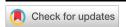


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Health risk assessment of heavy metals in sediment, shrimp (*Parapenaeopsis atlantica*), and periwinkles (*Tympanotonus fuscatus*) from Esuk Ibeno Beach, Akwa Ibom State, Nigeria

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ABSTRACT

Beaches play an important role in the survival of the world. They serve the purpose of water supply for domestic, industrial, agricultural, and power generation. Beaches are also used for the disposal of industrial and sewage waste, putting rivers under tremendous pressure due to human activities. This research assesses heavy metal contamination in sediments, shrimps (Parapenaeopsis atlantica) and periwinkles (Tympanotonus fuscatus) from Esuk Ibeno Beach, Akwa Ibom State, Nigeria, to ascertain their potential human health risks to consumers. Shrimp samples and periwinkle samples (at low tide) were obtained with the help of local fishermen from Esuk Ibeno beach. Sediment samples were collected at the same location as the periwinkles. Concentrations of chromium (Cr), iron (Fe), nickel (Ni), copper (Cu), lead (Pb), and cadmium (Cd) were analyzed using atomic absorption spectrometry. The sediments indicated heavy metal concentrations of Cr (0.24-0.32 mg/kg), Fe (25.0-41.4 mg/kg), Ni (0.27-0.38 mg/kg), Cu (0.05-0.11 mg/kg) Pb (0.03-0.09 mg/kg), and Cd (0.01-0.02 mg/kg), all below the quality standards of marine sediments. In the biota, Fe concentrations in shrimps (8.80±0.25 mg/kg) and periwinkles (0.90±0.03 mg/kg) exceeded the FAO/WHO limit of 0.5 mg/kg, while Cr, Ni, Cu, Pb and Cd were within the permissible limits. Biomagnification was apparent for Cr (1.00) and Cd (2.00) in the periwinkles. Dietary exposure assessments showed ingestion rates for adults and children, with the Exp_{diet} values for Cr, Fe, Ni, Cu, Pb and Cd being lower than the oral reference dose (RfD). The target hazard quotient (THQ) values were less than 1 for all metals, indicating that there were no significant health risks. The cumulative hazard indices for shrimps (1.56×10-2 in adults; 1.61×10⁻² in children) and periwinkles (1.11×10⁻² in adults; 1.15×10⁻³ in children) suggest potential long-term risks of bioaccumulation. Incremental lifetime cancer risk (ILCR) for all investigated metals were 1.0×10⁻⁶ and 1.0×10⁻⁴. This indicates that the consumption of Parapenaeopsis atlantica and Tympanostus fuscatus from the Esuk Ibeno beach was within the acceptable range. This study indicates a great impact of anthropogenic activities on Esuk Ibeno Beach and calls for sustainable industrial waste management to prevent environmental and public health hazards.

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1. Introduction

Pollution of the environment with toxic heavy metals is not only concerning in metropolitan cities, but also in remote and rural communities where anthropogenic activities are occurring. This environmental contamination is mainly due to industrial activities, such as mining, electroplating, gas exhaust, energy and fuel production, application of fertilizers and pesticides, and generation of municipal waste [1]. The uncontrolled dissemination of waste effluents to large bodies of water has negatively affected both water quality and aquatic life [2].

The Food and Agricultural Organization (FAO) of the USA revealed that in African countries, particularly Nigeria, water-

related diseases had been interfering with basic human development [3]. Different aquatic organisms often respond to external contamination in different ways, where the quantity and form of the element in water, sediment, or food will determine the degree of accumulation [2,4]. Rivers play a significant role in the survival of the world because they not only the purpose of water supply for domestic, industrial, agricultural and power generation, but are also used for the disposal of sewage and industrial waste. Therefore, this puts rivers under tremendous pressure due to human activities. Improper waste disposal systems from slaughterhouses could lead to the transmission of pathogens to humans and cause zoonotic diseases such as *E. coli, Bacillosis, Salmonellosis, Brucellosis,* and *Helminthes* [5,6].

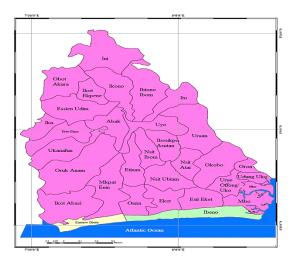


Figure 1. Map of Akwa Ibom state showing the location of the Study Area (Ibeno).

