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Assessment of Soil and Plant Heavy Metal Concentration in an Anthropogenic Impacted Area in Rivers State, Nigeria

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Abstract

Illegal crude oil refining, theft, and sabotage, amongst others, have assumed an advanced stage within the Niger Delta region, culminating in degradation of major biophysical environmental matrices such as soil and vegetation. Farmlands in Elele-Alimini and Ibaa in Emohua Area, Ogbodo in Ikwerre Area and Umuanyagu (control) in Etche Area of Rivers State, Nigeria, were sampled in this study. A total of fifty (50) sampling points in both test and control locations were randomly selected using a standard spatial (grid-based) sampling technique. Soil and plant samples within the farmlands were collected and analysed in the laboratory for heavy metals using an atomic absorption spectrophotometer (AAS). Mean values of Zn, Pb, Cd, Ni, Mn and Cu in test soil during the dry and wet seasons were in the ranges 7.34-13.37 mg/kg and 6.06-11.39 mg/kg; 4.53-5.87 mg/kg and 3.68-5.39 mg/kg; 1.78-2.85 mg/kg and 1.68-3.11 mg/kg; 5.09-6.02 mg/kg and 4.29-5.62 mg/kg; 103.60-149.1 mg/kg and 101.05-156.51 mg/kg, and 3.51-6.96 mg/kg and 2.77-3.70 mg/kg respectively. Mean values of Zn, Pb, Cd, Ni, Mn and Cu in test plants during the dry and wet seasons were in the ranges 13.26-69.30 mg/kg and 8.40-42.65 mg/kg, <0.001-6.61 mg/kg and <0.001-5.19 mg/kg; <0.001-0.51 mg/kg and 0.13-0.49 mg/kg; 0.36-1.99 mg/kg and <0.001-1.15 mg/kg; <0.001 mg/kg and <0.001; 13.14-139.74 mg/kg and 14.53-67.56 mg/kg, and 1.94-6.59 mg/kg and 1.28-5.48 mg/kg respectively. Levels of heavy metals generally were: Mn > Zn > Ni > Pb > Cu > Cd. Human health risk assessment, EDI values for all metals during dry and wet seasons fell within the recommended reference oral dose, except for Pb and Cd in adults and children at some study locations. To avoid future contamination, it is advised that artisanal refining activities in the area be avoided.

KEYWORDS: Artisanal, Crude Oil, Refining, Soil, Plant, Physicochemical, Toxic Metals

Introduction

Nigeria is well-endowed with a vast majority of mineral resources, among these is hydrocarbon, which is pivotal to the sustainability of the national economy and development. Petroleum exploration and production activities have brought economic boom to the nation, but not without associated problems [1]. One of such problems is the inequitable distribution of the gains of petroleum exploration and production, which leaves the areas where these resources are sourced and people underdeveloped, while bearing the full brunt of the exploration and production activities. A fallout of this is the coordinated vandalisation of oil and gas installations and theft of crude oil, which is either sold off or refined locally as “*kpo fire*”. In most communities where illegal oil refining takes place, such an act is considered a form of local ownership and utilisation of resources that are rightfully theirs for communal good [2].

This is the situation in the Niger Delta region, where militant groups, youths and community leaders, and interested investors have established over 20,000 artisanal refineries to take advantage of cheap labour and raw material availability in the area [3]. There has been a swell in the number of artisanal refineries in the Niger Delta in recent times, which is now a survival strategy for oil thieves who find it difficult to sell stolen crude offshore, and also because of the growing level of poverty in the region [4].

The artisanal refining process begins with crude oil theft through pipeline cannibalisation by the installation of a tap at the tapping point, and the crude is refined into various products such as diesel, premium motor spirit and kerosene. The distilleries are heated by open fires from an excavated pit oven, which is powered by crude oil and burns away, releasing dense smokes and fumes into the sky [5]. The crude oil is usually burnt either by firewood or the crude waste (bitumen).

Oil-hydrocarbons exert adverse effects on soil properties regardless of the means of entering the soil. There is a growing concern of severe pollution of the environment from the artisanal refining process, as evident by the growing incidence of black soot in the air of major cities within the Niger Delta [6]. The United Nations Development Programme report on the Niger Delta [7] warned that the continuous activities of makeshift refineries would lead to the eradication of mangrove habitat in the Niger Delta.

It is common knowledge that the artisanal petroleum refineries in Rivers State are now spreading across 14 of the 23 local councils, most noticeably in Port Harcourt, Obio/Akpor, Ikwere, Emohua, Eleme, Ogubolo, Oyigbo, Okrika and Ogba/Egbema, and have left residents at the mercy of frequent fire outbreaks and polluted air, as soot is seen everywhere in Port Harcourt in recent times. The crude distillation technique adopted for artisanal refining of crude oil discharges clouds of thick smoke into the environment, likened to the site of an inferno. The environmental quality and sustainability in this region are severely undermined. The people of Elele Alimini, Ibaa and Ogbodo are known to be farmers. The sudden spread of artisanal crude oil refineries into these areas poses great danger to the environmental quality, sustainability and soil chemistry, which could impact health quality, due to potential release of pollutants.

This study aimed to investigate heavy metal distribution in soils from the vicinity of an artisanal refining site in Elele Alimini, Ibaa and Ogbodo, Rivers State, Nigeria.

2. Materials and Methods

2.1 Study Area Description

The study area is on latitude 4°53’N - 4°54’N and longitude 6°52’30’E -7°1’30’E. The study area lies within the Niger Delta region. The area is dry, flat land and plain. The landscape is primarily level and slopes very slightly toward the Atlantic Ocean (Figure 1). A network of distributaries drains and criss-crosses the low-lying region, which is often little higher than 20 meters above sea level. The enormous plain that makes up the Niger Delta is occasionally swamped by flooding brought on by rivers and creeks that overflow their banks.

