Ecological Risk Assessment of Heavy Metals in Sediment from Oil-producing Regions of Ilaje Local Government Area of Ondo State, Nigeria.

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Abstract **-Nigeria is one of the developing countries that depend largely on oil exploration as major source of revenue for economic development. More than 400,000 tons of oil had spilled into the creeks and soils of most oil producing communities in Nigeria, thereby, affecting the livelihood of host communities. The study aimed at evaluating the present health status of water bodies proximate to oil wells located in Ilaje communities using six pollution indices which comprises of three single pollution indices {Contamination Factor (CF), Ecological Risk Factor (Er) and Index of Geo-accumulation (Igeo)} and three Integrated pollution indices {Pollution Load Indices (PLI), Potential Ecological Risk Index (RI) and Nemerow Pollution Index (Pnemerow)} to quantify the extent or degree of heavy metal contamination in the sediment. Eight (8) heavy metals (Cd, Fe, Cu, Pb, Ni, Mn, Cr, and Zn) from sediment taken for five (5) months from three different regions of Ilaje (Ayetoro, Orereara and Abereke) were analyzed using Atomic Absorption Spectrophotometer. Heavy metal concentrations range from: Cd (0.0607- 0.1067ppm), Fe (152.5404- 246.713ppm), Cu (0.5339- 1.3073ppm), Pb (0.2612- 0.5226ppm), Ni (0.1370- 0.2339ppm), Mn (0.5643- 0.7345ppm), Cr (0.1785- 0.2423ppm), Zn (1.0753- 1.7945ppm). All values were below the international standard for sediment and the pollution indices also reveals that the areas are not polluted with low potential ecological risk. Result of Pnemerow indicates the areas as safe domain for most benthic organmisms. Continuous monitoring of these areas, especially when there is oil spillage, is therefore, recommended.**

Keywords**: Heavy metals; Sediment; Pollution indices; Ilaje; Oil spillage**

I. INTRODUCTION

Environmental degradation as a result of oil exploration is one of the major problems faced by oil producing communities. This problem has been prevalent in Nigeria since1950s and more than 400,000 tons of oil had spilled into the creeks and soils of southern Nigeria as a result of several factors including overexploitation, corrosion and vandalisation of pipe lines, illegal mining activities [1],[2].Apart from degradation of water quality, contamination of sediment with heavy metals is a major environmental threat to most benthic organisms.

Heavy metals are part of the constituent of crude oil but the type and concentration level of these metals depend on several factors like the type of rock that serves as source for the oil and also during the extraction process [3]. Whenever there is spillage or during the drilling process, there is always release of some heavy metals into the water body, which later sink down into the sediment. Sediment is a home to many sedentary organisms which are depended on either directly or indirectly by organisms (including man) at the higher trophic level. Bioaccumulation of metals in these organisms is a pointer to great health risk for final consumers.

Ilaje community is one of the oil producing communities in the Niger Delta region of Nigeria that is faced with serious threat of environmental pollution. It is located in the Southern part of Ondo State along the coastal line of the Atlantic Ocean. Oil exploration and production started in this area in the 1960s by Gulf Oil Company and presently, there are over 14 Oil wells located in different parts of the region [4]. The area has one of the largest market for sea foods including crabs, periwinkles and fish of diverse species [5].

Pollution index is a powerful statistical index analysis tool used for processing, analyzing, and conveying raw environmental information to decision makers, managers, technicians, and the public. Pollution indices can be regarded as tools and guides for a comprehensive geochemical assessment of the environment. It assesses and quantify the extent and degree of heavy metal contamination/deposition in sediment. Pollution indices can either be used as single or integrated factor. Single index factors include Enrichment factor, Contamination factor, Index of Geoaccumulation and Ecological Risk Factors while integrated factors include Pollution load index, Potential Ecological Risk index and Nemerow Pollution Index [6]. Pollution Load Index (PLI) is one of the integrated tool for determining and comparing the severity of pollution on different sites/at the same site on temporal scale. It is usually obtained as concentration factor (CF) which is the quotient obtained by dividing the concentration of each metal while Ecological Risk factor (ER) and Potential Ecological Risk Index are used for evaluating heavy metal pollution and associating ecological and environmental effect with the toxic response factor. They can be used to quantitatively express the potential ecological risk of a given contaminant. Geo-accumulation index (I-geo) is used to quantify the extent of heavy metal contamination associating with the sediment. It determines the level of metal contamination in sediments by comparing current concentration with pre-industrial levels while Pnemerow index determines the safety of an area. All these indices can be used together to assess the degree of environmental contamination.

