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Prevalence of Some Heavy Metals in Mango and Pawpaw Found in Dumpsites of Obio/Akpo and Eleme Local Government Areas in River State, Nigeria

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Abstract

Concentrations of six heavy metals Pb, Cd, Zn, Mn, Cu, and Mg were investigated in dumpsites and non-dumpsites in parts of Rivers State. Similar sizes of two species of fruits mango (*Mangifera indica*) and pawpaw (*Carica papaya*) grown at these sites were used for the study. The levels of heavy metals were also investigated in the topsoil at each site. The samples were prepared and digested with mixture of mineral acids $HClO_4$, HCl, H_2SO_4 and HNO_3. They were analyzed by Atomic Absorption Spectrophotometer model 204. The results obtained in mg/Kg showed that heavy metals in mango occurred in the range; Pb (1.34-2.74), Cd (ND - 0.001), Zn (1.09-2.45), Mn (110-178), Cu (2.3-5.20), Mg (0.31-1.73). In paw paw the following were obtained Pb (1.24-1.57), Cd (ND -0.001), Zn (3.84-6.32), Mn (111-115), Cu (2.5-4.11), Mg (1.04-1.84) and in the top soil samples Pb (142-3.66), Cd (ND-0.001), Zn (5.27-8.63), Mn (106-179), Cu (1.24-6.84) and Mg (1.35-1.72). The results revealed that elevated concentrations of heavy metals were obtained in samples from dumpsites when compared to non-dumpsites. The results showed that samples from dumpsites will not be toxic to humans if consumed, as the levels of metals obtained were within standard set by WHO/FAO for daily intake of minerals except for Mn and Pb.

Keywords: Heavy metals; Dumpsites; Non-dumpsites; Mango; Pawpaw; Anthropogenic

Introduction

The Niger Delta area south-south Nigeria is located within the equator and it is characterized with both mangrove and tropical rain forest. In the area, several plants and aquatic organisms thrived due to the terrain. Seasonal, annual and biannual plants are grown in the area and most of them are of economic values. These fruit bearing plants and vegetables grown in the area form part the sources of minerals, vitamins and protein for humans. The anthropogenic activities such as exploration and exploitation of oil, discharge of industrial and domestic waste, road construction, dredging of river and creeks have all resulted in the introduction of toxic substance to the environment [1-3]. In addition, oil bunkery, oil spillage has also contributed to the pollution of both aquatic and terrestrial environment. Smith et al. reported that in 1992 some birds such as crow and the amedori drop into the sea while flying over Minamata bay in Japan as a result of the consumption of fish from the Minamata bay [4]. According to Chukwuma and Brandt et al. topsoil is the outer most parts of the earth where plants and animals survived [5,6]. Fruits and vegetables are grown along the road side, dumpsites, motor mechanic workshops, around residential buildings and household wastes such as battery, chips of paints, and damaged electronic materials are dumped near the fruits and vegetable gardens [7,8]. In the Niger Delta, it is often seen that plantain and pawpaw are cultivated at dumpsites. These fruits absorb the required nutrients through their roots to the entire system of the plant and bioaccumulate metals in their tissues. Goldwater had reported that fruits, grains, milk and vegetable contain less than 0.04 ppm of mercury (Hg) [9]. In Nigeria, the two fruits mango (*Mangifera indica*) and pawpaw (*Carica papaya*) are seasonal and non-seasonal fruits that are consumed regularly by the inhabitants of the area. It is on these bases that the researchers were interested in examining the levels of heavy metals in these two fruits grown at dumpsites and non-dumpsites.

The aim is to ascertain:

i. The concentration of heavy metals in the mesocarp of the two fruits mango (*Mangifera indica*) and pawpaw (*Carica papaya)* and in the topsoil from dumpsites and non-dumpsites

ii. compare the results obtained with the standard set by WHO.

