

Risk and Toxicity Assessments of Heavy metals in *Tympanotonus fuscatus* and sediments from Iko River, Akwa Ibom State, Nigeria

ABSTRACT

This study evaluates the physico-chemical parameters and heavy metals in water, sediments and *Tympanotonus Fuscatus* obtained from three sample sites along Iko River in Eastern Obolo LGA, Akwa Ibom State. The heavy metal analysis results on Pb, Cd and Ni in sediments and *Tympanotonus fuscatus* were used to estimate the human health and ecological risk assessment of the study area. The human health risk assessment tools utilized in this study were estimated dietary intake (EDI), total hazard quotient (THQ) and hazard index (HI) while sediment pollution parameters evaluated were contamination factor (CF), contamination degree (CD), pollution load index (PLI) and geoaccumulation index (I_{geo}). Results obtained showed that EDI of Cd in periwinkle in the study sites ranged from 0.2 – 6.4 $\mu\text{g/kg-bw/day}$ and exceeded the provisional tolerable dietary intake (PTDI), while EDI for Pb (0.0004 – 2.6 $\mu\text{g/kg-bw/day}$) and Ni (0.32 – 2 $\mu\text{g/kg-bw/day}$) was within the limit for all sites, except Ni in site II (34 $\mu\text{g/kg-bw/day}$) which was higher than the PTDI of 5 $\mu\text{g/kg-bw/day}$. The THQ of Cd in all sites was greater than 1, while Pb and Ni generally recorded $\text{THQ} < 1$. The hazard index (HI) was as follows: site I (2.36), sites II (24.44) and site III (6.5), highlighting a potential hazardous effect to humans as a result of the consumption of *Tympanotonus fuscatus* obtained from site II and III. The sediment pollution assessment revealed that the contamination factor (CF) and geoaccumulation index, I_{geo} of Cd were far above the permissible limits while Pb and Ni were mostly within limits. The estimated contamination degree (CD) and pollution load index (PLI) showed a high degree of pollution, which can be mainly attributed to the high degree of Cd contamination in the sediment. Therefore, the area under investigation is highly polluted and the periwinkle obtained from Iko river in the study area is unfit for human consumption.

Keywords: Heavy metals, *Tympanotonus fuscatus*, Risk Assessment, Total Hazard Quotient, Contamination, Pollution

1. INTRODUCTION

Marine pollution is however a critical environmental issue of concern across the globe when growing human population increases, the intensities of anthropogenic threat it exerts on the environment increases as a result of industrialization and agricultural activities [1]. Water, sediments and biota are generally metal reservoirs in aquatic environment. Researchers have revealed that nearly all metal content in aquatic environment reside in water sediments [2]. Bower [3] noted that sediments are the major depository of metals, in some cases holding up to 99% of the total amount in the system. The concentration of harmful and toxic substances is of many orders of magnitude higher in water, sediments and biological tissues than in water itself. Aquatic ecosystem is the ultimate recipient of almost everything including heavy metals. This has long been recognized as a serious pollution problem [4]. The input of

heavy metal in sediments is particularly of concern due to its toxic nature. Previous studies have shown that 30-90% of heavy metals in rivers are transported in sediments associated form [5]. Sediments particularly are regarded as any particulate matter that can be transported by fluid flow and which eventually is deposited as a layer of solid particles on the bed or bottom of body of water or other liquid. The contamination of aquatic system by heavy metals, especially in sediments has become one of the most challenging pollution issues owing to its toxicity, abundance, persistence and subsequent bio-accumulation [6]. When discharged into aquatic ecosystems heavy metals can be absorbed by suspended solids, then strongly accumulated in sediments and bio-magnified along aquatic food chains. Moreover, these sediments act as sink and may in turn acts as sources of heavy metals. Many aquatic organisms, like *Tympanotonus fuscatus* (periwinkle), have the ability to accumulate and biomagnifies contaminants like heavy metals, polycyclic aromatic hydrocarbons and PCB in the environment [7].

2. MATERIAL AND METHODS

2.1 Study Area

The study was conducted at designated sites along Iko river, Eastern Obolo LGA in Akwa Ibom State, Nigeria. Iko river is located in the eastern part of the Niger Delta between latitude 4° 30'N and 4°45'N and longitude 7°35'E and 7°40'E, the river has a shadow depth ranging from 1.0 meter to 7.0 meters at flood and ebb tide and an average width of 16metres. Iko River takes its rise from the Qua Ibo river catchment and drains directly into the Atlantic Ocean at the bight of bonny. Iko River has many adjoining tributaries and creeks, and part of it also drains into Imo river estuary, which opens into the Atlantic Ocean at the bight of bonny.

