Assessment of Heavy Metals in Selected Vegetables Sold at Owode Market in Ede North Local Government Area, Osun State, Nigeria

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Abstract — Heavy metals are non-biodegradable, toxic and persist for long durations in aquatic as well as terrestrial environments. They might be transported from soil to ground waters or may be taken up by plants, including agricultural crops. It is well known that high industrial and traffic activities contribute high levels of heavy metals to the environments. The Plants grown around such areas are likely to absorb these metals either from the soil through the roots or from atmospheric contaminants through the leaves. Consumption of contaminated vegetables constitutes an important route of heavy metal exposure to animals and humans. The present study is aimed at determine the heavy metal concentrations of selected vegetables in Owode markets in Ede, Osun state. Seven samples of the vegetables were purchased from Owode markets in Ede North Local Government, Osun State, Nigeria. The edible portion of the collected vegetable samples were properly separated, washed and chopped into small pieces using a knife. The vegetables were air-dried and then dried in an oven at 80 °C. Dried samples of the vegetables were ground into a fine powder (80 mesh) using a commercial blender. Heavy metals in vegetable samples were extracted by acid digestion and analyzed for Cadmium, Zinc, Cobalt and Cadmium using a flame atomic absorption spectrophotometer. The results obtained showed that Dandelion greens, Solanecio biafrae, Bitter leaf and African spinach had Cadmium (0.0313±0.01, 0.013±0.00, 0.0175±0.00 and 0.0097±0.00), Zinc (1.266±0.17, 1.7767±0.19, 1.175±0.12 and 1.14±0.09), Cobalt (0.0202±0.01, 0.0144±0.00, 0.0173±0.00 and 0.0087±0.00) and Copper (0.0201±0.02, 0.0120±0.00, 0.0178±0.00 and 1.1367±0.13) while Clove basil, water leaf and Fluted pumpkin had Cadmium (0.0181±0.00, 0.0794±0.05 and 0.8833±0.02), Zinc (1.2420±0.16, 1.9810±0.05 and 1.2970±0.21), Cobalt (0.0178±0.00, 0.0744 ± 0.05 and 0.0187 ± 0.07) and copper $(0.0181\pm0.00, 0.0764\pm0.04, \text{ and } 1.7226\pm0.31)$

Vegetables assessed for heavy metal are within the required regulatory standard for heavy metals permissible level except in few Cases.

Keywords— Vegetables, heavy metals, Acid digestion and flame atomic absorption spectrophotometer.

I. INTRODUCTION

Increase in awareness on food safety has enhanced studies about risk associated with consuming contaminated foods by trace metals (Gomiero, 2018). A significant route for human exposure to trace metals compared to other routes is food chain via soil-planthuman (Chen et al., 2016). Vegetables are important components of a healthy and perfect diet of human beings (Shagal et al., 2012). Recently, various studies have shown that consumption of vegetables can effectively prevent chronic heart diseases and some types of cancers, most especially cancers of the gastrointestinal tract such as colon cancer (Temple et al., 2012).

Vegetables are an important source of carbohydrates, vitamins, minerals, proteins, and fibers; hence they play a vital role in contributing to a healthful diet across the world. An important pathway for the intake of essential nutrients is through consumption of vegetables. The accumulation of trace metals via root or foliar uptake is influenced by the environment and crop species (Bakkali et al., 2012). Irrigation with contaminated water, addition of fertilizers and metal-based pesticides, and industrial emissions are the major sources of vegetables contamination by trace metals (Radwan and Salama, 2006).

There are several reports on adverse health effects associated with increase in level of trace metals found in our vegetables (Arora et al., 2008). This is unconnected to the fact that trace metals can induce damage in multiple organs even at low exposure, so they are systemic toxicants. According to the USEPA, they are classified as human carcinogens. The most affected population includes children and women. Therefore, dietary intake of vegetables containing metals may pose potential health risks to consumers, this is because once into human bodies via consumption, there is little physiological mechanism for their excretion, hence, they have a long half-life at 10e30 years (Gomiero, 2018).

