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Heavy metal and Total Petroleum Hydrocarbon Concentrations in Water, Sediment and Fauna of Okerenkoko Estuarine Delta State, Nigeria

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ABSTRACT

Heavy metal and total petroleum hydrocarbon (TPH) pollution of inland waters poses threat to aquatic life. Regular monitoring of heavy metal and TPH concentrations in surface water, sediment and fish of Nigeria aquatic ecosystems is germane to the management of its fishery resources. However, information on heavy metal and TPH pollution of Okerenkoko Estuarine (62.79 Km) are limited. This study was therefore undertaken to investigate the impact of pollution on water, sediment and fish of Okerenkoko Estuarine, Delta State, Nigeria. Okerenkoko Estuarine was spatially stratified into five stations (Z1 – Z5) based on key anthropogenic activities. Three sampling points per station were randomly selected. Temporal stratification covered wet (March – September) and dry (October – January) seasons. Water, sediment and fish samples were collected from each station monthly for 12 months following standard methods. Mercury, Chromium, Nickel and TPH in water (mg/L), sediment and fish (mg/Kg) were analysed by using standard procedures. Data were subjected to descriptive statistics and ANOVA at $\alpha_{0.05}$. In water, significantly highest and least mean of Hg in Water were 0.97±0.06 and 0.69±0.10 in Z4 and Z2 but ranged from 0.68±0.14 to 0.76±0.06 in wet and dry seasons. Highest (32.56±0.32) and least (26.72±0.09) concentrations of Cr in sediment were recorded in Z1 and Z4, while it ranged from 41.05±0.05 to 45.67±0.0 in wet and dry seasons. Highest and least concentration of Ni in Ethmalosa fimbriata were 1.51±0.01 and 0.08±0.01 in Z4 and Z5. Seasonally, it ranged from 0.78±0.01 to 0.98±0.03, 0.34±0.01 in dry and wet seasons, respectively. Spatially, the highest and least concentration of TPH in water (9.76±0.24, 6.97±0.03); sediment (0.67±0.09, 0.49±0.29) occurred in Z1 and Z4, while Ethmalosa fimbriata recorded 0.39±0.23 and 0.51±0.03 in Z5 and Z2, respectively. Seasonally, TPH concentrations in water ranged from 10.79±0.54 to 14.18±3.75; Sediment (5.80±0.19, 8.13±0.24) and Ethmalosa fimbriata (0.39±0.18, 0.43±0.14) in wet and dry seasons, respectively. Heavy metal and TPH levels of contamination Okerenkoko Estuarine was very high with Hg, Cr, Ni and TPH Hence, its biodiversity could be threatened. Regular monitoring is recommended to ensure the conservation of its biodiversity.

Keywords: Heavy metal, Surface water, Sediment, Okerenkoko Estuarine, Biodiversity

1. INTRODUCTION

Estuary constitutes an integral part of the aquatic habitats where waste products are disposed and recycled (Ewutanure and Binyotubo, 2021). The alteration of the aquatic ecosystem through the activities of man and nature is one of the major causes of diseases outbreak and death globally (Ewutanure and Olaifa, 2021). The rise in pollutant concentrations and the excessive exploitation of the water resources for crude oil production, potable water supplies, agriculture and power generation to meet the demand of the ever-increasing population, significantly reduce acceptable quality (Olaifa et al., 2019). Therefore, stress exerted on water courses is borne by the aquatic flora and fauna species within them (Ajayi, 2018).

As the sixth largest oil producing country in the world, Nigeria has most of her petroleum producing companies located within the Niger Delta Region (Ibeto and Okoye, 2010). The fishing communities of the Niger Delta are seriously hampered by petroleum production activities and heavy metal pollution (Ewutanure and Olaifa, 2018a). Annually, it has been reported that about ten million tonnes of crude oil spills into the aquatic environment of the Niger Delta Region due to accident, oil production, corrosion of pipelines, sabotage (Ajayi, 2018). In order to ensure good quality of water for the aquatic living resources, the United Nations sustainable development goals, dedicated Goal 14 of the (SDG) on life below water (Ewutanure and Olaifa, 2018a). It is concerned with the conservation and sustainable uses of the aquatic resources for sustainable development ((Ewutanure and Olaifa, 2018b). Globally, over 3 billion people depend on the aquatic habitat as means of livelihood (Ewutanure and Olaifa, 2021).