2.2 Sampling Techniques

Samples water, *Tympanotonus fuscatus* (periwinkle) and sediments were collected at three different sampling stations along the study site (Iko river) between the months of May and August in 2018. At each of the sampling points, six samples each of water, sediments and periwinkle were collected. Water samples were obtained at the depth of 20 cm below the surface using an acid prewashed 1litre polyethylene bottles; the water samples were then transported to the laboratory for analysis. Sediments samples were collected at a depth of 10 cm using soil augur, kept in a polythene bag and transported to the laboratory for analysis.

2.3 Samples Preservation and Pre-treatment

The water samples were placed in pre-cleaned plastic bottles and nitric acid was immediately added to prevent any microbial action on the water. They were then taken to the laboratory for digestion. Sediment sample was weighed and then air dried in the oven. After air-drying, the dried sediments was then meshed, pounded and sieved to fine powdered particles.

The *Tympanotonus fuscatus* (periwinkle) samples were washed thoroughly to clean and remove dirt and mud particles. The soft periwinkle tissues were removed from the shells with a clean sterilized steel needle. The periwinkle tissue was air dried in the oven. After air drying for three days the samples was collected and pounded into powdered form and then taken for digestion.

2.4 Analysis

2.4.1 Determination of Total metal content in water

EPA method 3005A was used in water digestion. 100 mL aliquot of well-mixed water sample was transfered to a beaker. Thereafter, 2 mL of concentrated HNO and 35mL of

concentrated HCl was added to the sample. The sample was covered with a ribbed watch glass and heated, without boiling, on a hot plate at 90 to 95°C until the volume was reduced to 15-20 mL. The beaker was removed from the hotplate; the digestate was allowed to cool and centrifuged to remove silicates and other insoluble material that could clog the AAS nebulizer. Heavy metal concentration was analysed with FAAS (Buck scientific model 210VGP-Variable Giant Pulse)

2.4.2 Determination of Total metal content in sediments

Nitric-perchloric acid digestion, with procedure outlined by AOAC [8], was performed on the sediment samples. 1g of sample was placed in a 100 ml digestion tube and 10 ml of concentrated HNO₃ was added. The mixture was boiled gently for 30 mins to facilitate the oxidization of all easily oxidizable matter in the sample. After cooling, 5 ml of 70% HClO₄ was added and the mixture was boiled cautiously until dense white fumes appeared. After cooling, 20 ml of distilled water was added and the mixture was boiled further to no fumes were released. The solution was cooled, filtered through Whatman No. 42 filter paper, transferred quantitatively to a 25ml volumetric flask and diluted to mark with distilled water.

2.4.3 Determination of Total metal content in *Typanotonus Fuscatus* (periwinkle)

0.5 g of each sample was digested with 10ml aqua regia (3:1 v/v HCl/HNO₃) and 1 ml HClO₄. The mixture was heated on a hot plate to near dryness and the digestate was cooled, diluted with 25ml distilled water and filtered with Whatman No. 42 filter paper into a 100 ml volumetric flask. Heavy metal concentrations in the digestate were measured with flame atomic absorption spectrophotometer

2.4.4 Determination of physico-chemical parameters

The parameters assessed were Salinity, TDS, Temperature, Conductivity, Current, and pH respectively. Water samples for the physicochemical analyses were done. Total dissolved solids (mg/l), Conductivity (µs/cm), and water temperature (°C), were conducted using the conductivity meter (DDST-3084) and salinity (%), current (nA) and dissolved oxygen were conducted using the DO oxygen meter DC analyzer JPS-605.

2.5 Human Health Risk Assessment

Human risk assessment utilizes some tools in evaluating the risk posed by a potentially hazardous agents to human health. The United States Environmental Agency (USEPA) models [9, 10] were employed in this study.

