



Heavy Metals Analysis and Health Risk Assessment of Three Fish Species, Surface Water and Sediment Samples in Ogbaru Axis of River Niger, Anambra State, Nigeria

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Abstract

Human activities on environmental resources have negatively affected floras and faunas in maintaining fair balance. In this research study, selected heavy metals (Al, As, Cd, Cr, Cu, Fe, Hg, Pb, Ni, Zn) concentration in three fish species (*Clarias gariepinus*, *Heterotis niloticus* and *Anguilla labiate*), surface water and sediment samples in Ogbaru axis of River Niger, Anambra State, Nigeria. We evaluated the samples using atomic absorption spectrophotometer (AAS). The result of heavy metal analysis in fish samples showed that in decreasing order in *Clarias gariepinus* in increasing order of Cu > Fe > Ni > Hg > Pb > Zn > As > Cd > Al > Cr, while *Heterotis niloticus* followed the order Cu > Zn > Fe > Ni > Pb > Cd > Al > As > Hg > Cr, and *Anguilla labiate* followed the pattern of Cu > Fe > Zn > Ni > Pb > Cd > Cr > As > Hg > Al. For surface water, As, Cd, Cr, Cu, Fe, Hg and Pb showed high concentration for the raining season compared to dry season, as Al, Ni and Zn were dominant during dry season, while sediment samples of Cr, Cu, Ni and Pb concentration in raining season were higher than dry season and vice versa for other As, Cd, Fe, Hg, Zn. Correlation matrices showed positive value showing that heavy metals were from a similar source with migration route and vice versa for negative correlation. Health and exposure risk assessment was conducted for carcinogenic and non-carcinogenic exposure in adults and children, where the cumulative cancer risk was within USEPA regulatory standard and cumulative hazard index were above 1 for adults (2.02) and children (4.93), implying that children are at risk of having adverse health issues compared to adults. Therefore, there is a need for regulatory advocacy and special care to mitigate anthropogenic release and safeguard the environment.

Keywords: River Niger; Fish Species; Surface Water; Sediment; Heavy Metal; Hazard Quotient

Introduction

The influence of human activities has been known to cause immerse environmental impact over a long period, which has made it difficult to contain pollution across environmental matrices especially in aquatic environment [1-3]. All over the world, water bodies are continuously overburdened with chemical effluents that have led to increase in heavy metals,

pesticides, aromatic and aliphatic hydrocarbons, making it unfit for survival of aquatic organisms and inhibit water aesthetic [4-7]. Heavy metals are metallic chemical element with relatively high density that are toxic or poisonous at low concentrations to organisms [8].

According to USEPA [9], heavy metals are classified as nutritional metals example are chromium (iii), copper, cobalt,

iron, manganese, molybdenum, selenium, zinc; non-essential metals are aluminum, arsenic, cadmium, lead, mercury, silver that is been debated by scientific critics [9,10]. Heavy metals in trace toxic amount can cause oxidative stress in relation to ecotoxicity in the aquatic organisms [11], as Woo, et al. [12] infers that degradation of bacteria is possible in marine environment. Due to anthropogenic releases, sediment and water sources are influenced negatively across various environmental factors such as temperature, dissolved oxygen, pH, and conductivity that in-turns causes potential threat to aquatic organisms and mammals over a period [13,14].

Aquatic organisms ingest phytoplankton and dissolved food source in water with high metallic ions via ion-exchange across lipophilic membranes or adsorption on tissue or membrane surface, as such leads to increase metallic bioaccumulation, which thereafter is eaten by other aquatic mammals and humans [15-17]. Fish has over the decade been a major protein source for humans, which entails that peradventure these aquatic organisms or mammals have extreme concentration of heavy metals, after human consumption, it can lead to adverse health effect from high toxicity and chemical interaction with human organs and tissues [18]. Several studies have conducted heavy metal assessment across different aquatic organisms, which gives divergent inference in relation to anthropogenic pollutants [18-21].

The purpose of this study is the evaluation and health risk assessment of heavy metals in selected fish species, water and sediment from Ogbaru axis of River Niger, Ogbaru local government area, Anambra state, Nigeria.

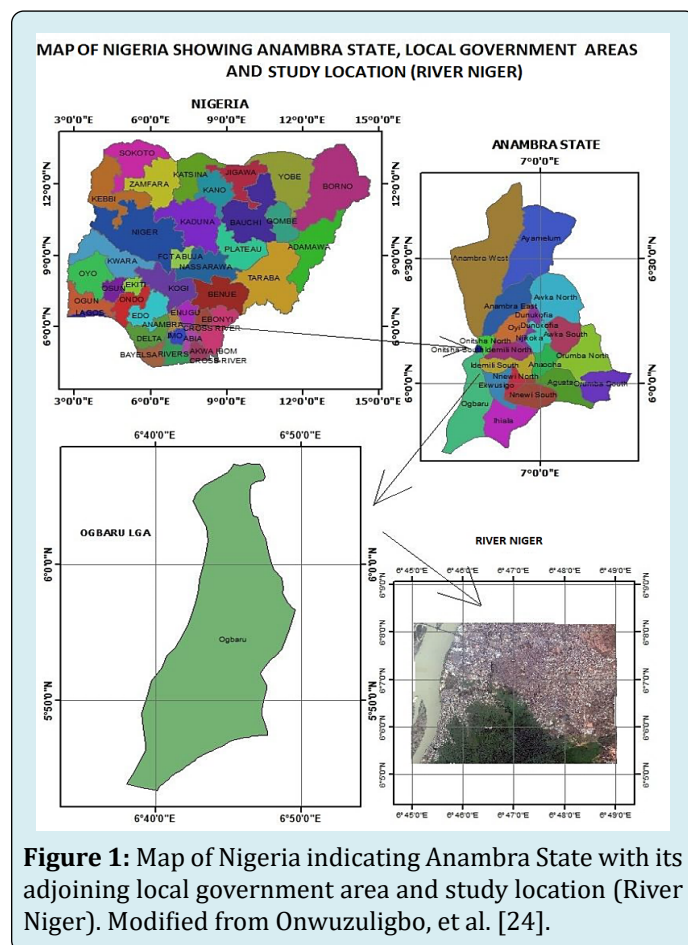
Materials and Methods

Study area

The study area was Ogbaru axis of River Niger as shown in Figure 1. Ogbaru local government area has an area of 453 km² in Anambra State, Nigeria, which is bounded to the north by Onitsha South local government area, in the west by the River Niger, in the south-east by Ihiala local government area, and in the east by Ekwusigo and Idemili South local government areas.