The climate is a humid tropical /equatorial zone with a mean annual temperature of about 29°C. The temperature ranges from 22°C - 35°C within the rainy and dry seasons, respectively. The highest rainfall occurs between the months of July and September, and decreases as the dry season approaches between December and January, with a mean annual rainfall of 2500mm [8,9].

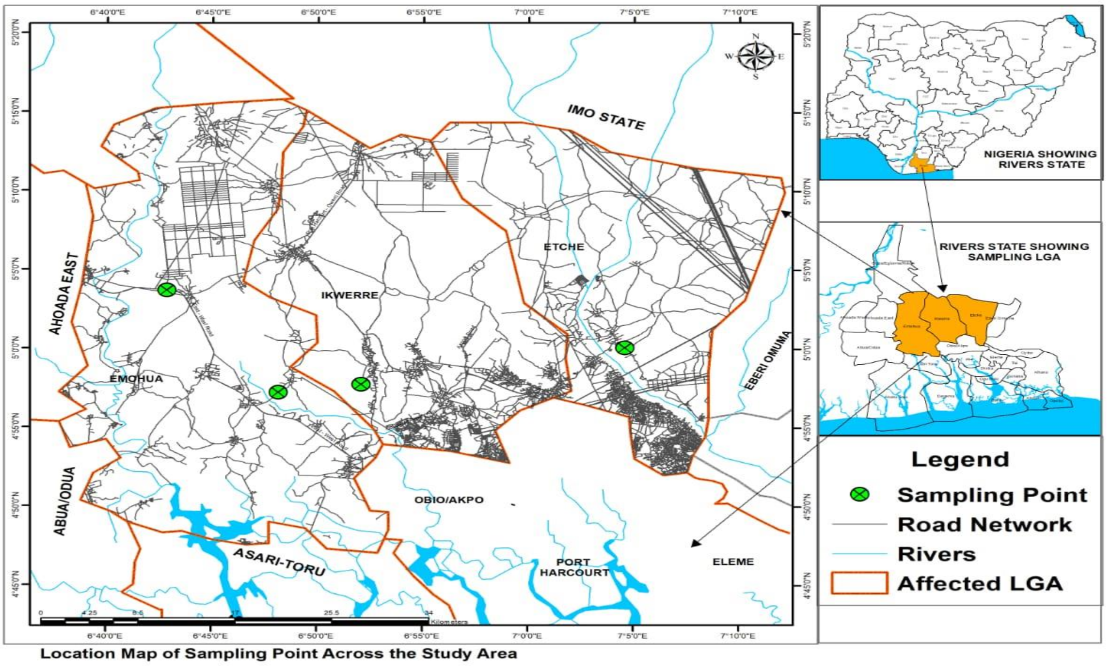

Figure 1: Map showing sampling sites

2.2 Sample Design and Collection

The sampling design and soil collection were carried out in the manner outlined by Osuji and Nwoye [10], with minor modifications. Soil samples were gathered from farmlands located near artisanal crude oil refining sites in Emuoha and Ikwerre LGA. Farmlands in Etche LGA served as control. Fifty (50) soil samples were collected at random from chosen farmlands measuring 100m x 100m using the grid sampling technique (Figure 2). The sampling area was then subdivided into 100 grid plots of 10m x 10m. were gathered using a conventional steel auger. Ten (10) replicate soil samples were collected from surface soils (0-15cm) and subsurface soils (15-30cm) and placed in well-labelled plastic bags before being transported to the laboratory for analysis.

Epicentre of artisanal refinery.

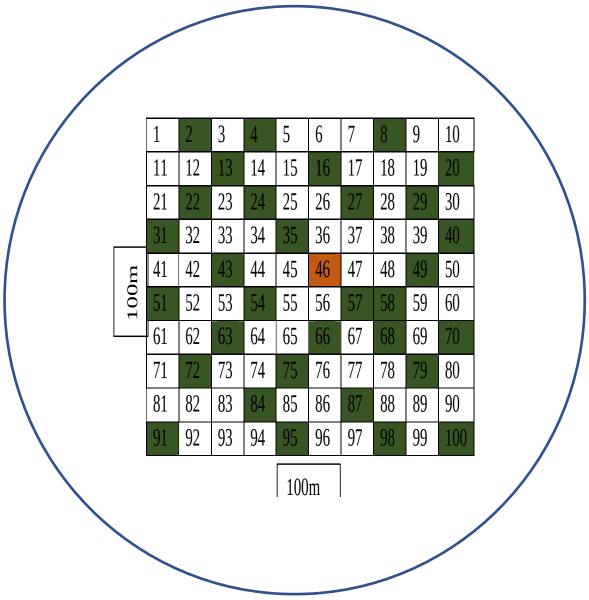

Fig 2: A schematic grid diagram showing randomly sampled plots

2.3 Analysis of Heavy Metal in Soil Samples

Concentrations of heavy metals in soil were determined by an atomic absorption spectrophotometer (AAS).

2.4 Health Risk Assessment Associated with Heavy Metal Exposure

This study used the human health risk assessment method established by the USEPA [11] with minor modifications to estimate the health consequences associated with exposure to non-carcinogenic and carcinogenic substances. The risk assessment procedure consisted of four basic steps: hazard identification, exposure evaluation, toxicity (dose-response) evaluation, and risk characterisation. Heavy metal concentrations in cassava tubers in the research areas were studied based on hazard identification. Cd, Pb, Cu, Cr, Mn, Ni, Cu, and Hg were identified as potential community hazards in the study sites.

2.5 Exposure to Heavy Metals Pathways

The study measured the mean expected daily intake (EDI) of heavy metals previously detected through ingestion and skin contact by adults and children from the study sites. According to Wang (2005), adults and children were separated due to behavioural and physiological differences. Dose-response assessment methods were used to quantify the toxicity of heavy metals according to exposure levels. The reference dose (RfD), a non-carcinogenic threshold, is a key toxicity metric. The "No observable effect level" principle is used to determine RfD values from animal research. To account for uncertainties, RfD values for humans are multiplied by ten. The children and adults of the research area were subjected to risk characterisation to forecast non-cancerous health risks. The information acquired is used to arrive at quantitative estimates of cancer risk and hazard indices. Heavy metal exposure pathways in polluted sediment matrices were calculated. DI (mg/kg-day) was determined for each route using Equations 1 and 2 as described by Kamunda et al. [12].

