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Bioaccumulation and Human Health Risk Assessment of Trace Metals in *Tympanotonus fuscatus* from Cross River Estuary, Niger Delta, Nigeria

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Abstract

This study was conducted to determine the levels of some trace metals in sediment and periwinkle (*Tympanotonus fuscatus*) from Cross River estuary (CRE) and estimate the human health risk associated with the consumption of *Tympanotonus fuscatus* from the estuary. The trace metals in sediment and periwinkle were determined using Atomic Absorption Spectrophotometer (AAS) and the human health risk assessment of the trace metals was carried out using models stipulated by United States Environmental Protection Agency (USEPA). The range for the results of trace metals in sediment (mg/kg) during the dry and wet seasons were as follows : Pb (19.836 -53.500), Cd (5.056 - 31.286), Ni (8.130 - 60.403), Fe (16.781-66.303), Zn (5.933-20.096), Cu (3.375-27.986) while the range for the results of trace metals in periwinkle(mg/kg) during both seasons were : Pb (0.836 - 4.020), Cd (0.270-4.650), Ni (0.430 - 4.363), Fe (0.396 -13.800), Zn (0.603-31.060), Cu (11.096 - 42.875). Apart from zinc and copper all the investigated metals in sediment during the dry and wet seasons were above the sediment quality guideline stipulated by National Oceanic and atmospheric administration (NOAA). Pb, Cd and Ni in periwinkle were above the Food and Agricultural organization standard (FAO) in both dry and wet seasons while Fe, Cu and Zn were below the FAO standard except in few stations were they exceeded the limit. The bioaccumulation factor for Zn and Cu were greater than unity for most of the stations in both seasons. Also, the linear regression models revealed positive relationships between the metals in the sediment and the periwinkle tissues in the dry season. The estimated daily intake, hazard index and target hazard quotient (THQ) via ingestion pathway for all the investigated metals were less than unity. Frequent monitoring of the aquatic environment is advocated to detect and prevent cumulative effect of trace metal pollutants in edible periwinkle which may result in health risk in humans.

1. Introduction

Shellfish for example periwinkle and crabs constitute cheap sources of animal protein and minerals such as zinc, copper and iron for the coastal communities [1-2]. They occur abundantly in brackish and fresh waters in coastal areas such as the Niger Delta in Nigeria. High levels of trace metals in environmental matrices such as water, sediment and biota such as periwinkle may be linked to human activities. Metal pollution results from direct atmospheric deposition, geologic weathering or through the discharge of industrial waste products [3].

The discharged trace metals from industrial effluents associates with particulates and ultimately settles in the bottom sediment of water bodies and may be taken up by aquatic organisms such as periwinkle and fish. Sediment are repositories for physical and biological debris and also act as sinks for a wide variety of pollutants such as trace metals and polycyclic aromatic hydrocarbons [4]. Periwinkles and other aquatic organisms can bioaccumulate and consequently biomagnify contaminants such as trace metals in their environment. The ingestion of these metals and their possible accumulation affect biological processes such as reproduction, feeding, growth and maturity etc in the mollusk [5]. Also, human beings and other animals at higher trophic levels are at great risk as a result of bioavailability and biomagnifiction of these contaminants. Edema and Ebong [6] reported the non-biodegradable and persistent nature of trace metals in the environment indicating that they can easily be assimilated and bioaccumulated in the protoplasm of aquatic organisms. The use of periwinkle as bioindicator in monitoring trace metals pollution in aquatic ecosystem has been reported by many authors [4, 7, 8].

Since periwinkle forms part of the daily staple food in the Niger Delta region of Nigeria, human exposure to trace metals contaminants through the consumption of periwinkle may result in adverse health effects. These health effects with varying symptoms depends on the nature and quantity of the metal ingested [9]. The nature and magnitude of possible risk from human exposure to environmental pollutants such as trace metals can be assessed using human health risk assessment models [10]. Four processes are involved in risk assessment and they include; hazard identification, exposure assessment, toxicity assessment and risk characterization. Usually the risk characterization is achieved by comparing the dose-response assessment with the exposure assessment [10].

Exposure of humans to copper has been linked with hyperactivity, schizophrenia**,** insomnia**,** autism**,** stuttering**,** postpartum psychosis**,** inflammation and enlargement of liver. Nickel is carcinogenic and long term exposure to nickel can result in skin irritation and reduction in body weight [11]. Chronic exposure to copper result in liver damage and gastrointestinal illness while high level of zinc leads to muscle pain, anaemia and renal failure [12].

Cross River estuary is located in the Niger Delta region of Nigeria and the water from the estuary is used for drinking, fishing activities, recreational activities like swimming and irrigation. Domestic wastes from homes, hotels and industrial waste water from a petrochemical industries located in the area are discharged directly into the estuary. In the Niger Delta, trace metals contamination by metals such as Pb, Ni, Cd, Zn, Cu, Fe and their elevated levels in the environment is primarily due to uncontrolled pollution levels linked to oil spill, indiscriminate discharge of domestic and municipal waste, agricultural run-offs and pipeline vandalisation [13].

Inengite *et al*. [14] reported that Pb, Ni, Cr, V are minor components of crude oil which is the major pollutant in the estuary. Also, the metals considered in this study were determined because of their association in piping system, oil exploration such as drilling mudand as anticorrosive agents in the marine environment. Pb, Cd and Zn are useful as pigment in marine corrosion inhibition paints and lead is also used as an antiknock agent in marine automobile engines. Copper is a major component of wood preservatives in boat making process while nickel is used as an alloy in steel [15].