The River Niger in Ogbaru axis arises from a combination of two springs from Cameroun mountain, Cameroun and Guinea Highland, Guinea, that co-joins in Kogi State, Nigeria [22]. The water is discharged into diverse tributaries in the Niger Delta, which thereafter is deposited into the Atlantic Ocean. A closer investigation into the Rivers Niger shows that several commercial activities such as farming and fishing activities, oil and gas exploration and solid mineral mining

is abundant across a large expanse of river lines, as such the water volume fluctuates significantly as a result of natural and man-made influences that causes extreme flooding in Niger Delta, Nigeria [23].



Sample Collection and Preparation

Three sample regiments (fish, surface water and sediment) were collected across Ogbaru axis of the River Niger. Three species of fish samples: *Clarias gariepinus* (Cat fish), *Heterotis niloticus* (African arowana) and *Anguilla labiata* (African mottled eel) were bought from the local market close to the study area. The fish samples were of similar size, which was labelled accordingly, packaged in a polyethene bag and transported to the laboratory for chemical evaluation.

The surface water and sediment samples were obtained via two seasons (wet and dry season), which was collected at different three (3) positions with a distance of five (5) meters and mixed to form a composite mixture, thereafter was packaged in a precleaned plastic container, labelled accordingly and subsequently sent to the laboratory for chemical evaluation [25].

Laboratory Analysis

Digestion of fish sample: Fish samples were dried at 105°C in a laboratory oven until they reach a constant weight. The dried samples were grounded using a porcelain mortar and a pestle, as 5g of ground fish samples were weighed into Teflon crucible with 10ml of freshly prepared concentrated HCl/HNO₃ (aqua-regia) in the ratios of 3:1 added to each sample, thereafter allow the crucible was covered and allowed to solubilize. The samples in the crucibles were heated in the oven at a constant temperature of 150°C for 2 hours until the solution became clear and completely digested as the samples were cooled. 10ml of deionized water was added to each sample and filtered using Whatman filter paper into 250ml volumetric flask, and made up to 250 ml level with deionized water for metal determination of arsenic (As), mercury (Hg), lead (Pb), aluminum (Al), cadmium (Cd), nickel (Ni), copper (Cu), chromium (Cr), zinc (Zn) and iron (Fe) using Varian AA240 atomic absorption spectrophotometer.

Digestion of surface water samples: 5 ml of 10 M concentrated HCl were added to 250 ml of surface water samples in 500 ml beaker, which was placed in water bath at 80°C and allowed to evaporate to 25ml. The concentrate was transferred to a 50 ml volumetric flask and diluted to mark with deionized water. Prior to analysis, the solution was filtered using Whatman filter paper as indicated by Izuchukwu, et al. [26]. Similar metal determination was done accordingly to Braid et al. [25] procedure.

Digestion of sediment samples: Sediment samples were dried at 105°C in a laboratory oven for 1 hour, thereafter the sediment was ground into fine powder using pestle and mortar. 5g of sediment sample were weighed into a 250ml beaker as 50ml deionized water, 0.5ml of concentrated HNO₃ and 5ml of concentrated HCl was added accordingly.

The beaker was thereafter placed on a hot plate in a fume cupboard for digestion to prevent chemical spillage and allowed to evaporate to 15ml. the beaker were removed and allowed to cool to room temperature, as the digestate were filtered into a 50ml volumetric flask and made up to 50ml mark with deionized water, then metal determination was conducted as done for water samples.

Data Analysis: Microsoft Excel 2019 data analysis was utilized for determination of correlation matrix, which evaluates the strength and direction of a linear relationship between two variables (or metal ions of interest). Correlation coefficient of value greater than 0.71 is accepted for correlation matrix at significance level of 0.05 [27].

Health risk assessment: Cancer risk (CR) and Hazard Quotient (HQ) are indices developed by USEPA risk assessment models for evaluation of carcinogenic and non-carcinogenic health risk in adults and children in relation to fish, surface water and sediment samples in Ogbaru axis of river Niger. Exposure route were employed which is Fish (dietary ingestion), surface water (dermal and ingestion) and Sediment (dermal, accidental ingestion and inhalation) [28,29]. The formulas are shown below:

Where C is the concentration of heavy metal in sample; EF is exposure frequency; ED is exposure duration; IR_x is ingestion rate of sample; SA is skin surface area; RBA*: relative bioavailability for sediment calculation only; AF: adherence factor; Kp: dermal permeability constant for sediment calculation only; GIABS is gastrointestinal absorption factor for sediment calculation only; ET is inhalation exposure time; AT: average time; BW is body weight; PEF is particulate emission factor; VF is volatilization factor Tables 1 & 2.

Parameter	Unit	Adult	Children
Concentration of heavy metals (C)	mg/kg	Laboratory data	Laboratory data
Exposure frequency (EF)	day/year	350	350
Exposure duration (ED)	years	30	6
Fish ingestion rate (IR _p)	mg/day	30400	12225
Water ingestion rate (IR _w)	L/day	1.704	2.88
Sediment ingestion rate (IR _s)	mg/day	100	200
Relative bioavailability (RBA)	unitless	See Table 2	See Table 2
Skin surface area for soil (SA _s)	cm ² /day	6,032	2,373
Skin surface area for water SA _w)	cm ²	19652	6365
Adherence factor (AF)	mg/cm ²	0.07	0.2
Skin adsorption factor ABS	unitless	See Table 2	See Table 2
Dermal permeability constant (Kp)	unitless	0.001	0.001

Gastrointestinal absorption factor (GIABS)	dimensionless	See Table 2	See Table 2
Inhalation exposure time (ET)	hr/day	6	9
Average time (AT) – carcinogen	days/yr	25,550	25,550
Average time (AT) – non-carcinogen	days/yr	10,950	2,160
Body weight (BW)	Kg	80	15
Volatilization factor (VF)	m ³ /kg	1.00×10 ⁵	1.00×10 ⁵
Particulate emission factor (PEF)	m ³ /kg	6.79×10 ⁸	1.36×10 ⁹
Cancer slope factor (CSF)	(mg/kg/day) ⁻¹	See Table 2	See Table 2
Refernce dose (RfD)	mg/kg/day	See Table 2	See Table 2
Cancer inhalation unit risk (IUR)	(mg/m ³) ⁻¹	See Table 2	See Table 2
Reference inhalation concentration (RfC)	mg/m ³	See Table 2	See Table 2

Table 1: Parameters used to evaluate health risk assessment [30-33].

