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RISK ASSESSMENT OF TRACE METALS IN *CHRYSICHTHYS NIGRODIGITATUS* AND *PACHYMELANIA AURITA* FROM CROSS RIVER, ITU, AKWA-IBOM STATE, NIGERIA



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ABSTRACT

The levels of six trace metals (Mn, Cu, Zn, Fe, Ni and Co) in *Chrysichthys nigrodigitatus* (Fish) and *Pachymelania aurita* (Periwinkle) from Cross River in Itu, Akwa-Ibom State, Nigeria were determined and recorded. The results gave the trend Mn>Cu>Zn>Fe>Ni>Co in *Pachymelania aurita* for both wet and dry seasons and Cu>Mn>Fe>Zn>Ni>Co and Mn>Cu>Fe>Zn>Ni>Co in *C. nigrodigitatus* for both wet and dry seasons respectively. The overall elevated level of these metals was observed during wet season particularly in periwinkle. Mn (29.44µg/g and 11.8µg/g) for both wet and dry seasons were respectively higher than the FAO/WHO maximum permissible limits of 1.00µg/g; Fe in fish (11.04µg/g) for only wet season was higher than the FAO/WHO maximum permissible limit of 10µg/g while the other metals were below the limits. Dietary intake and toxic risk were evaluated for both adults and children resident in the study area and all the values were below unity. The Hazard Quotients for adults consuming *Pachymelania aurita* only, *C. nigrodigitatus* only and those consuming both species ranged from 4.4 E-03 to 4.16 E-01, 2.86 E-04 to 1.67 E-01 and 4.69E-03 to 5.83E-01 respectively, were generally less than unity; and HQ for children consuming *Pachymelania aurita* only, *C. nigrodigitatus* only and those consuming both species ranged from 2.44 E-02 to 2.30 E+0, 1.58E-03 to 9.25E-01 and 1.22E-02 to 3.24E+0 respectively, were generally higher than unity. The Hazard Indices were less than unity for adults consuming *Pachymelania aurita* only, *C. nigrodigitatus* only and those consuming both species (6.20E-01, 2.44E-01 and 7.44E-01); and higher than unity for children (3.44E+0, 1.34E+0 and 4.74E+0) respectively. This implied that the trace metal contaminants posed hazards to local residents especially children associated with the consumption of *Pachymelania auritas*, *C. nigrodigitatus* and both species.

INTRODUCTION

Protein from aquatic animals remains one of the best and major ways to furnish the body with complete amino acids needed for tissue formation, growth, maintenance and repairs. Production, traffic utilization and disposal of wastes from many modern products release trace metals into the aquatic environment in addition to what already exists in nature. A lot of environmentalists are paying more attention to how humans are affected by this, which makes bio-monitoring of trace metals very essential to the assessment of ecosystem health (Yetimoglu *et al.*, 2007; Mico *et al.*, 2006). Metals enter into the food web through direct consumption of water organism or through uptake process and accumulation in fish and periwinkle and other sea foods (Paquin *et al.*, 2003).

Fish is a major part of the human diet because it represents the main part of many natural food chains. It has a high protein content, omega- 3 fatty acids, low saturated fat, amino acids and vitamins; it also contains several minerals including Ca, Fe, Cu, Zn, etc. (Aremu and Ekunode, 2008; Dural *et al.*, 2007). Periwinkles are mass-consumer products constituting relatively cheap

animal protein in Akwa-Ibom State and are one of the many delicacies in the Nigeria cuisines, especially in the Niger Delta region. Though the nutrient found in fish, periwinkle and other aquatic organisms supports good health, there is a growing concern that metals accumulated in fish and periwinkle muscle tissues may represent a health risk, especially for populations with high consumption rates (Burger and Gochfeld, 2009; Diez *et al.*, 2009). Consumption of these contaminated fishes showed the risk potential for humans (US EPA, 2000; Storelli, 2008; Imar and Carlos, 2011).

The Niger Delta region of Nigeria is among the most environmentally impacted regions in Nigeria considering such indices as increase in population rate, metal smelting, increase in coastal traffic and intense crude oil exploration over the years. Also, just like in most developing countries with increase in population, Nigeria is generally characterized by high loadings of increasing waste generation, most of which are disposed without treatment into aquatic environments (Arukwe *et al.*, 2012). As a result of these, natural surface waters in the region receive inorganic and organic pollutants from diverse sources (Sojину *et al.*, 2010). All these, in addition to occasional incidence of oil spills in the region have raised public concerns regarding the environmental status of the area.