2.5.1 Estimated Daily Intake (EDI): The EDI of heavy metals in the periwinkle consumed by the exposed populace was estimated using the formula,

$$EDI (\mu\text{g/kg-bw/day}) = \frac{EF \times ED \times MI \times MC}{ORD \times BW \times AT}$$

EF is the exposure frequency (365 days/year), ED is the exposure duration (51.86 yrs), which is the estimated average life span of a Nigerian [11], MC is the metal concentration in periwinkle (µg/kg), MI is the mass of periwinkle ingested. According to WHO [11], the per capital consumption of fish and shellfish in Nigeria for human food is averaged 9.0 kg, which is equivalent to 24.7 g (0.0247 kg) per day; average adult body weight (BW) is considered to be 60 kg; AT is the average exposure time for non-carcinogens (EF× ED, 365 days/year × 51.86 yrs).

2.5.2 Non-carcinogenic health effect

2.5.2.1 Target hazard quotient: Non-carcinogenic risk estimation of heavy metals consumption was determined using THQ values. THQ is a ratio of the determined dose of a

toxicant to a reference dose considered harmful. If the ratio is equal to or greater than 1, an exposed population is at risk.

$$THQ = \frac{EDI}{ORD}$$

where EDI is the estimated daily intake of heavy metals through consumption of periwinkle (as described in the previous equation); ORD is the Oral Reference Dose which is the daily dose of the metals that is likely to pose no appreciable risk of deleterious effects during a life time as recommended by USEPA, WHO and FAO. The following reference doses were used (Cd = 0.001 mg/kg/day, Ni = 0.02 mg/kg/day, Pb = 0.0035 mg/kg/day) [9, 10, 11].

2.5.2.2 Hazard index: Hazard index is used to evaluate the potential risk to human health when more than one heavy metal is involved. Hazard index was calculated as the sum of hazard quotients (HQs). Since different pollutants can cause similar adverse health effects, it is often appropriate to combine HQs associated with different substances.

$$HI = \sum THQ_i$$

where $\sum THQ_i$ is the sum total of THQ of individual metals in the periwinkles and i is the distinct heavy metal in consideration.

2.6 Sediment Pollution Indices and Ecological Risk Assessment

The following pollution indices were adopted to estimate heavy metal pollution of sediment samples obtained from the study area: (i) degree of contamination (CD) (ii) contamination factor (CF) (iii) pollution index (PI) (iv) geoaccumulation index (I_{geo})

2.6.1 Contamination factor (CF) is estimated as, $\left[\frac{M_c}{M_{bkg}} \right]$

Where M_c is the mean concentration of individual metal and M_{bkg} is the background value of individual metal. The gradation of CF is as follows: low ($CF < 1$), moderate ($1 \leq CF < 3$), considerable ($3 \leq CF < 6$) and high ($CF \geq 6$)

2.6.2 Contamination degree is estimated to give a holistic impact of multimetals on the environment [12, 13]. In this study CD was calculated using the formula developed by Hakanson [14], which states that CD is the sum total of CF of the individual metals

$$CD = \sum CF$$

The degree of contamination is categorized into low ($CD \leq 6$), moderate ($6 < CD \leq 12$), considerable ($12 < CD \leq 24$), and very high ($CD > 24$)

2.6.3 Pollution Load index is calculated using Tomlison's method [15] and is expressed as the n th root of the product of n CF

$$PLI = [CF_1 \times CF_2 \times \dots \times CF_n]^{1/n}$$

Where n corresponds to the number of metals and CF_n is the contamination factor of metal n. PLI is categorized as follows: background concentration ($PLI = 0$), unpolluted ($0 < PLI \leq 1$), unpolluted to moderately polluted ($1 < PLI \leq 2$), moderately polluted ($2 < PLI \leq 3$), moderately to highly polluted ($3 < PLI \leq 4$), highly polluted ($4 < PLI \leq 5$), and very highly polluted ($PLI > 5$)

2.6.4 Geoaccumulation index (I_{geo}) is usually employed to estimate metals enrichment above baseline concentration in sediments and soil. In this study, the I_{geo} was calculated using the method developed by Muller [16]

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right)$$

Where C_n is the concentration of metal (n) in the sediment sample and B_n is the geochemical background, which corresponds to metal (n) concentration in average shale. In this study the background sediment concentrations of Pb, Cd and Ni used were 20, 0.3 and 68 mg/kg respectively [17]. According to Muller (1969), the correlation between I_{geo} and degree of metal pollution are classified as follows: unpolluted ($I_{geo} \leq 0$), unpolluted to moderately polluted ($0 < I_{geo} \leq 1$), moderately polluted ($1 < I_{geo} \leq 2$), moderately to heavily polluted ($2 <$