Most rivers have been unmindfully used for the disposal of domestic and industrial effluents far beyond their assimilative capacities and have been severely polluted. The effect of water pollution on human health is of serious concern [7]. Shah et al. found that the presence of toxic heavy metals in the food chain causes ill health, resulting in the death of aquatic organisms [8]. Liu et al. and Ite et al. found that fish are the most affected [9,10]. Agah et al. proved that the concentrations of heavy metals in fish tissues were higher than those of their habitats [11]. In Akpan et al. carcinogenic risks due to dermal exposure calculated for both adults and children were higher than the US EPA acceptable cancer risk and much higher for children, suggesting that children could be prone to cancer [12]. Therefore, the risk assessment of PAHs exposure to children may be considered greater than those of adults and need to be monitored. The bioaccumulation of heavy metals in organisms is known to have resulted over the years in high concentrations of these trace metals at higher levels of the food chain [2,13]. In 2004 through various studies, they showed that heavy metals such as Hg, Ni, Cu, Cd, Pb, Fe, As, Mn, and Cr were contaminants in waste water, agricultural soil and green vegetables planted in an industrial area in Australia and New Zealand. Certain environmental conditions such as salinity, pH, and hardness of water hardness can play an important role in heavy metals accumulation up to toxic concentrations in living organisms and cause ecological damage [14]. Therefore, heavy metals acquired through the food chain as a result of pollution are potential chemical hazards that threaten consumers [1]. Sediment quality guidelines (SQGs) are essential tools for identifying contaminated sediment hotspots and also for assessing the possible effects of contaminated sediments on benthic organisms [15]. Sediment contamination is estimated by comparing the concentration of sediment contaminants with the corresponding quality guideline [16]. These guidelines are also designed to help interpret the quality of the sediment.

The Ibeno River in the Ibeno Local Government Area provides good water to the teaming population in Ibeno. However, the dream that this river would provide clean and safe water in the state is being threatened by metal pollutants and carcinogenic organic compounds. There have been industrial activities in the Ibeno Local Government Area of Akwa Ibom State for decades. Industrialization, like other human activities that impact the environment, often results in pollution and degradation [17-19]. Polluted water deteriorates, reduces water quality, thus generating negative effects on aquatic life, and transfers the same by bioaccumulation to humans, affecting public health [20-22]. The main hazardous content of water pollutants is heavy metals [23]. Monitoring the

pollution load of industrial activity effluents in the Ibeno River, as well as its effect on aquatic life, becomes necessary for the above reasons. The aim of the research is to determine the heavy metal concentrations in sediment, shrimp, and periwinkles from the Ibeno rivers in the Ibeno local government area of Akwa Ibom State. The objectives of this study are to determine the concentrations of Cr, Fe, Ni, Cu, Pb and Cd in sediment, shrimp and periwinkle samples to know the metal transfer factors from sediment to periwinkles and shrimps and their potential human health risks to consumers.

2. Experimental

2.1. Description of the study area

Ibeno is located in the south east of Nigeria and is a local government area of Akwa Ibom State. The town of Ibeno is on the eastern side of the Qua Ibo River, about 3 km from the mouth of the river and is one of the largest fishing settlements on the Nigerian coast. As seen in Figure 1, Ibeno lies in the mangrove forest belt of the Niger Delta region of Nigeria, bounded to the west by the Eastern Obolo Local Government Areas, to the north by Onna, Esit Eket and the Eket Local Government Area, and to the south is the Atlantic Ocean. The main occupation of the Ibeno people is fishing. However, farming and petty trading enjoy appreciative notice. The presence of oil exploration activities by the oil giant Exxon Mobil and other service companies influences the activities upstream and downstream. The areas of interest in this investigation were stations chosen along the course of the river that channel their waste into the river (Figure 1).

2.2. Sample collection, preparation and digestion

Shrimp samples were obtained with the help of local fishermen from Esuk Ibeno beach. The periwinkle samples were collected at low tide using a boat to access the shorelines. Periwinkles and shrimp were purchased from the fishermen as soon as they were harvested. They were rinsed and stored in self-sealable polyethylene bags and transported to the laboratory in an ice chest.

Sediment samples were collected at the same location as the periwinkles. About 1 kg of sediment samples were collected at six different points (in triplicate), five meters away from each other. Sediment samples were collected using the Van Veen grab sampler and then stored in self-sealable polyethylene bags, kept in an ice chest, and transported to the laboratory for

storage in freezers awaiting analysis. Each of the sediment samples was acidified with 3 mL of concentrated nitric acid.