The defunct Oku-Iboku paper mill industry is located about 2km from the study area. Wastes from this industry and other workshops close to the Cross river tend to pollute this aquatic environment and since fish is one aquatic animal whose movement cannot be restricted as they have to go out of their habitat in search of food, they could be adversely affected.

MATERIALS AND METHODS

Study Area

The study area (Cross River) is located in Akwa Ibom State Nigeria. It is between latitude 5.765N and longitude 8.941E with an area of about 1400km² (Essien, 2013). It is a fresh water ecosystem with several aquatic animals such as fishes, crayfish, shrimps and periwinkles among others. The major occupation of the people around the creek is fishing. There are also artisans, automobile repairers, iron benders and welders as well as petty traders and timber dealers. In this study, the conventional framework was adopted for assessing the health risk connected with the consumption of fish and periwinkle contaminated with some trace metals. The hazard identification step has been accomplished through the collection of fish samples and subsequent analysis to quantify the contamination level of trace metals. In order to estimate the toxic risks, the dose-response assessment was carried out using standard Reference Dose (RfD) values for the trace metals considered in this work.

Sample Collection, Treatment and Instrumental analysis

The collection of fish was carried out by the use of local traps which were set at dusk and inspected at dawn while the periwinkles were collected by hand picking around the muddy areas at the bank of the river. These samples were collected during wet and dry seasons covering July 2014 to January 2015. Sixty fish samples and sixty periwinkle samples made up of thirty samples of each per season were collected.

The samples were thoroughly washed using de-ionized water. The fish was filleted by taking out the muscle which is the edible part while the periwinkle muscles were removed from their shells and oven dried between 80⁰-105⁰C overnight. Both samples were ground to powder separately using ceramic mortar and pestle. 1g of the samples was digested with 5cm³ of 6M HCl and then the solution was made up to 50cm³ with de-ionized water. The already digested samples were stored in polyethylene bottles with lid at room temperature until ready for use.

Further analysis for the various metals (copper, zinc, iron, manganese, cobalt and nickel) in both species was carried out using UNICAM 939/959 Atomic Absorption Spectrophotometer (AAS) as recorded in the AOAC (2010).

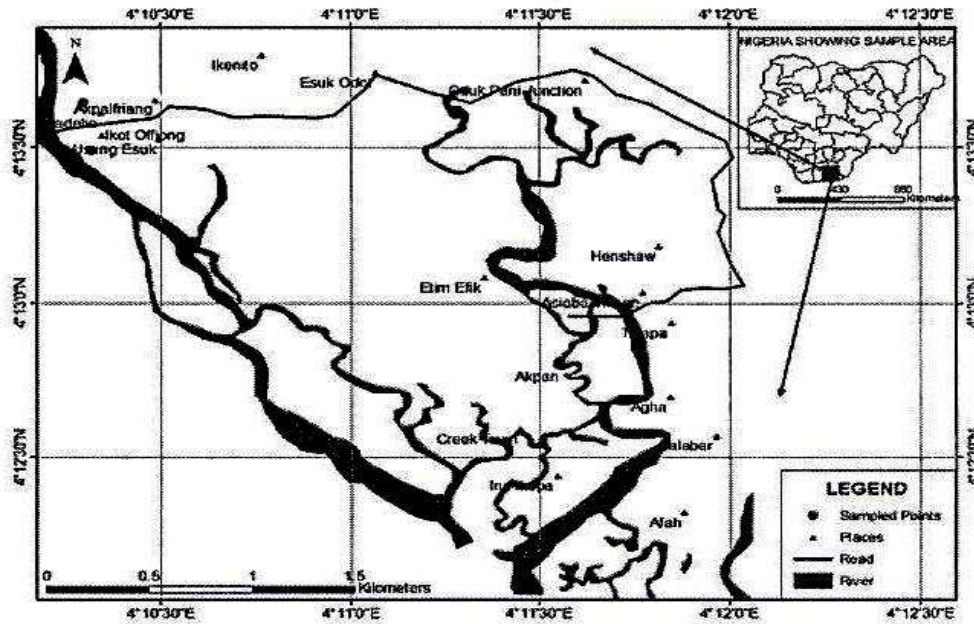


Figure 1: Sampling locations at Cross river, Itu LGA in Akwa Ibom State

Risk Assessment Procedure

A Risk assessment procedure was done in four-steps namely: (1) hazard identification, (2) exposure assessment, (3) dose-response or toxicity assessment, and (4) risk characterization. The hazard identification stage was accomplished by measuring the environmental concentrations of the contaminants in fish and periwinkle of the chosen study area. On the other hand, the dose-response or toxicity assessment was largely based on existing toxicity information developed for specific metals which refer to non-carcinogenic effects that would arise as a result of the exposure to contaminants (Lee *et al.*, 2005). The magnitude of the effects is estimated in terms of Hazard Quotients (HQ) (Shah *et al.*, 2012) while the risk characterization stage involves the process of estimating the probable incidence of adverse impacts on potential receptors under the various exposure conditions (Udosen *et al.*, 2014).