2.6 Consumption of Heavy Metals via Cassava Tuber

$$EDI_{ing} = \frac{CxIRxEFxEDxCF}{BWxAT} \quad \text{-------------------------------------} \textbf{Eqn 1}$$

where EDI_{ing} is the mean daily intake of heavy metals ingested from soil in mg/kg-day, C = concentration of heavy metal in mg/kg for soil. IR in mg/day is the ingestion rate, EF in days/year is the exposure frequency, ED is the exposure duration in years, BW is the body weight of the exposed individual in kg, and AT is the time period over which the dose is averaged in days. CF is the conversion factor in kg/mg.

2.7 Dermal Contact with Heavy Metals via Cassava Tuber Consumption

$$EDI_{derm} = \frac{CxSAxFExAFxABSxEFxEDxCF}{BWxAT}$$

where EDI_{derm} is the exposure dose via dermal contact in mg/kg/day. C is the concentration of heavy metal in sediment in mg/kg, SA is the exposed skin area in cm^2, FE is the fraction of the dermal exposure ratio to soil, AF is the soil adherence factor in mg/cm^2, and ABS is the fraction of the applied dose absorbed across the skin. EF, ED, BW, CF and AT are as defined in the previous equation. The exposure parameters used for the health risk assessment through different exposure pathways in cassava are presented in Table 1.

Table 1: Exposure parameters used for the health risk assessment through different exposure pathways for sediment

S/N	Parameter	Unit	Child	Adult
1	Body weight (BW)	Kg	15	70
2	Exposure frequency (EF)	days/year	350	350
3	Exposure duration (ED)	Years	6	30
4	Ingestion rate (IR)	mg/day	200	100
5	Inhalation rate (IRair)	m^3/day	10	20
6	Skin surface area (SA)	$Cm^{2`}$	2100	5800
7	Sediment adherence factor (AF)	mg/cm^2	0.2	0.07
8	Dermal Absorption factor (ABS)	none	0.1	0.1
9	Particulate emission factor (PEF)	m^3/kg	1.3E09	1.3E09
10	Conversion factor (CF)	kg/mg	1.0E-06	1.0E-06
11	Average time (AT) for non-carcinogens	days	365 x ED	365 x ED

Source: Kamunda et al. [12]

2.8 Non-Carcinogenic Risk Assessment

The hazard quotient (HQ) and hazard index (HI) are used to classify non-carcinogenic risks. HQ is a unitless quantity that expresses the likelihood of a person receiving a negative consequence. As illustrated in Equation 3, it is defined as the quotient of EDI or dosage divided by the toxicity threshold value, which is referred to as the chronic reference dose (RfD) in mg/kg-day of a certain heavy metal.

$$HQ = \frac{DI}{RfD} \quad \text{------------------------------------}\textbf{Eqn 3}$$

HI, on the other hand, is the population's non-carcinogenic effect for n number of heavy metals, given as the sum of all the HQs caused by individual heavy metals (Equation 4).

$$HI = \sum_{k=0}^{n} HQ \quad \text{-------------------------------}\textbf{ Eqn 4}$$

Where HI and HQ are the health index and hazard quotient, respectively. Please note that HQ values are obtained up to the k^{th} heavy metal. If the HI value is less than one, the exposed population is unlikely to experience adverse health effects. If the HI value exceeds one, then there may be concern for potential non-carcinogenic effects [13].

2.9 Carcinogenic Risk Assessment

The cancer risk (CR) posed to human health by each probable carcinogenic metal was calculated. The cumulative cancer risk (TCR), which may increase carcinogenic effects depending on exposure dose, was then determined from heavy metal consumption (Cr, Ni, As, Pb, and Cd).

CR = EDI x CSf

TCR = $\sum^{i}_{n=1}$ CR

where CR = cancer risk over a lifetime due to individual heavy metal consumption, EDI = estimated daily metal intake of the population/day/kg body weight, CSF = oral cancer slope factor in (mg/kg/day), and n = number of heavy metals considered for cancer risk calculation. Cr, Ni, As, Pb, and Cd CSF levels were 0.5,1.7,1.5,0.38, and 0.01mg/kg/day, respectively [13]. The acceptable limits for single carcinogenic metals and multiple carcinogenic metals are 106 and 104, respectively [14].

2.10 Data Analysis

Analysis of data obtained in the study was done using descriptive and inferential statistical methodologies in the SPSS Statistics software package. One-way analysis of Variance (ANOVA) and Student's T-test were used to test for significant difference ($p=0.05$) in concentrations of heavy metals across sampling locations and seasonal variations.

3. Results

3.1 Heavy metal concentrations in soils in dry and wet seasons

Table 2 shows data on heavy metal concentrations during the wet and dry seasons. Mean values of Zn in test soil during the dry season ranged from 7.34-13.37 mg/kg, Pb from 4.53-5.87 mg/kg, Cd from 1.78-2.85 mg/kg; Ni from 5.09-6.02 mg/kg, Mn from 103.60-

149.1 mg/kg and Cu from 3.51-6.96 mg/kg. The concentration of Zn, Pb, Cd, Ni, Mn and Cu in the control soil ranged from 7.01-7.90 mg/kg, 3.84-4.61 mg/kg, 1.34-1.93 mg/kg, 5.31-6.86 mg/kg, 49.17-65.88 mg/kg and 3.61-3.67 mg/kg. Mean values of Zn in test soil during the wet season ranged from 6.06-11.39 mg/kg, Pb from 3.68-5.39 mg/kg, Cd from 1.68-3.11 mg/kg; Ni from 4.29-5.62 mg/kg, Mn from 101.05-156.51 mg/kg and Cu from 2.77-3.70 mg/kg. The concentration of Zn, Pb, Cd, Ni, Mn and Cu in the control soil ranged from 5.34-5.79 mg/kg, 4.35-4.61 mg/kg, 1.27-1.92 mg/kg, 5.13-6.49 mg/kg, 59.23-64.65 mg/kg and 1.99-2.49 mg/kg.