Materials and Methods

Study area

The study area comprises of Obio/Akpor and Eleme local government areas of Rivers State. Obio/Akpor is located within Port Harcourt city, while Eleme is outskirts of Port Harcourt. Most of the industries in Rivers State are cited in these two local government areas. These industries include Indorama Petrochemical Company Eleme, Gas free zone Onne, where Intel Nigerian services is located, and Port Harcourt Refinery Company. The wastes generated from these companies are deposited at dumpsites within these local government areas. Four locations were chosen from the two local government areas. The stations were Choba (station 1) and Ozuoba (station 2), Alesa (station 3) and Nchia (station 4) in Obio/Akpor and Eleme local government areas respectively.

Sample collection

Similar sizes of the two species of fruits, mango and pawpaw were harvested by hand from the four stations of the dumpsites and non-dumpsites in May 2016. The samples were placed in different bagco sack bags that were labeled according to the various sites. The topsoil samples were also collected from each site with a plastic pipe at the

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depth of about 5.0 cm. The soil samples were wrapped in aluminum foil labeled according to the sites. They were transported to the Chemistry research laboratory of Ignatius Ajuru University of Education.

Sample collection: Pawpaw, mango and soil samples were collected from five different dumpsites (Choba and Alesa) and non-dumpsites (Ozuoba and Nchia) in parts of Obio/Akpo and Eleme Local Governments Areas of the Rivers State at monthly intervals for three months.

Sample preparation and digestion

The mesocarp of pawpaw and mango were sliced with a stainless knife into small chips and were oven dried at 105°C. This was to ensure that all the water content was completely driven off. The dried samples were weighed and the drying was repeated until a constant weight was obtained. The same procedure was repeated for the topsoil samples. The dried samples were homogenized with mortar and pestle and 5.0 g of the ground samples (fruits and soil) were measured with electronic weighing balance and placed in a 250 ml volumetric flask. Thereafter, 30 ml of aqua regia was added to the content of the flask containing the fruits, while 15 ml of perchloric acid ($HClO_4$) and 5 ml of hydrochloric acid (HCl) and tretraoxosulplate (vi) acid (H_2SO_4) were added to the soil samples. Each was placed in a water bath and heated for 1 h until the contents of the flasks were almost dry. Precisely 20 ml of de-ionized water was added to each flask and was stirred with a glass rod. This was later filtered with Whatman filter paper. The filtrate was preserved in sample bottles and kept in a refrigerator pending analysis. The samples were than analyzed using Atomic Absorption Spectrophotometer mode 204. The results obtained were then expressed as mean ± Std of the determinations.

Results and Discussion

The results of the analysis of the two species of fruits mango, pawpaw and soil samples are shown in Tables 1-3. The results showed the mean, standard deviation and range of each element.

Metal		Location			
		Dumpsite		Non-dumpsite	
		Choba	Alesa	Ozuoba	Nchia
Pb	$\bar{X}$	1.34	2.74	1.27	2.02
	Std	0.21	1.21	0.54	0.56
	RG	1.0-1.72	2.02-2.87	1.02-1.43	1.95-2.32
Cd	$\bar{X}$	0.01	0.20	0.001	ND
	Std	0.00	0.01	0.000	0.00
	RG	0.001-0.00	0.01-0.23	0.001-0.010	ND
Zn	$\bar{X}$	2.45	1.98	2.32	1.09
	Std	0.35	0.72	1.21	0.83
	RG	2.11-2.75	1.33-2.20	1.53-3.20	1.02-2.51
Mn	$\bar{X}$	110	178	104	160
	Std	23	43	38	38
	RG	45-130	148-192	98-150	150-171
Cu	$\bar{X}$	2.3	4.03	3.84	5.20
	Std	0.21	0.11	0.25	2.7
	RG	21-4.2	3.21-514	2.44-3.97	3.5-7.3
Mg	$\bar{X}$	0.31	1.70	1.73	1.54
	Std	0.01	0.56	0.11	0.67
	RG	0.22-0.53	1.60-1.90	1.21-1.96	1.4-1.54

Table 1: Heavy metals concentrations in mango (*Mangifera indica*) of dumpsites and non-dumpsites in mg/Kg. Mean ± Std of 5 determinations, $\bar{X}$ =mean, std=standard deviation, RG=range.