Exposure Assessment

The exposure assessment for the inhabitants of the area was carried out using a model provided in the literature (Atul *et al.*, 2012; Udosen *et al.*, 2014; US EPA, 2001) as shown:

$$\text{Intake (mg/k-day)} = (\text{CF} \times \text{IR} \times \text{FI} \times \text{EF} \times \text{ED}) / \text{BW} \times \text{AT}$$

where CF is the chemical concentration of fish (mg/kg), IR is ingestion rate (Kg/day), FI is the fraction ingested, EF is exposure frequency (365 days/year), ED is exposure duration, BW is body weight and AT is the averaging time (period over which exposure is average in days). Specific values for each of the exposure parameters are shown in Table 1.

Table 1: Summary of risk assessment parameters

Symbol	Description	Unit	Value(s)
CF	Metal concentration in fish	mg/Kg	Presented in Table 2
IR	Ingestion rate	Kg/day	Adults = 0.024, children = 0.019
FI	Fraction ingested	Unitless	1, assuming that the whole muscle fillet of fish is consumed.
EF	Exposure frequency	Days/year	365 days/year
ED	Exposure duration	Years	Adults = 70, children = 10
BW	Body weight	Kg	Adults = 70, children = 10
AT	Averaging time	Days	ED × EF
^a RfD	Reference dose	µg/g/day	Co=0.06 ^b , Cu=0.037, Mn=0.14, Ni=0.02, Fe=0.8 and Zn=0.3

(Udosen *et al.*; 2014)

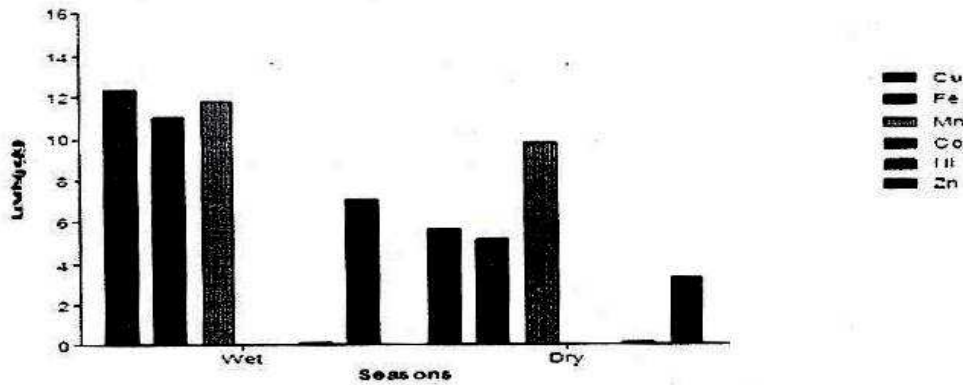


Figure 3: Seasonal variation of trace metal levels ($\mu\text{g/g}$) in *Chrysichthys nigrodigitatus* from Cross river.

It was also noted that the levels of the trace metals in periwinkle were generally higher in both seasons than those in fish except for Fe whose values were higher during the wet season (Figures 4 and 5). This could be attributed to sample habitats.