1.1 Heavy metal

Metals with densities greater than $5gcm^{-3}$ are referred to as heavy metals (Olaifa, 2004). They are among the transition metals and metals of higher atomic weights in groups III through IV in the periodic table (Odiete, 1999). They can also be referred to as large class of inorganic chemicals which are toxic to the aquatic flora and fauna (Ogaga et al. 2015). It has been reported that heavy metal pollution is one of the major causes of low primary production and mortality in aquaculture (Ewutanure and Olaifa, 2018a). Metal distribution in the aquatic environment is influenced by two main factors which include areas of metal entry into surface water and the uptake of these metals by aquatic biota and demineralization (Yi et al. 2008). Many heavy metals tend to be sequestered in sediment because sediment exhibit high binding characteristics (Ewutanure and Olaifa, 2018b). The aquatic organisms are highly susceptible to the harmful effects of heavy metals pollution because they are in close and prolonged contact with the soluble metals (Ewutanure and Olaifa, 2018a).

The distribution and impact of heavy metals in the aquatic ecosystem depends on pH, vegetation, hydrocarbon, organic matter contents, total suspended solid and sediment particle sizes (Gupta, 2001). The rapid increased in industrialization and urbanization has led to an increase in the production of anthropogenic effluents thereby causing environmental pollution (Ogaga et al. 2015). Petroleum industries represent a major source of aquatic environmental pollution in the Niger Delta Region of Nigeria (Ajayi, 2018). Pollution of the inland rivers, estuaries and streams in this region is a daily occurrence as some industries discharged their effluents directly into them (Adewuyi and Olowu, 2012). There has been reports of heavy metal contamination of the surface water of the Niger Delta Region of Nigeria (Adewuyi et al. 2011). Ewutanure and Olaifa, (2021) reported that visible impact of industrial development on Okerenkoko Estuarine range from stench, colouration to the presence of oil sleeks on surface water.

1.2 Total Petroleum Hydrocarbons (TPH)

The petroleum industries are the major sources of total petroleum hydrocarbon pollution (TPH) in both lotic and lentic water bodies (Anifowose, 2008). It has been reported that TPH is a measurable amount of petroleum – based hydrocarbon in the aquatic environment (Auquo et al. 1999). Total petroleum hydrocarbon is a family of large chemical compounds that are of crude oil origin (Ogamba, 2015). The amount of TPH found in a sample is a major indicator of petroleum contamination within such an estuary (Salman et al. 2011). Waste waters released by oil processing and petrochemical industries are characterized by high amounts of oil products such polycyclic aromatic hydrocarbons, phenols, surface-active substances, sulfides, naphthylenic acids, metal derivatives, and other chemicals (Odiete, 1999).

1.3 How TPH Enters And Leaves Aquatic Fauna

Certain concentrations of TPH could enter and leave the blood stream of aquatic fauna during drinking of water, food and sediment ingestion (Atunbi, 2011). The concentrations of TPH compounds are highly distributed through the blood into the entire body of an organism and are absorbed more slowly (Olowu et al. 2010).

1.4 Sources of Aquatic Pollutants

Ewutanure and Olaifa, (2018a) reported that the two main sources of aquatic pollutants are point source. Pollutants flowing from this source into the aquatic environment are specific and traceable. The identifiable sites could be from surface run – off, pipes or direct discharge of effluents, while the source is the non – point source (WHO, 2008). Effluents or Pollutants from this source originate from different discrete points which cannot be traced to any single site of discharge and it is often the cumulative effects of little quantity of pollutants gathered from a large area (WHO, 2008).

Literature shows that studies have been conducted on the pollution status of Gbalegbe River, Delta State (Ewutanure and Olaifa, 2020), Warri River (Ogaga et al. 2015), Iffie River, Delta State (Atunbi, 2011), Edo River, Edo State (Ize – Iyamu et al. 2007), but not much has been done on the Okerenkoko Estuary with regards to its heavy metal and TPH concentrations and their negative impact on the surface water, sediment and the fauna community. Therefore, this study was undertaken to investigate the level of heavy metals and TPH in water, sediment and the fauna community of Okerenkoko Estuary, Delta State, Nigeria.

