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# Comparing Levels of Some Heavy Metals in Rivers and Sediments from Two South-Western States of Nigeria

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**ABSTRACT**

Ten water and ten sediment samples from both Igbokoda and Apapa in South west, Nigeria were collected between March and August, 2018 for heavy metal analysis. The study aimed at using Potential Ecological Risk (PER) index to characterize rivers sediments and waters for possible environmental impact. The sampling span industrial, domestic and recreational areas. The water and sediment grab samples were treated using standard procedures. The filtrate from sediment was made up to 50 cm3 mark with distilled water and used for seven heavy metals determination using atomic absorption spectrophotometry (AAS). Contamination factor (CF) and Pollution load index (PLI) calculated for each metal in the sediments indicate moderate contaminations. However, Cd in exception showed the highest potential ecological risk factor of 42.3 in Igbokoda. PER value of the Igbokoda sediment is 45.37 while that of Apapa sediment is 6.79. The potential risk pose by Cd alone in the sediment suggests that the Igbokoda water is unsafe for recreational and other beach activities. The recommendation from the study will suggest a proper treatment of wastewater and sewages before fluxing into both the Igbokoda and Apapa water bodies.

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## Introduction

Pollutants, the elements of pollution, can be either foreign substances/energies or naturally occurring contaminants [1]. Environmental pollution has been a major concern because of the increasing growth of urbanization and industrial development [2]. Most of the industries discharged their waste directly (without been treated) into the stream, lakes, oceans as well as in the open land and that contaminate the ground water [3]. These metals can enter the water supply by industrial or consumer waste or even from acidic rain, breaking down soils and releasing other heavy metals into streams, lakes, rivers and ground waters [4]. The environmental problem of soil and sediment pollution by heavy metals has always received increased attention in the last few decades in both developing and developed countries throughout the world [5].

Heavy metals are so dangerous because they tend to bio-accumulate [6]. Once they accumulate in living things, they are taken up and stored faster than they are used, broken down or extracted. Some of these heavy metals are further classified as hazardous owing to the detrimental impact on the biotic components of the ecosystem.

Furthermore, the amount of metals entering the environment through anthropogenic activities is considerably high owing to their prevalence, therefore the risk of human exposed to such metals continue to be on the increase. In the past, inadequate regulation of recycling programs has led to accidental exposure, but of recent, multiple sources of exposures has become problems of increasing significance from ecological, evolutionary, nutritional, and environmental perspective [7].

The metals are usually present in trace amounts in natural waters but many of them such as arsenic, lead, cadmium, nickel, mercury, chromium, cobalt, zinc, antimony and selenium are highly toxic even in minute concentrations. Heavy metals in general, can directly influence negative behavior by impairing mental and neurological function, influencing neurotransmitter production and utilization, and also altering numerous metabolic body processes. Systems in which these elements can induce impairment and dysfunction include the blood and cardiovascular, eliminative pathways (colon, liver, kidneys, skin), endocrine (hormonal), energy production pathways, enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive, and urinary [1].

Sediments are sensitive indicators that can be used in monitoring contaminants in aquatic environments. They are considered integrators and amplifiers of the concentrations of heavy metals in the waters which pass over and transport them [8]. Sediments when polluted with different types of heavy and toxic substances often accumulate them through several pathways which include the disposal of liquid effluent, terrestrial run-off and leachate-carrying chemicals originating from numerous urban, industrial activities, agricultural activities and atmospheric deposition. Sediments also serve as sink and reservoir for a variety of contaminants and thereby providing record of catchments input into aquatic ecosystems [9-11]. The favourable physicochemical conditions of the sediment can thus be remobilized and they release the metals

into the water column. They sometimes accumulate heavy metals to levels many times higher than the water column concentration [12]. In such cases, sediments become a secondary source of pollution, leading to the possible contamination of benthic organisms living in contact with them and, finally of all of the benthic food chain. The present study is targeted at establishing and comparing the levels of contamination of sediments under two of the coastal rivers in south western part of Nigeria using the potential ecological risk PER methods. PER status may show specific metal pollution status of general pollution by contributions of individual metal loading.