Heavy metals are considered as one of the most significant environmental concerns because of their toxicity and accumulation in the tissues of living organisms which even at low levels can endanger human health (Heshmati, 2014). The existence of heavy metals in the food chains and their critical concentration can have adverse metabolic and physiological effects on human body (Rowland and McKinstry, 2006). The absorption of metals can be affected by several factors such as pH, ionic concentration of the solution, cationic concentration of metal, the presence of competitive

metal cations, and organic and inorganic ligands (Gupta et al., 2012). Moreover, the shapes and different species of plants can create differences in their ability to absorb and accumulate heavy metals (Nazemi and Khosravi, 2011).

World Health Organization (WHO) estimates that about a quarter of the diseases facing mankind today occur due to prolonged exposure to environmental pollution. Heavy metal pollution of the environment, even at low levels, and their resulting long-term cumulative health effects are among the leading health concerns all over the world. Heavy metals are known as nonbiodegradable, and persist for long durations in aquatic as well as terrestrial environments. They might be transported from soil to ground waters or may be taken up by plants, including agricultural crops (Oluyemi et al., 2008).

It is well known that high industrial and traffic activities contribute high levels of heavy metals to the environments. Plants grown around such areas are likely to absorb these metals either from the soil through the roots or from atmospheric contaminants through the leaves. The soil contamination by heavy metals can transfer to food and ultimately to consumers. For instance, plants accumulate heavy metals from contaminated soil without physical changes or visible indication, which could cause a potential risk for human and animal (Osma et al., 2012).

As a result on its persistent and cumulative nature, as well as the probability of potential toxicity effects of heavy metals as a result of consumption of leafy vegetables and fruits, there is a need to test and analyzed this food item to ensure that the levels of these trace elements meet the agreed international requirements.

Based on the stated problem, the present study was design to assess the level of heavy metals in selected vegetables from Owode market, Ede, Osun State, Nigeria. The objectives of this study includes determination of heavy metal contamination in vegetables sold at Owode market in Ede, compare the results of heavy metals obtained from vegetables with the required regulatory standard.

II. MATERIALS AND METHODS

A. Collection of samples

Seven samples of the vegetables (Table 1) were purchased from markets in Owode market, Osun State, Nigeria. The samples were taken to the Laboratory for analysis.

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Sample	English	Local	Botanical
	Name	Name	Name
Sample1	Dandelion	Efo Yarin	Taraxacum
-	greens	(Wild	officinale
	-	lettuce)	
Sample2		Worowo	Solanecio
-			biafrae
Sample3	Bitter leaf	Efo Ewuro	Solanecio
-			biafrae
Sample4	African	Efo Tete	Amaranthus
-	spinach		hybridus
Sample5	Clove	Efirin	Ocimum
_	basil		gratissimum
Sample6	Water leaf	Gbure	Talinum
			Triangulare
Sample7	Fluted	Ugu	Telfairia
	pumpkin	-	occidentalis
	leaf		

B. Pretreatment

After collection, the samples were brought to the laboratory and processed further for analysis. Edible portions of the samples were used for analysis while bruised or rotten samples were removed.

C. Washing of samples

The edible portion of the collected vegetable samples were properly separated and washed to remove dust particles. The samples were then chopped into small pieces using a knife. The vegetables were air-dried and then dried in an oven at 80 $^{\circ}$ C.

D. Grinding of samples

Dried samples of the vegetables were ground into a fine powder (80 mesh) using a commercial blender and stored in polyethylene bags, until used for acid digestion.

E. Acid Digestion

Heavy metals in vegetable samples were extracted following acid digestion procedure as follows: 1.0 g of the dry weight of each the sample collected at those markets was weighed into a digestion tube and 10ml of 98% nitric acid was added. This was then placed in a water bath and allowed to boil for about 72 hours. After which digestion was completed, the resulting pale yellow solution was made up to 25ml with de-ionized water and stored. The composite of the samples were made for each market.