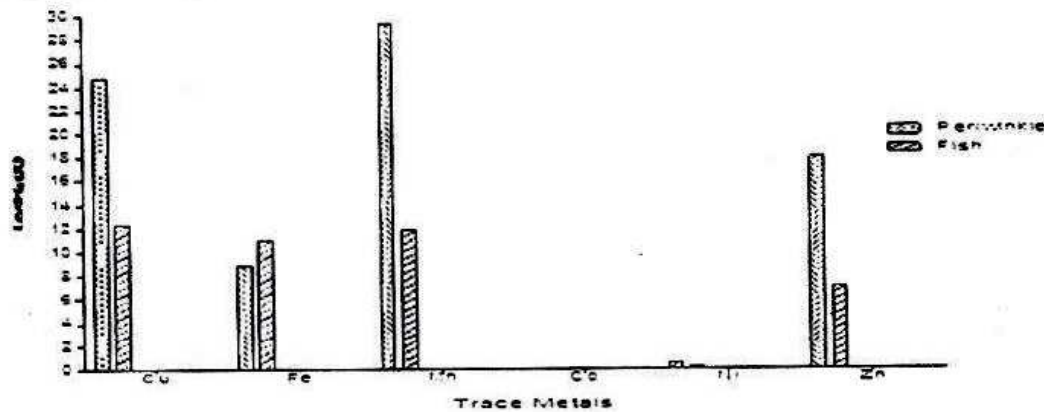


Figure 4: Seasonal Variation of Trace Metal Levels ($\mu\text{g/g}$) between *Pachymelania aurita* and *Chrysichthys nigrodigitatus* (Wet Season)

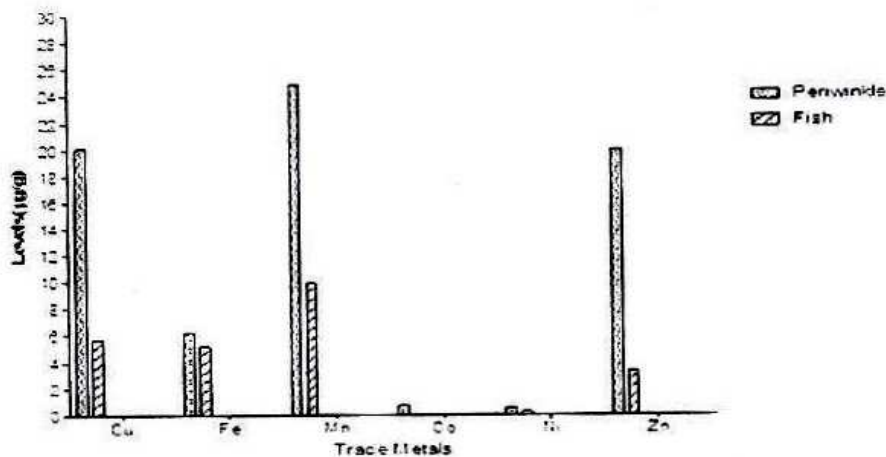


Figure 5: Seasonal Variation of Trace Metal Levels ($\mu\text{g/g}$) between *Pachymelania aurita* and *Chrysichthys nigrodigitatus* (Dry Season)