## Materials and Methods

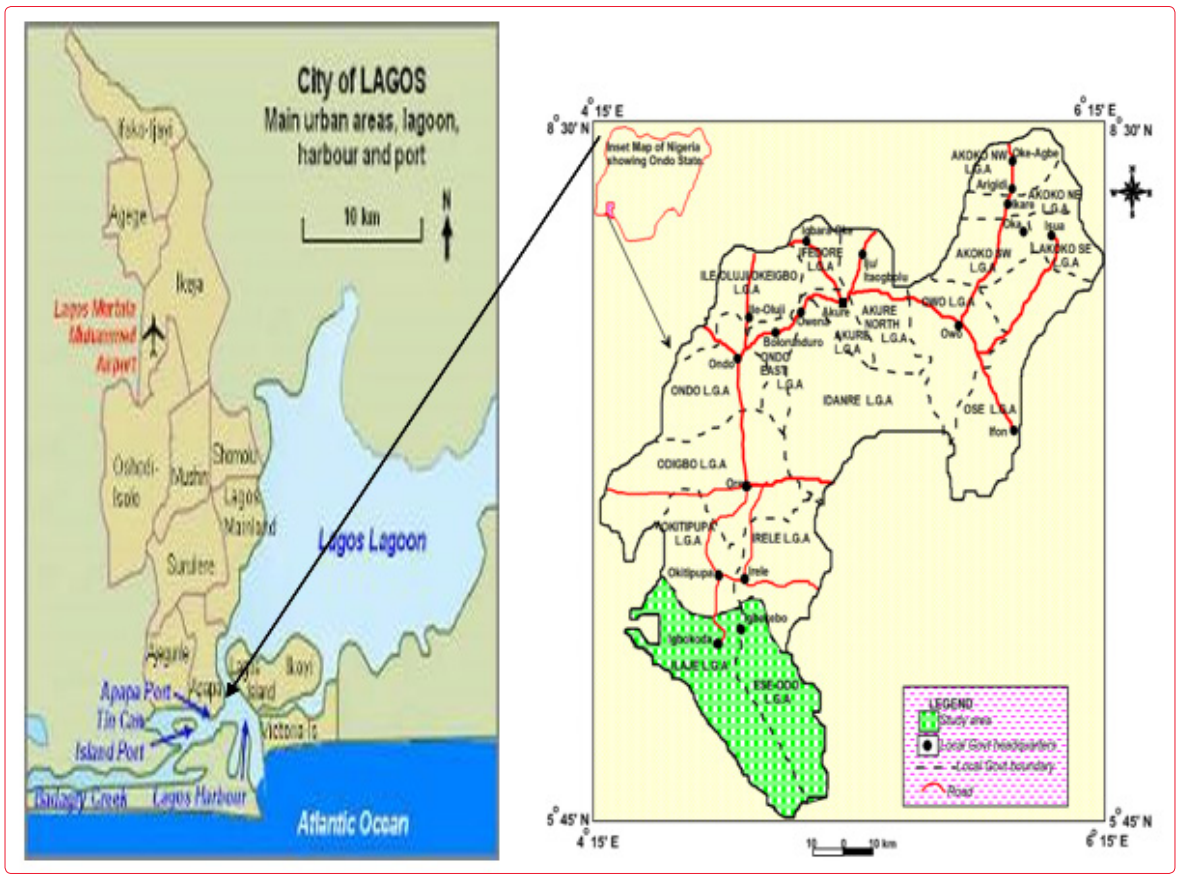
### Materials

### Sampling Location

Apapa with geographical coordinate of 6027'N, 3022'E is located to the west of Lagos Island. Apapa contains a number of ports and terminals operated by the Nigerian Ports Authority (NPA), including the major port of Lagos State and Lagos Port Complex (LPC). The region of Apapa used for this study lies near the mouth of Lagos lagoon, and contains ports and terminals for various commodities such as containers and bulk cargo, houses, offices and a small old disused railway station (Apapa North). It is the site of a major container terminal which are owned and/or operated by the Federal Government of Nigeria. Adjacent to the container port is the Tin Can Island Port, which has 'ro-ro' facilities. On the other hand, Igbokoda is in Ilaje Local Government Area of Ondo State, known for its large fishing activities. The geographical coordinate of Igbokoda is 6021'N, 4048'E. Igbokoda, is fast becoming an international trade centre as its popular market attracts traders not only from other part of Nigeria, but also from other African countries such as Togo, Benin, Ghana, Cameroon and Gabon. Igbokoda is only about 75 kilometers from Victoria Island, Lagos (Plate 1) and its aquatic environment presents the area as a suitable environment for tourism.

