18mg/kg Ogbete market). Pineapple samples showed the lowest concentration of Pb in all the three markets compared to the other fruits investigated. In all the markets, Nsukka market representing Enugu North Senatorial zone showed the highest concentrations of heavy metals in all the fruits analyzed. Cd concentration in all the three fruits were also above the WHO maximum allowed concentration (0.05mg/kg) except for pineapple sample from Nsukka market which showed the same concentration of Cd as of the maximum allowed concentration (0.05mg/kg). Similar to lead, the concentration of Cd in all the fruit samples were highest in Nsukka market, followed by samples from Ogbete market. Ezeagu market showed the least Cd concentration. Ni concentrations in all the fruits analyzed were below the WHO maximum allowed concentration (0.8mg/kg). Ogbete market showed the highest concentrations of Ni in all the three fruits analyzed. Co concentration was highest in banana samples from the three markets, while pineapple showed the least Co concentration. Cu concentrations in the three fruit samples from the three markets were far below the WHO maximum allowed concentration (4.5mg/kg). High levels of Zn were observed in all the three fruit samples. Ezeagu market showed the highest concentration of Zn in banana and pineapple samples while Nsukka market showed the highest concentration of Zn in watermelon sample. In all the fruit samples analyzed, banana showed the highest Zn concentration followed by pineapple. Watermelon showed the least concentration of Zn in all the three markets.

ANOVA at 95% confidence level revealed no significant difference ($p<0.05$) in the mean concentration of Pb in pineapple and watermelon samples from Nsukka market but varied significantly ($p>0.05$) from the concentration of Pb in banana sample from Nsukka market. Similar levels of significance were observed for the three fruit samples from Ezeagu market. The concentrations of Pb in banana sample and watermelon sample from Ogbete market was not significantly different ($p<0.05$) but varied significantly ($p>0.05$) from the concentration of Pb in pineapple sample from Ogbete market. Cd concentrations in banana and watermelon sample were not significantly different ($p<0.05$) but varied significantly ($p>0.05$) from Cd concentration in pineapple sample; this level of significance in Cd concentration was observed in all the three markets. No significant difference ($p<0.05$) was observed in the concentrations of Ni for the three fruit samples in Nsukka market. The concentration of Ni observed in banana and watermelon sample were not significant ($p<0.05$), but the concentration of Ni observed in pineaaple sample varied significantly ($P>0.05$) from the other two fruit samples; as observed in Ezeagu and Ogbete market.

Fruit samples from Nsukka and Ogbete market showed no significant difference ($p<0.05$) in the concentration of Co observed in pineapple and watermelon sample but varied significantly ($p>0.05$) from Co concentration observed in banana sample. Fruit sample from Ezeagu market showed no significant difference ($p<0.05$) in the concentration of Co observed in banana and watermelon samples but varied significantly ($p>0.05$) from Co concentration observed in pineapple sample. There were significant differences ($p>0.05$) observed in the concentration of Cu observed in all the fruit samples from Nsukkaand Ogbete markets. Whereas the concentration of Cu observed in pineapple and watermelon samples from Ezeagu market was not significantly different ($p<0.05$) but the concentration of Cu observed in banana sample from Ezeagu market varied significantly ($p>0.05$) from the other two fruit samples. Zn concentration in all the three fruit samples varied significantly ($p>0.05$) from one another in the three markets.

Table-3. Heavy metal concentration in fruit samples from three market locations in enugu state for the month of January.