F. Heavy Metals Analysis

The vegetal solution were analyzed for Cd, Zn, Co and Cd using a flame atomic absorption spectrophotometer (AAS, Perkin Elmer model 2130). A certified standard reference materials was used toensure accuracy and the analytical values were within the range of certified value. Blank and standards were run after five determinations to calibrate the instrument.

G. Statistical Analysis

Data were subjected to appropriate analysis

III. RESULT AND DISSCUSSION

A. Cad<mark>mium</mark>

In this study, the values recorded for cadmium in vegetables examined ranges between $0.0097\pm0.00 - 0.0313\pm0.01$ mg/kg, with least concentration of 0.0097 ± 0.00 mg/kg for African spinach (Amaranthus hybridus), follow by 0.0131 ± 0.00 mg/kg for Worowo (Solanecio biafrae), Bitter leaf (Vernonia Amygdalina) had 0.0175 ± 0.00 mg/kg cadmium concentration while the highest concentration of 0.0313 ± 0.01 mg/kg was found in Dandelion greens (Taraxacum officinale) Table 2a. The values recorded for Cadmium for all vegetables examined in the study are below the maximum standard limit of 0.1mg/kg (within and not beyond permissible limit) Table 2a.

Various values have been previously reported for fruits and leafy vegetables which include 0.05, 0.14 and 0.003 mg/kg for apple by Radwan and Salama (2006), Parveen et al. (2003) and Karavoltsos et al. (2002), respectively; watermelon (0.02 and 0.0004 mg/kg); orange (0.04 and 0.0009 mg/kg) and banana (0.02 and 0.001 mg/kg) by Radwan and Salama (2006) and Karavoltsos et al. (2002), respectively. However, Radwan and Salama (2006) and Karavoltos et al. (2002) also reported Cd values of 0.02 and 0.0004 mg/kg for watermelon, 0.04 and 0.0009 mg/kg for orange as well as 0.02 and 0.001 mg/kg for banana. Similarly, Divrikli et al. (2006) have recently reported 0.002 mg/kg as cadmium level in Indian basil which is similar to values reported in this study.

Various sources of environmental contamination have been implicated for its presence of cadmium in foods (Adriano, 1984). The range of Cadmium observed for the vegetables in this study is between 0.0181 ± 0.00 and 0.8833 ± 0.02 mg/kg Table 2b. The highest concentration of 0.8833 ± 0.02 mg/kg was recorded for fluted pumpkin leaf (Telfairia occidentalis), follow by Water leaf (Talinum Triangulare) with 0.0794 ± 0.05 mg/kg while the least concentration of 0.0181 ± 0.00 mg/kg was obtained for clove basil (Ocimum gratissimum)) Table 2b.

Previous studies has revealed different values for leafy vegetables which include 0.090 mg/kg for fluted pumpkin by Sobukola et al. (2010), 0.049 mg/kg (Muhammed and Umer, 2008) for lettuce. According to FAO/WHO, the safe limit for Cd consumption in vegetables is 0.2mg/kg. The result recorded for vegetable in this study fall within the required standard by regulatory bodies except fluted pumpkin leaf (Telfairia occidentalis) with 0.8833±0.02mg/kg.

Cadmium can be absorbed via the alimentary tracts, penetrate through placenta during pregnancy, and damage membranes and DNA, hence they are dangerous and hazardous element. It may remain in the metabolism from 16 to 33 years, once it enters human body and is linked to several health problems, including renal damages and ab-normal urinary excretion of proteins. Decrease in bone calcium concentrations and increase of urinary excre-tion of calcium and death linked to these cases are attributed to exposure to Cadmium. It also affects reproduc-tion and endocrine systems of women (WHO, 2004). Vegetables ma may contribute to about 70 % of Cd intake by humans, varying according to the level of consump-tion (Wagner, 1993). The values of cadmium recorded for all seven vegetables examined in the present study were with the required standard for human body as stipulated by WHO and other health agencies.