Table 2: Heavy metal levels in soils in the farm sites of the study area during dry and wet seasons

Location/Nature of Farm Soil	Zn (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Ni (mg/kg)	Mn (mg/kg)	Cu (mg/kg)
Dry Season (mean value ± SE)						
Elele Top Soil	10.37 ± 0.78 ^{a}	5.63 ± 0.43 ^{b}	2.39 ± 0.25 ^{a}	5.93 ± 0.35 ^{b}	149.1 ± 7.25 ^{b} (88.40 –	4.12 ± 0.45 ^{b}
Elele Sub-Soil	9.66 ± 0.63 ^{b}	4.57 ± 0.32 ^{b}	2.41 ± 0.29 ^{a}	5.35 ± 0.25 ^{b}	136.54 ± 10.70 ^{b}	3.25 ± 0.29 ^{b}
Ibaa Top soil	8.86 ± 0.22 ^{b}	5.87 ± 0.65 ^{a}	2.85 ± 0.99 ^{b}	6.02 ± 0.65 ^{b}	118.80 ± 32.48 ^{b}	6.72 ± 0.63 ^{a}
Ibaa Sub-soil	7.34 ± 0.62 ^{b}	5.45 ± 0.13 ^{b}	2.28 ± 0.60 ^{b}	5.55 ± 1.01 ^{b}	104.16 ± 36.97 ^{b}	6.96 ± 1.42 ^{a}
Ogbodo Topsoil	13.37 ± 0.09 ^{a}	4.69 ± 0.34 ^{a}	2.74 ± 0.44 ^{a}	5.81 ± 0.33 ^{b}	145.27 ± 8.58 ^{b}	3.67 ± 0.36 ^{b}
Ogbodo Sub-soil	10.00 ± 3.07 ^{b}	4.53 ±1.23 ^{b}	1.78 ± 0.51 (1.27 –	5.09 ± 0.38 ^{b}	103.60 ± 4.94 ^{b}	3.51 ± 0.27 ^{b}
Control Top soil	7.01 ± 1.17 ^{b}	4.61 ± 1.08 ^{b}	1.93 ± 0.37 ^{a}	6.86 ± 0.16 ^{b}	65.88 ± 15.04 ^{a}	3.61 ± 0.48 ^{b}
Control Sub-soil	7.90 ± 0.57 ^{b}	3.84 ± 0.28 ^{b}	1.34 ± 0.30 ^{b}	5.31 ± 0.09 ^{b}	49.17 ± 10.95 ^{a}	3.67 ± 0.36 ^{b}
Wet Season (mean value ± SE)						
Elele Top Soil	11.39 ± 2.77 ^{a}	5.39 ± 0.49 ^{a}	2.43 ± 0.25 ^{a}	5.62 ± 0.44 ^{b}	124.95 ± 17.83 ^{b}	3.70 ± 0.31 ^{b}

Elele Sub-Soil	8.51 ± 2.00 ^{b}	4.21 ± 0.29 ^{b}	1.90 ± 0.21 ^{b}	4.46 ± 0.30 ^{b}	112.19 ± 15.28	2.77 ± 0.11 ^{b}
Ibaa Topsoil	6.87 ± 0.73 ^{b}	5.28 ± 0.66 ^{b}	3.11 ± 0.94 ^{b}	5.10 ± 0.48 ^{b}	156.51 ± 7.92 ^{b}	3.57 ± 0.86 ^{b}
Ibaa Sub-soil	6.06 ± 0.71 ^{b}	4.54 ± 0.56 ^{b}	2.23 ± 0.7 ^{b} (0.82 –	4.29 ± 0.51 ^{b}	128.74 ± 2.48 (126.25 –	1.99 ± 0.26 ^{b}
Ogbodo Topsoil	10.27 ± 1.87 ^{b}	4.49 ± 0.27 ^{a}	2.37 ± 0.44 ^{b}	5.33 ± 0.53 ^{b}	123.86 ± 14.99 ^{b}	3.54 ± 0.37 ^{b}
Ogbodo Sub-soil	8.73 ± 1.22 ^{b}	3.68 ± 0.21 ^{b}	1.68 ± 0.15 ^{b}	4.58 ± 0.44 ^{b}	101.05 ± 11.94 ^{b}	2.97 ± 0.32 ^{b}
Control Top soil	5.34 ± 0.02 ^{b}	4.61 ± 1.08 ^{b}	1.92 ± 0.35 ^{a}	6.49 ± 0.32 ^{b}	64.65 ± 10.99 ^{a}	2.49 ± 0.36 ^{b}
Control Sub-soil	5.79 ± 0.79 ^{b} (5.70 –	4.35 ± 0.62 ^{b} (3.73 –	1.27 ± 0.29 ^{a} (0.12–	5.13 ± 0.11 ^{b} (5.02 –	59.23 ± 4.74 ^{a} (49.84 – 65.05)	1.99 ± 0.26 ^{b} (1.52 –
F-value	17.261	6.370	32.844			
P-value	P = 0.006	P = 0.045	P = 0.000	P > 0.05		
DPR	**140**	**85**	**0.8**	**35**	**-**	**36**
****WHO**	**50**	**85**	**0.8**	**35**	**-**	**10**
TCL	**-**	**5**	**-**	**-**	**-**	**-**