$I_{geo} \leq 3$), heavily polluted ($3 < I_{geo} \leq 4$), heavily to extremely polluted ($4 < I_{geo} \leq 5$), or extremely polluted ($I_{geo} > 5$)

3. RESULTS AND DISCUSSION

3.1 Water Analysis

The values of the physico-chemical and heavy metals analysis of the water samples obtained from the study and control sites are presented in tables 1 and 2 respectively

Table 1 Physico-chemical parameters of water sample

	Site I	Site II	Site III
Salinity	0.08%	0.01%	0.03%
TDS (mg/l)	762	134.8	324
Temperature (C)	27.1	26.8	27.1
Conductivity (us/cm)	1529	269	645
Current I (nA)	1343	1132	1295
pH	6.5	6.6	6.9
DO(Dissolved Oxygen)	52.1	52.2	46.7

Table 2 Heavy metals in water sample (mg/l)

Site	Pb	Cd	Ni
I	9.865 ± 0.001	4.174±0.002	0.985±0.001
II	15.413±0.001	11.929±0.0012	1.645±0.002
III	12.107±0.001	8.649±0.043	1.126±0.001

Physico-chemical parameters: Table 1 shows that the salinity of sampling sites I, II and III were 0.08%, 0.01% and 0.03% respectively. This can be attributed to the proximity of the sampling sites to the river source, the Atlantic ocean, which is a saline water body. Site I was the closest to the ocean, followed by site III while site II was farthest from the ocean. The salinity parameter also correlates with other physico-chemical parameters namely total dissolved solid (TDS), conductivity and current, which gave the trend as follows: I > III > II. Table 1 indicates that dissolved oxygen was least in site III, which can be attributed to higher eutrophication process due to the presence of phosphates and nitrates, especially since this area is closest to human settlements and farmlands. Dissolved oxygen concentration and the pH of water bodies are important parameters that determine the spatial and temporal

distribution of aquatic organisms, particularly the fish fauna [18]. Dissolved oxygen is required for respiration by most aquatic animals. Apart from this, dissolved oxygen combines with other important elements such as carbon, sulphur, nitrogen and phosphorous to form carbonates, sulphates, nitrates and phosphates, respectively, which constitute the required compounds for the survival of aquatic organisms. In the absence of adequate oxygen levels, the above elements, among others, could form compounds which are toxic to the aquatic biota [19].

Lead: Lead concentration in water sample varied between 9.86 ± 0.001 , 15.413 ± 0.001 and 12.107 ± 0.001 mg/l in sites I, II and III respectively (table 2). The lead content was observed to be highest in water samples obtained from site II, which was the downward region and closest to an illegal oil bunkering area. This indicates that Pb pollution was much higher in this region than the upwind regions. Generally, the mean lead content for the water samples were above the permissible limit set by WHO [20] at 0.001mg/l, NSDWQ at 0.01mg/l and FMENV at 0.05mg/l and the values were above stipulated limits respectively.

Cadmium: The mean Cd concentration varied from 4.17 ± 0.001 (Site I), 8.65 ± 0.04 (Site III) and 11.93 ± 0.001 (Site II). The Cd concentration was found to be highest in site II, which is closest to a suspected illegal bunkering site. Furthermore, the mean cadmium concentration for the water samples were all above the permissible limit set by WHO (0.003mg/l), NSDWQ (0.003 mg/l) and FMENV at (1.0 mg/l), making it unsafe for humans.

Nickel: Table 2 indicates that the nickel concentration in the water samples ranged from 0.99 ± 0.001 mg/l in site I, to the highest value in site II (1.64 ± 0.002 mg/l). It was observed that nickel concentrations were lower when compared to Ni and Pb.

