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Seasonal Variation of Heavy Metals in Sediments, Water, Shiny Nose Fish, Shrimp, and Periwinkle in Esuk Ekpo Eyo Beach, Akpabuyo, South-East Nigeria

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Abstract

The seasonal variations of heavy metals (Cr, Cu, Pb, Cd, Ni, Fe, Hg, and Zn) in sediments, water samples, and shiny nose fish (*Polydactylus quadrifilis*), shrimp (*Parapenaeopsis atlantica*) and periwinkle (*Tympanostonus fuscatus*) of Esuk Ekpo Eyo Beach, Akpabuyo, Cross River State, South East Nigeria were investigated using AAS spectrophotometer. The mean concentrations (mg/l) of Cr, Cu, Pb, Cd, Fe, and Ni in sediments for the dry and wet seasons were 1.004±0.658 mg/l, and 0.546±0.406 mg/l for Cr, 0.46200±0.071 mg/l and 0.020±0.010 mg/l for Cu, 0.344±0.01594 mg/l and 0.0285±0.0062 mg/l for Pb, 0.01917±0.01693 mg/l and 0.02133±0.01089 mg/l for Cd, 0.1752±0.0112mg/l and 0.1503±0.1216mg/l for Ni, 64.00±3.964 mg/l and 39.91±4.187 mg/l for Fe. The mean concentrations (mg/l) of Cr, Cu, Pb, Cd, Fe, Zn, and Hg in water samples during dry and wet seasons were 0.1238±0.0866 mg/l and 0.19766±0.1644 mg/l for Cr, 0.02866±0.0060 mg/l and 0.0382±0.0265 mg/l for Cu, 0.03083±0.01721 mg/l and 0.03683±0.0225 mg/l for Pb, 0.03716±0.0301 and 0.042166±0.01701 mg/l for Cd, 4.3525±2.27mg/l and 7.221±2.49 mg/l for Fe, 0.0508±0.0214 mg/l and 0.071166±0.00702mg/l for Zn, 0.014±0.0010 mg/l and 0.02400±0.0077 mg/l for Hg. The concentrations (mg/l) for Cr in shiny nose fish, Fe in shrimp, and Cd in periwinkle for the dry and wet seasons were 0.019±0.007 mg/l and 0.036± 0.001 mg/l for Cr, 0.327±0.001 mg/l and 0.740±0.001 mg/l for Fe, 0.021±0.007 and 0.009±0.004 for Cd in periwinkle. The estimated daily intake of these metals in fish, shrimp, and periwinkle analyzed using the estimated daily intake formula were all below the Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives (JECFA) recommended daily intake limits. Physicochemical analysis was carried out to determine the values of pH, TOC, TOM, silt, clay, and sand for sediments, also pH, turbidity, TDS, TSS, EC, and salinity for water samples. The pollution load index calculated for sediment showed moderately severe enrichment for the dry season and minor enrichment for the wet season while the modified degree of contamination of the geo-accumulation index in the sediments was less than 1.5, hence no contamination. The results of Pearson's correlation matrix showed that significant correlations were observed among variables at 0.05 levels.

Keywords: Seasonal Variation, Heavy Metals, Shrimp, Periwinkle, Pollution Load Index

1 Introduction

Pollution is the introduction of contaminants into the natural environment that cause adverse changes. Pollution can take the form of chemical substances or energy, such as noise, heat, or light. The components of pollution can be either foreign substances/energies or naturally occurring contaminants [1]. Heavy metal pollution in an aquatic ecosystem is a worldwide environmental problem that has received increasing attention over the last few decades because of its adverse effects [1]. Heavy metal contamination affects humans, flora, and fauna. They are toxic to living organisms. The contamination of aquatic systems by heavy metals especially in sediments and biota and has become one of the most challenging pollution issues due to the toxicity, abundance, persistence, and consequent bioaccumulation of these metals [2]. When discharged into the water ecosystems, heavy metals can be adsorbed by suspended solids, and then they strongly accumulate in sediments and became biomagnified among food chains [3]. Moreover, these sediments act as absorbing mediums and may in turn act as sources of heavy metals [4].

1.1 Biota

Biota may refer to the plant and animal life of a region (eg tropical region). This may include plants like seaweeds, zooplankton, and phytoplankton and animals like fishes, oysters, prawns, and periwinkle [2].

1.2 Sediments

Sediment is a naturally occurring material that is broken down by the processes of weathering and erosion and is subsequently transported by the action of wind, water, or ice and/or by the force of gravity acting on the particles. For example, sand and silt can be carried in suspension in river water and on reaching the sea bed deposited by sedimentation

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and if buried may eventually become sandstone and siltstone (sedimentary rocks). Sediments are most often transported by water (fluvial process) but also by wind (Aeolian processes) and glaciers. Beach sands and river channel deposits are examples of fluvial transport and deposition through sediment also often settle out of slow-moving or standing water in lakes and oceans. A beach is a sandy shore, especially by the sea between high and low water marks. Desert dunes and loess are examples of Aeolian transport and deposition, and glacial moraine deposits, and till are ice-transported sediments [4].

1.3 Heavy Metal Pollution

Heavy metals are known as metallic entities that have a relatively high density compared to water [5]. With the assumption that the weight of the metals and their poisonous effects are interrelated, heavy metals also include metalloids, such as Nickel, that can induce virulent effects at a low level of exposure. In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals. Also, human exposure has risen dramatically as a result of an exponential increase in their use in several industrial, agricultural, domestic and technological applications [5].

1.4 Entry Routes

Heavy metals enter the plant, animal, and human tissues via air inhalation, diet, and manual handling. Motor vehicle emissions are a major source of airborne contaminants including arsenic, cadmium, cobalt, nickel, lead, antimony, vanadium, zinc, platinum, palladium, and rhodium [6]. Water sources (groundwater, lakes, streams, and rivers) can be polluted by heavy metals leaching from industrial and consumer waste, acid rain can increase this process by releasing heavy metals trapped in soils. Plants are exposed to heavy metals through the uptake of water, animals eat these plants; ingestion of plant and animal-based foods are the largest sources of heavy metals in humans. Absorption through skin contact, for example from contact with soil or metal-containing toys and jewelry, is another potential source of heavy metal contamination. Toxic heavy metals can bio-accumulate in organisms as they are hard to metabolize [7].

1.5 Sources of Heavy Metal Pollution

Heavy metals are found in the earth and become concentrated as a result of human activities [42]. Common sources are mining and industrial wastes: vehicle emissions: lead acid batteries: fertilizers, paints, treated wood, aging water supply infrastructure, and microplastics floating in the world's oceans [8]. Arsenic, cadmium, and lead may be present in children's toys at levels that exceed regulatory standards. Lead can be used in toys as a stabilizer, color enhancer, or anti-corrosive agent. Cadmium is sometimes employed as a stabilizer or to increase the mass and luster of toy jewelry. Arsenic is thought to be used in connection with coloring dyes. Regular imbibers of illegally distilled alcohol may be exposed to arsenic or lead poisoning the source of which is arsenic-contaminated lead used to solder the distilling apparatus [8].

1.5.1 Natural Sources

The basic source of heavy metal pollution in the Environment is by weathering of rocks like sedimentary rock, dolomite, shale, and sandstone. Interaction of water with igneous rocks such as granite, gabbro, nephelite, syenite, and basalt. The most natural sources of metal inputs into the ecosystem are Natural weathering [9]. It is the source of baseline or background levels. It's to be expected that in areas characterized by metal bearing-formations, these metals also will occur at elevated levels within the water and bottom sediments of the actual areas. Mineralized zones end in regional pollution. In consequence, the final limitation arises out of the way to distinguish between metal input in a locality be it a natural input or man-made input. According to Irabien *et al.* (1999) not several examples are known of interactions between natural weathering processes and anthropogenic inputs. Arruti *et al.* (2010) tried to elucidate the interactions of naturally associated anthropogenic metal inputs into water. They argued that the pollution of the stream (which is assumed to be a natural source) doesn't presently originate utterly from natural weathering processes only but sources of polluted depositions can also be a result of man-made input. This discovery provides initial insight into man's first impact on water.

1.5.2 Anthropogenic Sources

Heavy metals are discharged into the atmosphere by several human activities. They're conjointly utilized in an oversized form of industrial product that in the future gets to be deposited as waste. Heavy metal unleashed into the atmosphere happens at the start of the assembly/production chain, whenever ores are mined throughout the manufacturing of products containing them in the industries. The natural sources are dominated by parent rocks and aluminiferous minerals, whereas the most anthropogenic sources are agricultural activities such as the application of fertilizers, animal manures, and pesticides containing Heavy metals which are widely used in crop production, metallurgic activities that embody mining, smelting, metal finishing and others, energy production and transportations, electronic product and eventually waste disposals [11]). Heavy metals can be discharged into the atmosphere in aerosolized, particulate, aqueous, or in solid forms and can emanate from a variety of sources. The speedy rates of manufacturing and urbanization increase the carrying capacity of heavy metals in water sharply [42]. The concentration level of Hg in water will increase principally because of agricultural activities, human activities such as tillage and work, domestic biodegradable pollution discharge, part deposition from solid waste combustion, coal and oil combustion, pyro-metallurgical processes (Fe, metallic element, and Zn) and mining activities. Surface run-off from rain or snow brings Hg-contaminated soil to adjacent water systems. Industrial processes that are accountable for polluting water with Hg include chloralkali, batteries, fluorescent lamps, thermometers, and electronic switch production [43]. Most of these Industries for example the mining industry, petroleum industry, paint industry, etc. have been among the most important direct polluting supply of Heavy metals in the world. The earliest source of lead pollution is from the unsound metal pipes and compounds of Lead in the aquatic atmosphere which comes from compounds like paints and gasoline additives and precipitation of aerosols fashioned from extreme temperature processes, also coal combustion, smelting, and cement production [12].

1.6 Impacts of Heavy Metal Toxicity on the Environment

The main threats to human health from heavy metals are associated to exposure to mercury, arsenic, lead and cadmium compounds. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as WHO and FAO etc. The aim of this research is to determine the levels of heavy metals in the Esuk Ekpo Eyo Beach, Akpabuyo Cross River State, Southern Nigeria and to establish their variation during the dry and wet season. To achieve this the following objectives are considererd

1. To determine the levels of six heavy metals in sediments, Biota and water samples of the Esuk Ekpo Eyo Beach. Biota samples include shrimp (*Parapenaeopsis atlantica*), periwinkle (*Tympanotonus Fuscatus*), and shiny nose fish, locally called 'Edéng' (*Polydactylus quadrifilis*) of Akpabuyo Local Government of Cross River State.
2. To ascertain the pH, salinity, turbidity of the water and total organic carbon content, and total organic matter content of the sediments in the study area.
3. To ascertain the degree of sediment texture, ranging from silt size, clay size, and sand size of the sediments in the beach in the Esuk Ekpo Eyo community
4. Determination of the pollution load index and geo-accumulation index of the sediments of the Esuk Ekpo Eyo Beach.
5. Assessment of the estimated daily index consumption rate (Health implication) of shiny nose fish (*Polydactylus quadrifilis*), shrimp (*Parapenaeopsis atlantica*), and periwinkle (*Tympanotonus Fuscatus*) in Esuk Ekpo Eyo Beach.

1.7 The Study Area

The Esuk Ekpo Eyo Beach lies on the South-Eastern Nigerian coastline; it is part of the Great Kwa river which flows through Cross River State Nigeria. The Esuk Ekpo Eyo Beach town is located within latitude 4°56̍34''N and longitude 8°23'34''E. The climate of the area is characterized by long rainy/wet seasons usually lasting from April to November and a short duration of dry periods/weather from December to March. In the rainy season, when the water level is high, the river and creek channels are fringed with mangrove swamps in which various arthropods like crustaceans, diplopods, dipterans, etc, are the dominant fauna elements. Rhizophora *spp* and Nypa *fruticans* are the dominant floral elements. Human activity in the Esuk Ekpo Eyo Beach has traditionally been limited to small-scale farming, aquaculture, and artisanal fisheries. The map of the study area is shown on the next page.