Metal		Location			
		Dumpsite		Non-dumpsite	
		Choba	Alesa	Ozuoba	Nchia
Pb	$\bar{X}$	1.42	1.41	1.05	1.57
	Std	0.221	0.35	0.10	0.66
	RG	1.1-1.41	1.37-1.53	1.02-1.30	1.40-1.68
Cd	$\bar{X}$	0.001	ND	ND	0.010
	Std	0.00	0.00	0.00	0.00
	RG	0.001-0.010	ND	ND	0.001-0.012
Zn	$\bar{X}$	6.32	4.92	6.31	3.84
	Std	1.21	1.01	1.22	0.19
	RG	4.56-6.82	4.22-4.99	5.21-6.45	3.27-3.92
Mn	$\bar{X}$	120	141.92	111	115
	Std	42	23	24	17
	RG	117-128	138-156	101-116	101-123
Cu	$\bar{X}$	2.5	4.01	3.89	4.11
	Std	0.3	0.03	0.52	0.21
	RG	2.2-2.6	3.01-4.11	3.66-3.97	4.09.4.46
Mg	$\bar{X}$	1.04	1.63	1.84	1.73
	Std	0.20	0.41	0.21	0.17
	RG	1.01-1.11	1.41-1.70	1.53-1.97	1.62-1.83

Table 2: Heavy metals in pawpaw (*Carica papaya*) of dumpsites and non-dumpsite in mg/Kg. Mean ± Std of 5 determinations, $\bar{X}$ =mean, std=standard deviation, RG=range.

Metal		Location			
		Dumpsite		Non-dumpsite	
		Choba	Elesa	Ozuoba	Nchia
Pb	$\bar{X}$	2.41	3.66	1.42	2.01
	Std	0.27	0.71	0.22	0.1
	RG	2.05-2.47	3.62-3.70	1.38-1.48	1.99-2.23
Cd	$\bar{X}$	ND	ND	ND	ND
	Std	0.00	0.00	0.00	0.00
	RG	ND	ND	ND	ND
Zn	$\bar{X}$	8.63	6.04	5.27	6.65
	Std	0.18	0.11	0.18	0.31
	RG	2.52-2.80	2.32-2.72	3.2-3.48	3.01-3.45
Mn	$\bar{X}$	112	193	106	135
	Std	40	14	2.32	21
	RG	105-138	187-191	1.01-1.62	128-137
Cu	$\bar{X}$	1.24	4.54	1.56	6.43
	Std	0.11	0.61	0.22	0.41
	RG	1.11-1.27	4.50-4.62	1.37-1.62	6.20-6.54
Mg	$\bar{X}$	1.52	4.54	1.35	1.72
	Std	0.72	0.31	0.74	0.25
	RG	1.42-1.63	4.30-4.63	1.30-1.47	1.68-1.78

Table 3: Heavy metal concentrations in topsoil of dumpsites and non-dumpsites in mg/Kg. Mean ± Std of 5 determinations, $\bar{X}$ =mean, std=standard deviation, RG=range.

Levels of Pb and Cd in mango, pawpaw and top soil

The concentrations of Pb and Cd which are potential toxic element occurred in variable levels in both categories of sites (dump and non-dump). Elevated levels of Pb was recorded in all the sites when compared to the levels of Cd at the dumpsite, the samples from Alesa contained the highest mean levels of Pb than those of Choba (station 1). Concentrations of Pb occurred in the range (1.0-2.32 mg/Kg) in mango at dumpsites and non-dumpsites, while in pawpaw the range (1.02-1.68 mg/Kg) was observed. The highest mean concentration of 1.57 mg/