3. 2 Heavy metals in Sediment and *Tympanotonus fuscatus*

Table 3 Heavy metals in *Tympanotonus fuscatus* and Sediment (mg/kg)

Sample	Site	Pb	Cd	Ni
Perewinkle	I	<0.001	5.43 ± 0.1	0.77 ± 0.3
	II	6.23 ± 0.2	54.4 ± 0.2	83.6 ± 0.2
	III	<0.001	15.6 ± 0.2	4.8 ± 0.5
Sediment	I	<0.001	4.57 ± 0.1	2.42 ± 0.3
	II	5.4 ± 0.2	31.8 ± 0.5	91.6 ± 0.2
	III	<0.001	23.25 ± 0.1	17.3 ± 0.2

Lead: The Pb concentration in *Tympanotonus fuscatus* and sediment obtained in sites I and III were very minimal and below standard permissible limit, which indicates low geo-accumulation and bioaccumulation in the sediment and *Tympanotonus fuscatus* samples respectively. Meanwhile, Pb concentration of periwinkle and sediment in site II was 6.23 ± 0.2 mg/l and 5.4 ± 0.2 mg/l respectively, indicating a high bio-accumulation of this toxic metal in the periwinkle samples, which is an important delicacy of the populace and exposing them to numerous health hazards. Chronic exposure to high levels of lead may cause weakness, anemia, kidney and brain damage and even death. It has been reported that lead can cross the placental barrier, implying that pregnant women exposed to Pb may result in defects (like brain damage) to the unborn foetus. [21].

Cadmium: Cd concentration in *Tympanotonus fuscatus* at the three study sites were as follows: Site I (5.43 ± 0.1 mg/kg), Site II (54.4 ± 0.1 mg/kg) and Site III (15.6 ± 0.1 mg/kg)

while Cd in sediments ranged from 4.57 ± 0.1 mg/kg in Site I to 31.8 ± 0.5 mg/kg in Site II. Generally, it was found that site II recorded the highest Cd levels in both sediments and periwinkle. Sediments are the ultimate sink of pollutants in the aquatic system, which implies that the metals in the water will ultimately end up in the sediments, which are taken up by bottom feeders like periwinkle. International Agency for Research on Cancer (IARC) has introduced cadmium as a carcinogenic agent which is a major cause of kidney dysfunction [22]

Nickel: Ni in *Tympanotonus fuscatus* ranged from 0.77 ± 0.3 mg/kg (Site I) to 83.6 ± 0.2 mg/kg (Site II) and in sediment, Ni ranged from 2.42 ± 0.3 mg/kg (Site I) to 91.6 ± 0.2 mg/kg (Site II). It can be observed from table 3 that the Ni concentrations in sediments were generally higher than in periwinkle. The presence of Ni in the study sites may be attributed to industrial activities around the area, which generate polluted waste that is discharged into the river. The most common harmful health effect of nickel in humans is an allergic reaction. For example, eczema and asthma is can result from nickel exposure through inhalation. Other serious harmful health effects from nickel exposure include chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus. According to ASTDR [23], oral exposure of humans to high levels of soluble nickel compounds through the environment is extremely unlikely. However, eating or drinking levels of nickel much greater than the levels normally found in food and water have been reported to produce lung disease in dogs and rats and to affect the stomach, blood, liver, kidneys, and immune system in rats and mice, as well as their reproduction and development [23].

Generally, it can be observed that metal bio/geoaccumulation was higher in low salinity aquatic system (Site II) than in high salinity system (Site I). This observation correlates with the finding of Pierron et al [24], who stated that at low salinity, bioavailability of Cd in shrimp *Palaemon longirostris* is increased. Fritioff et al. [25] also opined that metal concentration at low salinity aquatic system was twice higher than in high salinity water.

3.3 Human Health Risk Assessment

Table 4 Estimated Dietary Intake (EDI) and Estimated Weekly Intake (EWI) of metals in *T. fuscatus* ($\mu\text{g/kg-bw/day}$ and week)

Sample ID	Pb		Cd		Ni	
	EDI	EWI	EDI	EWI	EDI	EWI
I	4.1×10^{-4}	2.9×10^{-3}	2.2	15.4	0.32	2.24
II	2.6	18	22	154	34	238
III	4.1×10^{-4}	2.9×10^{-3}	6.4	44.8	2.0	14
Guidelines	PTDI	PTWI	PTDI	PTWI	PTDI	PTWI
WHO 1993	3.57	24.9	-	-	-	-
JECFA 2010	-	-	0.829	5.8	-	-
WHO 1997	-	-	-	-	5	35

Table 5 Target Hazard Quotient (THQ) and Hazard Index (HI) for metal intake (consumption of 24.7 g/day)