Assessment of pollution status of ilaje oil producing communities have been limited to assessing the physicochemical parameters of water bodies [7] and quantification of Total Polycyclic Hydrocarbon [5], little have done on using pollution indices to quantify the extent of pollution in the sediment. It is, therefore, imperative to assessthe present level of heavy metal contamination in sediment which house most of the seafood like crab and periwinkle sold in Ilaje.

II. METHODOLOGY

Study Area

Field study was conducted on the coastal water of Ilaje area of Ondo State, Nigeria. Ilaje area is made up of several communities that settled along the rivers and estuaries and this define their primary occupation as cash crops farmers and fishermen. The choice of the sampling area is based on the long history of various anthropogenic inputs from oil exploration activities through pipeline seepages and vandalization, illegal mining activities and transportation. In addition, this area is noted for sea foods like fish (of divers species), crabs, periwinkles which are consumed within and outside the state. This mean that its pollution may have national and global healtheffects. There is, therefore, the need to assess and monitor the aquatic ecosystem.

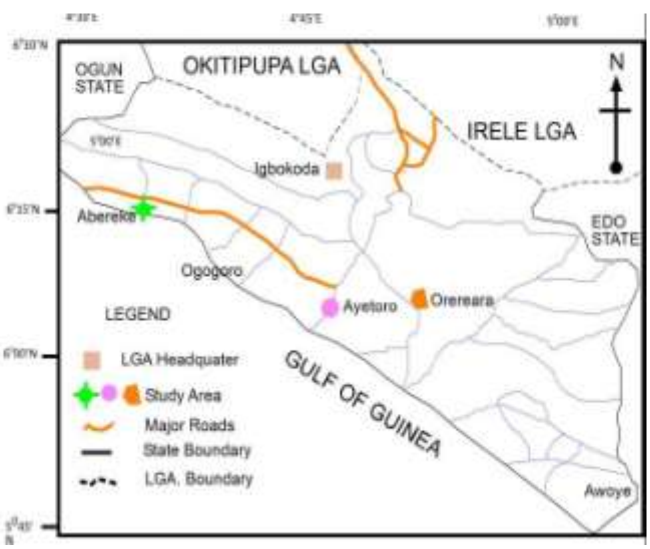


Fig.. 1: Map of Ilaje Local Government Area showing the three different study sites

Sampling and Preservation

Three (3) representatives' sites in the coastal region; Ayetoro, Orereara and Abereke were considered. Sampling was carried out for five months (May-September, 2018). Sediment was taken using Van veen grab (250 litre), kept in a pre-cleaned Polythene bag and transported to the laboratory of the Department of Animal and Environmental Biology, Adekunle Ajasin University where it was air-dried.

Procedure for the Digestion of Sediment Samples for Heavy Metal Analyses

Sediment from each station was spread on a tray and air dried. After air drying, sediment samples were crushed into smaller particles using crucible mortar and pestle, and sieved. 2 g of the sediment sample was weighed and poured into a beaker. 5 ml of hydrogen trioxonitrate (v) acid (HNO_3) was added together with 2 ml of perchloric acid ($HClO_4$) and 5 ml of hydrogen fluoride (HF) was also added and heated for 1 hour on a heater at 160°C. After proper digestion, the sample was allowed to cool down and filtered with a Whatman Filter paper. The filtrate was transferred into 100 ml volumetric flask and made up to mark with distilled water. The prepared sample solution was transferred into a pre-cleaned labeled sample bottles in readiness for Atomic Adsorption Spectrophotometer (AAS) analysis. Eight heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, Zn, Fe) were analyzed.