Different authors have reported on the level of trace metals in periwinkle from the Niger delta region [5, 16-18] while other authors studied the possible accumulation or transfer of trace metals from the sediment to the tissues of periwinkle [4, 8, 19-20], and human health risk in one location along CRE reported by Udousoro *et al*. [11]. However, there is little or no data on the risk assessment based on human exposure to trace metals via periwinkle consumption from five different locations along CRE in both dry and wet season.

The objective of this study is to assess the levels of some trace metals (Pb, Cd, Ni, Fe, Zn and Cu) in sediment and periwinkle (*Tympanotonus fuscatus* radula var) collected from five locations along Cross River estuary and estimate the human health risk induced by the consumption of periwinkle contaminated by these trace metals.

2. Material and Methods

2.1 Description of study area

The Cross River estuary takes it rise from Cameroon Mountains. It meanders into Nigeria and then Southwards through high rainforest formations before discharging into the Atlantic Ocean through the Cross River at the Gulf of Guinea (Figure 1 & Table 1). Within the lower brackish water reaches of the River, the Vegetation changes to mangrove forest. It is the biggest estuary in the Gulf of Guinea. The detailed description of this study area has been reported in our previous work [13].

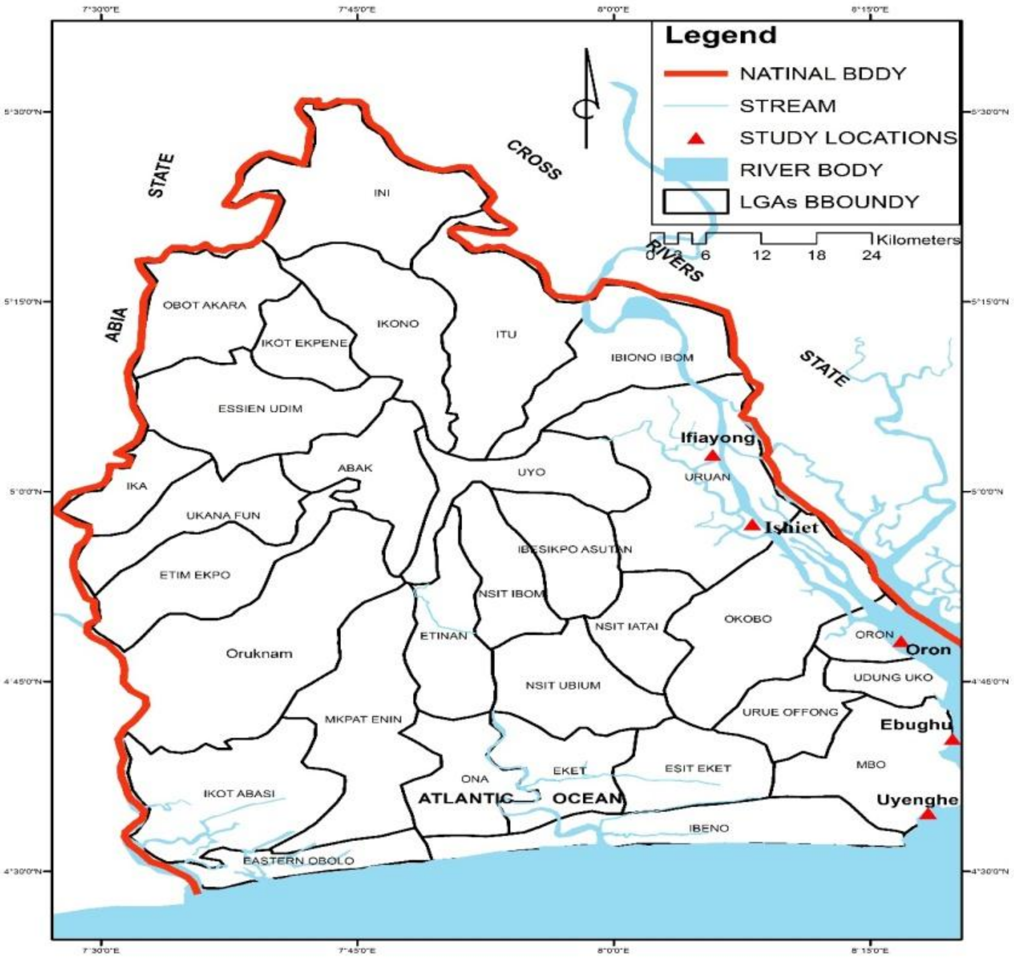

Figure 1: Map of Akwa Ibom state showing the study locations

Table 1:GPS coordinates of sampling locations along from Cross River Estuary

Study location	Longitude (E)	Latitude (N)
Ebughu	8.32470	4.6786
Ishiet	8.1357	4.9555
Oron	8.2770	4.7887
Uyenghe	8.30533	4.5726
Ifiayong	8.096904	5.04701