Sample ID	Total Hazard Quotient (THQ)			Hazard Index (HI)
	Pb	Cd	Ni	
I	0	2.2	0.16	2.36
(%) HI	-	93.2	6.8	
II	0.74	22	1.7	24.44
(%) HI	3.03	90.02	6.96	
III	0	6.4	0.1	6.5
(%) HI	-	98.46	1.54	

% HI = Percent (%) contribution of each metal to the hazard index

Estimated Dietary Intake (EDI): EDI of Pb, Cd and Ni in *Tympanotonus fuscatus* obtained from the study area are shown in table 4 and Intake estimates are expressed in mg/kg-bw/day or weekly. These values are compared with the recommended guidelines as stipulated by environmental safety institutions. The joint FAO/WHO Expert Committee on Food Additives (JECFA) stipulated a Provisional Tolerable Daily Intake (PTDI) of 3.57 µg/kg body weight for lead [22] and 0.83 µg/kg body weight for cadmium [26]. These translate to 214.2 µg/ day lead for a 60 kg adult while for cadmium, it is 49.8 µg/day for a 60 kg adult. WHO [27] has given a Tolerable Daily Intake (TDI) of Ni to be 5 µg/kg body weight, which translates to 300 µg/day for a 60kg adult. The daily lead intakes for an adult, due to the consumption of periwinkle obtained in this study sites were: I (4.1×10^{-4} µg/kg/day), II (2.6 µg/kg/day), III (4.1×10^{-4} µg/kg/day) which indicates that the EDI or lead in the three sample sites were below the recommended PTDI (3.57 µg/kg-bw/day) for lead; EDI for Cd in the sites were as follows; I (2.2 µg/kg/day), II (22 µg/kg/day), III (6.4 µg/kg/day) which all exceed the PTDI of cadmium (0.829 µg/kg/day). The EDI (EWI) for Ni were 0.32 µg/kg/day (22 µg/kg/week) in Site I; 34 µg/kg/day (238 µg/kg/week) in site II and 2.0 µg/kg/day (14 µg/kg/week) in site III. The estimated dietary/weekly intake of Ni in site I and III were lower than the provisional tolerable daily intake of 5 µg/kg-bw/day, suggesting no potential adverse effects to the exposed populace from Ni contamination. However, EDI and EWI of cadmium were higher than the recommended PTDI and PTWI indicating hazardous potential of the consumption of the periwinkle. In the subsequent section, the hazard posed by the heavy metals to humans will be quantified using the total hazard quotient and hazard index parameters.

Target Hazard Quotient (THQ) and Hazard Index (HI): This parameter assesses the non-carcinogenic health risk posed by the metal exposure from the consumption of *Tympanotonus fuscatus* in Iko river, as presented in table 5. The THQ of metals in periwinkle are in the order Cd > Ni > Pb with values in site I (2.2, 0.16, 0), site II (22, 1.7, 0.74) and site III (6.4, 0.1, 0). With the exception of Cd, the THQ for the metals were generally below 1. Cadmium gave a very high THQ indicating extreme pollution and health risk to exposed populace; THQ of Cd contributed to over 90% of the hazard index in all the study sites. Hazard index (HI) is the combined effects of the heavy metals assessed in the study sites and it was found in this study that sites I, II and III recorded HI of 2.36, 24.44 and 6.5 respectively, which is above the maximum acceptable limit of 1 and implies that the *Tympanotonus fuscatus* (periwinkle) obtained in these location are not fit for human consumption. In all three sites investigated, Cd contributed to over 90% of the recorded HI

while Ni and Pb gave minimal contributions to the hazard index of the periwinkle obtained from the sites.

3.4 Sediment Pollution Indices and Ecological Risk Assessment

Table 6 Contamination factor (CF), Contamination degree (CD) and Pollution load index (PLI) of heavy metals in sediment

Sample ID	Contamination factor (CF)			CD	PLI
	Pb	Cd	Ni		
I	0	14.9	0.04	14.94	0.7720
II	0.27	106.0	1.35	107.62	3.3807
III	0	77.5	0.25	77.75	4.4017

Table 7 Geoaccumulation index (I_{geo}) values for heavy metal concentration obtained in sediment samples

Sample ID	Pb	Cd	Ni
I	0	3.0568	0.00714
II	0.05418	21.271	0.27031
III	0	15.5519	0.05105

