JCHR (2021) 11(1), 1-15

Journal of Chemical Health Risks

www.jchr.org

ORIGINAL ARTICLE

Petroleum Hydrocarbons and Heavy Metals Risk of Consuming Fish Species from Oguta Lake, Imo State, Nigeria

Verla Andrew Wirnkor[1], Opara Alexander Iheanyichukwu[2], Enyoh Christian Ebere[*1],Verla Evelyn Ngozi[3], Ohazurike Natheniel C[4] , Okoro U. Kingsley[5], Ibe Francis Chizoruo[1], Ahuocha Pauline Amaka [6]

[1]Group Research in Analytical Chemistry, Environment and Climate Change (GRACE & CC),
Department of Chemistry, Faculty of Science, Imo State University Owerri, P. M. B 2000, Imo State, Nigeria
[2]Department of Geology, Federal University of Technology Owerri, Imo State, P. M. B. 1526, Nigeria
[3]Department of Environmental Technology, Federal University of Technology Owerri, Imo State, P. M. B. 1526, Nigeria
[4]Department of Crop Science and Biotechnology, Faculty of Agriculture, Imo State University Owerri, Imo State, P. M. B 2000, Nigeria
[5]Department of Physics, Faculty of Science Imo State University Owerri, P. M. B 2000, Imo State, Nigeria
[6]Department of Microbiology, Faculty of Science Imo State University Owerri, Imo State, P. M. B 2000, Nigeria

(Received:10 February 2019 Accepted: 7 October 2020)

KEYWORDS

Assessment;
Health;
Permissible levels;
Pollution;
Hazard Quotient

ABSTRACT: Oguta lake has experienced lots of oil spills and heavy metals and petroleum hydrocarbons could constitute fish contaminants. In order to assess the potential danger associated with consumption of fish from the lake by children and adults the current research was conducted. 6 g of each fish species from the lake were homogenized and divided into two portions. One was digested with aqua-regia while the other was extracted with hexane using a soxhlet extractor. Extracts were analyzed for heavy metal and hydrocarbons concentrations with AAnalyst Perkin Elmer 400 AAS and Buck 530 GC respectively. Data was interpreted with pollution and risk assessment models. Results revealed that except for Hg and Ni all other metals were below permissible levels by Food and Agricultural Organization (FAO). Estimated dietary intakes (EDI mg/kg day^{-1}) were high in children (110.157) for *C. spectaculurus* to (25.212) for *H. fossilis* while adult (18.885) *C. spectaculurus* to (7.951) for *H. fossilis*. EDI varied for children (Fe > Hg > Zn > Ag > Pb > Ni > Cu > Cd) and (Fe > Zn > Hg > Ag > Pb > Ni > Cu > Cd) for adults. Target Hazard Quotient (THQ) was highest for Cd in both adults and children. Total petroleum hydrocarbon (µg/l) was high in *O. leucosticus* (11113755.94) > H. fossilis (40210.66) > C. spectaculums (35184.44) > *M. salmoides* (6373.27). Fish species from Oguta lake could constitute a health risk with significant potential carcinogenic risk both in children and adults as estimated from fish consumption.

INTRODUCTION

The presence of Shell Petroleum Development Corporation (SPDC) and Nigerian Agip oil Company (NAOC) within Oguta Lake vicinity could be a major source of both petroleum hydrocarbons and heavy metals in waters of when found in the water considers fish and other aquatic life will be expose to some level of risk

---

*Corresponding author: cenyoh@gmail.com (E. Christian Ebere)

DOI: 10.22034/jchr.2020.584959.1017

resulting from petroleum hydrocarbons and heavy metal contaminants. There are reports of incessant oil spill and the count is well over 500 oil spills since 1960 when oil exploration and exploitation began in the area [1]. Recently oil spills at Umuezechi farmlands have been attributed to ruptured pipelines due to aging as opposed to NAOC's claim of sabotage. Records show more than 3 million barrels lost with 60% of the oil spills taking place off-shores. However researchers claim that these are due to criminal activities rather than accident [2]. Whatever the cause of these spills the effects do not select between sabotage and natural cause and so urgent attention is needed. Contaminants and toxic substances abound in crude oil.

Heavy metal contamination has been identified as a major environmental problem arising from industrialization, urbanization and anthropogenic sources. The activities around the lake have been known to impact negatively on the water. Dumping of refuse, construction, transportation and social activities all leave huge amounts of water in the lake. Oguta lake is one of the largest lakes in the state and receives visitors from all over the Nigeria and beyond. Therefore potential pollution that could hurt aquatic life is eminent [3]. Odoemelam have reported some heavy metals content of rivers is as a result of industrial effluents [4] in some Nigerian cities. It was ascertained that metal toxicity arise due to organisms mobility to cope with excess body levels of metals [5]. Other researchers have identified some metal toxic at low concentrations while others are toxic at elevated concentration [5-7].

A mixture of hydrocarbon compounds found in crude oil can be referred to as total petroleum hydrocarbon (TPH) and is easily analyzed by gas chromatography after extraction with appropriate solvents. Compounds grouped together from large groups of organic compounds that are found in TPH. Many of these compounds have public health concerns such as carcinogens, mutagens presence of oxygenated neutral nature [7].

Cadmium and other metals have been fingered in cancer inducement; it is thought that the presence of organic carcinogens and inorganic carcinogens could be synergistic in action or complementary to a level that spelt danger for consumers of fish that accumulate these pollutants [8]. Therefore the present research was to analyze fish species from aquatic lake for the presence of heavy metals and hydrocarbons with a view to assessing the potential toxicity to both children and adults.

Everyone is exposed to TPH from many sources, including gasoline pumps, spilled oil on pavement, and chemicals used at home or work. Some TPH compounds can affect your nervous system, causing headaches and dizziness. TPH has been found in at least 23 of the 1,467 National Priorities List sites identified by the Environmental Protection Agency [7].The people within the surrounding villages of Oguta (Orsu Obodo, Nkwesi and Awo Omama) use the lake as a source of water, fish, tourism, marine transport and also as an outlet for sewerage. There is thus possible pollution of the lake in a manner that could be dangerous to both aquatic life and humans. Health risk assessment models have been developed basically in Europe and in the United States and are now being used worldwide [9]. Comparing Legal limits for hazardous substances in fish and fish products, an assessment of risk can be made. According to [9] risk is a multi-step procedure. It comprise of collection of data, assessment of exposure, and toxicity. Such analysis are lacking in Nigeria. And so we set out here to contribute in risk assessment.The aim of this study was therefore to determine if the concentrations of Fe, Cr, Ag, As, Hg, Pb, Cd, Cu, Ni, Zn and petroleum hydrocarbons in fish from Oguta lake and the assess the potential toxicity associated with consumption of fish species and finally determine the risk of consuming fish species caught from the lake. It is expected that baseline data, contamination factors and models such as estimated dietary intake and Target hazard quotient could assist in determining the level of remediation needed by polluted lake and aquatic products over time. Thus the health implication of this research is obvious.