2.2 Sample collection, preparation and digestion

The periwinkle samples were collected at low tide from the five fishing beaches along Cross River estuary (CRE) using quadrat sampling method reported by Ikpe *et al*. [19]. Boats were used to access the shorelines during sample collection from the selected locations. *Typanotonus fuscatus* radula (var) from the study sites is brownish in colour with spikes and sharp pointed shells. Sampling was conducted monthly from December, 2018 to February, 2019 for the dry season and May, 2019 to July, 2019 for the wet season. The periwinkle samples were purchased from the fishermen as soon as they were collected. They were rinsed and stored in polyethylene bags and transported to the laboratory in a flask filled with ice. Surface sediment (1-15 cm depth) were collected at each location. Twenty samples (200 g) each from five sampling points per sampling sites were randomly homogenized to form a composite sample. The sediment samples were stored in polyethylene bags and transported in an ice-chest to the laboratory. In the laboratory, the periwinkle samples were washed with tap water, followed by distilled water and allowed to dry. The edible tissues were removed from the shells with a needle and dried in an oven at 60^oC to a constant weight. The dried samples were ground to powder with plastic mortar and pestle, passed through 0.5 mm mesh sieve and stored in a well-labelled plastic container for digestion. The sediment samples were air-dried for seven days and each sample was ground with plastic mortar and pestle, passed through 2 mm mesh and stored in well-labelled plastic for digestion.

2.3 Digestion of Sediment samples

Digestion of sediment was carried out according to the ISO 11466 procedure which involves the digestion of 2 g of sediment (dry weight) with aqua regia acid mixture [21]. The blank was digested using similar procedures.

2.4 Digestion of periwinkle samples

A modified method of De wolf *et al*. [22] was used for the digestion of periwinkle tissues. 2g each of periwinkle samples were weighed into 50ml Teflon beaker. The digestion was done using 20 ml mixture of nitric acid and perchloric acid (2:1) boiled on a hot plate in a reflux system to obtain a clear solution, which was then evaporated to near dryness in a fume cupboard. The cooled residue was dissolved in 0.5M nitric acid filtered into 50ml standard flask using Whatman no 42 filter paper and made up to the mark with dilute 0.5M nitric acid. The same procedure was used for the bank digest.

2.5 Determination of trace metals

After appropriate digestion of the sample, the trace metals were determined using Buck atomic absorption spectrophotometer (Unicam939/959 model). Before the determination of the trace metals concentration in the samples, a calibration curve was prepared from a standard stock solution of the metals. Buck certified standards were used for the respective trace metals while the working solutions were prepared by dilution of the stock solution. A hollow cathode lamp for each of the metal was used for each analysis. Each of the working standard was sprayed or aspirated into the flame and the corresponding absorbance for each concentration was recorded. A blank was similarly determined. Blanks were used to reset the instrument prior to each analysis to avoid matrix interference. The analysis was carried out three times for reproducibility, accuracy and precision.

2.6 Statistical analysis

All values were expressed as mean of three determinations ± standard deviation. One way ANOVA and linear regression analysis were performed using Excel spreadsheet of window 10. This application was used to compare the mean between stations and a $P < 0.05$ was considered statistically significant. Linear regression was performed using SPSS statistics version 22 for windows.

2.7 Estimation of bioaccumulation factor

Bioaccumulation factor (BAF) describes the absorption and distribution of a substance in an organism after exposure in a given environmental matrix [11] and was used to ascertain possible bioaccumulation of the toxicant in the periwinkle tissue. Chindah *et al*. [20], reported that BAF can be calculated as the ratio of pollutant levels in the periwinkle tissues to those in sediments as shown in equation 1 below:

$$\text{BAF} = \text{Concentration of trace metals in periwinkle} \,/\, \text{concentration of trace metals in sediment} \ldots\ldots \ (1)$$

2.8 *Health risk assessment of trace metals in sea food*

Human health risk assessment is a process that involves the characterization of the probability of adverse human health effect associated with exposure to environmental chemicals. Different models have been postulated for different pollution pathway. The exposure assessment for ingestion of contaminated periwinkle was calculated using the model in equation (2) postulated by USEPA [23].

2.8.1Pollution pathway

Usually pollutants gain entry into the body through different exposure or contact pathways which include inhalation, ingestion and dermal contacts.

Ingestionpathway

2.8.2 Ingestion pathway

A typical risk for oral exposure (ingestion) of some trace metals may be defined by equation 2 below:

$$\text{EDI}_{\text{ingestion}} = \frac{\text{C x IR x EF x ED x CF}}{\text{Bw x AT}} \ldots\ldots \ (2)$$

Where $\text{EDI}_{\text{ingestion}}$ = estimated daily intake via ingestion(mg/kg/day)

C =Concentration of trace metal or other pollutants in periwinkle(mg/kg),

IR = Periwinkle ingestion rate(0.036kg/person/day) for periwinkle

EF =Exposure frequency (365 days/year)

ED = Exposure duration (70 years)

BW= Body weight (70kg)

AT= Average time (25550 days)

CF = Conversion factor of fresh weight to dry weight intake rates of periwinkle tissues using moisture percentage in periwinkle and is 0.17 for *Tympanotonus fuscatus* [24].

The periwinkle ingestion rate is obtained from one-on-one interview and questionnaire survey of 110 adult participants, aged 17 to 60 years reported by Udousoro *et al*. [11] was adopted in this study because periwinkle consumption pattern of 60 – 70 years adults are assumed to be the sam in the locality.