B. Zinc

Concentration of Zn in the samples of vegetables in this study varied between 1.1400 ± 0.09 and 1.266 ± 0.17 mg/kg with the lowest value of 1.14 ± 0.09 mg/kg in African spinach (Amaranthus hybrids), 1.175 ± 0.17 mg/kg was recorded for Bitter leaf (Vernonia Amygdalina), Worowo (Solanecio biafrae) had 1.7767 ± 0.19 mg/kg value for zinc and the highest concentrations of 1.266 ± 0.17 mg/g was recorded in Dandelion greens (Taraxacum officinale) Table 2a.

However, the value reported in this study is contrary to values reported by Divrikli et al. (2006) and Ozcan (2004) that recorded lower values of 0.011 and 0.014 mg/kg for zinc in Indian basil. The daily metal intake of zinc was found to be below the recommended RDI of 8-11mg/day (FNB, 2001). Results from this study was in

line with studies done by Akubugwo et al. (2012) on Amaranthus hybridus vegetables which reported values of zinc of 1.06 ± 0.02 to 2.82 ± 0.01 mg/kg. Muhammad et al. (2008) also reported the amount of zinc in leafy vegetable samples as 0.461(spinach), 0.705 (coriander), 0.743 (lettuce), 1.893 (radish), 0.777 (cabbage) and 0.678 (cauliflower) mg/kg, respectively.

In this study, the concentration of Zinc in Vegetables varied between 1.242±0.16 and 1.981±0.05 mg/kg with highest value recorded in Water leaf (Talinum Triangulare) and least concentrations in Clove basil (Ocimum gratissimum) Table 2b.

The contents of Zinc reported in this study are generally higher than the permissible levels by FAO/WHO in vegetables (0.2mg/kg). This study is not in line with the work by Muhammad et al. (2008) that reported level of Zinc in vegetables as 0.777mg/kg for cabbage.

Zinc plays a vital role in the immune system and is an antioxidant in vivo (Strachan, 2010). Zinc deficiency can disturb zinc maintenance in human body.

The clinical manifestations of zinc deficiency in humans are growth retardation, neuropsychiatric disturbances, dermatitis, alopecia, diarrhoea, increased susceptibility to infections, and loss of appetite (Michael et al., 2009). The concentrations of zinc obtained for all the vegetables assessed in the current study were beyond 0.2mg/kg level required in human.

B. Cobalt

The concentration of cobalt obtained in this study varied between 0.0187±0.00 and 0.0202±0.01 mg/kg with the lowest in African spinach (Amaranthus hybridus) and the highest observed in Dandelion greens (Taraxacum officinale) Table 2a. The daily recommended range of cobalt in human diet is 0.005 mg/day (ATSDR, 2004b). In this study, the DIMetal recorded was above the recommended RDI; however, the DImetal values were less than 30 mg/day which can cause digestive and skin disorders in humans (ATSDR, 2004 b).

The concentration of cobalt recorded for vegetables in this study ranges from 0.0178 ± 0.00 to 0.0744 ± 0.05 mg/kg with highest concentration in Water leaf (Talinum Triangulare) and minimum value in Clove basil (Ocimum gratissimum) Table 2b.

The values recorded for all vegetable samples in this study are within the permissible level of Cobalt (0.2mg/kg) set by regulatory authority. This is in line with the work of Sobukola et al. (2010) that reported Co levels 0.015 and 0.046 mg/kg with the lowest in Indian Basil and the highest observed in pumpkin with range

values of 0.024-0.031 mg/kg and 0.041-0.050 mg/kg, respectively.

Animal studies showed that cobalt has been confirmed to be a carcinogen and is considered a possible carcinogen in humans. Fatigue, nausea, vertigo and problems with balance, poor memory and cognitive function, tinnitus and hearing problems, blindness, headaches, cardiomyopathy, hypothyroidism, peripheral neuropathy with tremors and loss of coordination, rashes, kidney failure, anxiety and irritability are symptoms of cobalt toxicity.