MATERIALS AND METHDS

Site description

Oguta lake is located at coordinates 5’42’24”N 6”47’33”E.Oguta oil field was chosen because the area has a history of oil spills from the oil fields mentioned above as well as some human activities that pose health hazard to the community.

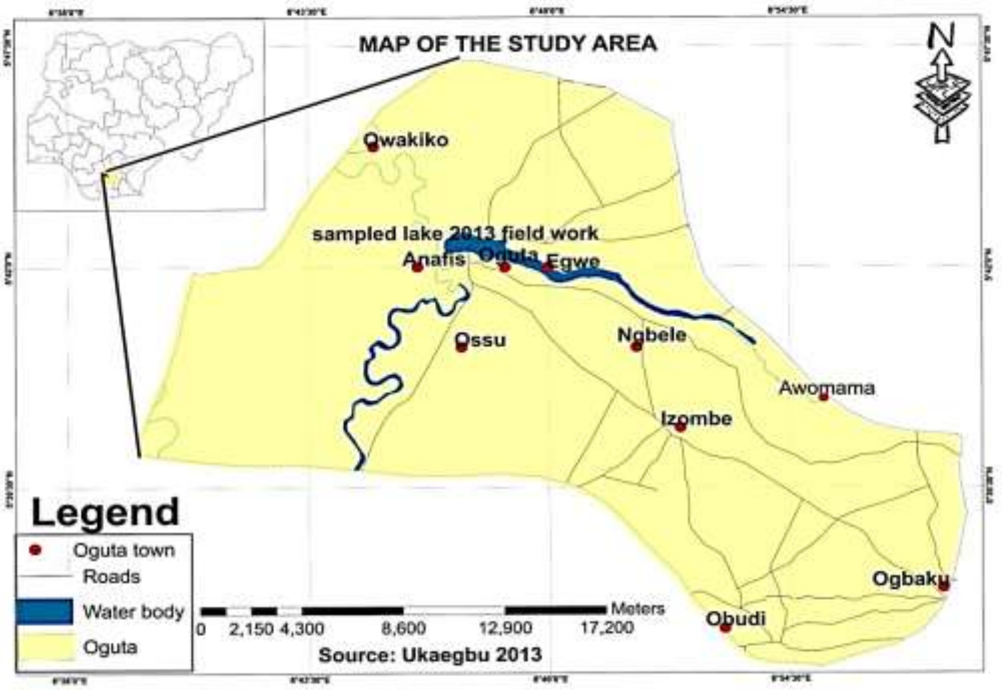

Figure 1. Map of Oguta lake and adjoining communities

Sample collection

Fish was bought from fishermen at the bank of the lake (at various sampling points). Samples were collected in triplicates from 3 different sampling sites along Oguta, Egbema and Orsu. Four fish species *O. leucostictus, H. fossilis, M. salmoides* and *C. spectaculurus* were bought from fishermen at the bank of the lake and identifications done by the experts in fish and fish products at the department of agriculture, Imo state Nigeria. Three samples of each fish species were analyzed to give a total of 12 fish samples.

Digestion of fish samples

3g of each fish sample was accurately weighed after pulverization and homogenization. The homogenized samples were weighed into the digestion tubes. 10ml conc. H_2SO_4 and 5ml conc. HNO_3 was added. The sample was digested and its volume was reduced to 2 cm^3. The digestion was continued until the solution was colourless. This ensured the removal of all HNO_3.The sample was allowed to cool and 15 ml of water was added with gentle swirling. 1 M NaOH was added dropwise until a pink tinge, brown or colourless solution was produced. The solution was filtered using a Whatman filter paper No.42 followed by dilution to the mark in a 25ml volumetric flask. The digested fish samples were analysed for Pb, Cd, Fe, Cu, Zn, Ag, Ni, As and Hg concentration using AAnalyst Perkin Elmer 400 Atomic Absorption Spectrophotometer. All determinations were carried out in triplicate and reported as heavy metal concentration in parts per million.

Method of PHC determination

The fish samples were dissected and soft tissue wrapped in aluminum foil, sealed and packaged in thick polythene bag with zip and pressure at -20 ^oC awaiting analysis [7]. The tissue was latter thawed and homogenized and saponified with KOH- methyl alcohol mixture. The mixture was centrifuge at 3000 rpm and then filtered. The filtrate was extracted with n-hexane (using soxhlet extractor at a temperature of 50-60 ^oC for 4hrs) and the organic layer washed with distilled water and evaporated to a small volume which was chromatographed on alumina using Buck 530 Gas Chromatograph.

The samples were carefully injected using a 10 µL syringe (by carefully piercing the septum in the inlet) following the sandwich injection technique. After injection, acquisition was started immediately to get accurate retention times. The Buck 530 Gas Chromatograph used was equipped with an on-column, automatic injector, Electron capture detector, and HP 88 capillary column (100 m x 0.25 µm film thickness). The detector temperature was set at 280 ^{o}C, column temperature was set at 210 ^{o}C, and injector temperature was set at 250 ^{o}C while the integrated chart speed was set at 2 cm/min. The chromatograms were interpreted using tabulated standards. Blank samples were run in the same way as the samples to check for accuracy.

Determination of heavy metals

This was done by the use of AAnalyst Perkin Elmer 400 Atomic Absorption Spectrophotometer. Heavy metal pollution index of the water and fish were calculated by averaging the ratios of the heavy metal concentrations to their permissible level.

AAnalyst Perkin Elmer 400 Atomic Absorption Spectrophotometer with acetylene gas was used in the determination of the heavy metal absorbance. Concentration of each metal was calculated with reference to a standard curve. Calibration of the instrument was done by preparing standard solutions of the metal in concern by diluting their Certified Reference Material (CRM). The standard concentration prepared were 0.1 mg/l and 0.01 mg/l for the points to draw the calibration curve. Instrumental conditions with Signal output of 90 % and above was considered good for analysis.

Statistical analysis

Analytical Quality Assurance (AQA)

All glasswares were soaked overnight in 10% (v/v) nitric acid, followed by washing with 10% (v/v) hydrochloric acid and rinsed with double deionized water and dried before use. All other quality control measures were carried out according to [10].

Data obtained from this study were analyzed using the statistical package for social sciences (SPSS) version 18.0 for windows. Statistical analysis was carried out to show correlation details where appropriate and values were considered significant at $p< 0.05$. The concentrations of heavy metals in various matrices are presented as arithmetic mean with standard error (mean ± SE) and results are presented in tables.