In the laboratory, the shrimp and periwinkle samples were thoroughly washed with tap water and allowed to drain. Shrimps were dried in air at room temperature for three days after which the samples were pulverized and refrigerated at 4 $^{\circ}\text{C}$ until analysis. The periwinkles were randomly selected and transferred to a pot of boiling water (100 $^{\circ}\text{C}$) in a 4:1 ratio. The periwinkles were allowed to boil for twenty minutes and then turned into a sieve. The tissues (edible portions) were removed from the shells with a needle and dried in an oven at 60 $^{\circ}\text{C}$ to a constant weight. The dried samples were ground to power with a plastic mortar and pestle, passed through 0.5 mm mesh sieves, and stored in well-labeled plastic containers for digestion.

2.2.1. Sample digestion

The sample digestion was carried out according to reference [24]. One g portion of crushed dry sediment was accurately weighed into a conical flask. 15 mL of aqua regia (HNO3:HCl, 1:3, v:v) was added slowly, followed by 5 mL of concentrated perchloric acid (HClO4) and placed on a slow heat burner at 120 $^{\circ}$ C for 2-3 hours until a clear solution was obtained. The digested sample was allowed to cool and quantitatively filtered into a 50 mL volumetric flask using Whatman no. 42 filter paper and made up to mark with deionized water. The same procedure was used for the blank digest without sample.

One g of dry crushed biota samples was measured in a conical flask and 20 mL aliquot of aqua regia (HNO₃:HCl, 1:3, v:v) was added and left to stand at room temperature for an hour. The flask was slowly heated on a hot plate at 90 °C for 2-3 hours to ensure a clear sample solution was obtained. The biota sample was then allowed to cool and then the sample mixture was filtered and transferred to a 50 mL volumetric flask and volume adjusted to mark with deionized water. The same procedure was used for the blank digest without sample.

2.3. AAS analysis of samples

The digested sediment, shrimp, and periwinkle tissue samples were analyzed for chromium, iron, nickel, copper, lead, and cadmium using atomic absorption spectrometry (Agilent Technology, Spectra 55b Australia). Specific metal standards (AccuStandard, USA) were used to calibrate the instrument. Working solutions were prepared by dilution of stock solutions. A blank was similarly determined to reset the instrument prior to each analysis to avoid matrix interference. The analysis was carried out in triplicate for reproducibility and accuracy was carried out in triplicate for reproducibility, accuracy, and precision. Before the determination of the heavy metal concentration in the samples, a calibration curve was prepared from a standard stock solution of the metals.

2.4. Estimation of the transfer factor (TF)

Metal transfer factor (TF) describes the absorption and distribution of a substance in an organism after exposure in a given environmental matrix [25] and was used to determine possible biomagnification of the toxicant in shrimp and periwinkle tissues. It is calculated as the ratio of contaminant levels in shrimp and periwinkle tissues to those in sediments [25-27] as shown in Equation 1.

$$TF = \frac{C_{Periwinkle}}{C_{Environmental matrix}} \tag{1}$$

where $C_{Periwinkle)}$ and $C_{Environmental\ matrix}$ are the concentrations of heavy metals in periwinkle and sediment, respectively.

2.5. Human health risk assessment of heavy metals in Biota

Human health risk assessment is a process that involves characterization of the probability of adverse human health effects associated with exposure to environmental chemicals.

2.5.1. Exposure assessment

Usually pollutants enter the body through different exposure or contact pathways that include inhalation, ingestion and dermal contacts. The ingestion pathway is the primary pathway of biota exposure to the body. Dietary intake of contaminated foods has been implicated as a primary source of human exposure to toxic chemicals, including heavy metals. The exposures through ingestion of contaminated *Parapenaeopsis atlantica* and *Tympanotonus fuscatus* were calculated using Equation 2.

$$EXP_{lng} = \frac{C \times 1R_{Biota} \times ED \times EF \times CF}{BW \times AT}$$
 (2)

where C is the concentration of the medium (mg/kg), IR is the ingestion rate of the medium (kg/day/person) (adult = 0.036 kg and children = 0.016 kg, the ingestion rate is obtained from a one-on-one interview and questionnaire survey of 110 participants (aged 8 to 70 years). The number of periwinkles and shrimps eaten in breakfast, lunch, and dinner was averaged and used to calculate the ingestion rate per day. ED is the duration of exposure (years) (adult = 70 years and children = 8 years), EF is the frequency of exposure (days / year) = 365 days/year, CF is the conversion factor of the fresh weight to dry weight intake rates of biota issues using the moisture percentage in the biota = 0.17, BW is the body weight (kg) (adult = 70 kg and children = 30 kg) and AT is the average time (days) = $EF \times ED$ days.