2. 9 Non-*carcinogenic* risk assessment

Non-carcinogenic risk of some trace metal in contaminated periwinkle may be predicted from their target hazard quotient (THQ) in equation 3[23].

$$\text{THQing} = \frac{\text{EDIing}}{\text{RfD}} \ldots\ldots \ (3)$$

EDIing = estimated daily intake via ingestion (mg/kg /day) RfD = reference dose of the contaminant (mg /kg/ day)

The values for Hazard index (HI) was obtained from the model of USEPA [25] and Naveedullah *et al*. [26].

$$\text{HI} = \text{THQ}_{(\text{Toxicant 1})} + \text{THQ}_{(\text{Toxicant 2})} + \ldots\ldots \text{THQ}_{(\text{Toxicant n})} \ldots\ldots (4)$$

If the THQ and HI are greater than unity there might be concerns for non-carcinogenic risk, which indicates potential adverse effect on human health. HI is the sum of THQs from all applicable pathways and different pollutants. It is used to evaluate the total potential non-carcinogenic risk posed by more than one pathway and more than one pollutant.

3. Results and discussion

3.1 Levels of trace metals in sediment

The level of trace metals in sediment from the study sites are presented in Tables 2 and 3.

Table 2: Mean concentrations of trace metals in sediment from Cross River estuary (CRE) during the dry season (mg/kg dw)

Location	Pb	Cd	Ni	Fe	Zn	Cu
Oron	21.690±1.810	22.243±3.430	8.130±0.302	16.781±1.096	15.216±4.329	8.113±0.897
Ebughu	20.225±1.294	12.546±1.954	14.206±1.103	59.346±2.007	20.096±1.666	5.980±0.334
Uyenghe	53.50±2.185	5.056±0.876	22.333±0.804	29.336±5.720	5.933±0.960	3.375±1.634
Ifiayong	23.300±0.871	11.613±1.059	25.470±0.883	18.676±2.365	15.293±3.560	6.450±0.713
Ishiet	20.701±0.871	31.166±0.850	36.001±1.527	20.016±7.017	11.003±0.005	4.483±0.025
NOAA standard	12.8	4.95	16	10.38	111	29.7

Table 3: Mean concentrations of trace metals in sediment from Cross River estuary (CRE) during the wet season (mg/kg dw)

Location	Pb	Cd	Ni	Fe	Zn	Cu
Oron	33.760±3.418	30.433±3.909	45.180±3.310	44.836±8.492	12.653±3.642	26.100±3.642
Ebughu	35.283±2.693	31.286±3.354	41.716±4.889	47.869±2.782	13.056±1.293	19.653±1.293
Uyenghe	42.250±9.562	30.471±1.234	45.943±7.212	48.943±3.410	12.686±1.787	27.986±1.787
Ifiayong	19.836±7.629	20.062±8.045	32.566±10.245	32.823±10.498	15.220±3.860	14.153±3.860
Ishiet	32.360±9.364	13.003±2.412	60.403±19.297	66.303±13.490	14.936±4.527	23.313±4.527
NOAA standard	12.8	4.95	16	10.38	111	29.7

As presented in Tables 2 and 3, the variation for trace metals in the dry season was Fe > Ni >Pb> Cd > Zn > Cu while the variation for the wet season was Fe > Ni >Pb> Cu >Zn > Cd. One way analysis of variance (ANOVA) at 95% confidence level, using Microsoft excel revealed significant differences between the mean of five sampling sites for sediment during the dry and wet seasons ($P < 0.05$).

The highest value was recorded for iron in the wet season while the least value was recorded for copper in the dry season. The levels of trace metals in sediment during the wet season were generally higher than values in the dry season. This corroborates the research findings reported elsewhere [4, 27]. However, Ikpe *et al.* [19] recorded higher values in the dry season compared to the wet season. Chindah *et al.* [20] reported that increase volume of suspended particulate matter in sediment and run-offs with municipal and industrial wastes into the aquatic ecosystem were responsible for higher wet season values compared to dry season while Freeman and Ovie, [27] confirmed that contaminants bioavailability increases with increase in water volume from their anthropogenic sources. Nwadinigwe *et al.* [28] reported that the variability in levels of trace metals in the dry and wet season and between sampling stations might be due to the geological distribution of minerals from one study site to the other.

The result for iron in this study is comparable to the work of Ikpe *et al.* [19] and Nwadinigwe *et al.* [28]. Iron in the environment originates from both anthropogenic and natural sources. Iron is the second most abundant element and the most abundant transition metal in the earth crust and high levels of iron in sediments might be due to the discharge of iron-laden waste and effluents with corroded iron pipes. Nwadinigwe *et al.* [28] attributed the high level of iron to the nature of the soil along the river course leached into the river system. The level of Fe in Ebughu, Ishiet and Uyenghe were higher than the probable effect concentration (PEC) stipulated by NOAA [29] while the level at Oron and Ifiayong were higher than the lowest effect level (LEL) and the threshold effect level (TEL) for the dry season. An elevated level of iron is toxic to intracellular organelles such as mitochondria and lysosomes. It produces hydrogen free radical that results in the oxidation of DNA molecules leading to cellular damage and cell death [30]. The level of Cd in this study is similar to the findings of Udousoro*et al*. [11]. Cd in the wet season was higher than the level in the dry season. The results for Cd in sediments were higher than the standard stipulated by NOAA [29]. Cd binds to cysteine-rich protein such as metallothlonein and could lead to nephrotoxicity. Cd replaces zinc in the metallothlonein since they have the same oxidation state as zinc, thereby inhibiting it from acting as free radical scavenger within the cell. Long term exposure to Cd results in kidney damage, fragile bones, lung disease and reduced weight and premature death during pregnancy [12].Cd is used as pigment in paint and released into the environment through fertiliser production, river transport and incineration of municipal waste.