Kg for Pb was recorded at Nchia one of the non-dumpsites (Table 2). Elevated levels of Pb at this station may be attributed to the fact that (Nchia) is located along a major junction where heavy traffic occurred. According to Mmolawa et al. of all the eight heavy metals examined along roadside in Botswana, Pb had the highest concentration in the top soil due to vehicular emissions [10]. This station (Nchia) is located in an industrial area where Indorama Petrol Chemical Company is situated. This implies that the levels of Pb at this site may have emanated from vehicular emission and industrial wastes. However, in Table 2, similar distribution trend of Pb also occurred at the various sites. In addition, Pb recorded the highest concentration of 3.66 mg/Kg in the topsoil at Alesa dumpsite when compared to the levels at Ozuoba and Nchia the non-dumpsites. The study revealed that Pb in the three samples occurred in the order, soil >mango>pawpaw, and no significant differences in the mean levels of Pb occurred in both mango and pawpaw.

The concentrations of Cd in the three samples were generally low when compared to Pb. Cadmium concentration occurred in the range ND-0.023 as shown in Tables 1-3. The concentrations of Cd occurred at both dumpsites and non-dumpsites in similar manner. The results of heavy metals Pb and Cd obtained in this study were low when compared to the levels reported by Beavington, in vegetables and soils [11]. The major source of Cd at Alesa is household waste such as batteries and other electrical that were dumped over the past decades. According to Smith, Cd has been shown to be easily absorbed by plants and the edible parts accumulate significant concentrations. In humans, Pb affects the central nervous system, kidney and the reproductive system, while Cd could cause irritation to stomach resulting in vomiting and diarrhea [12]. The concentrations of Pb and Cd are shown in Figures 1 and 2, the figures revealed that the concentration of the elements in the samples varied with the stations (Table 4).

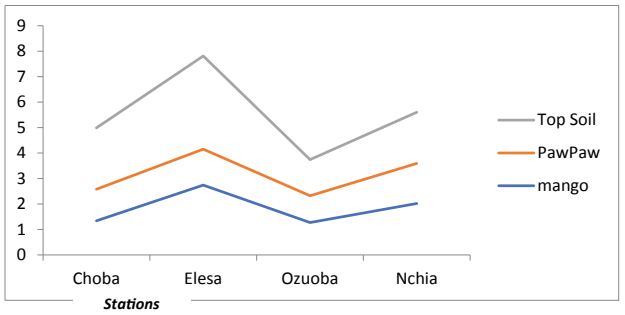

Figure 1: Lead (Pb) concentrations in mango, paw-paw and topsoil.

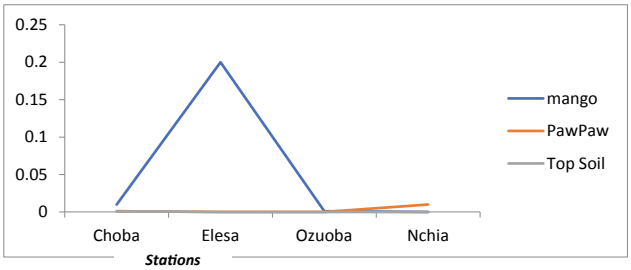

Figure 2: Cadmium (Cd) concentrations in mango, paw-paw and topsoil.

Metal	Recommended daily Allowances	Tolerable Upper Intake Limit	FAO/WHO (1984)	FAO/WHO (2001)
Mn	1.8	11	-	-
Zn	1500	2300	0.60	0.30
Mg	310	40	-	-
Cu	900 µg	10000 µg	40	20
Pb	0.10	-	0.50	0.1
Cd	60 µg	-	0.30	0.30

Table 4: Safe Limits in mg/Kg Recommended by regulatory bodies. -=not available.