Pollution Indices

Pollution index is a powerful statistical index analysis tool used for processing, analyzing, and conveying raw environmental information to decision makers, managers, technicians, and the public [6]. The six pollution indices used in this study are listed below:

Contamination factor (Cf)

The level of contamination of soil by metal is expressed in terms of contamination factor as follows:

$$\text{Contamination factor (Cf)} = \frac{C_i}{C_{ri}}$$

Where C_i = content of metal I

C_{ri} = reference value/ baseline level of metal i

Table 1: Range of contamination factor

CLASS	RANGE	INTERPRETATION
1	$C^i_f<1$	Low contamination factor
2	$1\leq C^i_f<3$	Moderate contamination factor
3	$3\leq C^i_f<6$	Considerable contamination factor
4	$C^i_f\geq 6$	Very high contamination factor

Pollution Load Index

Pollution Load Index (PLI) is one of the integrated tool for determining and comparing the severity of pollution on different sites/at the same site on temporal scale. It is usually obtained as concentration factor (CF) which is the quotient obtained by dividing the concentration of each metal. The pollution load indexes of the study sites will be calculated by obtaining the n-root from the n-CFs that was obtained for all the metals.

The formula developed by [8] was used in this study as shown in equation below:

$$PLI = n\sqrt{(C^i_f 1 \times C^i_f 2 \times C^i_f 3 \times \ldots \times C^i_f n)}$$

Where

C^i_f= Contamination factor

n= number of metals

The PLI represents the number of times by which the metal content in the soil exceeds the average natural background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample.

Table 2: Different classes of PLI

CLASS	RANGE	INTERPRETATION
1	PLI>1	Polluted
2	PLI<1	Not polluted
3	PLI=1	Heavy metal loads close to the background level

Ecological Risk Factor and The Potential Ecological Risk Factor

Ecological Risk factor (ER) is a single tool for evaluating heavy metal pollution and associating ecological and environmental effect with the toxic response factor. It is used to quantitatively express the potential ecological risk of a given contaminant.

$$Er^i = Tr^i \times C^i_f$$

Where

Tr^i = toxic response factor for a given metal

C^i_f= contamination factor

Table 3: Classes for Ecological Risk Factor (Er)

CLASS	ErVALUES	GRADES
1	$Er^i<40$	Low potential ecological risk
2	$40\leq Er^i<80$	Moderate potential ecological risk
3	$80\leq Er^i<160$	Considerable potential ecological risk
4	$160\leq Er^i<320$	High potential ecological risk
5	$Er^i\geq 320$	Very high potential ecological risk

The Potential Ecological Risk Index (RI) is another potent integrated tool used for assessing the degree of toxic metal pollution in sediments. It is defined as the sum of the risk factors (Er)

$$RI = \sum_{i=1}^{m} Er^i$$

Where Er^i=Single index of ecological risk factor

m= count of the heavy metal species

Table 4: Grades for RI values

CATEGORIES	RI VALUES	GRADES
1	RI<150	Low ecological risk
2	150≤RI<300	Moderate ecological risk
3	RI>600	Very high ecological risk

Index of geo-accumulation

The geo-accumulation index (I-geo) is used to quantify the extent of heavy metal contamination associating with the sediment. It helps to determine the level of metal contamination in sediments by comparing current concentration with pre-industrial levels.

$$I\text{-}geo = \log_2 (Ci / 1.5\, Cri)$$

Where Ci = Measured concentration of theexamined metal *i*in the sediment

Cri= Geochemical background concentration or reference value of the metal *i*.

Factor 1.5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences.

Table 5: Classes for Geo-accumulation index by [9].

CLASS	Igeo VALUES	SEDIMENT QUALITY
0	Igeo≤0	Unpolluted
1	0< Igeo≤1	From unpolluted to moderately polluted
2	1< Igeo≤2	Moderately polluted
3	2< Igeo≤3	From moderately polluted to strongly polluted
4	3< Igeo≤4	Strongly polluted
5	4< Igeo≤5	From strongly polluted to extremely polluted
6	Igeo>5	Extremely polluted

Nemerow Pollution Index

This is a comprehensive pollution index equation based on single pollution index. Nemerow composite index method not only takes account all the individual evaluation factor which also highlights the importance of the most contaminated elements [10]. In this study the single pollution index that was used to calculate Nemerow pollution index is the contamination factor.