Heavy metal	CSF (mg/kg/day) ⁻¹	RfD (mg/kg/day)	IUR (mg/m ³) ⁻¹	RfC (mg/m ³)	RBA	GIABS
Al	No CSF	1.00	No IUR	0.005	1	1
As	1.5	0.0003	4.3	0.000015	0.6	1
Cd (dietary)	No CSF	0.001	1.8	0.00001	1	0.025
Cd (water)	6.3	0.0005	1.8	0.00001	1	0.05
Cr (III)	No CSF	1.50	No IUR	0.005	1	0.013
Cr (VI)	0.5	0.003	84	0.0001	1	0.025
Cu	No CSF	0.04	No IUR	0.004	1	1
Fe	No CSF	0.70	No IUR	0.8	1	1
Hg	No CSF	0.0003	No IUR	0.0003	1	0.07
Ni	0.84	0.02	0.26	0.00009	1	0.04
Pb	0.0085	0.0035	0.0085	0.0035	1	1
Zn	No CSF	0.30	No IUR	0.03	1	1

No CSF; No IUR – reference value unavailable

Table 2: Reference values for health risk assessment [30-33].

Results

Heavy metal concentration in fish samples

Table 3 and Figure 2 shows the concentration of heavy metals in different fish species assessed in Ogbaru axis of River Niger. The highest concentration of aluminum (Al) was indicated in *Clarias gariepinus*, followed by *Heterotis niloticus* with the concentration 0.019mg/kg and 0.005mg/kg respectively, as Ismaniza, et al. [5] observed a concentration range of 15.39 – 320.6 mg/kg for aluminum that was attributed to industrial waste, erosion, dissolution of minerals and salts, atmospheric dust pollution and rain [34]. Highest concentration of arsenic (As) was seen in *Clarias gariepinus* having 0.093mg/kg while the lowest concentration of 0.002mg/kg was found in *Anguilla labiate* which was lower than those reported in Zrnčić, et al. [35]

study ranging between 0.021–0.048 µg/g for *Cyprinus carpio*. Ashraf, et al. [1] observed a concentration of 0.87 mg/kg for *Hampala macrolepidota* from a tin mining catchment area.

Chromium (Cr) concentration was 0.001mg/kg in *Clarias gariepinus* and *Anguilla labiate*. The mean concentration of Cu ranged 2.16mg/kg – 10.56mg/kg as the highest value was found in *Anguilla labiate* with the lowest in *Clarias gariepinus*, which was far below Cu in Ikema and Egieborb [36] assessment in fish sample having 0.03mg/kg. Mercury concentration was highest in *Clarias gariepinus* having 0.311mg/kg, which is lower than commission of the European communities [37] guideline of 0.5mg/kg. The mean lead concentration of *Heterotis niloticus* had highest concentration of 0.394mg/kg followed by *Anguilla labiate* with a concentration of 0.299mg/kg and the least value of 0.276mm/kg in *Clarias gariepinus*, which was below FAO/

WHO limit of 0.4mg/kg for fish species [38].

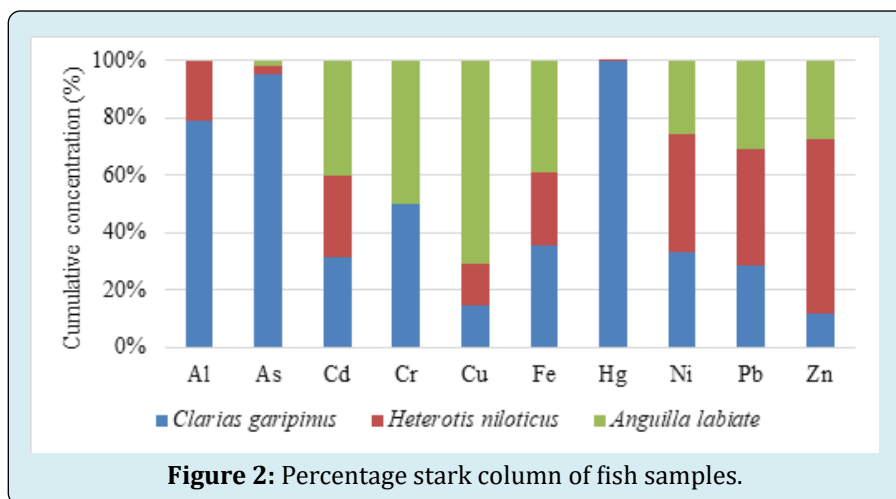
The concentrations of Cadmium ranged between 0.020mg/kg - 0.028mg/kg. The highest concentration was measured in the muscles of *Anguilla labiate* while the lowest was recorded from *Heterotis niloticus*. For zinc, the value recorded ranged between 0.245mg/kg - 1.242mg/kg for

all three fish species. The highest concentration of nickel (0.514 mg/kg) was measured in *Heterotis niloticus* while the lowest concentration of 0.322mg/kg was detected in *Anguilla labiate*. The highest concentration of iron (Fe) was predominant in *Anguilla labiate* having 1.93mg/kg, while the lowest value of 1.23mg/kg was recorded in *Heterotis niloticus*.

Heavy metal (mg/kg)	<i>Clarias garipinus</i> (Cat fish)	<i>Heterotis niloticus</i> (African Arowana)	<i>Anguilla labiate</i> (African mottled eel)
Al	0.019±0.027	0.005±0.002	0.000±0.000
As	0.093±0.004	0.003±0.002	0.002±0.002
Cd	0.022±0.004	0.020±0.004	0.028±0.001
Cr	0.001±0.002	0.000±0.000	0.001±0.002
Cu	2.161±0.033	2.197±0.007	10.560±0.306
Fe	1.755±0.028	1.234±0.006	1.927±0.022
Hg	0.311±0.00058	0.00067±0.001	0.000±0.000
Ni	0.419±0.009	0.514±0.004	0.322±0.006
Pb	0.276±0.003	0.394±0.1	0.299±0.061
Zn	0.245±0.04	1.242±0.03	0.556±0.008

Presented values shown as mean ± SD

Table 3: Mean concentration of heavy metals in fish species.