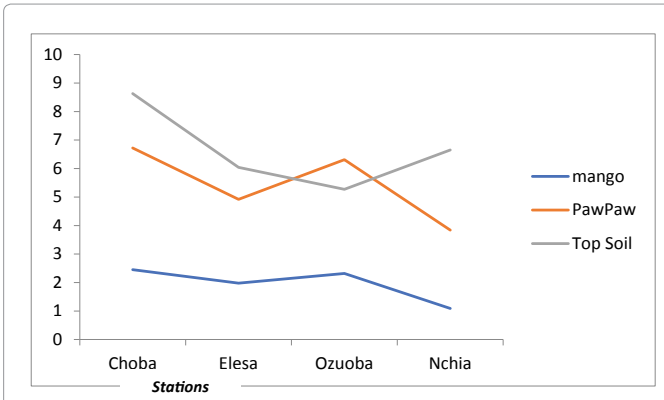

Figure 3: Zinc (Zn) concentrations in mango, paw-paw and topsoil.

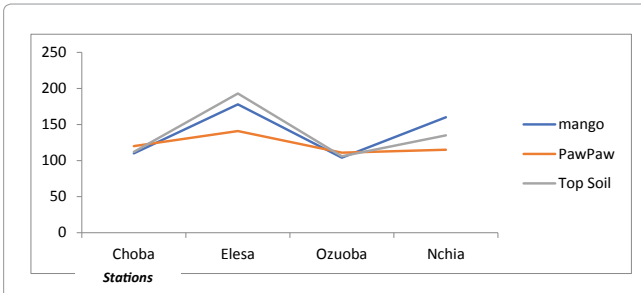

Figure 4: Manganese (Mn) concentrations in mango, paw-paw and topsoil.

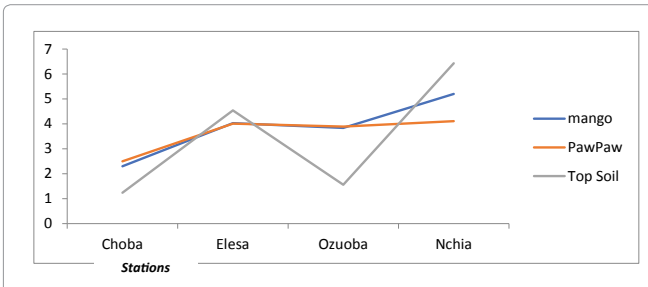

Figure 5: Copper (Cu) concentrations in mango, paw-paw and topsoil.

Distribution of Zn, Mn, Cu and Mg in paw paw, mango and soil

The concentrations of Zn, Mn, Cu and Mg in the three samples are shown in Tables 1-3 and Figures 3-6. These elements (Zn, Mn, Cu and Mg) are essential to human and are required in trace amount. However, elevated concentrations could be harmful. Generally, low levels of these metals were reported in both the mango and paw

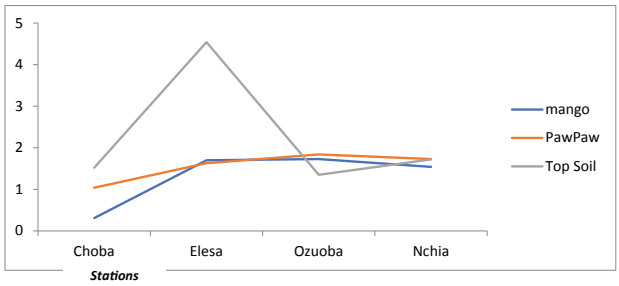

Figure 6: Magnesium (M) concentrations in mango, paw-paw and topsoil.