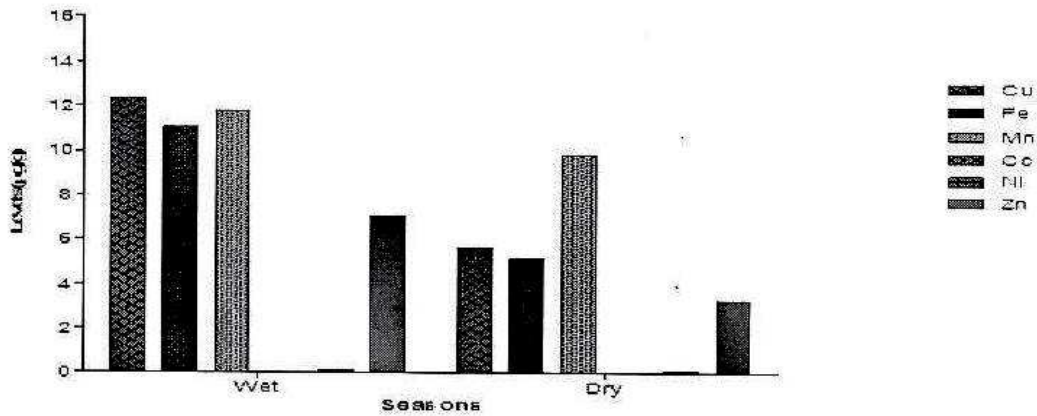


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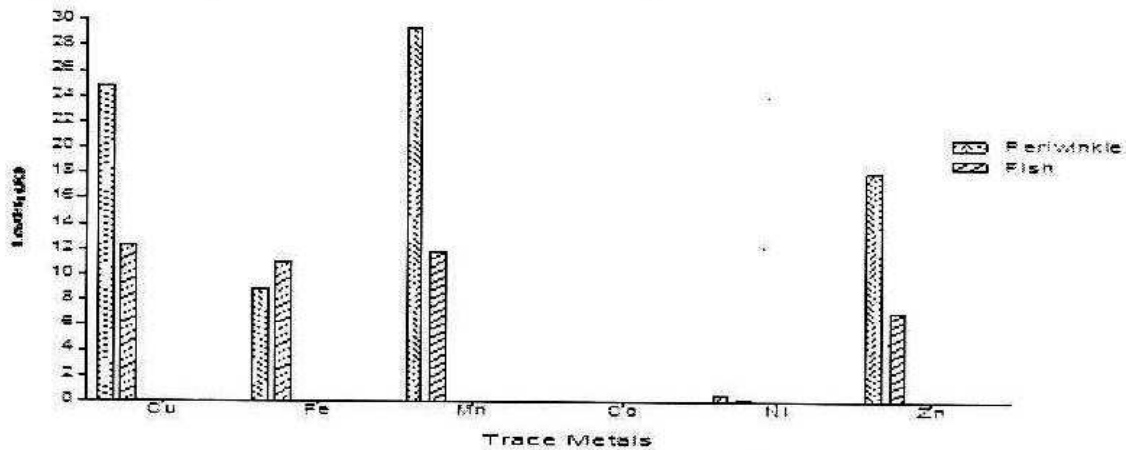


Figure 4: Seasonal Variation of Trace Metal Levels ($\mu\text{g/g}$) between *Pachymelania aurita* and *Chrysichthys nigrodigitatus* (Wet Season)

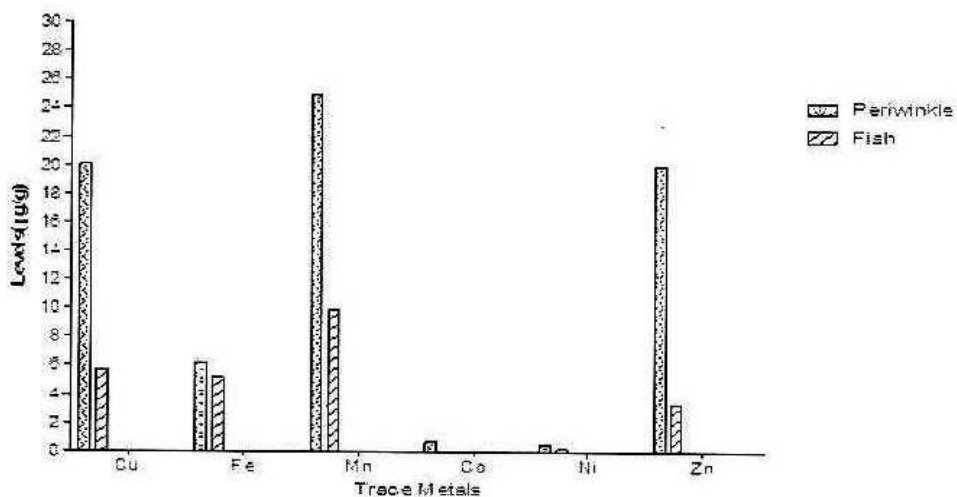


Figure 5: Seasonal Variation of Trace Metal Levels ($\mu\text{g/g}$) between *Pachymelania aurita* and *Chrysichthys nigrodigitatus* (Dry Season)

In this study, Mn was detected at a high level in both samples, exceeding the WHO/FAO maximum permissible limit in both wet and dry seasons (Table 2). The high levels of Mn could be attributed to the indiscriminate dumping of domestic waste, sewage, inappropriate use of fertilizer, pesticides and insecticides from agricultural activities. Atmospheric deposition of the exhaust fumes from moving vehicles also probably contributed to the high levels since there is a major busy road across the river This conforms with studies by Santa-Maria, (2008) and Nagajyoti *et al.* (2010). Comparing the highest level of Mn (Table 2) of fish and periwinkle in this study with those collected from Ondo coastal river during wet and dry seasons, it was observed that our values were high (Table 3), but the highest Mn values for both seasons (51.17µg/g) and (44.36 µg/g) reported by Rahman *et al.*, (2012) for fish collected from Bangshi River , Bangladesh were higher than our values. The values of Mn (86.62µg/g for dry and 68.60µg/g for wet) in *Rutilus rutilus* collected from a pond in Etueffort, France were higher than ours (Zohra *et al.*, 2014) and also the wet and dry seasonal values of Mn (715.72 µg/g and 689.90 µg/g) in *tympnotonus fuscatus* collected from Qua Iboe river estuary in Niger Delta Region of Nigeria were far higher than ours (Udosen *et al.*, 2005). The value of Mn in this study has raised serious concern, for even though it is known as an essential element at a low concentration, it could also cause effect such as gastro-intestinal irritation, respiratory disease and neuropsychiatric disorder (Udosen,2015), as well as Parkinson's disease (Carpenter, 2001), when large levels are ingested.