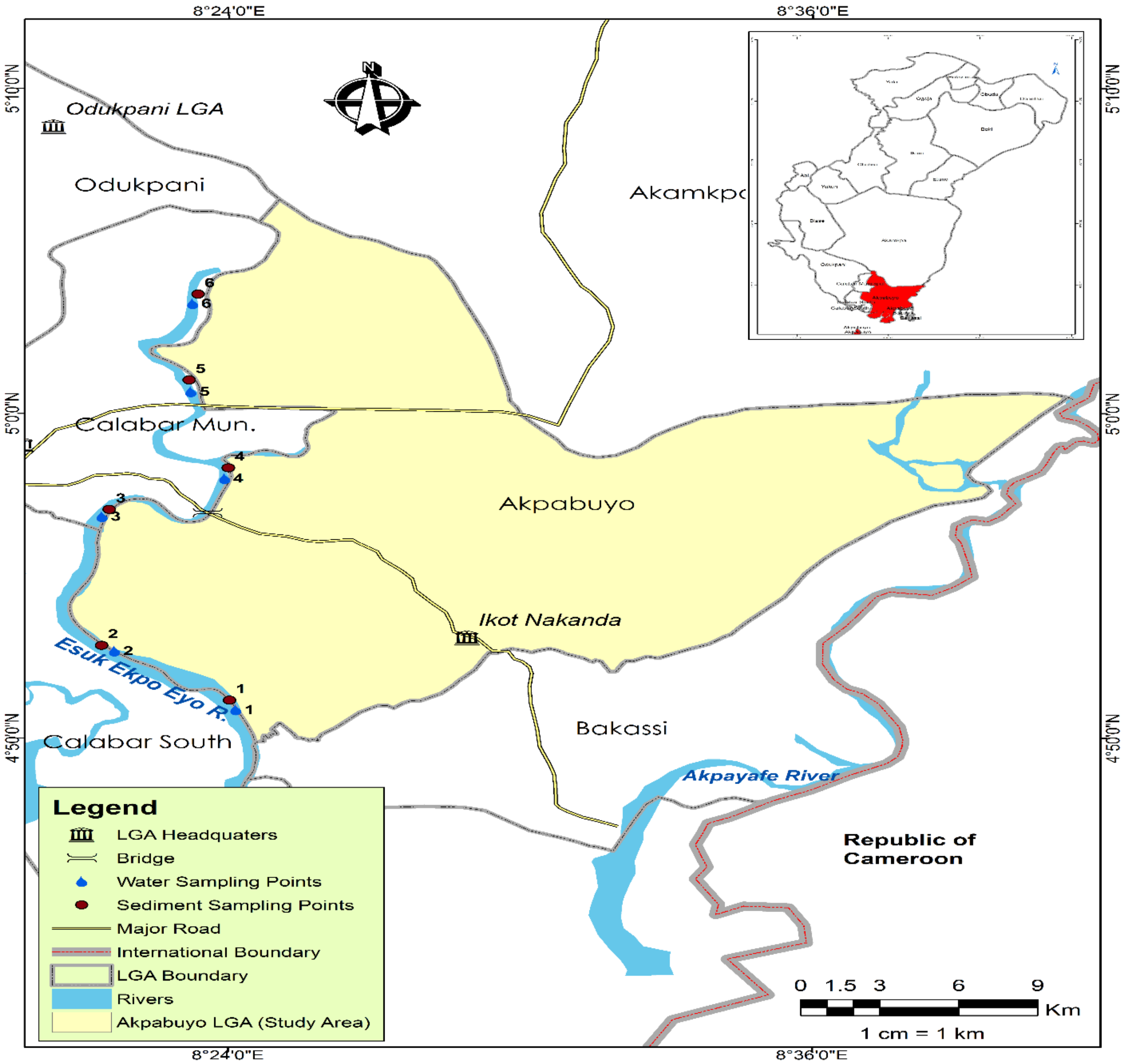


Figure 1: Map of the Study Area

1.8 Scientific Classification of Periwinkle

Domain: *Eukaryota*
Kingdom: *Animalia*
Phylum: *Mollusca*
Class : *Gastropoda*
Order: *Cacnogastropoda*
Family: *Potanididae*
Genus: *Tympanotonos*
Species: *Tympanotonos fuscatus*

Figure 1 is a picture showing periwinkles that live in swampy cities in the freshwater habitat of West Africa. Most animal periwinkles live in less deep areas of the coast i.e. Locations where rocks are dominated. The species live in water with laminar waves where the bottom of the water is fairly concentrated in dendritic. Periwinkles feed on deposits, most especially around the river coast [49].

1.9 Scientific Classification of the Giant African Threadfin, commonly known as 'Shiny Nose Fish'

Kingdom: *Animalia*
Phylum: *Chordata*
Class: *Actinopterygii*
Order: *Perciformes*
Family: *Polynemidae*
Genus: *Polydactylus*
Species: *Polydactylus quadrifilis*

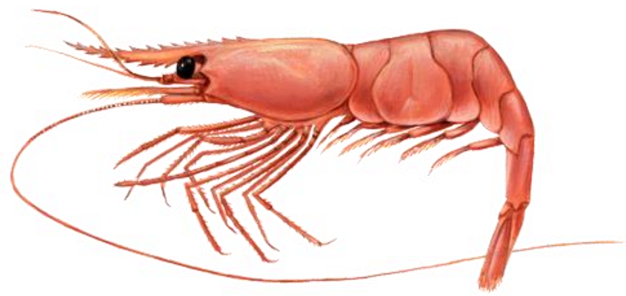
The giant African threadfin commonly known as shiny nose fish (*Polydactylus quadrifilis*) is a fish species in the family *Polynemidae*. It is native to coastal parts of western and eastern Africa. This fish can reach up to 6.6ft in length.

Shiny nose fish (scientific name: *Polydactylus quadrifilis,* commonly called Edeng**)**

1.10 Scientific Classification of Shrimp (Guinea Shrimp)

Kingdom: *Animalia*
Phylum: *Arthropoda*
Class: *Malacostraca*
Order: *Decapoda*
Family: *Penaeidae*
Genus: *Parapenaeopsis*
Species: *Parapenaeopsis atlantica*

The Guinea shrimp is native to the western and eastern Atlantic Ocean and Indian ocean, its common total length is from 6.0 to 9.0 cm (male) and 9.0 to 14.0 cm (female) it is widely distributed within the west African coast from Senegal to Angola and around the South African cape to Mozambique. It is mostly found in bottom mud or sandy mud in marine and estuarine environment [51].



Shrimp (Scientific name: *Parapenaeopsis atlantica*)

2 Materials and Methods

2.1 Sediment Sample Collection/Storage

Six sediment samples were collected from six locations along the Esuk Ekpo Eyo beach using the Van Veen grab sampler across the two seasons(that is from November to March for the dry season and April to October for the rainy season). The samples were placed in polythene bags and placed in a cooler and transported within hours to the laboratory for analysis. The sediment samples on reaching the laboratory were air dried, disaggregated on an agate mortar, and sieved to 2mm sizes. Each of the samples was sealed in a properly closed beaker. The sealed samples were kept for at least 28 days to allow a state of secular equilibrium to be reached.

2.1.1 Digestion of Sediment Samples for AAS analysis

One gram portion of crushed dry sediment was accurately weighed into a conical flask. Then 15ml aliquot of aqua regia (HNO_3: HCl, 1:3 v/v) was added slowly followed by 5ml of concentrated perchloric acid ($HClO_4$) and it was allowed to stand at room temperature for an hour before the mixture was then emptied into a Teflon vessel where it was properly corked and placed on a slow heat burner for at 120^oC for 2-3 hours until a clear solution was obtained. The sediment mixture was then transferred into a 50 ml volumetric flask and was allowed to cool and the volume was made up to mark with de-ionized water. The prepared samples were finally transferred into corked glass containers, labeled, and stored for AAS analysis [13].

2.2 Biota sample collection/preparation

The biota samples, notably shrimp and fish were caught with the aid of local fishermen from Esuk Ekpo Eyo Beach. The samples were stored in a cooler and transferred to the laboratory immediately. The periwinkles on the other hand were handpicked along the shores of the beach and stored in a cryogenic condition to avoid biodegradation. The shrimp and fish were dried in air at room temperature for three days after which the samples were pulverized and refrigerated at 4^oC until analysis, while the periwinkle tissues were removed from the shell, air-dried, homogenized, and stored for analysis [13].

2.2.1 Biota Sample Digestion for AAS Analysis

One gram of dry crushed biota samples was measured into a beaker and 20 ml aliquot of aqua regia (HNO_3: HCL, 1:3 v/v) was added and left to stand at room temperature for an hour. The beaker was slowly heated on a hot plate at 90ºC for 2-3 hours ensuring a clear sample solution was obtained. The biota sample was then allowed to cool and then the sample mixture was transferred to a 50ml volumetric flask and volume adjusted to mark with de-ionized water.

2.3 Water sample collection

Six water samples were randomly collected from the upstream, middle-stream, and downstream along Esuk Ekpo Eyo Beach. Sampling was carried out across the two major seasons in the study area, before this, the glass bottles were rinsed with 1ml of HNO_3 (nitric acid) to maintain the constant pH and minimize loss of sample because of variation in pH, evaporation, and precipitation, etc. The bottles were filled and then sealed tightly to avoid headspace that causes loss of sample because of oxidation.

2.3.1 Physicochemical Analysis of Water

The physicochemical analysis of water such as pH, turbidity, and electrical conductivity (EC) was done by using a pH and electrical conductivity meter.

2.3.2 Water Sample Pre-treatment for AAS Analysis

The digestion procedure for the Esuk Ekpo Eyo beach was carried out by transferring a measured volume (50ml) of well-mixed acid–preserved water sample to a beaker. Then 5ml of concentrated nitric acid (HNO_3) was added and the mixture was boiled and evaporated on a hot plate to the lowest possible volume (10 to 20 ml) Once digestion was completed by the presence of clear colored solution. After this, the beaker was washed down with water and filtered and then the filtrate was transferred into a 100ml volumetric flask and then made up of 50 ml mark with de-ionized water. A portion of this solution was taken for the required metal determination [13].

2.4 Particle Size Analysis

Particle size was determined using the Bouyocous hydrometer method. 50g of each sample was soaked in a dispersant of sodium metabisulphite followed by the addition of 200 ml of water and stirred vigorously. The mixture was allowed to stay overnight. The mixture was then transferred to a measuring cylinder and made up to 1000ml by the addition of water. The resulting mixture was shaken vigorously and allowed to stand for 40 seconds. The hydrometer was inserted and the first reading was taken. The second reading was taken after 2 hours. The particle size in percent of each constituent in each sample of sediment was then determined from the expression.

$$H_1 + [0.3(T_1\text{-}20)\text{-}2]$$

where H = hydrometer reading T= temperature reading in ^{0}c. Results obtained from the calculation were recorded accordingly.

2.5 Determination of Total Organic Carbon by The Walkley Black Method

Total organic carbon content was determined by weighing 2.0 g of sieved air-dried sample and it was placed in a 250cm^3 conical flask and 5cm^3 of 0.17M solutions of potassium heptaoxodichromate (VI) ($K_2Cr_2O_7$) was added to it followed by the addition of 10cm^{3}concentrated sulphuric acid from a burette. To improve the digestion process (complete oxidation), the aid of an electro-thermal magnetic stirrer with its temperature set at 100̊C to prevent unnecessary decomposition of $K_2Cr_2O_7$ at 150̊C was employed [44]. The solution was then allowed to stand for about 30 minutes. The resulting solution was diluted with 100cm^3 of distilled water to halt the reaction; 9.5cm^3 of 85% of syrupy orthophosphoric acid was added to prevent the iron (III) ions which are formed in the course of the titration of the iron (II) salt from oxidizing the diphenylamine prematurely. 0.2g sodium fluoride was then added to bind the refractory metals such as calcium and magnesium. Two drops of diphenylamine indicator were then added to the contents of the flask resulting in a purple-blue coloration. The indicator was chosen due to the difficulty in judging quantitatively the color of the $K_2Cr_2O_7$ solution unlike the potassium oxomanganate (VII) solution ($KMnO_4$). The resultant solution was then titrated with 0.25M ferrous ammonium tetraoxosulphate (VI) ($Fe\ (NH_4)_2(SO_4)_2.6H_2O$) solution with the aid of an electro-thermal magnetic stirrer to allow for even interaction of constituents with the titrant. A bright green coloration was observed at the endpoint. The procedure was repeated twice to enable average titer value calculations. The entire process was then repeated for all the remaining samples. The percentage of total organic carbon in each sample was then calculated using the equation below;

$$\%\ OrganicCarbon = 10\left(1 - \frac{T}{S}\right) \times F$$

where T is the sample titer value, S is the blank titer value, and F is the factor derived as follows; (1.0×12)/4,500))×((1.72×100)/W), and W is the weight (in grams) of the crushed samples used. Results obtained from the calculation were recorded accordingly.