3.2 Heavy metal concentrations in selected plants during dry and wet seasons

Table 3 shows the results of heavy metal concentration in selected crops. Mean values of Zn in test plants during the dry season ranged from 13.26-69.30 mg/kg, Pb from <0.001-6.61 mg/kg, Cd from <0.001-0.51 mg/kg; Ni from 0.36-1.99 mg/kg, Hg <0.001 mg/kg, Mn from 13.14-139.74 mg/kg and Cu from 1.94-6.59 mg/kg. The concentration of Zn, Pb, Cd, Ni, Hg, Mn and Cu in the control soil ranged from 712.06-30.76 mg/kg, <0.001-4.74 mg/kg, 0.13-0.56 mg/kg, 0-2.86 mg/kg, <0.001 mg/kg, 14.53-109.93 mg/kg and 1.55-7.29 mg/kg. Mean values of Zn in test plants during the wet season ranged from 8.40-42.65 mg/kg, Pb from <0.001-5.19 mg/kg, Cd from 0.13-0.49 mg/kg; Ni from <0.001-1.15 mg/kg, Hg <0.001 Mn from 14.53-67.56 mg/kg and Cu from 1.28-5.48 mg/kg. The concentration of Zn, Pb, Cd, Ni, Hg, Mn and Cu in the control soil ranged from 18.56-32.20 mg/kg, <0.001-2.47 mg/kg, 0.17-0.38 mg/kg, <0.001 mg/kg, <0.001 mg/kg, 31.85-67.56 mg/kg and 1.54-7.53 mg/kg.

Table 3: Heavy metal levels in selected crops during dry and wet seasons

Location	Plant	Zn (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Ni (mg/kg)	Hg (mg/kg)	Mn (mg/kg)	Cu (mg/kg)

	Dry Season (mean value)							
Elele	Elephant	69.30	6.61	<0.001	1.99	<0.001	48.31	5.77
Ibaa		33.18	4.78	0.35	0.67	<0.001	32.17	3.56
Ogbodo		30.07	4.29	<0.001	0.46	<0.001	13.14	2.57
Control		24.25	4.31	0.30	1.79	<0.001	67.50	6.59
Elele	Independent	27.78	3.98	<0.001	1.66	<0.001	18.69	6.04
Ibaa		15.78	3.14	<0.001	1.32	<0.001	14.32	4.56
Ogbodo		13.26	5.18	<0.001	1.22	<0.001	16.36	4.97
Control		28.02	3.98	0.05	0.60	<0.001	89.50	3.85
Elele	Cassava	34.61	0.33	0.22	0.36	<0.001	31.82	2.58
Ibaa		17.95	<0.001	0.33	0.64	<0.001	65.08	2.43
Ogbodo		18.56	0.01	0.29	0.82	<0.001	21.95	1.94
Control		12.06	<0.001	0.13	0	<0.001	14.53	1.55
Elele	Stem-Leaf	27.31	0.81	0.37	0.64	<0.001	23.90	2.34
Ibaa		33.33	0.10	0.27	0.26	<0.001	57.91	2.62
Ogbodo		57.09	2.18	0.51	1.72	<0.001	139.74	3.89
Control		30.76	4.74	0.56	2.86	<0.001	109.93	7.29
	Wet Season (mean value)							
		Zn (mg/kg)	**Pb (mg/kg)**	**Cd (mg/kg)**	**Ni (mg/kg)**	**Hg (mg/kg)**	**Mn (mg/kg)**	**Cu (mg/kg)**
Elele	Elephant	8.40	<0.001	0.29	0.81	<0.001	24.11	1.28
Ibaa		10.87	<0.001	0.19	0.23	<0.001	34.66	1.93
Ogbodo		39.39	1.02	0.50	1.15	<0.001	45.05	4.03
Control		22.74	0.77	0.17	<0.001	<0.001	29.81	1.54
Elele	Independent	34.51	3.06	0.31	0.26	<0.001	16.62	4.15
Ibaa		42.65	1.68	0.46	<0.001	<0.001	45.26	5.48
Ogbodo		38.05	<0.001	0.29	0.33	<0.001	45.56	4.97
Control		31.52	2.47	0.38	<0.001	<0.001	31.85	7.53
Elele	Cassava	34.61	0.33	0.22	0.36	<0.001	31.82	1.55
Ibaa		17.95	<0.001	0.13	0.64	<0.001	14.53	2.43
Ogbodo		12.06	0.01	0.29	0.82	<0.001	21.95	1.94
Control		18.56	<0.001	0.33	<0.001	<0.001	65.08	2.58
Elele	Stem-Leaf	45.52	5.19	0.52	1.05	<0.001	61.41	3.19
Ibaa		27.29	<0.001	0.19	0.24	<0.001	27.80	3.40
Ogbodo		39.13	1.83	0.28	0.85	<0.001	67.56	2.87
Control		32.20	<0.001	0.24	<0.001	<0.001	61.30	2.46
WHO*		0.60	0.30	0.02	10	-	-	10

*WHO (1996) permissible limits of heavy metals in plants

3.3 Human Health Risk Assessment via Heavy Metals in Cassava Tuber

In conducting an assessment of the health risk of adults and children of Elele Alimini, Ogbodo, Ibaa and Etche (Control) due to the consumption of cassava products harvested from the impacted soils, estimated daily intake of metals (EDI), target hazard quotient (THQ) and health risk index (HRI) were calculated during both seasons and presented in Tables 4 and 5, respectively. Estimated Daily Intake were compared with the recommended daily intake of metals established by the Institute of Medicine for people between the ages of 15 to 70 years [15,16].

During the dry and wet seasons, EDI of Zn, Ni and Cu in cassava were below the RDI of 8.0 mg day^{-1} person-1, 0.5 mg day^{-1} person and 0.9 mg day^{-1} person, respectively. EDI of Pb and Cd were above the RDI of 0 mg day^{-1} person.

THQ values for Zn, Pb, Ni, Cu, Cd, and Mn in adults ranged from 4.02E-05 to 1.15E-04, 0.0 to 9.42E-05, 0.0 to 4.1E-05, 3.88E-05 to 6.45E-05, 1.33E-04 to 3.3E-04, and 1.04E-04 to 4.65E-04, respectively.