2.6. Risk characterization

2.6.1. Non-carcinogenic risk

The potential non-cancer risk of heavy metal concentrations in sediments and biota is characterized using a target hazard quotient (THQ). The target hazard quotient (THQ) assumes that there is a level of exposure known as the reference dose (RfD). It is estimated that daily oral intake of the heavy metal at the reference dose will not pose a reasonable risk even to sensitive populations, over a 70-year lifetime [28]. The US EPA defines hazard quotient (THQ) as the ratio of the estimated daily intake by ingestion (EXP $_{lng}$) (mg/(kg/day)) to the reference dose (RfD, mg/(kg/day)). It was estimated using the formula in Equations 3 and 4.

$$THQ = \frac{EXP_{Ing}}{RfD}$$
 (3)

where THQ = Hazard quotient (unitless), RfD = Reference dose (mg/kg/day). For n numbers of heavy metals, the non-carcinogenic effect to the population is as a result of the summation of all the THQs due to individual heavy metals.

HI (Hazard index) =
$$THQ_{Toxicant 1} + THQ_{Toxicant 2} + THQ_{Toxicant 3} + \cdots + THQ_{Toxicant n}$$
(4)

If the THQ (target hazard quotient) and HI (hazard index) are less than 1.0, it is highly unlikely that significant additive or toxic interactions would occur, so no further evaluation is necessary. When THQ and HI exceed 1.0, there may be concern about a potential non-cancer health effect.

Table 1. pH and concentration of heavy metals in sediment samples *.

Stations	pН	Cr (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
SIR1	5.74	0.27	31.0	0.27	0.07	0.03	0.02
SIR2	5.20	0.24	25.0	0.38	0.05	0.03	0.01
SIR3	5.56	0.32	41.4	0.32	0.11	0.09	0.01
MSQS	-	16	>25,000	-	38	28	0.5
WHO/FAO MPL	6.5-8.5	0.05	0.3	0.07	2	0.01	0.003

^{*} SIR 1, SIR 2 and SIR 3: Sediment sample station 1, 2 and 3 respectively; MSQS: Marine sediment quality standard; WHO/FAO MPL: World Health Organization/Food and Agricultural Organization Maximum permissible limit.

Table 2. Heavy metal concentrations in shrimps and periwinkles in mg/kg *.

BIOTA	Cr (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
SHRIMPS (CIR)	0.33±0.01	8.80±0.25	0.64±0.01	0.02±0.02	0.05±0.02	0.01±0.01
Range	0.32-0.34	8.50-9.00	0.62-0.65	0.00-0.04	0.03-0.07	0.01-0.02
WHO/FAO MPL	0.15-1.0	0.5	-	-	1.0	2
PERIWINKLE (PIR)	0.28±0.04	0.90±0.03	0.13±0.05	0.02 ± 0.02	0.02 ± 0.01	0.02±0.01
Range	0.25-0.32	0.87-0.92	0.09-0.18	0.00-0.03	0.01-0.02	0.01-0.03
WHO/FAO MPL	0.5	0.5	-	-	1.0	2

^{*} WHO/FAO MPL: World Health Organization/Food and Agricultural Organization Maximum permissible limit.

Table 3. Descriptive statistics of sediment physicochemical parameters and heavy metals (Valid N (listwise) = 3).

	N	Range	Minimum	Maximum	Mean	Std. error	Std. deviation	Variance
pН	3	0.54	5.20	5.74	5.5000	0.15875	0.27495	0.076
Cr	3	0.08	0.24	0.32	0.2767	0.02333	0.04041	0.002
Fe	3	16.40	25.00	41.40	32.4667	4.79073	8.29779	68.853
Ni	3	0.11	0.27	0.38	0.3233	0.03180	0.05508	0.003
Cu	3	0.06	0.05	0.11	0.0767	0.01764	0.03055	0.001
Pb	3	0.06	0.03	0.09	0.0500	0.02000	0.03464	0.001
Cd	3	0.01	0.01	0.02	0.0133	0.00333	0.00577	0.000

2.6.2. Incremental Lifetime Cancer Risk (ILCR)

The cancer risk from heavy metals in sediment and biota is calculated following Equation 5.

$$ILCR = EXP_{Ing} \times CSF$$
 (5)

where $\mathrm{EXP}_{\mathrm{Ing}}$ (Estimated Daily Intake Through Ingestion) is the daily exposure to the contaminant and CSF (Cancer Slope Factor) is the risk per unit dose of the contaminant (mg/kg/day). CSF for Cd = 6.3, Ni = 0.017, Cr = 0.5. Fe, Cu, and Pb are not classified as human carcinogens.