All values obtained in this study for vegetables were within the acceptable level of cobalt (0.2kg/mg) in human.

D. Copper

In this study, African spinach (Amaranthus hybridus) had the highest values of copper concentration (1.1367 ± 0.13) in this study, follow by Dandelion greens (Taraxacum officinale) with $0.0201\pm0.02mg/kg$, 0.0178 ± 0.00 mg/kg concentration of cobalt for Bitter leaf (Vernonia Amygdalina) while the least value of 0.0120 ± 0.00 mg/kg was recorded for Worowo (Solanecio biafrae) Table 1a. So, the value of copper recorded for vegetables in this study varies between 0.0120 ± 0.00 to 1.1367 ± 0.13 mg/kg Table 2a.

This is in line with the work of Divrikli et al. (2006) and Ozcan (2004) that reported Cu contents of 0.02 and 0.0081 mg/kg, respectively for Indian Basil.

In Contrary to the above work, Uwah et al. (2011) recorded copper values of between 0.81 mg/kg and 1.75 mg/kg in spinach and lettuce grown in Nigeria. Similarly, Akubugwo et al. (2012) and Muhammad et al. (2008) also show related results in the ranges of 1.20 to 3.42 mg/kg and 0.25 mg/kg to 0.92 mg/kg, respectively, in vegetables studied.

The highest value observed for copper in this study was found in fluted pumpkin leaf (Telfairia occidentalis) with 1.7226±0.31 mg/kg; follow by 0.0181±0.00 mg/kg value found in Clove basil (Ocimum gratissimum) with least concentration of 0.0764±0.04mg/kg in Water leaf (Talinum Triangulare) Table 2b.

This is within safe limit with respect to FAO/WHO-Codex alimentarius commission, 2001 (0.2mg/kg) except concentration of 1.7226 mg/kg recorded for copper in fluted pumpkin leaf (Telifairia occidentalis).

Table 2a: Concentration of Heavy metals in selected vegetables (Dandelion greens, Worowo, Bitter leaf and African spinach) at Owode Market, Ede, Osun state

Sample	Cadmiu	Zinc	Cobalt	Copper
	m			
Dandeli	0.0313±0	1.2660±0	0.0202±0	0.0201±0
on	.01	.17	.01	.02
greens				
Worow	0.0131±0	1.7767±0	0.0144±0	0.0120±0
0	.00	.19	.00	.00
Bitter	0.0175±0	1.1750±0	0.0173±0	0.0178±0
leaf	.00	.12	.00	.00
African	0.0097±0	1.1400±0	0.0087±0	1.1367±0
spinach	.00	.09	.00	.13

Table 2a: Concentration of Heavy metals in selected vegetables (Dandelion greens, Worowo, Bitter leaf and African spinach) at Owode Market, Ede, Osun state

Samp le	Cadmiu m	Zinc	Cobalt	Copper
Clove Basil	0.0181± 0.00	1.2420± 0.16	0.0178± 0.00	0.0181± 0.00
Water leaf	0.0794± 0.05	1.9810± 0.05	0.0744± 0.05	0.0764± 0.04
Flute d pump	0.8833± 0.02	0.8833± 0.02	0.0187± 0.17	1.7226± 0.31
kin leaf			×	

IV. CONCLUSION

The levels of heavy metals examined in this study were low in most cases and within the acceptable standard as required by regulatory agencies. This might be linked to absence of pollution in the areas where they were planted. However, there is no compliance to regulatory permissible in some instances, for example all vegetables tested in this study were not within permissible level of zinc (0.2 mg/kg) rather the values obtained were beyond the acceptable range. Also, all vegetables analyzed were within acceptable standard for copper concentration except values recorded for Africa spinach and fluted pumpkin leaf. The values of heavy metals observed in this work from vegetables obtained from Owode market, Osun state Nigeria can be valuable in the food composition tables for Nigerians and the West African sub-region. Further works should be carried out in the soil samples were the vegetables are grow

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