### Sampling of Water and Sediment

Ten sediment samples representing large area of the two contaminated environments in Nigeria were sampled during the second and third quarters of the year 2018. Five sediment samples were collected from Tin-can Liverpool river, Apapa, Lagos and another five sediments were also collected from Igbokoda river in Ondo State, Nigeria. The sediment areas in Lagos included Location (1) that receives drainage water from industries in Apapa, while locations (2) and (3) are recipients of domestic (household) waste water, location (4) and (5) are recreational beaches. Water samples were also collected from these locations for analysis using 2L Polypropylene plastics previously soaked in dilute acid bath and later rinsed thoroughly with distilled water thrice.




(1) (2)

**Plate 1:** Map of the study area (1) Map of Lagos state showing Apapa (2) Map of Ondo showing Igbokoda

At each location, sediment samples were collected from the surface layer (0-15cm depth) using a stainless steel Peterson grab sampler (20 x 12 cm). The samples were immediately stored in an ice-cooled box and transferred to the laboratory. The samples were air dried for two weeks by spreading on aluminum trays in a well ventilated room until a constant weight is achieved and finally powdered in a mortar and packaged for subsequent analysis.

## Methods

### Heavy metals determination in water

The water samples were first digested with conc. $HNO_3$ and pre concentrated before analysis using Atomic Absorption spectrophotometry (AAS). 100 $cm^3$ of well-mixed water sample was measured into a 250 $cm^3$ beaker and 10 $cm^3$ conc. $HNO_3$ was added. The solution was evaporated to near dryness in a beaker on hot plate under a medium heat of approximately 60 °C temperatures (solution not allowed to boil). The beaker with the content was allowed to cool to room temperature after which another 10 $cm^3$ portion of conc. $HNO_3$ and 5 cm3 $H_2O_2$ were added. The beaker was immediately covered with a watch glass and returned to the hot plate and increasing the temperature of the hot plate set a gentle reflux action. This was continued until a whitish residue was obtained. The residue was dissolved using 5 $cm^3$ conc. $HNO_3$ and 20 $cm^3$ of distilled water. The solution was then filtered after cooling through What man filter paper # 42 into a 50 $cm^3$ volumetric flask and made to the mark with distilled water. The solution was then transferred into another 50 $cm^3$ standard polythene flask prior to AAS analysis. Reagent blanks were prepared in similar manner. All solutions were analysed for seven heavy metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) using AAS BuckScientific 210 VGP model. Analyses of the metal standards (Cd, Cr, Cu, Mn, Ni, Pb and Zn) serially diluted from their stock solutions were also carried out and the data used to prepare a calibration curve from where the concentrations of the metals in the samples were extrapolated.

### Heavy metals determination in sediment

The sediment samples were air dried in the laboratory for 2 weeks. They were then ground into fine particles in a mortal, sieved through a 2 mm sieve and about 200 g of the sieved samples were sub-sampled by quartering for analysis. Extraction of metals from the sediment samples was by mixed acid digestion [13]. About 2 g of each air dried sample was weighed into a 250 cm3 conical flask. The digestion was carried out with 20 cm3 of a mixture of conc. $HClO_4$ and $HNO_3$ at a 2:1 ratio (v/v) on a hot plate and the mixture heated to almost dryness. This was followed by the addition of 20 $cm^3$ of 0.5 M $HNO_3$ and the solution filtered into a 50 $cm^3$ volumetric flask through Whatman # 42 filter paper. The filtrate obtained was made up to 50 $cm^3$ mark with distilled water and used for metals determination against those of the blank and calibration standards using a flame atomic absorption spectrophotometer (AAS), BuckScientific 210 VGP

### Calculation

$$\text{Metal Concentration in } \mu g/g = \frac{\text{AAS Reading in } {}^{\mu g}/_{ml} \times \text{volume of digest in ml}}{\text{Weight of sample in g}} \quad \text{(i)}$$

### Contamination factor

The contamination factor (CF) was calculated as described by Tomlinson et al. modified by [2,14].

$$CF = \frac{\text{Metal concentration in sediment}}{\text{Base value for the metal}} \quad \text{(ii)}$$

The base value for each metal was reported by Martin and Meybeck, modified by and represents the average composition of the surface rocks [2,15]. The terminologies used to describe CF are:

CF < 1, low contamination; 1 < CF < 3, moderate contamination; 3 < CF < 6, considerable contamination; and CF > 6, high contamination [16].