Heavy Metal Concentrations in Surface Water and Sediment Samples

Table 4 and Figure 3 shows the concentration of heavy metals in surface water (mg/l) and sediments (mg/kg) in seasonal variations (raining and dry seasons). For water samples, As, Cd, Cr, Cu, Fe, Hg and Pb showed high concentration for raining season in comparison to dry season, as Al, Ni and Zn were dominant during dry season respectively. Using percentage stark column arrangement (Figure 3i), we can see that Al and Zn was 100% at dry season,

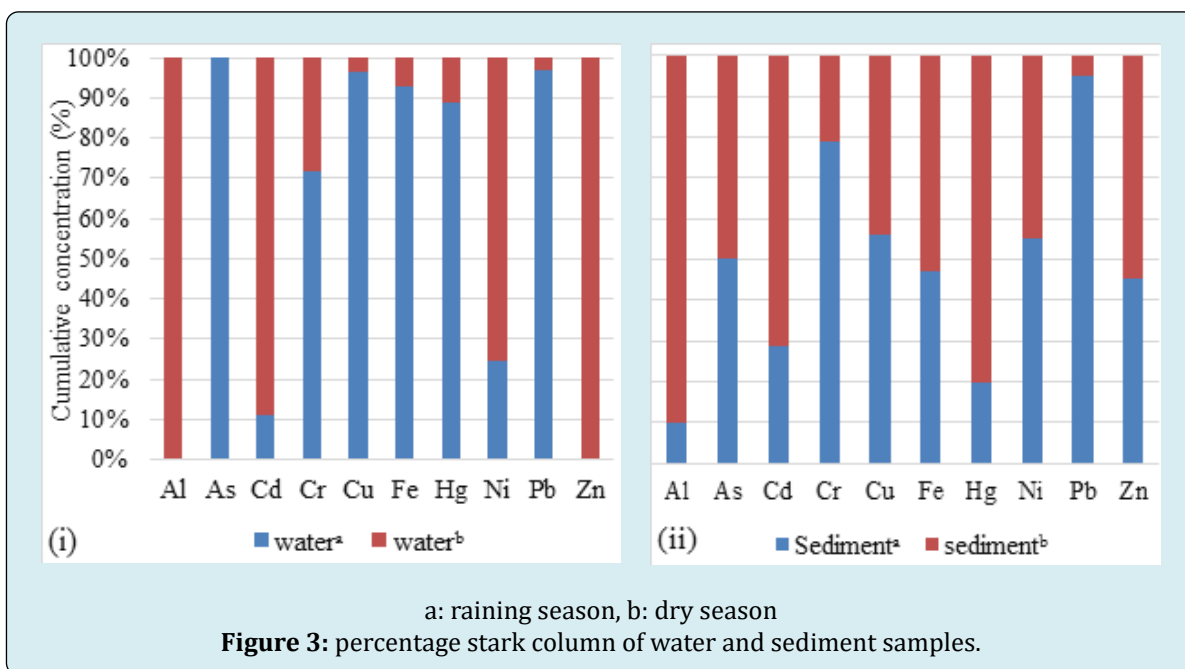
while As. was 100% at raining season; Cu and Pb had 96% for raining season and 4% for dry season. For sediment samples (Figure 3ii), Cr, Cu, Ni and Pb concentration in raining season were higher than dry season, and vice versa for dry season that is As, Cd, Fe, Hg, Zn were dominant, although As were similar in concentration for both season at 0.001 mg/kg. A view at Figure 3ii shows that As, Fe and Zn had 50%, 46% and 45% cumulative concentration for raining season as Al and Hg had 10% and 19% for raining season, while 90% and 81% for dry season respectively.

Heavy metal	water ^a	water ^b	Sediment ^a	sediment ^b
Al	0.000±0.000	0.246±0.058	0.160±0.018	1.458±0.892
As	0.005±0.003	0.000±0.000	0.0006±0.0009	0.001±0.003
Cd	0.032±0.026	0.270±0.190	0.316±0.059	0.788±0.131
Cr	0.099±0.084	0.039±0.023	0.112±0.052	0.030±0.023
Cu	0.186±0.167	0.007±0.011	0.029±0.042	0.022±0.033
Fe	2.308±0.823	0.180±0.063	2.371±0.216	2.653±0.918
Hg	1.501±1.093	0.195±0.017	0.150±0.035	0.614±0.302
Ni	0.254±0.067	0.773±0.464	0.945±0.189	0.781±0.134
Pb	0.724±0.789	0.023±0.014	0.039±0.024	0.002±0.003
Zn	0.000±0.000	2.903±1.263	0.766±1.016	0.931±1.397

a: raining season, b: dry season

Presented values shown as mean ± SD

Table 4: The concentrations of heavy metals in surface water and sediment samples.



Correlation Matrix of Fish, Surface Water and Sediment Samples

Pearson correlation was conducted for the heavy metal concentration in fish samples in relation to water and sediment as presented in Table 5. The correlation coefficient was significant at $p \leq 0.05$ in most cases with presence of positive and negative correlation. A review of the three fish samples depicts that they had similar correlation matrices across all metal substrates in water and sediment samples attributed to bioaccumulation and bio-speciation of heavy metals and other pollutants in tandem to seasonal variation

[39-42].

A strong correlation indicates that metals across both fish and water/sediments have common pollution source and similar migration behavior, while if there is medium or weak correlation, it depicts that there is slight or no influence associated between the fish and water/sediment samples [43,44]. In view of this correlating regression, positive values show that they are from similar or mutual source and reaction mode, while negative is associated to different polluting or interacting source and biochemical interaction taken place no associated to water and sediment samples [44-46].