2. MATERIALS AND METHODS

The study area has a common link with the Eschravos River situated in Delta State, Niger Delta Region of Nigeria. Okerenkoko Estuarine with an average depth of 35 m and of a total length of 62.79 Km is located on latitudes 5°30′0″N and 5°50′0″N of the Equator and Longitudes 5°10′0″ E and 5°40′0″ E of the Greenwich meridian (Figure 1). Most of the Nigeria's oil and gas companies in Nigeria which account for over 70 % of the federal government revenue are located within the Niger Delta Region (Ewutanure and Olaifa, 2018b).

The Okerenkoko Estuarine is located in a mangrove swamp forest. The major species of mangrove identified were the red and white. Rhizophora racemose (red), Avicennia africana (white) mangroves and flood plain border the estuarine and its surrounding creeks, while the major occupation of Okerenkoko dwellers is fishing (Ewutanure and Olaifa, 2021). Okerenkoko Estuarine was spatially stratified into five stations (Z1, Z2, Z3, Z4 and Z5) based on proximity to key anthropogenic activities. Three sampling points per station were randomly selected. Temporal stratification covered wet (March – September) and dry (October – January) seasons.

Water, sediment and fish samples were collected from each station monthly for 12 months following standard methods (APHA, 1992), while the exact locations of all sampling stations were determined by using Garmin GPSMAP eTrex 10 type sensors.

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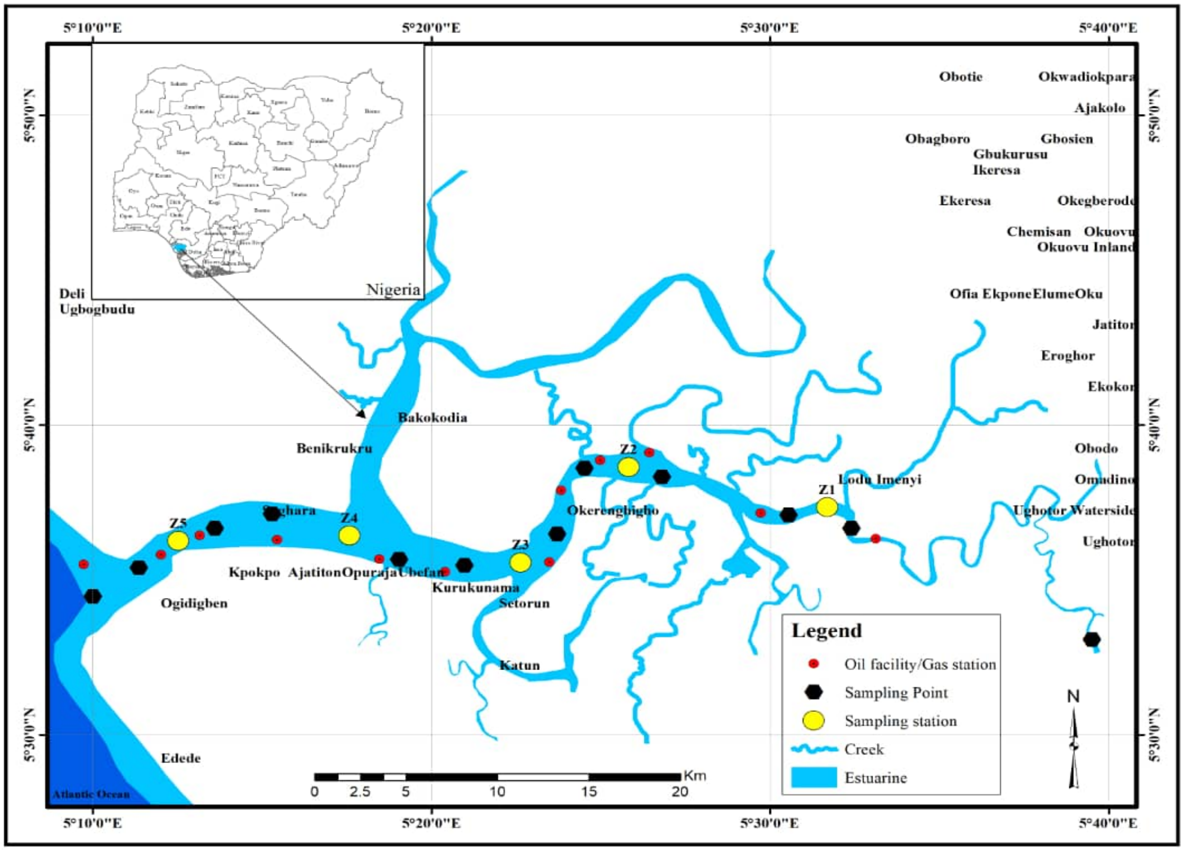