2.6 Determination of Total Organic Matter (TOM)

The organic matter was extracted from the sediment sample by ultra-sonication. 2.0 g of the sample was introduced in 15 ml of solvent (acetone/hexane) (1:1) v/v in an ultrasonic cleaning bath with an average power output of 360W and a mean operating frequency of 40 kHz. After the mixture was exposed to the ultrasound for 30 minutes, it was centrifuged at 3500rpm for 10 minutes, after which the clear supernatants were removed and the combined extract was concentrated to dryness. Total organic matter (TOM) was obtained after air drying the extracts in a pre-weighed test tube using analytical balance [45].

2.7 Determination of pH

A buffer solution with pH 7.0 was added to a beaker and the pH electrode was then inserted to calibrate the pH meter to a pH of 7.0. 20g of each sample was placed in a container; 50ml of distilled water was added to each of the samples and stirred for 30 minutes before inserting the pH probe into the system. The values were then read off from the electronic meter attached to the probe and the data obtained was recorded [46].

2.8 Determination of conductivity

Apparatus: clean properly sterilized beaker, water sample (ideally the water sample should be at 25ºC at the time of analysis), and an electrical conductivity meter. The conductivity meter was turned on and then the measuring lead was placed into the water sample the reading on the conductivity meter was taken after the reading was stabilized, and the measurement displayed on the electrical conductivity meter showed the purity of the water measured in micro-siemens.

2.9 Turbidity Determination

25 cm^3 of distilled water was measured into a cuvette and read at a wavelength of 450nm. The standard was also read at the same wavelength. Then 25ml water samples were poured into the turbidimeter tube and the results were recorded.

2.10 Salinity determination

Materials: Conductivity meter, beaker samples, and measuring cylinder. Method: 100cm^3 of water sample was measured with a measuring cylinder (100cm^3) into a beaker. The conductivity meter was switched on and the probe (electrode) was dipped in the water sample after the calibration of the equipment. The readings displayed were recorded, repeating the process two other times to obtain two other values, salinity increases with a corresponding increase in electrical conductivity.

2.11 Determination of Total Dissolved Solids (TDS)

The evaporating dish was weighed in milligrams (mg) after ensuring that it was completely dry and clean of extraneous particulate matter. The water sample in the beaker was stirred with a stirring rod, it was stirred vigorously enough to agitate the solution to ensure that any particulate matter is more or less evenly distributed throughout the sample. 50 ml of the water sample was then pipetted while stirring took place and then the 50 ml water sample was then passed through a filter paper into an evaporating dish, the evaporating dish with the filtrate was then weighed. TDS is [(A-B) × 1000]/ml sample, A is the Weight of the evaporating dish+ filtrate, and B is the weight of the evaporating dish on its own.

2.12 Determination of Total Suspended Solids (TSS)

50 cm^3 of water sample was measured after properly shaken and filtered with a pre-known weight filter paper into a beaker. The filter paper was then dried in an oven at 60ºC and thereafter was transferred into a desiccator for two hours. Then it was weighed and the reading was subtracted from the pre-weighed filter paper.

Calculation: TSS (ppm) = $W_2 – W_1/V \times 10^3$

where W_1 is the weight of the pre-weighed filter paper, W_2 is the weight of the filter paper residue, and V is the volume of the filtered sample.

2.13 Heavy Metal Determination Using Atomic Absorption Spectrophotometer

The methods of A.O.A.C (2000) were used in these determinations. The principle of this method is based on the absorption property of the elements. The vapor of the elements containing free atoms absorbs light having a wavelength like that which the atoms of the elements are capable of emitting. When the light of this wavelength is passed through a flame containing free atoms of the respective elements, the intensity of the ray was diminished due to absorption. The measured decrease in the intensity of the light was proportional to the concentration of the atoms in the solution. The standard solutions of different elements were prepared for each element and the calibration curve for each element was plotted as described in the operational manual. Heavy metals of interest were analyzed in the digested state using an Atomic Absorption spectrophotometer AAS (Agilent Technology, Spectra 55b Australia). Specific metal standards (AccuStandard, USA) were used to calibrate the instrument.

2.14 Sediment Pollution Indices

The geo-accumulation index (I-geo) and pollution load index (PLI) were employed to assess the pollution of metals in the sediment of Esuk Ekpo Eyo Beach.

2.14.1 The Pollution Load Index (PLI)

The Pollution Load Index (PLI) is obtained as a concentration factor (CF). This CF is the quotient obtained by dividing the concentration of each metal by the background value The PLI of the sediment is calculated by obtaining the n-root from the n-CFs that were obtained for all the metals. Generally, the pollution load index (PLI) is calculated by the method of Tomlinson *et al.* (1980) in which CF is C metal / C background value, PLI is $\sqrt{(CF1xCF2xCF3x…xCFn)}$. where CF is the contamination factor, n is the number of metals, C metal is the metal concentration in polluted sediments, and C Background value is the background value of that metal. The PLI value of > 1 is polluted, whereas < 1 indicates no pollution.

2.14.2 Geo-accumulation Index (Igeo)

The degree of contamination from the heavy metals could be assessed by measuring the geo-accumulation index (Igeo). The index of geo-accumulation has been widely used to assess sediment contamination (Ahmed *et al*., 2015). This was introduced by Muller in 1979 to characterize the level of pollution in the sediment; geo-accumulation index (Igeo) values were calculated using the equation,

$$Igeo = Log_2[Cn/1.5Bn]$$

where Cn is the measured concentration of metal n in the sediment and Bn is the geochemical background value of element n in the background sample (Ahmed, *et al*., 2015). Factor 1.5 is introduced to minimize the possible variations in the background values which may be attributed to lithogenic effects. The I_{geo} has seven grades as shown in Table 1.

Table 1: Classification of the Modified Degree of Contamination (MCD)

MCD VALUES	SEDIMENT QUALITY (SQ)
Mcd <1.5	Nil to the low degree of contamination
1.5<mcd<2	Low degree of contamination
2<mcd<4	A moderate degree of contamination
4<mcd<8	The high degree of contamination
8<mcd<16	The very high degree of contamination
16<mcd<32	The extremely high degree of contamination
Mcd>32	Ultra-high degree of contamination

Sources: Hakanson, 1980; Abrahim *et al*., 2007

Table 2: Dry Season Sediment Bulk Properties and Concentration of Heavy Metals

ST	SAND (%)	SILT (%)	CLAY (%)	pH	TOC (%)	TOM (%)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Cd (mg/L)	Ni (mg/L)
ST 1	73.31	8.29	18.40	5.21	0.31	12	0.312	0.013	23.21	0.086	0.001	0.036
ST 2	70.12	12.37	17.51	5.18	0.25	18	0.639	0.018	49.11	0.117	0.006	0.028
ST 3	68.73	12.14	19.13	5.20	0.25	18	0.611	0.022	77.22	0.131	0.011	0.111
ST 4	9.99	11.78	78.31	5.19	0.24	15	0.813	0.077	64.77	0.152	0.017	0.089
ST 5	26.70	10.01	63.29	5.20	0.27	18	1.913	1.231	88.22	0.384	0.035	0.341
ST 6	9.04	7.85	83.11	5.22	0.25	19	1.738	1.411	81.49	1.192	0.044	0.446

Table 3: Wet Season Sediment Bulk Properties and Concentration of Heavy Metals

ST	SAND (%)	SILT (%)	CLAY (%)	pH	TOC (%)	TOM (%)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Cd (mg/L)	Ni (mg/L)
ST 1	65.43	11.62	22.95	6.11	0.57	20	0.126	0.005	14.31	0.007	0.007	0.011
ST 2	67.33	14.47	18.20	6.13	0.47	25	0.235	0.013	16.11	0.022	0.024	0.053
ST 3	62.13	20.63	17.24	6.16	0.41	25	0.374	0.018	22.31	0.018	0.021	0.133
ST 4	26.57	19.13	54.30	6.32	0.38	23	0.612	0.016	41.89	0.041	0.030	0.232
ST 5	21.15	11.31	67.54	5.87	0.40	24	0.673	0.026	67.21	0.037	0.043	0.264
ST 6	5.13	6.14	88.73	6.07	0.51	20	1.254	0.044	77.63	0.046	0.069	0.282

Table 4: Dry Season Bulk Properties and Heavy Metal Concentration of Water Samples

ST	pH	EC (uS/cm)	Salinity	TDS (mg/L)	TSS (mg/L)	FTU	Cr (mg/l)	Cu (mg/L)	Fe (mg/l)	Pb (mg/L)	Cd (mg/L)	Zn (mg/L)	Hg (mg/L)
ST 1	6.05	3.41	0.047	221	102	0.351	0.056	0.017	2.190	0.008	0.011	0.038	ND
ST 2	6.10	4.11	0.052	315	130	0.290	0.068	0.022	4.630	0.017	0.022	0.047	ND
ST 3	6.12	3.53	0.049	295	173	0.350	0.087	0.031	3.349	0.023	0.034	0.043	0.010
ST 4	6.09	3.48	0.068	326	223	0.380	0.099	0.039	4.311	0.034	0.042	0.054	0.015
ST 5	6.21	4.08	0.053	311	210	0.619	0.219	0.025	5.513	0.046	0.053	0.058	0.021
ST 6	6.15	3.79	0.061	417	236	0.587	0.214	0.038	6.122	0.057	0.061	0.065	0.019

ND- Not Detected

2.15 Health risk analysis

Estimated Daily Intake (EDI): The Estimated daily intake for shiny nose fish, shrimp, and periwinkle was estimated by conducting a random survey of people living within the study area by the use of a generated list of questions (Wang *et al.*, 2005). Hence the formula for calculating the EDI is EDI = DFC × MC/BW. Where DFC is the daily average fish/shrimp/periwinkle intake, MC is metal concentration, and BW is average body weight. The average body weight taken for children/Adolescents between the age ranges of 10-25 years was 40kg and adults between the age ranges of 26-35 years were 70 kg and an adult that was above 36 years was 75 kg.

3 Results and Discussion

3.1 Results

The levels of the parameters in various matrices from Esuk Ekpo Eyo Beach are presented in tables 2-18 and Fig 2-5. Table 2 and 3 shows the physicochemical parameters and concentrations of heavy metals in sediments from station 1 to 6 for both the dry and wet season. Sand concentration ranged from 73.31% in ST1 to 9.04% in ST6, silt concentration ranged from 8.29% in ST1 to 7.85%in ST 6, clay concentration ranged from 5.21 to 5.22, TOM concentration ranged from 12% in ST1 to 19% in ST 6, Cr concentration ranged from 0.312mg/L to1.738mg/L, Fe concentration ranged from 23.21mg/L to 81.49mg/L, etc. in table 3 sand concentration ranged from 65.43% in ST 1 to 5.13% in ST 6, clay concentration ranged from 22.95% to 88.73%, TOC concentration ranged from 0.57% to 0.51%, Fe concentration ranged from 14.31mg/L to 77.63mg/L, Cr concentration ranged from 0.126mg/L to 1.254 mg/L, etc. Tables 4 and 5 show the dry and wet season physicochemical parameters and Heavy metal concentration in water samples of Esuk Ekpo Eyo Beach. The concentration values of pH, electrical conductivity, salinity, turbidity, Cr, Fe, and Zn in the dry and wet seasons are as follows; pH ranged from 6.05 to 6.15, electrical conductivity ranged from 3.41 to 3.79uS/cm, salinity ranged from 0.047 to 0.061, Cr ranged from 0.056 mg/L to 0.214 mg/L, Fe ranged from 2.190 mg/L to 6.122 mg/L, Cd ranged from 0.011 to 0.061 mg/L. in the wet season Fe concentration ranged from 3.131 mg/L to 10.21 mg/L, Zn ranged from 0.033 to 0.092 mg/L, electrical conductivity ranged from 0.98 uS/cm to 1.68 uS/cm, etc. Table 6 shows the wet and dry season heavy metal concentration in Fish, Shrimp, and Periwinkle of Esuk Ekpo Eyo Beach. The concentration of Cr in the Fish samples during the dry and wet seasons was 0.826±0.005 mg/L and 0.534±0.007 mg/L. The concentration of Fe in the periwinkle sample during the dry and wet seasons was 0.826±0.005 mg/L and 0.534±0.007 mg/L, also the concentration of Ni in shrimp during the dry and wet seasons was 0.045±0.003 mg/L and 0.023±0.004 mg/L, etc. Table 7 shows the pollution load index of sediments in the wet and dry season and their mean values during the wet and dry season was given as 2.89 and 4.08 respectively. Table 8 shows the geo-accumulation index (I-geo) of heavy metals in sediments for both dry and wet seasons and the mean values recorded were all negative values. Tables 9 and 11 shows the descriptive statistics of the physicochemical parameters and Heavy Metal concentration in sediments during the dry and wet season. The mean concentration values of Sand, Clay, Ph, Fe, Cr, and Ni for both dry and wet seasons are as follows 42.98±1.49% and 41.29±3.04%, 46.60±0.09% and 44.83±2.11%, 5.200±0.00577 and 6.1100±0.0595, 64.00±4.9600 mg/L and 39.91±9.1620 mg/L, 1.004±0.269 mg/L, and 0.546±0.166 mg/L and for Ni, it is given as 0.1752±0.0715 mg/L and 0.1503±0.0497 mg/L. Tables 10 and 12 shows Pearson's correlation matrix on bulk properties and Heavy Metal of sediments in both dry and wet season. Tables 13 and 15 shows the descriptive statistics of the physicochemical parameters and Heavy Metal concentration in water samples during the dry and wet season. The mean concentration values of salinity, and turbidity. TDS, Fe, Cr, and Zn for both dry and wet seasons are as follows 0.0545±0.00145 and 0.02600±0.00255, 0.4295±0.0202 Ftu and 0.3795±0.0338