The contamination factor values calculated for studied trace metals in the sediment sample were in the following order: Cd (77.5, 106.0, 14.9) > Ni (0.04, 1.35, 0.25) > Pb (0, 0, 0.27); generally, site II had the highest contamination factor while site III had the least. CF for Ni and Pb were mostly below 1 which indicates low degree of contamination, according to Hanson (1980); while the CF for Cd at all sites exceeded 6 which implies a very high degree of contamination. The high amount of cadmium in the sediments may have been due to discharges from the illegal bunkering and other industrial activities into the Iko river. This pollutant is subsequently deposited on the river sediments, which acts as a pollutant sink, and are taken up by benthic organisms. Cadmium is a well known carcinogen than has harmful effects to human lungs, bones and kidney. The Contamination degree (CD) of the metals at the sampling sites was as follows: Site I (14.94), Site II (107.62), Site (77.75) which were all above 24 and implies a very high degree of contamination, according to the formula developed by Hakanson [14]. The high contamination degree in all sample sites may be attributed to the high degree of cadmium contamination in the sampling area. Table 6 shows that the Pollution Load Index (PLI) of site I is 0.7720, which according to Tomlison [15], infers no pollution; site II – 3.38, implying moderately to high pollution; site III – 4.47, indicating high pollution of the sediment obtained at the sample site.

Table 7 shows the result of the estimated geoaccumulation index, I_{geo} values of Pb, Cd and Ni in sediment samples in the sites under investigation. The I_{geo} values for Pb and Ni were within $0 < I_{geo} \leq 1$ implying that the sediment samples were unpolluted to moderately polluted. The calculated I_{geo} values of Cd for the sites I, II and III were 3.0568, 21.271 and 15.552, respectively. These values are higher 5, implying that the sites are extremely

polluted with Cd [16]. The extreme cadmium pollution is likely from anthropogenic sources and it poses a problem for the ecosystem, since cadmium has adverse effects on both flora and fauna.

4. CONCLUSION

The human and ecological risk assessment of the study area has revealed an alarming degree of pollution of the study sites. The estimated dietary intake of Cd in periwinkle obtained sites I, II, III and Ni in site II exceeded the provisional tolerable dietary intake, while EDI for Pb was within the limit for all sites. The Total hazard quotient of Cd in all sites was much higher than 1, while THQ for Pb and Ni were less than 1. The hazard index (HI) of consuming *Tympanotonus fuscatus* (periwinkle) in sites I (2.36), II (24.44) and site III (6.5) were higher than 1, highlighting a potential hazardous effect from the consumption of periwinkle obtained from these sites. The ecological risk assessment of sediment samples showed that the contamination factor (CF) and geoaccumulation index, I_{geo} of Cd were far above the permissible limits while Pb and Ni were mostly within limits. Due to the high degree of Cd pollution in the sediment, the estimation of contamination degree (CD) and pollution load index (PLI) revealed a high pollution of the sampling sites, which followed the order: Site II > Site III > Site I. Therefore, the area under investigation is highly polluted and the *Tympanotonus fuscatus* (periwinkle) obtained from Iko river is unfit for human consumption.

REFERENCES

- [1] Raja P, Veerasingam S, Suresh G, Marichamy G, Venkatachalapathy R. Heavy metals concentration in four commercially valuable marine edible fish species from Parangipettai Coast, South East Coast of India, Int J. of Animal and Vet. Adv. 2009;1(1):10 -14.
- [2] Ademoroti CMO Standard methods for water and effluents analysis. Foludex Press Ltd., Ibadan. 1996;3:29-118.
- [3] Bower HJ. Heavy metals in Sediments of Founary cover cold spring, New York, *Environ Sci Technol.* 1979;13:683-687
- [4] Farombi EO, Adelowo OA, Ajimoko YR. Biomarkers of oxidative stress and heavy metals levels as indicator of environmental pollution in African Catfish (*Clarias gariepinus*) from Nigeria Ogun River. Int. J. of Environ. Res. and Pub. Health, 2007;4:158-165
- [5] Wang Y, Yang Z, Shen Z, Tang Z, Niu J, Gao F. Assessment of heavy metals in sediments from a typical catchment of the Yangtze River, China *Environ Monit. Assess.* 2011;172(1-4):407-417
- [6] Fu J, Tao X, Yu H, Zhang X. Risk and Toxicity Assessments of Heavy metals in sediments and fishes from the Yangtze River and Taihu Lake, China, *Chemosphere*, 2013;93(9): 1887-1895
- [7] Davies OA, Allison ME, Uyi HS. Bioaccumulation of Heavy Concentration of Lead in Perwinkle (*Tympanotonos Fuscatus*) and River Sediments in Eagle Island River, Rivers, American. J. Environ. Prot. 2006;2:37-40
- [8] AOAC. Official Methods of Analysis of the Association of Analytical Chemists. 1990; edited by Kenneth Helrich.
- [9] USEPA. *Mercury update: impact on fish advisories*. US Environmental Protection Agency, Washington DC. 2001 (<http://www.epa.gov/waterscience/fishadvice/mercupd.pdf>,
- [10] USEPA. Risk-based concentration table. United State Environmental Protection Agency, Washington, DC. 2001
- [11] FAO/WHO. Joint Food Standards Program Codex Committee on contaminants in foods. Fifth session, the Hague, Netherlands, 21 – 25 March 2011.