Hazard index of heavy metal intake via consumption of cassava by adult and children in test and control locations during dry season (Fig. 3) and wet season (Fig. 4). Hazard index of potential heavy metals pollution in adults and children during dry season showed values as (0.000739438 and 0.009464808), (0.00094744 and 0.012127238), (0.00060101 and 0.007692922) and (0.000312736 and 0.004003017) at Elele Alimini, Ibaa, Ogbodo and Control, respectively. In the same vein, hazard index of heavy metals consumed by adults and children during the wet season showed values as (0.000854978, 0.009464808), (0.001216022 and 0.012127238), (0.000738626 and 0.007692922) and (0.000373374 and 0.004003017) at Elele Alimini, Ibaa, Ogbodo and Control, respectively.

Table 4: Estimated Daily Intake and Target Hazard Quotient of Heavy Metal Intake from Cassava Tuber in Dry Season

Heavy metal	**Location -Dry Season**	**EDI Adult**	**THQ Adult**	**EDI Child**	**THQ Child**	**Recommended Daily Intake (RDI: mg day^{-1} person $^{-1}$) in cassava**
Zn	Elele Alimini	0.00003461	0.000115367	0.00044301	0.0014767	8.0
	Ibaa	0.00001795	5.98333E-05	0.00022976	0.0007659	
	Ogbodo	0.00001856	6.18667E-05	0.00023757	0.0007919	
	Control	0.00001206	0.0000402	0.00015437	0.0005146	
Pb	Elele Alimini	0.00000033	9.42857E-05	4.224E-06	0.0012069	0.00
	Ibaa	0	0	0	0	
	Ogbodo	0.00000001	2.85714E-06	1.28E-07	3.657E-05	
	Control	0	**0**	0	0	
Cd	Elele Alimini	0.00000022	0.00022	2.816E-06	0.002816	0.00
	Ibaa	0.00000033	0.00033	4.224E-06	0.004224	
	Ogbodo	0.00000029	0.00029	3.712E-06	0.003712	
	Control	0.00000013	0.00013	1.664E-06	0.001664	
Ni	Elele Alimini	0.00000036	0.000018	4.608E-06	0.0002304	0.5
	Ibaa	0.00000064	0.000032	8.192E-06	0.0004096	
	Ogbodo	0.00000082	0.000041	1.0496E-05	0.0005248	
	Control	0	0	0	0	
Mn	Elele Alimini	0.00003182	0.000227286	0.0004073	0.0029093	NS
	Ibaa	0.00006508	0.000464857	0.00083302	0.0059502	

	Ogbodo	0.00002195	0.000156786	0.00028096	0.0020069	
	Control	0.00001453	0.000103786	0.00018598	0.0013285	
Cu	Elele Alimini	0.00000258	0.0000645	3.3024E-05	0.0008256	0.9
	Ibaa	0.00000243	0.00006075	3.1104E-05	0.0007776	
	Ogbodo	0.00000194	0.0000485	2.4832E-05	0.0006208	
	Control	0.00000155	0.00003875	0.00001984	0.000496	

Table 5: Estimated Daily Intake and Target Hazard Quotient of Heavy Metal Intake from Cassava Tuber in Wet Season

Heavy metal	Location - Wet Season	EDI Adult	THQ Adult	EDI Child	THQ Child	Recommended Daily Intake
Zn	Elele Alimini	4.74E-05	0.000158	0.000443	0.00148	8.0
	Ibaa	2.46E-05	8.20E-05	0.000230	0.000766	
	Ogbodo	1.65E-05	0.0000551	0.000154	0.000515	
	Control	2.54E-05	8.478E-05	0.000238	0.000792	
Pb	Elele Alimini	4.52E-07	0.000129	0.0000042	0.00121	0.00
	Ibaa	0	0	0	0	
	Ogbodo	1.37E-08	3.91E-06	0.000000128	3.66E-05	
	Control	0	0	0	0	
Cd	Elele Alimini	3.01E-07	0.000301	0.00000282	0.00282	0.00
	Ibaa	1.78E-07	0.0001781	0.00000166	0.00166	
	Ogbodo	3.97E-07	0.0003973	0.00000371	0.00371	
	Control	4.52E-07	0.0004521	0.00000422	0.00422	
Ni	Elele Alimini	4.932E-07	0.0000247	0.000004608	0.000230	0.5
	Ibaa	8.768E-07	0.0000439	0.00000819	0.0004096	
	Ogbodo	1.123E-06	0.0000562	0.0000105	0.000525	
	Control	0	0	0	0	
Mn	Elele Alimini	4.36E-05	0.000311	0.000407	0.00291	NS
	Ibaa	1.99E-05	0.000142	0.000186	0.00133	
	Ogbodo	3.007E-05	0.000215	0.000281	0.00201	

	Control	8.916E-05	0.000635	0.000833	0.00595	
Cu	Elele Alimini	2.124E-06	5.31E-05	0.00001984	0.000496	0.9
	Ibaa	3.329E-06	8.33E-05	0.000031104	0.000778	
	Ogbodo	2.658E-06	0.0000664	0.000024832	0.0006208	
	Control	3.54E-06	0.0000884	0.000033024	0.0008256	