Location	Samples	Heavy metals (mg/kg)					
		Pb	**Cd**	**Ni**	**Co**	**Cu**	**Zn**
Nsukka market	Banana	0.27±0.01[a]	0.16±0.01[ac]	0.08±0.01[ac]	0.59±0.14[a]	0.51±0.11[ac]	9.02±0.60[a]
	Pineapple	0.20±0.00[bc]	0.09±0.01[b]	0.04±0.00[b]	0.44±0.01[b]	0.10±0.01[b]	4.65±0.53[bc]
	Watermelon	0.21±0.00[bc]	0.17±0.01[ac]	0.07±0.00[ac]	0.52±0.11[c]	0.24±0.01[c]	3.28±0.13[bc]
Ezeagu market	Banana	0.22±0.01[a]	0.14±0.01[ac]	0.10±0.01[ac]	0.50±0.10[ac]	0.67±0.14[a]	12.61±0.80[a]
	Pineapple	0.17±0.01[bc]	0.08±0.01[b]	0.03±0.00[b]	0.42±0.01[b]	0.11±0.01[b]	2.63±0.14[bc]
	Watermelon	0.19±0.01[bc]	0.12±0.01[ac]	0.07±0.01[ac]	0.53±0.13[ac]	0.17±0.01[c]	2.62±0.14[bc]
Ogbete market	Banana	0.20±0.00[ac]	0.19±0.01[ac]	0.12±0.01[a]	0.57±0.13[a]	0.46±0.02[a]	9.78±0.62[a]
	Pineapple	0.15±0.01[bc]	0.11±0.00[b]	0.06±0.00[bc]	0.42±0.01[b]	0.08±0.01[b]	4.06±0.13[b]
	Watermelon	0.18±0.01[ac]	0.16±0.00[ac]	0.09±0.01[bc]	0.49±0.03[c]	0.20±0.01[c]	2.46±0.15[c]
MAC [16]		0.1	0.05	0.8	2	4.5	

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

Table 3 above revealed that Pb concentrations in all the fruit samples from the three markets to be slightly above the WHO maximum allowed concentration (0.1mg/kg). Fruit samples from Nsukka market showed the highest level of lead contamination, while Ezeagu market showed a contamination level slightly below that of Nsukka market but above Ogbete market. Banana sample showed the highest Pb contamination level in all the three markets (Nsukka 0.27 mg/kg, Ezeagu 0.22 mg/kg and Ogbete 0.20 mg/kg) while pineapple sample showed the least (Nsukka 0.20 mg/kg, Ezeagu 0.17 mg/kg and Ogbete 0.15 mg/kg). Similarly, the Cd concentrations detected in all the samples were above the WHO maximum allowed concentration (0.05mg/kg). Banana showed the highest level of Cd contamination in all the markets except for Nsukka market, of which watermelon has the highest Cd concentration (0.17mg/kg). Pineapple showed the least level of Cd in all three markets. Cd concentration observed in Watermelon sample was below the concentration observed in banana sample but above pineapple sample. In Nsukka market, the concentration of Ni detected in all the fruits were below the WHO maximum allowed concentration (0.8mg/kg) except for banana which is the same with the maximum allowed concentration (0.8mg/kg). Co detection levels in banana samples were highest for Nsukka (0.59 mg/kg) and Ogbete market (0.57 mg/kg); watermelon samples showed the highest Co concentration in Ezeagu market (0.53 mg/kg). The levels of Cu contamination in all the samples from the three markets were far below the WHO maximum allowed concentration (4.5mg/kg). Similar to December results, Zn detection level in all the samples were high, of which banana showed the highest level of contamination for all three markets.

ANOVA at 95% confidence level revealed that the concentration of Pb in watermelon and pineapple samples from Nsukka market were not significantly different ($p<0.05$) but varied significantly from banana sample ($p>0.05$). Similar level of significance was observed for fruit samples from Ezeagu market. The concentrations of Pb in banana and watermelon samples from Ogbete market were not significantly different ($p<0.05$) but varied significantly ($p>0.05$) from the concentration of Pb observed in pineapple sample. The concentrations of Cd observed in banana and watermelon samples were not significantly different ($p<0.05$) but varied significantly ($p>0.05$) from the concentration of Cd observed in pineapple sample. This level of significance in the concentration of Cd in the fruit samples were observed for all the three markets.