samples from dumpsites and non-dumpsites. As shown in Tables 1-3. The mean concentration of Zn in Table 1 varied from 1.09 to 2.45 mg/Kg. The highest mean concentration was recorded at Choba dumpsite. In pawpaw the mean levels of Zn ranged from 3.84-6.32 mg/Kg. The highest concentration of the metal (Zn) occurred at Choba. However, in Table 3, elevated levels of Zn were obtained in the topsoil when compared to the levels in mango and pawpaw. The excessive concentrations of Zn in the topsoil could result from migration of the metals from batteries, electronic, alloys and solders. In a similar study, Brant and Rickard, (1996) reported elevated levels of metals in wild Asparagus near waste disposal site. In Table 1, Mn concentrations in mango ranged from 104 to 178 mg/Kg. The results revealed that Alesa dumpsite recorded the highest concentrations of Mn while the lowest concentration was recorded at Ozuoba one of the non-dumpsites. The concentration of Mn in pawpaw occurred in the range 111 to 141 mg/Kg, where the lowest concentration occurred at Ozuoba and the highest concentration was obtained at Alesa dumpsite. The mean levels of Mn in the topsoil ranged from 106 to 193 mg/Kg and the results showed that the topsoil recorded the highest concentrations of the six elements. The highest concentrations of Mn in the samples may be attributed to the fact that manganese (Mn) occurs naturally and its application in the manufacturing of many substances such as batteries, electronics, pigments, paints, biocides, textile materials and fuel which are commonly found in the environment. The levels of Mn obtained in this study was higher when compared to the results reported by Audu and Lawal and Kpee et al. in Kano and Niger Delta respectively [2,13]. The mean levels of Cu and Mg in the samples showed significant difference at all the stations. The results revealed that Cu had the range of 2.3-5.20 mg/Kg, 2.5-4.11 mg/Kg and 1.24-6.84 mg/Kg in mango, pawpaw and the topsoil respectively. On the other hand, Mg concentration occurred in the range 0.31-1.73 mg/Kg, 1.04-1.83 mg/Kg and 1.35-1.72 mg/Kg in mango, pawpaw and topsoil as shown in Table 1-3. Highest levels of Cu was obtained at Alesa, this site is located near Indorama Petrochemical Company, Onne Wharf and Port Harcourt refinery. This implies that, both domestic and industrial wastes are dumped at this site when compared to other sites; Choba, Ozuoba and Nchia. Copper is one of the transition metals used as catalysts in industrial processes such as catalytic cracking of petroleum. The accidental discharge of fuel (kerosene, diesel and petrol) may have contributed to the elevated concentrations of Cu at both dumpsites and non-dumpsites. Cu is an essential element required for metabolism of cells. However, elevated levels in food can cause irritation of the nervous system, depression, necrotic changes in liver and kidney. The results revealed that low levels of magnesium (Mg) were reported in the two species of fruits and the topsoil. In the fruits, the concentration range of 0.31 to 1.84 mg/Kg was recorded, while in the top soil the range of 1.35 to 1.72 mg/Kg of Mg was obtained. The results revealed that an elevated level of Mg was reported in the non-dumpsite when compared to dumpsite. Magnesium compound $Mg(OH)_2$ is important to human as it act as antacid, also Mg^{2+} is present in green parts of plants especially in the chlorophyll and act as lewis acid in porphyrin. Generally, the results obtained in this study revealed that elevated concentrations of heavy metals were more in the dumpsites than non-dumpsites. The relative abundance of the heavy metals in mango occurred in the order Mn>Cu>Zn>Mg>Pb>Cd, while in pawpaw the order was Mn>Zn>Cu>Mg>Pb>Cd. Similar distribution trend of heavy metals was reported in the topsoil.

Conclusion

The results of the study revealed the occurrence of heavy metals at both dump and non-dump sites. Elevated levels of essential metals Zn, Mn, Cu and Mg was recorded when compared to the concentration of Pb and Cd in the two species of fruits (mango and pawpaw). However, elevated concentrations of heavy metals were obtained at the dumpsites when compared to the non-dumpsite. Manganese Mn recorded the highest mean concentrations of the elements investigated while Cd had the lowest. The results revealed that the concentration of the non-essential metals Pd and Cd were low. This implies that there was no point source of the metals. The results obtained revealed that, it would be necessary for the inhabitants of the area not to consume fruits grown at dumpsites, since they contained elevated levels of some of the heavy metals. Since Cd and Pb are potentially hazardous metals, it would be necessary for companies and industries located in the area to recycle their waste before disposal. In addition, government should set up agencies that will educate residents of the area against the consumption of fruits and vegetables grown at dumpsites.

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