Nickel and lead in the wet season were higher than values in the dry season. The finding in this study is similar to values reported by Udousoro *et al.* [11] and Okorafor *et al.* [31]. Nickel is said to be from chronic discharge of petroleum waste into the ecosystem [32]. Lead laden waste discharged into the aquatic ecosystem is responsible for the high levels of lead in the environment. Lead is used in industrial activities and consumer products such as storage batteries, gasoline additives, rolled and extruded products, paints, alloys and pigments. Lethal doses of lead affect sperm shape, mobility and DNA integrity resulting in male infertility. Lead accumulation affects cellular functions such as growth and immune responses. Also, lead can substitute calcium even in picomolar concentration affecting protein kinase C which regulates neural excitation and memory storage [33].

Cu and Zn were higher in the wet season compared to the dry season. The result for zinc in this study was comparable to the values reported for Ibeno and lower than value reported for Ishiet by Udousoro *et al*. [11]. The results for zinc and copper were lower than the sediment quality guidelines stipulated by NOAA, [29], while the result for Cu in this study was higher than values reported by other authors [7, 19, 27, 31]. Generally, the level of trace metals in sediment was higher than the level in periwinkle except Cu and Zn in some stations. Sediments serve as sink or reservoirs for aquatic pollutants such as trace metals and holds up to 90% of the total amount of metals in an aquatic system [31, 34]. Bazzil [35] confirmed that sediments act as reservoir for all contaminants and dead organic matter from the ecosystem.

3.2 Levels of trace metals in Periwinkle

The trend for the levels of trace metals in periwinkle during the wet season was Cu > Zn > Fe > Ni >Pb> Cd while the pattern for the dry season was Cu > Zn > Fe >Pb> Ni > Cd. The result for the levels of trace metals in periwinkle in both the dry and wet seasons are presented in Tables 4 and 5 respectively. One way analysis of variance (ANOVA) at 95% confidence level, using Microsoft excel revealed significant differences between the mean of five sampling sites for periwinkle during the dry and wet seasons ($P < 0.05$).

The highest value was recorded for Copper with the least value recorded for Cadmium. Pb, Cu, Fe and Zn recorded higher values in the dry season compared to wet season while the values of Cd and Ni were higher in the wet season than the dry season. The result for Pb and Fe were comparable to the result reported by Ikpe *et al.* [19] while other investigated metals were higher than the results reported by the following researchers [27, 31].

Apart from the level in sample from Ebughu, Pb at all the stations was above FAO standard in the dry season and wet season [36]. Cd in the sample from Oron and Ifiayong in the dry season and Cd at Ifiayong during the wet season were below than standard. Ni in all the stations in both seasons was above the stipulated standard except at Ifiayong during the wet season. The levels of Fe, Zn and Cu in this study were below the FAO limit, apart from Cu at Ebughu and Ifiayong during the dry season and Zn at Ifiayong during the dry season.

Table 4: Mean concentrations of trace metals in periwinkle from Cross River estuary (CRE) during the dry season (mg/kg dw)

Location	Pb	Cd	Ni	Fe	Zn	Cu
Oron	2.106±0.066	0.415±0.033	2.550±0.070	3.31±0.585	0.603±0.044	27.255±2.146
Ebughu	0.836±0.065	0.510±0.038	0.586±0.022	10.133±0.375	26.535±3.951	40.150±3.597
Uyenghe	4.020±0.783	2.506±0.257	4.183±0.920	13.800±1.633	5.525±0.085	11.960±0.461
Ifiayong	11.213±1.050	0.476±0.032	0.630±0.025	0.396±0.027	31.060±2.693	42.875±3.571
Ishiet	3.610±0.346	4.650±0.427	1.023±0.415	1.026±0.026	14.666±1.527	6.500±0.802
FAO/WHO 1983	1	0.5	0.5	30	30	40

Table 5: Mean concentrations of trace metals in periwinkle from Cross River estuary (CRE) during the wet season

Location	Pb	Cd	Ni	Fe	Zn	Cu
Oron	1.812±0.029	1.330±0.216	1.860±0.570	3.673±0.403	11.74±0.496	22.260±0.141
Ebughu	2.06±0.669	2.953±0.518	1.883±0.160	3.66±0.330	13.890±3.120	25.916±1.480
Uyenghe	3.631±0.573	3.713±0.216	4.363±0.502	4.856±0.608	15.290±6.861	25.566±4.722
Ifiayong	1.230±0.025	0.270±0.002	0.430±0.263	3.293±0.042	7.230±0.342	11.096±0.838
Ishiet	1.180±0.918	0.567±0.221	1.303±0.803	7.425±1.125	1.148±0.148	33.143±1.086
FAO/WHO 1983	1	0.5	0.5	30	30	40