- [12] Li X, Liu L, Wang Y. Heavy metal contamination of urban soil in an old industrial city (Shenyang) in Northeast China. *Geoderma*, 2013;192(1):50-58
- [13] Benson NU, Enyong PA, Fred-Ahmadu, OH. Trace metal contamination and Health Risks Assessment of *Commelina Africana* L. and *Psammitic Sandflats* in the Niger Delta, Nigeria. *App. and Environ. Soil Sc.* 2016; Article ID 8178901, <http://dx.doi.org/10.1155/2016/8178901>
- [14] Hakanson L. Ecological risk index for aquatic pollution control: A sedimentation approach. *Water Res.* 1980;14:975 – 100
- [15] Tomlison DC, Wilson JG, Harris CR, Jeffrey DW. Problems in the assessment of heavy metals levels in estuaries and the formation of pollution index. *Helgoland Mar. Res.* 1980;3: 566 – 575
- [16] Muller G. Index of geoaccumulation in sediments of Rhine River. *GeoJournal*, 1969;2: 108 – 118
- [17] Turekian KK, Wedepohl KH. Distribution of the elements in some major units of the earth's crust. *Geol. Soc. of Amer. Bull.* 1961;72(2):175 – 192
- [18] Araoye PA. The seasonal variation of pH and dissolved oxygen (DO₂) concentration in Asa lake Ilorin, Nigeria, *Int. J. of Phy. Sc.* 2009;4(5): 271-274.
- [19] Jenyo-Oni A, Oladele AH. Heavy Metals Assessment In Water, Sediments And Selected Aquatic Organisms In Lake Asejire, Nigeria. *European Scient. Journ.* 2016;12(24):339–351
- [20] WHO. Guideline for drinking water quality (3rd ed). Incorporating 1st and 2nd Agenda. Vol. 1: Recommendation. World Health Organisation, Geneva, 2008.
- [21] National Institute for Occupational Safety and Health (NIOSH) 1995. Report to Congress on Workers' Home Contamination Study Conducted Under The Workers' Family Protection Act (29 U.S.C. 671a), 1995; DHHS (NIOSH) Publication No. 95-123 Available: <https://www.cdc.gov/niosh/docs/95-123/pdfs/95-123.pdf>
- [22] WHO. Evaluation of certain food additives and contaminants. 41st Report of the Joint FAO/WHO Expert Committee on Food Additives. Tech. 1993; Report Series, 837.
- [23] Agency for Toxic Substances and Disease Registry (ATSDR). [Toxicological profile for Nickel](#). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service, 2005.
- [24] Pierron F, Baudrimont M, Boudou A, Massabuau JC. Effects of salinity and hypoxia on cadmium bioaccumulation in the shrimp *Palaemon longirostris*. *Environ. Toxicol. Chem.* 2007;26(5):1010-1017
- [25] Fritoff A, Kautsky L, Greger M. Influence of temperature and salinity on heavy metal uptake by submerged plants. *Environ. Poll.* 2005;133(2): 265 – 74
- [26] Joint FAO/WHO Expert Committee on Food Additives (JECFA). Evaluation of certain Food additives and contaminants: Summary and conclusion on the Seventy-third meeting. World Health Organization, Geneva. 2010
- [27] World Health Organization (WHO). Guideline for drinking water quality, 2nd ed., volume 1, Recommendations. World Health Organization, Geneva, 1997.