Figure 1. Map of Okerenkoko Estuarine, Delta State, Nigeria
Source: Ewutanure and Binyotubo, (2021)

2.1 Experimental Procedure and Sampling Techniques

All equipment used for sample collection, storage and analysis of heavy metals were pre-cleaned using high – purity nitric acid (GFS Chemicals Inc.). Proper cleaning and storage procedures eliminates detectable metal contaminants in the sampling equipment (ASTM, 2006; ISO, 2006). Samples of water for heavy metal and TPH analyses were collected in polypropylene bottles and filtered immediately through 0.45 µm Waltman filter paper and acidified with ultra – pure HNO_3 at a concentration of 1ml per litre of sample to pH< 2, labelled, dated and stored at 4°C prior to heavy metal and TPH analyses (Odiete, 1999). In the laboratory, the water samples were transferred into the refrigerator until needed for analyses (AOAC, 1990; FAO/SIDA, 1983). A pre – cleaned van Veen bottom grab (van Veen, 1933) sampler was used to collected sediment samples from each station. Samples of fish were obtained from the local fishers. Fish and sediment samples were preserved following the methods described by Gupta, (2001). Fish samples were identified by using standard keys (Idodo – Umeh, 2003; Olaosebikan and Raji, 2004).

2.2 Analyses of the concentrations of heavy metals and TPH in water, sediment and fish samples of Okerenkoko Estuarine

In the laboratory, collected water, sediment and fish samples were processed according the methods described by AOAC, (1990). Concentrations of heavy metals in water, sediment and fish were then analysed by using Atomic Absorption Spectrophotometer (AAS) as described by American Public Health Association (APHA, 1998). The concentrations of TPH in water, sediment and fish samples were determined using volumetric method (Etim, 2009). The concentration of TPH in water sample was the calculated by using:

$$\text{TPH (mg/L)} = \frac{\text{weight of TPH from tarred bottle x extract dilution factor}}{\text{volume of sample (L)}}$$ Etim (2009) …………….(1)

The concentrations of TPH in fish and sediment samples were determined by using formula as described by Etim (2009); AOAC, (1990).

$$\text{TPH } (\mu\text{g/Kg}) = \frac{\text{weight of TPH in tarred flask x 1000}}{\text{weight of specimen sample(kg)}}$$ (ASTM, 2006) ……………………………..…..(2)

2.3 Statistics

Data were analysed by using descriptive statistics and ANOVA at $\alpha_{0.05.}$

3. RESULTS

The concentrations of heavy metals recorded in water of Okerenkoko Estuarine among stations and between seasons during the study period are presented in Tables 1 and 2. Means of heavy metals obtained were higher than the recommended values of < 0.0001 mg/L, 0.002 mg/L, 0.003 mg/L, 0.05 and < 0.02 mg/L for Hg, Ni, Cd, Cr and Pb, respectively (NIS, 2007). There were no significant differences (P>0.05) in the concentrations of heavy metals recorded among stations and between seasons.

Table 1. Concentrations of heavy metals in water of Okerenkoko Estuarine among stations

Heavy metals	Stations					P – values
	Z1	Z2	Z3	Z4	Z5	
Hg (mg/L)	0.74±0.05	0.69±0.10	0.78±0.11	0.97±0.06	0.88±0.09	0.03**
Ni (mg/L)	0.55±0.03	0.57±0.11	0.85±0.31	0.90±0.19	0.68±0.14	0.00**
Cd (mg/L)	0.27±0.01	0.23±0.05	0.29±0.14	0.36±0.04	0.29±0.07	0.01**
Cr (mg/L)	0.63±0.02	0.21±0.10	0.38±0.12	0.25±0.09	0.35±0.11	0.02**
Pb (mg/L)	0.50±0.04	0.51±0.14	0.59±0.10	0.66±0.02	0.49±0.13	0.06**