3.3 Bioaccumlation factor

Bioaccumulation factor (BAF) explains the potential of a biota to accumulate trace metals [20], [37]. Also, Moslen *et al*. [8] reported that BAF results gives information on the assimilation and excretion rate of trace metals in organisms with respect to their surrounding environment. According to Wokoma [34], BAF values greater than one indicates bioaccumulation or how probable a pollutant is to bioaccumulate. The order of bioaccumulation of periwinkle from sediment in this study was Cu> Zn > Fe >Ni >Pb>Cd for the dry season while the variation for the wet season was Cu > Zn > Fe > Ni > Cd >Pb (Tables 6 and 7). Higher bioaccumulation was recorded for Zn and Cu during the wet season in this study. However, Chindah *et al.* [20], reported opposite findings. The result for BAF in this study corroborated the findings of Davies *et al*. [37] who reported that the BAF values decreases with increasing metal concentration in sediments. The BAF for Zn at Ebughu, Ishiet and Ifiayong during the dry season and the BCF for Cu in all the study locations were above one while the BAF value for Zn at Oron, Ifiayong and Ishiet during the wet season and Cu for Ebughu and Ishiet during the wet season were above unity.

In this study, the BAF values in dry season were observed to be higher than the values in the wet season. This might be due to differences in metal uptake by *Tympanotus fuscatus*. Chindah *et al.* [20] listed various factors that affect the uptake of metals in the tissue of *Tympanotus fuscatus* to include reproductive conditions, metabolic activities, feeding habits, age and developmental stages. Davies *et al*. [37] confirmed that the biological availability of metals in sediment is a function of above listed physiochemical parameters and that only solubilised or leacheable metals are bioavailable. Moslen *et al.*, [8], attributed the body contents of metals in organism to the net balance between the processes of metal uptake and metal loss.

Ikpe *et al.* [19] recorded values for BAF greater than one for copper and arsenic while other investigated metals were less than one. The result in this study implies that sediment to biota transfer of Zn and Cu is a pathway or route of human exposure to sediment contamination. Davies *et al.* [8] also reported bioaccumulation of Cu and zinc in periwinkle from Elechi Creek, Upper Bonny in Rivers state, Nigeria. The high BAF values of zinc and Cu inspite of their low concentration in sediment reveal their high bio-magnification ability. This might be due to their importance as co-factor in biochemical and physiological functions in the body as essential trace metals. The result in this study is similar to the findings of Nwoko *et al.* [18], who reported very high level of copper accumulation as observed in this study. Also, high levels of Cu and zinc in the soft tissue transferred from sediment might be due to anthropogenic activities such as effluents discharged from industries located close to the sampling sites. This accumulation of zinc and Cu may result in copper and zinc toxicity induced by the consumption of periwinkle from the study sites.

Zinc toxicity results in vomiting, diarrhoea, abdominal cramping and intestinal haemorrhage. High levels of zinc have antagonistic effect on other essential elements such as copper and iron. Acute effect of inhaled zinc results in pulmonary stress, chills, fever and gastroenteritis in industrial workers exposed to zinc fumes [38]. High zinc diet has been linked with hypocalcaemia and bone resorption in rats [39]. Short-term exposure to high levels of copper can cause gastrointestinal distress while long-term exposure and severe cases of copper poisoning can cause anaemia, Wilson's disease (genetic disorder resulting in abnormal copper absorption and metabolism) and disrupt liver and kidney functions [40].

Zinc is widely used in industrial products such as paints, rubber, wood preservatives and dyes while copper is widely used in the production of many items including electrical wiring and plumbing materials such as household water pipes.

Table 6: Bioaccumulation factors for trace metals in *Tympanotonus fuscatus* from CRE during the dry season

Location	Pb	Cd	Ni	Fe	Zn	Cu
Oron	0.097	0.018	0.313	0.185	0.039	8.699
Ebughu	0.041	0.040	0.041	0.170	1.320	6.714
Uyenghe	0.751	0.495	0.187	0.470	0.931	3.543
Ifiayong	0.480	0.040	0.024	0.021	2.030	6.638
Ishiet	0.173	0.149	0.028	0.051	1.332	1.449

Table 7: Bioaccumultion factors for trace metals in *Tympanotonus fuscatus* from CRE during the wet season

Location	Pb	Cd	Ni	Fe	Zn	Cu
Oron	0.053	0.043	0.041	0.081	1.077	0.845
Ebughu	0.058	0.094	0.045	0.076	0.939	1.318
Uyenghe	0.085	0.121	0.094	0.099	0.829	0.913
Ifiayong	0.062	0.013	0.0193	0.100	2.104	0.784
Ishiet	0.036	0.044	0.021	0.112	1.632	1.421

3.*4 Predictive linear regression models for trace metals in periwinkle and sediment from CRE*

The use of the linear regression model to predict contaminants concentration in tissues and organs of aquatic biota (fauna) has been reported by many authors [19, 20]. Regression model is used to predict the relationship between pairs of variables, where one is a dependent variable and the other is an independent variable [41]. In this study, the level of contaminants in the tissues of periwinkle, the dependent or response variable (y) was plotted against the level of contaminants in the sediment the independent or predictor variable (x). In the dry season, there was a positive correlation between the tissue concentration of the Pb, Cd, Ni, Fe and Zn and the concentration in the sediment. The unit increase for the concentration of pollutants in the tissue of periwinkle attributable to the contaminant in the sediment was (0.105, 0.089, 0.035, 0.211, and 1.349) respectively for the above mentioned metals. The concentration of copper in the tissue decreased by 7.635 per unit increases in sediment copper concentration.