RESULTS AND DISCUSSION

Petroleum Hydrocarbon

Table 1 shows the various petroleum hydrocarbons that were detected in the fish samples. The values ranged from octane (0.360 µg /ml) in *leucostictus* specie to decane (11112309.012 µg/ml) in same fish species. It was observed that 11 hydrocarbons were detected in *C. spectaculurus*, 6 in *M. salmoides*, 10 in *O. leucostictus* and 7 in *H. fossilis*. This suggests that the fish species were were good reservoir for hydrocarbons. Petroleum hydrocarbons are of concern for three main reasons: firstly, low molecular weight petroleum hydrocarbons can be directly toxic to marine animals; secondly, because metabolites of some of the high molecular weight hydrocarbons are potent animal and human carcinogens; thirdly, low molecular weight petroleum hydrocarbons can cause taint in the fish resulting in consumer rejection of the product and an associated loss in consumer confidence which is an obvious impact on the fish industry.

Table 1. Concentration of hydrocarbons in fish samples

Carbon chain	**Hydrocarbon**	**Concentrations (µg/kg)**			
		O. leucostictus	***H. fossilis***	***M. salmoides***	***C. spectaculurus***
C_8	Octane	ND	312.68	0.36	259.08
C_{12}	Dodecane	1007.27	ND	11112309.0	ND
C_{14}	Tetradecane	ND	352.622	ND	ND
C_{15}	Pentadecane	ND	ND	ND	2655.04

C_{17}	Heptadecane	ND	1461.37	179.00	ND
C_{18}	Octadecane	2202.94	ND	70.27	ND
C_{19}	Nonadecane	ND	ND	294.39	26.66
C_{20}	Eicosane	ND	ND	ND	ND
C_{21}	Heicosane	ND	ND	283.78	ND
C_{23}	Tricosane	2781.18	ND	15.709	ND
C_{24}	Tetracosane	544.26	ND	ND	ND
C_{26}	Hexacosane	ND	1863.32	ND	ND
C_{27}	Heptacosane	ND	ND	305.48	ND
C_{28}	Octacosane	ND	ND	3.49	ND
C_{29}	Nonacosane	2462.36	2224.87	294.44	ND
C_{31}	Hentriacotane	22542.99	ND	ND	ND
C_{32}	Dotriacotane	1194.06	ND	ND	813.22
C_{34}	Tetratriacotan	788.95	ND	ND	26999.5
C_{36}	Hexatriacosane	233.17	ND	ND	ND
C_{37}	Heptatriacosane	892.02	ND	ND	ND
C_{38}	Octatriacotane	535.24	ND	ND	4355.29
C_{39}	Nonatriacosane	ND	158.41	ND	5101.79
TPH		11113755.9	40210.66	6373.27	35184.44

ND: Not detected, TPH: Total petroleum hydrocarbon

Petroleum hydrocarbons have been particularly studied as an important pollutant due to their toxicity as mutagens, carcinogens and nervous system toxicant. Veerasingam and coworkers [11] proposed that *S. Longiceps* could be used as a good biological indicator for PHC pollution of water. Except for *M. salmoides* all other fish species studied could be used as biological indicators. The order of H.C concentrations in fish species decrease in the order; *O. Leucostictus* (1113755.94 µg/kg) > *H. fossilis* (40210.66 µg/kg) > *C. spectaculurus* (35184.44 µg/kg) > *M. salmoides* (6373.27 µg/kg). Various hydrocarbons groups are capable of causing stress to aquatic organisms and subsequent death [12-13]. Grouping fish species according to presence of carbon group/ hydrocarbon concentration revealed the following groups *O. leucosticus* appeared on six groups. It was most contaminated species with hydrocarbons.

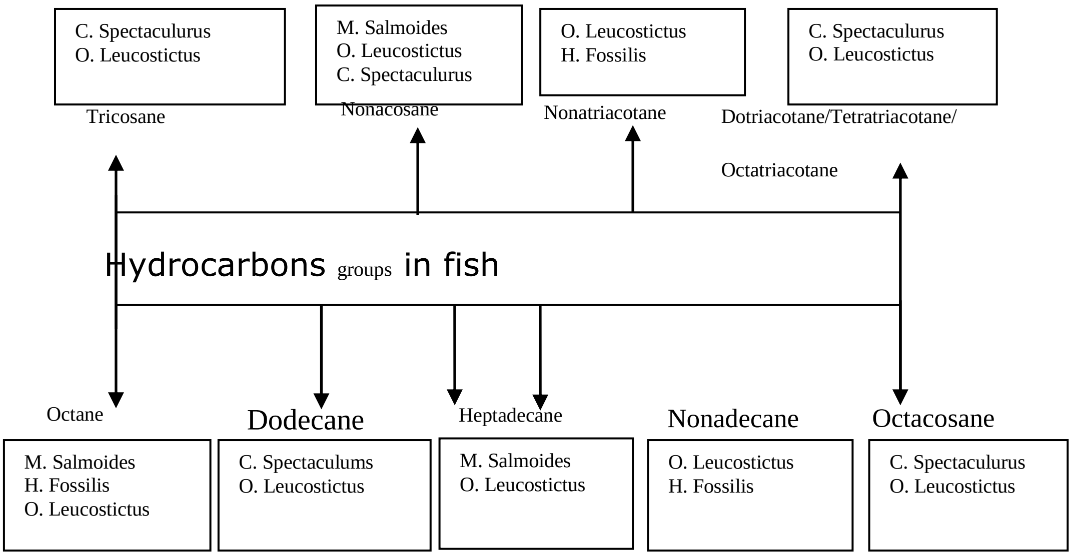

Figure 2. Groups of fish species with similar predominant hydrocarbon

A careful assessment of figure 2 shows that there groups had some relevance with water and sediments. For instance heptadecane group had high concentrations of PHC in water (4549.176 µg/ml) and sediment (71341.44 µg/ml) while the nonacosane group showed sediments (24611.34 µg/ml) rich in PHC to have PHC of the heptadecane, eicosane and tetracosane while other hydrocarbons were below detection limits. PHC in the order 0.1 – 10 µg/kg in marine fish is typically while values of 10 – 1000 times higher are typical for fish in polluted water [7, 13].The concentration of PHC in this study revealed that all fish samples at all sampling locations were high than hazardous levels should be a public health concern.

Table 2. Mean concentration (mg/kg) of some heavy metals in fish samples with corresponding permissible limit.