### Pollution load index

Pollution load index (PLI) was computed according to Tomlinson et al., 1980 using equation (iii).

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots CFn)^{(1/n)}, \quad \text{(iii)}$$

where PLI=pollution load index; CF=contamination factor; and n = the number of investigated metals. The overall toxicity status of hazardous materials in sediments may be assessed from Pollution load index (PLI) calculation. The PLI value of >1 is considerably polluted while <1 is considerable no pollution on a study site.

### Potential ecological risk (PER)

The degree of hazardous elements contamination in sediments from the two sites was determined by PER index. Guo et al., proposed equations (iv) and (v) which were used to calculate PER [17].

$$C_f^i = \frac{C^i}{C_n^i}, C_d = \sum_{i=1}^{n} C_f^i \quad \text{(iv)}$$

$$E_r^i = T_r^i \times C_f^i, PER = \sum_{i=1}^{m} E_r^i \quad \text{(v)}$$

where,

$C_f^i$ is the single element contamination factor, Ci is the content of the element in samples and

$C_n^i$ is the background value of the element.

The sum of $C_f^i$ for all metals represents the integrated pollution degree ($C_d$) of the environment. $E_r^i$ is the potential ecological risk index and $T_r^i$ is the biological toxic factor of an individual element. The toxic-response factors for Cd, Cr, Cu, Ni, Zn and Pb were 30, 2, 5, 6, 1 and 5, respectively [17-19].

*PER* is the comprehensive potential ecological risk index, which is the sum of $E_r^i$. Sensitivity of the biological community is represented by it to the toxic substance and indicates the potential ecological risk caused by the overall contamination.

### Statistical analysis

The data were statistically analyzed for variations in the means between the two contaminated sites using the statistical package, SPSS 22.0 (SPSS, USA). Some figures representation was plotted using the same software. Mean of the heavy metal concentrations in sediments are recorded as Mean ±S.D of five determinations from each sampling point area. Other calculations and Figure plotting were performed using Microsoft Excel 2010 (Microsoft Comp. Inc).

## Results and Discussion

### Heavy Metals in Water and Sediment Samples

The mean metal concentrations for the water and sediment samples are shown in Figure 1 (a-f). Five water and five sediments samples per site were analyzed. Except for few of the heavy metals whose concentration was below the detection limit of the AAS used for the analysis, all the seven metals were present in all the samples. Zn is the most abundant metal in both Igbokoda and Apapa water and sediments analyzed. Overall, the concentration of Zn (mg/Kg) is about 100 order >Cr; 67 order > Cd; 50 order>Ni; 40 order >Mn; 30 order >Pb and 13 order>Cu in the sediments. The concentration of all the metals in the river water samples in both sites were less than 0.5mg/Kg.

Figure 2 depicts the partitioning of the metals between

the river waters and sediments in the two sites. Igbokoda showed that the sequence of the metals in decreasing order is Cr>Ni>Cd>Mn>Pb>Cu>Zn for the % concentration of the metals while the reverse Zn>Cu>Pb>Mn>Cd>Ni>Cr is true for the sediments. In Apapa site, the sequence of the % composition of metals water is in the decreasing order of Ni>Mn>Zn>Cu>Pb>Cd>Cr while the reverse is obtainable with the sediments i.e. Cr>Cd>Pb>Cu>Zn>Mn>Ni. The sequence of these metals in different orders and % composition may serves as an impetus towards source apportionment of the heavy metals, since the two different locations are distinctively different.