The coefficient of determination measures the extent that the dependent variable is predicted by the independent variable. It assesses how well a model explains or predict future outcome. According to Chinda *et al*. [20], the coefficient of determination (R^2) reveals the percentage variation in the concentration of the metal in the tissue attributable to the sediment concentration. In this study, 49 % of the variation in the concentration of copper in the organism is attributable to sediment copper load while the variation for Pb, Cd, Ni, Fe and Zn were 36%, 23.9%, 5%, 39.3% and 3% respectively.

In the wet season, positive correlation between the tissue concentration and concentration in the sediment was recorded for Ni, Cu, Zn while Pb, Cd and Fe recorded negative correlation. The unit increase for the concentration of pollutants in the tissue of the organism attributable to the contaminant in the sediment was 0.22 for Ni, 2.356 for Zn and 0.913 for Cu. The unit decrease in the concentration of the organism asa result of the concentration in the sediment was 0.097 for Pb, 0.2265 for Cd and 0.13 for Fe. The percentage variation in the tissue of periwinkle is indicated by the R^2 values presented in Table 8 and 9. Higher variation was observed in the wet season compared to the dry season. The R^2 values of 0.60 mean that 60% of the dependent variable is predicted by the independent variable. In this study, 63.7% of Pb, 60.6% of Cd, 2.49% of Ni, 84.46% of Fe, 80.7% of Zn and 39.6% of the investigated trace metals in the tissues of periwinkle was predicted by the concentration of the respective metals in the sediment.

The intercept in a regression model is the value of y when the value for x is zero. Values for the intercept and below are not dependent on sediment concentration. For example, copper values in the periwinkle tissue of 3.236 mg/kg and below are not dependent on the concentration of copper in the sediment.

Table 8: Regression analysis between trace metals concentration in the tissues of periwinkle and sediment during the dry season

Metal	Regression equation	Coefficient of determination (R^2)
Pb	$Y = 0.105x + 2.435$	0.0363
Cd	$Y = 0.0892x + 0.236$	0.2394
Ni	$Y = 0.035x + 2.494$	0.0514
Fe	$Y = 0.211x + 0.393$	0.3953
Zn	$Y = 1.349x + 2.546$	0.3003
Cu	$Y = 7.635x - 10.270$	0.4914

Table 9: Regression analysis between trace metals concentration in the tissues of periwinkle and sediment during the wet season

Metal	Regression equation	Coefficient of determination (R^2)
Pb	$Y = 0.097x - 1.194$	0.630
Cd	$Y = 0.226x - 4.290$	0.606
Ni	$Y = 0.022x + 1.019$	0.024
Fe	$Y = 0.130x - 1.676$	0.846
Zn	$Y = 2.356x + 43.763$	0.807
Cu	$Y = 0.913x - 3.236$	0.390

3.5 *Human risk assessment of trace metals via the consumption of tympanotonus fuscatus*

3.5.1 Estimated daily intake

The estimated daily intake (EDI) of metals is the milligram per body weight per day of a pollutant and it is usually compared with the oral reference dose for risk characterization. The oral reference dose is the maximum tolerable daily intake of a specific metal that does not result in any deleterious health effect [42]. The EDI (mg/kg bw/day) of the six investigated metals were computed based on daily consumption of 0.036 kg/person/day of *Tympanostus fuscatus* from the five locations along Cross River estuary and the result is presented in Tables 10 and 11 for both the dry and wet season respectively. In this study, the EDI of the investigated metals (Pb, Cd, Ni, Zn, Fe and Cu) were lower than the oral reference dose (RFD) suggesting that the trace metals in periwinkle tissues may not pose any health risk. Saha and Zaman [43], reported that oral reference dose is the estimated daily exposure to which the human population may be continually exposed over a life time without appreciable risk.

The result in this study is similar to the findings of Udousoro *et al.* [11], who determined the EDI of Pb, Cd, Ni, Fe, Zn and Cu for both *Tympanostus fuscatus* and *Pachymelenia fusca* from two coastal areas of Akwa Ibom State, Nigeria. However, the EDI values in this study are lower than the result reported by Markmanuel *et al*. [44], for EDI for two species of periwinkle from Bayelsa, Nigeria. The EDI values recorded in this study are lower than the data for provisional tolerable daily intake for the investigated metals as suggested by the Joint FAO/WHO Expert Committee for Food Additives [45]. The trend for the variation of EDI in the dry season was Cu > Zn > Fe > Pb> Cd > Ni while the trend for the wet season was Cu > Zn > Fe > Ni > Pb > Cd.