It is calculated by the following equation:

$$Pnemerow = \sqrt{[(1/n\Sigma P)^2 + (Pmax)^2] / 2}$$

Where, Pnemerow = Nemerow pollution index

P = single pollution index (contamination factor)

n = number of elements analyzed

Table 6: Classes for Nemerow pollution index

S/N	Grade of $P_{Nemerow}$	Terminology for pollution grade
1	$P_{nemerow}<0.7$	Safety domain
2	$0.7\leq P_{nemerow}<1.0$	Precaution domain
3	$1.0\leq P_{nemerow}<2.0$	Slightly polluted domain
4	$2.0\leq P_{nemerow}<3.0$	Moderately polluted domain
5	$P_{nemerow}>3.0$	Seriously polluted domain

Data analysis

Data were subjected to One-way ANOVA to get the mean and standard deviation while six pollution indices were used to access the degree of contamination in thesediments.

III. RESULTS AND DISCUSSION

Metal Concentration in sediment from three study sites

Average concentration of different heavy metals assessed from the three study sites are presented in Table 7. The occurrence of the measured heavy metal is in the decreasing order of Fe>Zn>Cu.Mn>Pb>Cr>Ni>Cd. Fe had the highest mean concentration of 246.7130±68.1064 ppm while Cd had the lowest value of 0.0607±0.0455 ppm.

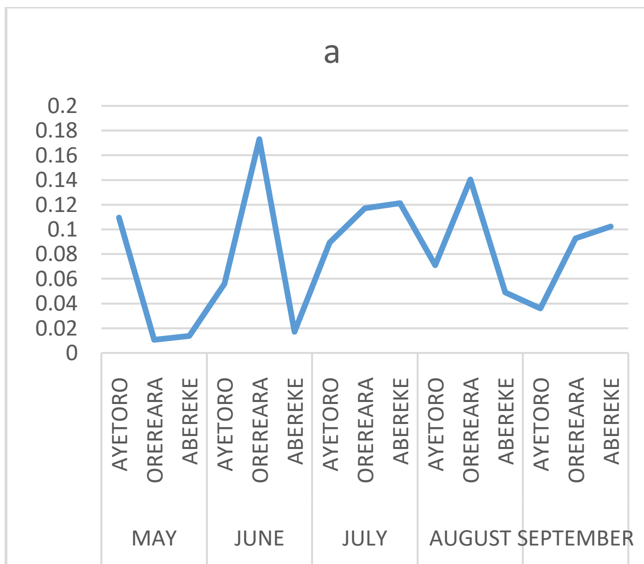
Table 7: Comparison of the average concentration of metals (ppm) from different study sites with international standard for sediment