Table 2: Comparison of result with WHO/FAO maximum permissible limits (µg/g)

Species	Trace metals						
	Cu	Fe	Mn	Co	Ni	Zn	
<i>Pachymelania aurita</i> (n=5)	24.80 (20.06)	8.91 (6.18)	29.44 (24.97)		0.06 (0.17)	0.54 (0.45)	18.00 (19.00)
<i>Chrysichthys nigrodigitatus</i> (n=5)	12.35 (5.67)	11.04 (5.51)	11.8 (9.85)		0.03 (0.02)	0.14 (0.15)	7.08 (3.30)
WHO/FAO	30.0 ^a	10 ^b	1.00 ^a		1 ^b	5 ^b	50.0 ^b

^aUdosen *et al.*, 2014; ^bAtul *et al.*, 2012; WHO 2011, values in parentheses are for dry season.

The level of copper was the second highest in the examined species of fish and periwinkle samples in this work. The levels were 24.80 µg/g and 20.06 µg/g for periwinkle, and 12.35 µg/g and 5.67 µg/g for fish during wet and dry seasons respectively. The maximum permissible limit of Cu proposed by the WHO/FAO (30.00 µg/g) was higher than values obtained from this study. The levels of Cu in fish and periwinkle from this study were higher than levels in *Cyprinus Carpio* collected from Sikkak dam, Tlemcen Algeria and in mullet fish from Musa estuary, Persian Gulf for both wet and dry season (Table 3). They were also higher than those reported for *tympnotonus fuscatus* (6.51 µg/g and 6.41µg/g) collected from Qua Iboe river in Akwa Ibom State Nigeria for both wet and dry season respectively (Udosen *et al.*, 2005) and those in common roach fish (*Rutilus rutilus*) (3.80µg/g and 4.47µg/g) from ponds in Etueffort, France as reported by Zohra *et al.* (2014).. However our values were lower than those in fish and periwinkle collected from Ondo coastal river, Nigeria as shown in Table 3. If the level of Cu in this biota is not monitored, with time it could pose health threat such as gastro-intestinal bleeding, acute renal failure, liver and kidney failure amongst others ((Udosen, 2015; Arayal, 2003) in humans.

Though with levels quite lower than the FAO/WHO maximum permissible limits of 50.0 µg/g, Zn occurred as the third highest level observed in the study (18.00µg/g and 19.96µg/g) for periwinkle and (7.08µg/g and 3.30µg/g) for both wet and dry seasons respectively. Compared to reported values, the values of Zn in the species of both fish and periwinkle studied were higher than those reported by Ololade *et al.* (2008) but lower than those species of fish from Bangshi, river Sava, Dhaka, Bangladesh, Sikkak dam in Algeria (Table 3), pond in Etueffort,

France with values (566.58µg/g and 576.15) for wet and dry respectively (Zohra et al., 2014) and *tympantonus fuscatus* from Qua Iboe river estuary in Niger Delta Region of Nigeria with values of 109.95µg/g and 119.22µg/g for wet and dry season respectively. Although Zn is an essential element needed by humans in trace amount, it is also a neurotoxin.. It causes neuronal cell death in a dose dependent manner (Udosen, 2015) and it could also reduce the immune system functions in large amount if the levels are not monitored in the aquatic environment.

Table 3: Comparison of results with those reported in literature (µg/g)

Sample location	Species	Cu	Fe	Mn	Co	Ni	Zn	References
Cross river, Itu Nigeria	<i>Pachymelania aurita</i>	24.80 (20.06)	8.91 (6.18)	29.44 (24.97)	0.06 (0.17)	0.54 (0.45)	18.00 (19.00)	This work
	<i>C. nigrodigitatus</i>	12.35 (5.67)	11.04 (5.51)	11.8 (9.85)	0.03 (0.02)	0.14 (0.15)	7.08 (3.30)	
Ondo coastal River Nigeria	<i>Tilapia Zilli</i>	271.14 (194.45)	261.13 (204.72)	1.76 (1.05)	0.11 (0.18)	— —	0.16 (0.23)	(Ololade et al., 2008)
	<i>Littorina Litorea</i>	351.5 (310.2)	1052.6 (1315.5)	0.99 (0.78)	0.24 (0.33)	— —	0.11 (0.10)	
*Bangshi River,Savar, Dhaka, Bangladesh	VSA	8.33- 43.18	—	9.43- 51.17	—	0.69- 4.36	42.83- 418.05	(Rahman, Molla and Arafat 2012)
Sikkak Dam of Tlemcen, Algeria	<i>Cyprinus Carpio</i>	0.11 (0.09)	55.29 (69.70)	—	—	0.84 (0.67)	14.58 (18.80)	(Derragzineb, Dali, Nacera and Meslilotfi, 2014)
*Musa Estuary, Persian Gulf	Mullet fish	0.89- 4.28	—	—	ND- 1.63	0.48- 2.73	—	(Doroghi, Monikh, Safahieh and Savari, 2011)