Table 10: Estimated daily intake of trace metals via the consumption of *Tympanostus fuscatus* from CRE during the dry season

Location	Pb	Cd	Ni	Fe	Zn	Cu
Oron	1.840E-04	3.628E-05	3.172E-06	2.720E-04	5.271E-05	2.383E-03
Ebughu	7.309E-05	4.458E-05	3.897E-06	8.860E-04	2.319E-05	3.510E-03
Uyenghe	3.514E-04	2.190E-04	1.915E-05	1.207E-04	4.830E-04	1.046E-03
Ifiayong	9.803E-04	4.166E-05	3.638E-06	3.460E-05	2.715E-03	3.744E-03
Ishiet	3.147E-04	4.665E-04	3.554E-05	8.970E-05	1.282E-03	5.683E-04
RfD	4.000E-03	1.000E-03	2.000E-02	7.000E-01	3.000E-01	4.000E-02

RfD is the oral reference dose

Table 11: Estimated daily intake of trace metals via the consumption of *Tympanostusfuscatus*from CRE during the wet season

Location	Pb	Cd	Ni	Fe	Zn	Cu
Oron	1.584E-04	1.160E-04	1.650E-04	3.210E-04	1.026E-03	1.929E-03
Ebughu	1.804E-04	2.580E-04	1.65E-04	3.200E-04	1.214E-03	2.260E-03
Uyenghe	3.173E-04	3.250E-04	3.810E-04	4.250E-04	1.337E-03	2.235E-03
Ifiayong	1.075E-04	2.370E-04	5.510E-05	2.881E-04	6.320E-04	9.700E-04
Ishiet	1.031E-04	5.040E-05	1.140E-04	6.490E-04	8.000E-04	2.895E-03
RfD	4.000E-03	1.000E-03	2.000E-02	7.000E-01	3.000E-01	4.000E-02

3.5.2 Target hazard quotient

Target hazard quotient (THQ) has been recognized as one of the methods for the evaluation of risk associated with intake of metals via the consumption of contaminated food such as fish and shell fish [46], [47]. The THQ value proposed by USEPA compares the amount of the ingested product with a standard reference [15]. The target hazard quotient and the hazard index of periwinkle harvested from the study locations are presented in Tables 12 and 13 for the dry and wet season respectively. The highest value was recorded for Cd at Ishiet while the least value was recorded for Ni at Uyenghe during the dry season. In the wet season, the highest value was recorded for Fe at Ifiayong. The trend for the THQ in the dry season was Cd > Pb > Cu > Zn > Fe > Ni while the variation for the wet season was Cu > Pb> Cd > Ni > Zn > Fe. The THQ for all the investigated metals during the dry and wet seasons were less than unity. This indicates that there might be no considerable health hazard from the consumption of *Tympanostus fuscatus* from the study area. The high level of THQ for Cd in the dry season recorded in this study is similar to the findings of Udousoro *et al.* [11]. The cumulative THQ (Hazard index) was less than one for both the dry and wet season. The HI value for Ishiet during the dry season was 0.505, this indicate possible risk in the future as a result of bioaccumulative and non-biodegradable nature of trace metals. Markmanuel *et al*. [44], recorded THQ values less than one which is similar to this study. However, the hazard indices values for their study were greater than one.

Table 12: Target hazard quotient (THQ) and hazard index (HI) of trace metals via the consumption of *Tympanostus fuscatus* from CRE during the dry season

Location	Pb	Cd	Ni	Fe	Zn	Cd	Hazard index
Oron	4.603E-02	3.620E-02	1.594E-04	3.880E-04	1.760E-04	5.950E-02	8.890E-02
Ebughu	1.827E-02	4.450E-02	1.950E-04	1.266E-03	7.732E-03	8.770E-02	1.596E-01
Uyenghe	8.786E-02	2.190E-01	9.580E-04	1.610E-03	1.610E-03	2.614E-02	3.372E-01
Ifiayong	2.456E-01	4.161E-02	1.823E-04	9.052E-03	9.052E-03	9.366E-02	3.395E-01
Ishiet	7.868E-02	4.065E-01	1.777E-03	4.274E-03	4.274E-03	1.420E-02	5.054E-01

Table 13: Target hazard quotient (THQ) and hazard index (HI) of trace metals via the consumption of *Tympanostus fuscatus* from CRE during the wet season

Location	Pb	Cd	Ni	Fe	Zn	Cu	Hazard index
Oron	3.960E-02	1.160E-02	8.260E-03	4.590E-04	3.421E-03	4.823E-02	2.084E-01
Ebughu	4.500E-02	2.580E-02	8.230E-03	4.570E-04	4.048E-03	5.664E-02	1.401E-01
Uyenghe	7.930E-02	3.240E-01	1.900E-02	6.070E-04	4.456E-03	5.580E-02	1.916E-01
Ifiayong	2.680E-02	2.300E-03	2.740E-03	4.110E-04	2.105E-03	2.425E-02	5.860E-02
Ishiet	2.570E-02	5.005E-03	5.690E-03	9.270E-04	2.666E-03	7.244E-02	1.124E-01

Conclusion

Appreciable amounts of the investigated metals were recorded in sediments and *Tympanotonus fuscatus* from Cross River estuary in both dry and wet seasons. The levels of trace metals in sediment during the wet season was higher than the level in the dry season while trace metals level in periwinkle was higher in the dry season than the wet season. All the investigated metals in sediment in both dry and wet seasons were above the sediment quality guideline stipulated by NOAA apart from zinc and copper. Pb, Cd and Ni in periwinkle were above the FAO standard in both dry and wet seasons while Fe, Cu and Cu were below the standard.

In this study, the sediment to biota (periwinkle) transfer of trace metals in the study locations were higher in zinc and copper than other trace metals in both seasons while the linear regression model predicted positive relationships between the metals in the sediment and the periwinkle tissues in the dry season compared to the wet season. The estimated daily intake of the investigated metals was lower than the oral reference dose while the target hazard quotient (THQ) and hazard index induced by the consumption of periwinkle for all the investigated metals were less than unity.

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