Metals	*O. leucostictus*	*H. fossilis*	*M. salmoides*	*C. spectaculurus*	PL
Fe	17.436±0.854	8.201±0.547	19.650±0.823	48.535±7.415	48.000
Cu	0.609±0.059	0.287±0.135	0.419±0.154	0.321 ±0.06	10.000
Zn	6.167±0.646	3.856±0.752	7.102±1.134	6.177±0.694	40.000
Cr	ND	ND	ND	ND	1.000
Ag	2.013±0.530	0.656±0.195	0.522±0.102	0.619±0.020	NF
Ni	0.482±0.204	0.360±0.186	0.118±0.019	0.471±0.179	0.140
Pb	0.523±0.122	0.273±0.059	0.399±0.083	0.701±0.031	1.500
As	0.167±0.079	0.529±0.138	0.371±0.102	0.733±0.106	1.000
Hg	13.137±0.615	12.510±1.27	7.650±0.953	5.937±1.071	1.000
Cd	0.471 ±0.174	0.069±0.057	0.488±0.267	0.058±0.029	0.500

Bioconcentration factors (BCF)

Bioconcentration factors estimates the amount of metal that is possibly stored in a fish due to accumulation [14]. Various metals have different potentials of being stored in the fish to become toxic and so the permissible levels define some level at which the metal is not toxic. Therefore expressing the metal concentration determinant in fish as a factor of the permissible limits can enable the fish species to be ranked according to their tendency to accumulate a particular metal.

$$\boldsymbol{BCF} = \frac{\boldsymbol{Concentration\ of\ metal\ in\ fish}}{\boldsymbol{Permissible\ limit\ for\ the\ metal}} \times 100 \quad (2)$$

Toxicity index (TL)

Heavy metal toxicity index (HMTI) of the fish samples were estimated by averaging the ratios of metal concentration to assumed permissible levels for each metal divided by the total number of heavy metals analyzed [15]. The mathematical expression used is;

$$\mathrm{HMTI} = \frac{[\boldsymbol{Fe}]}{\boldsymbol{PL}} + \frac{[\boldsymbol{Cu}]}{\boldsymbol{PL}} + \frac{[\boldsymbol{Zn}]}{\boldsymbol{PL}} + \frac{[\boldsymbol{Ni}]}{\boldsymbol{PL}} + \frac{[\boldsymbol{Pb}]}{\boldsymbol{PL}} + \frac{[\boldsymbol{As}]}{\boldsymbol{PL}} + \frac{[\boldsymbol{Hg}]}{\boldsymbol{PL}} + \frac{[\boldsymbol{Cd}]}{\boldsymbol{PL}}/7 \quad (3)$$

The mean toxicity index of the various samples of fish species was calculated and contribution by each metal in a species of fish was expressed as a percentage. The HMTI followed the pattern as metal concentrations, as follow: $\mathrm{HMTI}_{\mathrm{OL}} > \mathrm{HMPI}_{\mathrm{HF}} > \mathrm{HMPI}_{\mathrm{CS}} > \mathrm{HMPI}_{\mathrm{MS}}$

Table 3. Bioconcentration factors and toxicity index of fish from Oguta lake

Metals	*O. leucostictus*	*H. fossilis*	*M. salmoides*	*C. spectaculurus*
	Bioconcentration factors in of fish species			
Fe	36.33	17.10	40.90	101.10
Cu	60.90	28.70	41.90	32.1 0

Zn	15.40	9.64	17.80	15.40
Cr	0.00	0.00	0.00	0.00
Ag	2.01	0.66	0.52	0.62
Ni	344.30	257.10	8.43	336.40
Pb	34.90	0.18	0.27	0.47
As	16.70	0.53	0.37	0.73
Hg	1313.70	1251.00	765.00	593.70
Cd	94.20	13.80	97.60	11.60
Toxicity index of fish species				
HMTI	2.068	1.803	1.193	1.313

Heavy metal Risk assessment

Estimated Dietary Intake (EDI)

The EDI of metals in fish after consumption was calculated using the mathematical expression

$$\text{EDI (ug/kgbw)/day)} = (MIxCM)/BWA \qquad (4)$$

MI= mass of fish ingested per day, CM = concentration of metal in fish, BW = body weight for average adult is 70 kg. The mass of the fish ingested per day in Nigeria is 7.6 kg which is equivalent to 20.8 g per day. In the case of children the mass of BWC was taken as 12 kg. RFD = oral reference dose. This is an estimate of daily exposure to human population that is likely to be without an appreciable risk of deleterious effect during life time. Some oral reference dose include Pb 1.5 (mg/kg/day), Cd 0.001 (mg/kg/day), Fe 0.7 (mg/kg/day) while USEPA [16] recommends Cu 4.0 mg/kgBWday^{-1} , Zn 30 mg/kgBWday^{-1}, Ni 2.0 mg/kgBWday^{-1}.

Table 2 shows the provisional tolerable daily intake in adult and children who consumed fish species from Oguta Lake *C. spectaculus* showed highest daily dietary intake amongst all fish species with up to 83.13 mg/kg/Bw/day in children , while adults EDI had 14.422 mg/kgBWday^{-1} of Fe. Other fishes showed much lower values of EDI in the following order: *C. Spectaculurus* < *M. Salmoides* < *O. Leucostictus* < *H. fossils*. All fish exhibited recommended daily intake (12500 ug/day) set by NRC, 1989. Copper showed mean EDI values ranging from *H. fossils* (0.291) to *O. leucostictus* (0.619) while zinc had mean EDI values of *H. fossils* (3.915) to *M. salmoides* (7.210). Nickel showed mean EDI of 0.628 mg/kgBw/day for *C. spectaculums* and the lowest value of mean EDI amongst all metals was 0.071 mg/kgBw/day for *H. fossils*.

EDI for fish species from Oguta Lake showed that amongst the heavy metals toxic to living systems Hg had highest values ranging from *O. leucosticus* (13.337 mg/kg/Bwday^{-1}) to H. fossils (2.995 mg/kg/Bwday^{-1}) values of EDI for Pb followed same trend in fish species as for Hg, while cadmium showed highest value of EDI in *M. salmoides* (0.989) and lowest for *C. spectaculurus*. Arsenic revealed mean EDI values in fish species to follow the order; *C. spectaculurus* (0.745) < *M. salmoides* (0.405) < *O. leucostictus* (0.169) < *H. fossils* (0.134). This trend in mean EDI was repeated for many metals. Amongst all metals Ag showed relatively high values of mean EDI ranging from 3.915 mg/kgBwday^{-1} in *H. fossils* to 7.201 mg/kgBwday^{-1} in *M. salmoides*. When compared, results revealed that the mean EDI for all fish species was generally in the order; *H. fossils* < *O. leucostictus* < *M. salmoides* < *C. spectaculurus*. Cadmium is one of the most toxic metals and showed EDI ranging from *C. spectaculurus* (0.059) to *M. salmoides* (0.989). These values though low, could constitute a source of danger for consumers of fish. Amongst the essential trace elements in human metabolism Fe had highest values both in the case of children and adults respectively while Nickel had lowest values.