		Al	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn	
<i>C. garipinus</i> and water	Al		-0.574	0.954	-0.181	-0.576	0.797	0.906	0.260	-0.671	0.747	<i>C. garipinus</i> and sediment
	As	-0.481		-0.792	-0.702	0.999	-0.952	-0.173	-0.940	0.992	-0.970	
	Cd	0.994	-0.573		0.121	-0.793	0.941	0.739	0.536	-0.862	0.911	
	Cr	-0.197	-0.765	-0.090		-0.700	0.449	-0.580	0.903	-0.608	0.519	
	Cu	-0.505	0.999	-0.595	-0.747		-0.952	-0.176	-0.939	0.993	-0.970	
	Fe	-0.979	0.292	-0.951	0.393	0.318		0.467	0.790	-0.983	0.997	
	Hg	-0.625	-0.383	-0.537	0.888	-0.358	0.771		-0.173	-0.294	0.395	
	Ni	0.970	-0.252	0.937	-0.431	-0.278	-0.999	-0.797		-0.890	0.836	
	Pb	-0.818	-0.111	-0.750	0.725	-0.084	0.918	0.961	-0.934		-0.990	
	Zn	0.999	-0.475	0.993	-0.204	-0.499	-0.980	-0.630	0.971	-0.822		
<i>H. niloticus</i> and water	Al		-0.580	0.956	-0.166	-0.582	0.723	0.990	0.183	-0.648	-0.267	<i>H. niloticus</i> and sediment
	As	-0.925		-0.793	-0.707	0.999	-0.982	-0.688	-0.907	0.996	0.940	
	Cd	0.998	-0.898		0.130	-0.794	0.893	0.988	0.462	-0.842	-0.537	
	Cr	-0.139	0.506	-0.076		-0.705	0.562	-0.026	0.939	-0.644	-0.906	
	Cu	-0.548	0.188	-0.600	-0.752		-0.983	-0.69	-0.906	0.997	0.939	
	Fe	-0.864	0.991	-0.830	0.618	0.053		0.8123	0.812	-0.995	-0.859	
	Hg	-0.412	0.728	-0.352	0.960	-0.537	0.814		0.318	-0.748	-0.399	
	Ni	0.874	-0.993	0.841	-0.602	-0.072	-0.999	-0.802		-0.867	-0.996	
	Pb	-0.891	0.997	-0.860	0.574	0.107	0.998	0.781	-0.999		0.907	
	Zn	0.912	-0.999	0.884	-0.533	-0.156	-0.995	-0.749	0.996	-0.999		
<i>A. labiate</i> and water	Al		-0.583	0.959	-0.170	-0.583	0.851	0.990	0.327	-0.672	0.880	<i>A. labiate</i> and sediment
	As	-0.803		-0.788	-0.702	0.999	-0.923	-0.689	-0.959	0.993	-0.899	
	Cd	0.999	-0.792		0.115	-0.789	0.965	0.989	0.581	-0.854	0.978	
	Cr	-0.129	0.694	-0.111		-0.702	0.373	-0.032	0.876	-0.616	0.318	
	Cu	-0.513	-0.100	-0.528	-0.785		-0.923	-0.69	-0.959	0.994	-0.899	
	Fe	-0.982	0.902	-0.978	0.315	0.340		0.915	0.775	-0.961	0.998	
	Hg	-0.395	0.865	-0.378	0.962	-0.586	0.563		0.455	-0.768	0.937	
	Ni	0.993	-0.869	0.990	-0.247	-0.406	-0.997	-0.503		-0.92	0.736	
	Pb	-0.799	0.999	-0.788	0.699	-0.107	0.899	0.868	-0.865		-0.943	
	Zn	0.984	-0.897	0.980	-0.305	-0.349	-0.999	-0.554	0.998	-0.894		

Correlation significant at $p \leq 0.05$

Table 5: Correlation matrix between fish samples in relation to water and sediment.

Table 6 represents correlation conducted for water and sediment samples during wet and dry season. We can see therefore that there was presence of positive and negative correlation across all heavy metals accessed. Al correlated with Cd (0.961) and Cr (-0.71) strongly, with As correlating with Cu (0.993), Hg (0.952), Ni (-0.911), Pb (0.976) and Zn (-0.772). vertical correlation of Cd and Cr produced

medium and weak correlation, while Cu, Fe, Hg, Ni, Pb correlated strong, medium and weak accordingly, as there were presence of negative and positive correlation signifying all metal components were not from the same source and biochemical interaction mode between water and sediment samples [47-50].

	Al	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
Al	1									
As	-0.367	1								
Cd	0.961	-0.567	1							
Cr	-0.710	0.533	-0.652	1						
Cu	-0.442	0.993	-0.644	0.524	1					
Fe	0.333	0.472	0.278	0.395	0.368	1				
Hg	-0.14	0.952	-0.390	0.248	0.943	0.426	1			
Ni	0.296	-0.911	0.547	-0.200	-0.930	-0.168	-0.962	1		
Pb	-0.497	0.976	-0.699	0.499	0.994	0.268	0.929	-0.949	1	
Zn	0.018	-0.772	0.121	-0.617	-0.700	-0.914	-0.679	0.482	-0.619	1

Correlation significant at $p \leq 0.05$

Table 6: Correlation matrices of water and sediment.

Health Risk Assessment of Fish, Surface Water and Sediment Samples

Cancer risk: The result of carcinogenic risk assessment was conducted heavy metals (Al, As, Cd, Cr (III), Cr (VI), Cu, Fe, Hg, Ni, Pb, Zn) in fish samples, surface water and sediment in Ogbaru axis of River Niger as presented in Tables 7 & 8 across different exposure pathways in adults and children. Using USEPA reference range of $1.00\text{E}-06$ – $1.00\text{E}-04$ [51], one can see that both children and adults were within and above the range, which entails that there will be no associated cancer issues across different exposure pathways. The total exposure pathway (total CR) for adults is Al, Cr (III), Cu, Fe, Hg, Zn ($0.00\text{E}+00$), As ($2.30\text{E}-05$), Cd ($1.74\text{E}-05$), Cr (VI) $1.12\text{E}-06$, Ni ($1.72\text{E}-04$), Pb ($1.33\text{E}-06$), while children is Al, Cr (III), Cu, Fe, Hg, Zn ($0.00\text{E}+00$), As ($9.90\text{E}-06$), Cd ($2.14\text{E}-05$), Cr (VI) ($1.68\text{E}-06$), Ni ($7.83\text{E}-05$), Pb ($5.96\text{E}-07$). The cumulative cancer risk for adults is $2.15\text{E}-04$, while children is $1.12\text{E}-04$, which entails that there is likelihood that children will encounter cancer health risk compared to adults even though the value is within USEPA reference

range [32].