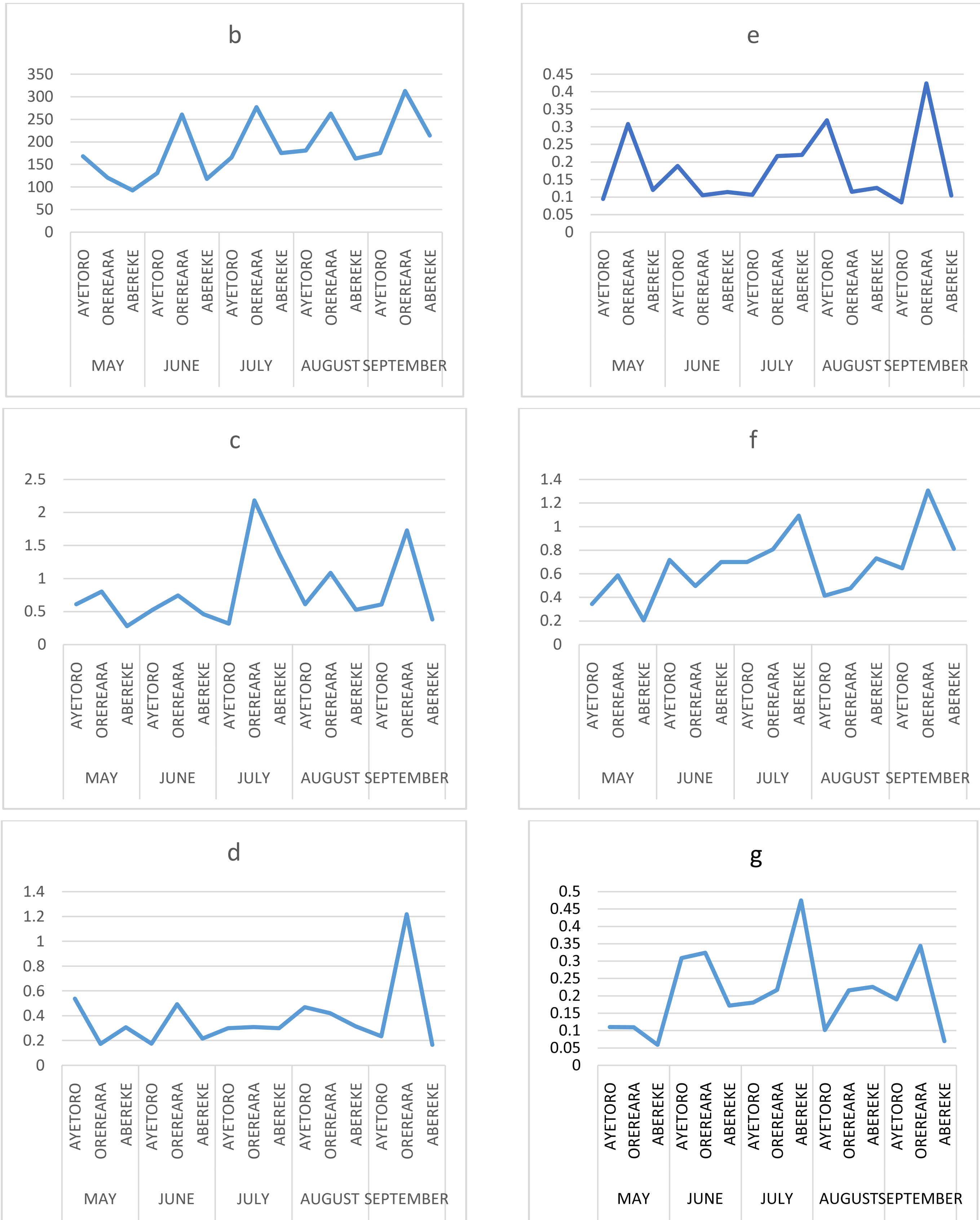
	AYETORO	OREREARA	ABEREKE	ASV	TRV	LEL	SEL	**
Cd	0.0724±0.0267	0.1067±0.0568	0.0607±0.0455	0.3	0.6	0.6	10	0.000-0.095
Fe	164.0577±18.1259	246.7130±68.1064	152.5404±44.3834	46000				0.339-1.623
Cu	0.5339±0.1180	1.3073±0.5790	0.5999±0.4017	45	16	16	110	0.021-0.157
Pb	0.3431±0.1436	0.5226±0.3770	0.2612±0.0617	20	31	31	250	0.036-0.403
Ni	0.1587±0.0913	0.2339±0.1248	0.1370±0.0448	68	16	16	75	0.024-0.182
Mn	0.5643±0.1607	0.7345±0.3207	0.7081±0.2974	850		460	1100	0.002-0.095
Cr	0.1785±0.0771	0.2423±0.0879	0.2004±0.1562	90	26	26	110	-
Zn	1.3800±0.2781	1.7945±0.8405	1.0753±0.6147	95	110	120	820	0.072-0.178

ASV: Average Shale Value; TRV: Toxicity Reference Value; LEL:Lowest Effect Level and SEL: Severe Effect Level [11]; **Range of heavy metal from sediment of Ugbo river in Ilaje LGA, Nigeria [12].

Values for all metals were below the international standards while Zn, Cu, Fe and Mn exceeded the range of heavy metals from reference study. Most importantly, they were below Average Shale Values and the Lowest Effect Level values, thereby, indicating that the present level of contamination are below levels that can be hazardous to health of majority of the benthic organisms. That is, the contamination level can still be tolerated by most of the aquatic lives present in these study sites. This study corroborates the findings of [13] that reported that all the metals analyzed in sediment from three locations along the Atlantic Ocean shoreline in Ilaje LGA were below the Probable Effect Concentration (PEC) level in sediment. However, when compared with range of heavy metal reported from Ugbo river, which is one of the waterbodies from Ilaje LGA (Local Government Area of this present study), most of the heavy metals (Zn, Cu, Fe, Mn), Pb and Ni (Orereara only) from this study exceeded the reference study [12].