3. Results and discussion

3.1. Distribution of heavy metals in sediment, shrimps and periwinkle

The levels of heavy metals in the sediment and biota of the Esuk Ibeno beach are presented in Table 1 for stations 1 through 3. The concentrations of heavy metals in sediment ranged from 0.24 to 0.32 mg/kg in Cr, 25.0 to 41.4 mg/kg in Fe, 0.27 to 0.38 mg/kg in Ni, 0.05 to 0.11 mg/kg in Cu, 0.03 to 0.09 mg/kg in Pb and the concentration ranged from 0.01 to 0.02 mg/kg in Cd.

As seen in Table 2, the heavy metal concentration in Shrimp was 0.33 ± 0.01 mg/kg in Cr, 8.80 ± 0.25 mg/kg in Fe, 0.64 ± 0.01 mg/kg in Ni, 0.02 ± 0.02 mg/kg in Cu, 0.05 ± 0.02 mg/kg in Pb and 0.01 ± 0.01 mg/kg in Cd. The Cr concentration in the periwinkle sample was 0.28 ± 0.04 mg/kg, Fe was 0.90 ± 0.03 mg/kg, Ni was 0.13 ± 0.05 mg/kg, Cu was 0.02 ± 0.02 mg/kg, Pb was 0.02 ± 0.01 mg/kg and Cd was 0.02 ± 0.01 mg/kg. Table 3 shows the descriptive statistics of the physicochemical parameter and the heavy metal concentration in sediment. The mean concentration values of pH, Cr, Fe, Ni, Cu, Pb, and Cd were as follows: 5.50 ± 0.2 , 0.28 ± 0.04 , 32.47 ± 8.30 , 0.32 ± 0.06 , 0.08 ± 0.03 , 0.05 ± 0.03 , and 0.01 ± 0.01 mg/kg, respectively.

The mean concentration of Cr in the sediment samples was 0.28±0.04 mg/kg. This value was higher than the allowable limit given by the Standard Organization of Nigeria and also higher than the allowable limits given by the World Health Organization (0.05 mg/kg). This indicates that the sediment in

the study area was polluted, which is in line with the research carried out by [24,29,30], who reported high Cr concentrations. The concentration of Cr in shrimps (0.33 \pm 0.01 mg/kg) and periwinkle (0.28 \pm 0.04 mg/kg) did not exceed the permissible limit (0.15-1.00 mg/kg and 0.5 mg/kg) for Cr in shrimps and periwinkle respectively according to FAO/WHO standards. Hence, shrimp and periwinkle were not polluted in the study area.

Iron is a very critical element in biological systems [31]. Iron is widely distributed in the earth's crust and is found in several ferromagnetic minerals. Pyrite is a common form of iron in sedimentary materials, whereas ferric oxides and hydroxides are important iron-bearing minerals [31]. The iron concentration value in the sediment is 32.47±8.29 mg/kg as seen in Table 1. This mean concentration was higher than the maximum allowed limits recorded by the FAO and WHO. This may be due to the flow of Fe-containing water materials. It also suggests that the Fe concentration is at toxic levels in the beach water [32]. The high amounts of iron present as pollutants in the atmosphere can cause deleterious effects on humans, animals, and materials. Excess Fe leads to tissue damage as a result of the formulation of free radicals. Table 2 shows that the iron concentration in shrimps (8.80±0.25 mg/kg) and periwinkle (0.90±0.03 mg/kg) were above the FAO/WHO recommended limit of 0.5 mg/kg. Therefore, shrimp and periwinkle had high concentrations of iron and therefore were polluted with Fe.

Sources of Ni in the aquatic environment include industrial discharge, sewage, and runoff [33]. The mean concentration of 0.32±0.06 mg/kg was recorded in sediment, respectively (Table 1). This value was higher than the permissible limits of Ni of FAO and WHO [3] (0.07 mg/kg). In Table 2, the concentration of nickel in shrimp and periwinkle were 0.64±0.01 and 0.13±0.05 mg/kg, respectively. The maximum allowable limit of nickel for humans is not known. Therefore, shrimp and periwinkle from the Esuk Ibeno Beach cannot be said to be polluted or unpolluted.

As seen in Table 1, the mean concentrations of Cu $(0.08\pm0.03 \text{ mg/kg})$ in sediment samples were lower than the permissible limits of 2 mg/kg given by FAO, 2007 for sediment quality [3].

Table 4. Calculated transfer factor values for the investigated metals

Metals	Sediment	Periwinkle	Periwinkle/Sediment
Cr	0.28	0.28	1.00
Fe	32.47	0.90	0.03
Ni	0.32	0.13	0.41
Cu	0.08	0.02	0.25
Pb	0.05	0.02	0.40
Cd	0.01	0.02	2.00

Table 5. Dietary intake of heavy metals via the consumption of Parapenaeopsis atlantica and Tympanostus fuscatus from Esuk Ibeno Beach *.