Hazard quotient (HQ): The result of heavy metals (Al, As, Cd, Cr (III), Cr (VI), Cu, Fe, Hg, Ni, Pb, Zn) in Ogbaru axis of River Niger is presented in Tables 9 & 10. A review of hazard quotient evaluated for all exposure pathways in fish, surface water and sediment shows that HQ were less than 1 for adults, while for children were less than 1 except for fish dietary exposure (*Anguilla labiate*) in Cu having 2.09. The total exposure pathway (total HQ) of heavy metals for adult is Al ($1.26\text{E}-05$), As ($1.19\text{E}-01$), Cd ($2.82\text{E}-02$), Cr (III) ($1.61\text{E}-06$), Cr (VI) ($3.01\text{E}-04$), Cu ($1.36\text{E}+00$), Fe ($2.59\text{E}-03$), Hg ($3.82\text{E}-01$), Ni ($2.30\text{E}-02$), Pb ($1.01\text{E}-01$), Zn ($2.57\text{E}-03$), which shows that Cu is greater than 1 and vice versa for others heavy metals. For children, the total HQ is Al ($4.39\text{E}-05$), As ($2.60\text{E}-01$), Cd ($1.11\text{E}-01$), Cr (III) ($8.93\text{E}-06$), Cr (VI) ($4.45\text{E}-03$), Cu ($2.96\text{E}+00$), Fe ($5.89\text{E}-03$), Hg ($1.30\text{E}+00$), Ni ($5.42\text{E}-02$), Pb ($2.37\text{E}-01$), Zn ($6.36\text{E}-03$), which shows that Cu and Hg were greater than 1 and less than 1 for other heavy metals. Therefore, we can see that the cumulative hazard quotient for adults is 2.02, while children are 4.93 implying children are extremely at risk in tandem to adults.

	Fish Exposure pathway			Surface water Exposure pathways				Sediment Exposure pathways						Total CR
	Dietary Ingestion			Ingestion		Dermal		Ingestion		Dermal		Inhalation		
	<i>C.garipinus</i>	<i>H. niloticus</i>	<i>A. labiate</i>	Water ^a	Water ^b	Water ^a	Water ^b	Sediment ^a	Sediment ^b	Sediment ^a	Sediment ^b	Sediment ^a	Sediment ^b	
Al	No CSF	No CSF	No Data	No Data	No CSF	No Data	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
As	2.18E-05	7.03E-07	4.68E-07	6.57E-11	0	5.30E-08	0	4.62E-10	4.62E-10	3.25E-12	3.25E-12	1.56E-10	1.56E-10	2.30E-05
Cd	No CSF	No CSF	No CSF	1.82E-09	1.49E-08	1.47E-06	1.20E-05	1.02E-06	2.55E-06	8.64E-08	2.15E-07	2.07E-08	5.15E-08	1.74E-05
Cr (III)	No CSF	No Data	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
Cr (VI)	7.81E-08	No Data	7.81E-08	4.33E-10	1.71E-10	3.50E-07	1.38E-07	2.88E-08	7.71E-09	4.86E-09	1.30E-09	3.42E-07	9.15E-08	1.12E-06
Cu	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
Fe	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
Hg	No CSF	No CSF	No Data	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
Ni	5.50E-05	6.74E-05	4.22E-05	1.87E-09	5.68E-09	1.51E-06	4.59E-06	4.07E-07	3.29E-07	4.30E-08	3.47E-08	8.91E-09	7.19E-09	1.72E-04
Pb	3.66E-07	5.23E-07	3.97E-07	5.39E-11	1.71E-12	4.35E-08	1.38E-09	1.70E-10	8.73E-12	7.19E-13	3.69E-14	1.20E-11	6.17E-13	1.33E-06
Zn	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
Σ HM	7.72E-05	6.87E-05	4.32E-05	4.24E-09	2.07E-08	3.42E-06	1.67E-05	1.46E-06	2.89E-06	1.34E-07	2.51E-07	5.42E-07	1.96E-07	2.15E-04

No data – Analytical data unavailable; No CSF; No IUR – reference value unavailable; Total CR: total cancer risk; Σ HM: sum total of heavy metals.

Table 7: Cancer risk (CR) of heavy metal exposure matrix in adults.

	Fish Exposure pathway			Surface water Exposure pathways				Sediment Exposure pathways						Total CR
	Dietary Ingestion			Ingestion		Dermal		Ingestion		Dermal		Inhalation		
	C.garipinus	H. niloticus	A. labiate	Water ^a	Water ^b	Water ^a	Water ^b	Sediment ^a	Sediment ^b	Sediment ^a	Sediment ^b	Sediment ^a	Sediment ^b	
Al	No CSF	No CSF	No Data	No Data	No CSF	No Data	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
As	9.34E-06	3.01E-07	2.01E-07	1.18E-10	No Data	5.23E-08	No Data	9.86E-10	9.86E-10	3.90E-12	3.90E-12	4.68E-11	4.68E-11	9.90E-06
Cd	No CSF	No CSF	No CSF	3.28E-09	2.68E-08	1.45E-06	1.19E-05	2.18E-06	5.44E-06	1.04E-07	2.58E-07	6.20E-09	1.55E-08	2.14E-05
Cr (III)	No CSF	No Data	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No IUF	No CSF	0.00E+00
Cr (VI)	3.35E-08	No Data	3.35E-08	9.84E-09	3.88E-09	3.45E-07	1.36E-07	7.73E-07	2.07E-07	5.83E-09	1.56E-09	1.02E-07	2.75E-08	1.68E-06
Cu	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
Fe	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
Hg	No CSF	No CSF	No Data	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
Ni	2.36E-05	2.89E-05	1.81E-05	3.37E-09	1.02E-08	1.49E-06	4.53E-06	8.69E-07	7.01E-07	5.16E-08	4.16E-08	2.67E-09	2.16E-09	7.83E-05
Pb	1.57E-07	2.24E-07	1.70E-07	9.71E-11	3.09E-12	4.29E-08	1.36E-09	3.63E-10	1.86E-11	8.62E-13	4.42E-14	3.61E-12	1.85E-13	5.96E-07
Zn	No CSF	No CSF	No CSF	No Data	No CSF	No Data	No CSF	No CSF	No CSF	No CSF	No CSF	No IUR	No IUR	0.00E+00
Σ HM	3.31E-05	2.94E-05	1.85E-05	1.67E-08	4.10E-08	3.38E-06	1.65E-05	3.83E-06	6.35E-06	1.61E-07	3.01E-07	1.63E-07	5.88E-08	1.12E-04

No data – Analytical data unavailable; No CSF; No IUR – reference value unavailable; Total CR: total cancer risk; Σ HM: sum total of heavy metals.

Table 8: Cancer risk (CR) of heavy metal exposure matrix in children.