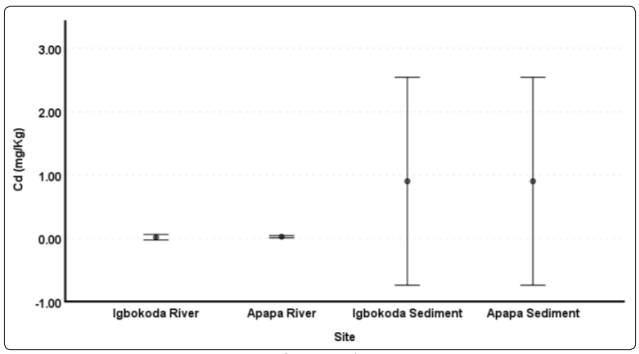



**Figure 1a**

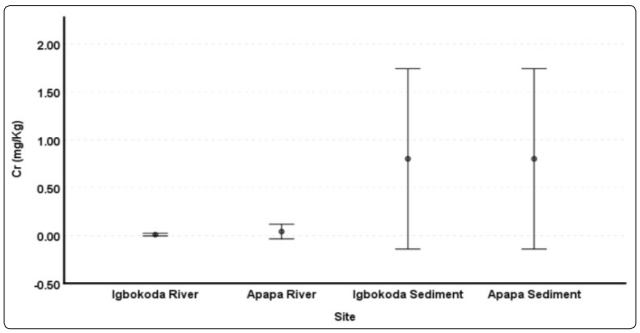
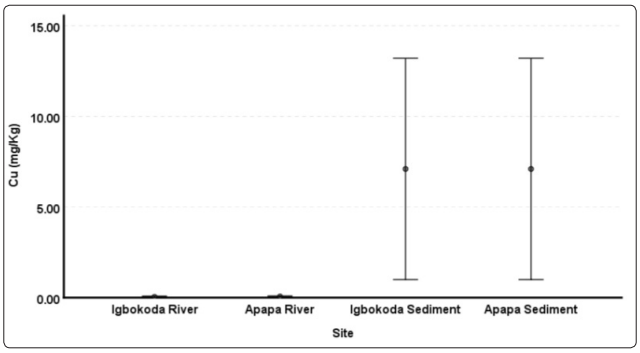



**Figure1b**

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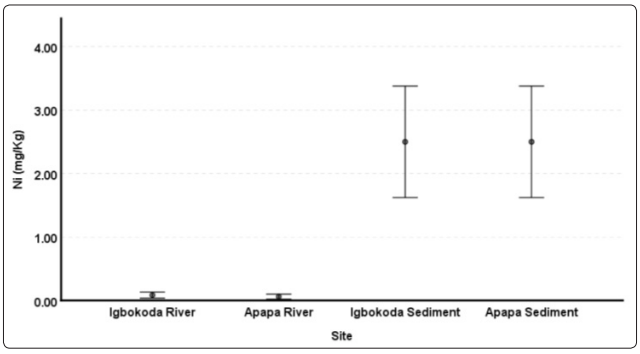


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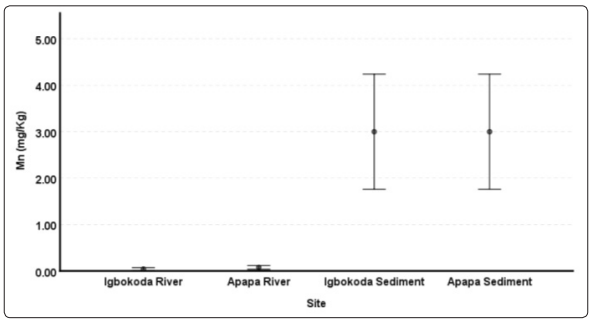


**Figure 1e**

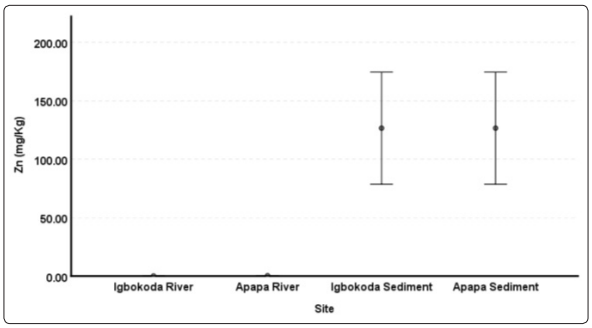


**Figure 1f**

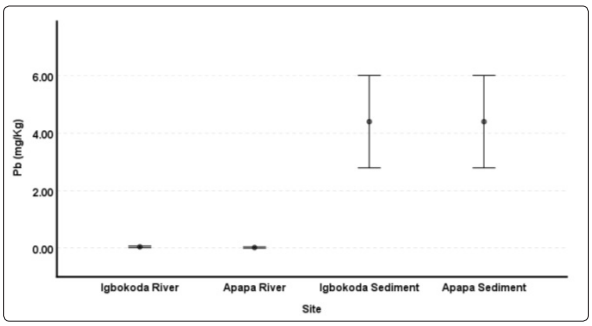


**Figure 1g**

**Figure 1(a-g):** Comparative mean metal concentration of hazardous metals in rivers and sediments from Igbokoda and Apapa. Values are Mean ± S.D for five sample number (n=5)