Biota	Cr	Fe	Ni	Cu	Pb	Cd
Shrimps (Adults)	2.89×10 ⁻⁵	7.70×10 ⁻⁴	5.60×10 ⁻⁵	1.75×10-6	4.37×10-6	8.74×10 ⁻⁷
Shrimps (Children)	2.99×10 ⁻⁵	7.98×10 ⁻⁴	5.80×10 ⁻⁵	1.81× 10 ⁻⁶	4.53× 10 ⁻⁶	9.07× 10 ⁻⁷
Periwinkle (Adults)	2.45×10 ⁻⁵	7.87×10 ⁻⁴	1.14×10-5	1.75×10-6	1.75×10-6	1.75×10 ⁻⁶
Periwinkle (Children)	2.54×10 ⁻⁵	8.16×10 ⁻⁵	1.18×10 ⁻⁵	1.81×10-6	1.81×10-6	1.81×10 ⁻⁶
RfD (mg/kg/day)	3.00×10 ⁻³	7.00×10 ⁻¹	2.00×10-2	4.00×10 ⁻²	4.00×10 ⁻³	1.00×10 ⁻³
CSF (mg/kg/day)	0.5	-	1.70×10 ⁻²	-	-	6.3

^{*} RfD is the oral reference dose.

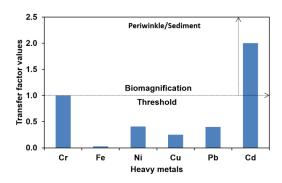


Figure 2. Transfer factor of heavy metals in the periwinkle.

These findings are in agreement with the studies carried out by Ong *et al.* on the distribution of heavy metals in the New Calabar River which recorded low levels of copper in the study area [34]. Table 2 shows that the Cu concentration in both shrimp and periwinkle were 0.02±0.02 and 0.02±0.02 mg/kg, respectively and these values were lower than the WHO recommended standard as well as the FAO standard of 3.0 mg/kg. Therefore, with respect to copper, shrimps remain unpolluted. There are no known standards for periwinkle by WHO/FAO, hence the standard for fish and shrimp is used.

A high dose of lead causes damage to the central nervous system, affects intelligence, and causes attention deficiency. Lead also causes cancer, interferes with vitamin D metabolism, and affects mental development in infants [31]. The mean concentration of lead in sediment samples recorded in Table 1 was 0.05±0.03 mg/kg. However, the maximum allowable limit of Pb for humans has not been recorded by FAO/WHO, and therefore it cannot be decided whether Pb in sediments was polluted or not. In Table 2, the concentration of Pb in shrimp and periwinkle was shown as 0.05±0.02 and 0.02±0.01 mg/kg, respectively which is lower than the maximum limit of FAO/WHO of 1.0 mg/L. Therefore, the shrimp and periwinkle were not polluted with regard to Pb.

The mean concentration of cadmium in sediment samples as shown in the descriptive statistics was 0.01 ± 0.01 mg/kg (Table 3). The mean concentration was lower than the sediment quality standard (0.5 mg/kg). According to FAO/WHO, the maximum limit of cadmium in shrimp and periwinkle is 2.0 mg/kg. This value was higher than the values recorded for shrimps and periwinkle (0.01 \pm 0.01 and 0.02 \pm 0.01 mg/kg, respectively) in this study (Table 2). Shrimps and periwinkle were not polluted with cadmium.

3.2. Transfer factor of heavy metals in the periwinkle

The metal transfer factor from sediment to periwinkle is considered a major pathway of human exposure to heavy metals through the food chain. It is an essential tool for investigating the human health risk index [35]. The calculated transfer factor values (Table 4 and Figure 2) indicate the level of biomagnification that has occurred in *Tympanotonus fuscatu*. A transfer factor of 1 and above indicates that the metal is biomagnified [36]. Except for Cr (1.00) and Cd (2.00), all other transfer factors in Tympanotonus fuscatus were below 1 indicating that there was no biomagnification of the other heavy metals. Bioconcentration and biomagnification could lead to high toxicity of these metals in organisms, even when the exposure level is low. Under such conditions, the toxicity of a moderately toxic metal could be enhanced by synergism, and the aquatic population may decline. In addition to destabilizing the ecosystem, the accumulation of these toxic metals in the aquatic food web is a threat to public health and therefore its potential long-term impact on ecosystem integrity cannot be ignored [37].