	Fish Exposure pathway			Surface water Exposure pathways				Sediment Exposure pathways						Total HQ
	Dietary Ingestion			Ingestion		Dermal		Ingestion		Dermal		Inhalation		
	<i>C.garipinus</i>	<i>H. niloticus</i>	<i>A. labiate</i>	Water ^a	Water ^b	Water ^a	Water ^b	Sediment _a	Sediment _b	Sediment _a	Sediment _b	Sediment _a	Sediment _b	
Al	6.92E-06	1.82E-06	No Data	No Data	5.02E-09	No Data	1.74E-06	1.92E-07	1.78E-06	3.47E-10	3.22E-09	1.36E-08	1.26E-07	1.26E-05
As	1.10E-01	3.64E-03	2.43E-03	3.4E-07	No Data	3.53E-08	No Data	2.04E-06	2.40E-06	2.17E-12	2.17E-12	8.47E-11	8.47E-11	1.19E-01
Cd	8.02E-03	7.29E-03	1.02E-02	1.35E-06	1.1E-05	2.33E-07	1.91E-06	7.58E-04	1.89E-03	1.37E-08	3.42E-08	2.68E-08	6.68E-08	2.82E-02
Cr (III)	2.43E-07	No Data	2.43E-07	1.35E-09	5.31E-10	7.00E-07	2.76E-07	8.95E-08	2.40E-08	1.87E-08	5.01E-09	9.49E-09	2.54E-09	1.61E-06
Cr (VI)	1.21E-04	No Data	1.21E-04	6.74E-07	2.66E-07	7.00E-07	2.76E-07	4.47E-05	1.20E-05	9.72E-09	2.6E-09	9.49E-09	2.54E-09	3.01E-04
Cu	1.97E-01	2.00E-01	9.62E-01	9.50E-08	3.57E-09	1.31E-06	4.95E-08	8.39E-07	6.59E-07	6.07E-11	4.77E-11	2.37E-09	1.86E-09	1.36E+00
Fe	9.14E-04	6.42E-04	1.00E-03	6.91E-08	5.25E-09	1.67E-05	1.27E-06	4.06E-06	4.54E-06	5.14E-09	5.75E-09	2.01E-07	2.25E-07	2.59E-03
Hg	3.77E-01	1.22E-03	No Data	1.02E-04	1.31E-05	1.06E-05	1.36E-06	5.99E-04	2.45E-03	4.65E-09	1.9E-08	1.27E-08	5.19E-08	3.82E-01
Ni	7.63E-03	9.37E-03	5.87E-03	2.59E-07	7.89E-07	1.79E-06	5.46E-06	5.66E-05	4.57E-05	5.12E-08	4.13E-08	8.00E-08	6.46E-08	2.30E-02
Pb	2.87E-02	4.10E-02	3.11E-02	4.22E-06	1.34E-07	5.12E-06	1.63E-07	1.34E-05	6.85E-07	8.46E-11	4.34E-12	3.30E-09	1.69E-10	1.01E-01
Zn	2.98E-04	1.51E-03	6.75E-04	No Data	1.98E-06	No Data	2.05E-05	3.06E-05	3.72E-05	1.66E-09	2.02E-09	6.49E-08	7.89E-08	2.57E-03
Σ HM	7.33E-01	2.65E-03	1.01E+00	1.09E-04	2.73E-05	3.72E-05	3.30E-05	1.51E-03	4.44E-03	1.05E-07	1.13E-07	4.24E-07	6.20E-07	2.02E+00

No Data: Analytical data unavailable; Total HQ: total hazard quotient; Σ HM: sum total of heavy metals.

Table 9: Hazard quotient (HQ) of heavy metal exposure matrix in adults.

	Fish Exposure pathway			Surface water Exposure pathways				Sediment Exposure pathways						Total HQ
	Dietary Ingestion			Ingestion		Dermal		Ingestion		Dermal		Inhalation		
	<i>C.garipinus</i>	<i>H. niloticus</i>	<i>A. labiate</i>	Water ^a	Water ^b	Water ^a	Water ^b	Sediment _a	Sediment _b	Sediment _a	Sediment _b	Sediment _a	Sediment _b	
Al	1.51E-05	3.96E-06	No Data	No Data	4.59E-08	No Data	2.03E-05	4.09E-07	3.80E-06	4.92E-09	4.57E-08	2.06E-08	1.91E-07	4.39E-05
As	2.46E-01	7.92E-03	5.28E-03	3.11E-06	No Data	1.38E-03	No Data	5.11E-06	5.11E-06	1.03E-07	1.03E-07	1.29E-10	1.29E-10	2.60E-01
Cd	1.74E-02	1.58E-02	2.22E-02	1.23E-05	1.01E-04	5.45E-03	4.46E-02	0.001616	4.03E-03	9.72E-07	4.85E-05	4.07E-08	1.02E-07	1.11E-01
Cr (III)	5.28E-07	No Data	5.28E-07	1.23E-08	4.85E-09	5.45E-06	2.15E-06	1.91E-07	5.11E-08	2.99E-11	6.15E-10	1.44E-08	3.87E-09	8.93E-06
Cr (VI)	2.64E-04	No Data	2.64E-04	6.16E-06	2.43E-06	2.72E-03	1.07E-03	9.55E-05	2.56E-05	2.87E-08	3.08E-07	1.44E-08	3.87E-09	4.45E-03
Cu	4.28E-01	4.35E-01	2.09E+00	8.68E-07	3.27E-08	3.84E-04	1.44E-05	1.79E-06	1.41E-06	2.15E-08	1.69E-08	3.61E-09	2.84E-09	2.96E+00
Fe	1.99E-03	1.40E-03	2.18E-03	6.31E-07	4.80E-08	2.79E-04	2.12E-05	8.66E-06	9.69E-06	1.04E-07	1.17E-07	3.06E-07	3.42E-07	5.89E-03
Hg	8.21E-01	2.64E-03	No Data	9.34E-04	1.19E-04	4.13E-01	5.28E-02	0.001279	5.23E-03	1.08E-06	6.29E-05	1.93E-08	7.90E-08	1.30E+00
Ni	1.66E-02	2.04E-02	1.28E-02	2.37E-06	7.21E-06	1.05E-03	3.19E-03	1.21E-04	9.74E-05	5.81E-08	1.17E-06	1.22E-07	9.82E-08	5.42E-02
Pb	6.25E-02	8.92E-02	6.77E-02	3.86E-05	1.23E-06	1.71E-02	5.42E-04	2.85E-05	1.46E-06	3.43E-07	1.76E-08	5.03E-09	2.58E-10	2.37E-01
Zn	6.47E-04	3.28E-03	1.47E-03	No Data	1.81E-05	No Data	7.98E-04	6.53E-05	7.94E-05	7.85E-08	9.55E-08	9.87E-08	1.20E-07	6.36E-03
Σ HM	1.59E+00	5.76E-01	2.20E+00	9.98E-04	2.49E-04	4.41E-01	1.03E-01	3.22E-03	9.48E-03	2.79E-06	1.13E-04	6.44E-07	9.43E-07	4.93E+00

No data – Analytical data unavailable; Total HQ: total hazard quotient; Σ HM: sum total of heavy metals.