Table 4. Estimated Dietary intake (μg/kgbw/day) and Target Hazard Quotient of metals from fish species

Metal	**O. leucostictus**		**H. fossils**		**M. salmoides**		**C. spectaculums**		**Mean ± SD**	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Estimated Dietary intake of metals from fish species										
Fe	5.481	30.16	2.437	14.215	5.8	34.06	14.422	84.13	7.04±5.15	40.64±30.24
Cu	0.181	1.056	0.085	0.497	0.125	0.726	0.095	0.556	0.15±0.07	0.71±0.25
Zn	1.832	10.586	1.146	6.684	2.110	12.310	1.836	10.707	1.73±0.41	10.07±2.39
Cr	-	-	-	-	-	-	-	-	-	-
Ag	0.598	3.489	0.195	1.137	0.155	0.905	0.184	1.072	0.28±0.21	1.65±1.23
Ni	0.143	0.836	0.107	0.035	0.035	0.205	0.140	0.816	0.11±0.05	0.47±0.41
Pb	0.155	0.906	0.086	0.118	0.119	0.691	0.209	1.215	0.14±0.05	0.73±0.46
As	0.049	0.289	0.157	0.110	0.110	0.643	0.218	1.271	0.13±0.07	0.58±0.51
Hg	3.903	22.771	3.717	2.273	2.273	13.20	1.764	10.290	2.91±1.06	12.13±8.46
Cd	0.320	0.320	0.021	0.143	0.143	0.846	0.017	0.1001	0.13±0.14	0.35±0.34
∑EDI	12.66	70.41	7.951	25.212	10.87	63.586	18.885	110.157	1.262±0.7	6.73±4.43
Target Hazard Quotient of metals from fish species										
Fe	0.0078	0.0431	0.0035	0.0203	0.0083	0.0490	0.0206	0.1202	0.0101±0.00	0.0582±0.04
Cu	0.0045	0.0264	0.0021	0.0124	0.0031	0.0182	0.0024	0.0139	0.0030±0.00	0.0177±0.01
Zn	0.0061	0.0353	0.0038	0.0223	0.0070	0.0410	0.0061	0.0357	0.0058±0.00	0.0336±0.01
Cr	-	-	-	-	-	-	-	-	-	-
Ag	0.1196	0.6978	0.039	0.2274	0.031	0.181	0.0368	0.2144	0.0566±0.01	0.3302±0.25
Ni	0.0072	0.0418	0.0054	0.0018	0.0018	0.0103	0.007	0.0041	0.0054±0.00	0.0145±0.02
Pb	0.0001	0.0006	0.0001	0.0001	0.0001	0.0005	0.0001	0.0003	0.0001±0.00	0.0038±0.00
As	0.1633	0.9633	0.5233	0.3667	0.3667	2.1433	0.7267	4.2367	0.445±0.24	1.9275±1.71
Hg	7.806	45.542	7.434	4.546	4.546	26.400	3.528	20.580	5.8285±2.12	24.267±16.9
Cd	0.320	0.320	0.021	0.143	0.143	0.846	0.017	0.1001	0.1253±0.14	0.3523±0.34
∑THQ	8.435	47.670	8.032	5.340	5.108	29.689	4.345	25.305	6.48±2.06	27.001±17.4
Potential carcinogenic risk of metals from fish species										
Cr	-	-	-	-	-	-	-	-	-	-
Pb	0.0013	0.0077	0.0007	0.0010	0.0010	0.0059	0.0018	0.0103	0.0012	0.0062
Cd	0.1216	0.1216	0.0080	0.0543	0.0543	0.3215	0.0065	0.0380	0.0494	0.1330

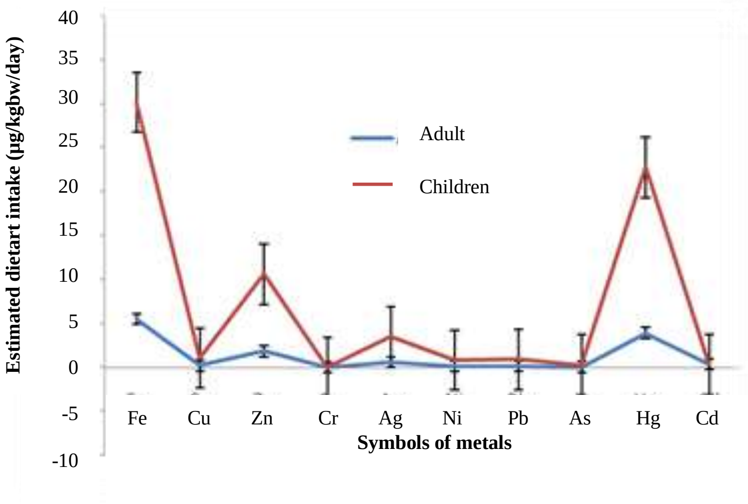

Figure 2. Estimated dietary intake of metals from *O. leucostictus* species

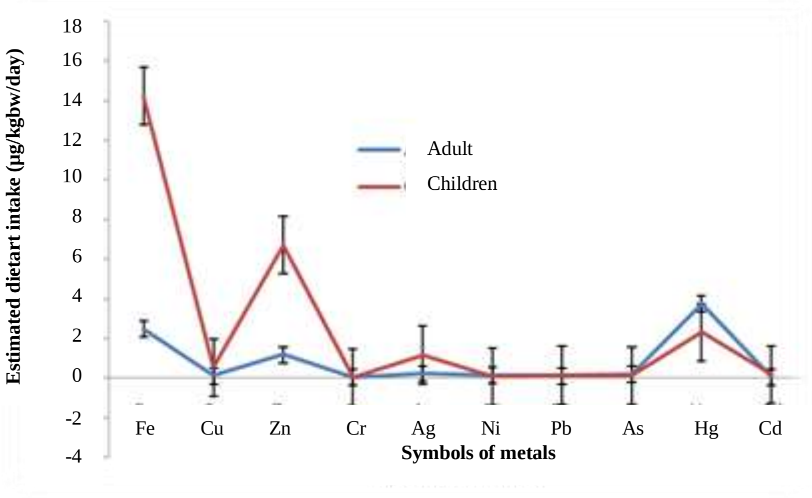

Figure 3. Estimated dietary intake of metals from *H. fossilis* species

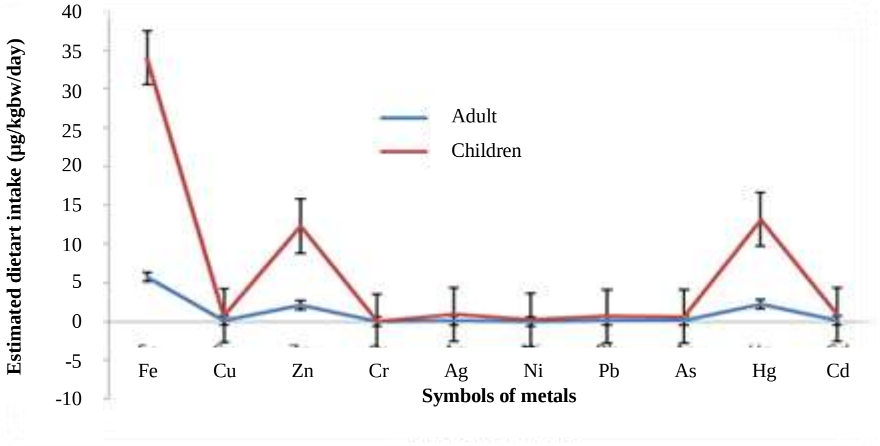

Figure 4. Estimated dietary intake of metals from *M. salmoides* species.