Ftu, 314.2±28.6 mg/L and 246.2±35.5 mg/L, 4.3525±1.31 mg/L and 7.221±1.44 mg/L, 0.1238±0.0866 mg/L and 0.19766±0.1644 and for Zn, it is given as 0.0508±0.0214 mg/L and 0.071166±0.00702 mg/L. Tables 14 and 16 shows Pearson's correlation matrix on bulk properties and Heavy Metal of water samples in both dry and wet season. Tables 17 and 18 show the estimated daily intake of heavy metals in Fish. Shrimp and Periwinkle during the dry and wet seasons in the Esuk Ekpo Eyo Community, some of which are summarized below; Cr intake in fish during the dry season for children was recorded as 7.1E-4 mg/kg, Cr intake in Shrimp for children was recorded as 2E-4 mg/kg, Cr intake in Periwinkle for children was recorded as 1.9E-4 mg/kg. During the wet season, Fe intake in Fish for children was recorded as 7.4E-2 mg/kg. Fe intake in shrimp for children was recorded as 1.5E-2 mg/kg, and Fe intake in Periwinkle for children was recorded as 1.6E-3 mg/kg. Figures 2 to 5 show the bar chart of dry and wet seasons of heavy metal concentrations (mg/L) in sediments and water samples of Esuk Ekpo Eyo Beach.

3.2 Discussion

The concentration of heavy metals in sediments, shiny nose fish (*Polydactylus quadrifilis*), shrimp (*Parapenaeopsis atlantica*), and periwinkle (*Tympanostonus fuscatus*), in Esuk Ekpo Eyo Beach, Akpabuyo Local Government of Cross River State, Southern Nigeria were presented in section 4.1. Also presented in that section was the associated pollution load index and geo-accumulation indices for both dry and wet season.

3.2.1 Physicochemical parameters and distribution of heavy metals in sediment samples of Esuk Ekpo Eyo Beach

Table 2 shows the results of the geochemical bulk properties of the sediments ranging from sand, silt, clay, pH, TOC, and TOM during the dry season

Table 5: Wet Season Bulk Properties and Heavy Metal Concentration of Water Samples

ST	pH	EC (S/m)	Salinity	TDS (mg/l)	TSS (mg/l)	FTU	Cr (mg/l)	Cu (mg/l)	Fe (mg/l)	Pb (mg/l)	Cd (mg/l)	Zn (mg/l)	Hg (mg/l)
ST 1	5.79	0.98	0.029	150	209	0.317	0.067	ND	3.131	0.013	0.020	0.033	0.009
ST 2	5.84	1.19	0.020	210	319	0.330	0.072	0.019	5.214	0.018	0.031	0.040	0.013
ST 3	5.97	1.57	0.026	273	214	0.420	0.133	0.024	6.141	0.024	0.043	0.091	0.020
ST 4	5.51	1.63	0.024	252	229	0.390	0.146	0.034	8.341	0.037	0.048	0.088	0.027
ST 5	5.73	1.59	0.032	281	241	0.433	0.379	0.055	8.069	0.058	0.052	0.083	0.034
ST 6	5.78	1.68	0.029	311	247	0.387	0.389	0.059	10.21	0.066	0.059	0.092	0.041

ND- Not Detected

Table 6: Wet and Dry Season Heavy Metal Concentrations in Fish, Shrimp, and Periwinkles in mg/L

	Biota	Chromium (mg/L)	Copper (mg/L)	Iron (mg/L)	Lead (mg/L)	Cadmium (mg/L)	Nickel (mg/L)
Dry season	Fish	0.019±0.007	0.008±0.001	0.821±0.003	0.010±0.001	ND	0.078±0.007
	Shrimp	0.010±0.001	0.005±0.002	0.327±0.001	0.022±0.005	0.005±0.001	0.045±0.003
	periwinkle	0.064±0.012	0.011±0.006	826±0.005	0.013±0.002	0.021± 0.007	0.089±0.003
Wet season	Fish	0.036±0.001	0.012±0.001	1.979±0.002	0.024±0.003	0.041±0.013	0.057±0.002
	Shrimp	0.025±0.003	0.009±0.001	0.740±0.001	0.030±0.009	0.013±0.002	0.023±0.004
	Periwinkle	0.013±0.007	0.006± 0.002	0.534±0.007	ND	0.009±0.004	0.026±0.008

ND- Not Detected

Table 7: Pollution Load Index (PLI) of Sediments in Wet and Dry Season

Stations	Wet Season	Dry season
1	1.85	2.33
2	2.37	2.13
3	2.79	3.62
4	2.63	4.24
5	3.41	7.03
6	4.30	5.14
Mean Value	2.89	4.08

Table 8: Geo-accumulation Index (I-geo) of Heavy Metals in Sediments

	Wet Season						Dry Season					
Stations	Cr	Cu	Fe	Pb	Cd	Ni	Cr	Cu	Fe	Pb	Cd	Ni
1	-10.1	-12.34	-16.35	-10.8	-8.82	-13.2	-2.64	-4.13	-2.61	-2.54	-1.81	-3.45
2	-9.17	-12.5	-15.9	-9.87	-7.82	-10.9	-2.33	-3.57	-1.46	-2.41	-1.27	-3.56
3	-8.49	-12.2	-14.5	-9.23	-6.81	-9.58	-2.34	-3.49	-2.35	-2.36	-1.33	-2.97
4	-7.79	-12.0	-14.24	-9.55	-4.91	-8.78	-2.22	-2.94	-1.32	-2.29	-1.17	-3.06
5	-7.65	-11.34	-14.10	-7.94	-3.60	-8.59	-1.85	-1.73	-1.13	-1.89	-1.02	-2.48
6	-6.75	-10.7	-13.50	-7.81	-3.39	-8.49	-1.89	-1.68	-1.01	-1.40	-0.82	-2.36
Mean	-8.33	-11.8	-14.8	-9.20	-5.89	-9.92	-2.21	-2.92	-1.65	-2.15	-1.24	-2.98

Table 9: Descriptive Statistics of the Physicochemical Parameters of Sediment in Dry Season (n=6)

Parameters	Mean (mg/l)	SE Mean	St Dev	Minimum	Q1	Median	Q3	Maximum
SAND	42.98	1.49	2.10	9.04	68.60	9.99	80.12	73.31
SILT	10.407	0.815	1.996	7.850	8.180	10.895	12.198	12.370
CLAY	46.600	0.09	4.66	17.51	10.41	78.31	19.35	83.11
pH	5.2000	0.00577	0.0141	5.1800	5.1875	5.2000	5.2125	5.2200
TOC	0.2617	0.0105	0.0256	0.2400	0. 2475	0.2500	0.2800	0.3100
TOM	16.67	1.09	2.66	12.00	14.25	18.00	18.25	19.00
Cr	1.004	0.269	0.658	0.312	0.536	0.726	1.782	1.913
Fe	64.00	4.9600	3.964	23.21	23.20	64.70	64.77	88.22
Pb	0.344	0.00651	0.01594	0.00900	0.00375	0.01700	0.2750	1.192
Cd	0.01917	0.00691	0.01693	0.00300	0.00375	0.01400	0.03850	0.04300
Ni	0.1752	0.0715	0.0112	0.0280	0.0340	0.1000	0.36673	0.446
Cu	0.46200	0.274	0.071	0.004	0.005	0.050	1.276	0.038

Table 10: Pearson's Correlation Matrix on Bulk Properties and Heavy Metals of Sediment in Dry Season

	Sand	Silt	clay	pH	TOC (%)	TOM (%)	Cr(mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Cd (mg/L)
Silt	-0.798										
clay	-0.966**	0.616									
pH	0.721	-0.888*	0.563								
TOC (%)	0.173	-0.581	0.123	0.386							
TOM (%)	0.356	0.227	-0.562	-0.053	-0.695						
Cr(mg/l)	0.737	-0.442	0.775	0.541	-0.448	0.561					
Cu (mg/l)	0.908*	-0.645	0.911*	0.687	-0.195	0.516	0.949**				
Fe (mg/l)	0.649	-0.332	0.706	0.514	0.501	0.589	0.972**	0.890*			
Pb (mg/l)	0.867*	-0.451	0.940**	0.517	-0.244	0.667	0.870*	0.920**	0.869*		
Cd (mg/l)	-0.862*	-0.513	0.908*	0.517	-0.227	0.518	0.912*	0.934**	0.891*	0.965**	
Ni (mg/i)	0.544	-0.172	0.637	0.293	-0.530	0.540	0.883*	0.766	0.938**	0.836*	0.889*

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (2-tailed)

Table 11: Descriptive Statistics of the Physicochemical Parameters of Sediment Samples in Wet Season (n=6)

Parameters	Mean (mg/l)	SE Mean	St Dev	Minimum	Q1	Median	Q3	Maximum
SANDw	41.29	3.04	7.44	5.13	64.61	26.57	78.90	67.33
SILTw	13.88	2.20	5.39	6.14	10.02	13.05	19.50	20.63
CLAYw	44.83	2.11	5.16	17.24	10.29	54.30	19.39	88.73
PHw	6.1100	0.0595	0.1457	5.8700	6.020	6.1200	6.2000	6.3200
TOCw	0.4567	0.0301	0.0737	0.3800	0.3950	0.4400	0.5250	0.5700
TOMw	22.833	0.946	2.317	20.000	20.000	23.500	25.000	25.000
Crw	0.546	0.166	0.406	0.126	0.208	0.493	0.818	1.254
Cuw	0.020	0.013	0.010	0.005	0.005	0.016	0.018	0.044
Few	39.91	9.1620	4.187	14.30	14.31	41.90	41.89	77.63
Pbw	0.0285	0.719	0.0062	0.0400	0.0475	0.0870	0.2255	0.04600
Cdw	0.02133	0.00812	0.01089	0.00500	0.00575	0.1250	0.04450	0.04900
Niw	0.1503	0.0497	0.1216	0.0110	0.0425	0.1460	0.2685	0.2820

3.2.2 Particle size

This comprises sand, silt, and clay. The mean concentration values of sand, silt, and clay in the dry and wet seasons were (table 9) 42.98±2.10% and (table 11) 41.29±7.44, while the mean concentration values of silt were (table 9) 10.407±1.996% and (table11) 13.880±5.39%, also clay mean concentration value was recorded as (table 9) 46.600±4.66% and 44.83±5.16% (table 11). From the above concentration values, it is observed that sand and clay had higher concentration values than silt and were higher in the dry season. This could be a result of the high frequency of sand mining activities and higher evaporation of water moisture during the dry season leaving higher deposits of sand and clay particles along the shoreline [16].