There was variation in the concentration of each metal over the sampling periods (May-September) per site as shown Fig. 2a-h.

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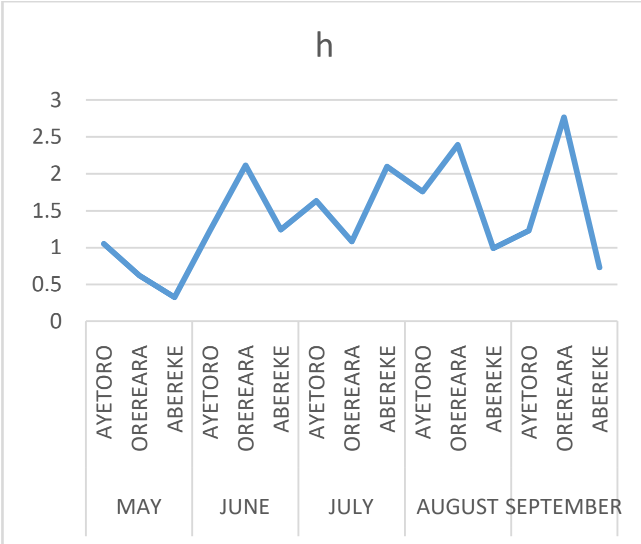

Fig. 2a-h: Variations in the concentration of Cd, Fe, Cu, Pb, Ni, Mn, Cr and Zn respectively during sampling periods

The highest value for Cd (0.1730±0.001 ppm) was recorded in Orereara during the month of June while the lowest (0.0107±0.0025 ppm) was recorded in the month of May at the same site (Fig. 2a). Apart from the month of May, Cd was relatively high in Orereara throughout the sampling periods. There was steady increase in the mean concentration of Fe present in Orereara with the highest concentration (312.7007±0.1534 ppm) recorded in September. Fe concentration was relatively low in Abereke when compared with other sites (Fig. 2b). Orereara had the highest value of Cu throughout the months with the highest value recorded in July (2.1810±0.0036 ppm) while the lowest value was recorded in Abereke in the month of May (0.2780±0.0036 ppm). Orereara had the highest value of Pb, Ni, Mn, and Zn in the month of September with 1.2177±0.0143, 0.4240±0.002, 1.3060±0.0121 and 2.7670±0.0187 ppm respectively while Abereke recorded the highest value (0.4757±0.003 ppm) for Cr in the month of July followed by Orereara (0.3443±0.0031 ppm) in the month of September.

Metal pollution indices

Pollution indices are ecological tools used to quantify the extent and degree of heavy metal contamination in sediment and have been used by several researchers to assess specific locations [14]-[21]. Results of the Contamination Factor (CF) and Pollution Load Index (PLI) are presented in Table 8. All values for the three study sites were below 1(<1) for both CF and PLI. The PLI values ranged between 0.0069 – 0.0110 for Abereke and Orereara respectively.

Table 8: Contamination factor and Pollution Load Index of the measured metals

STATION	Contamination Factor (Cf)								PLI	PL*
	Cd	Fe	Cu	Pb	Ni	Mn	Cr	Zn		
AYETORO	0.2413	0.0036	0.0119	0.0172	0.0023	0.0007	0.0020	0.0145	0.0073	N P
OREREARA	0.3557	0.0054	0.0291	0.0261	0.0034	0.0009	0.0027	0.0189	0.0110	N P
ABEREKE	0.2023	0.0033	0.0133	0.0131	0.0020	0.0008	0.0022	0.0113	0.0069	N P

*PL: Pollution Level, N P: Not Polluted

This correlate with the findings of[15] who reported that the CF value for Zn, Ni, Cu, Cr and Mn in surface sediment from the Aden coast of the Southern Yemen were less than 1. The PLI reported for sediment from an urban river and Karnaphuli River in Bangladesh were above 1, thus, indicating a serious progressive deterioration of the sediment quality [16], [17]. However, the present study indicates that all the study sites are not polluted with heavy metals. This may be as result ofdecrease in the incidence of oilspillage, which had been the major source of pollution, in these areas.