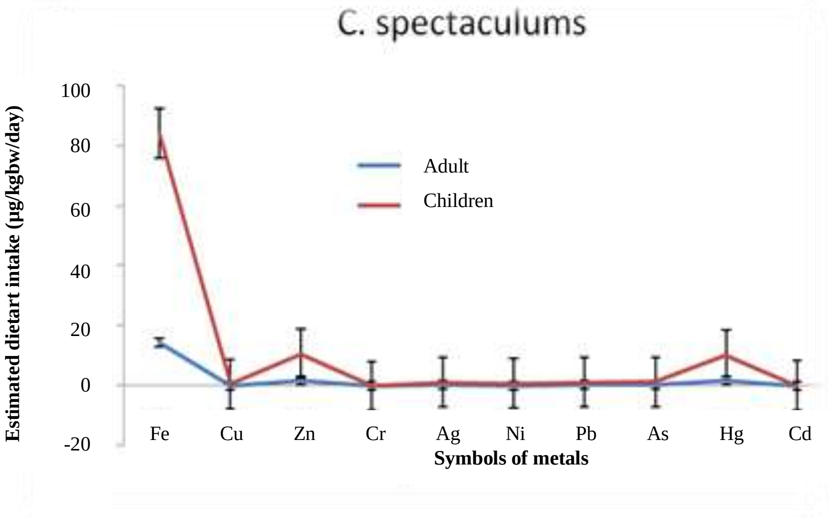

Figure 5. Estimated dietary intake of metals from *C. spectaculums* species

Target Hazard Quotient (THQ)

This refers to the ratio between measured concentration and oral reference dose weighed by the length and frequency of exposure, amount ingested and body weight. According to Islam *et al*., [17],

$$THQ = {E_F \times E_D \times ED_I}/{RFD_S \times T_A} \times 10^{-3} \qquad (5)$$

E_F = exposure frequency 365 days, E_D = exposure duration which corresponds to average life expectancy in Nigeria (54.5 years), T_A = averaging exposure time for non-carcinogens (365 days/years x ED), ED_I=estimated daily intake, RFD_S=reference dose of a metal

THQ concept was developed by USEPA [16] for estimating potential health risk associated with long term exposure to chemical pollutant. The THQ is a dimensionless index of risk due to long periods of exposure to chemical based upon reference upper safe limits. THQ above 1 indicates reason for imminent health concern and seek immediate action to alleviate the situation. Table 4 shows that all fish species exhibited THQ bellow 1 except for Hg in all fish species few species in the case of As.

In other to compare THQ in adults and children the pyramidal plots was created (Figures 6-9).

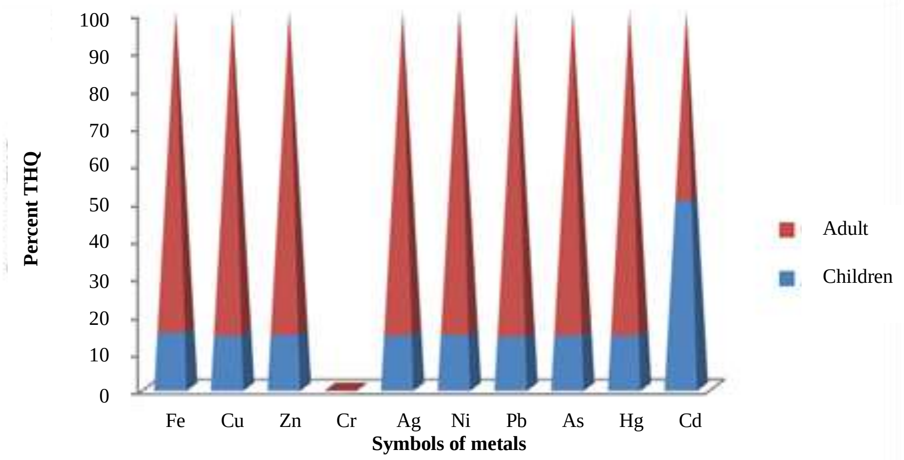

Figure 6. Percentage Target Hazard Quotient of metals for *O. leucostictus*

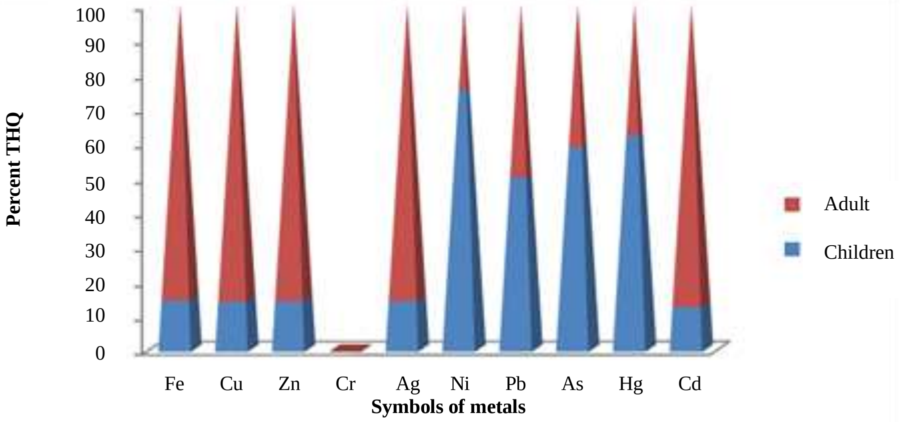

Figure 7. Percentage Target Hazard Quotient of metals for H. fossilis.

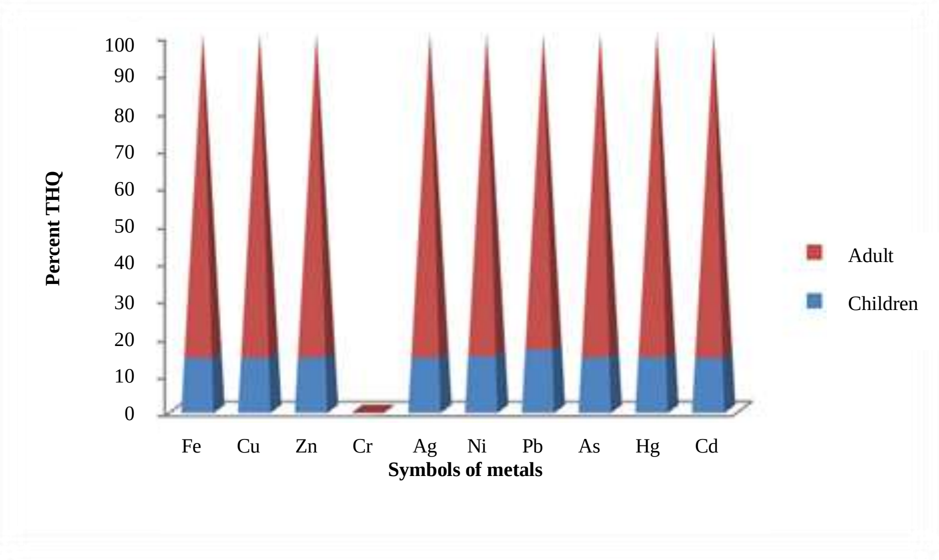

Figure 8. Percentage Target Hazard Quotient of metals for *M. salmoides*.