Note: ** = There are no significant differences (p>0.05) between means along the rows

Table 2. Concentrations of heavy metals in water of Okerenkoko Estuarine between seasons

Heavy metals	Seasons		P – values	NIS, (2007)
	Wet	Dry		
Hg (mg/L)	0.68±0.14	0.76±0.06	0.06**	< 0.0001
Ni (mg/L)	0.59±0.04	0.77±0.06	0.02**	0.002
Cd (mg/L)	0.57±0.10	0.68±0.07	0.00**	0.003
Cr (mg/L)	0.71±0.04	0.88±0.06	0.04**	0.005
Pb (mg/L)	0.27±0.12	0.34±0.06	0.03**	<0.02

Note: ** = There are no significant differences (p>0.05) between means along the rows

The concentrations of heavy metals in sediment of Okerenkoko Estuarine among stations and between seasons obtained during the study period are presented in Tables 3 and 4. Concentrations obtained were higher than the acceptable limits of < 0.001 mg/Kg, 16 mg/Kg, 0.6 mg/Kg, 25 mg/Kg and 40 mg/Kg for Hg, Ni, Cd, Cr and Pb, respectively (NIS, 2007). There were no significant differences (P>0.05) in the concentrations of heavy metals recorded among stations and between seasons.

Table 3. Concentrations of heavy metals in sediment of Okerenkoko Estuarine among stations

Heavy metals	**Stations**					**P – values**
	Z1	Z2	Z3	Z4	Z5	
Hg (mg/Kg)	0.92±0.03	0.82±0.04	0.71±0.03	69.15±0.02	0.66±0.08	0.43**
Ni (mg/Kg)	21.45±0.21	25.42±0.04	18.52±0.01	17.21±0.02	19.37±0.05	0.00**
Cd (mg/Kg)	0.40±0.21	0.38±0.01	0.32±0.11	0.37±0.77	0.44±0.19	0.01**
Cr (mg/Kg)	32.56±0.32	28.94±0.29	27.68±0.02	26.72±0.09	30.71±0.01	0.02**
Pb (mg/Kg)	47.23±0.01	41.36±0.03	49.7±0.13	50.56±0.07	45.84±0.02	0.08**

Note: ** = There are no significant differences (p>0.05) between means along the rows

Table 4. Concentrations of heavy metals in sediment of Okerenkoko Estuarine between seasons

Heavy metals	Seasons		P – values	FEPA, (1991)
	Wet	Dry		
Hg (mg/Kg)	0.24±0.03	0.20±0.09	0.43**	< 0.001
Ni (mg/Kg)	23.76±0.02	21.90±0.37	0.00**	16
Cd (mg/Kg)	31.98±0.10	27.32±0.16	0.01**	0.6
Cr (mg/Kg)	41.05±0.10	38.97±0.47	0.02**	25
Pb (mg/Kg)	47.02±0.02	45.67±0.03	0.08**	40

Note: ** = There are no significant differences (p>0.05) between means along the rows

The concentrations of heavy metals recorded in the muscles of Ethmalosa fimbriata obtained from Okerenkoko Estuarine among stations and between seasons during the study period are presented in Figures 1 and 2. Means of heavy metals obtained from the fish muscles were higher than the recommended values of < 0.01 mg/Kg, 1.00 mg/ Kg, 0.02 mg/ Kg and 0.2 mg/ Kg for Hg, Ni, Cd, Cr and Pb, respectively (NIS, 2007). There were no significant differences (P>0.05) in the concentrations of heavy metals recorded among stations and between seasons.