3.3. Human risk assessment of trace metals through the consumption of Parapenaeopsis atlantica and Tympanotonus fuscatus

3.3.1. Exposure assessment

Dietary intake of contaminated food has been implicated as a primary source of human exposure to toxic chemicals including heavy metals. The exposures through ingestion (Exp_{Diet}) of contaminated *Parapenaeopsis atlantica* and *Tympanotonus fuscatus* were calculated for both adults and children and shown in Table 5. The Exp_{Diet} (mg/kg bw/day) of the six investigated metals were calculated based on the daily consumption of 0.036 kg/person/day of *Parapenaeopsis atlantica* and *Tympanotonus fuscatus* on the beach of Esuk Ibeno.In this study, the Exp_{Diet} of the investigated metals (Cr, Fe, Ni, Cu, Pb, and Cd) was lower than the oral reference dose (RfD), suggesting that the heavy metals in shrimp and periwinkle tissues may not pose any health risk.

Table 6. Target hazard quotient (THQ) and hazard index (HI) of heavy metals through the consumption of *Parapenaeopsis atlantica* and *Tympanostus fuscatus* from Esuk Ibeno Beach.

Biota	Target hazard quotient							
	Cr	Fe	Ni	Cu	Pb	Cd	<u>—</u>	
Shrimps (Adult)	9.63×10 ⁻³	1.10×10 ⁻³	2.80×10-3	4.38×10-5	1.09×10-3	8.74×10-4	1.56×10 ⁻²	
Shrimps (Children)	9.97×10 ⁻³	1.14×10-3	2.90×10-3	4.53×10 ⁻⁵	1.13×10-3	9.07×10 ⁻³	1.61×10-2	
Periwinkle (Adult)	8.17×10 ⁻³	1.12×10-4	5.70×10 ⁻⁴	4.38×10-5	4.38×10-4	1.75×10 ⁻³	1.11×10-2	
Periwinkle (Children)	8.46×10 ⁻³	1.17×10-3	5.89×10 ⁻³	4.53×10 ⁻³	4.53×10-3	1.81×10-3	1.15×10 ⁻³	

Table 7. Incremental lifetime cancer risk (ILCR) of heavy metals via the consumption of *Parapenaeopsis atlantica* and *Tympanostus fuscatus* from Esuk Ibeno Beach *.

beach .						
Biota	Cr	Fe	Ni	Cu	Pb	Cd
Shrimps (Adults)	1.40×10 ⁻⁵	-	9.52×10 ⁻⁸	-	-	5.51×10 ⁻⁶
Shrimps (Children)	1.50×10 ⁻⁵	-	9.86×10 ⁻⁷	-	-	5.71× 10 ⁻⁶
Periwinkle (Adults)	1.23×10 ⁻⁵	-	1.94×10 ⁻⁷	-	-	1.10×10 ⁻⁵
Periwinkle (Children)	1.27×10 ⁻⁵	-	2.01×10 ⁻⁷	-	-	1.14×10 ⁻⁵
CSF (mg/kg/day)	0.5	-	1.70×10 ⁻²	-	-	6.3

^{*} CSF is the cancer slope factor [42].

Reference [38] reported that the oral reference dose is the estimated daily exposure to which the human population can be continually exposed over a life time without appreciable risk. The result of this study is similar to the findings of [25], who determined the estimated dietary intake of Pb, Cd, Ni, Fe and Cu for both *Tympanostus fuscatus* and *Pachymelenia fusca* from two coastal areas of Akwa Ibom state, Nigeria. The EXP_{Diet} values recorded in this study are lower than the data for the provisional tolerable daily intake of the investigated metals as suggested by the Joint FAO/WHO Expert Committee for Food Additives [3].

3.3.2. Target hazard quotient (THQ)

The target hazard quotient (THQ) has been recognized as one of the methods for evaluating the risk associated with the intake of metals through the consumption of contaminated foods such as shrimp and periwinkle [39,40]. The THQ value according to USEPA is used to compare the amount of the ingested product with a standard reference. The target hazard quotient and the hazard index of shrimps and periwinkle harvested from the study locations are presented in Table 6. The lowest value was recorded for adults and children for Cu (4.38×10⁻⁵) in both shrimp and periwinkle and the highest value recorded for Cr in both shrimps (9.97×10-3) and periwinkle (8.46×10-3) in children. The THQ values for all the investigated metals were less than unity. This indicates that there could be no considerable health hazard from the consumption of Parapenaeopsis atlantica and Tympanostus fuscatus from the beach of Esuk Ibeno. The cumulative THQ (hazard index) was less than one for both Parapenaeopsis atlantica and Tympanostus fuscatus. The HI value for Parapenaeopsis atlantica and Tympanostus fuscatus was 1.56×10⁻² and 1.11×10⁻², respectively, in adults and 1.61×10⁻² and 1.15×10-3, respectively, in children. This indicates possible risk in the future as a result of the bioaccumulative and nonbiodegradable nature of heavy metals. References [41,42] recorded THQ values less than one, which is similar to this study. However, the hazard index values for their study were not greater than one.