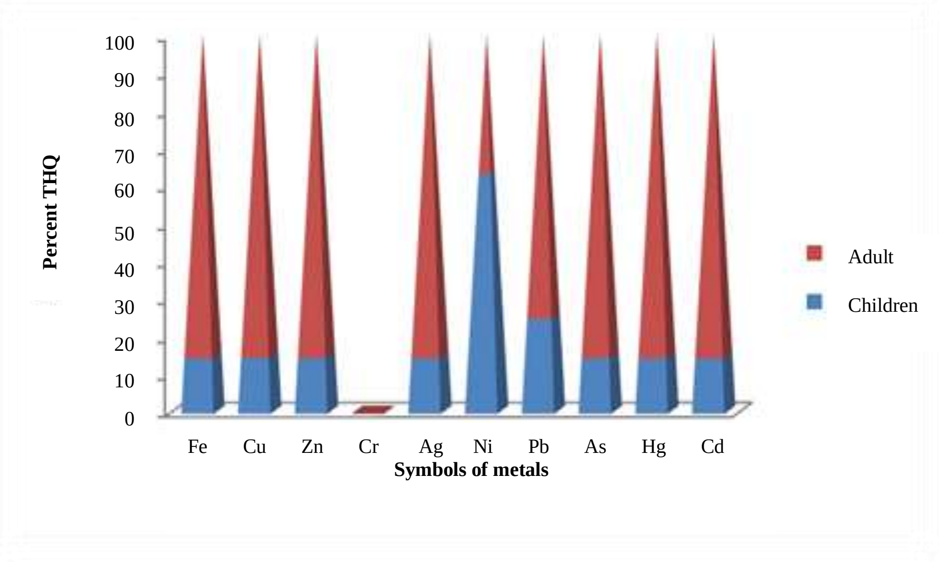

Figure 9. Percentage Target Hazard Quotient of metals for *C. spectaculums*.

The THQs were expressed as percentages (Figures.6 -9) to show the contribution of each heavy metal to total THQ for children and adults.

Hazard index

When considering the overall potential risk to human health of many heavy metals, Hazard index is used .Hazard index is usually calculated by summation of hazard quotients (HQs) [18-19]. Different heavy metals can cause similar adverse health effects, it is appropriate to combine HQs associated with different substances [20, 21] as in equation.

$$HI=\Sigma THQ\ (THQ_1+THQ_2+THQ_3\dots\dots\dots THQ_n)\ (7)$$

HI shows when a population stands a risk. Values of HI calculated for fish species ranged between4.345 to 47.679 with mean values for children 27.001±17.4 more than 4 times the value for adults 6.48±2.06. The present study for both adults and children, show that the HI values for all the fish species sampled were greater than

(>) 1 which indicates a potential health risk to those consuming these fish species.

Potential carcinogenicity

Potential carcinogenicity was calculated as an incremental lifetime probability cancer health risk [16]. This is because an individual could develop a cancer as a result of daily exposure to carcinogen for a lifetime. Thus that individual's lifetime cancer risk (ILCR) can be obtained from the Cancer Slope Factor (CSF). According to ASTDR 2010, the CSF can be used to estimate an individual's probability of developing cancer due to oral exposure to carcinogen [22].The estimated probability is carcinogen specific and in this work the cancer slope factor was expressed in mg/kg/day. Consequently the Potential carcinogenic risk was calculated as

$$\mathrm{PCR} = \mathrm{ED_I} \times \mathrm{CSF_I} \qquad (8)$$

where $\mathrm{ED_I}$ refers to estimated daily intake through ingestion and $\mathrm{CSF_I}$ refers to cancer slop factor for injestion with units mg/kg/day and $(\mathrm{mg/kg/day})^{-1}$ respectively.

Amongst metal analyzed, three are carcinogens namely Cr, Pb and Cd and are therefore used in determining Potential Carcinogenic risk of fish species. Though Cr was not detected in all four fish species it is noteworthy that the European Community/CODEX standard [23] of 0.3 mg/kg for Cr was never exceeded and so cancer risk arising from Cr was not noted. As an essential micronutrient Chromium (III) helps in sugar, protein and fat uses in human body. Despite this Institute of Medicine, 2002 has fingered Chromium (VI) to be carcinogen while the Agency for Toxic Substances and Disease Registry, 2004 maintains that there could be adverse health effects if chromium (III) becomes excessive in the body [24-25].

Lead concentration in all four fish species sampled and studied were lower than the 2.0 mg/kg value as recommended by WHO/FAO but values were not insignificant at $P<0.05$ [23].

The concentration of Cadmium did not exceed the permissible limit of 1.0 mg/kg and 0.2 mg/kg as recommended by WHO/FAO and EC/CODEX respectively [23, 26]. However by using the cancer slope factor of ingestion of Pb: 0.0085 and Cd: 0.38 the PCR for fish species was shown to range of 0.0007 to 0.0103 in Pb and 0.0065 to 0.3215 in Cd for all species of fish consumed by both adults and children. The maximum value for Pb and minimum and maximum values for Cd are within the dangerous range. This represents a call for concern. According to [16] values of 10^{-6} (1 in 1,000,000) to 10^{-4} (1 in 10,000) represent a range of permissible predicted lifetime risks of carcinogens. Cd has been lined to lung cancer, prostate cancer and cancer of testes by such mechanisms as oxidative stress induction, DNA repair inhibition, apoptotic tendencies and aberrant gene expression (PJEAC) [16]. Therefore there was significant potential carcinogenic risk arising from fish consumption in this study area. Chemical for which the risk factor falls below10^{-6} may be eliminated from further consideration as a chemical of concern.

CONCLUSIONS

Among all four fish species *O. leucosticus* had the highest THQ in children followed by *M. salmoides,* while *H. fosillis* had lowest THQ both in children and adults. Both petroleum hydrocarbons and heavy metals pollutants have been found in significant quantities in fish probably due to their bioaccumulation tendencies. However, children are most at risk as confirmed by the THQ values in the current study. Fish species of Oguta Lake could constitute health risk arising from petroleum hydrocarbons and heavy metals. Therefore consumption of fish species from Oguta lake needs to be minimized while the sources the two sets of pollutants can be minimized. Since the risk factor falls below 10^{-6} there is a need to carry out more test on Pb and Cd for further consideration as a chemical of concern for carcinogenicity arising from consumption of fish species at Oguta lake. As a recommendation results have revealed the need to monitor extensively and occasionally heavy metals in fish and waters especially at Oguta lake in order to reduce the potential health risk of the population.