3.2.3 pH

The mean concentration values for pH in the dry season was (table 9) 5.200±0.0141 while in the wet season, the mean concentration value was (table 11) 6.110±0.1457. The mean concentration of pH in the dry season is lower than the mean value in the wet season, Normally with a reduction in pH in sediment during the dry season the competition between H^+ and the dissolved metals for ligands (eg., OH^-, CO_3^{2-}, SO_4^{2-} and phosphates) become more significant. The adsorption abilities and bioavailabilities of the metals subsequently decrease and then increase the mobility of heavy metal, moreover, H^+ occupies more adsorption sites at lower pH values which results in soluble and carbonate-bound heavy metals being precipitated more easily than at higher pH values [17]. Both of these processes result in a rapid heavy metal discharge rate with lower pH as can be seen in the observed mean concentration results (Tables 9 and 11).

3.2.4 Total organic carbon content (TOC)

The mean concentration values for TOC in sediments during the dry season was 0.2617±0.0256% (Table 9) while in Table 11, the mean concentration was 0.4567±0.0737%. This shows that the concentration of total organic carbon in sediments was higher in the wet season than in the dry season, this means a reduced amount of carbon compounds present in the sediments and high precipitation of carbon compounds from agricultural activities and sewage by-products into the beach water during rainfall and increase in water volume [18].

Table 12: Pearson's Correlation Matrix on Bulk Properties and Heavy Metals of Sediments in Wet Season

	Sand	Silt	Clay	pH	TOC (%)	TOM (%)	Cr(mg/ L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Cd (mg/L)
Silt	-0.721										
Clay	-0.690	-0.005									
pH	-0.473	0.606	0.050								
TOC (%)	-0.057	-0.621	0.731	-0.125							
TOM (%)	-0.368	0.675	-0.174	0.012	-0.731						
Cr (mg/l)	0.920**	-0.582	-0.719	-0.656	-0.258	-0.096					
Cu (mg/l)	0.926**	-0.751	0.551	-0.685	-0.003	-0.319	0.962**				
Fe (mg/l)	0.885*	-0.619	0.629	-0.399	-0.079	-0.318	0.891*	0.928**			
Pb (mg/l)	0.902*	-0.616	0.658	-0.250	-0.074	-0.277	0.824*	0.839*	0.940**		
Cd (mg/l)	- 0.936	0.529	0.797	-0.423	-0.297	-0.081	0.947*	0.896*	0.921*	0.942**	
Ni (mg/l)	- 0.887*	0.674	0.576	0.587	-0.048	-0.321	0.938*	0.981**	0.970*	0.857*	0.890*

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (2-tailed)

Table 13: Descriptive Statistics of Bulk Properties and Heavy Metals of Water Samples in Dry Season

Parameters	Mean	SE Mean	St Dev	Minimum	Q1	Median	Q3	Maximum
pHd	6.122	0.0536	0.0929	6.050	6.0450	6.100	6.120	6.210
Ecd	3.733	0.212	0.367	3.410	3.410	3.570	3.533	4.110
Salnityd	0.0545	0.00145	0.00252	0.0470	0.0470	0.04900	0.04900	0.06100
TDSd,	314.2	28.6	49.5	221.2	221.0	295.0	295.2	417.0
TSSd	178.6	35.9	62.1	102.2	102.0	223.0	173.0	236.0
FTUd	0.4295	0.0202	0.0349	0.2900	0.3510	0.3800	0.3510	0.6190
Crd	0.1238	0.0500	0.0866	0.0560	0.0560	0.0870	0.2190	0.2190
Cud	0.02866	0.00346	0.00600	0.01700	0.01700	0.02500	0.03100	0.03900
Fed	4.3525	1.31	2.27	3.131	3.131	4.311	3.349	6.122
Pbd	0.03083	0.0994	0.01721	0.0800	0.0800	0.03400	0.04600	0.04600
Cdd	0.03716	0.0174	0.0301	0.0110	0.0110	0.0530	0.0340	0.0610
Znd	0.0508	0.0181	0.0214	0.0380	0.0380	0.0540	0.0430	0.0650
Hgd	0.0140	0.000577	0.00100	0.0100	0.0100	0.0100	0.1100	0.0210

Table 14: Pearson's Correlation Matrix on Bulk Properties and Heavy Metals of Water Samples in Dry Season

	pH	**EC (uS/cm)**	**salinity**	**TDS (mg/L)**	**TSS (mg/I**	**FTU**	**Cr (mg/L)**	**Cu (mg/L)**	**Fe (mg/L)**	**Pb (mg/L)**	**Cd (mg/L)**	**Zn (mg/L)**
EC (uS/cm)	0.997											
Salinity	-0.157	0.982										
TDS (mg/L)	0.559	0.812	0.907									
TSS (mg/L)	0.209	0.984	0.933	0.694								
FTU	0.235	-0.979	-0.923	-0.675	-1.000*							
Cr (mg/L)	0.996	-0.123	0.065	0.480	-0.299	0.323						
Cu (mg/L)	0.269	0.954	0.993	0.949	0.885	-0.873	0.179					
Fe (mg/L)	0.962	0.245	0.422	0.765	0.067	-0.041	0.932	0.523				
Pb (mg/L)	0.999*	0.069	0.119	0.527	-0.246	0.271	0.999*	0.232	0.950			
Cd (mg/L)	0.866	0.472	0.629	0.898	0.307	-0.282	0.817	0.714	0.970	0.847		
Zn (mg/L)	0.620	0.765	0.872	0.997*	0.638	-0.617	0.545	0.923	0.812	0.590	0.929	
Hg (mg/L)	0.963	-0.299	-0.115	-0.315	-0.465	0.488	0.984	-0.011	0.852	0.973	0.700	0.386

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (2-tailed)

Table 15: Descriptive Statistics of Physical and Chemical Parameters of Water Samples in Wet Season

Parameters	Mean	SE Mean	St Dev	Minimum	Q1	Median	Q3	Maximum
pH w	5.777	0.146	0.252	5.51	5.79	5.51	5.97	5.97
Ec w	1.440	0.181	0.314	0.980	0.980	1.630	1.570	1.680
Salinity w	0.02600	0.00255	0.00458	0.02000	0. 02900	0. 02600	0.02600	0.03200
TDS w	246.2	35.5	61.5	150.0	150.0	252.0	273.0	311.0
TSS w	243.2	21.2	36.7	209.0	208.5	229.0	214.0	319.0
FTU w	0.3795	0.0338	0.0586	0.3170	0.3170	0.4200	0.4200	0.4330
Cr w	0.19766	0.0949	0.1644	0.0670	0.0670	0.1330	0.1330	0.3890
Cu w	0.0382	0.0153	0.0265	0.0190	0.0190	0.0235	0.02400	0.0590
Fe w	7.221	1.44	2.49	3.131	3.131	6.141	6.141	10.21
Pb w	0.03683	0.00120	0.0225	0.0130	0.0130	0.0370	0.0240	0.0660
Cd w	0.042166	0.00982	0.01701	0.02000	0.02000	0.04800	0.04300	0.05900
Zn w	0.071166	0.04406	0.00702	0.0330	0.0330	0.08800	0.09100	0.0920
Hg w	0.02400	0.0110	0.0077	0.0090	0.0090	0.01950	0.0200	0.0410

Table 16: Pearson's Correlation Matrix on Bulk Properties and Heavy Metals of Water Samples in Wet Season

	pH	EC (uS/cm)	Salinity	TDS (mg/L)	TSS (mg/L)	FTU	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Cd (mg/L)	Zn (mg/L)
EC (uS/cm)	0.037											
Salinity	0.095	0.014										
TDS (mg/L)	0.915	0.145	-0.314									
TSS (mg/L)	0.947	-0.970	-0.229	-0.996								
FTU	1.000**	0.998*	0.074	0.924	0.954							
Cr (mg/L)	0.994	1.000*	-0.012	0.953	0.976	0.996						
Cu (mg/L)	0.938	-0.963	-0.257	0.221*	1.000**	0.945	0.969					
Fe (mg/L)	0.850	0.890	-0.443	0.990	0.261	0.861	0.902	0.980				
Pb (mg/L)	0.976	0.990	-0.126	0.781	0.995	0.980	0.993	0.991	0.945			
Cd (mg/L)	0.714	-0.769	-0.629	0.336	0.601	0.729	0.785	0.913	0.976	0.851		
Zn (mg/L)	0.941	0.965	-0.249	0.798*	0.982*	0.948	0.972	1.000**	0.978	0.992	0.910	
Hg (mg/L)	0.981	0.093	-0.102	0.977	0.992	0.984	0.996	0.988	0.937	0.570*	0.838	0.989

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

Table 17: Estimated Daily Intake (EDI) for Heavy Metal (Mg/kg) in Dry Season

Categories	Seafood	Cr	Cu	Fe	Pb	Cd	Ni
Children/Adolescent Bt 10-25 yrs	Fish	7.1E-4	3E-4	3E-2	3.8E-4	-	2.9E-3
Adult (b/w 26-35yrs)	Fish	4.1E-4	1.7E-4	1.8E-2	2E-4	-	1.6E-3
Adult (>36 yrs)	Fish	3.8E-4	1.6E-4	7.4E-2	4.8E-4	-	1.5E-3
Children/Children/Adolescent (btw 10-25yrs)	Shrimp	2E-4	1E -4	6.5E-3	4.4E-4	1E-4	9E-4
Adult (btw 26-35 yrs)	Shrimp	1.1E-4	5.7E-5	3.7E-3	2.5E-4	5.7E-4	5.1E-4
Adult (>36 yrs)	Shrimp	0.9E-4	5.3E-5	3.5E-3	2.3E-4	5.2E-4	4.8E-4
Children/Adolescent Children/Adolescent (Btw 10-25yrs)	Periwinkle	1.9E-4	3.3E-5	2.5E-3	3.9E-5	6.3E-5	2.7E-5
Adult(btw 26-35 yrs	Periwinkle	1.1E-4	1.9E-4	1.4E-3	2.2E-5	3.6E-5	1.5E-4
Adult (>36 yrs)	Periwinkle	1.0E-4	1.7E-4	1.3E-3	2.1E-5	3.4E-5	1.4E-4
JECFA (2009)	Daily Seafood intake	0.20	0.5	20.5	0.06	0.03	-

(E = Exponential)

Table 18: Estimated Daily Intake (EDI) for Heavy Metal (Mg/kg) in the Wet Season

Categories	Seafood	Cr	Cu	Fe	Pb	Cd	Ni
Children/Adolescent Bt 10-25yrs	Fish	1.4E-3	4.5E-4	7.4E-2	9E-4	1.5E-3	5.9E-3
Adult (b/w 26-35yrs)	Fish	7.7E-4	2.6E-4	4.2E-2	5.1E-4	8.8E-4	3.4E-3
Adult (>36 yrs)	Fish	7.2E-4	2.4E-4	4.0E-2	4.8E-4	8.2E-4	3.1E-3
Children/Adolescent (btw 10-25yrs)	Shrimp	5E-4	1.8E-4	1.5E-2	6E-4	2.6E-4	4.6E-4
Adult (btw 26-35 yrs)	Shrimp	2.9E-4	1.0E-4	8.5E-3	3.4E-4	1.5E-4	2.6E-4
Adult (>36 yrs)	Shrimp	2.7E-4	9.6E-5	7.9E-3	3.2E-4	1.4E-4	2.5E-4
Children/ Adolescent (Btw 10-25yrs)	Periwinkle	3.9E-5	1.8E-5	1.6E-3	-	2.7E-5	7.8E-5
Adult (btw 26-35 yrs	Periwinkle	2.2E-5	1.1E-5	9.2E-4	-	1.5E-5	4.5E-5
Adult (>36 yrs)	Periwinkle	2.1E-5	9.6E-6	8.5E-4	-	1.4E-5	4.2E-5
JECFA (2009)	Daily seafood intake	0.20	0.5	20.5	0.06	0.03	-

(E = Exponential)