VSA: Various species analyzed, Values with * are given in ranges, values in parentheses are for dry season

Iron is an essential micro nutrient in human diet but at high levels could be toxic to humans. In this study, the mean level of Fe was the fourth in ranking the concentration of the metals in both fish (8.91µg/g and 6.18µg/g) and periwinkle (11.04µg/g and 5.51µg/g) for wet and dry seasons respectively. The values from this study were lower than those of species collected from Ondo coastal river, Nigeria and those from Qua-Iboe river estuary in Niger Delta, Nigeria(Udosen et al., 2005). The FAO/WHO maximum permissible limit of 10.0µg/g was also higher except for the value recorded for fish (11.04µg/g) during the wet season and this could be attributed to the corroded metal rods from the Calabar - Itu Bridge. Discharge of iron-laden waste could also be a contributing factor.

Nickel is one of the carcinogenic metals determined in this study. It was the fifth highest (0.54µg/g and 0.45µg/g) for periwinkle and (0.14µg/g and 0.15µg/g) for fish in both seasons. Comparing the values obtained for Ni accumulation in muscles of the species of fish and periwinkle with those of literature, our data were lower than those reported by Udosen et al.(2005) with 19.12µg/g for wet and 19.15µg/g for dry seasons and by Rahman et al.(2012) with 4.13µg/g and 4.36µg/g for wet and dry seasons respectively but our values were higher than 0.027 µg/g recorded for dry season only by Andem et al. (2013). The levels for both fish and periwinkle investigated were quite lower than the FAO/WHO maximum permissible limits of 5µg/g.

Based on the total metal levels in the species of fish and periwinkle, cobalt was observed to have accumulated the least with values of 0.06µg/g and 0.17µg/g for periwinkle and 0.03µg/g

and 0.02µg/g for fish in both wet and dry seasons. Our data were below the FAO/WHO maximum permissible limit and also below those reported in literature (Table 3) as well as those reported by Udosen et al. (2005) with 0.98µg/g and 0.97µg/g for both seasons respectively.

Human Health Risk Assessment

Exposure assessment for fish consumption

The evaluation of human exposure to trace metals in the species of both fish and periwinkle were obtained for adults and children, the estimated dietary intake of trace metals in the edible muscles of fish and periwinkle are summarized in Table 5. The results revealed that intake values for trace metals due to consumption of the investigated species collected from the study area were of the trend Mn>Cu>Zn>Fe>Ni>Co for both adults and children (Table 5). Mn, Cu, Zn and Fe showed major contribution through the consumption of fish and periwinkle for both adults and children than other metals analysed. Contribution to trace metals intake through the consumption of seafood were of the trend *Pachymelania aurita* (PA)>*Chrysichthys nigrodigitatus* (CN) for adults and children respectively (Table 5). The implication of these results is that the consumption of more TP would lead to more intake of trace metals and vice versa.

Table 5: Estimated dietary intake of trace metals in some edible muscles of seafood

Species/Metals	Cu	Fe	Mn	Co	Ni	Zn
Adults						
<i>P. aurita</i>	1.54E-02	5.17E-03	1.87E-02	2.64E-04	3.39E-04	1.30E-02
<i>C. nigrodigitatus</i>	6.18E-03	5.55E-03	7.42E-03	1.71E-05	9.94E-05	3.56E-03
PA and CN	2.16E-02	1.07E-02	2.61E-02	2.81E-04	4.39E-04	1.66E-02
Children						
<i>P. aurita</i>	8.52E-02	2.86E-02	1.03E-01	1.47E-03	1.90E-03	7.21E-02
<i>C. nigrodigitatus</i>	3.42E-02	3.07E-02	4.11E-02	9.5E-05	5.1E-04	1.96E-02
PA and CN	1.19E-01	5.94E-02	1.45E-01	1.56E-03	2.43E-03	9.18E-02

PA = *Pachymelania aurita*, CN = *Chrysichthys nigrodigitatus*.