ACKNOWLEDGEMENTS

We thank Prof. V. O. Nwaugo of Department of Resourse Management, Abia State University Uturu who assisted in designing and criticizing the writing of this paper. TETFUND Nigeria is acknowledged for the sponsorship of the trip to India where lots of criticisms improved the manuscript.

REFERENCES

1. Cosmas A. A., Godwin I.N., Chukwuma J.I., Emmanuel N.E., Samuel O.O., 2012. Water quality monitoring of a tropical lake and associated rivers: a case study of Oguta Lake and its tributaries, Niger Delta Basin, Southeastern Nigeria. J Environ. Sci. Eng., 1:818-826.

2. IUCN Niger – Delta Panel, 2013. Sustainable Remediation and Rehabilitation of Biodiversity and Habitats of Oil Spill Sites in the Niger Delta. Main Report including recommendations for the future. A report by the independent IUCN - Niger Delta Panel (IUCN-NDP) to the Shell Petroleum Development Company of Nigeria (SPDC). January 2013.Gland, Switzerland: IUCN. Pp 75.

3. Ahmad M.K., Islam S., Rahman S., Haque M.R., Islam M.M., 2010. Heavy metals in water, sediment and some fishes of Buriganga River, Bangladesh. Int J Environ Res. 4(2), 321-332.

4. Odoemelam S.A., 2005. Bioaccumulation of trace elements in fish from Oguta Lake in Nigeria. J Chem Soc Nigeria. 30(1), 18-20.

5. Walter F.A., Kingsly R.I., Allan W.Y., 2005. Heavy metal concentrations and burden in the bivalves (*Anadara (Senilia) senilis, Grassostrea tulipa and Perna perna*) from lagoons in Ghana: Model to describe mechanism of accumulation/excretion. Afr J Biotechnology. 2(9), 280-287.

6. Hauser R., Hauser M., 2009. Articles on natural medicine, 'The dangers of heavy metals. Retrieved on 20-11-2017 from http://www.heart-disease-bypass-surgery.com/data/articles/141.htm.

7. Nwabueze A.A., Nwabueze E.O., Okonkwo C.N., 2011. Levels of Petroleum Hydrocarbons and some Heavy Metals in Tissues of *Tympanotonus fuscatus*periwinkles from Warri river of Niger Delta Area of Nigeria. J Appl Sci Environ Manage. 15(1), 75-78.

8. Iwegbue C.M.A., Nwanjei G.E., Eguavoen I.O., 2004, 'Distribution of Cadmium, Chromium, Iron, Lead and mercury in water, Fish and aquatic plants from Ewalu River, Nigeria, Advances in Natural and Applied Science Research. 2(1), 72-82.

9. FAO (1983). Compilation of Legal limits for hazardous substances in fish and fishery products, Food and Agriculture Organization, FAO Fish Circ., 464:5-100.

10. Horsfall M. Jr., Spiff A.I., 2013. Principles of environmental pollution, toxicology and waste management. Onyoma research publications, Port Harcourt. pp. 13.

11. Veerasingam S., Venkatachalapathy R., Raja P., Sudhakar S., Rajeswari V., MohamadAsanulla R., Mohan R., Sutharsan P., 2011. Petroleum hydrocarbon concentrations in ten commercial fish species along Tamilnadu coast, Bay of Bengal, India. Environmental Science and Pollution Research 18, 687- 693.

12. Shriadah M.M.A., 2001. Petroleum hydrocarbons concentrations in Arabian Gulf Fish tissues. Bulletin of Environmental Contamination and Toxicology. 67, 560-567.

13. Tolosa I., de Mora S.J., Fowler S.W., Villeneuve J.P., Bartocci J., Cattini C.,2005. Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from the Gulf and the Gulf of Oman'. Mar Pollut Bull. 50,1619-1633.

14. Alinnor I.J., Obiji I.A., 2010. Assessment of Trace Metal Composition in Fish Samples from Nworie River. Pakistan Journal of Nutrition. 9(1), 81-85.

15. Verla E.N., Horsfall M. Jnr., Verla A.W., Spiff A.I., 2015. Assessment of some heavy metals in children's playground in owerri metropolis, Imo State, Nigeria. J Chem Soc Nigeria. 40(1), 44-50.

16. USEPA, 2011. Risk-based concentration table.United State Environmental Protection Agency, Washington, DC.

17. Islam S. Md, Md Kawser A., Al-Mamun Md H., 2014. Determination of Heavy Metals in Fish and Vegetables in Bangladesh and Health Implications,

Human and Ecological Risk Assessment: An International Journal. 1-35.

18. Singh A, Sharma RK, Agarwal M, Marshall FM (2010) Riskassessmentofheavy metal toxicity through contaminated vegetables from waste water irrigated area of Varanasi, India.Trop Ecol 51: 375-387.

19. Abou-Arab A.A.K., 2001. Heavy metal contentsin Egyptian meat and the role of detergent washing on their levels. Food ChemToxicol. 39, 593-599.

20. Al-Jassir M.S., Shaker A., Khaliq M.A., 2005. Deposition of heavy metals on green leafy vegetables sold on roadsides of Riyadh City, Saudi Arabia. Bull Environ Contam Toxicol. 75, 1020-1027.

21. Antonious G., Kochhar T., 2009. Mobility of heavy metals from soil into hotpepper fruits: A field study. Bull Environ Contamin Toxicol. 82, 59-63.

22. Asegbeloyin J.N., Onyinonyi A.E., Ujam O.T., Ukwueze N.N., Ukoha P.O., 2010. Assessment of Toxic Trace Metals in Selected Fish Species and Parts of Domestic Animals. Pakistan Journal of Nutrition. 9(3), 213-215.

23. Laganà P., Avventuroso E., Romano G., Gioffré Maria E., Patanè P., Parisi S., Moscato U., Delia S., 2017. The Codex Alimentarius and the European Legislation on Food Additives, Chemistry and Hygiene of Food Additives. Chemistry of Foods. 1-11.

24. Codex Alimentarius (1995) General standard for food additives CODEX STAN 192-1995, adopted in 1995, revision 2015. Food and Agriculture Organization of the United Nations, Rome, and World Health Organization, Geneva.

25. Institute of Medicine (IOM)., 2001. Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Cadmium, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc. Washington, DC: National Academy Press.

26. ATSDR 2004. Toxicological profile for manganese Agency for toxic substances and disease Registry, US department of Health and human services, public health services, G. A.