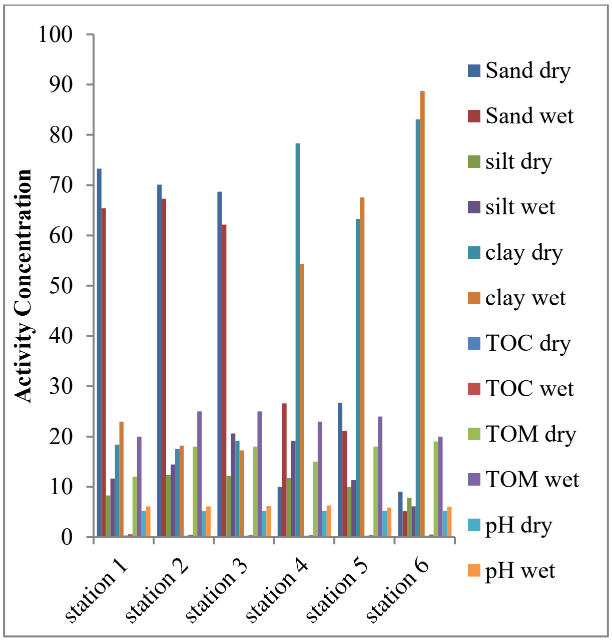


Fig 8: Multiple bar chart showing the comparison of the activity concentration of the physicochemical parameters of sediments obtained from Esuk Ekpo Eyo Beach, Akpabuyo local Government, Cross river state for both dry and wet season

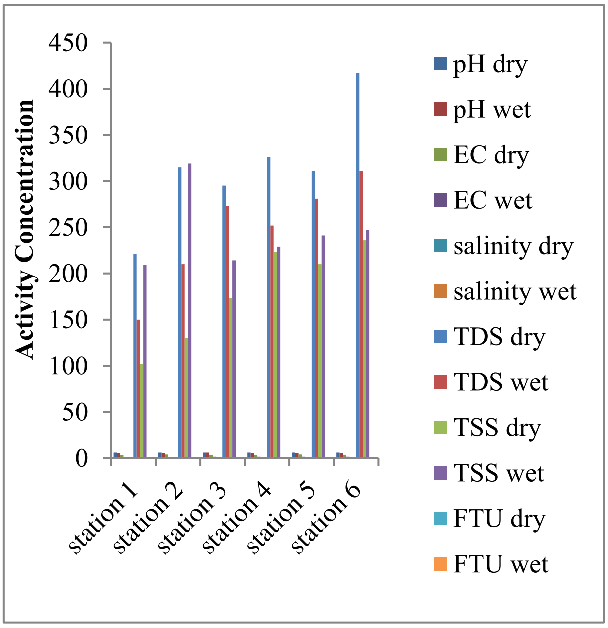


Fig 9: Multiple bar chart showing the comparison of the activity concentration of the physicochemical parameters of water samples obtained from Esuk Ekpo Eyo Beach, Akpabuyo local Government, Cross river state for both dry and wet seasons.

3.2.5 Total Organic Matter (TOM)

The mean concentration values for TOM in sediments during the dry season as shown in table 9 is 16.67±2.66% and in the wet season, the mean value recorded in table 11 is 22.83±2.317%. hence the organic material present was dissolved in the beach water than in the sediment and some heavy metal compounds could have dissolved with the organic matter into the beach water, also according to Hart *et al*. (2005), this could also be a result of an increase in dissolved oxygen in the wet season which can increase the total organic matter. A similar trend was also reported by Davies *et al*. (2005) who also reported that at a high temperature which is usually observed in the dry season, the solubility of oxygen decreases, resulting in the reduction of tidal organic matter, while at lower temperatures (rainy season) dissolved oxygen increases.

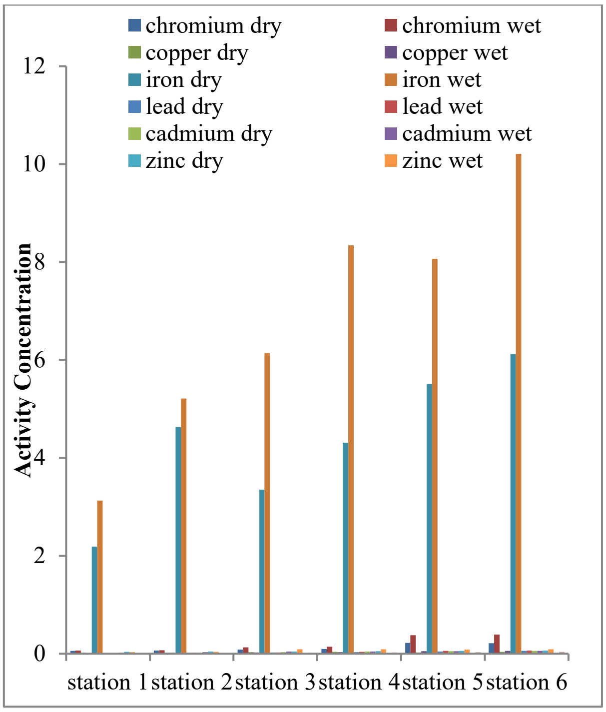


Fig 10: Multiple bar chart showing the comparison of the activity concentration of Heavy metals of water samples in Mg/l obtained from Esuk Ekpo Eyo Beach, Akpabuyo local Government, Cross river state for the both dry and wet season

3.2.6 Chromium

Concentrations of chromium in sediments in the dry season ranges from 0.312 to 1.913mg/l (table 2) at the stations with a mean concentration of 1.004±0.658mg/l (Table 9). Then in the wet season Cr concentration levels ranged from 0.126 to 1.254mg/l (Table 3) at the different stations with a mean concentration of 0.546±0.406mg/l (Table 11). The mean value of chromium for the dry season was slightly above the recommended limits of 0.05 mg/l in water and higher during the dry season but lower than the marine sediment quality standards of 16 ppm (Appendix 1).

3.2.7 Copper

Mean concentrations of copper in dry season was 0.46200±0.071 mg/l (Table 9) and 0.020 ± 0.010 mg/l (Table 11) in wet season (Table 11). In dry season the concentration was higher than the WHO (2011) recommended value of 0.033mg/l in water but far lower than the marine sediment quality standards of 390mg/l (Appendix 1) These findings show that there is very little Cu-containing discharge waste make-up in the estuary but regular monitoring of the Esuk Ekpo Eyo beach banks should be initiated. Sources of Copper contamination within the study area may be due to weathering of rocks within the sediments and surface run of

3.2.8 Iron

The mean concentration of Fe in the dry season was 64.00mg/L (Table 9) while in the wet season the mean concentration was 39.91mg/L (Table 11) the mean concentration of Fe in the wet season was lower than in the dry season but was still far below the marine sediment quality standards by Burton (2002). This finding is in agreement with Banu 2013, in the sediments of the Karnafully river mouth, Iron has always been used as an indication of natural changes in the heavy metal carrying capacity of the sediment and its concentration has been related to the abundance of metal reactive compounds not significantly affected by the action of human beings [22]. However the higher levels of Fe in the sediments may be attributed to the discharge of Fe – laden wastes and effluents from corroded pipes, and iron smelting scraps into the water body which then settles in the sediment.

3.2.9 Lead

The concentrations of lead in sediments of Esuk Ekpo Eyo Beach in the dry season (Table 2) ranged from 23.21mg/l in station 1 to 81.49mg/l in station 6 with a mean concentration of 0.344±0.01594mg/l (table 9), while in table 3, the concentrations ranged from 0.007mg/l in Station 1 to 0.046mg/l in Station 6 with a mean concentration of 0.0285±0.0062mg/l (Table 11). The observed trends in the seasonal distribution of Pb-containing waste may be attributed to lead-based paints used in houses situated around the beach banks which wash down into the beach during rainfall and also lead-based wastes in the estuarine environment, Hence during high tides and high levels of water rise and rainwater from lead pipes and wastes wash into the river through the water tributaries and channels and drainage systems, then in the dry season due to the fact that water levels decrease, the higher concentration of lead toxic metals settle more in the bottom sediments. The presence of Pb is risky to live since fishes and aquatic fauna are particularly vulnerable to Pb and often retain about a percent of ingested lead which could be taken by man through the food chain [23].

3.2.10 Cadmium

Cadmium is regarded as one of the most harmful trace elements in the environment. The increased emissions resulting from its production, use, and disposal combined with its persistence in the environment, and its comparatively rapid uptake and accumulation through the food chain add to its potential environmental hazards. The descriptive statistics of the dry and wet season shown in Tables, 9 and 11 revealed that mean concentrations of Cadmium are slightly higher in the wet season than in the dry season i.e. 0.01917± 0.01693mg/L(Table 9) in the dry season and 0.02133± 0.01089mg/L(Table 11) in the wet season. This could be a result of the wind tidal direction of the river water washing down cadmium-containing compounds in the rainy season which settles in the sediments. The mean concentrations were below the marine sediment quality standard of 0.2 mg/L (Appendix 10) indicating that the sediment is not polluted concerning cadmium.

3.2.11 Nickel

The concentration of Ni in sediments of Esuk Ekpo Eyo Beach in the dry season ranged from 0.036mg/l in Station 1 to 0.446mg/l in Station 6 with a mean concentration of 0.1759±0.0112mg/l (table 9) while in the wet season (table 3) the concentration of Ni ranged from 0.011mg/l in station 1 to 0.282 in station 6 (table 3) with a mean concentration of 0.1503±0.1216mg/l (table 11) these findings are in agreement with Chindah *et al*. (2004) and Sibeudu *et al*.(2003) whose findings based on heavy metal pollution studies done in Calabar river suggest that with the exception of Cr, Ni, and Fe, other metals like Pb, Cd, Zn, and Cu occur in relatively low concentrations.

3.3 Physicochemical Parameters and Distribution of Heavy Metals in Water Samples of Esuk Ekpo Eyo Beach

3.3.1 Salinity

Salinity is a measure of the dissolved salts in the water salinity is usually highest during periods of low river flows and increases as water levels drop. Conductivity is related to TDS (Total dissolved solids) which measures the amount of dissolved salts in the river water or EC (Electrical conductivity) which is the characteristic of a substance that enables it to serve as a channel or medium for electricity. Salt water conducts electricity more readily than pure water because of the presence of dissolved ions in it [26]. The values of salinity ranged from 0.047 to 0.061 mg/L from stations 1 to 6 respectively in the dry season and from 0.029 to 0.032mg/l in the wet season (Tables 2 and 3) hence the concentration was higher in the dry season than in the wet season. These could be attributed to high evaporation and saltwater intrusion [27]. The water salinity during the dry season may also be increased by several human activities such as loading of salt from seawater irrigation and intensive agricultural activities can also lead to saline water seeping into the river estuary. During the wet season, the low levels of salinity may be attributed to the low rate of surface water evaporation and the low presence of insoluble metallic compound discharges. [28].

3.3.2 pH

pH levels vary naturally within rivers as a result of photosynthesis, geology, and soils of the study area and runoff from bushland areas. This particularly introduces tannic acid (tannins) which also account for the tea-like the colour of seas [29]. in table 3 pH values range from 6.05 in Station 1 to 6.21 in station 5 in the dry season and 5.51 to 5.79 in station 1 in the wet season (Table 4). The highest pH value indicates alkalinity and may be attributed to the contribution made by basic rocks such as limestone and surface run-offs which may contain detergents and fertilizers. The wet season was enriched more with heavy metals as compared to the dry season and this may be due to low pH values. This is particularly important because the solubility of metal hydroxides increases as pH decreases [30].

3.3.3 Conductivity

Conductivity is the ability of a substance to discharge electricity. The conductivity of water is a function of the concentration of dissolved ions. Conductivity is not of adequate health concern. But because it is easily measured. It can serve as an indicator of other water quality problems if the conductivity of a river increases. It indicates that there is a source of dissolved ions in the vicinity. The mean concentration values (table 13) obtained during the dry season was 3.733±0.767uS/cm while in the wet season (table 15) it was 1.440±0.314uS/cm. the lower concentration value seen in the wet season may be due to the dilution of metal ions due to higher water volume [28].

3.3.4 Turbidity

The degree of clearness and purity of river water measured is determined by estimating the turbidity of the river [30]. Turbidity levels in water most times increase directly with the amount of suspended solids in the water, the more a river body is polluted with waste disposal or high movement of suspended particles as a result of high tides and other river tributaries that empties into the ocean the more turbid the ocean. In Esuk Ekpo Eyo Beach it was observed that the mean turbidity values (Table 13) during the dry season was 0.429±0.0349ftu, while in the wet season (Table 15) the turbidity means value was 0.3795±0.0586ftu. This could be due to reduced water flow which can lead to a low level of dilution of metallic composites and also due to nondissolvable leachates from drainage systems into the beach water leading to an increase in turbidity in the dry season [30].