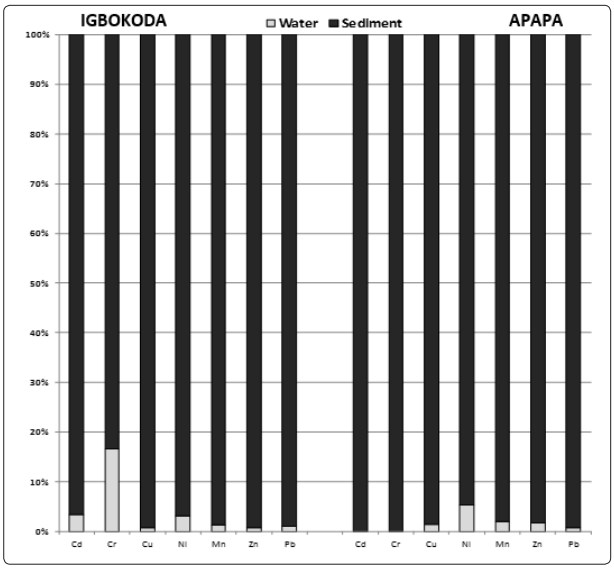


**Figure 2:** Percentage composition of hazardous metals in river water and sediments from Igbokoda and Apapa, south west, Nigeria

**Assessments of Contamination and Pollution in Sediments**

The contamination factor (Cif ) for individual metal and degree of contamination ( Cd ) are presented in Table 2. The two sites, Igbokoda and Apapa showed low contamination (Cd < 6) for all the metals in the sediments. The table can be interpreted as shown in Table 3, that the contaminated sites pose low potential risk to the surrounding ecosystems. This observation is akin to that reported by Rahed (2010). Overall, the Cif for investigated metals were in the descending order: Zn >Cd>Cu>Mn>Ni>Cr> Pb for Igbokoda and Zn>Cu>Cd>Ni>Mn>Cr>Pb for Apapa. The assessment of sediment contamination was based on the degree of contamination (Cd) showed low degree of metal contamination (Table 2).

Pollution load index (PLI) value equal to zero (0) indicates perfection; value of one (1) indicates the presence of only baseline level of contaminants and values above one (>1) indicates progressive deterioration of soil due to metal contamination [18,19]. Extent of pollution increases with the increase of numerical PLI value. As per above grade system, the sediments are not polluted, since PLI of most sediments are lower than 1 (Figure 3). Such low PLI value predicts that no drastic rectification measures are needed for the sediments at present. However, continued discharge of effluents and other wastes could actually increase these values unless waste and effluents coming from the anthropogenic activities in the coastal rivers drastically reduced and wastewater get treated for heavy metals removal before being discharged to the water bodies. This is reasonably unlikely to happen in view of the recent civilization and increased industrial activities and high economic potential of these two sites in the country.

Proshad et al., defines four categories of Cif, four categories of Eir, and four categories of PER, as shown in Table 3 [21]. Combining the potential ecological risk index of individual metals (Eir) and the potential ecological risk index (PER) (Table 4) with their grades (Table 3), sediments from Igbokoda sampling are classified as moderate ecological risk by Cd but low potential ecological risk by the remaining six hazardous metals. Similarly, sediments from Apapa are classified as having low ecological risk by all the seven hazardous metals.

**Table 2: Contamination factor, degree of contamination and contamination level of heavy metals in sediments from Igbokoda and Apapa, South west, Nigeria**

| Contamination factor (CF) | | | | | | | | Degree of Contamination | Contamination level |
|---|---|---|---|---|---|---|---|---|---|
| Site | Cd | Cr | Cu | Ni | Mn | Zn | Pb | | |
| Igbokoda | 1.41 | 0.01 | 0.18 | 0.04 | 0.05 | 1.89 | 0.004 | 3.6 | Low |
| Apapa | 0.13 | 0.03 | 0.24 | 0.05 | 0.04 | 1.58 | 0.004 | 2.1 | Low |