Evaluation of toxic (non-carcinogenic) risks

The hazard quotient helps in the evaluation of the magnitude of harm posed to the consumers of fish and periwinkle contaminated with trace metals. In this study, all the HQ values calculated for adults consuming the sea-foods analysed, were all below unity indicating that low or no toxic risks are associated with them (Table 6) while the HQ calculated for children consuming *Pachymelania aurita* for both season were higher than unity indicating possible risk associated with their consumption while those consuming *Chrysichthys nigrodigitatus* were less than unity indicating low or no risk associated with their consumption. The HQ values were highest for Cu, Mn, and Zn for both adults and children and lowest in Co.

In the study it was assumed that the toxic risk due to potentially hazardous chemicals in the same medium was cumulative; therefore, the summation of the HQs gave the overall toxic risk, which is the hazard index (Table 6). On a general note, all the computed HI values for *Pachymelania aurita* and *Chrysichthys nigrodigitatus* were above unity for children and below unity for adults (Table 6). There is every possibility that same persons consuming fish could also consume periwinkle from the same studied biota.

Table 6: Estimated hazard quotients (HQ) and hazard index (HI) for adults and children due to dietary intake of trace metals in fish and periwinkle species.

Species	HQ						HI
	Cu	Fe	Mn	Co	Ni	Zn	
Adults							
<i>Pachymelania aurita</i>	4.16E-01	6.47E-03	1.33E-01	4.4E-03	1.60E-02	4.35E-02	6.20E-01
<i>C. nigrodigitatus</i>	1.67E-01	6.94E-03	5.30E-02	2.86E-04	4.97E-03	1.19E-02	2.44E-01
PA and CN	5.83E-01	1.34E-02	6.63E-02	4.69E-03	2.19E-02	5.53E-02	7.44E-01
Children							
<i>Pachymelania aurita</i>	2.30E+0	3.58E-01	7.38E-01	2.44E-02	9.41E-02	2.40E-01	3.44E+0
<i>C. nigrodigitatus</i>	9.25E-01	3.85E-02	2.94E-01	1.58E-03	2.76E-02	6.57E-02	1.35E+0
PA and CN	3.24E+0	7.42E-02	1.03E+0	2.59E-02	1.22E-02	2.60E-01	4.74E+0

PA = *Pachymelania aurita*, CN = *Chrysichthys nigrodigitatus*.

Relationship between metals

The Hierarchical cluster analysis and the Pearson's correlation considered in this study were evaluated using the SPSS statistical software package version 20.0. The results revealed that the metals correlated with each other (Table 7). In correlation analysis, some trace metals pairs may have strong correlation with each other and so form primary cluster pairs (Shah et al., 2012). The primary cluster pairs were found for Co-Ni and Cu-Mn in the species of fish and periwinkle studied, this could be because they occur in the same ore in nature or they are by-product of other metals. This is in conformity with what Peltone, et al. (2006) said. According to them pure cobalt is not found in nature but always occur with nickel in iron meteorites. Co is also regarded as always being a by-product of other metals, primarily nickel. According to Smith, et al. (2001) oceanic tholelites is an ore of copper and manganese and ferromanganese contains Mn and Cu as well as other minor trace metals. The cluster analyses reveal that the presence of one metal may have interactive effect on each other within the grouping.

Table 6: Correlation coefficient matrix of trace metals in fish and periwinkle from Cross river.

	FD	PD	FW	PW
FD	1			
PD	.821(*)	1		
FW	.045	.773	1	
PW	.898(*)	.071	.848(*)	1
	.015	.980(**)	.033	
	.894	.001		

*Correlation is significant at the 0.05 level (2-tailed), ** Correlation is significant at the 0.01 level (tailed). Seasonal values for sample: FD: Fish values for dry, PD: periwinkle values for dry, FW: Fish values for wet, PW: Periwinkle values for wet.

CONCLUSION

The present study revealed that trace metals are widely spread in Cross River at various levels and ranged from very low to high levels particularly the non-carcinogenic metals. The contamination sources could be linked to the indiscriminate dumping of domestic, agricultural, and metallic wastes (which could be from the automobile repair shops) and run-off from the various outlets within the community. Oral ingestion was the only pathway for humans (since the samples studied are edible) and therefore pose some degree of toxic risk to humans with children being the most vulnerable.

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