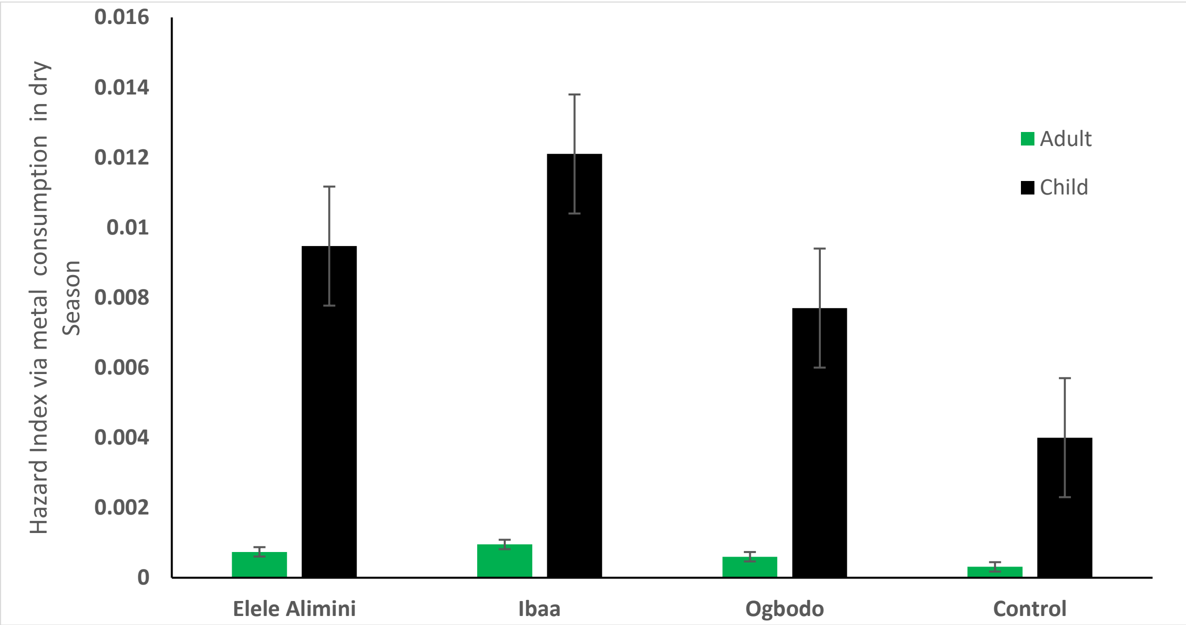

Fig. 3: Hazard index (± SE at 95% Confidence Level) of heavy metal intake via consumption of cassava by adults and children in test and control locations during the dry season

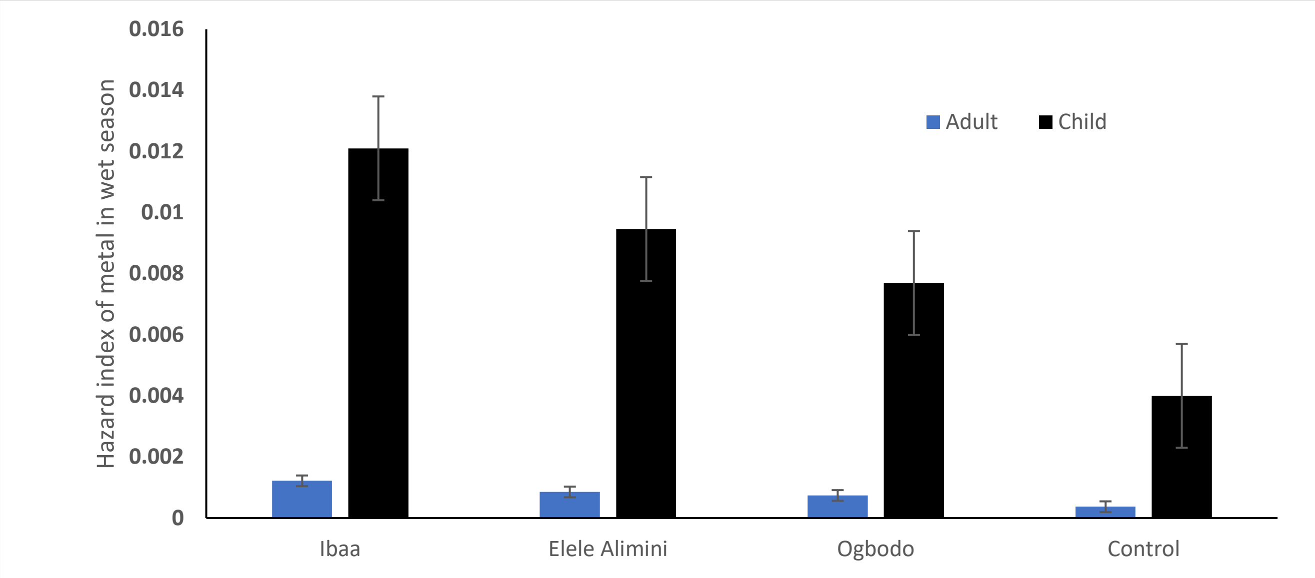

Fig. 4: Hazard index (± SE at 95% Confidence Level) of heavy metal intake via consumption of cassava by adults and children in test and control locations during the wet season

4. Discussion

This study assessed the heavy metal distribution in soils from the vicinity of an artisanal refining site in Rivers State, Nigeria. The distribution showed that heavy metal concentrations were lower in Control locations than in test locations, except for Ni and Mn, which showed slight disparity. In the distribution of heavy metal micro-pollutants in test soil samples and Control samples, there is a prevalent drop in concentrations of the trace metals at further soil depths (0 -15cm and 15 – 30cm) during both seasons, although with an exception to Zn, which depicted an increasing trend in the Control station. Cadmium also depicted an inverse or increasing trend at further soil depth (15 – 30cm) in the Control station only during the dry season. Aigberua [17] and Iwegbue [18] in their report gave higher fractional metal concentration in top soils (0 -15 cm) in comparison to the bottom soils (15-30 cm) for impacted soils in the region of the Niger Delta. However, the concentrations of potentially toxic metals in the test as well as the Control locations were within stipulated soil intervention limits of Zn (140 mg/kg), Pb (85 mg/kg), Cd (0.8 mg/kg), Cu (36 mg/kg), Ni (35 mg/kg) and Cd [19] and the heavy metal standard in soil; Zn (50 mg/kg), Pb (85 mg/kg), Cr (100 mg/kg), Cu (36 mg/kg), Ni (35 mg/kg) and Cd (0.8 mg/kg) [20]. Results revealed a considerable presence of heavy metals in the soil. This can be attributed copious use of chemicals with heavy metals in the course of petroleum production activities. Udoetok and Osuji [21] posited that these metals may be absorbed by plants, thus causing potential bioaccumulation impact on crops and animals depending on the plants for survival, hence, resulting in toxic effects on the food chain.