The Ecological Risk factor (Er) and Potential Ecological Risk Factor (RI) are also presented in Table 9. RI value ranged between 6.2286 – 10.9882 for Abereke and Orereara respectively. The mean Er^i value for each metal were in the decreasing order Cd>Pb>Cu>Zn>Ni>Cr>Mn. All the Er values were below 40 while the highest value recorded was 10.6700 for Cd in Orereara

Table 9: Evaluation on potential risk of heavy metal pollution in sediment

STATION	Ecological Risk Factor Er^i							RI	Risk Grade
	Cd	Cu	Pb	Ni	Mn	Cr	Zn		
AYETORO	7.2400	0.0593	0.0858	0.0117	0.0007	0.0040	0.0145	7.4159	Low Ecological Risk
OREREARA	10.6700	0.1453	0.1307	0.0172	0.0009	0.0054	0.0189	10.9882	Low Ecological Risk
ABEREKE	6.0700	0.0667	0.0653	0.0101	0.0008	0.0045	0.0113	6.2286	Low Ecological Risk

Naturally, Cd is dangerous and very toxic to the environment and health of human and other organisms. It is, therefore, necessary to caution any activity that can lead to the uprising of Cd in this site (Orereara). However, all RI values were also below 150, thereby, indicating that these areas have low ecological risk for aquatic biota. This agreed with the findings of [19], [21] that also reported that both $Er^i$and RI for the examined heavy metals were below 40 and 150 respectively.

The Geo-accumulation index results for all the study sites were less than 0 (<0) as shown in Fig. 3. I_{geo} is one of the most viable tools used in comparing present heavy metals concentration levels with pre-industrial levels.

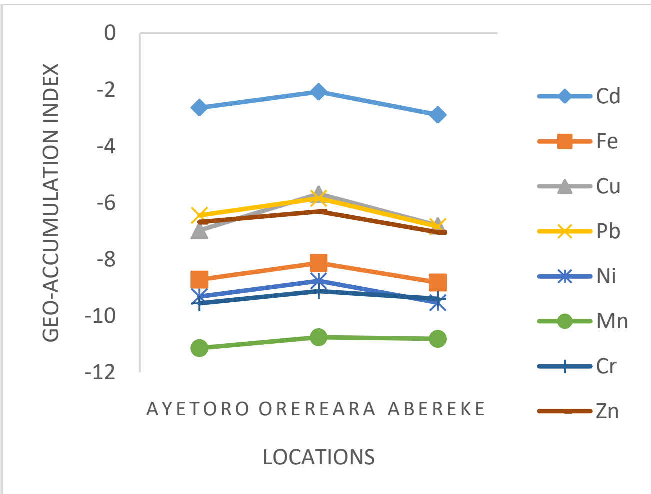

Fig. 3: Geo-accumulation Index (I_{geo}) of the measured metals in sediments of study sites

Negative values recorded for I_{geo}in all the sites also indicate that the areas are not polluted with heavy metals when compared with background values (Average Shale Values). This agreed with the report of[15, 22] and also, most of the I_{geo}values recorded for seven metals (Fe, Cu, Zn, Cr, Co, Cd and Pb) analyzed in the sediment of Burullus lake, Egypt were negative [18]. Pnemerow values ranged between 0.1721-0.1721 for Abereke and Orereara respectively (Table 10).

Table 10: Interpretation of Pnemerow value for the study sites

Ayetoro	Orereara	Abereke	Pnemerow grade	Interpretation
0.1726	0.1751	0.1721	<0.7	Safety domain

Finally, Pnemerow, which is used to assess the safety of an area, also reveals that the study areas are safe for most benthic organisms.

IV. CONCLUSION AND RECOMMENDATION

From this present study, it is evident that the heavy metal concentrations are not higher than the regulatory limits stipulated for sediment but constant monitoring of these study sites are necessary so that the level do not shoot go above the limits.

Further study can be carried out by National Oil Spill Detection and Response Agency (NOSDRA) and National Environmental Standards Regulatory and Enforcement Agency (NESREA) so as to be able to regulate the activities of the oil companies situated in the LGA. Community members in the area should also be educated on dangers that can result from vandalism and sabotage, as these may affecttheir means of livelihood and the aquatic system.

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