Ni concentration observed in banana and watermelon samples were not significantly different ($p<0.05$), but a significant difference ($p>0.05$) was observed for Ni concentration of pineapple sample for both Nsukka and Ezeagu market. For Ogbete market sample, the concentration of Ni in banana sample varied significantly ($p>0.05$) from the concentrations of Ni observed in pineapple and watermelon samples which showed no significant difference ($p<0.05$) in their Ni concentrations. The concentration of Co observed in all the fruit samples from Nsukka and Ogbete market varied significantly ($p>0.05$) from each other. For Ezeagu market samples, the concentration of Co observed in banana and watermelon samples were not significantly different ($p<0.05$) but varied significantly ($p>0.05$) from Co concentration in pineapple sample. The concentration of Cu observed in all the fruit samples from the three markets were significantly different ($p>0.05$) from one another. For Nsukka and Ezeagu market samples, the concentration of Zn in pineapple and watermelon samples were not significantly different ($p<0.05$) but varied ($p>0.05$) from banana samples. Zn concentration in fruit samples from Ogbete market varied significantly ($p>0.05$) from one another Table 3.

Table-4. Heavy Metal concentration in fruit samples from three market locations in Enugu State for the month of February.

Location	Samples	Heavy metals (mg/kg)					
		Pb	Cd	Ni	Co	Cu	Zn
Nsukka market	Banana	0.28 ± 0.01^{a}	0.18 ± 0.01^{ac}	0.08 ± 0.01^{ac}	0.64 ± 0.13^{a}	0.50 ± 0.11^{a}	10.26 ± 0.62^{a}
	Pineapple	0.18 ± 0.01^{b}	0.12 ± 0.01^{b}	0.05 ± 0.01^{b}	0.47 ± 0.03^{b}	0.14 ± 0.01^{b}	6.22 ± 0.42^{b}
	Watermelon	0.22 ± 0.01^{c}	0.21 ± 0.01^{ac}	0.10 ± 0.01^{ac}	0.55 ± 0.13^{c}	0.27 ± 0.01^{c}	3.71 ± 0.13^{c}
Ezeagu market	Banana	0.20 ± 0.00^{ac}	0.15 ± 0.01^{ac}	0.13 ± 0.01^{a}	0.52 ± 0.11^{ac}	0.69 ± 0.14^{a}	13.88 ± 0.81^{a}
	Pineapple	0.14 ± 0.01^{b}	0.10 ± 0.01^{bc}	0.06 ± 0.01^{bc}	0.45 ± 0.01^{b}	0.12 ± 0.00^{b}	3.41 ± 0.13^{b}
	Watermelon	0.19 ± 0.00^{ac}	0.13 ± 0.01^{bc}	0.09 ± 0.01^{bc}	0.54 ± 0.13^{ac}	0.25 ± 0.01^{c}	2.89 ± 0.14^{c}
Ogbete market	Banana	0.22 ± 0.01^{a}	0.22 ± 0.01^{a}	0.12 ± 0.01^{ac}	0.58 ± 0.14^{a}	0.54 ± 0.11^{a}	10.40 ± 0.62^{a}
	Pineapple	0.14 ± 0.00^{bc}	0.14 ± 0.00^{b}	0.08 ± 0.01^{b}	0.44 ± 0.01^{b}	0.09 ± 0.01^{b}	4.63 ± 0.53^{b}
	Watermelon	0.16 ± 0.01^{bc}	0.18 ± 0.01^{c}	0.11 ± 0.00^{ac}	0.53 ± 0.13^{c}	0.23 ± 0.00^{c}	2.93 ± 0.15^{c}
MAC [16]		0.1	0.05	0.8	2	4.5	

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

The concentrations of Pb, Cd, Co, Cu and Zn detected in banana samples Table 4 were higher than those detected in watermelon and pineapple samples in all the three markets. Pineapple samples showed the least concentrations of most these metals analyzed except for Zn where the concentration observed in pineapple samples were greater than the concentrations observed in watermelon samples from all the three markets. The concentrations of Pb and Cd in all the fruit samples from the three markets were above the WHO maximum allowed concentration (0.1mg/kg and 0.05mg/kg respectively). Ni concentration in watermelon samples from Nsukka market (0.21±0.011mg/kg) exceeded that of the other fruit samples. However, Ezeagu and Ogbete market showed higher concentration of Ni in banana samples (0.13mg/kg and 0.12mg/kg respectively).