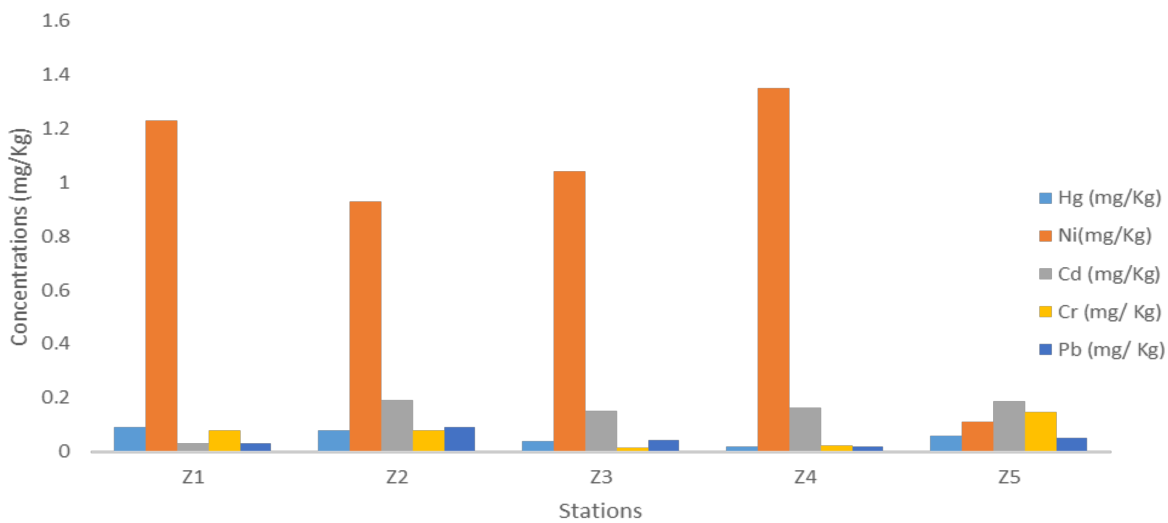

Figure 1. Concentrations of heavy metals in the muscle of Ethmalosa fimbriata obtained from Okerenkoko Estuarine among stations

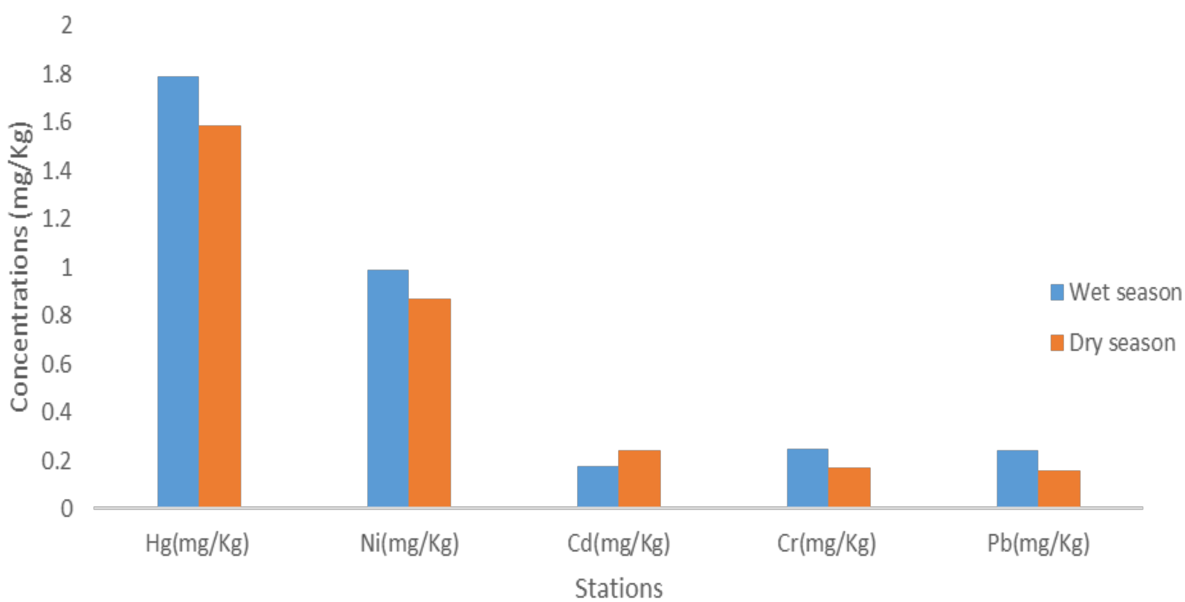

Figure 2. Concentrations of heavy metals in the muscle of Ethmalosa fimbriata obtained from Okerenkoko Estuarine between seasons

The concentrations of TPH in biota of Okerenkoko Estuarine among stations and between seasons recorded during the study duration are shown in Tables 5 and 6. Higher concentrations than recommended values for water (< 0.001 mg/L), fish (< 0.001 mg/Kg and sediment (0.002 mg/Kg) were recorded, respectively (FEPA, 1991; NIS, 2007).