3.3.3. Incremental Lifetime Cancer Risk (ILCR)

To calculate the cancer risk of contaminants in shrimp and periwinkle ingested, an incremental lifetime cancer risk (ILCR) model was used. The ILCR value according to USEPA is used to compare the amount of the ingested product with a standard reference. The ILCRs of shrimps and periwinkle harvested from the study locations are presented in Table 7. The lowest value for adult and children was recorded for Ni (9.52×10-8 in shrimp) and Ni (9.86×10-7), respectively. The highest value recorded for Cr in shrimps (1.50×10-5) and periwinkle (1.27×10-5) in

children. The ILCR for all the investigated metals were 1.0×10^{-6} and 1.0×10^{-4} . This indicates that the consumption of *Parapenaeopsis atlantica* and *Tympanostus fuscatus* on the beach of Esuk Ibeno was within the acceptable range [2,43].

4. Conclusions

This study was carried out to investigate the health risk associated with heavy metal concentrations in sediments, shrimp, and periwinkle on the Esuk Ibeno beach, as these delicacies provide a relatively cheap source of animal protein for Ibeno community residents. The results of this study showed that the contamination of sediment and biota (P. atlantica and T. fuscatus) from the Esuk Ibeno River with heavy metals (Cd, Cu, Cr, Fe, Pb and Ni) was largely from anthropogenic sources. However, the metals in the sediment were all below the marine sediment quality standard. In biota, Fe concentrations in shrimp and periwinkle exceeded the permissible limit, but all other metal concentrations were within the limits. Cr and Cd in T. fuscatus, and Fe and Ni in P. atlantica were biomagnified when the calculated transfer factors were greater than 1. The human health risk assessment showed that in this study, the Exp_{Diet} of the investigated metals (Cr, Fe, Ni, Cu, Pb and Cd) was lower than the oral reference dose (RfD), suggesting that the heavy metals in shrimps and periwinkle tissues may not pose any health risk. The THQ values for all the investigated metals were less than unity. This indicates that there could be no considerable health hazard from the consumption of Parapenaeopsis atlantica and Tympanostus fuscatus from Esuk Ibeno Beach. The cumulative THO (hazard index) was less than one for both *Parapenaeopsis* atlantica and Tympanostus fuscatus. The HI value for Parapenaeopsis atlantica and Tympanostus fuscatus was 1.56×10⁻² and 1.11×10⁻², respectively. This indicates possible risk in the future as a result of the bioaccumulative and nonbiodegradable nature of heavy metals. The ILCR for all the investigated metals were 1.0×10^{-6} and 1.0×10^{-4} . This indicates that the consumption of Parapenaeopsis atlantica and Tympanostus fuscatus from Esuk Ibeno beach was within the acceptable range. Industries operating in this community should adopt more sustainable and eco-innovative management options to reduce the potential risks of metal pollution on ecology and human health.

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Disclosure statement os



Conflict of interests: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered to. Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement GR

Conceptualization: Akanimo Dianabasi Akpan, Patience Okon Asuquo; Methodology: Akanimo Dianabasi Akpan, Patience Okon Asuquo, Bassey Sam-Uket Okori; Software: Akanimo Dianabasi Akpan, Bassey Sam-Uket Okori; Validation: Akanimo Dianabasi Akpan, Patience Okon Asuquo; Formal Analysis: Patience Okon Asuquo, Bassey Sam-Uket Okori; Investigation: Akanimo Dianabasi Akpan, Patience Okon Asuquo, Bassey Sam-Uket Okori; Resources: Akanimo Dianabasi Akpan, Patience Okon Asuquo, Bassey Sam-Uket Okori; Data Curation: Akanimo Dianabasi Akpan, Patience Okon Asuquo, Bassey Sam-Uket Okori; Writing - Original Draft: Akanimo Dianabasi Akpan; Writing - Review and Editing: Akanimo Dianabasi Akpan, Patience Okon Asuquo, Bassey Sam-Uket Okori; Visualization: Akanimo Dianabasi Akpan, Bassey Sam-Uket Okori; Funding acquisition: Akanimo Dianabasi Akpan, Patience Okon Asuquo, Bassey Sam-Uket Okori; Supervision: Akanimo Dianabasi Akpan, Bassey Sam-Uket Okori; Project Administration: Akanimo Dianabasi Akpan, Patience Okon Asuquo, Bassey Sam-Uket Okori.

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