ANOVA at 95% confidence level revealed the concentration of Pb in fruit samples from Nsukka market to vary significantly ($p>0.05$) from each other. The concentrations of Pb in Banana and Watermelon sample from Ezeagu market were not significantly different ($p<0.05$) but varied significantly ($p>0.05$) from the concentration observed in pineapple sample. Pb concentrations in watermelon and pineapple samples from Ogbete market were significantly different ($p<0.05$) but varied significant ($p>0.05$) from the Pb concentration observed in Banana sample. The differences in the concentration of Cd in banana and watermelon samples from Nsukka market were not significant but varied significantly from Cd concentration in pineapple sample. The concentration of Cd in pineapple and watermelon samples from Ezeagu market were not significantly different ($p<0.05$) but varied significantly ($p>0.05$) from Cd concentration in banana sample. The concentration of Cd in all the fruit samples from Ogbete market varied significantly ($p>0.05$) from one another. For samples from Nsukka and Ogbete market, the concentrations of Ni observed in banana and watermelon samples were not significantly different ($p<0.05$) but varied significantly ($p>0.05$) from the Ni concentration observed in pineapple for samples from Nsukka and Ogbete market. The concentration of Ni in banana sample from Ezeagu market varied significantly ($p>0.05$) from the concentration of Ni observed in pineapple and watermelon samples. Co concentration in all the fruit samples from Nsukka and Ogbete market showed significant differences ($p>0.05$) from one another. The concentration of Co observed in fruit samples from Ezeagu market showed pineapple sample to vary significantly from banana and watermelon samples. The concentrations of Cu and Zn in all the fruit samples from all the three markets varied significantly ($p>0.05$) from one another.

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 sate (Nsukka market, Ezeagu market and Ogbete market) during the dry season (December, January and February). These study areas were characterized by high anthropogenic activities that cause environmental pollution, which are source of trace metals pollution to the environment. According to Shen, et al. [17] 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. Fruit samples from Nsukka market showed the highest concentrations of heavy metals investigated while fruit samples from Ogbete market showed the least concentrations of all the heavy metals investigated except for Nickel concentration.

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. [18] 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 rate of accumulation of heavy metals in the fruit samples are in the order; Zn>Co>Cu>Pb>Cd>Ni. The highest concentrations of Zn (13.88mg/kg), Cu (0.69mg/kg) and Ni (0.13mg/kg) were observed in banana sample from Ezeagu market in the month of February. The highest concentrations of Co (0.64mg/kg) and Pb (0.28mg/kg) were observed in banana sample from Nsukka market in the month of February. Cd concentration was highest

(0.22mg/kg) in banana sample from Ogbete market in the month of February Table 4. Heavy metals affect the nutritive values of agricultural materials and also have deleterious effect on human beings. National and international regulations on food quality set the maximum permissible levels of toxic metals in human food; hence an increasingly important aspect of food quality should be to control the concentrations of heavy metals in food [19].

5. CONCLUSION

Data obtained in this work indicate that there is a considerable amount of heavy metals in the fruit samples from all three markets. Metals in banana were higher followed by watermelon and pineapple respectively. In all the analysis, Zinc was the heavy metal with the highest concentration in the fruit samples for the markets. This effect could be attributed to the use of domestic or industrial waste water for plants irrigation during the dry seasons. Another factor could be the higher concentration of toxic heavy metals in the air and dust, and poor transportation methods during the dry season.

REFERENCES

[1] J. P. F. D'Mello, *Food safety: Contamination and toxins.* Wallingford, Oxon, UK, Cambridge: CABI Publishing, 2003.

[2] A. Yusuf, T. Arowolo, and O. Bamgbose, "Cadmium, copper and nickel levels in vegetables from industrial and residential areas of Lagos City, Nigeria," *Food and Chemical Toxicology,* vol. 41, pp. 375-378, 2003.

[3] U. Divrikli, S. Saracoglu, M. Soylak, and L. Elci, "Determination of trace heavy metal contents of green vegetables samples from Kayseri- Turkey by flame atomic absorption spectrometry," *Fresenius Environmental Bulletin,* vol. 12, pp. 1123-1125, 2003.

[4] M. S. Dundar and H. B. Saglam, "Determination of cadmium and vanadium in tea varieties and their infusions in comparison with 2 infusion processes," *Trace Element Elect,* vol. 21, pp. 60-63, 2004.