3.3.5 Total Dissolved Solids

Oxygen is an important element in seawater. The amount of oxygen in the water to a degree shows its overall health, i.e. if oxygen levels are high, then it is assumed that pollution levels in the water are low. Conversely, if oxygen levels are low one can presume this is a high oxygen demand and that the body of water is not in optimal health. Apart from indicating pollution levels, oxygen in water is required by aquatic fauna for survival in conditions of no or low oxygen availability fish and other organisms will die [31]. Table 5 shows lower levels of TDS during the wet season than dry season (Tables 4 and 5). This could be due to high temperatures during the dry season for the dissolution of ions and the presence of insoluble metallic compounds or ions during the wet season [31]. Higher TDS values were recorded during the dry season than during the wet season as we observe the mean concentration values of 314.2±49.5mg/l and 246.2± 35.5mg/l in Tables 14 and 15 respectively

3.3.6 Total suspended solids

The total suspended solids may enter the water body through surface runoff i.e erosion by rainwater, upland soil erosion, and land sliding. TSS reduces light penetration and reduction in aquatic invertebrates [31]. During the dry season the mean concentration value of TSS was (table 13) 178.6±62.1mg/l while in the wet season it was 243.2±36.7mg/l hence the mean concentration value is higher in the wet season than in the dry season. This could be due to the presence of agricultural surface run-off, leachates from underground drainage systems [31].

3.3.7 Chromium

Mean concentrations of chromium in the water samples from Esuk Ekpo Eyo Beach were higher during the wet season than in the dry season. Tables 13 and 15 recorded the mean Cr concentration values as 0.1238±0.0866 mg/l and 0.19766±0.1644 mg/l for dry and wet seasons respectively. The mean concentration values for chromium in the wet season were 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 (50ug/l= 0.05mg/l) this indicates that the water of the study area is polluted, this is in line with the research carried out by Chindah et al (2004) on the distribution of heavy metals in the upper Calabar river in which he reported that Cr concentration was high.

3.3.8 Copper

Copper concentrations in the water of the study areas were higher during the wet season compared to the dry season (Tables 4 and 5) The mean concentrations (0.02866±0.00600mg/L in the dry season and 0.0382±0.0265mg/L in the wet season, (Tables 13 and 15) values were lower than the permissible limits given by WHO, (2011) (Appendix 2) for water quality. These findings are in agreement with the studies carried out by Sibeudu & Chindah (2003) on the distribution of Heavy Metals in the New Calabar River which recorded low levels of copper in the study area.

3.3.9 Iron

Iron is a very critical element in biological systems and is present in the river water in the form of hydrates $Fe(OH)_2$ and $Fe(OH)_4$ The mean concentrations (4.2525±2.27mg/l) recorded during the dry season were lower than the mean concentration (7.221±2.49mg/l) recorded during the wet season these mean concentrations were higher than permissible limits recorded by the NIS-2007 and WHO-2011 this may be due to Fe containing water materials influx during the wet season it also suggests that Fe concentration is in toxic levels in the beach water [35].

3.3.10 Lead

Concentrations of lead recorded during the wet season were higher than dry season in Tables 4 and 5, the mean concentrations recorded in tables 13 and 15, 0.03083±0.01721mg/l and 0.03683±0.0225 mg/l shows the difference. However, 0.03683mg/l for the wet season is higher than the permissible limit of 0.01mg/l given for lead in drinking water by WHO indicating slightly high levels of pollution of lead-containing materials on the beach.

3.3.11 Cadmium

Concentrations of cadmium in the wet season were higher than the dry season at Esuk Ekpo Eyo beach Tables 4 and 5. The mean concentrations as shown in the descriptive statistics in Tables 13 and 15, 0.04216±0.01701 mg/l higher in the wet season and 0.03716± 0.0301mg/l and lower in the dry season. The mean concentration was slightly higher than the permissible limits recorded by NIS-2007 and WHO 2011 they are lower than ones in heavily industrialized estuaries E.g. the seine (Chiffoleau *et al.,* 1997) these concentrations may therefore be detrimental to the water ecosystems and other users of the beach water

3.3.12 Zinc

Concentrations of zinc in Esuk Ekpo Eyo Beach during the wet season were higher than those obtained in the dry season, Tables 4 and 5, sources of zinc in the aquatic environment include industrial discharge, sewage, and runoff (Burgmann, 2011) the mean concentrations (0.0508±0.0214mg/l) recorded during the dry and wet season (0.071166±0.00702mg/l) Table 13 and Table 15 were lower than the WHO (2011) and SON (2007) permissible Limits of zinc in water.

3.3.13 Mercury

The sources of mercury in the aquatic environment are mainly anthropogenic such as waste incineration, broken thermometers, lawn fungicides, amalgam tooth filings, and drug products [37]. The concentration of mercury during and during wet seasons was high. The mean concentration of Hg during the dry season was 0.0140±0.0100mg/l and wet season was 0.02400± 0.0077mg/l. During the wet season, the mean concentrations were higher than that recommended by the standard organization of Nigeria NIS-2007 of 0.001mg/l and higher than the WHO permissible limit for drinking water. This could be due to mercury-containing wastes such as disposed car batteries and waste drug products around the beach [37].

3.4 Distribution and Seasonal Variations of Heavy Metals in Shiny nose fish (Polydactylus quadrifilis), Shrimp(Parapenaeopsis atlantica) and Periwinkle (Tympanostonus fuscatus)

3.4.1 Chromium

High doses of chromium lead to necrosis and cancerous tumors in the stomach. Hence Chromium levels in fish are monitored by the World Health Organization and the Food and Agricultural Organization accordingly. The concentration of Cr in both dry and wet seasons did not exceed the permissible limit for Cr in fish according to World Health Organization standards. Hence the shiny nose fish sample and shrimp were not polluted concerning Cr in both the dry and wet seasons (Table 6) which had values of 0.019 ± 0.007 in the dry season and 0.036 ± 0.001 mg/L respectively and 0.005 ± 0.001 for shrimp dry season and 0.025 ± 0.003 mg/L in the wet season. The results of the chromium content of *Tympanotonus fuscatus* are also presented in table 6. The levels of Cr in this study revealed a value of 0.064± 0.012mg/l in the dry season while that of the wet season showed 0.013± 0.007mg/l. These values are lower than the maximum permissible limit of 0.5 mg/l set by FAO/WHO (2011). Therefore periwinkle from the Esuk Ekpo Eyo Beach is not polluted concerning Cr.

3.4.2 Copper

Excessive copper intake can lead to muscle weakness, paleness, neurological issues, and anemia. Hence in high doses, it is very toxic. (Table 6) shows that the highest concentration of Cu in both shrimp and *Polydactylus quadrifilis* (shiny nose fish) in the dry and wet seasons was 0.005±0.002mg/l and 0.009± 0.001mg/l respectively for shrimp and 0.008±0.001 mg/l and 0.012±0.001 mg/l for shiny nose fish and this is lower than the World Health Organization recommended standard as well as the Food and agricultural organization (FAO/WHO 2011) standard of 3.0mg/l. Hence with respect to copper, fish and shrimp remains unpolluted. The results of the copper content of *Tympanotonus fuscatus* are also presented in Table 6. The levels of Cu in this study revealed a value of 0.011± 0.006 mg/l in the dry season while that of the wet season showed 0.006±0.002mg/l. There are no known standards for periwinkle by WHO/FAO, hence the standard for fish and shrimp is used. Therefore periwinkle from the Esuk Ekpo Eyo Beach is not polluted concerning Cu.

3.4.3 Iron

Iron is one of the most abundant heavy metals on earth and even in the sea. Iron is a vital element in life, due to the insolubility of iron oxides and sulfides; the implication is that dissolved iron was fairly abundant. High amounts of iron can be present as pollutants in the atmosphere and can cause deleterious effects on humans, animals, and materials. Excessive iron leads to tissue damage as a result of the formulation of free radicals. The highest concentration of iron (Table 6) of fish and shrimp for both dry and wet seasons was 0.821±0.003 mg/L and 1.979 ±0.002mg/L respectively for shiny nose fish and 0.327 ±0.001mg/L and 0.740±0.001mg/L for shrimp. These values were above the FAO/WHO (2011) recommended limit of 0.5mg/L therefore the shiny nose fish and shrimp had high concentrations of iron. The results of the iron content of *Tympanostonus fuscatus* were also presented in table 6. The levels of Fe in this study revealed a value of 0.534± 0.007mg/L in the wet season while that of the dry season showed 0.826±0.005mg/L. These values are higher than the maximum permissible limit of 0.25 mg/L set by FAO/WHO (2011). Therefore periwinkle from the Esuk Ekpo Eyo Beach is polluted concerning Fe.

3.4.4 Lead

Lead is a dangerous element, it is harmful even in small amounts, Pb enters the human body in many ways, and most of the Pb we take in is removed from our bodies in urine. High concentrations of Pb in the body can cause death or permanent damage to the central nervous system. In Table 6, the highest concentration of lead in shiny nose fish is in the wet season which is shown as 0.024±0.003 mg/L and for shrimp, it was recorded as 0.030±0.009 mg/L which is lower than the Maximum limit of FAO/WHO (2011) of 1.0mg/L hence the Shiny nose fish and shrimp were not polluted concerning lead. The results of the Pb content of *Tympanotonus fuscatus* were also presented in table 6. The levels of Pb in this study revealed a value of 0.013± 0.002mg/L in the dry season while that of the wet season was not detected. These values were lower than the maximum permissible limit of 1.0mg/L set by FAO/WHO (2011). Therefore periwinkle from the Esuk Ekpo Eyo Beach is not polluted concerning Pb.

3.4.5 Cadmium

Cadmium considerably exists in the environment as a result of human activities such as the use of fossil fuels, metal ore combination and sewage sludge to agricultural soil may cause the transfer of cadmium compounds adsorbed by plants that may play a significant role in the food chain and accumulate in various human organs. It has a very long biological half-life (10- 30 years) (Ghrefat & Yusuf 2006) and human activities related to cadmium should be restricted to a minimal or not harmful level. According to FAO/WHO (2011), the maximum limit of cadmium in fish and shrimp is 0.5mg/L. In Table 6 the highest concentration of cadmium is in fish at 0.041±0.012 mg/L. The fish was not polluted concerning cadmium. The results of the Cd content of *Tympanostonus fuscatus* were also presented in Table 6. The levels of Cd in this study recorded a value of 0.021± 0.007mg/L in the dry season while that of the wet season showed 0.009±0.004mg/l. These values were lower than the maximum permissible limit of 2.0 mg/L set by FAO/WHO (2011). Therefore periwinkle from the Esuk Ekpo Eyo Beach is not polluted concerning Cd.

3.4.6 Nickel

An excessive amounts of Nickel can be mildly toxic studies have shown that the carcinogenicity of Nickel-containing compounds levels is very low. In Table 6 the highest concentration of Nickel in fish and shrimp is 0.078±0.007mg/L for shiny nose fish in the dry season and 0.045±0.004mg/L for shrimp also in the dry season. The results of the Ni content of *Tympanotonus fuscatus* are also presented in table 6. The levels of Ni in this study revealed a value of 0.026± 0.005mg/L in the wet season while that of the dry season showed 0.089±0.003mg/L. The permissible limit for Nickel in Fish, shrimp, and periwinkle is not known Therefore periwinkle from the Esuk Ekpo Eyo Beach cannot be said to be either polluted or unpolluted.

3.4.7 Estimated Daily Intake Rate of Fish, Shrimp, and Periwinkle in Adults (between the ages of 26-35 years).

The calculated estimated daily intake rate of adults between the ages of 26-35 years for the heavy metals chromium, copper, iron, lead, cadmium, and nickel (Tables 17 and 18) were all below the permissible daily intake recommended by the evaluation of the joint FAO/WHO expert committee on food additives ([39]. See (appendix 5) for the daily consumption of seafood.

3.4.8 Estimated Daily Intake Rate of Fish, Shrimp, and Periwinkle in children/adolescent (between the ages of 10-25 years)

The calculated estimated daily intake rate of children/adolescents between 10-25 years of age for the heavy metals chromium, copper, iron, lead, cadmium, and nickel (Tables 17 and 18) were all below the permissible daily intake of these metals recommended by evaluation of the joint FAO/WHO expert committee on food additives [39]. See (appendix 5), for the daily consumption of seafood.