Table 5. Concentrations of TPH in biota of Okerenkoko Estuarine water among stations

TPH	Stations					P – values	FEPA, (1991)
	Z1	Z2	Z3	Z4	Z5		
TPH – water (mg/L)	9.76±0.24	7.92±0.33	8.49±0.07	6.97±0.03	7.68±0.16	0.00**	< 0.001
TPH – muscle of Ethmalosa fimbriata (mg/Kg)	0.46±0.20	0.39±0.23	0.45±0.21	0.44±0.25	0.51±0.30	0.05**	< 0.001
TPH – sediment (mg/Kg)	0.67±0.09	0.58±0.19	0.53±0.03	0.49±0.29	0.50±0.01	0.04**	0.002

Note: ** = There are no significant differences (p>0.05) between means along the rows

Table 6. Concentrations of TPH in biota of Okerenkoko Estuarine water between seasons

Seasons	TPH-Water (mg/L)	TPH – muscle of Ethmalosa fimbriata (mg/Kg)	TPH – Sediment (mg/Kg)
Wet season	14.18±3.75 (12.80 – 24.57)	0.39±0.18 (0.24 – 0.36)	8.13±0.24 (4.38 – 15.45)
Dry season	10.79±0.54 (3.07 – 11.75)	0.43±0.14 (0.39 – 1.56)	5.80±0.19 (1.40 – 8.67)
P – values	0.00**	0.03**	0.09**
FEPA, (1991)	< 0.001	< 0.001	0.002

Note: ** = There are no significant differences (p>0.05) between means along the rows

4. DISCUSSION

Bioaccumulation seemed to occur in the muscle of Ethmalosa fimbriata as higher concentrations of heavy metals than recommended were recorded. Heavy metals absorption depend on their chemical forms and properties (Olaifa et al., 2004). Heavy metal assimilation into the body through the pulmonary veins could results into speeds up a rate of absorption and distribution through circulatory system (Salman et al. 2011).

The passage of heavy metals via the intestinal tract could be governed by pH level and movement along the tract (Ewutanure and Olaifa, 2018a). The aggregation of these factors could either decrease or increase the rate of absorption (Ewutanure and Olaifa, 2018b). The effect of heavy metals on any organ is determined by the form of the metal. For example, organometallic mercury could cause brain and nervous system damage, while mercury ion can attack the kidneys (Olaifa et al., 2004).

Increased concentration of heavy metals could inhibit red blood cell formation, increased urinary excretion of acid and interference with haemobiosynthesis (Odiete, 1999; Ewutanure and Olaifa, 2021). Toxic effect of heavy metals on aquatic flora and fauna is enhanced by increased temperature, pH and decrease in dissolved oxygen level (Ewutanure and Binyotubo, 2021).

Total petroleum hydrocarbon is the quantity of hydrocarbon that can be determined in an aquatic system and it is a combination of various chemicals (Ajayi, 2018). The quantity of TPH contained in an aquatic sample is an indication of petroleum pollution within such an environment (Atunbi, 2011). Certain TPH fractions float in water and form thin surface films while heavier fractions accumulate in the sediment thereby affecting the feeding and biological systems of aquatic flora and fauna (WHO, 2008).
In Okerenkoko Estuarine, characteristic gasoline, kerosene, or oily odour is a daily occurrence due to the incessant discharge of crude oil into its water. Okerenkoko Estuarine acts as a major sink for pollutants (Ewutanure and Binyotubo, 2021). Sublethal concentrations of TPH could disrupt various physiological and behavioural processes of different aquatic flora and fauna (Aremu, 2002). The presence of TPH in a fish could lead to peripheral neuropathy (nerve disorder), damages to the lungs, brain, skin, circulatory and immune systems and deformities in fish larvae (Aghoghovwia, 2008).

5. CONCLUSION

Due to the importance of water, sediment and fish to the Okerenkoko dwellers, it is therefore, necessary that biological monitoring of the water and fish meant for consumption be done regularly to ensure continuous safety of food. Safe disposal of anthropogenic effluents should be practiced. An urgent step should be taken by the federal government of Nigeria to ensure that Okerenkoko Estuarine is properly cleaned up so as to ascertain the safety of its aquatic living resources and the lives of humans that depend on it for survival. Laws enacted to protect the aquatic environment should be enforced.

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