The mean concentration of Zn in the sampled soil was highest at Ogbodo Top soil (13.37 + 0.09 mg/kg), which was not statistically ($p > 0.05$) different from Elele Alimini Topsoil (10.37 + 0.78 mg/kg) and lowest in the Control Samples (7.01 +.17 mg/kg). Values were within the stipulated range of 1.00 to 900 mg/kg in soil [22], the WHO intervention value of(140mg/kg) and the DPR limit of 50 mg/kg. The concentrations of Zn obtained by Otaiku [23] (1.52-2.05 mg/kg) were lower than those obtained in this study. The report of Udoetuk et al. [24], 9.84 ± 0.93mg/kg, who measured heavy metal (Zn) concentrations in an oil spill site in the Niger Delta region of Nigeria, conformed with this report. Zinc is required in our diet. Nwankwo et al. [25] measured higher values of Zn above standard limits (50mg/kg) in the range of 33.2 to 235.98mg/kg values while analysing oil-impacted soil at Akinima, Rivers State, Nigeria. Too little zinc might cause issues, but too much zinc can also be dangerous. Harmful effects typically begin at levels 10 to 15 times higher than what is required for healthy health. Large amounts taken by mouth, even for a short period of time, might produce stomach cramps, nausea, and vomiting. If taken for an extended period of time, it can induce anaemia and lower your good cholesterol levels. Although it is unknown whether high zinc levels affect human fertility, rats fed substantial doses of zinc were infertile [26]. Inhaling significant amounts of zinc (as dust or fumes) might result in a short-term sickness known as metal fume fever. Zinc is a contaminant in locations near petroleum processing plants.

The level of lead in test locations (soils) was lower than in the Control. The highest lead concentrations were found in Ibaa during the dry season and Elele Alimini during the wet season. The values at Ibaa in the dry season and Elele Alimini in the rainy season were statistically ($p < 0.05$) different; however, both were within the WHO intervention limit (85mg/kg) for agricultural soil. These findings are above the toxicity characteristic leachate limits (TCL) for lead of 5.00 mg/kg [22]. Waste products from the usage of chemicals such as pipe lax, lube 106, and other lubricants, such as diesel oil used in the manufacturing of petroleum contaminated soils with lead. Although lead has been reported to be hazardous to many plant species although a few relatively tolerant species exist. When lead is consumed, it develops a sickness known as plumbism. When exposed to lead, the brain, central nervous system, kidneys, liver, and reproductive system are all jeopardised [27]. Lead has no biological function and may be hazardous to microorganisms [25,28].

The concentrations of copper (Cu) were highest at Ibaa and lowest in the Control (uncontaminated soil samples). Values were within the normal ranges required by plants for a natural soil concentration (5.10 to 49.80 mg/kg), Bowen [22]; DPR intervention values of 30mg/kg and WHO limits of 10mg/kg. This study showed Cu values that were higher than those presented by Udoetuk et al. [24] (0.32 ± 0.07mg/kg) and less than those of Adewuyi et al. [29] (5.00 to 35.28 mg/kg). Copper levels are often greater in volcanic rock soils and lower in extremely acidic soils.

Some of these heavy metals (Cu, Zn, Fe, Mn, Mo, Ni, and Co) are recognised to be important for plant and animal growth, but only at trace levels over which they become poisonous [30]. Zinc concentrations in selected crops during the dry season were highest (69.3mg/kg) in elephant grass at Elele Alimini and lowest (0.19mg/kg) in cassava tuber at Ibaa. Spatially, on the other hand, in the wet season, Zn was highest (45.52mg/kg) in stem leaf cassava at Elele Alimini and lowest (8.40 mg/kg) in the same location in elephant grass. Concentrations of Zn in plants of the study area were within the FAO/WHO acceptable limit of 99.4mg/kg. Zn transfer factor from soil to the plants was> 1 except for cassava tuber in the dry season at Elele (0.66), Ibaa (0.04), Ogbodo (0.91), Control (0.87) season and Elephant grass at Elele (TF = 0.65) and Ibaa (TF = 0.84) in the wet season.

Toxicological risk associated with heavy metals was analysed by comparing it to legal limits and estimating dietary intake and non-carcinogenic risks in cassava tuber eaters from study and control sites. During the dry and wet seasons, EDI of Zn, Ni and Cu in cassava were below the RDI of 8.0 mg day^{-1} person $^{-1}$, 0.5 mg day^{-1} person $^{-1}$ and 0.9 mg day^{-1} person $^{-1}$ respectively. EDI of Pb and Cd were above the RDI of 0 mg day^{-1} person $^{-1}$.

The THQ was calculated to estimate the health risk of metal(oid) ingestion through cassava consumption for both Adult and Child residents of the study area. The THQs of Zn, Pb, Ni, Cu, Cd, and Mn were found to be less than unity in cassava consumed in all locations. THQ values for Zn, Pb, Ni, Cu, Cd, and Mn in adults ranged from 4.02E-05 to 1.15E-04, 0.0 to 9.42E-05, 0.0 to 4.1E-05, 3.88E-05 to 6.45E-05, 1.33E-04 to 3.3E-04, and 1.04E-04 to 4.65E-04, respectively, indicating the serious potential health risks associated with these elements. The risk posed in the consumption of cassava was significantly higher in Children than in Adults from the data obtained. Baghaie and Fereydoni [31] found greater THQ levels in a comparable investigation involving coriander and lettuce. THQs for V, Cr, Ni, Cd, and Pb were discovered to be less than one.

In both seasons, the hazard index of heavy metal intake via consumption of cassava by adults was much more than for Children. However, the hazard index was less than unity, implying no serious health risk concern due to heavy metals.

Conclusion

Data showed that during wet and dry seasons, EDI values for all metals fell within the recommended reference oral dose except for the EDI Pb and Cd in adults and Children at Elele Alimini, Ibaa and Ogbodo. In both seasons, the hazard index was less than unity, implying no serious health risk concern due to heavy metal consumption via cassava. The risk posed by heavy metals via consumption of cassava was significantly higher in Children than in Adults from the data obtained in both seasons.

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