**Table 3: Indices and grades of potential ecological risks of heavy metal pollution [21].**

| Contamination factor $C^i_f$ | Contamination degree of individual metal | Degree of Contamination | Contamination degree of the environment | $E^i_r$ | Grade of Ecological risk of individual metal | Risk index (PER) | |
|---|---|---|---|---|---|---|---|
| $C^i_f < 1$ | Low | Cd <5 | Low contamination | $E^i_r$ <40 | Low risk | RI <40 | Low risk |
| $1 \leq C^i_f < 3$ | Moderate | 5≤Cd <10 | Moderate contamination | 40≤ $E^i_r$ <80 | Moderate Risk | 65≤RI <130 | Moderate risk |
| $3 \leq C^i_f < 6$ | Considerable | 10≤Cd <20 | Considerate contamination | 80≤ $E^i_r$ <160 | Considerable risk | 130≤ RI <260 | Considerable risk |
| $C^i_f \geq 3$ | High | Cd ≥5 | High contamination | 160≤ $E^i_r$ <320 | High risk | RI≥5 | Very high risk |
| | | | | $E^i_r \geq 5$ | Very high risk | | |

The PER represents the sensitivity of various biological communities to different toxic substances and illustrates the potential ecological risk caused by hazardous materials. According to Islam, et al., 2018 and two others (Mass et al., 2011; Luo et al., 2012) Cd contributes significantly to the PER of the environment and may originate from anthropogenic activities. The maximum value of PER for Cd is 45.4 in the sediment from Igbokoda. This denotes low potential ecological risk for the fauna and flora elements of the river and other even those on/in the sediment.

**Table 4: Potential Ecological risk factor, risk index and pollution degrees of heavy metals in sediments collected from Igbokoda and Apapa, South west, Nigeria**

| Site | Potential ecological risk factor (Eir) | | | | | | Potential Risk PER | Pollution degree |
|---|---|---|---|---|---|---|---|---|
| | Cd | Cr | Cu | Ni | Zn | Pb | | |
| Igbokoda | 42.3 | 0.02 | 0.9 | 0.24 | 1.89 | 0.02 | 45.37 | Low Risk |
| Apapa | 3.9 | 0.06 | 1.2 | 0.30 | 1.58 | 0.02 | 6.79 | Low Risk |

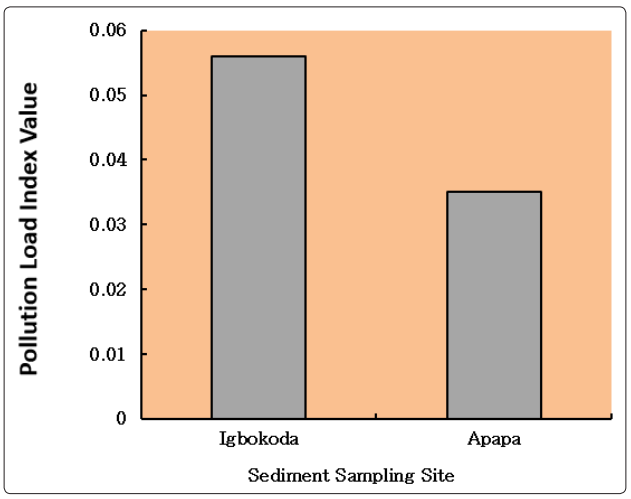


**Figure 3:** Pollution load index (PLI) of hazardous metals in sediments from two sites in South Western Nigeria

## Conclusion

For the study of the pollution status of sediments con¬taminated by some heavy metals the method of potential ecolog¬ical risk indices was used. According to the method used, the concentration of heavy metals in the sediments from Igbokoda and Apapa pose a low ecological risk to both the Igbokoda and Apapa Rivers. The potential ecological risk indices were found in the following order Cd > Zn > Cu > Ni > Cr/Pb in Igbokoda sediments but with the order Cd > Zn > Cu > Ni > Cr>Pb in Apapa Sediments.

The results of sediments quality assessment from the two locations had shown that the sediments are moderately contami¬nated by the metals and their pollution can be attributed to industrial pollution through anthropogenic activities. Contamina¬tion assessment of sediments may provided substantial evidence useful in water management techniques and indicates the need of remediation and protection of surface river water. Further works on the dynamics of heavy metals between the water and the sediments may be required to fully understand the contribution of sediments to river or other surface water contamination processes. A metal speciation study is also vital for understanding its transport and fate in the water and sediments. Specifically and relating to Cd metal, there is need to place a caution on the consumption of sea foods from the region examined for Cd if its PER value is on the increase. Further study into the healthy levels of Cd or its bioaccumulation factor in the aquatic animals consumed from this river is highly expedient [24].

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