[5] A. Navas-Acien, E. Guallar, E. K. Silbergeld, and S. J. Rothenberg, "Lead exposure and cardiovascular disease—a systematic review," *Environmental Health Perspectives,* vol. 115, pp. 472-482, 2007. Available at: https://doi.org/10.1289/ehp.9785.

[6] M. K. Monali, "Quantitative analysis of heavy metals from vegetable of Amba Nalain Amravati District," *Der Pharma Chemica,* vol. 4, pp. 2373-2377, 2012.

[7] C. D. Klaassen, J. Liu, and B. A. Diwan, "Metallothionein protection of cadmium toxicity," *Toxicology and Applied Pharmacology,* vol. 238, pp. 215-220, 2009.

[8] L. Patrick, "Toxic metals and antioxidants: Part II. The role of antioxidants in arsenic and cadmium toxicity," *Alternative Medicine Review,* vol. 8, pp. 106–128, 2003.

[9] M. A. Rahman, M. M. Rahman, S. M. Reichman, R. P. Lim, and R. Naidu, "Heavy metals in Australian grown and imported rice and vegetables on sale in Australia: Health hazard," *Ecotoxicology and environmental safety,* vol. 100, pp. 53-60, 2014. Available at: https://doi.org/10.1016/j.ecoenv.2013.11.024.

[10] L. M. Gaetke and C. K. Chow, "Copper toxicity, oxidative stress, and antioxidant nutrients," *Toxicology,* vol. 189, pp. 147-163, 2003. Available at: https://doi.org/10.1016/s0300-483x(03)00159-8.

[11] M. Harmanescu, L. M. Alda, D. M. Bordean, I. Gogoasa, and I. Gergen, "Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area; A case study: Banat County, Romania," *Chemistry Central Journal,* vol. 5, pp. 64-73, 2011. Available at: https://doi.org/10.1186/1752-153x-5-64.

[12] P. Alexander, B. Alloway, and A. Dourado, "Genotypic variations in the accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables," *Environmental Pollution*, vol. 144, pp. 736-745, 2006. Available at: https://doi.org/10.1016/j.envpol.2006.03.001.

[13] F. Zhu, W. Fan, X. Wang, L. Qu, and S. Yao, "Health risk assessment of eight heavy metals in nine varieties of edible vegetable oils consumed in China," *Food and Chemical Toxicology*, vol. 49, pp. 3081-3085, 2011. Available at: https://doi.org/10.1016/j.fct.2011.09.019.

[14] A. S. Ogbuagu, A. O. Onyema, U. E. Ekpunobi, and C. T. Onyema, "Nutritional and heavy metals analysis on four local fruits in Awka South Eastern Nigeria," *International Journal of Chemical and Biochemical Science*, vol. 1, pp. 83-88, 2015.

[15] Food Safety and Standards Authority of India (FSSAI), *Manual of methods of analysis of foods*. New Delhi, India: Food Safety and Standards Authority of India, 2012.

[16] WHO, "Codex alimentarius commission: Food additives and Contaminants Joint FAO/WHO Food Standard Programme: 1-289," 2002.

[17] Z.-G. Shen, X.-D. Li, C.-C. Wang, H.-M. Chen, and H. Chua, "Lead phytoextraction from contaminated soil with high-biomass plant species," *Journal of Environmental Quality*, vol. 31, pp. 1893-1900, 2002. Available at: https://doi.org/10.2134/jeq2002.1893.

[18] N. Zheng, Q. Wang, X. Zhang, D. Zheng, Z. Zhang, and S. Zhang, "Population health risk due to dietary intake of heavy metals in the industrial area of Huludao city, China," *Science of the Total Environment*, vol. 387, pp. 96-104, 2007. Available at: https://doi.org/10.1016/j.scitotenv.2007.07.044.

[19] O. P. Sobukola, O. S. Awonorin, A. M. Idowu, and O. F. Bamiro, "Chemical and physical hazard profile of 'Robo'processing–a street-vended melon snack," *International Journal of Food Science & Technology*, vol. 43, pp. 237-242, 2008. Available at: https://doi.org/10.1111/j.1365-2621.2006.01424.x.