3.4.9 Estimated Daily Intake Rate of Fish, Shrimp, and Periwinkle in Adults (greater than 36 years)

The calculated estimated daily intake rate of adults older than 36 years of age for the heavy metals chromium, copper, iron, lead, cadmium, and nickel (Tables 17 and 18) were all below the permissible daily intake of these metals recommended by evaluation of the joint FAO/WHO expert committee on food additives [39]. See (appendix 5) for the daily consumption of seafood.

3.5 Pollution Load Index

The pollution load index (PLI) (Table 7) proposed by Tomlinson *et al.,* (1980) was used to estimate the concentrations of pollutants in the beach sediment by calculating the n-root of Contamination Factors (Cf) of the studied metals in each station. The results obtained revealed the following trend for wet season station 6>5>4>3>1>2 while the trend for the dry season was 6>5>4>3>2>1. The mean pollution calculated for the wet season (2.890mg/g) according to Appendix 6 showed minor enrichment and in the dry season (4.080mg/g) indicates moderately severe enrichment.

3.6 Geo- accumulation index

The Geo-accumulation index (Igeo), (Table 8) was used to estimate the degree of anthropogenic influence on heavy metal concentration in sediments from Esuk Ekpo Eyo Beach, According to the Mcd values in Table 1 were less than 1.5, hence nil to low degree of contaminations.

3.7 Pearson Correlations for Sediment Samples

The analysis of the data using Pearson's correlation matrix among the concentration of Cr, Cu, Fe, Pb, Cd, Ni, pH, TOC, TOM, sand, silt, and clay in sediment samples is presented in Tables 10 and 12 for dry and wet season respectively. In Table 10, strong positive correlations were observed between Cr with Cu (r=0.949), Fe (r=0.972), Pb (r=0.920), Cd (r=0.912), Ni (r=0.883), sand (r=0.737), clay (r=0.775), pH (r=0.541), TOM (r=0.561), Fe showed positive correlations with TOC (r=0.501), TOC with clay (r=0.123), TOC with sand (r=0.173), TOM showed a positive correlation with sand (r=0.356), Pb with sand(r=0.867), Ni with sand(r=0.544), Cu with clay (r=0.911). Pb with clay (r=0.940), Ni with clay (r=0.637), and Fe with pH (r=0.514). In Table 12, strong positive correlations were observed between Cr with Cu (r=0.926), Fe (r=0.811), Pb (r=0.824), Cd (r=0.947), Ni (r=0.938), sand (r=0.920), weakly with pH (r=0.012), pH with Ni (r=0.576), clay correlated positively with Fe (r=0.629), with Pb (r=0.658), with Cd (r=0.797) with Ni (r=0.674), with sand (r=0.885), Pb with sand(r=0.902), TOM correlated strongly with silt (r=0.675), TOC correlated strongly with clay (r=0.731), pH correlated strongly with silt (r=0.606). It is well established that sediment texture, TOC, and TOM with pH are important regulatory factors in the distribution of heavy metals in sediments [41].

3.8 Pearson correlations for water samples

The analysis of the data using Pearson's correlation matrix among the concentration of heavy metals Cr, Cu, Fe, Pb, Cd, Zn, Hg, TDS, TSS turbidity (FTU), and electrical conductivity (EC) in water samples are presented in Tables 14 and 16 for dry and wet season respectively. In Table 14, strong positive correlations were observed between Cr with pH (r=0.996), TDS (r=0.480), turbidity (FTU) (r=0.323), weakly with salinity (r=0.065), with Cu (r=0.179), Fe (r=0.932), Pb (r=0.999), Cd (r=0.817), Zn (r=0.545), Hg (r=0.984). strong positive correlations were observed between EC and pH (r=0.997), salinity (r=0.982), EC and TSS (r=0.984), EC and Cu (r=0.954), EC and Fe (r=0.245), strong positive correlations were observed between pH and Pb (r=0.999). Strong correlations were observed between TDS and Cd (r=0.898), and TDS and Zn (r=0.997). In table 16, strong positive correlations were observed between Cr with pH (r=0.994), EC (r=1.000), TDS (r=0.953), TSS (r=0.976), turbidity (r=0.996), Cu (r=0.969), Fe (r=0.902), Pb(r=0.993), Cd (r=0.785), Zn(r=0.972), Hg(r=0.996). strong positive correlations were observed between turbidity(FTU) with pH (r=1.000), EC (r=0.998), TDS (r=0.924), TSS (r=0.954).In all cases, strong positive correlations were observed among some variables which are indicative of a common point input and they are independent of each other while some variables that did not correlate have separate input sources and are completely independent of each other.

4 Conclusion

The seasonal variation of heavy metal pollution in sediments, water, shiny nose fish (*Polydactylus quadrifilis*), shrimp (*Parapenaeopsis atlantica*), and periwinkle (*Tympanotonus fuscatus*) using atomic absorption spectrophotometer were analyzed to ascertain the different concentration levels of Cr, Cu, Pb, Fe, Cd, Ni, Zn, and Hg for both dry and wet seasons. For sediments, the result showed that the concentration of heavy metals was much higher in the dry season than in the wet season. This could be because sediments act as a storage reservoir for heavy metal pollutants as well as agricultural surface-run etc, although cadmium concentrations were higher in the wet season than in the dry season. However, the metals were all below the marine sediment quality standard. Most of the heavy metals in the water samples were above the water standards, for example, Fe, Pb, Cr, Cd, and Hg except for Cu which was below the permissible limits. In biota, Fe concentrations in fish, shrimp, and periwinkle exceeded the permissible limit. Cr, Cu, Cd, Ni, and Pb were all below the limits; also the concentrations of these metals in fish and shrimp were higher in the wet season than in the dry season except for periwinkle which was higher in the dry season than in the wet season. The results of the pollution load index showed that the enrichment factor during the dry season was moderately severe and in the wet season showed no enrichment while the geo-accumulation index results of the study area showed no contamination. The estimated daily intake of fish shrimp and periwinkle were all below the tolerable daily intake limits. Pearson correlation carried out on the sediment and water variables demonstrated that their physicochemical properties played a large role in the distribution of the heavy metals in the study area. Sediments, water, and biota samples (shiny-nose fish, shrimp, and periwinkle) in Esuk Ekpo Eyo Beach, Akpabuyo Local Government of Cross River State were analyzed for Heavy metals in both dry and wet seasons using an Atomic absorption spectrometer, from the results obtained, the following was observed:

1. Sediment samples were found to have higher concentrations of Cr, Cu, Fe, Pb, Cd, and Ni in the dry season compared to the wet season. This supports the findings that sediments act as storage sinks/reservoirs for pollutants.
2. In the water samples, the concentration of Fe, Pb, Cd, Hg, and Cr were all slightly above the recommended water standards while Cu and Zn were all below the permissible limits, although the concentration of heavy metals in the wet season was higher than the dry season which could be due to the movement of heavy metals pollutants from the Atlantic ocean during high tides and strong wind currents into the study area.
3. In the Biota (shiny nose fish, shrimp, and periwinkle), most of the metal concentrations like Cr, Cu, Cd, Ni, and Pb were below the permissible limit, except for Fe which exceeded the limit. Also, the concentration of heavy metals in fish and shrimp was higher in the wet season than in the dry season, which could be a result of the movement of aquatic life from more polluted areas into the Esuk Ekpo Eyo Beach but the concentration of heavy metals in periwinkle

was higher in the dry season than in the wet season. The results of the Pollution Load Index showed that the enrichment factor during the dry season was moderately severe and in the wet season showed no enrichment while the Geo-accumulation Index results of the study area showed no contamination.

4. Health risk assessment of the estimated daily intake or consumption of shiny nose fish, shrimp, and periwinkle containing Cr, Cu, Fe, Pb, Cd, and Ni show that the daily intake limits lie below the tolerable limits for children/adolescents and adults.
5. Pearson correlation analysis revealed that some variables are positively correlated while some are negatively correlated at a 0.05 significant level (2-tailed).

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Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically about authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that the submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that no conflict of interest would prejudice the impartiality of this scientific work.

Authors' contribution

Daniel C. Ekpechi performed the experimental design, prepared the manuscript text, and compiled the data. Bassey S. Okori performed the literature review and manuscript edition.

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APPENDIX I: Marine sediment quality standards

CHEMICAL	Permissible Limits MG/L
PARAMETER	(PARTS PER MILLION (PPM)
CADMIUM	0.5
CHROMIUM	16
COPPER	38
LEAD	28
MERCURY	0.15
SILVER	6.1
ZINC	80
IRON	>25000

(Allen Burton, 2002)

APPENDIX II: Standard organization of Nigeria (maximum Permissible limits of some Heavy metals in water)

PARAMETER	UNIT	MAXIMUM PERMISSIBLE LIMITS	HEALTH IMPACT
Aluminum	mg/l	0.2	Potential neurodegenerative disease
Arsenic	Mg/l	0.01	Cancer
Cadmium	Mg/l	0.03	Toxic to the kidneys
chromium	Mg/l	0.05	Cancer
Copper	Mg/l	1	Gastrointestinal disorder
Iron	Mg/l	0.01	Cancer, and interference with vitamin D metabolism affect mental development in infants, toxic to the central and peripheral nervous system.
Mercury	Mg/l	0.001	Affects the kidneys and central nervous system
Nickel	Mg/l	0.02	Possible carcinogenic
Zinc	Mg/l	3	None

(Nigerian Industrial standards, NIS 554:2007) Current drinking water quality guidelines (µg L-1) for heavy metals (HM), published by several organizations, committees, or agencies throughout the world. There are no drinking water quality guidelines for bismuth, cerium, cobalt, gallium, gold, platinum, tellurium, tin, and vanadium.

APPENDIX III: Heavy metal concentration in drinking water by international health agencies

HEAVY METALS	WHO ug/l	USEPA ug/l	ECE ug/l	FTP-CDW ug/l	ADWG ug/l
Arsenic	10	10	10	10	10
Cadmium	3	5	5	5	2
Chromium	50	100	50	50	50
Copper	2000	1300	2000	1000	2000
Iron	300	300	200	300	300
Lead	10	15	10	10	10
Manganese	100	50	50	50	500
Mercury	6	2	1	1	1
Nickel	70	-	20	-	20
Zinc	5000	500	-	5000	3000

(a) World Health Organization (WHO 2011); (b), United States Environmental Protection Agency (USEPA, 2011); (c), European Commission Environment (ECE, 1998); (d), Federal-Provincial-Territorial Committee on Drinking Water (CDW), Health Canada (FTP-CDW, 2010);(e) Australian Drinking Water Guidelines (DDWG, 2011)

APPENDIX IV: Table A: Maximum Limit WHO/FAO (Mg/L) In Fish/Shrimp

Heavy Metals	Permissible Limits in Mg/L
Zinc	30
Manganese	0.5
Copper	2.0
Iron	0.5
Lead	1.0
Cadmium	2
Chromium	0.15-1.0
Nickel	-

Table B Maximum Limit of Heavy metals WHO/FAO in periwinkle (Tympariostomus spp) (FAO/WHO-2011)

Heavy Metals	Permissible Limits (Mg/L)
Zinc	0.3-1.0
Manganese	0.8
Copper	-
Iron	0.5
Lead	1.0
Cadmium	2
Chromium	0.5
Nickel	-

APPENDIX V:Tolerable Daily intake for metals in seafood

Heavy Metals	Recommended Daily intake Mg/day/person
Iron (Fe)	**20.5**
Copper (Cu)	**0.5**
Lead (Pb)	**0.06**
Cadmium (Cd)	**0.03**
Chromium (Cr)	**0.20**
Nickel	**--**

(Source: JECFA; 2009)

JECFA (2009), Evaluation of the joint FAO/WHO Expert committee on food additives

APPENDIX VI: Interpretation of enrichment factor

Enrichment Factor	Implication
< 1	No enrichment
1-3	Minor enrichment
5-10	Moderately Severe enrichment
10-25	Severe enrichment
25-50	Very severe enrichment
>50	Extremely severe enrichment

(Chen et al,2007)

APPENDIX VII: Some metals and their average crustal values

METAL	AVERAGE CRUSTAL VALUE (ppm)
Lead (pb)	20
Cadmium (Cd)	0.3
Zinc (Zn)	95
Nickel (Ni)	68
Cobalt (Co)	19
Chromium (Cr)	90
Copper (Cu)	45
Manganese (Mn)	850
Iron (fe)	47000

(Some Metals and their average crustal value, Turekian and Wedepohl 1961)