Table 10: Hazard quotient (HQ) of heavy metal exposure matrix in children.

Discussion

Heavy metals in diverse concentration are released from a host of natural and anthropogenic source that pose negative environmental and health-based risk over a period of time [52,53]. According to Vu, et al. [54], anthropogenic activities lead to the release of heavy metals that are readily mobile in surface water, which thereafter suspend and deposit them on sediment fine grains. As these anthropogenic metals reach high threshold, aquatic organism is impacted negatively via bioactivity and mobile bio-accessibility from contaminated sediment finegrains and water body [55,56]. In this study, heavy metal concentration varied over fish, surface water and sediment samples, thus implies that biochemical transformation and geochemical interaction has great impact to florae and faunas in relation to humans [57-59].

According to WHO [60], arsenic (As) is found in diet, mostly in fish and shells, which exist as less toxic organic form in comparison to inorganic form, as such limited data has suggested that natural and anthropogenic source could impact on the concentration depending on the location. Arsenic in high concentration is known to cause short- and long-term health risks such as tissue and organ cancer, dermal lesion and vascular diseases, although arsenic exposure in humans are excreted via urine or sweat as organic acids in minute concentration [60-63].

Aluminum (Al) and iron (Fe) are known to exist in water and sediment as combined component of carbonates, sulphates, chlorides, oxides that are easily absorbed in tissues and bones of aquatic organisms and humans also. Similarly, they both impact water quality such as color, turbidity, hardness, conductivity and dissolved oxygen [64,65]. There is little indication that aluminum and iron have health implication, but hypothetically, it has been said that extreme *aluminum exposure leads to Alzheimer diseases in humans* [66]. Iron (Fe) is an essential element in human nutrition, which estimated daily requirement depends on age, sex, physiological status and iron bioavailability [60].

Cadmium (Cd) and zinc (Zn) in high concentration is an indication of pollution from each other, as they are released into the environment from several industrial activities such as steel, plastics, fertilizer that get absorbed and/or assimilated by aquatic organism and agricultural plants. Zinc impacts taste at minimum concentration of 4mg/l (as sulphate, carbonate and chloride). In humans, cadmium and zinc accumulate in kidney after exposure leading to cytotoxicity induced tumors in urinary tract and development of hyperplasia and subsequently neoplasia [67-69].

Cadmium (III) and (VI) are known valence group of chromium that are prevalent different in biochemical interaction in human body [70]. Chromium (III) is a vital

source of nutrient that exist in food source, although chromium (VI) is known to be carcinogenic via different exposure route (inhalation, oral and dermal). A national toxicology program (NTP) study shows that chromium (VI) is reduced to chromium (III) in human stomach and gastrointestinal tract in a dose-response interaction at very low concentration, but at high concentration can lead to tumor and cancer in organs and tissues in humans [71].

Copper (Cu) and lead (Pb) are released into the environment from natural and anthropogenic sources, as its solubility is initiated by pH dominant anions (sulphate, nitrate, phosphate, chloride, carbonate) that impacts water quality (temperature, taste, color, dissolved oxygen) over a period of time [72,73]. Short-term exposure of copper leads to gastrointestinal irritation (diarrhea), which is concentration dependent, as long-term effect can lead to metabolic homeostasis and trigger Wilson disease in gene carriers [60].

Exposure to lead has been known to cause neurodevelopmental issues, cardiovascular diseases, impaired renal function and fertility, hypertension, as lead in blood is known to cause blood cell-tumor and systolic blood pressure [38,65,74]. In children, lead decreases intelligence quotient (IQ) point by at least two (2) point and increase systolic blood pressure by about 3 mmHg [75].

Mercury exist as organic and inorganic forms in aquatic environment as inorganic mercury exposure in human causes genotoxic health activities (tissue and organ tumor) as oral exposure above recommended guideline of 0.0006mg/l result in hemorrhagic gastritis in stomach and intestinal tissue and kidney damage [63,76-79].

Nickel exist predominantly in food source as water and sediment exposure is a minor contributor to adult and children over a period of time. Although presence of steel industries can lead to increase nickel pollution from industrial effluents, which impacts the aquatic and land environment. High concentration of nickel causes dermal allergies (dermatitis) [80].

The correlative review as shown in Table 5 and 6 shows that diverse activities such as industrial effluents and emission, agricultural land use, sanitary landfill, mining activities, fishing and water-land transport has negative influence on surface water and sediment, which in turn leads to exposure to florae and faunas over a period of time [30,31]. As the aforementioned activities takes place, it leads to the release of chemical toxins in high concentration that has the potential to cause immense health risk to a population, which leads to carcinogenesis, mutagenesis and non-carcinogenesis (adverse health effect) [51]. The calculated total cancer risk

(Table 7 and 8) suggest that children will have cancer-based symptoms as compared to adults from fish dietary exposure, surface water (ingestion and dermal) exposure and sediment (ingestion, dermal and inhalation) exposure [51,81].

The calculated total hazard quotient Tables 9 & 10 suggest that both adult and children are at risk of having adverse health issues from all exposure pathways for fish most especially, as such special care is advocated [31,32].

Conclusion

The study evaluated significant concentration of heavy metals in three fish species, surface water and sediment samples from Ogbaru axis of River Niger. However, the concentration was low or moderate within set WHO standard, as correlation showed positive and negative regression indicating that they were from similar source and vice-versa thus lead to bioaccumulation and increased toxicity in fish samples. Cancer risk and hazard quotient showed that fish dietary exposure is a major contributor compared to surface water and sediment exposure for both adults and children respectively. Children are more prone to have adverse health effect from consumption of fish samples exposed to low or moderate heavy metal concentration in comparison to adults. Based on these results, one can draw that fish samples were immensely impacted by anthropogenic activities that are released into the River Niger that span over a wide distance. Therefore, the following recommendations are advocated:

- a) Further evaluation of pollutants in microscale and nanoscale is advocated to derive required information on the exposure medium of environmental matrices to human.
- b) Regulatory action and proactive attention should be enforced on environmental polluters involved in diverse activities.
- c) Regular public health check on the level of heavy metals among the populace in the communities that border the study area should be employed in order to safeguard health and wellbeing.

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